

In Situ Synthesis and Characterization of Ethylene-based Copolymers, Terpolymers and Composites

BY

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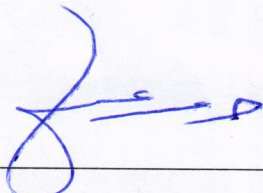
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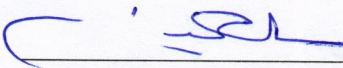
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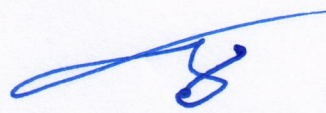
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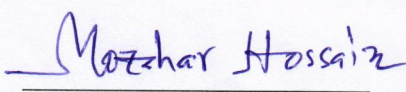

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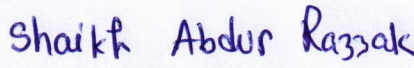

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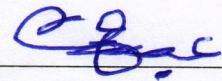
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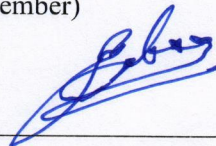



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Dedication

Dedicated to My Family, Advisor and Colleagues

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All praise due to Allah who gave me the ability to accomplish my work. Blessing and salutation to the final prophet Muhammad (pbuh) whose teaching shows the path in day and night.

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LIST OF ABBREVIATIONSs

<i>TM</i>	:	Transition Metal
<i>ETM</i>	:	Early Transition Metal
<i>LTM</i>	:	Late Transition Metal
<i>P-S</i>	:	Phosphne-Sulfonate
AN	:	Acrylonitrile
Ar ^F	:	3,5-bis(trifluoromethyl)phenyl
DFT	:	Density Functional Theory
FG	:	Functional group
HDPE	:	High-density polyethylene
MA	:	Methyl acrylate
MAO	:	Methylaluminoxane
MMA	:	Methyl methacrylate
MMAO	:	Modified Methylaluminoxane
M_n	:	Number-average molecular weight
M_w	:	Weight-average molecular weight
ROMP	:	Ring-opening metathesis polymerization
SHOP	:	Shell higher olefin process
T_m	:	Melting temperature
VAc	:	Vinyl acetate
VC	:	Vinyl chloride
VE	:	Vinyl ether
VF	:	Vinyl fluoride
CBP	:	Carbon Black Powder
CF	:	Carbon Fiber
MWCNT	:	Multiwalled carbon nanotube

SWCNT	:	Single wall carbon nanotube
GO	:	Graphene Oxide
rGO	:	Reduced Graphene Oxide
GNP	:	Graphene Nano particles
EP	:	Ethylene Propylene
EPS	:	Ethylene Propylene Styrene
LDH	:	Layered Double Hydroxide
T _m	:	Melting Temperature
T _c	:	Crystalline Temperature
T _{0.9}	:	Temperature at 10% degradation
NiCr LDH	:	Nickel Chromium Layered Double Hydroxide
DSC	:	Differential Scanning Calorimetry
TGA	:	Thermogravimetric Analysis
CRYSTAF	:	Crystallization Fractionation Analysis
XRD	:	X-Ray Diffraction Analysis
FTIR	:	Fourier Transformed Infra-Red
NMR	:	Nuclear Magnetic Resonance
SEM	:	Scanning Electron Microscopy
EDX	:	Energy Dispersive X-Ray Analysis
PE	:	Polyethylene
MOF	:	Metal Organic Framework
RM	:	Red Mud
RMR	:	Reduced Red Mud

ABSTRACT

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Thesis Title : In Situ Synthesis and Characterization of Ethylene-based Copolymers, Terpolymers and Composites.

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Polyolefin and their derivatives are an important commercial product since their invention. Hence, it is crucial to study their co and terpolymers due to their extensive use. In this research, *in situ* synthesis of ethylene-propylene copolymer, their terpolymer with styrene, and composites with nickel-chromium layered double hydroxide (LDH) has been reported along with their thermal properties. Styrene had a significant impact on the activity, increasing the yield by 195 % and 235% with an addition of 0.5 mL and 1.0 mL styrene, respectively, compared to neat ethylene-propylene (EP). The crystallinity, melting temperature, and thermal stability decreased due to styrene, nevertheless, it performed better compared to similar work of terpolymer where α -olefin was the third monomer. The incorporation of nickel-chromium (NiCr) LDH as a drop-in filler during *in situ* polymerization affected adversely on the thermal stability of the terpolymer. However, the ultrasonication treatment improved the thermal stability of the final product.

Along with the co and terpolymers of ethylene, polymerization of ethylene with different fillers were also investigated using the same *in-situ* technique. The interested fillers were two metal organic frameworks and a waste materials. The composites showed better crystallinity and the thermal stability compared to neat polyethylene. The composites with metal organic frameworks outperformed slightly the composites with the waste materials. The composites with the waste materials showed highest crystallinity of 93% at a very low

level of loading of the material as drop-in filler. However, there was no distinguishable difference in melting temperature, crystallization temperature and morphological properties of the composites compared to the control sample. In brief, the obtained polyethylene composite had better thermal stability and crystallinity with respect to polyethylene.

ملخص الرسالة

الاسم الكامل: محمد خير البحر

عنوان الرسالة: التوليف الموضعي وتوصيف البوليمرات المشتركة القائمة على الإيثيلين والبوليمرات التربينية والمركبات.

التخصص: الهندسة الكيميائية

تاريخ الدرجة العلمية: مايو ٢٠٢٣

البولي أوليفين ومشتقاتها هي منتج تجاري مهم منذ اختراعها. لذا، من الضروري دراسة تراكيب البوليمرات المختلطة الثنائية والثلاثية لهذه المركبات نظرًا لاستخداماتها الواسعة. في هذه الدراسة، تم رصد التوليف في الموقع لبوليمر الإيثيلين - البروبيلين المشترك وثلاثيمره مع الستايرين، والمركبات المترابطة مع هيدروكسيد مزدوج الطبقات من النيكل والكروم (LDH) مع تحليل خصائصهم الحرارية. كان للستايرين تأثير كبير على الفعالية، حيث زاد الإنتاج بنسبة 195% و235% بإضافة 0.5 مل و 1.0 مل ستايرين على التوالي، مقارنة بالإيثيلين - البروبيلين النقي. انخفضت درجة البلورية ودرجة الانصهار والاستقرارية الحرارية بسبب الستايرين، ومع ذلك، كان أدائها أفضل بالمقارنة مع الأعمال المماثلة لثلاثي البوليمر حيث كانت أحد مونومرات α -أولفين الثالثة. من وجهة نظر أخرى، أثرت إضافة هيدروكسيد النيكل-الكروم (LDH) كمادة حشو بالتتنقيط "Drop-in" خلال البلمرة على الاستقرارية الحرارية لثلاثي البوليمر بشكل سلبي. ومع ذلك، تحسنت الاستقرارية الحرارية للمنتج النهائي بعد المعالجة بالموجات فوق الصوتية.

بالإضافة إلى الكوبوليمرات وثنائي البوليمرات من الإيثيلين، تمت دراسة تفاعل الإيثيلين مع حشوات مختلفة باستخدام التقنية نفسها. كانت الحشوات المثيرة للاهتمام عبارة عن اثنين من الأطراف العضوية المعدنية ومواد نفايات. أظهرت المركبات ذات تراكيب الأطراف العضوية المعدنية تحسناً طفيفاً في التبلور والاستقرار الحراري مقارنةً بالبولي إيثيلين الخام. ولكن المركبات مع مواد النفايات أظهرت أعلى درجة تبلور بنسبة 93% عند مستوى منخفض جداً من تحميل المادة كحشو بالتتنقيط "Drop-in". ومع ذلك، لم تكن هناك فروق جلية في درجة الانصهار ودرجة التبلور وخصائص

الشكل الخارجي للمركبات مقارنةً بالعينة الضابطة. بدون الخوض بالتفاصيل، يعتبر المركب البولّي إيثيلين المحصل عليه ذو استقرار حراري وتبلور أفضل بالمقارنة مع البولّي إيثيلين الخام.

CHAPTER 1

INTRODUCTION

In the period of pandemic and post pandemic, the use of polyolefins has been increased due to their low cost, single use, a noncorrosive character, high strength, low weight, and simplicity of processing. Polyethylene is the mostly used polyolefin. [1], [2] The worldwide polyethylene market was estimated at US\$139.95 billion in 2021 and is anticipated to increase to US\$186.16 billion by 2027 at a CAGR of 4.87%.*(Global Polyethylene Market: Analysis By Demand)* The post pandemic scenario shows there is an in jump in use of polyethylene in the upcoming years.*(Polyethylene Market Size, Share, Trends | Analysis Report [2029])*

Polyethylene covers more than 50% of total plastic is covered by polyethylene. So, the various properties in this polymer are highly expected. Polyolefins have a disadvantage, notwithstanding their relevance. Because they are hydrophobic hydrocarbon compounds with modest hydrophilicities, their applications are limited because some need hydrophilic qualities. As a result, polymer chemists are interested in developing functionalized polyolefins with numerous polar functional groups in their main chains. [3] However, homopolymerization of ethylene lacks required qualities, and polyolefins with polar functional groups are thought to have not only unique bulk properties, but also changed surface properties such as dyeability, adhesion, and wettability.[4] A radical-initiated procedure or, more typically, a coordination/insertion process by transition metals are used

to make polyethylene (PE).[5] Metal-mediated coordination polymerization has piqued attention since the discovery of Ziegler-Natta polymerization and has emerged as the most potent approach for manipulating polymerization stereochemistry.[6] Polar vinyl monomers behold a electron-withdrawing or -donating groups directly to the olefin moiety. For this reason fundamental polar vinyl monomers have different reactivities than ethylene. [7]

PE copolymers offer improved characteristics over PE and are produced using radical polymerization techniques that need extremely high pressures and temperatures. [5] The drawbacks associated with the low hydrophilic polyolefins compatibility , sustainability, adhesion, gas barrier properties is solved either through radical polymerization or coordination-insertion polymerization while the later removes the drawback of radical of not producing well defined polymers.

Early transition metal (ETM) catalyst contributed significantly in the polymerization and copolymerization. Among them Zeigler-Natta, Metallocene and Philips catalyst are the major groups. The catalysts are mainly Ti and Zr based. They are very good at handling non polar monomers and it is a proved technology. Zeigler Natta is the pioneer of this type of organometallic catalyst and for their contribution they got Nobel prize in 1963. Later on several Nobel prize has been given in this field. But the ETM can not handle polar monomers due to high oxophilicity of the metals.

Copolymerization of monomers, specially polar vinyl monomers with ethylene is a matter of great interest. A more functional group-tolerant late metal catalysts potentially offer an attractive alternative in this regard for generating such value-added copolymers . Late transition catalysts are mainly Ni ,Pd ,Co, Fe and Rh based

Polyolefin elastomers are one of the most important commercial synthetic rubbers due to their excellent physical and chemical properties at a very low cost. They have contributed to modern human life for various applications including transportation, building materials, industries, piping and instrumentation, sports, etc. However, ethylene-propylene (EP) with a third monomer has been the centre of interest due to the versatile properties of EP terpolymers ranging from thermoplastic to elastomers.[8] The EP terpolymer exhibits good elastic and mechanical properties, good aging resistance, excellent resistance to heat, oxygen, and ozone, excellent resistance against polar solvents and aqueous media, and the capacity to incorporate very large amounts of fillers and oil plasticizers, leading to affordable rubber compounds.[9], [10] In the EP terpolymer, the third monomer remains mainly dienes, higher α -olefins.[9], [11]–[17] Upon polymerization, there might still remain unsaturated bonds in the terpolymer.[18] These terpolymers with a large proportion of ethylene or propylene (or other -olefins) and a small amount of a monomer whose molecule contains more than one double bond also exhibit good elastic and mechanical properties. Different monomers could be used to produce terpolymers with a low degree of unsaturation which is suitable for the traditional vulcanization processes used for rubbers. EP copolymers are generally processed for excellent elastomeric properties by two methods; vulcanization and peroxide curing where in peroxide curing, the unsaturated double bond in the macromolecule has the ability to open the door for good product.[10], [14] Despite reported literature on terpolymers, there is still required investigation about terpolymerization of ethylene- propylene and a monomer that contains unsaturated bonds to substantially subject to react for vulcanization or peroxide curing.[8], [14], [19], [20]

Although there is availability of plenty of suitable aromatic comonomers, the terpolymerization of such species with EP is however under-investigated. Poly (styrene-butadiene-styrene), or SBS rubber, is a form of hard rubber that contains styrene as one of its constituents.[21] In this work, the effect of styrene in EP terpolymerization and the properties of the produced terpolymers were investigated.

A narrow distribution in polydispersity index (PDI) has been found to be crucial for the ethylene-propylene copolymer-derived synthetic rubbers' mechanical qualities, however, moderately high molecular weight is crucial for the rubbers' processability. The homogeneity in the structure of the EP micro chain is also crucial.[10], [22] Metallocene catalysts, in contrast to typical Ziegler-Natta catalysts, may copolymerize with high homogeneity and provide high polymer yields with low polydispersity indices (PDI). [9], [12], [23]

Additionally, metallocene has the advantage to use different cocatalysts[18] including Isobutylaluminum aryloxides,[24]triisobutylaluminium (TIBA),[12] TIBA/borate,[25] triethylaluminium (TEA),[26] and (modified) methyaluminoxane (MMAO/MAO). However, the most effective cocatalyst remains methyaluminoxane based i.e., MAO/MMAO ,[24] Borates can be used as activators.[26]

Although the characteristics of polymers produced using homogeneous metallocene catalysts have improved, nevertheless, these polymers still have inferior thermal and mechanical properties for uses needing greater thermal and mechanical durability. Fillers can add or boost up the desired properties of the polymer. The inorganic fillers can greatly influence the mechanical, thermal and electrical properties, flame retardance, barrier properties of the polymer composite.[27]–[29] Different types of fillers like ceramic based

i.e. Aluminum Nitride, Silicon Nitride, Calcium Zirconate,[30]–[33] oxide based nanofillers i.e. TiO_2 , Al_2O_3 , ZrO_2 , [29], [34], [35] nano carbon based i.e. carbon black, multiwalled carbon nano tube (CNT), graphene, CNT, [36]–[38] Layered double hydroxide (LDH), [39], nanofiller composite (rGO-CNT-Fe) [40] had been used to improve the polymer thermal and mechanical properties. Depending on the desired properties fillers can be selected for the polymer specially for polyethylene. In this regard, the size, shape, loading, dispersion of fillers can influence significantly the properties of the polymer composite. [28] Despite the fact that some fillers performed well, the polymer composite continues to require improved thermal characteristics.

By *in situ* polymerization, LDHs have been employed as nanofillers and catalyst supports in polymer nanocomposites (polyethylene i.e., PE, and polypropylene i.e., PP). The MWD, crystallinity, polymer morphology, catalytic activity, and flame retardancy are all affected by LDHs. [11] Metal Organic Framework (MOFs) has attracted the researchers for last two decades extensively for its various properties like thermal, mechanical, high surface area and porosity. [41] It is gradually emerging to industrial scale. Due to the extremely strong metal ligand binding, zirconium-based MOFs stand out among other kinds of MOFs for their exceptional thermal, chemical, acidic, aqueous, and water vapor stability. [42], [43] Most famous zirconium based MOF is UiO-66 and UiO-66- NH_2 . Apart from its ease of synthesis it also exhibits higher chemical and thermal stability with high porosity and surface area which makes it appealing for using various applications. [41], [43] Waste management had been a big issue for decades and red mud utilization is one of the major concern in this respect. [44], [45] Red mud after some simple modification can be utilized as a filler. This has the potential to avoid expensive fillers as well as waste management.

In this work our aim was to in situ synthesis ethylene propylene copolymer, ethylene propylene styrene terpolymer and their composites with nickel chromium LDH. The thermal and crystallization behavior of the synthesized polymers was studied. Besides terpolymer composites, the composite of only polyethylene with two category (three fillers i.e. UiO-66, UiO-66-NH₂ and reduced red mud) were synthesized and studied as well. To our best of knowledge nobody has ever used those materials as drop-in filler for polyethylene.

CHAPTER 2

LITERATURE REVIEW

2.1 Development of Transition Metal Based Catalyst

2.1.1 Historical Background

Early transition metal (ETM) catalyst contributed significantly in the polymerization and copolymerization. Among them Zeigler-Natta, Metallocene and Philips catalyst are the major groups. The catalysts are mainly Ti and Zr based. They are very good at handling non polar monomers and it is a proved technology. Zeigler Natta is the pioneer of this type of organometallic catalyst and for their contribution they got Nobel prize in 1963. Later on several Nobel prize has been given in this field. But the ETM can not handle polar monomers due to high oxophilicity of the metals.

Copolymerization of monomers, specially polar vinyl monomers with ethylene is a matter of great interest. A more functional group-tolerant late metal catalysts potentially offer an attractive alternative in this regard for generating such value-added copolymers . Late transition catalysts are mainly Ni ,Pd ,Co, Fe and Rh based.

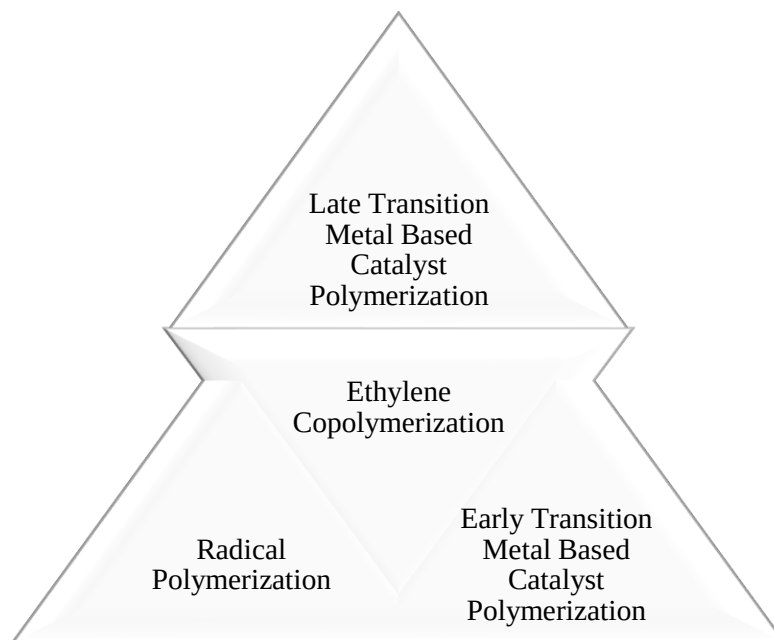


Figure 1 Methods of Ethylene Copolymerization with Polar Monomers.

The development of late transition based metal catalyst started with Klabunde in 1987 when he pointed nickel catalysts of the shell higher olefin process (SHOP) . This type of catalyst showed potential to copolymerize ethylene with certain polar monomers.[46] The major and significant breakthrough was made by Brookhart in 1996 where α -diimine Pd catalyst successfully copolymerized ethylene with methyl acrylate (MA) and Vinyl ketone monomer and some other copolymer incorporation was developed eventually.[47]–[49] Jonson and Grubbs used Ni phenoxymine catalyst to copolymerize. The limitation of comonomer variation was yet to be solved. Drent and colleagues announced yet another big accomplishment in this sector in 2002. Drent-type catalysts (Pd-Phosphine-Sulfonate) allowed ethylene copolymerization with a remarkable array of fundamental polar monomers, according to research.[50] Nozaki et al. copolymerized ethylene with methyl methacrylate (MMA), which has greater steric needs owing to 1,1-disubstitution and certain related comonomers, in 2018. In that work an imidazo[1,5-a]quinolin-9-olate-1-

ylidene supported palladium catalyst was used. Chen & Chen directly copolymerized ethylene with polar-functionalized 1,2-disubstituted ethylene effectively by combining ruthenium-catalyzed ethenolysis with palladium-catalyzed copolymerization. [51]

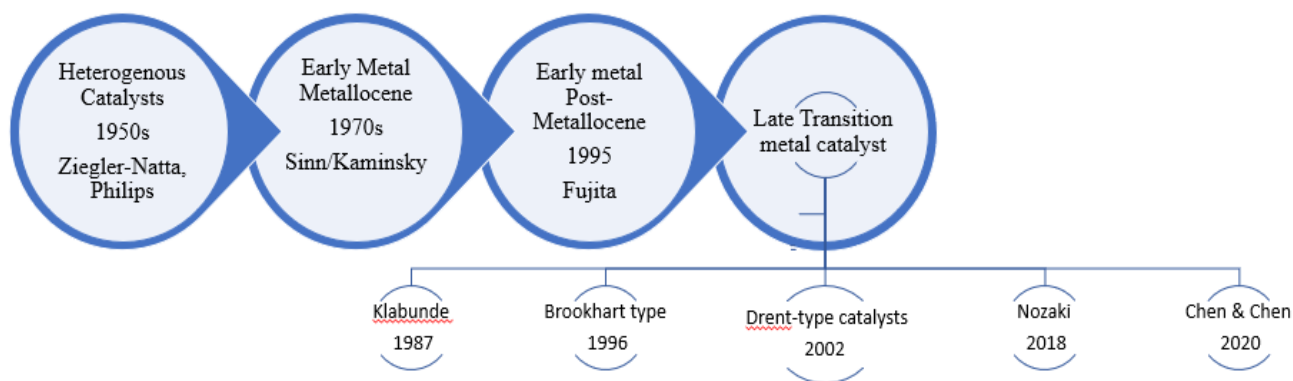


Figure 2 History of development of catalysts for ethylene polymerization.

