

**APPLICATION FOCUSED DESIGN AND
DEVELOPMENT OF POLYMER MATRIX COMPOSITES
FOR THERMAL APPLICATIONS**

BY

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DHAHRAN- 31261, SAUDI ARABIA
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2020

|Dedicated to my parents and family |

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LIST OF ABBREVIATIONS AND SYMBOLS

<i>SPHM</i>	:	Single-phase homogeneous material
<i>LED</i>	:	Light emitting diode
<i>CPV</i>	:	Concentrated photovoltaic
<i>STHE</i>	:	Shell and tube heat exchanger
<i>PHE</i>	:	Polymer Heat Exchanger
<i>GMI</i>	:	Materials Genome Initiative
<i>PMC</i>	:	Polymer matrix composite
<i>TC</i>	:	Thermal conductivity
<i>PSU</i>	:	Polysulfone
<i>CNT</i>	:	Carbon nanotube
<i>GNP</i>	:	Graphene Nano particle / platelet
<i>EG</i>	:	Expanded Graphite
<i>SE</i>	:	Synergic Effect in thermal conductivity
<i>EMT</i>	:	Effective medium theory
<i>HJ</i>	:	Hesselman and Johnson (Model)
<i>HS</i>	:	Hashin-Shtrikman (Model)
<i>MT</i>	:	Mori-Tanka (Model)
<i>HDPE</i>	:	High density polyethylene
<i>PP</i>	:	Polypropylene
<i>DSC</i>	:	Differential Scanning Calorimeter
<i>PPNS</i>	:	Polypropylene – Aluminum Nitride Small (A composite system)

<i>PPNL</i>	:	Polypropylene – Aluminum Nitride Large (A composite system)
<i>PPOS</i>	:	Polypropylene – Aluminum Oxide Small (A composite system)
<i>PEOS</i>	:	High Density Polyethylene – Aluminum Oxide Small (A composite system)
<i>PEOL</i>	:	High Density Polyethylene – Aluminum Oxide Large (A composite system)
<i>PENL</i>	:	High Density Polyethylene – Aluminum Nitride Large (A composite system)
<i>ITR</i>	:	Interfacial or Interface thermal resistance
<i>TCR</i>	:	Thermal contact resistance
<i>FESEM</i>	:	Field Emission Gun Scanning Electron Microscope
<i>AMM</i>	:	Acoustic Mismatch Model
<i>CTE</i>	:	Coefficient of thermal expansion
<i>CPV</i>	:	Concentrated photovoltaic
<i>TPU</i>	:	Thermoplastic polyurethane
<i>PDMS</i>	:	Polydimethylsiloxane
<i>EVA</i>	:	Ethylene vinyl acetate
<i>PVB</i>	:	Polyvinyl butyral
<i>Al₂O₃</i>	:	Alumina
<i>AlN</i>	:	Aluminum Nitride
ρ	:	Density
C_p	:	Specific heat at constant pressure
<i>T</i>	:	Absolute temperature

$\mathbf{q}$	:	Heat flux
Q	:	Extra heat source = 0 in this case (chapter 6)
k	:	Thermal conductivity (tc)
$\{s\}$	:	Stress vector
F_v	:	Body force per unit deformed volume
$[C]$	:	Stiffness matrix
$\{\epsilon^{el}\}$	:	Mechanical strain vector
ϵ	:	Total strain vector
$\{\epsilon^{th}\}$	:	Thermal strain vector
α_i	:	Coefficient of thermal expansion in ith direction
T_{ref}	:	Temperature of zero strain and stress
G_∞	:	Long term shear modulus
α	:	Coefficient of thermal expansion (CTE)
E	:	Young's modulus
ν	:	Poisson's ratio
G	:	Shear Modulus
σ_0	:	Yield strength
M	:	Tangent Modulus
$\Delta\epsilon$	:	Strain range
σ'_f	:	Fatigue strength coefficient = 345 MPa
σ_m	:	Mean stress
N_f	:	Number of reversals
b	:	Fatigue strength exponent = -0.05

ε'_f	:	Fatigue ductility coefficient =0.3
c	:	Fatigue ductility exponent =-0.6
$\mathbf{n}$	:	Surface normal
η_{pv}	:	Electrical efficiency of the cells
A_{module}	:	Top surface area of the PV module
V_{module}	:	Volume of the module
G	:	Solar Irradiance
h	:	Heat loss coefficient
α_b	:	Absorbance of the PV module
T_{amb}	:	Ambient temperature
T_s	:	Surface temperature
Nu	:	Nusselt Number
Re	:	Reynolds number
Pr	:	Prandtl number
μ_b/μ_w	:	Ration of fluid viscosities (viscosities of shell side fluid at average temperature the same at wall temperature)
ΔP_s	:	Shell side pressure drop
F	:	Friction factor
G	:	Mass flux [kg.s-1.m-2]
D_s	:	Shell diameter
N_b	:	Number of baffles
D_e	:	Equivalent diameter

ABSTRACT

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Engineering community is in a constant pursuit of new materials for high-tech applications. Numerous materials' combinations are possible for the development of new materials at micron to nano – scale. However, none of these combinations could be a universal material, which can be suitable for all applications. The material's combination and their scale of mixing depends upon the required material properties, which in turn depends upon the target application. Finding the right combination of materials leading to enhanced suitability should be *application-focused*. Efficient computational tools can be developed based on effective medium theories, atomistic simulations etc. which can enable the *design of application-focused* discovery of material's combination.

In this dissertation, an integrated scheme for the design and development of polymer-composites has been developed focused on target applications. The entire '*application-focused design*' scheme is mainly divided into four steps namely setting the target properties, designing the polymer-composite, developing the representative compositions, and evaluating the performance. '*Setting the target properties*' is established by analyzing the effect of material properties using mathematical models of the selected applications.

The target properties are expected to provide enhanced performance of the material in application. '*Designing the polymer-composite*' is established through properties estimation models, which are based on differential effective medium theory and Mori-Tanaka's homogenization scheme. '*Developing the polymer-composite*' includes pre-treatments, mixing, processing, casting / molding, sample preparation, measurements, characterizations, and finally validation and calibration of computational design. '*Evaluating the performance*' is established using the measured properties of developed polymer-composite as inputs to the mathematical model used in '*Setting the target properties*'.

Though the proposed scheme of design and development is a generalized scheme, this dissertation mainly encompasses thermal applications, i.e. wherein increasing thermal conductivity could lead towards enhanced performance provided the other properties are kept within some bounds. Therefore, as contribution to the second step of design and development scheme, new models for estimating thermal conductivity of composites have been developed. In this way, the dissertation can be divided into two major parts: development of *thermal conductivity models* and implementation of *application-focused design* scheme.

Thermal conductivity models are derived based on percolation theory and differential effective medium theory. The model based on percolation theory is derived for dilute hybrid percolating fillers. The model is validated, calibrated through experiments, and used to design the best composition of polysulfone (PSU) matrix - 10% Graphene nano-platelets (GNPs) / Carbon nano-tubes (CNTs) composite for the maximum thermal conductivity. The other proposed model is based differential effective medium theory and it is

generalized for non-dilute filler concentrations. The proposed model is able to handle particulate fillers of variable geometry. The proposed model is validated by producing different polymer-composite systems with ceramic filler concentrations up to 50% by volume. The effects of different parameters have been elucidated through parametric studies in both the models. In the percolation model, the dimensional parameters and the interface resistance of the platelet shaped fillers are the most sensitive to control the effective thermal conductivity. In the non-dilute model, the aspect ratio of particulates is found the most sensitive parameter. The proposed models are expected to open new doors for the researchers and the industry to develop new polymer composites with tailorable ultrahigh thermal conductivity in corrosive environment-heat transfer applications. Later, as a direct application of thermal conductivity models, polymer-composites with ultra-high thermal conductivity were designed and developed leading to non-conventional microstructures with segregated thermally conductive phase.

The scheme of design and development of composite material has been successfully implemented for two applications namely backside *encapsulant* of concentrated photovoltaic (CPV) modules and *tubes* of shell and tube heat exchanger. For the encapsulant, thermal conductivity (k), coefficient of thermal expansion (α), and long-term shear modulus (G_∞) were considered as the target properties with focus on improved module life and electrical power. The target values were established through finite element (FE) simulations of thermal stress problems in a three-cell model of CPV module. For the tubes of heat exchangers, thermal conductivity and yield strength were considered as target properties. The target thermal conductivity was decided based on estimation of heat transfer coefficient using well-known Kern and Bell-delaware methods and target yield

strength was decided based on Barlow's formula. In both implementations, composite materials were computationally designed to achieve target properties based on properties estimation models and representative compositions were developed in line with the computational design. Finally, the measured properties of the representative samples were used to evaluate the actual performance of material and hence to validate the entire scheme.

In view of the outcomes of these applications, it is concluded that a successful design and development of polymer-composites can provide significant enhancement in the performance for any particular applications by tailoring the properties for desired target properties. It is expected that this approach will allow cost-effective production of polymer composites in various industrial applications.

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ملخص الرسالة

الاسم الكامل: حافظ كبير رضا شيشتى

عنوان الرسالة: تصميم و تطوير من وجهة تطبيقية لمركبات قوالب البوليمر المستخدمة للتطبيقات الحرارية

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المجتمع الهندسي في سعي مستمر للمواد الجديدة للتطبيقات ذات التقنية العالية. تركيبات عديدة من المواد ممكنة لتطوير مواد جديدة على نطاق ميكرون إلى نانو. ومع ذلك ، لا يمكن لأي من هذه التركيبات أن تكون مادة عالمية ، والتي يمكن أن تكون مناسبة لجميع التطبيقات. تعتمد تركيبة المادة وحجم الخلط على خصائص المواد المطلوبة ، والتي تعتمد بدورها على التطبيق المستهدف. عملية إيجاد التركيبة الصحيحة من المواد التي تؤدي إلى تحسين الملاءمة يجب أن تكون تركز على التطبيق. يمكن تطوير أدوات حسابية فعالة استنادًا إلى نظريات متوسطة فعالة ، ومحاكاة ذرية وما إلى ذلك ، والتي يمكن أن تتيح تصميم اكتشاف تركيبة المواد التي تركز على التطبيق.

في هذه الرسالة ، تم تطوير مخطط متكامل لتصميم وتطوير مركبات البوليمر المركزة على التطبيقات المستهدفة. ينقسم مخطط "التصميم الذي يركز على التطبيق" بالكامل إلى أربع خطوات وهي تحديد الخصائص المستهدفة ، وتصميم مركب البوليمر ، وتطوير التراكيب التمثيلية ، وتقييم الأداء. يتم إنشاء "تعيين الخصائص المستهدفة" من خلال تحليل تأثير خصائص المواد باستخدام النماذج الرياضية للتطبيقات المحددة. من المتوقع أن توفر الخصائص المستهدفة أداءً محسناً للمادة الموجودة في التطبيق. يتم إنشاء "تصميم البوليمر المركب" من خلال نماذج تقدير الخصائص ، التي تستند إلى نظرية الوسط التفاضلي الفعال ومخطط Mori-Tanaka للتجانس. يتضمن "تطوير البوليمر المركب" المعالجات الأولية والخلط والمعالجة والسباكة / الصب وإعداد العينات والقياسات والتوصيفات وأخيرًا التحقق من التصميم الحسابي ومعايرته. تم إنشاء "تقييم الأداء" باستخدام الخصائص المقاسة لمركب البوليمر المطور كمدخلات للنموذج الرياضي المستخدم في "تعيين الخصائص المستهدفة".

على الرغم من أن مخطط التصميم والتطوير المقترح هو مخطط معمم ، فإن هذه الرسالة تشمل بشكل أساسي التطبيقات الحرارية ، حيث يمكن أن تؤدي زيادة الموصلية الحرارية إلى تحسين الأداء بشرط الاحتفاظ بالخصائص الأخرى داخل بعض الحدود. لذلك ، كمساهمة في الخطوة الثانية من مخطط التصميم والتطوير ، تم تطوير نماذج جديدة لتقدير الموصلية الحرارية للمركبات. بهذه الطريقة ، يمكن تقسيم الرسالة إلى قسمين رئيسيين: تطوير نماذج الموصلية الحرارية وتنفيذ مخطط التصميم الذي يركز على التطبيق.

يتم اشتقاق نماذج الموصلية الحرارية بناءً على نظرية الترشيح ونظرية الوسط التفاضلي الفعال. يتم اشتقاق النموذج القائم على نظرية الترشيح من أجل الحشوات المتقشرة الهجينة المخففة. تم التحقق من صحة النموذج ومعايرته من خلال التجارب ، ويستخدم لتصميم أفضل تكوين لمصفوفة البولي سلفون 10 - (PSU)٪ من صفائح الجرافين النانوية (GNPs) / أنابيب الكربون النانوية (CNTs) للحصول على أقصى توصيل حراري. النموذج المقترح الآخر يستند إلى نظرية الوسط التفاضلي الفعال التفاضلي ويتم تعميمه لتركيزات الحشو غير المخفف. النموذج المقترح قادر على التعامل مع حشوات الجسيمات المتغيرة الشكل الهندسي. يتم التحقق من صحة النموذج المقترح عن طريق إنتاج أنظمة مختلفة من البوليمر المركب بتركيزات حشو خزفي تصل إلى 50٪ من حيث الحجم. وقد تم توضيح آثار العوامل المختلفة من خلال الدراسات البارامترية في كلا النموذجين. في نموذج الترشيح ، تكون معلمات الأبعاد ومقاومة الواجهة للحشوات على شكل الصفائح الدمية هي الأكثر حساسية للتحكم في الموصلية الحرارية الفعالة. في النموذج غير المخفف ، تكون نسبة أبعاد الجسيمات هي العامل الأكثر حساسية. من المتوقع أن تفتح النماذج المقترحة أبواباً جديدة للباحثين والصناعة لتطوير مركبات بوليمر جديدة ذات موصلية حرارية فائقة مصممة خصيصاً لتطبيقات نقل الحرارة في البيئة المسببة للتآكل. في وقت لاحق ، كتطبيق مباشر لنماذج الموصلية الحرارية ، تم تصميم وتطوير مركبات البوليمر ذات الموصلية الحرارية العالية للغاية مما أدى إلى إنشاء تركيبات مجهرية غير تقليدية مع مرحلة توصيل حراري منفصلة.

تم تنفيذ مخطط تصميم وتطوير المواد المركبة بنجاح لتطبيقات هما الغلاف الخلفي للوحدات الكهروضوئية المركزة (CPV) وأنابيب المبادل الحراري من نوعية ال Shell and tube. بالنسبة للمغلفات ، تم اعتبار الموصلية الحرارية (k) ومعامل التمدد الحراري (α) ومعامل القص طويل المدى (G_{∞}) من الخصائص المستهدفة مع التركيز على تحسين عمر الوحدة والطاقة الكهربائية. تم تحديد القيم المستهدفة من خلال محاكاة العناصر المحدودة (FE) لمشاكل الإجهاد الحراري في نموذج ثلاثي الخلايا من وحدة CPV. بالنسبة لأنابيب المبادلات الحرارية ، تم اعتبار التوصيل الحراري

ومقاومة الخضوع من الخصائص المستهدفة. تم تحديد الموصلية الحرارية المستهدفة بناءً على تقدير معامل انتقال الحرارة باستخدام طرق Kern و Bell-delaware المعروفة ، وتم تحديد قوة العائد المستهدف بناءً على صيغة Barlow. في كلا التطبيقين ، تم تصميم المواد المركبة حسابياً لتحقيق الخصائص المستهدفة بناءً على نماذج تقدير الخصائص وتم تطوير التراكيب التمثيلية بما يتماشى مع التصميم الحسابي. وأخيراً ، تم استخدام الخصائص المقاسة للعينات التمثيلية لتقييم الأداء الفعلي للمادة وبالتالي للتحقق من المخطط بأكمله.

في ضوء نتائج هذه التطبيقات ، تم استنتاج أن التصميم والتطوير الناجح لمركبات البوليمر يمكن أن يوفر تحسناً كبيراً في الأداء لأي تطبيقات معينة من خلال تكييف الخصائص لتوافق الخصائص المطلوبة للهدف. من المتوقع أن يسمح هذا النهج بالإنتاج الفعال من حيث التكلفة لمركبات البوليمر في مختلف التطبيقات الصناعية. |

CHAPTER 1

INTRODUCTION

1.1 Polymer matrix composites

Polymer based advanced materials are attractive for many industrial and domestic applications due to their lightweight. The remarkable new developments of computational theories and tools of evolving materials has amazingly resulted polymer-based light emitting diodes (LEDs), [1] and self-repairing bio-compatible materials [2]. It is well accepted that universal materials do not exist i.e. there is no material which can be said to be suitable for every application. Applications of materials are wide spread with each application having its own requirements. A single-phase homogeneous material (SPHM) cannot necessarily possess all the required thermal and mechanical properties for a target application. Therefore, certain properties of an SPHM are enhanced by adding suitable reinforcements to make it suitable for the particular application. The motive behind the development of composite materials is to find a more suitable material, which can provide a longer life, a higher efficiency, a higher output, a small carbon footprint etc. In the composite materials, two or more immiscible materials are purposely mixed to get a composite, which in application provides the best out of each individual component material for the target application. Steel bars reinforced concrete is a well-known example, where we combine the high rigidity of concrete with the high strength of steel.

Polymer matrix composites (PMCs) are the focus of recent developments in many structural and electronic applications. Due to their high strength to weight ratio PMCs are highly desired for structural applications. PMCs are also attractive for corrosive environments due to their excellent resistance to chemical reactions. The properties of PMCs can be tailored by tuning different material and processing parameters, similar to the other types of composites [3]. A set of material properties are tailored to be suitable for the target application. For example, in electronic packaging and thermal interface materials thermal conductivity (TC) and coefficient of thermal expansion (CTE) are tailored such that TC is increased while CTE is decreased. However, improvement of one property by the additions of fillers may deteriorate the other the other property and hence, fail to serve the purpose. Therefore, the composite materials should be designed for improvement of all the target properties leading to enhanced performance. The performance evaluation may be based on parameters such as fatigue life, efficiency, effectiveness etc.

1.2 Design and Development Scheme

The purpose of this work is to propose a systematic design and development scheme to make composite materials for target applications. The design part of the scheme utilizes computational methods including mathematical models and finite element simulations. The design part is further divided into two sections including identification of optimized material properties [target properties] and design of composite material with the optimized material properties. The identification of optimized material properties is based on the solutions of finite element and mathematical models of the applied-problem. The

composite materials are designed using the properties estimation models, which are based on effective medium theories and Mori-Tanaka mean field homogenization scheme.

The development part of the scheme utilizes experimental tools including pretreatments, processing, sampling, molding, testing, and characterizations. The phase compositions, particle size, and types of fillers etc. for the development of composites are based on the results of design of composite materials. Finally, the performance of new composite material is evaluated by means of finite element simulations and lab scale models. For implementation of the proposed design and development scheme, two applications have been selected namely encapsulant of solar cells for concentrated photovoltaic (CPV) module and tubes of plastic-shell and tube heat exchangers (STHEs). Based on the developed computational scheme, the materials for these applications are designed and developed followed by validation through thermal and structural properties measurements.

1.3 Motivation for the research

1.3.1 Development of thermally conductive polymer matrix composites

Polymeric materials are rapidly replacing the metals due to their extraordinary acceptability. Their lightweight, low temperature processibility and unbeatable corrosion resistance are the most attractive features. Unlike metals, polymers have the potential to be used in a wide spectrum of applications. Building structures, packaging, bioactive, biocompatible, textile, and reducing friction are among the few fast-growing areas of polymers.

Due to the weak vander Waal forces between the molecular chains in the polymeric materials, their mechanical properties like tensile strength, elastic modulus, hardness and wear resistance are very low as compared to metals. Similarly, the electrical and thermal conductivity of polymers are very low due to unavailability of free electrons and having small mean free path of phonons.

PMCs are widely accepted in many heat transfer applications such as heat exchangers, thermal management of electronics and thermal interface materials. For such applications, TC must be good enough to dissipate the waste heat. In this view, scientists are working to enhance the TCs of PMCs synergistically. Synergistic enhancement in TC of PMCs has been reported by using hybrid fillers such as mixtures of differently composed [4], differently sized [5,6], or differently shaped [7–9] particles. The key to synergistic enhancement in TC is to develop a percolating network of high TC fillers in the final product [10–12]. Among different approaches, one is to follow a methodology in which the particulate fillers are forced to connect each other, for example, layer-by-layer fabrication by doctor blading [13], and structuring of flakes by high-speed mixing and hot compressing [14–17]. Another way is to use expandable graphite (EG). Once expanded, EG forms a fully connecting skeleton and leads to high TC [18–20]. Similarly, foams or porous structures of thermally conducting ceramics can be infiltrated with polymeric materials to have inter-connecting heat pathways throughout [21–23]. On the same lines, forming a segregated structure of thermally conductive fillers following a two-stage mixing route can lead to ultrahigh TCs [10,24]. The main concern of this work is to design and develop for thermal applications i.e. where the heat transfer property of the material is

crucial. Nevertheless, the other properties such as elastic moduli, yield strength and thermal expansion coefficient should be within the design-allowed window. Therefore, this work is dedicated to improve the thermal and mechanical properties particularly thermal conductivity of polymer composites with the purpose to use them in designated applications.

1.3.2 Application-focused design

There are certain material selection criteria that should be considered for a particular application. One of the selection criteria is to check material properties, which can affect the performance parameters such as structural life, efficiency, output power, heat-transfer, effectiveness etc. for the target application. Most of the available literature in this area focuses on improvement of certain material properties that are expected to improve the performance. However, the quantification of the improved performance is mostly missing. One of the major objectives of this work is to address this gap by systematically designing the composite materials for target applications (encapsulant of CPVs and tubes of STHes) in conjunction with quantifying and evaluating the improved thermal and structural performance. In this context, an integrated design, development and performance evaluation scheme is used whereby predictive computational tools are developed and used to optimize material properties. Then the samples are produced in line with the predictions of computational tools to validate the design. The designed and produced composites are then used for quantifying the target performance.

1.3.3 Reducing the number of experiments

In general, the effective properties of any composite material depend on many competing factors such as the intrinsic properties of individual phases, shape morphology, interface conditions of the fillers etc. In order to achieve certain properties, many hit and trail combinations of matrix and second phase fillers need to be tried through experiments. This type of approach leads to unnecessary consumption of material, energy, efforts and time to explore the best out of the combination. Through proper use of computational material design tools, optimum composites can be designed with desired target properties.

In this work, the design of composite materials is based on the predictions of properties estimation numerical and mathematical models, where the target material properties are taken as inputs while the material design parameters such as phase compositions, types of fillers, and volume fractions etc. are the outputs. The presented models are validated through experiments by synthesizing some representative composite samples in line with designed parameters. This integrated design-lead approach significantly reduces the experimental cost as mentioned earlier.

1.3.4 Development of computational design models

A significant work related to computational design of material is available in the open literature focusing on many design aspects pertaining to thermal and structural properties. However, the existing computational models still have some limitations, which need to be addressed for accurate predictions. These limitations are mostly related to interaction among the second phase particles.

Effective TC of composites is controlled by many parameters, but particle size and aspect ratio of the particulate fillers are the most sensitive parameters because the formation of a percolating network depends on these parameters [25,26]. Most of the estimation models used for predicting effective TC of composites are limited to dilute concentrations (low volume fractions) of fillers i.e. where the field of one particle does not interact with that of its neighboring particle [27–31]. On the other hand, the available models for composites with non-dilute concentrations (high volume fractions) of fillers are limited to particles with irregular shapes and cannot handle the variable orientation of the high aspect ratio particles [32,33]. Hence, there is a need to develop a model for estimating effective TC of composite, which includes the effects of non-dilute filler concentrations, and orientation and aspect ratio of particles all-in-one.

This work is intended to develop a more realistic effective medium theory-based TC estimation model that can be equally used for percolating fillers at dilute and non-dilute concentrations with particles of variable shapes and orientations.

1.4 Selected applications for model implementation

1.4.1 Encapsulant of Concentrated Photovoltaic modules

Over the period of last decade, the cost of electricity obtained from PV systems is decreasing at a fast descending rate. On the other hand, the total global capacity of the PV installations around the globe have doubled within only five years from 2012 to 2017. The total global installed solar photovoltaic (PV) capacity of the world was only 100.9 GW at the end of 2012. The PV installations are growing so rapidly that the capacity of

installations within the historic year of 2017 were close to the total PV capacity of the world until 2012 i.e. 99.1 GW. By having 30% more installations than 2016, the total PV capacity of the world was over 400 GW, which is expected to cross 1 TW by 2022. ACWA power, a Saudi company has won a tender of 300 MW Solar Power at the lowest price of only 2.34 US cents/kWh in February 2018. The decreasing cost and increasing demand have boosted the development for high efficient PV modules [34]. The PV efficiency is improved by concentrating PV modules. However, the CPV systems are less common due to the required additional costs of concentrating optics and cooling systems. CPV systems are categorized based on their concentration factor, optical standard, focal shape, and distribution of illumination, etc. Having a lower concentration factor of 1 to 30, CPV systems are classed as low concentration PV (LCPV) modules and those with a concentration factor of more than 300 are said to be high concentration PV (HCPV) modules. The former (i.e. LCPV) type of modules use high-efficiency Si-Cells and are linear systems that concentrate the incident solar radiation in only one axis [35,36]. The PV efficiency is severely affected by high cell temperature or non-uniform cell temperature distribution. Moreover, the cells are prone to degradation if the temperature goes beyond a certain limit. Therefore, an appropriate cooling system is one of the major concerns in the design of CPV systems. Moreover, a higher thermal conductivity of encapsulant can help faster cooling of the modules for having a better production of electrical power [37–39].

1.4.1.1 Structural components of PV Modules

The PV modules consists of different components and each of them has a specified objective. The heart of the module is the solar cell, which converts the solar radiation into

electricity. The solar cells are connected in series to build a PV module. The entire solar cell assembly has to be electrically insulated in order to avoid leakage of current. In addition, the insulation should have high transmittance from front side, certain level of strength and adhesion to serve for reasonable life. For this purpose, the popular encapsulant materials are ethylene vinyl acetate (EVA) and silicone. However, EVA is more common in the PV industry because of its lower cost. Besides being electrical insulator and adequately strong, the encapsulant must be transparent from front side so that it may transmit the solar radiation unaffected. From front side, the encapsulated module is covered with glass sheets. The glass sheet protects the module from mechanical attacks and reflects some amount of ultraviolet radiations, which cause degradation of the encapsulant. From the backside, the module is supported by a backsheet of suitable material like polyester or tedlar. The function of the backsheet is to provide adequate mechanical stability to the entire structure. A set of modules makes a panel and a set of panels makes a solar array [40,41].

1.4.1.2 Commercially used encapsulant materials of PV modules

Hasan et al. [42] have compared the performance of different encapsulant materials which are used for the encapsulation of solar cells. The performance criteria were light transmittance, UV durability, electrical insulation, moisture ingress, structural life, and cost. It was concluded that the increasing order of overall performance is Polyvinyl butyral (PVB) < thermoplastic polyurethane (TPU) < Polydimethylsiloxane (PDMS) < ethylene vinyl acetate (EVA) < ionomer. However, EVA is much popular in the solar industry because its cost is almost half as compared to ionomer.

1.4.1.3 Essential Properties of an encapsulant

The encapsulant has to encapsulate the functional components of PV modules. The word “encapsulation” is meant for protection i.e. the encapsulant has to protect the solar cells from environmental effects, electrical leakage, and mechanical damage. The main objective of the encapsulant is to insulate the assembly of solar cells electrically. To protect from environmental effects, the encapsulant material must have high resistance to penetration and ingress of water and high resistance to yellowing due to UV-rays in the solar radiations. To avoid leakage of current, the encapsulant must be a good electrical insulator i.e. high volume resistivity is required. The encapsulant should have low damping response and low CTE to reduce the hysteresis of thermal cycling and improve fatigue life.

In the CPV systems as compared with the non-concentrated systems, the thermal stresses are relatively worse due to higher working temperature and irregular distribution. Hence, it may cause overheating and untimely breaking of cells or interconnects due to thermal fatigue or some other thermomechanical reasons. Therefore, the requirement of high thermal conductivity, low elastic modulus and low coefficient of thermal expansion becomes vital for the efficient performance of CPV systems. This work is focused on designing potential composite materials as backside encapsulant for CPV systems with best combinations of thermal and structural properties, which could lead to improved overall performance [37,42].

Due to their high thermal conductivity, metals are the materials of choice for the heat exchangers. However, metals have several disadvantages such as high density, high cost, high temperature process-ability, low fouling and corrosion resistances. Polymer based

materials can effectively overcome the disadvantages offered by metals with lower production cost, low temperature and easy process-ability and very good corrosion and fouling resistances.

1.4.2 Tubes used in shell and tube heat exchangers (STHEs)

Heat exchanger is a device, which is used to transfer heat between two fluids through a separating surface. The assembly of a heat exchanger is such that the hot and cold fluids are kept separated from each other by means of thin separating solid surfaces. Most commonly used assemblies of heat exchangers are the “plate and frame” and “shell and tube” types, where the separating surfaces are plates or tubes respectively [43]. Heat exchangers are one of the core components of many engineering systems for example space heaters, air conditioning, power stations, chemical and petrochemical plants, refineries, food processing, and thermal desalination etc.

1.4.2.1 Polymer heat exchangers

Polymer heat exchangers are accepted in many industrial and engineering applications. Polymer based heat exchangers have been studied by scientists and engineers since 1960 and since then have been magnificently employed for many applications. These applications include but not limited to heat recovery systems [44,45] HVAC & R [46–49], evaporative cooling systems [50,51], seawater desalination [52–56], solar water heating [57–59], and condensing boilers [60].

1.4.2.2 Essential properties of tubes in STHEs

The heat transfer surface of heat exchanger must be capable of transferring the heat at the quickest, which is the core function of heat exchanger. In order to perform this function for a reasonable life-time, it should have a good thermal conductivity and adequate strength over the working temperature range of the fluids [49].

To be used for thermal management, the low thermal conductivity of the polymers is a big hurdle. Furthermore, their low mechanical properties put a limit on the allowable fluid pressure in the heat exchangers. Thanks to thermally conductive carbonaceous fillers, which can dramatically change the behavior if added in polymer matrix leading to enhanced thermal and mechanical properties without compromising on the characteristic advantages of polymers. The properties of polymer matrix composites can be tailored by tuning different material and processing parameters [3]. The purpose of the proposed work is to ‘design’ a polymer matrix composite initially that would have a combination of high thermal conductivity, and adequate tensile strength. On the other hand, the processing related material properties such as melt viscosity, processing temperature and cooling time etc. should be un-affected [49,61].

The properties of composites are the complex functions of many different parameters. These include but not limited to volume fractions, shape morphology, distribution, and interface condition of the fillers. Without a computational design methodology, one can try many different combinations of volume fractions, types and shapes of filler particles, and processing parameters for the synthesis of composite that may or may not successfully lead to the material with target set of properties. This may be lots of time consuming and

utilization of resources unnecessarily. On the other hand, analytical and/or numerical models can effectively predict the required material (such as filler type, volume fraction, distribution, shapes and particle size etc.) and processing (such as interface condition and porosity etc.) parameters [29,62,63]. Most of the literature related to the polymeric heat exchanger, mainly focuses on the design of heat exchanger without coupling to the design of composite material. In this work, the two designs i.e. of heat exchanger at macroscopic level and of composite material at microscopic level are coupled to provide both optimized heat exchanger and optimized composite material leading to overall heat transfer coefficients comparable to those of metals.

1.5 Problem statement

The behavior of any structure predicted through numerical and mathematical models significantly depends upon the constituent materials and their respective property combinations. These models are used to identify the optimum combination of material properties, which can lead to enhanced performance. However, designing of such material with optimum combination of properties is a crucial prerequisite for the development of material and the resulting structure. No systemic work is available in the open literature focusing on the all aspect of design and development. Most of the existing literature is focused on the individual aspects of the properties optimization, material design, development, and performance evaluation. There is still a lack of research in finding the interaction between various stages of material design and development as mentioned earlier. There is a strong need to integrate the experiments, theories, simulations and

computational tools for application-focused developments of engineering materials. In this work, a scheme has been proposed wherein the results of performance evaluation through numerical and mathematical models for finding the optimum material properties are coupled with the design of composite materials through properties estimation models. Accordingly, the results of computational design then lead to the development of samples followed by performance evaluation.

As stated earlier, two applications are selected in the current research for implementation of the proposed integrated approach, namely encapsulant for CPV and tubes used in heat exchangers. The purpose of modifying the backside encapsulant of CPV systems is to improve the production of electrical power and module life while TC, CTE and long-term shear modulus of the encapsulant are considered for improvement. The purpose of considering PMCs-made plastic tubes is to prove the feasibility of replacing metallic tubes by polymeric tubes in the shell and tube heat exchanger with minimum disturbance of the design and flow parameters. This methodology is systematically integrated through the objectives outlined in the following section.

1.6 Main objectives of the work

1. To develop material properties estimation tools for the application focused design of polymer matrix composites.
2. To analyze and set the target values of essential material properties for selected application through mathematical tools.
3. To design and develop polymer matrix composites with target properties.

4. To evaluate the performance of synthesized polymer matrix composite for target applications.

1.6.1 Specific objectives with respect to selected applications

1.6.1.1 Encapsulant for CPV modules

1. To set the target properties of backside encapsulant leading towards enhanced electrical power produced and increased module life of CPV system.
2. To design and develop a new composite material for the encapsulation of CPV modules.
3. To evaluate the improvement in electrical power and module life provided by the new composite material as an encapsulant for the CPV system.

1.6.1.2 Tube material for STHEs

1. To study the feasibility of replacing metallic tubes with enhanced TC polymeric composite tubes.
2. To set the target tube wall TC by analyzing the effects of different design and operating parameters of HEs upon threshold TC for a lab-scale STHE.
3. To design and develop a new composite material for the tubes of lab-scale STHE.
4. To evaluate and compare the heat transfer performance of commercially available polymer-based thermally conductive tubes to that of metallic tubes.

1.6.2 Scope of the work

This work is focused on developing an integrated material design and development methodology for designing PMCs for target applications. The improvements in the existing models are made to enable prediction for low to high volume fraction composites and with irregular shaped fillers. The design tools are validated from in-house experiments as well as from experimental data available in the literature. The methodology has been applied to the development of composite materials for backside encapsulant of CPV modules and tubes of STHes.

1.7 Dissertation Outline

The dissertation is structured such that each chapter can be read independently. However, recurring/ repeating sections/subsections are handled separately. The dissertation is organized as follows and the mapping of chapters to the achievement of objectives is presented in Figure 1-1;

The research topic is introduced in the start of chapter 1 with brief explanation of the selected applications and their functional requirements. The motivations and problem statement are also portrayed and finally the chapter 1 is concluded with objectives and scope.

Chapter 2 is written to have an overview of the current state of the art available in the literature. An objective-wise literature review is presented and explained.

The overall step-by-step research methodology for the application focused design and development of polymer matrix composites is described in Chapter 3.

Chapters 4 and 5 address objective 1 i.e. the development of properties estimation tools. Chapter 4 is related to the thermal conductivity model for composites percolating hybrid fillers while chapter 5 is related to the thermal conductivity model for composites with high volume fractions.

Chapter 6 and Chapter 7 address objectives 2, 3 and 4 pertaining to target applications. Chapter 6 is focused on encapsulation of concentrated PV modules while chapter 7 covers polymeric-composite tubes used in shell and tube heat exchanger.

Chapter 8 is to introduce some novel approaches for the development of ultra-high thermal conductivity polymer-matrix composites.

Finally, chapter 9 concludes the important outcomes of the work followed by future recommendations.

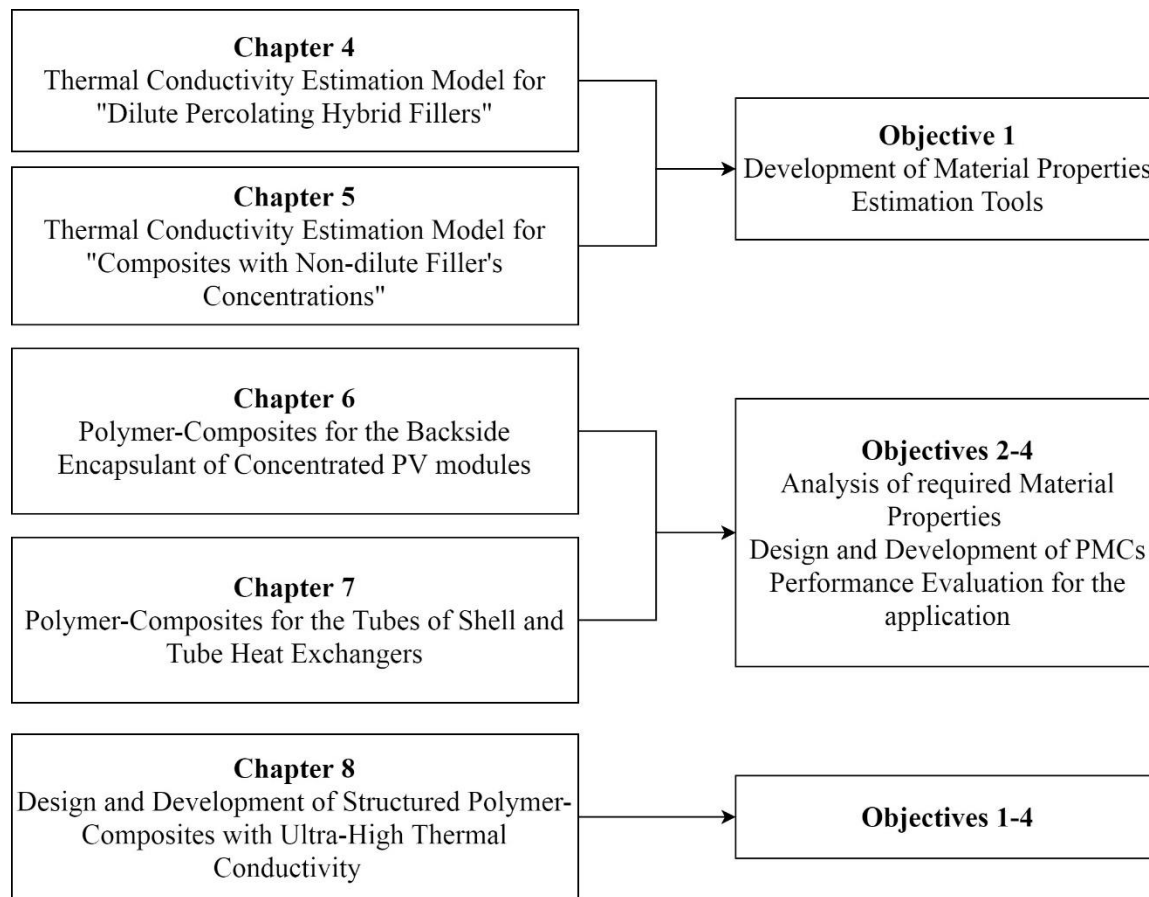


Figure 1-1 Arrangement of topics in the chapters and their mapping to the objectives

CHAPTER 2

LITERATURE REVIEW

This chapter summarizes the published work related to different steps involved in the proposed scheme of application-focused design and development of composite materials. First, the property estimation models for predicting the thermal properties of composites with focus on polymer matrix composites reported in the literature are discussed. Second, different aspects of synthesis and characterization of polymer matrix composites are explored. Finally, different methods for performance evaluation of various thermal and structural applications are discussed.

2.1 Finding the optimum material properties

Hasan et al. [42,64] have published several articles on the effect of material properties on the module life and overall performance of PV modules through FE models. In their work, a three-cell representative PV module was exposed to direct sunlight of four representative days of the year and sequentially thermal stress problem was solved. The effect of encapsulant constituent behavior on thermal stress and strain was analyzed to estimate the structural life (fatigue life) of the module. Moreover, the properties of different encapsulants such as glass transition temperature, light transmittance, ultra-violet (UV) rays-durability, volume resistivity, moisture ingress, and cost were considered to rank and compare different encapsulant materials. Finally, ionomer was recommended to be the

best neat encapsulant. However, thermal performance such as efficiency and electrical power were not considered in their work for ranking of the encapsulants. All components of PV modules are bound together by the encapsulant. The encapsulant should have comparable refractive index to the top cover, glass. The electrical resistivity (volume resistivity) and dielectric breakdown of encapsulant should be very high to resist leakage of current. Furthermore, high adhesion strength, high tearing strength, high resistance to water absorption, high resistance to UV-induced yellow-browning, and high resistance to UV and moisture -induced delamination are required for the encapsulant to be reasonably efficient [65]. There are many environmental induced phenomena, which deteriorate the properties of encapsulant with the passage of time and hence decrease the performance. Properties of encapsulant need to be optimized for the best electrical, thermal and structural performance. The evolving technology of composite materials-made encapsulants can address many environment-related degradation issues [66].

Hülsmann et al. [67] have simulated water ingress into PV modules using FE model based on the permeability and diffusion behavior of the encapsulant materials and suggested improvements in permeability related material properties and overall structure of the modules. Koehl et al. have considered absorption and transport of water into and within the module as affected by the ambient climate to estimate the hydrolysis of polymeric components, and corrosion of glass and metallic components [68]. However, finding the optimum combination of thermal and mechanical properties through numerical models has never been reported in the literature. In this work, the optimum properties of backside encapsulant for CPVs have been determined through FE models.

Lee et al. [37] have produced composites of ethylene vinyl acetate (EVA) with ceramic fillers such as SiC, Al₂O₃, ZnO, BN, AlN, and MgO up to 60 vol.% with the objective to use them as backside encapsulant. TC and volume resistivity of the composites were measured. Furthermore, a single-cell laminate was produced and tested under irradiation intensity of 1000 W/m². Finally, composites with ZnO fillers were reported to be the best in terms of high TC, volume resistivity and electrical power. On the same lines, Allan et al. [69] have produced EVA-BN composites to be used as backside encapsulant and evaluated the performance of using finite difference method of a linear solar cell model. A decrease in cell temperature and an increase electrical power (by 0.3%) was reported and this improvement was attributed to the increased TC of backside encapsulant. Sebastian et al. [70] have produced EVA composites with ZnO nanoparticles up to 4% by weight and evaluated the dielectric, optical, thermal, tensile and adhesion properties. Though all properties of the composites were found to be more suitable for encapsulation, the practical improvement in the performance of the module was not quantified.

As an outcome of this PhD research work, we have recently published and presented a work for the determination of optimum thermal and mechanical properties of encapsulant used in CPV modules [71]. The material properties (TC, G_{∞} , and CTE) for backside encapsulant are varied in the FE model and their effect on electrical power and module life is observed. The effect of increased TC appears in terms of decreased cell temperature and hence increased electrical power. Similarly, the effect of decreased CTE and G_{∞} is to reduce thermal strains and stresses on the surrounding components including inter-cell connections, which are the critical regions. A sub-model around the inter-cell connections

produced more accurate values of thermal stress and strain variations. Finally, the module life was taken as the number of on-off cycles which could cause fatigue fracture of the inter-cell connections based on Morrow's mean stress correction model for the strain life equation [72]. Conclusively from this study, it is determined that a TC of around $0.75 \text{ Wm}^{-1}\text{K}^{-1}$, $\text{CTE} < 200 \text{ K}^{-1}$ and $G_{\infty} < 0.2 \text{ MPa}$ can provide both increased production of electrical power and module life of the CPV systems as compared with neat EVA. These are the suggested properties to be achieved by the computationally designed and experimentally developed composite material in the present work. The complete analysis, design and development has become the chapter 6 of this dissertation.

Polymer heat exchangers (PHE) are accepted in many industrial and engineering applications. Polymer based heat exchangers (HE) have been studied by scientists and engineers since 1960 and since then have been magnificently employed for many applications. These applications include but not limited to heat recovery systems [44,45] HVAC & R [46–49], evaporative cooling systems [50,51], seawater desalination [52–56], solar water heating [57–59], and condensing boilers [60].

The heat transfer performance of HE greatly depends upon the TC of heat transfer surface. Therefore, metals are the materials of choice for HEs owing to their high TCs. However, it has been identified that minimum threshold TC required to achieve the heat transfer performance as high as those of metals is much less than the TCs of metals. Luckow et al. [47] have compared the performance of PHE to that of corrosion resistant titanium-HE for application in natural gas liquefaction industry. It is reported that a polymer composite with a TC of 10 W/mK can provide nearly identical heat transfer rate to that of titanium for the

typical operating conditions of target industry (natural gas liquefaction). Chen et al. [73] have developed a finned-tube cross flow HE using tubes of polypropylene (PP) or PP-based composites with different TCs for various low-temperature heat transfer applications such as heat recovery, water source heat pump and sea water desalination. A detailed analysis upon the effect of tube-TC was conducted. It was demonstrated that there exists a threshold value of TC which divides the performance curve into two parts. Enhancing the TC of polymers from around 0.2 W/mK to the threshold value of TC significantly contributes to the HE performance while further increasing TC above the threshold value of TC provides very little contribution to the HE performance. Moreover, a PHE with tubes having a TC of 15 W/mK can provide nearly 84% of the performance of copper or aluminum tube HEs under the same design and operating conditions. On the same lines, Trojanowski et al. [60] have shown through computational fluid dynamics (CFD) simulations that a TC = 2.5 W/mK of polymer composite tube is good enough to offer an effectiveness equivalent to that of stainless steel in flue gas heat recovery applications. In the present work, the author has conducted a detailed parametric studies to find out the effect of different design and operating parameters on the required minimum threshold TC [also called as target TC] in Chapter 8 of this dissertation. It is shown that the target TC greatly depends upon the flow rates on hot and cold side of the HE, while other design and operating parameters have a little effect on target TC. Therefore, in the literature cited above, the target values of TC are different from each other depending upon operating conditions and design of the HE in the particular case.

The heat transfer performance of HE greatly depends upon the TC of heat transfer surface. Therefore, metals are the materials of choice for HEs owing to their high TCs. However, it has been identified that minimum threshold TC required to achieve the heat transfer performance as high as those of metals is much less than the TCs of metals.

2.2 Current approaches used for material design

The bulk properties of composite materials are complex functions of their constituents at atomic and microstructural levels. The selection of exact constituents, which can lead to the target properties, can be very tedious and time consuming without using computational tools. Abundant efforts are going on to develop computational tools that can predict the constituents at atomic and microstructural levels for multifunctional materials with tailorable bulk properties. Numerous contributions have been made by the “Materials Genome Initiative (GMI)” to accelerate the discovery of new materials by tightly-integrated efforts in experiment, theory and computation [74]. The theories and computational models for the maximization of material performance are evolving very fast owing to the increased available computational power. For example, thermal and electrical transport in thermoelectric material can be optimized via computational models to enhance thermoelectric performance [75]. Similarly, molecular dynamics and continuum mechanics-based models have been used to explore atomic-scale deformation mechanisms in self-folding graphene reinforced composites, and to optimize the self-folded length and the interface for enhancing ductility without losing strength [76]. The development of material design models to improve magnetoelectric coupling in magnetoelectric

composites is also a fast-evolving field for energy harvesting [77–79]. Another way of computational material design is to use data-driven machine learning [80,81].

The type of computational design and simulation method depends upon the length and time scales at which the properties are required to be controlled [82]. Molecular dynamics simulations and continuum mechanics-based models are used for the cases where properties are controlled at atomic/molecular levels [76,83]. Finite element models [84–87] and homogenization schemes [84,88–90] are used to predict the properties which are controlled at the microstructural level. The purpose of the current work is to present an approach for the design and development of composite materials for the backside encapsulant of CPV systems.

Design of composite materials using computational methods is the current approach towards satisfying the demands of high performance engineering components. The concept behind the composite materials is that, two or more phases are mixed and bound together in such a way to get the best final properties out of all the phases. The multiple phases assist/support each other in property enhancement. For thermal management, as an example, high TC combined with low coefficient of thermal expansion (CTE), moderate stiffness and low cost is required and that can be achieved by making a composite of copper matrix reinforced with artificial diamond particles. Diamond particles play a dual role; not only increase the TC but also lower the CTE of copper owing to their high TC and low thermal expansion respectively [91,92].

The critical thing is that the design engineer has to identify the important variables, which play role in the development of microstructure. Microstructure constitutes the texture, distribution, interfaces and it tells whether there is a percolating phase available or not. Based on the *effect* of each variable researchers have proposed different mathematical models which are capable of predicting the mechanical and physical properties of composite systems with more or less accuracy [29,93,94]. Another method of material design is by making use of commercial FE codes with more accuracy. For example, a multi-scale approach can be used to compute the TC of nanocomposite. Multi-scale is meant for computing the TC at a micro-scale using theoretical models in a representative volume element and then projecting the micro-scale to a macro-scale using a homogenization scheme in order to tackle the effects of inhomogeneity [29].

2.3 Computational models used for predicting properties of composites

This section briefly describes the recently developed property estimation analytical models for thermal, electrical and mechanical properties like thermal conductivity (TC), electrical conductivity (EC), elastic modulus (E), coefficient of thermal expansion (CTE).

2.3.1 Thermal conductivity

Proposition of theoretical models for the prediction of thermo-physical properties of composite materials began in late 19th century, when Maxwell proposed his models capable of predicting promising results for dilute volume fraction of non-interacting spherical particles [95]. TC of composites is affected by the shape of particles, relative density, thermal contact resistance and volume fraction of the reinforcing phase. Over a period of

more than 100 years the modifications of the theoretical models have been coming up incorporating the effect of these different parameters [96]. Without going in to the details of next generations of these models, only a recently published model is described here.

Siddiqui et al. [29] have recently published their work for the prediction of TCs of nanocomposites. Their work is a unique mix of analytical and numerical methods. The analytical part is capable of handling multiple inclusion types, different shapes, anisotropy, nanometer sized inclusions while the non-uniform dispersion is handled by a two scale approach. Using effective medium theory (the analytical part), the TC was determined at each point of representative volume element (RVE) and then computational homogenization was used to numerically estimate the effective TC of the composite. Their analytical part states the equations from (2-1) to (2-10).

$$k_{eff,11} = k_{eff,22} = k_{mat} \frac{2 + \sum_{i=2}^N \varphi^i \left[\beta_{11}^i (1 - L_{11}^i) (1 + \langle \cos^2 \theta \rangle^i) + \beta_{33}^i (1 - L_{33}^i) (1 - \langle \cos^2 \theta \rangle^i) \right]}{2 - \sum_{i=2}^N \varphi^i \left[\beta_{11}^i L_{11}^i (1 + \langle \cos^2 \theta \rangle^i) + \beta_{33}^i L_{33}^i (1 - \langle \cos^2 \theta \rangle^i) \right]} \quad (2-1)$$

$$k_{eff,33} = k_{mat} \frac{1 + \sum_{i=2}^N \varphi_i \left[\beta_{11}^i (1 - L_{11}^i) (1 - \langle \cos^2 \theta \rangle^i) + \beta_{33}^i (1 - L_{33}^i) \langle \cos^2 \theta \rangle^i \right]}{1 - \sum_{i=2}^N \varphi_i \left[\beta_{11}^i L_{11}^i (1 - \langle \cos^2 \theta \rangle^i) + \beta_{33}^i L_{33}^i \langle \cos^2 \theta \rangle^i \right]} \quad (2-2)$$

$$\langle \cos^2 \theta \rangle^i = \frac{\int \rho^i(\theta) \cos^2 \theta \sin \theta d\theta}{\int \rho^i(\theta) \sin \theta d\theta} \quad (2-3)$$

$$L_{11}^i = L_{22}^i = \begin{cases} \frac{(p^i)^2}{2((p^i)^2 - 1)} - \frac{p^i}{2((p^i)^2 - 1)^{1.5}} \cosh^{-1} p^i, & \text{for } p^i \geq 1 \\ \frac{(p^i)^2}{2((p^i)^2 - 1)} + \frac{p^i}{2(1 - (p^i)^2)^{1.5}} \cos^{-1} p^i, & \text{for } p^i < 1 \end{cases} \quad (2-4)$$

$$p^i = a_3^i / a_1^i \quad (2-5)$$

$$L_{33}^i = 1 - 2L_{11}^i \quad (2-6)$$

$$\beta_{kk}^i = \frac{k_{c,kk}^i - k_{mat}}{k_{mat} + L_{kk}^i (k_{c,kk}^i - k_{mat})} \quad (2-7)$$

$$k_{c,11}^i = \begin{cases} k_{inc}^i / (1 + \gamma_{11}^i L_{33}^i k_{inc}^i / k_{mat}), & \text{for platelet inclusions} \\ k_{inc}^i / (1 + \gamma_{11}^i L_{11}^i k_{inc}^i / k_{mat}), & \text{for other shapes} \end{cases} \quad (2-8)$$

$$k_{c,33}^i = \begin{cases} k_{inc}^i / (1 + \gamma_{33}^i L_{11}^i k_{inc}^i / k_{mat}), & \text{for cylindrical inclusions} \\ k_{inc}^i / (1 + \gamma_{33}^i L_{33}^i k_{inc}^i / k_{mat}), & \text{for other shapes} \end{cases}$$

$$\gamma_{kk}^i = \begin{cases} \alpha_k (2 + 1/p^i), & \text{for } p^i \geq 1 \\ \alpha_k (1 + 2p^i), & \text{for } p^i < 1 \end{cases} \quad (2-9)$$

$$\alpha_k^i = R_{TB}^i k_m^i / a_k^i \quad (2-10)$$

The superscript i represents the associated property with i th inclusion. The other parameters are listed as follows.

ϕ^i	Volume fraction of i th inclusion
$\langle \cos^2 \theta \rangle^i$	Orientation factor of i th inclusion
p^i	Aspect ratio of i th inclusion
a_k^i	Particle radius of i th inclusion in k th direction
R_{TB}^i	Interfacial thermal resistance of i th inclusion with the matrix
k_{inc}^i	Thermal conductivity of i th inclusion
k_{mat}	Thermal conductivity of the matrix

There model has a few limitations as listed below;

1. Their model is only valid for dilute volume fractions of inclusions where the particles are far much away from each other and do not interact.
2. The model is designed for prolate to oblate morphology of the inclusions, which is seldom the real case. Most of the time the inclusions particles are of random and irregular shapes.
3. For handling the nanometer-sized inclusions, it involves complex estimations of mean free path with an assumption that a heat carrier of matrix collides with all the inclusion particles in a given volume. In this way, the model requires input of a few parameters, which are hard to determine experimentally or empirically.

