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Preparation of PP/PP-g-MAH/C15A Nanocomposite by Melt Extrusion Process and Comparative Study of its Mechanical and Non-Isothermal Crystallization Behaviour

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Abstract: Nanocomposite films have been prepared by melt blending method with the help of twin screw extruder using polymer polypropylene(PP)nucleating agent like organically modified nanoclay at optimum loading condition. Compatibilizers such as polypropylene grafted maleic anhydride (PP-g-MAH) were used for better compatibility between polymer matrix and filler. The effect of organoclay on nucleation effect and subsequent incremental values in mechanical and thermal behavior of different nanocomposite films has been investigated and explained with justifications. The tensile properties have shown to be improved in presence of clay nanoparticles due to resistance exerted by clay layers against plastic deformation of the polymer. Thermal properties measured by differential scanning calorimeter shows increased crystallization temperature of the nanocomposites in presence of clay particles and compatibilizer of optimum concentration.

Keywords: Polypropylene, organoclay, Nanocomposite, crystallization, nucleation, interlayer, compatibilizer

I. INTRODUCTION

The commercial production of polypropylene by using Zeigler-Natta Catalysts has revolutionized the mass exploitation and its use in polymeric world with respect to automotive and packaging applications [1]. The main cause of its huge commercial use in variety of applications; is of its low cost, light weight, heat distortion temperature above 100°C and amazing properties with its recycling behaviour. In recent years, polymer researchers have developed various techniques to prepare composites comprising polyolefins and organically modified filler such as clay. The advantages of using fibers in composites are many such as durability, competitive specific mechanical and thermal properties, reduced energy consumption and eco-friendliness [2-3]. Incorporation of fillers in composites comprising base polymer such as polyolefins has been proven to be an effective way in improving mechanical properties such as tensile strength, toughness of base polymer polypropylene. Clays like montmorillonite, hectorite, saponite and surface modified clay by using maleic anhydride are important minerals. Among various kinds of clay as mentioned above, the most common nanoscopic filler is resulting from montmorillonite clay [4-7] .It is found naturally in a layered silicate structure with a high aspect ratio and surface area. The surface area of montmorillonite clay is nearly about 750 m^2/gm. Greater surface area means grater dispersion during mixing with polymer matrix [5]. The clay particles normally consist of platelet tactoids structure of 20-25 layers. These clay particles are widely used in macro/ micro composite and nanocomposites because of their natural occurrence, high aspect ratio, low cost, good heat resistance, light weight, stiffness and morphological structural importance even at very low content of clay (<5 weight %) [6-7]. The issue lies with the preparation of polymer-clay nanocomposites (e.g. Polypropylene/clay nanocomposites) due to very low intermolecular interaction between the non-polar hydrophobic polypropylene and hydrophilic clay particles. Exchanging the cations in between the silicate layers with bulkier and organophilic cations, such as long chain alkyl ammonium ion which modified the clay platelet structure and make it organophilic so called organoclay [8]. The cation expands the silicate layer spacing which helps the clay layers to be intercalated or exfoliated. An exfoliated clay particle means platelets of thickness in the order of 1 nanometer and with aspect ratio in the order of 100. Good clay dispersion in nanocomposite can potentially overcome achieved by preparing nanocomposites by twin screw extrusion, conventional shear mixing technique [2-3]. These methods have been successfully used to prepare intercalated/exfoliated nanocomposite structure. However melt intercalation is the dominant way of preparing polymer/clay nanocomposites due to their cost effectiveness and less time consuming process. The melt intercalation takes place in twin screw extruder machine where the mixing of polymer matrix with clay particles takes place.

The proper mixing of clay particles in molten polymer depends on screw speed, establishment of favorable system energy reduction mechanism and many other related factors [8, 9]. The inter layer spacing in clay platelets and favorable interaction with polymer matrix is the key to get intercalated or exfoliated structure. In recent times melt intercalation technique by using twin screw extruder is being accepted as an encouraging approach because of its ease by retaining conventional polymer mixing and its environmental friendly behaviour. In this process, the polymer matrix and clay particles are forced through a nozzle that creates tensile stress which partially aligns its molecules. This alignment can be assumed to be crystallization and it affects the material properties. When polymers crystallize from an isotropic bulk of melt, the lamellae having thickness 10 to 20 nm in thickness are typically organized into a spherulitic morphology. However when polymer chains are confined in a space with dimensions of a few tens of nanometers, comparable to or less than that the lamellar crystal thickness, nucleation and growth can be dramatically affected [10-13].

Considering the technical aspect of preparation, two stage mechanisms have been proposed. In the first stage, polymer melts and intercalated into the stretched clay galleries. Further, the bulk polymer matrix got transferred into the silicate interlayer spacing. This particular pathway need not require high shear. The important driving force is either the chemical or physical affinity of the polymer matrix for the organoclay surface and the heat (enthalpy) of mixing. The enthalpy of mixing must be favorable so as to maximize the driving force required for transport of polymer bulk into the clay galleries. Addition of compatibilizer during melt blending is the direct way to increase the compatibility between polymer matrix and clay particles. The non-polar polymer like polypropylene must be further treated with compatibilizer by applying high shear intensity during melt processing without which clay tactoids do not delaminate. Several efforts have been made to improve the mixing of clay particles in polypropylene matrix by using functional oligomers as compatibilizer [11-12]. Maleic anhydride grafted polypropylene (PP-g-MAH) is one of the best compatibilizer which is used to enlarge the interlayer spacing in bulk polymer matrix and facilitate the penetration of clay particles. Hence it helps in binding non-polar hydrophobic polypropylene with hydrophilic clay particles and produced partially intercalated or exfoliated structure. In brief, the addition of compatibilizer creates more favorable polymer–clay interaction which leads to exfoliation of the clay particles and helps in maximizing the mechanical and barrier properties.

The properties of the compatibilizer i.e. PP-g-MAH that influences its efficiency in preparing polypropylene/organoclay nanocomposite are a) molecular weight b) maleic anhydride content which relates to the volume of functionality present in the compatibilizer. Different researchers reported the effect of addition of compatibilizer on the clay dispersion in polymer matrix during melt blending. The molecular weight of the compatibilizer and its loading percentage with maleic anhydride content has been summarized in table-1.

Table-1: Molecular weight of the compatibilizer and its loading percentage

Trade Name	Molecular Wt.	Acid value	MA content	PP-g-MAH (w/w)	Reference
PPMA-100	30,000	32	-	3/1,1/1 and 1/3	
PPMA-1010	30,000	52	-	3/1	
PPMA-1001	40,000	26	-	-	
PPMA-100	30,000	52		3/1,2/1 and 1/1	
PPMA-110TS	12,000	7	-		

From analysis with respect to the data as specified in **table-1,** it has been reported that the effect of maleic anhydride content on the clay dispersion is not consistent. It is revealed that, high maleic anhydride content generally enhances the intercalation of polypropylene into clay galleries but with possibility of immiscibility with polymer matrix. Further, it also harms the mechanical properties of the nanocomposite. Some researchers reported that high maleic anhydride content (nearly 4.2%) has enhanced the mechanical properties as compared to low compatibilizer loading under the same experimental condition. However the consequence of using compatibilizer having low molecular weight is less clear. Wang et al. found that using low molecular wt. oligomers (Mw= 9100) has resulted in better dispersion and high molecular weight of the compatibilizer (Mw= 330,000) has improved mechanical strength of the composite. In the study published by Kim et al., it is reported that compatibilizer (with lowest maleic anhydride content of 0.55%) and polypropylene having low viscosity resulted in the greatest improvement in storage modulus. It is to be noted that without mentioning the molecular weight of the compatibilizer, it is difficult to critic the significance of viscosity of components. Viscosity plays vital role in dispersion of polymer with clay particles during melt blending.

In the second stage, the clay tactoids are exfoliated under the optimum shear and by increasing the contact area between the polymer matrix and clay platelets. High shear intensity would support the formation of polymer/clay hybrid by breaking up clay particles and increasing uniform mixing. This process is facilitated by both residence time and screw configuration in the twin screw extruder. The process is thus facilitated by both residence time and screw configuration [2]. Although the preparation of complete clay exfoliated polypropylene/clay nanocomposite is the most favorable morphology but the same has not yet been experimentally achieved. However the partial intercalation/exfoliated structure has enhanced the properties such as stiffness and strength at low loading of clay content which is still very attractive from the industrial and manufacturing point of view [7-8].

