

**Impact Modification of Reinforced Polypropylene Composites
Through Hybridization with Various Fillers and Fibers
for Automotive Applications**

BY

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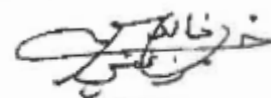
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Dedicated to

My beloved parents, brothers and sisters whose boundless encouragement
has been the driving force behind my academic journey.

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Above all, I express my gratitude to Allah Almighty for his guidance and the numerous blessings he has bestowed upon me.

I express my profound thanks and gratitude to my beloved parents for their enduring love and unwavering support.

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LIST OF ABBREVIATIONS

CaCO ₃	Calcium Carbonate
CF	Carbon fibers
T _c	Crystallization Temperature
EPDM	Ethylene Propylene Diene Monomer
EPR	Ethylene Propylene Rubber
GF	Glass fibers
hPP	Homopolymer Polypropylene
ICP	Impact Copolymer Polypropylene
T _m	Melting Temperature
PET	Polyethylene Terephthalate
POE	Polyolefin Elastomer
POE-g-MA	Polyolefin Elastomer grafted Maleic Anhydride
PP	Polypropylene
PP-g-GMA	Polypropylene grafted Glycidyl Methacrylate
PP-g-MA	Polypropylene grafted Maleic Anhydride
PVA	Polyvinyl Alcohol
SEBS	Styrene Ethylene Butylene Styrene
SEBS-g-MA	Styrene Ethylene Butylene Styrene grafted Glycidyl Methacrylate
SEEPS	Styrene [Ethylene (Ethylene-Propylene)] Styrene
SEM	Scanning Electron Microscope

ABSTRACT

Full Name : Faisal Abdullah AlSuhaibani
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Polypropylene reinforced composites mostly exhibit a trade-off between stiffness and toughness. In this study, the impact of incorporating Polyolefin Elastomer and Polyvinyl Alcohol fibers as individual and hybrid reinforcement to Glass fiber and Talc reinforced polypropylene composites, in the presence of a compatibilizer, was explored. The main attention was focused on achieving an optimal stiffness/toughness balance. Several ternary and quaternary hybrid composite systems were developed and analyzed. A twin-screw extruder was used to melt mix all of the components, then injection molded for subsequent mechanical and morphological analysis. Tensile, flexural and izod impact tests were utilized to assess the mechanical properties of the developed composites. Scanning Electron Microscope helped to identify the micromechanical deformation processes contributing to the impact toughening mechanism for composites. Different local deformation processes were identified in the deformed samples. These processes can occur simultaneously or sequentially within the composite. However, one of them usually dominates the failure mechanism, although the effects of other processes should not be ignored. The predominant energy absorbing mechanism for glass fibers was found to be fiber fracture, due to the strong adhesion achieved through the adoption of Silane sizing treatment as well as the use of a coupling agent. For PVA fibers, the dominating

micromechanical deformation process was pull-out, while for Talc it was mainly debonding. Unlike the other fibers' deformation processes, the debonding mechanism of the Talc particles did not contribute to improve the impact strength of PP. For POE, the primary source of energy absorption was the cavitation of elastomer particles. The mechanical results revealed that glass fibers, Talc and PVA fibers increase the stiffness of composites, yet to different extents. The hybridization of Talc and PVA fibers has significantly boosted the stiffness and toughness of PP to high levels, exceeding the properties of individual filler reinforcements. Moreover, a large stiffness of approximately 2.4 GPa Young's modulus, and Izod impact strength ranges between 250 and 400 J/m can be attained with the quaternary hybrid system, PP/GF/POE/PVA fibers. Its performance can be controlled by altering the POE/PVA fibers ratio to achieve the targeted stiffness/toughness balance. These values represent a remarkable increase, with the Young's modulus being 120% higher and the izod impact strength surpassing that of the control sample by over 800%. The enhanced macroscopic properties of the composites are attributed to the high inherent rigidity of the reinforcing fillers and the considerable energy absorption ability associated with various micromechanical deformation mechanisms occurring during failure. Also, Differential Scanning Calorimetry results revealed that Talc has the strongest nucleation effect in PP, evident by the 12 °C increase in the crystallization temperature. Furthermore, in addition to imparting strength and toughness to PP, PVA fibers have lower density than other conventional reinforcements, like Glass fibers and Talc. The low density of PVA fibers contributes to reducing the overall hybrid composite density, leading to lighter weight parts and, consequently, lower fuel consumption. This is achieved while still satisfying the high rigidity needed for automotive applications.

ملخص الرسالة

الاسم الكامل : فيصل السحيباني
عنوان الرسالة : الأثر المترتب على مركبات البولي بروبيلين المُعززة من خلال التهجين بأنواع مختلفة من الحشوات والألياف لتطبيقات السيارات
التخصص : علوم و هندسة المواد
تاريخ الدرجة العلمية : ديسمبر 2023

تُظهر مركبات البولي بروبيلين المقواة في الغالب مفاضلة بين الصلابة والمرونة. في هذا البحث، تم دراسة تأثير دمج مطاط البولي أوليفين وألياف البولي فينيل الكحول كتعزيز فردي وهجين لمركبات البولي بروبيلين المقواة بألياف الزجاج والتالك. كان التركيز الرئيسي في هذه الدراسة على تحقيق التوازن الأمثل بين الصلابة والمرونة. تم تطوير وتحليل العديد من العينات المركبة الهجينة الثلاثية والرباعية. تم خلط جميع المكونات باستخدام آلة البثق، ثم تم تشكيلها بالحقن للتحليل الميكانيكي. تم استخدام اختبارات تأثير الشد والانحناء والإرتطام المرن لتقييم الخواص الميكانيكية للمركبات المطورة، كما ساعد المجهر الإلكتروني الماسح على تحديد عمليات التشوه الميكروميكانيكية التي أسهمت في آلية تحسين الصلابة والمرونة للمركبات. تم تحديد عمليات تشوه ميكروميكانيكية مختلفة في العينات المشوهة. يمكن أن تحدث هذه العمليات بشكل متزامن أو متتابع داخل المركب. ومع ذلك، عادة ما يهيمن أحدهم على آلية الفشل، ولكن ينبغي عدم تجاهل آثار العمليات الأخرى. تبين أن آلية امتصاص الطاقة المهيمنة في عينة الألياف الزجاجية هي كسر الألياف، نتيجة للالتصاق القوي الذي تم تحقيقه من خلال المعالجة المسبقة لسطح الألياف بالإضافة إلى تواجد مادة لتحفيز الإقتران والربط. بينما كانت عملية التشوه الميكروميكانيكية السائدة لألياف البولي فينيل الكحول هي سحب الألياف، في حين أن جزيئات التالك كان بفك الارتباط بشكل أساسي. خلافا لعمليات تشوه الألياف الأخرى، لم تسهم آلية فك ارتباط جزيئات التالك في تعزيز مقاومة البولي بروبيلين للصدمات. بالنسبة لمطاط البولي أوليفين، كان المصدر الرئيسي لامتصاص الطاقة هو تكوين التجويفات لجزيئات المطاط. كشفت النتائج الميكانيكية عن أن الألياف الزجاجية و ألياف البولي فينيل الكحول وجزيئات التالك تزيد من صلابة المركبات، ولكن بدرجات متفاوتة. وقد أدى تهجين ألياف البولي فينيل الكحول والتالك إلى زيادة كبيرة في صلابة ومرونة مركبات البولي بروبيلين محققة مستويات عالية، متجاوزة بذلك خصائص تعزيزات الحشو الفردية. علاوة على ذلك، مع النظام الهجين الرباعي المكون من: البولي بروبيلين/ألياف زجاجية/مطاط البولي أوليفين/ألياف بولي فينيل الكحول يمكن تحقيق صلابة كبيرة تصل إلى 2.4 جيجا

باسكال لمُعامل يونغ، بالإضافة إلى قوة ارتطام مرن عالية تصل إلى 400 جول/متر. تُمثل هذه القيم زيادة كبيرة ملحوظة مقارنة بالعينة الأساسية الغير مدعّمة، بحيث يكون معامل يونغ أعلى بـ 120 في المائة وقوة امتصاص الارتطام أعلى بأكثر من 800 في المائة. كما يُمكن التحكم في الأداء من خلال تغيير نسبة مطاط البولي أوليفين إلى ألياف البولي فينيل الكحول لتحقيق التوازن المستهدف بين الصلابة والمرونة. يُعزى الأداء المحسن بالنسبة للمركبات المدعّمة إلى الصلابة المتأصلة العالية للألياف والحشوات المعززة، بالإضافة إلى القدرة الكبيرة على امتصاص الطاقة المرتبطة بآليات التشوه الميكانيكية الدقيقة المتنوعة التي تحدث أثناء الفشل. بالإضافة إلى منح القوة والمتانة للبولي بروبيلين، تتمتع ألياف البولي فينيل الكحول بكثافة أقل بكثير من الألياف والمعززات التقليدية الأخرى، مثل ألياف الزجاج والتالك. تُساهم الكثافة المنخفضة لألياف بولي فينيل الكحول في تقليل الكثافة الكلية للمركب الهجين، مما يؤدي إلى أجزاء أخف وزناً وبالتالي انخفاض استهلاك الوقود، ويتحقق ذلك مع الاستمرار في تلبية الصلابة العالية والمرونة اللازمة لتطبيقات السيارات.

CHAPTER 1

INTRODUCTION

1.1 Polypropylene

Polymers are chemical compounds in which molecules are bonded together in long repeating chains. They demonstrate distinctive characteristics and can be modified based on their intended applications. Polypropylene (PP) is a polymer composed of propylene monomer units. Propylene, the monomer used in its production, can be sourced from natural gas or obtained as a co-product with ethylene through the cracking of petroleum (naphtha). Polypropylene is a semi-crystalline thermoplastic linear polymer that was initially developed in the 1950s by Giulio Natta in Italy. Polypropylene is among the most widely produced thermoplastics globally because of its distinctive properties, which include ease of processability, low density, low specific energy, and cost-effectiveness in production [1]. Polypropylene holds high significance due to its diverse applications, including food packaging, textiles, automotive, packaging films, clear and rigid food containers, appliances, and medical equipment.

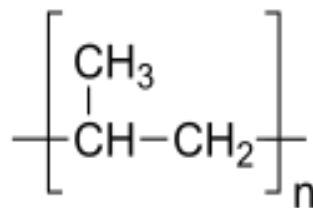
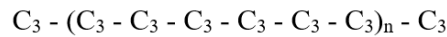
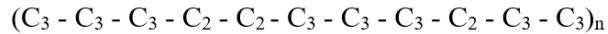


Figure 1 Polypropylene chemical structure [2]

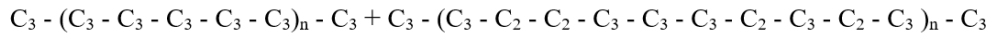
Polypropylene is available in two main forms: homopolymer and copolymer, derived from ethylene-propylene monomers. The copolymer can be further classified as either a Random copolymer or a Block copolymer, commonly known as Impact PP. Homopolypropylene consists of only propylene (C3) monomer and is manufactured in a single-reactor system. Random polypropylene copolymer consists of two different monomers, in which ethylene (C2) randomly distributed along the growing C3 polymer chain, typically produced in a single-reactor system. Impact polypropylene copolymer, also known as heterophasic PP, is composed of blocks of Ethylene-Propylene Rubber (EPR) distributed within the PP homopolymer matrix, and usually is produced in a two-reactor system operated in series [1], [3], [4]. PP homopolymer, random, and impact copolymers each possess distinct properties. The selection among them should be based on the specific application requirements and the desired properties.



Homo Polypropylene



Random Polypropylene copolymer



Impact Polypropylene copolymer

Figure 2 Structure of the different PP types

Furthermore, different factors are affecting the mechanical characteristics of homopolymer polypropylene, including the morphological and crystallization behavior, along with the processing conditions. The primary factor affecting the physical and

mechanical properties is the degree of crystallinity. As crystallinity increases, stiffness rises, but generally at the expense of decreased toughness [5]. The ability of a material to resist deformation when force is applied is known as stiffness. In some cases, neat polymers may not fully meet the requirements of the end application. Consequently, the introduction of polymer composites becomes necessary.

1.2 Polymer composites in the automotive industry

Plastics are widely utilized in the automotive industry because of their ease of manufacture and comparatively lower cost compared to other conventional materials. Over the previous few decades, numerous research studies have been directed towards enhancing the mechanical attributes of automotive components, while simultaneously seeking more environmentally friendly and cost-effective solutions [6]. Compared to traditional materials, polymer composites offer several advantages, including higher specific strength, resistance to corrosion, reduced weight, and enhanced resistance to various static and dynamic loads that car structures may encounter. Due to the reduced weight, energy consumption is lowered. To illustrate, according to some published reports, a reduction of one kilogram in a vehicle's weight results in approximately 20 kilograms less carbon dioxide emissions [7]. Figure 3 illustrates various components of a car in which polymers, including polypropylene, are employed.

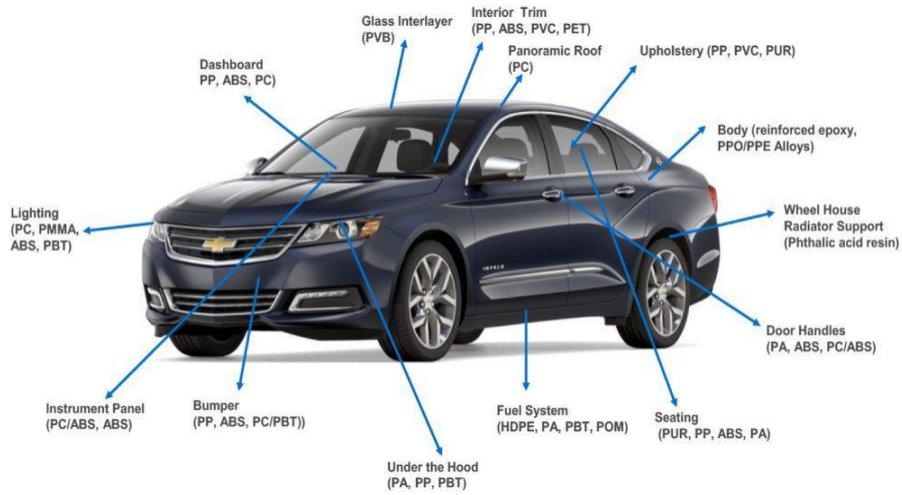


Figure 3 Polypropylene applications in automotive parts [8]

According to Nexant, Polypropylene represents about 32% of the plastics consumed in the automotive industry in north America, and it is expected to grow even further with the rising production of electric vehicles, as these vehicles will demand lighter components to counterbalance the weight of the heavy batteries [8].

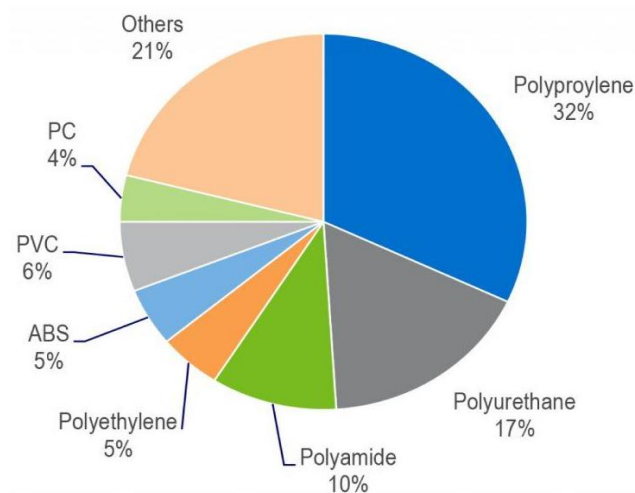


Figure 4 Polymers consumption in automotive industry in north America [8]

1.3 Polymer hybrid composites

Polymer composites are materials created by blending polymers with reinforcing phases such as fibers, fillers, or nanoparticles. These tailored combinations are designed to achieve specific properties or characteristics that may be challenging to attain with neat polymers alone. Polypropylene (PP) is a commonly used polymer in the automotive sector. Its production continues to grow and expand worldwide due to its attractive balance between cost and mechanical performance. Along with its easy processing and recyclability, one of the main advantages of polypropylene is that it can be further modified and tailored in several ways to widen its application through incorporation of fibers and fillers by forming composites [9]. To illustrate, PP toughness can be improved via blending with elastomers, while strength and stiffness can be enhanced by filler addition. The high standards in the automotive industry require products with increased strength. Parts designed for the automotive sector typically need to exhibit both high toughness and good stiffness simultaneously. However, fulfilling this requirement is challenging as these two properties are inversely related [10], [11], [12]. Hybrid composites are reinforced materials achieved by incorporating two or more distinct fillers or fibers into the matrix. The hybridization of these additives within the polymer matrix helps maintain a favorable balance between stiffness and toughness [11], [13], [14].

1.4 Mechanisms of Reinforcement in Polymer Composites

The incorporation of fillers and fibers to polymers, including thermoplastics, helps to enhance their stiffness and strength. The mechanism involves strong inclusions bearing the load while the matrix serves to bind those particulates or fibres and facilitates load transfer between them. So, the matrix phase will only sustain a small fraction of the externally applied stress, while the majority is borne by the inclusions. This mechanism functions optimally when the fillers/fibers are inherently strong and stiff, well dispersed, possess sufficient content and length, and exhibit strong adhesion with the polymer matrix [15], [16]. Since the stress is transmitted from the matrix to the embedded particles/fibers across the interface, it is critical to improve the bonding between the matrix and fillers to ensure efficient load transfer. The bonding strength between the two constituents can be enhanced by the addition of coupling agent as well as treating the fibers' surface with a chemical. Silane coating is widely used for glass fibers sizing. Adopting both treatments options will result in improved synergistic effects concerning the interfacial adhesion [1]. In addition, the length of the fibers, as well as their aspect ratio, is of paramount importance in altering the mechanical characteristics of the composite. When subjected to stress, the bond between the fiber and matrix discontinues at the very ends of the fiber, which implies that there is no transmission of load from the matrix at both fiber's tips. So, the fiber ends or particles sharp edges act as stress concentration points, where crack starts from [16], [17], [18], [19]. Thus, to achieve effective reinforcement and enhanced stiffness in the composite, a specific critical fiber length is required. This critical length varies depending on factors such as the fiber's ultimate strength, interfacial bonding strength, and fiber diameter. To understand the importance of fiber length, three cases are assumed; if the fiber

length is exactly equal to the critical length, then the maximum load on the fiber is attained solely at the central axis of the fiber which is equal to the ultimate tensile strength of the fiber. For attaining more effective reinforcement, the fiber length should be larger than L_c , where the stress axial position covers major portion of the fiber's axial length. The last case is when the fiber is shorter than the critical length. In this situation, only minimal reinforcement is provided by the fiber, which is much less than the ultimate tensile strength of the fiber, hence the matrix will bear majority of the applied load [15], [16]. Therefore, the number of fiber ends, which corresponds to the length of fibers, is closely linked to the composite overall performance and occurrence of its failure. The following schematic diagram summarizes the three cases.

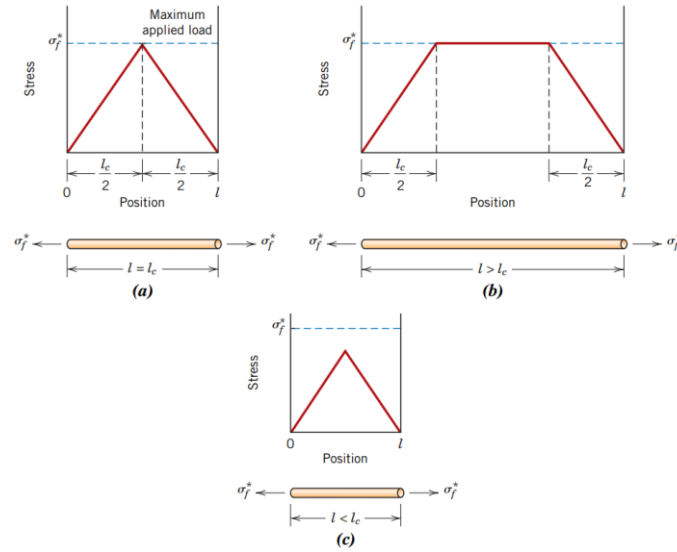


Figure 5 Fiber axial stress position for different fiber lengths (adopted from [16])

where (a) fiber length = L_c (b) fiber length > L_c (c) fiber length < L_c

Furthermore, fibers' attrition during the processing stage is a crucial factor in controlling the ultimate properties of the composite material. Fiber breakage occurs due to a combination of factors, including interactions between the fibers and the polymer matrix,

interactions between adjacent fibers, and the interaction between the fibers and the surfaces of the processing machine. In addition, increasing fiber content in the composite proved to lead to severe damage to the final fiber length due to the increased fiber-fiber interaction [20].

Moreover, rigid fibers typically demonstrate a lower fracture strain than that of the polymer matrix in most cases. As a result, the point at which composite failure initiates is marked by the moment when the fibers begin to break. However, failure of the composite is not considered catastrophic due to the fact that not all fibers break at the same stress, and even after breakage, those shorter fibers can still continue to bear a lower load while the matrix undergoes plastic deformation [16].

1.5 Mechanical properties

Materials are subjected to different types of loads while in use, and they will deform according to their mechanical characteristics. The applied load can manifest as compression, tension, or shear forces, and its intensity may either remain constant over time or fluctuate continuously. All these factors, along with the service temperature, will influence the behavior of the material throughout its service life. Furthermore, material properties such as morphological and molecular characteristics play a significant role in determining the deformation behavior of the material [16].

1.5.1 Tensile properties

A sample is typically subjected to deformation, often resulting in fracture, by applying a steadily increasing tensile force uniaxially along the specimen's long axis. The following section will introduce some important properties related to deformation under tensile force.

