

**MICROCRYSTALLINE CELLULOSE-FILLED ENGINEERING
THERMOPLASTIC COMPOSITES**

By

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By Alper Kiziltas

Thesis Advisor: Dr. Douglas J. Gardner

An Abstract of Thesis Presented
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The overall objective of this study was to investigate the influence of microcrystalline cellulose (MCC) filler loading on the mechanical and thermal properties of MCC-filled engineering thermoplastic composites. MCC and engineering thermoplastics (nylon 6 and a polyethylene terephthalate (PET)/polytrimethylene terephthalate (PTT) blend) were chosen as the filler/matrix combination. Engineering thermoplastic composites have attracted much interest over the past several decades due to potentially superior material properties and a wide range of applications such as in automotive, electrical and aerospace materials. MCC is thermally stable compared to other wood constituents and has the advantage of high specific surface area in comparison with conventional cellulose fibers. Because of these properties, MCC can use as a filler in polymer matrices.

Differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA) were used to determine thermal

properties of the composites. Infrared Spectroscopy (diffuse reflectance infrared Fourier transform (DRIFT)) was also used to identify chemical differences between the neat PET-PTT blend and MCC filled composites. The DSC results indicated that there was not a significant change in the glass transition (T_g) or melting temperature (T_m) of the nylon 6 and PET/PTT blend with the addition of MCC. With increasing MCC content, dynamic mechanical properties improved because of the reinforcing effect of the MCC. The TGA data show that as the MCC filler loading increased, the thermal stability of the composites decreased slightly because of the lower thermal stability of MCC compare to neat nylon 6 and PET/PTT blend. Thermogravimetric analysis also indicated that the MCC did not show significant initial degradation under 300°C, which implies thermal stability so that MCC-filled composites could be used for high temperature circumstances, like in “under the hood” applications in the automobile industry. No significant chemical changes were observed in the DRIFT spectra of the composites.

Tensile, flexural and impact tests were used to evaluate the mechanical properties of the composites as well as determining the composite densities. The composites reinforced with higher MCC filler loadings displayed enhanced tensile and flexural properties in comparison with the neat nylon 6 and PET/PTT blend. The Izod impact strength of the composites decreased in comparison with the neat nylon 6 and PET/PTT blend. The density of the composites increased slightly with increased MCC loading.

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BACKGROUND/MOTIVATION

Many materials, including inorganics and organics such as glass fibers, carbon fibers and wood flour, are currently used as fillers in thermoplastic composites. These organic and inorganic fillers can increase stiffness, decrease thermal expansion, improve long term mechanical performance and reduce cost of composite materials (Chen and Gardner 2008). Over the past several decades, interest in the development of new composite materials derived from wood fiber and thermoplastic polymer matrices has received remarkable attention in the marketplace. Wood fiber-filled thermoplastic composites are lightweight, low cost, offer high strength to weight ratios, are less abrasive to processing equipment than mineral and glass fillers and can be recycled (Chen and Gardner 2008; McHenry and Stachurski 2003). In spite of these attractive properties, wood fiber-filled thermoplastic composites have some challenges. These challenges are moisture and high processing temperatures (Azizi Samir et al. 2005). Moisture can cause complications during the compounding process especially polyamide-based composite production (Chen and Gardner 2008). The processing temperature of these composites is restricted to about 200°C because the hemicellulose components of wood fibers degrade above 180°C and the melting temperature of selected plastics should not be over 200°C, which restricts the use of engineering thermoplastics such as polyamides and polyesters (Chen and Gardner 2008; Azizi Samir et al. 2005; Jacobson et al. 2001; Sears et al. 2001; Sears et al. 2004). Although thermogravimetric analysis studies of wood component polymers show that the purified cellulosic component is

thermally more stable than other wood component polymers, the earliest reports, which attempted to use cellulose flour and cellulosic fibers to reinforce engineering thermoplastic (polyamide 6), exhibited severe discoloration and pronounced pyrolytic degradation (Jacobson et al. 2001). Because of these initial experiments, the common belief is that wood/natural fiber as reinforcement is limited to low melting commodity thermoplastics such as PE, PP and PVC (Sears et al. 2001). Moreover, it has been commonly believed that the engineering thermoplastics, which have higher melting temperatures, are not suitable for wood/natural fiber-filled plastic production (Caulfield et al. 2001)

1.1. Overview of the Project

1.1.1. Why Engineering Thermoplastics and Microcrystalline Cellulose?

Engineering thermoplastic composites have attracted a great deal of interest over the last decades as a result of the potentially superior properties (excellent chemical resistance, high thermal stability, low creep compliance and high tensile, flexural and impact strength) and wide range of industrial and consumer applications such as automotive, electrical and aerospace applications. These materials can also show relative properties to commodity plastic composites (Field 2003). In spite of the attractive properties of engineering thermoplastics, there is limited information related to cellulose-filled engineering thermoplastic composites in the literature. Microcrystalline cellulose (MCC) is a naturally occurring substance and crystalline cellulose obtained from high

quality wood pulp (Azizi Samir et al. 2005; Mathew et al. 2004). MCC has the advantage of high specific surface area and thermally stable structure in comparison with other conventional cellulose fibers and can be used as a cellulosic reinforcement for polymer matrices (Mathew et al. 2004). The physical and chemical characteristics of MCC versus other cellulosic fibers are summarized in Table 1.1 (Mathew et al. 2005; Kothari et al. 2002; Andersson et al. 2003; Oporto et al. 2009). MCC has been incorporated into a number of different matrices including poly (lactic acid) (Mathew et al. 2004; Petersson and Oksman 2006), polystyrene (Laka and Chernyavskaya) and polyethylene (Maskavs et al. 1999; Maskavs et al. 2001; Panaitescu et al. 2007a; Panaitescu et al. 2007b]. However, there is lack of information about MCC-filled engineering thermoplastics in the literature.

Table 1.1 MCC versus other cellulosic fillers

Characteristics	MCC	CF	WF
Appearance	Particles	Single fibers	Fiber Bundles
Surface topography	Rough	Smooth	Rough
Crystallinity (%)	70-85	30-60	25-35
Particle size/diameter (μm)	10-15	20-30	150-750
Surface energy (mJ/m^2)	54	49	38

1.1.2. Project Motivation

The automobile and construction markets need high specific strength and modulus, low density and inexpensive reinforcements for engineering thermoplastics. Because of this demand, researchers have examined cellulose-filled engineering thermoplastics recently (Xu 2008). Polymer composites with cellulose fibers are materials with unique properties compared to inorganic materials. The main advantages of cellulose is its renewable nature, high specific strength and modulus (the elastic modulus for cellulose whiskers is about 145 GPa while that of glass fibers averages about 70 GPa), low density ($\sim 1.6\text{g/cm}^3$ for cellulose and $\sim 2.5\text{g/cm}^3$ for glass fiber) compared to materials reinforced by inorganic substances, low thermal conductivity and a possibility of recycling (Azizi Samir et al. 2005; Goodrich 2007; Eichhorn et al. 2001; Starcova et al. 2005). Because of the high surface area and thermally stable structure of MCC, it could be a good candidate as reinforcement for engineering thermoplastics.

1.1.3. Objectives

The main objective of this research is to develop a method to process low cost, low density and high specific strength and modulus composites using melt blending followed by injection molding of MCC-filled nylon 6 and MCC-filled polyethylene terephthalate (PET)-polytrimethylene terephthalate (PTT). The specific objectives in this study can be summarized as follows.

- To develop methods and procedures for the melt blending of MCC and nylon 6, and MCC and PET-PTT blend on the bench scale.
- To evaluate the mechanical and thermal properties of these composites using different test methods.

It is expected that a large synergetic effect will be present between the MCC and engineering thermoplastic polymer matrices. The synergy is expected to obtain essential properties for engineering thermoplastic applications.

1.2. Structure of Thesis

In this thesis, the production of engineering thermoplastic composites is described. The effect of the filler loading of MCC on the properties of nylon 6 and PET/PTT blends are investigated. A general overview of natural fiber-filled engineering thermoplastic composites is given chapter 2. In general, the properties of filler-reinforced thermoplastic composites are mostly affected by the size, shape, aspect ratio and volume fraction of reinforcements, degree of crystallinity of the matrix, filler agglomeration, compatibility of composite components and processing parameters (Mathew et al. 2005). This thesis is basically divided into two parts. Part I deals with engineering thermoplastic composites based on MCC-filled PET/PTT blends and Part II on MCC-filled nylon 6.

1.2.1. Engineering Composites Based on MCC-filled PET/PTT Blends

In chapter 3 the effects of MCC loading on the thermal properties of PET/PTT was investigated. The thermal properties were studied by means of dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The degree of crystallinity of the engineering composites was also determined by means of DSC. In addition, infrared spectroscopy (Diffuse reflectance infrared Fourier transform (DRIFT)) was used to identify chemical differences between the neat polymer blend and MCC-filled PET/PTT composites. In chapter 4 the mechanical properties of MCC-filled PET/PTT blends were studied using mechanical tests including tensile, flexural and impact test and density measurements.

