

Extrusion and Properties of Nanoclay Added Composite Polypropylene Monofilaments

by

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Abstract

This study focuses on combining traditional polymeric materials with nanoclays to engineer new composite monofilaments for nontraditional industries using extrusion process. Polypropylene/nanoclay composite monofilaments were produced using single and twin screw extruders, and the structure and properties of the new monofilaments were characterized using scanning electron microscopy (SEM), X-Ray diffraction (XRD), Fourier transform infrared spectrometry (FTIR), thermal gravimetric analyzer (TGA), differential scanning calorimeter (DSC), and Instron universal testing machine. Composite monofilaments were prepared at different weight percentage (1, 2, and 3%) of nanoclay (Cloisite 15A) and different amount of compatibilizer (10, 15, and 20%) contents with single screw extruder. Twin screw extruder was used to produce composite monofilaments with different weight percentage (0.5, 1, and 1.5 %) and types of nanoclay (Cloisite 15A and 30B). The results showed that the amount of nanoclay and compatibilizer affect the formation and final properties of the new monofilaments. It was observed that tensile strength of composite monofilament decreased compared to pure polypropylene monofilaments. Melting temperature and degree of crystallinity were not affected much; however, there was significant increase in decomposition temperature of composite polypropylene monofilaments.

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CHAPTER 1

INTRODUCTION AND BACKGROUND

Polymer-layered silicate (PLS) nanocomposites have been investigated by academic and industrial researches in recent years because the final composites often provide a desired enhancement of mechanical, molecular barrier, thermal, flame retardant, corrosion protection properties and/or other properties relative to the original polymer matrix, even at very low clay contents [1-8]. Nanoparticles may dominate the behavior of materials because of their sizes, nanoscale dimensions, and relatively huge surface areas per unit weight. Carbon nanotubes, montmorillonite type clays and biomolecules such as protein and DNA are used in many nanostructures [3, 9].

Polymeric properties can be improved even at low loading without negative effects on density, transparency and processability. Basically, nanoparticles are dispersed in a polymer matrix at low amounts, most of the time less than 6% by weight [10]. The conditions for successful reinforcement and good properties are the homogeneous distribution and dispersion of the reinforcing components, high aspect ratio of the nanolevel fillers, and good adhesion between polymer matrix and fillers [11]. Many thermoplastic and thermosetting polymers with different polarities including polystyrene, polycaprolactone, polypropylene, poly(ethylene oxide), epoxy resin, polysiloxane and polyurethane can be used to form nanocomposite structures. The first commercial product of clay-based polymer nanocomposites was the timing belt cover made from

PA6 nanocomposites by Toyota Motors in the early 1990s. This timing-belt cover exhibited good rigidity, excellent thermal stability and no wrap. It also saved weight by up to 25% [3].

Twin and single screw extrusion machines are mainly used for filament and film manufacturing. Nanocomposite structures can be produced by extrusion machines because of their good mixing characteristic and processing efficiency compared to other methods. The features of the extruder and screw configuration are important to obtain good dispersion. Better dispersion may be achieved with longer residence times in the extruder [12]. In some cases, having a higher melt viscosity is useful in obtaining dispersion, because of the higher stresses that can be enforced on the nanoparticles [8]. Other parameters such as barrel and die temperatures, draw-down ratio, and heater temperature can be adjusted for better dispersion. Correct settings of these parameters can change the reinforcing effect, agglomeration of particles, and synergistic effect of nanoparticles.

Polypropylene/nanoclay nanocomposites are being investigated in recent years. Polypropylene and nanoclays have advantages to be used in forming of nanocomposite structures. Nanoclays have high aspect ratios and plate morphology. Their low cost and environmental friendly characteristics make them very attractive. On the other hand, polypropylene is one of the most widely used polyolefin because of the low cost, low density, high thermal stability and easy processibility. For example, Sharma and Nayak [1] obtained 95% enhancement in tensile strength and 152% in tensile modulus of clay modified polypropylene. Shariatpanahi et al. [13] observed improvement in tensile modulus and impact strength by 15 and 22%, respectively, with the addition of montmorillonite clay into polypropylene matrix via direct melt mixing method. Baniasadi et al. [14] reported improvement of thermomechanical properties of nanocomposites by introducing small amount of clay into polymer matrix. Zhang et al. [15]

successfully prepared polypropylene (PP)/organomontmorillonite (OMMT) nanocomposites via melt intercalation by using conventional twin screw extrusion technique, and dispersed organoclay layers were observed in the PP resin at the nanometer level. Wenyi et al. [16] investigated the dispersion of organo-montmorillonite (Org-MMT) in polypropylene matrix and observed an increase in melting and crystallinity point of the nanocomposites. Joshi et al. [17] characterized monofilaments which contain polypropylene/clay, and obtained improved tensile strength, modulus, thermal stability, and reduced elongation at break. Horrocks et al [18] successfully produced polypropylene filaments that contained Cloisite 20A nanoclay, and observed that filament modulus was increased to some degree. In addition, Kumar et al. [4] added small carbon fibers to the nanoclay filled PA66/PP and extruded them in order to improve mechanical properties.

1. Nanocomposite Structures

A nanocomposite can be defined as a particle-filled polymer which has at least one dimension of dispersed particles in the nanometer range [19]. We can classify the nanocomposites according to the dimension ranges of the dispersed particles. When we mention the three dimensions which are all in the order of nanometers, we are talking about isodimensional nanoparticles, such as spherical silica nanoparticles, semiconductor nanoclusters, and others [20, 21]. Carbon nanotubes or cellulose whiskers can be classified separately in which two dimensions are in nanometer scale, and the third one is larger while forming an elongated structure [22, 23]. In the last group, one dimensional fillers exist which are typically a few nanometers thick and a few thousand nanometers long. Polymer-layered crystal or clay nanocomposite is the general name of this group [24].

Nanocomposites cannot be formed only by physical mixing of the polymer and inorganic materials. The problem is the polymer blends; most of the time immiscible systems cause poor mechanical attraction and particle agglomeration between the polymer and inorganic materials. Therefore, phase separated composite, which is similar to the traditional microcomposites, is obtained when the polymer is not capable to intercalate between silicate sheets [3, 20]. The polymer layered silicate nanocomposites are based on separation and dispersion of the clay platelets in polymer matrix, and this dispersion range goes from simple intercalation to complete exfoliation of the silicate layers [2, 3, 6, 12, 17]. Clay layers are placed within the structure and they exist as particles containing tactoids at immiscible nanostructures (Figure 1(a)). Clays are separated more at intercalated systems and penetration of the polymer chain may occur in the interlayer spacing (Figure 1 (b)). Clay layers are separated individually and better dispersions are achieved in exfoliated nanostructures compared to the other two systems as shown in figure 1(c) [25, 26]. However, it is very difficult to obtain full exfoliation due to poor affinity between nanofillers and polymer matrix [2, 27, 28]. There is a separation of less than 20–30 Å between the platelets in intercalation, but the polymer separates the clay platelets by 80–100 Å or more during exfoliation [3]. The exfoliated system is the main interest in nanocomposites because it maximizes polymer-clay interaction and makes the whole surface of layers available for the polymer. This helps to improve mechanical and thermal properties better than intercalated structures [3].

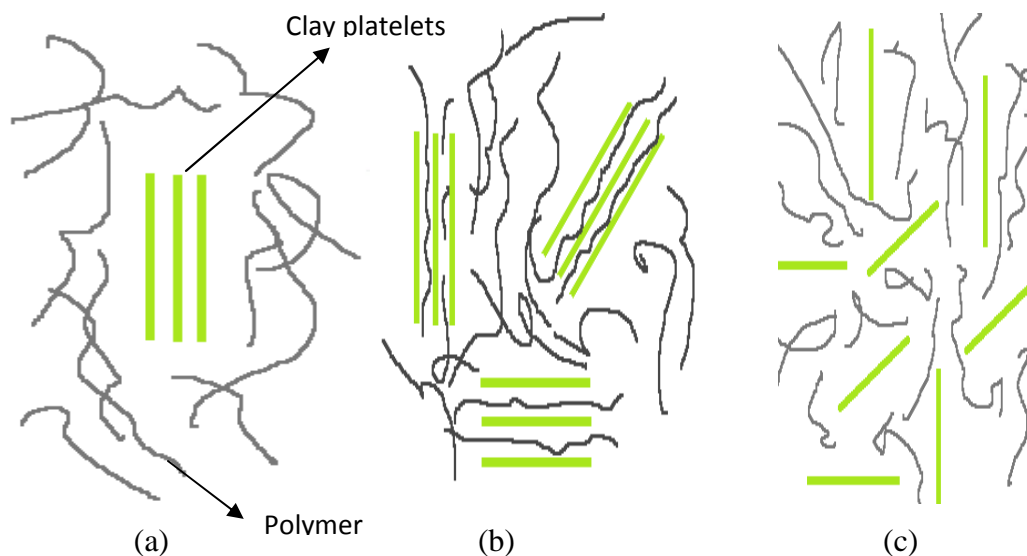


Figure 1. Level of nanoclay dispersion: a) Immiscible Nanostructure, b) Intercalated Nanostructure, c) Exfoliated Nanostructure [2, 29]

1.1. Layered Silicates

Layered silicates are commonly used in nanocomposites and they are known as the 2:1 phyllosilicates. Table 1 shows some common phyllosilicates.

Table 1. Chemical structure of phyllosilicates

2:1 phyllosilicates	General Formula
Montmorillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$
Saponite	$M_xMg_6(Si_{8-x}Al_x)O_{20}(OH)_4$

M=monovalent cation; x=degree of isomorphous substitution (between 0.5 and 1.3) [6]

One of the most widely used layered silicates (nanoclays) is montmorillonite as shown at Figure 2. It has two silicate tetrahedral layers sandwiching an inner octahedral layer which

consist of either alumina or magnesia [2, 26]. The duty of the Na^+ is to counterbalance the Al or Mg for generation of negative charge in the platelet. Montmorillonite has many platelets (layers), and there are Van der Waals forces between these layers [29]. The gaps between the layers are called interlayer or gallery. For example, the X-ray d-spacing of completely dry sodium montmorillonite is 0.96 nm while the platelet itself is about 0.94 nm thick [2]. The initial interlayer space is about 3.15 nm for Cloisite 15A and 1.85 nm for Cloisite 30B [12].

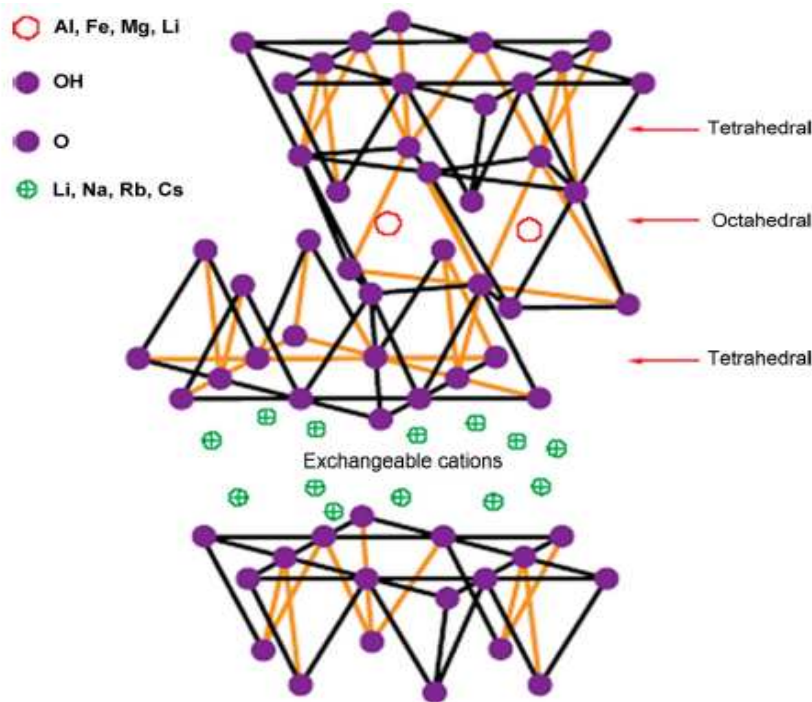


Figure 2. Structure of a 2:1 layered silicate [3]

Montmorillonite is in powder form with a mean particle size of about $8\mu\text{m}$, and in each particle of powder there are more than 3000 platelets [30]. The thickness of each layer is around 1nm, and the length of these layers can vary from 300\AA to several microns [31], i.e., it has high aspect ratio.

Generally, there are two main considerations for polymer/layered silicate nanocomposites. The first one is dispersion of silicate particles into individual layers. The second is the ability of improving the surface chemistry through ion exchange reactions with organic and inorganic cations [32]. Pretreatment of clays using ammonium salts or alkyl phosphonium makes the clays organophilic; the modified clays are called organoclays [25, 33]. Figure 3 shows the exchange process between alkylammonium ions and metallic cations. After exchanging the ions, surface energy of inorganic host decreases and wetting properties of polymer matrix are improved. Larger interlayer spacing is obtained as a result [34].

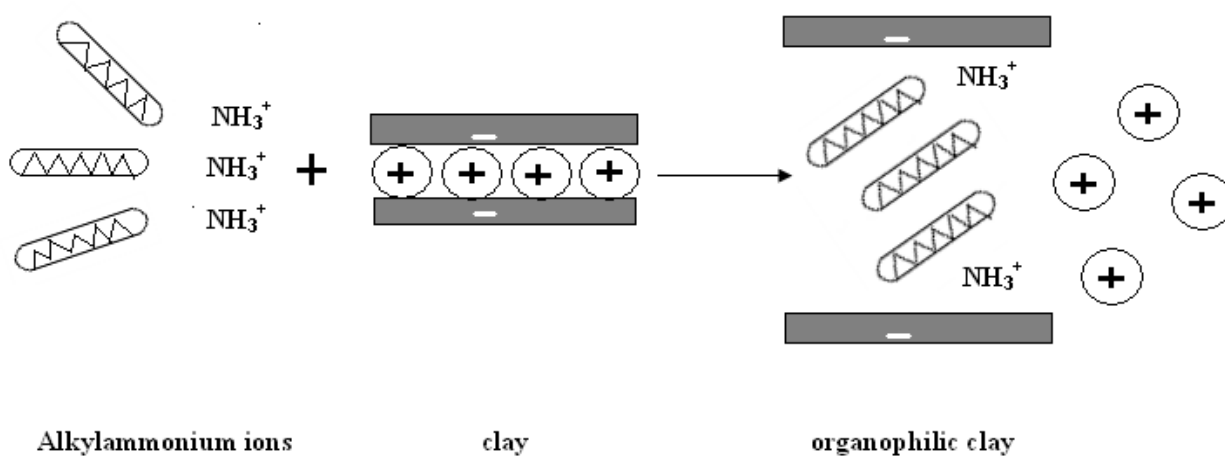


Figure 3. Cation-exchange process between alkylammonium ions and metallic cations [34].

Most of the time, polymer/clay nanocomposites have the combination of good processibility characteristic of the polymers, and great physical properties of the clays such as mechanical, thermal, and electrical properties [35-37]. As mentioned before, polypropylene-nanoclay nanocomposites are interesting for industrial applications because PP is one of the most widely used thermoplastic polymer and nanoclays are effective as filler materials [32]. However,

there are some difficulties to form these nanostructures. Nanoclays are known to be naturally hydrophilic while PP has no polar groups in its backbone and therefore, it is a hydrophobic polymer [10, 38]. Most of the time, poor interfacial bonding between the PP matrix and clay surface is obtained with low level of dispersion of the clay plates [39]. Compatibilizers (PP-g-MA) are used to improve intercalation/exfoliation of the organoclay and maximize its interfacial contact with polymer matrix [1, 25]. PP-MA has polar groups (-OH, COOH) which increases the polarity of the polypropylene [40]. They help to bond the clay and PP together with hydrogen bonds between the polar carboxylic group of PP-MA and oxygen or hydroxyl group in silicates [41]. The interlayer spacing of the montmorillonite increases, and interaction between the silicate layers gets weaker. Dispersion of silicate layers dispersion in polymer matrix via PP-MA is illustrated in Figure 4.

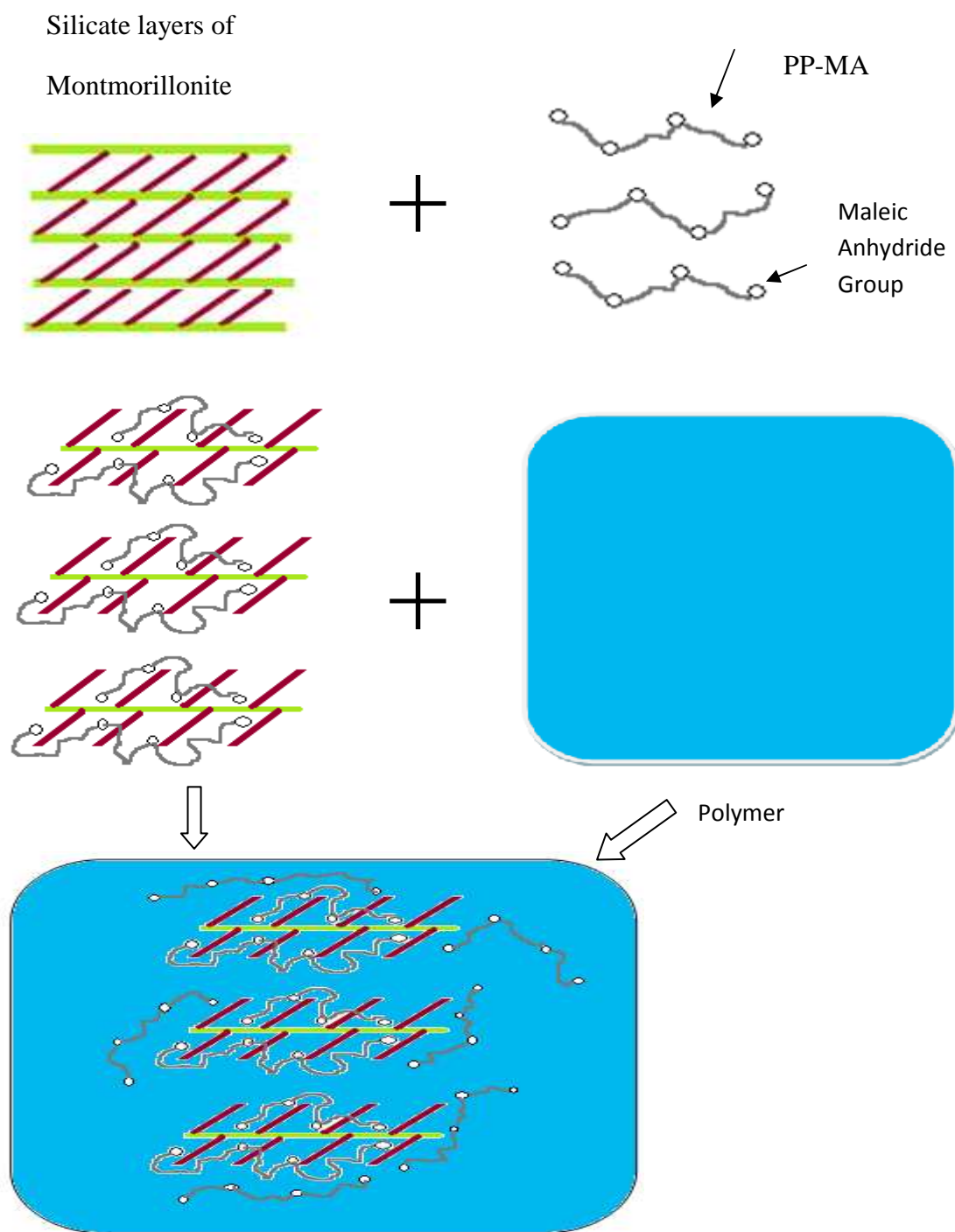


Figure 4. Dispersion of silicate layers in polymer matrix via PP-MA [40]

1.2. Nanoparticle Dispersion

There are different techniques to disperse nanofillers at nanoscales in a polymer matrix.