1.5.1A Elastic Modulus

When a polymer is subjected to a relatively low level of stress, it will deform elastically. This means that the polymer chains temporarily stretch in response to the applied force, resulting in a change in the material's shape or size. Once the stress is removed, the polymer returns to its original shape and size without any permanent deformation. The elastic modulus is usually calculated based on the slope of the stress-strain curve at low elongation, typically in the region between 0.05% and 0.25% strain. It serves as an indicator of a sample's stiffness, with higher modulus values indicating greater rigidity in the material [2], [16].

$$\text{Elastic Modulus (EM)} = \frac{\text{Stress } (\sigma)}{\text{Strain } (\epsilon)} \quad (1)$$

1.5.1B Yield point

When the applied stress on a polymer surpasses its elastic limit, it undergoes plastic deformation. In such cases, polymer chains may break or slip past each other, leading to permanent changes in shape. The yield point represents the onset of plastic deformation, and the corresponding stress is referred to as the yield strength [2], [16].

1.5.1C Tensile Strength

Tensile strength, also known as the ultimate tensile strength, corresponds to the maximum stress that a polymer can withstand [16].

1.5.1D Fracture Strength

Fracture strength corresponds to the stress at which the material fractures under a tensile load [16].

1.5.1E Elongation percentage

Elongation percentage is defined as the strain at break divided by the original gauge length [16].

$$\text{Elongation percentage} = \frac{\text{Elongation } (\Delta L)}{\text{Initial gauge length } (L_0)} \quad (2)$$

1.5.1F Toughness

Toughness is the ability of a material to absorb energy and undergo plastic deformation until reaching the point of fracture. The area under the stress-strain curve can be used to quantify it [16].

The following figure represents the different deformation stages of polymer sample being exposed to tension force.

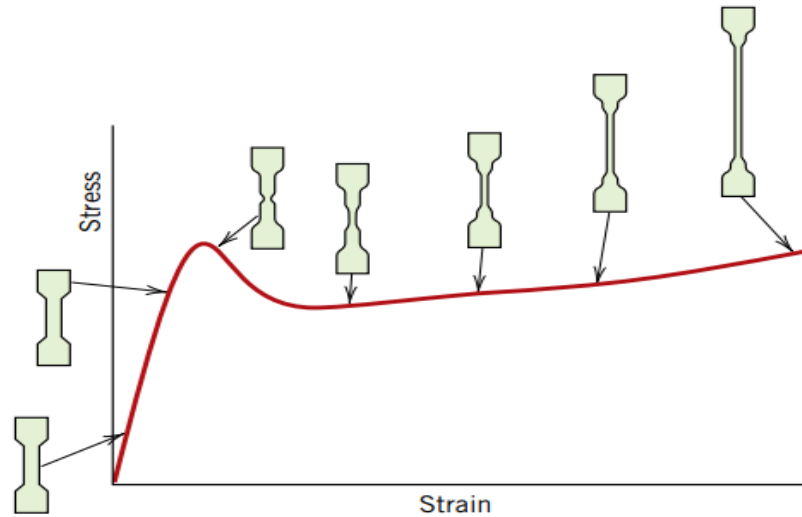


Figure 6 Schematic tensile stress–strain curve for a semicrystalline polymer [16]

1.5.2 Flexural test

Flexural test, also called bend test, evaluates how materials respond when subjected to beam load. During the test, the specimen undergoes bending, experiencing various types of forces such as tension, compression, and shear. Flexural test can be conducted either as a three-points or four-points bend test, with the latter typically employed for highly brittle materials. In the case of polymers, the 3-points bend test is commonly used. In this test, the specimen is positioned over two supporting noses, with a bending force applied via a single upper loading nose at the center. The test is concluded either when a maximum strain of 5.0% is reached or upon fracture, whichever occurs first [21]. The following properties are determined by the flexural test.

1.5.2A Flexural strength

Flexural strength is the maximum stress obtained during the bending test [22].

1.5.2B Flexural Modulus

Flexural modulus is determined from the initial linear segment of the stress-strain curve by calculating its slope, i.e. in the region between 0.5 to 1.0 strain %. It is an indication of the material's stiffness [22].

1.5.3 Impact strength

Impact strength measures the absorbed energy by the material upon a sudden impact, providing insights into how far the material is from brittle failure [1]. There are several methods for determining the impact strength, including Izod, Charpy, and drop weight impact tests. In the Izod impact test, the tested bar is placed vertically, with one end clamped while the other free end is struck by a heavy pendulum [2]. Higher Izod impact strengths indicate higher toughness and better impact resistance of the material. In automotive applications, knowing the impact strength of the material is crucial for predicting its behavior and response during use, such as in traffic accidents or instances of stone impact on a car bumper.

CHAPTER 2

LITERATURE REVIEW

2.1 State of art for properties enhancement of Polypropylene composites

Talc, kaolin, calcium carbonate, and mica are commonly employed to reinforce thermoplastics and decrease the production cost of molded samples. The addition of filler to the polymer can modify its crystalline structure, as it can act as a nucleating agent, leading to subsequent variations in its mechanical and thermal characteristics. Likewise, and in order to fulfill the requirements of withstanding higher loads in engineering applications, synthetic fibers, such as glass and carbon fibers, gained attention for reinforcing PP due to their high elastic modulus and strength. Rudrappa and Srinivasachar [23] explored the impact of adding glass fibers (GF) and carbon fibers (CF) to polypropylene composites. They observed an enhancement in tensile modulus/strength and flexural modulus with increasing fiber loading, while elongation at break of the compounds decreased, indicating a reduction in the ductility of the reinforced composites. A similar phenomenon was reported by Várdai et al. [24] and Rasana & Jayanarayanan [25]. Table 1 summarizes the mechanical properties of glass fiber reinforced polypropylene composites from various papers in the literature.

Table 1 Summary of mechanical properties of PP/Glass fibers composites

Glass fiber (wt.%)	10 %	20 %		30 %		Ref.
Property	Value	Value	Change*	Value	Change*	
Tensile Strength (MPa)	27.3	41.7	53 %	49.1	18 %	[26]
	50	67	34 %	75	12 %	[24]
Tensile Modulus (GPa)	5.1	8.5	67 %	10.6	25 %	[26]
	4.0	6.0	50 %	8.0	33 %	[24]
	2.4	4.5	88 %	6.5	44 %	[27]
Flexural Strength (MPa)	63.2	92.8	47 %	93.7	1 %	[26]
Flexural Modulus (GPa)	5.3	8.0	51 %	8.3	4 %	[26]
	2.2	4.3	97 %	6.3	45 %	[27]
Impact Strength (KJ/m ²)	4.4	4.0	- 9 %	4.6	15 %	[26]
	17	11	- 35 %	11	0 %	[27]

* Percentage change compared to the preceding loading

While fibers provide a higher degree of reinforcement for polypropylene, their cost is higher compared to particulates. Consequently, to optimize the cost/performance balance of the developed composite, the decision was made to also consider evaluating a particulate filler in addition to glass fibers. Talc, a hydrated magnesium silicate mineral with the

chemical formula $3\text{MgO}\cdot 4\text{SiO}_2\cdot 3\text{H}_2\text{O}$, and Calcium Carbonate (CaCO_3) are considered among the most widely used reinforcements for PP in the industry. They are relatively inexpensive, naturally available and exhibit high strength and good dimensional stability [28]. Several factors affect the stiffening efficiency of fillers, including their structure, size, and shape, along with the interfacial adhesion strength with the polymer matrix. Commercial fillers exhibit various shapes and aspect ratios. Generally, reinforcing efficiency improves with anisotropy, providing an advantage for platelet-like fillers such as Talc and Mica over spherical particles like CaCO_3 [29]. Due to its high aspect ratio, i.e., plate-like particles, Talc is known to improve the mechanical strength of polyolefins to a greater extent than CaCO_3 , which has round-shaped particles [28]. Several studies in the literature report better reinforcement of Talc over CaCO_3 in terms of stiffness for PP, while the latter contributes to higher impact strength [30], [31], [32]. Another study shows that the nucleation density, i.e. the number of nucleation sites, for Talc is significantly higher than for CaCO_3 . This indicates a higher crystallinity level and, hence, better stiffness [18]. Therefore, Talc was chosen as the reinforcing filler in this study. In addition, the size of filler particles influences reinforcement efficiency, with smaller particles demonstrating greater effectiveness owing to their larger surface area. The increased surface area facilitates enhanced stress transfer between the matrix and filler. Also, particle size influences debonding stress, with larger particles debond more easily from the matrix due to their lower debonding stress. It should be noted that commercial fillers typically have a wide particle size distribution, hence the debonding occurs across a broad strain range [33].

Moreover, PP homopolymer exhibits low impact strength, particularly at low temperatures, which can be enhanced by adding rubbers or impact modifiers to PP through

blending in the extruder. Impact modifiers have a low elastic modulus compared to the polymer matrix due to their rubbery nature. This rubbery phase absorbs impact energy, preventing the propagation of cracks and crazes within the PP composite [34]. Generally, the impact resistance of homo-Polypropylene can be modified either by copolymerizing propylene with other monomers, i.e. in-situ (in the reactor), or by blending with impact modifiers or other polymers, i.e. post-reactor (in the extruder) [34]. The latter is widely used in the plastic industry due to its lower cost and the variety of impact modifier options available. Several reports in the literature have studied the influence of incorporating different rubbers on PP toughness. For example, Styrene Ethylene Butylene Styrene (SEBS), Ethylene Propylene Diene Monomer (EPDM), Styrene [Ethylene (Ethylene-Propylene)] Styrene (SEEPS) and Ethylene Propylene Rubber (EPR) were blended with PP, and their mechanical behavior was reported [13], [35], [36]. In addition, Polyolefin Elastomers (POE), which are Ethylene-alpha-olefins copolymers (such as Ethylene-Butene or Ethylene-Octene copolymer) produced using Metallocene catalysts, are highly important in the plastic industry because they can be processed as thermoplastics while possessing elastic properties similar to rubbers. POE has replaced about 70% of traditional EPDM impact-modified polyolefins. This is mainly due to their low density, low crystallinity, and availability as free-flowing pellets, making POE easier to handle and process than standard rubbers [28]. Several reports in the literature have compared the impact modification efficiency of EPDM and POE. Results revealed that POE is more effective in enhancing the impact resistance of PP than the traditional modifier, EPDM [37]. In addition, Da Silva et al. [38] reported that POE viscosity is closer to PP than EPDM, hence better processability of PP/POE blend compared to PP/EPDM as confirmed by its

lower torque. Also, by varying the comonomer type, i.e. Ethylene-Butene vs. Ethylene-Octene, the performance of the POE differs because of the different densities and chemical structure, which in turn would dominate the performance of the PP/POE blend. To illustrate, Doan et al. [39] tested three different POEs, i.e. two C2-C8 copolymers and one C2-C3 copolymer. Results revealed that the Ethylene-Octene based POE significantly improved the impact toughness of the composite to a greater extent, i.e. 300 – 500%, compared to their rival. In addition, Liang [40] studied the impact of adding POE to PP at different loadings. Results revealed that upon increasing POE level in the blend, tensile modulus/ strength, flexural modulus/ strength and tensile elongation at break decreased, while impact resistance improved significantly. Sadeghi et al. [41] observed an improvement of about 115% in the elongation at break by adding 20 wt.% of POE to PP, but tensile strength and modulus decreased.

Furthermore, polymeric fibers can serve as reinforcing agents. Polyvinyl Alcohol (PVA) fibers, for example, are frequently employed to strengthen concrete and cementitious composites. Due to their high aspect ratio, large elastic modulus, excellent affinity with water, and compatibility with cement, PVA fibers have been used as a strengthening additive for concrete to effectively suppress crack propagation [42], [43]. According to Noushini et al. [44], compressive strength of concrete composites increased by 12% by adding 0.25 wt.% of PVA fibers. Another study showed an increase in flexural strength of about 48% for concrete/PVA fibers composite upon addition of 2 wt.% PVA fibers, and toughness improved 75 times compared to the control concrete sample [45]. However, the application of PVA fibers has been extended to the polymer industry as well. For example, Phong et al. [46] reported an increment in the elastic modulus and tensile

strength of about 5-8% with the addition of only 0.1 wt.% PVA fibers to an Epoxy/Carbon fibers composite. For thermoplastics, blending PP with PVA, where PVA is in pellet/granule form rather than fibers, has been thoroughly studied in the literature [47], [48], [49], [50] and proved to alter different properties, mainly barrier and thermal properties of the blend. For example, blending PP with PVA pellets, resulted in an immiscible blend because of the hydrophilic nature of PVA, resulting in lower mechanical properties compared to virgin PP. Yan et al. [47] reported lower Young's modulus of about 30% and elongation percentage by about 15% measured on melt spinning fibers of PP/PVA blend. They reported that the addition of a compatibilizer, i.e. Janus kaolinite particles, helped to improve the adhesion between the two polymers which led to better mechanical properties than the untreated PP/PVA blend, but still lower than virgin PP. In addition, another application of PVA in pellet form is for packaging, for example in food wrapping, where PP-PVA blend acts as a barrier layer. Jang and Lee [48] blended PP and PVA, both in pellet form and in the presence of a compatibilizer, then stretched the blend biaxially into a thin film. They reported higher oxygen barrier property by more than 130 times compared to the neat PP film, i.e. lower oxygen transmission rate, while moisture permeability increased. Moreover, Yan et al. [49] investigated the morphology of a PP/PVA blend with a 70/30 wt.% ratio. This blend can be used as a precursor to prepare a porous structure by incorporating 1 wt.% Silica nanoparticles, aiming to control the microstructure of the blend. Another study explored the impact of montmorillonite filler on the thermal properties and stability of a PP/PVA blend. The blend was subsequently spun using the melt spinning process, and the resulting fibers were tested. The results indicated that the crystallization temperature increased with the addition of

PVA/montmorillonite to PP, while the overall crystallinity level and thermal stability decreased [50].

On the other hand, the use of PVA in fiber form, in PP has started to be explored recently, and has been proven to have a positive influence on its mechanical properties. PVA fibers are very strong, demonstrated by their high Young's modulus, i.e. higher than 35 GPa. This could be attributed to the extensive hydrogen bonding that exists between the polymer chains, leading to strong intermolecular interactions [51]. In addition to having high strength, PVA fibers have much lower density than Carbon and Glass fibers, i.e. 1.3, 1.8, 2.5 g/cm³ for PVA, Carbon and Glass fibers, respectively. This low density of PVA fibers leads to lighter weight parts, thus resulting in less fuel consumption, while still satisfying the high rigidity needed for automotive applications. A recent study investigated the effect of two polymeric fibers, PVA and PET fibers, on homopolymer PP (hPP) and heterophasic PP copolymer (ICP) [52]. Results revealed that both fibers increased tensile modulus/strength and impact strength of PP composite, but the increment with PVA fibers was to a larger extent. To illustrate, PP homopolymer modified with PVA fibers exhibited a tensile modulus and impact resistance of about 3 GPa and 40 kJ/m², respectively, compared to 2 GPa and 15 kJ/m² with PET fibers. It is worth mentioning that the authors reported a decrease in impact resistance for the hPP/PVA fibers sample when a coupling agent is added, i.e. addition of PP grafted Maleic Anhydride, unlike the tensile modulus which was found to be independent of interfacial adhesion [52]. Sobczak et al. [53] have also examined the effect of PVA fibers in hPP and ICP, and a similar conclusion was drawn regarding the toughness and stiffness improvement for PP/PVA fibers composites, where tensile strength/modulus and impact strength increase significantly as a function of PVA

fibers loading level. Similarly, Vardai et al. [54] claimed more plastic deformation takes place for polypropylene composites prepared with PVA fibers compared to other natural stiff fibers, such as wood and flax fibers, which in turn shows better impact strength in addition to its reinforcing ability. Furthermore, in an attempt to enhance the dispersion of PVA fibers within the hydrophobic PP matrix, Nishikawa et al. [51] developed a technique where PVA powder is first diluted in an aqueous solution and then introduced into molten PP through a nozzle to the extruder. Excess moisture was removed through a wide vacuum venting port located at the end of the extruder. Due to the viscosity difference between PP and PVA, PVA takes on a fibrous form when subjected to flow within an extruder upon rapid solidification process. The achieved homogeneous dispersion of PVA fibers resulted in no agglomeration, and the composite exhibited higher Young's modulus, yield strength, flexural modulus, and heat deflection temperature compared to neat PP [51].

As presented above, the incorporation of solid fillers to PP would increase stiffness at the expense of toughness. However, elastomer-modified PP composites exhibit high impact strength but with decreased stiffness, especially at high elastomer loadings. This could impede the use of PP in some applications. Fortunately, the combination of elastomers and fibers/fillers, through hybridization, would retain toughness and strength of the PP composites. Hybrid composites are reinforced materials by incorporating two or more different fillers or fibers into the matrix. Various studies revealed that the concurrent addition of soft and rigid fillers into PP would result in a good stiffness/ toughness balance. According to Premphet and Horanont [37], a desired balance of toughness and strength, i.e. impact strength/ tensile modulus, of PP composite is achievable through the hybridization of CaCO_3 and POE. Results showed that the addition of 20 wt.% POE + 20

wt.% coated CaCO_3 exhibits a bit higher modulus with 2000% improvement in impact strength compared to the neat PP sample. Similar conclusion was made by Wu et al. [55] for the hybrid composite of PP/POE/Talc, where flexural modulus and impact strength improved by 80% and 60%, respectively, compared to neat PP. Yang and Xu [56] characterized the ternary composite system of PP/POE/GF. They observed that the hybrid composite, with the presence of a compatibilizer, exhibited a dramatic increase in impact toughness while maintaining the tensile properties within accepted ranges. In a similar manner, Vardai et al. [57] studied the mechanical and thermal properties of PP/Talc/PVA fibers hybrid composites. They concluded that Talc improved stiffness, PVA fibers primarily enhanced impact strength, and the hybridization of both fillers retained a good balance between stiffness and toughness. To illustrate, the Young's modulus (GPa) and impact strength (KJ/m^2) for PP with 20 vol.% Talc, PP with 20 vol.% PVA fibers, and PP with 20 vol.% talc/20 vol.% PVA fibers were as follows: 5.5 - 2, 2.5 - 27, and 4 - 18, respectively. They also tested PP/PVA fibers hybrid composites with three different reinforcements, i.e. GF, CF and wood [58]. They reported a possible combination of high impact strength (20–25 KJ/m^2) with enhanced stiffness (4–6 GPa) achieved with the hybrid systems. In addition, Ferdinand et al. investigated the efficiency of two impact modification approaches in Talc filled polypropylene composite [59]. Their results demonstrated that the PP/Talc/PVA fibers hybrid composite was more effective than the PP/Talc/POE hybrid composite in enhancing both stiffness and toughness.

Furthermore, the inclusion of a compatibilizer can enhance the interfacial adhesion between fillers/fibers and the polymer matrix, potentially resulting in improved mechanical properties. This is because the stress transfer through the interfaces is improved and borne

by the fibers/fillers. Polypropylene-grafted-Maleic Anhydride (PP-g-MA) and POE-g-MA, employed as coupling agents, were found to improve the interfacial adhesion between glass fibers and PP. The addition of PP-g-MA and POE-g-MA exerted a significant influence on the tensile strength and impact strength, with a slight effect observed on the tensile modulus of the PP/POE/GF hybrid composite [56]. Hassan et al. [60] reported an increase in tensile strength/modulus and flexural strength/modulus upon addition of PP-g-MA for PP/GF composite. Other coupling agents were also investigated. Zhang et al. [61] compared the efficiency of four different compatibilizers; PP-g-MA, POE-g-MA, PP-grafted-Glycidyl Methacrylate (PP-g-GMA), and SEBS-g-MA in PP/GF/wood hybrid composites. Results revealed that PP-g-MA outperformed all other tested compatibilizers in terms of improving tensile, flexural and impact properties of the hybrid composites. In addition, the effect of adding compatibilizers to some polymeric fiber-based PP composites was discussed in the literature. According to Várdai et al. [62], the addition of PP-g-MA demonstrated a pronounced improvement in the tensile strength of the PP/PET fiber hybrid composite reinforced with either CF, GF, or wood, while the effect was not as efficient for impact strength and tensile modulus. Also, a study showed that addition of PP-g-MA to hPP/PVA fiber composite significantly improved the tensile strength, while impact resistance was negatively affected [52]. Similarly, tensile properties of the hybrid composites of PP/PVA fiber with either CF, GF, or wood fibers were enhanced by adding PP-g-MA, while impact strength of notched samples for the hybrid composite decreased (unnotched samples behave contrarily) [58].

From the summarized literature review, and to the best of my knowledge, the literature lacks information on the potential synergistic effect between PVA fibers and POE on the mechanical properties of reinforced composites based on Polypropylene matrix.

2.2 Objective of present work

To the best of my knowledge, there is no published work in the literature which studied the effect of PVA fibers/POE hybridization on the properties of polypropylene composites. Accordingly, the aim of this study is to verify the possible synergistic effect between PVA fibers and POE on the mechanical properties of composites based on Polypropylene matrix through hybridization for the ternary and quaternary systems, i.e. PP/POE/PVA fibers and PP/POE/PVA fibers/filler. The main attention will be focused on achieving a good stiffness/toughness balance by studying the tensile and impact strengths properties of the developed composites.

In the above context, the present work is carried out. In this study, Talc, Glass fibers, POE and PVA fibers were selected to reinforce Polypropylene as single and hybrid reinforcements at different loading levels in the presence of PP-grafted-Maleic Anhydride as a compatibilizer.

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Methodology

Polypropylene and the different fillers/fibers were melt compounded using a co-rotating twin-screw extruder, in the presence of a compatibilizer to improve the adhesion between the polymer matrix and filler. The produced pellets were then injection molded into specimens with specific dimensions for subsequent mechanical, thermal and microstructure analysis. Due to the hydrophilic nature of PVA, samples containing PVA fibers were placed in the dryer for 4 to 6 hours at 80 °C prior of being injection molded in order to remove any residual moisture. The main characterization techniques are the following:

- Mechanical analysis:
 - Tensile test using Universal Testing Machine (Model: INSTRON® 3367) following ASTM D638 standard.
 - Three-point bend test for flexural properties using Universal Testing Machine (Model: INSTRON® 3367) following ASTM D790A standard.
 - IZOD impact test using pendulum impact tester (Model: Zwick HIP50P ML 010) following ASTM D256 standard.