The polar monomers are olefins with polar functional groups around the carbon–carbon double bond like (meth)acrylate, vinyl acetate, and vinyl halides. In modern industrial processes is primarily reliant on the utilization of those for the creation of synthetic polymers. [3] Manufacturers are highly interested in building composites of improved structural, physical, and aesthetic properties of polyolefins with other materials such as polar polymers, fibers, or talc . To create a good affinity of polyolefins with these day to used materials, polar functionalities must be included into the polymer chain. [52] However, when polar monomers with polar functional groups are used, side reactions such as -coordination and -elimination of the functional group cause the catalysts to deactivate. Nonetheless, recent advances in late transition metal catalysis have permitted the

coordination–insertion polymerization of many different forms of functional polymers from polar monomers.

2.1.2 Early Transition Metal Based Catalyst

Amongst the early transition metal-based catalyst Zeigler Natta is the most extensively studied[4], [53]–[60]. It is Titanium based catalyst. Other early transition metal based catalyst are Zr[61]–[64] , Cr , Nb based[65]–[67]. Lanthanides polymerize ethylene and acrylic esters because they are d-electron deficient metals akin to early transition metals like Ti and Zr.[68]

Despite metallocene catalysts, have provided exceptional prospects for the production of new olefin-based materials[69]–[72], they are typically viewed as unpromising for such copolymerization. Many works has been done to copolymerization of polar commoners and work in ongoing. [73]. The main reason for the failure of early transition metal catalyst is the high oxophilicity of them.

2.1.3 Late Transition Metal Based Catalyst

Late transition metal based catalyst performs several advantage over early transition metal based catalysts for ethylene copolymerization with polar monomers. The major other types radical copolymerization requires very undesired reaction condition while not having control over polymer branching. ETM catalyst becomes poisoned due to their high oxiphility. Low Oxophility, the capacity to copolymerize with polar monomers, the ability to create branched microstructures out of ethylene alone (methyl branches being the most prevalent), and the lack of the need for expensive comonomers etc. make LTM catalysts

very prone to be used. [74][75] For these LTM catalyst has high catalytic activity, high MW copolymer generation capacity with good copolymer incorporation ability.

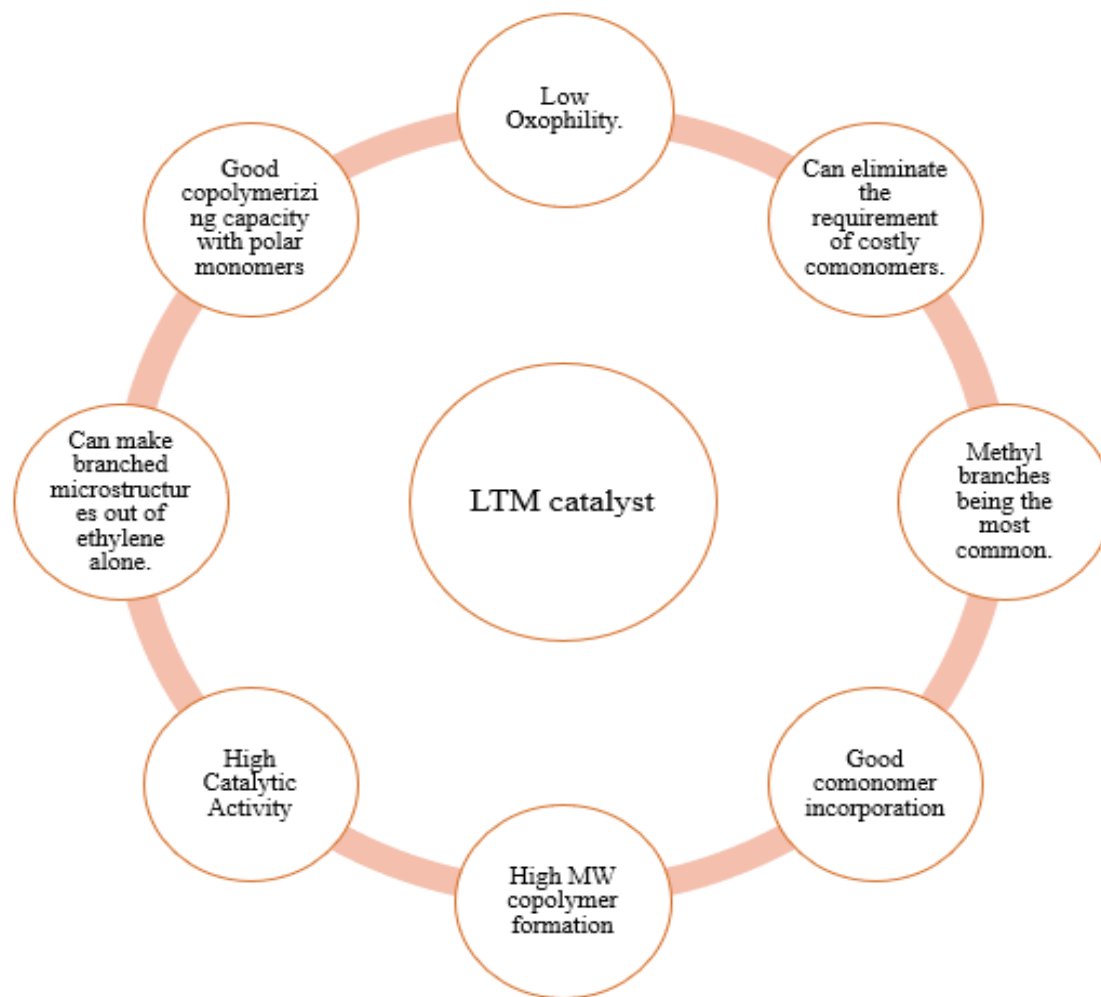


Figure 3 Advantages of using LTM based catalyst for ethylene copolymerization.

After the invention of Brookhart type catalyst more than 25 years intensive study was made on α -diimine based catalysts. In table 02 some of the major catalyst and corresponding ligand along with significance achievement is summarized. From that is evident that Ni and Pd based catalyst are very dominant and the use of other LTM catalyst is very limited and not improved.

Table 1 Significant Late Transition Metal Catalyst for ethylene copolymerization.

Metal base	Organic base	Major Findings	Reference
Ni, Pd	α -diimine	With this catalyst, only ethylene as feedstock is enough to generate branched polymer.	[74]
Pd	phosphine-sulfonate	Able to produce highly linear polyethylene main chains whereas α -diimine produce branched polyethylene.	[3]
Ni, Pd	diphosphazane monoxide ligands.	The nickel catalysts performs close to palladium analogues.	[76]
Ni	imine/phosphine-oxide ligand	In this nickel system, electronic effects outnumber steric effects and take precedence.	[77]
Ni	phosphino-naphtholate chelate ligands	High activity for ethylene, ethylene-methyl acrylate and ethylene-1,1-disubstituted difunctional ethylene comonomer with good comonomer incorporation and so on.	[78]
Ni	amidine/phosphine-oxide	High activity comparing to imine/phosphine-oxide Ni catalyst (approximately one order of magnitude higher)	[79]
Pd	alkylphosphine– sulfonate	Can produce high molecular weight polymer.	[80]
Fe	bis(imino)pyridyl	Chain walking Polymerization with low cost Fe catalyst.	[81]

Amongst Ni and Pd based catalysts α -diimine and Phosphine-Sulfonate ligand based catalyst are mostly studied due to their high performance where modification of the substituents of the ligand being one of the prime sector.

2.2 Novel Monomers and Copolymerization of Ethylene

There has been a lot of work on the copolymerization of PE with other monomers. Amongst them α -olefins i.e. propylene, 1-butene, 1-hexene, 1-octene, 1-decene etc. are the most. ETM catalyst performs outstanding performance for them. Apart from that, some monomers like dienes, aromatic monomers (Figure 04) also expected to be done smoothly by ETM catalysts due to their nonpolarity. In case of non polar comonomer many works has been done in situ and non in situ.

The copolymerization of ethylene and different polar monomers[41]–[48] had already been established by a number of research organizations. Table 02 includes the most common of them. Other than the listed commoners work with *N*-isopropylacrylamide and *N*-vinyl-2-pyrrolidinone has been done also. The controlled copolymerization of comonomers is very important to achieve desired polymeric properties. For example, ethylene-vinyl acetate copolymers can be used to improve the diesel property with methacrylate-acrylamide copolymers where ethylene-vinyl acetate (28 %) works best.[90]

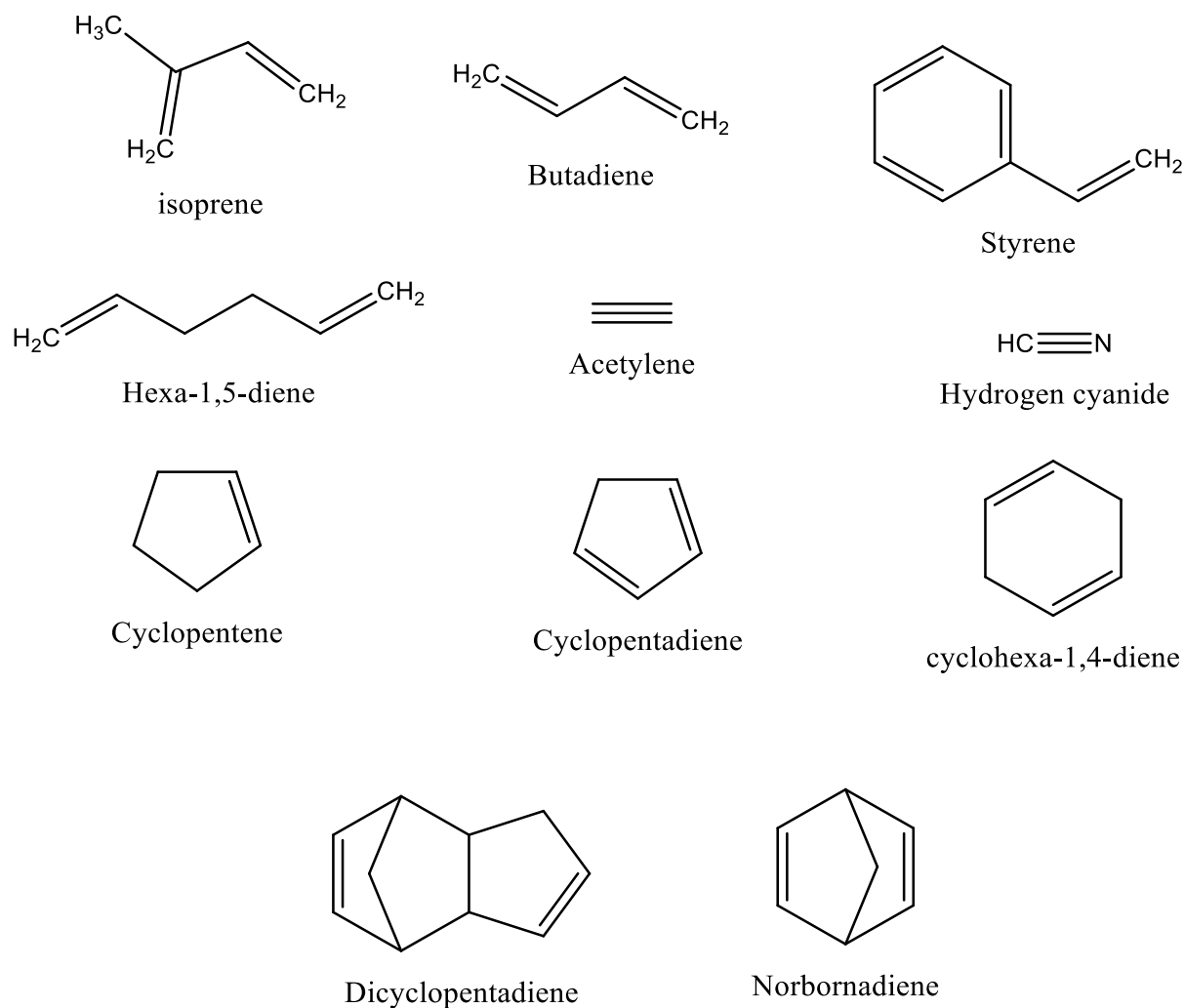
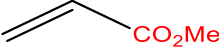
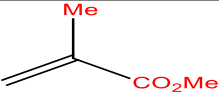
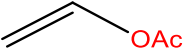
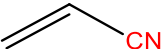
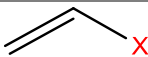
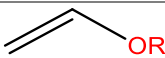
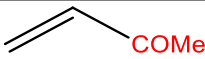
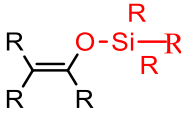
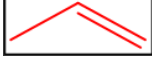
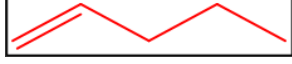
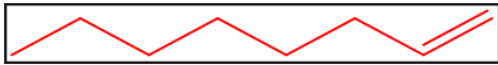
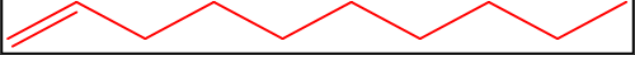


Figure 4 Non polar comonomers excepts alpha olefins.

Table 2 Polar monomers used for ethylene copolymerization.

<i>Polar Monomer</i>	<i>Formula</i>	<i>Reference</i>
Methyl Acrylates (MA)		[91]
Methyl Methacrylate (MMA)		[92]
Vinyl Acetate (VAc)		[93]
Acrylonitrile (AN)		[94]

Vinyl Halide (VX)		[95]
Vinyl Ether		[96]
Methyl Vinyl Ketones		
Silyl Vinyl Ether		[97]

Monomer	Formula	Reference
1-Hexene		H. Mazhar
5-ethylidene-2-norbornene (ENB)		A. Ali et al 2011
1-Hexene		H. Mazhar
Propene		Y. Jing et
ω -bromo- α -olefins		J. Wang et
1-pentene		N Luruli et
1-octene		J. Liu et al
1-decene		J. Liu et al

The key feature is the linear polyethylene main chain. General formula is given in fig 04.

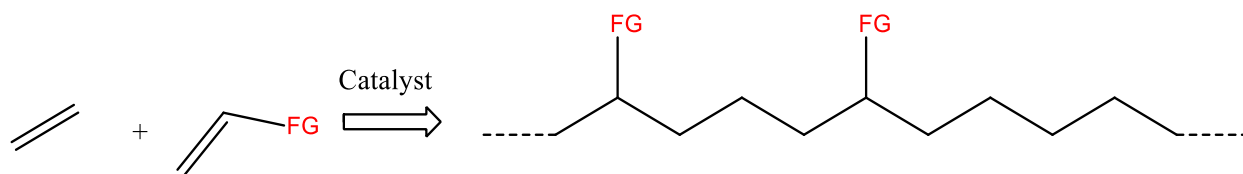


Figure 5 General formulae of ethylene copolymerization with comonomers.

2.3 Fillers

Fillers include metal powders, metal oxides, carbonates, talc, layered silica, silica, and fibers made of carbon nanotubes, carbon nanofibers, and polymer fibers. Because they provide a significant barrier against the permeation of gases and liquids, layered inorganic materials like multilayered silicates, clay, montmorillonite, or graphene are particularly interesting for use in this context.[98] In Table 03 used fillers for creating polymer composite has been listed.

Table 3 Fillers used in making polymer composites

Serial No	Nanofillers	Reference
	Carbon Nanotube (CNT)	[99]
	GO	[100]
	rGO	[101]
	ZnAl LDH	[11]
01	Ceramic Nanofiller (Aluminium Nitride)	[30]
02	Graphene/ MgAl LDH	[39]
03	TiO ₂ -Fe	[102]
04	Calcium Zirconate	[32]
05	Ceramic Nanofiller (Silicon Nitride)	[31]

06	TiO ₂ -Fe	[34]
07	Mn doped- Titania (1% Mn- TiO ₂)	[29] [28]
08	Fe doped- TiO ₂	[103]
09	Graphene oxide nanofillers	[104]
10	SiO ₂ - TiO ₂	[35]
11	Boehmite Nanorod	[105]
12	Nanosilica	[106] [107]
13	Silica , CBP, CF, MWCNT	[108]
14	glycidyl methacrylate (GMA) modified TiO ₂ and Clay nanofillers	[33]
15	EG(expanded graphaite)/SWCNT	[109]
16	SiO ₂ -ZrO ₂ (LLDPE)	[110]
18	Polyaniline/Graphite Oxide or rGO (PANI-GO/rGO)	[36]
19	Iron- Carbon	[111]
20	Carbon nanofillers (3 tyeps : 0D carbon black, 1D MWCNT, 2D graphene)	[37]
22	ZnO	[112]
23	Ag (Silver) Nanoperticles	[113]
24	Graphite nanocomposites	[114]
25	Carbon Nanotube (Metallocene)	[27]
26	Silica-Silver (SiAg)	[115]
Serial No	Nanofillers	Reference
27	CB–PET (Carbon Black-Poly ethylene terephthalate)	[116]
28	Clay nanocomposite (Bentonite type clay and MgCl ₂)	[117]
29	Clay Nanocomposite (Natural Palygorskite)	[118]
30	TiO ₂ -Based nanoparticles	[119]

31	Dimond nanocomposite (sol-gel surface modified)	[120]
32	Silica -clay-organo-heterostructures	[121]
33	Modified montmorillonite nanocomposites with an aluminosilicate content	[122]
34	Alumina Nano composite	[123]
35	Silica Nanosphere	[124]
37	Carbon Nanotube	[125]
39	Aluminum Nanoparticles	[126]
40	Na ⁺ -Montmorillonite Nanocomposites	[127]
41	graphite nanosheets, molybdenum disulfide, shungite, and montmorillonite	[128]
42	GO & rGO	[129]
44	CNT-Fe (modified)	[130]
45	Functionalized GO	[131]
46	Cellulose Nanocrystal	[132]
48	Graphite NP (GNP) & GO	[133]
49	GO	[134]
50	Iron oxide/cassava starch nanoparticles	[135]
51	Silver nanoparticles encapsulated in silica	[136]

CHAPTER 3

RESEARCH MEHODOLOGY

3.1 Materials

Ethylene and Ethylene-propylene (95:05) gas mixture (99% pure) were purchased from Igas (Dammam, Saudi Arabia). Styrene, Bis(cyclopentadienyl) Zirconium(IV)dichloride, modified-methylaluminoxane (MMAO), Nickel Chloride hexahydrate $[\text{NiCl}_2 \cdot 6\text{H}_2\text{O}]$, Chromium Chloride hexahydrate $[\text{CrCl}_3 \cdot 6\text{H}_2\text{O}]$, Sodium Carbonate (NaCO_3), Sodium hydroxide (NaOH), toluene, acetone, methanol, and all other chemicals were purchased from Sigma Aldrich (Darmstadt, Germany). Metal organic frameworks UiO-66 and UiO-66- NH_2 were collected from Research Institute , KFUPM and Red mud was collected from local industrial waste.

3.2 Synthesis of NiCr-LDH

Precursor Nickel and Chromium salt solution water were prepared in a 3:1 molar ratio. Then, to create mixed solution A, NiCl_2 (1 M) and CrCl_3 (1 M) were added to a beaker at a ratio of 3:1, respectively. Solution B was created by dissolving around 0.2 mol of Na_2CO_3 and 0.8 mol of NaOH in distilled water. Solution B was then slowly titrated into solution

A, and the pH of the reaction mixture was maintained at 8.5.[137]The reaction solution in the beaker was kept for 24 hours under vigorous stirring conditions. The obtained product was centrifuged and washed three times till the pH of the product reaches 7. The wet cake was dried under a vacuum at 40 °C for 24 hours. It was further acetone washed and the centrifugation and drying process was repeated. The resultant product was kept at 180 °C for the removal of water in it. The final product was kept in a nitrogen environment and used as filler.

3.3 Ethylene-Propylene and Ethylene-Propylene-Styrene

Polymerization

The ethylene-propylene-styrene polymerization was performed in a 250 mL Schlenk flask reactor. Inside the glovebox, the flask was charged with the 6 mg Cp_2ZrCl_2 catalyst and 80 ml anhydrous toluene solvent. A specified amount of Styrene and LDH were also added in this step. The sealed flask is taken out from the glove box and sonicated for 30 min. Post-sonication the reaction mixture was connected to the EP gas supply maintained at a pressure of 5 psi and the temperature of the reactor was maintained at 60°C. After 2 minutes of gas saturation, 5 mL of the MMAO co-catalyst was injected into the reactor to start the polymerization. The reaction was allowed to run for 30 minutes followed by termination by adding 100 mL of methanol that contained 5% by volume of HCl. The product was washed with excess methanol and filtered followed by drying in an oven at 40 °C for 16 hours.[11]

3.4 Polymerization of Ethylene

The polymerization of ethylene was done in a similar fashion that was done for ethylene-propylene polymerization with slight modification. Briefly, a 250 mL Schlenk flask was charged with 6 mg of Zirconocene catalyst (Cp_2ZrCl_2) and 80 mL anhydrous toluene solvent inside the glove box. For polymer composites specified amount of filler was added in the flask at that stage. The flask was sealed and after taking out of the glove box, ethylene gas was supplied at a pressure of 5 psi in the flask while maintaining the temperature at 30 °C. In order to begin the polymerization, 5 mL of the MMAO co-catalyst was added into the reactor after 3 minutes of gas saturation. Following the addition of 100 mL of methanol that contained 5% by volume of HCl, the reaction was stopped after being allowed to proceed for 30 minutes. The result was filtered after being rinsed with excess methanol, and it was then dried for 16 hours at 40 °C in the oven.[30]

3.5 Characterization Technique

The obtained layered double hydroxides, polymer and polymer composites were characterized by the following techniques

3.5.1 X-Ray Diffraction Spectrometry (XRD)

A Shimadzu diffractometer (XRD-6000, Japan) was used for X-ray diffraction (XRD) of the LDH sample. The XRD uses Cu K radiation operated at 40kV, 15mA. The sample was scanned in 2θ degree angle range of 3 to 90 degrees at 2 degree/minute scan rate.