Polymers can crystallize upon cooling from melting, mechanical stretching or solvent evaporation. The properties of semi-crystalline polymers **(Figure-1)** are determined are determined not only by the degree of crystallinity, but also by the size and orientation of the molecular chain.

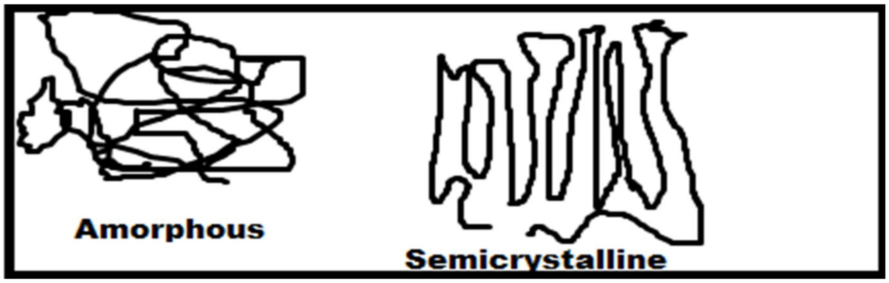


Figure-1: Arrangement of molecular chains in amorphous and semi-crystalline polymers

Nucleation starts with small, nanometer sized area where as result of heat motion some chains or their segments occur parallel. Those seeds can either dissociate, if thermal motion destroys the molecular order, or grow further, if the grain exceeds a certain critical value. Apart from the thermal mechanism, nucleation is strongly affected by fillers and other additives in the polymer. For example in this paper the nucleating effect of clay particles in polymer matrix during melt intercalation by melt blending has been explained in details. This effect is referred as heterogeneous nucleation. Figure-2 represents the lamellae obtained during crystallization from the melt [13].

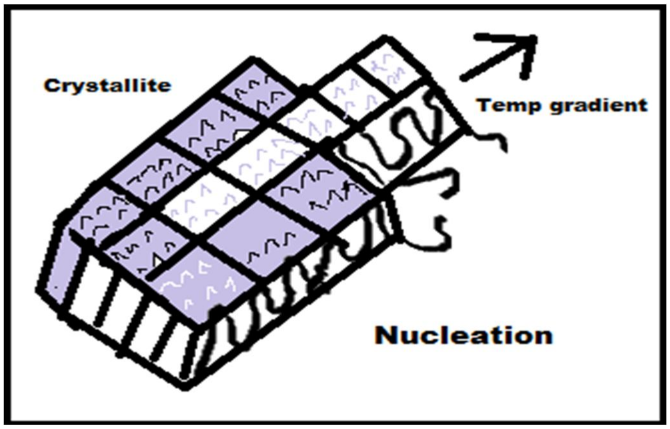


Figure-2 : Lamellae form during crystallization from the melt.

Crystal growth is achieved by the further addition of folded polymer chain segments and only occurs for temperatures below the melting temperature(Tm) and above the glass transition temperature (Tg). Further at higher temperature destroys the molecular arrangement and below the glass transition temperature, such movements of molecular chains are frozen. It is too worthy mentioned that, secondary nucleation can proceed even below Tg, as the process affects the mechanical and thermal properties of the composites. The molecular entanglements interact via different types of the van der Waals forces exist among the lamellas. Figure - 3 depicts schematic model of a spherulites and its direction of molecular alignment. The interaction forces and its strength depend on the distance between the parallel chain segments and it influences the mechanical and thermal behaviour of the polymer and its nanocomposites [5-6]. The growth of the crystalline regions preferably occurs in the direction of the largest temperature gradient. In case of strong gradient, the growth has a unidirectional character.

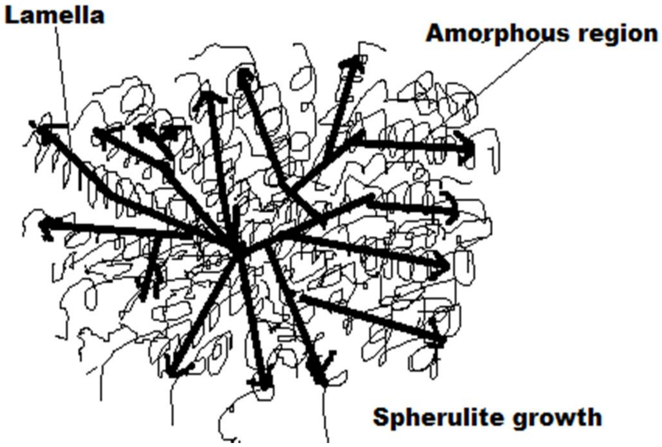


Figure-3: Schematic model of a spherulite .Black arrows represent the direction of molecular alignment

II. MATERIALS

A. Polypropylene

The PP homopolymer pellets (Repol H100EY) of density 0.96 and Melt Flow Index 11g/10min (230˚C/2.16 kg, ASTM D 1238) supplied by Reliance Polymers was used in this work which meets FDA requirements for all food contact and cooking application in the Code of Federal Regulations in 21 CFR 177.1520. The properties as supplied by the manufacturer are listed in table-2.

Table-2 General Properties of Polypropylene

Properties	*Values*	*Unit*	*ASTM test method*
Physical Properties			
Density	0.900	g/cm^3	D792B
Melt Flow	12.0	g/10 min	D1238
Mechanical Properties			
Hardness, Rockwell R	93	---	D785A
Tensile Strength, Yield	35.0	MPa	D638
Elongation at Yield	9.0	%	D638
Flexural Modulus	1.60	GPa	D790A
Izod Impact, Notched	0.320	J/cm	D256A
Thermal Properties			
Deflection Temperature at 0.46 MPa	94.0	°C	D648

B. Maleic Anhydride grafted Polypropylene (PP-g-MAH)

Maleic anhydride (MAH) grafted onto PP was used as a compatibilizer between nanofillers and matrices. Maleated polymers act as compatibilizer between the nonfunctional polymers and clay. Typical properties of used PP-g-MAH are shown in **table-3**.

Table-3: Properties of Maleic anhydride (MAH)

Maleic anhydride	Properties
Molecular Formula	$C_4H_2O_3$
Molar Mass	98.06g/mol
Density	$1.314 g/cm^3$
Melting point	60^0C
Boiling point	202^0C

The PP-g-MAH has been used as a coupling agent in the PP/clay nanocomposites. The PP-g-MAH exhibited both polar and non polar components. The maleic anhydride (MAH) is a polar component which grafts to the non polar PP backbone. Therefore, the MAH is compatible with the modified clay. The MAH group may be able to interact with the hydroxyl group (-OH) in the modified clay to form hydrogen bonding or covalent bonding. In addition, the PP backbone of the PP-g-MAH is miscible with the PP matrix. Therefore, PP-g-MAH leads to improvement of the dispersion of modified clay in the PP matrix.

C. Cloisite 15A (C15A) Nanoclay

The commercially modified clay mineral, Cloisite 15A (C15A), was purchased from Southern Clay Products, Inc., USA. The properties of C15A are given in **table-4**. The basal spacing (d_{001}) of the C15A is higher than in the other Cloisite products. This induces the PP to penetrate more easily in to the clay layers of the C15A rather than the other Cloisite products. Typical physical properties of C15A clay used are as follows.