- Morphological analysis:
 - Scanning Electron Microscope (SEM) test using JEOL Model JSM-6610LV.
- Thermal analysis:
 - Differential Scanning Calorimetry (DSC) test using TA Instrument Model Q1000 following ASTM D3418 standard.

3.2 Materials

Polypropylene homopolymer used as a matrix (grade code: PP 500P, melt flow index: 3 g/10min @230 °C/2.16 Kg, and density: 0.905 g/cm³) is produced by SABIC. The Polyolefin Elastomer (POE), SABIC FORTIFY™ C1070D, is an Ethylene-Octene copolymer produced by solution polymerization using Metallocene catalyst (melt flow index: 2 g/10min @230 °C/2.16 Kg, and density of 0.868 g/cm³). Polyvinyl Alcohol fibers are produced by BOC Science having an average original length of 6 mm and 55 µm average diameter. Glass fibers of around 6 mm initial length, 13 µm diameter and coated (sized) with Silane are obtained from Qingdao Segoe, China. The Talc masterbatch “PP-050” produced by Clariant, was used as received. The masterbatch contains approximately 58% Talc in a homo polypropylene carrier. A compatibilizer, “SCONA TPPP 6102GA”, which is a Polypropylene functionalized with Maleic anhydride masterbatch, is kindly provided by BYK with a melt flow rate (MFR) of 20-40 g/10min (@190 °C/2.16 Kg) and

Maleic anhydride content higher than 0.9 wt.%. The following table shows the characteristics of the glass and PVA fibers as received.

Table 2 Glass and Polyvinyl Alcohol fibers properties

Material	Glass fibers	Polyvinyl Alcohol fibers
Fiber length* (mm)	6	6
Fiber diameter* (μm)	13 - 15	50 - 60
Specific gravity*	2.5	1.3
Elastic Modulus* (GPa)	65-75	36.5
Tensile Strength* (MPa)	NA	1645
Elongation* (%)	5	6.5

* Average values as reported by supplier

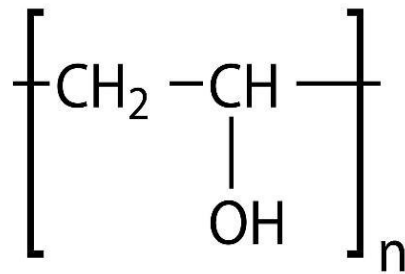


Figure 7 PVA Chemical Structure



Figure 8 PVA fibers used in this study

Furthermore, the following table shows the average market price of the used materials as indicated from different sources (December 2023).

Table 3 Average market price of the used materials

Material	Price (USD/Kg)	Ref.
PP	1.0 – 1.2	[63]
POE	2.2 – 2.6	[64]
PVA fibers	2.5 – 3.5	[65]
Glass fibers	1.5 – 2.5	[66], [67]
Talc	0.2 – 0.4	[66], [67]

3.3 Formulations

Based on the summarized data presented in Table 1 above, it has been decided to fix the loading of glass fiber at 20 wt.% of the total formulation, as it was found to be most efficient in increasing the stiffness of PP composites compared to other loadings. To illustrate, the percentage improvement in tensile and flexural properties at 20 wt.% glass fibers was higher than at 30 wt.% when compared to its preceding loading (i.e., 20 vs. 10 wt.% and 30 vs. 20 wt.%). The benefits gained at 20 wt.% GF loading are higher when comparing the improvement in stiffness obtained to the cost of adding 30 wt.%. With regards to the POE loading, McNally et al. [68] studied the effect of elastomer content on the impact strength and tensile elongation percentage of PP/POE blend over the whole range from 0 to 100 wt.% POE. Results revealed that at 23 °C, the highest impact strength and tensile elongation percentage were obtained at about 15 wt.% POE, after which the impact resistance declined mainly due to phase separation resulted at higher POE loading. So, in this study, POE loading will be kept at 15 wt.%. In addition, based on literature data [53] as well as the supplier's recommendation, a fixed amount of the coupling agent is added to all formulations, i.e. 2 wt.% of the total weight of the composite. The addition of PP-g-MA helps to improve the adhesion and compatibility between the polymer matrix and filler.

Therefore, the following tables show the proposed formulations to be evaluated. Table 4 for the binary and ternary composite systems measured in weight fraction (wt.%). For the quaternary composite systems, i.e. Table 5, volume fraction (vol.%) is used. Volume fraction (vol.%) is preferred over the weight fraction (wt.%) for composites with

multiple fillers/fibers, because the mechanical properties of composite materials depend on their volume, not their weight. In a composite material, the reinforcing fibers or particles occupy a certain volume within the composite, and it is this volume that contributes to the material's strength and stiffness. For example, Halpin-Tsai equation or the rule of mixture models depend on volume fraction to predict the mechanical strength of the composite material. Therefore, the volume fraction is a more accurate measure of the amount of reinforcement in a composite material than the weight fraction. In Table 5, the ratio of POE to PVA fibers changes (e.g. 75:25, 25:75, etc.) to study its effect on the mechanical properties. All samples contain a fixed amount of PP-g-MA, i.e. 2 wt.% out of the total weight of the composite, to improve the adhesion between the polymer matrix and filler.

Table 4 Proposed formulations for the binary and ternary systems

Sample code#	PP + PP-g-MA	POE	PVA fibers	Glass fibers	Talc
A	100				
B	85	15			
C	80		20		
D	80			20	
E	80				20
F	65	15	20		
G	65	15		20	
H	65	15			20
I	60		20	20	
J	60		20		20

* Note: Units are weight fraction wt.%

Table 5 Proposed formulations for the quaternary systems

Sample code #	PP + PP-g-MA	POE	PVA fibers	Glass fibers	Talc
K	55 (46.4)	27.08 (21.9)	9.03 (10.9)	8.9 (20.8)	
L	55 (45)	19.1 (15)	17 (20)	8.9 (20)	
M	55 (44.6)	17 (13.2)	19.1 (22.2)	8.9 (20)	
N	55 (43.3)	9.03 (6.8)	27.08 (30.6)	8.9 (19.3)	
O	55.5 (46.4)	27.3 (21.9)	9.1 (10.9)		8.1 (20.8)
P	55.5 (45)	19.3 (15)	17.1 (20)		8.1 (20)
R	55.5 (44.6)	17.1 (13.2)	19.3 (22.3)		8.1 (20)
S	55.5 (43.2)	9.1 (6.8)	27.3 (30.6)		8.1 (19.4)

* Note: Units are volume fraction vol.%. Values between brackets are weight fraction wt.%

3.4 Compounding process

A co-rotating twin-screw extruder manufactured by Brabender® (Model: TSE20/40, 20 mm screw diameter and a length to diameter ratio (L/D) of 40) was used. Table 6 shows the technical specifications of the used extruder.

Table 6 Brabender TSE 20/40 specifications

Property	Value
Motor power	16 KW
Maximum operating temperature	400 oC
Maximum operating melt pressure	350 bars
Screws	Two screws corotating to the left
Maximum torque	80 Nm
Maximum screw Speed	350 rpm



Figure 9 Brabender TSE20/40 extruder

Furthermore, due to the feeding difficulties encountered when dealing with low bulk density materials like PVA fibers, it was decided to prepare a masterbatch of PVA, which will then be added to the composite. In this work, the masterbatch of PVA fibers, which consists of 60 wt.% PVA fibers in 40 wt.% PP carrier, was prepared firstly at the following conditions: temperature profile 165-175-185-190-195-200 °C at 15 rpm screw speed. Then, the prepared PVA fiber masterbatch was compounded again with PP and the other fillers according to the formulations to obtain the corresponding compositions.

Prior to compounding, the required amounts of each component, as per the formulation, were initially weighed and dry-blended manually. Then, the mixture was fed into the main hopper. The mixture was loaded from the first top opening through the V-shape hopper (Figure 9) because there were no side feeding or alternative top feeding port openings available. The extruder was run at a screw speed of 25 - 30 rpm, throughput rate of 2.0 - 2.7 kg/hr and melt temperature of 203 - 206 °C (temperature profile: 170-175-185-190-195-200 °C, Die temperature 200 °C). The lowest possible processing temperatures were chosen, clearly over the melting temperature of polypropylene but securely below the PVA fibers melting point. The melt pressure ranged between 30 - 60 bar, and the torque was between 40 and 65 Nm. Three kilograms of pelletized material were collected for each formulation.

Moreover, the screw has a helical shape with channels, ensuring the melting and pushing of the molten polymer forward inside the barrel toward the die. This design helps to build up pressure to overcome the flow resistance from downstream units, including the die plate. Screw can be designed in different ways by altering its elements. In these experiments, the screw was designed to contain one kneading block, two left-handed

mixing elements, along with the conveying and mixing elements, to give enough intensity of mixing and residence time in the compounding process to ensure homogeneous product. It is to be mentioned that a couple of different screw configurations were assessed and tested before selecting above mentioned configuration in order to optimize the screw design to ensure optimum product homogeneity and best quality. For example, repositioning the one kneading block element, i.e. placed in the first third of the screw, and testing the installation of three different kneading blocks were considered. The selection of the screw configuration, as shown in Figure 10, was based on the dispersion and homogeneity of fillers/fibers, tested on a compressed thin film of about 250 microns thickness, as well as extrusion pressure and torque.

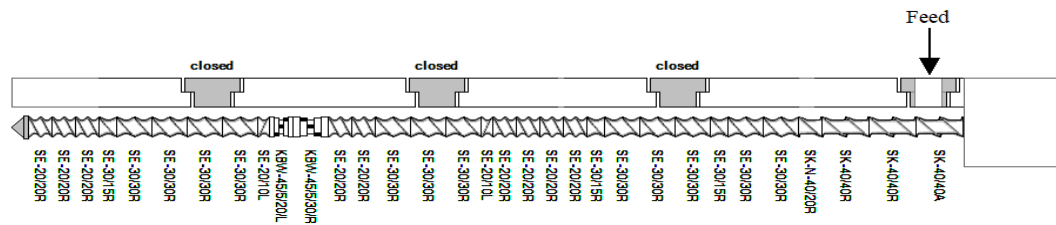


Figure 10 Screw configuration [adopted from Brabender screw configuration software]

Furthermore, the extruded polymer strand was then cooled down by passing through a water bath, after which it entered the granulator to pelletize the polymer strand into the specified pellet size. Pellet size was set to be about 6.5 mm in order to preserve the original length of glass and PVA fibers to the best of our ability.



Figure 11 Water bath to cool the extruded polymer strand as it emerged from the die



Figure 12 Granulator to pelletize the cooled polymer strand

3.5 Injection molding process

Injection molding is a process in which the polymer undergoes melting inside the barrel due to the heat generated by the heating bands and shearing force created by the rotating screw. This process results in a thoroughly melted and uniformly mixed polymer blend. Then, molten polymer is injected into the closed mold by a high injection pressure, after which it will be cooled down to take the final shape of the mold. Once the cooling step is completed, the mold opens and ejector pins will push the finished molded sample out of the mold. The injection molder used in this research is manufactured by Battenfeld, model HM 1000/750.



Figure 13 Battenfeld HM 1000/750 Injection molder

During the injection molding experiments, samples were prepared sequentially. Each sample underwent a sequence starting with the tensile mold, followed by the flexural mold, and finally the Izod mold. This sequence was repeated for subsequent samples after purging with a specific amount of the sample itself. The following table shows the injection molding conditions used to stabilize the process and get a well molded part.

Table 7 Injection molding conditions

Property	Value
Temperature profile	170 – 185 – 200 – 205 °C
Clamp force	1000 kN
Injection pressure	800 – 950 bar (depending on fibers/filler content)
Injection speed	50 mm/s
Holding pressure	600 - 800 bar (depending on fibers/filler content)
Back pressure	30 bar
Screw speed	200 rpm
Cooling time	15 sec.
Holding time	15 sec.
Injection time	1 sec.
Total cycle time	35 sec.
Mold temperature	60 °C



Figure 14 Izod, Flexural and Tensile molds

3.6 Tensile test

Tensile experiments were conducted using a universal testing machine “Instron 3367” at a crosshead speed of 5 mm/min according to ASTM D638. The following properties were obtained from the generated stress-strain curve: Tensile properties (modulus and strength), yield properties, and the elongation percent. Tensile results reported are the average of 8 specimens tested for each sample. The following picture shows the tensile tester used, indicating the main components. During tensile test, the crosshead moves upward at the pre-specified test rate.

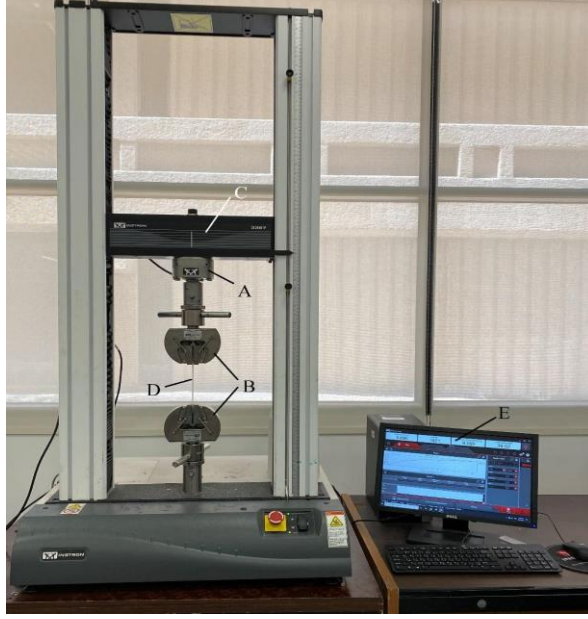


Figure 15 Tensile testing machine “Instron 3367”

where A: Load cell. B: Grips. C: Crosshead. D: Specimen for test. E: Bluehill Software

3.7 Flexural test

Flexural experiments were conducted using a universal testing machine “Instron 3367” following ASTM D790 Procedure A (strain rate of 0.01 mm/mm/min) type I, i.e. ASTM D790-AI. The strain is being determined from the crosshead displacement. According to the standard, specimens are having rectangular shape with the following dimensions: 127 mm length, 3.2 mm thickness, and 12.7 mm width. Support span is 16 times the specimen’s thickness, which is equal to 51.2 mm [69]. Test speed is a function of specimen’s thickness, support span and strain rate. It is calculated based on the following equation:

$$R = \frac{z L^2}{6 d} \quad (3)$$

where: R = test speed (mm/min), L = support span (mm), d = specimen's thickness (mm), Z = strain rate (which is equal to 0.01 mm/mm/min for procedure A) [69]. So, $R = 1.36$ mm/min. Flexural results reported are the average of 6 specimens tested for each sample.

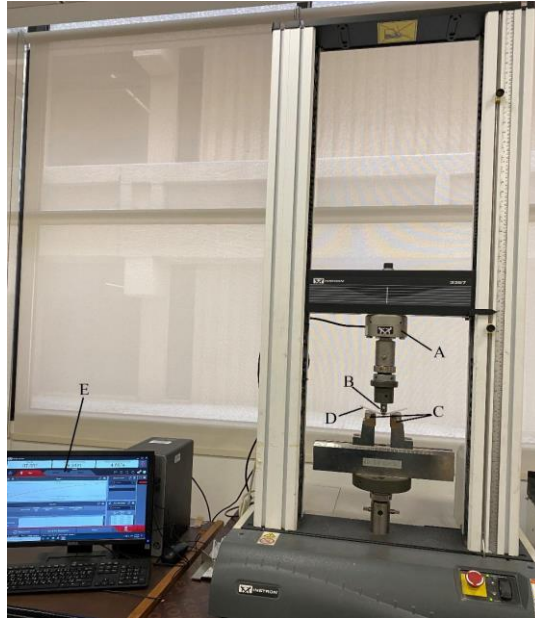


Figure 16 Flexural testing machine “Instron 3367”

where A: Load cell. B: Upper loading nose. C: Two support noses. D: Specimen. E: Bluehill Software

3.8 Izod impact test

Notched Izod impact strength was used to assess the impact resistance of the composites. Izod test was done using “Zwick, model: HIP50P ML 010” according to ASTM D256 with a V-notch shape of 2.54 mm notch depth, where the notching was done on a milling machine. The notched side is oriented toward the hammer's striking edge. The test was performed at room temperature. The impact strength is determined by dividing the

energy absorbed by specimen's thickness, i.e. J/m. The velocity of the striker is about 3.5 m/s. Izod impact results reported are the average of 8 specimens tested for each sample.

3.9 Scanning Electron Microscope test

The Scanning Electron Microscope (SEM) is considered a powerful and easily operated microscope that is widely used. It generates high-resolution pictures that enable the examination of microscopic structures and surface features. The SEM images are formed by applying a focused electron beam over continuous cross-sections of the sample to generate secondary electrons and back-scattered electrons. Depending on the operating mode, one type of the generated electrons is received and converted to photons to be displayed as a final image [70]. The broken surface of tensile tested specimens was sputtered with Gold before recording the micrographs by SEM to create a continuous conductive thin layer. SEM was performed using JOEL Model JSM-6610LV.

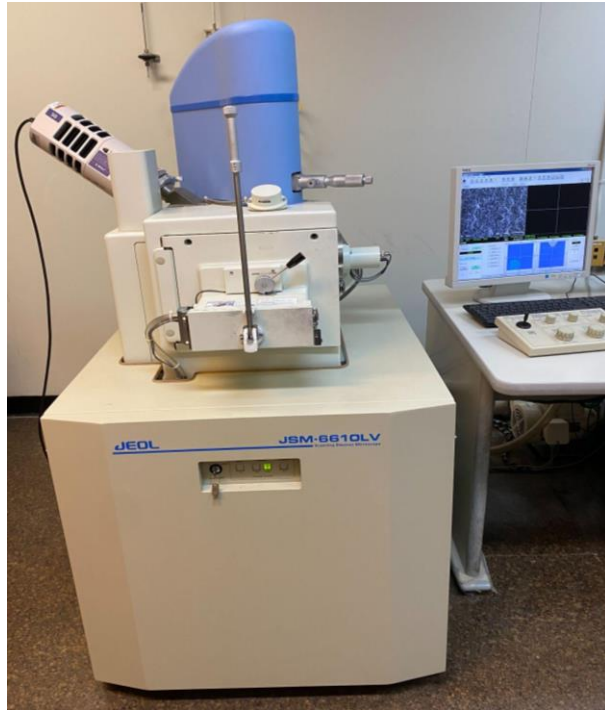


Figure 17 Scanning Electron Microscope machine “JEOL JSM-6610 LV”

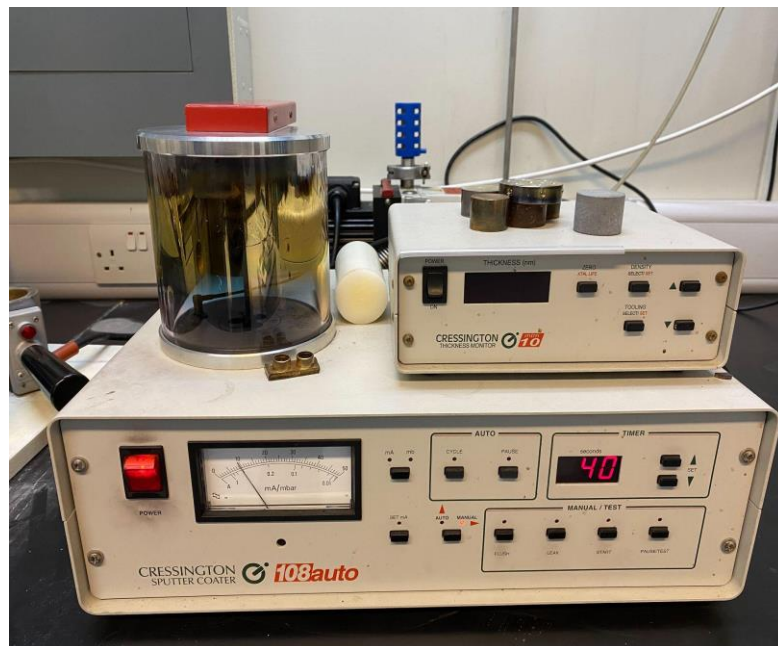


Figure 18 Sputtering machine

3.10 Differential Scanning Calorimetry test

Differential Scanning Calorimetry (DSC) test is used to determine the thermal properties of materials, including for example transition temperatures and enthalpies of crystallization/melting. According to ASTM D3418, DSC test for polymers follows this sequence: heating to X °C, hold the sample at X °C for 5 minutes, then cooling down to Y °C and hold at Y °C for 5 minutes. This cycle is repeated once. For Polypropylene, X was set to be 220 °C, and Y is 30 °C. The first cycle is intended to erase the thermal history of the sample, which it undergoes during the fabrication process. The heating and cooling rates were set to be 10 °C/min in Nitrogen atmosphere. Melting and crystallization temperatures, as well as the heating and crystallization enthalpies, are determined from the generated thermogram [71]. Crystallinity percentage can be calculated using the following equation:

$$Crystallinity \% = \frac{\Delta H_m}{\phi \Delta H_m^0} \times 100\% \quad (4)$$

where ΔH_m is the measured melting enthalpy, ϕ is the weight fraction of matrix PP in the composite, and ΔH_m^0 is melting enthalpy for 100% crystalline PP, which is around 207 J/g [72].

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of PVA fibers and POE hybridization on the mechanical properties

Mechanical results are divided into separate sections based on the composite type, i.e. the single-component (binary) composite systems and the hybrid composites. The latter will be further subdivided into two subsections: ternary and quaternary composite systems. It should be noted that the reported tensile, flexural, and Izod impact results in the figures below represent the averages of 8 specimens tested for each sample. The line above each bar indicates the standard deviation, i.e. sample standard deviation type is used.