2.3.2 Elastic modulus and coefficient of thermal expansion

Akhtar et al. [62] have found a good agreement between the experimentally measured CTE and the one predicted by mean field homogenization of Mori-Tanaka as outlined by Benveniste and Dvorak in a book chapter of the book titled “Micromechanics and Inhomogeneity” [97]. According to the mean field homogenization scheme the effective properties are estimated using the equations (2-11) to (2-13).

$$\overline{C_{eff}} = \varphi_{inc} C_{inc} : A_{inc} + (1 - \varphi_{inc}) C_{mat} : A_{mat} \quad (2-11)$$

$$\alpha_{eff} = \alpha_{inc} I_2 + \varphi_{inc} (C_{inc}^{-1} - C_{mat}^{-1}) W ((1 - \varphi_{inc}) I_4 + \varphi_{inc} W)^{-1} \quad (2-12)$$

$$\begin{aligned} A_{mat} &= [(1 - \varphi_{inc}) I_4 + \varphi_{inc} B_a]^{-1} \\ A_{inc} &= B_a : A_{mat} \\ B_a &= [I_4 + S : C_{mat}^{-1} (C_{inc} - C_{mat})]^{-1} \end{aligned} \quad (2-13)$$

$\overline{C_{eff}}$ is the homogenized stiffness tensor, α_{eff} is the effective CTE, C_{inc} and C_{mat} are the stiffness tensors of inclusion and matrix respectively, $W = C_{inc} A_{inc} C_{mat}^{-1}$, A_{mat} and A_{inc} are the strain localization tensors, I_2 and I_4 are the 2nd order and 4th order identities respectively, and S is the Eshelby's tensor.

2.4 Experimental approaches for enhancement of composites' properties

Lee et al. [98] have added AlN, wollastonite, SiC and BN fillers in HDPE matrix to produce PMCs with high TCs. They added single and hybrid fillers with low and high volume contents and produced composite samples with injection molding and compression molding techniques. They concluded that use of hybrid fillers and of large particle size is more effective for enhancement of TC. Similarly, synergistic enhancement of thermal and mechanical properties by adding multi-walled carbon nano-tubes (MWCNTs) and graphene nano platelets (GNPs) in epoxy matrix has been reported by Yang et al. [99]. They used functionalized MWCNTs with a diameter of around 20 nm and GNPs with thickness of 1 to 15 nm as single and hybrid fillers. The MWCNTs and GNPs were suspended in tetra hydro furan (THF) followed by dissolution of epoxy oligomer in this suspension. The solution was homogenized by ultra-sonication and then THF was evaporated in a vacuum oven. Then the mixture was homogeneously mixed with the epoxy hardener to make the final composite. The hybrid composite was observed to demonstrate around 36% and 147% improvements in tensile strength and TC, respectively. Similarly many other efforts have been reported for enhancement of TC in PMCs [99]. CoolPoly ® D-series is the trademark of Celanase for high TC and high electrical resistivity polymer matrix series; they claim a TC of up to 10 W/mK in a liquid crystalline polymer (LCP) based composite i.e. 5000% improvement [100].

For the selected applications in this research, i.e. for encapsulant of CPVs and tubes of STHs, primarily the TC needs to be enhanced with tailorable mechanical properties. Sebastian et al. [70] have reported significant increase in the TC of EVA composites by reinforcing with ZnO nanoparticles. In their work, ZnO nanoparticles were produced by sol-gel method and used as fillers in EVA matrix. ZnO has a combination of high TC and very low electrical conductivity. The matrix and ZnO nanoparticles were homogeneously mixed by solution compounding followed direct probe sonication and drying at 50 °C. Dielectric constant, dielectric loss, optical absorption, thermal stability, thermal diffusivity, TC and tensile properties of the samples were reported. The important thing related to the subject of this work is that increasing concentration of ZnO in EVA increased TC up to 7.98 W/mK in a 4 wt% composite while reduced electrical conductivity and retained tensile properties compared to pure EVA [70]. The EVA/Ceramic particulates composite particularly suits to the intended application of this work due to its unique combination of high TC, low electrical conductivity, and reasonable tensile properties. Hence, an inclusion similar to ZnO i.e. having high TC and low electrical conductivity is a potential reinforcement for the intended application of this work. A similar work has been published by Allan et al. [69] to prove the importance of replacing backside encapsulant by a thermally conductive composite layer. Composites of EVA with BN fillers up to 60% by weight were developed and followed by performance evaluation through finite different model of a linear geometry. Ghose and his co-workers [101] added different reinforcement in EVA matrix with the objective to increase TC without losing its flexibility for liquid cooling ventilation garments (LCVG) in space-craft applications. The composites were

produced with single and multiple filler types (hybrid composites) using Brabender mixer followed by extrusion through a laboratory mixing extruder. Among different reinforcements used were functionalized multiwalled carbon nanotubes (MWCNTS), carbon nano fibers (CNF), expanded graphite (EG), metallized CNFs, Nickel strands, boron nitride (BN) and Al powders. The maximum TC observed was to be 5.55 W/mK in a composite with 40 wt% EG parallel to the direction of extrusion [101]. Due to their high flexibility and glass transition behaviors, polymers are easily tailorable in terms of mechanical, thermomechanical and viscoelastic properties. Kuila et al. [102] and Yuan et al. [103] have reported the tailoring of mechanical properties via single and hybrid nano fillers, respectively.

2.5 Development of Polymer matrix composites

Development of composite materials, in general, constitutes mixing, consolidation and characterization. For PMCs, most of the methods used for mixing of components involve melt mixing followed by extrusion, casting or compression molding in desired shapes. The characterization involves measuring the properties desired for the intended application and relating the obtained properties to the microstructural features.

2.5.1 Production methods for PMCs

Different methods for the production of polymer matrix composites have been reported in the literature. The production method must be capable of handling and then uniformly distributing the inclusions. Among different methods for the production of thermoplastic PMCs melt mixing followed by compression molding is the most widely used method

reported in the literature. Melt mixing may be carried out by using one of twin screw extruder, two roll mill or Brabender Plasticoder (mixer). However, mixing may also be carried out by cryo-milling or solution casting. As an example, H. A. Khonakdar [104] melt-mixed surface treated nano-silica in the blends of EVA/LLDPE at different compositions using twin screw extruder and analyzed the effects on rheological, crystallization and thermal degradation properties of the composites. Brabender mixer was used by Sabet et al. [105] who produced composites of EVA with CNTs. In this work, effect of CNT addition on melt flow, tensile properties, electromagnetic shielding, electrical resistivity, thermal stability, and resistance to flammability was studied. Lee et al. [37] used two roll mill for making composite of SiC, ZnO, AlN and different other particulates ceramics in EVA matrix. They analyzed thermal conductivity and electrical resistivity of the produced composites. In a few others studies [70,106] researchers have used solution casting method for mixing and compounding. One of them used toluene while the other used tetrahydrofuran (THF) as solvents.

2.5.2 Surface treatment methods for inclusions

The effectiveness of a composite is proportional to the effectiveness of flux transfer from the matrix to the inclusions or vice versa. The flux may be of any type, for example stress or heat flux. Therefore, it is obligatory for the inclusions to be compatible with the matrix. The increasing compatibility is mostly meant for increasing adhesion between the matrix and inclusion particles. For the case of polymers, where the structure is composed of long chains of non-polar molecules, the inter-molecular forces are only the weak Van der Waals forces while the attraction for the foreign molecules/atoms follows the rule “like dissolves

like”. That is, the polymer molecules (being non-polar most of the time) will only attract and be compatible with the foreign molecule/atom if it is non-polar. On the other hand, the inclusions with high strength are generally polar or ionic in nature and hence possess weak compatibility with the polymers.

Normally, in making composite the particles of reinforcement are held by the continuous phase of matrix by only physical bonds. The physical bonds may be due to one or both of friction and Van der Waals forces and obviously these are weak bonds. It is well-established concept that in order to improve the properties of a composite, the loads (structural, thermal or electrical) must be effectively transferrable between the matrix and the reinforcements. In addition, for the effective transferability of loads to be achieved, the interface must be very strong for example in steel reinforced concrete; the interface bond is naturally very strong and hence the property enhancement is very effective. Ideally, if the interface (adhesive force) is stronger than the cohesive forces of the individual components (matrix and reinforcement) then the load transferability would be at its peak.

Most of the ceramic materials exist in their most stable form and therefore theoretically they are the least reactive materials but hydrophilic. On the other hand, polymers are hydrophobic due to their nonpolar nature. Therefore, a polymer/ceramic composite demands a surface treatment of the ceramic inclusions so that they become compatible with each other. This intermediate step cannot only improve the interaction or the load transferability between matrix and reinforcement but also help in retaining the structural and thermal properties over a prolonged period of thermal and structural stress cycling.

Ansari et al. [107] have added untreated and surface treated cellulose nanocrystals in a matrix of polyvinyl acetate (PVAc) and compared the effect on mechanical properties. It was observed that surface treatment dramatically improved the tensile strength of the composites. Similarly W. Di et al. [108] have used functionalized carbon fibers as reinforcements in EVA matrix and studied the electrical properties. They quantitatively evaluated the interaction of matrix with carbon fibers by a solvent extraction method and showed that the functionalization can improve the matrix/fiber interaction significantly and hence improve the interface-dependent properties of composites.

CHAPTER 3

RESEARCH METHODOLOGY

The flow chart of various steps involved in the design and development of polymer matrix composites is shown in the Figure 3-1. The flow chart is arranged in such a way that the boxes on left hand side (red colored texts) show computational work, while the boxes on right hand side (blue colored texts) explain experimental work.

3.1 Development of material properties estimation tools

The first objective of the dissertation is to develop material design tools that could predict the essential thermal properties of polymer composites taking into consideration two important aspects namely percolating hybrid fillers and non-dilute filler concentrations in polymer matrices. These models are validated through experiments. The derivation of these models have been explained in Chapters 4 and 5, respectively.

3.2 Finding the optimum combination of material properties

Mathematical models can be developed based on the physics of the problem. A steady state heat transfer mathematical model of concentrated photovoltaics (CPVs) can be developed based on heat balance equations. Similarly, well-known mathematical models are available in for solving heat transfer problems in shell and tube heat exchangers (STHEs) such as Kern and Bell-Delaware models. Alternatively, a finite element model of the problem can be solved with more accuracy. In the first step, the effect of different material properties on the overall performance of the system using these models is studied with the objective to maximize the performance. This step leads to set values of target properties for material design.

In this work, the thermal stress problem of CPVs was solved in numerically in three-dimensions using COMSOL Multiphysics. The detailed model, geometry, governing equations, life estimation model, meshing and boundary conditions have been explained in Chapter 6 of this dissertation. The problem was solved at different values of thermal conductivity (TC), long-term shear modulus and coefficient of thermal expansion to observe their effect on electrical power and module life.

The heat transfer problem of STHEs was solved using Kern and Bell-Delaware methods [109]. The equations of these models have been described in Chapter 7 of this dissertation. Initially, the problem was solved for a commercial STHE to find out the minimum threshold TC [target TC] required to achieve heat transfer performance comparable to that of a metallic STHE. Then the model was used to probe the effect of different design and

operating parameters on the performance and target TC and finally to design and optimize a lab scale STHE.

3.3 Material design using properties estimation models

The purpose of this step is to identify the type, compositions, and particle's geometry of the fillers, which can be added to the polymer matrix for achieving the target properties of selected applications. The details of material design pertaining to each particular application have been included in Chapters 6 and 7. The general material design methodology is described here.

Initially, the prospective matrices and fillers are listed along with their properties. In the initial listing, only those matrices and fillers are included, which are suitable for the application in terms of basic requirements. For example, the list of matrices and fillers includes only those with high volume resistivity. Then the equations of related properties estimation models (section 2.3) are solved to determine the range of material parameters (compositions, volume fractions, and particle's geometry of the filler and matrix) that is expected to offer all the target properties. The effectiveness of the same material design scheme has been recently reported by Akhtar et al. [62] for composite of Ni-droplet fillers in alumina matrix.

3.4 Development of composite materials

The development of composites include all the steps starting from raw materials to the characterization and measurement of material properties. A schematic flow chart of the steps involved in the development of composites is shown in Figure 3-2.

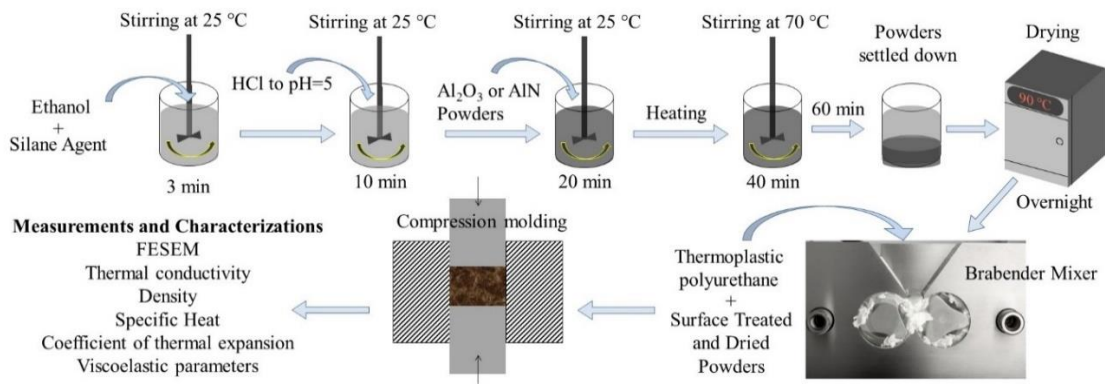


Figure 3-2 Schematic diagram for the route of composite sample's development

3.4.1 Surface treatment

The importance of surface treatment has been described in the section 2.5.2 concluding that a surface treatment is a pre-requisite for fillers in a polymer matrix. A surface treatment is carried out by refluxing the filler particles with a solution of the surface treatment chemical reagent. In this work, the ceramic fillers were treated by silane based reagents. During the treatment, silane end of the molecules is attached to the surface of filler particles, while the other end is connected to the polymer matrix during melt-mixing.

3.4.2 Synthesis

The most commonly used method for the synthesis of polymer matrix composites is by melt-mixing using internal mixers such as Bradender Mixer [105,110–113]. However,

melt-mixing can also be performed using two roll mill [114–116], and twin screw extruder. Polymer matrix composites can also be compounded via cryo-milling [117], and solution casting [70,106,118]. According to the literature, melt-mixing through internal mixers offer the best results in terms of handling high density fillers, avoiding contaminations, homogeneity of mixing, and producing bulk samples. On the other hand, Cryo-milling breaks the molecular chains during high speed mixing at cryogenic temperatures. Solution casting requires costly solvents and cannot handle large volume fractions of fillers [119,120]. Therefore, melt-mixing was selected for compounding the PMCs in this work. The temperature, speed and duration of mixing experiments have been mentioned in each Chapter.

3.4.3 Compression Molding

The output of melt-mixing is in the form of irregular shaped lumps that cannot be used for any type of testing. Therefore, the pre-weighed amount of the lumps, depending upon the required thickness was hot-compressed to make cylindrical samples (ϕ 31 mm) that could be cut further to get the desired shape for a particular measurement. Other hot-compression parameters have been outlined in each chapter.

3.4.4 Testing / Characterization

Measurement of target properties such as TC, long-term shear modulus, coefficient of thermal expansion, elastic moduli and yield strength is required to validate the material design. However, the other properties like heat capacity, density and viscoelastic parameters were also evaluated to be used as inputs finite element model the structure.

Moreover, the developed composites were characterized for their microstructures using FESEM. The machines used for different characterizations are listed in Table 3-1.

Table 3-1 List of equipment used for used in testing and characterization of synthesized samples

Property to be evaluated	Used equipment / machine
Long term shear modulus and viscoelastic behavior	Mettler Toledo DMA/SDTA 1+ - Dynamic Mechanical Analyzer
Coefficient of thermal expansion	Mettler Toledo TMA/SDTA 2+ - Thermo Mechanical Analyzer
Thermal Conductivity	TCi Thermal Conductivity Analyzer by C-Therm Technologies Ltd., Canada
Tensile / compression stress – strain behavior	30 kN Instron Universal Testing Machine
Heat capacity at constant pressure	Mettler Toledo DSC 3+ - Differential Scanning Calorimeter
Density	Archimedes Principle
Microstructural examination	FESEM Tescan Lyra 3 Olympus Metallurgical Microscope

3.5 Constitutive relationships and Performance Evaluation

The last objective of this work is to evaluate the performance of the material for the targeted application. The performance evaluation through thermal stress finite element problem of three-cell CPV laminate required complete set of thermomechanical properties as inputs. Particularly, the viscoelastic behavior of composite encapsulant is very important to affect the thermal stresses and strains in the surrounding components. The selected sample was subjected to measurement of storage modulus and damping factor by dynamic mechanical

analyzer. The measurements were conducted by generating isotherms of frequency scans at different temperatures. Then the curves were horizontally shifted on a log scale to generate the Master Curve. Then the master curve was fitted to the equation of generalized Maxwell model for 9 branches, which determines the Prony-parameters. The detailed determination of Prony-parameters is presented as part of Chapter 6. Development of constitutive behavior was not required for performance evaluation of STHEs since it was based on mathematical models and therefore elastic modulus and yield strength are required to be measured.

In the performance evaluation, the measured properties and the developed constitutive relationships are the inputs to the model used in finding the optimum combination of material properties. The thermal stress finite element model of encapsulant of CPVs and Bell-Delaware method of STHE was reused to evaluate the developed material in terms of performance. Furthermore, for STHE, a lab-scale model with single tube was developed to conduct heat transfer studies using a commercially available thermally conductive polymer-composite tube and the results were compared with a copper tube under same operating conditions.

CHAPTER 4

THERMAL CONDUCTIVITY MODEL AND DESIGN OF

POLYMER NANOCOMPOSITES WITH

PERCOLATING HYBRID FILLERS

A percolating network of hybrid fillers can provide significant synergic enhancement of thermal conductivity in polymer matrix composites. Especially, when platelets and fibers of high aspect ratios are mixed to form a percolating network, the percolation thresholds are small. However, the optimum ratio of platelets to fibers must be acquired for the maximum synergic enhancement. In this work, a thermal conductivity estimation model for composites with hybrid percolating fillers in dilute concentrations has been proposed and used to design the best composition of polysulfone (PSU) matrix - 10% Graphene nano-platelets (GNPs) / Carbon nano-tubes (CNTs) composite for the maximum thermal conductivity. Calibration of the proposed computational model with several experimentally measured thermal conductivities of polymer matrix-hybrid nanocomposites discloses the composition where maximum synergic effect / maximum thermal conductivity is expected. For the specific PSU–10% GNPs + CNTs hybrid composites synthesized in this study, the composition with maximum thermal conductivity as designed by the model is PSU / 8.4% GNPs / 1.6% CNTs. The samples produced experimentally around this composition have

shown close agreement with the predictions of the model. Sensitivity analyses and parametric studies conducted on the model highlight that the dimensional parameters and the interface resistance of the fillers are the most sensitive to enhance the effective thermal conductivity.

4.1 Introduction

Continued development in polymer based materials has enabled them to replace their metallic counter parts in many applications. The low density, excellent corrosion resistance and small carbon footprint are the primary advantages of polymeric materials. Polymer based materials are now available with high mechanical strength and high temperature stability. Polysulfone (PSU) is among those polymers, which can maintain their high strength, and high stiffness up to 150 °C and it has a glass transition temperature of higher than 190 °C. In addition, it is biocompatible combined with high resistance to change by many chemicals and radiations and hence can be sterilized repeatedly. However, the problem in PSU is that it has a low thermal conductivity [121]. The research community is in pursuit of finding a tailorable material for application where high thermal conductivity combined with high strength is desired, for example in heat exchangers. Similarly, high thermal conductivity materials are desired for thermal management in modern semiconductor devices where increased level of miniaturization has caused increased power densities [122,123]. Therefore, in this work the target was to enhance the thermal conductivity of PSU.

Traditional composites for thermal management applications include composites with large volume fractions of high conductivity ceramic fillers such as Alumina, Aluminum Nitride, Boron Nitride [37,124], Silicon Nitride and their hybrid mix [125,126]. These composites have the disadvantages of high cost and reduced processability. The use of reduced-dimension carbon fillers such as carbon nanotubes (CNTs), graphite nanoplatelets (GNPs) and graphene in polymer matrices have shown thermal conductivity enhancements greater than 1000% for GNPs and Graphene composites and conductivity enhancements of 100-200% for CNTs [127–130]. The use of hybrid fillers in a polymer matrix has also shown good promise for enhanced thermal conductivity at low concentrations. Three different types of hybrid fillers in polymer matrices have been widely reported in the literature. These include using CNTs with nanoparticles [7,131], Graphene or Graphite nanoplatelets (GNPs) with nanoparticles [8,132–134] and CNTs with Graphene or GNPs [99,135–140]. The use of other types of nanotubes and nanoplatelets in a polymer matrix composite has also been reported [141]. Moreover, the thermal and structural properties may also be enhanced by introducing a reaction layer at the matrix/filler interface [142].

The key to synergic enhancement in effective thermal conductivity is to develop a percolating network or so-called segregated structure of high thermal conductivity fillers in the final product [10–12]. Gu et al. [143,144], for example, have reported thermal conductivities up to 4.6 W/mK where the composites were developed by a two-step methodology of ball milling and hot pressing. Among different approaches reported in the literature, one way is to use expandable graphite (EG). Once expanded, EG can form a fully connecting skeleton and lead to a very high thermal conductivity [18,19]. Similarly,

high thermal conductivity has been reported by using Si_3N_4 foam as percolating filler in epoxy matrix [21]. A very high thermal conductivity can also be achieved by making a percolating network of graphene nanoparticles via specialized alignment procedure [142]. Different research groups [127,145] showed that in polymer composites with nanotube-nanoplatelet hybrid fillers, the nanoplatelets formed a percolating network through the nanotubes giving the synergic enhancement in the effective thermal conductivity of the composite. They showed that maximum thermal conductivity enhancement is achieved at an optimum ratio of the fillers in the hybrid mix. This optimization can either be carried out experimentally or numerically using prediction models for effective thermal conductivity.

Limited work has been reported on the thermal conductivity estimation models for polymer composites with hybrid fillers. Chu et al. [139] presented a modified effective medium theory model based on earlier work by Nan et al. [28] for the estimation of effective thermal conductivity of composites with hybrid fillers. Their model considered the effect of percolation but failed to identify the optimum ratio of hybrid fillers. Chen et al. [146] formulated a two-step approach based on thermal resistance method and effective medium theory for estimating the effective thermal conductivity of composites with hybrid fillers. Their model captures the effect of changing filler's ratio on the effective thermal conductivity of the composite but results in a large error when the nanotube to nanoplatelet ratio is either too low or too high. J. Yu et al. [145] modified the Mori-Tanaka scheme to include the effect of multiple fillers for the estimation of thermal conductivity. They found waviness of nanofillers the most sensitive for effective thermal conductivity. Finally,

Siddiqui and Arif [29,147] have recently published their models for the estimation and optimization of thermal conductivity in hybrid fillers – polymer matrix composites.

The number of experiments in the development of composite materials can be minimized by material design scheme. Material design scheme is a type reverse engineering approach i.e. to use the available models for computing the required filler, its composition and particle size etc that can lead to achieve the expected structural and thermal properties. Akhtar et al. [62], for example, have reported a design scheme for composite materials. Using the predictions of appropriate properties estimation models, they estimated the required particle size and volume fraction of filler for reaching a targeted set of structural and thermal properties. Similar to the Akhtar et al.'s work material design scheme can be used to find out the optimum ratio of fillers in a percolating network of thermally conductive hybrid-fillers. Such a material design scheme has never been found in the literature for maximizing the thermal conductivity with percolating hybrid fillers.

In the current work, a model for estimating the effective thermal conducting of polymer-composites reinforced by percolating hybrid fillers is proposed used to design and develop PSU matrix composites with GNPs and CNTs (platelets + fibers). The objective was to design the composition with maximum thermal conductivity using the proposed estimation model. The design methodology is portrayed and experimentally verified. To understand the effect of different parameters on effective thermal conductivity of hybrid-composites, sensitivity analyses and parametric studies are conducted and explained with theoretical reasoning.

4.2 Computational model

Siddiqui and Arif [29] have published their model for computing the effective thermal conductivity of polymer matrix composites with multiple fillers. In the present work, the aforementioned model is modified to work for percolating fillers by including the effect of percolation and reported as an outcome of this dissertation [25]. To include the percolation effect, the equation is modified with a critical exponent “ n ”, which is used with the filler that makes the skeleton of percolating network i.e. platelets in this work. After this modification, the equation takes the form of equation (4-1).

$$\begin{aligned} K_{eff,11} &= K_{eff,22} = K_m \frac{2 + \varphi_1^n X_{11}^1 + \varphi_2 X_{11}^2}{2 - \varphi_1 Y_{11}^1 + \varphi_2 Y_{11}^2} \\ K_{eff,33} &= K_m \frac{1 + \varphi_1^n X_{33}^1 + \varphi_2 X_{33}^2}{1 - \varphi_1 Y_{33}^1 + \varphi_2 Y_{33}^2} \end{aligned} \quad (4-1)$$

where, the double indices 11, 22, 33 represent the global x, y and z directions while the single indices 1 and 2 relate the parameter to platelets and fibers respectively. The subscripts *eff* and *m* refers to the effective property of composite and matrix while K and φ represent the respective thermal conductivities and volume fractions respectively. The parameters X_{kk}^i , Y_{kk}^i and the exponent n on φ_1 are described in the subsequent paragraphs. The latter is to include the effect of percolation while the others are to include the effects of intrinsic thermal conductivities of fillers, their shapes, orientation, particle size, particle size distribution, and thermal interface resistance.

$$\begin{aligned}
X_{11}^i &= \beta_{11}^i (1 - L_{11}^i) \left(1 + \langle \cos^2 \theta \rangle^i\right) + \beta_{33}^i (1 - L_{33}^i) \left(1 - \langle \cos^2 \theta \rangle^i\right) \\
Y_{11}^i &= \beta_{11}^i L_{11}^i \left(1 + \langle \cos^2 \theta \rangle^i\right) + \beta_{33}^i L_{33}^i \left(1 - \cos^2 \theta\right)^i \\
X_{33}^i &= \beta_{11}^i (1 - L_{11}^i) \left(1 - \langle \cos^2 \theta \rangle^i\right) + \beta_{33}^i (1 - L_{33}^i) \left(\langle \cos^2 \theta \rangle^i\right) \\
Y_{33}^i &= \beta_{11}^i L_{11}^i \left(1 - \langle \cos^2 \theta \rangle^i\right) + \beta_{33}^i L_{33}^i \langle \cos^2 \theta \rangle^i
\end{aligned} \tag{4-2}$$

$$n = m + \eta \exp(-10\varphi_2 / \varphi_{total}) \tag{4-3}$$

Where, i refers to i^{th} filler; $i=1$ for platelets and $i=2$ for fibers. The other parameters are listed as follows: β_{kk}^i = Non-dimensional thermal conductivity enhancement factor in filler's local kk direction and is a function of some materials and processing parameters, L_{kk}^i = well-known shape factors of filler's local kk direction and $\langle \cos^2 \theta \rangle^i$ = the effect of orientation, as described in references [28,147]. Lastly, η = critical exponent to include the effect of percolation, where in equation (4-3), m and η are model parameters, and φ_{total} is the total fillers volume fraction being added. Parameter m is defined in the range 0.8-0.9 while the parameter η is given by the equation (4-4).

$$\eta = 0.1 \times \left(1 - \frac{K_{eff}^{fibers} - K_{eff}^{platelets}}{K_{eff}^{fibers}} \times \frac{1}{100\varphi_{total}} \right) \tag{4-4}$$

where K_{eff}^{fibers} and $K_{eff}^{platelets}$ are the effective thermal conductivities of composites with single fillers; either fibers or platelets with a volume fraction equal to φ_{total} . This is worth noticing that the model used in this work is applicable to any type of matrix (polymers / ceramics /

metals) similar to the original models of Nan et al. [28] and Siddiqui et al. [29] with dilute concentrations ($< \sim 15$ volume %) of fillers. The Nan's model [28] is for composite with single type of filler and the Siddiqui's Model [29] is for composites with non-percolating hybrid fillers. Later, they extended their model to work for percolating hybrid fillers [147], where the fillers #1 and 2 are supposed to be platelets (aspect ratio $\ll 1$) and fibers (aspect ratio $\gg 1$) respectively.

4.3 Materials and methods

4.3.1 Materials

PSU was supplied by *Sigma-Aldrich*, USA. COOH-functionalized multi-walled carbon nanotubes (CNTs) were purchased from *Cheap Tubes Inc.*, USA and used as is. The graphene nanopowder (GNP) also referred as graphene nanoplatelets, was purchased from *Graphene Supermarket*, USA with the trade name "AO-3". The electron images of multi walled CNTs and GNPs are shown in Figure 4-1.

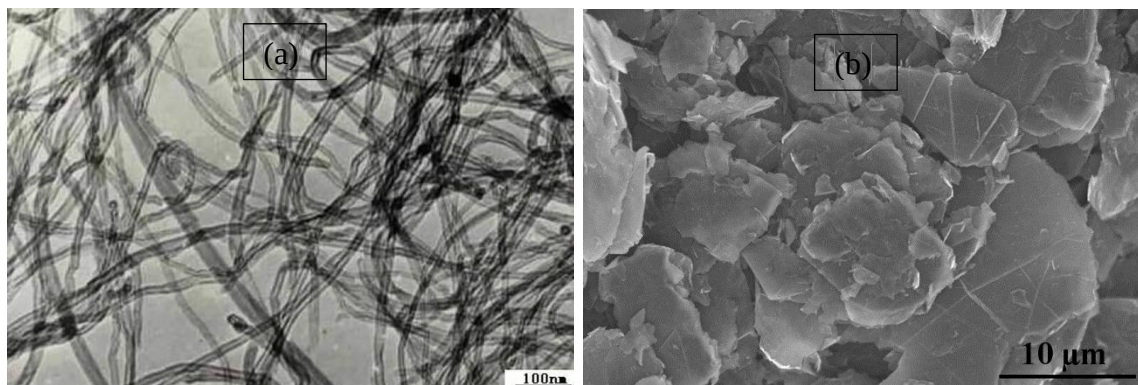


Figure 4-1 Electron images of particulate fillers: (a) TEM image of multi walled CNTs from Cheap Tubes Inc. ¹; SEM image of Graphene Nano Powder (AO-3) from Graphene Super Market Inc. ²

4.3.2 Material design scheme

The first step in material design is to calibrate the model with the experimental results. Initially four compositions; two with single fillers while the others with hybrid fillers were produced as listed in Table 4-1 for calibration in a range of 10 weight % filler. The input variables to the model are calibrated so that the predictions of the model are in close agreement with the experimental results. Once calibrated the model predicts the variation of effective thermal conductivity across a wide range of compositions. The maximum in this curve locates the maximum of synergic effect i.e. with maximum thermal conductivity.

¹ <https://www.cheaptubes.com/product/cooh-functionalized-graphitized-multi-walled-carbon-nanotubes-10-20nm/>

² <https://graphene-supermarket.com/Graphene-Nanopowder-AO-3-12-nm-Flakes-100-g.html>

Table 4-1. Compositions for hybrid nanocomposites in PSU matrix

Sr #	Weight % PSU	Vol% PSU	Weight % CNTs	Vol% CNTs	Weight % GNP	Vol% GNP	Name
1	100	100	0	0	0	0	PSU
2	90	91.04	10	8.96	0	0	0GNP10CNT
3	90	91.67	8	7.22	2	1.12	2GNP8CNT
4	90	92.94	4	3.66	6	3.40	6GNP4CNT
5	90	94.25	0	0	10	5.75	10GNP0CNT

4.3.3 Methodology of composite development

According to Table 4-1 each composite sample was produced with a filler weight fraction of 0.1 in a composite weight of 1.00 g, where two samples were produced only for compositions with hybrid fillers (2GNP8CNT and 4GNP6CNT). The entire process follows a three-step methodology. The required weight of CNT+GNP (0.10 g) was added in 10 mL of N-methyl-2-pyrrolidone (NMP) and sonicated with a probe-type sonicator for 2 hours to have a stable suspension within the solvent. Secondly, the required weight of PSU (0.90 g) was added into the suspension and dissolved. The dissolution was carried out by magnetic stirrer at 50°C for 12 hours. It is important to note that the PSU was completely dissolved in less than 4 hours for each composition; however, the stirring was continued for the mentioned time to have a fully homogenized mixture. Thirdly, the homogenized solution was cast in petri dishes and dried in a two-step heat treatment. Initially, the casted samples were kept at 80°C for 24 hours in a vacuum oven to slowly evaporate the solvent. Then the residual solvent, which was less than 6 % by weight, was evaporated by keeping the samples at 120°C for another 24 hours in vacuum oven. For reference, the neat PSU sample was also processed through the same procedure of dissolving and casting.

4.3.4 Characterizations: thermal conductivity, SEM, XRD

The thermal conductivity of the casted films was measured using *TCi Thermal Conductivity Analyzer* by *C-Therm Technologies Ltd.*, Canada, which uses the modified transient plane source method (MTPS) for the measurement. For microscopy, the films were broken under tensile force gently and the fractured surfaces were observed by field emission scanning electron microscope (FESEM) after gold sputtering of around 5 nm. The FESEM used was *Lyra3* of *Tescan*, Czech Republic and operated at an accelerating voltage 20 kV. The crystallinity status of the neat polymer and composites was observed by scanning the samples using *D8 Advance X-ray Powder Diffractometer* of *Bruker*.

4.4 Experimental Results

4.4.1 Thermal conductivity

Table 4-2 shows the measures of thermal conductivity of the samples produced for the calibration of model where the thermal conductivities of 2GNP8CNT and 4GNP6CNT are the average values. The synergic effect of hybrid fillers on thermal conductivity is very clear from the hybrid compositions; however, the optimum weight ratio of GNPs to CNTs cannot be assured from these results. It is also evident that addition of any filler has enhanced the thermal conductivity at least more than 200% i.e. in the compositions with either CNTs or GNPs. The higher thermal conductivity in hybrid compositions is attributed to the formation of percolating network as evidenced by the SEM observations (Figure 4-3).

Table 4-2. The measures of thermal conductivity in hybrid nanocomposites with total weight fraction of 0.1 of the samples produced for the calibration of model as listed in Table 4-1

Composition	Thermal Conductivity (W/mK)
PSU	0.17
0GNP10CNT	0.41
2GNP8CNT	0.60
6GNP4CNT	0.72
10GNP0CNT	0.67

4.4.2 Microscopy

Figure 4-2 and Figure 4-3 show the fractured surfaces of representative compositions. Figure 4-2a clearly shows the brittle fracture of the neat polymer viewed from the top where the flow of material prior to fracture is negligible and the fractured surface is almost perpendicular to the direction of applied force. Figure 4-2b shows that the CNTs are well-dispersed, their pull out from the matrix is only at a few locations (1, 2) and there is a bit increased flow of material (3) in 0GNP10CNT composition. The homogeneous distribution of CNTs can enable them to provide networking between themselves as well as other particles in their ways. The pull out only from few locations and increased flow of material indicate good adhesion between the functionalized CNTs and the polymer. Figure 4-2c is the fractograph of 10GNP0CNT composition, which shows a much-increased material flow prior to the fracture. In overall, the CNTs and GNP fillers are well bonded and well dispersed into the matrix as indicated by the increased flow of material observed in the fractographs.

Figure 4-3 shows the fractrographs of different samples of 6GNP4CNT representing the percolating network of CNTs with graphene. Figure 4-3a shows a CNT connecting between different particles of GNPs, Figure 4-3b shows embedded GNP particles over with distributed CNTs on it, and Figure 4-3c shows the pull of the graphene (2) and CNTs (1) on the fractured surface. The inter-connectivity of the CNTs and GNPs is the source of synergic effect on thermal conductivity as observed in the thermal conductivity results.

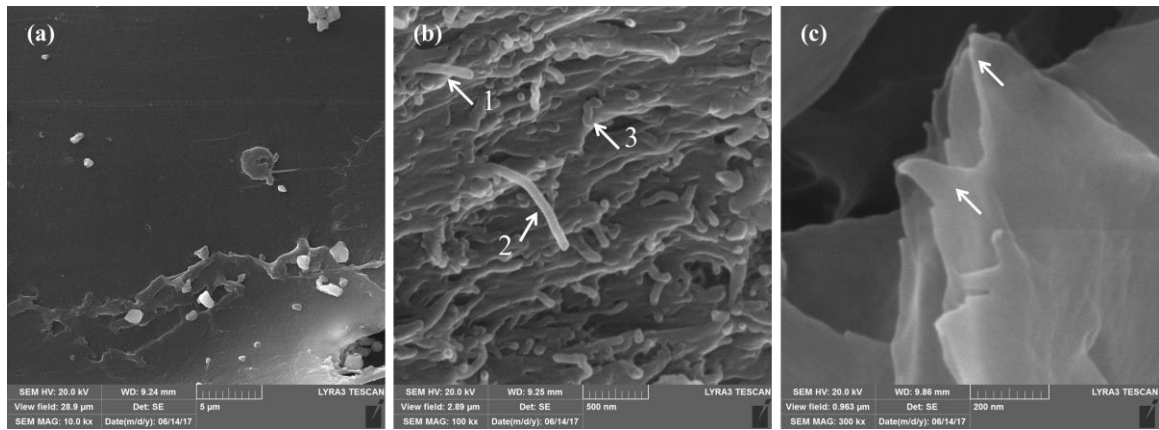


Figure 4-2 Fractured surfaces of (a) PSU (b) 0GNP10CNT and (c) 10GNP0CNT samples

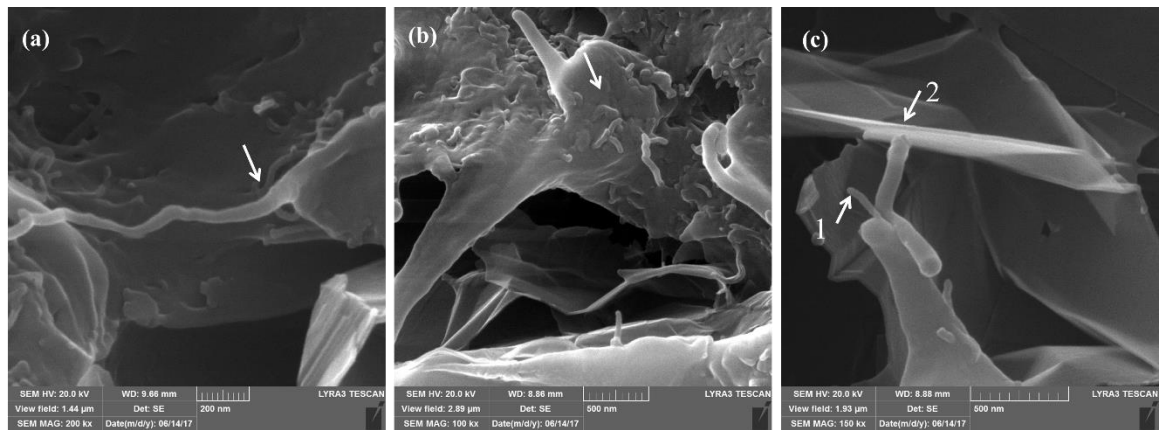


Figure 4-3 The representative fractrographs of 6GNP4CNT samples at different magnifications and locations

4.4.3 XRD

The X-ray diffraction spectra of pure PSU and 6GNP4CNT composition of hybrid nanocomposite are shown in Figure 4-4. The PSU spectrum is free of any peak showing the absence of any definite crystal structure and that is a well-known PSU being an amorphous thermoplastic polymer. The presence of crystalline carbon fillers (GNPs and CNTs) is very clear from the sharp peaks in the other spectrum. Similar spectra were observed in the compositions 0GNP10CNT and 10GNP0CNT but with lower peak heights in case of 0GNP10CNT.

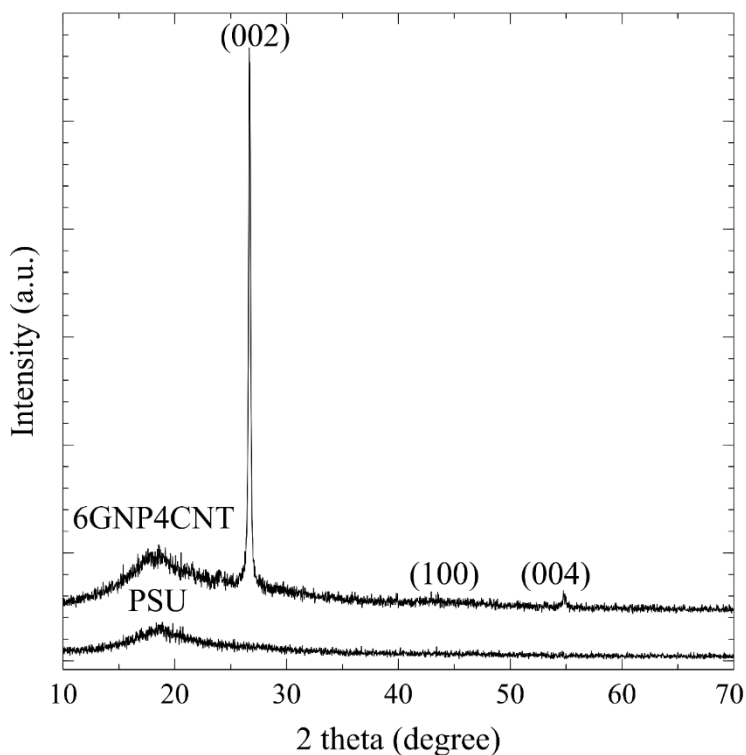


Figure 4-4 X-ray diffraction spectra of the PSU and 6GNP4CNT compositions

4.5 Calibration and Validation of the model

Figure 4-5 shows the comparison of the current model with the experimental results and several other models from the literature. The values of calibrated parameters are listed in Table 4-3 with the parameter m was taken as 0.87. Figure 4-5 shows that the current model captures the synergic enhancement and, the trend of effective thermal conductivity in the hybrid nanocomposites with a reasonable accuracy. On the other hand, the model by Nan et al. [28] does not capture the synergic effect at all while the other model by Chu et al. [139] over estimates the effective thermal conductivity beyond the optimum ratio. The current model has also been validated for two other published experimental results (Yu et al. [148] and Yan et al. [141]) of hybrid nano composites (Figure 4-6). The computed values of η from the equation (4-4) for the three works are listed in Table 4-4. In the experimental part of current work as well as in the other experimental works considered for validation, there was no preferred orientation of the fillers i.e. the fillers were randomly oriented completely. For such a case, Guo et al. [149] have recently reported a scheme to convert the three components of anisotropic thermal conductivity ($K_{eff,11}$, $K_{eff,22}$ and $K_{eff,33}$) into an overall isotropic thermal conductivity (K'). This scheme was derived from plane source method for measuring the thermal conductivity and therefore only suitable for the particular measurement method. However, in this work, the effect of random orientation was taken into account using the parameter $\langle \cos^2 \theta \rangle^i$. As suggested by [28,150], and hence throughout in this work, for randomly oriented particles $\langle \cos^2 \theta \rangle^i = 1/3$.

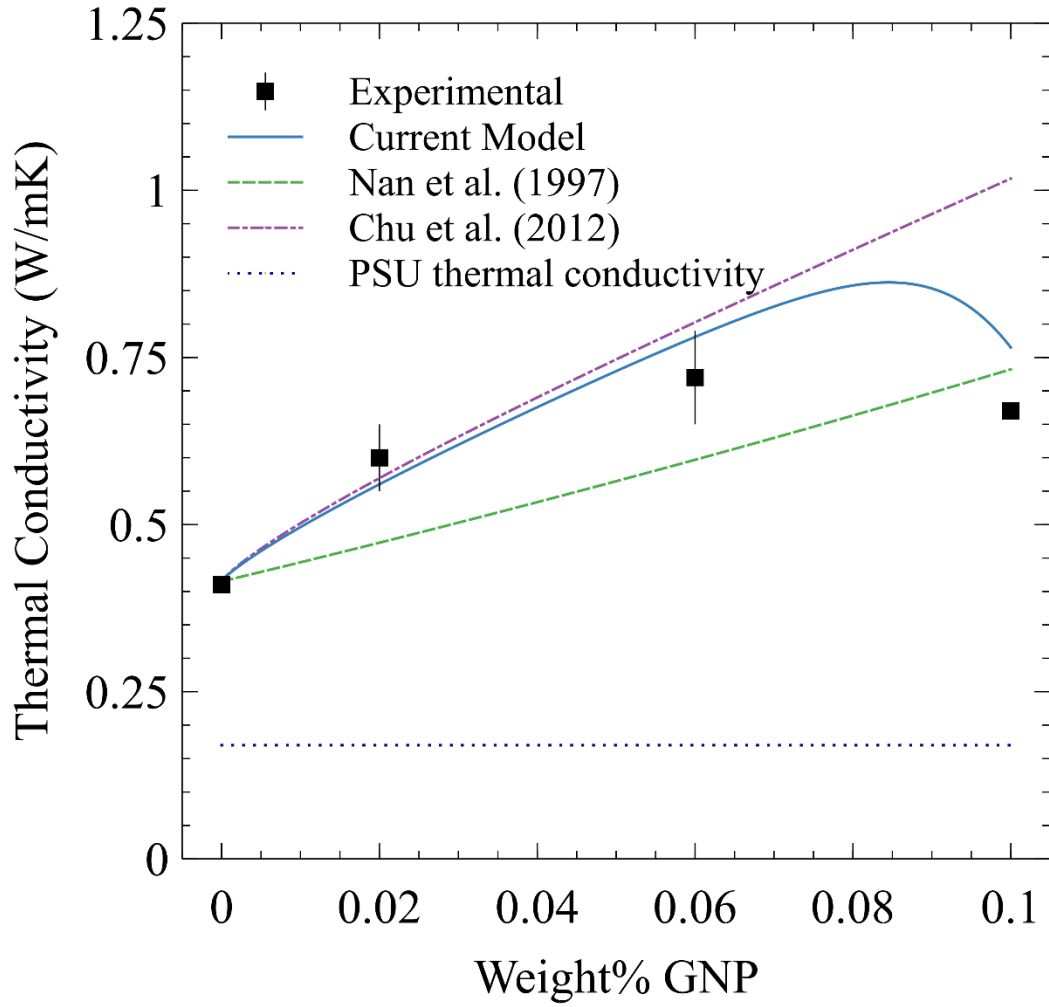


Figure 4-5 The comparison of thermal conductivity estimation by the current model with the experimental data and other published models

Table 4-3 Values of different model parameters used for the validation

Parameter	PSU	GNPs	CNTs
Intrinsic Thermal Conductivity [W/mK]	0.17	4000	3000
Polymer-filler Thermal Interface Resistance [$10^{-7} \text{ m}^2 \cdot \text{K/W}$]	-	1.1	2.2
Diameter [nm]	-	4500	10
Aspect Ratio	-	1/375	430

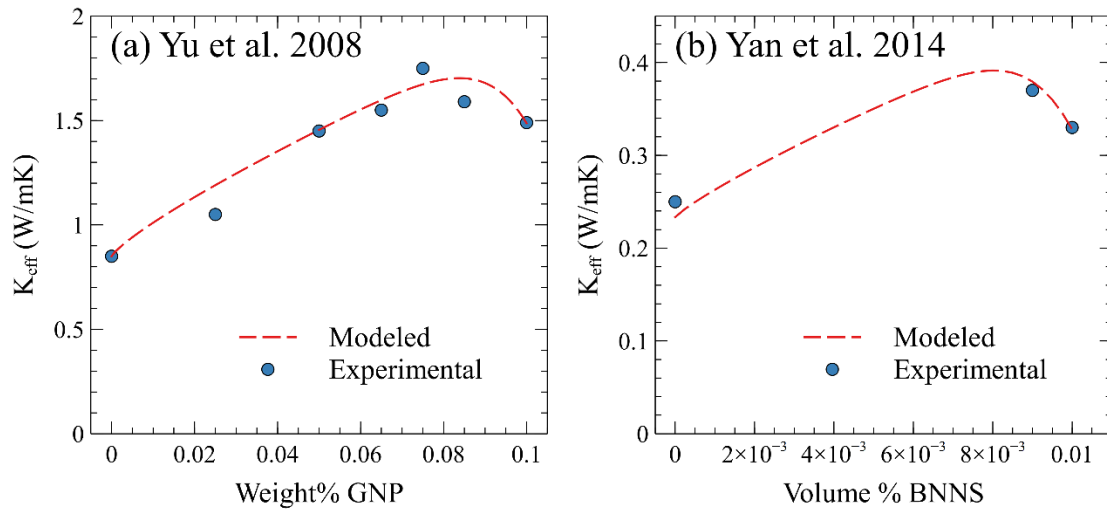


Figure 4-6 Comparison of the current model with the experimental results of (a) Yu et al. 2008 [148] (b) Yan et al. 2014 [141]

Table 4-4 Values of η for the current work and other experimental studies

Sr. #	Experimental	K_{eff}^{fibers} (W/mK)	$K_{eff}^{platelets}$ (W/mK)	φ_{total}	η
1	Current work	0.41	0.67	0.085	0.1074
2	Yu et al. 2008 [146]	0.85	1.49	0.085	0.1089
3	Yan et al. 2014 [139]	0.25	0.33	0.01	0.132

The models of Chu et al. [139] and Nan et al. [28] actually help in understanding the two extreme cases. With the Nan's model [28], $n=1$ indicates no synergic effect at all, while using $n=0.86$ with Chu's model [139] captures the synergic effect at low φ_1 very well but over-estimates at higher φ_1 . These two cases indicate that n is a variable which depends upon percolation. Hence, Siddiqui and Arif [147] in their model took n as the function of φ_2 ; equation (4-3) which results in the better accuracy of the model. The equation (4-3)

describes the parameter to be dependent upon the volume fraction of fibers type filler (φ_2) or indirectly upon φ_1 since $\varphi_2 = \varphi_{total} - \varphi_1$. As soon as φ_1 starts increasing from zero, the synergic effect is triggered (increased percolation) and after crossing the maximum, φ_2 becomes so small that the exponent n reaches close to 1 (decreased percolation). At these low values of φ_2 , the synergic effect is negligible. This ability of the model to capture the dependence of synergic effect on the volume fraction of fillers enables its use for the estimation of the optimum ratio in a hybrid composite.

4.6 Material design and development

As depicted in Figure 4-5, the optimum ratio predicted by the model for the PSU CNT/GNP composite studied experimentally in the current work is around 8.4 wt% GNPs with 1.6 wt% CNTs. A few samples were produced experimentally and tested for their thermal conductivity as listed in Table 4-5. These samples were produced following the same methodology used for the previously produced samples. The results of new samples not only validate the prediction of optimum ratio but also conform to the other compositions.

Table 4-5 The measures of thermal conductivity of the samples developed for the validation of the optimum ratio predicted by the model

Weight % Composition (vol %)			Thermal Conductivity (W/mK)				% deviation
PSU	GNPs	CNTs	Sample 1	Sample 2	Average experimental	Model prediction	
90 (93.59)	8 (4.56)	2 (1.84)	0.83	0.78	0.80	0.858	6.7
90 (93.72)	8.4 (4.80)	1.6 (1.48)	0.95	0.81	0.88	0.862	2.1
90 (93.92)	9 (5.15)	1 (0.92)	0.79	0.93	0.86	0.853	<1

4.7 Sensitivity Analysis

Sensitivity analysis is the study of how the uncertainty in the output of a model can be attributed to uncertainties in the model parameters [151]. For predictive models, it can help identify the relative dependence of the predicted output of a model on its parameters.

A sensitivity analysis can be carried out either locally or globally on a model. In a local sensitivity analysis, the sensitivity of the model output with respect to its parameters is equal to the partial derivative of the output with respect to each parameter while keeping the other parameters fixed. As such, the sensitivity of the model with respect to a parameter is dependent on the values of the other parameters. In a global sensitivity analysis, on the other hand, a Monte Carlo simulation is carried out in which all model parameters are varied at the same time as per predefined probability distributions. The sensitivity of the model with respect to the model parameters are calculated using statistical techniques.

In the current work, a global sensitivity analysis was carried out to determine the model sensitivity with respect to the model parameters m and η , material parameters p^1 , p^2 , and processing related parameters R_{TB}^1 and R_{TB}^2 . For details on sensitivity analysis, please see [152]. The steps involved in carrying out the global sensitivity analysis are listed below.

1. N parameter sets are randomly generated within a predefined parameter space. The parameter space was generated by first calibrating the model, material and processing parameters to accurately predict the effective thermal conductivity of Epoxy-10% CNT-GNP nanocomposite developed by Yu et al. [148]. The minimum

and maximum limits of the parameter space were defined by allowing for a 10% variation in the parameters. The calibrated material parameters are presented in Table 4-6. 100 samples were randomly generated in the sample space considered.

2. For each combination of parameter values, the effective thermal conductivity model is solved using Monte Carlo simulations for the entire range of hybrid filler's ratio $\phi_1:\phi_2$.
3. Two function outputs are considered in the analysis i.e. the maximum effective thermal conductivity of the hybrid composite possible for the given parameters set and the optimum hybrid fillers ratio for achieving maximum thermal conductivity enhancement defined here using ϕ_1/ϕ_{total} .
4. The sensitivity of the two model outputs with respect to the parameters is analyzed using linear and rank partial correlation. The partial correlation method measures the degree of association between two random variables (in this case, the model parameters and outputs), with the effects of other parameters removed.