3.5.2 Fourier Transformed Infra-Red (FTIR)

Nicolet iS10 Fourier Transform Infrared (FTIR) Spectrometer was used for the investigation of the LDH and the polymer samples. The FTIR was operated in attenuated total reflection (ATR) mode in a wavenumber range of 400 to 4000 cm^{-1} . For each sample, 64 scans were recorded with a resolution of 4 cm^{-1} .

3.5.3 Differential Scanning Calorimetry (DSC)

The thermal behavior of terpolymers was analyzed by DSC (TA Q1000). The equipment was operated in a temperature range of 30-180 $^{\circ}\text{C}$ with a ramp rate of 10 $^{\circ}\text{C}/\text{min}$ in a heat-cool-heat mode. About 5 mg of the sample was loaded in a non-hermetic pan and subjected to the heating mode of DSC. The first heating cycle removes the thermal history of the polymer, while the peak that appeared during the cooling was associated with the crystallization temperature (T_c). The polymer melting temperature (T_m) was evaluated as the peak of the second heating cycle curve.

3.5.4 Thermogravimetric Analysis (TGA)

The TGA (SDT-Q1000, TA Instruments) was used to examine the thermal stability of samples. The instrument was operated under a nitrogen environment in the temperature range of 30-850 $^{\circ}\text{C}$. About 10 mg of the polymer sample was heated to 800 $^{\circ}\text{C}$ at a heating

rate of 10°C/min with a nitrogen flow rate of 100 ml/min. The percentage weight-loss versus temperature plot was used to analyze the thermal stability of the polymer.

3.5.5 Crystallization Analysis Fractionation (CRYSTAF)

CRYSTAF (Polymer Char, Spain) was used to analyze the crystallinity of polymers. A very small amount of polymer samples were dissolved in 1,2,4-trichlorobenzene (TCB) forming a low concentration (~0.1 mg/mL) solution at 95°C. Further, the temperature was programmed to decrease slowly (0.1 °C/min) while the polymer fraction crystallizes gradually with a decrease in the temperature. An inline infrared detector was used to track changes in the polymer concentration in the solution. The CRYSTAF results are plotted in form of differential weight change versus temperature for analysis.

3.5.6 Nuclear Magnetic Resonance (NMR) Spectrometry

Bruker 400 MHz spectrometer was utilized to analyze the samples. The polymer samples were dissolved in deuterated chloroform in a quartz tube for ¹H NMR analysis.

3.5.7 Scanning Electron Microscope (SEM)

JEOL SEM (Model- JSM6610LV) was used for morphological analysis of the polymers and polymer composites. The solid samples were gold coated and inserted into the microscope for analysis.

CHAPTER 4

RESULTS AND CONCLUSION

4.1 Thermal Behavior and Crystallization Analysis Ethylene-Propylene (EP) Copolymer , EP-Styrene Terpolymer and their composites with Layard Double Hydroxide

4.1.1 NiCr LDH Characterization

The NiCr LDH was characterized by XRD and FTIR. XRD analysis was used to examine the crystallography of the produced samples. The specific characteristic peaks of the NiCr LDH were found at 2θ values of 10.7, 35.2, and 60.8°, as shown in Figure 6. Similar observations for NiCr LDH have been reported in the literature.[138], [139]

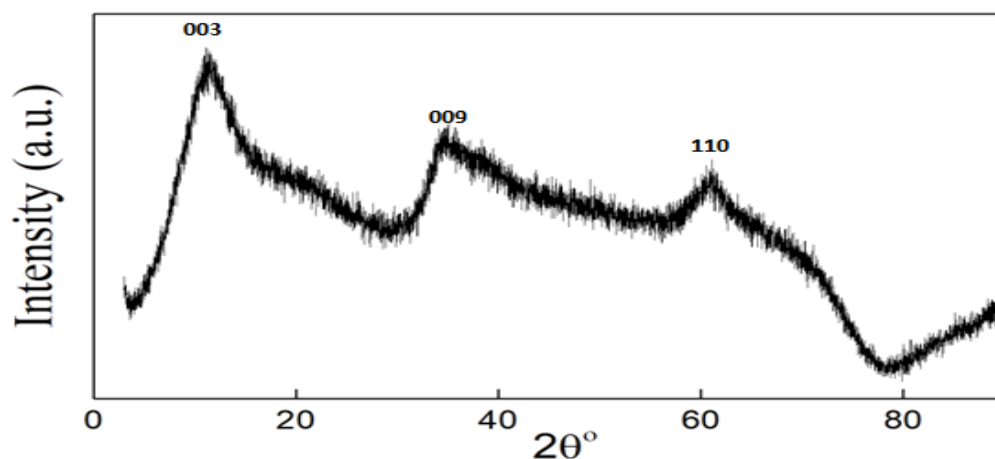


Figure 6 XRD plot of NiCr LDH.

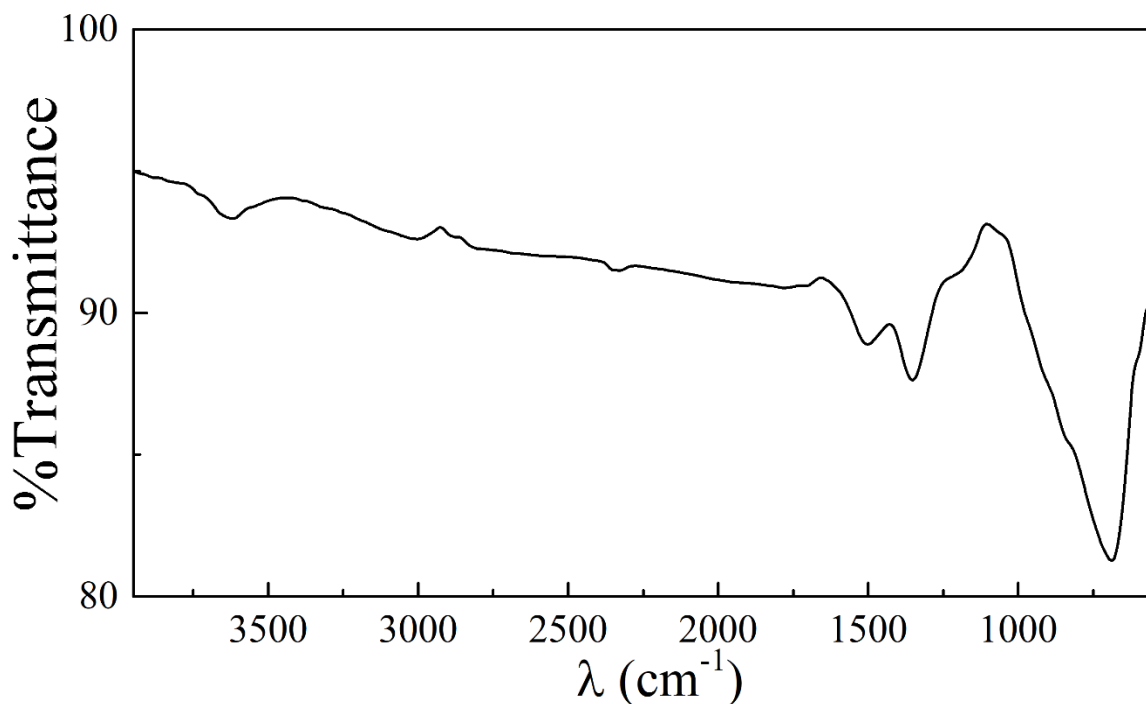


Figure 7 FTIR plot of NiCr LDH.

The existence of functional groups in LDH was evaluated from FTIR spectra, as shown in Figure 7. In the LDH, broad peak appearing at around 3450 cm^{-1} is associated with the hydroxyl group stretching. The presence of physically adsorbed interlayer H_2O molecules might have caused the O-H stretching vibration in LDHs. In addition, the M-O (M = Ni or Cr) bending and stretching modes were assigned to the peaks appearing below 750 cm^{-1} . [139] The antisymmetric stretching vibration of the interlayer NO_3 is primarily responsible for the band seen at around 1350 cm^{-1} . [140] In summary, XRD and FTIR data indicate successful synthesis of NiCr LDH that is added as a drop-in filler in styrene-ethylene-propylene terpolymerization, and the results are discussed in the activity section.

4.1.2 Activity

The nomenclature and activities of ethylene-propylene (EP) co-polymerization and ethylene-propylene-styrene (EPS) ter-polymerization with and without LDH and ultrasonication are summarized in Table 1 and Figure 3, respectively. The polymerizations were performed using metallocene catalysts and MMAO as a co-catalyst. The activity was increased by 2~2.4 times compared to the control sample upon the introduction of 0.5~1.0 mL of styrene (Figure 8 and Table 4). For instance, the control sample showed an activity of 878 kg/mol/h/bar while the addition of 0.5 mL of styrene increased activity to 1737 kg/mol/h/bar. Larger amounts i.e., higher than 1 mL of styrene might have an adverse impact on the activity during polymerization, [141] hence this work is investigated for styrene amounts of not more than 1.0 mL.

Introducing monomers in ethylene-propylene to synthesize terpolymer plays a role in influencing the polymerization activity as well as product yield. An increasing trend of the catalytic activity with comonomer addition has been reported and trends similar to this work were observed when α -olefin was incorporated in α -olefin-ethylene-propylene terpolymerization.[11], [142] The enhancement in the activity caused by the introduction of a comonomer has been referred to as the “comonomer effect”.[143] Nonetheless, styrene incorporation, in the current work, demonstrate higher activity (2070 kg/mol/h/bar) in comparison with incorporation of 1-hexene (1554 kg/mol/h/bar) and 1-pentene (424 kg/mol/h/bar).

In addition to introducing a comonomer, using LDH as a drop-in filler also affects the catalytic performance. For instance, using 15 mg LDH as filler in ethylene-propylene-

styrene terpolymer with 0.5 mL of styrene (EPS0.5) to synthesize EPS0.5L reduced 8% of the activity (from 1737 to 1631 kg/mol/h/bar) while an activity loss of approximately 23% was observed when LDH was added to EPS1.0 for the synthesis of EPS1.0L.

Table 4 Activity and thermal properties of the terpolymer.

Sample Name	Ethylene: Propylene	Styrene (mL)	NiCr LDH (mg)	Sonication	T_m (°C)^a	T_c (°C)^b	Crystallinity (%)^c	T_{0.9} (°C)^d
EP	95:05	0	0	No	123.1	113.4	46.3	442.6
EPS0.5	95:05	0.5	0	No	119.3	109.5	27.9	436.8
EPS1.0	95:05	1	0	No	118.8	110.9	24.1	429.2
EPS0.5L	95:05	0.5	15	No	119.7	111.1	29.7	427.2
EPS1.0L	95:05	1	15	No	119.7	110.4	24.4	423.6
EPS0.5LS	95:05	0.5	15	Yes	119.8	111.3	29.5	436.9
EPS1.0LS	95:05	1	15	Yes	119.5	110.6	24.9	426.8

^aCalculated from DSC; ^bCalculated from DSC; ^cCalculated from DSC; ^dCalculated from TGA

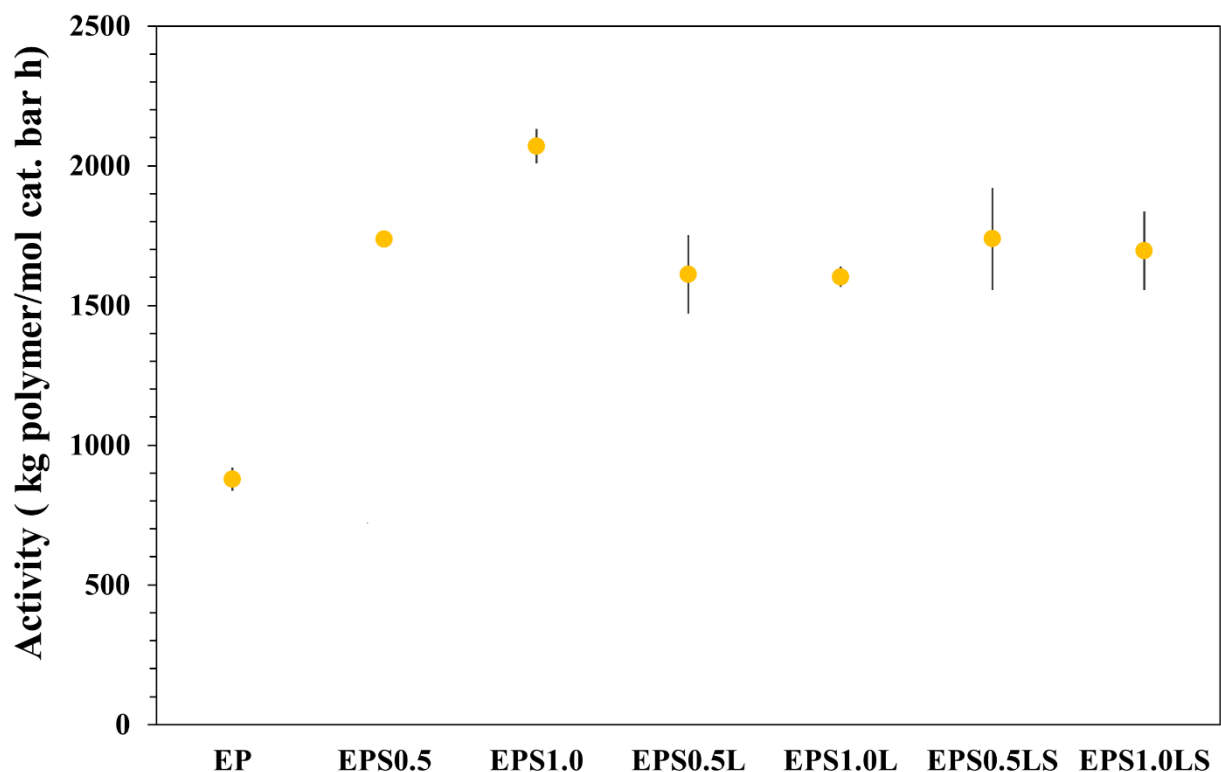


Figure 8 Activity plot for the co and terpolymers with their composites.

4.1.3 Thermal and Crystallization Properties

The thermal behavior and crystallinity of the resultant polymers were analyzed by TGA, DSC, and CRYSTAF. Figure 4 shows the DSC endotherms of all co- and ter-polymer samples. The DSC endotherms are usually associated with the melting temperature (T_m) while the DSC exotherms are related to the crystallization temperature (T_c) of the polymer. The DSC results showed a significant reduction in T_m , T_c , and the crystallinity of the EPS ter-polymer post styrene incorporation in comparison with EP copolymer. In the case of EP copolymer (control sample), a sharp T_m peak at $\sim 123^\circ\text{C}$ was observed whereas smaller, broader, and bimodal peaks were found corresponding to the terpolymer samples. The

peaks corresponding to T_m of terpolymer samples shifted to lower temperatures (118.8-119.8 °C) relative to the control sample (Figure 9). Styrene addition during polymerization promotes short-chain branching that could lead to a reduction in T_m values. These observations of reduction in T_m are in line with α -olefins-EP terpolymers reported earlier.[11], [144] For instance, in one of our previous works, 1-hexene addition to EP reduced the T_m from 123 °C to 114 °C.[11] A similar trend is observed for T_c and crystallinity that decreased with styrene introduction into EP. The loss in T_c and crystallinity is assigned to the formation of short-chain branching during terpolymerization post-styrene addition.[145] It is interesting to note that the addition of NiCr LDH as well as sonication treatment had an insignificant impact on the corresponding T_m , T_c , and crystallinity values.

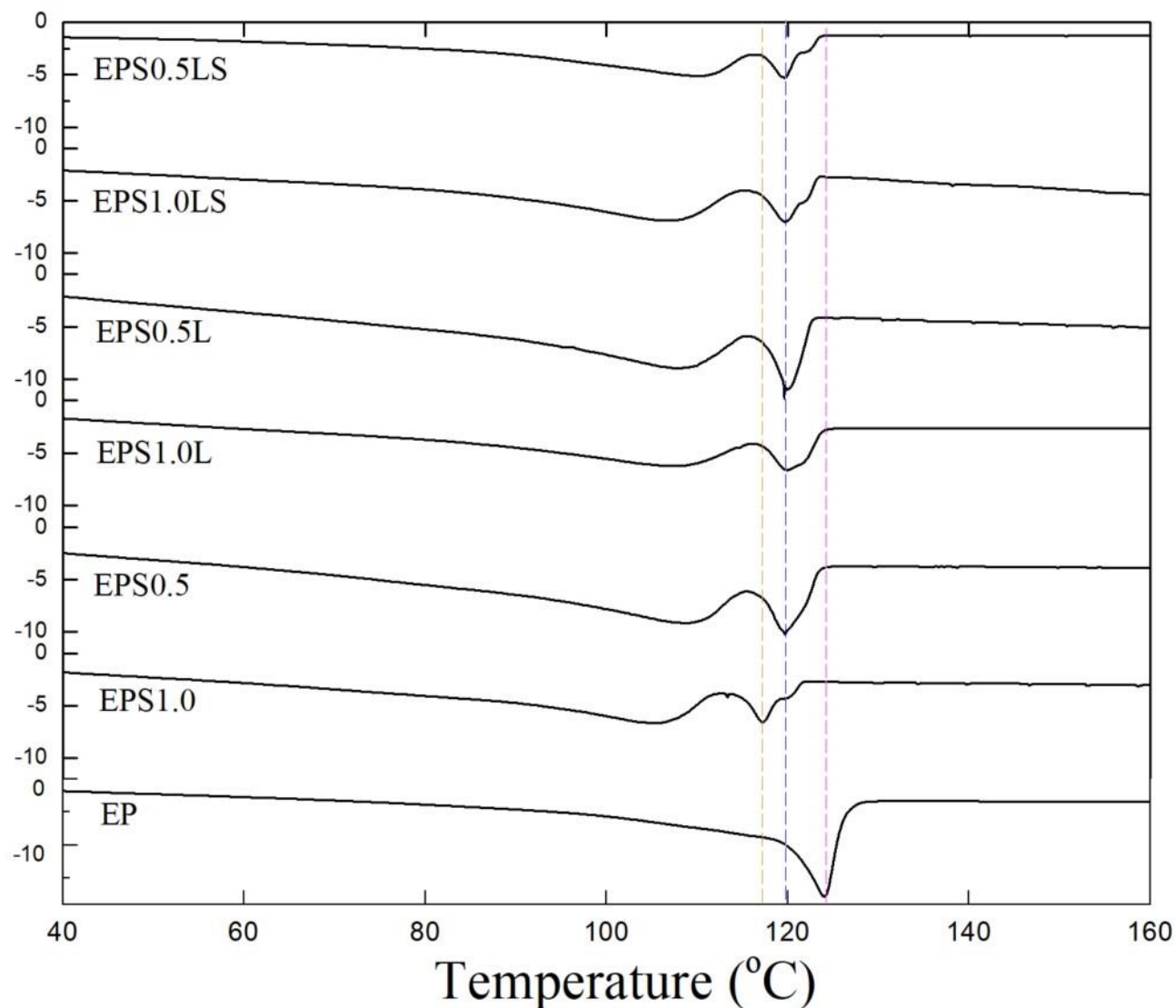


Figure 9 DSC heating cycle for copolymer, terpolymer and their composites.

CRYSTAF analysis was used to understand the SCB of the polymer chains (Figure 10). The study starts at 90 °C and temperature is reduced, during crystallization, to room temperature. The CRYSTAF analyzes the variation in the concentration of polymer solution during this temperature reduction. The reduction in temperature allows precipitation of the most crystalline portions, made up of molecules with no or few branches, prior to the molecules with higher number of branches.[141], [146], [147]

EP had the most intense peak at high temperatures (between 70 and 85 °C) and a few peaks also appear at a lower temperatures (between 40 to 70 °C) as shown in Figure 10. This result suggests that the EP control sample had a good number of longer chains (corresponding to high-temperature peaks) and less number of shorter chains were found as depicted from low-intensity peaks at lower temperatures. The addition of 0.5 mL of styrene to EP (EPS0.5) exhibited a peak with a relatively smaller intensity in comparison with the EP control sample. Hence, styrene addition reduced the number of longer chains in EPS0.5 as compared to the EP control sample. The peak shift of terpolymer towards lower temperature could be related to the reduction of melting temperature of the terpolymers along with SCB. The larger peak intensity and higher area under the curve, at lower temperatures, of the terpolymers as compared to the EP control sample confirmed higher SCB of the terpolymer. EPS1.0 also showed a lower-intensity peak at high temperatures depicting less number of longer chains. At lower temperatures, peaks intensity and area under the curve of EPS1.0 were larger than that of EPS0.5 demonstrating that SCB increased with respect to the amount of styrene. It has been reported that the addition of a third monomer alters the polymer's capacity to crystallize by introducing irregularities (side-chain branching) into its chains.[146] The drop-in filler i.e., LDH incorporation in the polymer lowered the number of longer chains portion for the terpolymer composites (EPS1.0L and EPS0.5L) as compared to its respective terpolymers (EPS1.0 and EPS0.5) corresponding to lower peak intensities at high temperature. However, no significant change in peak intensities of terpolymer composites, at the lower temperature, as compared to terpolymer was observed. Interestingly, the sonicated terpolymer composites (EPS1.0LS and EPS0.5LS) showed a lower number of longer

chains in contrast to the corresponding terpolymers (EPS1.0 and EPS0.5). This suggests that sonication influenced the crystalline behavior of terpolymer composites and might play a role in affecting the thermal characteristics of terpolymer composites post sonication as discussed in the TGA section.