1.2.2. Engineering Composites Based on MCC-filled Nylon 6

The ever increasing interest in engineering thermoplastics was the impetus for the research presented in chapter 5 addressing the manufacture of nylon 6 composites containing MCC filler. The composites were prepared using melt blending followed by injection molding. The thermal properties of the composites were investigated by DMTA, DSC and TGA. Chapter 6 covers the mechanical properties of MCC-filled nylon 6 composites. In chapter 7 general conclusions and recommendations for future studies are presented.

1.3. Economic Feasibility of MCC filled Engineering Composites

It is possible to estimate the cost of different blends of MCC-filled engineering thermoplastic composites (Rowell 1998). Cost of different loading levels of MCC filled engineering composites are shown Table 1.2 (The plastic web 2009)

$$\$/lb = \frac{ETP(X) + MCC(Y) + L(Z) + C}{E}$$

Where: \$/lb is the product cost in dollars per pound, ETP is the percent of engineering plastic in composite, X is the estimated cost of the engineering plastic in cents per pound, MCC is the percent of MCC filler in the composite, Y is the estimated cost of the MCC filler in cents per pound, L is the percent of lubricant in the composite, Z is the estimated cost of the lubricant in cents per pound, C is the cost of compounding in cents per pound, and E is the efficiency of operation.

Example for 20% MCC-filled Nylon 6 composites

If ETP for Nylon 6 = 75%; X = 1.50; MCC = 20%; Y = 1.81; L = 5%; Z = 1.2; C = 0.20, and E = 1 Then \$/lb is \$1.748.

Example for 20% MCC-filled virgin PET-virgin PTT blend composites

If ETP for PET-PTT Blend = 75% (50% PET: 25%PTT): X = (0.67 for PET; 0.87 for PTT): MCC = 20%; Y = 1.81; L = 5%; Z = 1.2; C = 0.20, and E = 1 Then \$/lb is \$1.175.

Example for 20% MCC-filled Recycled PET-virgin PTT blend composites

If ETP for Recycled PET-PTT Blend = 75% (50% PET: 25%PTT): X = (0.40 for PET; 0.87 for PTT): MCC = 20%; Y = 1.81; L = 5%; Z = 1.2; C = 0.20, and E = 1 Then \$/lb is \$1.041.

Table 1.2 Costs of different loadings of MCC-filled engineering composites.

Composite	Cost (\$/lb)
Neat Nylon 6 ^a	1.685
Nylon 6 – MCC2.5	1.692
Nylon 6 – MCC10	1.716
Nylon 6 – MCC20	1.748
Nylon 6 – MCC30	1.779
R ^{bc} Nylon 6	0.403
R Nylon 6 – MCC2.5	0.444
R Nylon 6 – MCC10	0.569
R Nylon 6 – MCC20	0.735
R Nylon 6 – MCC30	0.902
Neat PET/PTT ^d	0.961
PET/PTT – MCC2.5	0.987
PET/PTT – MCC10	1.068
PET/PTT - MCC20	1.175
PET/PTT - MCC30	1.284
R ^e PET/PTT	0.791
RPET/PTT – MCC2.5	0.821
RPET/PTT – MCC10	0.915
RPET/PTT - MCC20	1.041
RPET/PTT - MCC30	1.167

a: cost of nylon 6 is \$1.5/lb; b: R means recycled; c: cost of recycled nylon 6 is \$0.15/lb;

d: costs of PET and PTT are \$0.67/lb and \$0.87/lb; e: cost of recycled PET is \$0.4/lb.

1.4. References

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NATURAL FIBER-FILLED ENGINEERING THERMOPLASTIC COMPOSITES

The earlier research related to natural fiber-filled engineering thermoplastics did not give encouraging results. Materials exhibited severe discoloration and pronounced pyrolytic degradation because of the high melting point of engineering plastics (Caulfield et al. 2001a; Jacobson et al. 2001; Sears et al. 2001; Snijder et al. 1997). It is difficult to obtain high melting temperature polymer/natural fiber composites by conventional extrusion and injection molding processing because of the severe thermal degradation of the natural fibers that occurs at temperatures needed to process these composites. Therefore, there is lack of information about natural fiber-filled engineering thermoplastic composites (Xu 2008; Caulfield et al. 2001a). The automobile and construction markets need low density and cheap reinforcement for engineering thermoplastics. Because of this demand, researchers have recently looked again at cellulose-filled engineering thermoplastic (Xu 2008).

2.1. Thermoplastic Polyesters

Thermoplastic polyesters, including polyethylene terephthalate (PET) polytrimethylene terephthalate (PTT), polybutylene terephthalate (PBT), poly1,4-cyclohexylenedimethylene terephthalate (PCT) are important polymers and high-performance engineering plastics used in industry and are widely used in many areas including the textile, electronics, automotive industries, etc (Liang et al. 2007; Liang et al

2008; Wei et al. 2005; Son et al. 2002; Chen et al. 2007; Ge et al. 2007; Brink 2003). Of these, PET is the best known and the most studied thermoplastic polyester in the literature. The advantages of PET are a low material cost and higher strength and temperature resistance in comparison with other thermoplastic polyesters (Brink 2003). In spite of these attractive properties, PET has some disadvantages including slower crystallization rate and relative sensitivity to drying conditions. Slower crystallization rate and drying problems of PET can be improved with the proper addition of PTT which has similar mechanical properties and a lower heat deflection temperature (Brink 2003).

2.1.1 Natural Fiber-Filled Engineering Thermoplastic Polyester Composites

In 1997, Snijder et al. used flax, hemp and spruce fibers as reinforcing agents in a PBT matrix processed at 260°C. They found that the flexural modulus and strength increased with these fibers. They also did additional experiments with whiteners and successfully produced whitened composites without negatively affecting the mechanical properties. This finding indicates that discoloration is not an issue. As a result, their study suggests that natural fibers can be used as reinforcing agents in engineering thermoplastic composites (Snijder et al. 1997). In 2001, Caulfield et al. used cellulosic fibers as reinforcing agents in an aliphatic polyketone, which is identified in their research as ethylene-carbon-monoxide (ECM) and has a reported melting point of 220°C, and PBT matrices using low temperature processing techniques. They reported that these composites had stiffness and bending strength properties that were intermediate between

similar composites prepared with wollastonite and glass fiber composites without using any compatibilizers and other additives (Caulfield et al. 2001b).

2.2. Polyamides

Nylon 6, 7, 8, 9, 11, 12 and 66 are important polyamides and engineering plastics in industry (Garcia 2004). Of all these nylons, nylon 6 and nylon 66 are the best known and the most studied nylon types in the literature (Chavarria and Paul 2004). Nylon 6 and nylon 66 differ in terms of thermal, mechanical and structural properties. The glass transition temperature and melting temperature of nylon 66 are higher than nylon 6. Nylon 66 has a triclinic crystal structure while nylon 6 has a monoclinic crystal structure. The tensile modulus of nylon 66 is slightly lower than nylon 6 (Chavarria and Paul 2004). As a result, due to several advantages including good chemical resistance, good abrasion resistance, and good mechanical and thermal properties, nylon 6 and nylon 66 are widely used in many areas such as automobile and textile industries (Chavarria and Paul 2004; Fornes and Paul 2003).

2.2.1 Natural Fiber-Filled Engineering Polyamide Composites

Lower processing temperature and lower melting temperature by adding inorganic salts are two methods to get natural fiber-filled engineering thermoplastic composites (Xu 2008). In 2001, Jacobson et al. developed a unique compounding method called low temperature compounding to produce cellulose pulp fiber-filled nylon 6 composites.

They found that mechanical properties for the 33 percent cellulose fiber-filled nylon 6 composites were approximately twice as stiff as neat nylon composites, and had better strength properties than the neat nylon. The 33 percent cellulose fiber-filled nylon composites were also intermediate between approximately the same percent glass fiber and wollastonite, which are extensively used in the automobile industry as fillers. They also found that the density, color and surface appearance of these injection-molded materials appear suitable for some automobile applications (Jacobson et al. 2001). In another study, Misra et al. 2004 used small quantities of lithium chloride (LiCl) during melt extrusion processing to decrease the melting temperature of nylon 6. They determined that the addition of LiCl to nylon 6 also decreased the crystallization temperature and degree of crystallinity. They also demonstrated that both tensile modulus and strength increased with reinforcement of modified nylon 6 with 40% hemp fiber (Xu 2008; Misra et al. 2004).

The fiber/matrix interface and their adhesion properties can affect the processing and final properties of engineering thermoplastic composites. In 1994, Ramirez et al studied cellulose and nylon 66 blends. According to their study, each homopolymer, cellulose and nylon 66, was separately dissolved in a mixture of N-methyl morpholine N-oxide and phenol (80/20/w/w). Then, two solutions were mixed together. According to their studies, ^{13}C nuclear magnetic resonance indicates that the molecular mobility of nylon 66 is reduced by the presence of cellulose in comparison with neat nylon 66. In addition, elongation at break of blends was higher than for pure cellulose. Dynamic mechanical measurements also showed that part of the cellulose is homogeneously mixed

with amorphous nylon 66. As a result, they concluded that strong adhesion at the interface exists between cellulose and PA 66 in the blends prepared from solution (Ramirez et al. 1994; Ramirez et al. 1995). From a review of the literature, compatibilizers/coupling agents may increase mechanical properties of composites. Chen et al. used a coupling agent with carboxyl groups to increase compatibility between thermomechanical wood pulp and nylon 6. According to their study, strength and stiffness properties of the composites increased with coupling agent. They also observed that strength and stiffness properties of composites were lower than neat nylon 6 without coupling agent (Chen et al. 2004; Xu 2008).