1.2.1. In situ polymerization

In situ polymerization was the first method used to synthesize polymer–clay nanocomposites based on polyamide 6 [3]. In this technique, the layered silicate is swollen within the liquid monomer (or a monomer solution) so as the polymer formation can occur in between the intercalated sheets [3, 6, 24]. Mostly, the nanoparticles are pretreated with a chemical agent to improve their compatibility with the polymer matrix [8].

1.2.2. Solution blending

There are weak forces that stack the layers together, and they can be easily dispersed in an adequate solvent. It involves dissolution of polymers in adequate solvent with nanoscale particles and evaporation of solvent or precipitation [3, 24]. The final structure may be intercalated or exfoliated depending on the interaction between filler and polymer matrix.

1.2.3. Melt intercalation

The layered silicate is blended with the polymer matrix in the molten state. If there is sufficient affinity between polymer matrix and filler, either an intercalated or an exfoliated nanocomposite can be achieved [6]. Melt intercalation is the most widely used method for monofilament processing, and it is environmentally friendly due to lack of solvent during mixing or processing. It is compatible with the current industrial methods such as extrusion and injection

molding, and also allows polymer processing that is not suitable for in situ polymerization or solution intercalation [26].

1.2.4. Template synthesis

Clay minerals are synthesized within the polymer matrix, using an aqueous solution (or gel) containing the polymer and silicate building blocks [3, 6, 24].

The montmorillonite intercalated with the PP-MA oligomers have good contacts with PP under strong shear [33, 42]. Stacked platelets can be broken into smaller pieces and the interlayer spacing increases during extrusion process (Figure 5). The increase in interlayer space helps for better dispersion and distribution of the nanoclays in polymer matrix.

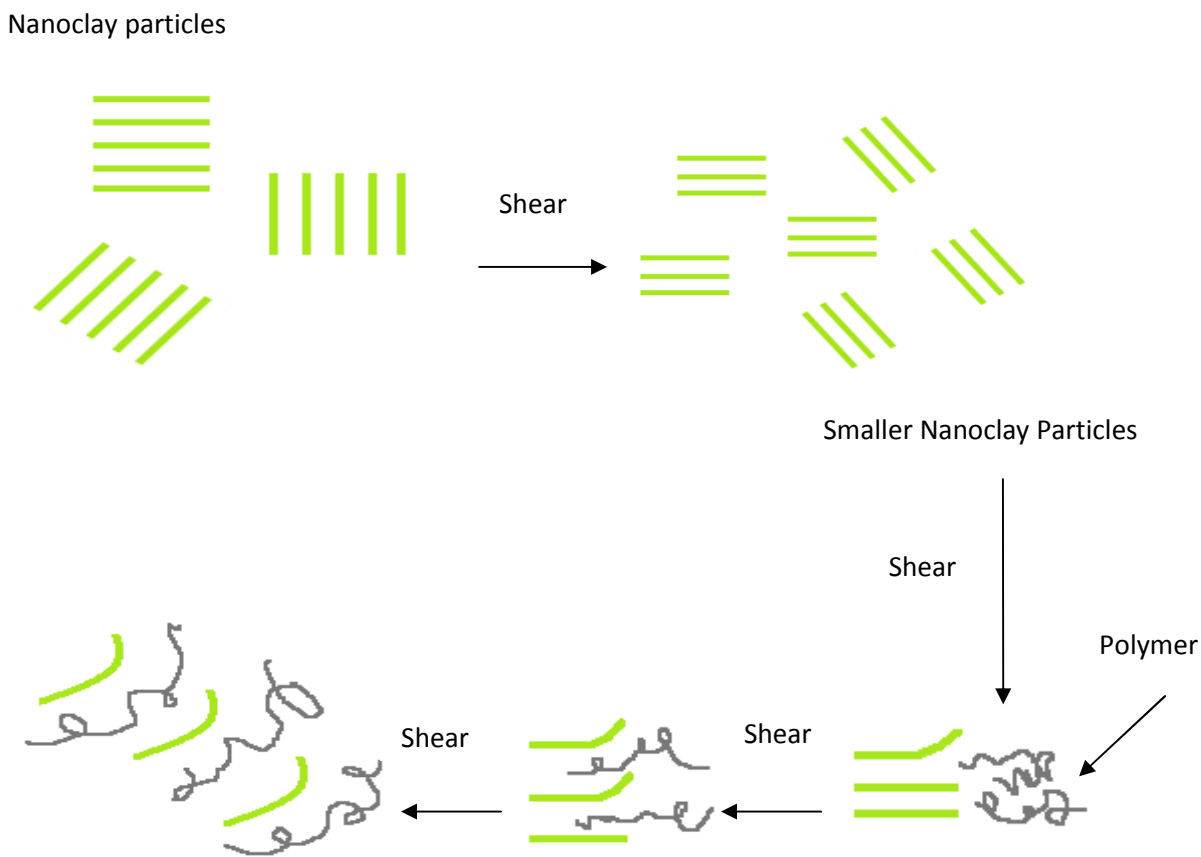


Figure 5. Organoclay dispersion and exfoliation during melt processing [6]

Some of the polypropylene monofilament application areas include nets and fabrics for agricultural end uses, geotextiles, sun breakers, sun blinds, shade nets, wind walls, safety nets, swimming pool covers, reinforcements in various coated products (such as plastics, and papers), filtration, carpeting, packaging, concrete reinforcement, and medical suture.

CHAPTER 2

MANUFACTURING AND CHARACTERIZATION OF PP/CLAY MONOFILAMENTS

1. Materials

- Polypropylene copolymer 30 Melt 2 Izod natural with melt flow index (MFI) of 30 g/10 min, and density of 0.91 g/cm³.
- Cloisite 15A as nanoclay which was already modified with a quaternary ammonium salt.
- Cloisite 30B as nanoclay which was already modified with a quaternary ammonium salt.
- Polybond 3200 (PP grafted with malefic anhydride; 1.0 weight % maleic anhydride level). It has 115 g/10 min MFI, and 0.91 g/cm³ density.

2. Machines Used For Manufacturing

All PP/Nanoclay monofilaments were prepared with melt intercalation method using single screw and twin screw extruders. Extrusion machines for the monofilament manufacturing are shown at Figure 6 and 7.



Figure 6. Single screw extrusion machine



Figure 7. Twin screw extrusion machine

2.1. Extrusion Machine

The common explanation of the extrusion is a process which plastic resins or pellets are used in a heated barrel or chamber, and carried along by a screw to the die which gives final shape of the products [43, 44]. Extrusion is one of the most efficient, most significant technologies of polymer processing. Almost 40% of polymer products are produced with extrusion. Extrusion has some advantages over other plastic processing techniques such as continuity, low cost, efficiency, broad raw material range, high production volume, and efficient mixing [45].

The first extruders were used in the food industry by bakers for noodle production. H. Bewley and R. A. Brooman made the first light industrial application in 1845, but the first extruder was patented by M. Grey [43]. These extruders were mainly used in the rubber industry.

Today, modern extruders are not very different than the old ones, but there have been a lot of changes at the geometry of the screws. Mainly, there are five considerations in an extrusion process for highly quality products:

- Appropriate polymer melt temperature
- Uniform/stable melt temperature
- Accurate melt pressure in the die
- Uniform/stable melt pressure in the die
- Well-mixed product [44].

2.1.1. Extruder Parts

Typical extruder mainly consists of hopper, barrel, screw, heaters, breaker plates, die, and melt pump (Figure 8).

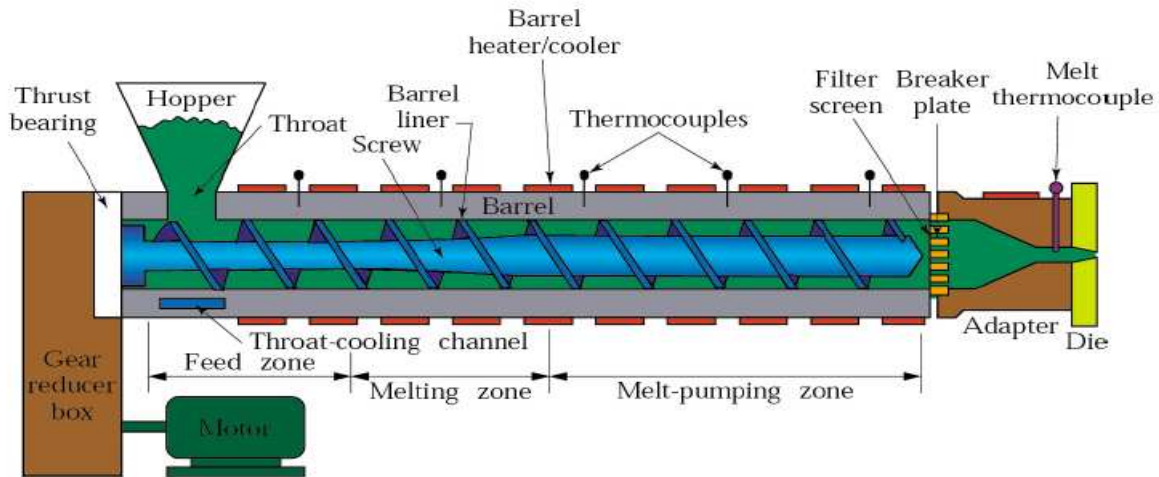


Figure 8. Longitudinal cross-section of an extruder [46]

2.1.1.1. Screw

Extruder screw is connected through a thrust bearing and rotates inside the barrel. The screw has important functions such as removing the pellets from the hopper, providing mechanical energy as part of the melting process, mixing pellets and additives, and generating pressure to push the melted polymer out of the die [45]. Figure 9 shows the main components of a single screw.

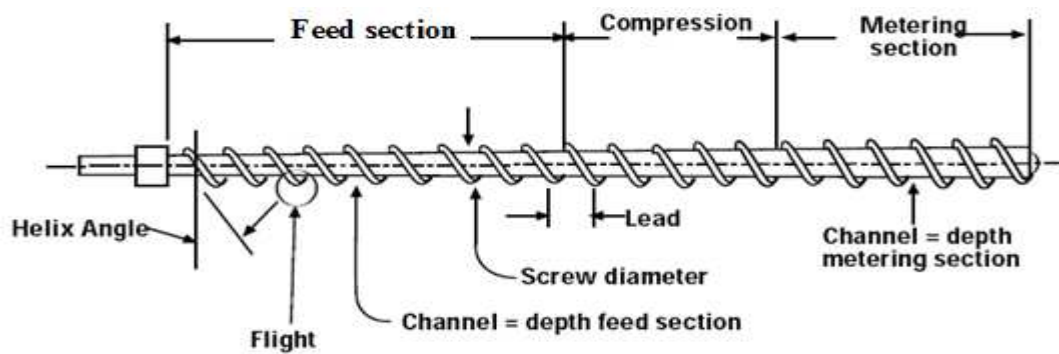


Figure 9. Schematic of a typical single screw [47]



Figure 10. A typical twin screw [48]

Twin screws provide better melting, mixing, and conveying in a shorter machine length than a single screw machine [49]. They also have ability to process the materials which are difficult to feed [50]. Figure 10 shows a twin screw.

2.1.1.2. Barrel

Barrel is expected to endure against high pressure and temperature. The screw is located inside the barrel. The barrel is made by hardened steel and lined with wear and corrosion resistant metal [45, 47].

2.1.1.3. Die

The die which determines the extruded plastic's cross sectional area is located at the end of heating zones (Figure 11). Monofilament diameters are affected by die diameter, screw speed, and the distance between die and water bath. Melted polymer falls down to the water with gravity effect, and solidifies there when contacts with water. If the distance between the die and water bath is short monofilaments will be thicker. When screw speed is increased monofilament diameter will be thicker because more polymers will be pushed to the die.

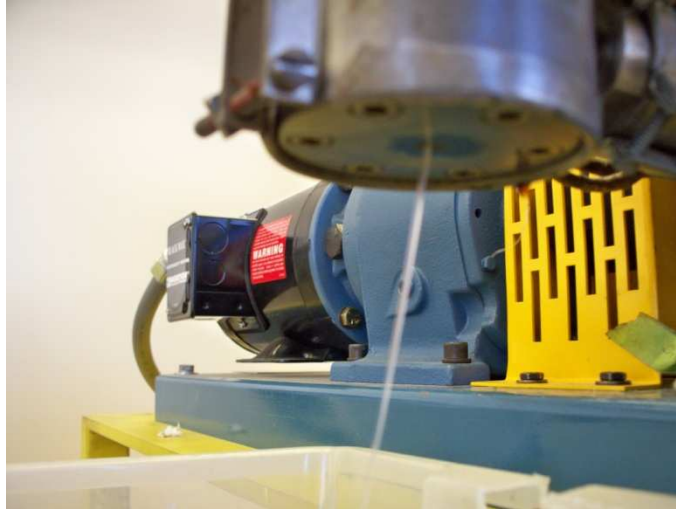


Figure 11. Single screw extruder die

2.1.1.4. Melt Pump

Most of the extruders have a melt pump which is used to prevent any pressure changes and transfer the melted polymer through the die. There are some cases that using gear pump provides advantages:

- Poor pressure-generating capability extruders (e.g., co-rotating twin screws, multi-stage vented extruders, etc.)
- When output stability is required to be better than 1%, i.e., in close tolerance extrusion (e.g., fiber spinning, cable extrusion, medical tubing, co-extrusion, etc.)[51].

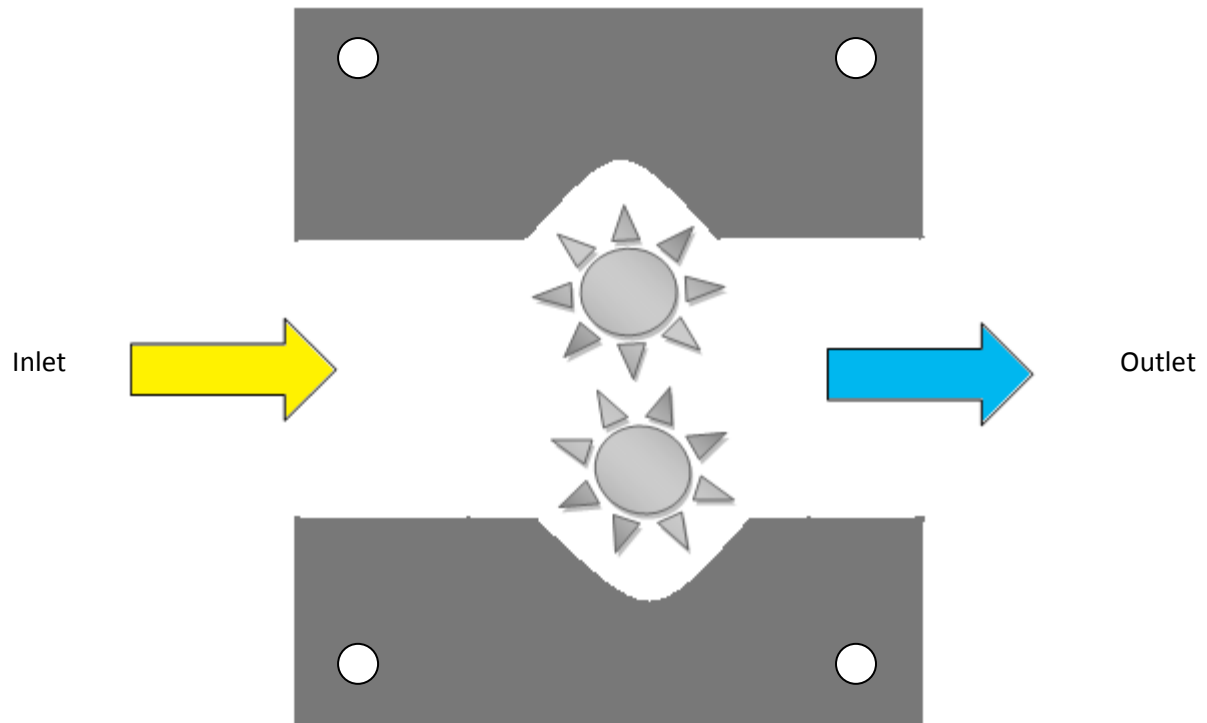


Figure 12. Operation of melt pump

Figure 12 shows a melt pump that contains two counter-rotating, intermeshing gears which produce a positive volumetric displacement of the melt. The molten polymer is used as lubricant for the bearings during process, and clearances are important at high pressure to avoid leakage. The melt pump also makes it possible for the extruder to run at lower head pressure, and this increases the specific output rate and decreases the melt temperature. A lower melt temperature is reduction of the possibility of thermal degradation during the extrusion process [52].

2.1.1.5. Breaker Plate

Breaker plates are used to prevent dusts, solids, or any foreign particles to pass through the die.



Figure 13. Breaker Plate

2.1.2. Processing

2.1.2.1. Raw Material Blending and Mixing

The feedstock is mostly used in pelletized form, but sometimes powder form is also used for good mixing with powder additives. These additives can be thermal stabilizers, nanofillers such as nanoclay or carbon nanotubes, UV stabilizers, plasticizers, and flame retardants. The best way to combine raw materials is mixing them prior to feeding into the extruder hopper. Some factors to be considered for material mixing are;

- Pellets and powder separation
- Appropriate mixing
- Particle size of the additives
- Uniform distribution of powders at low concentration [44].