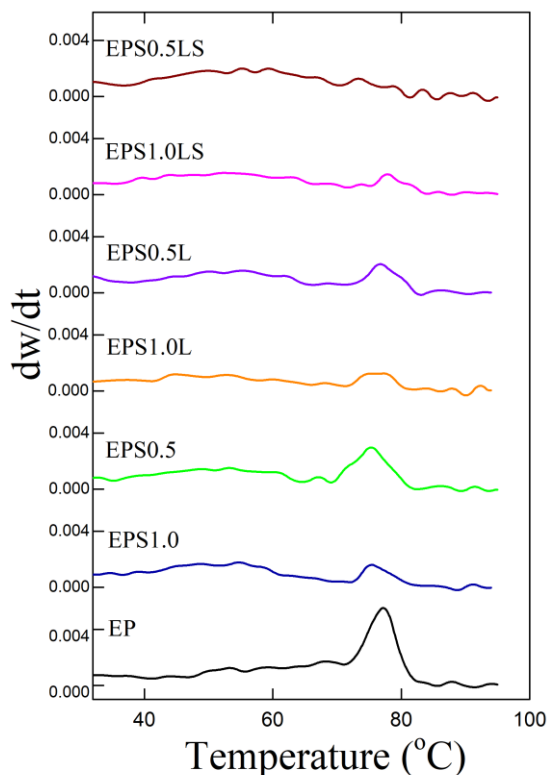


Figure 10 CRYSTAF plot for neat EP, EP-Styrene and its composites.

TGA was used to observe the thermal stability of the samples and plots of the samples are shown in Figure 11. From the weight loss curves, it was observed that the terpolymers degraded earlier than EP control sample exhibiting lower thermal stability after styrene was introduced into EP. Table 4 enlisted the temperature ($T_{0.9}$) at 10% weight loss. $T_{0.9}$ values of EP control, EPS0.5, and EPS1.0 remained 442, 437, and 429 °C, respectively. $T_{0.9}$ values of EPS0.5 (437 °C) and EPS1.0 (429 °C) showed that an increase in styrene

amount reduced the thermal stability of terpolymer. It is noteworthy that the styrene-based terpolymers investigated in this work demonstrate better thermal stability as compared to the α -olefin-based terpolymers reported earlier.^[4] For instance, the addition of 1 mL of 1-hexene to EP (EP-1-hexene) reduced the thermal stability of the resulting terpolymer by ~ 45 °C i.e., $T_{0.9}$ of EP-1-hexene was found to be 397 °C. On the contrary, the addition of a similar amount of styrene-producing terpolymer (EPS1.0) exhibited less reduction in the $T_{0.9}$ value (by ~ 13 °C). The incorporation of the LDH as drop-in filler to EPS terpolymers resulted in further reduction in the thermal stability of the resultant terpolymer composites (i.e., $T_{0.9}$ values reached 427 and 423 °C for EPS0.5L and EPS1.0L, respectively) in comparison with corresponding terpolymers. Thus, the filler addition negatively affected the terpolymer system with respect to thermal stability. It has been reported that uniformly dispersed LDH fillers improve the thermal stability of composites,[148], [149] the poor dispersion in the current work might be one of the reasons behind loss of thermal stability of terpolymer composites.

Sonication is one of the useful routes to have a uniform dispersion of the filler materials in the polymer composite system.[150], [151] It is interesting to note that sonication treatment had a positive impact on the thermal stability of terpolymer composites (EPS0.5LS and EPS1.0LS). $T_{0.9}$ values increased from 427 (EPS0.5L) to 436 °C (EPS0.5LS) and 423 (EPS1.0L) to 427 °C (EPS1.0LS), respectively. In summary, despite the fact that styrene addition reduced thermal stability, thermal degradation behavior was significantly influenced by filler incorporation as well as sonication treatment.

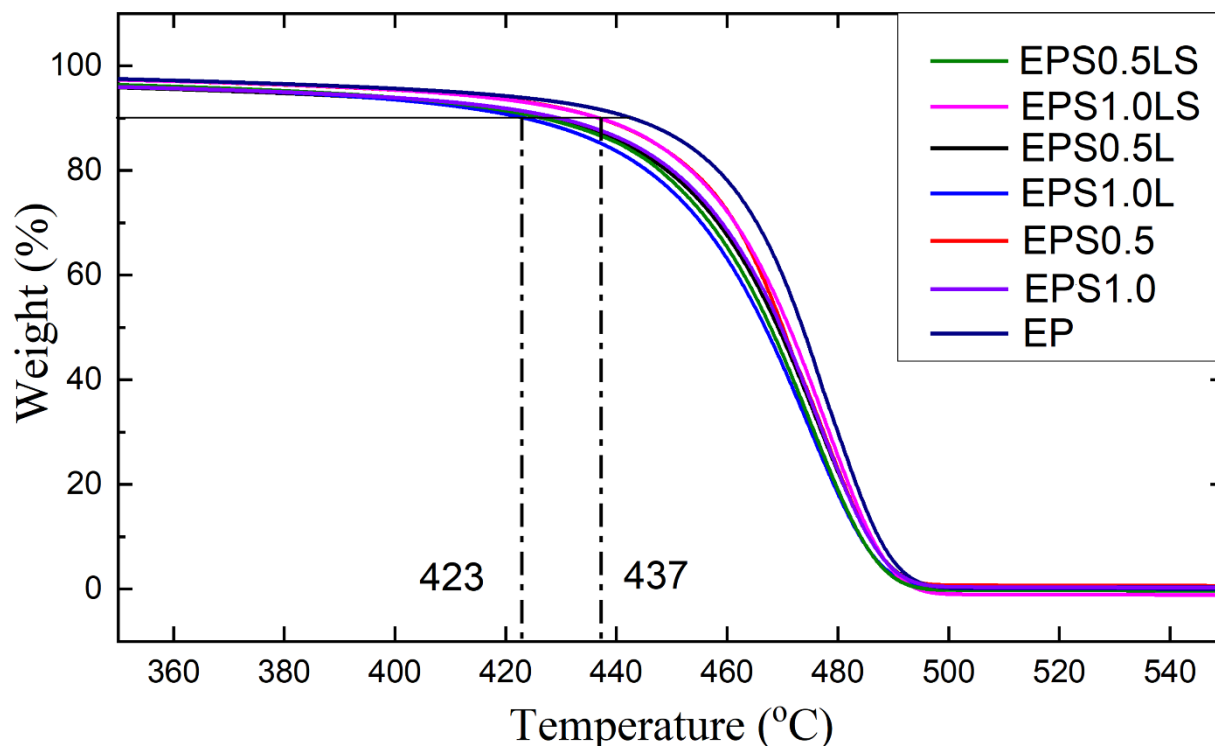


Figure 11 TGA plots for EP copolymer, EP-Styrene terpolymers and their composites.

4.1.4 FTIR and NMR Analysis

FTIR and NMR were done to assist the confirmation of styrene incorporation in the terpolymer. In FTIR plot (Figure 12), there was a peak around 1650 cm^{-1} which might be related to sp^2 hybridization of carbon due to some of the unreacted double bond of the ethylene/propylene/styrene.[152], [153] Though the above-mentioned peak (around 1650 cm^{-1}) was present for all the samples, the presence of small peaks at 1700 cm^{-1} onwards were absent for EP control sample. Also, a very small peak at 3060 cm^{-1} was present in the terpolymer samples which might be concluded as the indication of the presence of aromatic hydrogen i.e. styrene in the terpolymers and their composites.[154], [155] These two peaks (1700 cm^{-1} onwards and at 3060 cm^{-1}) were not present in the control sample.

The utmost left peak at 3450 cm^{-1} in every case was associated with the presence of -OH in the polymer as acidified methanol was used as a terminator for the polymerization.[156]

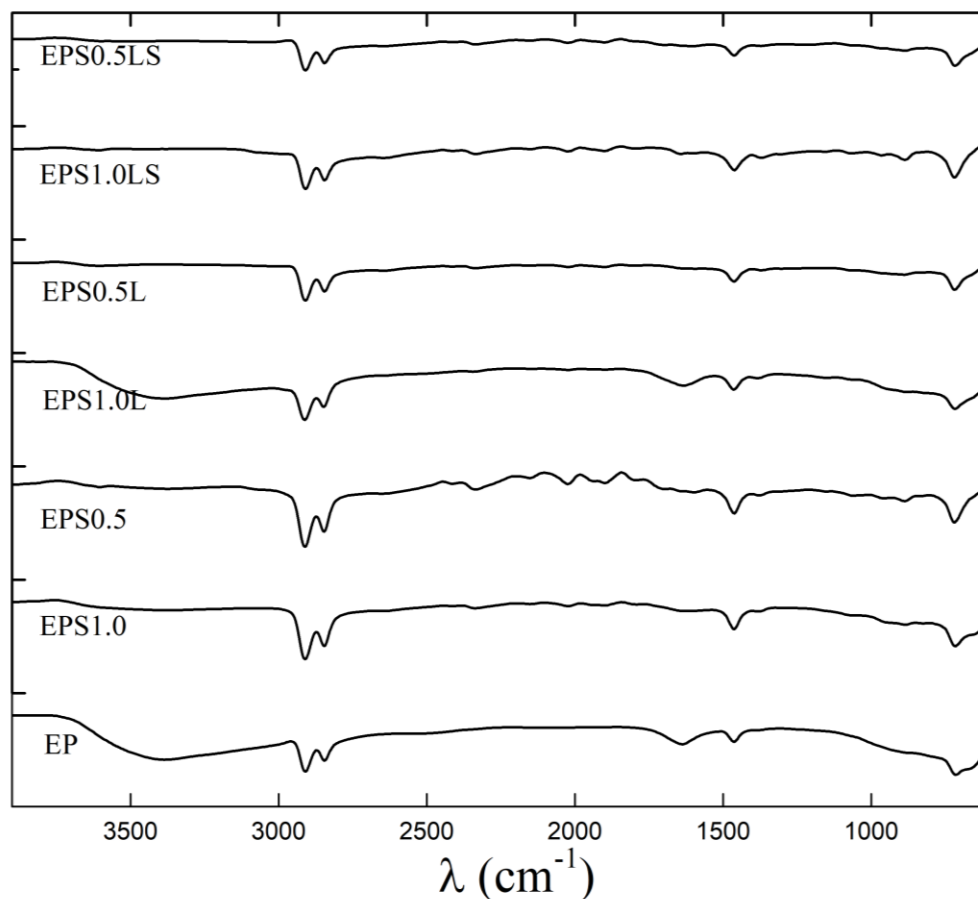


Figure 12 FTIR plots for neat EP, EP-Styrene and its' composites.

A representative NMR spectrum of EP control and EPS1.0 was shown in Figure 13 and Figure 14. There's a difference in the NMR spectrum of copolymer and terpolymer samples. The presence of peaks close to 6.7 ppm could be associated with styrene ($\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$) in the terpolymer which was absent in the EP control sample.[157] The higher ppm on the left (7.2 ppm onwards) was related to the solvent in both cases.

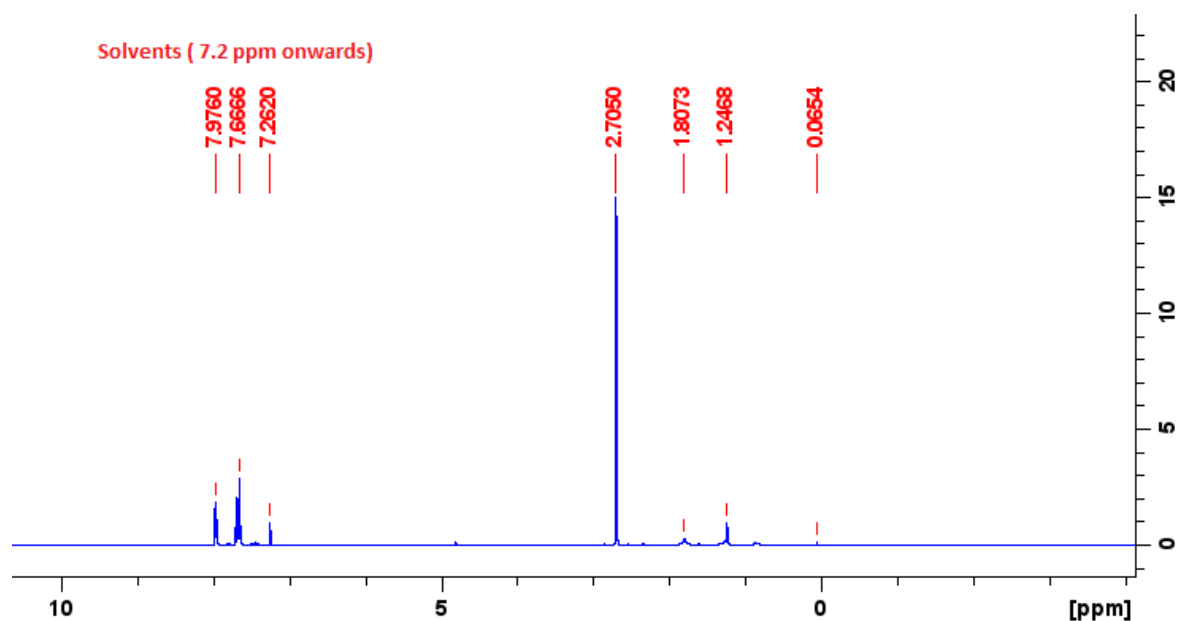


Figure 13 NMR Spectrum of neat EP.

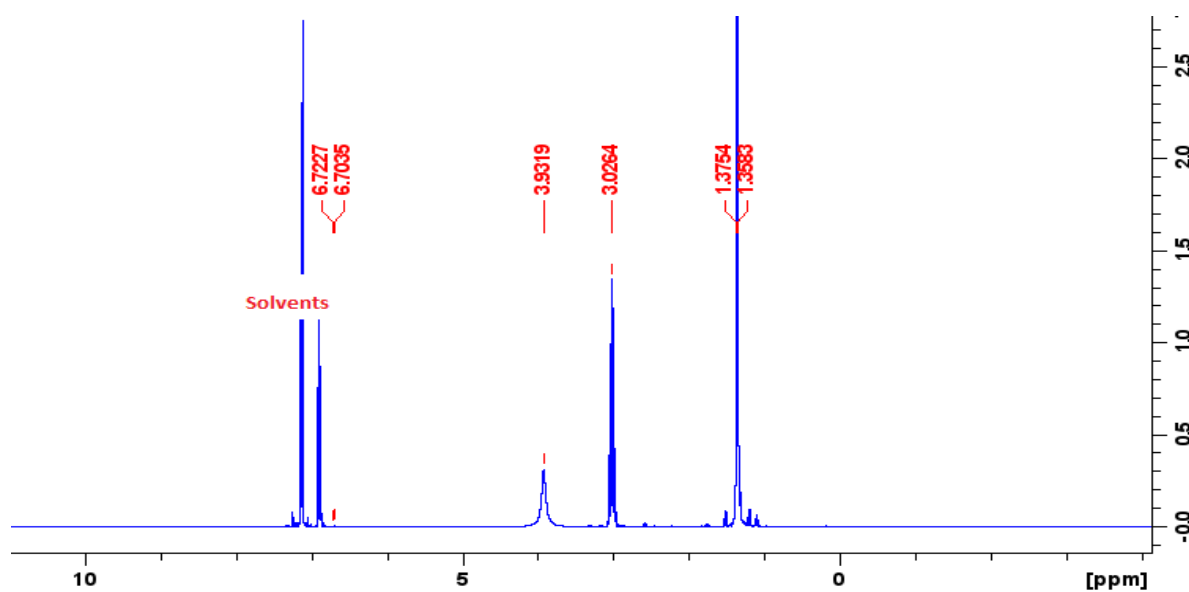


Figure 14 NMR spectrum of EPS1.0.

In conclusion, the results obtained from various characterization techniques like DSC , CRYSTAF , FTIR and NMR confirms the availability of styrene in the polymer more specifically the terpolymer. The reduction in the crystallinity confirmed by DSC, higher

short chain branching in the terpolymer, FTIR and NMR peaks relative to the styrene altogether add to the confirmation of the formation of terpolymer.

Ethylene-propylene copolymer and their terpolymer remain a subject of interest due to their versatile use. There has been less investigation using aromatic substances as the third monomer. This work dealt with styrene as a third comonomer and various properties of the resultant terpolymer have been investigated. Styrene showed a significant impact on the activity by increasing the yield just for a small amount of addition of styrene in the polymerization. As instance, only 1.0 mL of styrene increased the yield of the terpolymer by 2.4 four times higher compared to the neat ethylene-propylene copolymer. The incorporation of styrene affected the thermal properties of the resultant terpolymer where it decreased the melting temperature, crystallinity, and thermal stability. But when compared to other terpolymers of ethylene-propylene it shows improved properties of terpolymer. The melting temperature of the terpolymer was decreased by around 3 °C while the thermal stability was decreased by around a maximum of 15 °C. There was a significant decrease in the crystallinity of the terpolymer as compared to the copolymer which was mainly due to the short-chain branching. DSC, TGA, and CRYSTAF data helped to get the above observations. FTIR and NMR confirmed the incorporation of styrene in the polymer. The effect of nickel-chromium LDH as a drop-in filler in the terpolymer was also investigated in this work where it showed that the resultant LDH affected negatively the thermal properties of the polymer. But interestingly sonication improved the thermal property of the respective terpolymer composites.

4.2 Thermal and Crystalline Behavior of Polyethylene Composites with Metal Organic Frameworks

4.2.1 Activity

The polymer samples were named as PE where no drop in filler was used and polymer composite samples were named as PEM1xx where PE represents polyethylene matrix, M1 signifies MOF UiO-66 and xx denotes the amount MOF in mg used as drop in filler in the polymer. Figure 15 represented the activity of the polyethylene and its composites with drop in filler MOF 1 or UiO-66 upon different amount of loading of the filler. From the activity plot, it was observed that the activity of the polyethylene composites remains almost same with respect to the polyethylene control sample with slight improvement at higher amount of drop in filler. For example, the average activity of the polyethylene control sample was 483 kg PE / (mol cat. bar h) and the polyethene composites with 5, 15, 25 and 35 mg of UiO-66 as drop in filler were 475, 519, 531 and 615 kg PE / (mol cat. bar h). Maximum activity was observed with 35 mg filler where the increment in activity was 27% compared to the control sample. For other amount of fillers, the activity did not vary within $\pm 10\%$ compared to control. In brief, the activity of the polyethylene composites samples remained close to the activity of polyethylene composite samples when different amounts of UiO-66 was used as drop-in fillers.

Table 5 Thermal properties of polyethylene and polyethylene-UiO-66 composites.

Sample Name	Filler (mg)	T _m (°C) ^a	T _c (°C) ^a	Crystallinity (%) ^a	T _{0.9} (°C) ^b
PE	0	130.9	118.5	82.5	447.0
PEM105	5	131.1	119.1	88.1	447.9
PEM115	15	131.8	119.1	88.7	449.7
PEM125	25	132.2	119.6	90.8	460.1
PEM135	35	132.5	120.1	88.9	458.2

^a Calculated from DSC, ^b Calculated from TGA

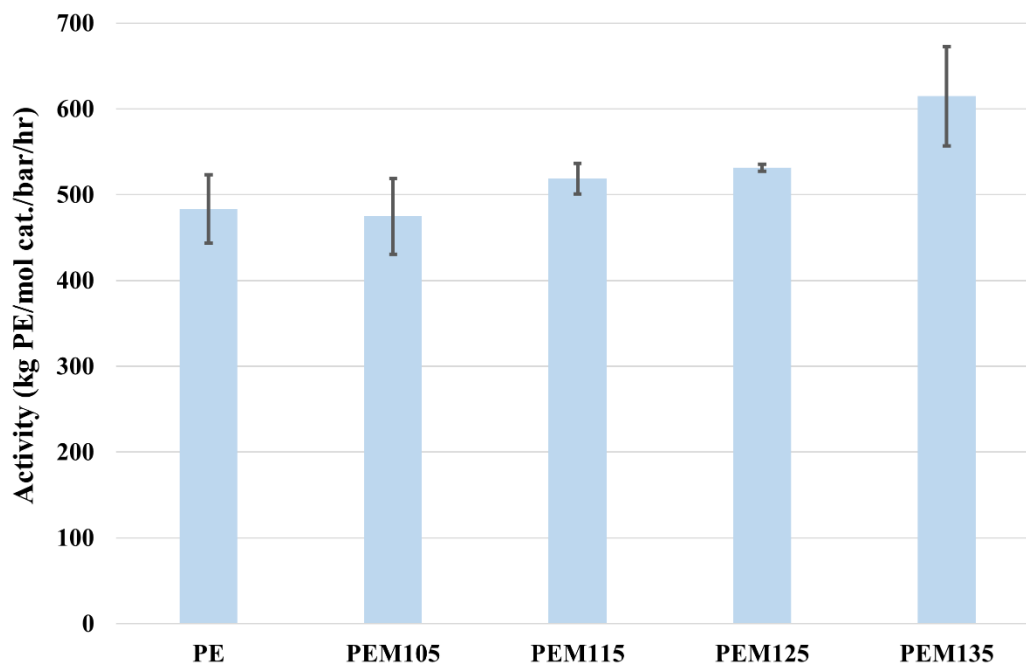


Figure 15 Activity of PE and PE-UiO-66 composites.