Table-4: Properties of Nanoclay (C15A)

Properties	Values
Treatment	
- Organic Modifier* (surfactant)	2M2HT
- Modifier Concentration	125 meq/ 100 g clay
- Moisture	< 2%
- Weight Loss on Ignition	43%
Typical Dry Particle Sizes (by volume)	
- 10% less than	2 µm
- 50% less than	6 µm
- 90% less than	13 µm
Density	
- Loose Bulk	10.79 lbs/ft^3
- Packed Bulk	18.64 lbs/ft^3
X Ray Result	1.66 g/cm^3
- d_{001}	
	3.15 nm

* 2M2HT: dimethyl, dihydrogenated tallow, quaternary ammonium

D. Sample Preparation

Preparation of virgin PP film and nanocomposite films of PP/organically modified nanoclay with PP-g-MAH as compatibilizer

Extrusion is a convenient method for mixing polymer and filler together, with melt compound flowing through a die to form a final product. In this work, prior to extrusion, the clay powder was dried in a vacuum chamber oven at 80°C for 12 hours to remove moisture. Then the PP pellets were mixed together with the C15A clay powder with and without PP-g-MAH as per composition shown in **table-5.** Three PP master batches were prepared containing PP and Cloisite 15A (C15A) along with virgin PP master batch. The composition of each master batch containing C15A was in the range of 3%, 5%, and 7% by weight without using compatibilizer. Nanocomposites were prepared by melt mixing of the two components using Torque rheometer (Haake Rheomix OS, Germany) with counter rotating roller rotors having a chamber size of 66 cm^3. The screw speed was maintained at 80 rpm and the mixing time was 15 minutes for all the compositions. The barrel temperature profile was optimized from 175°C to 190^{o}C from feed to die zone. After compounding, the mixed material was extruded to produce cylindrical extrudes. The optimized composition of the master batch was further mixed with PP-g-MAH as compatibilizer. The mixture was extruded after passing through twin screw extruder to homogenize the mixture thoroughly to get the pellets. The prepared pellets were further processed and the extruder was equipped with a blowing head having an orifice of 14 mm in diameter. The other parameters of the process were the temperature of blowing head of 190^o C, the temperature of cooling air: 22±2^{o}C, its relative humidity: 48 ± 3%. The extruder screw rotation speed was varied up to 200 rpm; the take-up velocity was set to such a rate to maintain the longitudinal draw ratio of 8:1 in either case and to get similar film thickness. The blowing ratio was set to 3:1 or 6:1, respectively. The small irregular extruded were obtained and left to cool at room temperature.

Optimized master batch sample was further mixed with different wt. % of compatibilizer and the blown films were prepared in similar procedure. Further the mechanical properties were analyzed to find out the optimum composition of compatibilized PP nanocomposite film master batch. The optimized samples of desired thickness were used for property evaluation. The virgin PP was extruded under the same conditions for comparison of property with respect to nanocomposite film. Figure-4 illustrates schematic presentation of twin screw extruder process with blown film set up for preparation of nanocomposite film samples.

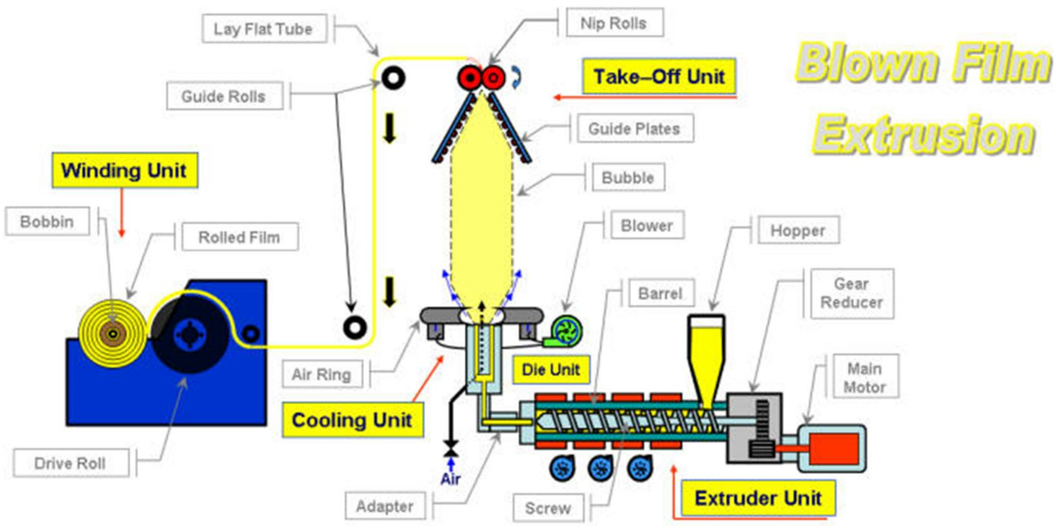


Figure-4: It shows schematic diagram of twin screw extruder process involved during compounding along with blown film set up for preparation of nanocomposite film

Table-5
Master batch compositions of developed PP/clay nanocomposite film films

Sample	Weight %		
	PP	PP-g-MAH	clay
Virgin PP	100	0	0
PP/clay	97	0	3
PP/clay	95	0	5
PP/clay	93	0	7
PP/ PP-g-MAH /clay	92	3	5
PP/ PP-g-MAH /clay	90	5	5
PP/ PP-g-MAH /clay	88	7	5

III. CHARACTERIZATION

A. Mechanical Properties

Tensile tests were carried out using UTM machine model 3382, USA, following ASTM-D 638 standard test method at 24˚C. The crosshead speed was 10 mm/min during tensile loading process. Prior to the testing, 07 nos. of samples were conditioned at 23 ± 2°C and 50 ± 5% relative humidity for 24 hours.

Testing was carried out in the tensile mode at 23°C at a speed of 50 mm/min using a load cell of 100 KN starting from a gauge length of 50mm. The Young's modulus of each specimen was determined using Instron strain gauge extensometer with a gauge length of 50 mm. Modulus, tensile yield strength, and percentage elongation at yield and at break was recorded. A minimum of four samples were evaluated for each batch. The gauge length was fixed at 50mm with a cross head of 5mm/min for conducting the test.

B. Differential Scanning Calorimetry (DSC)

DSC tests were carried out by a DSC Q2000 (TA Instruments- Waters LLC, New Castle, USA) under a constant nitrogen flow of 50 ml·min^{-1}. Two numbers of samples (one for virgin PP and another for the optimised nanocomposite film) were conditioned at 23 ± 2^{0}C and 50 ± 5% relative humidity for 24 hrs prior to test. Each sample of weight ~ 5-8 mg was heated up to 200°C at a rate of 10°C·min^{-1} and cooled to 0°C at a cooling rate of 10°C·min^{-1}. A second heating scan was then performed at 10°C min^{-1}. The melting enthalpy of 100% crystalline PE has been considered equal to ΔH_0 = 290 Jg^{-1} and that of PP is 310 Jg^{-1}. The crystallinity of nanocomposite film samples was estimated by taking the weight fraction of PE or PP in the composites into account. The melting temperatures Tm_1 and Tm_2 were recorded during the first and second heating scan, respectively. The crystallization enthalpy ΔH_c was measured by integrating the heat flow curve during the cooling scan. For measurement of non-isothermal crystallization kinetics, the samples were cooled at various cooling rates i.e. 5, 10, 15 and 20°C/min, respectively. The samples were initially melted at 200°C for 5 minutes in order to erase the previous thermal history. All measurements were carried out in nitrogen atmosphere from the temperature range -50°C to 200°C. The results were analyzed with different kinetic models. The evolution of crystallinity has been explained with the help of various mathematical models like Avrami, Ozawa and Mu.

IV. RESULT AND DISCUSSION

A. Mechanical Properties

PP and its nanocomposite films were prepared with variation of different weight % of clay and compatibilizer. **Table-6** depicts influence of different weight % of clay and compatibilizer content on the mechanical properties of PP. It is evident that there is an increase in tensile properties with a maximum, corresponding to the sample containing 5 weight % of clay. The tensile strength and modulus showed an improvement of 46.21 % and 70.09 % in comparison to virgin PP film with the decrease in elongation at break. It is further observed that tensile strength and modulus of PP nanocomposite film at 5 weight % clay loading was found to be 19.33 % and 24.38% higher in comparison to PP nanocomposite film with 3 weight % clay loading. The insertion of the polymer chains inside the silicate layers leads to an increase in the surface area of interaction between the clay and polymer matrix thereby leading to an increase in strength and modulus. The enhancement in the modulus of the nanocomposite film can also be ascribed to the resistance exerted by clay layers against plastic deformation of the polymer. In addition, the stretching resistance of polymer chains with an extended conformation in the gallery also contributed to the increase in modulus. At 5 weight % of clay loading, the sharp increase in tensile strength clearly indicates that there is an effective stress transfer exists from PP matrix to nanoscale clay platelets [17]. Further, it is revealed that the increment in strength and modulus is attributed to the reinforcing characteristics of dispersed nanolayers with high aspect ratio. Large number of nanoclay platelets present in the matrix acts as efficient stress transfer agent in the nanocomposites, including plastic deformation into the base polymer. It is expected that the macromolecules contacted to the clay layer would have different responses from those containing the matrix because of the mechanical displacement which is responsible for increase in modulus of the nanocomposite. Similar fact has been enumerated by Hidayat et al. [17] and Messersmith et al. [18]. However, there is a decline in both tensile and modulus with increase in clay loading to 7 weight %. Decrease in both, marked up to 65.51 % and 43.56 % in comparison to virgin PP film. This is possibly because of poor distribution of nanoparticles clusters present in the resulted hybrid and phase separation at higher clay loading. Further, at higher clay loading interaction between nanocomposite components is not thermodynamically favourable and therefore revealed decrease in tensile properties. Again the reason for reduction in elongation at break for the nanocomposite film is due to the presence of stacked silicate layers [19].