Manufacturers want to increase the flow rate, decrease energy cost, and have minimum irregularities during extrusion process. These irregularities are classified in two groups:

- Surface irregularities which happen because of constant shear stress perfunctory of extrusion temperature. Some types of surface irregularities are shark skin and roughness. They affect the final product properties.
- Flow irregularities which happen at unsteady flow conditions [53].

2.1.2.2. Drying

Some polymers need to be dried prior to extrusion to prevent polymer degradation. Nylon, polyester (PET and PBT), polycarbonates absorb moisture from the air [44]. Moisture may affect the molecular weight of these polymers, and result in poor polymer properties. The moisture in the polymer may change to steam and cause surface defects such as splay, holes or foamy product.

2.1.2.3. Feeding Polymer to Extruder

There are basically 4 ways to feed polymer to a single screw extruder;

a) Flood Feeding

The most common method is flood feeding (Figure 14); pellets or powders are placed directly in a hopper over the feed throat, and they are fed to the screw with gravity [44].

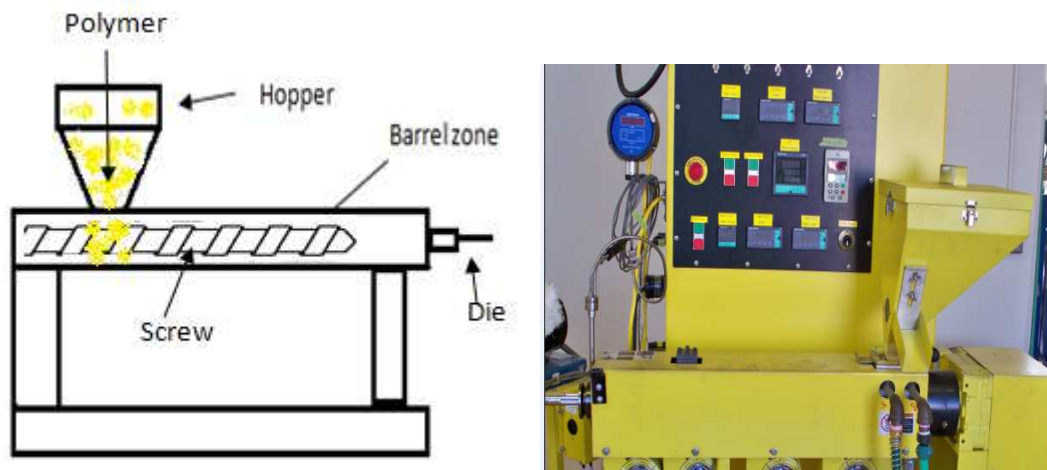


Figure 14. Flood feeding

b) Starve Feeding

Starve feeding is typically used in twin screw extrusion but can be employed in single screw extrusion as well (Figure 15) [44].

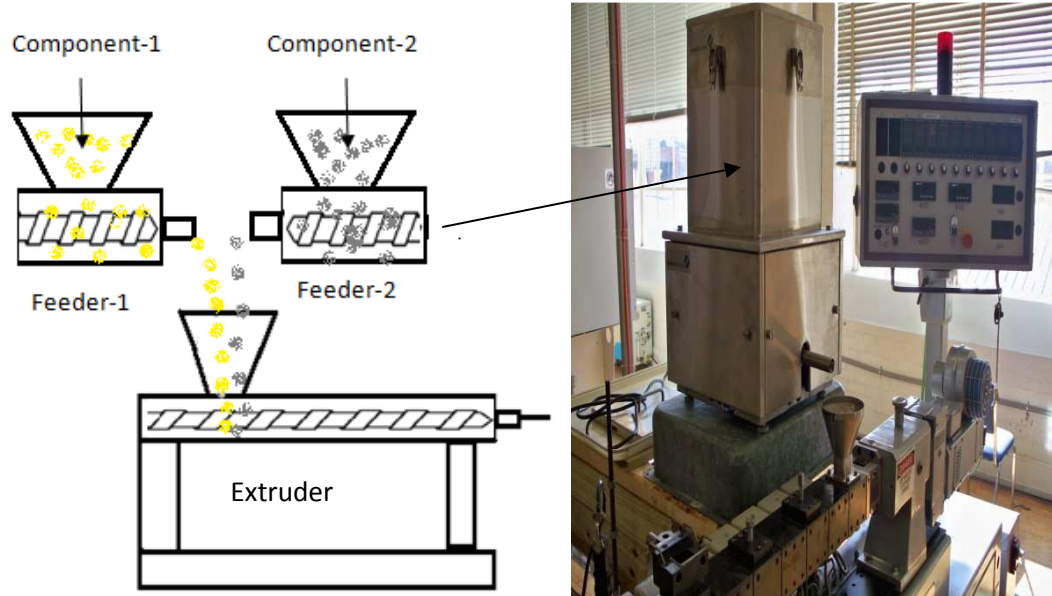


Figure 15. Starve feeding

c) Crammer Feeding

Crammer feeding is a positive system that works well with low bulk density materials, materials that tend to bridge and hard to feed materials. A screw mechanism inside the crammer positively conveys material to the extruder as shown in Figure 16 [44].

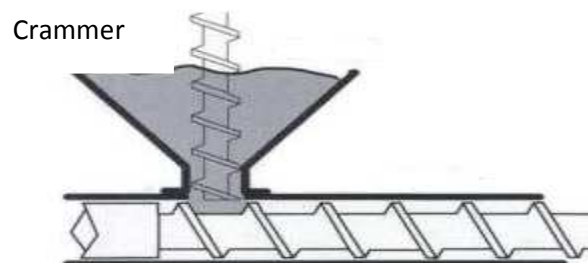


Figure 16. Crammer feeding [44]

d) Melt feeding

Molten polymers can be also fed from one extruder to another extruder. Basically, the feeder extruder is shorter, and develops uniform pressure and polymer melt temperature for the die (Figure 17) [44].

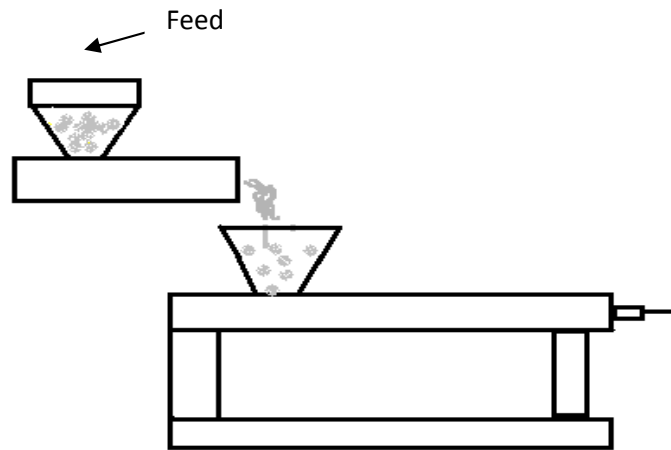


Figure 17. Melt feeding

2.1.2.4. Shaping and Drawing

Shaping is the last step in the extruder. When the polymer molecules relax and re-entangle at the end of the die, die swelling occurs as shown at Figure 18. Pullers (godets) have important role at this section (Figure 19).

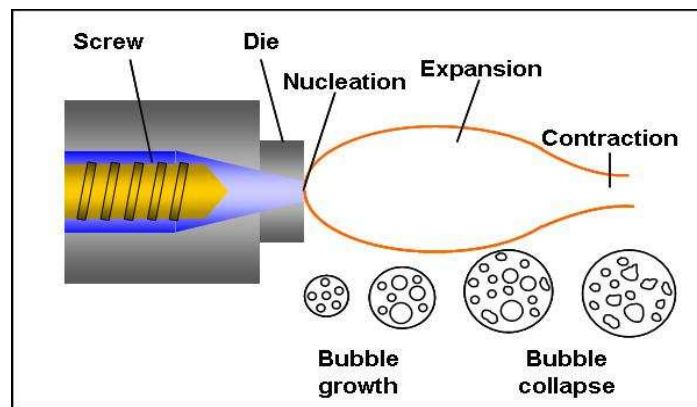


Figure 18. Extrudate expansion [54]

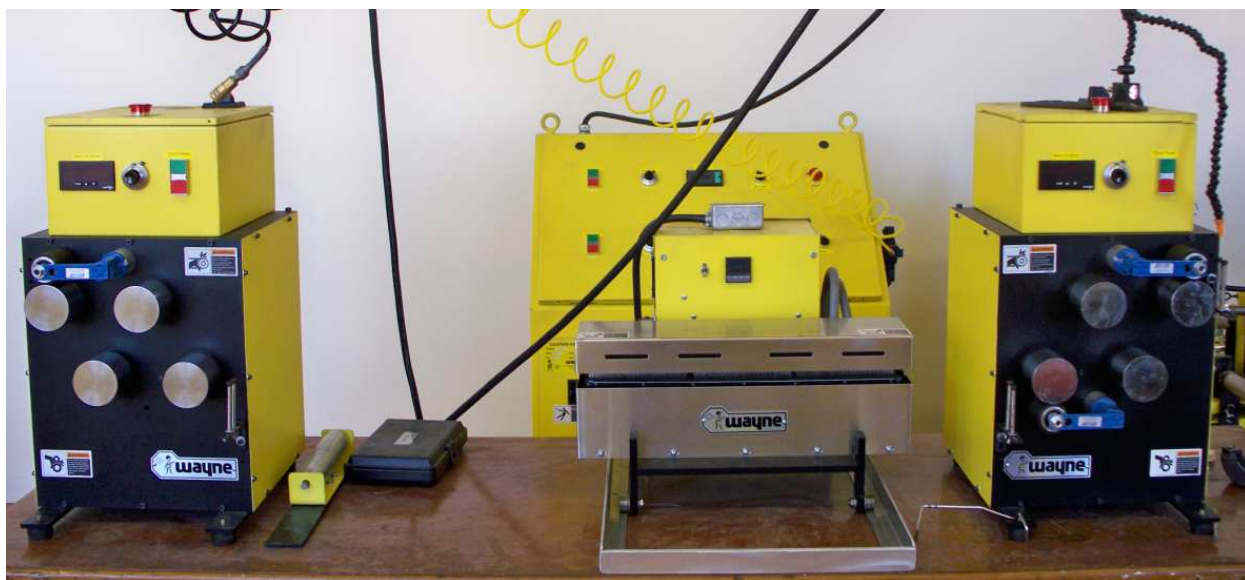


Figure 19. Godets and heater units of the single screw extruder

There must be a correlation between godets' speed and throughput rate to have the same dimensional product at the end of the process. Speed of the godets affects the molecular orientation of the polymers [44]. Molecular orientation can be increased or decreased by changing the draw-down ratio (Figure 20). Every polymer has a natural draw-down ratio, which changes the tensile and flexural properties [55]. Draw ratio can be calculated by the ratio of godets' speeds. Heaters can be used between two godets to have more uniform monofilaments.

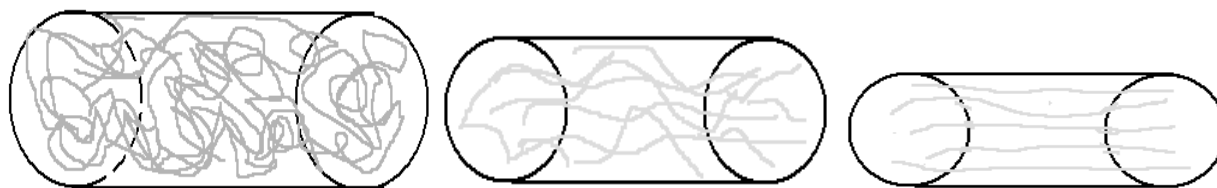


Figure 20. Molecular orientation of fibers during stretching

Draw-down ratio is one of the important considerations during monofilament manufacturing. Inaccurate ratios may results in diameter variations in the final product. Table 2 shows the processing parameters to produce monofilaments in this study.

Table 2. Parameter settings of monofilament processing

Sample	Barrel zone temperature °C (°F)	Die zone temperature °C (°F)	Motor speed (RPM)	Melt pump speed (RPM)	Heater temperature °C (°F)	Godet speeds (m/min)
1	204 (400)	216 (420)	220	13	177 (350)	15-30
2	204 (400)	216 (420)	220	13	177 (350)	15-45
3	204 (400)	216 (420)	220	13	177 (350)	15-60
4	204 (400)	216 (420)	220	13	177 (350)	15-90
5	204 (400)	216 (420)	220	13	177 (350)	15-105

Diameter variations were investigated and it was observed that uniformity was increased by increasing the draw-down ratio. Figure 21 shows the diameter changes by the draw-down ratio. It can be seen that when the draw-down ratio is 7, diameter variation is minimum.

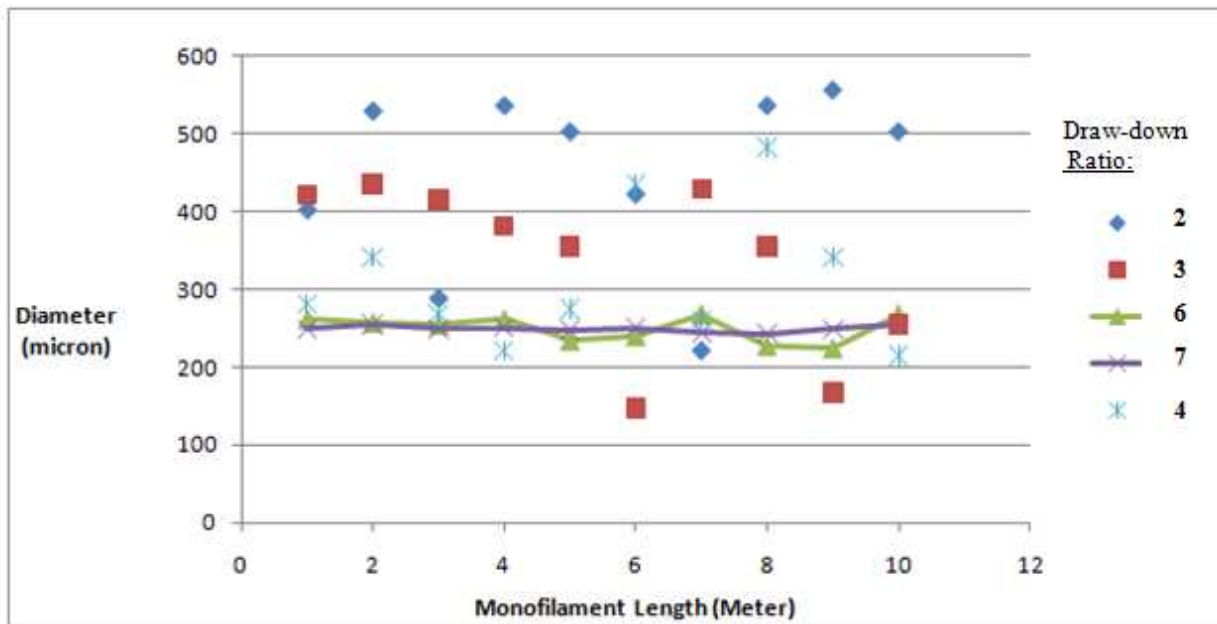


Figure 21. Diameter changes with different draw-down ratios

Experiments were done to examine the diameter variations when different heater temperatures were applied at a draw-down ratio 7. Polypropylene copolymer 30 Melt 2 Izod natural with melt flow index (MFI) of 30 g/10 min, and density of 0.91 g/cm³ was used. Table 3 shows parameter settings for monofilament processing for this purpose.

Table 3. Parameter settings of monofilament processing with different heater temperatures

Sample	Barrel zone temperature °C (°F)	Die zone temperature °C (°F)	Motor speed (RPM)	Melt pump speed (RPM)	Heater temperature °C (°F)	Godet speeds (m/min)
1	204 (400)	216 (420)	220	13	-	15-105
2	204 (400)	216 (420)	220	13	177 (350)	15-105
3	204 (400)	216 (420)	220	13	191 (375)	15-105
4	204 (400)	216 (420)	220	13	204 (400)	15-105

Four different monofilaments were manufactured with different heater temperatures. Then, diameters of the monofilaments were measured at every meter with microscopy. It can be seen in Table 4 that uniform monofilaments were obtained with low CV values. However, the monofilaments which were processed with heaters showed more uniform diameters compare to the ones manufactured without heater.

Table 4. Diameter variation of different monofilaments

	Sample 1	Sample 2	Sample 3	Sample 4
Distance (Meter)	Diameter (μm)	Diameter (μm)	Diameter (μm)	Diameter (μm)
1	260.63	256.61	258.62	249.24
2	253.93	245.89	254.6	254.6
3	244.91	251.25	255.94	249.24
4	256.61	248.57	249.91	250.58
5	247.90	247.23	251.25	247.23
6	253.93	247.9	253.26	250.58
7	257.95	244.55	253.26	244.55
8	253.26	249.91	253.26	243.21
9	245.91	252.59	249.24	249.24
10	249.91	249.91	260.63	255.94
Mean	252.49	249.441	253.997	249.441
C.V. (%)	2.07	1.39	1.42	1.57

Tensile properties can be affected by draw-down ratio and heater temperatures. Higher draw-down ratios results in higher tensile properties due to better molecular orientation of the monofilaments. Lower draw-down ratios cause necking which produces nonuniform structures with low tensile properties. Figure 22 shows the tensile strength changes at different draw-down ratios.

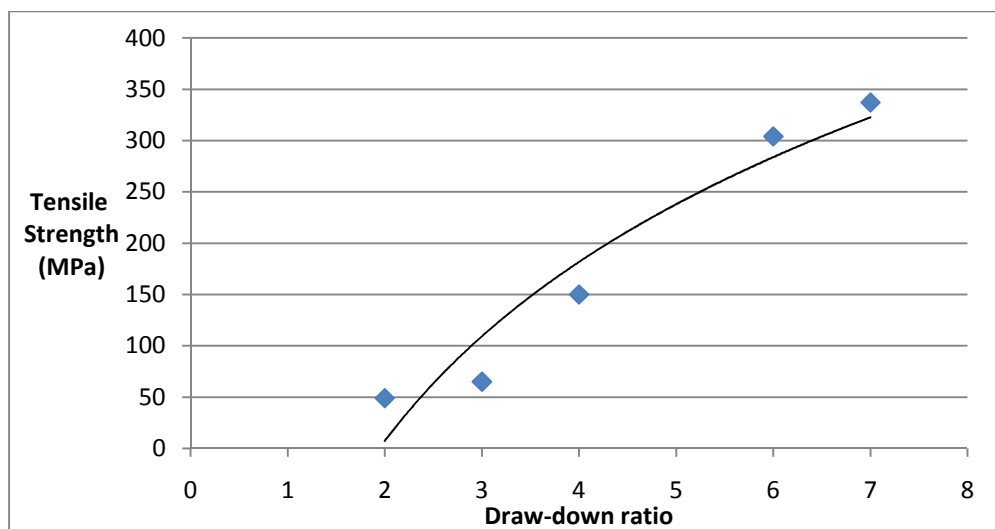


Figure 22. Tensile strength of monofilaments at different draw-down ratios

Heaters may affect the tensile strength of monofilaments. Figure 23 reflects the tensile strength values obtained with different heater temperatures. Monofilaments which were processed with higher heater temperatures had more tensile strength. As mentioned before, heaters helped to get more uniform monofilaments, which may result in higher tensile properties of the final products. Besides, heating makes the drawing of the monofilaments more efficient because of providing chain relaxation of the molecules.