The results of the sensitivity analysis are shown in Figure 4-7. The results for maximum effective thermal conductivity, given in Figure 4-7a, show that model parameter m with both linear and rank partial correlation coefficients equal to -1 plays an extremely important role in determining the maximum effective thermal conductivity of the hybrid composite. The negative sign highlights the fact that the maximum thermal conductivity of the composite increases with decreasing m . On the other hand, the maximum thermal conductivity has very low correlation with model parameter η . Among the material parameters considered, the maximum thermal conductivity shows high sensitivity to the

aspect ratio and interface thermal resistance of the platelets (p^1 and R_{TB}^1). The calculated correlation coefficients show that maximum thermal conductivity of the composite increases with reducing p^1 and R_{TB}^1 . Figure 4-7b presents the sensitivity analysis results for the optimum hybrid filler's ratio (defined by $\varphi_1/\varphi_{total}$). The results show that of the two model parameters m and η , the optimum filler's ratio shows a higher dependence on parameter η . The optimum filler's ratio shows moderate to high level of correlation with all four material parameters considered in the analysis. The results show that with increasing aspect ratio of both fibers (p^2) and platelets (p^1) and interfacial resistance of platelets (R_{TB}^1), the optimum fillers ratio reduces indicating higher φ_2 . This is because an increase in p^1 and R_{TB}^1 reduces the thermal conductivity enhancement due to platelets while an increase in p^2 results in an improvement in the thermal conductivity enhancement due to nanotubes. On the other hand, an increase in R_{TB}^2 (the fibers interfacial resistance) causes a decrease in the thermal conductivity enhancement due to nanotubes and therefore, results in an increase in φ_1 .

Table 4-6 Sample space for sensitivity analysis

Parameter	Calibrated Value	Lower Limit	Upper Limit
m	0.86	0.774	0.946
η	0.14	0.126	0.154
p^1	1/250	1/275	1/225
p^2	350	315	385
R_{TB}^1	$3.9 \times 10^{-8} \text{ m}^2\text{K/W}$	$3.51 \times 10^{-8} \text{ m}^2\text{K/W}$	$4.29 \times 10^{-8} \text{ m}^2\text{K/W}$
R_{TB}^2	$1 \times 10^{-7} \text{ m}^2\text{K/W}$	$0.9 \times 10^{-7} \text{ m}^2\text{K/W}$	$1.1 \times 10^{-7} \text{ m}^2\text{K/W}$

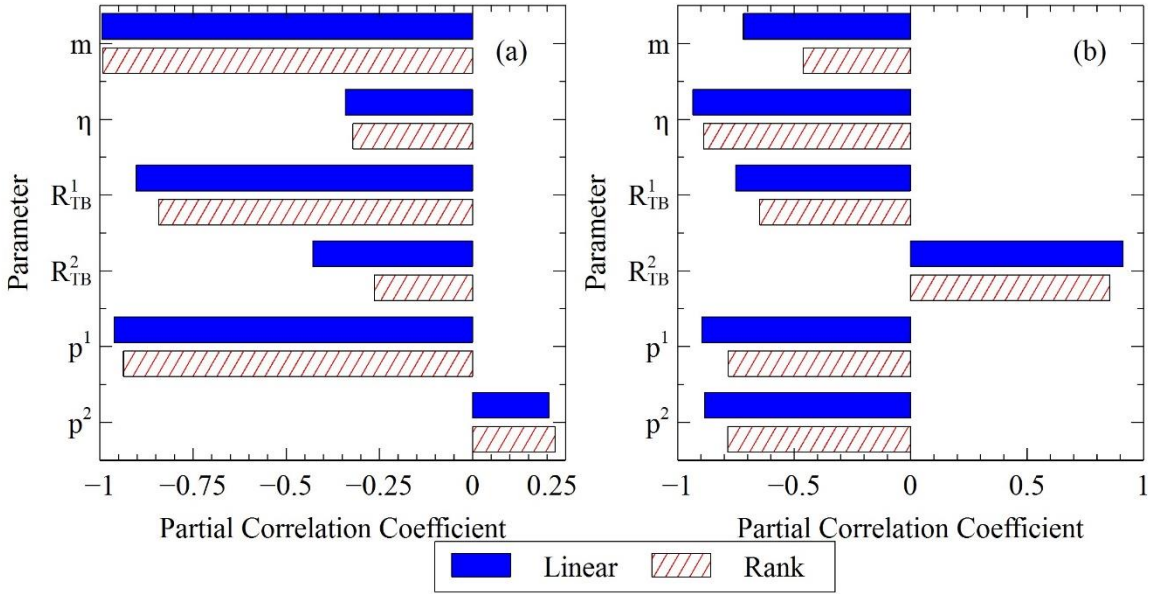


Figure 4-7. Sensitivity Analysis results for (a) maximum effective thermal conductivity and (b) optimum ratio of hybrid fillers

4.8 Parametric studies

To highlight the insights of the model, parametric studies were carried out by varying only one parameter at a time. In each case, the effective thermal conductivity of the composite,

K_{eff} , is plotted against weight fraction of platelets, ϕ_1 . Table 4-7 shows ranges of different parameters along with their types and values calibrated with the current experimental data and then used in the parametric studies. Figure 4-8 – Figure 4-11 present the different parametric studies. Each chart is dedicated to the study of one parameter keeping all other parameters constant as mentioned in Table 4-7 under the column “measured/calibrated value”. The black solid curve in each chart is the prediction of the current model for the thermal conductivity of GNP-CNT-PSU hybrid nanocomposites produced in the current work.

The selected range for K_m is 0.1 – 0.4 W/mK since most of the polymers fall in this range of thermal conductivity [61]. $K_{inc,1}$ and $K_{inc,2}$ are varied from 1 W/mK to the highest known thermal conductivity material of its own kind. Similarly, the GNPs and CNTs can have effective aspect ratios varying from 100 to 1000 [127] and hence the range is selected. Platelets and fibers of less than 100 nm size, as well as micron size range, are available in the market. Therefore, the thickness of platelets is varied from 12 nm (that of GNP in the current work) to more than 2.67 μm where the diameter of platelet becomes 1 mm and that of fibers is varied from 10 nm (that of CNTs in the current work) to 2.325 μm where the length of fiber becomes 1 mm as imposed by the constant aspect ratio. This parametric study elaborates the effect of moving from nano-fillers to micro-fillers on effective thermal conductivity. An effective functionalization or surface treatment can significantly reduce the matrix-filler interface resistance [153,154] and hence to observe its effect on thermal conductivity, a wide range of thermal interface resistance is selected that covers all

carbonaceous fillers along with ceramic fillers. The parameters m and η take care of the synergic enhancement indirectly through the critical exponent n . Within the selected ranges of m and η different types of synergic enhancement of thermal conductivities are covered. In all this discussion the term “synergic effect (SE) in thermal conductivity” is quantified as

$$SE = \frac{K_{\max} - K_{eff}^{fibers}}{K_{eff}^{fibers}} \times 100$$

Where $K_{\max}$ is the maximum achievable thermal conductivity, K_{eff}^{fibers} is thermal conductivity of composite with fibers (0 wt% platelets and 10 wt% fibers).

Table 4-7 Summary of the parametric studies conducted on the validated model for thermal conductivity of hybrid composites

Name of parameter (variable)	Type	Symbol	Figures	Measured/ Calibrated value	Range	Reason for the selected range
Thermal conductivity of matrix	Materials	K_m	Figure 4-8a	0.17 W/mK	0.1 – 0.4 W/mK	Most of the polymers fall in this range
Thermal conductivity of platelets		$K_{inc,1}$	Figure 4-8b	4000 W/mK	1 – 4000 W/mK	The lowest of fillers to the highest of its type
Thermal conductivity of fibers		$K_{inc,2}$	Figure 4-8c	3000 W/mK	1 – 3000 W/mK	
Aspect ratio of platelets		p^1 with a_1^1	Figure 4-9a	1/375	1/1000 – 1/100	The aspect ratios of GNP and CNTs can vary in this range
		p^1 with a_3^1	Figure 4-9b	1/375	1/1000 – 1/100	
Aspect ratio of fibers		p^2 with a_1^2	Figure 4-9c	430	100 – 1000	
		p^2 with a_3^2	Figure 4-9d	430	100 – 1000	
Particle size of platelets		a_1^1 with a_3^1	Figure 4-9e	12 nm, 4500 nm	12 – 4500 nm	Platelets and fibers of less than 100 nm size, as well as micron size range, are available in the market.
Particle size of fibers		a_1^2 with a_3^2	Figure 4-9f	10 nm, 4300 nm	12 – 2325 nm	
Matrix-platelets Interface resistance	Processing	R_{TB}^1	Figure 4-10a	1.1E-7 m ² K/W	1E-9 – 1E-5 m ² K/W	The wide range of this parameter can cover all the carbonaceous and ceramic fillers
Matrix-fibers Interface resistance		R_{TB}^2	Figure 4-10b	2.2E-7 m ² K/W	1E-9 – 1E-5 m ² K/W	
Parameter m	Model	m	Figure 4-11a	0.87	0.8 – 0.9	Can control variation in synergic enhancements
Parameter η		η	Figure 4-11b	0.11	0.05 – 0.3	

4.8.1 Thermal conductivities of constituents

Figure 4-8 shows how thermal conductivities of the constituents are important in achieving a high bulk thermal conductivity of the composites. Figure 4-8a shows that increasing or decreasing K_m does not modify SE and simply K_{eff} and K_{max} are proportional to K_m . Figure 4-8b shows the effect of thermal conductivity of platelet-type fillers ($K_{inc,1}$). It shows that SE is almost negligible at $K_{inc,1} = 10$ W/mK and increases with increasing $K_{inc,1}$. It also shows that a reasonable SE ($\sim 86\%$) can be achieved by using platelets with $K_{inc,1} = 100$ W/mK and a peak SE of around $\sim 106\%$ is reached for $K_{inc,1} \geq 1000$ W/mK. Any further increase in the GNP thermal conductivity has minimal effect on the synergic effect. Figure 4-8c shows the effect of $K_{inc,2}$ on K_{eff} . Quantitatively, SE decreases with increasing $K_{inc,2}$. However, the absolute value of K_{max} increases only a little from 0.83 W/mK to 0.862 W/mK when $K_{inc,2}$ increases from 1 W/mK to 3000 W/mK. The three parametric studies show that $K_{inc,1}$ is the most important among the thermal conductivities of the constituents to observe maxima of SE and K_{max} . Also, a platelet-thermal conductivity equal to 100 W/mK is enough for having a reasonable SE. The theoretical reasoning for $K_{inc,1}$ being the most influencing factor is that the platelets are the network formers through the fibers and the volume of a single platelet used in this study (GNP) is almost 550 times that of a single fiber (CNT). In other words, for equal bulk volumes of platelets and fibers, the ratio between the number of particles of platelets and fibers would be around 1:550. So, the fibers, being larger in number, provide a larger number of paths for the flow of heat carriers

and hence, a smaller thermal conductivity of fibers is less harmful to the effective thermal conductivity. However, a lower thermal conductivity of platelet will restrict the heat in itself and a larger thermal conductivity of fibers will not be able to provide much improvement for the heat flow. The matrix with K_m being very low acts like a high resistance in thermal circuit i.e. the heat carrier will only enter if a connecting platelet or fiber is not available. Therefore, the role of polymer matrix is just to provide a body to the thermal conducting networks.

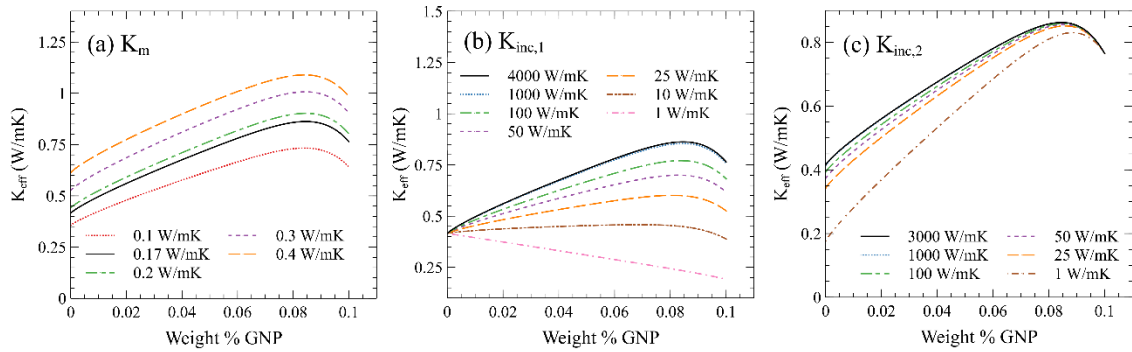


Figure 4-8 Effect of thermal conductivities of the constituents on the effective thermal conductivity of hybrid composites; (a) of matrix, K_m ; (b) of platelets, $K_{inc,1}$; (c) of fibers, $K_{inc,2}$

4.8.2 Dimensional parameters of the fillers

Dimensional parameters of constituents include aspect ratios (p^i) and particle sizes (a_1^i and a_3^i) of the platelets and fibers. $p^i = a_3^i / a_1^i$ where a_1^i is the diameter of platelet or fiber while a_3^i is thickness for the platelets or length for the fibers. The aspect ratios can be varied either by varying a_3^i or a_1^i . Since these parameters are interdependent, at least two parameters would be varied at a time. To have a deep insight of the dimensional parameters

six different parametric studies were carried out as outlined in Table 4-8 and presented in Figure 4-9.

Table 4-8 Parametric studies of dimensional parameters of fillers in Figure 4-9

Sr. #	Size related variable parameter	Related filler	Constants	Figure
1	p^1 by varying the diameter of platelets (a_1^1)	Platelets	a_1^2, a_3^1, a_3^2	Figure 4-9a
2	p^1 by varying the thickness of platelets (a_3^1)	Platelets	a_1^1, a_1^2, a_3^2	Figure 4-9b
3	p^2 by varying the diameter of fibers (a_1^2)	Fibers	a_1^1, a_3^1, a_3^2	Figure 4-9c
4	p^2 by varying the length of fibers (a_3^2)	Fibers	a_1^1, a_1^2, a_3^1	Figure 4-9d
5	a_1^1 and a_3^1	Platelets	a_1^2, a_3^2, p^1, p^2	Figure 4-9e
6	a_1^2 and a_3^2	Fibers	a_1^1, a_3^1, p^1, p^2	Figure 4-9f

Analysis of Figure 4-9a-d shows that for the synergic enhancement, the diameter of platelets (a_1^1) is the most influencing parameter. Decreasing aspect ratio by increasing a_1^1 (Figure 4-9a) can increase SE from 108% as seen in the current study to 373% with $p^1 = 1/1000$. However, decreasing aspect ratio with thickness (Figure 4-9b) does not bring much improvement in SE. The maximum SE is 114% with $p^1 = 1/1000$ compared to 108% for the fillers dimensions in the experimental study. Varying the aspect ratio of fibers (p^2) by varying the diameter (Figure 4-9c) has a negligible effect on SE and $K_{\max}$. Increasing p^2 by increasing the length of fibers (Figure 4-9d) decreases SE but increases the absolute value of $K_{\max}$. However, the relative increment in $K_{\max}$ with fibers as compared

to that with platelets is very low. The increase in SE with decreasing P^1 (Figure 4-9a) is due to the fact that a smaller aspect ratio with increased diameter enables the platelets to spread over a larger area and connect to a greater number of fibers and neighboring platelets i.e. increased percolation, which results in a larger SE in the effective thermal conductivity [155]. However, the increased SE by increased P^2 (Figure 4-9d) is attributed to the increased K_{eff}^{fibers} and not due to the increased percolation. Since increased fiber length can only help the heat carrier to travel over a longer distance with a less resistance which only contributes to K_{eff}^{fibers} but it cannot enhance the density of the network. Therefore, P^1 should be as low as possible with a larger diameter for maximum SE while $P^2 = 250$ is good enough to have a reasonable SE.

Figure 4-9e-f present the effects of varying particle sizes keeping aspect ratios constant as calibrated i.e. 1/375 of platelets and 430 of fibers on the effective thermal conductivity. The legends in the Figure 4-9e and Figure 4-9f indicate the smaller dimension of the fillers i.e. thickness of the platelets (a_3^1) in Figure 4-9e or diameter of the fibers (a_1^2) in Figure 4-9f.

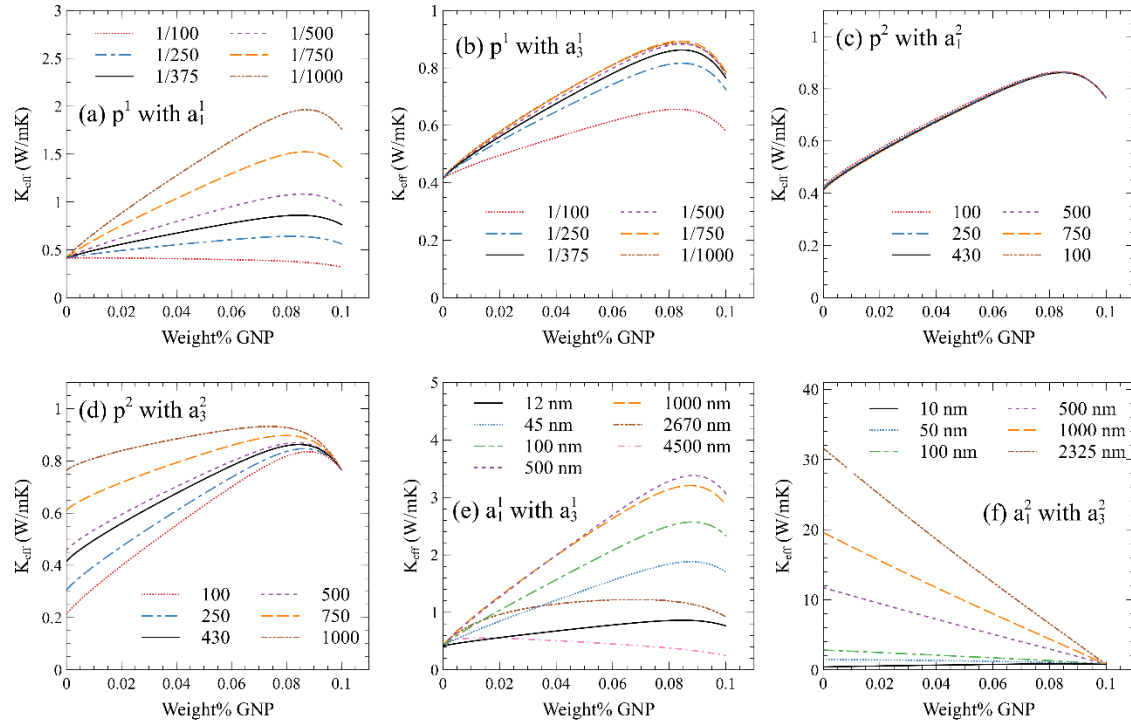


Figure 4-9 Effects of dimensional parameters of the fillers on the effective thermal conductivity; (a) varying p^1 with a_1^1 ; (b) varying p^1 with a_3^1 ; (c) varying p^2 with a_1^2 ; (d) varying p^2 with a_3^2 ; (e) varying a_1^1 and a_3^1 ; (f) a_1^2 and a_3^2

Figure 4-9e shows that increasing particle size of platelets is continuously increasing SE and $K_{\max}$ with maxima at a thickness of around 1 μm where the diameter would be around 375 μm and further increasing the particle size decreases both SE and $K_{\max}$. The increased SE and $K_{\max}$ are attributed to the increased percolation and increased $K_{\text{eff}}^{\text{platelets}}$. The increase in $K_{\text{eff}}^{\text{platelets}}$ with particle size of platelets is due to decreased total interfacial area and hence reduced overall interface resistance in the system. Moreover, a platelet with larger particle diameter ($=375 \times \text{thickness}$) can span over a larger area and can connect to a greater number of fibers and neighboring platelets i.e. more percolation. For a composition,

the *particle density* (the number of particles per unit volume) exponentially decreases with increasing particle size. Increasing the particle size of platelets decreases the *particle density* of platelets but increases the number of fibers connecting per platelet i.e. increased percolation and SE until the optimum ratio between the numbers of platelets and fibers is reached. Hence an increase in $K_{eff}^{platelets}$, SE and K_{max} is observed with increasing particle size of platelets. The decrease in SE and K_{max} by increasing the thickness above 1 μm is attributed to the decreased number of particles available for percolation i.e. decreased *particle density*. The decreased *particle density* with increased particle size changes the percolation behavior of platelets, as seen in the Figure 4-9e for $a_3^1 > 1000 \text{ nm}$ that the optimum ratio of platelets to fibers also changes. Further increasing the particle size of platelets decreases the *particle density* to a level where the number of available platelets is too small for the network to be percolating optimally. Figure 4-9e elaborates that for the maxima of SE and K_{max} , the system needs to be optimized in terms of the number of particles of fillers and this optimum ratio depends upon the dimensional parameters of the fillers and the total volume fraction of the fillers. Such high thermal conductivities of more than 5 W/mK in polymer matrix composites using graphite based fillers have been recently reported not only by researchers [10,18] but also by the polymers compounding industries [156].

Figure 4-9f shows that increasing particle size of fibers can give a very large boost to K_{eff}^{fibers} and even can bypass the synergic enhancement. For example, K_{eff}^{fibers} is expected to have a value of around 20 W/mK with fiber diameter and length of 1 μm and 430 μm respectively.

Even much higher than this thermal conductivity has been reported by using carbon fibers [157]. However, this would be the case when most of the fibers would maintain their shape in the final product the same as assumed in the model i.e. prolate to cylindrical in the final composite. However, in practice, the bends in fibers reduce the effective lengths and hence, the prediction of the model no longer remains valid. Practically, such a long effective length of fiber is not an easy task to be achieved with conventional processing methods and therefore this parametric study is of practical importance only for the special processing methods in which fibers may retain their shapes without bends.

4.8.3 Matrix-filler Interface resistance

Figure 4-10 show the effect of interface resistance of platelets and fibers. Like the previous parametric studies which highlighted the importance of platelet parameters, interface resistance of platelets is the sensitive factor for SE (Figure 4-10a). The SE can be enhanced from 108% to 770% by decreasing R_{TB}^1 from $1.1E-7$ to $1.0E-9 \text{ m}^2K / W$. On the other hand, $K_{eff}^{platelets}$ is increased by four folds. Figure 4-10b shows that decreasing R_{TB}^2 can lead to a very high value of K_{eff}^{fibers} . For the parameters considered in the study, K_{eff}^{fibers} increased from 0.41 to 30.8 W/mK when R_{TB}^2 is reduced from $2.2E-7$ to $1E-9 \text{ m}^2K / W$. A thermal conductivity value as high as this is only possible when the fibers are perfectly bonded to the matrix and form an interface with a thermal interface resistance as low as $1E-9 \text{ m}^2K / W$ along with other assumptions of the model are satisfied. However, for fibers like CNTs, 10 wt% is too high to avoid agglomeration. With agglomeration, CNT-CNT interface resistance comes into play and the assumptions of current model do not remain

valid. Hence, the case of very low R_{TB}^2 with long fibers is of less practical importance for the conventional polymer processing methods. Moreover, at higher values of R_{TB}^2 , the $K_{\max}$ is not much affected. It decreases from 0.862 to 0.827 W/mK when R_{TB}^2 increases from $2.2\text{E-}7$ to $1.0\text{E-}5 \text{ m}^2\text{K/W}$. Overall, this parametric study suggests that R_{TB}^1 should be as low as possible while a higher value of R_{TB}^2 will not cause much resistance to a high SE.

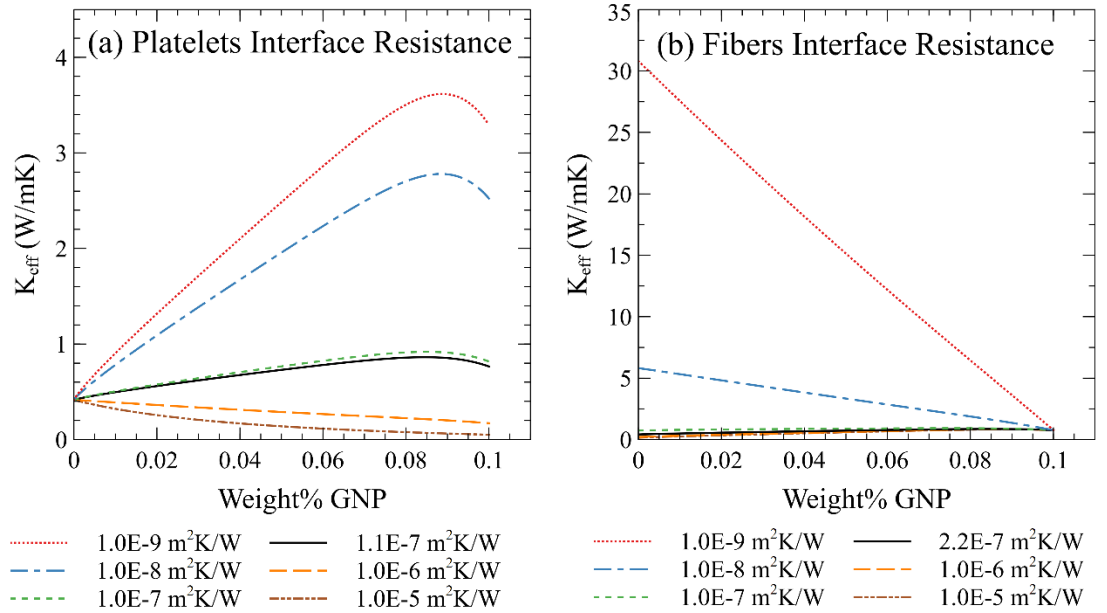


Figure 4-10 Effect of matrix-filler interface resistance on effective thermal conductivity (a) PSU-platelets interface resistance, R_{TB}^1 ; and (b) PSU-fibers interface resistance, R_{TB}^2

4.8.4 Model parameters m and η

Figure 4-11 shows the parametric studies conducted on the model parameters m and η . This study describes how these parameters affect the effective thermal conductivity and SE, what their role is in the material design process, what their ranges are, and how these

parameters can be determined. Figure 4-11a shows that varying the parameter m from 0.8 to 0.9 does affect the optimum ratio only slightly and varies the $K_{\max}$ from 0.804 to 1.02 W/mK. Therefore, an intermediate value of m can be used for material design, and the optimum ratio can be determined within an acceptable error. On the other hand, varying η (Figure 4-11b) affects $K_{\text{eff}}^{\text{platelets}}$, SE and the optimum ratio. For η , equation (4-4) has been proposed and validated in the current work.

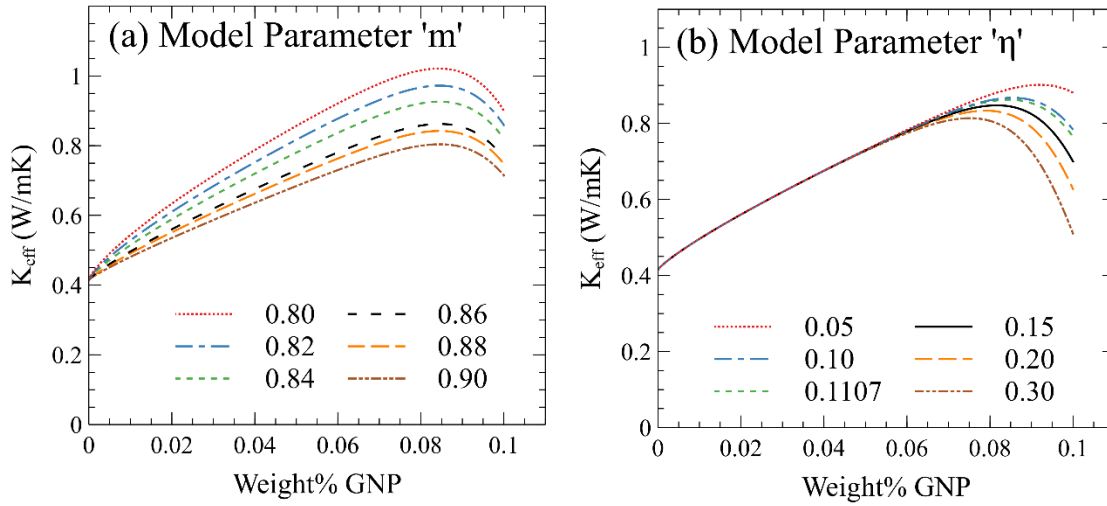


Figure 4-11 Effects of model parameters on effective thermal conductivity behavior; (a) effect of parameter m ; (b) effect of parameter η

4.9 Conclusions

The key to high thermal conductivity in polymer matrix composites is to form a percolating network of high thermal conductivity fillers. In this work, design and development of hybrid filler–PSU matrix composites are presented. The following conclusions may be drawn from the investigations.

- a) A computational model was used as a design tool to find out the optimum composition of hybrid fillers with best effective thermal conductivity.
- b) The implementation of this material design scheme requires calibration of the model with a few of the compositions. Then the model predicts the behavior of effective thermal conductivity over the selected range of hybrid compositions. The maximum of this curve points out the optimum composition. Following this scheme, the optimum composition found is PSU / 8.4 GNP / 1.6 CNT in wt% where the observed K_{eff} is 0.88 W/mK.
- c) Sensitivity analyses and parametric studies resulted that for hybrid composites, of the platelets, the thermal conductivity, diameter and interface resistance are the most influencing factors for synergic enhancement and the platelets with a thermal conductivity of 100 W/mK can provide a reasonable synergic enhancement. However, the size and interface resistance of the fibers are important for non-hybrid composites. In composites with alone fibers as fillers, high thermal conductivity fibers of reasonable aspect ratio and diameter of around micron can provide very high thermal conductivity provided with low interface resistance and the fibers are not bent.
- d) The model is found to have strong material design capability and therefore recommended for targeted material design using hybrid fillers in polymer matrices.

CHAPTER 5

A NEW PREDICTIVE MODEL FOR THERMAL CONDUCTIVITY OF POLYMER-COMPOSITES WITH NON-DILUTE FILLER CONCENTRATIONS

The recent approach for enhancing the thermal conductivity of polymer-composites is to generate an inter-connecting network of thermally conductive fillers. However, most of the existing predictive models for effective thermal conductivity of composites in general are based on the assumption of dilute filler concentration (low volume fraction) which leads to inaccurate predictions when filler concentration is non-dilute or making an inter-connecting network. In this work, an improved and more realistic model for effective thermal conductivity of polymer matrix composites is derived and validated considering *non-dilute filler concentration*. The model includes the effects of variable size and shape of particulate fillers. The derivation is based on the Bruggeman's differential effective medium theory wherein the *high volume fractions* can be obtained by incrementally adding '*small volume fractions*' into the '*existing composite*' at each stage. The proposed model is validated by synthesizing different series of ceramic reinforced polymer matrix composites. Using different combinations of Al_2O_3 or AlN as filler, and high-density polyethylene or polypropylene as the matrix, different series of composites were produced

with variable filler concentrations up to 50% by volume. The predictions of the proposed model are in agreement with the measured thermal conductivity. To elucidate the effects of different parameters, parametric studies are conducted. The aspect ratio of particulate fillers is the most sensitive parameter to enhance effective thermal conductivity. The proposed model is expected to open new doors for the researchers and the industry to develop new composite designs for achieving ultrahigh thermal conductivity.

5.1 Introduction

Polymers have the potential to replace metallic components in many engineering and real-life applications. Low density, small carbon footprint, high corrosion and chemical resistance, easy processing, and flexible manufacturability are the few advantages of polymer-based materials. Many heat transfer applications involve low working temperatures and therefore polymers can effectively replace their metallic counterparts with enhanced certain properties. For heat exchangers and thermal interface materials, the thermal conductivity (TC) of polymers must be enhanced to serve the purpose efficiently.

Polymer matrix composites (PMCs) are widely accepted in many heat transfer applications such as heat exchangers, thermal management of electronics and thermal interface materials. For such applications, TC must be good enough to dissipate the waste heat. In this view, scientists are working to enhance the TCs of PMCs synergistically. Synergistic enhancement in TC of PMCs has been reported by using hybrid fillers such as mixtures of differently composed [4], differently sized [5,6], or differently shaped [7–9] particles. The key to synergistic enhancement in TC is to develop a percolating network of high TC fillers

in the final product [10–12]. Among different approaches, one is to follow a methodology in which the particulate fillers are forced to connect each other, for example, layer-by-layer fabrication by doctor blading [13], and structuring of flakes by high-speed mixing and hot compressing [14–17]. Another way is to use expandable graphite (EG). Once expanded, EG forms a fully connecting skeleton and leads to high TC [18–20]. Similarly, foams or porous structures of thermally conducting ceramics can be infiltrated with polymeric materials to have inter-connecting heat pathways throughout [21–23]. On the same lines, forming a segregated structure of thermally conductive fillers following a two-stage mixing route can lead to ultrahigh TCs [10,24].

Effective TC of composites is controlled by many parameters, but particle size and aspect ratio of the particulate fillers are the most sensitive parameters because the formation of a percolating network depends on these parameters [25,26]. Most of the estimation models used for predicting effective TC of composites are limited to dilute concentrations (low volume fractions) of fillers i.e. where the field of one particle does not interact with that of its neighboring particle [27–29]. On the other hand, the available models for composites with non-dilute concentrations (high volume fractions) of fillers are limited to particles with irregular shapes and cannot handle the variable orientation of the high aspect ratio particles [32,33]. Hence, there is a need to develop a model for estimating effective TC of composite, which includes the effects of non-dilute filler concentrations, and orientation and aspect ratio of particles all-in-one.

This work is intended to present a more realistic effective medium theory-based TC estimation model that can be equally used for dilute and non-dilute volume fractions of

fillers with particles of variable shapes and orientations. The proposed model is presented and validated by experiments. The experiments include the development of different series of composites using different polymer matrices loaded with fillers of varying attributes. The insights of the model are highlighted through parametric studies and new materials designs are proposed for achieving ultrahigh TC.

5.2 Thermal conductivity estimation models

5.2.1 History

TC estimation models for composite materials have been reported in different generations. Mainly, these models are classed as simulation models or classical theoretical models. The classical theoretical models are further categorized as effective medium theory (EMT) and micromechanics methods [82]. The EMT was initiated by Maxwell [95] and Lord Raleigh [158]. They presented their works for the estimation of properties in composites with non-interacting spherical (3D) and rectangular (2D) fillers respectively. Maxwell's model was modified by Fricke [159] to work for ellipsoid shaped fillers. Various modifications of Maxwell's model have been reported over time. For example, Bruggeman's [160] modification was to enable the model for non-dilute concentrations of fillers, Hamilton and Crosser's [161] modification was to include a generalized shape factor and that of Hasselman and Johnson (HJ) [27] was to include the effect of interfacial thermal resistance (ITR).

The next generation of the effective medium theory was to update the existing model to include two or more of the aforementioned modifications. Hence, Every et al. [32]

modified the Bruggeman's model to include HJ's ITR and Jiajun et al. [33] further modified the Every's model to include a sphericity-dependent shape factor. The model proposed by Jiajun et al. [33] was capable to handle differently shaped particulate fillers and non-dilute concentrations with ITR. There was a need to model the effects of filler's aspect ratio and their orientation, since the interest in using the nano-fillers such as carbon nanotubes and graphene was growing rapidly. For this purpose, apart from the above-mentioned models, Nan et al. [28] published an effective medium theory that included more generalized parameters such as aspect ratio and orientation of the fillers with ITR. However, Nan's model was derived for regularly shaped ellipsoid fillers with the assumption of dilute concentrations. Later on, their model was modified by Siddiqui et al. [29] and Raza et al. [25] for *non-uniformly distributed dilute hybrid fillers* and *percolating dilute hybrid fillers*, respectively.

In contrast to EMT, variational principle and mean-field homogenization for the estimation of TC are the examples of micromechanics methods. The Hashin-Shtrikman (HS) bounding [162] and Mori-Tanaka (MT) [163] scheme were the first examples of using the variational principle and mean-field homogenization respectively. Later, Benveniste [164] combined the two approaches and included the effect of ITR. And the simulation models include molecular dynamics, Lattice Boltzmann and finite element methods that are time and length scale-dependent.

5.2.2 Effective medium theory – dilute filler concentrations

Different extensions of Nan's Model [28] have been previously reported by Siddiqui et al. [29,165] and Raza et al. [25]. The original model and its extensions are applicable to a wide

range of filler particle shapes, but these models are limited to dilute concentrations of fillers. The model is outlined in equations (5-1) to (5-10) as follows.

$$k_{eff,11} = k_{eff,22} = k_{mat} \frac{2 + \sum_{i=2}^N \varphi^i \left[\beta_{11}^i (1 - L_{11}^i) (1 + \langle \cos^2 \theta \rangle^i) + \beta_{33}^i (1 - L_{33}^i) (1 - \langle \cos^2 \theta \rangle^i) \right]}{2 - \sum_{i=2}^N \varphi^i \left[\beta_{11}^i L_{11}^i (1 + \langle \cos^2 \theta \rangle^i) + \beta_{33}^i L_{33}^i (1 - \langle \cos^2 \theta \rangle^i) \right]} \quad (5-1)$$

$$k_{eff,33} = k_{mat} \frac{1 + \sum_{i=2}^N \varphi_i \left[\beta_{11}^i (1 - L_{11}^i) (1 - \langle \cos^2 \theta \rangle^i) + \beta_{33}^i (1 - L_{33}^i) \langle \cos^2 \theta \rangle^i \right]}{1 - \sum_{i=2}^N \varphi_i \left[\beta_{11}^i L_{11}^i (1 - \langle \cos^2 \theta \rangle^i) + \beta_{33}^i L_{33}^i \langle \cos^2 \theta \rangle^i \right]} \quad (5-2)$$

$$\langle \cos^2 \theta \rangle^i = \frac{\int \rho^i(\theta) \cos^2 \theta \sin \theta d\theta}{\int \rho^i(\theta) \sin \theta d\theta} \quad (5-3)$$

$$L_{11}^i = L_{22}^i = \begin{cases} \frac{(p^i)^2}{2((p^i)^2 - 1)} - \frac{p^i}{2((p^i)^2 - 1)^{1.5}} \cosh^{-1} p^i, & \text{for } p^i \geq 1 \\ \frac{(p^i)^2}{2((p^i)^2 - 1)} + \frac{p^i}{2(1 - (p^i)^2)^{1.5}} \cos^{-1} p^i, & \text{for } p^i < 1 \end{cases} \quad (5-4)$$

$$p^i = a_3^i / a_1^i \quad (5-5)$$

$$L_{33}^i = 1 - 2L_{11}^i \quad (5-6)$$

$$\beta_{kk}^i = \frac{k_{c,kk}^i - k_m}{k_m + L_{kk}^i (k_{c,kk}^i - k_m)} \quad (5-7)$$

$$k_{c,11}^i = \begin{cases} k_f^i / (1 + \gamma_{11}^i L_{33}^i k_f^i / k_m), & \text{for platelet inclusions} \\ k_f^i / (1 + \gamma_{11}^i L_{11}^i k_f^i / k_m), & \text{for other shapes} \end{cases} \quad (5-8)$$

$$k_{c,33}^i = \begin{cases} k_f^i / (1 + \gamma_{33}^i L_{11}^i k_f^i / k_m), & \text{for cylindrical inclusions} \\ k_f^i / (1 + \gamma_{33}^i L_{33}^i k_f^i / k_m), & \text{for other shapes} \end{cases}$$

$$\gamma_{kk}^i = \begin{cases} \alpha_k (2 + 1/p^i), & \text{for } p^i \geq 1 \\ \alpha_k (1 + 2p^i), & \text{for } p^i < 1 \end{cases} \quad (5-9)$$

$$\alpha_k^i = R_{TB}^i k_m^i / a_k^i \quad (5-10)$$

$k_{eff,kk}$ in equations (5-1) and (5-2) represents the effective TC of composite in global kk (x,y or z) directions. The subscripts f and m relate the associated symbol to the fillers and matrix respectively. The superscript i relates the symbol to i th filler. The other parameters are described as;

φ^i	Volume fraction of i th filler
β_{kk}	Non-dimensional enhancement factor in filler's local kk direction. It's is a function of some materials and processing parameters; equation (5-7)
L_{kk}	Shape factors (also called polarization factors) of filler's in local kk direction; equation (5-4)
$k_{c,kk}$	In the units of TC, is a measure of how effectively, the fillers can modify the TC of matrix; equation (5-8)
$\langle \cos^2 \theta \rangle^i$	Orientation factor of i th filler; equation (5-3)
p^i	Aspect ratio of i th filler; equation (5-5)
a_k^i	Radius of i th ellipsoid shaped filler along local k th axis
R_{TB}^i	Interfacial thermal resistance (ITR) of i th filler with the matrix

k_f^i	TC of ith filler
k_m	TC of the matrix
α_k	Non-dimensional parameter, to include the effect of Kaptiza radius; equation (5-10)
γ_{kk}	Non-dimensional parameter, to include the combined effect of Kaptiza radius and aspect ratio; equation (5-9)

5.2.3 Effective medium theory – non-dilute filler concentrations

In the current work focused on composites with non-dilute filler concentrations (high volume fraction), equations (1) and (2) are modified following the Bruggeman's differential effective medium theory, by integrating the differential form of low volume fraction relationship. The Bruggeman's theory is based on the postulate that for high volume fractions, the fillers can be added incrementally by considering the existing composite as a new matrix for each increment. Hence, for low volume fractions, equation (5-1) can be simplified for small φ as

$$k_{eff,11} = k_{eff,22} = k_m \left(1 + \sum_{i=2}^N \frac{\varphi^i}{2} \left[\beta_{11}^i \left(1 + \langle \cos^2 \theta \rangle^i \right) + \beta_{33}^i \left(1 - \langle \cos^2 \theta \rangle^i \right) \right] \right) \quad (5-11)$$

For equation (5-11) using the analogy of Every's model [32] the differential form and its integral form for a single filler can be written as follows in equations (12) and (13) respectively.

$$dk = \left(\frac{d\varphi}{1-\varphi} \right) * \frac{k}{2} * \left(\beta_{11} \left(1 + \langle \cos^2 \theta \rangle \right) + \beta_{33} \left(1 - \langle \cos^2 \theta \rangle \right) \right) \quad (5-12)$$

$$\int_{k_m}^{k_{eff}} \frac{2}{k * (\beta_{11}(1 + \langle \cos^2 \theta \rangle) + \beta_{33}(1 - \langle \cos^2 \theta \rangle))} dk = \int_0^\varphi \left(\frac{1}{1 - \varphi} \right) d\varphi \quad (5-13)$$

Equation 13 can be solved to result as follows;

$$\left(\frac{k_{eff,11}}{k_m} \right)^2 = \frac{1}{(1 - \varphi)^{\beta_{11}(1 + \langle \cos^2 \theta \rangle) + \beta_{33}(1 - \langle \cos^2 \theta \rangle)}} \quad (5-14)$$

Equation (5-14) can be solved iteratively for $k_{eff,11}$. On the same lines, equation (5-2) can be derived to give equation (5-15) that can also be solved iteratively for $k_{eff,33}$.

$$\left(\frac{k_{eff,33}}{k_m} \right)^2 = \frac{1}{(1 - \varphi)^{\beta_{11}(1 - \langle \cos^2 \theta \rangle) + \beta_{33}\langle \cos^2 \theta \rangle}} \quad (5-15)$$

5.3 Material and Methods

In order to validate the proposed model, low and high volume fraction samples of PMCs were synthesized using different matrices and filler-attributes (Table 5-1). The information about the particle size listed in Table 5-1 was provided by the supplier. For comparison, samples of neat polymers (HDPE and PP) were also passed through all the processing steps.

5.3.1 Materials

AlN (powders) and HDPE (granules) were purchased from Surmet Corporation (USA) and SABIC (KSA) respectively, whereas Al_2O_3 (powders), γ -methylacryloxypropyl trimethoxy silane (liquid) and PP (granules) were purchased from Sigma Aldrich. The

experimentally measured melting points (DSC) of HDPE and PP were 150 °C and 160 °C respectively.

5.3.2 Surface modification of fillers

The fillers under consideration in this work (ceramics) were surface treated to enhance compatibility with the matrix (polymers). For the surface treatment, γ -methylacryloxypropyl trimethoxy silane equivalent to 2% by weight of the filler was added in ethanol and stirred for 3 minutes at room temperature to homogenize. The pH of the solution was adjusted to 5 by dropwise adding dilute HCl while continued stirring at room temperature. The pre-weighed amount of ceramic powders was added to the solution followed by vigorous stirring for 20 min at room temperature. The solution was then refluxed at 70 °C on a hot plate with continued stirring for 1 hour. After that, the particles were allowed to settle down for another 1 hour. Finally, the extra solution was poured out and the settled particles were dried overnight at 80 °C in a vacuum oven. The pre-treated powders were placed in a vacuum desiccator to avoid any moisture or dust contamination.

Table 5-1 Details of prepared PMC samples

Matrix	Filler	Particle Size	Compositions (vol. %)	Number of samples	Series name
PP	AlN-S	Mean = 5 μm	2, 5, 10, 15, 20, 30, 40, 50	8 $\times$ 2	PPNS-X
PP	AlN-L	Mean = 20 μm	10, 20, 35, 50	4 $\times$ 2	PPNL-X
PP	Al ₂ O ₃ -S	< 15 μm	10, 30, 50	3 $\times$ 2	PPOS-X
HDPE	Al ₂ O ₃ -S	< 15 μm	10, 20, 35, 50	4 $\times$ 2	PEOS-X
HDPE	Al ₂ O ₃ -L	< 45 μm	10, 20, 35, 50	4 $\times$ 2	PEOL-X
HDPE	AlN-L	Mean = 20 μm	10, 30	2 $\times$ 2	PENL-X

5.3.3 Melt mixing

The pre-treated ceramic powders were melt-mixed with the polymer matrix using Brabender Mixer. However, before melt mixing, the polymer granules were dried in a vacuum desiccator overnight. Initially, the temperature of the three zones of the mixing chamber was set to the processing temperature (180 °C). After attaining the set temperatures, the polymer granules, and pre-weighed ceramic powders were added at a slower rpm (30 rpm). Then the chamber was closed and mixing speed was increased to the processing speed of 60 rpm and the mixing was continued for 30 minutes. After each mixing experiment, the chamber was cleaned thoroughly to avoid any contamination to the next composition. The output of Brabender Mixer is in the form of irregular lumps that cannot be used for any type of testing. Therefore, these composite lumps were processed further to make samples of the desired shapes for measurements.

5.3.4 Compression-molding

Depending upon the required thickness, a pre-weighed amount of the lumps was hot-pressed in a compression-molding machine at the temperature slightly above the melting temperature of the matrix for the particular composition. The samples with HDPE and PP matrices were hot compressed at 160 and 170 °C, respectively at a pressure of 3 MPa for 15 min. This step produced samples of cylindrical shape that could be cut further to get the desired shape for a particular measurement.

5.3.5 Measurements and characterizations

TC of the samples was measured using TCi Thermal Conductivity Analyzer by C-Therm Technologies Ltd., Canada. Moreover, the heat transfer capabilities of the samples were compared using FLIR One thermal imaging camera. For imaging, a hot plate was initially set to a steady-state temperature of 80 °C. The samples were directly placed on the hot plate and the images were captured with a time interval of 5 sec until 60 sec. Filler's morphology and their distribution and interface condition in the composites were observed by Tescan Lyra 3 FESEM. The powders and fractured surfaces for microscopy were gold-coated using a sputter coater for 20 sec and FESEM was operated in BSE mode at 20 kV for all the composite samples.

5.4 Results and discussion

5.4.1 Powders morphology

Figure 5-1 shows the FESEM images of different ceramic powders used. All of the powers conforms to the particle size reported by the suppliers and reported in Table 5-1. Particle size in AlN-L is more homogeneous as compared with AlN-S. On the other hand, Al₂O₃-L particles are roughly equiaxed, whereas Al₂O₃-S are mostly oblates.

5.4.2 Composites Fractured Surfaces

Figure 5-2 and Figure 5-3 show the representative micrographs of composite samples with PP and HDPE matrices respectively. All of the images show a homogenous distribution of particles, which indicates the effectiveness of the synthesis route adapted in this work. The BSE color images enable the ceramic particulates to be clearly identified within the matrix and even particles of AlN embedded under the matrix are also visible (Figure 5-3c). In both Figures, the ceramic particles being higher in average atomic weight appear brighter as compared with the matrix. On the other hand, color images in parallel further clarify the matrix areas being more bluish due to lower signal intensity, whereas the ceramic particles appear green-red due to higher signal intensity.