In 2008, Xu studied cellulose-filled engineering thermoplastics with different production methods. Xu found that for cellulose fiber-filled nylon 6 and cellulose-filled nylon 66 composites, extrusion-injection molding gave better mechanical properties than extrusion-compression molding and low temperature extrusion exhibited better properties than high temperature extrusion. Xu also found that strength and stiffness of cellulose-filled nylon 6 composites increased with the increasing fiber content in the extrusion-injection molding system. On the other hand, Xu examined the effect of different plasticizers/modifiers (N-butylbenzenesulfonamide (NBBSA), LiCl and international technical polymer systems inc. (ITPS) claimed their product INTEC SB 94, which is a metallic complex based on oxides of Titanium, Aluminum and Magnesium, on the mechanical properties and processing temperature of cellulose-filled nylon 66 composites. Xu showed that 3%INTEC SB 94/3%NBBSA/3LiCl/nylon 66 gave better properties because it decreases the processing temperature and cooling time during

injection molding (Xu 2008). There is a lot of research focused on the thermal properties of filled engineering thermoplastics in the literature. Since there are few reports about natural fiber-filled engineering thermoplastic composites, there is a lack of information about the thermal properties of natural fiber filled engineering thermoplastics in the literature. In 2008, Chen and Gardner studied dynamic mechanical properties of extruded nylon-wood composites. They found that the storage modulus and thermal stability of the nylon is improved with addition of wood flour. They also found that aging affects are reduced by wood flour. They concluded that nylon-wood composites would be suitable in thermally challenging areas such as the manufacture of under-the-hood automobile components because of improved thermal and aging properties (Chen and Gardner 2008).

2.3. Conclusions

Latest studies showed that using natural fibers (cellulosic fibers) as reinforcing agents in engineering thermoplastics gave better mechanical properties in comparison with neat polymers. Studies also indicate that natural fiber reinforced engineering thermoplastic composites may also have potential for high temperature circumstances (under the hood applications in automobile industry) and structural applications instead of glass and wollastonite fillers. The engineering thermoplastic composite materials to be developed using MCC are expected to have significantly improved mechanical and thermal properties of composites compared to neat polymers.

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THERMAL PROPERTIES OF MCC-FILLED PET/PTT BLEND POLYMER COMPOSITES

3.1. Chapter Summary

Polymer composite materials were prepared from poly (ethylene terephthalate) (PET)/poly(trimethylene terephthalate) (PTT) blends as the matrix and different microcrystalline cellulose filler levels (0 to 40 weight percent) using melt compounding followed by compression molding. The composites were analyzed using dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The DSC results indicated that there was not a significant change in the glass transition (T_g), melting (T_m) and crystallization temperature of the composites with the addition of MCC. With increasing MCC content, dynamic mechanical properties improved because of the reinforcing effect of the MCC. The $\tan \delta$ peak values from the dynamic mechanical thermal analysis were not significantly changed as the MCC content increased. Thermogravimetric analysis indicated that the onset temperature of rapid thermal degradation decreased with increasing MCC content. It was also found that the thermal stability of the composites slightly decreased as the MCC content increase. No significant chemical changes were observed in the DRIFT spectra of the composites.

3.2. Introduction

Cellulose is among the most abundant natural, renewable and biodegradable materials in the world and can be obtained from many sources. It has been predicted that 10^{10} and 10^{11} tons of cellulose are produced and destroyed each year in the world (Helbert et al. 1996; Azizi Samir et al. 2005). Over the last few decades, interest in producing polymer composite materials with cellulose materials has received considerable attention (Petersson et al. 2007; Panaitescu et al. 2007a; Bondeson et al. 2006; Goodrich 2007; Panaitescu et al. 2007b). Polymer composites with cellulose fibers are materials with unique properties compared to inorganic materials. The main advantages of cellulose is its renewable nature, high specific strength and modulus (the elastic modulus for cellulose whiskers is about 145 GPa while that of glass fibers averages about 70 GPa), low density ($\sim 1.6\text{g/cm}^3$ for cellulose and $\sim 2.5\text{g/cm}^3$ for glass fiber) compared to materials reinforced by inorganic substances, low thermal conductivity and a possibility of recycling. In addition, because of the non biodegradability of most plastics, disposal is a significant challenge. As a solution, industrial and scientific research communities have shown great interest in blending plastic materials with natural biopolymers such as wood flour, cellulose and starch (Azizi Samir et al. 2005; 2006; Goodrich 2007; Panaitescu et al. 2007b; Sturcova et al. 2005; Eichhorn et al. 2004).

Synthetic and natural polymers are exposed to degradation under the effect of increased temperature. Therefore, it is extremely important to have information about the effect of the processing temperatures in regards to processing duration because thermal

stress can occur during the manufacturing of natural fiber reinforced composite materials with thermoplastic matrices (Wielage et al. 1999). Essential information regarding the thermal stability of the natural and synthetic polymers can be obtained by thermal analysis, which is based on analytical experimental techniques that measure thermal behaviors and interfacial characteristics of composite materials as a function of temperature (Wielage et al. 1999; Kim et al. 2005; Kim et al. 2006). The following techniques are often used for thermal analysis. Differential Scanning Calorimetry (DSC) can be used to determine melting temperature (T_m), glass transition temperature (T_g), crystallization temperature (T_c) and crystallinity (X_c) of composite materials, and is the easiest and most widely used thermal analysis technique in the world. Dynamic mechanical thermal analysis (DMTA) has become widely used and is an important technique in terms of determining the viscoelastic properties of composite materials for investigating their dynamic material behavior such as storage modulus (E) and loss factor ($\tan \delta$) as a function of temperature. Thermogravimetric analysis (TGA) can be used for determining the moisture content, thermal degradation temperature and thermal stability of composite materials (Kim et al. 2005; Kim et al. 2006). Infrared Spectroscopy (DRIFT) is a technique which yields both physical and chemical information about composite materials (Buckton et al. 1999). In the present study, infrared spectroscopy was used to identify chemical differences between the neat polymer blend and MCC filled composites.

Composite materials made from thermoplastic resins (polyethylene and polystyrene) and MCC have been studied (Panaitescu et al. 2007; Laka et al. 1996;

Maskavs et al. 1999; Maskavs et al. 2001). MCC is a purified, partially depolymerized cellulose, prepared by treating alpha-cellulose, obtained as a pulp from fibrous material with mineral acids and it used extensively in pharmaceutical, food, paper and the composite manufacturing industries (Azizi Samir et al. 2005]. The application of engineering thermoplastic polymer composites with MCC is limited by the lack of information about morpho-structural aspects and the behavior of such materials when mechanical and thermal stresses are applied. Aromatic polyesters, including PET, and PTT are important polyesters and high-performance engineering plastics used in industry and are widely used in many areas including the textile, electronics, automotive industries, etc (Liang et al. 2007; Liang et al. 2008; We et al. 2005; Son et al. 2003; Chen et al. 2007; Ge et al. 2007). In recent years, many researchers have been interested in blends or copolymers to increase the crystallization rate of PET or improve the mechanical and thermal properties of PTT (Liang et al. 2007; Liang et al. 2008; We et al. 2005; Son et al. 2003; Chen et al. 2007; Ge et al. 2007). In the present study, PTT was used to reduce the processing temperature and increase the crystallization rate of PET (Liang et al 2007). Liang et al., found that PET/PTT blends showed a single composition-dependent glass transition temperature and cold crystallization peak over all compositions, suggesting that PET and PTT were miscible in the amorphous state. Polymer miscibility of blends is determined by measuring their glass transition temperature (T_g) from DSC scans. In general, for immiscible blends, two or more T_g s generally appear in a DSC scan indicating phase separation whereas for miscible blends or copolymers only one T_g is observed in the amorphous phase (Liang et al. 2007).

The aim of this study was to investigate the effect of microcrystalline cellulose on the thermal properties of the PET/PTT composites. Microcrystalline cellulose was incorporated over a content ranging from 0 to 40 weight percent. Analyses were conducted using thermal tests including DMTA, DSC, TGA and FTIR. Thermal stability was also compared using the derivative thermogravimetric curve temperature (DTGmax), viscoelastic behavior (storage modulus (E') and loss factor ($\tan \delta$)) melting temperature (T_m), glass transition temperature (T_g), crystallization temperature (T_c) and crystallinity (X_c) of the neat PET/PTT blend and composites. In the present study, PET/PTT based composites were prepared with microcrystalline cellulose as the filler phase by thermal mixing followed by compression molding.