Table-6.
Effect of Organoclay and Compatibilizer loading on Mechanical properties of PP

Sample Type/composition	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
Virgin PP	19.134 ± 0. 1	501.674 ± 10	495.042 ± 4
PP/3wt.% clay	23.445 ± 2	470.145 ± 7	677.018 ± 5
PP/5wt.% clay	27.977 ± 3	336.583 ± 8	842.065 ± 9
PP/7wt.% clay	6.599 ± 0. 3	330.808 ± 9	279.356 ± 7
PP/PP-g-MAH/clay (92:3:5)	26.42 ± 2	330.80 ± 6	810.69 ±9
PP/PP-g-MAH/clay (90:5:5)	32.38 ± 3	382.31 ±8	1135.64 ±10
PP/PP-g-MAH/clay (88:7:5)	24.21 ± 2	328.42 ±7	780.91 ± 7

To increase the compatibility between the non-polar matrix polymer and the polar nanoclay, PP-g-MAH is used as compatibilizer at different weight % (3, 5, 7) with nanocomposites containing 5 weight % organically modified nanoclay. It is observed from figure-5 that the PP nanocomposite film prepared with 5 weight % of PP-g-MAH compatibilizer display enhanced tensile strength and modulus in comparison with virgin PP and PP nanocomposite film at 5 weight % of clay loading. At 5 weight % of PP-g-MAH compatibilizer, the tensile strength and modulus found to be higher by 13.93 % and 3.10 % respectively in comparison with PP nanocomposite film at 3 weight % compatibilizer loading [20]. This behaviour is probably due to the fact that incorporation of compatibilizer enhances adhesion of clay platelets with the PP matrix and conformational effects on the polymer at the polymer-clay interface, which enhances stress transfer from clay platelets to the matrix [21]. Addition of PP-g-MAH facilitates expansion of the gallery space of reinforcing nanolayers by inclusion of some polar groups (MAH) to intercalate between the silicate layers through hydrogen bonding to the oxygen groups of silicate tetrahedral. The miscibility of the maleated PP with polar groups of the nanoparticles and PP matrix mediate between the surface chemistry of the polymer and the nanoclay at the interface thus contributing to significant improvement in the mechanical performance [22]. This also results in enhancement of interlayer distance of stacked nanolayers, which in turn reduces interfacial energy of both phases, thereby increasing the strength of nanocomposite film. The miscibility of the compatibilizer with nanoclay and the PP matrix mediate the surface chemistry of the polymer, which contribute significantly towards increment in the strength. However, further increase in PP-g-MAH concentration from 5 to 7 wt. %, deterioration in mechanical properties was observed. The reason might me that PP-g-MAH has a lower molecular weight as compared to PP which seems to be responsible for plasticizing effect and causes self-entanglement among the compatibilizer chains rather than with PP. It is interesting to note that incorporation of 5 weight % of compatibilizer with 5 weight % of clay loading is sufficient for making interfacial saturation for nanocomposite film and to obtain optimized properties [23].

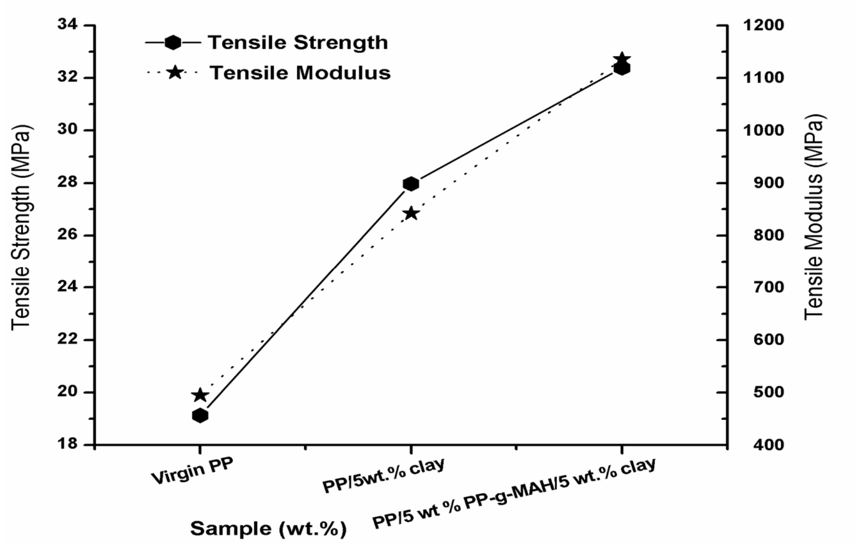


Figure-5: Tensile strength and modulus of virgin PP and PP nanocomposite film.

B. *Thermal Properties*

1) *Crystallization and Melting Behavior:* The crystallization temperature (T_c) of virgin PP film is 123^{o}C .The T_c of PP increases with the addition of compatibilizer and clay particles (Table-7). This increase in crystallization temperature indicates nucleating effect of the nanoclay of PP [24-25] .The extent of increase in T_c is varied slightly with the type of the filler. The order of magnitude of Tc in the different nanocomposite film system with variation of filler type is C15A clay > PP. It is observed that the degree of crystallinity increases from 30 % in virgin PP to 51 % in case of PP/PP-g-MAH/organoclay nanocomposite film. This increase in degree of crystallinity is mainly due to the dispersion of nanoclay platelets within the matrix which promotes heterogeneous nucleation resulting in an increase in the crystallization rate and crystallinity [25-30]. Presence of PP-g-MAH as compatibilizer has also a significant contribution towards the nucleation process, increasing the crystallinity of the polymer matrix. The difference in the degree of crystallinity arises due to the interfacial interaction between the filler and matrix, which plays an important role in the free energy of closure formation and the rate of nucleation. Weak interaction lowers the rate of nucleation, thereby leading to decrease in degree of crystallinity [31-33]. Non-isothermal crystallization kinetic of different nanocomposite films has been studied.

It is evident that there is a distinct exothermic crystallization peak in all the cooling scans. The crystallization temperature (T_c) of virgin PP was noticed at 123.42°C.Incorporation of organically modified nanoclay, results in increasing the T_c of the virgin matrix, thus indicating nucleation effect of the nanoclay. PP/clay nanocomposite film exhibits optimum T_c (125.07°C), which is probably due to the greater interaction of C15A clay with PP matrix. Further, the half-life time ($t_{½}$) of the PP matrix also decreases with the addition of nanoclay[. Hence, briefly summarizing, as evident from the test results reported in different chapters, PP/PP-g-MAH/clay (90:5:5) nanocomposite film exhibits a higher (125.07°C) $T_{c,}$ and a smaller ΔT_c than those of virgin PP, thereby demonstrating the fact that the nanoclay effectively acts as nucleating agent. These results further confirm that the crystallization of PP may be accelerated by means of blending with nanoclay [34-35].

Table-7

Crystallization behavior of PP and its nanocomposite films

Sample	Φ (°C/min)	Tc (°C)	T_p (°C)	ΔT (°C)	$t_{1/2}$ (min)
Virgin PP	20	119.38	111.9	7.48	0.42
PP/PP-g-MAH/clay(90:5:5)	20	121.26	114.23	7.03	0.382

Also from the table-8, it can be seen that the crystallization peak temperature (T_p) and the initial crystallization temperature for PP/clay, nanocomposite film systems are higher than those of virgin counterparts at the same cooling rate, thus indicating that the presence of the filler makes the crystallization process in the nanocomposite film easier compared with the virgin PP Further, $t_{1/2}$ (min) of the nanocomposite film are smaller than those of virgin PP, thereby indicating the introduction of nanoclay accelerate the crystallization of the respective polymer matrix in the nanocomposite film. This further confirms that the nanoscale layers of organoclay dispersed in the nanocomposite films act as nucleating agent [34-35].