The resultant samples of polymers were classified as polyethylene where no filler was added and as polyethylene composites where different amount of filler MOF (UiO-66-NH₂) was added. Bare polyethylene sample was named as PE or PE control and the polyethylene composites were named as PEM2XX where PE denoted polyethylene, M2 expressed MOF UiO-66-NH₂ and XX resembled the amount of filler (in mg) in the respective composites. For example, PEM225 represented polyethylene composite with 25 mg of drop in filler MOF UiO-66-NH₂ in the polyethylene matrix. The nomenclature depending on the amount of filler addition along with some thermal and crystalline properties were summarized in Table 6 while Figure 16 represented the activity plot of the same samples. From Figure 16 it can be observed that there was no significant change in activity of polyethylene composites compared to polyethylene control. Though the average activity of composites with 15 and 25 mg drop in filler increased slightly, it remained within limit of 7% compared to control sample. Average activity with 5 and 35 mg of filler remained very similar to one another with the control sample. So, MOF UiO-66-NH₂ did not alter the activity of the polyethylene composites compared to the bare polyethylene sample as drop in filler in it.

Table 6 Thermal properties of PE and polyethylene-UiO-66-NH₂ composites

Sample Name	Filler (mg)	T_m (°C)^a	T_c (°C)^a	Crystallinity (%)^a	T_{0.9} (°C)^b
PE	0	130.92	118.49	81.81	447.0
PEM205	5	131.14	118.24	86.58	458.4
PEM215	15	131.45	118.56	88.39	459.6
PEM225	25	131.85	119.39	89.15	461.6
PEM235	35	131.73	119.24	86.92	459.6

^a Calculated from DSC, ^b Calculated from TGA

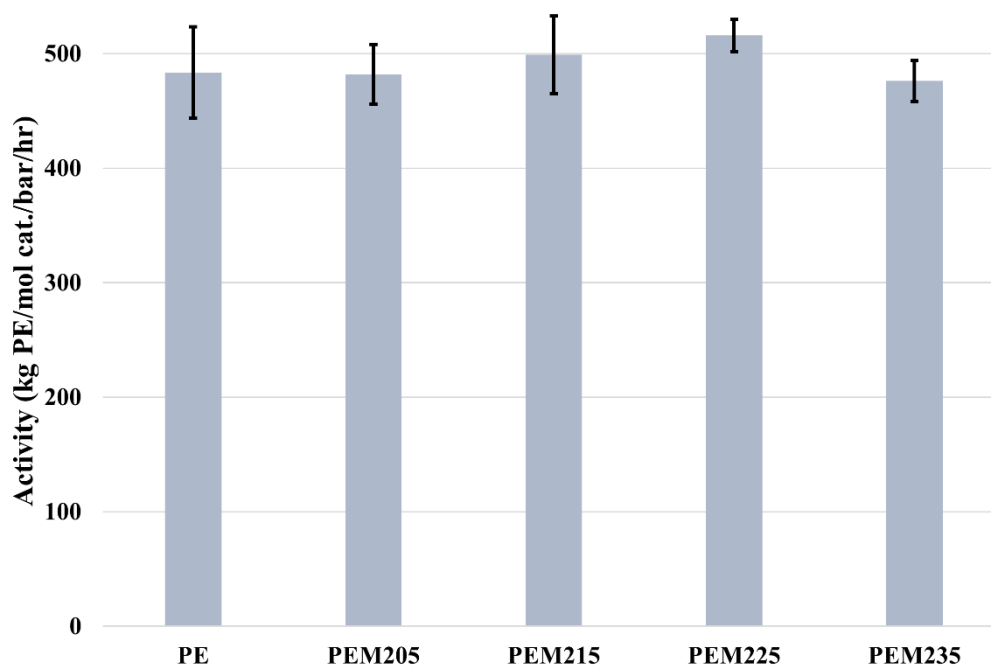


Figure 16 Activity of PE and PE-UiO-66-NH₂ composites.

4.2.2 Thermal and Crystalline Properties

While drop-in filler UiO-66 did not alter the activity of the polyethylene composites to a great extent compared to the polyethylene control sample, a significant change in the thermal properties and crystallinity were observed for the polyethylene composites compared to bare polyethylene sample. Table 5 melting temperature (T_m), crystalline temperature (T_c), percentage of crystallinity and temperature at 10% weight loss ($T_{0.9}$) of the polyethylene and its composite samples at different amount of fillers addition were summarized in Table 05. In Table 4 and Figure 17 it was demonstrated that the melting temperature (T_m) of the polyethylene composites remained close to the control sample with minor increases. As an instance, T_m of polyethylene control sample (PE) and its composite with 5 mg of drop -in filler (PEM105) were 130.9 and 131.1 °C respectively. Even though it was a little rise, the melting temperature of the polyethylene composites rose as the filler content grew. For example, polyethylene composites with filler amount of 15, 25 and 35 mg showed T_m at 131.8 , 132.2 and 132.5 °C respectively. Like melting temperature, similar trend of small increase in the crystalline temperature (T_c) was observed for the polyethylene composite samples compared to control sample. Crystalline temperature of the polyethylene composites with 5, 15, 25 and 35 mg drop-in filler showed 0.6, 0.6, 1.1 and 1.6 °C increase with respect to the polyethylene control sample where its T_c was observed to be 118.5 °C.

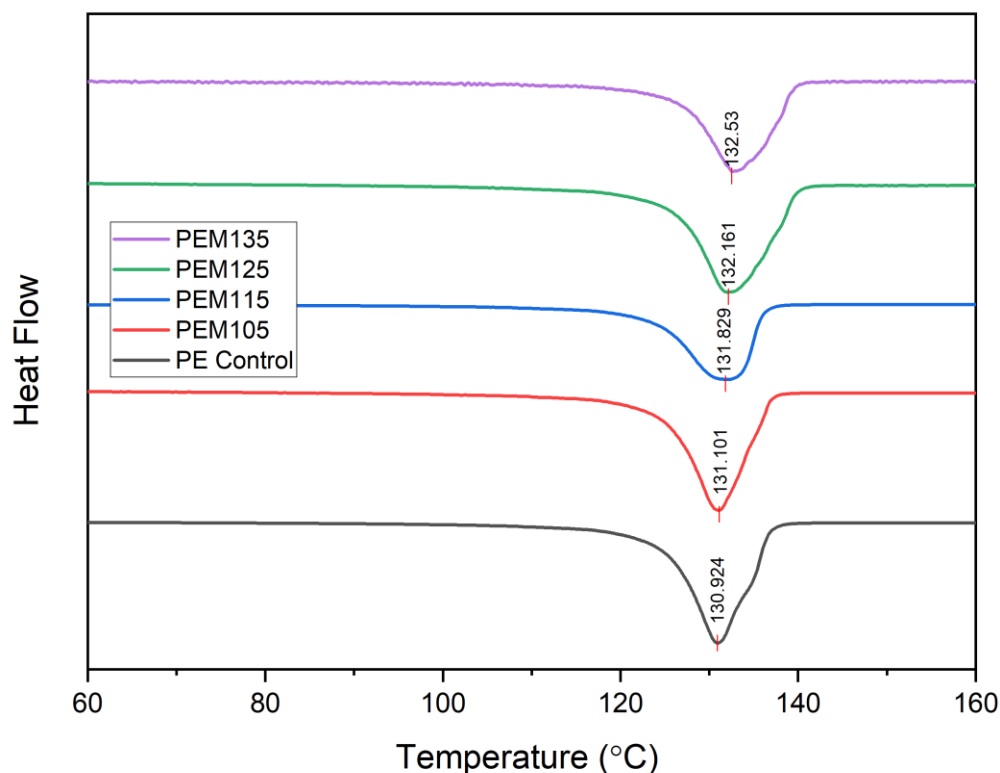


Figure 17 DSC plots for PE and PE-UiO-66 composites

Like activity, this filler did not alter significantly the melting and crystalline temperature of the composites compared to polyethylene control sample (Table 6). The melting temperature (T_m) of polyethylene control and composites with 5,15,25 and 35 mg of filler were 130.9, 131.1, 131.5, 131.9 and 131.7 °C respectively. There was a very small increment in the melting temperature as it remained increasing slightly from 5 mg to 25 mg of filler addition compared to polyethylene control. However, the melting temperature decreased insignificantly for 35 mg of filler addition compared to 25 mg of filler addition. Similar trend was followed for crystalline temperature where the crystalline temperature with 5, 15, 25 and 35 mg of drop-in filler were 118.2, 118.6, 119.4 and 119.2 °C

respectively. There was no significant change of the composites in crystalline temperature as the crystalline temperature of polyethylene control was 118.5 °C. Thus such insignificant improvement in melting and crystalline temperature of the composite resembled UiO-66-NH₂ had very small contribution in melting and crystalline temperature.

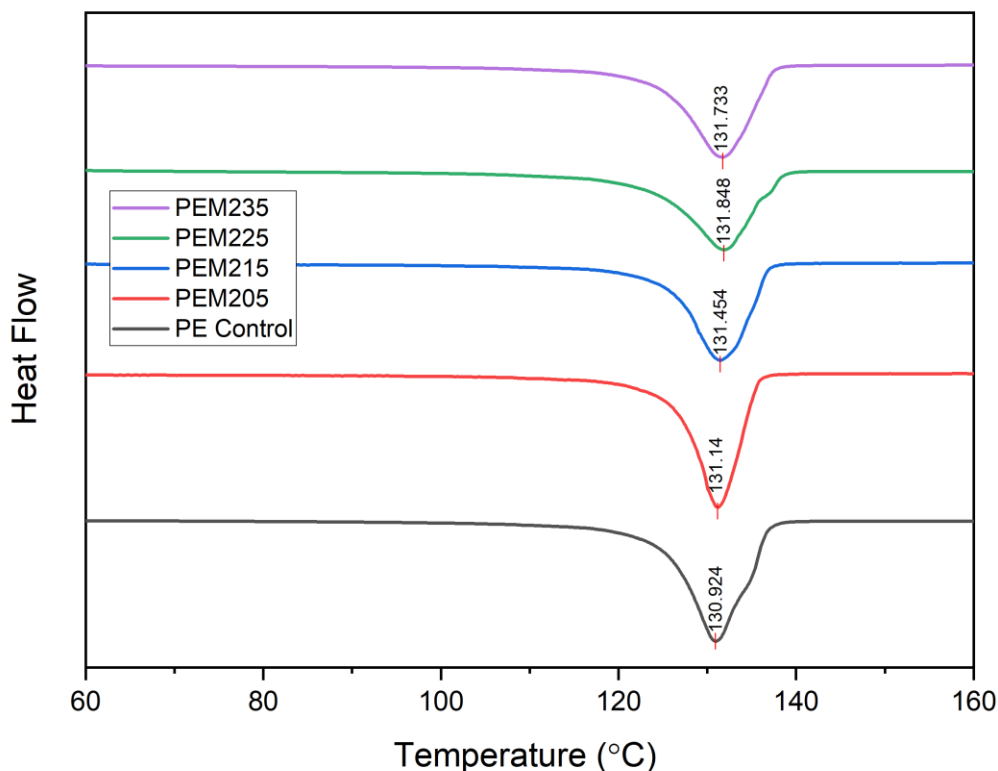


Figure 18 DSC plots for PE and PE-UiO-66-NH₂ composites

Although the crystallization and melting temperatures of the composites were nearly identical to those of the control sample, the thermal stability of the composites with higher amount of fillers (25 and 35 mg) improved by a significant number. The results obtained from thermogravimetric analysis (TGA) were demonstrated in Figure 19 and 10 % weight loss temperatures ($T_{0.9}$) were summarized in Table 5. From the figure and the table it was

noticed that there was no significant improvement in the thermal stability of the polyethylene composites compared to polyethylene control sample for addition of 05 and 15 mg of filler (PEM105 and PEM115). $T_{0.9}$ temperature of the control sample was 447.0 °C and there were 0.9 and 2.7 °C increase in for PEM105 and PEM115 respectively. When 25 mg of drop-in filler (PEM125) was used, the thermal stability significantly improved (by 13.1 °C) and reached a $T_{0.9}$ temperature of 460.1 °C. Even more filler, 35 mg, did not improve the composite's thermal stability (PEM135); rather, it lowered the $T_{0.9}$ temperature by 1.9 °C in comparison to PEM125. In short, by adding extra filler up to 25 mg, the polyethylene composite's thermal stability was enhanced to a maximum temperature compared to polyethylene control sample. The thermal stability of the polyethylene composite was not improved by adding more filler than 25 mg; instead, it slightly decreased. In summary, there was an insignificant improvement of melting temperatures, crystalline temperatures, and significant improvement in thermal stability of the polyethylene composites compared to polyethylene control sample when MOF UiO-66 was used as drop-in filler in different amount. These findings suggested that this MOF might have acted as a nucleating agent during the polymerization process.[103], [158]

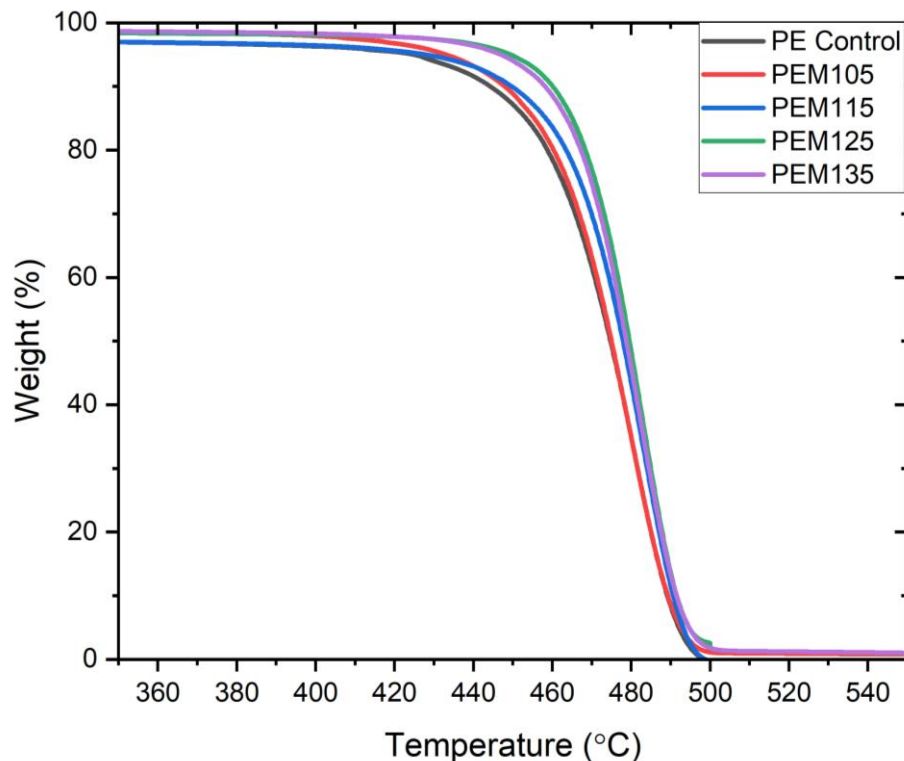


Figure 19 TGA plot for PE and PE-UiO-66 composites .

Although the crystallization and melting temperatures of the composites were nearly identical to those of the control sample, the thermal stability of the composites showed significant improvement even for small amount of filler (5 mg) addition like crystallinity. The results obtained from thermogravimetric analysis (TGA) were demonstrated in Figure 3 and 10% weight loss temperatures ($T_{0.9}$) were summarized in Table 6. Thermal stability of the polyethylene composites improved appreciably compared to only polyethylene sample which was well demonstrated in Figure 20. Regarding the $T_{0.9}$ temperature, 10% of polyethylene control sample degraded during TGA at 447.0 °C whereas only for 5 mg drop-in filler increased the thermal stability of the polymer composite PEM205 to 458.4 °C. Further increment in the filler amount did not increase the $T_{0.9}$ significantly. For example, $T_{0.9}$ temperature of the composites due to addition of 15,25 and 35 mg of drop-in

filler were 459.6, 461.6 and 459.6 °C respectively. The maximum increase in the thermal stability from the control sample was 14.6 °C due to addition of 25 mg of UiO-66-NH₂ as drop-in filler. The polymer composites exhibited an stable increase in thermal stability of around 12.5±1 for addition of 5,15 and 35 mg of drop-in filler compared to the polyethylene control sample. As a whole, when MOF UiO-66-NH₂ was used as a drop-in filler in various amounts, there was a negligible improvement in melting temperatures, crystalline temperatures, and a noteworthy improvement in crystallinity and thermal stability of the polyethylene composites compared to polyethylene control sample. According to these results, the UiO-66-NH₂ might have served as a nucleating agent throughout the polymerization process.

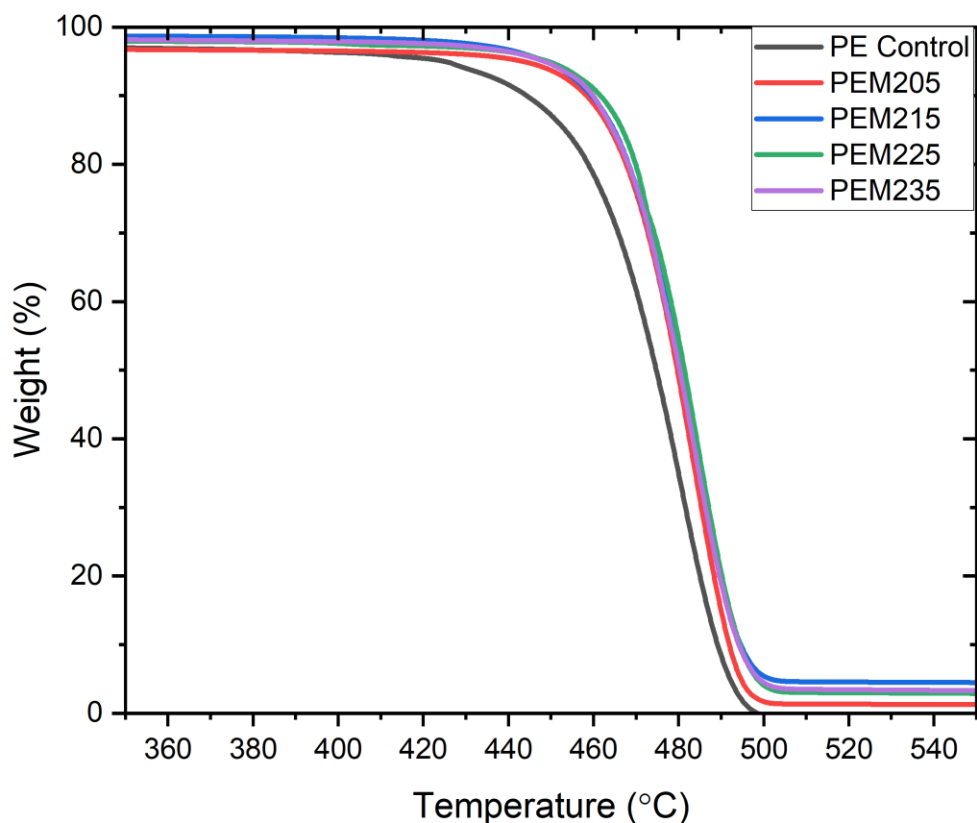


Figure 20 TGA plot for PE and PE-UiO-66-NH₂ composites .

Unlike melting temperature, crystalline temperature and thermal stability , even for a small amount (5 mg) of filler addition , the crystallinity of the polyethylene composites were improved significantly compared to polyethylene control. For example, the crystallinity of polyethylene control was improved from 82.5% to 88.1% in case of polyethylene composite PEM105 where 5 mg of MOF UiO-66 was added as drop-in filler. Further increase in the amount of filler up to 25 mg, improved the crystallinity of the polymer composites slightly. As an instance, polyethylene composites by addition of 15 and 25 mg MOF as drop-in filler demonstrated crystallinity by 88.7 and 90.8% respectively.

Increment in the filler amount beyond 25 mg decreased the crystallinity of the polyethylene composite a little as it was observed for composites with 35 mg of filler, had the crystallinity of 88.9%. Nevertheless, compared to the polyethylene control sample, the crystallinity of the polyethylene composites with various filler quantities was boosted up.

Though there was no obvious change in the crystalline temperature for the composites compared to polyethylene control sample, the crystallinity changed significantly. The crystallinity of the polyethylene control sample was 81.8 % and it increased to maximum 89.2 % for 25 mg of filler addition. Even for small amount of filler i.e. 5 mg it increased to 86.6%. For 15 and 35 mg of filler, the crystallinity of the composites were 88.4 and 86.9 respectively. In a nutshell, the crystallinity of the composites increased compared to the polyethylene control sample for all amount filler addition from starting 5 mg to 35 mg. Polyethylene composites showed 5~8% increase in crystallinity.

CRYSTAF analysis was carried out to determine whether the fillers had any other function in the structure of the polymer composites besides acting as a nucleating agent. More specifically CRYSTAF analysis was performed to understand branching in the polyethylene and its composites chains. In this analysis, the concentration of the polymer solution was monitored during decreasing the temperature. As the temperature of the solution was decreased, the most crystalline portion of the polymer chain precipitated first followed by the less crystalline portion of the polymer chain if any. For any polymer chain, the most crystalline portion has no or fewer branches and less crystalline portion has more branches. In the plot of CRYSTAF, polymer chains with no or few peaks appears in the high temperature side and peak for the most branched polymer chain appears in the lower temperature side. [141], [146], [147]

From Figure 21, it was observed that there was only one broad peak for polyethylene control sample and the polyethylene composite samples in upper temperature range i.e. 80 to 90 °C and no significant peak in the lower temperature range i.e. 30 to 80 °C . It resembled the polymeric chains for polyethylene control and polyethylene composite were long and there were no significant short chain branching for all the samples. Additionally, there was no discernible change in the peak of the composites in the temperature range when compared to the polyethylene control sample, suggesting that the chain length may be similar for all of the samples.[146], [159], [160] In a nutshell ,The results obtained from CRYSTAF signified that the chain length of the polyethylene and its composites with MOF UiO-66 were high and remained close to one another.