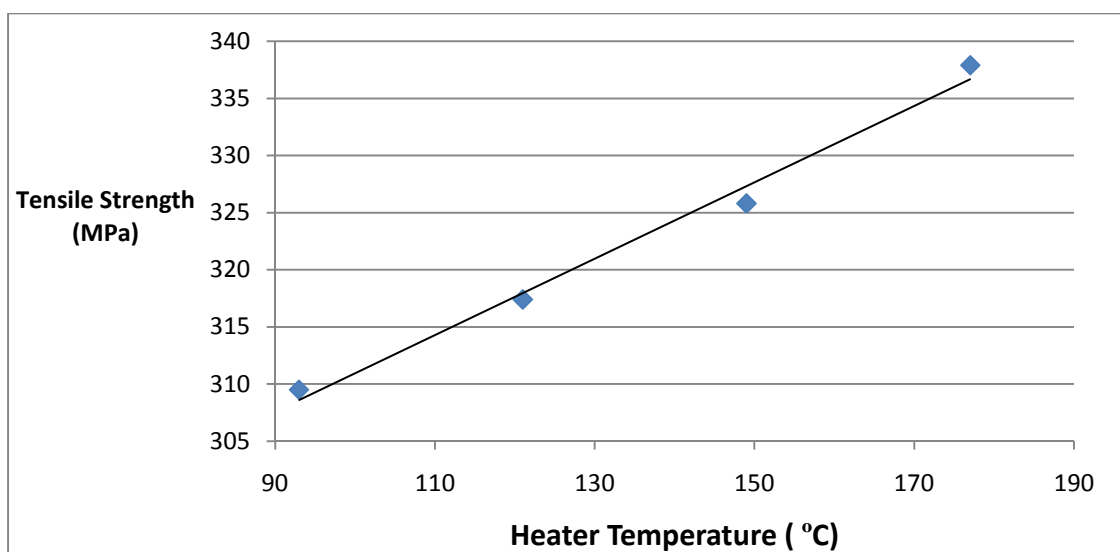


Figure 23. Tensile strength of monofilaments at different heater temperatures

2.1.2.5. Solidification and Cooling

After the die, filaments move through a water bath and solidify there. Instead of water, air can be used for cooling as well. Water temperature can be adjusted according to the polymer type. Sharp cooling can affect crystalline properties of polymers.

2.1.2.6. Winding

This is the final step of the extrusion process. Drawn filaments are rolled up on bobbins at winder (Figure 24). The winder speed can be adjusted; however, it should not be more than the final godet's speed. If it is higher, breakage may occur.

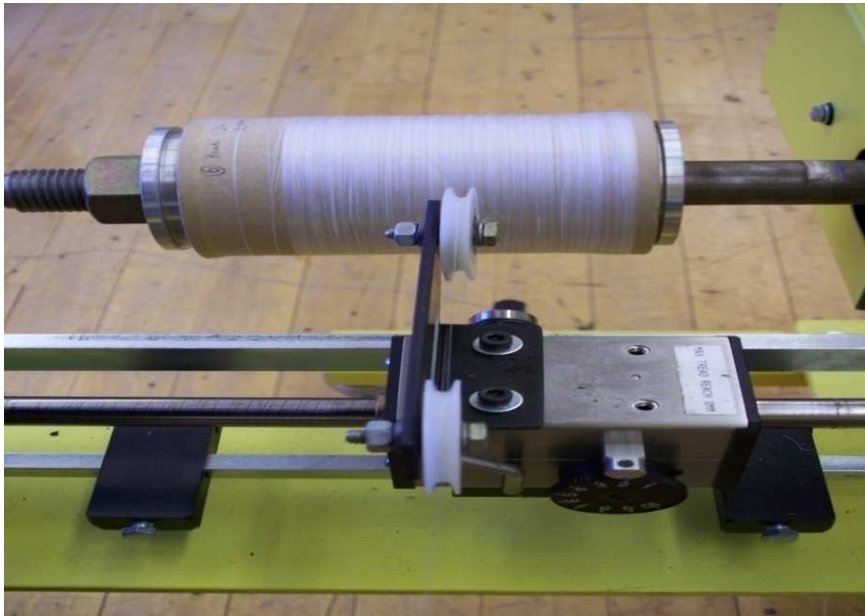


Figure 24. Winder section

2.1.3. Differences between Single and Twin Screw Extruders

There are some differences between twin and single screw extruders (Table 50). For instance, better feeding, easier processing with hard-to-feed materials (powders, slippery materials, etc.), short residence time and a narrow residence time distribution [56].

Table 5. Differences between single and twin screw extruders [56]

	Single screw	Twin screw
Flow type	drag	Near positive
Residence time and distribution	Medium/wide	Low/narrow(useful for reaction)
Effect of back pressure on output	Reduces output	Slight effect on output
Shear in channel	High (useful for stable polymers)	Low (useful for PVC)
Overall mixing	Poor /medium	Good (useful for compounding)
Power absorption and heat generation	High (may be adiabatic)	Low (mainly conductive heating)
Max. screw speed	High(output limited by melting, stability, etc)	Medium (limits output)
Thrust capacity	High	Low (limit pressure)
Mechanical construction	Robust, simple	Complicated
First cost	Moderate	High

3. Preparation of PP/Nanoclay Composite Monofilaments

First, monofilaments were produced with the single screw extruder. Then, twin and single screw extruders were used in sequence to have more efficient processing.

3.1. By Using Single Screw Extruder

Different amounts of nanoclay (Cloisite 15A) and compatibilizer (Polybond 3200) were used to form composite monofilaments by the single screw extruder. Attempts to produce polypropylene/nanoclay composite monofilaments without compatibilizer were unsuccessful.

Table 6 shows the master batches and sample codes.

Table 6. Sample codes and blends of master batches for single screw extruder

Sample Code	Clay Loading (%)	Compatibilizer Loading (%)
PP	-	-
P1-C10	1%	10%
P1-C15	1%	15%
P1-C20	1%	20%
P2-C10	2%	10%
P2-C15	2%	15%
P2-C20	2%	20%
P3-C10	3%	10%
P3-C15	3%	15%
P3-C20	3%	20%

Cloisite 15A was dried in a vacuum oven at 65 °C for 12 hours prior to manufacturing. Pure polypropylene pellets, Cloisite 15A, and Polybond 3200 were mixed manually before processing. Processing temperatures are given in Table 7.

Table 7. Temperature settings of the single screw extruder

Heating Zones	Temperature °C (°F)
Barrel zone-1	204 (400)
Barrel zone-2	204 (400)
Barrel zone-3	204 (400)
Barrel zone-4	204 (400)
Die zone-1	218 (425)
Die zone-2	218 (425)
Die zone-3	218 (425)
Die zone-4	218 (425)
Die zone-5	218 (425)
Die zone-6	218 (425)

The extruder screw speed was 100 rpm, and melt pump speed was set to 13rpm. A draw-down ratio of 7 was applied to the monofilaments. After the water tank, air was blown on the monofilaments to dry them before drawing section. After the drawing, all monofilaments, except pure polypropylene, were chopped and reextruded to obtain better dispersion and distribution of the nanoclays in polymer matrix.

3.2. By Using Twin and Single Screw Extruders in Sequence

Twin screw extruders are mainly used for mixing different components. They produce better shearing effect on nanoclays which means that more separation of nanoclay layers may occur. In addition, better distribution and dispersion may be obtained compared to single screw extruders.

Different types of nanoclays (Cloisite 15A and Cloisite 30B), and a compatibilizer (Polybond 3200) were used to form composite monofilaments. First, twin screw extrusion machine was used to make tape forms. Table 8 shows master batches and sample codes.

Table 8. Sample codes and blends of master batches for twin screw extruder

Sample Code	%15A	%30B	% Compatibilizer
P-A-5	0.5	-	10
P-A-10	1.0	-	10
P-A-15	1.5	-	10
P-A	1.0	-	-
P-B	-	1.0	-
P-B-5	-	0.5	10
P-B-10	-	1.0	10
P-B-15	-	1.5	10

Cloisite 15A and 30B were dried in a vacuum oven at 65 °C for 12 hours prior to manufacturing. Pure polypropylene pellets were fed to twin screw extruder with a pellet feeder (Figure 15). Nanoclay and compatibilizer were mixed prior to the processing, and then fed to the hopper while polypropylene pellets were being fed with the feeder. Extruder speed was set to 200 rpm. The temperature settings are given in Table 9. The tapes were cut with a chopper to have pellets that contained nanoclay and compatibilizer. These pellets were used in the single screw extruder to produce monofilaments. It was observed that manufacturing of monofilaments with the combination of twin and single screw extruder machines was easier than using only single screw extruder. Less breakage of monofilaments was noticed while drawing the

monofilaments. Besides, it was possible to produce monofilaments that do not have any compatibilizers (they could not be produced by using only single screw extruder).

Table 9. Temperature settings of the twin screw extruder

Heating Zones	Temperature (°C)
Barrel zone-1	220
Barrel zone-2	220
Barrel zone-3	220
Barrel zone-4	220
Barrel zone-5	220
Barrel zone-6	220
Barrel zone-7	220

4. Characterization

The surface morphology of the pure and composite monofilaments was investigated by using Zeiss EVO 50VP scanning electron microscopy (SEM). Probe current was adjusted between 700-900 pA. All specimens were coated with gold before the experiment.

Basic crystalline structures of pure and composite monofilaments were analyzed using Bruker APEX single crystal X-ray diffractometer. Sample collections were made between 2 θ range of 5-40° with CuK α 2 radiation at 40KV voltage, and 40 mA generators current. Scanning time was set to 750 seconds, and step size was 0.01°.

Melting behavior and degree of crystallinity measurements were made by using Perkin-Elmer DSC Q2000 instrument under nitrogen atmosphere. Sample sizes were between 5-10 mg. Samples were heated from 50 to 250 °C at 10°C/min, and held there 2 minutes, then cooled to

room temperature. The crystallinity of the samples was calculated according to the following formula:

$$X_c = \frac{\Delta H}{\Delta H_{PP}^0} \quad (1)$$

ΔH is the enthalpy of fusion of the sample (J/g) and ΔH_{PP}^0 is the enthalpy of fusion of completely crystalline PP (~209 J/g) [57].

Thermal stability of monofilaments was measured by using Perkin-Elmer TGA Q500 instrument. The heating rate was 20°C/min for all samples, and the temperature range was 50-600 °C under atmospheric air.

Nicolet 6700 FTIR spectrometer was used to characterize the molecular conformation of the pure and composite monofilaments. The number of each scan was 32, and experimental scan was set at 16.

Samples were tested according to the ASTM D-3822-07 Standard Test Method for Tensile Properties of Single Textile Fibers with Instron 5565 Testing Machine. The diameter of each sample was measured with a microscope. Five tests were done for each sample and the average values were used for the evaluation of the properties.

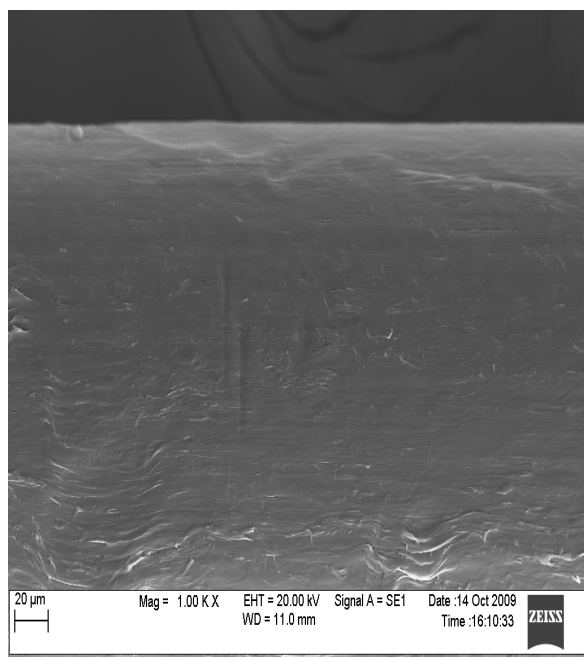
CHAPTER 3

RESULTS AND DISCUSSION

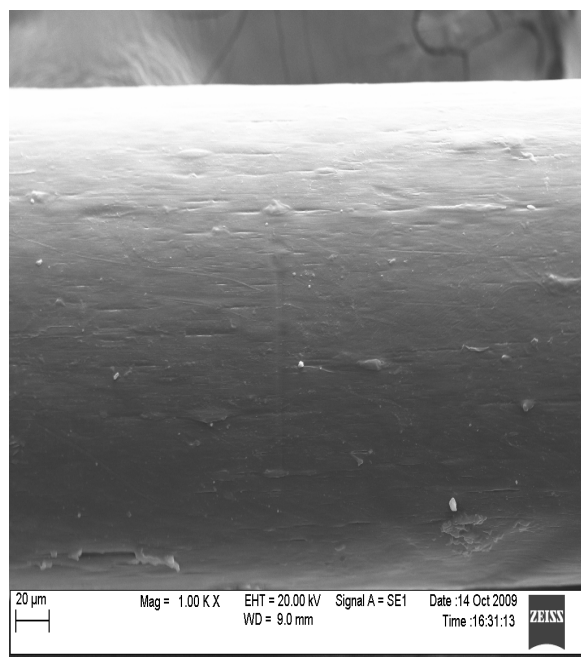
1. Single Screw Extrusion Results

1.1. SEM Microscopy

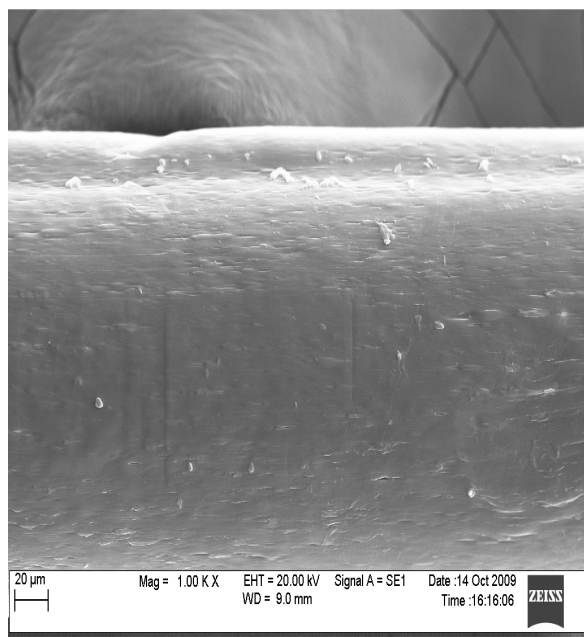
The surface morphology of pure polypropylene and some of the polypropylene/nanoclay composite monofilaments are presented in Figure 25 (a-d). SEM images show the distribution of nanoclay particles along the monofilaments. P3-C10 sample has bigger particles compared to P1-C10 and P2-C10. Agglomeration can be seen for P3-C10 sample due to low dispersion and distribution of nanoclay particles in the polymer matrix. Low shear effect of single screw extruder can also cause this agglomeration. P1-C10 and P2-C10 samples have almost the same level of nanoclay dispersion. The range of the particle size is between 700nm to 4 microns for P1-C10, and 3 to 10 microns for P2-C10. However, there are also smaller nanoscale particles which may help for reinforcement of the monofilaments. On the other hand, drawing of the monofilaments also helps with the distribution of nanoclay along the monofilament. In addition, sample P3-C10 could not be drawn well during processing compared to other samples due to agglomeration of the nanoclays.



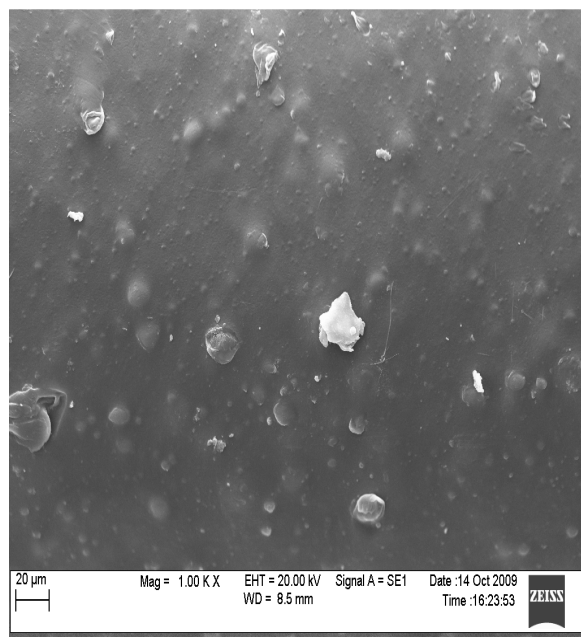
(a)



(b)



(c)



(d)

Figure 25. SEM images of surface views: (a) Pure PP Filament, (b) P1-C10, (c) P2-C10, (d) P3-C10.

1.2. FTIR

The FTIR spectrum of pure polypropylene and composite monofilaments is given in Figure 26. Si-O stretching (1005 cm^{-1}) and Si-O bending (480 cm^{-1}) can be observed for Cloisite 15A. There are vibration of peaks between 900 and 1000 cm^{-1} , and silicates and carboxyl groups might form bond in this range. However, all the peaks of composite monofilaments show similar characteristics compared to pure polypropylene monofilaments even if the clay loading is increased. This shows that there are weak bonds between nanoclays and polymer matrix due to agglomeration or lower dispersion of nanoclays.