Table-8

Parameters of non-isothermal crystallization of PP and its nanocomposite films

Sample	Cooling rate (°C/min)	T_c (°C)	T_p (°C)	ΔT (°C)	$t_{1/2}$ (min)
PP	5	128.21	122.94	5.27	1.018
	10	123.42	117.32	6.1	0.646
	15	121.16	115.15	6.01	0.478
	20	119.38	111.9	7.48	0.42
PP/PP-g-MAH/clay(90:5:5)	5	128.91	124.69	4.22	0.857
	10	125.07	120.4	4.67	0.449
	15	123.1	117.81	5.29	0.397
	20	121.26	114.23	7.03	0.388

2) *Non-isothermal cold Crystallization Behaviour:* The crystallization of isotropic polymers by heating above the Tg is referred as cold-crystallization. Unlike melt crystallization, in which the haphazard motion of polymer chains can be carried out exclusively through molecular repetitions, the polymer chain in the rubbery state complete the consequent conformational arrangements via supportive segmental movements. In view of this the crystal structure and morphology obtained from cold-crystallization may be predicted to be different from that obtained from melt-crystallization. Further, it is evident that the molecular motion of semi-crystalline polymers above Tg involves discrete interaction between amorphous and crystalline regions. The formation and its developments in crystalline regions certainly limit the random motion of the polymer chains in the amorphous regions. This is normally happen when low heating rate is used. PP manifests slow crystallization on cooling from the melt. However on subsequent heating after rapid cooling from the melt, the cold-crystallization phenomenon occurs [36]. The effects of clay on the crystallization behaviour of PP were quantitatively analyzed through non-isothermal DSC experiments. The crystallization thermograms of PP and PP/ PP-g-MAH/clay (90:5:5) nanocomposite film at a selected cooling rate of 10ºC/min is presented in figure-6. From these curves, some important parameters, such as the crystallization onset temperature (T_c) and crystallization peak temperature (T_p) and crystallization enthalpy (ΔH_c) of PP and PP/PP-g-MAH/clay(90:5:5) nanocomposite film have been determined. The results are summarized in table-8. For the same cooling rate the crystallization peak temperature, Tp of nanocomposites at a given organoclay C15A clay loading is higher than that of the virgin polymer and irrespective of cooling rate. Hence it is evident that the crystallization temperature of the virgin polymer increases with the incorporation of C15A clay. This increase in crystallization temperature indicates heterogeneous nucleating of PP initiated by the nanoclays which alters the crystallization process during cooling from a temperature above the melting point of virgin PP [37-38]. Nucleation occurs because the solid surface of clay particles and other impurities within the polymer act as nuclei on which PP chains can easily be absorbed. This leads to more rapid crystallization at higher temperatures. Many studies have shown nucleating effect of nanoclays for different polymers [38]. A nucleating agent has a surface charge opposite to partial charge of the chemical moiety of the base polymer. When semi-crystalline polymers crystallize from the melt, typically during the cooling phase of a process; the lamellae organize from a primary nucleus to form a complex macro-structure called spherulites. In nucleated polypropylene crystallization occurs earlier in the cooling process and happens at a faster rate [38].

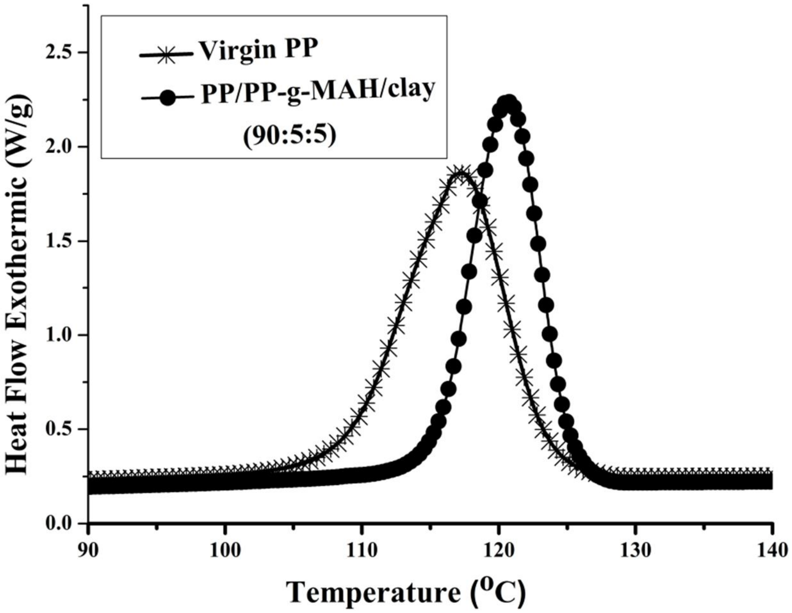


Figure- 6: DSC melting thermograms of virgin PP and PP/ PP-g-MAH/clay (90:5:5) nanocomposite film recorded under the exothermic condition at indicated heating rate after rapid cooling at 10°C/min.

Many studies on semi-crystalline polymer-clay nanocomposites describe that the nano-sized clay particles affect the crystallization behaviour and the crystal structure of the polymer matrix. It proves that nanoparticles of clay dispersed in polymer matrix acted as nucleating agent. Nucleating agent promote the crystallization of semi crystalline materials by creating numerous nucleating sites for the spherulites to form and grow [39]. The melting point of nucleating agent is higher than the melting point of matrix polymer because it has form nuclei (tiny particles) in order to be able to nucleate crystallization of polymer (which begins to form lamellae on the surface of nucleus formed by the nucleating agent). For the thermodynamic and kinetic control of the crystallization process (nucleation and growth of crystallizable polymers, nucleating agent are used in a combined form with a cooling gradient imposed to the polymer during its final processing stage, according to the desired crystalline morphology and degree of crystallinity) .This effect can be used to enhance the mechanical and thermal properties of the polymer. The degree of crystallinity (X_c) calculated from the melting curve by using the following equation

$$X_c=\frac{\Delta \mathrm{Hm}}{\Delta \mathrm{Hm}(1-\varnothing)}X100\% \qquad \text{-------------------------- (1)}$$

Where ΔH_m and ΔH are the heat of fusion of nanocomposite film and PP film with 100% crystallinity. According to literature, $\Delta H_m$of 100 % crystalline PP is estimated to be 240J/g. PP/clay nanocomposite film has higher X_c than virgin PP [11]. It is observed that the degree of crystallinity increases with from 29.5 % in virgin PP to 51 % in case of PP/PP-g-MAH/clay (90:5:5) nanocomposite film. This increase in crystallinity is mainly due to the dispersion of nanoclay platelets within the matrix which promotes heterogeneous nucleation resulting in an increase in the crystallization rate and crystallinity. Presence of PP-g-MAH as compatibilizer has also a significant contribution towards the nucleation process increasing the crystallinity of the matrix polymer. Similar observation, reported by researchers [39-40].It indicates a significant increase in crystallinity with the addition of nanoclay and compatibilizer irrespective of the processing condition.

Further, crystallization thermograms of virgin PP and PP/ PP-g-MAH/clay (90:5:5) nanocomposite film at different cooling rates (5^oc/min, 10^oc/min, 15^oc/min and 20^oc/min) are represented in **figure- 7 and 8.** It is observed that the exothermic trace become wider and the peak temperature (T_p) shifted to lower temperature when the cooling rate is increased. It has been observed that increasing the cooling rate during the crystallization process can decrease crystallinity effectively freezing the polymer microstructure in place before the polymer chain can be completely organized [40-41].