3.3. Experimental Procedures

3.3.1. Materials

The PET and PTT were supplied as homopolymer pellets by Shell Co. and Azom Co., USA respectively. The PET and PTT had densities of 1.3-1.4 and 1.35 g/cm³ and melt flow indices of 0.65 and 0.92 dl/g, respectively. The lubricant (TPW 113) used as an additives to improve processing conditions, was supplied by Struktol Co. The MCC used as the reinforcement was a powder with a particle size range from 26 μ m to 96 μ m. The average particle size was 50 μ m. The MCC is highly crystalline cellulose supplied by Sigma Aldrich Co. The MCC was stored in sealed containers after being oven dried for at least 16 hours at 105°C to obtain low moisture content which is less than 1 percent.

3.3.2. Sample Preparation

The MCC, PET and PTT, were dried until the moisture content reached less than one percent using an oven set at 105°C for 16-hrs. The matrix polymer PET/PTT blends were mixed with the MCC. The compounding was conducted using a Brabender Prep-mixer® equipped with a bowl mixer and the process temperature and torque changes were measured in real time. Melt temperature and torque changes for every run were recorded to determine optimum processability for the PET/PTT blend - MCC composites. The basic processing parameters are listed in Table 3.1. The mixer temperature was set to 270°C and the polymer melt temperature decreased to 230°C where the polymer blend appeared to experience good melting. The revolutions per minute (RPM) of the mix blades were increased from 60 to 70 so that the generated shear might facilitate polymer melting. MCC was added to the mixer when the polymer melt appeared well mixed. After addition of the MCC, the melt temperature dropped sharply to 200° C. and increased again as the mixing progressed. The melt mixture was released from the mixture immediately after the temperature reached 230° C. These temperature ranges and MCC residence times were recognized as a relatively safe temperature range to prevent severe thermal degradation with a guarantee of composite processability. The PET/PTT- MCC compounds were granulated using a lab scale grinder. The ground particles were dried at an oven at 105°C for 16 hours and placed on a steel mold heated up at 230°C. The mold was compressed at 60 tons for 5 minutes using 2'x 2' hot press and then cooled at the same pressure before release from the mold. Then the compressed panel samples were

continuously cooled down at room temperature. The compositions are shown in Table 3.2.

Table 3.1 Basic operating parameters of the brabender rheomixer for PET/PTT Blends.

Stage Level	Operating Parameters				
	Set Temp.	Melt Temp.	RPM	Mix Melt Temp.	Reaction Time
1 st stage (PET/PTT)	270	260	60-70	-	7 min
2 nd stage (with MCC)	230	200-230	50	Cont. under 230	2 min

Table 3.2 Composition of MCC-filled PET/PTT composites.

Sample Code	Compositions			
	MCC Contents	PET	PTT	Lubricant
Neat PET/PTT	0	63	32	5
PET/PTT – MCC2.5	2.5	61.5	31	5
PET/PTT – MCC5	5	60	30	5
PET/PTT – MCC10	10	56.5	28.5	5
PET/PTT - MCC20	20	50	25	5
PET/PTT - MCC30	30	43	22	5
PET/PTT - MCC40	40	37	18	5

Values are percentage by weight (wt. %)

3.3.3. Thermal Properties

DSC analysis was carried out using a Perkin Elmer Instrument Pyris DSC with a sample weight of 8 to 10 mg. Each sample was scanned from 30 to 300°C at a heating rate of 20°C/min and then cooled at the same rate under a nitrogen atmosphere to observe the T_m

taken as the peak temperature of the melting endotherm, T_g taken as the inflection point of the specific heat increment at the glass-rubber transition and crystallization behaviors of the composites. In addition, melting temperature and glass transition temperature were determined from a second scan. The specimens' relative degree of crystallinity (X_c) was calculated according to the following equation (Azizi Samir et al. 2004)

$$X_c = (\Delta H_f \times 100) / (\Delta H_f^\circ \times \omega)$$

where ΔH_f is the heat of fusion of the PET/PTT blend and composites, ΔH_f° the heat of fusion for 100% crystalline PET ($\Delta H_{100}=117.6$ J/g) and ω is the mass fraction for PET/PTT blends in the composites (Lee et al. 1999). At least three randomly picked specimens from ground samples were tested for each composition, and the results are presented as an average for tested samples.

The viscoelastic properties of the composites were determined using a Rheometric Scientific DMTA IV. The experiments were conducted in three point bending mode under isochronal conditions at a frequency of 1 Hz. The strain amplitude was fixed at 0.01% to be in the domain of the linear viscoelasticity of the composites. The composite materials were sawn into small strips on a vertical milling machine using a 1.45 mm x 75 mm, 36 tooth blade, attached to an arbor. The samples were cut in rectangular shape with dimensions about 42 mm x 3.2 mm x 1.8 mm. The temperature range was from -50 to 150°C at a scanning rate of 3°C/min. The storage modulus (E'), loss modulus (E'') and loss factor ($\tan \delta$) of the samples were measured as a function of temperature. At least three specimens were tested for each composition, and the results are presented as an

average for tested samples. TGA measurements were carried out using a Mettler Toledo analyzer on samples of about 10 mg. Each sample was scanned over a temperature range from room temperature to 600°C at heating rate of 10°C/min under nitrogen with a flow rate 20 ml/min to avoid sample oxidation. The samples used for the TGA measurement were randomly picked 5 individual samples from ground samples. The infrared spectra of the composites were obtained using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy on a Perkin Elmer Spectrophotometer equipped with a diffuse reflectance (DRIFT) cell. Approximately 250 mg of the composite mixture, which was composed of sample from composites ($\approx 15\text{mg}$) and KBr (≈ 235), was poured into a sample holder. The sample holder with sample and a second sample holder filled with pure KBr as the background were placed in the spectrometer and first background analyzed over the range of $400\text{--}4000\text{ cm}^{-1}$ under nitrogen atmosphere with a spectrum resolution 4 cm^{-1} and 200 scans total were combined. After obtaining the background spectra, composite samples were analyzed under the same experimental conditions.

3.4. Results and Discussion

3.4.1. Differential Scanning Calorimetry (DSC)

The effect of the microcrystalline cellulose on the thermal properties of the thermoplastic polymer composites was examined in non-isothermal DSC experiments. The values of glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c) and corresponding melting enthalpies (ΔH_m) and crystallization

enthalpies (ΔH_c) are presented in Table 3.3. The DSC thermograms of heating and cooling course of PET/PTT blend and composites are presented in Figure 3.1. The glass transition temperature provides important evidence for blend miscibility. If the blend is one phase, only one glass transition temperature is evident, and it could be concluded that two different polymers were miscible. If the blend is two phases, two glass transition temperatures are evident and it can be concluded that the blend is not miscible (Liang et al. 2007).

Table 3.3 Summary of T_g , T_m , T_c , ΔH_m (J/g), ΔH_c (J/g), and X_c for the MCC-filled PET/PTT blend composites.

Sample Code	Thermal Compositions					
	T_g (°C)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	ΔH_c (J/g)	X_c (%)
Neat PET/PTT	68.1 (0.1)	249.2 (0.2)	186.6 (2.6)	37.1 (1.4)	-52.2 (2.7)	31.5 (1.1)
PET/PTT – MCC2.5	68.4 (0.7)	244.9 (0.1)	186.3 (0.7)	34.9 (0.4)	-51.7 (1.1)	30.5 (0.3)
PET/PTT – MCC2.5	68.1 (1.1)	247.5 (0.5)	182.8 (0.2)	33.4 (0.5)	-49.2 (2.5)	30.0 (0.4)
PET/PTT – MCC10	68.3 (0.7)	248.1 (0.9)	183.8 (0.9)	31.9 (1.1)	-47.8 (1.7)	30.1 (1.0)
PET/PTT – MCC20	68.5 (0.2)	248.6 (0.9)	192.3 (0.9)	28.9 (1.5)	-44.9 (1.9)	30.7 (1.6)
PET/PTT – MCC30	68.8 (0.5)	249.3 (1.8)	194.4 (1.1)	26.6 (1.1)	-41.8 (1.6)	32.2 (1.3)
PET/PTT – MCC40	67.9 (1.4)	249.6 (1.1)	195.3 (0.4)	21.4 (0.5)	-35.7 (2.2)	30.2 (0.7)

Parenthesis indicates standard deviation.