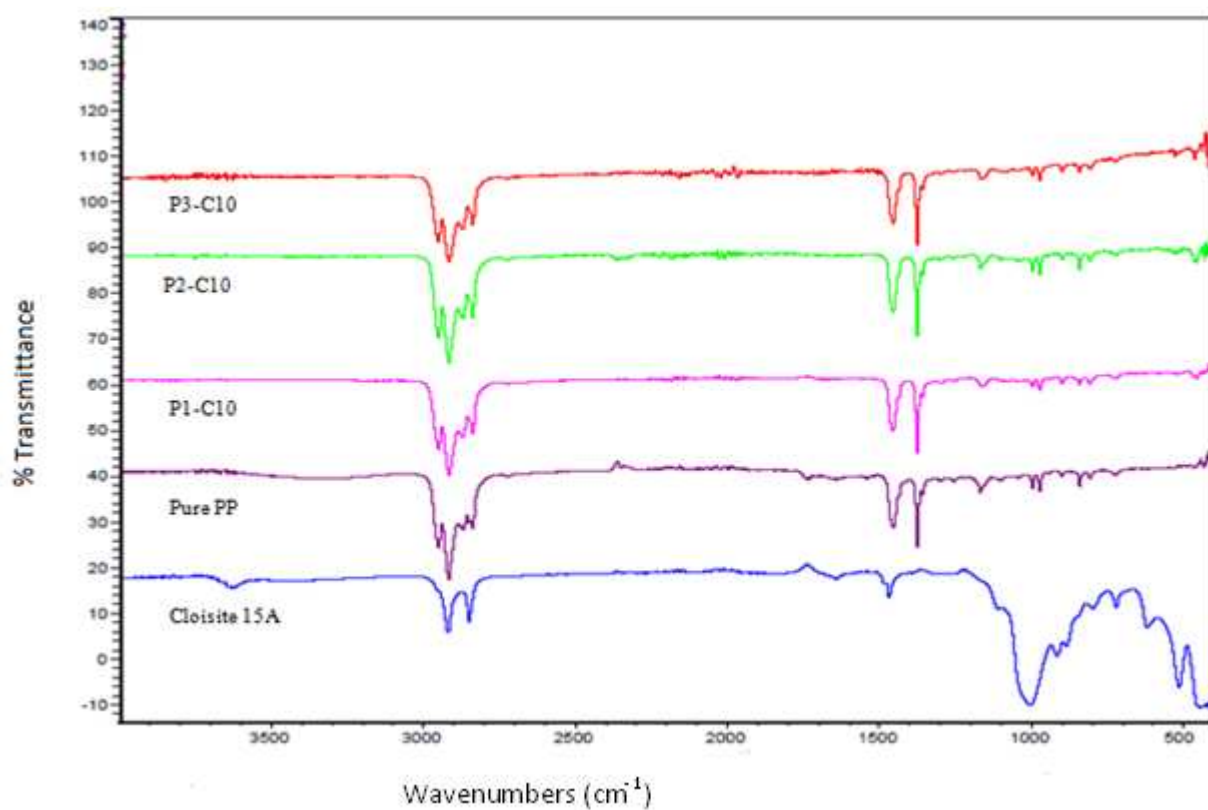


Figure 26. FTIR spectra of pure and composite monofilaments

1.3. X-Ray Diffraction

Figure 27 shows the X-ray diffraction of pure polypropylene monofilaments, P1-C10, P2-C10 and P3-C10 drawn monofilaments. The results can give a general view about the nanocomposite structure. The different peaks may indicate the distribution of clay layers and d-spacing which is the distance between the clay layers. Polymer nanocomposite peaks often show shifting to lower 2θ angle or larger d-spacing. Decrease or disappearance of characteristic peaks indicates the formation of intercalation or exfoliation nanostructures [58].

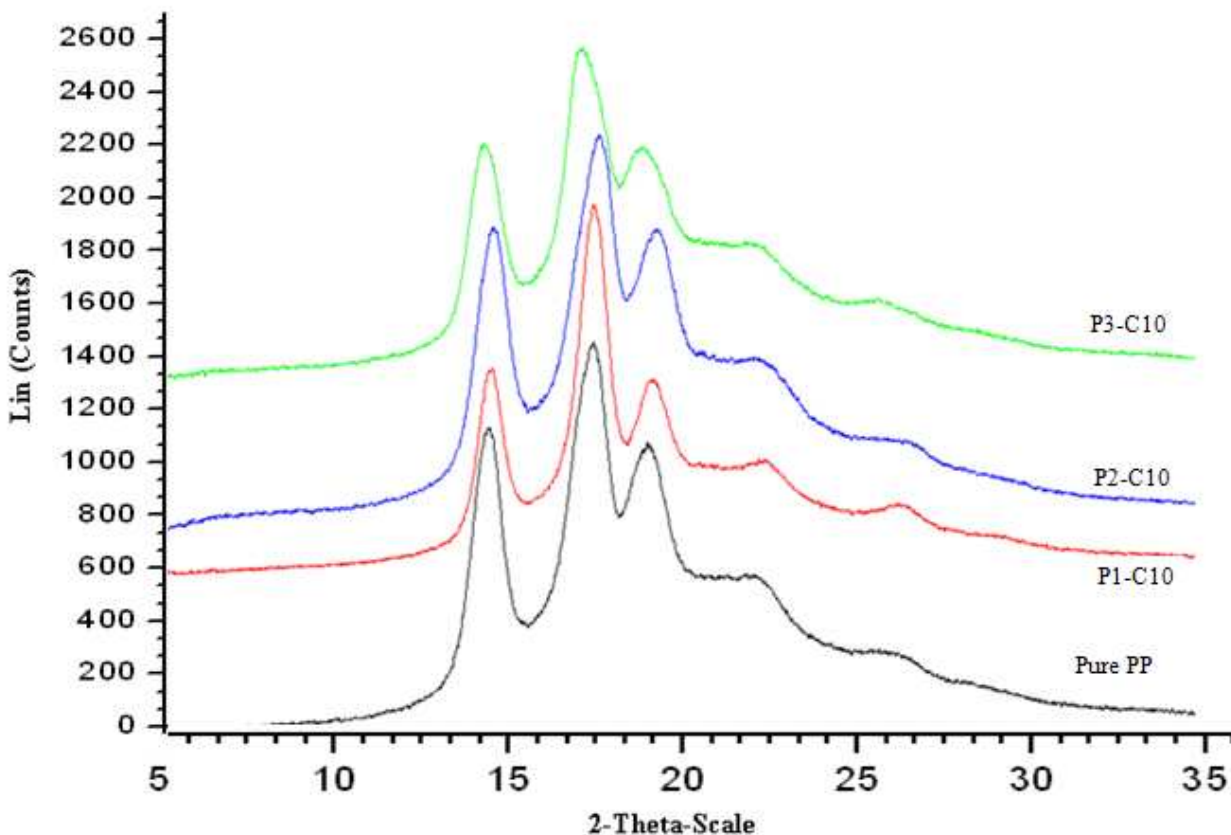


Figure 27. XRD curves of pure polypropylene and composite monofilaments

Table 10 shows the diffraction peaks of samples at 2θ angles. The results show that there is no significant change at peak characteristics of the samples. There is only little shifting at P3-C10 sample, and agglomerated clay particles may cause this difference. It can be concluded that addition of nanoclay did not affect basic crystal structure of the samples.

Table 10. Diffraction peaks of the samples at 2θ angle range

Pure PP	P1-C10	P2-C10	P3-C10
14.11	14.04	14.07	13.97
16.9	16.73	16.88	16.71
18.52	18.44	18.48	18.35
21.69	21.62	21.63	21.44

1.4. Thermal Behavior

Crystallization and melting behavior of the monofilaments with different nanoclay and compatibilizer loading are shown in Table 11. Most of the filament properties depend on crystallinity, spherulites size, and the size of lamellar crystals. Polypropylene is a semicrystalline polymer; on the other hand, nanoclays are known as nucleating agents and accelerate the crystallization process [59]. It was observed that melting point of pure polypropylene decreased slightly with the addition of nanoclay as shown in Figure 28. Melting point decrease may suggest a reduction of lamellar size; probably the clay can prevent the growth of individual lamellae, and more lamellae are formed with smaller sizes [60].

Table 11. Thermal and tensile results of composite monofilaments

Samples	Decomposition Temperature (°C)	Tensile Strength (MPa)	Elongation at Break (%)	T _m (°C)	T _c (°C)	X _c (%)
Pure PP	358.86	308.8	63.6	166.79	131.17	41.04
P1-C10	368.32	289.1	52.0	166.60	130.73	42.48
P2-C10	376.35	286.0	53.0	166.33	130.66	41.21
P3-C10	393.95	276.1	54.7	165.78	130.80	41.95
P1-C15	367.23	292.9	55.1	165.91	129.67	42.81
P2-C15	375.77	282.6	52.5	165.39	129.61	43.81
P3-C15	389.75	281.4	53.6	165.33	128.97	42.29
P1-C20	367.61	294.7	63.0	166.12	128.35	43.56
P2-C20	377.65	279.7	64.4	165.53	129.20	42.77
P3-C20	389.23	273.6	64.2	165.65	127.73	42.69
PP-MA	359.15	-	-	162.36	112.61	42.40

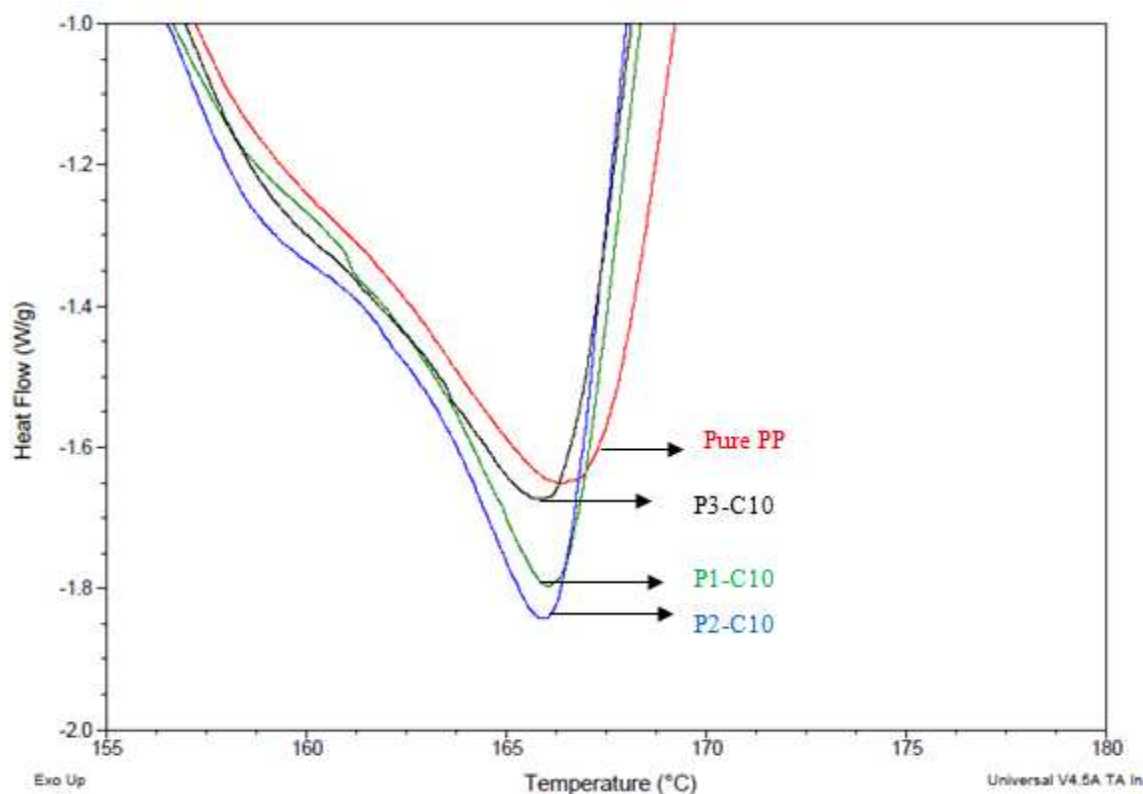


Figure 28. Melting behavior of pure and composite polypropylene monofilaments

Crystallization temperature (T_c) decreased slightly with the presence of nanoclay in the system. This also indicates the nucleating affect of nanoclays in crystallization of polypropylene. Addition of compatibilizer may also cause this reduction because of lower crystallization temperature (112.61 °C). The degree of crystallinity (X_c) was calculated according to the equation (1), and an increase (41.04 % to 43.81%) was observed with the addition of nanoclay. It was also observed that X_c increased by increasing compatibilizer amount in composite monofilaments.

Nanoclays are known as good heat insulators due to their good thermal resistance. Nanoclays can prevent the penetration of oxygen, and provide slower decomposition. TGA results are given in Table 11. The results show that addition of nanoclay increased decomposition temperature of the composite monofilaments compared to pure polypropylene

monofilaments. Figure 29 shows the comparison of pure and composite monofilaments during decomposition. Their onset temperatures are similar; after 300 °C, they start to lose their weight under temperature. Pure polypropylene shows rapid decrease of weight compared to composite monofilaments, and decomposes at 358.86 °C. The decomposition temperatures in the Table are the means of four samples' decomposition temperature for each monofilament. Figure 30 shows how to determine the decomposition temperature for one of the pure polypropylene monofilaments with the TGA instrument.

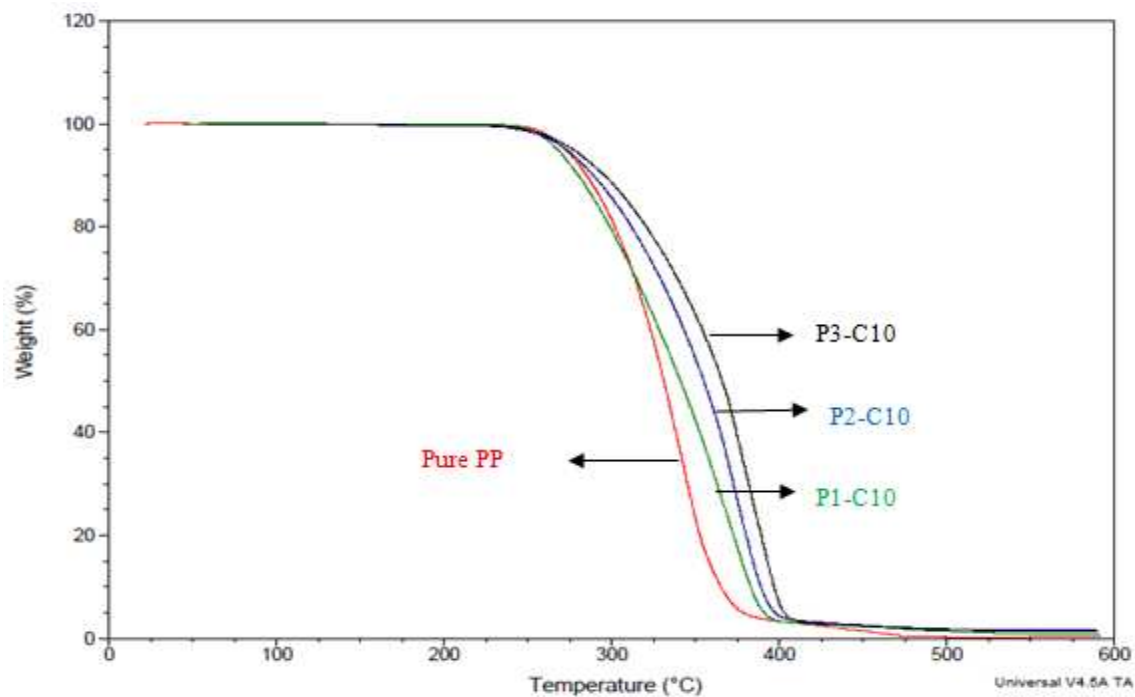


Figure 29. Decomposition behavior of pure and composite polypropylene monofilaments at different nanoclay loadings

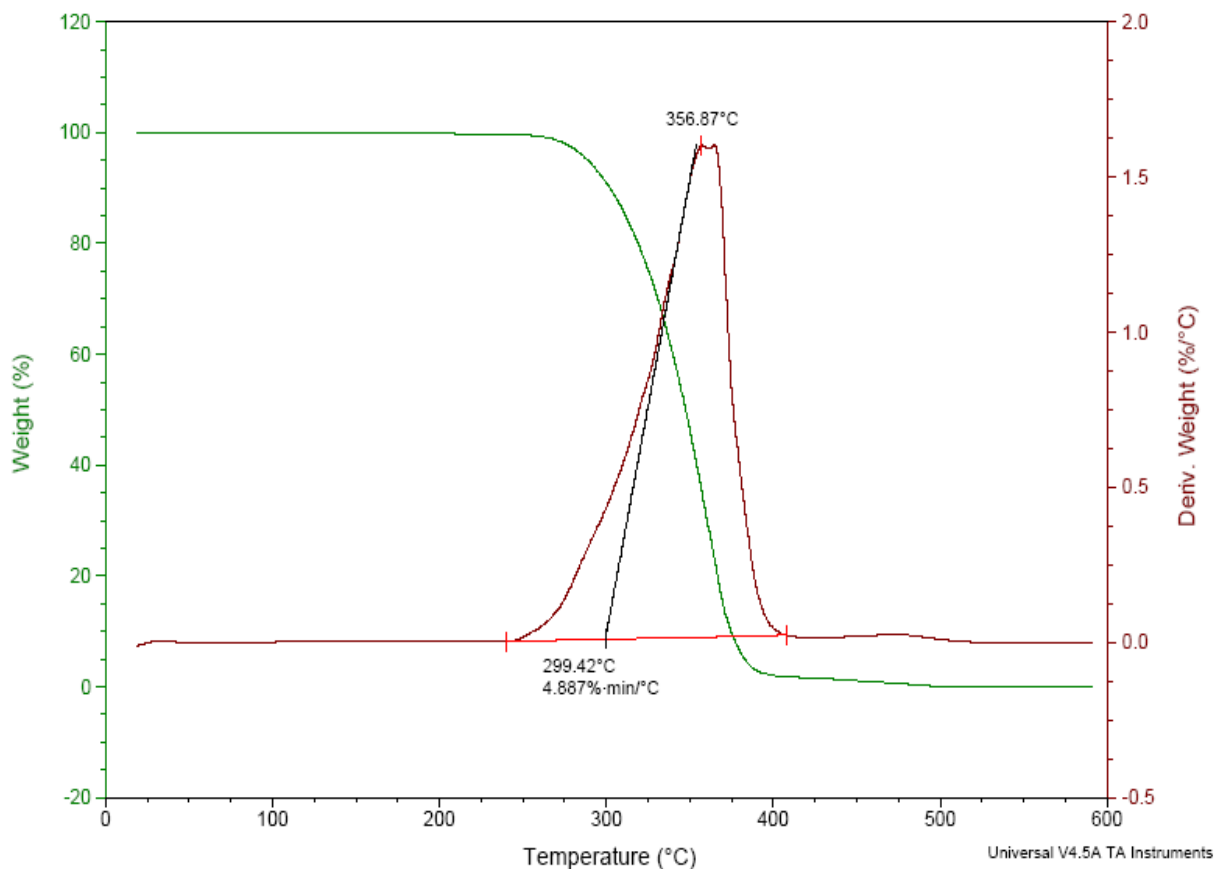


Figure 30. Determination of pure polypropylene monofilament's decomposition temperature

Figure 32 shows the effect of compatibilizer on decomposition behavior: all the samples with compatibilizers have higher decomposition temperature than pure polypropylene monofilament. However, the composite monofilaments have almost the same behavior which indicates that amount of compatibilizer may not have any significant effect on decomposition. The decomposition temperature of the compatibilizer (359.15 °C) is comparable to that of pure polypropylene (358.86 °C).