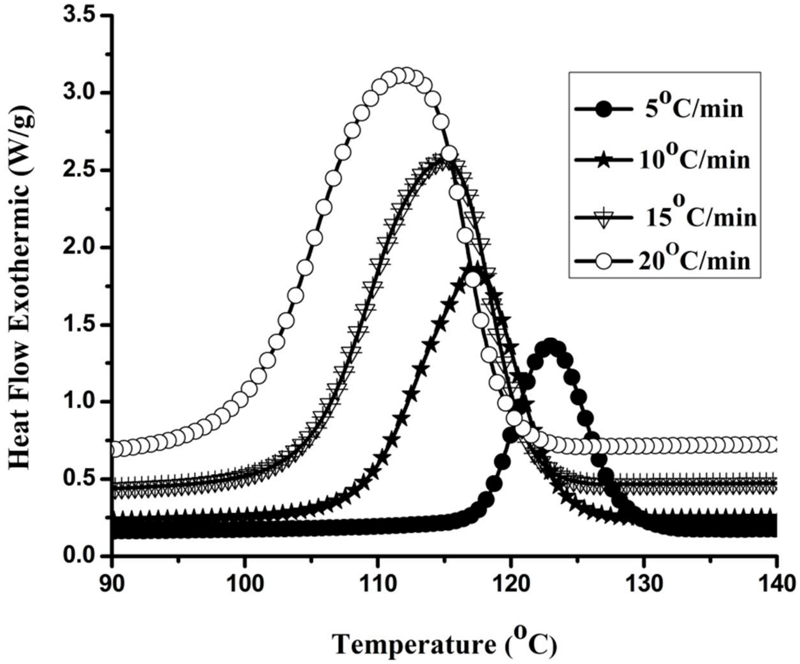


Figure-7: DSC thermograms of virgin PP recorded during non-isothermal crystallization at different cooling rates.

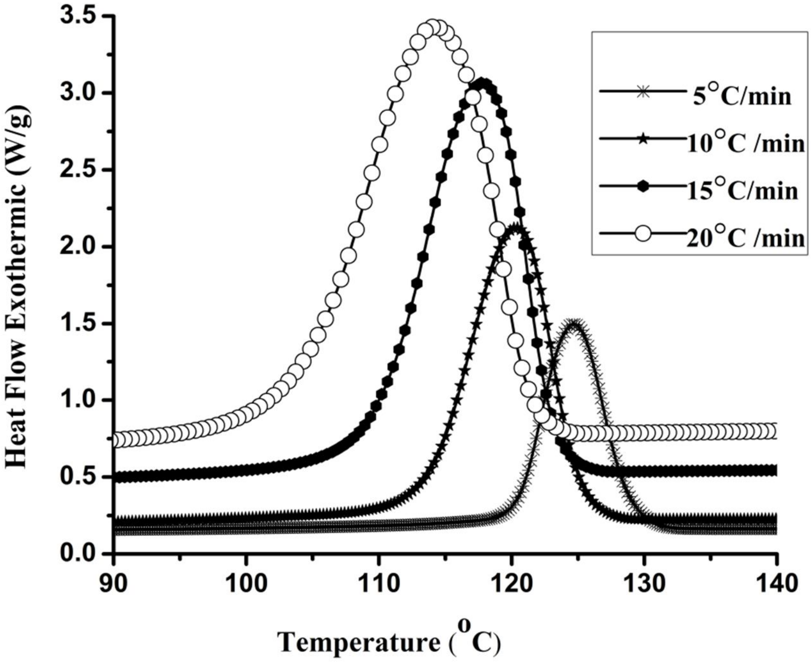


Figure-8 : DSC thermograms PP/PP-g-MAH/clay (90:5:5) nanocomposite film recorded during non-isothermal crystallization at different cooling rates.

Figure-9 shows the relationship between crystallization peak temperature (T_p) and the cooling rate for virgin PP and PP/ PP-g-MAH/clay (90:5:5) nanocomposite film. It is also seen that T_p decrease with increasing cooling rate. For example, T_p of virgin PP decreases about 11ºC, when cooling rate increases from 5 to 20ºC/min. Similarly T_p decreases about 10°C for the PP/PP-g-MAH/clay (90:5:5) nanocomposite film. When the cooling rate is low, polymer molecular chains get sufficient time to cross the nucleation energy barrier as a result of which the crystallization takes at higher temperature, raising the value of T_p. But when the cooling rate is increased polymers crystallize readily under super cooling temperature, as the molecular chains cannot enter into the crystal grains [42].

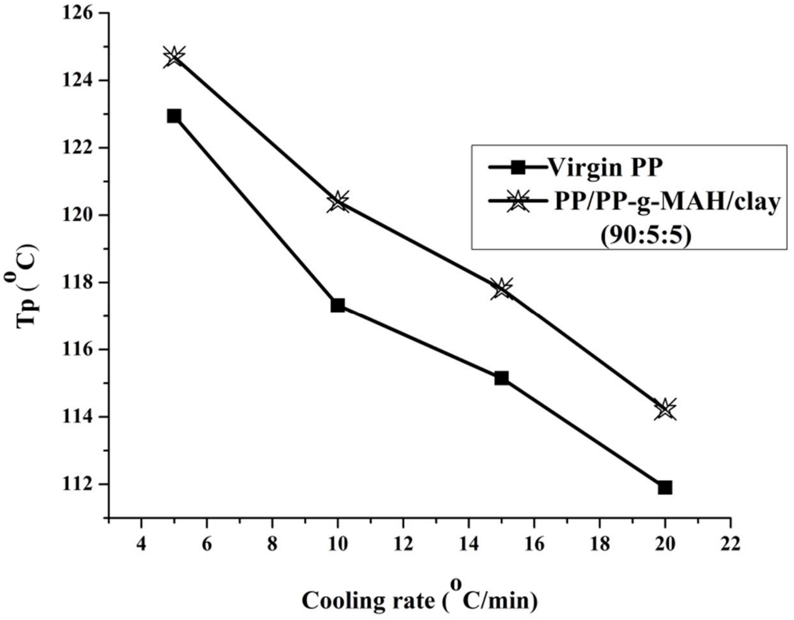


Figure - 9: Relationship between crystallization peak temperature (T_p) and the cooling rate for virgin PP and PP/ PP-g-MAH/clay (90:5:5) nanocomposite film

Under the same cooling rate, the T_p of PP/PP-g-MAH/clay (90:5:5) nanocomposite film is higher than that of virgin PP. Similar results have been reported earlier[228,22941-42].For example, at the cooling rate of 10ºC/min, crystallization peak temperature for virgin PP is 117ºC, while for PP/PP-g-MAH/clay (90:5:5) nanocomposite film, the value is 120.5ºC. This means that the nanoclays are the effective nucleating agent and reduces the degree of super cooling which is required for making crystallization. It facilitates and accelerates the crystallization process and also decreases the steric effect of exfoliated clay layers, which opposes polymer chain movements and retards the crystal growth during crystallization period. Aggregates of clay and other impurities can serve as nuclei on which the PP molecular chain can be easily absorbed which leads to quicker crystallization at higher temperature. Similar trend has been observed in the earlier report [38].This can also be attributed to the heterogeneous nucleation of clay particles on the polymer chain segments. It is reported that, the value of ΔH_c is decreased in the presence of clay particles in the nanocomposite. It is because, the clay (foreign body) destroys the integrity of PP matrix and decreases their activity and consequently leads to fewer crystallites in the nanocomposite film [38-39].

V. CONCLUSION AND FUTURE OUTLOOK

The pace of revolutionary discoveries now in nanotechnology is expected to accelerate in the next decades worldwide. Polymer nanocomposites can do much more than virgin polymers by enhancing mechanical, thermal and many other properties for various end user applications. Novel polymer-clay nanocomposites can be prepared by varying two parameters: one by optimizing polymer to clay ratio and second by varying the processing methods with optimum measurement conditions. An exploration in making the polymer-clay nanocomposites with different clay content, surfactants, compatibilizers and polymers is a ongoing subject of research and interest to both academicians and industry.

REFERENCES

[1] J. K. Lee and C.D. Han, "Evolution of polymer blend morphology during compounding in a twin-screw extruder," Polymer, vol. 41, pp.1799-1815, May. 2000, doi: 10.1016/S0032-3861(99)00325-0.

[2] A. Kaushaland and V. Singh, "Electromagnetic interference shielding response of multiwall carbon nanotube/polypropylene nanocomposites prepared via melt processing technique," Polymer Composites, vol. 42, pp. 1148-1154, March, 2021.doi:**10.1002/pc.25889**.