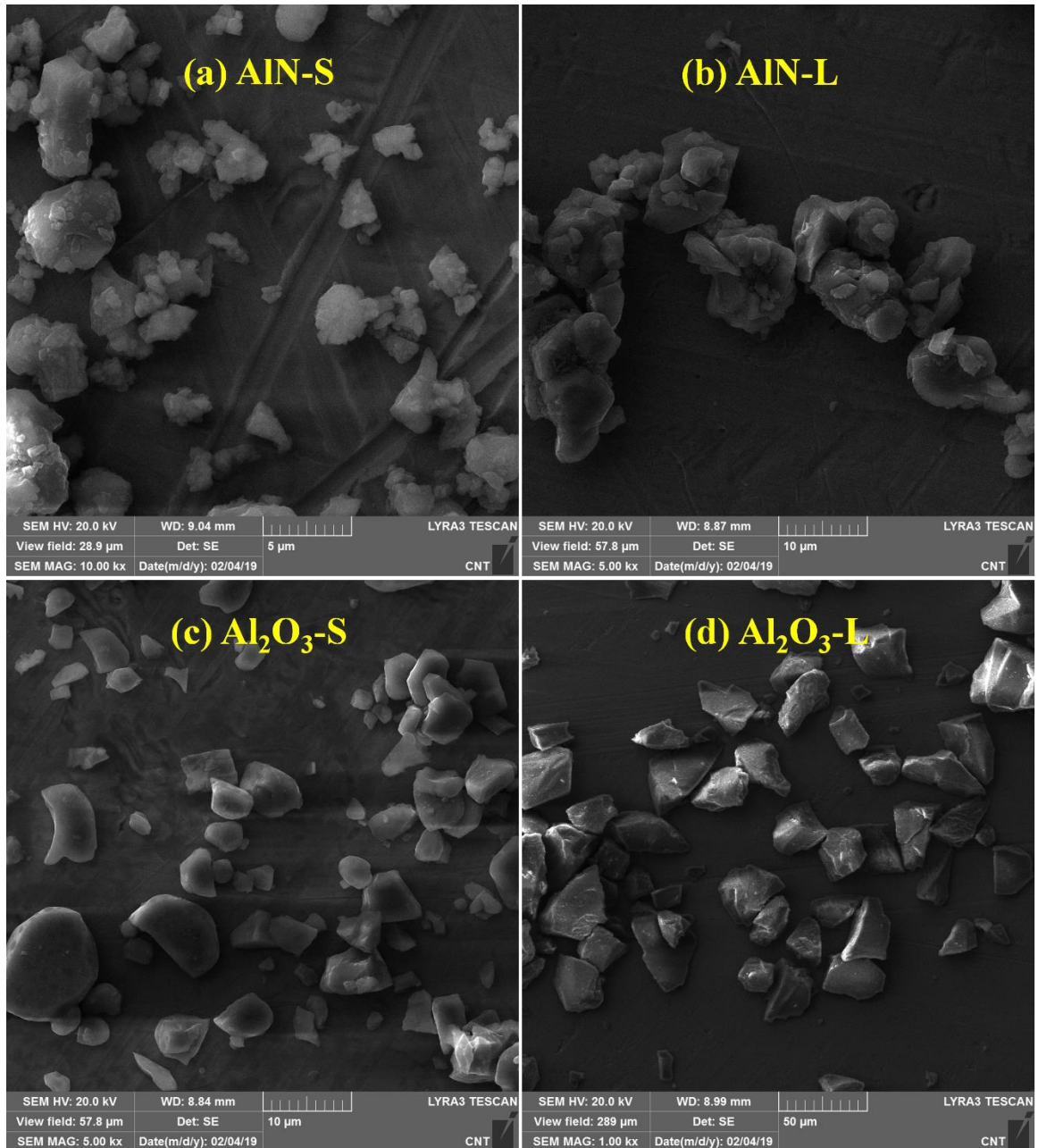


Figure 5-1 FESEM images of different ceramic particles used in samples listed in Table 5-1; (a) AlN-S; (b) AlN-L; (c) Al₂O₃-S; (d) Al₂O₃-L

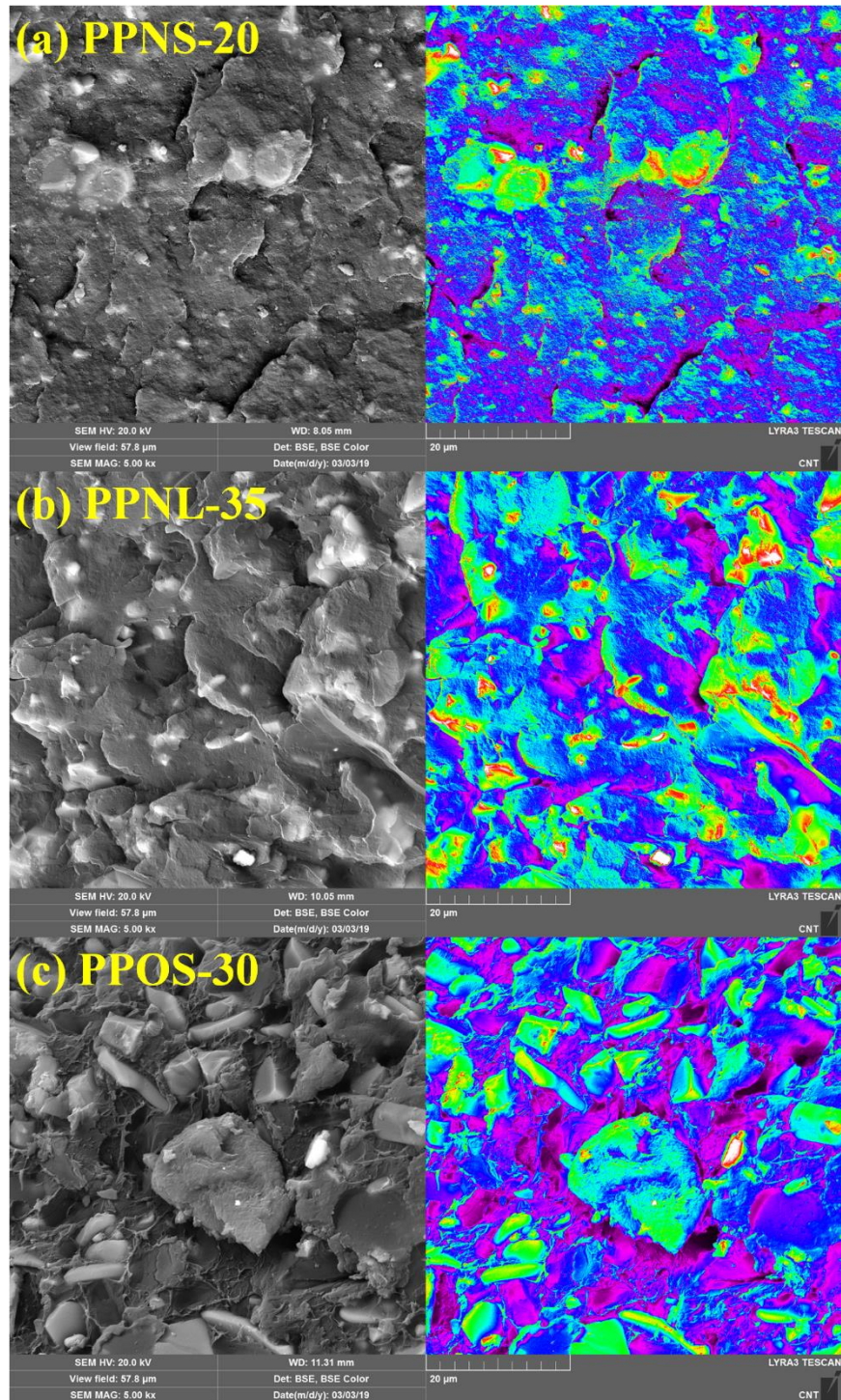


Figure 5-2 Representative FESEM images of composites fractured surfaces with PP as matrix and (a) 20% AlN-S, (b) 35% AlN-L, or (c) 30% Al₂O₃-S as filler

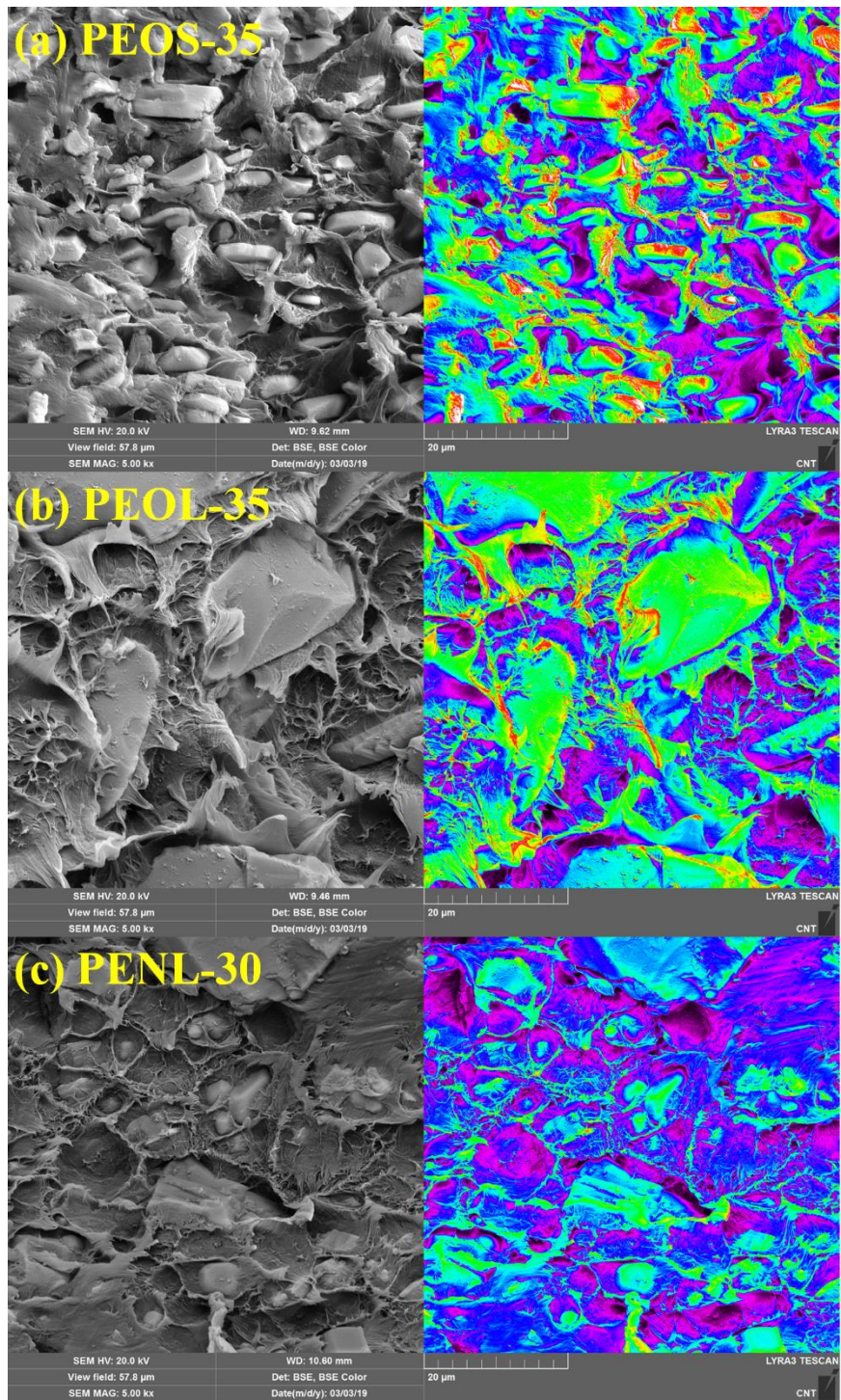


Figure 5-3 Representative FESEM images of composites fractured surfaces with HDPE as matrix and (a) 35% Al_2O_3 -S, (b) 35% Al_2O_3 -L, or (c) 30% AlN -L as filler

5.4.3 Thermal conductivity measurement and validation

5.4.3.1 Comparison of measured and model's estimated TCs

The measured TCs of the produced samples (as listed in Table 5-1) are presented and compared to the predictions of the dilute and non-dilute models in Figure 5-4. The predictions of dilute and non-dilute models are close to each other at lower volume fractions up to 0.2. However, the predictions of the dilute model are significantly less than the measured TCs at higher volume fractions as compared with the predictions of non-dilute model. The estimations of non-dilute model and measured TCs are in good agreement qualitatively in each of the series up to 40 vol.%, whereas, the deviations are mostly at $\phi = 50\%$. The higher deviations with the dilute model are associated with the ignored interactions among the effective fields of the neighboring particles. On the other hand, the non-dilute model is capable of accurately predicting the trend owing to the integration of the infinitesimally dilute additions of fillers into the homogeneous matrices. These results clearly indicate that the current model can be used for both dilute and non-dilute filler concentrations with high accuracy as compared to the dilute one, which underestimates the thermal conductivity especially at high volume fractions of fillers.

The higher TC in Figure 5-4 (d)-(f) as compared with (a)-(c) are due to the higher TC of matrix, HDPE (the continuous phase) in the former case. Comparing Figure 5-4 (a) with Figure 5-4 (b) confirms that larger particle size (in PPNL) can provide better TC enhancement. The same is the reason for the difference observed between Figure 5-4 (d) and (e). A larger particle size would have a smaller surface area per unit weight and hence,

a smaller thermal contact resistance leading to higher TC. Another important TC-controlling factor is the aspect ratio of the fillers; a near-spherical particle can provide the least enhancement as compared to prolate or oblate. Therefore, when Figure 5-4 (a) – (PPNS - equiaxed filler particles) is compared with Figure 5-4 (c) – (PPOS - oblate filler particles), the smaller Al_2O_3 particles are more capable in TC enhancement. The oblate or prolate particles have more tendency to form inter-connecting network and hence can provide a higher effective TC. The deviation of results at $\phi = 0.5$ is attributed to the processing-driven deviation of the final microstructure from the assumptions of model. The detailed effects and reasons for each parameter have been discussed in the parametric studies.

5.4.3.2 Input parameters to the model

The magnitudes of different matrix and filler –related input parameters required in the solution of equation 14 have been listed in Table 5-2. $k_f^{\text{Al}_2\text{O}_3}$ and k_f^{AlN} are the intrinsic TCs of the fillers and commonly reported in the literature. The intrinsic TCs are only sensitive to particle size if and only if the particle size is close to their mean free path but in this work are independent of particle size due to micron sized regime. k_m^{PP} and k_m^{HDPE} are the TCs of the PP and HDPE, respectively. The TCs of the phases “ k_f and k_m ” are variables among different series depending upon the matrix and the filler regardless of particle size and aspect ratio. $\langle \cos^2 \theta \rangle$ is assumed to be 1/3 for random orientation in each of the PMCs series because the mixing and sampling route adapted in this work does not cause any preferred orientation of the fillers in the final microstructure, as it is observed in the fractured surfaces of the samples (ref. Figure 5-2 and Figure 5-3). Moreover, the effect

of orientation is only sensitive with high aspect ratio filler particles at low volume fractions. At high volume fractions, the particle-particle connections are formed by default and the TC is enhanced in all directions isotropically or an-isotropically depending upon the preferred orientation. The model assumes the particles to be ellipsoidal shape with an average particle size. Hence, a_1 represents the average radius of the particle and a_3 represents either the average length of prolate (when $a_3 > a_1$) or the average thickness of oblate (when $a_3 < a_1$) shaped particles. The average values of particle size and aspect ratios for the four different types of particles used in the calculations of model are based on average size observed in FESEM images.

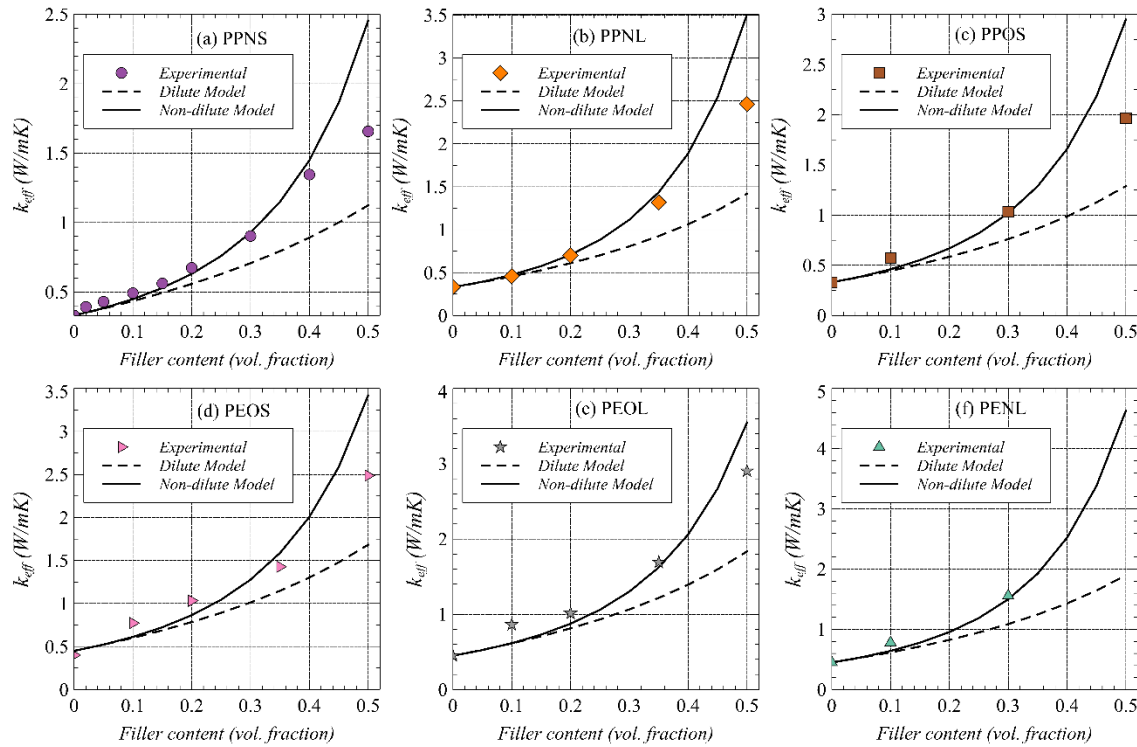


Figure 5-4 Measured and model-estimated values of thermal conductivities vs. fillers volume fraction in different composite systems showing a clear difference between the predictions of dilute and non-dilute models at higher volume fractions; (a) PPNS; (b) PPNL; (c) PPOS; (d) PEOS; (e) PEOL; and (f) PENL

The values of R_{TB} for a particular composite system depend upon the intrinsic thermal properties of matrix such as specific heat, density and Debye velocity, and some interface dependent properties such as acoustic impedance and critical angle for phonon-phonon coupling. Jiajun et al. [33] has reported that the theoretical value of R_{TB} based on the acoustic mismatch model (AMM) for polyimide-AlN composites is around $2.5 \times 10^{-7} \text{ m}^2\text{K/W}$ while R_{TB} determined by calibration of their model to the experimental data is $3.32 \times 10^{-7} \text{ m}^2\text{K/W}$. For the polymers, having smaller bulk densities and large heat capacities, the value of R_{TB} mainly depends upon the ratio of Phonon Velocities of the two phases; v_f/v_m . The range of v_f for AlN and Al_2O_3 is 6,300 – 10,000 m/s considering $v_f = (\text{Bulk_Modulus/Bulk_density})$ [166] and for polymers, such as HDPE and PP, v_m is $\sim 2500 \pm 100 \text{ m/s}$ [167]. Hence, the maximum variation of R_{TB} , for the composites under consideration is expected to be within a range of $1.15 \times 10^{-7} - 22.5 \times 10^{-7} \text{ m}^2\text{K/W}$ using the simplified expression of R_{TB} [equation (5-16)] using AMM [168].

$$R = \frac{2(\rho_m v_m + \rho_f v_f)^2}{C_m \cdot \rho_m^2 \cdot v_m^2 \cdot \rho_f v_f} \left(\frac{v_f}{v_m} \right)^2 \quad (5-16)$$

The exact data for the phonon velocities of materials is mostly unavailable, and therefore, the values of R_{TB} in the literature are mostly based on the calibration of theoretical models with the experimental data. In the current work, the ceramic powders were surface treated before mixing with the polymer matrix, therefore, R_{TB} is expected close to its lower limit. We have selected R_{TB} to be $3.32 \times 10^{-7} \text{ m}^2\text{K/W}$ which is a reported value for a similar composite system [33] and eventually, the experimental results are found in good agreement to the predictions of model.

Table 5-2 Values of the input parameters for different series of composites

Parameter	Value
k_f^{Al2O3}	33 W/mK
k_f^{AlN}	180 W/mK
k_m^{PP}	0.27 W/mK
k_m^{HDPE}	0.45 W/mK
Average $a_1^{Al2O3-S}$	10 μm
Average $a_1^{Al2O3-L}$	30 μm
Average a_1^{AlN-S}	2 μm
Average a_1^{AlN-L}	15 μm
$p^{Al2O3-S}$	0.5
$p^{Al2O3-L}$	2
p^{AlN-S}	2
p^{AlN-L}	2
$\langle \cos^2 \theta \rangle$	1/3 [for random orientation of particles]
R_{TB}	$3.32 \times 10^{-7} \text{ m}^2\text{K/W}$

5.4.3.3 Validation from literature with different cases of R_{TB} and $\langle \cos^2 \theta \rangle$

All of the results shown in Figure 5-4 are combined on a normalized scale and compared to the model as shown in Figure 5-5 (a). Moreover, the model is validated by experimental data of TCs with different cases of R_{TB} and $\langle \cos^2 \theta \rangle$ available in the literature as shown in Figure 5-5 (b). The solid line in Figure 5-5 (a) and (b) is the exact estimation of the model, whereas the other two straight lines are drawn to quantify the deviation. To avoid crowd of many lines and points, the charts in Figure 5-5 are log-normalized, and x and y -axes of the chart are taken to be the left and right hand side of the equation (5-14) respectively. For plotting each point in Figure 5-5 (a), the abscissa was calculated by the right hand side of

equation (5-14) with its own input parameters as listed in , and the ordinate was calculated by using the experimental values of k_m and k_{eff} . In this way, the points which are close to the prediction of model, would appear on or around the solid line and vice versa. Figure 5-5 (b) was generated on the same lines with the input parameters listed in Table 5-3. Three research publications [6,17,20] are selected to validate the model from the data published in the literature. Deng et al. [20] have produced composites with polyphenylene sulphide (PPS) as matrix and expandable graphite (EG) as filler. It is proved that a backbone structure of benzene rings in PPS develops a strong interaction of π - π electrons between PPS and EG. This interaction improves the crystallization behavior of the composite and segregates the EG in the amorphous regions to enhance the effective TC due to very low ITR. Moradi et al. [6] have published their work to show the effect of particle size of (hexagonal boron nitride) hBN fillers in epoxy matrix. This work is the case of high ITR due to weak interaction between hBN particles and epoxy matrix. On the other hand, Yu et al. [17] have reported a process-induced in-plane alignment of hBN particles and measured in-plane and through-plane TCs of composite films with thermoplastic polyurethane (TPU) matrix. This work is taken as the case to validate the effect of orientation captured by the model. Most of the measured TC values of the composites are within or close to bounds of $\pm 20\%$ of the exact estimation which indicates the strong capability of the model to include the effects of many different parameters.

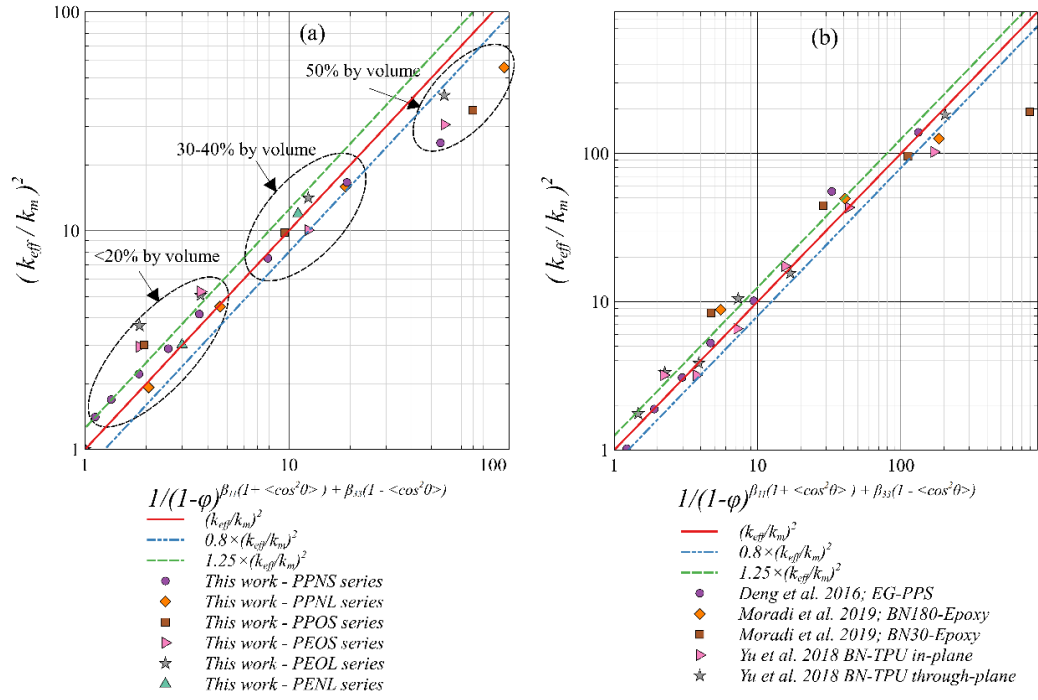


Figure 5-5 Model's estimated effective thermal conductivity compared to the measured thermal conductivity results of (a) different series of polymer-composites produced in the current work; (b) different cases of interface thermal resistance and orientation of the fillers in the literature

Table 5-3 Values of the input parameters for different cases available in the literature

References →		[20]	[6]	[6]	[17]	[17]
Parameters ↓	Symbol	Values				
TC Filler ($\text{Wm}^{-1}\text{K}^{-1}$)	k_f	200	600	600	600	600
TC Matrix ($\text{Wm}^{-1}\text{K}^{-1}$)	k_m	0.24	0.14	0.14	0.24	0.24
Particle's radius (μm)	Average a_1	5	50	10	15	15
Particles aspect ratio	p	0.05	0.1	0.095	0.2	0.2
Effect of orientation	$\langle \cos^2 \theta \rangle$	1/3	1/3	1/3	1	0
ITR ($\times 10^{-7} \text{ m}^2\text{KW}^{-1}$)	R_{TB}	1	23	23	16	16

5.4.4 Thermal imaging

To demonstrate the thermal management capability and physically observe the difference in thermal conduction of different composite series, the surface temperature variation of the samples is recorded using infrared camera. Figure 5-6 (thermal images), is a qualitative comparison of heat conduction in different PMC series namely PPNL, PEOS, and PEOL. For reference, the images at 10, 40 and 60 sec are presented in Figure 5-6. Clearly, the results conform to the TC results as shown in Figure 5-4 and Figure 5-5. The samples with higher volume fractions are capable to increase their temperature at a faster rate. PPNL as compared with PEOS and PEOL shows a lower temperature rise because of the lower matrix TC in PPNL. On the other hand, PEOL, because of its larger particle size, shows heat conduction rate more than PEOS.

5.4.5 Parametric studies

To explore various possible design alternatives, a detailed parametric analysis is performed by varying fundamental attributes of matrix and fillers (Figure 5-7). The parametric studies are conducted using the proposed model with reference values of particle size, aspect ratio and TCs of matrix and filler considered equal to those of PPOS-series (i.e. PP matrix with smaller sized Al_2O_3) as mentioned in Table 5-2. For example, in Figure 5-7a, the curves of are drawn for different values of k_m and rest of the parameters are for small sized Al_2O_3 i.e. $k_f = 33 \text{ W/mK}$, Average $a_1^{\text{Al}_2\text{O}_3-S} = 10 \text{ }\mu\text{m}$ and $p^{\text{Al}_2\text{O}_3-S} = 0.5$. Few terms to be used repeatedly in the following section are defined here. Percolation threshold (ϕ_c) is the volume fraction of filler at which effective TC starts increasing sharply due to the increased number of particle-particle connections. $k_{eff,max}$ is the maximum achievable effective TC

in the particular case at $\varphi > \varphi_c$ or maximum at $\varphi = 0.5$. The number density of particles is meant for the number of particles of the filler per unit volume of the composite.

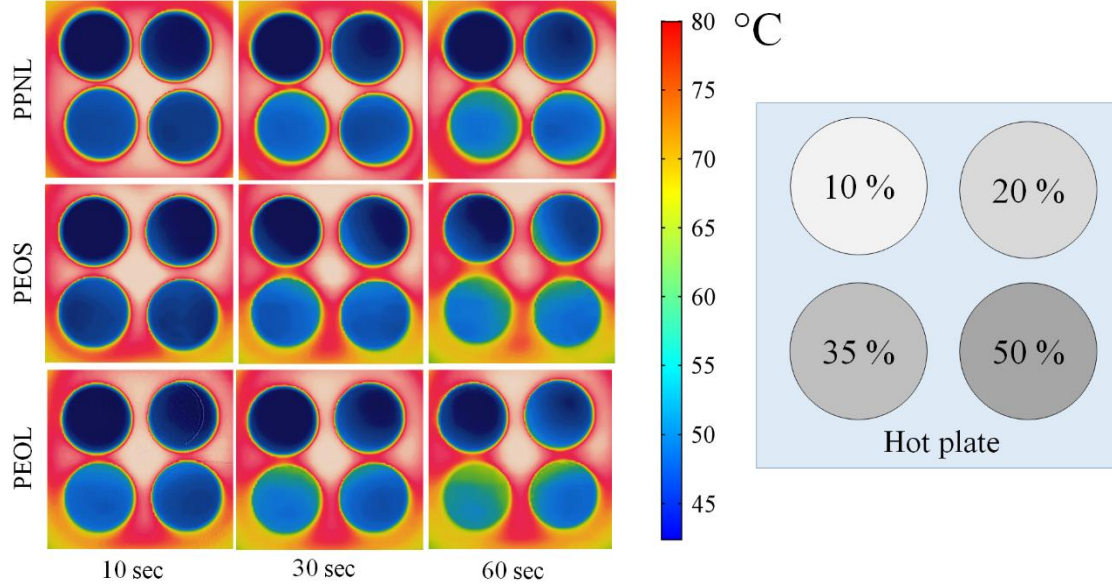


Figure 5-6 Infrared Camera images of different series of PMCs

5.4.5.1 Thermal conductivities of matrix and filler (k_m and k_f)

Figure 5-7 (a) shows the effect of k_m on k_{eff} . For a constant k_f there exist an optimum k_m that can lead to maximum absolute $k_{eff,max}$. A k_m close to k_f can decrease the effective TC rather. k_m in the range 1-2.5 W/mK is the best for $k_f = 33$ W/mK of Al_2O_3 . Figure 5-7 (b) shows the effect of varying k_f on k_{eff} . As expected, k_{eff} is increasing with k_f but only in the range of 1-30 W/mK and therefore $k_{eff,max}$ has almost been converged for the current set of parameters. Further increasing k_f up to 1000 W/mK does not bring a significant improvement to $k_{eff,max}$. k_f and k_m enter into the model – equation (5-14) through equation (5-7) for β_{kk} and equation (5-8) for $k_{c,kk}$ which are converging functions of k_f but not that of k_m and therefore it affects k_{eff} accordingly. In a continuous phase, heat is conducted without

any intervening resistance and hence heat flow depends only on intrinsic TC. However, by reinforcing the matrix, the interfering thermal contact resistance (TCR) tends to limit the enhancement provided by a thermally conductive discontinuous phase (reinforcement, filler or inclusion). The particles of discontinuous phase assist heat conduction in the continuous phase (matrix) and therefore, effective TC of the composite does greatly depend upon TC of continuous phase.

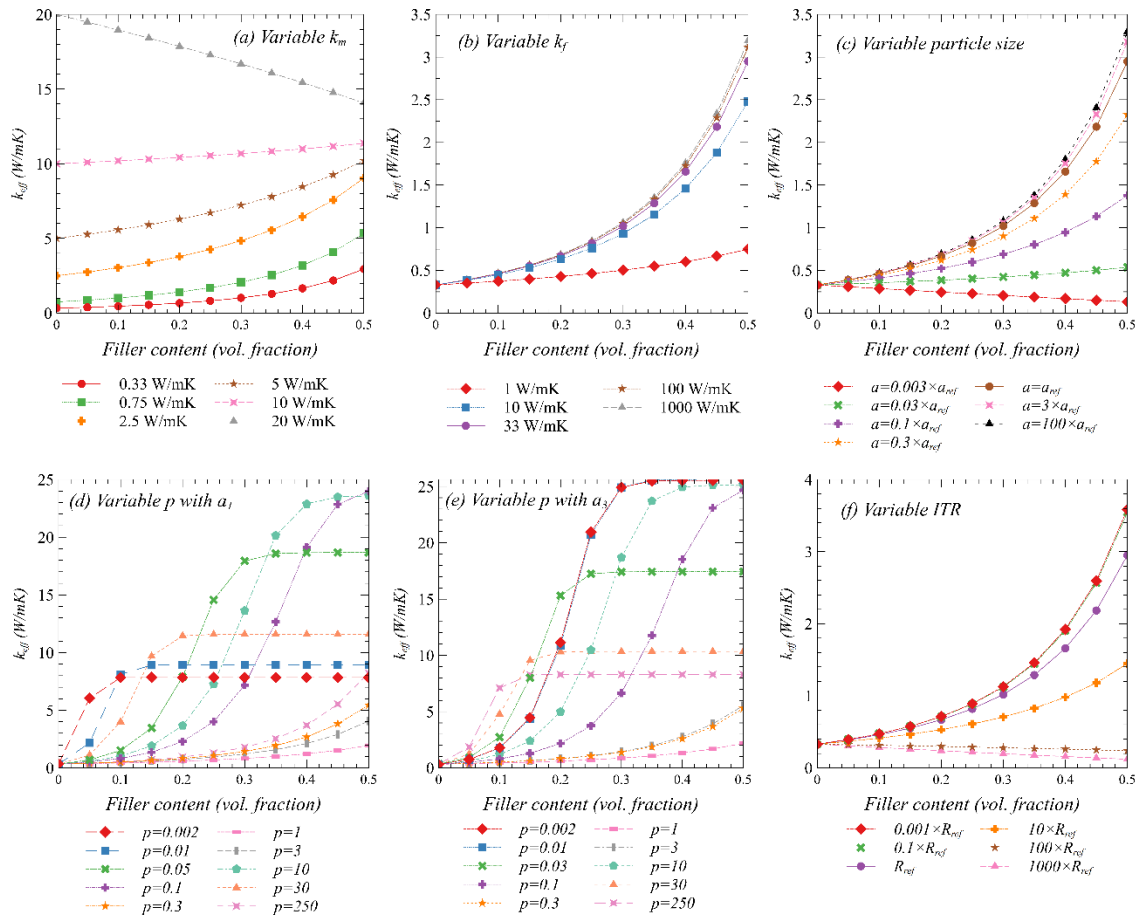


Figure 5-7 Results of parametric studies by varying one parameter at a time: (a) variable k_m , (b) k_f , (c) variable particle size, (d) variable p with a_1 , (e) variable p with a_3 , (f) variable ITR

5.4.5.2 Particle size (a_1 , a_3) and aspect ratio (p)

The parametric studies of varying dimensions of ellipsoid shaped fillers are shown in Figure 5-7 (c-e). Figure 5-7 (c) shows the effect of particle size using a ‘*size multiplying factor*’ to both of the radii without changing the aspect ratio. This factor enters into the model through equation (5-10). Decreasing the particle size increases the matrix–filler contact area and that is to increase the TCR of the system. Therefore, TC increases with particle size at a constant aspect ratio and vice versa (Figure 5-7 (c)). However, the effect of increasing particle size is almost converged at a multiplying factor of 3 due to a smaller value of k_m .

The filler’s aspect ratio (p) is the most sensitive. In Figure 5-7 (d-e) a_1 is the radius of the particles, whereas a_3 is length (for $p > 1$) or thickness (for $p < 1$). The aspect ratio is varied in the range of 0.002-250 by varying either a_1 or a_3 as shown in Figure 5-7 (d-e). The following facts are deduced from these two parametric studies;

- Particles with $p = 1$ can provide the least $k_{eff,max}$, and φ_c is not reached even at $\varphi = 0.5$. Due to their simplest geometry, the spherical particles have the least tendency to make particle-particle connections and hence could not percolate.
- Modifying the geometry of the particle to prolate ($p > 1$) or oblate ($p < 1$) increases the number of particle-particle connections and therefore with $p = 0.3$ and $p = 3$ increasing $k_{eff,max}$ is observed, but still φ_c is not reached even at maximum value of $\varphi = 0.5$.

- Further modifying the geometry increases the number of particle-particle connections and hence at $p \sim 0.1$ or 10, the maximum inter-particle connectivity can be achieved with $k_{eff,max}$ up to 25 W/mK using the current matrix and fillers.
- The lower value of φ_c for $p = 10$ as compared with that for $p = 0.1$ is attributed to the difference of geometries. A unit volume of a prolate ($p=10$) is much less as compared with that of an oblate ($p = 0.1$) and hence for a given volume fraction, fibers (prolates) are more capable to have a lower φ_c due to their higher number density than that for platelets (oblates).
- Reaching $p > 10$, by decreasing a_1 : for a given volume fraction, both the number density of particles and the tendency to percolate are increasing simultaneously, and hence, φ_c is decreased with $p = 30$ as compared with $p = 10$. However, maximum $k_{eff,max}$ is lowered due to the limited length ($a_3 = 5 \mu m$) of these particles. By further increasing p to 100 or more, the radius of the particles (a_1) becomes so small that the effect of TCR dominates and the system does not reach percolation stage.
- Reaching $p > 10$, by increasing a_3 OR reaching $p < 0.1$, by increasing a_1 : particles can easily percolate by connecting each other and this allows percolation at a lower φ_c . However, by increasing either a_3 or a_1 , the number density of particles is decreased and therefore $k_{eff,max}$ is lowered.
- Reaching $p < 0.1$, by decreasing a_3 : the increased number density of particles increases the number of particle-particle connections per unit volume and therefore φ_c decreases continuously until $p = 0.002$. However, in affecting $k_{eff,max}$, two factors

namely connections density and TCR due to the increased surface area are competing with each other. With $p = 0.03$ the effect of TCR dominates (a lower $k_{eff,max}$), whereas further decreasing to $p = 0.002$ the connection density among the particles dominate and a higher $k_{eff,max}$ can be achieved with a little compensation of ϕ_c .

5.4.5.3 Interface thermal resistance (ITR)

The effect of ITR (Figure 5-7 (e)) is analogous to reciprocal of particle size at constant p (Figure 5-7c). Increasing particle size and decreasing ITR have the same effect and hence the shape of the curves is the same. An increased ITR with constant matrix–filler contact area provides more resistance to the heat flow across the interfaces and therefore, tends to decrease the effective TC.

5.4.6 Recommendations for achieving ultrahigh thermal conductivity

The proposed model has the capability to handle a variety of materials and processing parameters in tailoring the TC of resulting composites. Furthermore, the model is also capable to find the percolation threshold for a particular combination of matrix and filler, which depends upon the particle size, shape, and preferred orientation. The current approach for achieving ultrahigh TCs is to reinforce matrix such that the particles of thermally conductive phase are interconnecting leading to create conductive pathways. The filler's aspect ratio can be tailored to minimize the percolation threshold for achieving maximum TC. The proposed model can also be used to optimize the filler-attributes in such composites. Similarly, the proposed model is also applicable to the composites with

segregated structures where compositions and proportion of segregated phase and distribution of segregating phase can be optimized for the best performance in heat conduction. In this way, the model is applicable to a wide variety of composite designs and finds its application for the estimation of effective TC and optimization of materials and processing parameters.

5.5 Conclusions

A new model is derived and validated for the estimation of effective thermal conductivity of composites. The proposed model is equally applicable for dilute and non-dilute concentrations of fillers in polymer matrix composites with wide ranges of filler particle sizes and shapes. Following are some of the major outcomes of this work.

- The model is validated by producing different series of polymer composites with variable matrix and filler-attributes. The model is also validated from literature with different cases of interface thermal resistance and orientation of the fillers.
- The material design capability of the model is demonstrated through parametric studies considering the thermal conductivity of matrix and filler, particle size, aspect ratio, and interface thermal resistance as variables. Increasing thermal conductivity of matrix and filler, increasing particle size, and decreasing interface thermal resistance have positive effects on the effective thermal conductivity of the resulting composites.
- The thermal conductivity of the continuous phase is a controlling factor for the overall enhancement of effective thermal conductivity.

- Among various filler-attributes, aspect ratio is the most sensitive parameter to the effective thermal conductivity, which significantly controls the formation of percolating network. The percolation threshold to achieve maximum effective thermal conductivity also greatly depends on the aspect ratio of particles.
- The model is applicable for material design in wide range of thermal management applications and can make a mathematical foundation for the current and future designs of polymer matrix composites with percolating non-dilute filler concentrations to achieve ultrahigh thermal conductivity.

CHAPTER 6

HIGH-PERFORMANCE POLYMER COMPOSITES AS NEW ENCAPSULANT MATERIALS FOR CONCENTRATED PHOTOVOLTAIC MODULES

A computational design methodology is reported to propose a high performance composite for backside encapsulation of concentrated photovoltaic (CPV) systems with focus on improved module life and electrical power. As first step sequentially coupled thermo-mechanical finite element (FE) simulations are run on CPV modules, to identify the optimum thermal conductivity (k), coefficient of thermal expansion (α), and long-term shear modulus (G_∞) of backside encapsulant. It is found that increasing k can improve electrical power, and decreasing α and G_∞ can improve service life. As second step, in-house built codes based on properties estimation models are used in line with target properties to design composites with suitable matrix and filler-attributes. Potential polymer composite systems that are expected to provide the target properties are proposed. The codes are based on differential effective medium theory and mean-field homogenization, which lead to the selection of matrix, filler, volume fractions, and type of particulates. Thermoplastic polyurethane loaded with ceramics fillers of designated particle size and shape morphology are found potential composites. As third step, some representative

samples are synthesized through melt-mixing and compression-molding route, and characterized. The target properties such as k , α , viscoelastic parameters, and G_∞ are measured to validate the computational design and used as inputs to the fourth step i.e. to evaluate the performance of CPV modules using the parent finite element model. A very good agreement is found between the predicted and measured properties. As fourth step, the parent finite element problem is solved using measured properties of encapsulant as inputs to predict the practical values of electrical power and module life. It is found that the proposed composite can drag the cell temperature down by 5.8 °C when compared with neat TPU which leads to a 4.3 % increase in electrical power along with a reasonable module life. It is expected that this approach will allow cost-effective production of polymer composites in various industrial applications.

6.1 Introduction

The total global installed solar photovoltaic (PV) capacity of the world was only 100.9 GW at the end of 2012. The PV installations are growing so rapidly that the capacity of installations within the historic year of 2017 were close to the total PV capacity of the world until 2012 i.e. 99.1 GW. By having 30% more installations than 2016, the total PV capacity of the world was over 400 GW which is expected to cross 1 TW by 2022. ACWA power, a Saudi company has won a tender of 300 MW Solar Power at the lowest price of only 2.34 US cents/kWh in February 2018. The decreasing cost and increasing demand have boosted the development for high efficient PV modules [34]. Figure 6-1 shows an

overview of the history and forecast of PV capacity and PV generation from 2017 to 2023 [169].

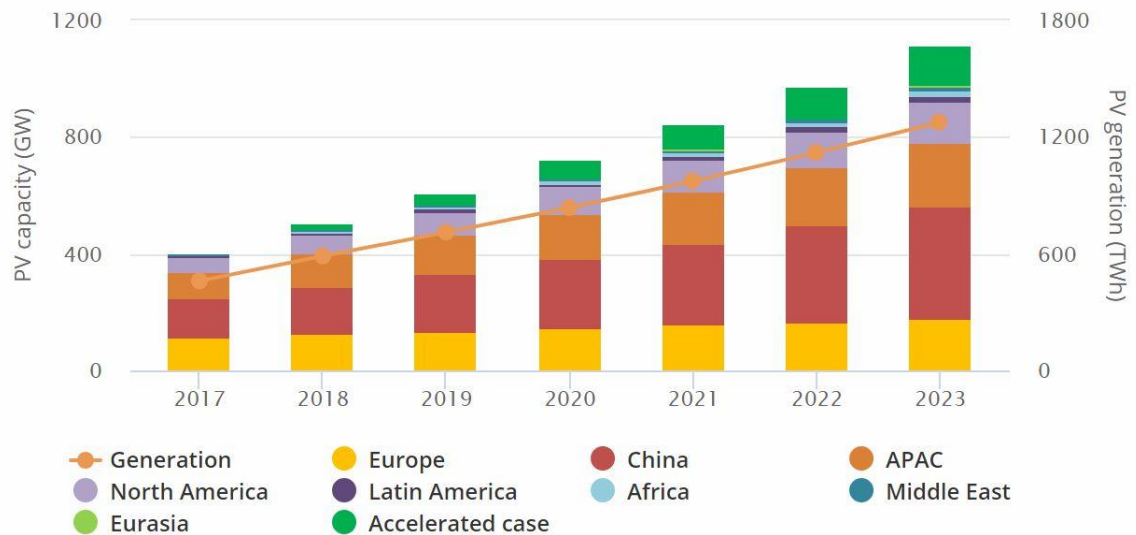


Figure 6-1 Growing and forecasted PV capacity and PV generation from 2017 to 2023 in different regions of the world [169]

The PV efficiency is improved by concentrating PV modules. However, the CPV systems are less-common due to the required additional costs of concentrating optics and cooling systems. CPV systems are categorized based on their concentration factor, optical standard, focal shape, and distribution of illumination, etc. Having a lower concentration factor of 1 to 30, CPV systems are classed as low concentration PV (LCPV) modules and those with a concentration factor of more than 300 are said to be high concentration PV (HCPV) modules. The former (i.e. LCPV) type of modules use high-efficiency Si-Cells and are linear systems that concentrate the incident solar radiation in only one axis [35,36]. The PV efficiency is severely affected by high cell temperature or non-uniform cell temperature distribution. Moreover, the cells are prone to degradation if the temperature goes beyond a certain limit. Therefore, an appropriate cooling system is one of the major concerns in the

design of CPV systems. Moreover, a higher thermal conductivity of encapsulant can help faster cooling of the modules for having a better production of electrical power [37,38].

The motive behind the development of any composite material is always to enhance the overall performance of a system, which is directly linked to the intrinsic properties of the composite constituents. For example, a combination of high thermal conductivity (TC) and low coefficient of thermal expansion (CTE) is required for the substrate material in thermal management of microelectronics [170]. For some other applications, the required set of properties and their range depend on the functions and conditions of the material in focus. The composite attributes such as type of matrix and fillers, their volume fractions, particle size etc. are selected based on a particular set of target properties for enhanced performance of intended application [62]. The purpose of the current work is to present an integrated approach for the design and development of composite materials for backside encapsulant of CPV systems.

Hasan et al. [42] have compared the structural performance of different encapsulants being used in the PV industry. The performance criteria were light transmittance, UV durability, electrical insulation, moisture ingress, structural life, and cost. It was concluded that the increasing order of overall performance is Polyvinyl butyral (PVB) < thermoplastic polyurethane (TPU) < Polydimethylsiloxane (PDMS) < ethylene vinyl acetate (EVA) < ionomer. However, EVA is much popular in the solar industry because its cost is almost half as compared to ionomer.

The main objective of the encapsulant is to electrically insulate the circuit of solar cells and electrical connections. In addition, it also protects the solar cells from environmental effects, electrical leakage, and mechanical damage. To protect from environmental effects, the encapsulant should be resistant to water penetration and yellowing caused by UV-rays. To avoid leakage of current, the encapsulant must be a good electrical insulator i.e. high volume resistivity is required. Moreover, low elastic modulus is desired to minimize thermal stresses on the surrounding components. A low CTE is also desired to reduce the hysteresis of interfacial stresses in thermal cycling. Furthermore, the encapsulant has to be transparent from front side so that maximum solar radiations can be transmitted to the cells with minimum absorbance and reflection [171].

As compared to non-concentrated systems, the CPV systems encounter higher thermal stresses due to high and irregular distribution of flux and temperature [172] which lead to overheating and premature breaking of cells and interconnects mainly due to thermal fatigue [42]. Therefore, the requirement of high TC, low elastic modulus and low CTE becomes vital for the continued efficient performance of CPV systems. High TC can help the cells cool faster while low elastic modulus and coefficient of thermal expansion can reduce the thermal stresses in the encapsulated components.

This work is divided in two parts; part 1 is focused to determine the best combinations of thermal and structural properties of backside encapsulant, which could lead to improved overall performance and part 2 is to focused to design and develop a composite material with the best combination of material properties determined in part 1. Overall, in the part 1, thermal stress problem of a representative three-cell laminate of cooled CPV module is

solved as a sequentially-coupled finite element problem. The variable inputs to the finite element model are the target properties including thermal conductivity, coefficient of thermal expansion and long-term shear modulus. The performance indicators are module life and electrical power which are estimated from the solutions of finite element problem. From this exercise i.e. by studying the effect of material properties on the performance indicators, the optimum values target properties are obtained which are required for enhanced overall performance. The optimum required target properties are the inputs to the part 2, whereas the output of this part 2 is the composite material with properties close to the target values. The core of part 2 is to design the composite material i.e. to find the ingredients (or the phases), their compositions, percent volumes, and other filler-attributes. The design of composite material is based on the properties estimation formulations of Mori-Tanaka's mean field homogenization and the generalized effective medium theory. The complete design scheme and its implementation is explained in this chapter. The phases, compositions, particle size and other material attributes are predicted using design codes to acquire the target properties. Some representative composite samples are synthesized in line with the predictions and the resulting properties are measured for validation. The viscoelastic properties of the samples are also estimated for performance evaluation. The performance evaluation of the developed composite systems is conducted through the parent finite element model developed in part 1 for finding the optimum target properties by taking into consideration the measured properties and constitutive behavior as inputs to propose some practical values of electrical power output and service life.

6.2 Design scheme

6.2.1 Finding the optimum combination of material properties (Step 1)

Finding the target material properties and setting the target range is the first step of ‘application-focused’ design and development. The material properties, which are sensitive for improved performance, can be called as target material properties. The problem of how the target material properties are affecting the performance is solved by analytical or numerical methods. The analytical or numerical solution of a problem solved with variable combinations of material properties would elucidate their effects and sensitivity for the performance of the system and hence would lead to set the target range of material properties. The flow chart for the entire methodology of this step is presented in Figure 6-2 with reference to encapsulant of CPV systems.

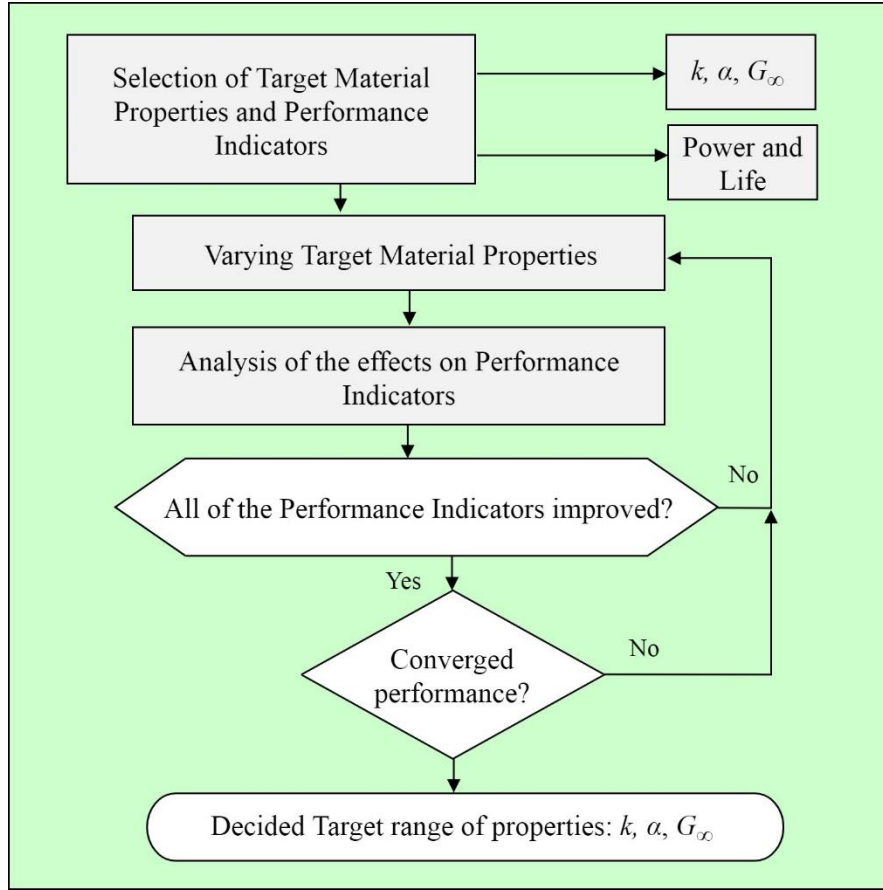


Figure 6-2 The flow chart for the step 1 of material design scheme i.e. Finding the optimum combination of material properties

6.2.2 Computational Design of composite material (Step 2)

The flow chart for the steps 2-4 of the design scheme are presented in Figure 6-3 with reference to encapsulant of CPV systems.

The second step is to design the material i.e. to select the material attributes such as the phases, their volume fractions, particle size, distribution and surface condition, etc. One of the solution strategies is to use property estimation models to predict the best combinations of material attributes for the intended properties. In order to implement this strategy, initially the possible phases including both matrices and fillers are identified such that their

combinations should not violate any major requirement. The essential requirement for any encapsulant material is to provide electrical insulation to the cells and hence the selected potential phases in the indented composite should have high volume resistivity. To meet this requirement, the best matrix is selected from the available candidates so that the loading of potential fillers lead to achieve the target material properties. In the next step of material design, the potential fillers, their required volume fractions, appropriate particle size, shape morphology, and distribution are selected by solving equations of material properties estimation models. The effective TC was estimated using the model for non-dilute concentrations explained in Chapter 5 and effective α and G_{∞} were estimated using the Mori-Tanaka's mean field homogenization explained in the section 2.3.2 in Chapter 2 of this dissertation.

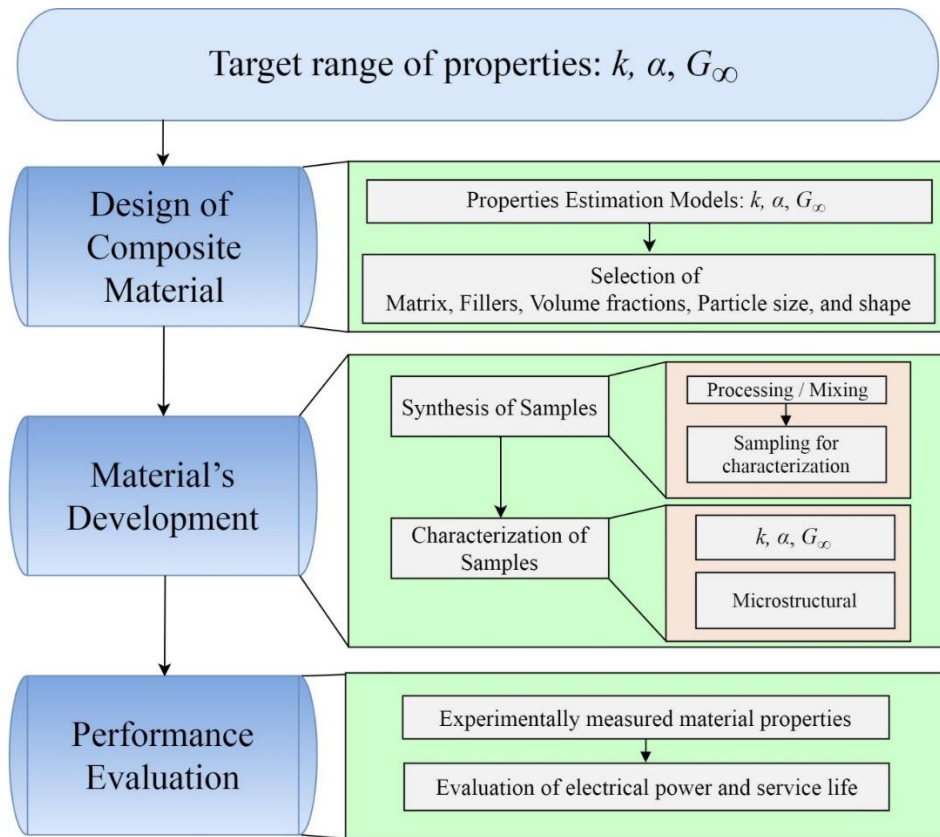


Figure 6-3 The flow chart for the steps 2-4 of material design scheme i.e. computational design of composite material, development of samples and performance evaluation

6.2.3 Development of representative composite samples (Step 3)

After the establishment of computational design of composite materials, few of the top potential candidates are experimentally developed. The development of samples includes processing from raw materials to the evaluation of material properties. For the polymer matrix composites, the raw materials are dried, the fillers are pretreated, the fillers + matrices are mixed by some appropriated techniques is the general route of processing. The processed and mixed polymer-composites are then molded to get the samples of desired geometry and gone through suitable application dependent properties evaluation. In this

work. Thermal conductivity, coefficient of thermal expansion, density, specific heat, viscoelastic parameters and long-term shear modulus are required to be evaluated.

6.2.4 Performance evaluation (Step 4)

This step is essentially a repetition of step 1, wherein the measured properties are going to replace the variable material properties. The performance evaluation can also be conducted by development of a lab-scale model of the problem under consideration.

6.3 Finite Element Model

6.3.1 Geometric Model

A representative 3D FE model of three-cell laminate was considered and solved using COMSOL Multiphysics. To have fully mapped mesh, the geometric model was divided into 7 layers as listed in Table 6-1 and shown in Figure 6-4. The geometry was created by generating the layers one-by-one starting from layer 4 followed by the neighboring three layers on both sides sequentially. The full model and through-thickness view of the geometric model is shown in Figure 6-4 (a) and (b). To have accurate results near the critical regions, the submodel as shown in Figure 6-4 (c) was solved for the structural part.

Table 6-1 Details of layers in the geometric model for finite element analyses

Layer #	Description
1	Back-sheet, 350 μm thick
2	Encapsulant bottom, 371 μm thick
3	Encapsulant + bottom connections, 129 μm thick
4	Encapsulant + cells, 200 μm thick
5	Encapsulant + top connections, 129 μm thick
6	Encapsulant top, 371 μm thick
7	Glass, 4 mm thick

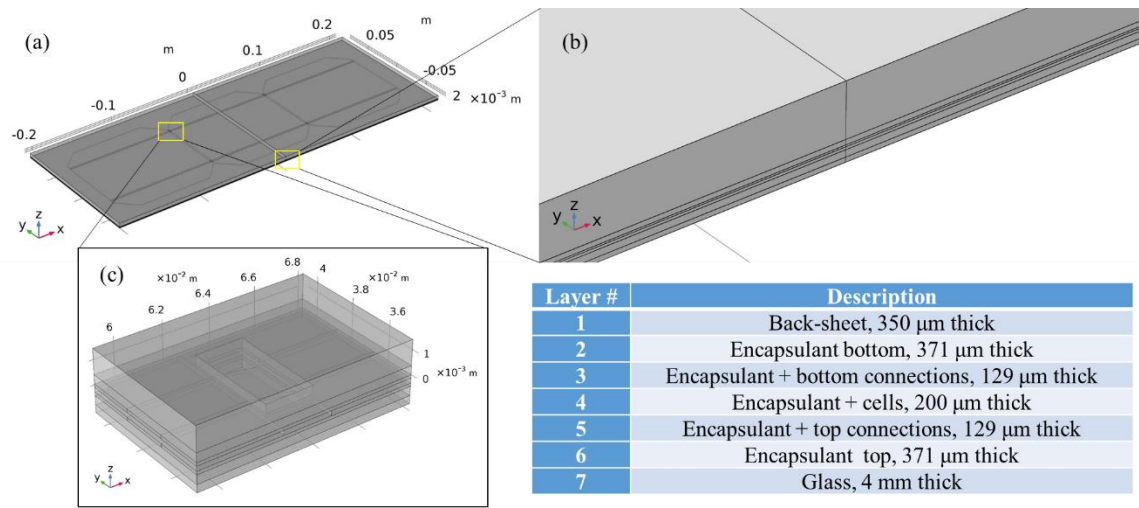


Figure 6-4 (a) Full three-cell model; (b) through thickness distribution of layers; (c) Sub-model around one of the inter-cell connection region of the full model

6.3.2 Material's models

The CPV module consists of five different materials each having different thermomechanical properties. The behaviors of different materials and their properties are listed in Table 6-2 and Table 6-3, respectively. The parameters of the Generalized Maxwell model for the viscoelastic behavior of EVA were taken from published literature [42]. The

material properties of backside encapsulant (layers 2 and 3) were varied in the ranges as listed in Table 6-4.