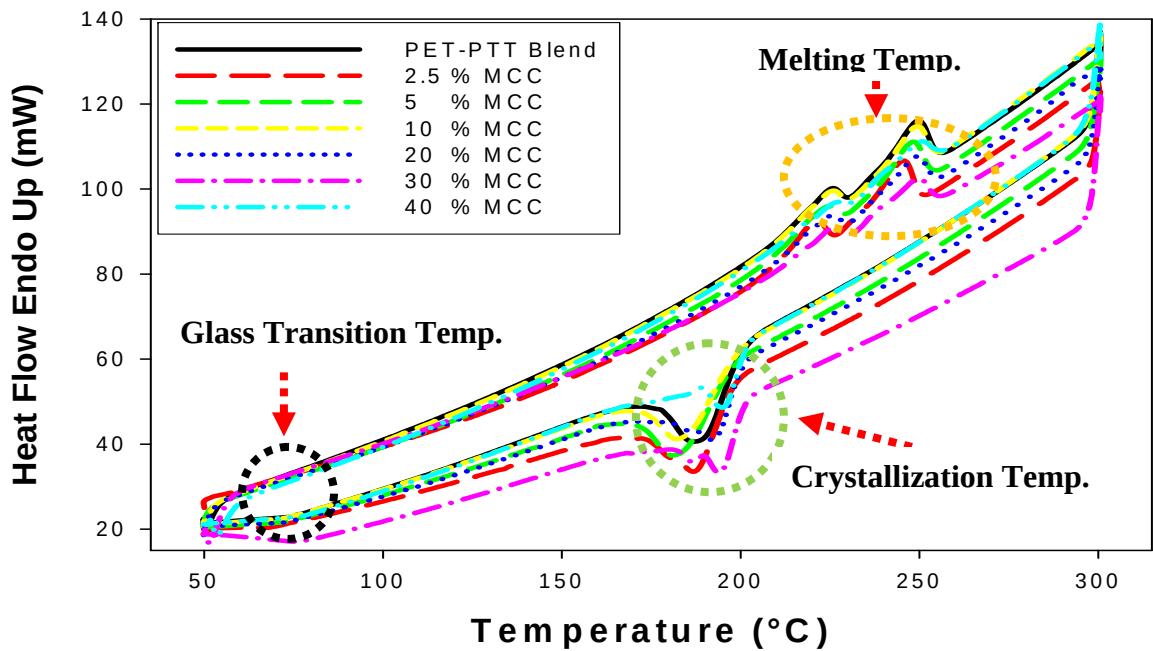


Figure 3.1 The DSC thermograms of heating and cooling course of PET-PTT blend and MCC- filled PET-PTT composites.

In Figure 3.1, all composites showed only one T_g value and the T_g values of composites are between 67 and 69°C and as MCC loading increased, the T_g of the composites slightly changed, but only marginally in Figure 3.2. Figure 3.2 also shows that there is not a good correlation between T_g obtained from DSC and DMTA. T_g by DMTA, loss factor ($\tan \delta$) measurements can differ by up to 25°C from DSC measurements (Wunderlich 2005).

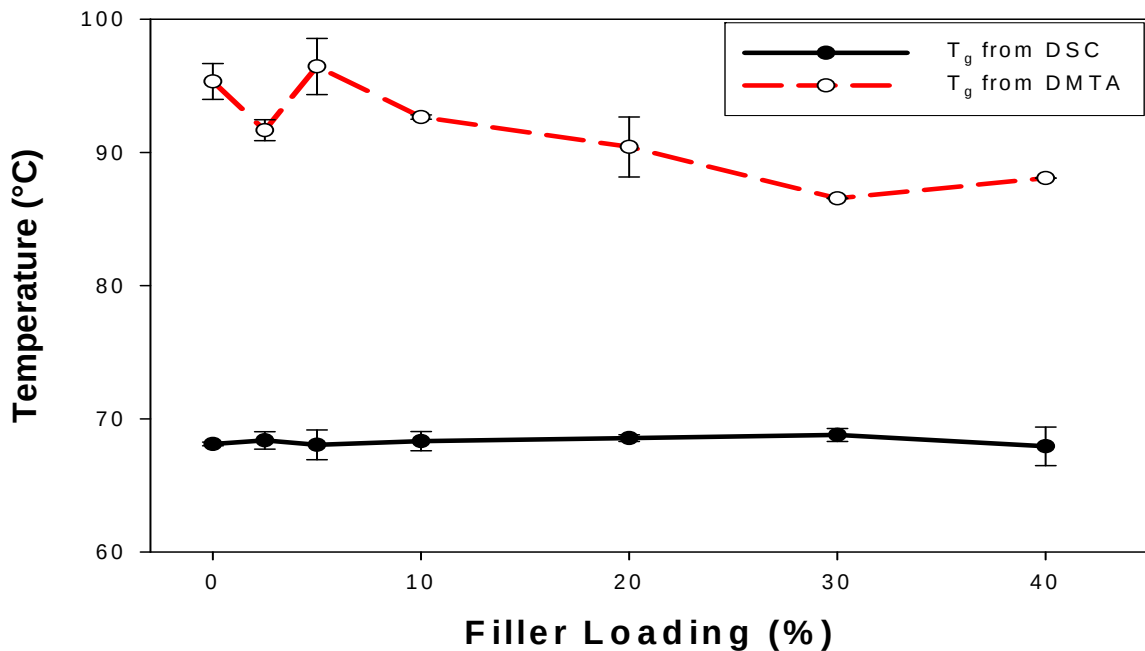


Figure 3.2 Tan $\delta_{\max}$ peak temperatures from DMTA and glass transition temperatures from DSC of the PET-PTT Blend and MCC-filled PET-PTT composites at different filler loadings.

Another evidence for miscibility is cold crystallization (Liang et al. 2007). Figure 3.1 showed only one cold crystallization temperature which is between 125 and 135°C for all composites. The single T_g and cold crystallization temperature shows that the PET-PTT blend and composites are compatible in the amorphous phase. This implies that no chemical bonding occurs at the interface between the matrix polymer and MCC. In other words, the MCC is physically encapsulated by the melted matrix polymer and physically inhibits the mobilization of the polymer chain. If interfacial adhesion such as chemical bonding were to occur between the matrix polymer and MCC, the T_g of the thermoplastic polymer composites would be substantially changed compared with that of the neat PET-PTT composites (Liang et al. 2007; Liang et al. 2008; Ge et al. 2007). The PET-PTT blend and MCC filled composites displayed similar thermograms and small

differences in their melting temperatures were within the experimental precision of the equipment. The melting point was taken as the main peak of the endothermic curve. Dual melting peaks can be observed from all composites. Because of melting peaks associated with the destruction of the crystalline region of polymer blend, the two melting peaks suggest that the chain segments of PET and PTT tend to crystallize in their crystal phase (Ge et al. 2007). The larger melting peak is associated with the PET because of its higher content in the composite blend. It can be seen for Figure 3.1 that the melting point of PET and PTT is about 250 and 225 °C, respectively. The effect of MCC on T_m of the composites is presented in Figure 3.3. It can be seen for the Figure 3.3 that the melting points of composites are between 244°C and 250°C. The addition of the MCC to composite has only a marginal effect on the melting temperature and no correlation of the results with the MCC loading can be established. This result means that the presence of the MCC does not affect the T_m of the composites. From these results, it can be concluded that the T_g and T_m values of the composites were strongly influenced by the matrix polymer. Furthermore, the T_m of the composites plays an important role in determining their processing temperature and thermal properties (Kim et al. 2005; Kim et al. 2006). Figure 3.3 also shows that the crystallization temperatures of PET/PTT blend and composites. Figure 3.3 illustrates that adding MCC does not change the crystallization temperature of the composites or it has a slight effect at most. However, increasing the MCC content in the composite, in all cases, results in smaller crystallization enthalpies (ΔH_c) and melting enthalpies (ΔH_m) (Table 3.3). A reason for this is that polymer chain mobility is hindered in highly filled composites. The degree of crystallinity of the composites was calculated using the heat of fusion determined from DSC measurements

and the one corresponding to a 100% crystalline PET reported by Lee et al (Lee et al. 1999]. These values are reported in Table 3.3. For low loading contents of MCC up to 30 wt%, the values are quite constant but after 30 wt%, crystallinity is slightly changed.

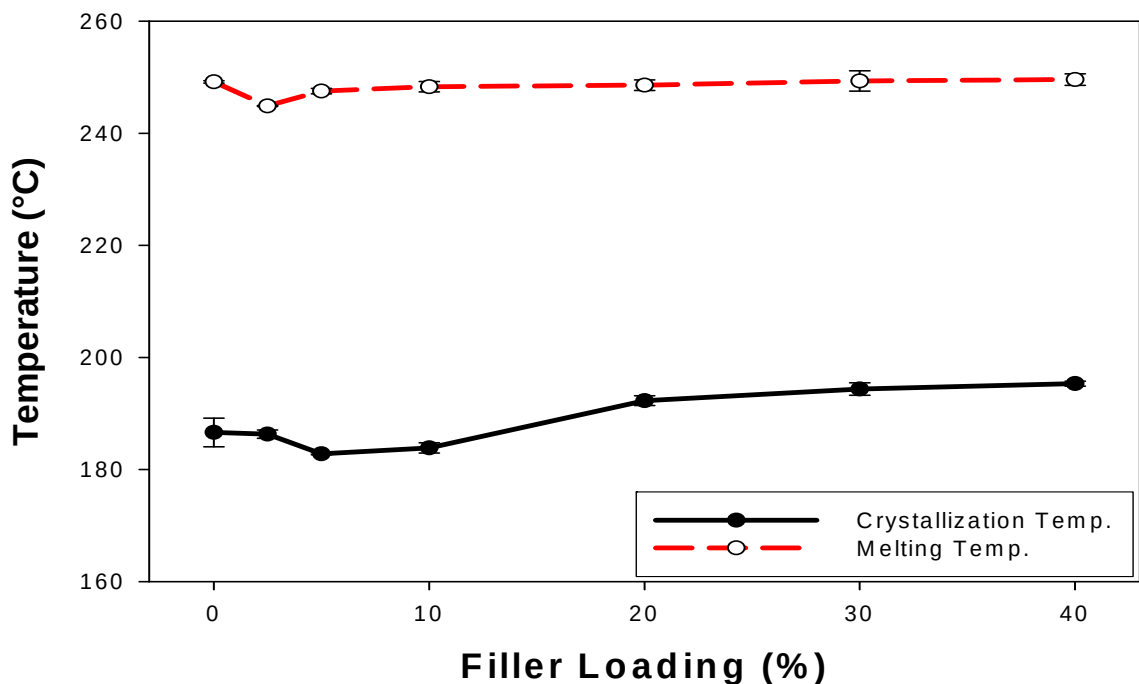


Figure 3.3 The effect of MCC loading on the melting and crystallization temperatures for the PET-PTT Blend and MCC-filled PET/PTT composites at different filler loadings.