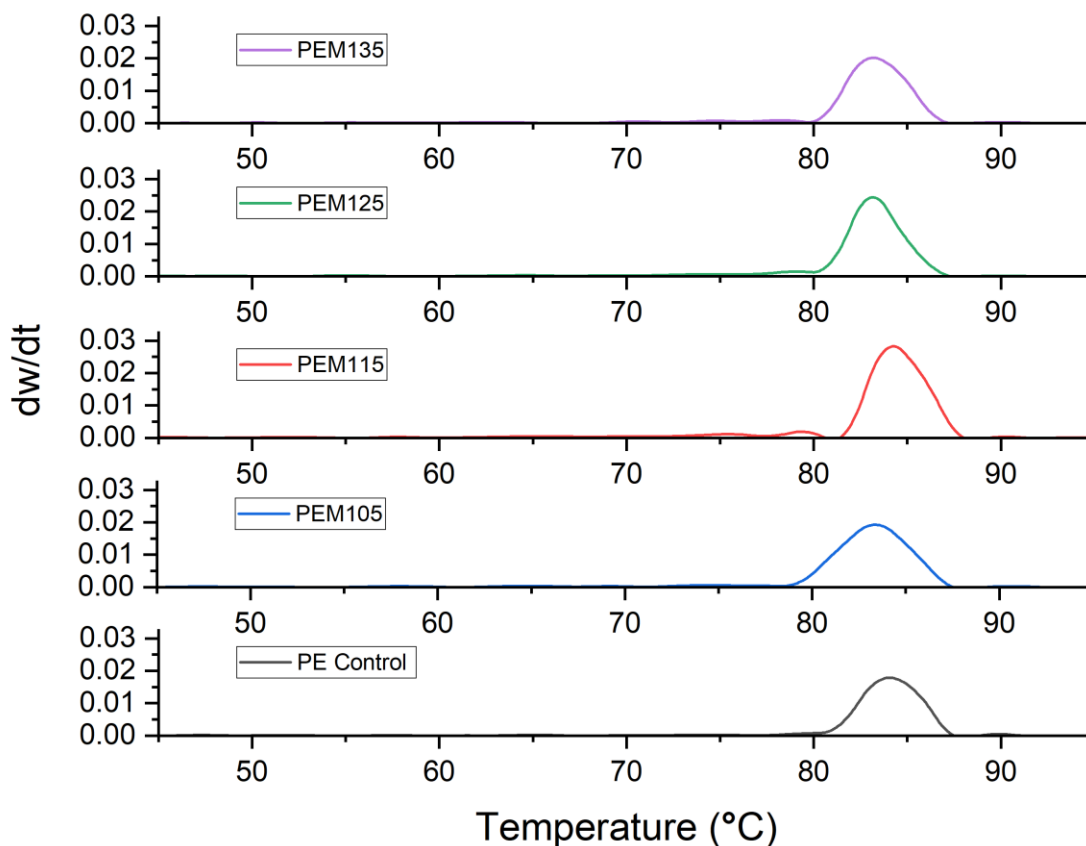


Figure 21 Figure obtained from data of CRYSTAF for PE and its composites

CRYSTAF analysis of polyethylene control and polyethylene composites at different loading of drop-in filler UiO-66-NH₂ was plotted in Figure 22. From the plotted data, it was clearly observed that there were only one single peak in high temperature side (80-90 $^{\circ}\text{C}$) for polyethylene control and its composites at various loading of filler. So, the polyethylene control sample contained longer polymeric chains with no or few branches. Also, the composites possessed long polymeric chains that were comparable to those in the control sample, demonstrating that the filler UiO-66-NH₂ had no effect on the polymeric chain branching for polyethylene composites.

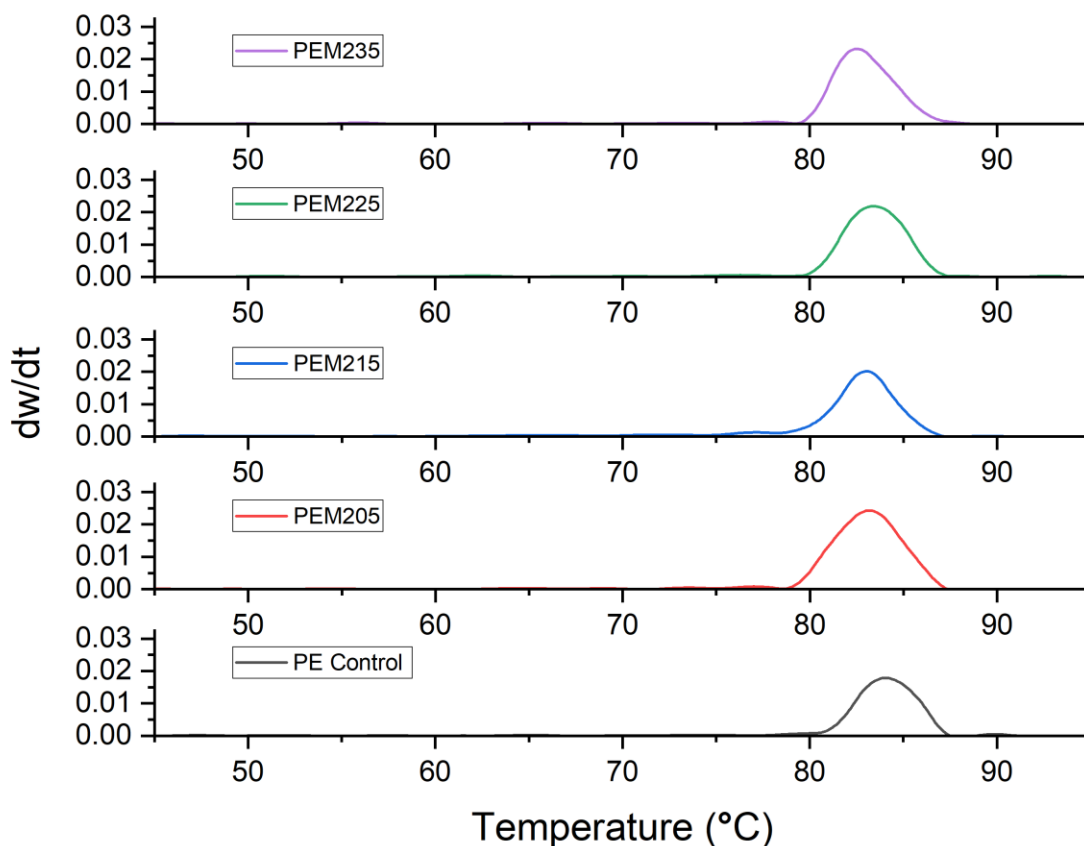


Figure 22 Figure obtained from data of CRYSTAF for PE and its composites.

4.2.3 FTIR Analysis

Figure 6 showed the FTIR spectra of Figure 23(a) PE control, Figure 23(b) PEM105, Figure 23(c) PEM115, Figure 23(d) PEM125, Figure 23(e) PEM135, Figure 23(f) UiO-66 alone. The FTIR spectra of PE control was similar to that published in literature. Strong peaks at 2911 and 2847 were due to symmetric and asymmetric stretching associated with CH₂, while strong peak at 1465 was associated with CH₂ scissoring. Weak bands in between 2970 and 3050 were associated with symmetric and asymmetric C-H stretching.

Further weak absorption bands in between 1301-1367 were due to CH₂ twisting deformation and wagging deformation . Peak at 719 was associated with CH₂ rocking. [161], [162]

The literature-published FTIR spectrum and the spectrum of UiO-66 are comparable. The bands between 1550 and 1630 cm⁻¹ and between 1450 and 1580 cm⁻¹ are caused by the symmetric and asymmetric stretching of the carboxylate ligands. Due to O-H stretching brought on by the water molecules in UiO-66, the wide peak in the region of 3400–3450 cm⁻¹ is the result. ZrO stretching in UiO-66 is what causes the medium intensity peak at 745 cm⁻¹. M-O stretching in UiO-66 also contributes to the peak at 728 cm⁻¹. [163]–[165]

Figures 23(b–e) had peaks similar to those of pure PE (Figure 23(a)), indicating that the support matrix remained unchanged. The main reason of such results was due to use of very small amount of drop-in filler.

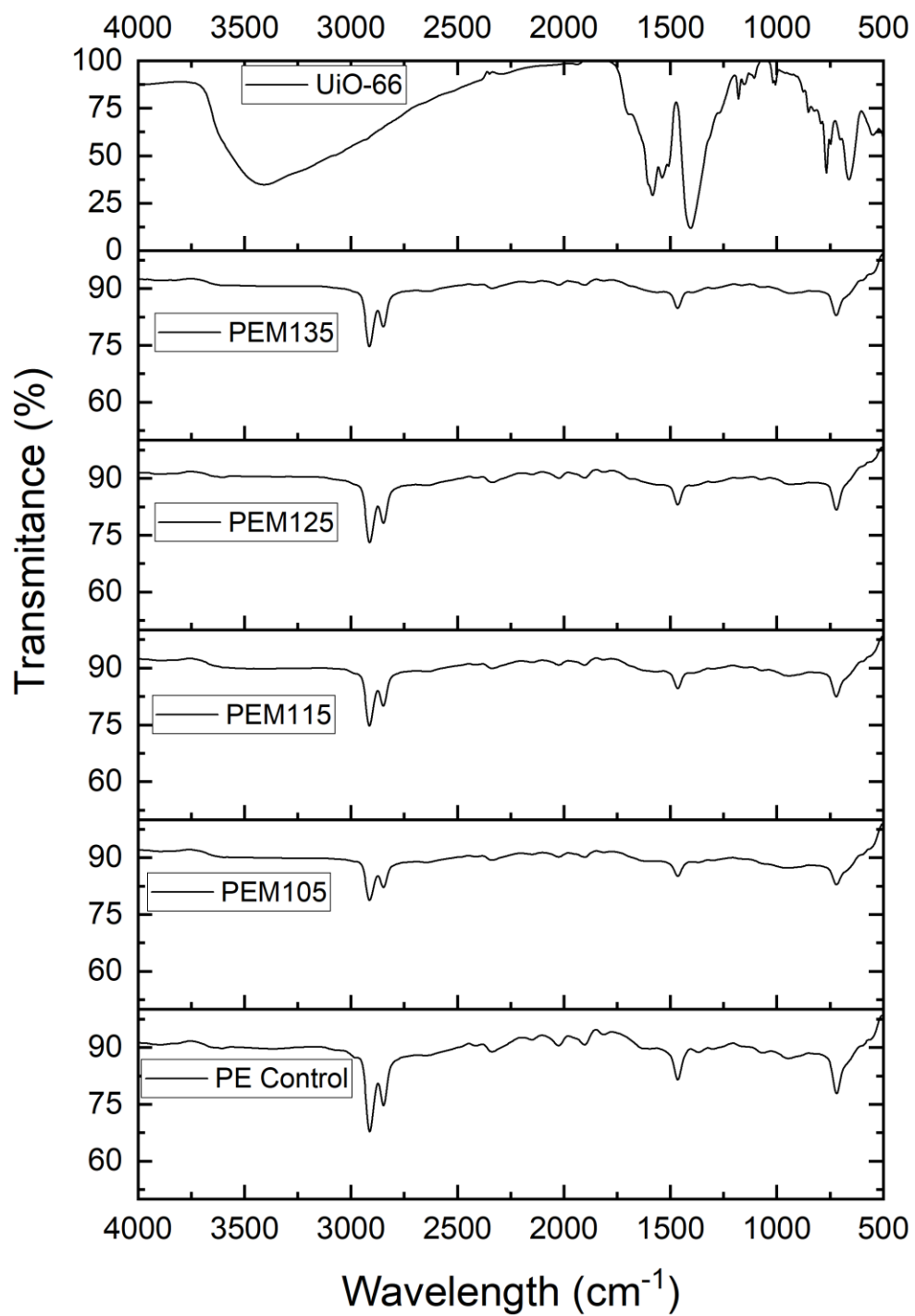


Figure 23 FTIR plot for PE and its composites with UiO-66.

Figure 6 showed the FTIR spectra of Figure 24(a) PE control, Figure 24(b) PEM2405, Figure 24(c) PEM215, Figure 24(d) PEM225, Figure 24(e) PEM235, Figure 24(f) UiO-66-NH₂ alone. The FTIR spectra of PE control was similar to that published in literature. Strong peaks at 2911 and 2847 were due to symmetric and asymmetric stretching associated with CH₂, while strong peak at 1465 was associated with CH₂ scissoring. Weak bands in between 2970 and 3050 were associated with symmetric and asymmetric C-H stretching. Further weak absorption bands in between 1301-1367 were due to CH₂ twisting deformation and wagging deformation. Peak at 719 was associated with CH₂ rocking. [161], [162]

The three zones of the IR spectra of UiO-66-NH₂ shown in Figure 2a are noticeably similar to those described in the literature. The first zone is below 1400 cm⁻¹, and it is made up of a number of bands that are attributed to the vibrations of 2-amino terephthalate. For example, the detected peak at 1261 and 1383 cm⁻¹ is related to the bonding of the amine's aromatic carbon and nitrogen. With respect to the carboxylate ligands, the second zone lies between 1400 and 1600 cm⁻¹. More specifically, the band between 1430 and 1533 cm⁻¹ was noticed, which denotes the presence of amino carboxylate compounds coordinated with the zirconium metal center by the -COO asymmetrical stretching with peaks at 1499 and 1570 cm⁻¹ and the -COO symmetrical stretching with peaks at 1383 and 1434 cm⁻¹. The symmetric and asymmetric vibrations of NH₂ on the organic linker allow the third zone's peaks at 3444 and 3361 cm⁻¹ to exist. [164]

Figures 24(b–e) had peaks similar to those of pure PE (Figure 24(a)), indicating that the support matrix remained unchanged. The main reason of such results was due to use of very small amount of drop-in filler.

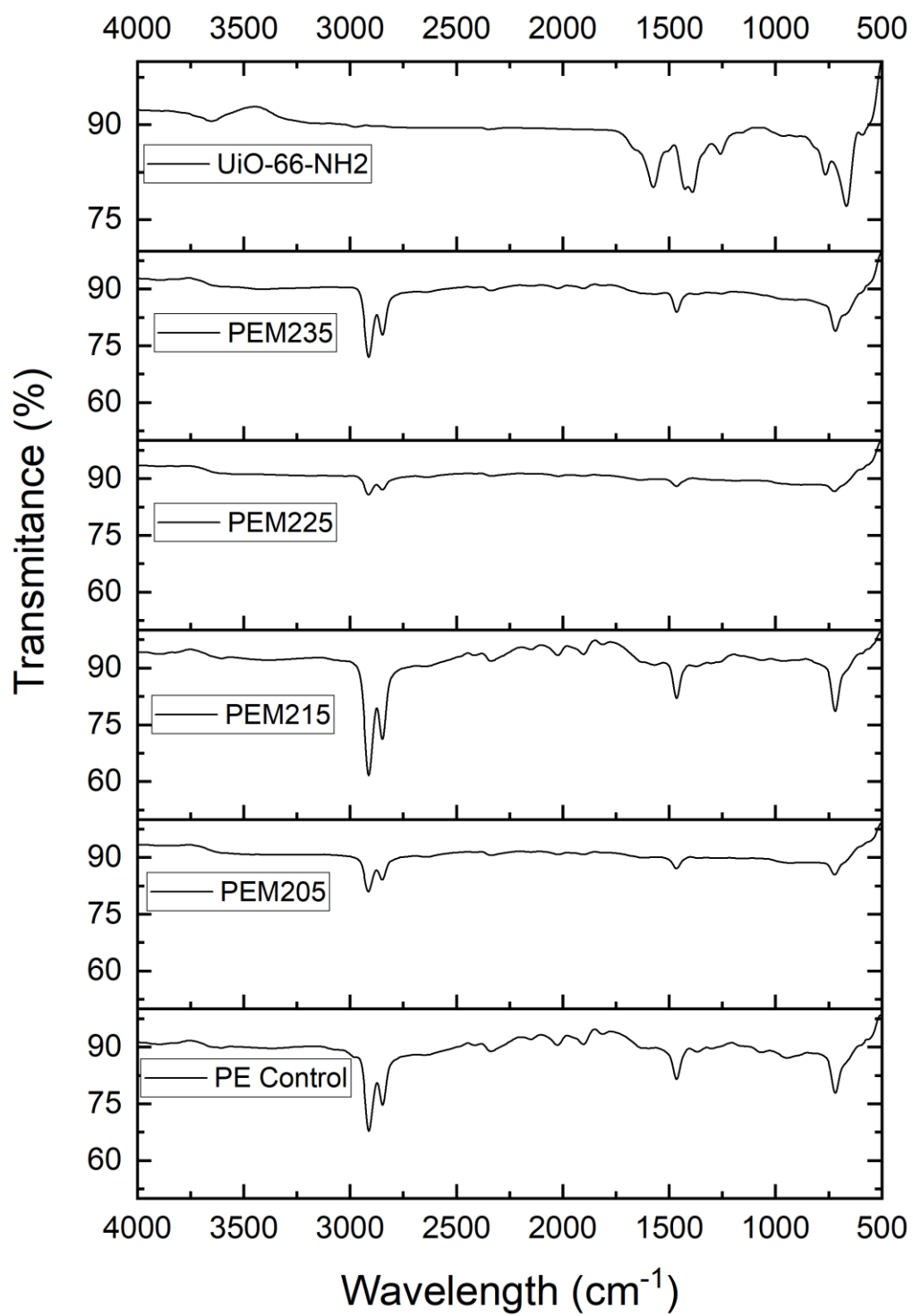
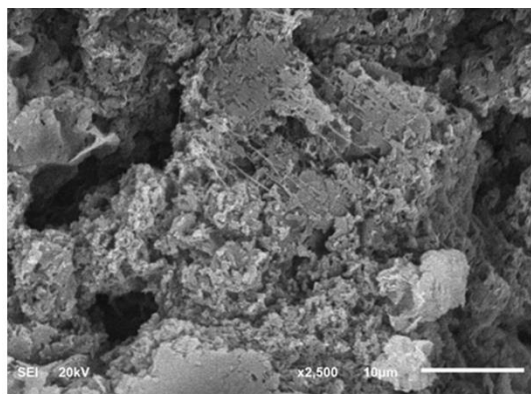


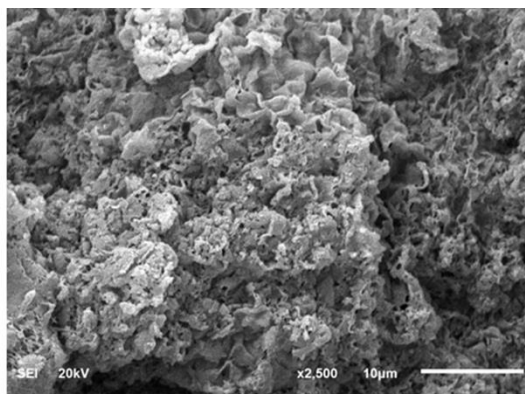
Figure 24 FTIR plot for PE and its composites with UiO-66-NH₂.

4.2.4 Morphological Analysis

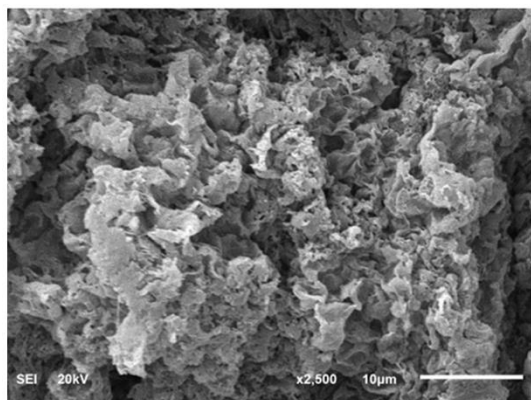
The morphologies of the virgin PE and its composite with MOF UiO-66 were observed by scanning electron microscopy (SEM) demonstrated in Figure 25 (a-d). Figure 25 (a) is for PE which predominantly showed spherical or unspecific particle growth mostly and in some places fibrils type. [32] Similar spherical or unspecific particle growth was observed polyethylene and its compound with nanocellulose at lower concentration (0.3%).[166] Figure 25 (b-d) also showed similar morphology where 25 (b) , (c) and (d) represented the SEM image of polyethylene composites with 15, 25 and 35 mg of drop in filler. The only notable difference was the exfoliation/(extra outer layer) in the composites seemed to be increased compared to neat polyethylene. As the filler amount was increased, it seemed the exfoliation increased which can be observed from Figure 25(b) and (d) where 15 and 35 mg of filler was used. Anyway, there was no huge change in the morphology as the amount of filler was very less compared to the polymer matrix. [166]



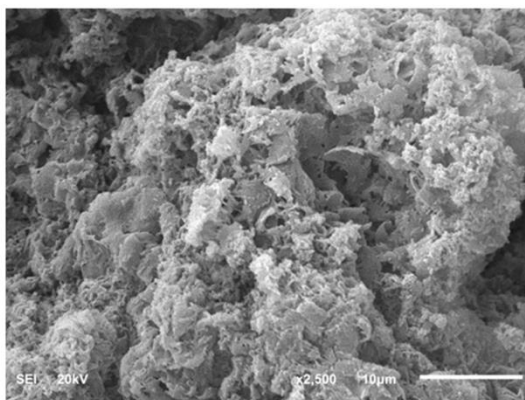
(a) PE



(b) PEM115



(c) PEM125



(d) PEM135

Figure 25 SEM image of polyethylene and its composites.