Table 6-2 Materials' constitutive behavior used in FE model

Material	Behavior
Glass	Isotropic, Linear elastic
Back-sheet	Isotropic, Linear elastic
Si – Cells	Orthotropic, Linear elastic
Cu – Connections	Isotropic, Bilinear Elastoplastic
Encapsulant	Isotropic, Linear Viscoelastic

Table 6-3 Material properties of various components used in FE model [64,173]

	Materials				
Properties	Glass	Back-sheet	Si – Cells	Cu – connections	EVA – encapsulant
CTE = α ($\times 10^{-6}$ K ⁻¹)	8.00	50.4	$\alpha(T)$	17.0	270
C_p (Jkg ⁻¹ K ⁻¹)	913	1010	677	385	2090
ρ (kgm ⁻³)	2500	2520	2329	8890	960
k (Wm ⁻¹ K ⁻¹)	0.937	0.36	130	400	0.311
E (GPa)	73.1		{130 130 130}	E(T)	0.644E-3
ν	0.23	0.29	{0.28 0.28 0.28}	0.34	0.4
G (GPa)	-	-	{79.6 79.6 79.6}	-	Viscoelastic
σ_0 (MPa)	-	-	-	$\sigma_0(T)$	-
M (MPa)	-	-	-	1000	-

Table 6-4 Ranges of different material properties used in FE model

Material Properties	Range
k	0.311 – 1.25 W/mK
G_{∞}	0.1 – 1 MPa
α	50 – 270 ($\times 10^{-6}$) m/mK

6.3.3 Governing Equations in FE modeling

In the heat transfer and solid mechanics physics of the problem, equations (6-1) to (6-3) were solved in three dimensions. Equation (6-1) is the energy equation of heat transfer, equation (6-2) is the Fourier's Law, and equation (6-3) is the equilibrium equation in three dimensions;

$$\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot \mathbf{q} = Q \quad (6-1)$$

$$\mathbf{q} = -k \nabla T \quad (6-2)$$

$$\nabla \cdot \mathbf{s} + \mathbf{F}_v = 0 \quad (6-3)$$

Wherein some of the variables are defined below and rest of the terms are listed under “Nomenclature and symbols” section of this chapter.

$\{\mathbf{s}\} = [\mathbf{C}] \{\boldsymbol{\varepsilon}^{\text{el}}\}$; is the equation of Hooke's Law

$\{\boldsymbol{\varepsilon}^{\text{el}}\} = \{\boldsymbol{\varepsilon}\} - \{\boldsymbol{\varepsilon}^{\text{th}}\}$; is the definition of mechanical strain

$\{\varepsilon^{th}\} = \{\alpha_x \quad \alpha_y \quad \alpha_z \quad 0 \quad 0 \quad 0\}^T \cdot (T - T_{ref})$; is the definition of thermal strain

6.3.4 Fatigue-Life estimation model

Breakage of inter-cell connections is one of the major causes of failure in PV modules. The number of ON-OFF cycles that can initiate a fatigue crack in the inter-cell connections is considered as the fatigue life of the module. The values of first principal stress and strain in the inter-cell connections are used to estimate their fatigue life using the fatigue-life model presented in this section. The commercially available PV modules are expected to have a life of 25 years i.e. around 9000 day-night ON-OFF cycles which is the category of low cycle fatigue [72]. In this study, the strain-based fatigue life model with Morrow's Mean Stress correction approach [equation (6-4)] is used to estimate the fatigue life. The variable inputs to this model are the maxima and minima of stress and strain and the rest of the parameters are constants except N_f . The first principal stress and strain at the midpoint of inter-cell connection are taken from the solutions of thermal stress FE problems and used as inputs to equation (6-4).

$$\frac{\Delta\varepsilon}{2} = \frac{\sigma_f' - \sigma_m}{E} (2N_f)^b + \varepsilon_f' (2N_f)^c \quad (6-4)$$

Where the terms $\Delta\varepsilon$ and σ_m are strain range and mean stress, respectively. N_f is the unknown to be determined by solving the equation iteratively. The values of other inputs are listed under “Nomenclature and symbols” section of this chapter [64].

6.3.5 Meshing

The meshing of full and sub-model was performed sequentially to make a fully mapped mesh using a bottom-up approach. The meshing of faces and domains was carried out in the following order; edges of the face at the end of connection → sweeping into the domains of connections → domains of inter-cell connections → faces and domains of the cells → surrounding encapsulant in layer 4 (layer 4 is completed at this step) → sweeping to layers 3 and 5 → sweeping to layers 2 and 6 → domains of encapsulant around inter-cell connections → sweeping to layers 1 and 7. The complete mesh on the full model was having 36,635 elements with an average quality of 0.83. The top view of mesh in the full model and its quality is shown in Figure 6-5 (a) and (b) respectively. On the other hand, the number of elements in the complete mesh of the sub-model was 14,529 with an average quality of 0.79. The mesh and its quality of the submodel is shown in Figure 6-5 (c).

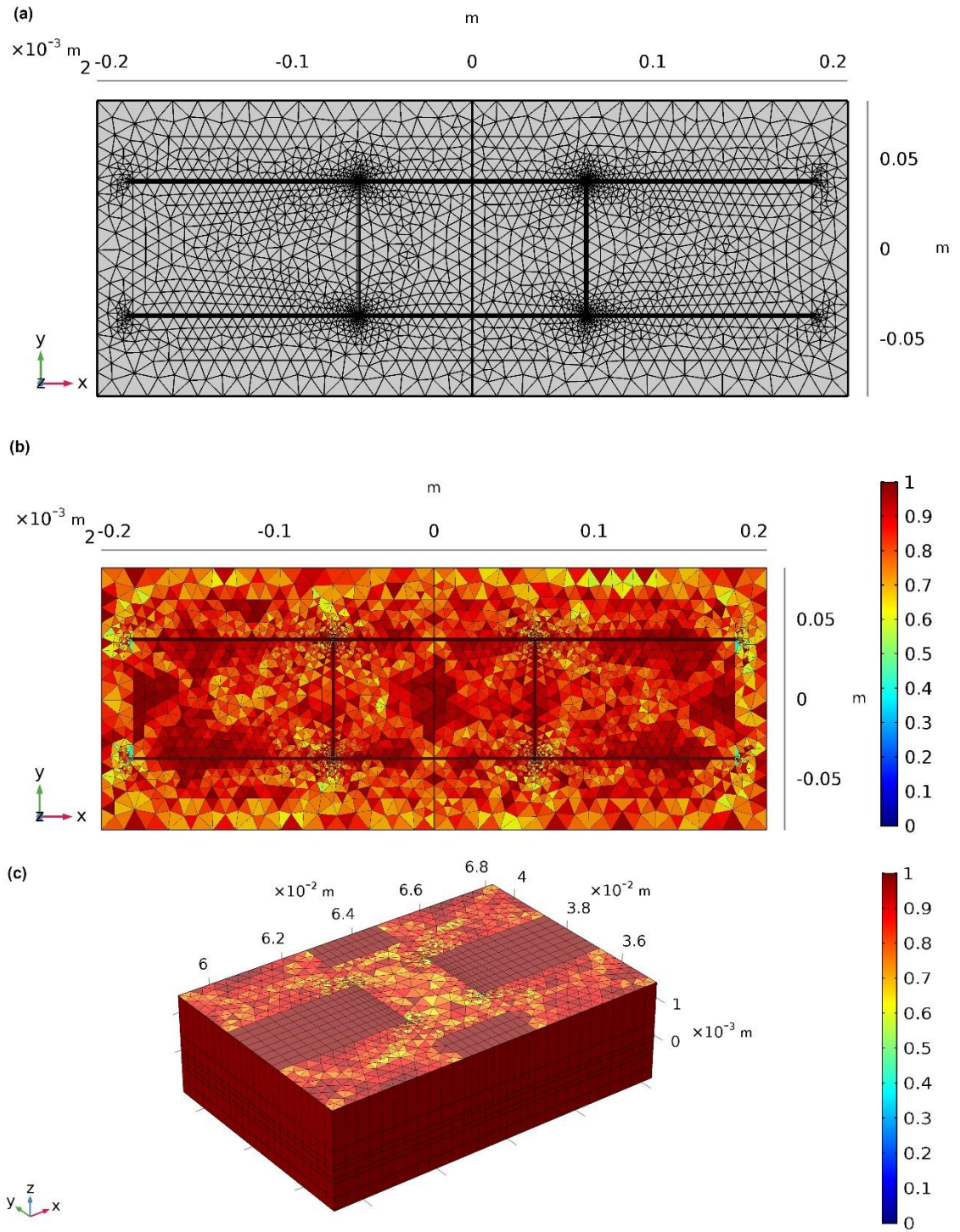


Figure 6-5 Meshing in the full model and the submodel; (a) top view of the full model (b) top of the full model with mesh quality and (c) mesh quality in the submodel

6.3.6 Boundary conditions

The heat transfer part of the FE problem was solved first and then coupled to the structural part for the estimation of thermal stress and strain. The thermal part was solved with exposure to variable solar flux ranging from 500 to 5000 W/m². The solar heat flux was applied to the top surface of the glass following the equations (6-5) and (6-6) [42];

$$-\mathbf{n} \cdot \mathbf{q} = q_0 \quad (6-5)$$

$$q_0 = \frac{(1-\eta_{pv}) * (1-\alpha_b) * G * A_{\text{module}}}{V_{\text{module}}} \quad (6-6)$$

For the CPV module in this study, perfect tracking conditions were assumed i.e. the solar irradiance, G , was considered perpendicular to the top surface of the module. In equation (6), the term $(1-\alpha_b)*G$ gives the amount of solar irradiance that is being absorbed by the module where α_b is the absorbance of the PV module. The equation, then, gives q_0 which is the amount of solar energy converted into heat per unit volume of the module and therefore $q=(1-\eta_{pv})*(1-\alpha)*G$ was applied as one of the boundary conditions at the top surface of the glass. In addition, constant convection boundary conditions were applied to the top (of glass) and bottom (of backside encapsulant) surfaces of the module with heat convection coefficients of 15.4 W/m²K and 100 W/m²K respectively. The heat transfer boundary conditions are shown in Figure 6-6 schematically. The convection boundary condition at the top and bottom surface of the module follows the energy balance equation (6-7).

$$-\mathbf{n} \cdot \mathbf{q} = h(T_{\text{amb}} - T_s) \quad (6-7)$$

For the structural part, all components of the full model were allowed to expand freely. The sub-model was only solved for the structural analysis. The temperature distribution in the domains of sub-model was copied from the full model. The displacements at the external boundaries of the sub-model were imposed from the full model so that the sub-model virtually may become the part of the full model.

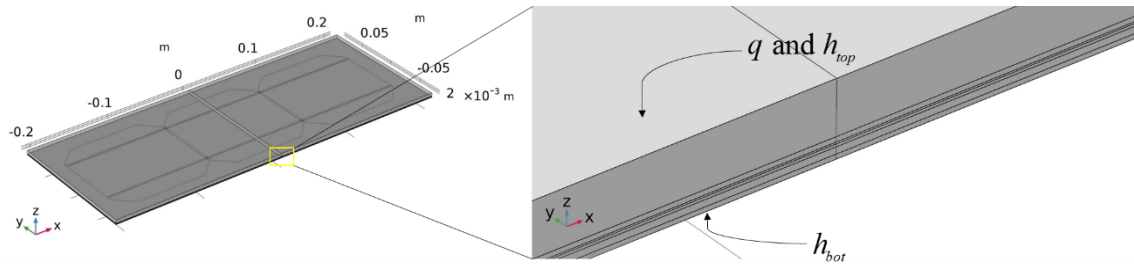


Figure 6-6 Boundary Conditions for Heat Transfer analysis

6.4 Prediction of optimum material properties from FE Analysis

6.4.1 The methodology of FE Analysis

To evaluate the performance of the CPV modules, the performance indicators were electrical power and module life. The electrical power was estimated based on cell temperature from steady-state heat transfer analysis and the module life was taken as the fatigue life of the inter-cell connections, which is the life (number of cycles) until crack initiation and it is a function of mean stress and strain amplitudes. Initially, the effect of varying thermal conductivity was observed by solving heat transfer problem and the corresponding change on the cell temperature and electrical power output was computed at different levels of incident solar flux with applied constant forced convection from the

backside. The incident solar flux was varied from 500 to 5000 W/m² where 5000 W/m² corresponds to a concentration ratio that can be easily achieved in LCPV modules.

The effects of G_{∞} and α of the encapsulant on thermal stresses and strains and corresponding module life were studied at an incident solar irradiance of 5000 Wm⁻² with thermal conductivity of 0.75 W/mK. The structural problems were solved, wherein the coefficient of thermal expansion and long-term shear modulus were varied simultaneously and a total of 16 structural problems were solved as listed in Table 6-5 along with their results. The solution of the full model with a coarser mesh identified the critical regions to be the small region between two cells where the two cells are connected by the copper inter-cell connections. Therefore, the sub-model was developed around the inter-cell connection as discussed above with reference to Figure 6-4 (c).

6.4.2 Results of FE Analysis

6.4.2.1 Electrical Power

The cell temperature as affected by the rising level of incident solar flux and varying thermal conductivity is shown in Figure 6-7 (a) where thermal conductivity of 0.311 W/mK refers to EVA. The increasing cell temperature with solar flux is due to the increased amount of heat input. The effect of increasing thermal conductivity of backside encapsulant is observed in terms of decreasing cell temperature as shown in Figure 6-8 wherein the temperature field in the domains of cells as affected by thermal conductivity of backside encapsulant are presented for $G=5000 \text{ Wm}^{-2}$. Increased thermal conductivity drags the temperature down by lowering the thermal resistance from the backside. The positive effect

of increasing thermal conductivity appears in the form of increased maximum power point by the PV module as shown in Figure 6-7 (b). Increasing thermal conductivity from 0.311 to 1.25 W/mK can decrease the cell temperature from 66.1 to 62.6 °C corresponding to an improvement of electrical power by 2.6%. However, increase in production of electrical power is converging above 0.75 W/mK because increasing from 0.311 to 0.75 W/mK can enhance the electrical power by 2% and further increasing to 1.25 W/mK can have 2.6% improvement as compared with 0.311 W/mK. This converging improvement is attributed to the small thickness of backside encapsulant, which is around 0.5 mm (Layers 2 + Layer 3 as mentioned in Table 6-1).

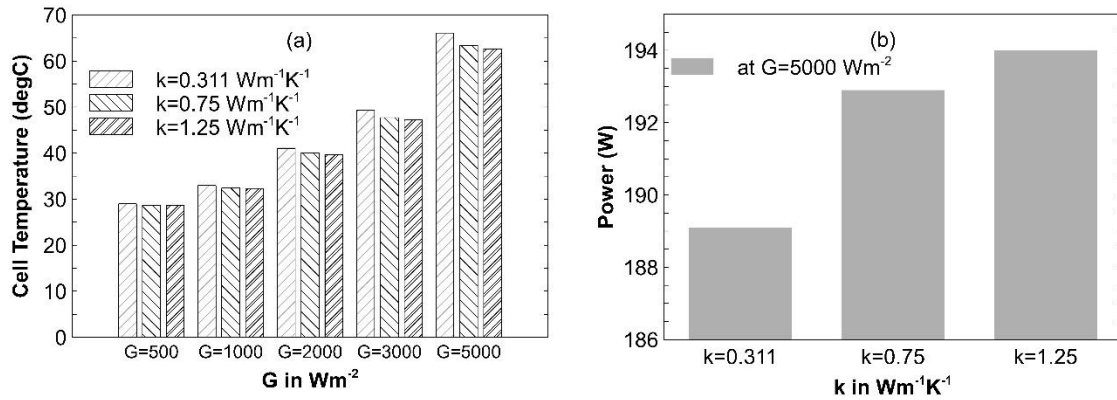


Figure 6-7 (a) Effect of varying incident solar irradiance on the cell temperature using different thermal conductivities of the back-side encapsulant and (b) the effect of varying thermal conductivity of back-side encapsulant on the amount of electrical power produced at G=5000 W/m²

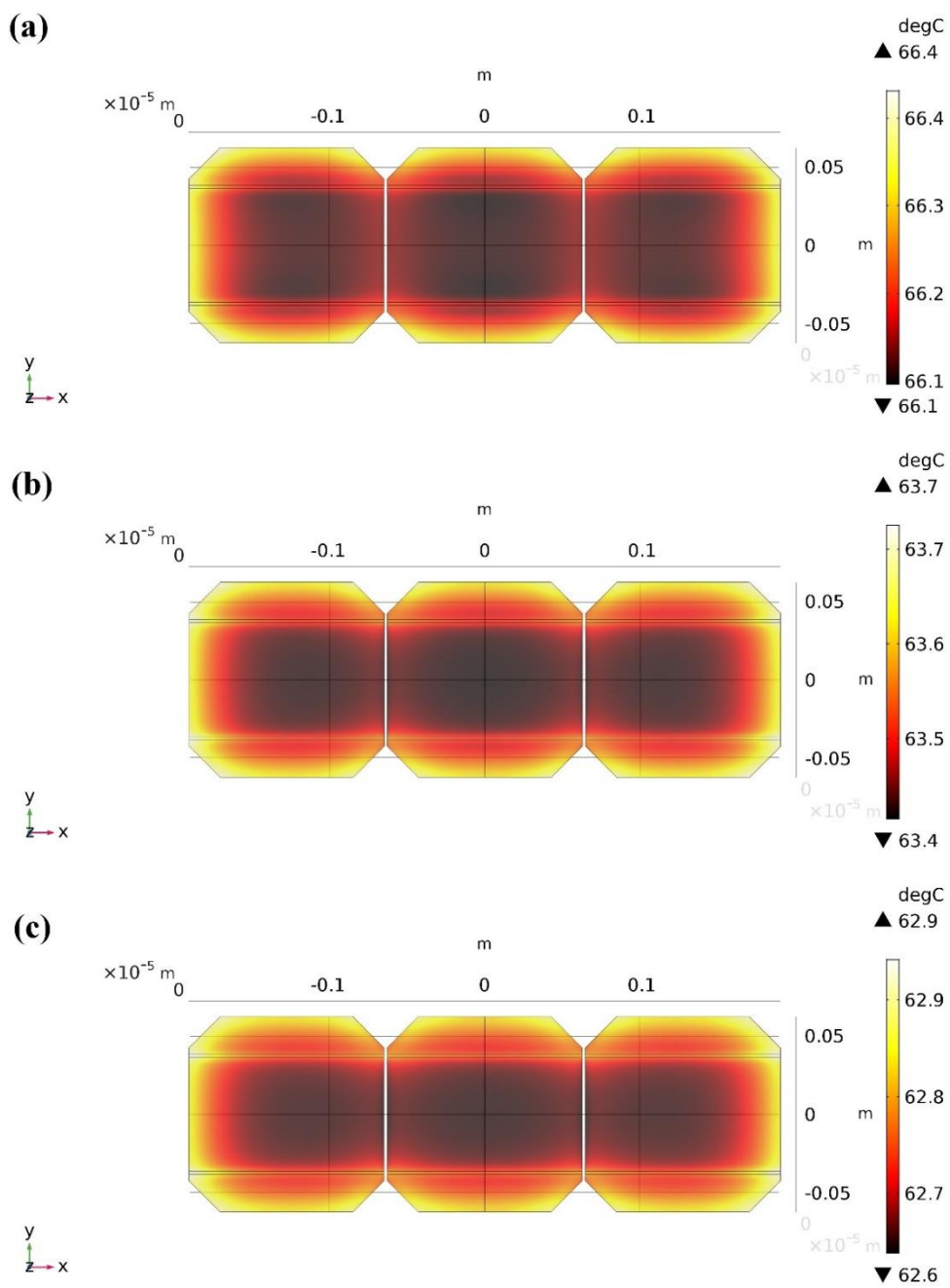


Figure 6-8 Temperature fields in the domains of cells with different thermal conductivities of backside encapsulant at $G=5000 \text{ Wm}^{-2}$; (a) $k=0.311 \text{ Wm}^{-1}\text{K}^{-1}$; (b) $k=0.75 \text{ Wm}^{-1}\text{K}^{-1}$; (c) $k=1.25 \text{ Wm}^{-1}\text{K}^{-1}$

6.4.2.2 Module Life

The number of cycles to failure for the copper inter-cell connection (module life) is the function of mean stress and strain range. From the solutions of thermal stress analysis on FE model, the first principal stresses and strains at the midpoint of inter-cell connection are taken as the maxima of stress and strain to be used in fatigue life equation. The mean stress and strain range are mainly affected by the long-term shear modulus and coefficient of thermal expansion. Therefore, a total of 16 cases of thermal stress problem were solved by simultaneous variation of long-term shear modulus and coefficient of thermal expansion as listed in Table 6-5. The contour plots of first principle stress and strain in a cut plane at mid of inter-cell connection of the submodel are presented in Figure 6-9 and Figure 6-10 respectively for case # 13 to 16, as representative cases. The contour plots of all the cases are essentially the same; the only difference is of the maxima and minima of stresses and strains. The encapsulant, due to its viscoelastic behavior, relaxes at the expense of high strain (Figure 6-10) and all this deformation is supported by the copper, and therefore the stress is mainly concentrated in the region of copper connection (Figure 6-9). Because the copper inter-cell connection is exceeding the yield strength in almost all the cases, the minimum strain is taken equal to the difference of first principle strain and effective plastic strain and accordingly the minimum stress is considered equal to zero. The mean stress and strain range from the FE solutions and the corresponding fatigue life are also listed in Table 6-5. Case 14 is the datum line in this discussion, as the module life is required to be increased to more than as achieved by using EVA. The fatigue life results (Table 6-5) show that as compared to current EVA only 4 cases (cases 1, 5, 9 and 13) are there in which the

life is improved. In all those cases G_{∞} is less than that of EVA. The increased life by decreased G_{∞} is attributed to reduced stress imposed by encapsulant on interconnects in cases 1, 5, 9 and 13.

Copper observes large strain fluctuations with small changes in stress owing to its bilinear elastoplastic material behavior and small tangent modulus. The effect of changing α is not significant due to viscoelastic behavior of encapsulant. Encapsulant being viscoelastic with temperature above glass transition (T_g) relaxes quickly and therefore a higher or lower thermal expansion does not make a significant difference in imposing strains on interconnects [42]. Hence, as compared with EVA (case 14), four out of sixteen cases lead to reasonably reduced levels of stress and strain and therefore improved module life.

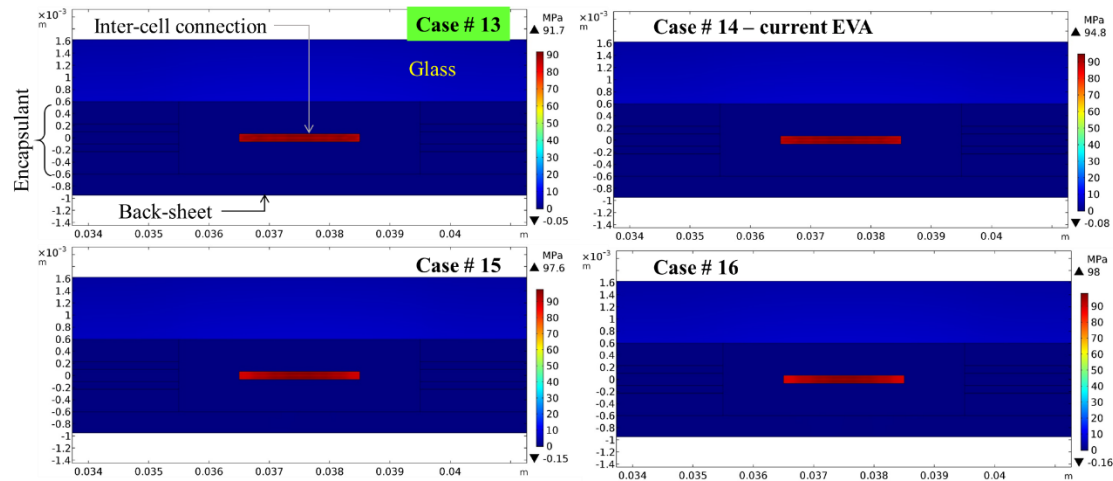


Figure 6-9 Contour plots of the first principal stress in a cut plane at mid of inter-cell connection of the submodel; (a) case # 13; (b) case # 14; (c) case # 15; (d) case # 16

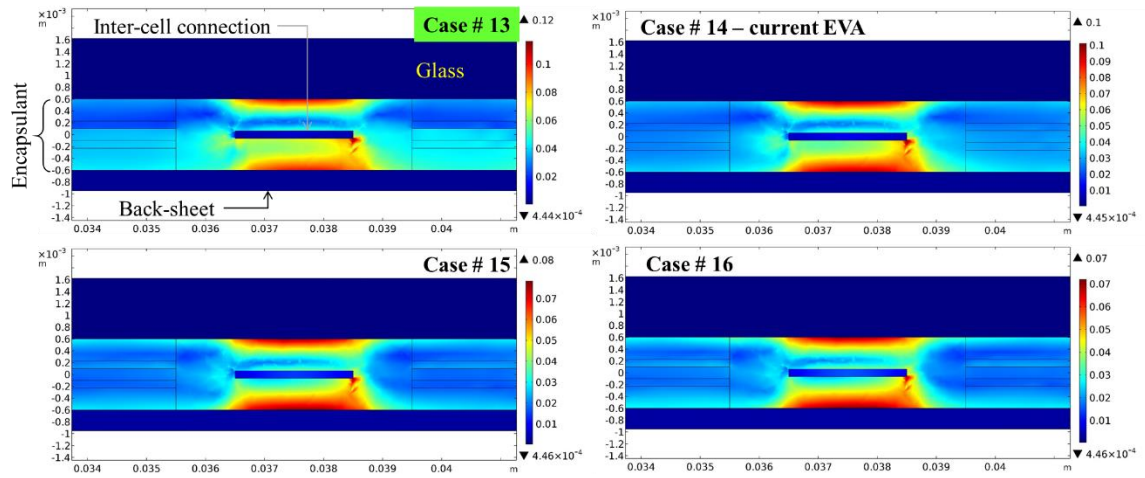


Figure 6-10 Contour plots of the first principal strain in a cut plane at mid of inter-cell connection of the submodel; (a) case # 13; (b) case # 14; (c) case # 15; (d) case # 16

Table 6-5 Results of structural problems to estimate the fatigue life of copper inter-cell connections as affected by σ_m and $\Delta\epsilon$

Case #	Material Properties		Input to Fatigue Life		Fatigue Life	
	G_∞ (MPa)	α ($\times 10^{-6} \text{ K}^{-1}$)	σ_m (MPa)	$\Delta\epsilon$ ($\times 10^{-3}$)	N_f	Life (years)
1	0.1	50	42.9	4.93	30313	41.52
2	0.23	50	44.4	5.90	9620	13.18
3	0.75	50	46.5	7.08	4232	5.80
4	1	50	47.1	7.31	3766	5.16
5	0.1	100	43.0	4.93	30313	41.52
6	0.23	100	44.4	5.91	10110	13.85
7	0.75	100	46.6	7.10	4232	5.80
8	1	100	47.1	7.34	3684	5.05
9	0.1	200	43.0	4.94	30313	41.52
10	0.23	200	44.4	5.92	10110	13.85
11	0.75	200	46.6	7.14	4133	5.66
12	1	200	47.2	7.39	3603	4.94
13	0.1	270	43.0	4.94	26345	36.09
14	0.23	270	44.4	5.93	9288	12.72
15	0.75	270	46.7	7.17	4039	5.53
16	1	270	47.2	7.43	3527	4.83

Decisively, it is observed from Figure 6-7 that for having a reasonable improvement in the electrical power the thermal conductivity must be raised to at least 0.75 W/mK from a current value of 0.311 W/mK for backside encapsulant. On the other hand, from Table 6-5, G_{∞} seems to be more sensitive than α and it should be less than the current value of 0.23 MPa. α does not have a reasonable sensitivity to the fatigue life of interconnects but reducing α is important for reducing thermal stresses on other parts like cells. The less sensitivity of α of the encapsulant is because of associated viscoelasticity and the slowly changing temperature during the day-night cycles.

6.5 Computational Design of Composite Material

The objective of computational design is to find the potential candidates that have the maximum probability to provide the desired target properties with minimum filler's content and available particle sizes/morphologies. The best combinations identified by the computational design should have the capability to achieve the predicted thermal and structural properties without disturbing the application dependent required functional properties such as electrical resistivity in this study. In this work, the target properties are decided to be $k \geq 0.75 \text{ W(mK)}^{-1}$, $G_{\infty} < 0.2 \text{ MPa}$ and $\alpha \leq 200 \times 10^{-6} \text{ K}^{-1}$ as discussed in the last section.

6.5.1 Selection of matrix

The encapsulant has to maintain its high electrical resistivity and simultaneously has to achieve the target properties. In addition, the structural compatibility should not be

affected. Therefore, the code, first of all, eliminates all those possible combinations that may cause a reduction in electrical resistivity or harm the structural compatibility. Different encapsulants used for the encapsulation of PV modules are selected as the potential matrices for the desired composite encapsulant. Hence, TPU, EVA, PVB, and PDMS come out to be the candidate matrices that possess structural compatibility. Material properties of these encapsulants are listed in Table 6-6. Among different encapsulants, PDMS and TPU are apparently the best candidates to reach the target range of G_{∞} based on their intrinsic material properties. However, to confirm this selection and elaborate the material design scheme, all candidate matrices are considered for the next steps of material design.

Table 6-6 Material properties of the prospective matrices for the composite encapsulant [37,174–177]

Encapsulant Matrix	k (Wm⁻¹K⁻¹)	Poisson's ratio	G_{∞} (MPa)	α ($\times 10^{-6}$ K⁻¹)
EVA	0.311	0.4	0.23	270
PVB	0.24	0.499	0.125	260
PDMS	0.15	0.44	0.0094	277
TPU	0.22	0.499	0.001124	190

6.5.2 Selection of fillers

Following the similar approach, all those fillers that have an electrical resistivity lower than those of any of the candidate matrices are eliminated and therefore, most of the ceramic particulates come out to be the candidate fillers. Due to the high electrical conductivity, metallic or carbon based fillers are not suitable to be used as fillers and hence not considered in the current design. On the other hand, ceramic fillers can enhance both

electrical resistivity and TC simultaneously owing to their very low electrical conductivity and high TC. Some potential ceramic fillers and their properties are listed in Table 6-7. The effect of fillers loading in respective polymer matrix on G_{∞} and CTE is studied. Figure 6-11 shows the effect of filler's volume fraction on G_{∞} and CTE of TPU as matrix. It is found that increasing the volume fraction tend to increase G_{∞} and decrease CTE following a same trend regardless of the filler type. Hence, in order to achieve the target properties, any kind of listed ceramic filler can be used depending upon the cost and availability. However, the values of G_{∞} and CTE are mainly related to the type of matrix which affect the overall effective values as a function of filler's loading as shown in Figure 6-12, wherein the effect of adding Al_2O_3 on G_{∞} and CTE of all the matrices under consideration is presented.

This behavior is attributed to the very large difference between the moduli and expansion coefficients of continuous (matrix) and discontinuous (fillers) phases. The effective properties such as CTE and G_{∞} of composites mainly depend upon the properties of the continuous phase (matrix). The comparative enhancement provided by different discontinuous phase particles (fillers) depends upon the relative numeric difference in the properties of matrix and fillers. The CTE of listed matrices is very high as compared with the ceramic fillers while the opposite is exact with G_{∞} . Therefore, the comparative enhancement provided by different fillers is almost unchanged. Ceramic fillers have very large moduli (and very small CTEs) as compared with polymers. Therefore, upon application of mechanical (or thermal strain), the ceramic particles will never deform (or expand a little bit) and all the deformations would be localized to the matrix. The only

strengthening mechanism is to restrict the motion of molecular chains at the interfacial boundaries and therefore, good interfacial strength is mandatory. Hence, it is observed that the type of matrix is the primary controlling factor for G_{∞} and CTE when the difference between the moduli of the matrix and fillers is very high [163,178].

Based on the maximum limits of G_{∞} and CTE as highlighted in Figure 6-12, EVA and PVB are not suitable candidate matrices as expected and hence can be omitted as far as G_{∞} and CTE are considered. However, a further investigation is needed to see their effect on TC (to be discussed later). This investigation leads to the fact that TPU and PDMS are the most suitable matrices that could be used with any of the listed fillers for further material design. Although the target values of G_{∞} and CTE can be achieved with using PVB as matrix at a filler volume content of 20 and 25 %, respectively, selecting any of these two compositions cannot satisfy the requirements of both G_{∞} and CTE simultaneously. For the required target values of CTE in PVB matrix, a threshold content of 25% Al_2O_3 is required. However, this significantly higher loading can lead to the value of G_{∞} that is expected to exceed the maximum limit, which is not recommended.

Table 6-7 Material properties of the prospective ceramic fillers

Filler material	k ($\text{Wm}^{-1}\text{K}^{-1}$)	Poisson's ratio	G_{∞} (MPa)	α (K^{-1})
Alumina (Al_2O_3)	33	0.21	88.0	4.40E-06
Aluminum Nitride (AlN)	177	0.23	126	4.30E-06
Boron Nitride (BN)	52	0.21	41.0	6.00E-06
Diamond	2000	0.2	440	8.00E-07
Fused Silica (SiO_2)	1.5	0.15	31.0	5.50E-07
Magnesium Oxide (MgO)	60	0.35	92.0	9.00E-06
Silicon Nitride (Si_3N_4)	43	0.23	65.3	1.40E-06
Titania (TiO_2)	11.8	0.27	90.0	8.40E-06
Zirconia (ZrO_2)	2.7	0.22	53.4	2.30E-06

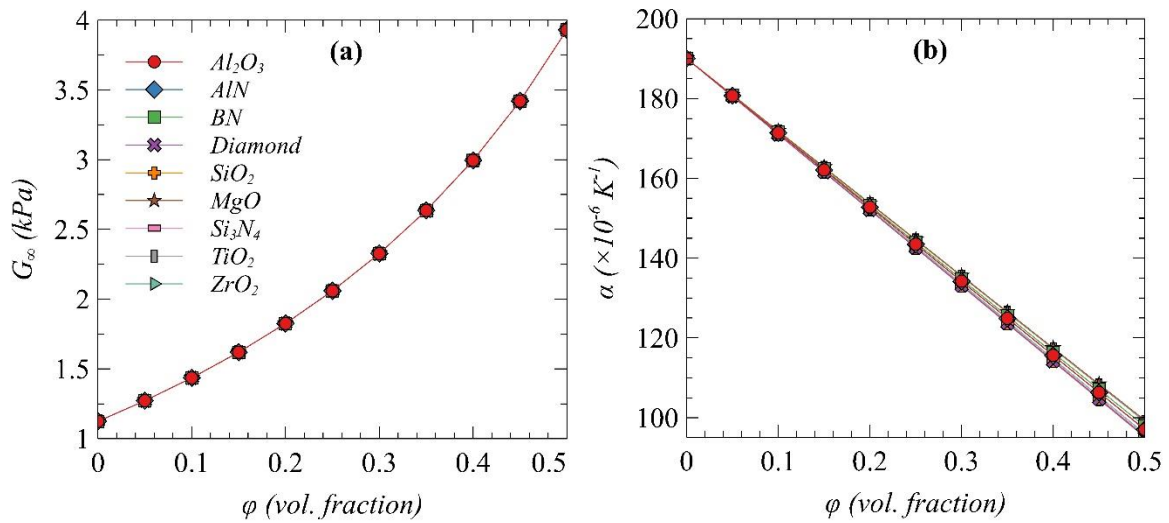


Figure 6-11 (a) G_{∞} and (b) α of TPU matrix composite as function of different filler's volume fraction

6.5.3 Selection of filler attributes

Finally, the computational design has to find the best combinations, estimate the relative compositions and particles size of the phases that can satisfactorily provide all the target properties with minimum addition of available fillers.

Filler attributes are finalized based on the estimations of effective TC model. It is discussed in detail in chapters 4 and 5 [25] that two of the most sensitive parameters affecting the TC in polymer composites are the interface thermal resistance and the particle size of the fillers. These parameters play their role in the estimation of effective TC through a parameter α defined by Equation (5-10), where the particle's radius (a) is the decision-making parameter. Initially the maximum allowed R/a ratio that can provide a reasonable enhancement of effective TC of the composite is determined, which depends upon the intrinsic TCs of phases (matrix and filler). The maximum R/a ratio indirectly identifies the minimum required particle radius (a). Based on the identified particle size, the final volume fraction of fillers is decided that can satisfy all the target values of the intended properties.

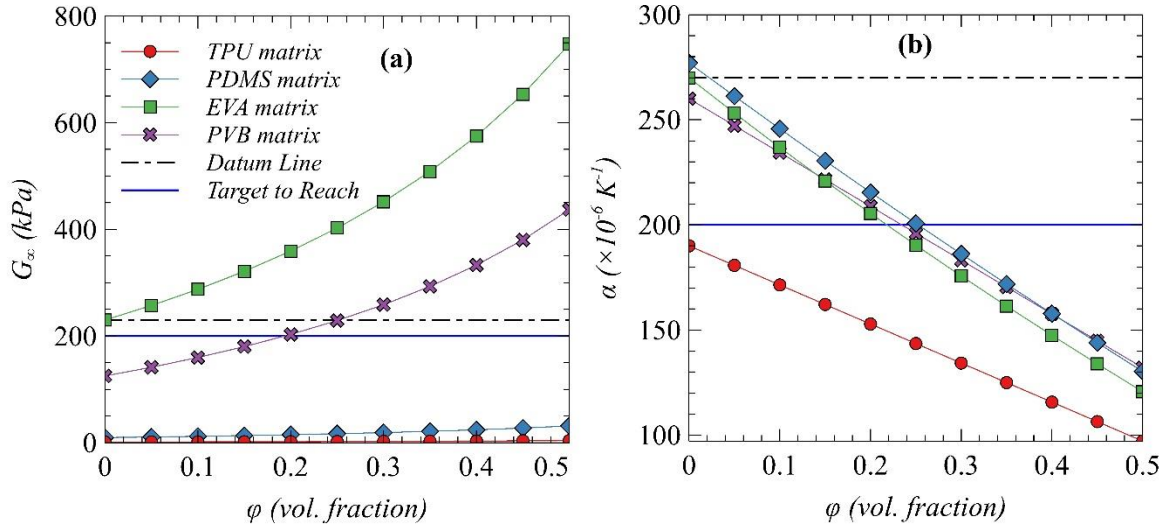


Figure 6-12 (a) G' and (b) α of composites with different matrices as function of volume fraction of alumina as filler

In order to find the maximum allowed R/a ratio, two combinations of matrices and fillers with lowest and highest individual TCs are used to evaluate the effective TC of composites at different R/a ratios as shown in Figure 6-13. The lowest TCs combination is fused silica with PDMS while the highest counterpart is diamond with EVA. It can be observed that the maximum allowed R/a ratio is close to unity in both of the combinations for a positive effect of fillers' loading on effective TC. However, the enhancement of effective TC is reasonable with $R/a = 0.1$. The commonly reported values for interface thermal resistance (R) between a polymer matrices and ceramic fillers is around $3 \times 10^{-7} \text{ m}^2 \text{KW}^{-1}$ [15,33] which results in a minimum required particle's radius of $3 \text{ }\mu\text{m}$ i.e. a particle size of $6 \text{ }\mu\text{m}$.

After identification of minimum particle size, all candidate matrices and fillers are used to predict the effective TC. The winner candidates and their required volume fractions that can satisfy all the targets of thermal and mechanical properties are finalized based on the

estimations of effective TC with the identified threshold particle size of fillers. Figure 6-14 presents effective TC as function of volume fraction in all possible combinations of listed matrices and fillers with $a = 3 \mu m$. It is depicted from Figure 6-14 that PDMS as a matrix, and ZrO_2 or SiO_2 as a filler are not recommended keeping in view the fact that a very high filler loading would be required to reach the target effective TC of $0.75 \text{ Wm}^{-1}\text{K}^{-1}$. On contrary, the other the fillers can provide nearly equal improvement in TC due to the converging effect of k_f [25,33]. Therefore, further shortlisting of the fillers is based on other factors such as cost per unit volume and availability. The desired target of TC is expected to be achieved with a volume fraction of 0.3 in EVA and 0.35 in TPU and PVB matrices with spherical particles. Moreover, larger particle size, particles with high aspect ratio or hybrid fillers can be used to decrease the required volume fraction [165].

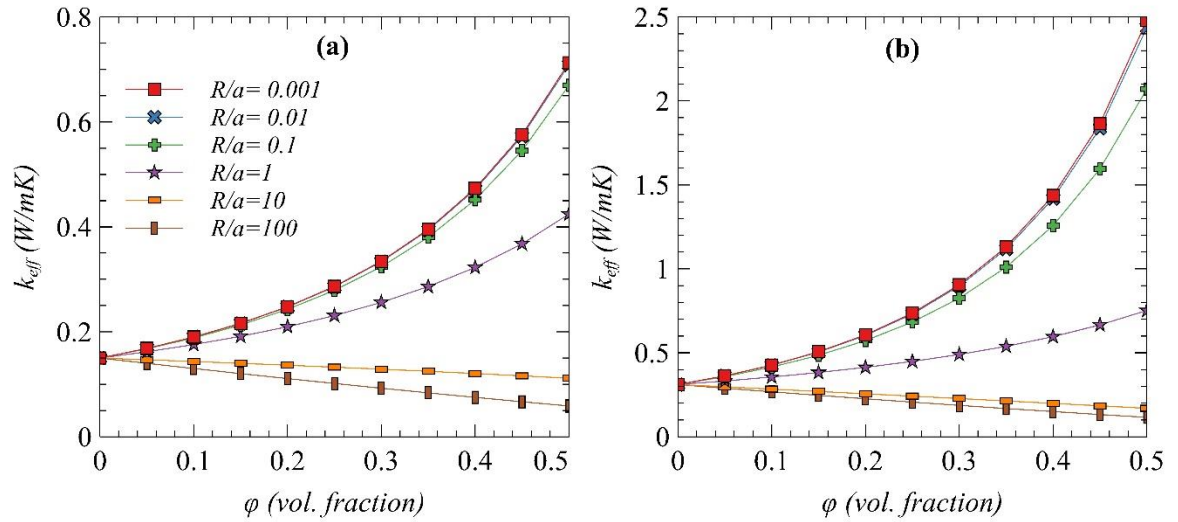


Figure 6-13 Estimation of effective thermal conductivity for the lowest and highest TCs combinations of matrices and fillers with different R/a ratios; (a) PDMS with spherical fused silica particulates (b) EVA with spherical diamond particulates

Decisively, from material design scheme, EVA and PVB are not recommended as far as the required values of G_{∞} and CTE are concerned. Similarly, PDMS as a matrix and ZrO_2 and SiO_2 as fillers are eliminated by the TC model owing to their lower intrinsic TC. The other candidate fillers (as listed in Table 6-7) can provide the desired values of TC, G_{∞} and CTE with a volume fraction of around 0.35 and a particle size of 6 μm . Among the remaining fillers, Al_2O_3 , AlN and MgO are the cheapest and readily available. However, for the development of composites only Al_2O_3 and AlN are considered in the present work. Based on the available particle size and approximate shape morphology, the required volume fraction is re-estimated for TPU matrix with Al_2O_3 and AlN as summarized in Table 6-8. The required estimated volume percent for the available Al_2O_3 and AlN is 22.5 and 23%, respectively.

6.6 Materials and Methods

The development of composites include all the steps starting from raw materials to the characterization and measurement of material properties. A schematic flow chart of the steps involved in the development of composites has been shown in Figure 3-2 [Chapter 3].

6.6.1 Materials

Al_2O_3 and Surface treating agent γ -methylacryloxypropyl trimethoxy silane were purchased from Sigma-Aldrich and AlN powders from Surmet Corporation (USA). TPU

was supplied by Taiwan PU Corporation. The information about the particle size has been listed in Table 6-8.

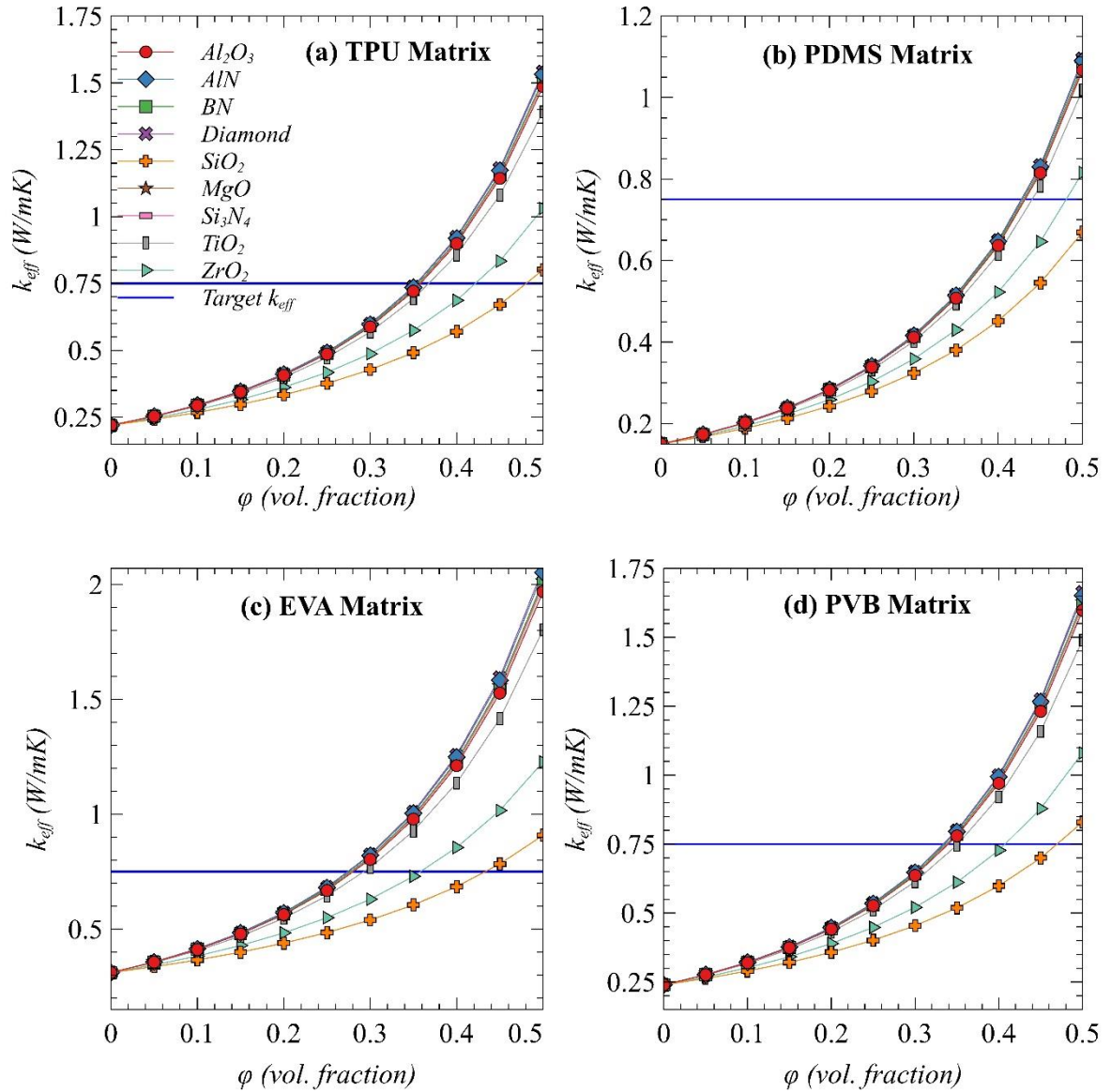


Figure 6-14 Estimation of effective thermal conductivities in different matrices and with different fillers at fixed $R/a=0.1$

Table 6-8 Results of Material design scheme for TPU matrix with the available particle sizes

Matrix	Filler	Size parameters		Estimated volume fraction	Experimentally mixed volume fraction	Name
		Radius = a_1	p			
TPU	AlN	3 μm	1.67	0.230	0.20	S1
TPU	Al ₂ O ₃	3 μm	2	0.225	0.20	S2
TPU	AlN	3 μm	1.67	0.230	0.25	S3
TPU	Al ₂ O ₃	3 μm	2	0.225	0.25	S4

6.6.2 Surface Treatment

The ceramic particles were surface treated before mixing with TPU to enhance interfacial compatibility. γ -methylacryloxypropyl trimethoxy silane equivalent to 2% by weight of the filler was mixed with ethanol for 3 minutes at room temperature. Then pH was adjusted to 5 by dropwise adding dilute HCl and stirred for another 10 minutes at room temperature. For surface treatment, initially, pre-weighed amounts of Al₂O₃ or AlN powder was added to the solution and stirred for 20 min at room temperature. The mixture was then heated to 70 °C on a hot plate with continued stirring for another 40 minutes. Heating and stirring was stopped and the particles were allowed to settle down for 1 hour. Finally, the solution was poured out and the settled particles were dried overnight at 90 °C in vacuum oven. The surface-treated powders were stored in vacuum desiccators to avoid any moisture or dust contamination.

6.6.3 Melt-Mixing

Before mixing, the TPU granules were dried by placing them in vacuum desiccator overnight. The pre-treated ceramic powders and TPU granules were mixed together in

molten state using Brabender Mixer. After the three zones of mixing chamber had attained the processing temperature of 150 °C, the dried TPU granules and the ceramic powders were added into the mixing chamber at a slower rpm (30 rpm) and the chamber was closed. The mixing speed was then increased to the processing speed of 60 rpm and continued for 20 minutes. After each mixing cycle, the chamber was cleaned thoroughly to avoid contamination to the next compositions. The output of the Brabender Mixer is in the form of irregular lumps that cannot be used for any type of testing or characterization. So these composite lumps are molded to make samples of desired shape for testing.

6.6.4 Compression Molding

A pre-weighed amount of the lumps, depending upon the required thickness was hot pressed in a compression-molding machine at 120 °C under a pressure of 3 MPa for 10 min. The produced samples were cylindrical (ϕ 31 mm and as desired thickness) that could be cut further to get the desired shape for a particular test.

6.6.5 Testing / Characterization

Measurement of TC, G_{∞} and CTE is required to validate the material design approach. However, the other properties like heat capacity, density and viscoelastic parameters were also evaluated to be used as inputs in sequentially coupled finite element thermal stress model of three-cell structure. Moreover, the developed composites were characterized for their microstructures using FESEM. The machines used for different characterizations are listed in Table 6-9.

Table 6-9 List of equipment used for used in testing and characterization of synthesized samples

Property to be evaluated	Used equipment / machine
Long term shear modulus and viscoelastic behavior	Mettler Toledo DMA/SDTA 1+ - Dynamic Mechanical Analyzer
Coefficient of thermal expansion	Mettler Toledo TMA/SDTA 2+ - Thermo Mechanical Analyzer
Thermal Conductivity	TCi Thermal Conductivity Analyzer by C-Therm Technologies Ltd., Canada
Heat capacity at constant pressure	Mettler Toledo DSC 3+ - Differential Scanning Calorimeter
Density	Archimedes Principle
Microstructural examination	FESEM Tescan Lyra 3

6.7 Results of Materials Development

6.7.1 Microstructural examination

The distribution of ceramic particles at microscopic level was observed to evaluate the effectiveness of melt-mixing and compression molding synthesis route. The compression-molded samples were brittle fractured after placing them in a chiller at -115 °C and the fractured surfaces were gold coated for electron imaging. The imaging was conducted in backscattered mode to have better contrast of ceramic vs. polymers. The fractured surfaces of samples S1 and S4 are shown in Figure 6-15. No porosity is observed and the particles are distributed very well which indicates that the synthesis route was good enough mix the ingredients.