4.1.1 Single component composites systems

Figure 19 shows the tensile properties for the reinforced composites along with the control sample, i.e. unfilled sample. As expected, results clearly revealed that the incorporation of Glass, PVA fibers and Talc led to an increase in composites' stiffness to different extents, while addition of the elastomer phase, i.e. POE, to PP lacks the capacity to bear any load, resulting in decreasing the rigidity of the composite. Addition of the rigid filler and fibers impart varying reinforcement effects to PP, where the addition of glass fibers yields composites that are stiffer than those obtained by adding PVA fibers or Talc. To illustrate, addition of 20 wt.% GF to PP increased the Young's modulus by about 110% over the control, i.e. 2.25 GPa, while the sample reinforced with 20 wt.% Talc had a

Young's modulus of 1.6 GPa, compared to 1.4 GPa for the sample reinforced with 20 wt.% PVA fibers. Addition of 15 wt.% of POE to PP decreased the elastic modulus to 0.84 GPa. Similar findings were reported for the tensile properties of Talc and PVA fibers, where Talc reinforced PP better while PVA fibers imparted higher toughness [57].

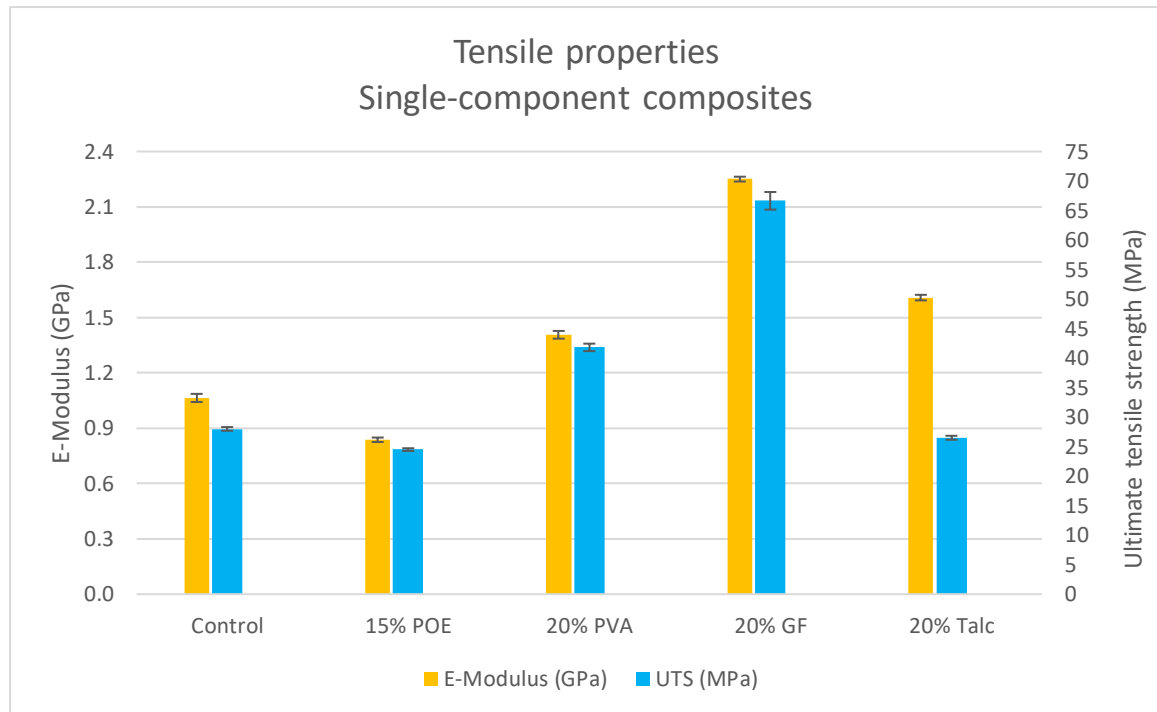


Figure 19 Tensile properties for the single-component composites systems

The higher reinforcing efficiency obtained with the glass fibers could be attributed to the fact that glass fibers inherently have higher strength than PVA fibers as shown previously in Table 2. In addition, unlike glass fibers, the polymeric fibers, PVA, are flexible and can spin, turn, bend and adjust easily without breaking which could affect their degree of orientation. Similar behaviour was observed for the flexible PET fibers in PP composites [73]. Conversely, glass fibers are more rigid hence they are more aligned in the flow direction. This will be clearly observed by the SEM images presented in the

microstructure characterization part (section# 4.2). Similarly, Talc plate-like particles are more rigid and can align along their major axis in the flow direction. Therefore, the higher degree of orientation achieved with glass fibers and Talc would impart a higher degree of reinforcement.

Moreover, like the Young's modulus, glass and PVA fibers improved the ultimate tensile strength, while with Talc, it slightly decreased compared to the control sample. The addition of POE lowered the ultimate tensile strength. For example, the ultimate tensile strength increased to 67 and 42 MPa for glass and PVA fibers composites, respectively, compared to 28 MPa for the control sample, while decreased to 26.5 and 24.5 MPa upon the addition of Talc and POE, respectively. The extent of increase is higher for the sample reinforced with glass fibers compared to PVA fibers. That is attributed to the same reasons discussed above concerning the increase in stiffness. In addition to that, the role of interfacial adhesion is critical in determining the ultimate tensile strength. That is because Young's modulus is calculated at very small strains, i.e. in the elastic region, where the effect of adhesion between fibers and matrix can be neglected, whereas fillers' rigidity is playing the significant role in affecting the modulus. Conversely, ultimate tensile strength is measured at higher deformations, where interfacial adhesion plays a critical role. In the case of glass fibers, excellent adhesion was achieved through fiber sizing as well as the addition of a coupling agent. Adopting both fiber surface coupling treatments results in fewer fibers debonding from the matrix, improving stress transmittance through the matrix-fiber interface and, consequently, results in a noticeable enhancement in strength. Bikiaris et al. [74] explored the impact of various treatments and sizing agents on glass fibers, including Silane-based components, in Polypropylene/glass fiber composites. Their

findings confirmed that the combination of polypropylene grafted Maleic anhydride compatibilizer and Silane-based sizing plays an effective role in enhancing stress transfer through the fiber-matrix interface, as indicated by the observed improvement in properties. Similar conclusion was reported elsewhere [75], where the degree of interfacial adhesion was improved upon the addition of PP-g-MA and treating the glass fiber with Silane-based sizing. In the absence of adhesion, or if it is insufficient, filler particles can debond from the polymer matrix under load at large strain ranges. When a substantial number of particles detach from the matrix due to external loading, the composite's tensile strength experiences a decline such as the case of the Talc filled sample. Such behaviour is commonly observed for particulate filled polypropylene composites [76], [77]. It is worth noting that the particle size of the filler may facilitate the debonding process making delamination from the matrix easier for larger particle sizes, hence yielding lower strength. The behaviour of Talc particles within the polymer matrix will be further explored in the morphology section.

Furthermore, and in order to validate the observed stiffness improvement from the tensile results, a flexural test was conducted. As shown in Figure 20, flexural modulus of PP/GF, PP/PVA fibers and PP/Talc composites are 130%, 34% and 68%, respectively, higher than the unfilled sample. Results confirmed that glass fibers provided the highest flexural modulus and strength, followed by Talc and PVA fibers, while the addition of POE reduced both properties.

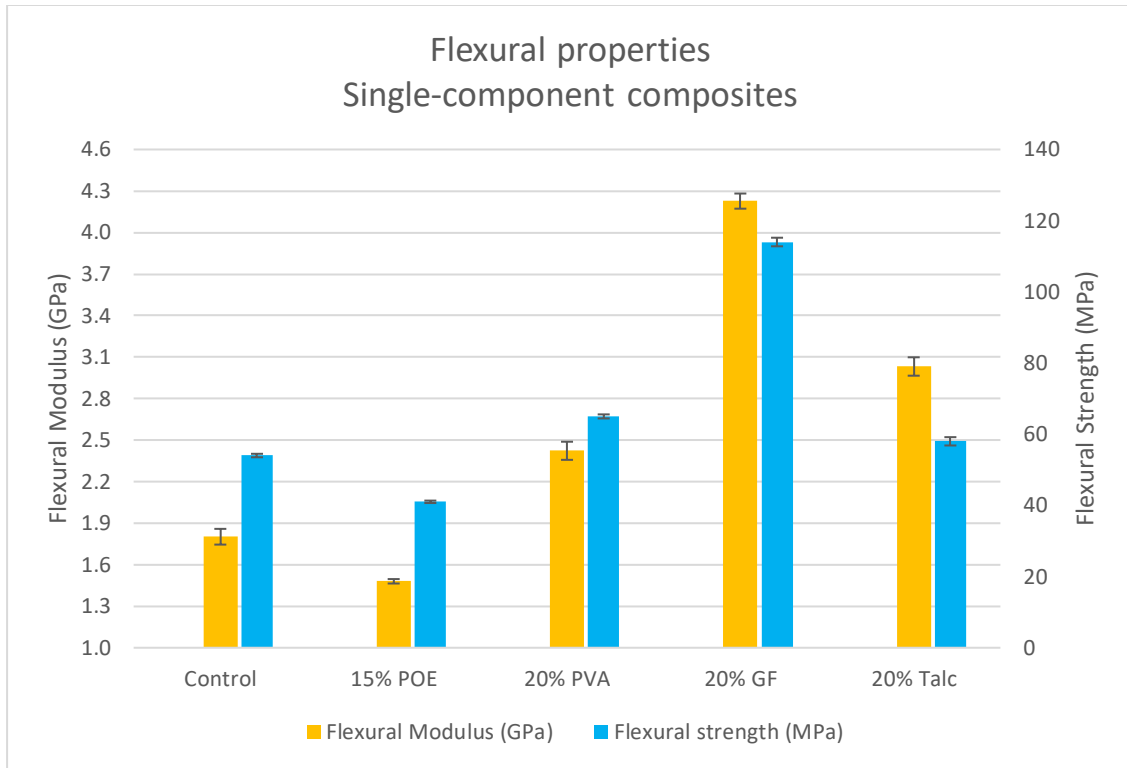


Figure 20 Flexural properties for the single-component composites system

Moreover, addition of rigid fillers and fibers to the polymer matrix causes a drastic decrease in the failure strain. That is because the presence of such rigid inclusions within the ductile polymer matrix restricts the mobility of the polymer chains and prevents the chains from sliding past each other, eventually decreasing the overall plastic deformation of the composite. Deformability is plotted in Figure 21. Composites containing 20 wt.% of GF and PVA fibers decrease the elongation at break to 9 and 23%, respectively, whereas both the control sample and composite containing POE have elongation percentage > 500%.

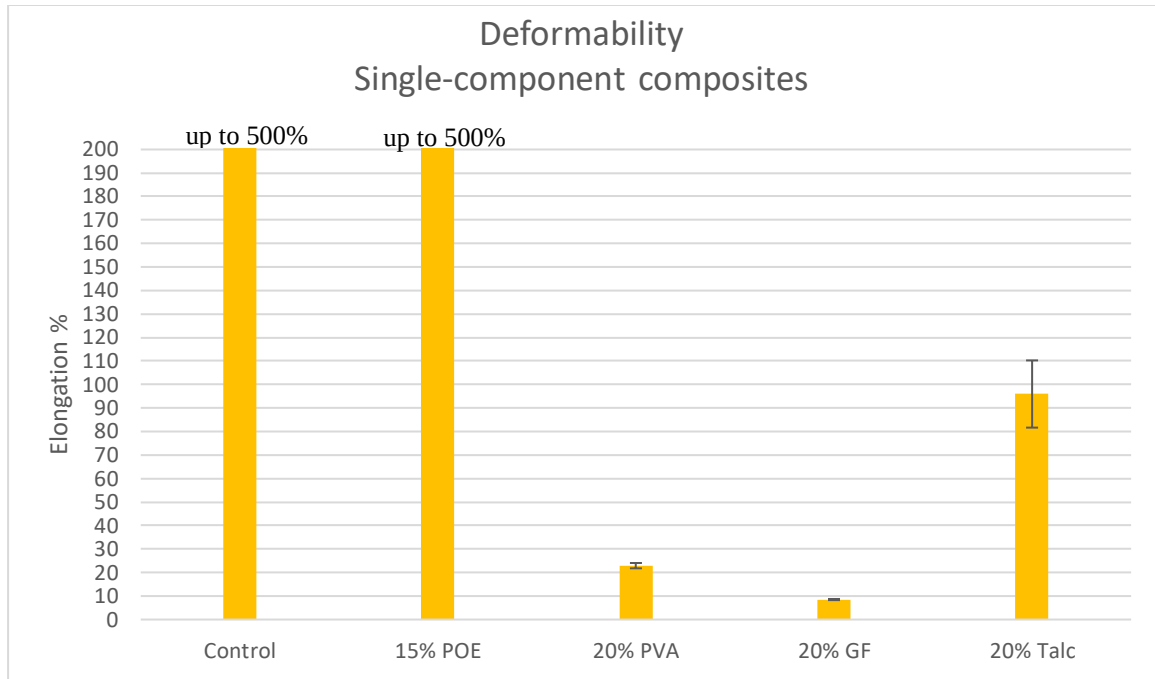


Figure 21 Elongation at break for the single-component composites systems

Additionally, presence of elastomer particles is considered as an intrinsic toughening, while inclusion of fibers, such as glass and PVA fibers, is considered as extrinsic toughening. The two principles differ in their toughening mechanism. To illustrate, when a composite is impacted by high energy, elastomer particles may debond and cavitate to dissipate the energy, so they affect both the crack initiation and propagation. Fibers, on the other hand, can retain the energy and then released after the occurrence of fiber fracture or pull out, a phenomenon known as bridging mechanism, so they only affect propagation of the cracks since cracks are initiated from fiber ends [78], [79], [80]. As depicted in Figure 22, the highest toughness was obtained by adding the elastomer phase, i.e. POE, where the notched izod impact strength increased more than 400 %. In contrast to what was anticipated, incorporation of glass fibers to PP increased the izod impact strength to a higher level than PVA fibers. For instance, izod impact strength of the notched

samples is 130, 80 J/m for glass and PVA fibers reinforced PP composites, respectively. It is noteworthy to mention that some studies in the literature have reported a decrease in the impact strength upon the addition of glass fibers to polypropylene [81]. Moreover, the addition of Talc reduced the izod impact strength, i.e. 27 J/m compared to 30 J/m for the control sample. The presence of sharp edges in Talc particles, where stress is concentrated, could facilitate crack initiation and propagation, thereby reducing the impact resistance [19]. The enhanced toughness associated with the addition of glass and PVA fibers should be attributed to the local deformation processes at the fiber's vicinity, which will be further discussed in section# 4.2.

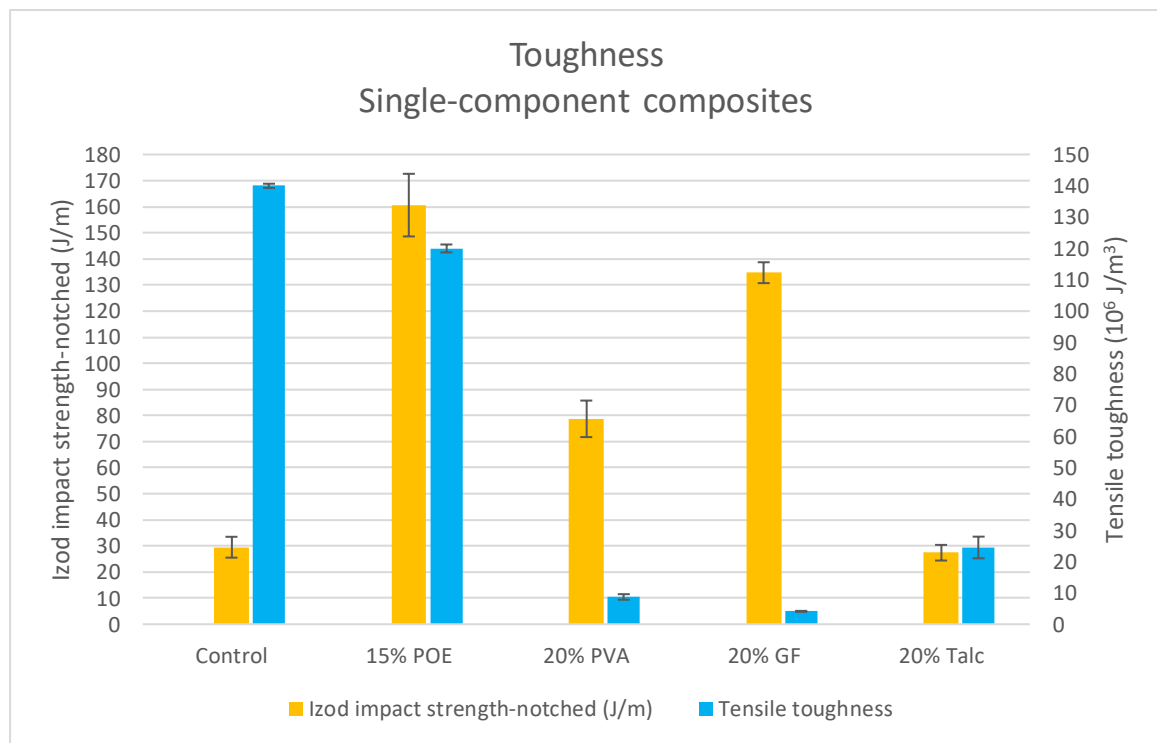


Figure 22 Toughness for single-component composites systems

Furthermore, tensile toughness as calculated from the area under the tensile stress-strain curve is also reported in Figure 22 for reference. The stress-strain behaviour of

polymers is greatly influenced by the temperature and strain rate at which the tensile test is carried. There are some major differences between tensile and impact resistance tests. In tensile test, the load is uniaxial force applied at a constant low strain rates with no notching or sharp corners in the specimen, while in the impact test, the force applied is a high sudden dynamic impact load. In the notched impact resistance test, mainly the energy absorbed during crack propagation is measured. Also, tensile toughness accounts for both the strength and ductility of the material.

4.1.2 Hybrid composites

In an attempt to enhance both stiffness and impact resistance to higher levels, the hybridization of two or more types of fillers/fibers was tested with the aim of improving the stiffness-toughness balance. In this section, we will discuss the mechanical properties of various ternary and quaternary composite systems composed of POE, Talc, glass, and PVA fibers.

4.1.2A Ternary composite systems

As mentioned earlier, there is no published work in the literature that has studied the effect of PVA fibers/POE hybridization on the properties of polypropylene composites. In this part, the ternary composite systems consisting of the elastomer material in combination with glass, Talc or PVA fibers, as well as the hybridization of glass/PVA fibers and Talc/PVA fibers in PP will be evaluated.

The addition of PVA fibers to the PP/POE composite improves its stiffness but remains lower than the single system of PP/PVA fibers composite (Figure 23). For instance, Young's modulus and ultimate tensile strength for PP/POE/PVA fibers and PP/POE composites are 1075, 36, and 840, 25 MPa, respectively, and 1400, 42 MPa for PP/PVA fibers composite. However, the impact strength significantly improved to about 290 J/m, a level that could not be achieved with either individual filler (Figure 25). Similarly, the hybridization of glass fibers and POE in the PP matrix (i.e., PP/POE/Glass fibers composite) imparts a strength that falls between the stiffness values of the single composite systems of both fillers. Nevertheless, and even though incorporating POE into PP/Glass fibers composite resulted in a reduction in the Young's and flexural moduli, the PP/POE/GF hybrid composite achieves a notably elevated impact strength, surpassing the

individual filler contributions. It can be concluded that the intrinsic toughening effect of POE works synergistically with the extrinsic toughening mechanism of glass and PVA fibers in polypropylene, resulting in a significant improvement in toughness. This conclusion will be further explored for verification through the analysis of morphology results.