[3] W.R. Córdova, J. Daniel, M. María, P. Jorge and G. M. Johann, "Effects of additives of organically modified montmorillonite and Octosilicate in a silica reinforced tire tread mixture." Applied Clay Science, vol. 200, (2021): pp. 105938, Jan,2021,doi:10.1016/j.clay.2020.105938

[4] S. Fan, X. Gao , D. Zhu and S. Guo,” Enhancement mechanism of the organic nano-montmorillonite and its effect on the properties of wood fiber/HDPE composite”, Industrial Crops and Products, vol.169, pp. 113634, Oct. 2021, doi:10.1016/j.indcrop.2021.113634

[5] L.J. Tan, Z. Wei and Z. Kun, “Development of organically modified montmorillonite/polypropylene composite powders for selective laser sintering," Powder Technology, vol. 369, pp. 25-37, Jun. 2020, doi: 10.1016/j.powtec.2020.05.005

[6] W.P. Zheng, Y. P. Ma, D. L. Du, A.H. He, H.F. Shao and C.G. Liu, "Polymerization Kinetics of Propylene with the MgCl 2-Supported Ziegler-Natta Catalysts—Active Centers with Different Tacticity and Fragmentation of the Catalyst," Chinese Journal of Polymer Science, vol. 39, pp. 70-80, Jan. 2021, doi: 10.1007/s10118-020-2473-z.

[7] Zhang G, Wu T, Lin W, Tan Y, Chen R, Huang Z, Yin X, Qu J. Preparation of polymer/clay nanocomposites via melt intercalation under continuous elongation flow. Composites Science and Technology. 2017 Jun 16; 145:157-64.

[8] S. Dixit, M. Gaurav and V.L. Yadav, "Optimization of novel bio-composite packaging film based on alkali-treated Hemp fiber/polyethylene/polypropylene using response surface methodology approach," Polymer Bulletin, pp. 1-25, Mar. 2021, doi: 10.1007/s00289-021-03646-5.

[9] G.Zhang ,T. Wu ,W. Lin ,Y. Tan ,R. Chen,Z. Huang ,X. Yin and J. Qu, “Preparation of polymer/clay nanocomposites via melt intercalation under continuous elongation flow,”. Composites Science and Technology, vol.145, pp. 157-64, Jun. 2017, doi: 10.1016/j.compscitech.2017.04.005.

[10] K. Zdiri, A. Elamri and M. Hamdaoui,”Advances in thermal and mechanical behaviors of PP/clay nanocomposites,” Polymer-plastics technology and engineering, vol. 24, pp. 824-40, May, 2017,doi :10.1080/03602559.2016.1233282.

[11] G.Liu , A.J. Müller and D,WangD,”Confined Crystallization of Polymers within Nanopores,”. Accounts of Chemical Research, pp. 181-184, Jul.2021,10.1021/acs.accounts.1c00242.

[12] W. Liu , L.Cheng ,X. Liu ,C. Liu ,X. Chi ,S. Li ,” Correlation between morphology and electrical breakdown strength of the polypropylene/maleic anhydride grafted polypropylene/nano-ZrO2 ternary system,” Journal of Applied Polymer Science, vol. 135, pp.46842, Nov. 2018,doi:**10.1002/app.46842**.

[13] C.A.Chatham,C.E. Zawaski ,D.C. Bobbitt ,R.B. Moore, T.E. Long ,C.B. Williams,”Semi-Crystalline Polymer Blends for Material Extrusion Additive Manufacturing Printability: A Case Study with Poly (ethylene terephthalate) and Polypropylene,” Macromolecular Materials and Engineering,Vol.304,pp.1800764,May.2019,doi:**10.1002/mame.201800764**

[14] J. Liu and H. Liang,” Heterogeneous nucleation and self-nucleation of isotactic polypropylene with addition of nano-ZnO,”Journal of Thermal Analysis and Calorimetry,pp. 1-2Jan.2021,doi:. 2021 doi: 10.1007/s10973-020-10446-y.

[15] D.G. Dikobe and A.S. Luyt, “Thermal and mechanical properties of PP/HDPE/wood powder and MAPP/HDPE/wood powder polymer blend composites,”.ThermochimicaActa, vol.654, pp. 40-50, Aug. 2017, doi:10.1016/j.tca.2017.05.002.

[16] R.V.de Camargo and C. Saron,”Mechanical–chemical recycling of low-density polyethylene waste with polypropylene,”Journal of Polymers and the Environment, vol.28,pp.794-802,Mar.2020,doi:10.1007/s10924-019-01642-5

[17] D. Stoofand K. Pickering,”Sustainable composite fused deposition modelling filament using recycled pre-consumer polypropylene,”Composites Part B:Engineering,vol.135, pp.110-118,Feb.2018 doi:10.1016/j.compositesb.2017.10.005

[18] A.T. Hidayat, H. Benten ,N. Ohta ,Y. Na ,A. Muraoka ,H. Kojima, M.C. Jung and M. Nakamura, “Enhancement of Short-Range Ordering of Low-Bandgap Donor–Acceptor Conjugated Polymer in Polymer/Polymer Blend Films. Macromolecules,” vol.53, pp. 6630-6639, Jul, 2020, doi: 10.1021/acs.macromol.0c00623.

[19] S. Pak, S. Park, Y.S. Song and D. Lee, “Micromechanical and dynamic mechanical analyses for characterizing improved interfacial strength of maleic anhydride compatibilized basalt fiber/polypropylene composites,”. Composite Structures, vol.193, pp.73-79, Jun.2018, doi: 10.1016/j.compstruct.2018.03.020.

[20] K.Zdiri, A. Elamri, M. Hamdaoui, N. Khenoussi, O. Harzallah and J. Brendle, “Impact of Tunisian clay nanofillers on structure and properties of post-consumer polypropylene-based nanocomposites,” Journal of Thermoplastic Composite Materials, vol.32, pp.1159-75, Sept.2019, doi:10.1177/0892705718792377.

[21] K. Zdiri, A. Elamri, and M. Hamdaoui. "Advances in thermal and mechanical behaviors of PP/clay nanocomposites." Polymer-plastics technology and engineering,vol. 56,pp. 824-840, May.2017, doi:10.1080/03602559.2016.1233282

[22] Y. Zare, M. Fasihi and K.Y. Rhee, "Efficiency of stress transfer between polymer matrix and nanoplatelets in clay/polymer nanocomposites," Applied Clay Science, vol. 143, pp. 265-272, Jul.2017, doi:10.1016/j.clay.2017.03.043.

[23] Y.Zare, and K. Y. Rhee, "Effects of critical interfacial shear strength between polymer and nanoclay on the Pukanszky's “B” interphase factor and tensile strength of polymer nanocomposites," Mechanics of Materials, vol. 149, pp. 103562, Oct. 2020, doi:10.1016/j.mechmat.2020.103562.

[24] P. Saha, T. Debnath, S. Das, S. Chatterjee and S. Sutradhar, "β-Phase improved Mn-Zn-Cu-ferrite-PVDF nanocomposite film: a metamaterial for enhanced microwave absorption." Materials Science and Engineering: B,vol. 245,pp.17-29, Jun.2017,doi:10.1016/j.mseb.2019.05.006.

[25] J. Bandyopadhyay, S. S. Ray, V. Ojijo, and M. Khoza, "Development of a highly nucleated and dimensionally stable isotactic polypropylene/nanoclay composite using reactive blending," Polymer, vol. 117, pp. 37-47, May.2017, doi:10.1016/j.polymer.2017.04.013.

[26] B. Kord, P. Ravanfar and N. Ayrilmis, "Influence of organically modified nanoclay on thermal and combustion properties of bagasse reinforced HDPE nanocomposites," Journal of Polymers and the Environment, vol.25, pp. 1198-1207, Dec.2017, doi:10.1007/s10924-016-0897-x.

[27] B. Wang, R.Utzeri, M.Castellano, P.Stagnaro, A.J. Müller, and Dario Cavallo. "Heterogeneous Nucleation and Self-Nucleation of Isotactic Polypropylene Microdroplets in Immiscible Blends: From Nucleation to Growth-Dominated Crystallization." Macromolecules, vol. 53, pp.5980-5991, Jul.2020, doi: /doi.org/10.1021/acs.macromol.0c01167.

[28] J. Liu and H. Liang, "Heterogeneous nucleation and self-nucleation of isotactic polypropylene with addition of nano-ZnO," Journal of Thermal Analysis and Calorimetry, pp. 1-12, Jan. 2021doi:10.1007/s10973-020-10446-y.

[29] S.A. Boyer, J.M. Haudin, V. Song, V.Bourassier, P. Navard, and C. Barron. "Transcrystallinity in maize tissues/polypropylene composites: First focus of the heterogeneous nucleation and growth stages versus tissue type." Polymer Crystallization vol.4, pp.e10155, Feb.2021, doi: 10.1002/pcr2.10155.