3.4.2. Dynamic Mechanical Thermal Analysis (DMTA)

Figure 3.4 shows the temperature dependence of the storage modulus and loss factor ($\tan \delta$) of PET-PTT blend and MCC filled composites. The PET/PTT blend shows a typical behavior of semi crystalline polymer with three distinct regions that could be identified as glassy, glass transition and rubbery regions. In the glassy region (temperature is below 30°C), the storage modulus (E') remains roughly constant. Around

35°C, the modulus decrease is related to the glass transition region of the PET/PTT blend amorphous phase. The magnitude of this storage modulus decrease is small due to the high degree of crystallinity of the blend. At higher temperatures after the glassy region (temperature is higher than 30°C), the storage modulus decreases sharply because of the increased viscosity and polymer chain mobility (Kim et al. 2005; Kim et al. 2006, Azizi Samir et al. 2003). The sharp decrease in the storage modulus is continued until the rubbery region. MCC filled composites show a similar behavior and have a higher modulus for all temperature ranges compared to the unfilled composites. The higher modulus for the composites could be a result of the high degree of crystallinity of the PET/PTT blend in the composite formulations, but DSC measurements show that the degree of crystallinity of the PET/PTT blend was composition-independent up to 30 wt% MCC, and then decreases for a high loading of MCC (Azizi Samir et al. 2003). It can be assumed that the increase in the composite modulus should be related to the reinforcing effect of MCC. A similar observation was reported for semi-crystalline poly (caprolactone) reinforced with chitin whiskers and poly (oxyethylene) reinforced with cellulose nanocrystals (Azizi Samir et al. 2003, Morin and Dufresne 2002). Also, it can be seen from the Figure 3.4 that the composites with MCC exhibit much better temperature stability than the PET/PTT blend in the rubbery region due to the percolating network effect (Seydibeyoglu and Oksman 2008).

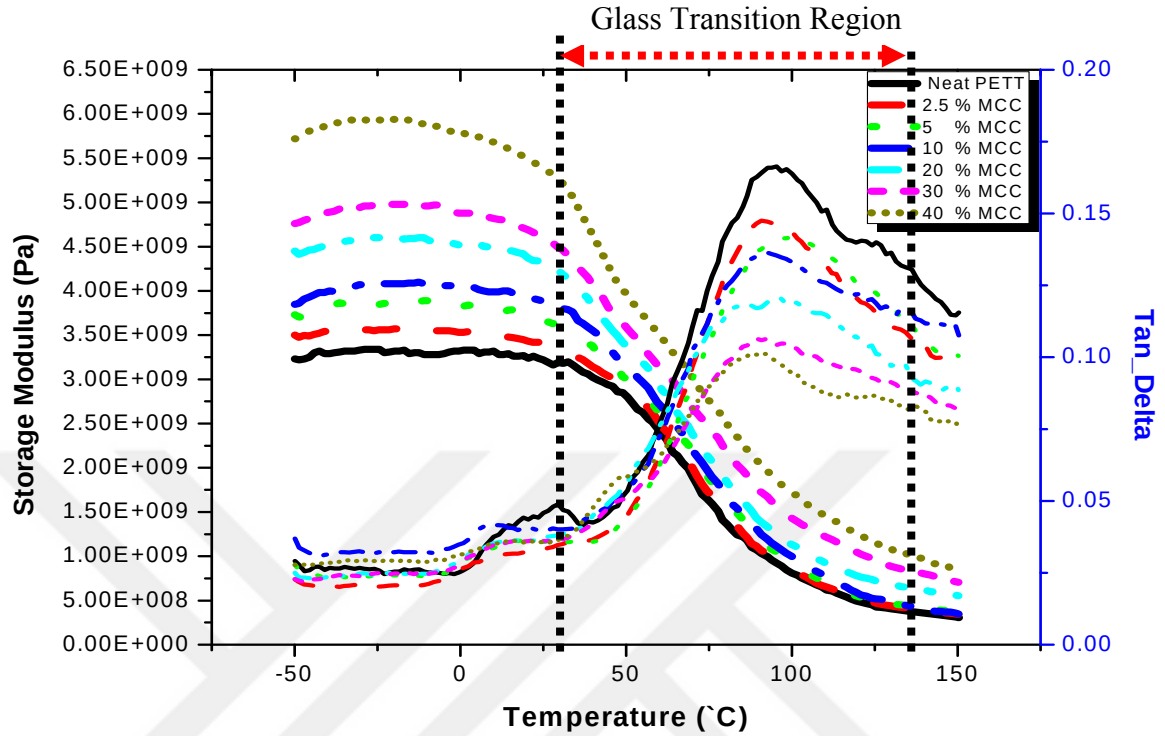


Figure 3.4 Storage modulus and loss factor ($\tan \delta$) of PET/PTT blend and MCC-filled PET-PTT composites from -50 to 150°C as a function of temperature.

Figure 3.5 shows that the storage modulus of the composites increased with increasing MCC percent at room (25°C) and glass transition (90°C) temperature. At 40% percent MCC loading, the storage modulus increased significantly. As the MCC loading increases, the stress is more evenly distributed throughout the composite and therefore the modulus increases with the addition of MCC compare to the PET/PTT blend. In addition, strong interactions, which arise from the hydrogen bonds between cellulose molecules and fibers and fibrils, lead to much a greater storage modulus (Seydibeyoglu and Oksman 2008).

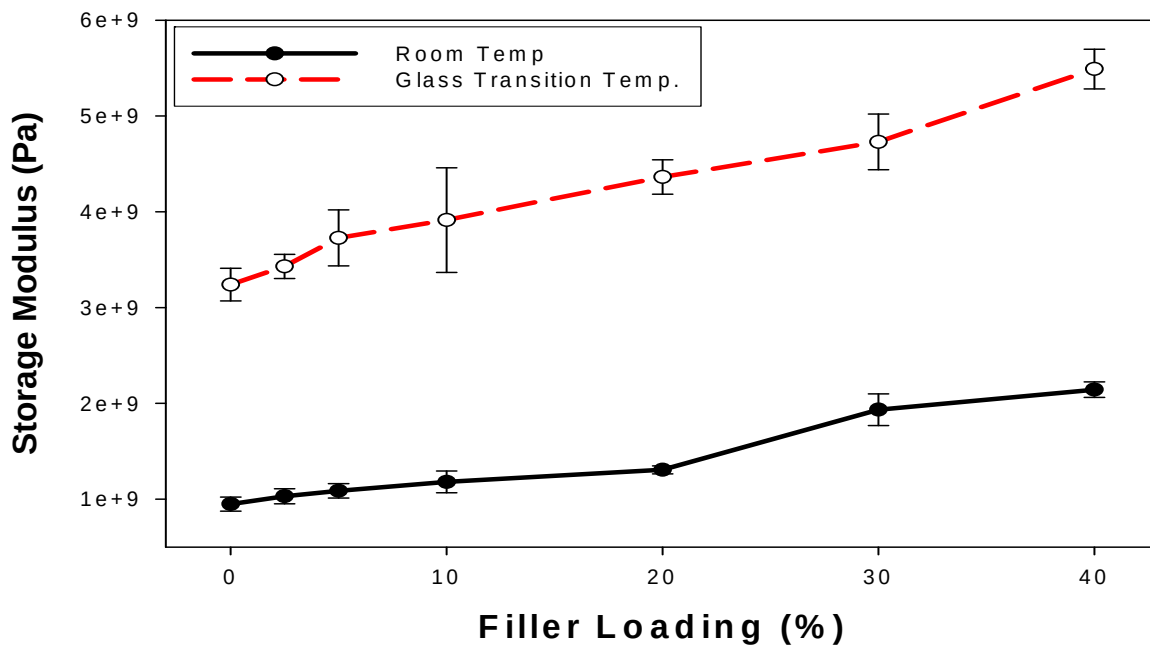


Figure 3.5 The storage modulus of PET/PTT blend and MCC-filled PET/PTT composites at the room temperature and glass transition temperature.

The temperature dependence of $\tan \delta$ versus for the MCC-filled PET-PTT composites as a function of temperature at a frequency of 1 Hz are presented in Figure 3.4. The shift in $\tan \delta$ peak temperature provides information about molecular interactions between the PET/PTT blend and MCC (Morin and Dufresne 2002). From the peak in the $\tan \delta$ curve, we can see that the incorporation of MCC does not significantly affect the glass transition temperature of the composite, but it does have a significant effect on the magnitude of $\tan \delta$ values. The $\tan \delta_{\max}$ peak values correspond to the glass transition temperature and these values are not significantly changed as the MCC content is increased because the viscoelastic properties of the composite are strongly influenced by the matrix polymer. Figure 4 indicates that the $\tan \delta$ peak did not exhibit any shift which indicates that there are no molecular interactions between the polymer matrix and MCC.