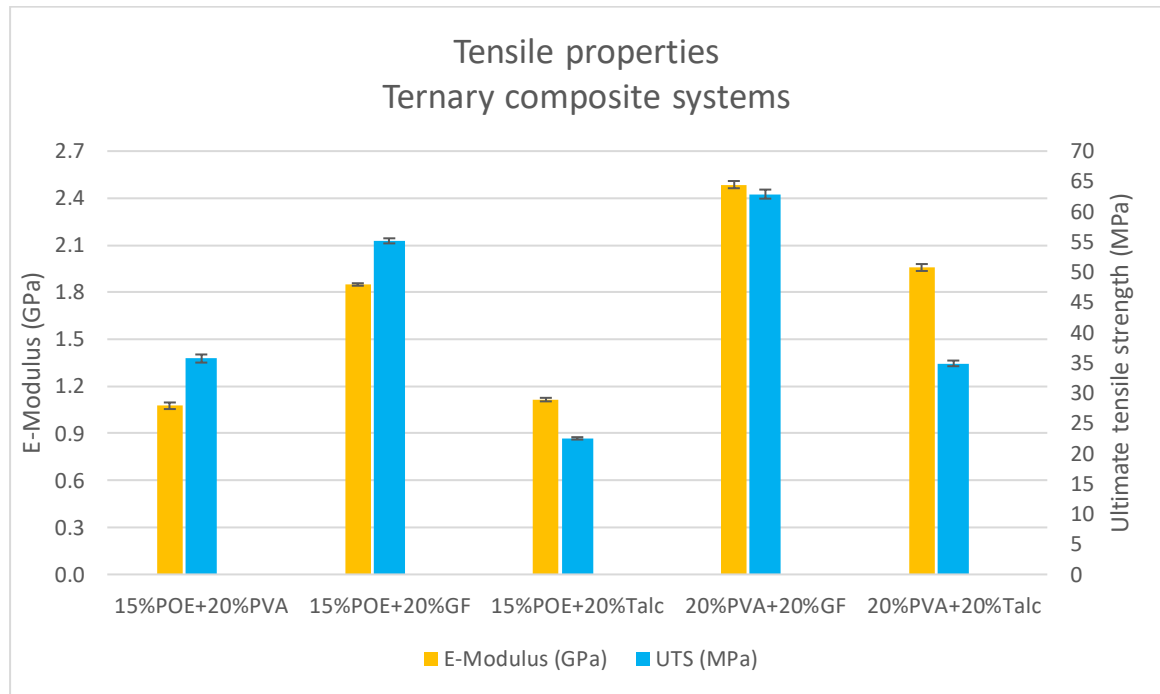


Figure 23 Tensile properties for the ternary composites systems

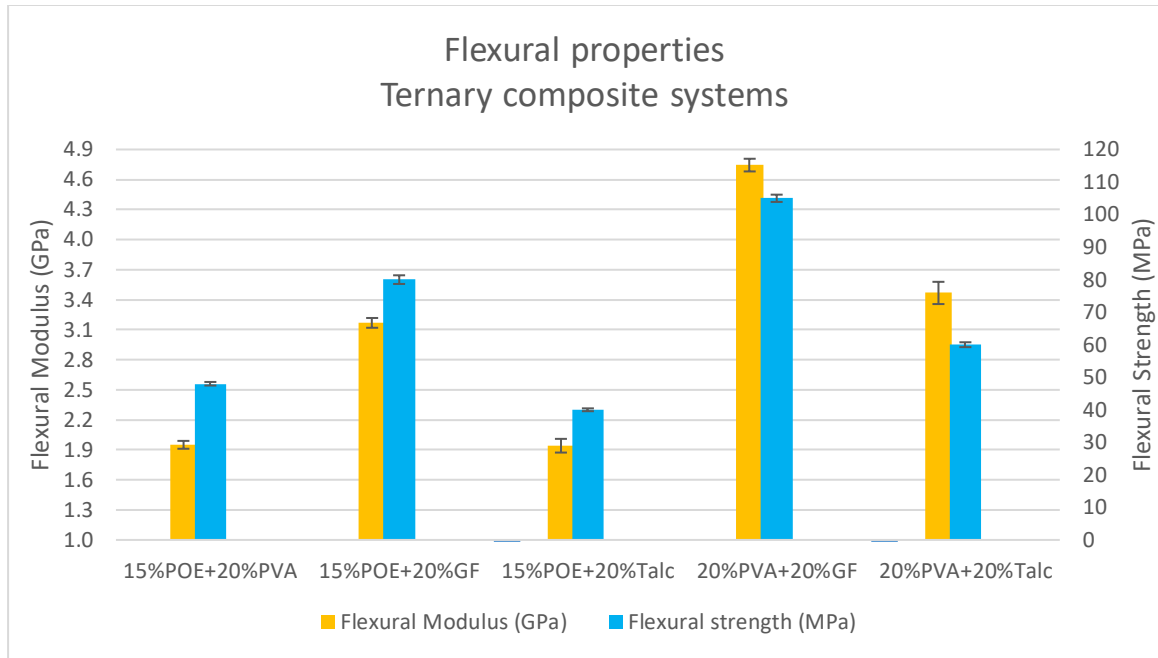


Figure 24 Flexural properties for the ternary composites systems

Additionally, the hybridization of glass and PVA fibers has significantly boosted the stiffness of PP to the highest level achieved in this study, exceeding the properties of individual fiber reinforcements. To illustrate, Young's and flexural moduli increased to approximately 2500 and 4750 MPa, respectively, for PP/glass/PVA fibers composite compared to 2250 and 4200 MPa for PP/Glass fibers, and 1400 and 2400 MPa of PP/PVA fibers samples (Figures 23 and 24). Other properties, including ultimate tensile strength, flexural strength and izod impact strength were comparable to the PP/glass fibers sample, yet higher than those of the PP/PVA fibers sample. Both glass and PVA fibers work synergistically; neither one overrides the other. The enhanced rigidity of the hybrid fibrous composite can be attributed to the collective influence of both glass and PVA fibers. Combining both fibers leads to an increase in the composite's stiffness, consequently

reducing its ductility resulting in low elongation percentage compared to the control sample.

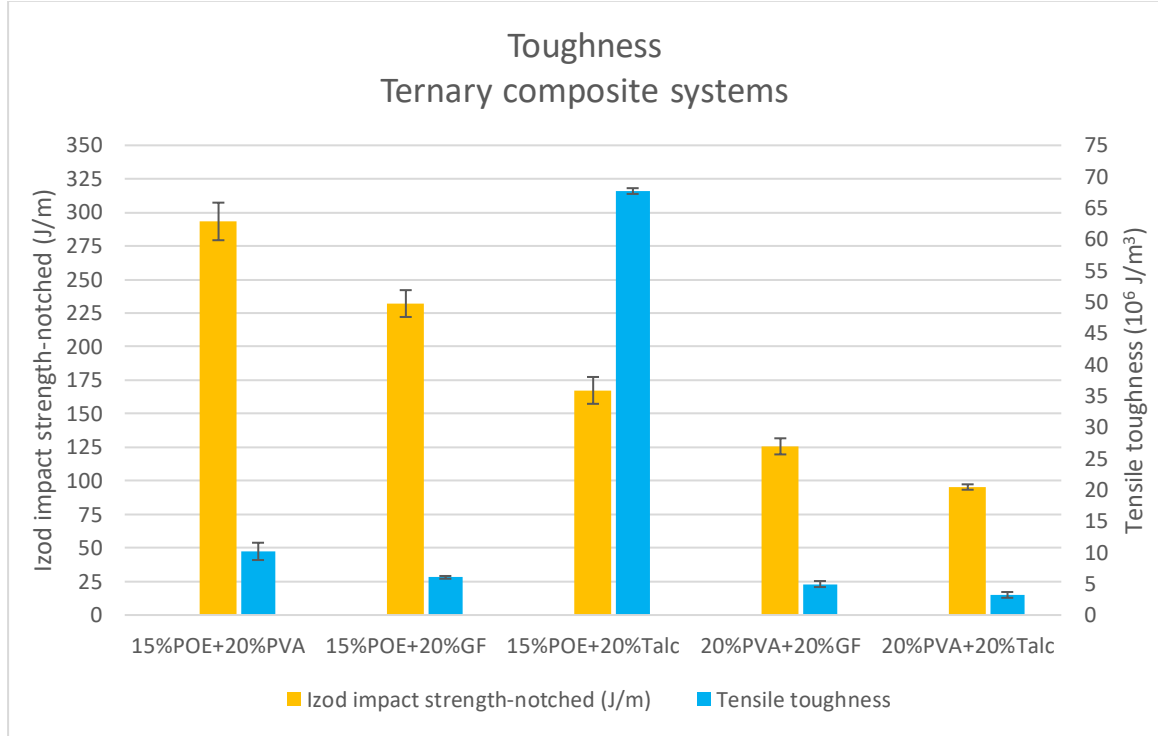


Figure 25 Toughness for the ternary composites systems

Moreover, the hybridization of Talc and POE in the PP matrix (i.e., 15 wt.% POE+20 wt.% Talc) imparts a strength that falls between the stiffness values of the single composite systems of both fillers. Nevertheless, and even though incorporating POE into PP/Talc composite resulted in a reduction in the Young's and flexural moduli, the composite exhibited 5 times higher impact strength than the unfilled PP.

Furthermore, the hybridization of Talc and PVA fibers improved the stiffness and toughness of PP, exceeding the properties of individual fillers reinforcements. To illustrate, Young's and flexural moduli increased to approximately 1950 and 3500 MPa, respectively,

for PP/Talc/PVA fibers composite compared to 1600 and 3000 MPa for PP/Talc, and 1400 and 2400 MPa of PP/PVA fibers samples. In addition, izod impact strength increased to 95 J/m compared to 78 and 27 for the individual PVA fibers and Talc composites, respectively. Ultimate tensile strength and flexural strength fall in between the values of the individual reinforcements. The enhanced rigidity of the hybrid PP/Talc/PVA fibers composite can be attributed to the collective influence of both Talc and PVA fibers. Combining both fillers leads to an increase in the composite's stiffness and toughness, surpassing the individual filler contributions.

4.1.2B Quaternary composite systems

In order to fulfill the requirements of withstanding higher loads in engineering applications, including automotive industry, the quaternary composite systems, i.e. PP/POE/Glass fibers/PVA fibers and PP/POE/Talc/PVA fibers, were prepared at different ratios and tested. In the quaternary composite system, glass fibers and Talc loadings were kept at 9 vol.% (about 20 wt.%) and 8 vol.% (about 20 wt.%), respectively, while different ratios of POE/PVA fibers, for example 75:25, 25:75 and so on, were developed in order to study its effect on the mechanical properties.

With regard to the quaternary hybrid system, the performance of the composites depends on the composition of their constituents. Increasing the POE/PVA fibers ratio enhances toughness, while decreasing it, i.e. by increasing the PVA fibers content in the composite, improves stiffness and rigidity. Overall, the simultaneous addition of POE, PVA, and glass fibers to PP resulted in an excellent balance between stiffness and

toughness, particularly in samples L and M. For example, the Young's modulus can reach values as high as 2.4 GPa, and the Izod impact strength ranges between 250 and 400 J/m (equivalent to approximately 25–40 kJ/m²). These values represent a remarkable increase, with the Young's modulus being 120% higher and the Izod impact strength exceeding the control sample by more than 800%.

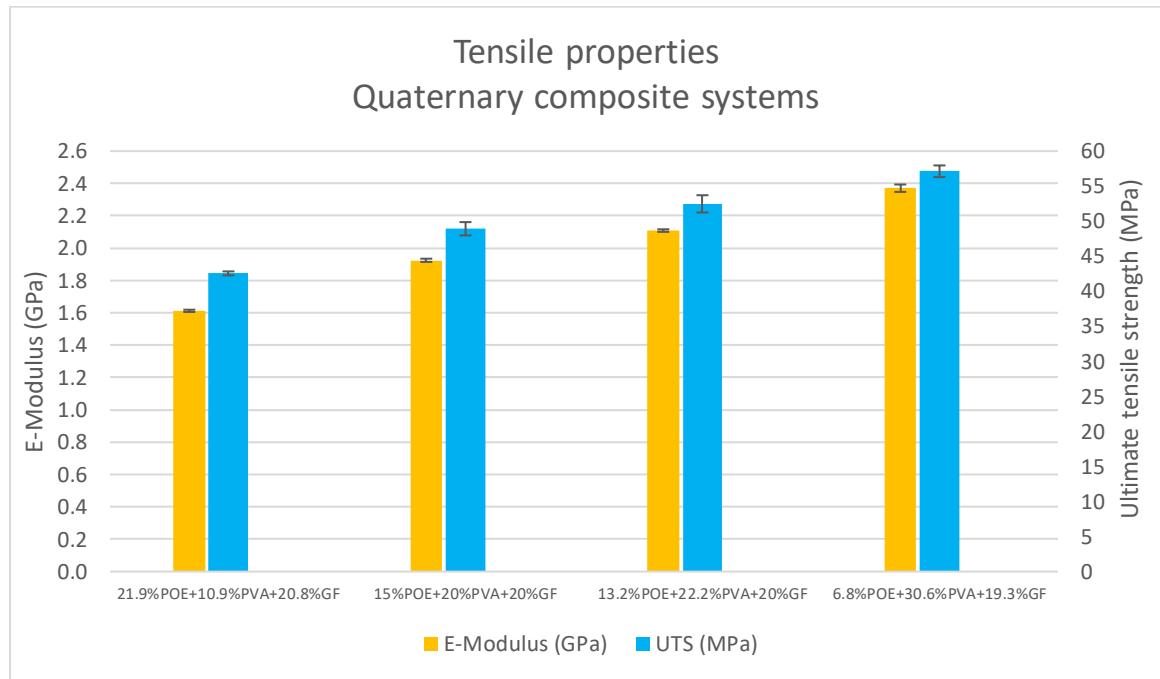


Figure 26 Tensile properties for the quaternary composites systems- Glass fiber reinforced PP

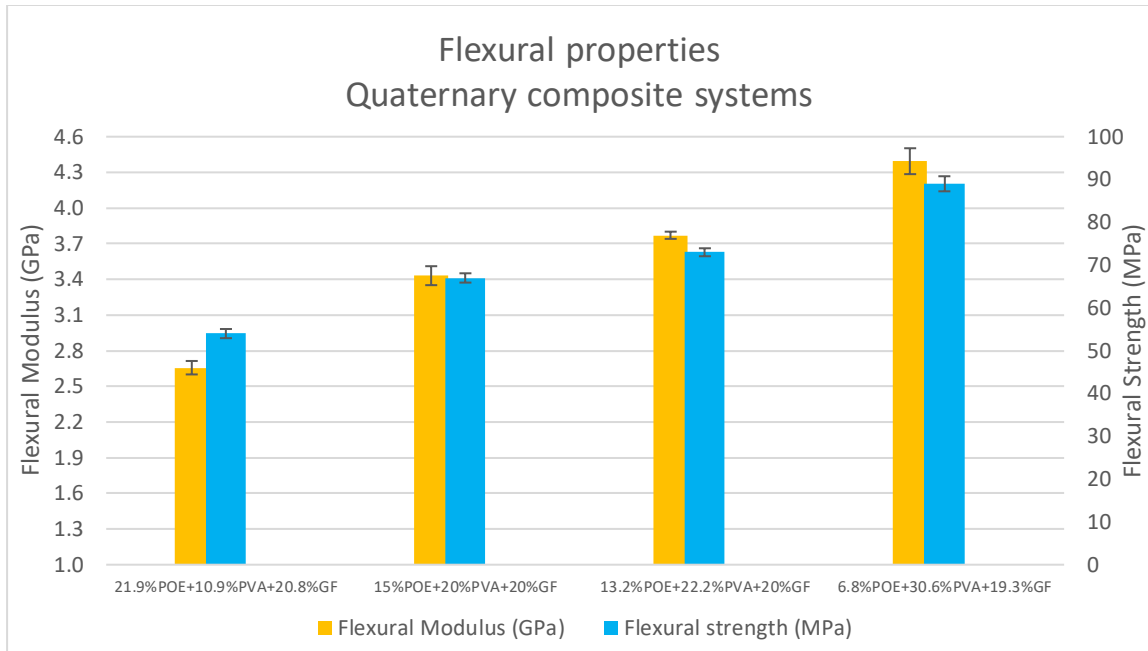


Figure 27 Flexural properties for the quaternary composites systems- Glass fiber reinforced PP

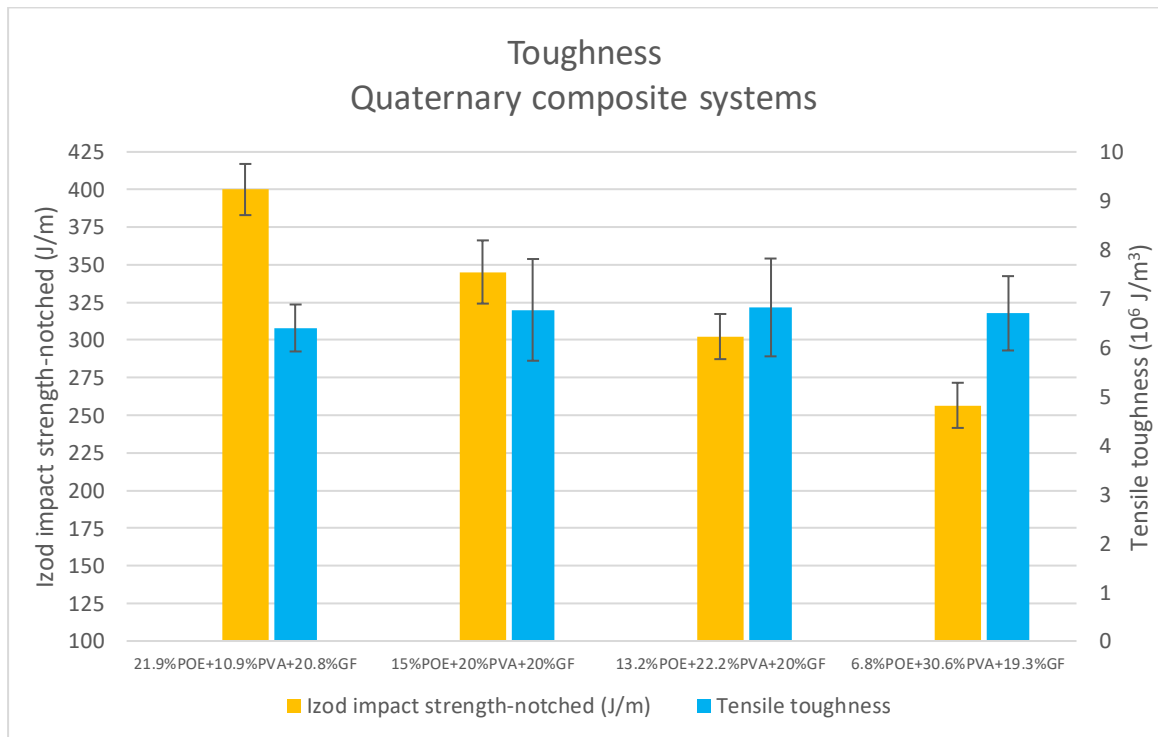


Figure 28 Toughness for quaternary composites systems- Glass fiber reinforced PP

Moreover, the critical length can be calculated using the following equation:

$$L_c = \frac{\sigma_f^* d}{2 \tau_c} \quad (5)$$

where σ_f^* is the ultimate tensile strength of the fiber, d is fiber diameter, and τ_c is the matrix-fiber interfacial shear strength. Fu et al. [82] measured the interfacial shear strength of PP/GF samples by performing pull-out experiments, and they reported an average τ_c value of about 15.2 MPa. The ultimate tensile strength for glass fibers is about 3450 MPa [16]. Therefore, using above equation, the critical length for the developed Glass fiber composites is:

$$L_c = \frac{(3450)(13)}{2 (15.2)} = 1.48 \text{ mm}$$

The calculated critical length is slightly higher than the reported value in the literature. The literature reports a critical length (L_c) for glass fibers in polypropylene composites in the range of 0.7 – 1 mm [16], [82], [83]. This discrepancy may be attributed to the higher ultimate tensile strength of the glass fibers used in our case, compared to the literature where the strength is approximately 2000 MPa [82], [83].

With regards to the quaternary system composed of PP/POE/Talc/PVA fibers, although its stiffness level did not reach the achieved Young's and flexural moduli of the PP/Talc/PVA fibers, i.e. ternary composite sample J, the simultaneous addition of POE, PVA, and Talc to PP resulted in an excellent balance between stiffness and toughness, particularly in samples P and S. For example, the Young's modulus can reach values of about 1.30 – 1.65 GPa, and the Izod impact strength ranges between 170 - 250 J/m (equivalent to approximately 17–25 kJ/m²). These values represent a notable increase, with

the Young's modulus being about 50% higher and the Izod impact strength exceeding the control sample by more than 500%.

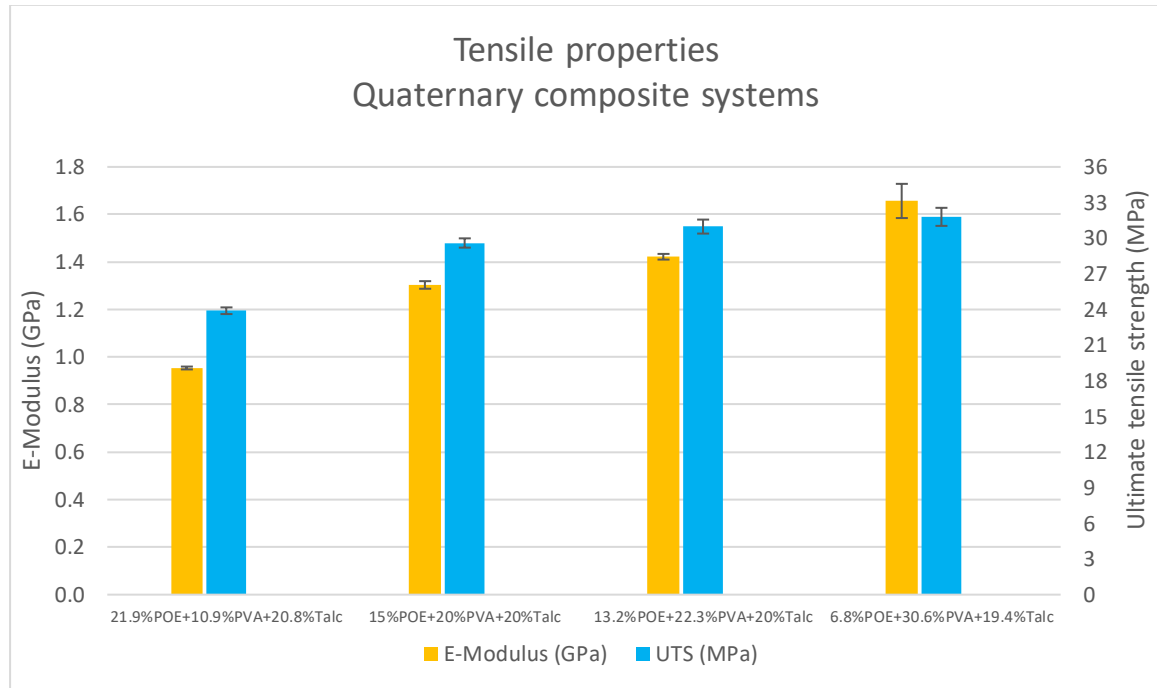


Figure 29 Tensile properties for the quaternary composites systems- Talc filled PP