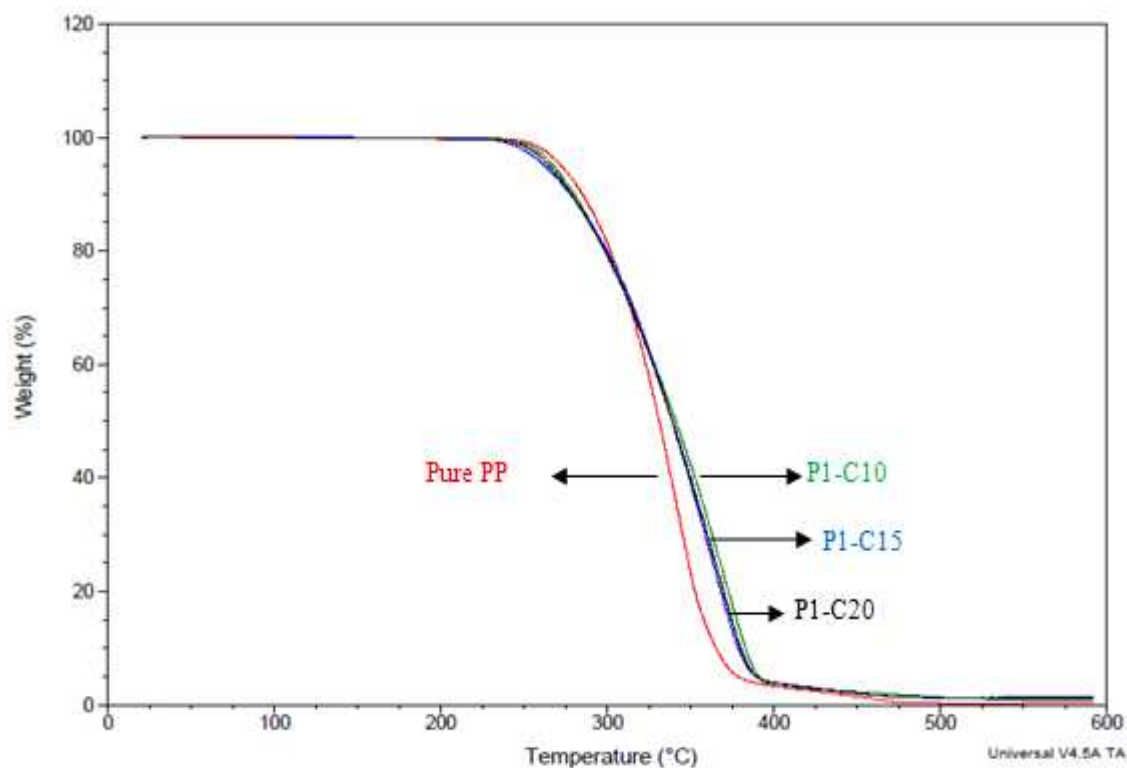


Figure 31. Decomposition behavior of pure and composite polypropylene monofilaments at different compatibilizer loadings

1.5. Mechanical Behaviors

Table 11 shows the tensile properties of pure and composite monofilaments. It was observed that addition of the nanoclay caused lower tensile properties. The reduction is almost 10 % at 3 % clay loading. Higher nanoclay containing samples showed more reduction compared to the lower ones. SEM results also indicate some agglomeration in the monofilaments. These agglomerated particles, which are in micron sizes, can reduce interaction between nanoclay and polymer matrix, and the result will be interfacial debonding under load. Besides, these particles can cause voids and act as a crack initiator under the load. Figure 32 shows the decrease in tensile stress of the pure and composite monofilaments.

Nanoclay particles are stiff materials with no elongation properties; therefore addition of these particles can lower elongation behavior of the monofilaments. Elongation at break values decreased in the presence of nanoclays except at 20% compatibilizer content as shown in Table 11. Samples containing 20% compatibilizer showed higher elongation properties compared to 10% and 15% ones. Compatibilizer might have contributed to the elongation values after certain amount of loading at composite monofilament manufacturing.

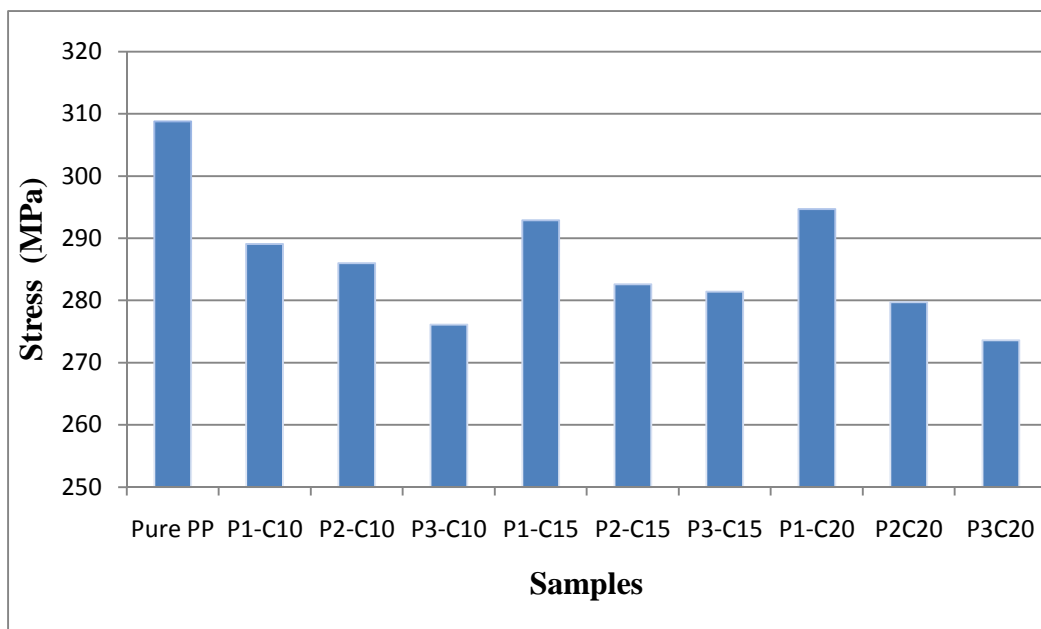


Figure 32. Tensile behavior of pure and composite monofilaments

2. Twin and Single Screw Extruder Results

2.1. Thermal Behavior of Pellets

First, the pellets (Figure 33), which were produced with the twin screw extruder, were analyzed. Table 12 shows some of the thermal properties of these pellets. It can be seen that melting temperature of the pellets decreased slightly by addition of nanoclay particles except P-A and P-B which do not contain any compatibilizers (Figures 34 and 35). As mentioned before, nucleating agent effect of nanoclay may be the reason for this small change. Crystallization temperature (T_c) of nanoclay contained pellets mostly showed reduction. However, pellets P-A and P-B had higher T_c than other pellets. This may be due to not having any compatibilizer in the system. The degree of crystallinity (X_c) was calculated according to the equation (1), and lower values were obtained for composite monofilaments except P-A-15, compared to the pure polypropylene pellets.



Figure 33. Polypropylene pellets after chopping

Table 12. Thermal behavior of pure polypropylene and nanoclay added pellets

Sample code	Melting temperature (°C)	Decomposition temperature (°C)	T _c (°C)	% X _c
PP	165.08	358.86	131.69	% 37.99
P-A-5	163.93	421.42	130.18	%36.84
P-A-10	164.52	425.75	130.68	%37.42
P-A-15	164.82	430.44	131.21	% 39.08
P-A	165.34	412.19	132.17	% 37.54
P-B	165.52	409.10	132.21	% 36.14
P-B-5	164.80	410.41	130.74	% 36.69
P-B-10	165.07	417.37	130.55	%35.55
P-B-15	164.62	429.68	130.70	%35.48

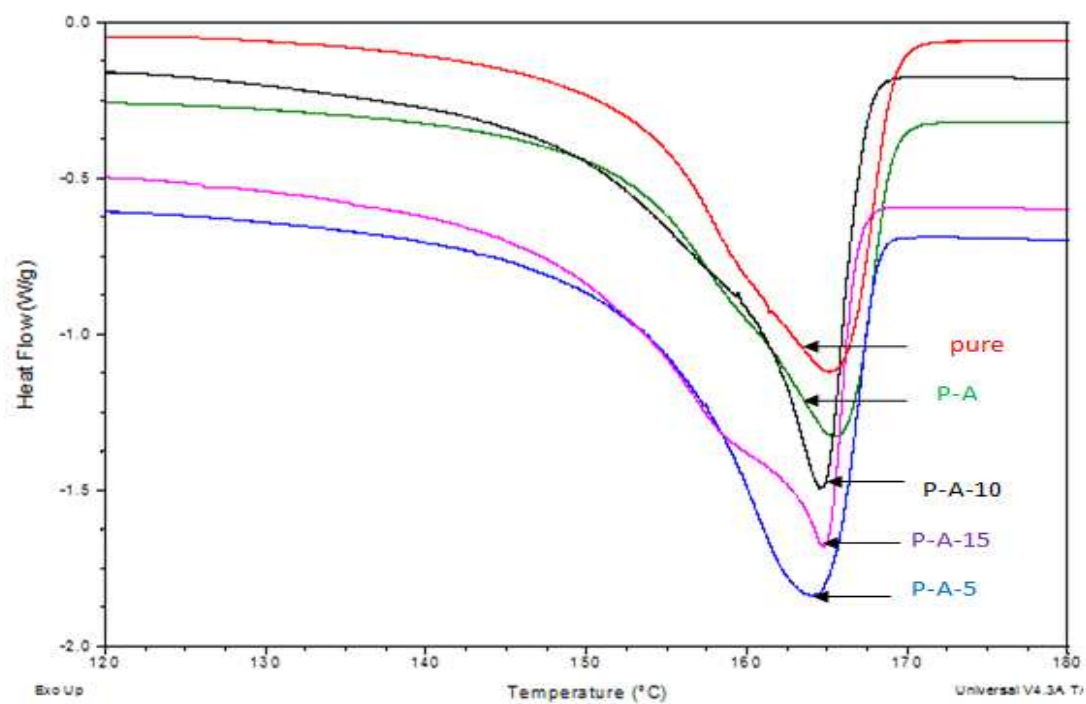


Figure 34. Melting temperature behavior of pure polypropylene and nanoclay (Cloisite 15A) added pellets

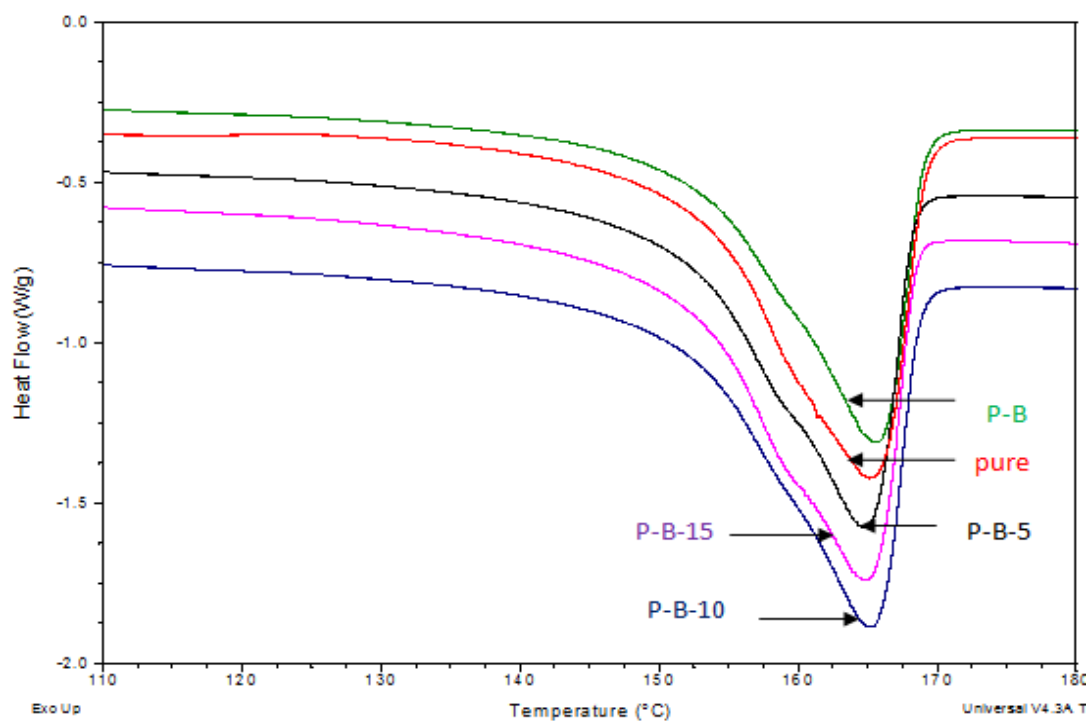


Figure 35. Melting temperature behavior of pure polypropylene and nanoclay (Cloisite 30B) added pellets

The decomposition temperature increased as shown in Figures 36 and 37 for the nanoclay added pellets. Cloisite 15A increased the decomposition temperature more than Cloisite 30B. This is probably due to better interaction occurred between Cloisite 15A and polypropylene polymer matrix compared to Cloisite 30B.

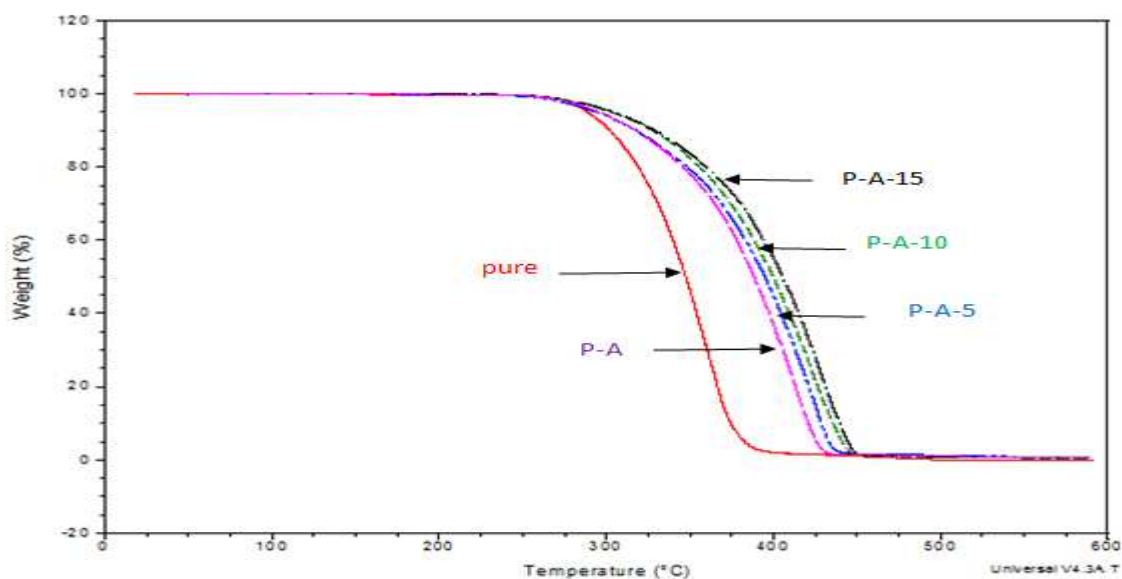


Figure 36. Decomposition behavior of pure polypropylene and nanoclay (Cloisite 15A) added pellets

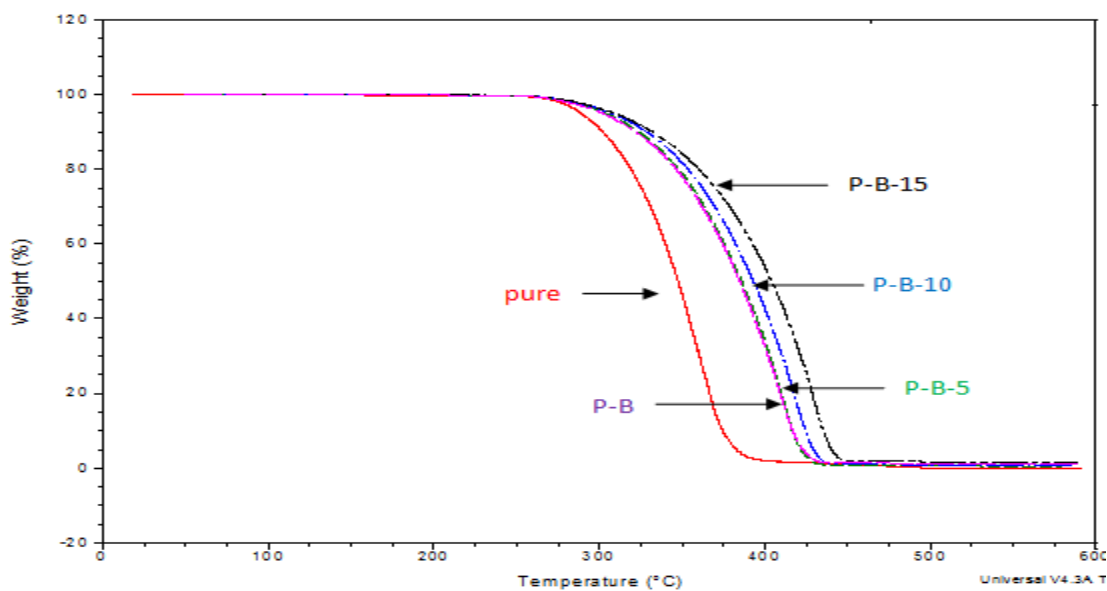


Figure 37. Decomposition behavior of pure polypropylene and nanoclay (Cloisite 30B) added pellets

2.2. Mechanical and Thermal Behavior of the Composite Monofilaments

After the pellets were chopped, they were used at single screw extruder to produce monofilament structures. Same machine settings were the same as in the previous experiments as can be seen in Table 7. Some of the mechanical and thermal test results are presented in Table 13.

Table 13. Thermal and mechanical properties of the composite monofilaments

Samples	Decomposition temperature (°C)	Tensile strength (MPa)	Elongation at break (%)
Pure PP	358.86	308.8	63.6
P-A-5	398.88	296.8	39.7
P-A-10	406.86	281.8	31.1
P-A-15	425.73	272.5	27.0
P-A	397.61	275.4	46.3
P-B	394.12	258.4	36.3
P-B-5	399.66	283.2	22.3
P-B-10	404.15	272.4	39.2
P-B-15	417.94	261.8	35.6

Figures 38 and 39 indicate the decomposition behavior of different nanoclay added monofilaments. Decomposition temperatures of the monofilaments were increased by addition of nanoclay compared to pure polypropylene monofilaments. Nanoclays are known as good heat insulators and therefore may have contributed to the thermal stability of the system. They may also behave as a wall to prevent the products from escaping the matrix and lower oxygen

penetration into the matrix. Different nanoclay added composite monofilaments showed different characteristics. Cloisite 15A enhanced the decomposition temperatures more than Cloisite 30B. This is probably better due to distribution and dispersion of Cloisite 15A obtained along the monofilaments.