[30] Y.Wang, G. He, Y. Shao, D. Zhang, X. Ruan, W. Xiao, X. Li, X. Wu, and X. Jiang, "Enhanced performance of superhydrophobic polypropylene membrane with modified antifouling surface for high salinity water treatment." Separation and Purification Technology, vol. 214, pp. 11-20 May.2019, doi:10.1016/j.seppur.2018.02.011.

[31] H. M. Shaikh,"Thermal, rheological, and mechanical properties of polypropylene/phosphate ore composites, "Construction and Building Materials, vol.263, pp.120151, Dec.2020, doi: 10.1016/j.conbuildmat.2020.120151.

[32] B. Liu, T. Jiang, X. Zeng, R. Deng, J. Gu, W. Gong, and L. He, "Polypropylene/thermoplastic polyester elastomer blend: Crystallization properties, rheological behavior, and foaming performance," Polymers for Advanced Technologies, vol. 32, pp.2102-2117, May.2021, doi: 10.1002/pat.5240.

[33] Y. Qiao, A. Jalali, J. Yang, Y. Chen, S. Wang, Y. Jiang, J. Hou, J. Jiang, Q. Li and C. B. Park, "Non-isothermal crystallization kinetics of polypropylene/polytetrafluoroethylene fibrillated composites," Journal of Materials Science, vol. 56, pp.3562-3575, Feb. 2021, doi:10.1007/s10853-020-05328-5.

[34] Y. Yan, R. Zhang, Q. Liang, J. Liu and Y. Han, "Control the interplay of crystallization and phase separation of conjugated polymer blends by the relative rate of nucleation and growth," Polymer, vol.182.pp. 121827, Nov.2019, doi: 121827.10.1016/j.polymer.2019.121827.

[35] X. Wen, Y. Su, Y. Shui, W. Zhao, A.J. Müller and D. Wang, "Correlation between grafting density and confined crystallization behavior of poly (ethylene glycol) grafted to silica," Macromolecules, vol. 52, pp. 1505-1516 Feb.2019, doi:.10.1021/acs.macromol.8b02007.

[36] M.Y. Ong and W. S. Chow, "Kinetics of crystallization for polypropylene/polyethylene/halloysite nanotube nanocomposites," Journal of Thermoplastic Composite Materials, vol. 33, pp.451-463, Apr. 2020 , doi:10.1177/0892705718807953.

[37] M. Nofar, "Synergistic effects of chain extender and nanoclay on the crystallization behaviour of polylactide," Int. J. Mater. Sci. Res, vol.1, pp.1-8, Apr.2018, doi: 10.18689/ijmsr-1000101.

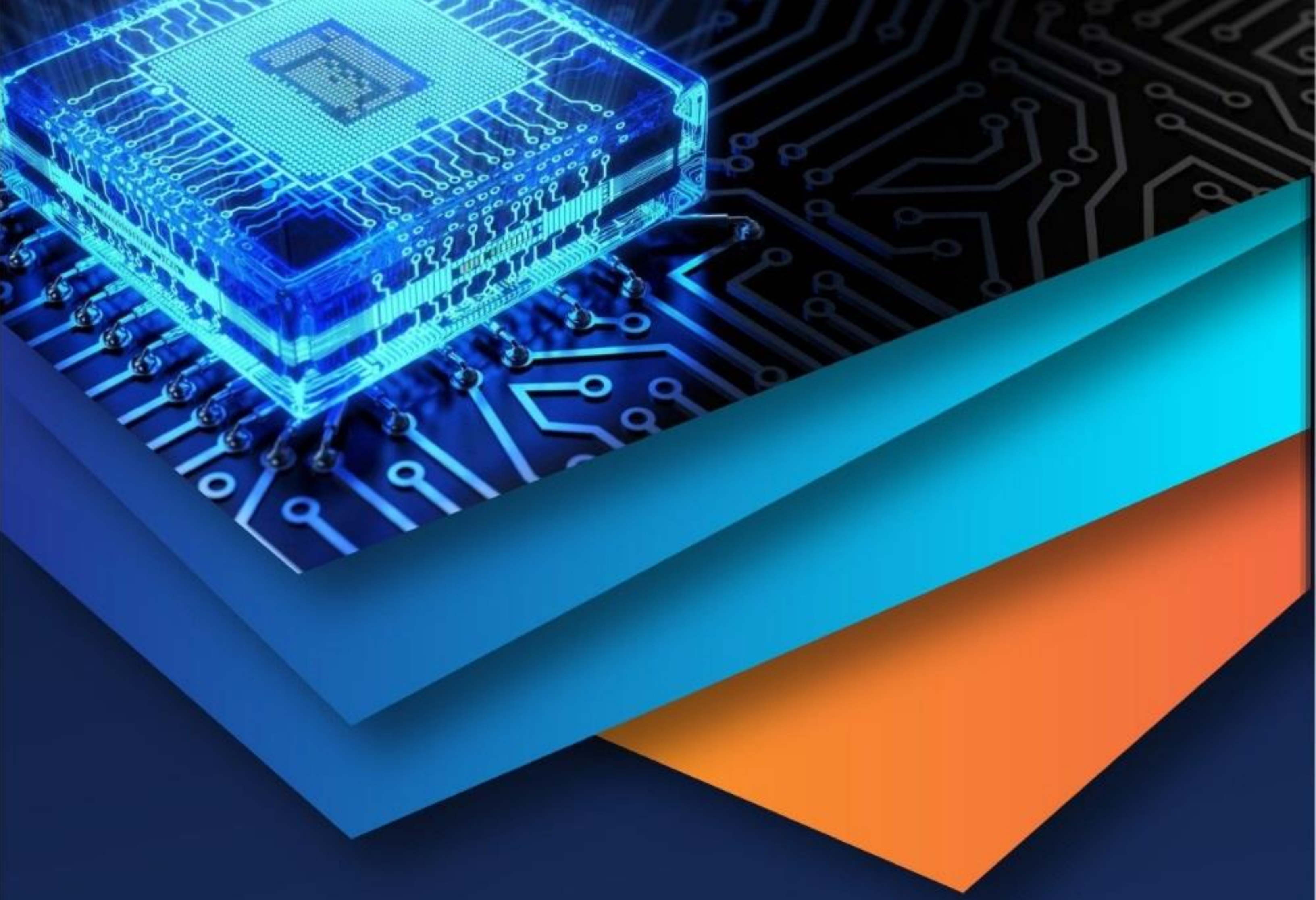
[38] F. Hemmati, O.Y. Farkhondeh, and H. Garmabi, "Compatibilized low-density polyethylene/linear low-density polyethylene/nanoclay nanocomposites: II. Opposing effects of nanofiller on quiescent and shear-induced crystallization," Advances in Polymer Technology, vol. 37, pp. 1345-1355, Sept. 2018, doi: 10.1002/adv.21793.

[39] B.D. Zhu, J.Y. Zhang, C.H. Lin, H.L. Chen, and J. Wang, "Nonisothermal crystallization kinetics of ethylene vinyl alcohol copolymer with poly (oxypropylene) diamine intercalated montmorrilonite," Journal of Macromolecular Science, Part B , vol.57, pp. 333-347,May.2018, doi:10.1080/00222348.2018.1460971.

[40] T.G. Mofokeng, S. S. Ray and V. Ojijo, "Influence of selectively localized nanoclay particles on non-isothermal crystallization and degradation behaviour of PP/LDPE blend composites, " Polymers, vol. 10, pp.245- 2018, doi: 10.3390/polym10030245.

[41] J. Li, Z. Jiang and Z. Qiu, "Isothermal melt crystallization kinetics study of cellulose nanocrystals nucleated biodegradable Poly (ethylene succinate)," Polymer, vol., pp.123869, Mar. 2021, doi:10.1016/j.polymer.2021.123869.

[42] Y. Fan, J. J. Lou, J. Jamali, Y. C. Lu and J. T. Wood, "Effect of clay dispersion on the nonisothermal and isothermal crystallization behaviors of polyethylene composites," Polymer-Plastics Technology and Engineering, vol. 56, pp. 1646-1656,Oct.2017, doi:10.1080/03602559.2017.1289393.



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