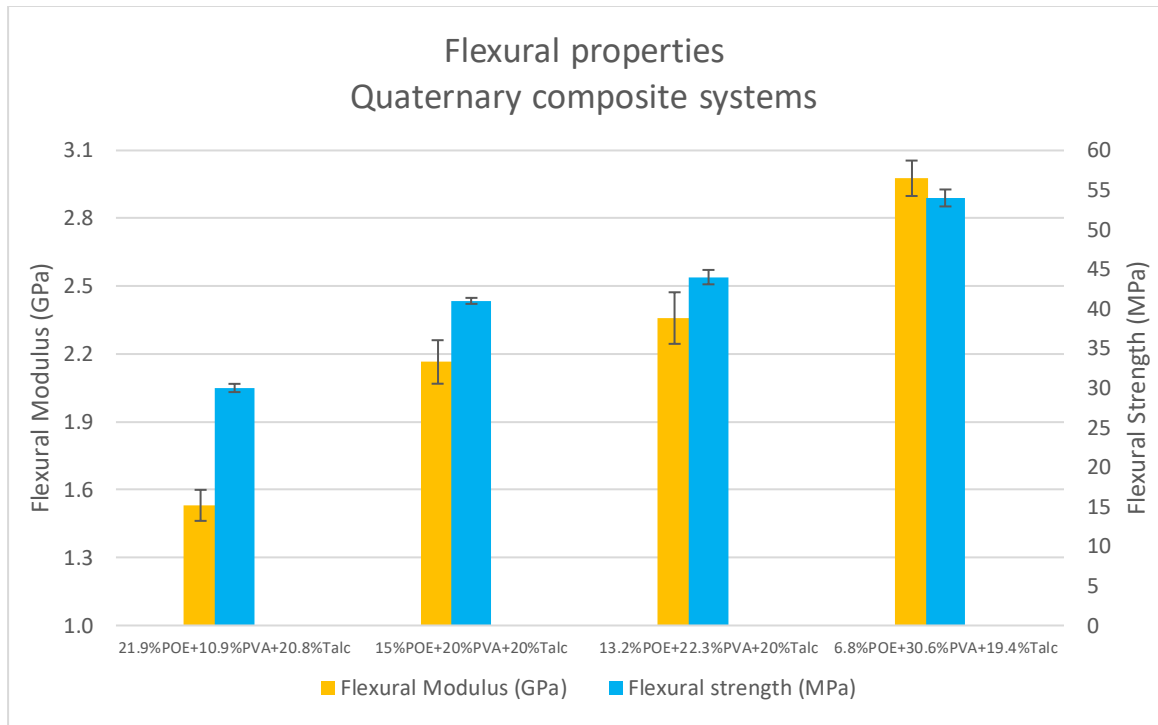


Figure 30 Flexural properties for the quaternary composites systems- Talc filled PP

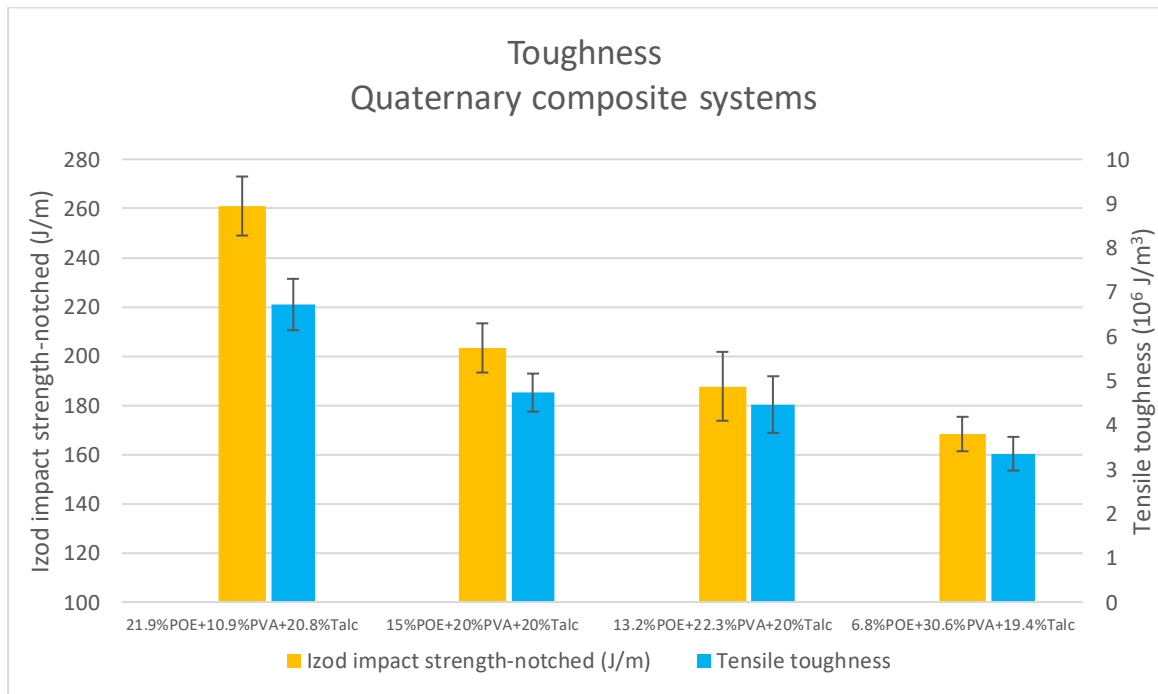


Figure 31 Toughness for the quaternary composites systems- Talc filled PP

It is worth noting that, for all hybrid samples, the notched specimens exhibited partial breakage under impact loading at room temperature, in contrast to the complete break observed in the control and single composite specimens. This suggests a ductile failure mode, as illustrated in Figure 32, where the failure exhibits a tortuous path.

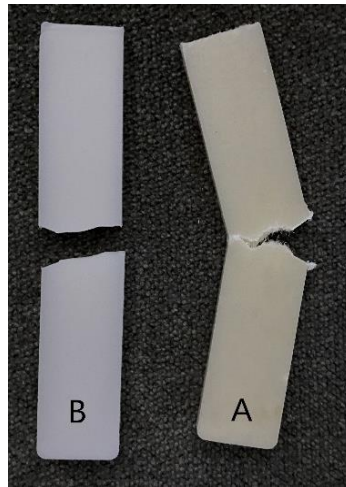


Figure 32 Izod impact specimens- notched; A: Partial break, B: Complete break

4.2 Microstructure analysis of the hybridized PP composites

The macroscopic characteristics of a composite are dictated by its microscopic structure. The addition of fillers, fibers, or elastomers into a polymer matrix is considered to create a heterogeneous structure because they have different elastic properties, resulting in the formation of a stress field around the filler particles in their vicinity when exposed to an external load. Due to this stress concentration, different micromechanical deformation processes are taking place, to relieve the concentrated stresses, in close proximity to the fillers/fibers which eventually determine the failure mechanism [84], [85], [86]. The stress magnitude is influenced by the geometric characteristics of particles (including shape and diameter), the strength of interfacial adhesion, and the relative properties of the composite's constituents [87]. For reinforced polymer composites, the main micromechanical deformation mechanisms are; Matrix shear yielding, debonding, pull-out and fracture of filler or fiber. Matrix shear yielding is the process in which polymer chains slide past each other, resulting in plastic deformation and a permanent change in the sample's shape. Matrix shear yielding is the main deformation mechanism for unfilled polypropylene. The other filler-related processes, i.e. debonding, pull out and fracture, are initiated by the filler/fiber itself. At low deformation strain and stress, debonding, which is the detachment of the fiber from the surrounding matrix, takes place if the fiber-matrix adhesion is poor. Upon increasing the load further, fiber pullout could occur following the debonding process. In the case of a good interfacial adhesion between the fiber and polymer matrix, fiber fracture would result upon applying a large stress [87], [88], [89], [90].

During deformation, those different processes can occur either simultaneously or sequentially within the composite. Micromechanical deformation processes directly affect

the composites' toughness and strength. The occurrence of the above-mentioned processes contributes to the absorption of energy during deformation by resisting the crack propagation, thus enhancing the fracture resistance and influencing the impact strength value to varying extents. Therefore, and since more than one process may coexist, the change in the composite properties are highly related to the prevailing local deformation mechanism [91], [92], [93].

The broken surface from the tensile test was studied using SEM, trying to correlate the observed macroscopic properties with the microscopic structure. The micrograph depicted in Figure 33 shows the broken surface of the glass fiber reinforced PP composite. The figure revealed that some pulled out fiber can be indicated, whereas the dominating micromechanical deformation process for the glass fibers is the fiber breakage. Clearly, fibers' breakage absorbs a substantial amount of energy during the failure process, which is reflected by the large impact strength observed for PP/glass fibers composite.

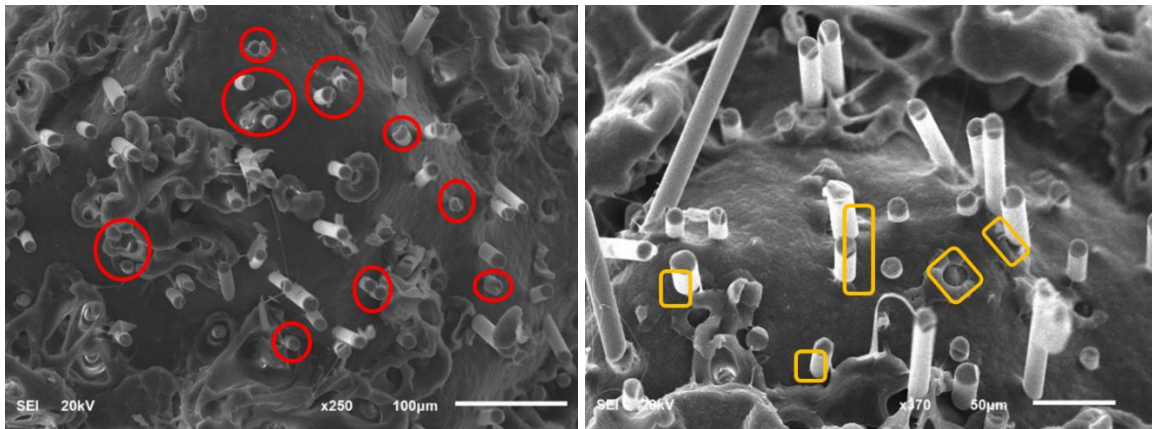


Figure 33 SEM micrographs for the tensile broken specimen of sample D – glass fibers fracture

In addition, it can be noted from above micrographs that glass fibers are well attached to the polymer matrix. The good adhesion between glass fibers and the PP matrix

results from the surface coupling treatment of the fibers, achieved through both silane sizing and the addition of a coupling agent. Adoption of both treatments results in fewer fibers debonding from the matrix, enabling the composite to withstand higher applied loads, thereby better reinforcement and toughening abilities. This high degree of adhesion had promoted the fiber fracture mechanism rather than fiber pull-out during failure. A closer look at the glass fiber surface shows the fiber is coated with a thin layer of the matrix material, which also indicates a strong bonding between the glass fibres and the surrounding matrix (Figure 34). Hence, it is a combination of the adhesion strength between the fibre and the matrix, and the fibre tensile strength which will decide the final toughness of the composite.

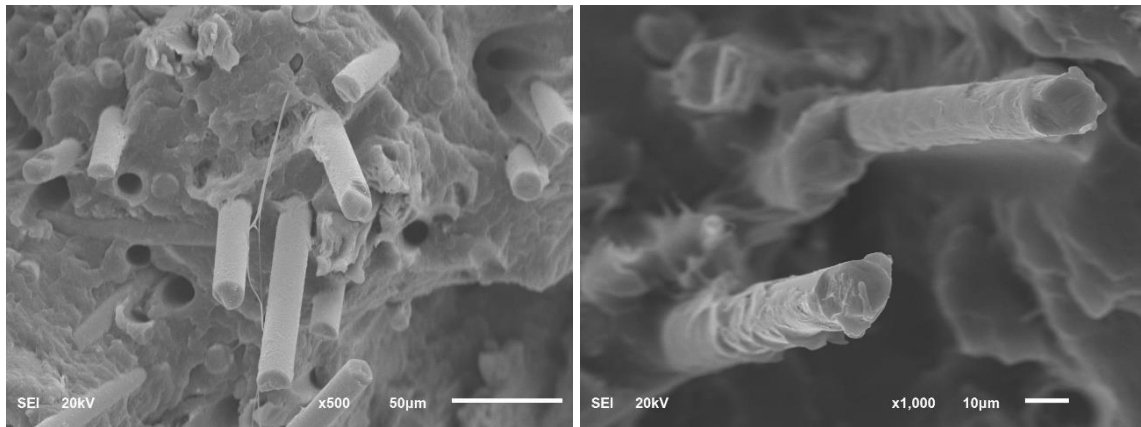


Figure 34 SEM micrographs for the tensile broken surface at high magnification for glass fibers surface

Moreover, given that the predominant failure mechanism observed for glass fibers is fiber breakage, it can be claimed that final length of glass fibers in the developed composites after processing is necessarily higher than the critical length value. Several studies from literature support this claim. For example, Fu et al. [82] reported that if the fiber length after processing is less than the critical length, then glass fibers will not experience fracturing; but instead, they will pulled-out. They reported a pull-out

mechanism as the predominant deformation process for the studied PP/GF composite, and proved that the measured final fiber length was indeed less than the calculated critical length. Similar conclusion was also reported elsewhere [83]. Also, another study tested short and long GF reinforced polypropylene composites. They reported that fiber fracture mechanism was only observed with the long glass fiber composite, which obviously longer than the critical length, while the short GF composite failed mainly by pull-out mechanism [94]. Fibers' attrition during the processing stage is a crucial factor in controlling the ultimate properties of the composite material. Fiber attrition occurs due to a combination of factors, including interactions between the fibers and the polymer matrix, interactions between adjacent fibers, and the interaction between the fibers and the surfaces of the processing equipment. In addition, increasing fiber content in the composite proved to lead to severe damage to the final fiber length due to the increased contact between the fibers [20]. It is believed that the used processing conditions in the compounding and injection molding stages, i.e. low extrusion speed, the gentle mixing induced by the employed screw configuration, and the low back pressure, helped to minimize fiber length breakdown in these experiments. So, retaining longer fibers in the final composite supported the high stiffness and toughness values observed for the composites prepared with glass fibers in this study, i.e. PP/GF, PP/GF/PVA fibers, and PP/GF/POE/PVA fibers composites.

Furthermore, Figure 35 represents the tensile broken surface of the PP/PVA fibers composite. It can be noticed that the two major local deformation processes are debonding and fiber pullout, with very few fractured fibers observed in the presented micrograph. Debonding can be clearly seen in the micrograph, as PVA fibers are detached from the polymer matrix creating a cavity around the fiber which is a result of the low degree of

adhesion between the two phases. Fiber pullout is the dominant deformation mechanism for the PP/PVA fibers composite as evidenced by the presence of many holes that correspond to the pulled-out fibers.

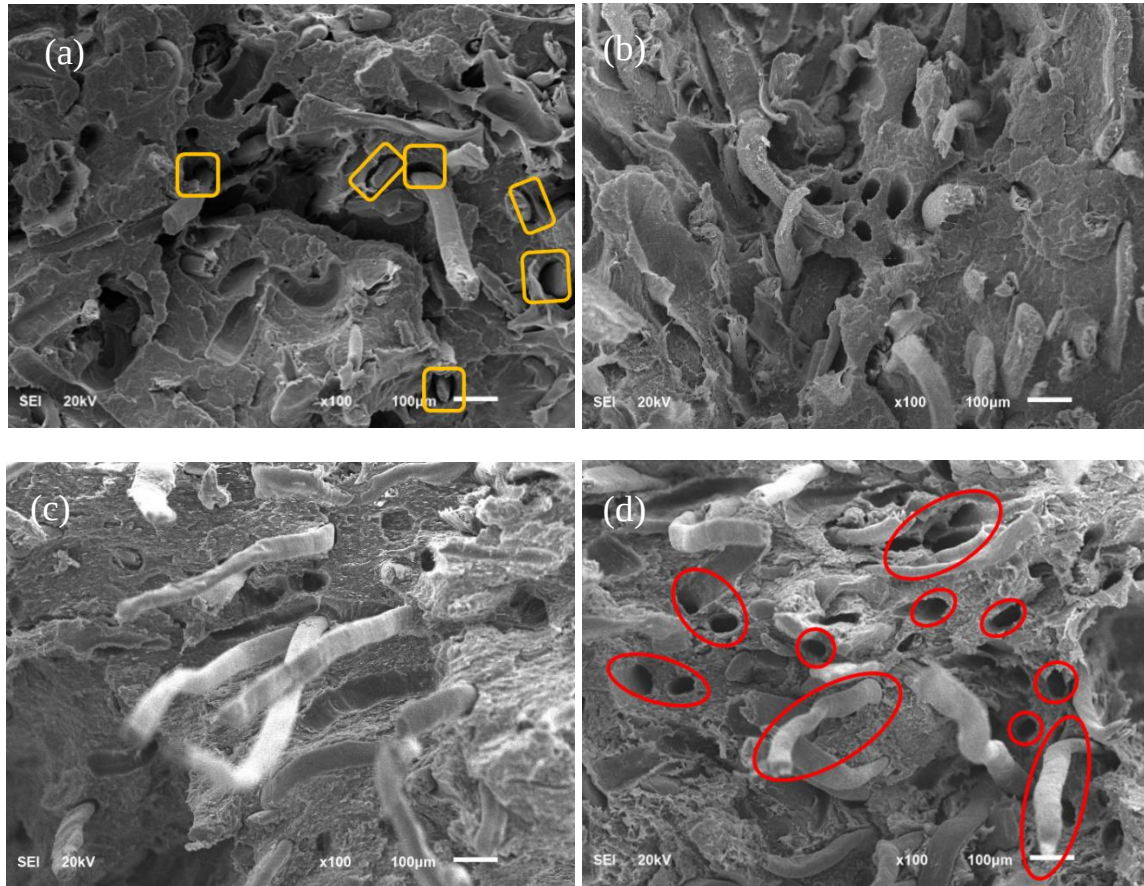


Figure 35 SEM micrographs for the tensile broken surface; (a) and (b): sample C , (c) and (d): sample P – PVA fibers pull-out

Moreover, Figure 36 represents the tensile broken surface of sample P. SEM micrograph showed the debonding of Talc particles from the polymer matrix, and some observed voids which correspond to the pulled out filler particles, while some Talc particles are still intact. This could indicate that the level of coupling agent added is insufficient. The limited strength in the interfacial adhesion between PP and Talc would hinder the enhancement in the ultimate tensile strength of the composites. Similar findings were

documented elsewhere for PP [30], [95], [96], [97]. Ashenai Ghasemi et al. [19] reported that the existence of such cavities clearly indicates a poor interfacial bonding within the Talc/polymer interface. They reported that upon the addition of 4 wt.% of a coupling agent to the composite, the number of Talc particles which had undergone debonding was reduced. It is noteworthy to mention that debonding is considered as the predominant local deformation process in majority of the particulate filled polymer composites [31], [76], [89], [90], [91], [97], [98].

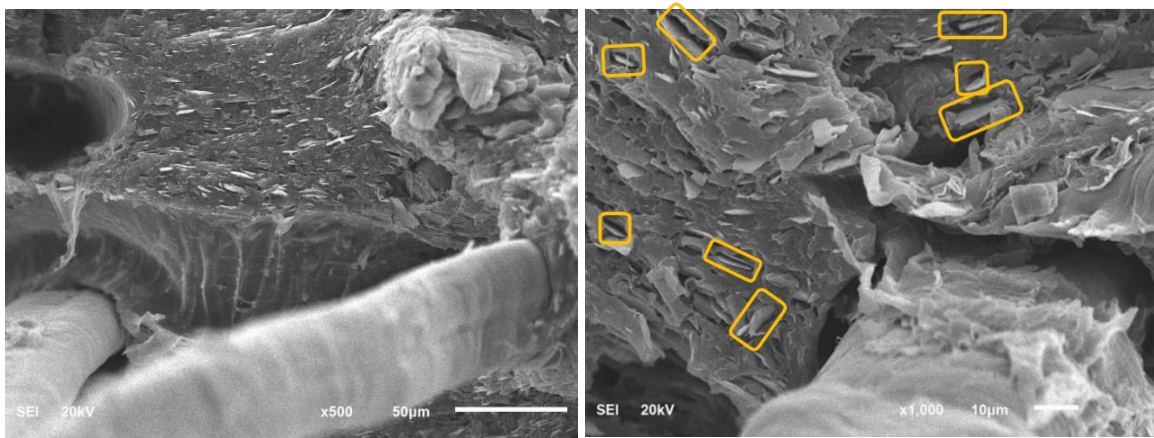


Figure 36 SEM micrographs for the tensile broken specimen of sample P – Talc particles debonding

Overall, the presence of Talc particles and the initiated debonding deformation process seem to impede the shear yielding of the surrounding matrix, thereby decreasing plastic deformation and impact resistance. Similarly, Ferdinand et al. [99] reported that debonding and fracture of wood particles did not contribute to enhancing the impact strength of PP/wood composite.

In addition, Figure 37 demonstrates the flexibility of PVA fibers, which can bend, turn, and spin. This flexibility could affect the orientation of PVA fibers, resulting in reduced stiffening ability. On the other hand, glass fibers are more rigid and partially

oriented in the direction of flow, which is perpendicular to the impact force direction, and that could help to absorb more energy during failure process.