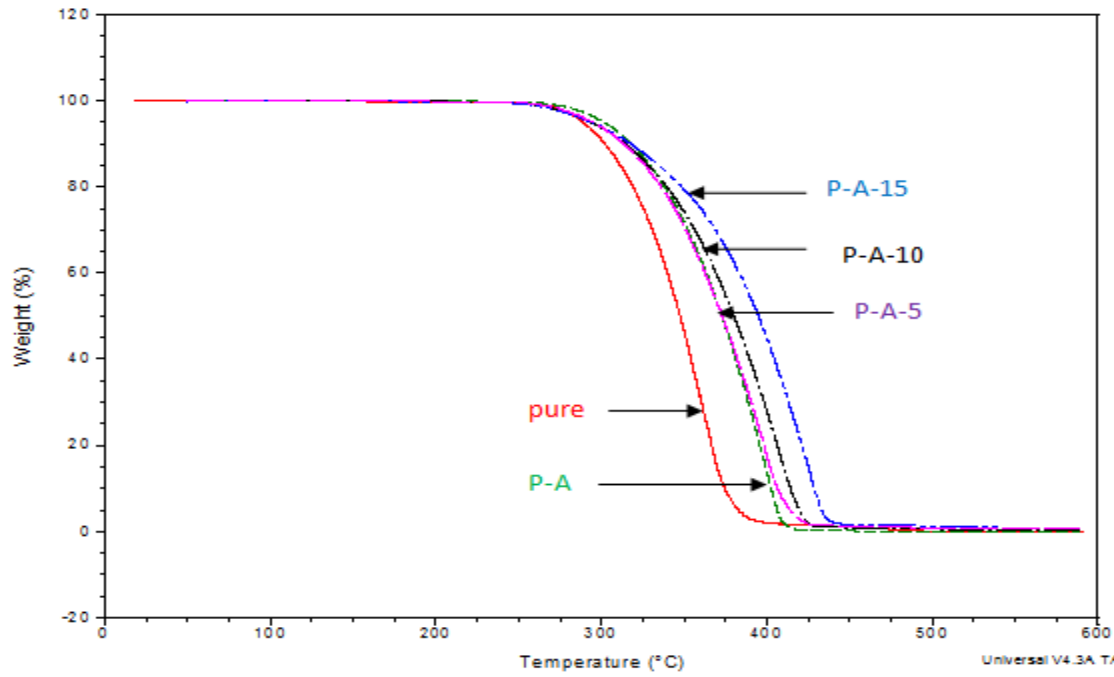


Figure 38. Decomposition behavior of pure polypropylene and nanoclay (Cloisite 15A) added monofilaments

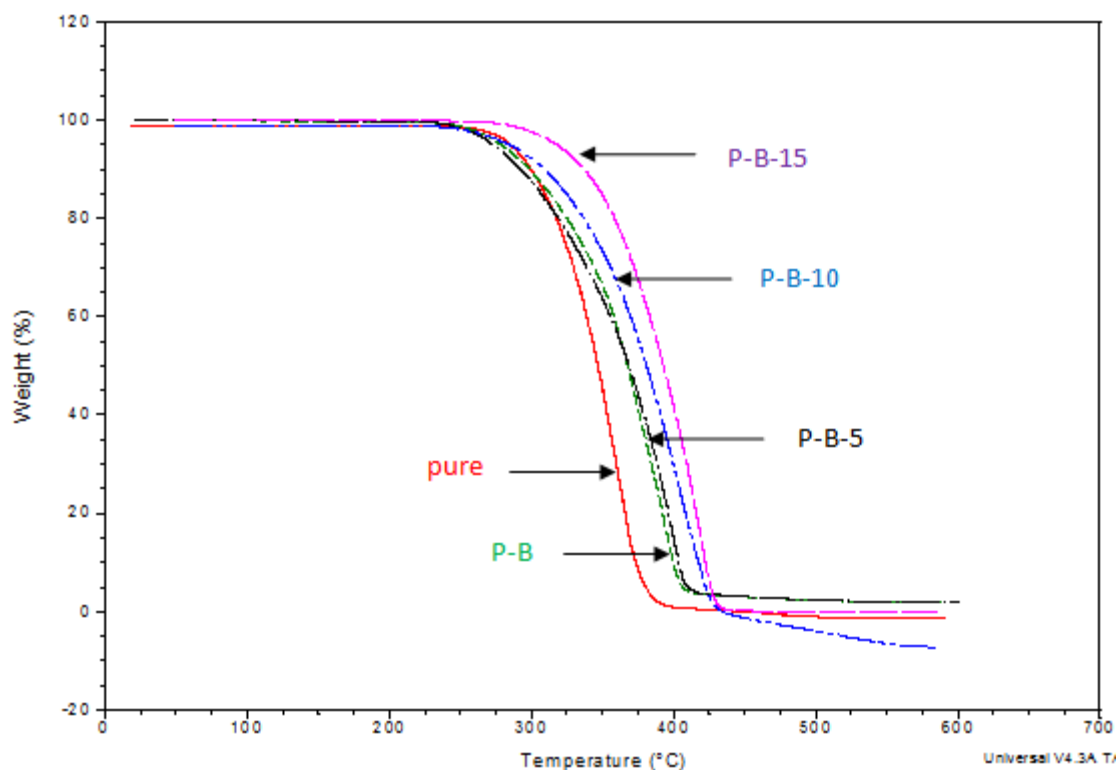


Figure 39. Decomposition behavior of pure polypropylene and nanoclay (Cloisite 30B) added monofilaments

Figures 40 and 41 show the tensile stress-strain behavior of composite filaments compared to pure polypropylene monofilaments. The tensile strength values decreased compared to the pure polypropylene monofilaments for all composite samples. This is probably due to interfacial debonding and incoherence between nanoclay particles and polymer matrix. Addition of more nanoclay caused more decrease as seen in Table 13. Cloisite 30B caused more reduction in tensile properties compared to Cloisite 15A. More agglomeration of Cloisite 30B or bigger dispersed particles in the system may cause this difference. Elongation values decreased compared to the pure polypropylene monofilaments because nanoclay does not have any elongation properties. The results also show that samples P-A and P-B, which do not have any compatibilizer, had lower tensile strength compared to the samples with compatibilizers. This is

probably due to more agglomeration, and lower interaction between the polymer matrix and nanoclay.

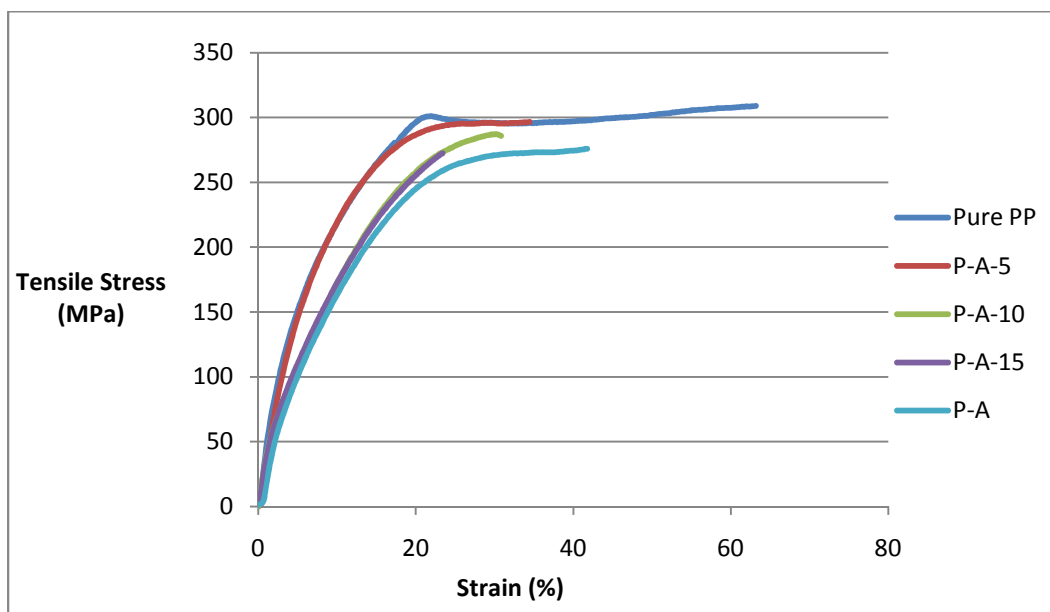


Figure 40. Stress-strain behavior of Cloisite 15A added composite and pure polypropylene monofilaments

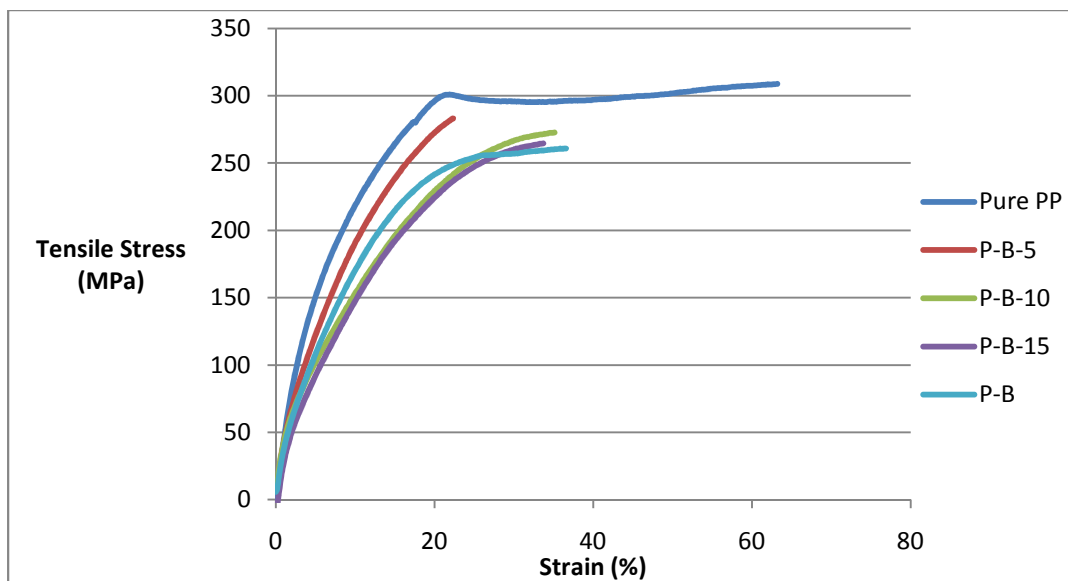
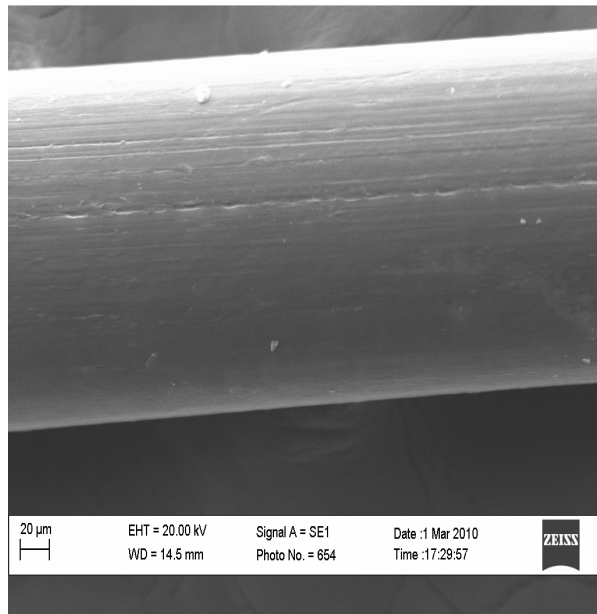
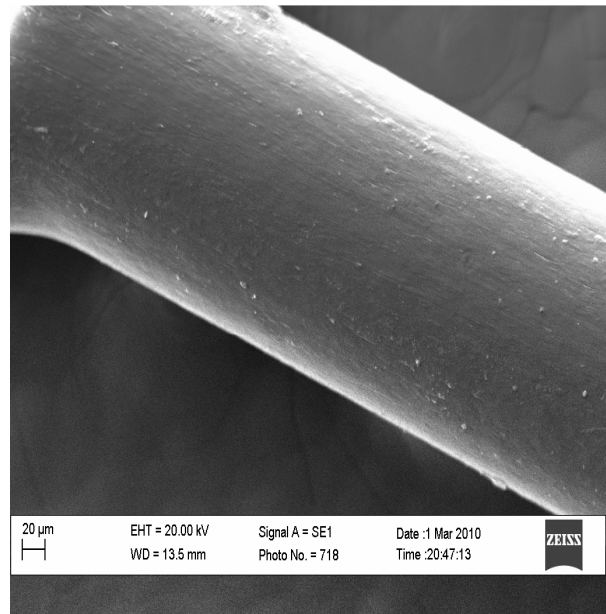


Figure 41. Stress-strain behavior of Cloisite 30B added composite and pure polypropylene monofilaments

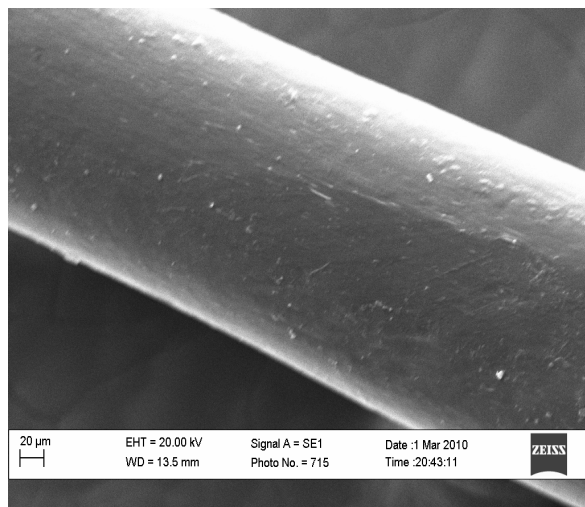
2.3. SEM Results of Composite Monofilaments



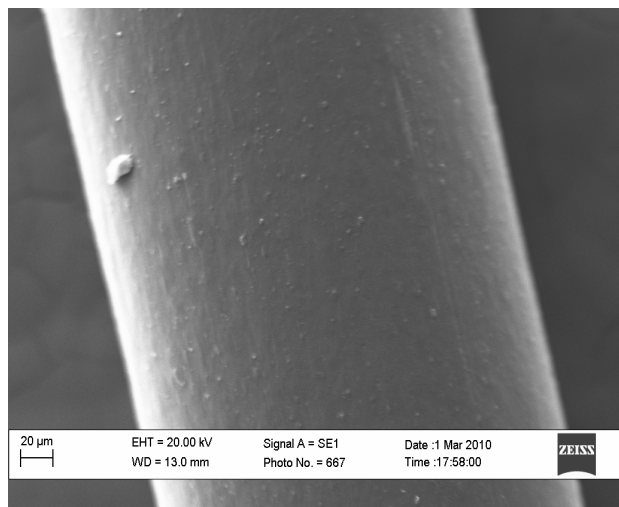
(a)



(b)

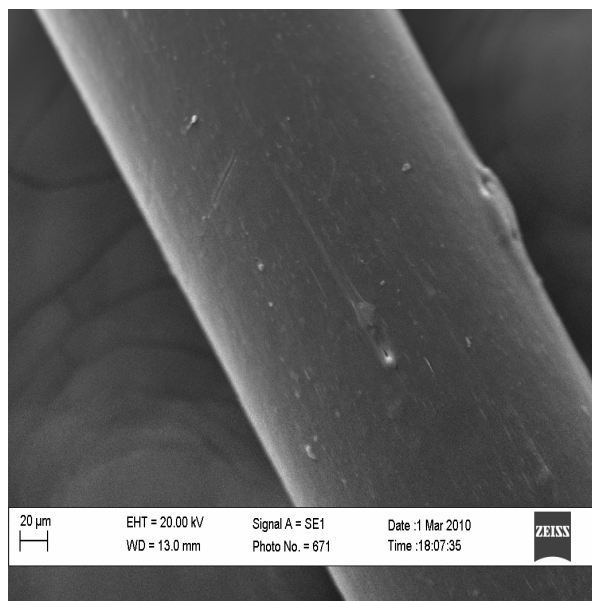


(c)

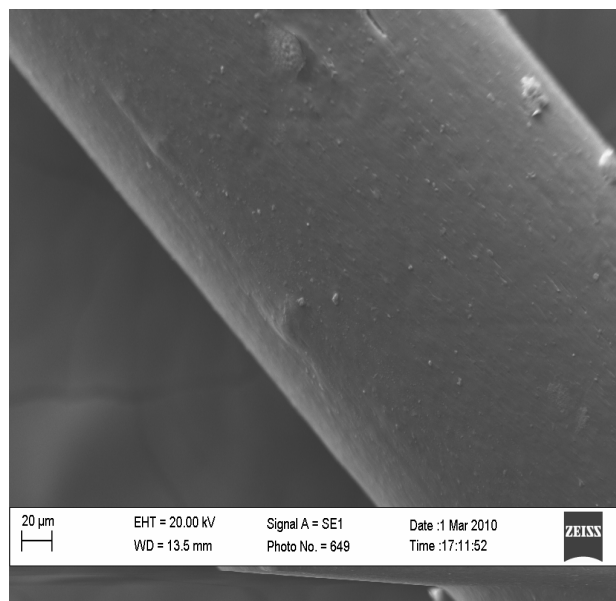


(d)

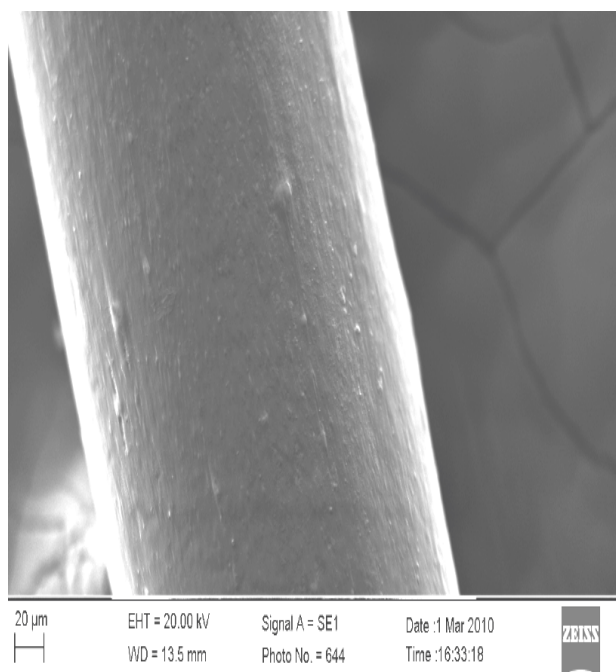
Figure 42. SEM surface view of: a) P-A-5, b) P-A-10, c) P-A, d) P-A-15