As a result, we can see that the reinforcing effect is related mainly to the cellulose network and strong interaction of the cellulose particles (Kim et al. 2005; Kim et al. 2006, Seydibeyoglu and Oksman 2008). The neat PET/PTT blend presents a $\tan \delta$ peak temperature of about 95°C and composites present $\tan \delta$ peak temperatures between 86 and 95°C. On the other hand, the difference in the $\tan \delta$ values between the neat PET/PTT blend and the composites at low temperature is only marginal. At higher temperatures, however, this difference is more predominant. The magnitude of $\tan \delta$ peak values of MCC-filled composites were significantly decreased around the glass transition temperature in Figure 3.6. Because of the restriction in the chain segment mobility in the amorphous region of the PET/PTT blend brought about by the incorporation of MCC (Kim et al. 2006). There is a small peak at around 30°C which is the effect of lubricant.

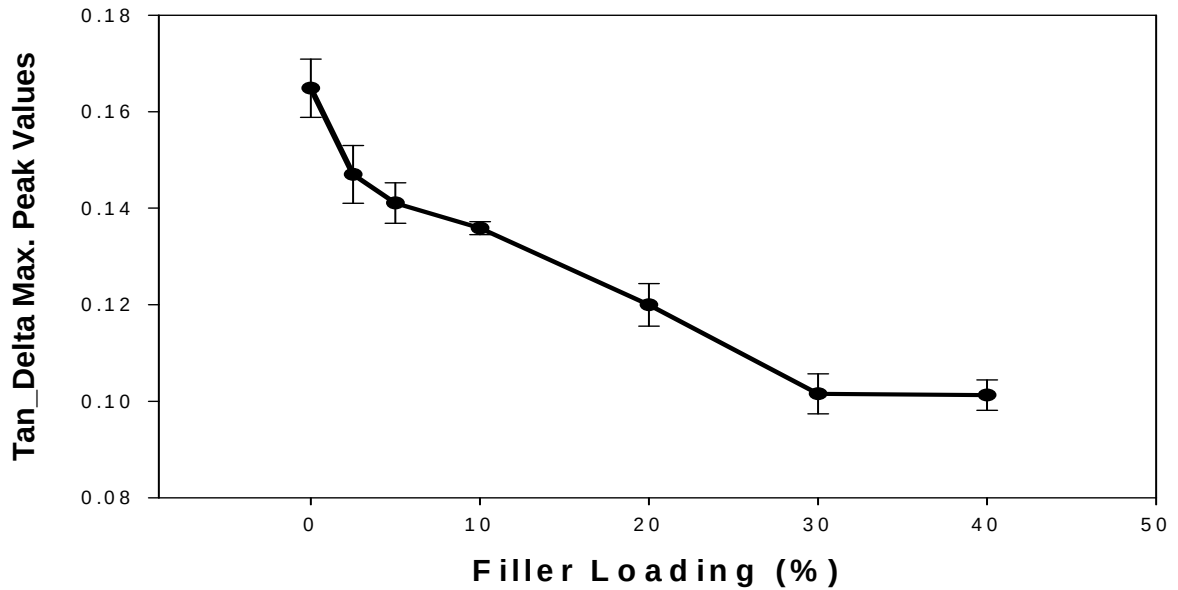


Figure 3.6 The effect of MCC loading on magnitude of $\tan \delta$ peak values for PET/PTT blend and MCC-filled PET/PTT composites.

3.4.3. Thermogravimetric Analysis (TGA)

Because of greater thermal stability compared to wood flour, microcrystalline cellulose can be used with engineering thermoplastics. Figure 3.7 provides evidence that MCC is thermally more stable and has less weight loss in comparison with similar sized wood filler particles at 270°C for 1 hour.

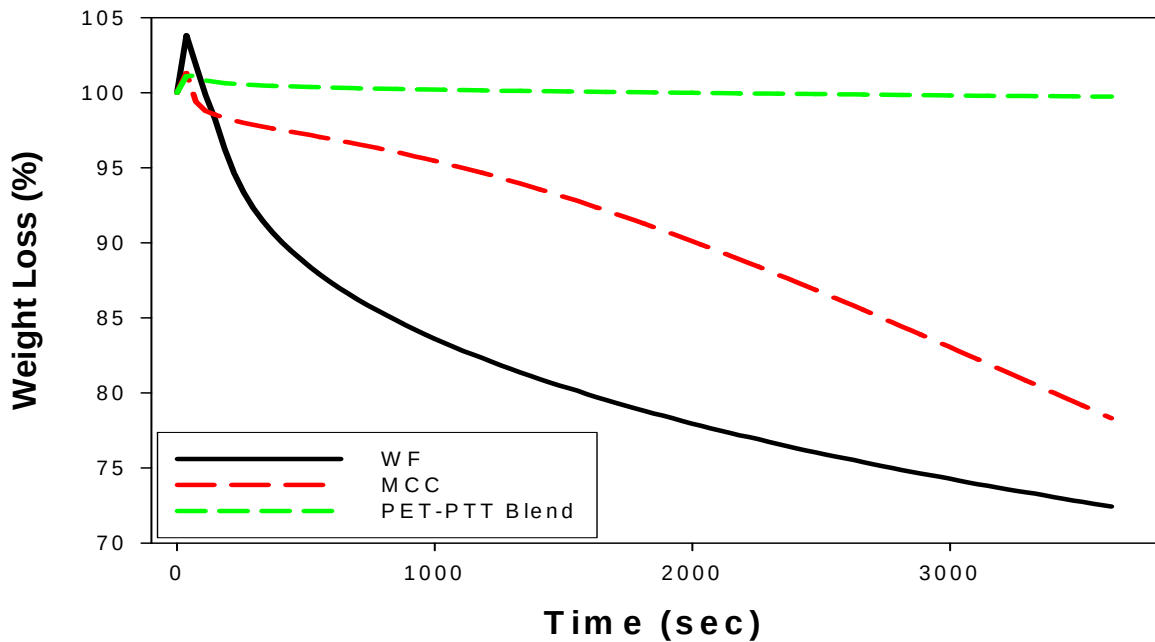


Figure 3.7 Weight Loss in % vs. time of MCC, wood flour and PET-PTT Blend by isothermal TGA.

The TGA and DTGA curves for PET/PTT blend and MCC-filled composites are shown Figure 3.8. The degradation temperatures of the PET/PTT blend and MCC-filled composites are different. The PET/PTT blend and 2.5% MCC-filled composites undergo a single stage degradation with a single peak at 410°C, whereas high MCC-filled composites show two degradation peaks in the range 340°C - 415°C.

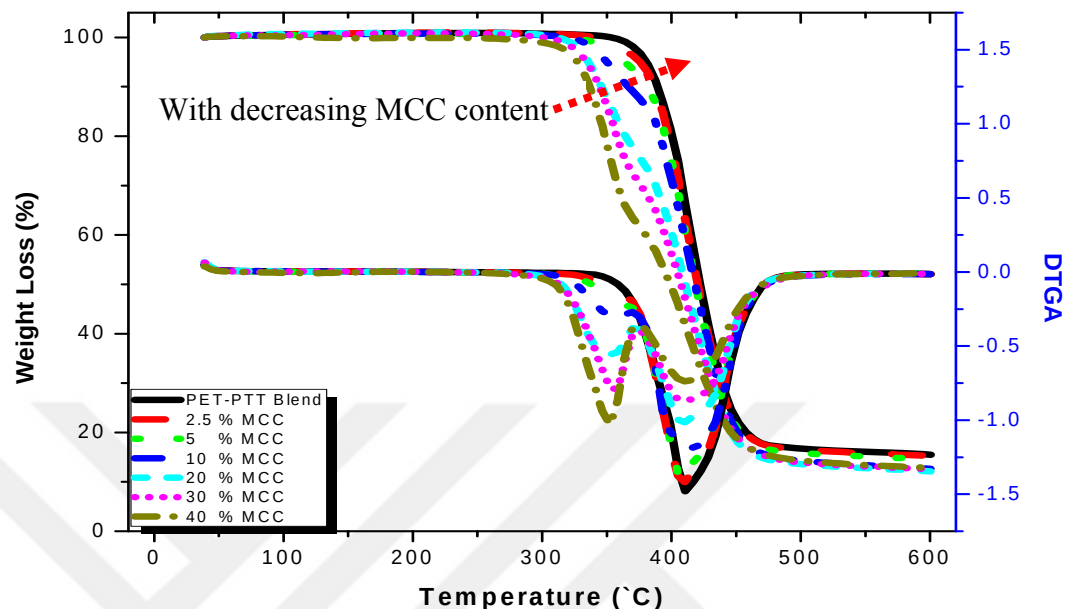


Figure 3.8 TGA and DTGA curves of PET/PTT blend and MCC-filled PET/PTT composites.