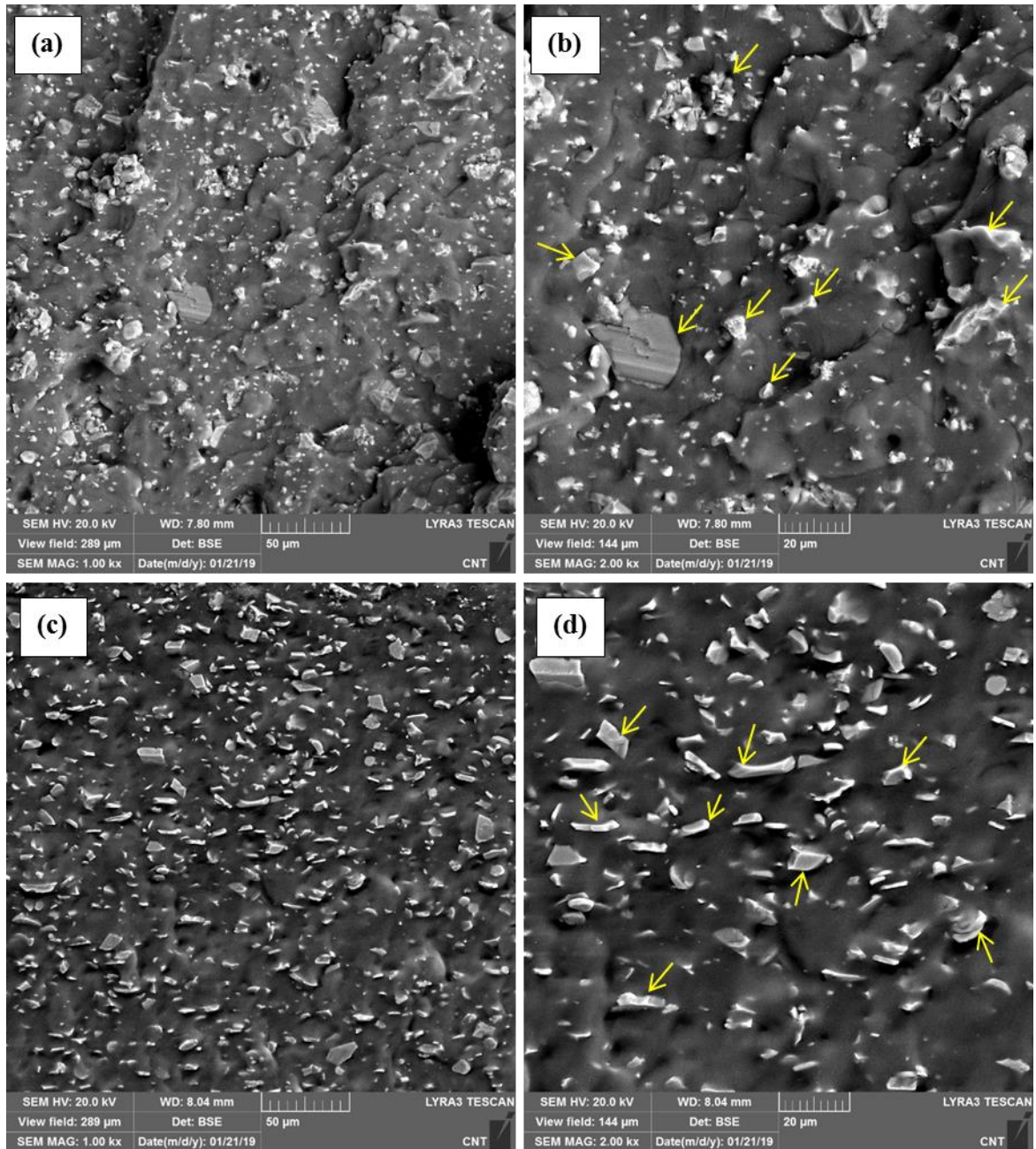


Figure 6-15 FESEM fractured surface of samples S1 (a) & (b) and S4 (c) & (d) taken at different magnifications; the arrow marks indicate the AlN particles in (b) and Al_2O_3 particles in (d)

6.7.2 Validation of Material design

6.7.2.1 Measured TCs, CTEs, densities and specific heat

The estimated and measured thermo-physical properties of the produced samples are listed in Table 6-10. A reasonable agreement between the measured and estimated TCs and CTEs is observed. Similarly, the measured densities and specific heats of the samples are also close the theoretical values indicating almost fully densified samples supported by the FESEM observations. The higher values of TCs and lower values of CTEs in the samples S3 and S4 are due to higher volume fractions of filler comparatively. AlN has a higher intrinsic TC than Al₂O₃, therefore the samples S1 and S3 are expected to possess higher TCs, but the unexpected results of TC values are dedicated to the disc-like shape of Al₂O₃ particles used in this work. The density and specific heat of the samples were estimated so that the real properties can be used in the finite element model for performance evaluation.

Table 6-10 Measured thermal and physical properties of the samples listed in Table 6-8

Name	Effective TC= k_{eff} (Wm ⁻¹ K ⁻¹)		Effective CTE= α_{eff} (*10 ⁻⁶ K ⁻¹)		ρ (gcm ⁻³)	C_p (Jkg ⁻¹ K ⁻¹)
	Estimated	measured	estimated	Measured	Measured	measured
S1	0.72	0.703	160	180	1.605	1290
S2	0.72	0.718	160	192	1.721	1055
S3	0.78	0.768	136	150	1.705	1240
S4	0.78	0.793	136	158	1.881	1025

6.7.2.2 Measurements of Dynamic mechanical analyzer and viscoelastic behavior of developed composite

The sample S1 was selected for measurement of G_{∞} and viscoelastic parameters using dynamic mechanical analyzer (DMA). Cuboid samples with a geometry factor of at least 30 as recommended by the manufacturer were used for DMA measurements. The samples were cooled to -20 °C using liquid nitrogen. At different temperatures, isotherms of storage modulus (G') and $\tan\delta$ were generated as function of oscillating frequency ranging from 0.1 to 200 Hz (Figure 6-16(a) and Figure 6-16(b) for G' and $\tan\delta$ respectively). For each isotherm, the system was allowed to settle for 5 minute to homogenize temperature in the entire sample. A typical behavior of viscoelastic polymers is observed in the sample i.e. a stiffer response at higher oscillating frequency and vice versa.

The curves are similar to “thermo-rheologically simple” polymers and therefore, the master curve of G' as function of a wide range of frequency can be generated by horizontal shifting of the curves. The curves of G' were horizontally shifted on a log scale to make a continuous curve for $T_{ref} = -11^{\circ}\text{C}$ which is the glass transition temperature of TPU (for the particular grade used in this study). The applied shift factors (a_T) for -20, -14, 0 and 10 °C were 2, 0.5, -2 and -4.1, respectively. The corresponding master curve of G' is shown in Figure 6-16(c) that makes a continuous curve, which can be simplified by Generalized Maxwell Model for linear viscoelastic materials [179,180]. The Williams–Landel–Ferry equation (WLF) constants of shift factor determined by linear curve fitting are $C_1=20$ and $C_2=80$ K. In Figure 6-17, the values of actually used shift factors are compared to the WLF shift function which are closely fitting. Finally, Prony series coefficients for 9-term

Generalized Maxwell Model are determined using an error minimization code in MATLAB (Table 6-11) and the resulting Prony fit is compared to the master curve of G' in Figure 6-17 (b). G_{∞} estimated by the Master Curve method for S1 comes out to be 0.18 MPa. The parameters listed in Table 6-11 and the constants of WLF shift function were used as inputs to model the thermomechanical (constitutive) behavior of developed composite and finally to evaluate the performance in the finite element model already published [71].

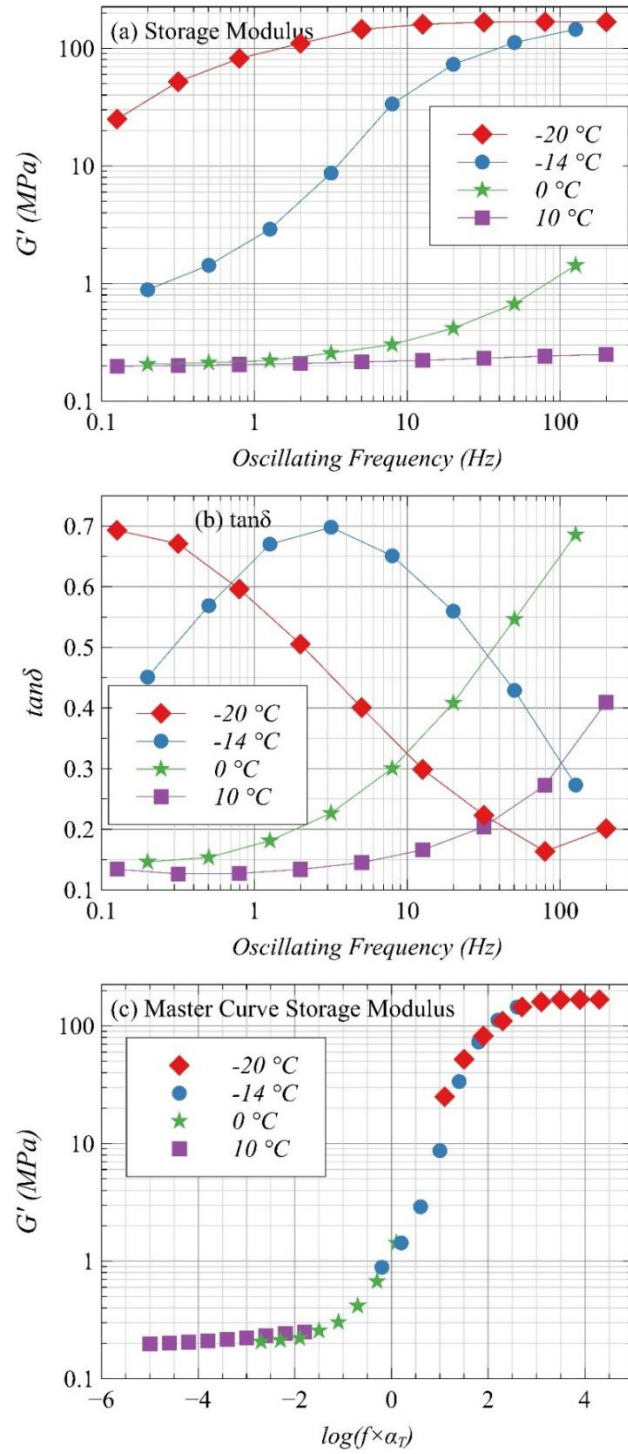


Figure 6-16 (a) The storage modulus (G') and (b) $\tan\delta$ of S1 measured as function of temperature and oscillating frequency; (c) Master Curve of Storage Modulus for S1 generated for $T_{ref} = -11$ °C by horizontal shifting of the measured curves

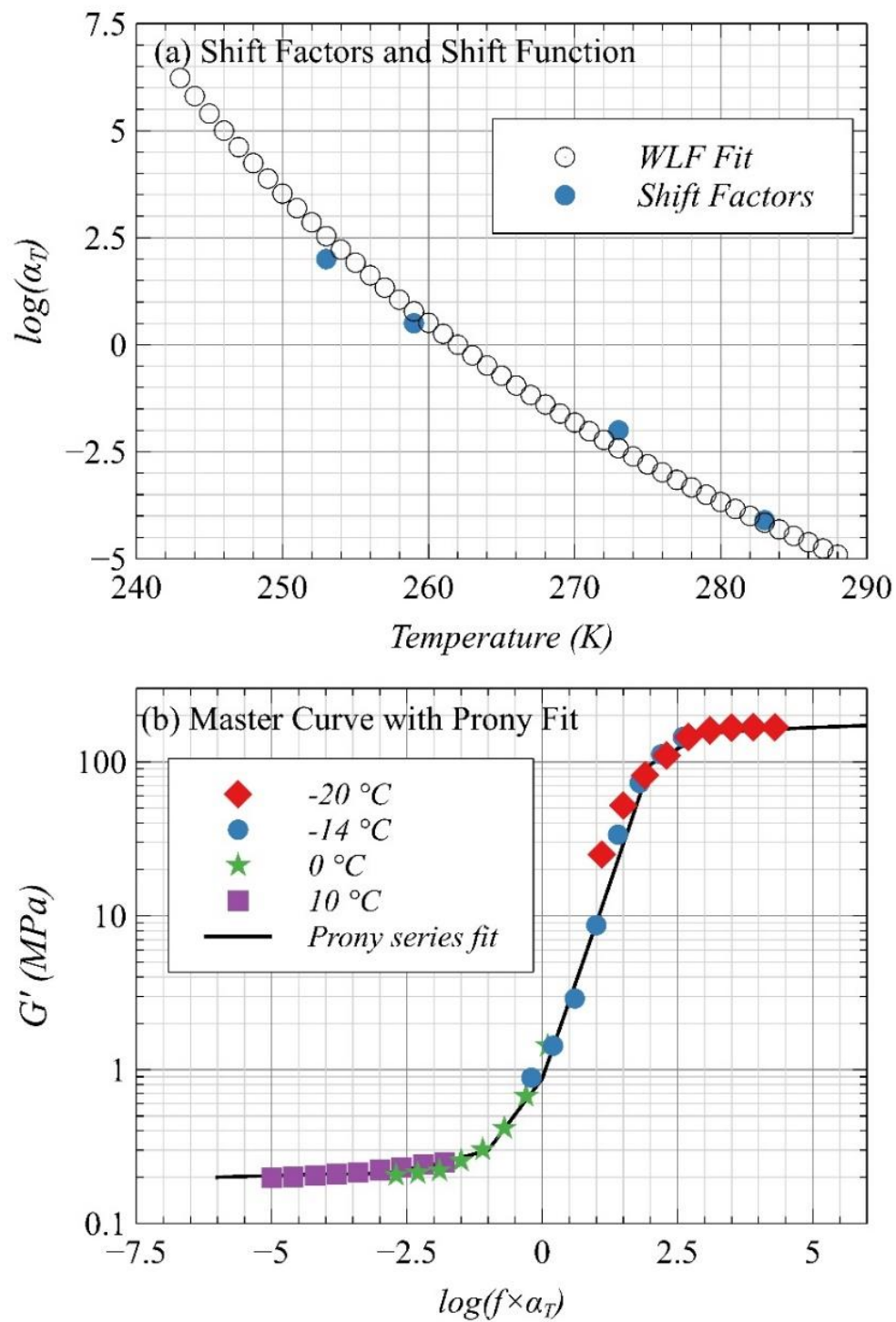


Figure 6-17 (a) Shift factors plot and WLF fit of Storage Modulus Master Curve (b) Prony series fit of Storage Modulus data for S1 at $T_{\text{ref}} = -11^\circ\text{C}$

Table 6-11 The 9-Term Coefficients of Prony Series for S1 at $T_{ref} = -11\text{ }^{\circ}\text{C}$

Branch #	G_i (MPa)	τ_i (sec)
Pure elastic	$G_{\infty} = 0.18$	-
1	30	1.00E-09
2	10	1.00E-06
3	12	1.00E-04
4	60	5.00E-03
5	90	3.00E-02
6	4	1.00E-02
7	1	1.00E+00
8	0.08	8.00E+01
9	0.01	1.00E+05

6.8 Performance Evaluation

The measured properties of the developed S1 (TPU + 20% AlN) sample were used in the finite element model developed for setting the target range of properties and the problem was solved to estimate the electrical power output and the life corresponding to 5000 W/m^2 . The thermal conductivity and specific heat was the input to the heat transfer study, and the other properties were input to the thermal stress study. With reference to Table 6-10 and discussion in the last section, the sample S1 has all the target set of properties i.e. $k \geq 0.75\text{ W(mK)}^{-1}$, $G_{\infty} < 0.2\text{ MPa}$ and $\alpha \leq 200 \times 10^{-6}\text{ K}^{-1}$ have been achieved. In this step, the measured properties (Table 6-10) were used in the parent FE model to evaluate the performance. The TC and specific heat were the inputs to the heat transfer study while the other properties were inputs to the thermal stress and strain study and finally, the obtained

results are summarized in Table 6-12. The results in Table 6-12 shows a good agreement to the predictions of FE solutions presented in Figure 6-7 and Table 6-5.

The highest cell temperature with neat TPU is attributed to its lowest TC as compared with neat EVA and proposed composite. Due to its highest TC, the proposed composite is capable to offer the lowest cell temperature and hence enhanced electrical power by 4.3% when compared with neat TPU. The highest mean stress and strain range are imposed by EVA because its CTE and G_{∞} values are the highest while the opposite is exact with neat TPU. The estimated life of 17.8 years with the proposed composite is good enough to pay back with a reasonable profit. On the other hand, the estimated life of ~61 years with TPU is too high to cope with the advancement of technology and degradation caused by other factors. Overall, the encapsulant with modified properties supports the production of electrical power and module life.

Table 6-12 Results of the performance evaluation using the properties of sample S1 in the finite element model

Name of the parameter	Magnitudes obtained			
	Using neat TPU	Using neat EVA	Using proposed composite (S1)	
Cell Temperature	68.8 °C	66.1 °C	63 °C	
Electrical Power	185 W	189 W	193 W	
% improvement in power output as compared with neat polymers	-	-	TPU	EVA
			4.3%	2.1%
Mean stress	37.5 MPa	44.4 MPa	44.3 MPa	
Strain range	0.004	0.00593	0.00542	
Estimated fatigue life	61.3 Years	12.7 Years	17.8 Years	

6.9 Conclusions

A computational approach is presented for the design of high-performance polymer composites for backside encapsulant of CPV systems. The design starts from selecting performance indicators and target material properties. In this study, for CPV systems, the performance indicators are electrical power and module life, while, target material properties are thermal conductivity, coefficient of thermal expansion, and long-term shear modulus. Target properties of intended composites such as thermal conductivity (k), coefficient of thermal expansion (α) and long-term shear modulus (G_∞) for improved performance of encapsulant are first identified by conducting sequentially-coupled thermo-mechanical finite element analyses in conjunction with Morrow's fatigue life approach. The finite element thermal stress problems were solved with variable input target properties taking into consideration the properties of ethylene vinyl acetate (EVA) as reference. It is found that, k should be increased for increasing the production of electrical power while G_∞ and α should be decreased for enhancing the module life. The required targets of the target properties are selected to be $k \geq 0.75$ W/m.K, $G_\infty < 0.2$ MPa and $\alpha \leq 200 \times 10^{-6}$ K⁻¹.

Based on target properties as predicted from FE-based performance evaluation, various candidate polymer matrices and fillers are considered at the material design stage. Thermal conductivity estimation is based on the differential effective medium approximation for non-dilute filler concentrations (Chapter 5) while the estimation of coefficient of thermal expansion and long-term shear modulus is based on mean-field homogenization (Chapter 2). Thermoplastic polyurethane (TPU) as matrix and ceramics (such as Al₂O₃ and AlN) as

fillers are the best among various candidates with designated filler attributes such as particle size and geometric shape. For validation of the design, some representative composites are synthesized and characterized. The properties such as thermal conductivity, coefficient of thermal expansion, viscoelastic behavior and long-term shear modulus are measured which are found in close agreement with the predictions. Moreover, the parameters of 9-term Generalized Maxwell Model and WLF shift function are determined by generating the master curve method. The performance of the module with the designed composite as encapsulant is assessed by using the measured properties in the finite element model for three-cell CPV structure. The measured properties of developed composites are used as input in the developed FE model to get some expected practical values of power output and life of CPV modules. A reasonable agreement between the measured and predicted values affirms the generalized use of this methodology for application-focused design and development of polymer matrix composites. The proposed TPU-composite is more capable and results in a temperature drop of 5.8 and 3.1 °C leading to an increased electrical power by 4.3 and 2.1 % when compared with neat TPU and EVA, respectively along with a more practical module life. The presented computational design and development strategy can serve as a useful guideline for composite manufacturers in developing new potential polymer composites for target applications. It is expected that the current design and development approach will also provide a useful guideline for the CPV modules manufacturers.

CHAPTER 7

POLYMER COMPOSITE TUBE MATERIAL FOR

SHELL AND TUBE HEAT EXCHANGERS

Heat exchanger is one of the core components of many engineering and industrial units. Commonly employed heat exchangers are made of metals, so that the purpose of effective heat transfer can be established easily owing to the high thermal conductivity of metals. However, there are several issues associated with metals such as high production cost, difficult processing, high corrosion, and high cost of maintenance. Therefore, the concerned community is in a constant pursuit of replacing metals in heat transfer applications especially when working in corrosive environment. Due to their easy and low temperature processing, low density, and matchless corrosion resistance, polymeric materials are the most suitable candidates to replace metals in such applications. In this work, the feasibility of replacing metallic tubes by polymeric tubes has been systematically investigated through mathematical models and experimental means. The critical performance indicators acquired by the tubes of shell and tube heat exchanger are the thermal and mechanical stability at the working temperature and pressure for a reasonable life time and the ability to transfer heat between hot and cold side fluids as per design requirements. Accordingly, the required target properties (strength and thermal conductivity) for the tubes of heat exchanger are identified through well-established

mathematical models. The well-known Kern and Bell-Delaware methods are used to study the effects of different design and flow parameters upon heat transfer coefficient while Barlow's formula is used to estimate the target strength. It is realized that the target strength and thermal conductivity of prospective polymer-composite are much less than those of metals to achieve equivalent performance of metals. The target thermal conductivity strongly depends upon the flow rates on both sides of the heat exchanger while the design parameters have a little effect. Hence, the target thermal conductivity for a lab scale heat exchanger having flow rates in the laminar regime, and transient regime is 1.5 and 3.6 W/mK, respectively. The target tensile strength depends upon the working temperature and pressure of the two flow streams. Based on Barlow's formula and creep life data of polypropylene a room temperature tensile strength of 20 MPa is good enough to provide a creep life of at least 25 years at a maximum design pressure of 1.00 MPa and average working temperature of 60 °C with tubes of ϕ 10 mm and 1.25 tube-wall thickness (maximum allowed hoop stress is 5.5 MPa). Following the author's previously established composite materials design scheme, a filler with aspect ratio < 0.1 (oblate) or > 10 (prolate) is required while the polymer matrix and the filler with thermal conductivity as low as 0.2 W/mK and 33 W/mK can be used to make the composite. And the recommended volume fraction for filler is 15%. Finally, composite samples in line with computational design are developed with PP and expanded graphite as matrix and filler, respectively with a volume fraction ranging from 10 to 20% and their performance is evaluated for heat transfer using a double pipe lab scale heat exchanger with replaceable tube. The effectiveness and

temperature drop observed with a commercial thermally conductive tube and a copper tube are found in close agreement under same operating conditions.

7.1 Introduction

Thermally conductive polymer matrix composites have become the focus of recent research and development of materials for heat transfer surfaces. The attraction of polymer matrix composites is attributed to their wide acceptability in many engineering, biomedical and domestic applications. Polymer based materials are light weight, corrosion-resistant, anti-fouling, inert to most of the chemicals and can be processed very easily at low working temperatures. However, due to the weak Vander Waal forces between the molecular chains in the polymeric materials, their mechanical properties like tensile strength, elastic modulus, hardness and wear resistance are very low as compared with metals. Similarly, the polymeric materials have small electrical and thermal conductivities due to unavailability of free electrons and small mean free path of phonons. Hence, the enhancement of thermal conductivity is one of the prime goals of the recent developments in polymer matrix composites. With enhanced thermal conductivity, polymer matrix composites are accepted for many thermal management applications such as thermal interface materials, heat transfer surfaces and heat spreaders.

Due to their high thermal conductivity, metals are the materials of choice for the heat exchangers. However, metals have several disadvantages such as high density, high cost, high temperature process-ability, low fouling and corrosion resistances. Polymer based materials can effectively overcome the disadvantages offered by metals with lower

production cost, low temperature and easy process-ability and very good corrosion and fouling resistances.

Heat exchanger is a device, which is used to transfer heat between two fluids through a separating surface however, the term “heat sink”, is used for a device in which heat is transferred between a solid and a fluid. The assembly of a heat exchanger is such that the hot and cold fluids are kept separated from each other by means of thin separating solid surfaces. Most commonly used assemblies of heat exchangers are the “plate and frame” and “shell and tube” types, where the separating surfaces are plates or tubes respectively [43]. Heat exchangers are one of the core components of many engineering systems for example space heaters, air conditioning, power stations, chemical and petrochemical plants, refineries, food processing, and thermal desalination etc. The heat transfer surface of heat exchanger must be capable of transferring the heat at the quickest, which is the core function of heat exchanger. In order to perform this function for a reasonable life-time, it should have a good thermal conductivity and adequate strength over the working temperature range of the fluids [49].

Polymer heat exchangers are accepted in many industrial and engineering applications. Polymer based heat exchangers have been studied by scientists and engineers since 1960 and since then have been magnificently employed for many applications. These applications include but not limited to heat recovery systems [44,45] HVAC & R [46–49], evaporative cooling systems [50,51], seawater desalination [52–56], solar water heating [57–59], and condensing boilers [60].

To be used for thermal management, the low thermal conductivity of the polymers is a big hurdle. Also, their low mechanical properties put a limit on the allowable fluid pressure in the heat exchangers. Thanks to thermally conductive carbonaceous fillers; their suitable addition in a polymer matrix can dramatically change the behavior leading to high thermal, mechanical properties without losing the characteristic advantages of polymers. The properties of polymer matrix composites can be tailored by tuning different material and processing parameters [3]. The purpose of the proposed work is to ‘design’ a polymer matrix composite initially that would have a combination of high thermal conductivity, and adequate tensile strength. On the other hand, the processing related material properties such as melt viscosity, processing temperature and cooling time etc. should be un-affected [49,61].

The properties of composites are the complex functions of many different parameters. These include but not limited to volume fractions, shape morphology, distribution, and interface condition of the fillers. Without a computational design methodology, one can try many different combinations of volume fractions, types and shapes of filler particles, and processing parameters for the synthesis of composite that may or may not successfully lead to the material with target set of properties. This may be lots of time consuming and utilization of resources unnecessarily. On the other hand, analytical and/or numerical models can effectively predict the required material (such as filler type, volume fraction, distribution, shapes and particle size etc.) and processing (such as interface condition and porosity etc.) parameters [29,62,63]. Most of the literature related to the polymeric heat exchanger, mainly focuses on the design of heat exchanger without coupling to the design

of composite material. In this work, the two designs i.e. of heat exchanger at macroscopic level and of composite material at microscopic level are coupled to provide both optimized heat exchanger and optimized composite material leading to overall heat transfer coefficients comparable to those of metals.

This work is a design methodology leading to the development of new polymer matrix composite material suitable for heat exchanger application. The new composite material acquires better thermal and structural performance as compared with the neat polymer. The thermal conductivity, tensile strength and thermal expansion are the main properties under consideration. For this purpose, previously developed codes based on Kern and Bell-Delaware methods [181] are used to explore and optimize among various heat exchanger designs, and to find out the required minimum threshold thermal conductivity and fluid pressure drop. This first step, identifies the target of required properties for the heat exchanger tubes. Then in the second step, the prospective composite material which can provide the target properties is designed using mean-field homogenization and effective medium theory -based material design codes. In the third step, the designed prospective composites are developed and their properties are characterized experimentally. Finally, in the fourth step, the performance of experimentally developed materials is evaluated through experimental and mathematical methods. A lab-scale double-pipe heat exchanger is developed using commercially available extruded composite tube for experimental performance evaluation, whereas Bell-Delaware method is used for mathematical performance evaluation.

7.2 Mathematical models

This section summarizes the equations of mainly heat exchanger design. The equations of material design have been already explained in Chapter 6. To design the heat exchanger two well-known methods were used; Kern and Bell-Delaware methods. These two methods have been investigated in detail for baffled shell and tube heat exchangers by Abdelkader et al. [109]. It was concluded that Bell-Delaware method is the most accurate to calculate the pressure drop and heat transfer coefficients. However, in this work, both of these methods provide nearly same results because of small heat exchanger and negligible leakage among shell-baffles-tubes.

7.2.1 Kern method

In a baffled heat exchanger, the fluid velocity is highly changing along the length due to confined areas at baffles. Moreover, the counter-flow becomes a mix of counter-flow and cross flow due to the baffles. The following correlations have been suggested for calculating the heat transfer coefficient and pressure drop on the shell side.

$$Nu = 0.36 Re^{0.55} Pr^{1/3} \left(\frac{\mu_b}{\mu_w} \right)^{0.14} \quad (7-1)$$

$$\Delta P_s = \frac{f G^2 D_s (N_b + 1)}{7.5 \times 10^{12} D_e \left(\frac{\mu_b}{\mu_w} \right)} \quad (7-2)$$

$$f = 0.4137 Re^{-0.2585} \quad (7-3)$$

7.2.2 Bell-Delaware method

Bell-Delaware method is based on the assumption that the fluid follows the path with least resistance and hence, the non-ideal flow streams can be up to 40% of the total flow rates. In this method, the total flow is divided into several streams and then calculations are performed for each stream separately. Finally, these calculations are summed up to calculate the overall heat transfer coefficient and pressure drop.

For heat transfer coefficient on shell side, the Bell-Delaware method uses the following equation;

$$h_s = h_c J_C J_L J_B J_R J_S J_\mu \quad (7-4)$$

Where h_s and h_c represent the overall shell side, and cross flow heat transfer coefficients, respectively, and each J is a correction factor calculated separately for each different stream. J_C is baffle window correction factor, J_L is the baffle leakage correction factor, J_B is the tube bundle bypass correction factor, J_S is the unequal baffle spacing correction factor, J_R is the laminar flow correction factor, and J_μ is the wall viscosity correction factor.

For pressure drop on shell side, this method uses the following equation;

$$\Delta P_s = \Delta P_{cb} + \Delta P_w + \Delta P_e \quad (7-5)$$

Where each ΔP is a pressure drop, and the subscripts s , cb , w and e relates the pressure drop to shell side, central baffle spaces, baffle windows and “entrance + exit” baffle spaces, respectively. The detailed equations of each of the correction factors and pressure drop can be found elsewhere [109,181].

7.3 Methodology

Overall, this work can be divided into four parts/steps as described in the previous chapter for encapsulation of concentrated photovoltaic modules. As a first step, the mathematical models of heat exchanger design are used to explore different design aspects of shell and tube heat exchanger. In all different designs, the effect of tube-wall thermal conductivity upon the overall heat transfer coefficient is investigated and analyzed. In parallel to the effect of tube-wall thermal conductivity, the pressure drop is also estimated which can be used to set the required tube-thickness and mechanical properties such as tensile yield strength. The analysis conducted in the first step leads to set the targets of thermal conductivity and yield strength.

As a second step, composite material is designed using the codes based on properties estimation models. The smartness of computational design of material is that it can predict the required material attributes without experimentation. The material attributes include but not limited to the required filler, its relative fractions, interface condition and geometric shape of the filler's particles.

As a third step, few samples from the top candidates among the computationally designed composites are synthesized and characterized. Overall, this step is named as “development” of samples. The experimental data obtained from this step plays a dual role; it validates the computational design of composite material and the values of measured properties become the inputs for the fourth step.

Finally, as a fourth step, the practical performance of the developed composite samples is evaluated using experimental and computational tools. For the experimental performance evaluation, a lab-scale single-tube heat exchanger with baffles as optimized through Kern or Bell-Delaware methods is constructed and heat transfer experiments are performed using different tubes including thermally conductive polymer composite tube and copper tube. For the computational performance evaluation, the problem was solved numerically in commercially available finite element software. The geometric model was developed in line with the heat exchanger design finalized in the first step and the boundary conditions were imposed accordingly. Overall, this step validates the first step of the overall methodology.

7.4 Optimizing the heat exchanger design and target properties

The first step in optimization of heat exchanger is to check the feasibility of replacing metallic tubes with polymeric tubes. The second step is to design a lab-scale heat exchanger and find the threshold material properties of prospective composite.

7.4.1 Feasibility study

7.4.1.1 Required tensile strength

Figure 7-1 shows the feasibility of using polymer-composite tubes and the identification of threshold yield strength. In Figure 7-1 (a) the creep data of polypropylene (PP) polymer has been considered as an example. The red dashed lines are to indicate the threshold quantities. The average working temperature in the application considered in this work is around 60 °C. An operational life of 25 years is expected for this polymer (PP) operating under an allowable hoop stress of 5 MPa at 60 °C. It is also approximated from Figure 7-1 (a) that a polymer for which the allowable hoop stress at room temperature is around 16 – 18 MPa is expected to have a life of 25 years under 5 MPa hoop stress at 60 °C with a factor of safety. The allowable working temperatures of thermoplastic polymers are wide spread, and now, polymers are commercially available that have service temperatures up to 300 °C with high values of hoop stress allowed. The required OD and tube wall thickness can be selected based on Barlow's formula [equation (6)]. Figure 7-1 (b) shows hoop stress in the tubes as function of tube's diameter at a high working pressure of 1 MPa for different tube wall thicknesses. It is observed, that nominal polymeric materials (such as PP) can provide the required mechanical strength without even reinforcing with fillers. For higher working temperatures or pressures polymers with higher mechanical strengths could be used. And reinforcing with high aspect ratio particulate fillers, normally enhance the yield strength of the polymeric materials and hence higher working pressures and temperatures could be allowed even with PP matrix.

$$\sigma = \frac{p(d-t)}{2t} \quad (6)$$

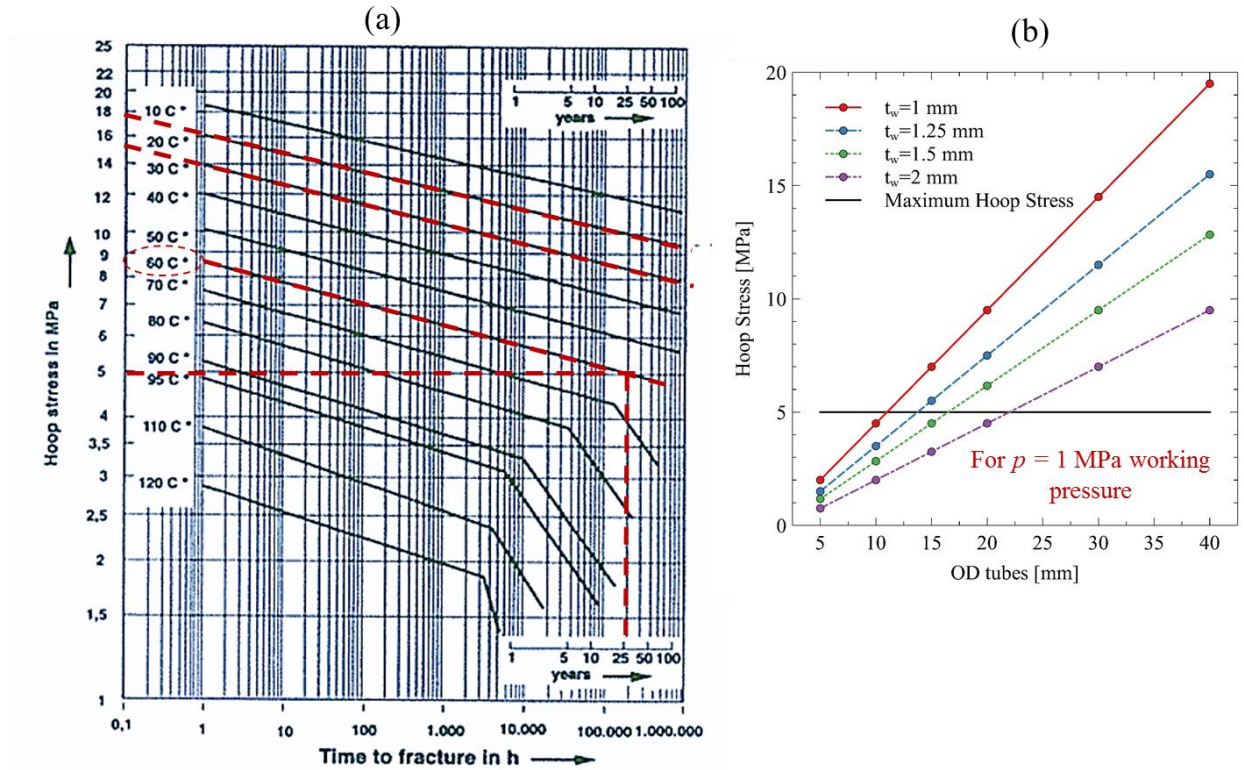


Figure 7-1 (a) Creep life data of polypropylene polymer to estimate required threshold of room temperature tensile strength; (b) Hoop stress as function of tube diameter at working pressure of $p = 1$ MPa for different tube wall thicknesses

7.4.1.2 Required thermal conductivity

The overall heat transfer coefficient is defined by equation (7-6), where R_{total} is the sum of all the convective and conductive resistances as defined in equation (7-7). Hence, R_{fi} and R_{fo} are the fouling resistances on tube and shell sides respectively and R_i and R_o are the convective resistances on tube and shell sides respectively, whereas R_w is the conductive resistance of the tube wall.

$$UA = \frac{1}{R_{total}} \quad (7-6)$$

$$R_{total} = R_{fi} + R_i + R_w + R_o + R_{fo} \quad (7-7)$$

$$R_w = \frac{\ln\left(\frac{D_{to}}{D_{ti}}\right)}{2\pi k_w L N_t} \quad (7-8)$$

R_w is defined by equation (7-7) which indicates that this resistance depends upon ratio of the tube outer diameter (D_{to}) to the tube inner diameter (D_{ti}), wall thermal conductivity (k_w), heat exchanger length (L), and the number of tubes (N_t). In order to replace the metallic tubes, for a particular case/application, the only parameter which is going to change is k_w . Therefore, the heat transfer equations of Kern and Bell-Delaware methods are solved as function of k_w for a commercial heat exchanger with three baffles, two passes and 158 tubes in the tube bundle. The other design parameters of heat exchanger are listed in Table 7-1. Different parameters of equations (7-6) and (7-7) as solved by heat exchanger equations as affected by k_w are shown in Figure 7-2. The feasibility of replacing metallic tubes is well-understood from Figure 7-2 (a), which shows that without changing the geometric design of heat exchanger it is only feasible to replace the metallic tubes, if and only if the thermal conductivity of tube wall, k_w , is increased to certain minimum threshold. For the heat exchanger under consideration in this feasibility study, $k_w = 10 \text{ Wm}^{-1}$

$^1\text{K}^{-1}$ is good enough to achieve an overall heat transfer coefficient (UA) equal to 80% as compared to that with metallic tubes with $k_w = 50 \text{ Wm}^{-1}\text{K}^{-1}$. Moreover, k_w is much sensitive for UA at smaller values up to $2.0 \text{ Wm}^{-1}\text{K}^{-1}$. Figure 7-2 (b) shows that among different resistances of equation (7-7), only R_o and R_i are unaffected by k_w because the geometry and flow rates on both sides of the heat exchanger are unchanged. However, R_w is the only parameter which is largely changed at lower values of k_w and converges later on similar to UA . Quantitatively, R_w decreases quickly with increasing k_w until $R_w = R_i$ at $k_w = 5 \text{ Wm}^{-1}\text{K}^{-1}$ as shown in Figure 7-2 (c). In parallel, UA increases quickly until at $k_w = 5 \text{ Wm}^{-1}\text{K}^{-1}$, UA reaches $44.7 \times 10^3 \text{ W/K} = 60\%$ of UA with $k_w = 50 \text{ Wm}^{-1}\text{K}^{-1}$. Further increasing k_w to $10 \text{ Wm}^{-1}\text{K}^{-1}$ decreases R_w and hence increases UA to reach $55.7 \times 10^3 \text{ W/K} = 80\%$ of UA with $k_w = 50 \text{ Wm}^{-1}\text{K}^{-1}$.

Table 7-1 The heat exchanger design parameters for different heat exchangers

Design parameter	Commercial heat exchanger	Lab-scale heat exchanger
Layout	90°	90°
Shell Length	4.8768 m	1.00 m (Parametric Study)
Baffle Cut	25%	25%
Number of Baffles	3	8 (Parametric Study)
Shell Diameter	534 mm	110 mm
Tube Wall Thickness	2.413 mm	1.25 mm (Parametric Study)
Tube Inner Diameter	20.574 mm	7.5 mm
Number of tubes	158	4 (Parametric Study)
Number of Passes	4	1
Shell Side		
Shell-side Fluid	Water	Water
Shell-in Temperature	67 °C	67 °C
Shell-out Temperature	53 °C	53 °C
Shell-side mass flow rate	5.52 kg/s	0.1 kg/s (Parametric Study)
Tube side		
Tube-side fluid	Water	Water
Tube-in Temperature	17 °C	17 °C
Tube-out Temperature	40 °C	40 °C
Tube-side mass flow rate	1 kg/s	0.0167 kg/s (Parametric Study)

Therefore, the feasibility study (step 1) concludes that the metallic tubes with high thermal conductivity up to $50 \text{ Wm}^{-1}\text{K}^{-1}$ can be replaced with tubes any other material that can have a thermal conductivity of $10 \text{ Wm}^{-1}\text{K}^{-1}$ without changing the operating conditions, the flow rates, and the geometric design of this particular heat exchanger under consideration and this replacement can lead to $UA = 80\% UA$ with $k_w = 50 \text{ Wm}^{-1}\text{K}^{-1}$. To avoid repetition of

words, UA with $k_w = 50 \text{ Wm}^{-1}\text{K}^{-1}$ will be called as UA_{50} from here so on. Further enhance of UA , depends upon the value of R_w which can be further decreased by reducing the wall thickness or by increasing length or the number of tubes according to equation (7-8). Most of the polymers have very low thermal conductivity ranging from 0.15 to 0.5 W/mK. However, polymers are easily processed at low temperatures and can accommodate large volume fractions of fillers, where thermal conductivity can be enhanced to very high values by using high aspect ratio inter-connecting thermally conductive fillers [10,24]. On the other hand, the typical pressure used in the shell and tube heat exchangers is close to 600 kPa which may cause a maximum hoop stress of 3 MPa in the tubes (only for the heat exchanger under consideration). A normal stress of 3 MPa is easily manageable with Polymer-composites.

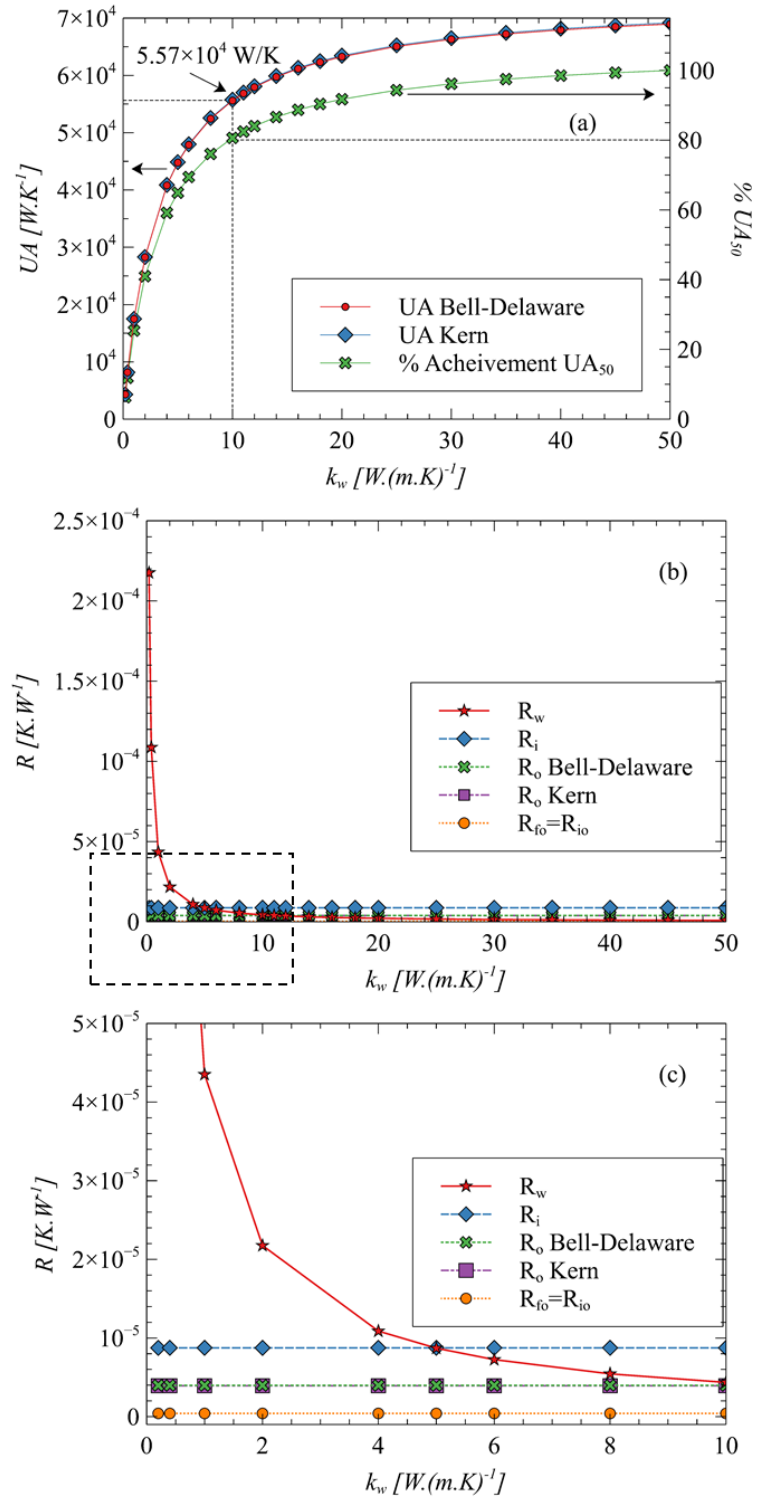


Figure 7-2 (a) Overall heat transfer coefficient and (b) Heat exchanger resistances as functions of k_w (c) zoomed in part of image (b) to show the critical values of R

7.4.2 Heat exchanger Design optimization

The second step in the optimization of heat exchanger is to work for Lab-Scale heat exchanger. For the lab-scale, some constraints are imposed upon the design of heat exchanger based on the available facilities. For example, the maximum tube length is limited to only 1.00 m and the flow rates are also small due to the small capacity water circulator heating units available where it is possible to test the heat exchanger at different inlet temperatures.

For the lab-scale heat exchanger, the code used to study the feasibility was modified to reach the minimum possible numbers of tubes and passes. Hence, the equations of Bell-Delaware and Kern methods are solved with number of passes reduced to one only and the number of tubes reduced to four only with 90° layout. The other baseline design parameters of the lab-scale heat exchanger are listed in Table 7-1. For the lab-scale heat exchanger the effects of tube thickness, heat exchanger length, number of tubes, number of baffles, and mass flow rates are analyzed through parametric studies. The objective of each parametric study is to observe the effect of k_w and look for the target value of k_w at which $UA = 80\% UA_{50}$ can be achieved. After the parametric analyses, the design which can provide the maximum absolute value of UA and lies within the lab-scale dimensional limits is selected for the development.

7.4.3 Parametric studies

7.4.3.1 Tube wall thickness

Tube wall thickness had a little effect on you a values as shown in Figure 7-3 (a). It is further shown in Figure 7-3 (aa) that target value of k_w for $UA = 80\% UA_{50}$ can be decreased by a little extent only by increasing or decreasing the wall thickness. The decrease in target k_w by decreasing wall thickness is associated with the decreased R_w while the same effect by increasing the wall thickness is associated with increased tube side turbulence and hence decreased R_i .

7.4.3.2 Heat exchanger length

The effect of heat exchanger length is much more significant as compared to tube wall thickness as it is shown in Figure 7-3 (b). The significant change in the values of UA by changing the heat exchanger length is due to the dependence of R_w on heat exchanger length [equation (7-8)]. By doubling the length from 1.0 m to 2.0 m, the target k_w is reduced from 1.5 W/mK to 1.0 W/mK without changing the number of baffles and using the baseline design flow rates mentioned in Table 7-1 as shown in Figure 7-3 (bb). The target k_w can be further reduced to < 0.75 W/mK by increasing the number of buffers, along with increasing length. Actually, the increased number of baffles will decrease the shell side convective resistance (R_o) due to the increase shell side turbulence.

7.4.3.3 Number of baffles

Figure 7-3 (c) shows the effect of number of the baffles (N_b) without changing the other parameters. Obviously, the number of baffles does not change the conductive resistance (R_w) of the tubes. Increased N_b only increases the flow length and the contact time of the shell side stream. The increased Re# on shell side is associated with the increased turbulence and flow length and hence UA is increased by increasing the number of baffles. However, target k_w is also affected to a little extend only as shown in Figure 7-3 (cc) which can be explained by equations (7-6) and (7-7). The decrease in R_o provided by increased number of baffles will increase the value of target $UA = 80\% UA_{50}$ and hence a larger k_w would be required to reach the target.

7.4.3.4 Number of tubes and tube side flow rates

The effects of number of tubes (N_t) and the tube side flow rate ($\dot{m}_{tube}$) are shown in Figure 7-3 (d) and (dd). Only N_t is increased in some cases while in the other cases, $\dot{m}_{tube}$ is also changed to keep the constant mass flux and Re# on the tube side in those cases. The effect of increased N_t appears in the form of decreased R_w referred by equation (8). In all of the cases shown in Figure 7-3 (dd), the target k_w is decreased by increased N_t because R_w is decreasing with increasing N_t . However, when $\dot{m}_{tube}$ is also increased, the effect of increased N_t on target k_w is somehow suppressed and that is associated with increased values of UA.

To optimize the overall design and flow parameters of the lab-scale heat exchanger, a few cases were solved as listed in Table 7-2 and their UA values as function of k_w are plotted and shown in Figure 7-4. In the case 1, the flow rates on both sides were increased to the level that Re# on both side was greater than 5000 and that is to have fully developed turbulent flow. It is observed that the target k_w is increased to 5.8 W/mK as compared to 1.6 W/mK for the baseline design. It has been already observed in Figure 7-3 (d) and now from Figure 7-4 as compared to Figure 7-2 it is confirmed that target k_w for having UA= 80% UA₅₀ significantly depends upon the flow rates. Case 1 to case 4 show that for Re# >5000 on both sides, the target k_w must be close to 5.5 W/mK while case 5 shows that target k_w can be reduced to 3.6 W/mK by having intermediate flow rates.

Conclusively, from all these parametric analysis it is observed that

1. The design thickness of the tubes should be close to 1.25 mm
2. The heat exchanger length (L) should be 2.0 m or more with N_b / L should be 8 to 10 per meter to have more values of UA and less value of target k_w .
3. Increasing N_t would add complexity to the design and it is obvious that increasing N_t will improve UA values but its role in controlling target k_w is not significant at the practical flow rates. Therefore N_t is left for the availability of tubes and other design restrictions.

4. The higher the flow rates the higher would be the target k_w for $UA = 80\% UA_{50}$ and vice versa. It is more practical to rely on intermediate flow rates for which the $Re\#$ is comparable to the commercially available HX. Moreover, if solved in simulation software with intermediate flow rates, the experimental data are easily available for validation.

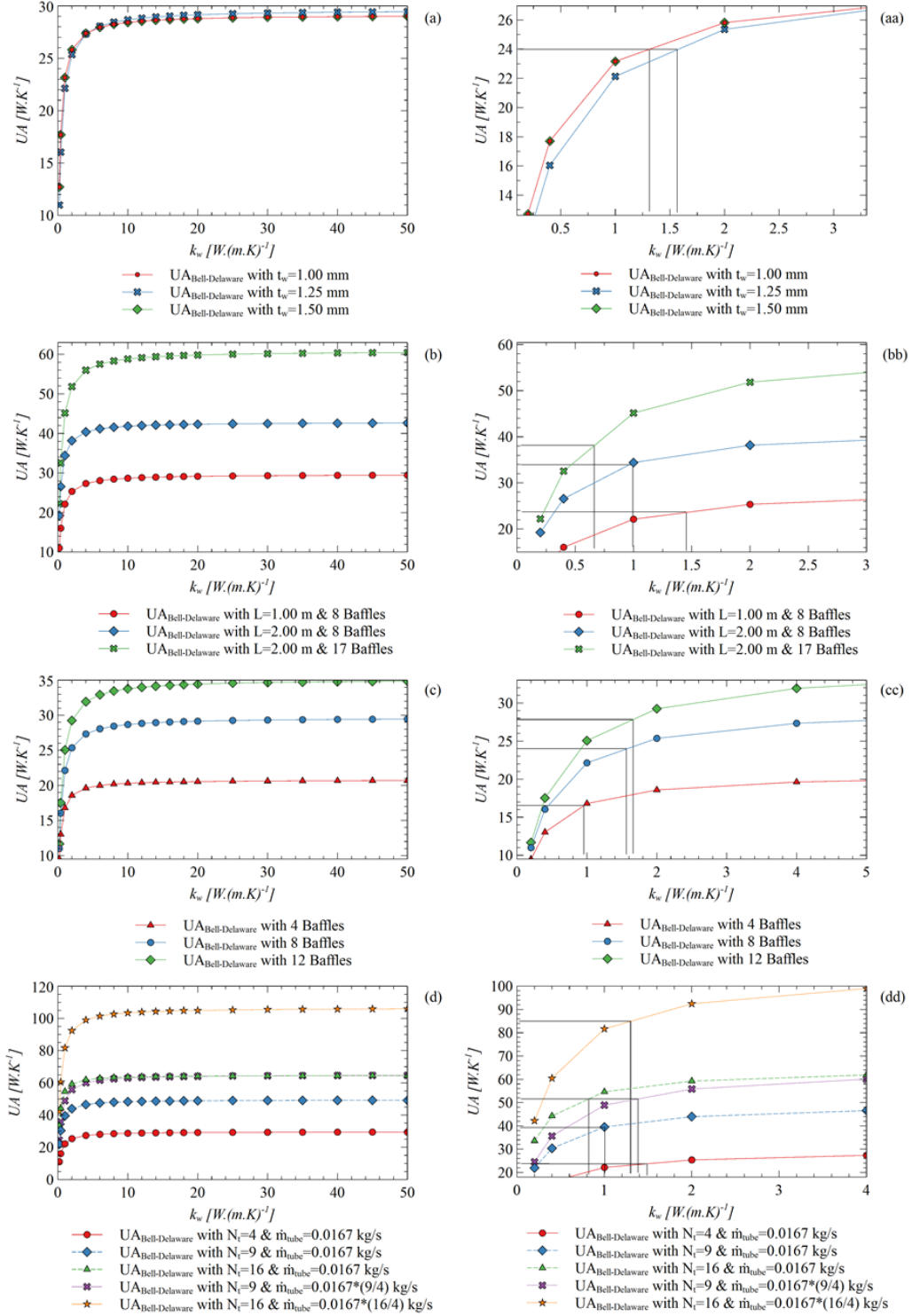


Figure 7-3 Parametric Studies to observe the effects of different heat exchanger design parameters on target wall thermal conductivity (k_w) and heat transfer coefficient (UA); (a, aa) tube wall thickness (t_w); (b, bb) heat exchanger length (L); (c, cc) number of baffles (N_b); (d, dd) Number of tubes (N_i)

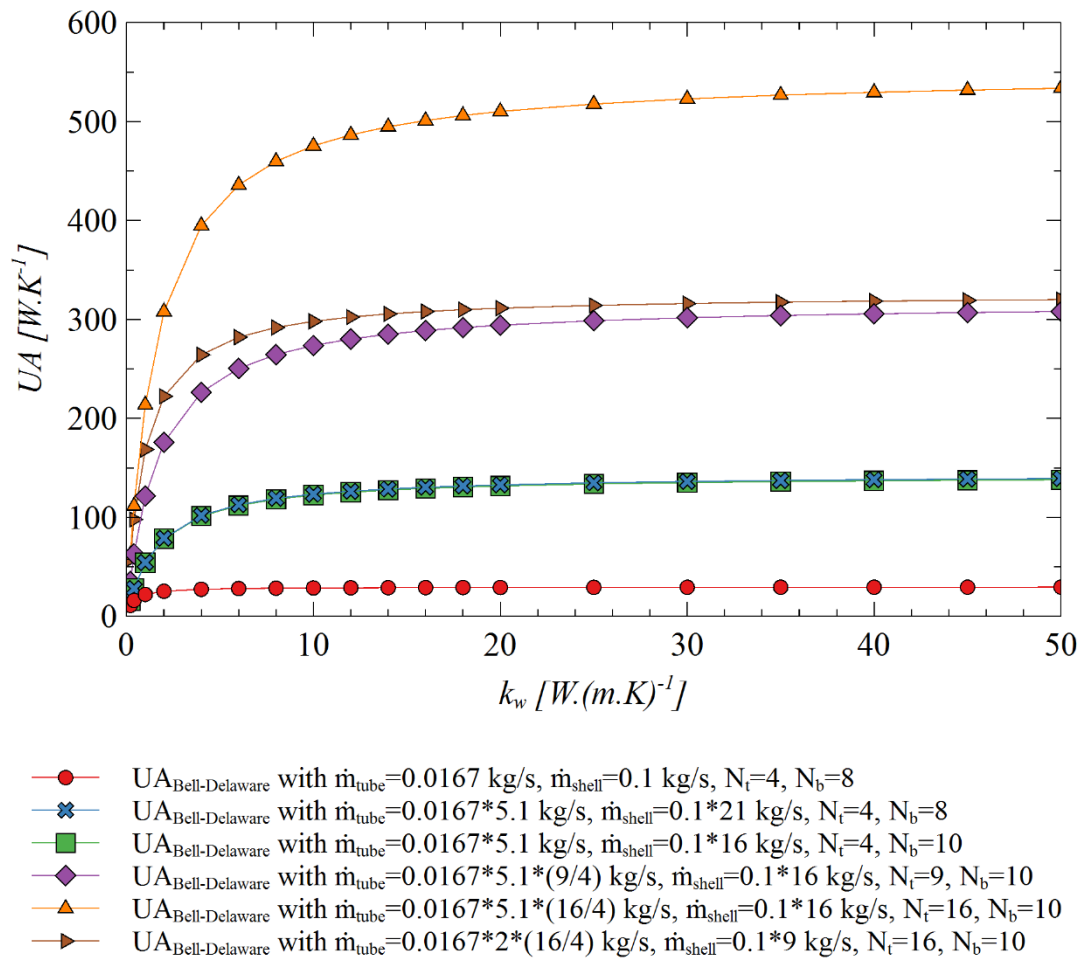


Figure 7-4 Heat transfer coefficient (UA) as function of tube wall thermal conductivity (k_w) for different cases of heat exchanger design as listed in Table 7-2 to finalize the lab-scale heat exchanger design

Table 7-2 Different cases of heat exchanger design and the corresponding 80% UA_{50} and Target k_w

Design	$\dot{m}_{\text{tube}}$ (kg/s)	$\dot{m}_{\text{shell}}$ (kg/s)	N_t	N_b	80% UA_{50} (W/K)	Target k_w (W/mK)
Baseline	0.0167	0.1	4	8	23.6	1.6
Case 1 ³	0.0852	2.1	4	8	111.4	5.8
Case 2 ⁴	0.0852	1.6	4	10	110.4	5.7
Case 3 ⁵	0.192	1.6	9	10	246.4	5.25
Case 4 ³	0.341	1.6	16	10	426.9	5.6
Case 5 ⁶	0.134	0.9	16	10	256	3.6

7.5 Computational Design of Composite Material

From the discussions made in the last section, it is well understood that the target k_w is strongly dependent upon design and input parameters of the HX. These target properties

³ As compared to baseline design, flow rates are increased to have fully developed turbulent flow in this design i.e. $Re\# > 5000$ on both sides.