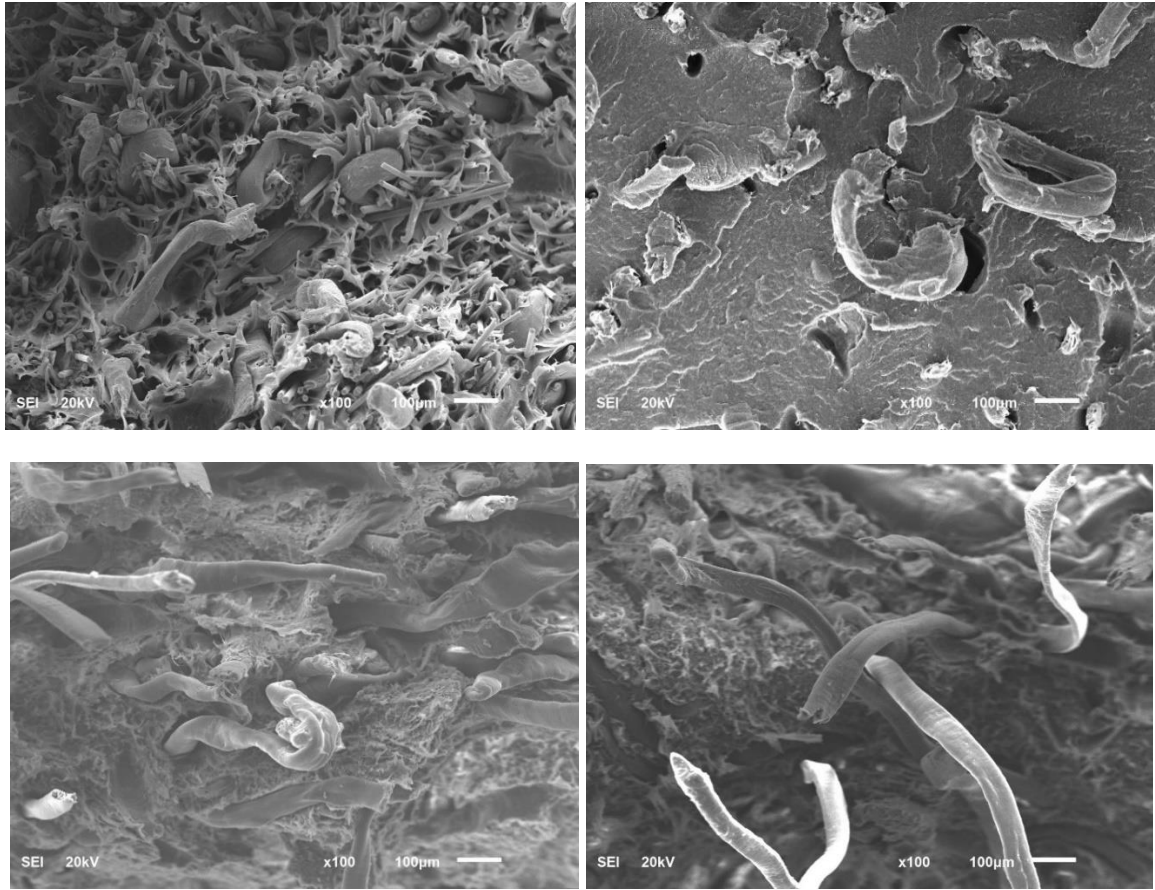


Figure 37 SEM micrographs of the tensile broken specimens showing the flexibility of PVA fibers

Also, Talc platelets were preferentially oriented in the flow direction along their major axis as shown in Figure 38 (note: the flow direction is out-of-plane to the SEM image). Due to the alignment of the Talc platelets in the flow direction, the crack propagation would be anisotropic, i.e. easier parallel to the Talc plates than perpendicular to them because of less crack blocking chances [18]. Therefore, the reduced impact resistance of Talc could be attributed to this factor.

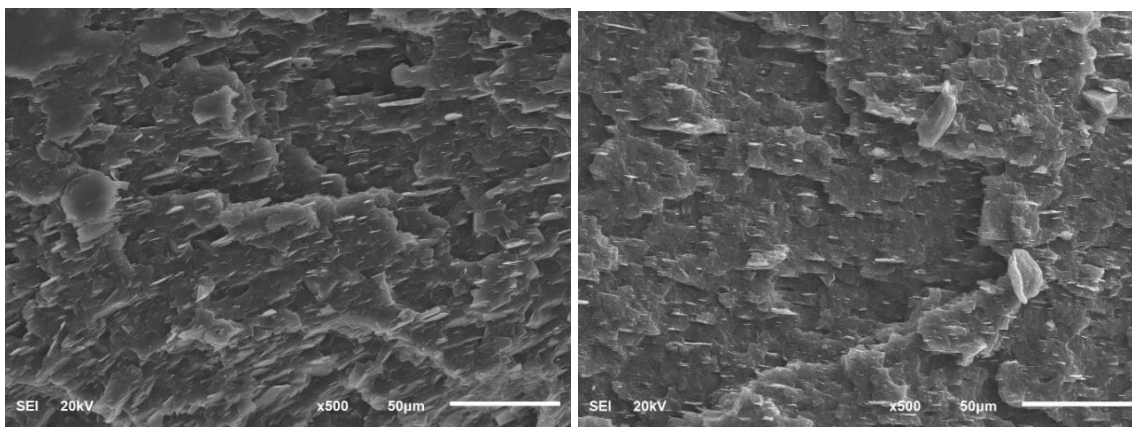


Figure 38 SEM micrographs for the tensile broken surface of sample E

Moreover, one of the most encountered issues with particulate filled polymers is the tendency of the particles to aggregate or agglomerate, especially for small size particles. Such structural defects will negatively impact the reinforcing efficiency of the filler [29]. Therefore, it is always good to observe the dispersion and distribution of the fillers within the polymer matrix. It can be noted from Figure 38 that Talc particles were homogenously dispersed; there is no sign of aggregates.

Additionally, for polypropylene toughened with elastomer, i.e. PP/POE composite, cavitation of the elastomer particles along with the subsequent plastic yielding were recognized as the main sources for energy absorption (Figure 39). Although POE is immiscible with PP, it can be observed that the two phases are well dispersed. SEM micrographs show that POE particles are predominantly spherical in shape, yet some ellipsoids are also noted. During fracture, energy will be absorbed as the propagating crack encounters the rubbery phase, where it will be dissipated through deformation [100].

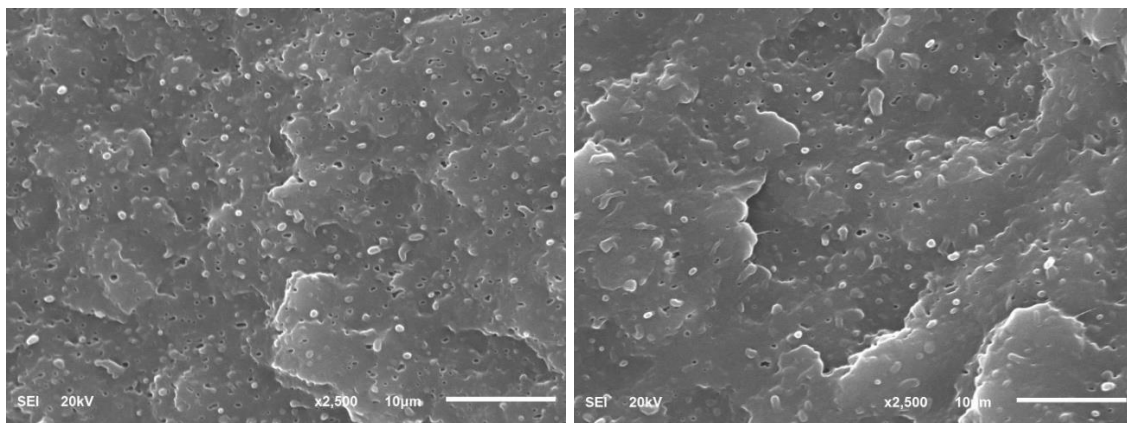


Figure 39 SEM micrographs for the tensile broken surface of sample B

Overall, the excellent performance in terms of impact resistance and high modulus observed in the quaternary composite systems, i.e., PP/POE/GF/PVA fibers and PP/POE/Talc/PVA fibers, is attributed to the high inherent rigidity of the filler and fibers, and the considerable energy absorption ability associated with the local deformation mechanisms explained in the morphology study above. It is the combination of all the aforementioned micromechanical deformation processes associated with Glass fibers, Talc, PVA fibers, and POE that has led to such high levels of stiffness and toughness.

Finally, considering the typically encountered inverse relationship between stiffness and toughness in polymer composites, the two properties are plotted below. It is clear that the hybridization of various fillers/fibers within the polymer matrix helps to maintain a favorable balance between Young's modulus and impact strength. This is illustrated by some of the developed ternary and quaternary composite samples moving towards the upper right corner, as desired. This simultaneous combination of high toughness and good stiffness is expected to meet the high standards required in the automotive industry.

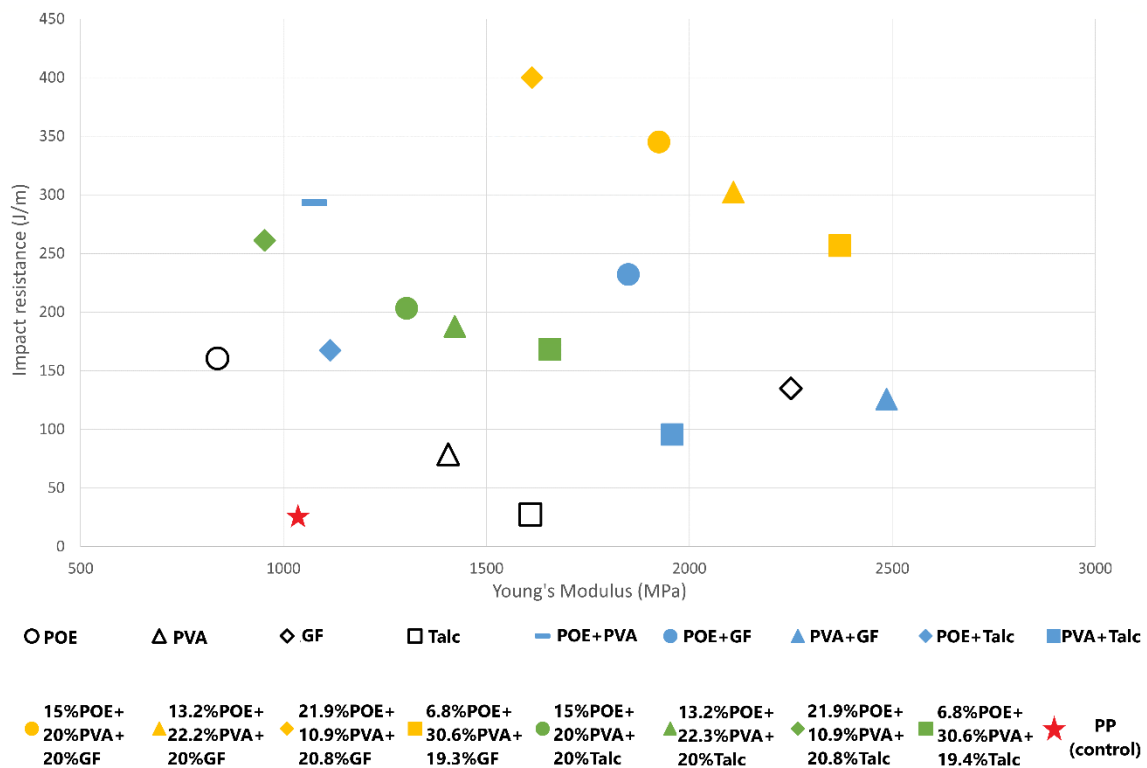


Figure 40 Stiffness/toughness balance for the developed composites (compositions are in wt.%)

4.3 Thermal analysis of the hybridized PP composites

Addition of solid fillers is known to nucleate Polypropylene where the crystallinity structure can change. One of the commonly used techniques to assess the nucleation effects of fillers in PP is DSC test, by studying the effect of filler addition on the crystallization temperature (T_c). Crystallinity percentage is calculated using equation (4). The following table summarizes the major thermal properties of the tested samples. It is to be noted that the reported melting temperature is obtained from the second heating cycle.

Table 8 Thermal properties of developed composites by DSC test

Sample	Melting Temperature (°C)	Crystallization Temperature (°C)	Crystallinity degree (%)
PP (control sample)	160.0	115.5	47.9
PP + 20 wt.% PVA fibers	162.7	117.1	45.4
PP + 20 wt.% Glass fibers	161.2	116.7	54.9
PP + 20 wt.% Talc	161.8	127.5	58.5
PP+6.8 wt.% POE+30.6 wt.% PVA+19.3 wt.% Glass fibers	161.9	118.0	57.3
PP+6.8 wt.% POE+30.6 wt.% PVA+19.4 wt.% Talc	162.5	127.9	58.6

DSC results clearly demonstrate that Talc exerts the most pronounced nucleation effect among other fillers/fibers in PP, evident by the substantial increase in the crystallization temperature by 12 °C. This effect also persists in the quaternary composite sample. Both glass and PVA fibers exhibit a marginal nucleation in PP, with T_c increasing by 1 - 2 °C. The higher crystallization temperature is indicative of thicker lamella [101].

Furthermore, addition of the studied fillers/fibers alters the crystallinity structure as indicated by the change in the crystallinity degree. Notably, the inclusion of PVA fibers leads to a slight reduction in the crystallinity percentage based on the calculated crystallinity degree. This reduction can be attributed to the low degree of compatibility between PP and PVA, which disrupts the crystalline structure of PP, thereby interfering with the packing of PP chains and resulting in a decrease in the crystallinity percentage. A similar observation was reported by Yan et al., where blending PP with 30 wt.% PVA led to a reduction in the overall crystallinity degree of the blend [47]. DSC thermograms for the tested samples are included in the appendix for reference.

CHAPTER 5

CONCLUSION

The high demand for polypropylene is expected to keep increasing, especially as polypropylene composites demonstrate their ability to replace expensive materials in some applications due to their lighter weight and high strength. Achieving a good balance between stiffness and impact strength is becoming a fundamental requirement for various applications, especially in the continuously growing automotive industry. Polypropylene hybrid composites proved to be a good candidate to attain high stiffness/toughness balance. The goal of this work was to study the impact of incorporating Polyolefin Elastomer and Polyvinyl Alcohol fibers as individual and hybrid reinforcement to Glass fibers and Talc reinforced polypropylene composites, in the presence of a compatibilizer. The main attention was focused on maximizing the stiffness/toughness balance by studying the tensile and impact characteristics and correlating those observed properties to the microscopic structure of the developed composites. In this study, several ternary and quaternary hybrid composite systems were developed and analyzed. The addition of Glass fibers (GF) results in stiffer composites than addition of Talc or PVA fibers. Nevertheless, the hybridization of Talc-PVA fibers and GF-PVA fibers has significantly boosted the stiffness/toughness of PP to levels 80%/200% and 130%/300% higher, respectively, than the control sample; a level that could not be achieved with either individual filler. Different micromechanical deformation processes were identified in the deformed samples. Those processes can occur either simultaneously or sequentially within the composite, yet one of

them usually dominates the failure mechanism, but the effect of other processes should not be ignored either. The micrograph indicates that predominant energy absorbing mechanism for glass fibers is fiber fracture, for PVA fibers is pull out, while Talc mainly deformed by debonding from the polymer matrix. Furthermore, a large stiffness of approximately 2.4 GPa Young's modulus, and notched Izod impact strength ranges between 250 and 400 J/m was achieved with the quaternary hybrid system, PP/GF/POE/PVA fibers. Its performance can be controlled by altering the POE/PVA fibers ratio to achieve the targeted stiffness/toughness balance. Generally, increasing the soft rubber loading into the composite yields better impact resistance. These values represent a remarkable increase, with the Young's modulus being 120% higher and the izod impact resistance surpassing that of the control sample by over 800%. The enhanced macroscopic properties of the composites are attributed to the high inherent rigidity of the reinforcing fibers and the considerable energy absorption ability associated with the various micromechanical deformation mechanisms that occur during failure. Differential Scanning Calorimetry test results revealed that Talc has the strongest nucleation effect in PP, evident by the 12 °C increase in the crystallization temperature, whereas glass and PVA fibers have only slight nucleation effect in PP. Furthermore, in addition to imparting strength and toughness to PP, PVA fibers have much lower density than other conventional fillers, including Talc and Glass fibers. This low density of PVA fibers would contribute in reducing the overall hybrid composite density, leading to lighter weight parts and hence lower fuel consumption, while still satisfying the high rigidity needed for automotive applications. The outcomes of this study offer valuable insights to develop polymer-based composites with favorable properties that align with the requirements for automotive industry.

CHAPTER 6

RECOMMENDATIONS FOR FUTURE WORK

Future work can tackle several aspects toward the primary goal of developing polymer composites with improved stiffness/toughness balance. The following are some recommendations to be considered for future research:

- Consider recycled PP instead of virgin PP as the matrix, in order to promote environmental sustainability by reducing the ecological impact of plastics waste.
- Incorporate advanced techniques to study micromechanical deformation processes, such as acoustic emission or volume strain measurements. These techniques could aid in predicting the failure mechanism, thereby assisting in estimating the material's behavior under practical conditions.
- Explore other advanced reinforcing solutions, such as Carbon fibers or nano fillers.
- Before implementation, it is crucial to study scalability and conduct a cost evaluation/assessment for the explored hybrid composites to ensure their economic feasibility.

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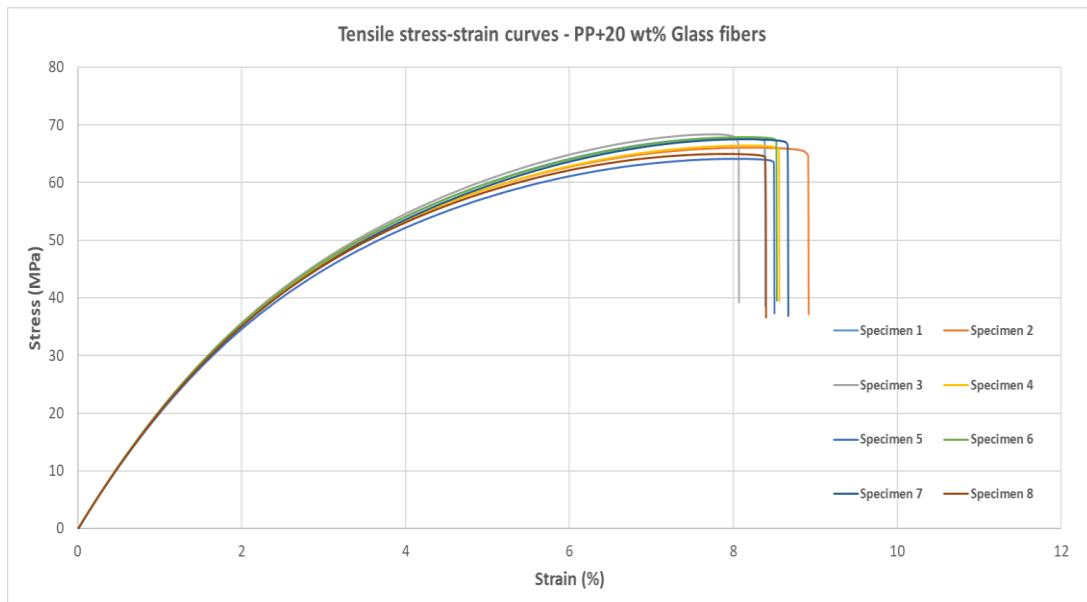
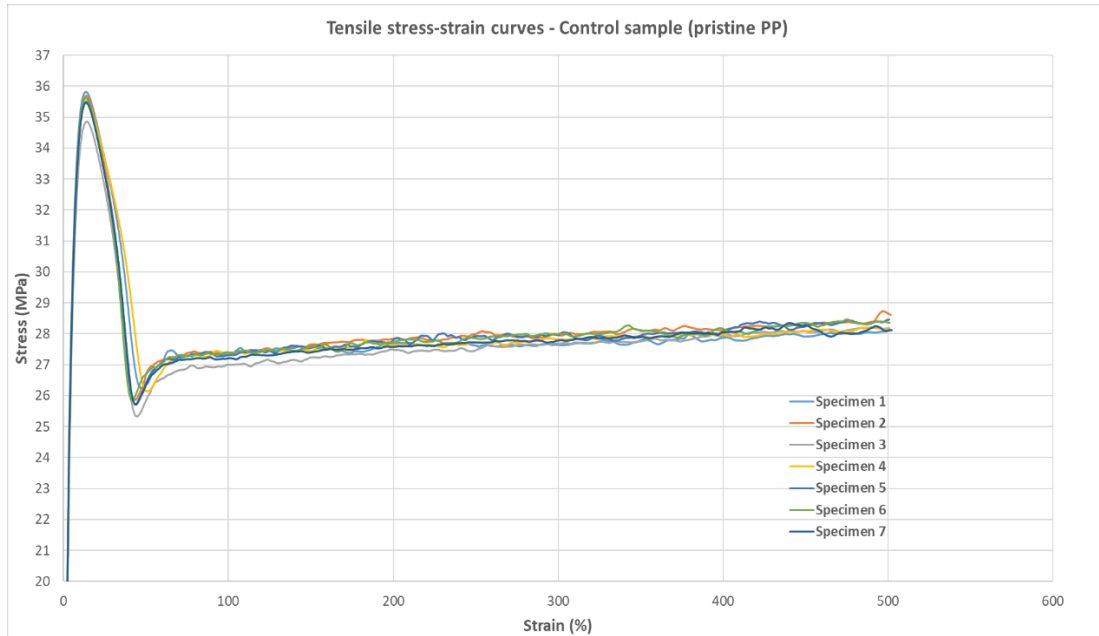
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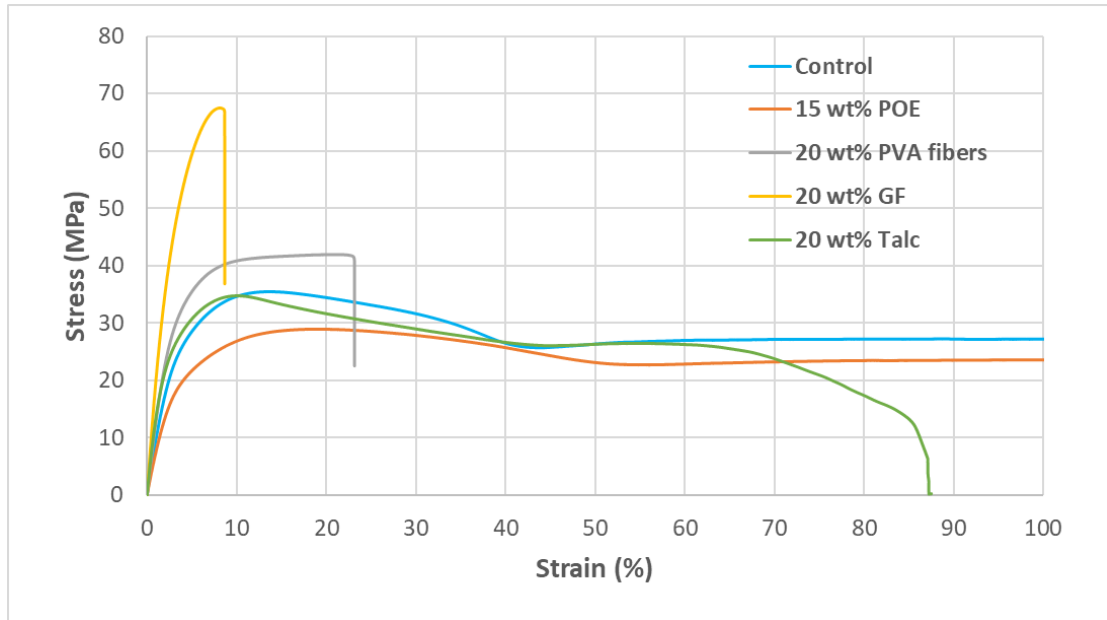
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APPENDIX