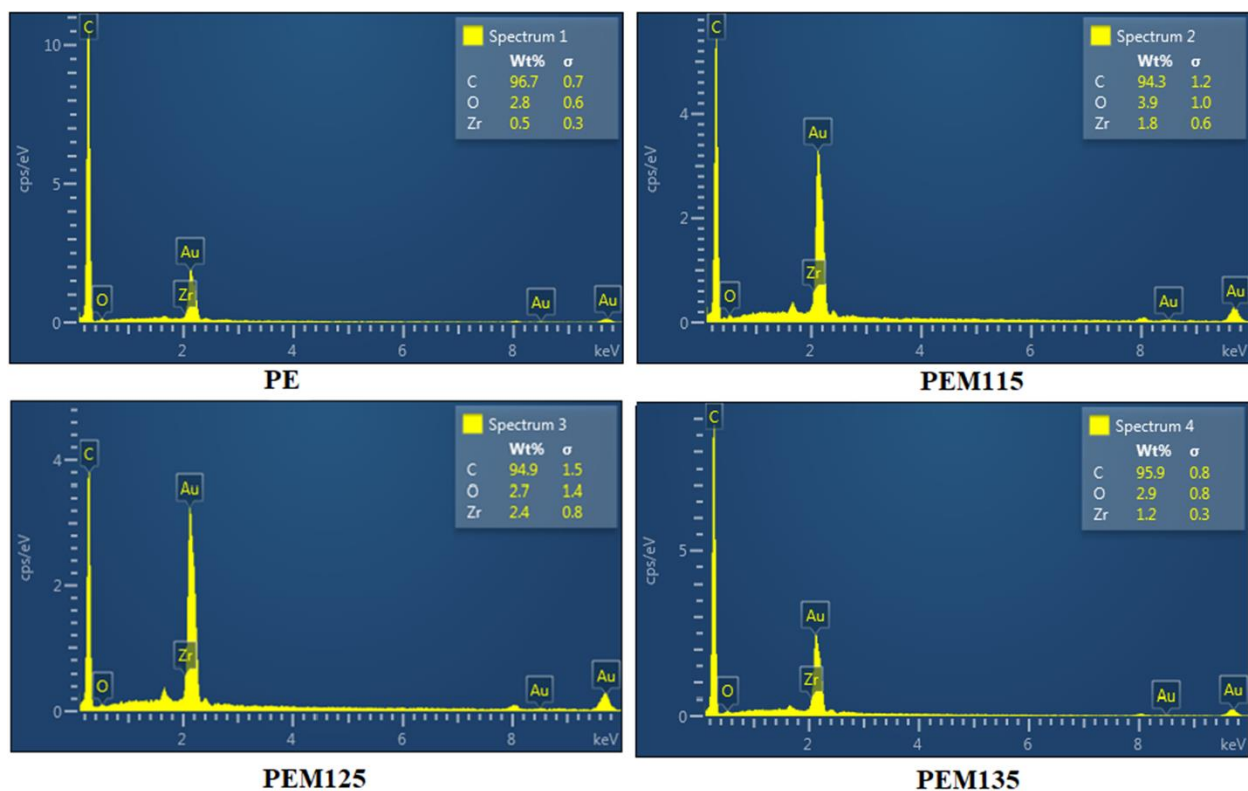


Figure 26 EDX analysis of PE and its composites with UiO-66.

The amount of Zr increased in the surface as the amount of drop-in filler increased for 15 and 25 mg of drop in filler addition. But for 35 mg of drop in filler the amount of Zr in the surface was decreased. The possible reason might be due to agglomeration of filler at higher amount than 25 mg.[167]

The morphologies of the virgin PE and its composite with MOF UiO-66-NH₂ were observed by scanning electron microscopy (SEM) demonstrated in Figure 27 (a-d). Figure 27 (a) is for PE which predominantly showed spherical or unspecific particle growth mostly and in some places fibrils type. [32] Similar spherical or unspecific particle growth was observed polyethylene and its compound with nanocellulose at lower concentration (0.3%).[166] Figure 27 (b-d) also showed similar morphology where 27 (b) , (c) and (d)

represented the SEM image of polyethylene composites with 15, 25 and 35 mg of drop in filler. The only notable difference was the exfoliation/(extra outer layer) in the composites seemed to be increased compared to neat polyethylene. As the filler amount was increased, it seemed the exfoliation increased which can be observed from Figure 27 (b) and (d) where 15 and 35 mg of filler was used. Anyway, there was no huge change in the morphology as the amount of filler was very less compared to the polymer matrix. [166]

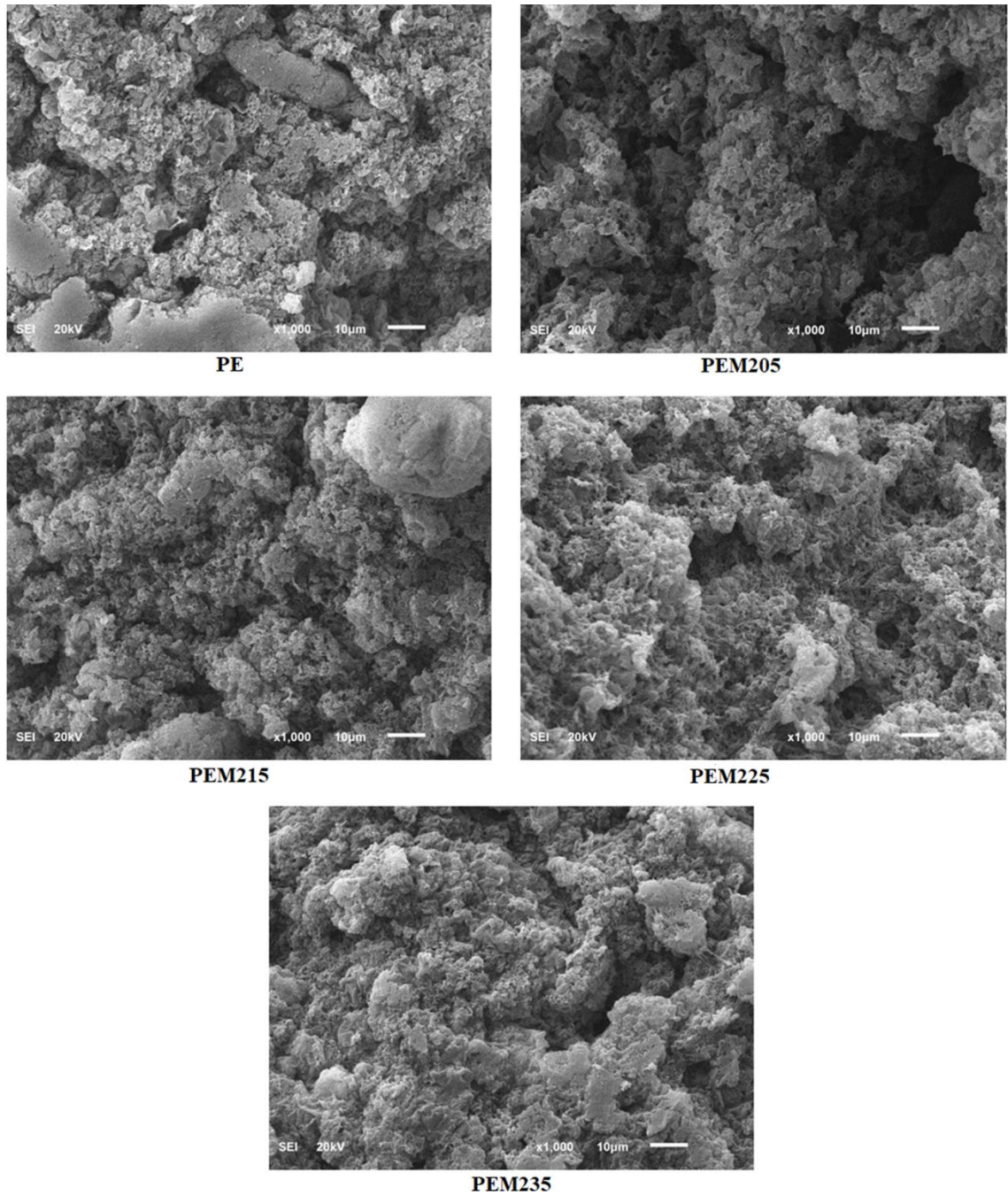


Figure 27 SEM image of polyethylene and its composites with UiO-66-NH₂.

The amount of Zr increased in the surface as the amount of drop-in filler 5, 15 and 25 mg.

For example. But for 35 mg of drop in filler the amount of Zr in the surface was decreased.

The possible reason might be due to agglomeration of filler at higher amount than 25 mg as stated above for filler UiO-66 also.

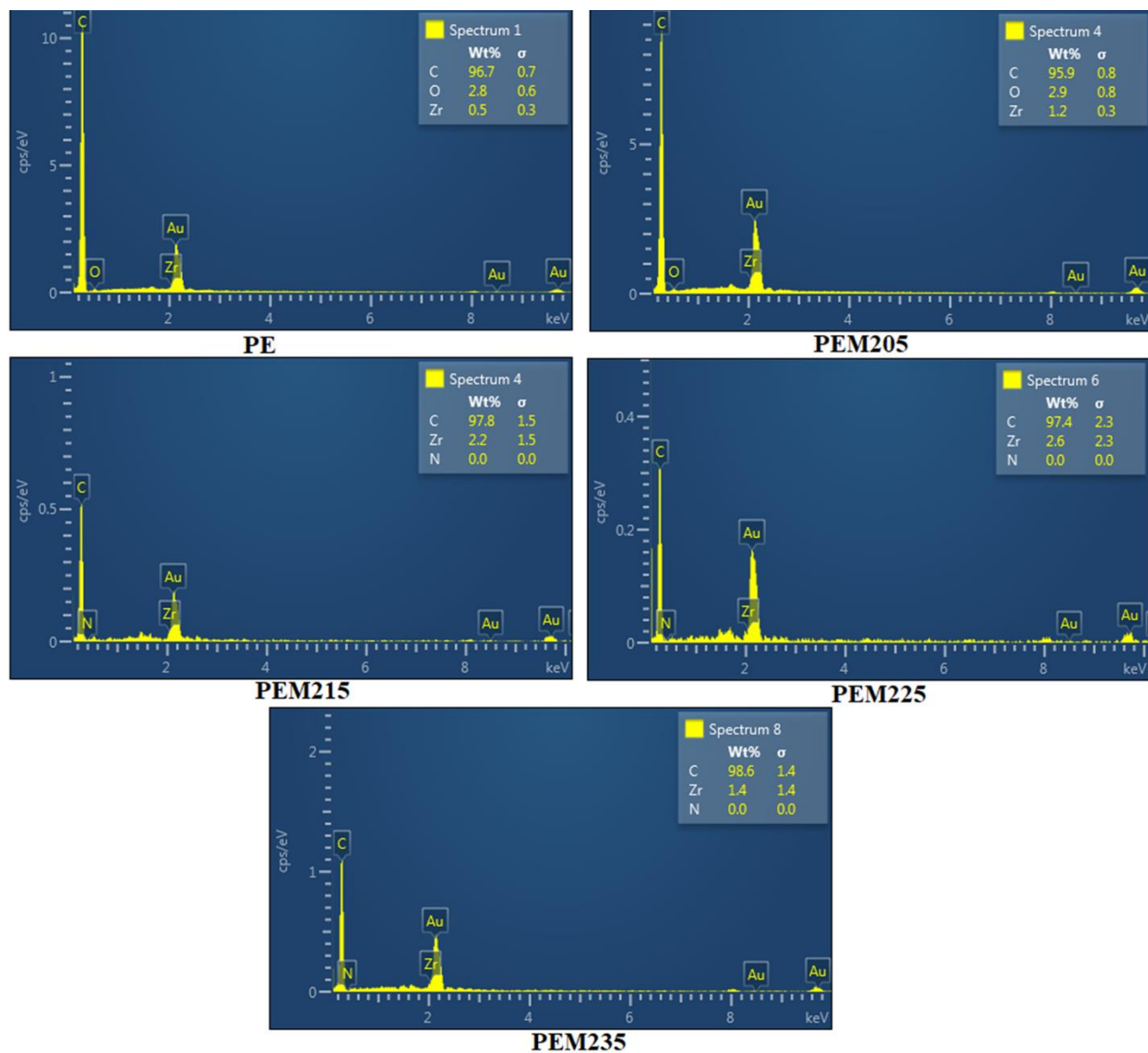


Figure 28 EDX analysis of PE and its composites with UiO-66-NH₂.

4.3 Thermal and Crystalline Behavior of Polyethylene Composites with Reduced Red Mud

4.3.1 Activity

The resulting polymer samples were divided into two groups: polyethylene without filler and polyethylene composites with varying amounts of filler reduced red mud (RMR). Pure polyethylene sample was referred to as PE or PE control, while polyethylene composites were referred to as PERMRXX, where PE stood for polyethylene, RMR stood for reduced red mud, and XX represented the quantity of filler (in mg) in each composite. For instance, PERMR15 indicated a polyethylene composite containing 15 mg of drop-in reduced red mud filler in the polyethylene matrix. Figure 29 showed the activity map of the identical samples and Table 7 summarized the nomenclature based on the quantity of filler addition as well as various thermal and crystalline parameters. Figure 1 shows that, in comparison to polyethylene control, the activity of polyethylene composites did not significantly vary. Though the average activity seemed to increase by 6-9 % for the composites compared to polyethylene control, considering the standard deviation the maximum activity for the composites remained very close to the control sample. From the plot it might be concluded that after addition of filler the activity became more stable as the standard deviation is small. In a nutshell, RMR as drop-in filler did not affect the activity of the polyethylene composite, rather the average activity was improved slightly.

Table 7 Thermal properties of PE and PE-RMR composites.

Sample Name	Filler (mg)	T_m (°C)	T_c (°C)	Crystallinity (%)	T_{0.9} (°C)
PE	0	130.9	118.5	82.5	447.0
PERMR05	5	132.0	120.9	93.0	458.7
PERMR15	15	132.2	119.7	89.9	458.5
PERMR25	25	131.7	118.6	88.1	456.4

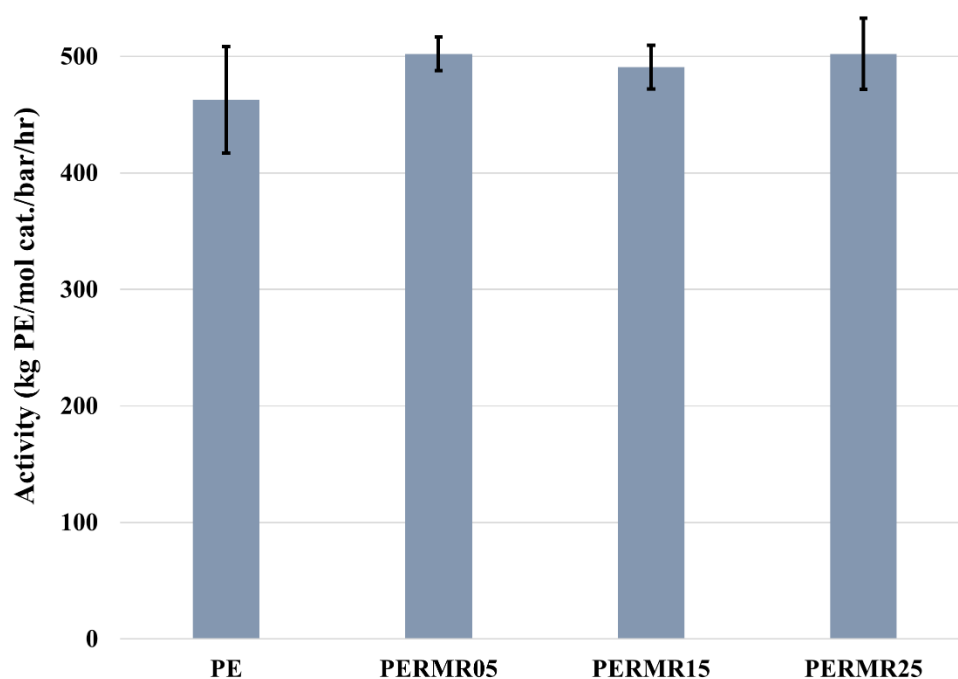


Figure 29 Activity of PE and PE-RMR composites.

4.3.2 Thermal and Crystallization Properties

Similar to activity, this filler had no discernible impact on the composites' melting and crystallization temperatures as compared to the polyethylene control sample. Table 1 summarized the melting and crystallization temperature of the polyethylene and its composites with RMR while Figure 30 displayed the heating cycle of DSC to determine the melting temperature of the samples. Polyethylene and its composites at different loading of RMR demonstrated a single sharp peak in between 120-140 °C in the heating cycle (Figure 30). After determining the signal maximum/ minimum the melting temperature of polyethylene control was 130.9 °C while polyethylene composites melting temperature for loading 5, 15 and 25 mg RMR as drop-in filler were 132.0, 132.2, 131.7 °C respectively. The melting temperature for loading of 5 mg of RMR improved the melting temperature of the composite to 132.0 °C from 130.9 °C. Increment in the filler amount to 15 mg increased very slightly the melting temperature to 132.2 °C and further increment in the filler amount to 25 mg decreased slightly melting temperature of the composite to 131.7 °C. The melting temperature of the composites differed by 1 ± 0.3 °C only from the polyethylene control sample. Thus, drop-in filler RMR did not alter the melting temperature of the composites significantly from its polyethylene control sample. Similar insignificant change in crystalline temperature was for polyethylene composites compared to polyethylene control sample. The crystalline temperature of the bare polyethylene samples was found to be 118.5 °C. After addition of 5 mg RMR as drop-in filler the crystallization temperature of the composite increased to 120.9 °C. Further increment in the filler amount decreased the composites' crystalline temperature. For example,

increment of filler from 5 mg to 15 and 25 mg decreased the crystalline temperature from 120.9 °C to 119.7 and 118.6 °C respectively. Though a small change was observed in the crystalline and melting temperature for the composites, the deviation was not far away from the polyethylene control sample.

Although the melting and crystalline temperature of the composites were close to polyethylene control there was a significant improvement in the crystallinity and thermal stability of the composites compared to the control sample. As an instance the crystallinity of the polyethylene control sample was 82.5% , whereas addition of only 5 mg RMR as drop-in filler improved the crystallinity of the composite PERMR05 to 93.0%. When the amount of drop-in filler was increased the crystallinity of the composites did not increase rather decreased slightly compared to PERMR05. It was observed that, composites obtained from 15 and 25 mg drop-in filler in the polyethylene matrix demonstrated crystallinity 89.9 and 88.1% respectively. So there was a maximum 10.5% improvement in the crystallinity by adding only 5 mg of RMR as drop-in filler while all composites showed better crystallinity for any loading of filler up to 25 mg.

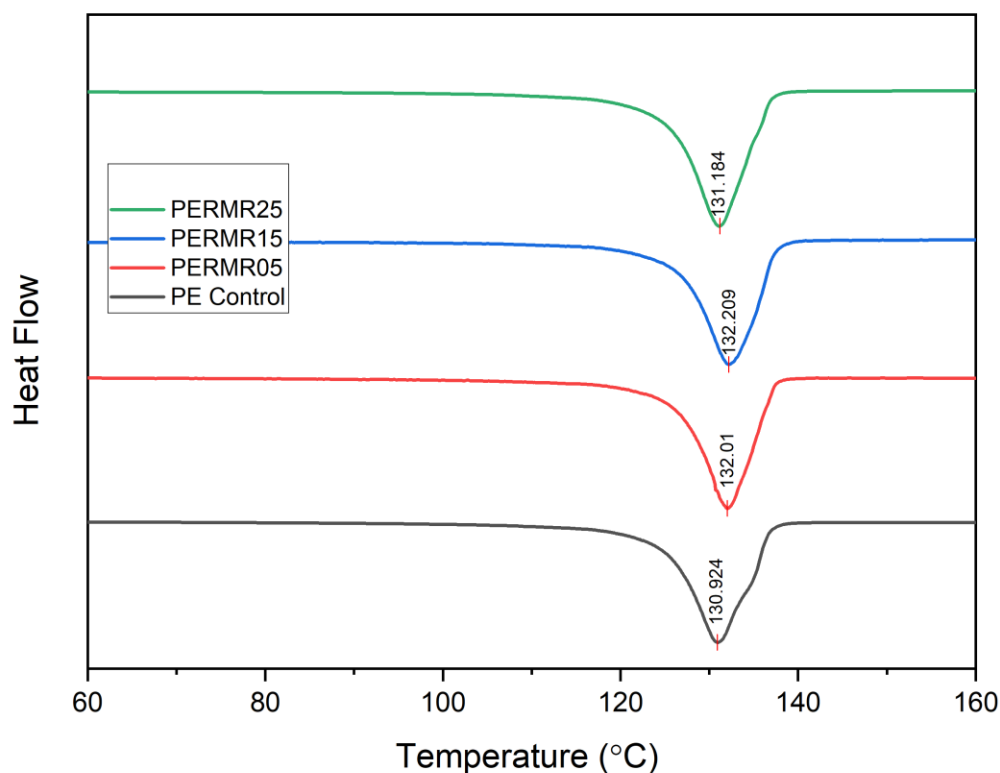


Figure 30 DSC plots for PE and PE-RMR composites.