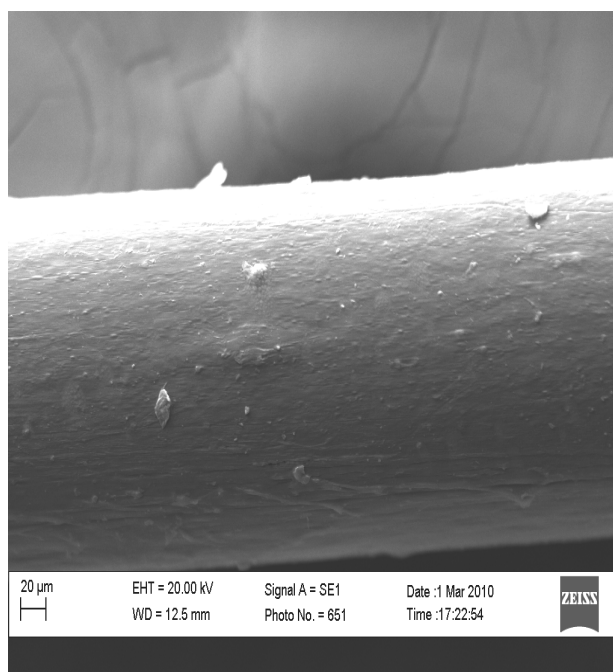
(a)



(b)



(c)



(d)

Figure 43. SEM surface view of: a) P-B-5, b) P-B-10, c) P-B, d) P-B-15

Figures 42 and 43 illustrate the SEM images of the composite monofilaments. Nanoclay distribution along the monofilaments seems quite uniform. It can be seen that monofilaments which contain 0.5% of nanoclay (sample P-A-5 and P-B-5) have smaller particles in their surfaces. Larger particles along the monofilament were achieved by addition of more nanoclay content (Fig 42-b-c-d and fig 43 b-c-d). These larger particles also caused lower tensile strength values compared to the smaller ones (Table 13). Probably bigger particles caused more voids and these voids made lower interaction between polymer chains. Figure 42 (b-c) and Figure 43 (b-c) can be used to evaluate the effect of compatibilizer on nanoclay distribution or particles sizes. Smaller particles were obtained along the monofilament (Figure 42-b) by addition of compatibilizer compared to the samples without any compatibilizer (Figure 42-c). The same result was also observed in Figure 43 (b-c). These results show that using compatibilizer helped for better dispersion of nanoclay particles. Particle sizes can be seen in Figures 44 and 45 for 0.5% nanoclay added composite monofilaments. There are particles less than 500 nm, however; there are larger particles at micron sizes (almost 3-4 microns in same monofilaments). These larger particles were formed probably by agglomeration of nanoclay layers during processing. Bigger particle sizes were achieved for monofilaments that contain Cloisite 30B; this might be the reason why monofilaments that contain Cloisite 30B have lower tensile strength than the ones with Cloisite 15A.

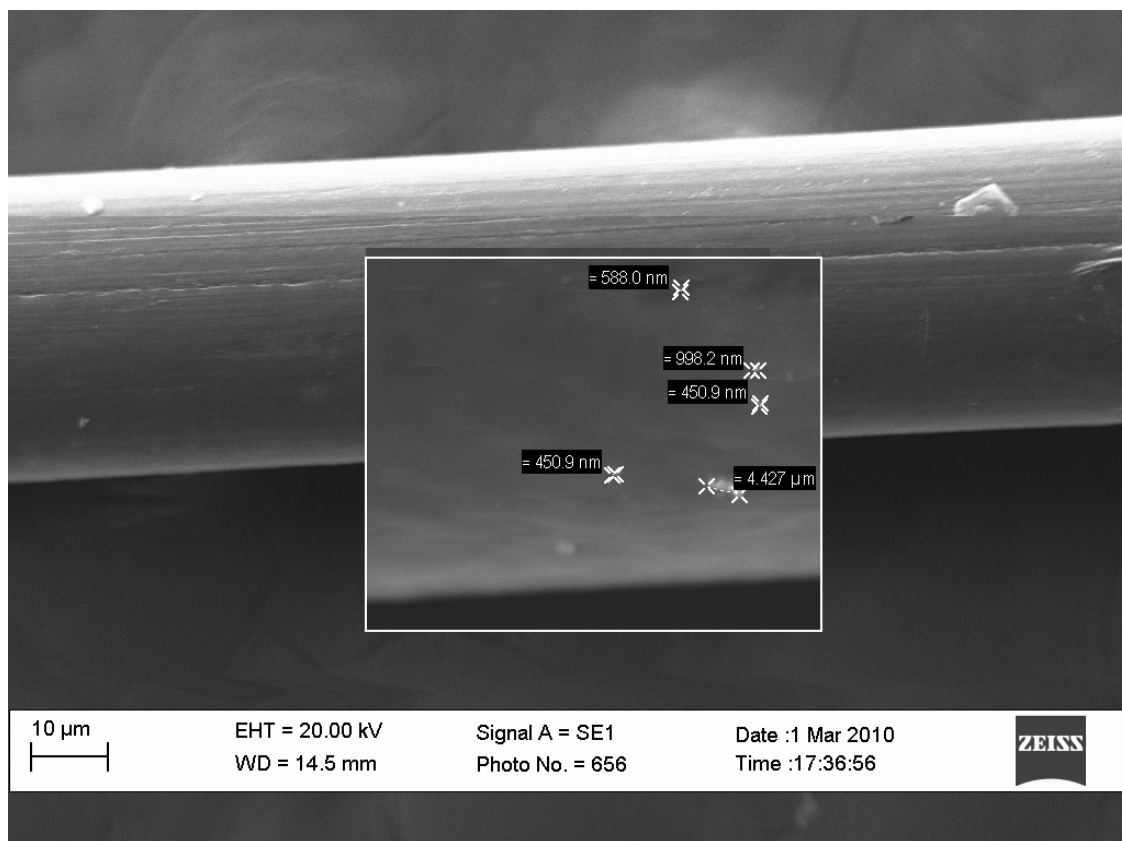


Figure 44. Particle size distribution of 0.5% Cloisite 15A added composite monofilament

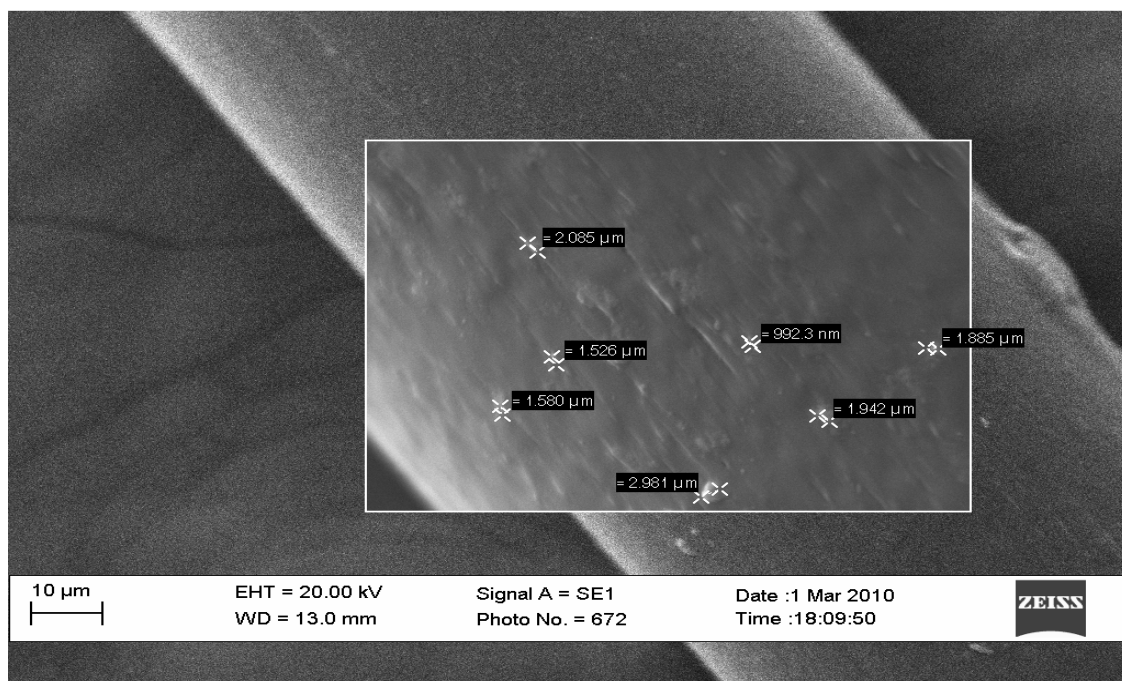


Figure 45. Particle size distribution of 0.5% Cloisite 30B added composite monofilament

CHAPTER 4

NANOCLAY AND POLYPROPYLENE MARKETS

1. Nanocomposite Market

Nanocomposite structures have been used at many industrial applications in recent years. Clay nanocomposites are the biggest market among all other nanocomposites (Table 14). Global consumption of nanocomposites has increased rapidly, reaching 23 million pounds in 2005, with an estimated value of \$252 million. By 2011, it is expected to reach almost 95 million pounds worth some \$857 million (Table 15) [61].

Table 14. Nanocomposite consumption by % (2005-2011) [61]

Year	Clay nanocomposites	Metal and metal oxide nanocomposites	Carbon nanotube composites
2005	24%	19%	15%
2011	44%	20%	11.5%

Table 15. Global consumption of nanocomposites (2005-2011) [61]

Year	Amount kg-millions (lb-millions)		Value (\$ millions)
2005	10.45	(23)	252
2011	43.18	(95)	857

The main nanocomposite applications areas were automotive parts, energy, and packaging in 2005, with market shares of 29%, 28%, and 19%, respectively. Other application areas were coatings (14%) and ESD (Electrostatic discharge) (8%) in 2005.

It is expected that packaging will be the leader in nanocomposite applications with over 28% of the market by 2011. Energy applications will be in second place with more than 26% of the market, and automotive applications will be the third-largest application with over 15% of the market, followed by coatings with 14% in 2011 [61].

2. Polypropylene Market

There was an increase in chemical fiber production compared to 2006 by 3.5 million tons or 8%, and to become 48.0 million tons in 2007. However, it decreased by 2.2 million tons or 6% to become 45.8 million tons in 2008. This increase occurred all around the world except China [62]. Table 16 shows chemical fiber production in 2007 around the world.

Table16. World chemical fiber production in 2007 [63]

Types of fibers and threads	Production, thousands of tons			2007/2006±%
	Complex fiber	Stable fiber and twist	Total	
Synthetic	23848	16536	40374	+7.9
Polyester	18253	12416	30670	+11.7
Polyamide	3633	353	3986	-1.1
Polypropylene	1543	1315	2858	-4.4
Polyacrylonitrile	-	2376	2376	-4.9
Other	420	66	468	+12.6
Cellulose	440	3273	3712	+9.0
Total	24288	19799	44037	+8.0

Table 17 shows global production of the most widely used synthetic fibers according to their manufacturing origins in 2007 and 2008. China is the biggest producer among all the countries. USA is also one of the biggest manufacturers with 1.2 million metric tons follows by India and Taiwan.

Table 17. Global production of synthetic fibers (1,000/kg tons) [64]

	Polyester			Polyolefins			Polyamide		
	2007	2008	%	2007	2008	%	2007	2008	%
W. Europe	677	566	-16	1,590	566	-11	451	415	-8
Turkey	401	339	-15	624	339	-8	51	41	-20
E. Europe	272	266	-2	190	266	-2	166	154	-7
USA	1,240	1,060	-15	1,298	1,060	-14	937	741	-21
Canada	-	-	-	86	73	-15	143	122	-15
Mexico	149	112	-25	87	81	-7	43	29	-33
S. America	311	273	-12	322	312	-3	104	96	-8
PR China	19,251	20,046	+4	1,053	997	-5	1,007	1,083	+8
India	2,272	2,090	-8	114	112	-2	95	90	-5
Taiwan	1,813	1,522	-16	171	158	-8	408	302	-26
Korea	1,245	1,157	-7	129	121	-6	145	131	-10
Japan	465	435	-6	179	176	-2	122	114	-7
Other Asia	2,709	2,536	-6	424	394	-7	145	131	-10
Others	290	248	-14	502	496	-1	76	63	-17
Total	31,095	30,065	-2	6,467	5,939	-8	3,891	3,512	-10

Table 18 reflects the global polyolefin fibers (polyethylene and polypropylene) production in 2008.

Table 18. Global production of polyolefin fibers (2008) [64]

	Yarns		Staple Fibers		Tapes		Total	
	1000	%	1000	%	1000	%	1000	%
	metric tons		metric tons		metric tons		metric tons	
W. Europe	678	-10	441	-13	229	-9	1,418	-11
Turkey	142	-16	31	-18	125	-2	298	-8
E. Europe	53	±0	44	-2	91	-1	187	-2
USA	611	-14	221	-17	284	-11	1,116	-14
Canada	28	-15	20	-13	25	-17	73	-15
Mexico	39	-2	12	-20	31	-3	81	-7
S. America	116	-5	36	-10	160	-1	312	-3
Asia	804		181		973		1,958	
- PR China	499	-6	81	-10	417	-4	997	-5
- Taiwan	68	-7	12	-25	78	-5	158	-8
- Japan	78	-4	53	±0	45	±0	176	-2
- Korea	58	-8	15	-6	48	-4	121	-6
- India	24	-17	6	-14	81	+4	112	-2
- Others	77	-13	14	-12	304	-5	394	-7
Africa	185	-3	58	-5	253	+1	496	-1
Total	2,656	-9	1,044	-12	2,239	-5	5,939	-8

In 2008, PP textile materials production was over 7 million tons which is almost 10% of the amount of natural and chemical fibers and yarns manufactured in 2007 [65]. It is expected that world PP consumption should reach 50 million of tons at 80-85% utilization capacities in 2010. Products obtained by injection molding (the combined increase here is estimated at 6.4%/year) and extrusion, will remain the fastest growing market for PP in the future; the share of these two sectors is 90-95% of PP processing [66].

Consumption of PP for extrusion (fibers, films, spunbond, yarn, etc.) in China is at 68% (app. 60% in the world average). Almost 2 million tons (25%) is used for woven textiles, 1.4 million tons (17%) for biaxially oriented films, and 1 million tons (12%) for rigid packing. In Europe, North America, and Japan 50% of the PP is used for injection molding, %23 is used for fiber production, and 15% for films, 8% extruded articles, 2% blow molding, and 2% for other purposes [66].

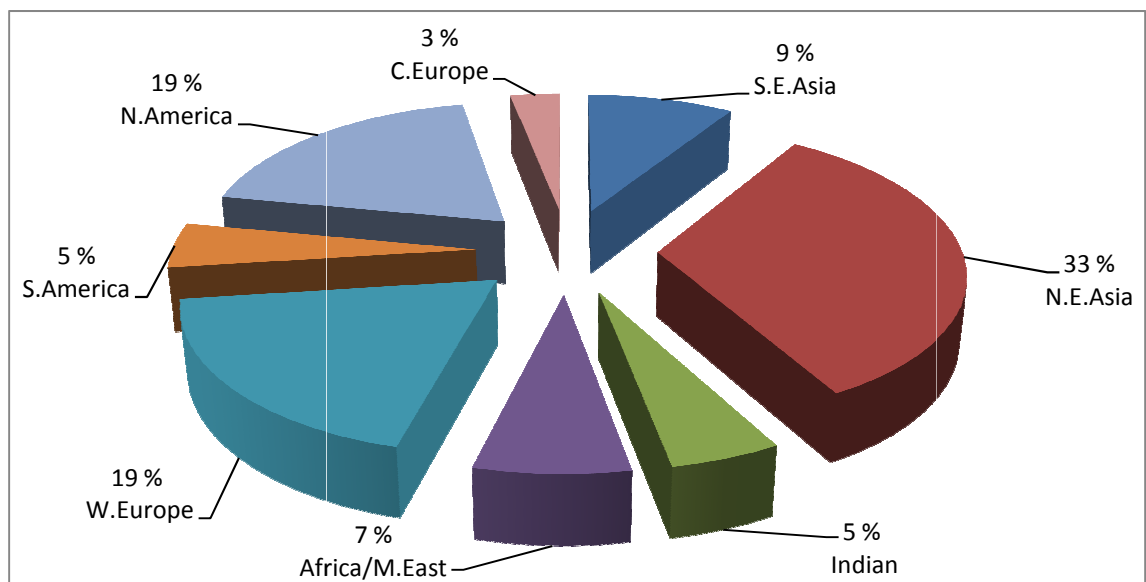


Figure 46. World polypropylene demand by region in 2009 [67]

Figure 46 shows the World polypropylene market, which indicates that Asia is still the biggest market (total 42%) and followed by N. America and W. Europe.

CHAPTER 5

CONCLUSIONS AND FUTURE RECOMMENDATIONS

Nanoclay added PP monofilament structures were successfully produced using twin and single screw extruder machines. Commercial nanoclays were used in this study. Draw-down ratio was set to 7. The formation of composite monofilament structures is affected by the amount of nanoclays, compatibilizers, and polarity of the polymer. It was more difficult to manufacture composite monofilaments with higher % nanoclay content because they caused more breakage during processing. There were mechanical and thermal changes in PP properties with the addition of nanoclays. Tensile strength decreased with the addition of nanoclays due to some agglomerated particles in the system. Decomposition temperature increased compared to pure polypropylene monofilament because of good heat insulation properties of nanoclays. Even if the tensile strength decreased, these monofilaments are still strong enough with higher decomposition temperatures and can be used in many industrial applications.

Proper mixing is very important to disperse nanoclays and compatibilizer uniformly during the process. More nanoclay dispersion can be achieved by increasing the space between clay layers and having higher shearing effect during processing. Monofilament production using both twin and single screw extruders was easier than only using single screw extruder. Less breakage occurred during processing because of having smaller nanoclay particles in the system.

For the future work, different types of polymers, rather than polypropylene, can also be used, and they may provide different compatibility with nanoclays. Besides, different

nanoparticles such as carbon nanotubes or metal particles added composite monofilaments can be produced to achieve different final properties using twin and single screw extruders.

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