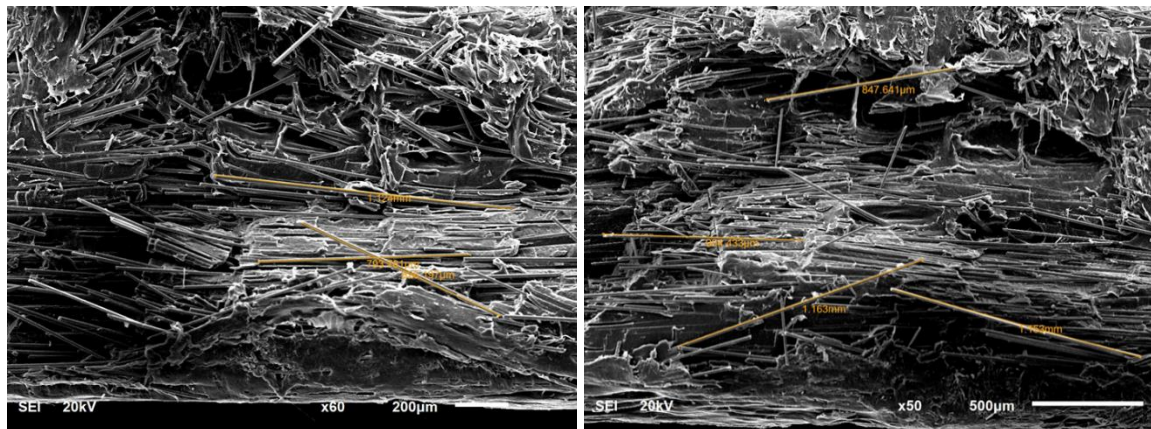
A – Tensile stress-strain curves for selected samples:



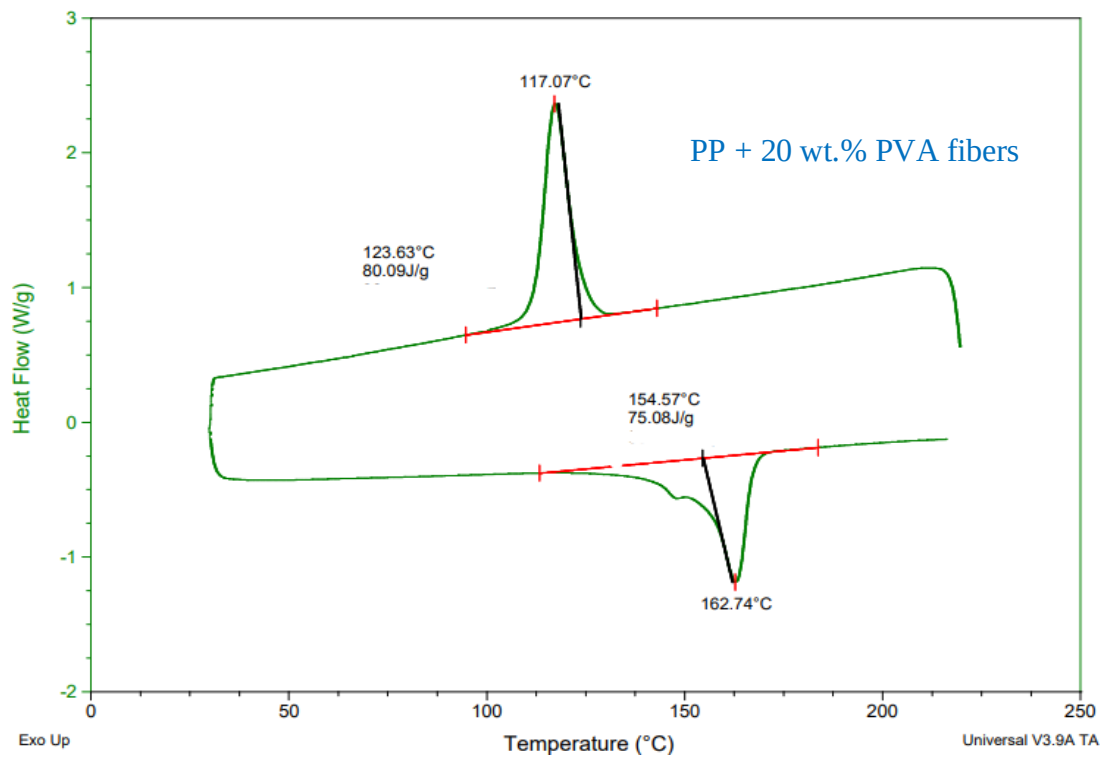
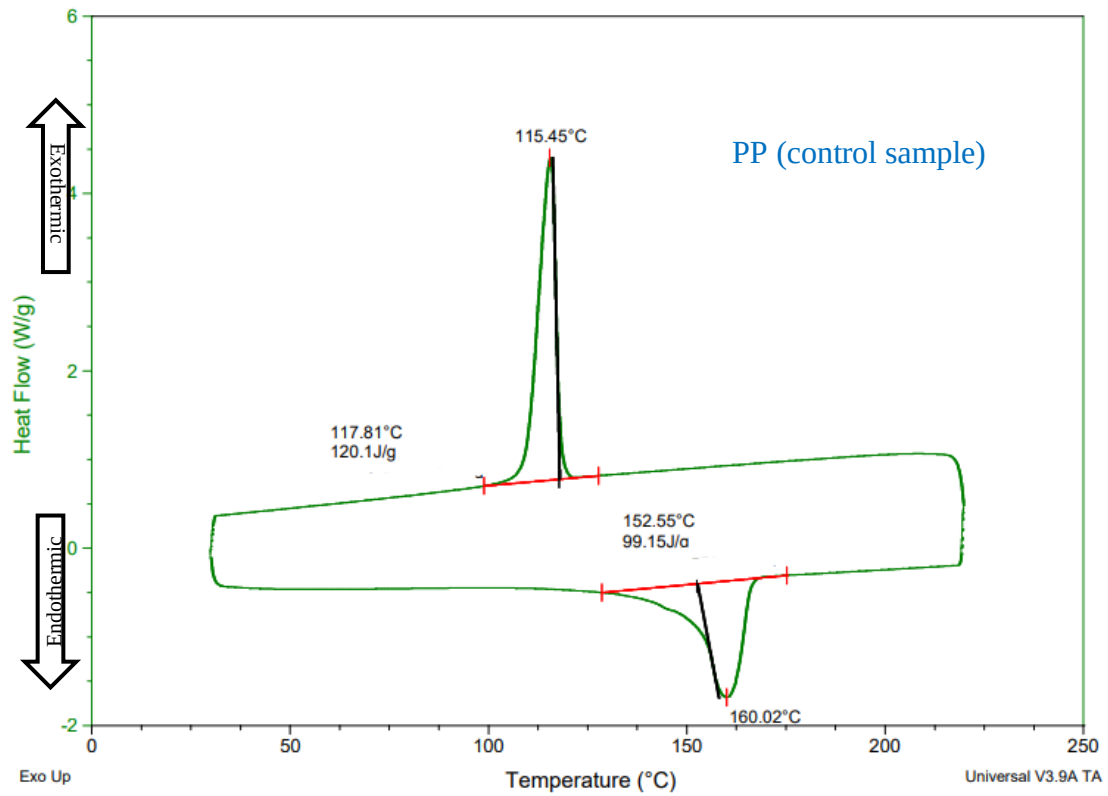


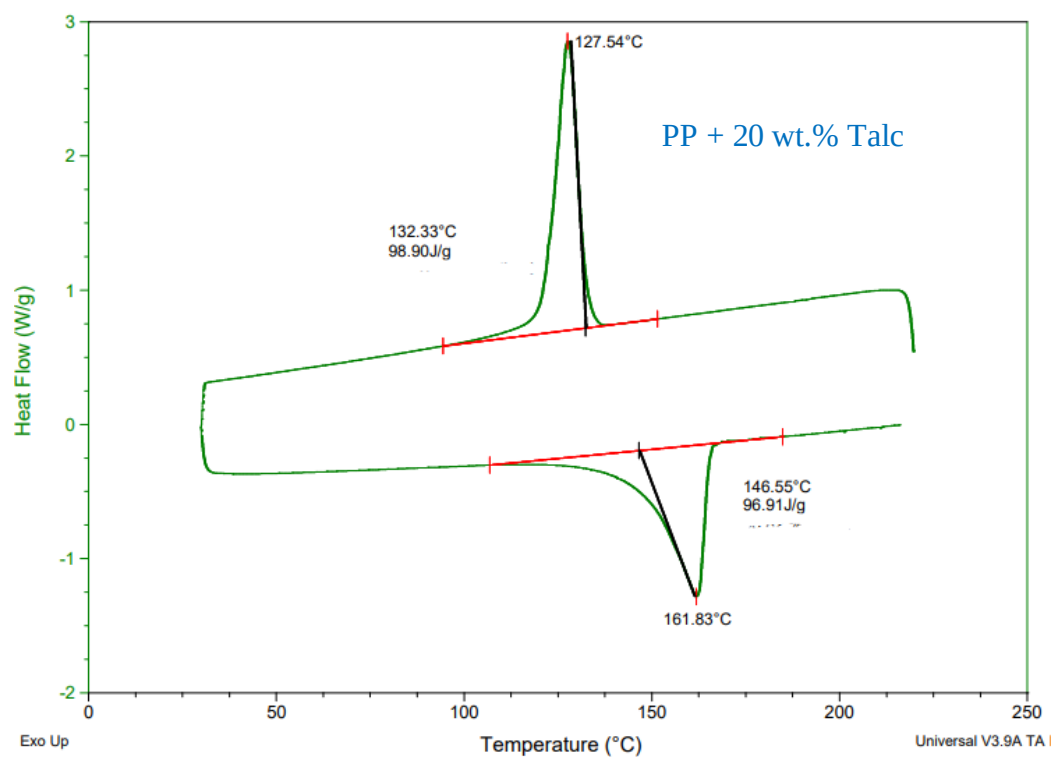
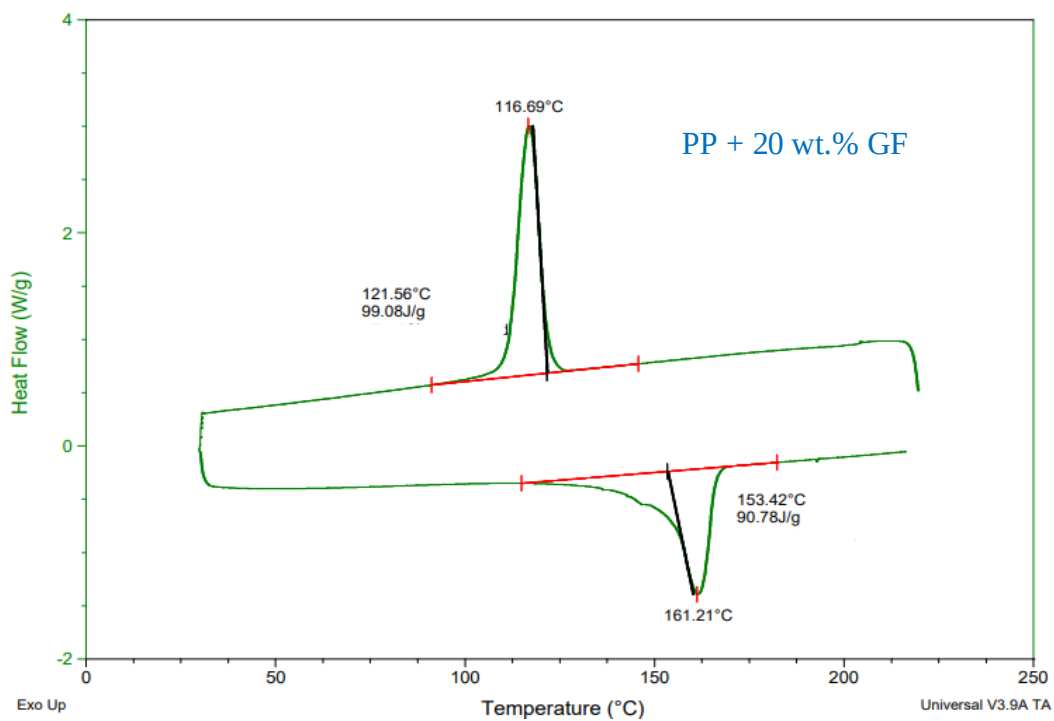
B – Residual Glass fiber length after extrusion:

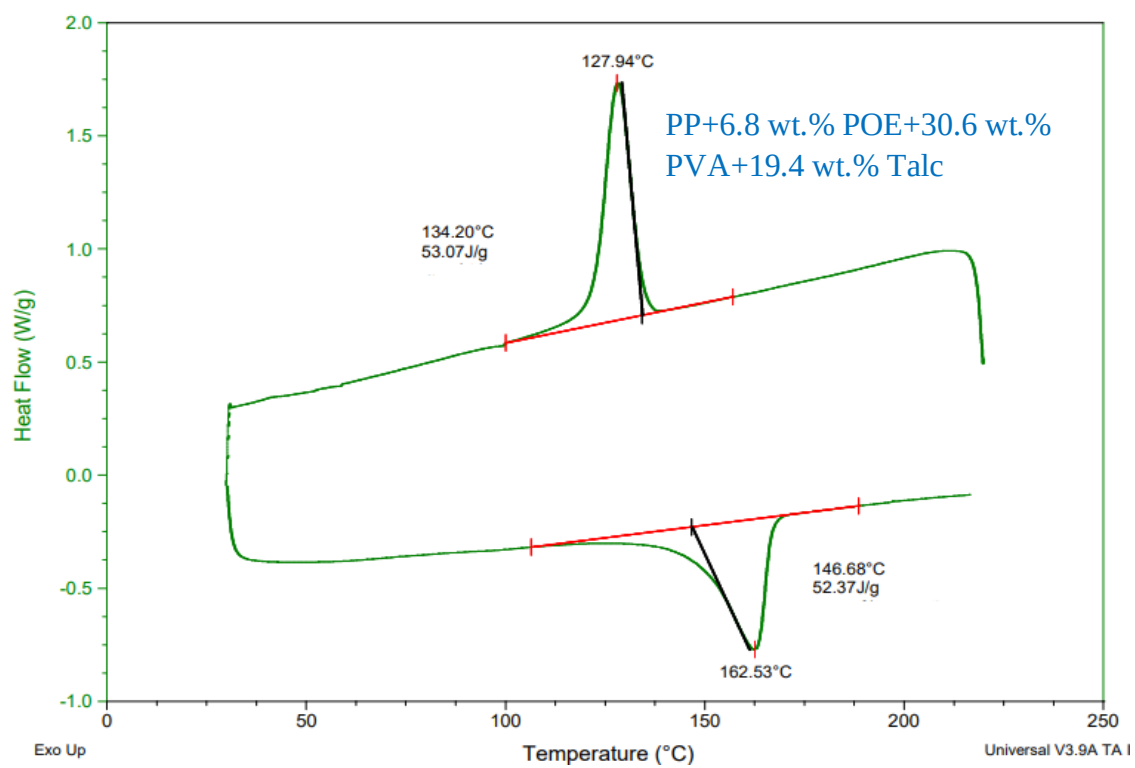
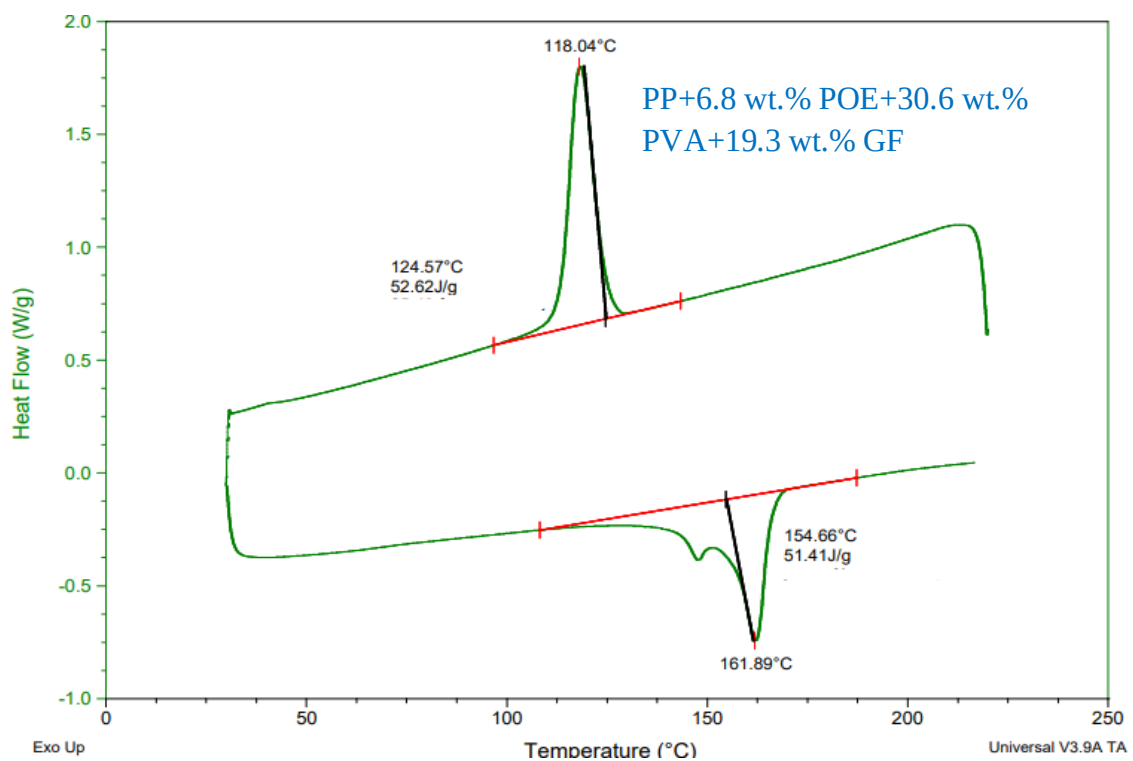
As a preliminary attempt to measure the residual fiber length of glass fibers after processing, a polymer strand sample of PP+30 wt.% GF was collected as the extrudate exited the die. Subsequently, the sample was fractured axially in liquid Nitrogen, and the broken surface was examined under the microscope to measure the length of some fibers. For more precise measurements, a sophisticated characterization technique can be employed in the future to accurately determine the final fiber lengths.



C – Differential Scanning Calorimetry test - thermograms:







D – Tensile test results: (reported results are the average values of the 8 tested specimens along with the standard deviation values between brackets)

Sample#	E-Modulus [MPa]	UTS [MPa]	Elongation [%]	Area under stress-strain curve [10 ⁶ J/m ³]
A	1064.1 (22)	28.0 (0.3)	500.0	140.0 (0.7)
B	837.2 (12)	24.5 (0.2)	500.0	120.0 (1.3)
C	1406.3 (21)	41.8 (0.6)	22.9 (1.1)	8.7 (0.9)
D	2250.6 (13)	66.6 (1.5)	8.5 (0.2)	4.1 (0.2)
E	1608.4 (15)	26.5 (0.3)	95.9 (14.2)	24.5 (3.5)
F	1075.7 (21)	35.7 (0.7)	34.0 (2.8)	10.2 (1.4)
G	1849.4 (8)	55.2 (0.4)	13.6 (0.4)	6.0 (0.2)
H	1115.1 (12)	22.5 (0.2)	300.0	67.7 (0.5)
I	2486.3 (23)	62.9 (0.7)	10.0 (0.7)	5.0 (0.5)
J	1957.7 (22)	34.9 (0.5)	10.5 (1.0)	3.2 (0.5)
K	1612.4 (7)	42.6 (0.3)	18.6 (1.2)	6.4 (0.5)
L	1924.8 (10)	48.9 (0.9)	17.0 (2.1)	6.8 (1.0)
M	2108.7 (8)	52.5 (1.2)	16.0 (1.8)	6.8 (1.0)
N	2370.7 (23)	57.1 (0.8)	14.4 (1.3)	6.7 (0.8)
O	953.8 (6)	23.9 (0.3)	33.1 (1.7)	6.7 (0.6)
P	1303.3 (16)	29.6 (0.4)	19.0 (1.4)	4.7 (0.4)
R	1422.0 (12)	31.0 (0.6)	17.1 (2.0)	4.5 (0.6)
S	1656.8 (72)	31.8(0.8)	12.3 (1.1)	3.4 (0.4)

E – Flexural and notched Izod impact tests results: (reported results are the average values along with the standard deviation values between brackets)

Sample#	Flexural Modulus [MPa]	Flexural strength [MPa]	Izod Impact Strength [J/m]
A	1802 (56.9)	53.8 (0.5)	29.5 (4)
B	1480.5 (16.0)	41.3 (0.3)	160.6 (12)
C	2423.8 (65.5)	65.0 (0.6)	78.7 (7)
D	4226.7 (54.8)	114.0 (1.2)	134.7 (4)
E	3032.3 (66.4)	58.3 (1.2)	27.4 (3)
F	1949.7 (39.3)	47.5 (0.6)	293.3 (14)
G	3168.7 (48.9)	80.2 (1.3)	232.1 (10)
H	1941.0 (68.4)	39.7 (0.4)	167.4 (10)
I	4744.2 (63.2)	104.5 (1.1)	125.7 (6)
J	3467.3 (111.1)	60.5 (0.8)	95.4 (2)
K	2656.6 (56.7)	54.3 (1.1)	400 (17)
L	3431.2 (79.7)	67.2 (1.1)	345.2 (21)
M	3771.4 (30.4)	72.9 (0.9)	302.3 (15)
N	4394.2 (109.6)	89.2 (1.8)	256.6 (15)
O	1531.2 (68.6)	30.3 (0.5)	261 (12)
P	2165.7 (96.2)	41.4 (0.4)	203.3 (10)
R	2358.8(114.1)	44.0 (0.9)	187.7 (14)
S	2977.0 (78.3)	54.4 (1.1)	168.3 (7)

Vitae

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