As stated earlier, thermal stability of the composites improved significantly compared to bare polyethylene sample like crystallinity. The thermogravimetric analysis (TGA) findings were displayed in Figure 31 and the 10% weight loss temperatures ($T_{0.9}$) were compiled in Table 7. The improvement in thermal stability of the polyethylene composites over the pure polyethylene sample has been clearly shown in Figure 31. All the polyethylene composites demonstrated better thermal stability compared to pure polyethylene. 10% Weight loss of the polymers was another indicator where 10% degradation of the polyethylene control sample occurred at 447.0 °C. But only 5 mg of the filler improved the $T_{0.9}$ temperature by 11.7 °C of the composite PERMR05 to 458.7 °C.

Interestingly, further increment in the filler amount slightly decreased the $T_{0.9}$ temperature like the slight decrease in the crystallinity of the same composites. For example, $T_{0.9}$ temperature for addition of 15 and 25 mg of filler amount were 458.5 and 456.4 °C respectively. Clearly, 5 mg RMR as drop in filler outperformed the other composites and control samples in terms of crystallinity and thermal stability. As comparison to the polyethylene control sample, the polyethylene composites showed a notable improvement in crystallinity and thermal stability as well as a marginal improvement in melting and crystalline temperatures when RMR was employed as a drop-in filler in varied proportions. These findings suggest that the RMR may have functioned as a nucleating agent during the polymerization process.

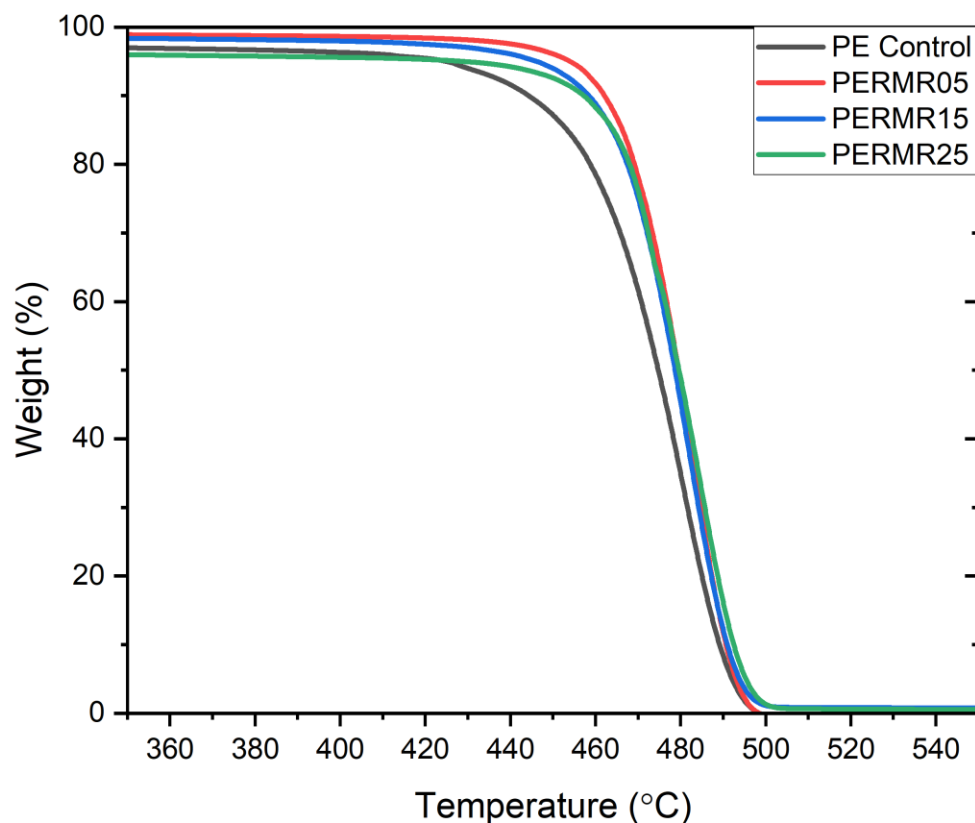


Figure 31 TGA plot for PE and PE-RMR composites

Apart from the thermal characteristics of the polymers by DSC and TGA, to understand the branching in the polyethylene and the chains of its composites required CRYSTAF analysis. When the temperature was being lowered in this analysis, the polymer solution's concentration was being watched. The polymer chain's most crystalline section precipitated first, followed by any less crystalline sections, as the solution's temperature dropped. Any polymer chain has a section that is most crystalline, which has no or few branches, and a region that is less crystalline, which has more branches. In the CRYSTAF plot, polymer chains with no or few peaks show on the high temperature side, while the peak for the most

branched polymer chain appears on the lower temperature side in the displayed data from CRYSTAF. CRYSTAF analysis of polyethylene control and polyethylene composites at different loading of drop-in filler RMR was plotted in Figure 32. Only one single peak was observed for polyethylene control sample as well as for the composites. The peak for each sample was in the high temperature zone (80-90 °C) which resembled longer chains with no or few branches in the polyethylene and its composites. There was no noticeable peak in the lower temperature zone (30-80 °C) representing no substantial short chain branching. So the RMR as drop-in filler did not alter the branching of polyethylene in its composites. This further supported the filler's role as a nucleating agent because it meant that the structure of the polyethylene composites remained the same as it was in the polyethylene control sample.

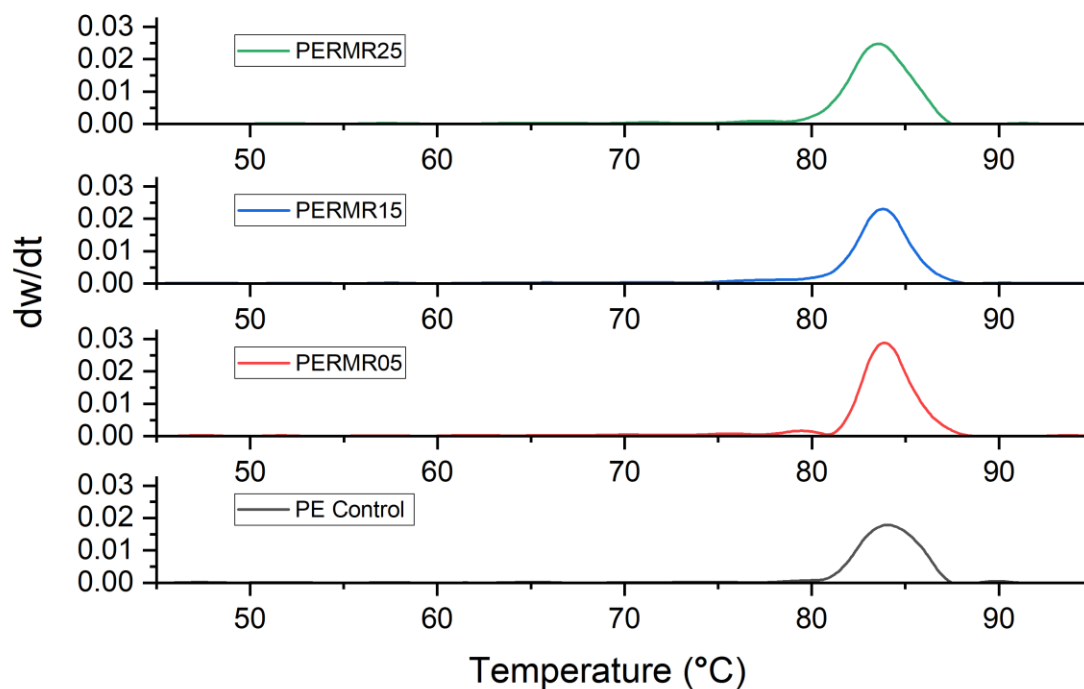


Figure 32 Figure obtained from data of CRYSTAF for PE and its composites.

4.3.3 FTIR Analysis

Figure 33 showed the FTIR spectra. The FTIR spectra of PE control was similar to that published in literature. Strong peaks at 2911 and 2847 cm^{-1} were due to symmetric and asymmetric stretching associated with CH_2 , while strong peak at 1465 cm^{-1} was associated with CH_2 scissoring. Weak bands in between 2970 and 3050 cm^{-1} were associated with symmetric and asymmetric C-H stretching. Further weak absorption bands in between 1301-1367 cm^{-1}

were due to CH₂ twisting deformation and wagging deformation . Peak at 719 was associated with CH₂ rocking. [161], [162]

Polyethylene composites with RMR has peaks similar to those of pure PE (Figure 33), indicating that the support matrix remained unchanged. The main reason of such results was due to use of very small amount of drop-in filler.

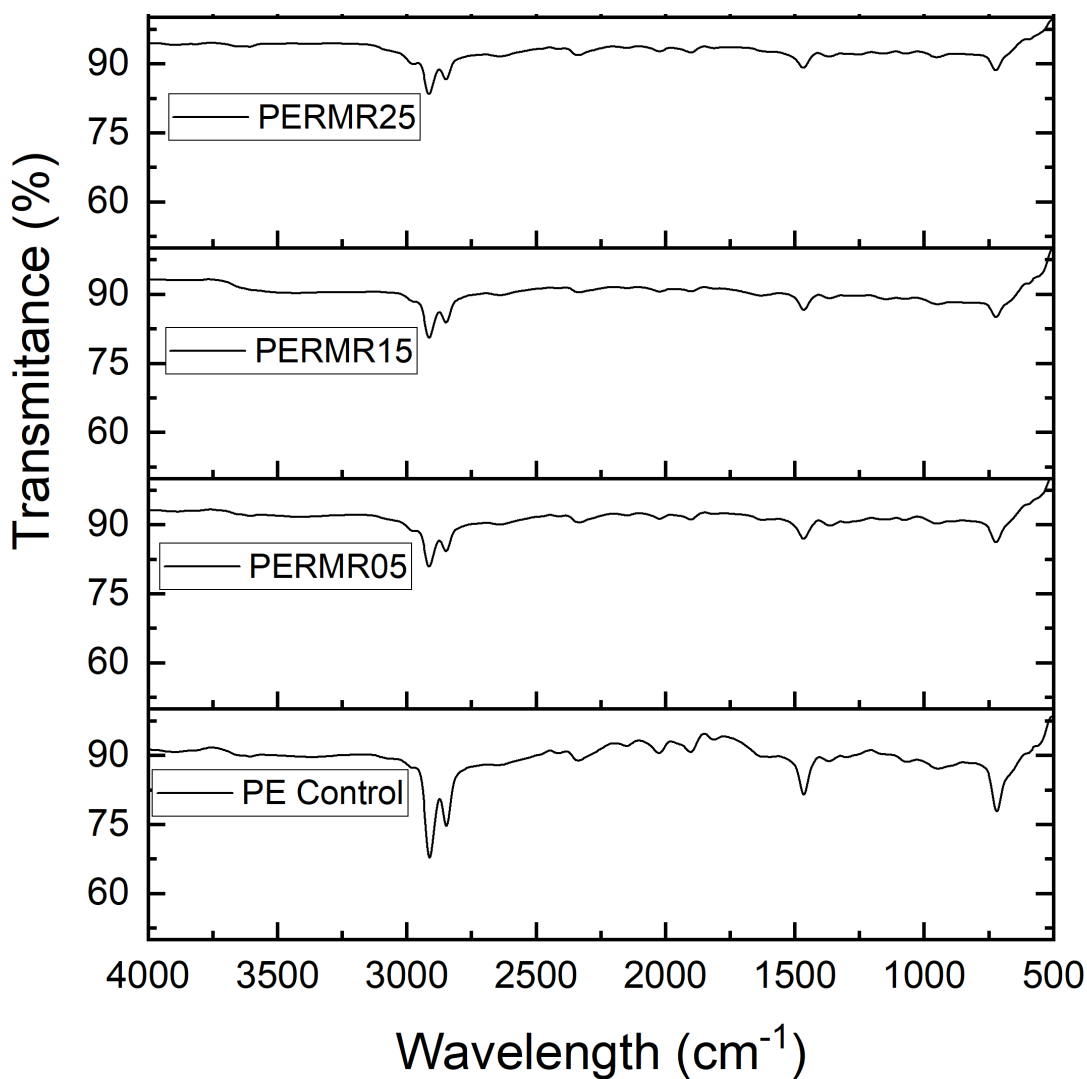


Figure 33 FTIR plot for PE and its composites.

4.3.4 Morphological Analysis

The morphologies of the virgin PE and its composite with RMR were observed by scanning electron microscopy (SEM) demonstrated in Figure 34 (a-d). Figure 34 (a) is for PE which predominantly showed spherical or unspecific particle growth mostly and in some places fibrils type. [32] Similar spherical or unspecific particle growth was observed polyethylene and its compound with nanocellulose at lower concentration (0.3%).[166] Figure 34 (b-d) also showed similar morphology where 34 (b) , (c) and (d) represented the SEM image of polyethylene composites with 05, 15 and 25 mg of drop in filler. The only notable difference was the exfoliation/(extra outer layer) in the composites seemed to be increased compared to neat polyethylene. As the filler was added, it seemed the exfoliation increased which can be observed from Figure 34(b) and (d) where 05 and 25 mg of filler was used. Anyway, there was no huge change in the morphology as the amount of filler was very less compared to the polymer matrix. [166]

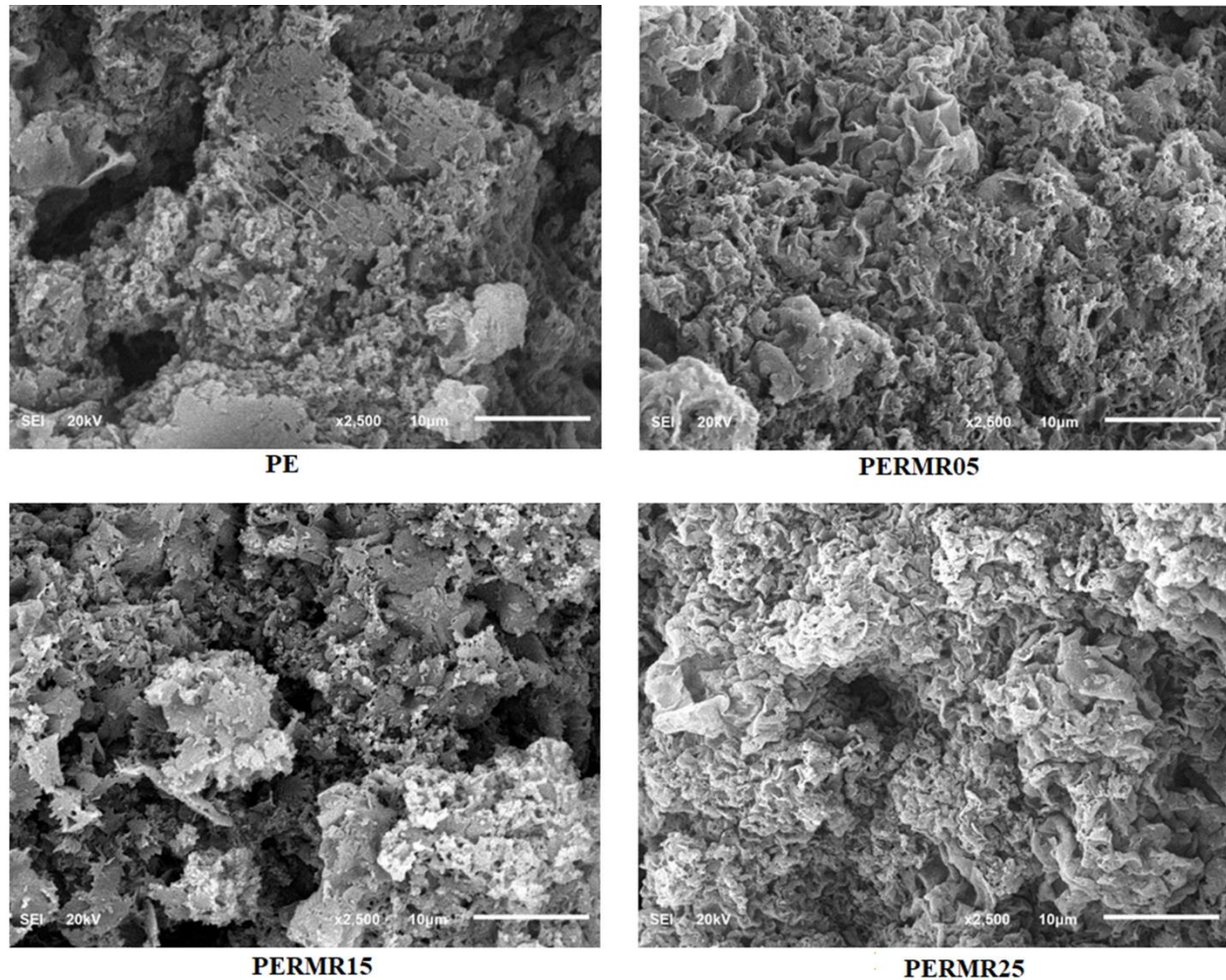


Figure 34 SEM image of PE and PE-RMR composites.

The EDX results clearly demonstrated that the amount of different inorganic/metals molecules increased as the filler amount was increased. It was a clear indication of the filler remained as drop in in the polymer matrix.

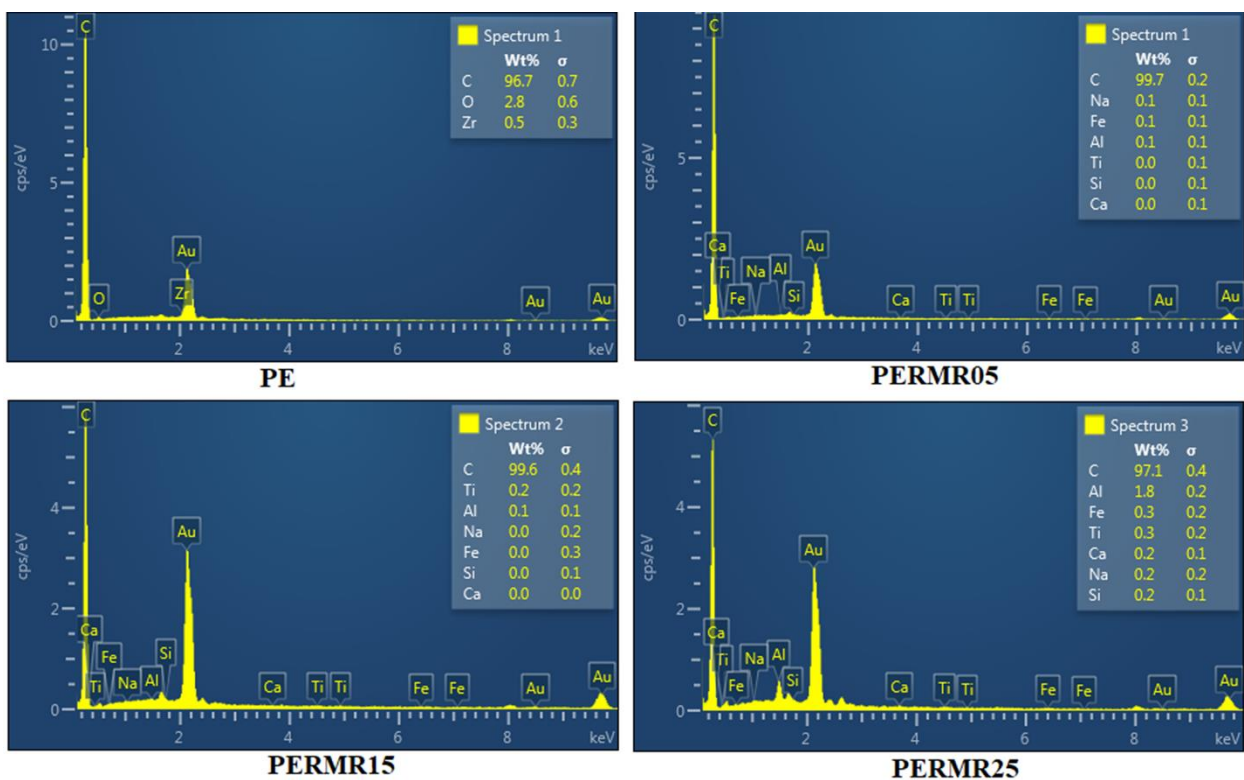


Figure 35 EDX analysis of PE and PE-RMR composites.

4.4 Conclusion

Polyolefins and their derivatives have been a crucial commercial product since they were first invented. These materials are used in a wide range of applications, including packaging, construction, and automotive industries. As a result, there is a great deal of interest in studying the copolymers and terpolymers of these materials due to their extensive use.

In this research, the focus was on synthesizing copolymers and terpolymers of ethylene and propylene, along with composites that incorporate nickel-chromium layered double

hydroxide (LDH) as a filler. Additionally, the researchers investigated the effect of adding different fillers to pure polyethylene using the same in-situ technique.

The copolymers were synthesized using styrene as a third monomer. The addition of styrene had a significant impact on the activity of the copolymerization reaction, resulting in an increase in yield of up to 235% when 1.0 mL of styrene was added. However, this increase in yield came at the cost of decreased crystallinity, melting temperature, and thermal stability. Despite this, the copolymers with styrene still performed better than similar terpolymers where α -olefin was used as the third monomer.

The research also explored the use of nickel-chromium LDH as a filler in the terpolymers. Unfortunately, this had a negative effect on the thermal stability of the resulting composites. However, the thermal stability of these composites could be improved through ultrasonication treatment.

In addition to exploring copolymers and terpolymers, the researchers also looked at incorporating different fillers into pure polyethylene using the same in-situ technique. Two metal organic frameworks and waste materials were used as fillers. The resulting composites showed better crystallinity and thermal stability compared to pure polyethylene, with the composites with metal organic frameworks performing slightly better than those with waste materials. Interestingly, the composites with waste materials showed the highest crystallinity at a low level of filler loading, but there were no significant

differences in melting temperature, crystallization temperature, or morphological properties compared to the control sample.

Overall, this research provides valuable insights into the synthesis and properties of polyolefins and their derivatives, as well as the use of different fillers to improve their properties.

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