⁴ Requirement of high flow rates on shell side is decreased by increasing the number of the baffles in this design

⁵ Number of tubes are increased to improve the values of UA in these designs

⁶ The flow rates are adjusted to have $Re\#$ comparable to those of commercial HX of Table 7-1

are easily achievable in polymer matrix composites. The material design methodology of polymer matrix composite has been explained very well in previous chapters. As already discussed, only k_w is the material property which is of main concern in this study. The target level of k_w is dependent upon HX design. Therefore, depending upon the target level of k_w various design alternatives are possible which can lead to achieve the target k_w . For example, the TC of continuous phase (the matrix) can be enhanced, high volume content of fillers can be added into to the matrix, or high aspect ratio filler particles can be used to achieve the desired high effective TC [25].

Figure 7-5 shows the availability of various design alternatives for enhancing effective TC. The reference values of different parameters used in the parametric studies shown in Figure 7-5 are listed in Table 7-3. Figure 7-5 (a) and (b) show that it is more important to enhance the TC of continuous phase (the matrix). By increasing the volume content of high TC near spherical filler particles up to 50% in a low TC continuous phase, such as polymer matrix, does not provide much enhancement of effective TC. On the other hand, enhancing the thermal conduction of continuous phase appears more effective for enhancement of effective TC even with low TC fillers such as alumina with 33 W/mK.

The other design possibilities are shown in Figure 7-5 (c) and (d) wherein the effect of different aspect ratio of oblate ($p>1$) type particles is shown in Figure 7-5 (c) and the same effect by using different aspect ratio of prolate ($p<1$) type particles is shown in Figure 7-5 (d). The use of high or low aspect ratio particles increases the number of particle–particle connections, promote heat conduction and hence improve the effective TC. The details of

this particle to particle connection and effects of high and low aspect ratio has been explained in chapters 4 and 5.

The shaded areas in different Figure 7-5 (a), (c) and (d) show the regions where the desired minimum target $k_w = 3.6$ W/mK can be achieved. It is clear that enhancing the TC of spherical fillers only cannot lead to reach the minimum target. On the other hand, if the continuous phase is reached to a TC of 2.5 W/mK, spherical particles alumina filler with low TC of 33 W/mK can cross the minimum target of k_w at 25 vol%. As discussed already, the effect of aspect ratio is much more sensitive for enhancement of effective TC. With a low TC matrix of 0.2 W/mK high (prolate) or low (oblate) aspect ratio particles can provide much more enhancement of effective TC [Figure 7-5 (c) and (d)]. However, this would be only true if the particles do not bend and remain randomly oriented in the final microstructure of the composite.

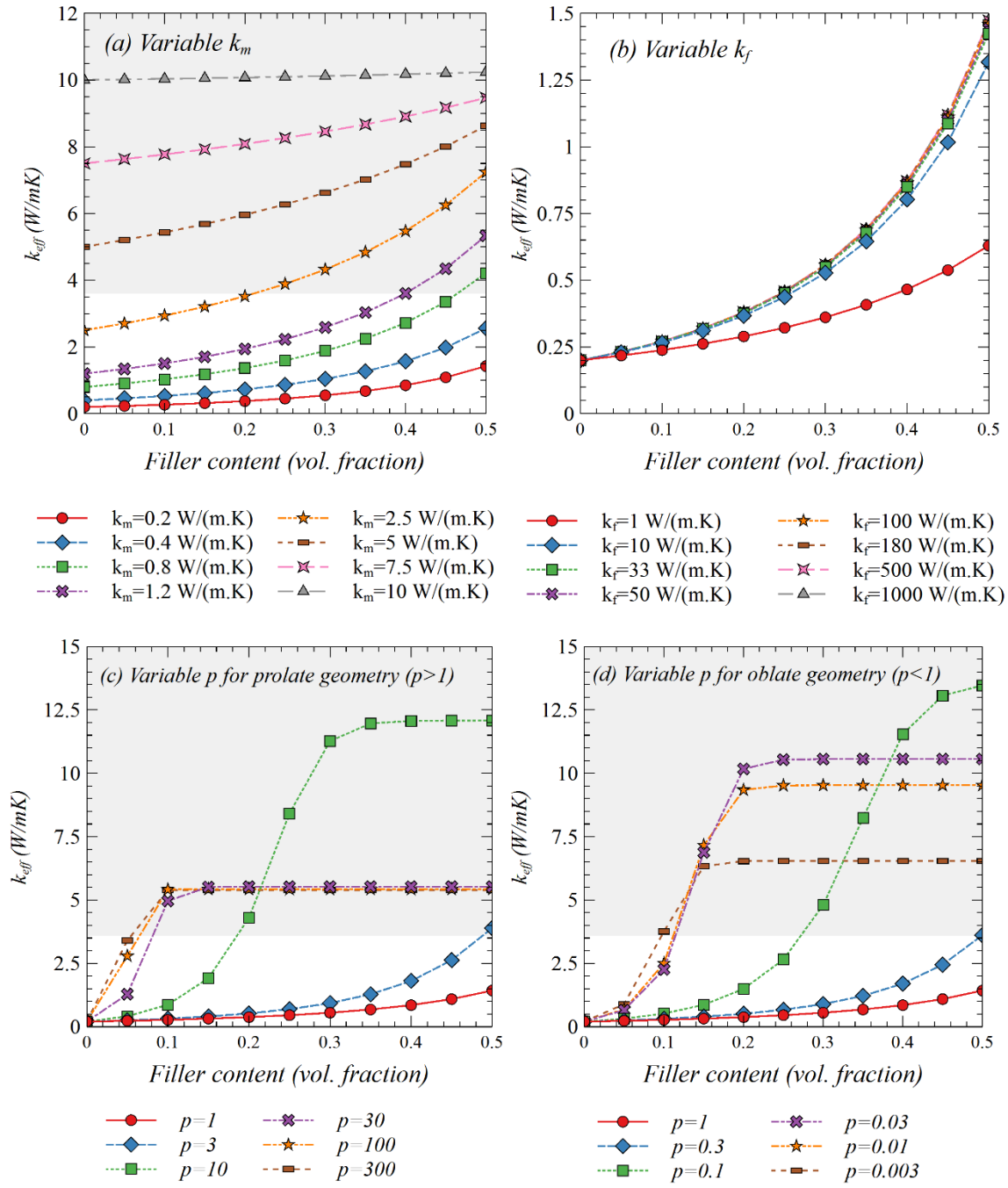


Figure 7-5 Computational Design of Composite Material with minimum Target $k_w = 3.6$ W/mK

From Figure 7-5 (c) and (d), it is suggested to use the filler particles with aspect ratio (p) should be either >10 or <0.1 . Accordingly the recommended volume content is $>15\%$ to accommodate the bending of particles and misalignment caused by processing-related limitations. And a polymer matrix with TC as low as 0.2 W/mK can be used in combination with the suggested filler particle attributes. In addition, the polymer matrix should be low cost, possess easy processing, and resistant to chemical attack by the tube and shell –side fluids. In this work, the working fluid on both sides is water, and hence most of the polymer matrices can be used; only those polymers which are water-soluble such as PVA (poly vinyl alcohol) cannot be used as matrix. The possibility of enhancing the TC of continuous phase has been explored and discussed in detail in the next chapter (Chapter 8).

Table 7-3 Reference values of the parameters of computational material design used in Figure 7-5

Figure #	Study	Reference values				
		k_m	k_f	$p > 1$	$p < 1$	Particle's radius
Figure 7-5 (a)	k_m	-	33 W/mK	1	1	$5 \mu\text{m}$
Figure 7-5 (b)	k_f	0.2 W/mK	-	1	1	$5 \mu\text{m}$
Figure 7-5 (c)	$p > 1$	0.2 W/mK	33 W/mK	-	1	$5 \mu\text{m}$
Figure 7-5 (d)	$p < 1$	0.2 W/mK	33 W/mK	1	-	$5 \mu\text{m}$

7.6 Development of composite materials

This section explains the processing, characterization and testing of composite material samples in line with the target properties and computational design of materials. From the computational design of materials polypropylene (PP) has been selected matrix which is

low cost, inert to most of the chemicals and has a TC of more than 0.2 W/mK. And a range of volume contents of graphite flakes have been selected as fillers and to synthesis the samples experimentally.

7.6.1 Materials

Isotactic PP was purchased from a local supplier of Sigma-Aldrich with a weight-average molecular weight of 250,000 g/mol and a density of 0.9 g/cm³. The graphite flakes was kindly supplied by Imerys Graphite & Carbon from Switzerland with trade name Timrex C-Therm 011 which is type a high aspect ratio and extremely high surface area filler specifically produced to make thermally conductive polymer matrix composites.

7.6.2 Drying

Both of the graphite powder and PP granules were dried in vacuum oven at 90 °C before mixing in the Brabender Mixer. The purpose of drying was to eliminate any water contamination.

7.6.3 Mixing

The melt mixing of the ingredients was conducted using Brabender Mixer 50 EHT. The graphite flakes were of very high surface area and the Scott density of the powder was as low as 0.19 g/cm³. Therefore, the mixing was managed to avoid air trapping during mixing. Initially, the temperature of the three zones of mixing chamber was set to 190 °C and left for some time to attain the temperature. Then the motor was switched on to rotate the mixer blades (roller blades) at a slower speed of only 10 rpm. Then pre-weighed amount of PP granules was added into the mixing chamber and allowed to melt. Finally, the pre-weighed

amount of C-Therm 011 graphite was added slowly at the same mixing speed. Then the mixing chamber was closed and the mixing speed was increased to 60 rpm and continued for 20 minutes. Experimentally, the samples were produced with 10, 15, and 20 vol % of C-therm 011 graphite in PP matrix. The calculations of conversion from volume % to mass % was performed considering the densities of PP and graphite to be 0.900 and 2.266 g/cm³, respectively.

7.6.4 Molding

The output the Brabender Mixer is in the form of irregular composite lumps of mixed ingredients. These irregular lumps are required to be shaped for measurements and characterization. For this purpose, the pre-weighed amount (depending upon the required thickness) of irregular lumps was hot-compressed in a compression molding machine at 170 °C for 10 min under a pressure of 3 MPa. The irregular lumps were shaped into disk shaped and cylindrical shaped samples. The disk shaped samples were brittle-fractured to observe under microscope while the cylindrical samples were used for mechanical testing and thermal conductivity measurement.

7.6.5 Testing

Thermal conductivity of the samples was measured using TCi Thermal Conductivity Analyzer by C-Therm Technologies Ltd., Canada. The measurement of TCi thermal conductivity analyzer is based on modified transient plane source method. The machine requires only one sample which is placed under weight on the spiral shaped heater + sensor during measurement.

7.7 Conclusions

To resolve the problems associated with metallic shell and tube heat exchangers, the metallic tubes can be replaced by polymeric materials. Heat exchanger with polymeric tubes is more advantageous in terms of providing high corrosion and fouling resistance, low manufacturing and maintenance costs, and light-weightiness.

1. In this work applicability of polymer-composites as tubes of plastic shell and tube exchangers has been proved through modeling and experimental means. Kern and Bell-Delaware methods are used as mathematical models for heat transfer calculations to check the feasibility of polymer-composite tubes and to optimize the design of lab heat exchanger. The minimum required thermal conductivity and strength for the tubes are much less than those of commonly used metallic tubes.
2. The target value of heat transfer coefficient is set to be $0.8UA_{50}$; where UA_{50} is the heat transfer coefficient with a metallic tube of tube wall thermal conductivity = 50 W/mK. Accordingly the target value of thermal conductivity at which $UA = 0.8UA_{50}$. The target thermal conductivity for a particular commercial heat exchanger is found to be 10 W/mK with both sides Re# in transient flow regime. The target thermal conductivity strongly depends upon the flow rates on both sides of the heat exchanger while the design parameters such as heat exchanger length, tube wall thickness, number of baffles, and number of tubes can also change required target value of tube wall thermal conductivity. Finally, the target thermal

conductivity for a lab scale heat exchanger having flow rates in the laminar regime, and transient regime is 1.5 and 3.6 W/mK, respectively.

3. The required tensile strength as estimated by Barlow's formula depends upon the working pressure of the two flow streams. The maximum allowed hoop stress is 5.5 MPa for tubes with ϕ 10 mm and 1.25 tube-wall thickness to have a life of 25 years for at average working temperature of 60 °C. Accordingly, the target room temperature tensile strength is 20 MPa based on the creep life data of neat polypropylene with a factor of safety 1.25.
4. Following the author's previously established composite materials design scheme, a filler with aspect ratio < 0.1 (oblate) or > 10 (prolate) is required while the polymer matrix and the filler with thermal conductivity as low as 0.2 W/mK and 33 W/mK can be used to make the composite. And the recommended volume fraction for filler is 15%.
5. Finally, composite samples in line with computational design are developed with PP and expanded graphite as matrix and filler, respectively with a volume fraction ranging from 10 to 20% and their performance is evaluated for heat transfer using a double pipe lab scale heat exchanger with replaceable tube. The effectiveness and temperature drop observed with a commercial thermally conductive tube and a copper tube are found in close agreement under same operating conditions.

CHAPTER 8

DESIGN OF STRUCTURED POLYMER COMPOSITES

WITH ULTRA-HIGH THERMAL CONDUCTIVITIES

This work aims to design and develop a polymer matrix composite with ultrahigh thermal conductivity by developing a continuous network of composite phase segregated with highly conducting graphite. The design of the composite material is based upon previously published thermal conductivity estimation model for non-dilute filler concentrations. The model explicates that for achieving ultrahigh thermal conductivity in polymer matrix composites, it is more effective to increase the thermal conductivity of the continuous phase (matrix) itself than that of discontinuous phase (fillers). Therefore, the composites are designed to have a continuous phase with high thermal conductivity using a multistep development approach. Graphite flakes (GF) are dispersed in polypropylene (PP) matrix in molten state as a first step to prepare a GF-PP mixture. In the second step, GF-PP mixture is mixed with polycarbonate (PC) at a temperature such that the former is kept in molten state while the latter remains solid. This scheme leads to the development of a continuous thermally conductive phase of GF-PP around the particles of PC. Effect of variables such as type of graphite and size of PC particles at constant overall GF volume fraction on the effective thermal conductivity is studied. It is found that a smaller size of PC and high surface area GF is more effective for enhancing the thermal conductivity. A practical value

of thermal conductivity more than 3.5 W/mK has been achieved with smaller size of PC particles and high surface area expanded graphite. Moreover, the heat-conduction behavior of different compositions has been demonstrated by thermal imaging. Finally, hardness measured by Shore's D method indicates that this methodology does not cause a significant loss to the mechanical properties.

8.1 Introduction

Due to their lightweight, high fouling and corrosion resistances, geometric flexibility and ease of processing, polymeric-based materials offer various advantages over metals in heat transfer applications. However, low thermal conductivity of polymers, which is less than 0.4 W/mK in general, is a major challenge to overcome [61]. Thermal conductivity of polymers can be easily enhanced by incorporating thermally conductive fillers. The enhancement in thermal conductivity strongly depends upon the intrinsic thermal conductivity of constituents, matrix/filler interface thermal resistance and geometric characteristics of the filler particles [182].

On incorporating fillers into polymer matrices, there are several factors influencing the degree of thermal conductivity improvement among which are: filler type, shape, size, orientation and the interfacial resistance between the filler and the matrix. Fillers could be metallic, ceramics or carbon based. Metals and carbon-based fillers have relatively higher thermal conductivities. However, in some applications, ceramics are particularly desired due to requirement of high electrical resistivity [183]. Carbon-based fillers such as graphite, carbon nanotubes and graphene are more attractive due to their low density and

the ability to make percolating networks [184]. Filler shape could be close to spherical, platelet or fiber shapes. Fillers of non-spherical shapes can be oriented during processing such that thermal conductivity is enhanced anisotropically [184]. Thermal conductivity of the final composite is most sensitive to interfacial resistance, particle size and particle orientation. Thermal conductivity of continuous phase in a composite plays a key role in the enhancement of effective thermal conductivity [185].

In literature, several methodologies are employed to enhance thermal conductivity of polymeric composite materials including hybrid fillers, surface treatment and alignment of fillers and formation of continuous filler network. Mixing fillers of different types, shapes, and sizes helps building thermally conductive network by forming connections between fillers and increasing the packing density, for instance, a thermal conductivity of 4.321 W/mK via inclusion of anisotropic aluminum nitride and isotropic spheres on epoxy and polyvinylidene fluoride in a 1:1 ratio and 60% by volume has been reported [186]. Another hybrid filler work of [145] incorporated graphene nanoplatelet (GNP) and multi wall carbon nanotubes (MWCNT) fillers with polycarbonate reaching a maximum of 1.39 W/mK. High effective thermal conductivity of polymer composites can be achieved by coating the polymer granules with conductive fillers and then compressing them to make solid samples. This method happens to be more promising as thermal conductivity could improve with lower filler content [182].

The aim of this work is to build a thermally conductive composite material consisting of polycarbonate (PC), polypropylene (PP) and graphite as the conductive filler. The composite system will be made via constructing a conductive phase out of graphite and

polypropylene (PP) through mixing at temperatures higher than the melting point of (PP) and mixing the resultant graphite-PP composition with (PC) at temperatures lower than the melting point of PC such that a continuous graphite-PP phase is formed around solid PC particles. Compositions with different types of graphite and different size of PC particles are developed and subjected to characterization.

8.2 Model for Thermal conductivity estimation

The model for thermal conductivity estimation with non-dilute filler concentration (presented in Chapter 5) was used in this study in two steps.

8.3 Design of Polymer Matrix Composites with High Enhancement

Before designing the composite, effects of filler and matrices thermal conductivities on the degree of enhancement on effective thermal conductivity as filler content increases is studied. Figure 8-1 a presents that the effect of increasing filler content on effective thermal conductivity has more significant effect as filler type possesses higher thermal conductivities. However, increasing filler thermal conductivity above 30 W/m.K has no significant effect on effective thermal conductivity, suggesting that filler thermal conductivity has no significant effect on effective thermal conductivity as most fillers has more than 30 W/mK thermal conductivity.

On the other hand, effect of increasing filler content on effective thermal conductivity becomes more significant because the matrix possesses higher thermal conductivities as shown in Figure 8-1 (b). This relationship continues as value of matrix thermal

conductivity is increased, suggesting that effective thermal conductivity is more sensitive to matrix thermal conductivity which lay on the range between 0.01 to 0.5 W/m.K. This is attributed to the fact that the matrix is the main path through which heat transfers.

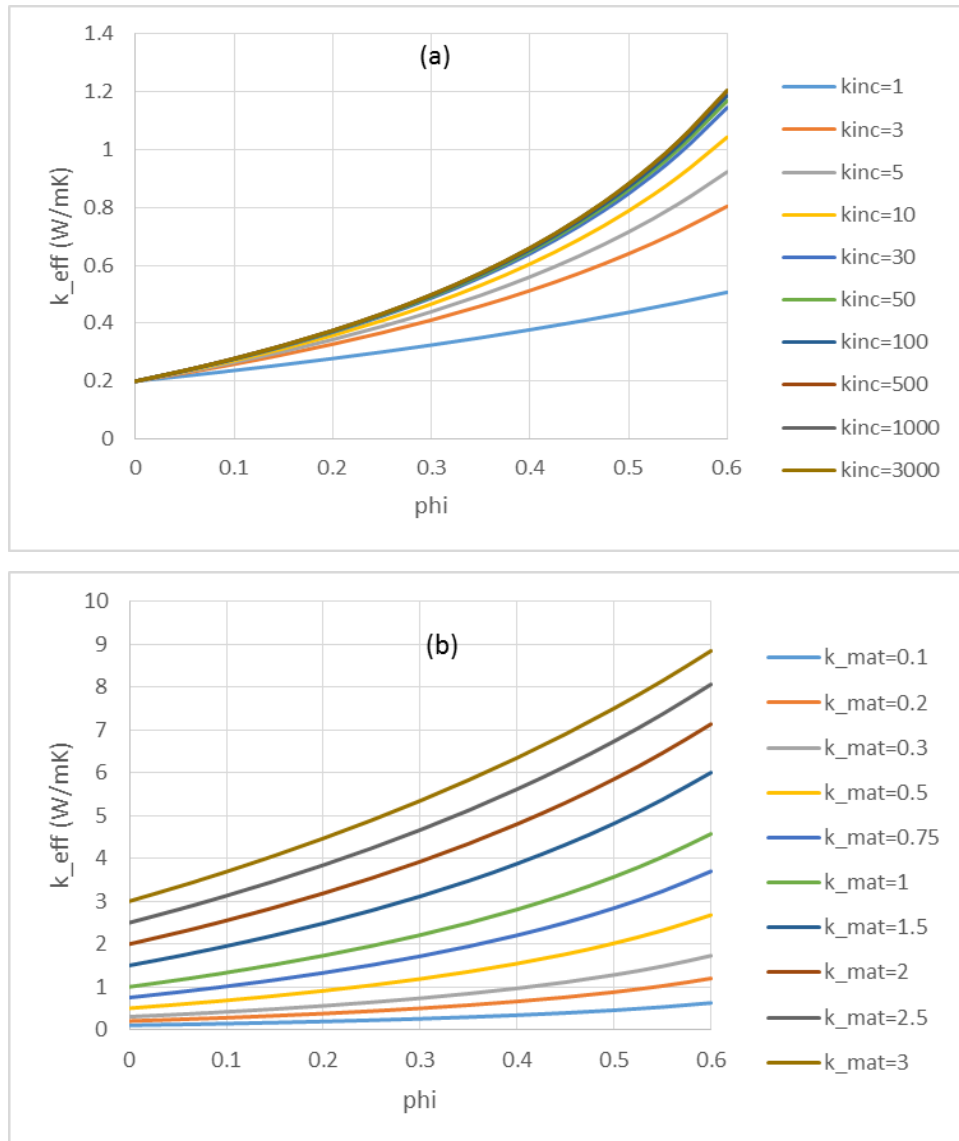


Figure 8-1 Thermal conductivity as function of volume fraction at different values of (a) filler thermal conductivity and (b) matrix thermal conductivity

8.4 Materials and Methods

8.4.1 Materials

Two different types of graphite flakes were used. One of them was high surface area synthetic graphite with the trade name C-Therm 011 kindly supplied by Imerys Graphite & Carbon, Switzerland. The other type of graphite was -325 mesh size high purity natural graphite purchased from Sigma Aldrich through its local supplier. PP and PC were also supplied by Sigma Aldrich with melt flow indices of 12 and 6.5 g/10 min respectively.

8.4.2 Processing

In the first step of processing, equal volumes of PP and the graphite were melt mixed using Brabender Mixer E50 equipped with roller blades. Mixing in the first step was performed at 190 °C at 60 rpm for 20 minutes. The output of first step mixing was named as GF-PP. In the second step of processing, GF-PP was mixed with PC particulates at 170 °C for 10 minutes with a volume ratio of 50:50. This step of mixing was performed at two different rpms so as to break or not to break the particles of PC during mixing. The detailed compositions and parameters of the samples are listed in the Table 8-1. In all the compositions listed in Table 8-1, the overall volume fraction of GF was 0.25. For reference, composites with 0.25 fraction of GF in GF-PP were also developed. The mixed samples were compression molded at 165 °C and 3 MPa pressure for 15 min to get at least 6 mm thick two cylindrical samples for measurements and microscopy.

Table 8-1 List of the samples, their compositions and variable parameters

Sample #	Type of Graphite	Overall Fraction of PP	Overall Fraction of PC	Mixing speed in second step (rpm)	Particle size of PC
C1	C-Therm 011	0.75	0.0	NA	NA
S1	Sigma	0.75	0.0	NA	NA
C2	C-Therm 011	0.25	0.5	30	Fine
S2	Sigma	0.25	0.5	30	Fine
C3	C-Therm 011	0.25	0.5	10	Coarse
S3	Sigma	0.25	0.5	10	Coarse

8.4.3 Measurements and characterization

The compression molded samples surfaces were fine grinded to have a very smooth surface for measuring thermal conductivity. Thermal conductivity of the samples was measured using *TCi Thermal Conductivity Analyzer by C-Therm Technologies Ltd., Canada*, in which the measurement is based on transient plane source method. Shore's D hardness of the samples was measured using a *Digi Test Motorized Durometer*. Heat transfer property of the samples was examined using an *FLIR one thermal imaging camera* by placing the samples on a set temperature hotplate covered with aluminum foil. The sample's surface was further polished to look at the microstructure and distribution of different phased in the composite. Finally, the microstructural examination was done using an *Olympus Metallurgical Microscope* equipped with camera.

8.5 RESULTS AND DISCUSSION

8.5.1 Macro and micro –structure

Figure 8-2 shows the camera pictures of the samples produced according to Table 8-1. It is important to note that the samples C1, C2, S1 and S2 are homogeneous at macroscopic level. However, PC particles are not broken in C3 and S3 and their size is approximately 3 mm due to very slow mixing speed used in the second step of the process. The optical micrographs of polished surfaces (Figure 8-3) shows that the composites are not homogeneous at microscopic level. Figure 8-3 (a) shows C1, where graphite is observed to be dispersed homogeneously in all directions. Figure 8-3 (b) shows the interface area between GF-PP and PC particles in C3. Finally, the microstructure of C2 (Figure 8-3 (c)) shows that high mixing speed during the second step of the process has broken the particles of PC and distributed them all around in the continuous phase of GF-PP. The particle size of PC in C2 ranges from 30 to 200 μm .

More details of the microstructures are revealed in FESEM images of fractured surfaces shown in Figure 8-4. The microstructure of C2 was captured at low magnification to show the particle size of segregating phase i.e. PC particles as shown in Figure 8-4 (b). The same observation has been discussed with reference to Figure 8-3 (c). The sample C1 is without PC particles; the fractured surface clearly shows mostly embedded sheets of C-therm expanded graphite within the matrix and a little pull out of inter-connecting sheets. Figure 8-4 (d) shows a localized segregated area in samples C3, which also indicates mostly embedded sheets with small pull outs. On the other hand, Figure 8-4 (c) shows a localized

segregated area where most of the graphite sheets are pulled out of Sigma graphite. These observations indicate that C-therm expanded graphite has a much better compatibility and a strong interface with the matrix as compared with Sigma graphite.

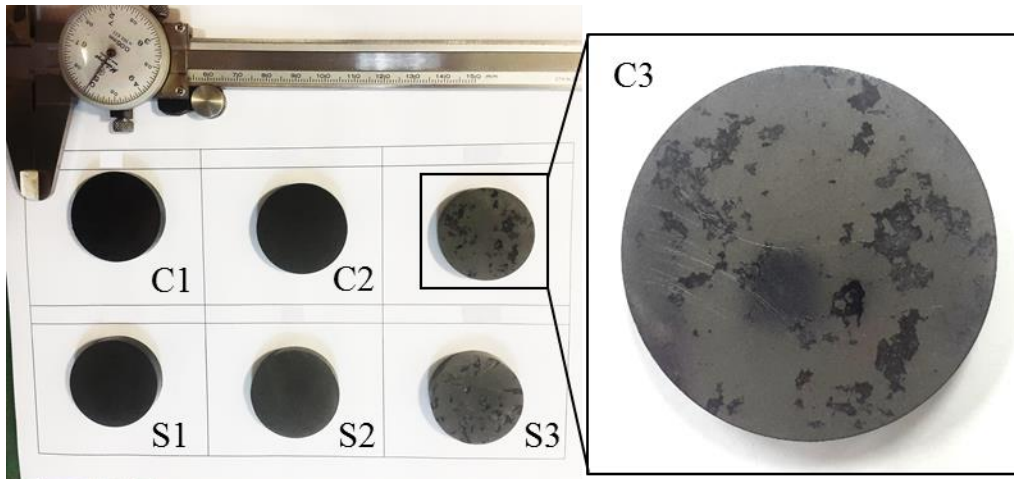


Figure 8-2 The Macrostructures of the samples produced listed in Table 1

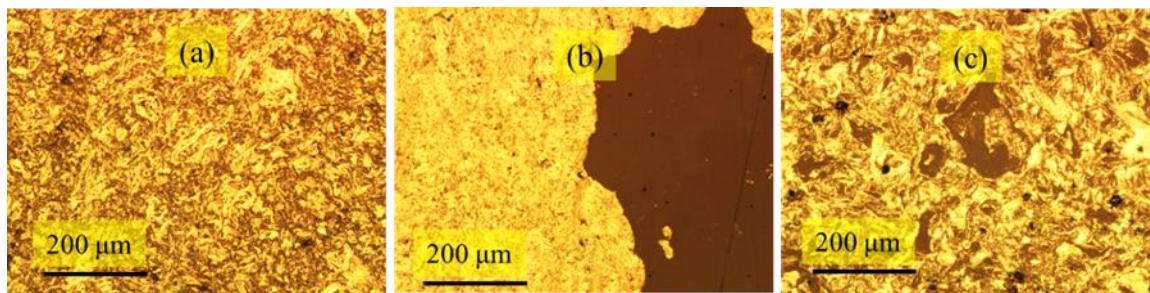


Figure 8-3 Optical micrographs of polished samples at 100X (a) C1 (b) C3 (c) C2

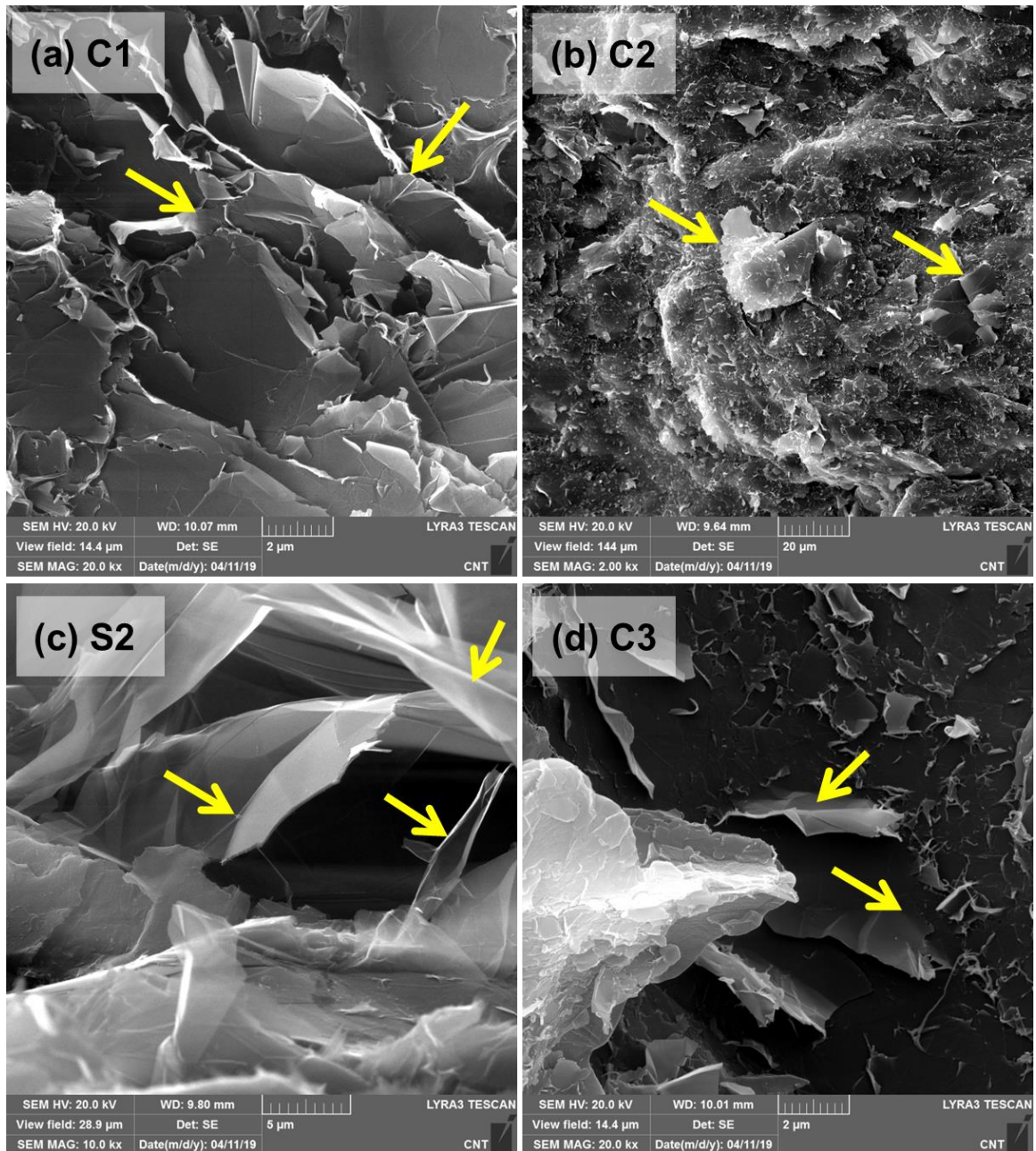


Figure 8-4 FESEM images of different samples listed in Table 8-1; C1 shows mostly embedded and little pull out of C-therm expanded graphite layers on the fractured surface; C2 show the microstructure at a low magnification to illustrate the size of fine PC particles; S2 shows pull out of separated Sigma graphite layers indicating a weak bond with polymer; image in C3 is the localized segregated area where the pull out of C-therm expanded graphite sheets is very less as compared to S2

8.5.2 Thermal conductivity

It is important to note that all of the six samples have a constant overall volume fraction of GF i.e. 0.25 and the samples are different from each other in terms of distribution of GF and the type of GF. The out of plane measured thermal conductivities of the samples are shown in Figure 8-5. Both of the compression molded samples were tested from both of their sides and at least three readings were taken on each side and hence the values shown in the Figure 8-5 are average of at least 12 measurements. The results indicate that graphite supplied by Imerys (C-therm 011) can perform much better as compared to the one purchased from Sigma. C-therm 011 has a very high surface area due to its expanded nature. This leads to have a denser inter-connectivity between the reinforcing flakes and hence higher thermal conductivity. Similarly, it is also evident that the multiscale approach of structuring the composite is also effective since the thermal conductivity of C1 is less than C2 and C3 and that of S1 is less than S2 and S3. That is according to the concept developed in the design of composite that enhancing the thermal conductivity of continuous phase is much more important to reach a higher target of thermal conductivity. The effect of particle size of the discontinuous phase is also clear from the Figure 8-5 that a smaller particle size of discontinuous phase allows faster heat flow i.e. higher thermal conductivity since $C2 > C3$ and $S2 > S3$ in terms of thermal conductivity. This is attributed to the fact that a smaller particle size of PC will generate more number of parallel connections and hence reduces the overall the thermal resistance.

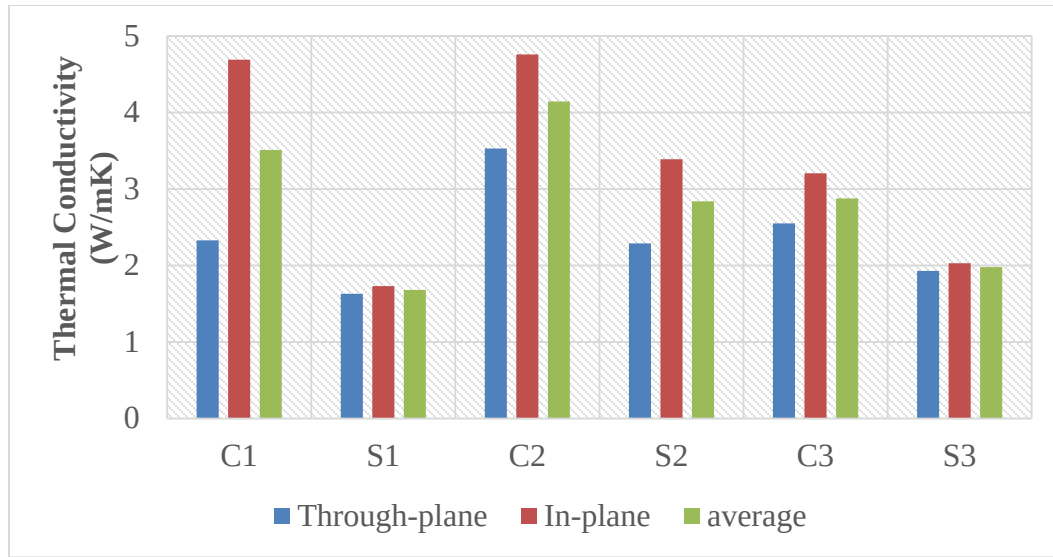


Figure 8-5 Measured thermal conductivities of the samples

8.5.3 Thermal imaging

Figure 8-6 shows thermal images of the samples placed for 30 min on a hot plate set at 110 °C. The images support the results of microstructure and measured thermal conductivity. C2 being the most thermal conductive appears brighter than all others indicating its highest ability of faster heat conduction. While the inhomogeneous distribution of PC is evident from the irregular temperature contours in C3 and S3.

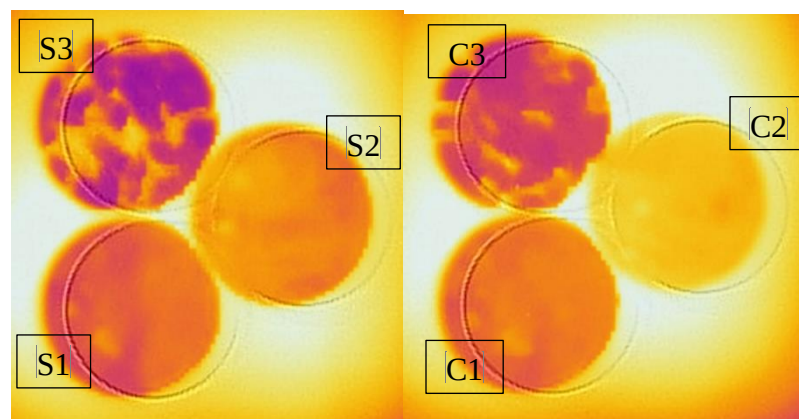


Figure 8-6 Thermal images of the samples placed on hotplate for 30 min

8.5.4 Hardness

The results of hardness on Shore's D scale are presented in the Table 8-2. Each of the reported value is an average of at least six readings taken on the same composition. All of the samples have nearly equal hardness values. This is a sign of the effectiveness of multi stage development approach that high thermal conductivity is achieved with a minimal loss to hardness properties.

Table 8-2 The measured hardness of the samples on Shore D Scale

Sample	Hardness Shore D
C1	77.3
S1	74.3
C2	73.8
S2	69.8
C3	77.2
S3	75.3

8.6 Conclusions

The purpose of this work was to design a polymer matrix composite that can provide high thermal conductivity with a lower filler loading. Using a thermal conductivity estimation model for polymer matrix composites, it was inferred that for achieving a reasonable improvement in thermal conductivity, enhancing the thermal conductivity of continuous phase in the composite has more potential. So a multistep development scheme was used that successfully led to have a thermally conductive continuous phase of GF-PP with PC particles as discontinuous phase as demonstrated by optical micrographs. Different types

GF and differently sized PC particles were used to see the effect on effective thermal conductivity and hardness. For the best thermal conductivity graphite should be C-therm 011 and particle size of PC should be smaller. Hardness is found to be not affected by any of these parameters indicating a minimum loss of mechanical properties. The scheme can be used to enhance thermal conductivities to much better levels.

CHAPTER 9

CONCLUSIONS AND FUTURE RECOMMENDATIONS

The demand of high-performance materials with target properties is ever growing. The design and development of new materials are driven by new applications with enhanced performance. However, achieving the right properties for any particular application is a cumbersome process, which claim significant experimental efforts and cost. In this context, analytical and computational models, which explain the behavior and properties of materials, are always considered useful tools. These models, which are based on scientific theories, are expected to improve the material design and narrowed down the selection of candidate ingredients for the discovery of new materials. Material design of *polymer-composites* is the focus in this dissertation where existing models are improved and some new models are proposed together with validation of these models and performance evaluation of some selected applications with designed composites.

In order to get enhanced performance, it is generally required to improve certain essential properties by keeping the other functional properties at their desired levels simultaneously. It is quite possible that gain in on material property will entail a loss in the other. However, right combinations of matrix and second phase particles in any composites can lead to overcome issue. In the current work, practical usage of effective medium theories, and other properties estimation models have been explored to find out the material's

constituents, which can provide the target properties for a certain application with enhanced performance.

In this dissertation, an application-focused design and development scheme for polymer-composites has been established leading to novel thermal conductivity estimation tools for polymer-composites. Consequently, the work can be divided into three major studies; (1) development of material design models; and (2) Implementation of application-focused design and development scheme considering some practical applications and 3) the development of ultra-high thermal conductivity polymer-composites based novel designs proposed by newly proposed material design models. The conclusions based on the outcomes of these studies have been summarized in the following sections.

9.1 Thermal conductivity estimation models

9.1.1 Model for dilute hybrid percolating fillers

The key to high thermal conductivity in polymer matrix composites is to form a percolating network of high thermal conductivity fillers. Hybrid fillers with low and high aspect ratios can easily form a percolating network leading to high thermal conductivity. A thermal conductivity model for percolating hybrid fillers was derived, validated and used to design and optimize the composition of hybrid nanocomposite with PSU matrix and carbon nanotubes (CNTs) + graphene nano platelets (GNPs) as hybrid fillers. Initially, the model was calibrated by few randomly produced relative CNT/GNP compositions and validated by several data available in the literature. The curve of calibrated model discloses the optimum composition with the best thermal conductivity. Following this scheme, the

optimum composition found was PSU / 8.4 GNP / 1.6 CNT in wt% where the observed K_{eff} was 0.88 W/mK. Insights of the model were elaborated through sensitivity analyses and parametric studies. Thermal conductivity, diameter and interface resistance of the platelet and fibers are the most influencing factors for synergic enhancement and the platelets with a thermal conductivity of 100 W/mK can provide a reasonable synergic enhancement.

9.1.2 Model for non-dilute filler concentrations

This part includes the derivation, explanation and implementation of a more realistic model for the estimation of effective thermal conductivity of composites. The proposed model is equally applicable for dilute and non-dilute concentrations of fillers in polymer matrix composites. Moreover, the model is capable to handle wide ranges of filler particle sizes and shapes. The model is validated by producing different series of polymer composites with variable matrix and filler-attributes. The material design capability of the model is demonstrated through parametric studies considering the thermal conductivity of matrix and filler, particle size, aspect ratio, and interface thermal resistance as variables. The thermal conductivity of the continuous phase is a controlling factor for the overall enhancement of effective thermal conductivity. Among various filler-attributes, aspect ratio is the most sensitive parameter to the effective thermal conductivity, which significantly controls the formation of percolating network. The percolation threshold to achieve maximum effective thermal conductivity also greatly depends on the aspect ratio of particles.

9.2 Implementation of application-focused design and development scheme

9.2.1 Encapsulant for Concentrated Photovoltaic (CPV) Modules

The backside encapsulant of CPV modules is improved following the application design and development scheme, leading to enhanced performance. In this study, for CPV systems, the performance indicators are electrical power and module life, while, target properties of the encapsulant are thermal conductivity (k), coefficient of thermal expansion (α), and long-term shear modulus (G_∞). The target values of these properties are identified by evaluating the performance through sequentially-coupled thermo-mechanical finite element (FE) analyses in conjunction with Morrow's fatigue life approach. The finite element thermal stress problems were solved with variable input target properties considering the properties of ethylene vinyl acetate (EVA) and thermoplastic polyurethane as reference. It is found that, k should be increased for increasing the production of electrical power while G_∞ and α should be decreased for enhancing the module life. The required values of the target properties are selected to be $k \geq 0.75$ W/m.K, $G_\infty < 0.2$ MPa and $\alpha \leq 200 \times 10^{-6}$ K⁻¹.

Based on target properties as predicted from FE-based performance evaluation, various candidate polymer matrices and fillers are considered at the material design stage. Thermal conductivity estimation is based on the differential effective medium approximation for non-dilute filler concentrations while the estimation of coefficient of thermal expansion

and long-term shear modulus is based on mean-field homogenization. Thermoplastic polyurethane as matrix and ceramics (such as Al_2O_3 and AlN) as fillers are the best among various candidates with specified filler attributes such as particle size and geometric shape. For validation of the material design, some representative composites are synthesized and characterized. The target properties (k , α and G_∞) are measured which are found in close agreement with the predictions. Moreover, the parameters of Generalized Maxwell Model and WLF shift function are determined by generating the master curve method. To get some expected practical values of power output and life of CPV modules with the designed composite as encapsulant is assessed by using the measured properties in the finite element model developed for setting the target properties. A reasonable agreement between the measured and predicted values affirms the generalized use of this methodology for application-focused design and development of polymer matrix composites. The proposed TPU-composite is more capable results in a temperature drop of 5.8 and 3.1 °C leading to an increased electrical power by 4.3 and 2.1 % when compared with neat TPU and EVA, respectively along with a more practical module life.

9.2.2 Tubes of Shell and Tube Heat Exchanger

To resolve the problems associated with metallic shell and tube heat exchangers (STHX), the metallic tubes can be replaced by polymeric materials. STHX with polymeric tubes is more advantageous in terms of providing high corrosion and fouling resistance, low manufacturing and maintenance costs, and light-weightness. In this work applicability of polymer-composites as tubes of plastic STHX has been proved through mathematical and experimental means. Kern and Bell-Delaware methods are used for heat transfer

calculations to check the feasibility of polymer-composite tubes and to optimize the design of lab-scale STHX, while Barlow's Formula to find the average stress in the tubes. The minimum required thermal conductivity and strength for the tubes are found much less than those of commonly used metallic tubes. Taking 80% UA value of a metallic STHX as target value, the target thermal conductivity for a particular commercial heat exchanger is found to be 10 W/mK with both sides Re# in transient flow regime. The target thermal conductivity strongly depends upon the flow rates on both sides of the heat exchanger while the design parameters have a little effect. Hence, the target thermal conductivity for a lab scale heat exchanger having flow rates in the laminar regime, and transient regime is 1.5 and 3.6 W/mK, respectively. The target tensile strength depends upon the working temperature and pressure of the two flow streams. Based on Barlow's formula and creep life data of polypropylene a room temperature tensile strength of 20 MPa is good enough to provide a creep life of at least 25 years at a maximum design pressure of 1.00 MPa and average working temperature of 60 °C with tubes of ϕ 10 mm and 1.25 tube-wall thickness (maximum allowed hoop stress is 5.5 MPa). Following the author's previously established composite materials design scheme, a filler with aspect ratio < 0.1 (oblate) or > 10 (prolate) is required while the polymer matrix and the filler with thermal conductivity as low as 0.2 W/mK and 33 W/mK can be used to make the composite. And the recommended volume fraction for filler is 15%. Finally, composite samples in line with computational design are developed with PP and expanded graphite as matrix and filler, respectively with a volume fraction ranging from 10 to 20% and their performance is evaluated for heat transfer using a double pipe lab scale heat exchanger with replaceable tube. The effectiveness and

temperature drop observed with a commercial thermally conductive tube and a copper tube are found in close agreement under same operating conditions.

9.3 Development of ultra-high thermal conductivity polymer-composite

The purpose of this work was to design a polymer matrix composite that can provide high thermal conductivity with a lower fillers' loading (volume fraction). Using thermal conductivity model for non-dilute filler concentrations presented in chapter 5, it was inferred that enhancing thermal conductivity of continuous phase is more important for leading to ultrahigh effective thermal conductivity. So a multistep development scheme is used to design a continuous phase with high thermal conductivity. In the first step of processing, graphite (GF) is mixed with polypropylene (PP) leading to GF-PP phase which is homogeneous at microstructural level. In the second step, GF-PP is mixed with polycarbonate (PC) particles leading to a segregated GF-PP phase around PC particles. Different types GF and differently sized PC particles were used to see the effect on effective thermal conductivity and hardness. For the best thermal conductivity graphite should be C-therm 011 and particle size of PC should be smaller. Hardness is found to be not affected by any of these parameters indicating a minimum loss of mechanical properties. This scheme can be used to enhance thermal conductivities to much better levels.

9.4 Future recommendations

- Thermal conductivity estimation model for non-dilute filler concentrations is applicable for material design in wide range of thermal management applications and can make a mathematical foundation for the current and future designs of polymer matrix composites with percolating non-dilute filler concentrations. The model should be used to explore new designs leading to achieve ultrahigh thermal conductivity.
- Thermal conductivity estimation model for non-dilute filler concentrations is capable of finding the percolation threshold for a particular combination of matrix and filler, which depends upon the particle size, shape, and preferred orientation. This ability of the model should be implemented in various cases and refined for accurate predictions.
- The presented computational design and development strategy can serve as a useful guideline for composite manufacturers in developing new potential polymer composites for target applications. The methodology should be implemented to other thermomechanical applications such as thermal interface materials and cutting tool inserts.
- There is strong need to develop estimation models for other material properties such as flame resistance and magneto-electric behavior, particularly for the composite materials used in energy harvesting.

References

- [1] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns, A.B. Holmes, Light-emitting diodes based on conjugated polymers, *Nature*. 347 (1990) 539–541. doi:10.1038/347539a0.
- [2] B.K. Ahn, D.W. Lee, J.N. Israelachvili, J.H. Waite, Surface-initiated self-healing of polymers in aqueous media., *Nat. Mater.* 13 (2014) 867–872. doi:10.1038/nmat4037.
- [3] M.R. Kessler, Polymer Matrix Composites: A Perspective for a Special Issue of *Polymer Reviews*, *Polym. Rev.* 52 (2012) 229–233. doi:10.1080/15583724.2012.708004.
- [4] B.L. Zhu, J. Wang, H. Zheng, J. Ma, J. Wu, R. Wu, Investigation of thermal conductivity and dielectric properties of LDPE-matrix composites filled with hybrid filler of hollow glass microspheres and nitride particles, *Compos. Part B Eng.* 69 (2015) 496–506. doi:10.1016/j.compositesb.2014.10.035.
- [5] M. Rosinski, L. Ciupinski, J. Grzonka, A. Michalski, K.J. Kurzydowski, Synthesis and characterization of the diamond/copper composites produced by the pulse plasma sintering (PPS) method, *Diam. Relat. Mater.* 27–28 (2012) 29–35. doi:10.1016/j.diamond.2012.05.008.
- [6] S. Moradi, Y. Calventus, F. Román, J.M. Hutchinson, Achieving High Thermal Conductivity in Epoxy Composites: Effect of Boron Nitride Particle Size and

- Matrix-Filler Interface, *Polymers* (Basel). 11 (2019) 1156. doi:10.3390/polym11071156.
- [7] T. Zhou, X. Wang, X. Liu, D. Xiong, Improved thermal conductivity of epoxy composites using a hybrid multi-walled carbon nanotube/micro-SiC filler, *Carbon* N. Y. 48 (2010) 1171–1176. doi:10.1016/j.carbon.2009.11.040.
- [8] T. Zhou, X. Wang, P. Cheng, T. Wang, D. Xiong, X. Wang, Improving the thermal conductivity of epoxy resin by the addition of a mixture of graphite nanoplatelets and silicon carbide microparticles, *Express Polym. Lett.* 7 (2013) 585–594. doi:10.3144/expresspolymlett.2013.56.
- [9] Y. Xu, D. Chung, D.D.L. Chung, C. Mroz, Thermally Conducting Aluminum Nitride Polymer-Matrix Composites, *Compos. Part A Appl. Sci. Manuf.* 32 (2001) 1749–1757. doi:10.1016/S1359-835X(01)00023-9.
- [10] H. Zhou, H. Deng, L. Zhang, Q. Fu, Significant Enhancement of Thermal Conductivity in Polymer Composite via Constructing Macroscopic Segregated Filler Networks, *ACS Appl. Mater. Interfaces.* 9 (2017) 29071–29081. doi:10.1021/acsami.7b07947.
- [11] J. Gu, Y. Guo, X. Yang, C. Liang, W. Geng, L. Tang, N. Li, Q. Zhang, Synergistic improvement of thermal conductivities of polyphenylene sulfide composites filled with boron nitride hybrid fillers, *Compos. Part A Appl. Sci. Manuf.* 95 (2017) 267–273. doi:10.1016/j.compositesa.2017.01.019.

- [12] U. Szeluga, B. Kumanek, B. Trzebicka, Synergy in hybrid polymer/nanocarbon composites. A review, *Compos. Part A Appl. Sci. Manuf.* 73 (2015) 204–231. doi:10.1016/j.compositesa.2015.02.021.
- [13] X. Han, L. Wu, H. Zhang, A. He, H. Nie, Inorganic–Organic Hybrid Janus Fillers for Improving the Thermal Conductivity of Polymer Composites, *ACS Appl. Mater. Interfaces*. 11 (2019) 12190–12194. doi:10.1021/acsami.8b22278.
- [14] G. Pan, Y. Yao, X. Zeng, J. Sun, J. Hu, R. Sun, J.-B. Xu, C.-P. Wong, Learning from Natural Nacre: Constructing Layered Polymer Composites with High Thermal Conductivity, *ACS Appl. Mater. Interfaces*. 9 (2017) 33001–33010. doi:10.1021/acsami.7b10115.
- [15] S. Yang, W. Li, S. Bai, Q. Wang, Fabrication of Morphologically Controlled Composites with High Thermal Conductivity and Dielectric Performance from Aluminum Nanoflake and Recycled Plastic Package, *ACS Appl. Mater. Interfaces*. 11 (2019) 3388–3399. doi:10.1021/acsami.8b16209.
- [16] S. Yang, W. Li, S. Bai, Q. Wang, High-performance thermal and electrical conductive composites from multilayer plastic packaging waste and expanded graphite, *J. Mater. Chem. C*. 6 (2018) 11209–11218. doi:10.1039/C8TC02840K.
- [17] C. Yu, W. Gong, W. Tian, Q. Zhang, Y. Xu, Z. Lin, M. Hu, X. Fan, Y. Yao, Hot-pressing induced alignment of boron nitride in polyurethane for composite films with thermal conductivity over $50 \text{ W m}^{-1} \text{ K}^{-1}$, *Compos. Sci. Technol.* 160 (2018) 199–207. doi:10.1016/j.compscitech.2018.03.028.

- [18] H. Wu, C. Lu, W. Zhang, X. Zhang, Preparation of low-density polyethylene/low-temperature expandable graphite composites with high thermal conductivity by an in situ expansion melt blending process, *Mater. Des.* 52 (2013) 621–629. doi:10.1016/j.matdes.2013.05.056.
- [19] F. Meng, F. Huang, Y. Guo, J. Chen, X. Chen, D. Hui, P. He, X. Zhou, Z. Zhou, In situ intercalation polymerization approach to polyamide-6/graphite nanoflakes for enhanced thermal conductivity, *Compos. Part B Eng.* 117 (2017) 165–173. doi:10.1016/j.compositesb.2017.02.043.
- [20] S. Deng, J. Wang, G. Zong, F. Chen, S. Chai, Q. Fu, Effect of chain structure on the thermal conductivity of expanded graphite/polymer composites, *RSC Adv.* 6 (2016) 10185–10191. doi:10.1039/C5RA26272K.
- [21] L. Yin, X. Zhou, J. Yu, H. Wang, C. Ran, Fabrication of a polymer composite with high thermal conductivity based on sintered silicon nitride foam, *Compos. Part A Appl. Sci. Manuf.* 90 (2016) 626–632. doi:10.1016/j.compositesa.2016.08.022.
- [22] Y. Yao, X. Zhu, X. Zeng, R. Sun, J.-B. Xu, C.-P. Wong, Vertically Aligned and Interconnected SiC Nanowire Networks Leading to Significantly Enhanced Thermal Conductivity of Polymer Composites, *ACS Appl. Mater. Interfaces.* 10 (2018) 9669–9678. doi:10.1021/acsami.8b00328.
- [23] J. Hu, Y. Huang, Y. Yao, G. Pan, J. Sun, X. Zeng, R. Sun, J.-B. Xu, B. Song, C.-P. Wong, Polymer Composite with Improved Thermal Conductivity by Constructing a Hierarchically Ordered Three-Dimensional Interconnected Network of BN, *ACS*

- Appl. Mater. Interfaces. 9 (2017) 13544–13553. doi:10.1021/acsami.7b02410.
- [24] K. Wu, C. Lei, R. Huang, W. Yang, S. Chai, C. Geng, F. Chen, Q. Fu, Design and Preparation of a Unique Segregated Double Network with Excellent Thermal Conductive Property, ACS Appl. Mater. Interfaces. 9 (2017) 7637–7647. doi:10.1021/acsami.6b16586.
- [25] K. Raza, M.U. Siddiqui, A.F.M. Arif, S.S. Akhtar, A.S. Hakeem, Design and development of thermally conductive hybrid nano- composites in polysulfone matrix, Polym. Compos. 40 (2019) 1419–1432. doi:10.1002/pc.24879.
- [26] T. Wieme, D. Tang, L. Delva, D.R. D’hooge, L. Cardon, The relevance of material and processing parameters on the thermal conductivity of thermoplastic composites, Polym. Eng. Sci. 58 (2018) 466–474. doi:10.1002/pen.24667.
- [27] D.P.H. Hasselman, L.F. Johnson, Effective Thermal Conductivity of Composites with Interfacial Thermal Barrier Resistance, J. Compos. Mater. 21 (1987) 508–515. doi:10.1177/002199838702100602.
- [28] C.-W. Nan, R. Birringer, D.R. Clarke, H. Gleiter, Effective thermal conductivity of particulate composites with interfacial thermal resistance, J. Appl. Phys. 81 (1997) 6692–6699. doi:10.1063/1.365209.
- [29] M. Siddiqui, A.F.M. Arif, Generalized Effective Medium Theory for Particulate Nanocomposite Materials, Materials (Basel). 9 (2016) 694. doi:10.3390/ma9080694.

- [30] I. Sevostianov, S.G. Mogilevskaya, V.I. Kushch, Maxwell's methodology of estimating effective properties: Alive and well, *Int. J. Eng. Sci.* 140 (2019) 35–88. doi:10.1016/j.ijengsci.2019.05.001.
- [31] A. Trofimov, S. Abaimov, I. Sevostianov, Inverse homogenization problem: Evaluation of elastic and electrical (thermal) properties of composite constituents, *Int. J. Eng. Sci.* 129 (2018) 34–46. doi:10.1016/j.ijengsci.2018.04.001.
- [32] A.G. Every, Y. Tzou, D.P.H. Hasselman, R. Raj, The effect of particle size on the thermal conductivity of ZnS/diamond composites, *Acta Metall. Mater.* 40 (1992) 123–129. doi:10.1016/0956-7151(92)90205-S.
- [33] W. Jiajun, Y. Xiao-Su, Effects of interfacial thermal barrier resistance and particle shape and size on the thermal conductivity of AlN/PI composites, *Compos. Sci. Technol.* 64 (2004) 1623–1628. doi:10.1016/j.compscitech.2003.11.007.
- [34] S. Europe, SolarPower Europe's Global Market Outlook 2018 – 2022, 2018. <https://www.solarpowereurope.org/wp-content/uploads/2018/09/Global-Market-Outlook-2018-2022.pdf>.
- [35] M. Khamooshi, H. Salati, F. Egelioglu, A. Hooshyar Faghiri, J. Tarabishi, S. Babadi, A review of solar photovoltaic concentrators, *Int. J. Photoenergy.* 2014 (2014). doi:10.1155/2014/958521.
- [36] M. Wiesenfarth, I. Anton, A.W. Bett, Challenges in the design of concentrator photovoltaic (CPV) modules to achieve highest efficiencies, *Appl. Phys. Rev.* 5

- (2018). doi:10.1063/1.5046752.
- [37] B. Lee, J.Z. Liu, B. Sun, C.Y. Shen, G.C. Dai, Thermally conductive and electrically insulating EVA composite encapsulant for solar photovoltaic (PV) cell, *Express Polym. Lett.* 2 (2008) 357–363. doi:10.3144/expresspolymlett.2008.42.
 - [38] M.U. Siddiqui, A.F.M. Arif, Electrical, thermal and structural performance of a cooled PV module: Transient analysis using a multiphysics model, *Appl. Energy*. 112 (2013) 300–312. doi:10.1016/j.apenergy.2013.06.030.
 - [39] U.S.E.I. Administration, Chapter 5. Electricity, in: *Int. Energy Outlook 2016*, 2016: pp. 81–99. <http://www.eia.gov/forecasts/ieo/electricity.cfm>.
 - [40] Madehow, Solar Cell, (2016). <http://www.madehow.com/Volume-1/Solar-Cell.html> (accessed October 11, 2016).
 - [41] PVEducation.org, Module Materials, (2016). <http://www.pveducation.org/pvcdrom/modules/module-materials> (accessed October 11, 2016).
 - [42] O. Hasan, A.F.M. Arif, Performance and life prediction model for photovoltaic modules: Effect of encapsulant constitutive behavior, *Sol. Energy Mater. Sol. Cells*. 122 (2014) 75–87. doi:10.1016/j.solmat.2013.11.016.
 - [43] Heat exchanger, (n.d.). https://en.wikipedia.org/wiki/Heat_exchanger (accessed March 29, 2020).
 - [44] D.R. Rousse, D.Y. Martin, R. Thériault, F. Léveillé, R. Boily, Heat recovery in

- greenhouses: a practical solution, *Appl. Therm. Eng.* 20 (2000) 687–706.
doi:10.1016/S1359-4311(99)00048-4.
- [45] L. Jia, X.F. Peng, J.D. Sun, T.B. Chen, An experimental study on vapor condensation of wet flue gas in a plastic heat exchanger, *Heat Transf. Res.* 30 (2001) 571–580. doi:10.1002/htj.10000.
- [46] J. Cevallos, S.K. Gupta, A. Bar-Cohen, Incorporating moldability considerations during the design of polymer heat exchangers, *J. Mech. Des. Trans. ASME.* 133 (2011) 1–9. doi:10.1115/1.4004583.
- [47] P. Luckow, A. Bar-Cohen, P. Rodgers, Minimum mass polymer seawater heat exchanger for lng applications, *J. Therm. Sci. Eng. Appl.* 1 (2009) 1–10. doi:10.1115/1.4001239.
- [48] P. Luckow, A. Bar-Cohen, P. Rodgers, J. Cevallos, Energy efficient polymers for gas-liquid heat exchangers, *J. Energy Resour. Technol. Trans. ASME.* 132 (2010) 0210011–0210019. doi:10.1115/1.4001568.
- [49] A.R.J. Hussain, A.A. Alahyari, S.A. Eastman, C. Thibaud-Erkey, S. Johnston, M.J. Sobkowicz, Review of polymers for heat exchanger applications: Factors concerning thermal conductivity, *Appl. Therm. Eng.* 113 (2017) 1118–1127. doi:10.1016/j.applthermaleng.2016.11.041.
- [50] W.J. Dartnall, A. Revel, V. Giotis, Air-Conditioning Employing Indirect Evaporative Cooling Can Be Shown to Derive Its Energy From the Solar Source, in:

- Vol. 6 Emerg. Technol. Altern. Energy Syst. Energy Syst. Anal. Thermodyn. Sustain., ASME, 2009: pp. 575–580. doi:10.1115/IMECE2009-10928.
- [51] S.S. Kachhwaha, S. Prabhakar, Heat and mass transfer study in a direct evaporative cooler, *J. Sci. Ind. Res. (India)*. 69 (2010) 705–710.
- [52] T.B. Scheffler, A.J. Leao, Fabrication of polymer film heat transfer elements for energy efficient multi-effect distillation, *Desalination*. 222 (2008) 696–710. doi:10.1016/j.desal.2007.02.076.
- [53] J.B.P. Christmann, L.J. Krätz, H.J. Bart, Falling film evaporation with polymeric heat transfer surfaces, *Desalination*. 308 (2013) 56–62. doi:10.1016/j.desal.2011.05.027.
- [54] K. Bourouni, R. Martin, L. Tadrist, H. Tadrist, Experimental investigation of evaporation performances of a desalination prototype using the aero-evapo-condensation process, *Desalination*. 114 (1997) 111–128. doi:10.1016/S0011-9164(98)00003-4.
- [55] H.T. El-Dessouky, H.M. Ettouney, Plastic/compact heat exchangers for single-effect desalination systems, *Desalination*. 122 (1999) 271–289. doi:10.1016/S0011-9164(99)00048-X.
- [56] J.B.P. Christmann, L.J. Krätz, H.-J. Bart, Novel polymer film heat exchangers for seawater desalination, *Desalin. Water Treat.* 21 (2010) 162–174. doi:10.5004/dwt.2010.1325.

- [57] Z. Antar, J.F. Feller, G. Vignaud, Eco-friendly conductive polymer nanocomposites (CPC) for solar absorbers design, *Polym. Adv. Technol.* 24 (2013) 638–645. doi:10.1002/pat.3126.
- [58] W. Liu, J. Davidson, S. Mantell, Thermal analysis of polymer heat exchangers for solar water heating: A case study, *J. Sol. Energy Eng. Trans. ASME.* 122 (2000) 84–91. doi:10.1115/1.1288027.
- [59] R. Raman, S. Mantell, J. Davidson, C. Wu, G. Jorgensen, A Review of Polymer Materials for Solar Water Heating Systems, *J. Sol. Energy Eng.* 122 (2000) 92–100. doi:10.1115/1.1288214.
- [60] R. Trojanowski, T. Butcher, M. Worek, G. Wei, Polymer heat exchanger design for condensing boiler applications, *Appl. Therm. Eng.* 103 (2016) 150–158. doi:10.1016/j.applthermaleng.2016.03.004.
- [61] X. Chen, Y. Su, D. Reay, S. Riffat, Recent research developments in polymer heat exchangers - A review, *Renew. Sustain. Energy Rev.* 60 (2016) 1367–1386. doi:10.1016/j.rser.2016.03.024.
- [62] S.S. Akhtar, M.U. Siddiqui, R. Kabeer, A. Hakeem, L. Kareem, A.F. Arif, A computational and experimental study on the effective properties of Al₂O₃-Ni composites, *Int. J. Appl. Ceram. Technol.* 14 (2017) 766–778. doi:10.1111/ijac.12674.
- [63] S. Zhou, J. Xu, Q.H. Yang, S. Chiang, B. Li, H. Du, C. Xu, F. Kang, Experiments

- and modeling of thermal conductivity of flake graphite/polymer composites affected by adding carbon-based nano-fillers, *Carbon* N. Y. 57 (2013) 452–459. doi:10.1016/j.carbon.2013.02.018.
- [64] O. Hasan, A.F.M. Arif, M.U. Siddiqui, Finite Element Modeling and Analysis of Photovoltaic Modules, in: Vol. 8 Mech. Solids, Struct. Fluids, ASME, Houston, Texas, USA, 2012: p. 495. doi:10.1115/IMECE2012-89429.
- [65] J. Pern, Module Encapsulation Materials, Processing and Testing, Natl. Renew. Energy Lab. (n.d.).
- [66] M.C.C. de Oliveira, A.S.A. Diniz Cardoso, M.M. Viana, V. de F.C. Lins, The causes and effects of degradation of encapsulant ethylene vinyl acetate copolymer (EVA) in crystalline silicon photovoltaic modules: A review, *Renew. Sustain. Energy Rev.* 81 (2018) 2299–2317. doi:10.1016/j.rser.2017.06.039.
- [67] P. Hülsmann, K.A. Weiss, Simulation of water ingress into PV-modules: IEC-testing versus outdoor exposure, *Sol. Energy.* 115 (2015) 347–353. doi:10.1016/j.solener.2015.03.007.
- [68] M. Koehl, M. Heck, S. Wiesmeier, Modelling of conditions for accelerated lifetime testing of Humidity impact on PV-modules based on monitoring of climatic data, *Sol. Energy Mater. Sol. Cells.* 99 (2012) 282–291. doi:10.1016/j.solmat.2011.12.011.
- [69] J. Allan, H. Pinder, Z. Dehouche, Enhancing the thermal conductivity of ethylene-

vinyl acetate (EVA) in a photovoltaic thermal collector Enhancing the thermal conductivity of ethylene-vinyl acetate (EVA) in a photovoltaic thermal collector, AIP Adv. 6 (2016) 1–9. doi:10.1063/1.4944557.

- [70] J. Sebastian, E.T. Thachil, J.J. Mathen, J. Madhavan, P. Thomas, J. Philip, M.S. Jayalakshmy, S. Mahmud, G.P. Joseph, Enhancement in the Electrical and Thermal Properties of Ethylene Vinyl Acetate (EVA) Co-Polymer by Zinc Oxide Nanoparticles, Open J. Compos. Mater. 5 (2015) 79–91. doi:dx.doi.org/10.4236/ojcm.2015.53011.
- [71] K. Raza, S.S. Akhtar, A.F.M. Arif, A.S. Hakeem, Design of Composite Encapsulation for Concentrated Photovoltaic Systems with Improved Performance, in: Int. Mech. Eng. Congr. Expo., 2019.
- [72] A. Ince, G. Glinka, A modification of Morrow and Smith-Watson-Topper mean stress correction models, Fatigue Fract. Eng. Mater. Struct. 34 (2011) 854–867. doi:10.1111/j.1460-2695.2011.01577.x.
- [73] L. Chen, Z. Li, Z.Y. Guo, Experimental investigation of plastic finned-tube heat exchangers, with emphasis on material thermal conductivity, Exp. Therm. Fluid Sci. 33 (2009) 922–928. doi:10.1016/j.expthermflusci.2009.04.001.
- [74] J.J. de Pablo, N.E. Jackson, M.A. Webb, L.-Q. Chen, J.E. Moore, D. Morgan, R. Jacobs, T. Pollock, D.G. Schlom, E.S. Toberer, J. Analytis, I. Dabo, D.M. DeLongchamp, G.A. Fiete, G.M. Grason, G. Hautier, Y. Mo, K. Rajan, E.J. Reed, E. Rodriguez, V. Stevanovic, J. Suntivich, K. Thornton, J.-C. Zhao, New frontiers

- for the materials genome initiative, *Npj Comput. Mater.* 5 (2019) 41. doi:10.1038/s41524-019-0173-4.
- [75] J. Yang, L. Xi, W. Qiu, L. Wu, X. Shi, L. Chen, J. Yang, W. Zhang, C. Uher, D.J. Singh, On the tuning of electrical and thermal transport in thermoelectrics: An integrated theory-experiment perspective, *Npj Comput. Mater.* 2 (2016). doi:10.1038/npjcompumats.2015.15.
- [76] X. Jia, Z. Liu, E. Gao, Bio-inspired self-folding strategy to break the trade-off between strength and ductility in carbon-nanoarchitected materials, *Npj Comput. Mater.* 6 (2020) 13. doi:10.1038/s41524-020-0279-8.
- [77] X. Zhang, J.-P. Zhou, X. Yao, Z. Yang, G.-B. Zhang, Comprehensive analysis of direct and converse magnetoelectric effects in S-S mode bilayered composites, *J. Magn. Magn. Mater.* 501 (2020) 166411. doi:10.1016/j.jmmm.2020.166411.
- [78] M. PourhosseiniAsl, X. Gao, S. Kamalishahrudi, Z. Yu, Z. Chu, J. Yang, H.-Y. Lee, S. Dong, Versatile power and energy conversion of magnetoelectric composite materials with high efficiency via electromechanical resonance, *Nano Energy.* 70 (2020) 104506. doi:10.1016/j.nanoen.2020.104506.
- [79] J.-M. Hu, C.-G. Duan, C.-W. Nan, L.-Q. Chen, Understanding and designing magnetoelectric heterostructures guided by computation: progresses, remaining questions, and perspectives, *Npj Comput. Mater.* 3 (2017) 18. doi:10.1038/s41524-017-0020-4.

- [80] S. Wu, Y. Kondo, M. aki Kakimoto, B. Yang, H. Yamada, I. Kuwajima, G. Lambard, K. Hongo, Y. Xu, J. Shiomi, C. Schick, J. Morikawa, R. Yoshida, Machine-learning-assisted discovery of polymers with high thermal conductivity using a molecular design algorithm, *Npj Comput. Mater.* 5 (2019). doi:10.1038/s41524-019-0203-2.
- [81] R. Ramprasad, R. Batra, G. Pilania, A. Mannodi-Kanakkithodi, C. Kim, Machine learning in materials informatics: Recent applications and prospects, *Npj Comput. Mater.* 3 (2017). doi:10.1038/s41524-017-0056-5.
- [82] S. Zhai, P. Zhang, Y. Xian, J. Zeng, B. Shi, Effective thermal conductivity of polymer composites: Theoretical models and simulation models, *Int. J. Heat Mass Transf.* 117 (2018) 358–374. doi:10.1016/j.ijheatmasstransfer.2017.09.067.
- [83] B. Arash, Q. Wang, V.K. Varadan, Mechanical properties of carbon nanotube/polymer composites, *Sci. Rep.* 4 (2015) 6479. doi:10.1038/srep06479.
- [84] S. Lee, J. Lee, B. Ryu, S. Ryu, A micromechanics-based analytical solution for the effective thermal conductivity of composites with orthotropic matrices and interfacial thermal resistance, *Sci. Rep.* 8 (2018) 7266. doi:10.1038/s41598-018-25379-8.
- [85] H. Ahmadi Moghaddam, P. Mertiny, Stochastic Finite Element Modelling of Char Forming Filler Addition and Alignment – Effects on Heat Conduction into Polymer Condensed Phase, in: *Flame Retard.*, IntechOpen, 2019: p. 13. doi:10.5772/intechopen.82878.

- [86] H. Ahmadi Moghaddam, P. Mertiny, Stochastic Finite Element Analysis Framework for Modelling Mechanical Properties of Particulate Modified Polymer Composites, *Materials (Basel)*. 12 (2019) 2777. doi:10.3390/ma12172777.
- [87] D. Klein, W. Malezki, S. Wartzack, Introduction of a computational approach for the design of composite structures at the early embodiment design stage, in: *Proc. Int. Conf. Eng. Des. ICED*, 2015: pp. 105–114.
- [88] Q. Chi, T. Ma, J. Dong, Y. Cui, Y. Zhang, C. Zhang, S. Xu, X. Wang, Q. Lei, Enhanced Thermal Conductivity and Dielectric Properties of Iron Oxide/Polyethylene Nanocomposites Induced by a Magnetic Field, *Sci. Rep.* 7 (2017) 3072. doi:10.1038/s41598-017-03273-z.
- [89] H.S. Kim, H.S. Bae, J. Yu, S.Y. Kim, Thermal conductivity of polymer composites with the geometrical characteristics of graphene nanoplatelets, *Sci. Rep.* 6 (2016) 26825. doi:10.1038/srep26825.
- [90] B. Abad, J. Maiz, A. Ruiz-Clavijo, O. Caballero-Calero, M. Martin-Gonzalez, Tailoring thermal conductivity via three-dimensional porous alumina, *Sci. Rep.* 6 (2016) 38595. doi:10.1038/srep38595.
- [91] K. Raza, F.A. Khalid, Optimization of sintering parameters for diamond–copper composites in conventional sintering and their thermal conductivity, *J. Alloys Compd.* 615 (2014) 111–118. doi:10.1016/j.jallcom.2014.06.139.
- [92] L. Weber, R. Tavangar, On the influence of active element content on the thermal

- conductivity and thermal expansion of Cu–X (X=Cr, B) diamond composites, *Scr. Mater.* 57 (2007) 988–991. doi:10.1016/j.scriptamat.2007.08.007.
- [93] Y. Agari, A. Ueda, S. Nagai, Thermal Conductivity of Polymer Composite, *J. Appl. Polym. Sci.* 49 (1993) 1625–1634.
- [94] M. Zain-Ul-Abdein, W.S. Awan, H. Ijaz, A.A. Taimoor, A. Muhammad, S.U. Rather, Effect of micro- to nanosize inclusions upon the thermal conductivity of powdered composites with high and low interface resistance, *J. Nanomater.* 2015 (2015). doi:10.1155/2015/843914.
- [95] J.C. Maxwell, *A treatise on electricity and magnetism*, 3rd ed., Oxford University Press, Oxford, UK, 1904, 1884.
- [96] M. Zain-ul-abdein, K. Raza, F.A. Khalid, T. Mabrouki, Numerical investigation of the effect of interfacial thermal resistance upon the thermal conductivity of copper/diamond composites, *Mater. Des.* 86 (2015) 248–258. doi:10.1016/j.matdes.2015.07.059.
- [97] Y. Benveniste, G.J. Dvorak, On a Correspondence Between Mechanical and Thermal Effects in Two-Phase Composites, in: *Micromechanics and Inhomogeneity*, 1990: pp. 65–81.
- [98] G.W. Lee, M. Park, J. Kim, J.I. Lee, H.G. Yoon, Enhanced thermal conductivity of polymer composites filled with hybrid filler, *Compos. Part A Appl. Sci. Manuf.* 37 (2006) 727–734. doi:10.1016/j.compositesa.2005.07.006.

- [99] S.Y. Yang, W.N. Lin, Y.L. Huang, H.W. Tien, J.Y. Wang, C.C.M. Ma, S.M. Li, Y.S. Wang, Synergetic effects of graphene platelets and carbon nanotubes on the mechanical and thermal properties of epoxy composites, *Carbon N. Y.* 49 (2011) 793–803. doi:10.1016/j.carbon.2010.10.014.
- [100] Celanese, CoolPoly (R) D5506 Thermally conductive liquid crystalline polymer, (2016) 1–2. http://www.coolpolymers.com/files/ds/Datasheet_d5506.pdf (accessed October 10, 2016).
- [101] S. Ghose, K.A. Watson, D.C. Working, J.W. Connell, J.G. Smith, Y.P. Sun, Thermal conductivity of ethylene vinyl acetate copolymer/nanofiller blends, *Compos. Sci. Technol.* 68 (2008) 1843–1853. doi:10.1016/j.compscitech.2008.01.016.
- [102] T. Kuila, P. Khanra, A.K. Mishra, N.H. Kim, J.H. Lee, Functionalized-graphene/ethylene vinyl acetate co-polymer composites for improved mechanical and thermal properties, *Polym. Test.* 31 (2012) 282–289. doi:10.1016/j.polymertesting.2011.12.003.
- [103] B. Yuan, C. Bao, X. Qian, S. Jiang, P. Wen, W. Xing, L. Song, K.M. Liew, Y. Hu, Synergetic Dispersion Effect of Graphene Nanohybrid on the Thermal Stability and Mechanical Properties of Ethylene Vinyl Acetate Copolymer Nanocomposite, *Ind. Eng. Chem. Res.* 53 (2014) 1143–1149. doi:10.1021/ie403438k.
- [104] H.A. Khonakdar, Dynamic mechanical analysis and thermal properties of LLDPE/EVA/modified silica nanocomposites, *Compos. Part B Eng.* 76 (2015) 343–353. doi:10.1016/j.compositesb.2015.02.031.

- [105] M. Sabet, H. Soleimani, S. Hosseini, Properties and characterization of ethylene-vinyl acetate filled with carbon nanotube, *Polym. Bull.* 73 (2015) 419–434. doi:10.1007/s00289-015-1499-9.
- [106] K. Czaniková, Z. Špitalský, I. Krupa, M. Omastová, Electrical and mechanical properties of ethylene vinyl acetate based composites, *Mater. Sci. Forum.* 714 (2012) 193–199. doi:10.4028/www.scientific.net/MSF.714.193.
- [107] F. Ansari, M. Salajková, Q. Zhou, L.A. Berglund, Strong Surface Treatment Effects on Reinforcement Efficiency in Biocomposites Based on Cellulose Nanocrystals in Poly(vinyl acetate) Matrix, *Biomacromolecules.* 16 (2015) 3916–3924. doi:10.1021/acs.biomac.5b01245.
- [108] W. Di, G. Zhang, Z.-D. Zhao, Y. Peng, Ethylene–(vinyl acetate) copolymer/carbon fiber conductive composite: effect of polymer–filler interaction on its electrical properties, *Polym. Int.* 53 (2004) 449–454. doi:10.1002/pi.1403.
- [109] B.A. Abdelkader, S.M. Zubair, The Effect of a Number of Baffles on the Performance of Shell-and-Tube Heat Exchangers, *Heat Transf. Eng.* 40 (2019) 39–52. doi:10.1080/01457632.2017.1404806.
- [110] M.A. Bahattab, J. Mosna, A.A. Basfar, T.M. Shukri, Cross-linked poly(ethylene vinyl acetate) (EVA)/low density polyethylene (LDPE)/metal hydroxides composites for wire and cable applications, *Polym. Bull.* 64 (2010) 569–580. doi:10.1007/s00289-009-0194-0.

- [111] N.C. Das, T.K. Chaki, D. Khastgir, Effect of Filler Treatment and Crosslinking on Mechanical and Dynamic Mechanical Properties and Electrical Conductivity of Carbon Black-Filled Ethylene – Vinyl Acetate Copolymer Composites, *J. Appl. Polym. Sci.* 90 (2003) 2073–2082.
- [112] N.C. Das, S. Maiti, Electromagnetic interference shielding of carbon nanotube / ethylene vinyl acetate composites, *J. Mater. Sci.* 43 (2008) 1920–1925. doi:10.1007/s10853-008-2458-8.
- [113] M. Pracella, M. Haque, V. Alvarez, Functionalization, Compatibilization and Properties of Polyolefin Composites with Natural Fibers, *Polymers (Basel)*. (2010) 554–574. doi:10.3390/polym2040554.
- [114] B. Jin, W. Zhang, G. Sun, H.-B. Gu, Fabrication and characterization of ethylene-vinyl acetate copolymer / Al₂O₃ nano- composites, *J. Ceram. Process. Res.* 8 (2007) 336–340.
- [115] D. Lopes, M.J. Ferreira, R. Russo, J.M. Dias, Natural and synthetic rubber / waste e Ethylene-Vinyl Acetate composites for sustainable application in the footwear industry, *J. Clean. Prod.* 92 (2015) 230–236. doi:10.1016/j.jclepro.2014.12.063.
- [116] K. Mitsuishi, S. Kodama, H. Kawasaki, Mechanical Properties of Polyethylene/Ethylene Vinyl Acetate Filled With Calcium Carbonate, *Polym. Compos.* 9 (1988) 112–118.
- [117] J. Gonzalez-Benito, E. Castillo, J.F. Caltido, Coefficient of thermal expansion of

- TiO₂ filled EVA based nanocomposites . A new insight about the influence of filler particle size in composites, *Eur. Polym. J.* 49 (2013) 1747–1752. doi:10.1016/j.eurpolymj.2013.04.023.
- [118] M. Shen, J. He, Y. Cui, Y. Zhang, Preparation of an Al₂O₃–EVA Co-film and its Thermal Conductivity, *J. Elastomers Plast.* 42 (2010) 499–516. doi:10.1177/0095244310376922.
- [119] F. Delogu, G. Gorrasi, A. Sorrentino, Fabrication of polymer nanocomposites via ball milling: Present status and future perspectives, *Prog. Mater. Sci.* 86 (2017) 75–126. doi:10.1016/j.pmatsci.2017.01.003.
- [120] G. Gorrasi, A. Sorrentino, Mechanical milling as a technology to produce structural and functional bio-nanocomposites, *Green Chem.* 17 (2015) 2610–2625. doi:10.1039/c5gc00029g.
- [121] S.H. Teoh, Z.G. Tang, G.W. Hastings, Thermoplastic Polymers In Biomedical Applications : Structures , Properties and Processing, in: J. Black, G. Hastings (Eds.), *Handb. Biomater. Prop. Part II*, Springer, Boston, MA, 1998: pp. 270–301. doi:10.1007/978-1-4615-5801-9.
- [122] Semiconductor Industry Association - 2015 International Technology Roadmap for Semiconductors (ITRS), (n.d.).
- [123] R. Courtland, Transistors could stop shrinking in 2021, *IEEE Spectr.* 53 (2016) 9–11. doi:10.1109/MSPEC.2016.7551335.

- [124] X. Huang, T. Iizuka, P. Jiang, Y. Ohki, T. Tanaka, Role of Interface on the Thermal Conductivity of Highly Filled Dielectric Epoxy/AlN Composites, *J. Phys. Chem. C.* 116 (2012) 13629–13639. doi:10.1021/jp3026545.
- [125] Z. Gao, L. Zhao, Effect of nano-fillers on the thermal conductivity of epoxy composites with micro-Al₂O₃ particles, *Mater. Des.* 66 (2015) 176–182. doi:10.1016/j.matdes.2014.10.052.
- [126] Z. Shi, R. Fu, S. Agathopoulos, X. Gu, W. Zhao, Thermal conductivity and fire resistance of epoxy molding compounds filled with Si₃N₄ and Al(OH)₃, *Mater. Des.* 34 (2012) 820–824. doi:10.1016/j.matdes.2011.07.012.
- [127] A. Yu, P. Ramesh, M.E. Itkis, E. Bekyarova, R.C. Haddon, Graphite Nanoplatelet - Epoxy Composite Thermal Interface Materials, *J. Phys. Chem. C.* 111 (2007) 7565–7569. doi:10.1021/jp071761s.
- [128] A. Yu, M.E. Itkis, E. Bekyarova, R.C. Haddon, Effect of single-walled carbon nanotube purity on the thermal conductivity of carbon nanotube-based composites, *Appl. Phys. Lett.* 89 (2006) 1–3. doi:10.1063/1.2357580.
- [129] M.J. Biercuk, M.C. Llaguno, M. Radosavljevic, J.K. Hyun, a. T. Johnson, J.E. Fischer, Carbon nanotube composites for thermal management, *Appl. Phys. Lett.* 80 (2002) 2767–2769. doi:10.1063/1.1469696.
- [130] K.M. Shahil, V. Goyal, A. Balandin, Thermal Properties of Graphene: Applications in Thermal Interface Materials, in: *ECS Trans.*, The Electrochemical Society, 2011:

pp. 193–199. doi:10.1149/1.3569911.

- [131] K. Yang, M. Gu, Enhanced thermal conductivity of epoxy nanocomposites filled with hybrid filler system of triethylenetetramine-functionalized multi-walled carbon nanotube/silane-modified nano-sized silicon carbide, *Compos. Part A Appl. Sci. Manuf.* 41 (2010) 215–221. doi:10.1016/j.compositesa.2009.10.019.
- [132] V. Goyal, A. a. Balandin, Thermal properties of the hybrid graphene-metal nano-micro-composites: Applications in thermal interface materials, *Appl. Phys. Lett.* 100 (2012) 073113. doi:10.1063/1.3687173.
- [133] F. Du, W. Yang, F. Zhang, C.-Y. Tang, S. Liu, L. Yin, W.-C. Law, Enhancing the Heat Transfer Efficiency in Graphene–Epoxy Nanocomposites Using a Magnesium Oxide–Graphene Hybrid Structure, *ACS Appl. Mater. Interfaces.* 7 (2015) 14397–14403. doi:10.1021/acsami.5b03196.
- [134] Z. Li, D. Wang, M. Zhang, L. Zhao, Enhancement of the thermal conductivity of polymer composites with Ag-graphene hybrids as fillers, *Phys. Status Solidi.* 8 (2014) n/a-n/a. doi:10.1002/pssa.201431054.
- [135] S.H. Xie, Y.Y. Liu, J.Y. Li, Comparison of the effective conductivity between composites reinforced by graphene nanosheets and carbon nanotubes, *Appl. Phys. Lett.* 92 (2008) 8–11. doi:10.1063/1.2949074.
- [136] I. Sagalianov, L. Vovchenko, L. Matzui, O. Lazarenko, Synergistic Enhancement of the Percolation Threshold in Hybrid Polymeric Nanocomposites Based on Carbon

- Nanotubes and Graphite Nanoplatelets, *Nanoscale Res. Lett.* 12 (2017) 140.
doi:10.1186/s11671-017-1909-z.
- [137] X. Huang, C. Zhi, P. Jiang, Toward Effective Synergetic Effects from Graphene Nanoplatelets and Carbon Nanotubes on Thermal Conductivity of Ultrahigh Volume Fraction Nanocarbon Epoxy Composites, *J. Phys. Chem. C.* 116 (2012) 23812–23820. doi:dx.doi.org/10.1021/jp308556r.
- [138] H. Im, J. Kim, Thermal conductivity of a graphene oxide–carbon nanotube hybrid/epoxy composite, *Carbon N. Y.* 50 (2012) 5429–5440.
doi:10.1016/j.carbon.2012.07.029.
- [139] K. Chu, W. Li, C. Jia, F. Tang, Thermal conductivity of composites with hybrid carbon nanotubes and graphene nanoplatelets, *Appl. Phys. Lett.* 101 (2012) 211903.
doi:10.1063/1.4767899.
- [140] Q.H. Zeng, a. B. Yu, G.Q. Lu, Multiscale modeling and simulation of polymer nanocomposites, *Prog. Polym. Sci.* 33 (2008) 191–269.
doi:10.1016/j.progpolymsci.2007.09.002.
- [141] H. Yan, Y. Tang, J. Su, X. Yang, Enhanced thermal-mechanical properties of polymer composites with hybrid boron nitride nanofillers, *Appl. Phys. A Mater. Sci. Process.* 114 (2014) 331–337. doi:10.1007/s00339-013-8149-6.
- [142] K. Chu, F. Wang, X. Wang, Y. Li, Z. Geng, D. Huang, H. Zhang, Interface design of graphene/copper composites by matrix alloying with titanium, *Mater. Des.* 144

(2018) 290–303. doi:10.1016/j.matdes.2018.02.038.

- [143] J. Gu, N. Li, L. Tian, Z. Lv, Q. Zhang, High thermal conductivity graphite nanoplatelet/UHMWPE nanocomposites, *RSC Adv.* 5 (2015) 36334–36339. doi:10.1039/C5RA03284A.
- [144] J. Gu, J. Du, J. Dang, W. Geng, S. Hu, Q. Zhang, Thermal conductivities, mechanical and thermal properties of graphite nanoplatelets/polyphenylene sulfide composites, *RSC Adv.* 4 (2014) 22101–22105. doi:10.1039/C4RA01761G.
- [145] J. Yu, H.K. Choi, H.S. Kim, S.Y. Kim, Synergistic effect of hybrid graphene nanoplatelet and multi-walled carbon nanotube fillers on the thermal conductivity of polymer composites and theoretical modeling of the synergistic effect, *Compos. Part A Appl. Sci. Manuf.* 88 (2016) 79–85. doi:10.1016/j.compositesa.2016.05.022.
- [146] L. Chen, Y.-Y. Sun, J. Lin, X.-Z. Du, G.-S. Wei, S.-J. He, S. Nazarenko, Modeling and analysis of synergistic effect in thermal conductivity enhancement of polymer composites with hybrid filler, *Int. J. Heat Mass Transf.* 81 (2015) 457–464. doi:http://dx.doi.org/10.1016/j.ijheatmasstransfer.2014.10.051.
- [147] M. Siddiqui, A.F.M. Arif, Estimation and optimisation of effective thermal conductivity for polymer matrix composites with hybrid inclusions, *J. Compos. Mater.* 52 (2018) 2139–2148. doi:10.1177/0021998317741953.
- [148] A. Yu, P. Ramesh, X. Sun, E. Bekyarova, M.E. Itkis, R.C. Haddon, Enhanced thermal conductivity in a hybrid graphite nanoplatelet - Carbon nanotube filler for

- epoxy composites, *Adv. Mater.* 20 (2008) 4740–4744.
doi:10.1002/adma.200800401.
- [149] Y. Guo, G. Xu, X. Yang, K. Ruan, T. Ma, Q. Zhang, J. Gu, Y. Wu, H. Liu, Z. Guo, Significantly enhanced and precisely modeled thermal conductivity in polyimide nanocomposites with chemically modified graphene via in situ polymerization and electrospinning-hot press technology, *J. Mater. Chem. C.* 6 (2018) 3004–3015.
doi:10.1039/C8TC00452H.
- [150] K. Chu, X. Wang, F. Wang, Y. Li, D. Huang, H. Liu, W. Ma, F. Liu, H. Zhang, Largely enhanced thermal conductivity of graphene/copper composites with highly aligned graphene network, *Carbon* N. Y. 127 (2018) 102–112.
doi:10.1016/j.carbon.2017.10.099.
- [151] A. Saltelli, *Global sensitivity analysis : the primer*, John Wiley, 2008.
- [152] J.P. Guilford, Benjamin Fruchter, *Fundamental Statistics in Psychology and Education*, 5th Ed., McGraw Hill, New York, 1973.
- [153] J. Gu, C. Liang, X. Zhao, B. Gan, H. Qiu, Y. Guo, X. Yang, Q. Zhang, D.Y. Wang, Highly thermally conductive flame-retardant epoxy nanocomposites with reduced ignitability and excellent electrical conductivities, *Compos. Sci. Technol.* 139 (2017) 83–89. doi:10.1016/j.compscitech.2016.12.015.
- [154] J. Gu, X. Yang, Z. Lv, N. Li, C. Liang, Q. Zhang, Functionalized graphite nanoplatelets/epoxy resin nanocomposites with high thermal conductivity, *Int. J.*

- Heat Mass Transf. 92 (2016) 15–22. doi:10.1016/j.ijheatmasstransfer.2015.08.081.
- [155] M.A. Raza, A. Westwood, A. Brown, N. Hondow, C. Stirling, Characterisation of graphite nanoplatelets and the physical properties of graphite nanoplatelet/silicone composites for thermal interface applications, Carbon N. Y. 49 (2011) 4269–4279. doi:10.1016/j.carbon.2011.06.002.
- [156] Imerys Graphite & Carbon, Specialty Carbons for Polymer Compounds, Imerys. (2014). http://www.imerys-graphite-and-carbon.com/wordpress/wp-app/uploads/2014/04/Polymer_compounds1.pdf.
- [157] T.J.-M. Chen Y-M, Ultra high thermal conductivity polymer composites, Carbon N. Y. 40 (2002) 359–62.
- [158] Lord Rayleigh, LVI. On the influence of obstacles arranged in rectangular order upon the properties of a medium, London, Edinburgh, Dublin Philos. Mag. J. Sci. 34 (1892) 481–502. doi:10.1080/14786449208620364.
- [159] H. Fricke, The Maxwell-Wagner Dispersion in a Suspension of Ellipsoids, J. Phys. Chem. 57 (1953) 934–937. doi:10.1021/j150510a018.
- [160] D.A.G. Bruggeman, Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. I. Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen, Ann. Phys. 416 (1935) 636–664. doi:10.1002/andp.19354160705.
- [161] R.L. Hamilton, O.K. Crosser, Thermal Conductivity of Heterogeneous Two-

- Component Systems, *Ind. Eng. Chem. Fundam.* 1 (1962) 187–191.
doi:10.1021/i160003a005.
- [162] Z. Hashin, S. Shtrikman, A Variational Approach to the Theory of the Effective Magnetic Permeability of Multiphase Materials, *J. Appl. Phys.* 33 (1962) 3125–3131. doi:10.1063/1.1728579.
- [163] T. Mori, K. Tanaka, Average stress in matrix and average elastic energy of materials with misfitting inclusions, *Acta Metall.* 21 (1973) 571–574. doi:10.1016/0001-6160(73)90064-3.
- [164] Y. Benveniste, Effective thermal conductivity of composites with a thermal contact resistance between the constituents: Nondilute case, *J. Appl. Phys.* 61 (1987) 2840–2843. doi:10.1063/1.337877.
- [165] M. Siddiqui, A.F.M. Arif, Estimation and optimisation of effective thermal conductivity for polymer matrix composites with hybrid inclusions, *J. Compos. Mater.* 52 (2018) 2139–2148. doi:10.1177/0021998317741953.
- [166] E.T. Swartz, R.O. Pohl, Thermal boundary resistance, *Rev. Mod. Phys.* 61 (1989) 605–668. doi:10.1103/RevModPhys.61.605.
- [167] M. Sinha, D.J. Buckley, Acoustic Properties of Polymers, in: J. E. Mark (Ed.), *Phys. Prop. Polym. Handb.*, 2nd ed., Springer, 2007: pp. 1021–1032.
- [168] Q. Kang, X. He, S. Ren, L. Zhang, M. Wu, C. Guo, W. Cui, X. Qu, Preparation of copper–diamond composites with chromium carbide coatings on diamond particles

- for heat sink applications, *Appl. Therm. Eng.* 60 (2013) 423–429.
doi:10.1016/j.applthermaleng.2013.05.038.
- [169] I.E. Agency, Renewables 2018 Market analysis and forecast from 2018 to 2023, 2018. <https://www.iea.org/renewables2018/>.
- [170] X. Huang, P. Jiang, T. Tanaka, A review of dielectric polymer composites with high thermal conductivity, *IEEE Electr. Insul. Mag.* 27 (2011) 8–16.
doi:10.1109/MEI.2011.5954064.
- [171] C. Peike, I. Hädrich, K.-A. Weiß, I. Dürr, Overview of PV module encapsulation materials, *Photovoltaics Int.* 19 (2013) 85–92.
- [172] J.A. Duffie, W.A. Beckman, Concentrating Collectors, in: *Sol. Eng. Therm. Process.*, 2013: pp. 322–372.
- [173] H. Watanabe, N. Yamada, M. Okaji, Linear Thermal Expansion Coefficient of Silicon from 293 to 1000 K, *Int. J. Thermophys.* 25 (2004) 221–236.
doi:10.1023/B:IJOT.0000022336.83719.43.
- [174] U. Eitner, Thermomechanics of photovoltaic modules, der Martin-Luther-Universität Halle-Wittenberg, 2011. <https://d-nb.info/1025202627/34%0Ahttp://d-nb.info/1025202627/34>.
- [175] D.A. Dillard, L. Yan, R.L. West, G. V. Gordon, L.D. Lower, Estimating the Stresses in Linear Viscoelastic Sealants Subjected to Thermally-Driven Deformations, *J. Adhes.* 87 (2011) 162–178. doi:10.1080/00218464.2011.545624.

- [176] Thermoplastic Polyurethanes Thermal Properties, (n.d.).
<https://www.tpu.covestro.com/en/Technologies/Properties/Thermal-Properties>
(accessed October 10, 2019).
- [177] C. Zhi, Y. Bando, T. Terao, C. Tang, H. Kuwahara, D. Golberg, Towards thermoconductive, electrically insulating polymeric composites with boron nitride nanotubes as fillers, *Adv. Funct. Mater.* 19 (2009) 1857–1862. doi:10.1002/adfm.200801435.
- [178] I. Doghri, L. Tinel, Micromechanical modeling and computation of elasto-plastic materials reinforced with distributed-orientation fibers, *Int. J. Plast.* 21 (2005) 1919–1940. doi:10.1016/j.ijplas.2004.09.003.
- [179] G. Bódi, T. Goda, Parameter identification methods for generalized Maxwell models: Engineering approach for small-strain viscoelasticity, *Mater. Sci. Forum.* 659 (2010) 379–384. doi:10.4028/www.scientific.net/MSF.659.379.
- [180] G.C. Papanicolaou, S.P. Zaoutsos, Viscoelastic constitutive modeling of creep and stress relaxation in polymers and polymer matrix composites, 2nd ed., Elsevier Ltd., 2010. doi:10.1533/9780857090430.1.3.
- [181] R. Serth, T. Lestina, Process Heat Transfer Principles, Applications and Rules of Thumb, 2nd ed., Academic Press, 2014.
- [182] C. Huang, X. Qian, R. Yang, Thermal conductivity of polymers and polymer nanocomposites, *Mater. Sci. Eng. R Reports.* 132 (2018) 1–22.

doi:10.1016/j.mser.2018.06.002.

- [183] K. Raza, S.S. Akhtar, A.F.M. Arif, A.S. Hakeem, Computational design and development of high-performance polymer-composites as new encapsulant material for concentrated PV modules, *Sci. Rep.* 10 (2020) 5304. doi:10.1038/s41598-020-62191-9.
- [184] H. Chen, V. V. Ginzburg, J. Yang, Y. Yang, W. Liu, Y. Huang, L. Du, B. Chen, Thermal conductivity of polymer-based composites: Fundamentals and applications, *Prog. Polym. Sci.* 59 (2016) 41–85. doi:10.1016/j.progpolymsci.2016.03.001.
- [185] K. Raza, S.S. Akhtar, A.F.M. Arif, A.S. Hakeem, An Improved Predictive Model for Effective Thermal Conductivity of Polymer Composites With Non-Dilute Filler Concentrations, in: Vol. 12 *Adv. Mater. Des. Process. Charact. Appl.*, American Society of Mechanical Engineers, 2019. doi:10.1115/IMECE2019-10960.
- [186] J.-F. Yang, D.-H. Yoon, T.M.L. Dang, C.-Y. Kim, Y. Zhang, T. Masaki, Enhanced thermal conductivity of polymer composites via hybrid fillers of anisotropic aluminum nitride whiskers and isotropic spheres, *Compos. Part B Eng.* 114 (2017) 237–246. doi:10.1016/j.compositesb.2017.02.008.

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Published Journal Articles:

Journals

1. M.T.S. Chani, K.S. Karimov, F. Ahmad Khalid, **K. Raza**, M. Umer Farooq, Q. Zafar, Humidity sensors based on aluminum phthalocyanine chloride thin films, Physical E: Low-Dimensional Systems and Nanostructures. 45 (2012) 77–81. doi:10.1016/j.physe.2012.07.012.
2. **K. Raza**, F.A. Khalid, Optimization of sintering parameters for diamond–copper composites in conventional sintering and their thermal conductivity, Journal of Alloys and Compounds. 615 (2014) 111–118. doi:10.1016/j.jallcom.2014.06.139.
3. M. Zain-ul-abdein, **K. Raza**, F.A. Khalid, T. Mabrouki, Numerical investigation of the effect of interfacial thermal resistance upon the thermal conductivity of copper/diamond composites, Materials & Design. 86 (2015) 248–258. doi:10.1016/j.matdes.2015.07.059.

4. S.S. Akhtar, M.U. Siddiqui, **K. Raza**, A. Hakeem, L. Kareem, A.F. Arif, A computational and experimental study on the effective properties of Al₂O₃ -Ni composites, *Internal Journal of Applied Ceramic Technology* 14 (2017) 766–778. doi:10.1111/ijac.12674.
5. M. Zain-ul-Abdein, H. Ijaz, W. Saleem, **K. Raza**, A.S. Bin Mahfouz, T. Mabrouki, Finite element analysis of interfacial debonding in copper/diamond composites for thermal management applications, *Materials (Basel)*. 10 (2017) 1–18. doi:10.3390/ma10070739.
6. **K. Raza**, M. Shamir, M.K.A. Qureshi, A.S. Shaikh, M. Zain-ul-abdein, On the friction stir welding, tool design optimization, and strain rate-dependent mechanical properties of HDPE–ceramic composite joints, *Journal of Thermoplastic Composite Materials*. 31 (2018) 291–310. doi:10.1177/0892705717697779.
7. **K. Raza**, M.U. Siddiqui, A.F.M. Arif, S.S. Akhtar, A.S. Hakeem, Design and development of thermally conductive hybrid nano-composites in polysulfone matrix, *Polymer Composites*. 40 (2019) 1419–1432. doi:10.1002/pc.24879.
8. **K. Raza**, S. Sohail, A. Fazal, M. Arif, A. Saeed, Computational design and development of high-performance polymer-composites as new encapsulant material for concentrated PV modules, *Scientific Reports*. **10**, 5304 (2020) doi: 10.1038/s41598-020-62191-9.
9. **K. Raza**, S.S. Akhtar, A new model for thermal conductivity of polymer-composites with non- dilute filler concentrations based on differential effective medium approximation, *International Journal of Thermal Sciences* (2020) [Submitted].

Conference Proceedings

10. **K. Raza**, F.A. Khalid, Fabrication and Characterization of coated and un-coated SiC reinforced copper matrix composites, in: *National Symposium on Materials Technologies*, 2013 GIK Institute, Topi, Pakistan.

11. S.S. Akhtar, A.F.M. Arif, M.U. Siddiqui, **K. Raza**, L.T. Kareem, A.S. Hakeem, Computational design and development of alumina-nickel droplet composites, in the proceedings of ASME International Mechanical Engineering Congress and Exposition, 2016. <https://doi.org/10.1115/IMECE2016-67071>
12. **K. Raza**, S.S. Akhtar, A.F.M. Arif, A.S. Hakeem, Design of Composite Encapsulation for Concentrated Photovoltaic Systems with Improved Performance, in the proceedings of ASME International Mechanical Engineering Congress and Exposition, 2019. <https://doi.org/10.1115/IMECE2019-11720>
13. **K. Raza**, S.S. Akhtar, A.F.M. Arif, A.S. Hakeem, An Improved Predictive Model for Effective Thermal Conductivity of Polymer Composites with Non-Dilute Filler Concentrations, in the proceedings of ASME International Mechanical Engineering Congress and Exposition, 2019. <https://doi.org/10.1115/IMECE2019-10960> |