The temperature at 10% weight loss (T_{10}) and the temperature at 50% weight loss (T_{50}) for the neat PET/PTT blend and MCC-filled composites are shown Figure 3.9. Both T_{10} and T_{50} values for the composites decreased monotonically from the PET/PTT blend to 40% MCC addition. It is obvious from Figure 3.10 that the percentage of weight loss for composites increased from around 84% for the neat PET/PTT blend to 87% for 20% MCC addition. Beyond the 20% MCC addition, weight loss in the composites decreased. The results also show that as the filler loading increased, the thermal stability of the composites slightly decreased as the MCC content increased because of the lower thermal stability of MCC compare to the PET/PTT blend. Summary of weight loss (%), peak temperature and residual weight after 600°C of the composites are given in Table 3.4.

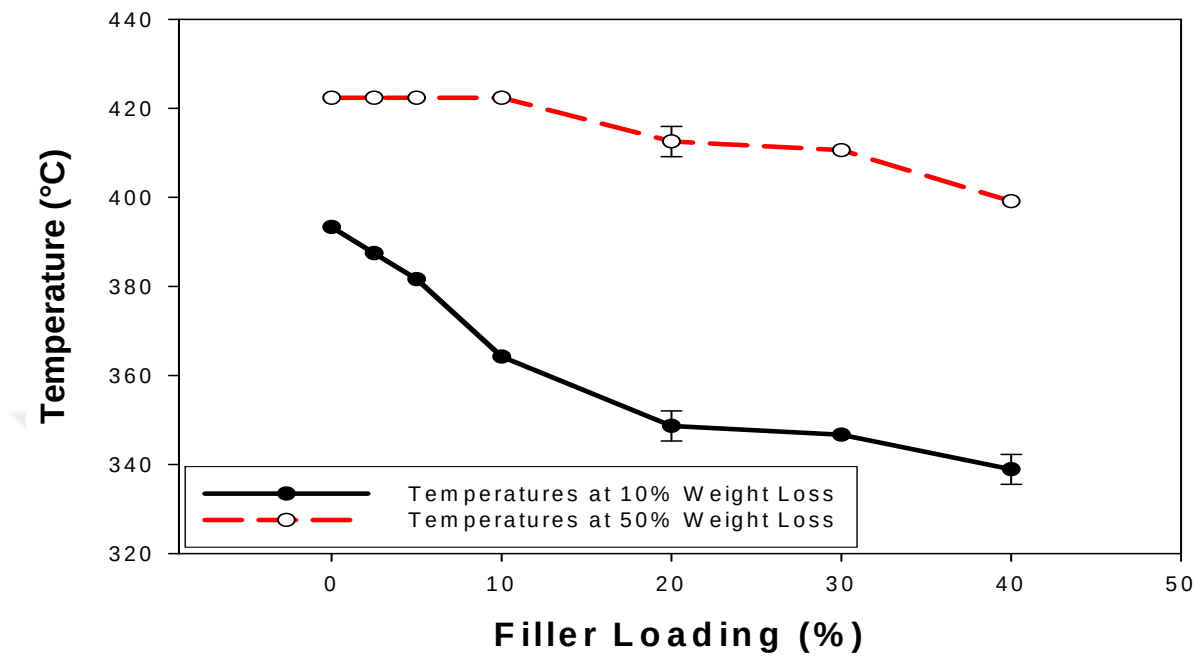


Figure 3.9 Temperatures at 10% and 50% weight loss for PET/PTT blend and MCC-filled PET/PTT composites.

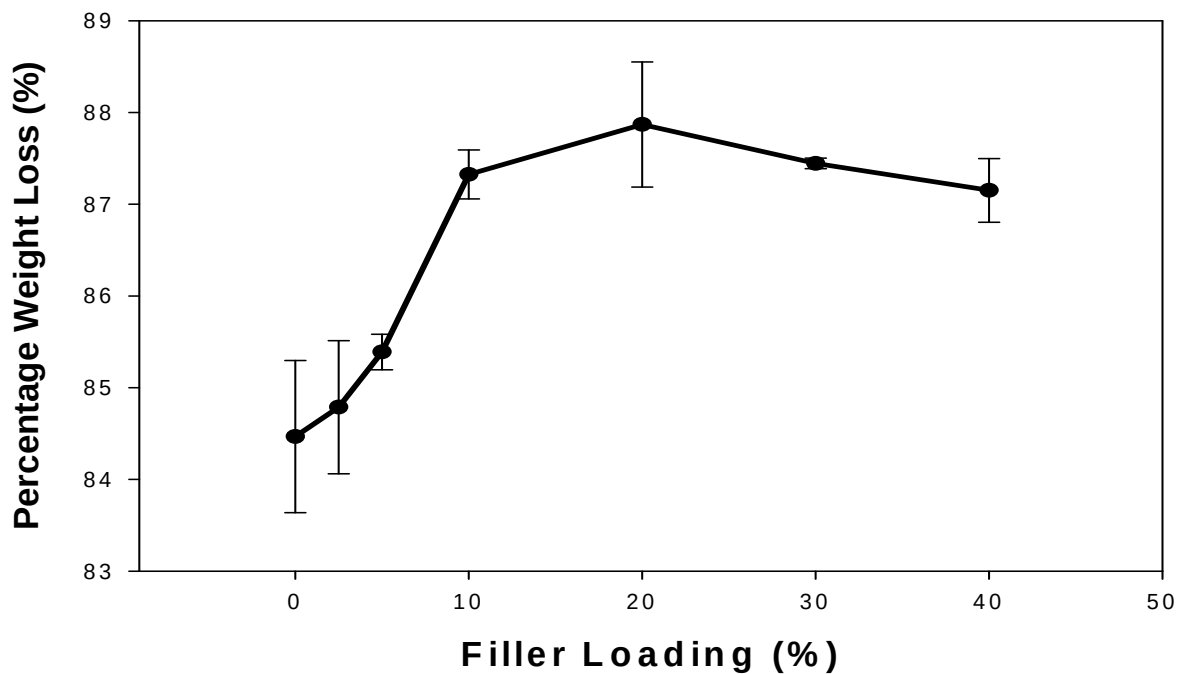


Figure 3.10 Ultimate percentage of weight loss for PET/PTT Blend and MCC-filled PET/PTT composites

Table 3.4 Thermogravimetric data for PET/PTT blend and MCC-filled-PET/PTT composites.

Sample Code	DTGA Temp. (°C)		W.L. (%)		Residue (%)	
PET/PTT Blend	410.8 (0.2)		33.7 (1.1)		15.5 (0.8)	
PET/PTT – MCC2.5	410.8 (0.2)		37.0 (1.7)		15.2 (0.7)	
	1 st Peak	2 st Peak	1 st Peak	2 st Peak		
PET/PTT – MCC5	369.3 (0.5)	410.8 (0.2)	6.4 (0.4)	39.5 (0.2)	14.6 (0.2)	
PET/PTT – MCC10	358.4 (0.6)	409.8 (1.6)	9.3 (0.2)	41.0 (0.1)	12.7 (0.3)	
PET/PTT – MCC20	352.3 (2.1)	408.8 (2.2)	17.0 (2.1)	50.7 (2.5)	12.1 (0.7)	
PET/PTT - MCC30	353.3 (0.5)	410.8 (0.0)	20.6 (0.5)	52.0 (1.2)	12.6 (0.1)	
PET/PTT – MCC40	352.5 (0.5)	410.8 (0.2)	24.1 (0.3)	58.3 (0.3)	12.8 (0.3)	

Parenthesis indicates standard deviation.

3.4.4. Infrared Spectroscopy (DRIFT)

Figure 3.11 shows the DRIFT spectra of MCC, PET, PTT, PET-PTT blend and composites. The DRIFT spectra of MCC exhibited the following absorption bands: 2895 cm^{-1} (C-H symmetric stretching), 2130 cm^{-1} (O-H and C-O-O symmetric stretching, 1630 cm^{-1} (O-H symmetric stretching), 1330 cm^{-1} (O-C-O symmetric bending) and four bands between from 1000 to 1200 cm^{-1} (C-C and C-O stretching) (Buckton et al. 1999; Tobyn et al. 1998). The DRIFT spectra of PTT showed the following absorption bands: 2960 and 2900 cm^{-1} (asymmetric and symmetric stretching vibration of methylene group respectively), 1718 cm^{-1} (stretching vibration of C=O group), 1504 and 1270 cm^{-1} (stretching vibration of C-O in carboxyl group) and 1460 cm^{-1} (vibration of the methylene group) (Silva Spinace et al. 2006). The DRIFT spectra of PET showed the following absorption bands: 3755 and 3683 cm^{-1} (anti symmetric and symmetric OH

stretching), 3430 cm^{-1} (second C=O stretching), from 3100 to 2660 cm^{-1} (C-H stretching), 1735 cm^{-1} (C=O stretching), 1289 cm^{-1} (asymmetric C-C-O stretching) and 1134 cm^{-1} (asymmetric O-C-C stretching) (ShuYong et al. 2008). There is no evidence of spectral difference between neat PET/PTT blend and MCC-filled PET/PTT composites in 2895 and $1000\text{--}1200\text{ cm}^{-1}$ region where hydrogen bonding in samples is generally apparent. A summary of infrared vibrations and assignments for PET, PTT and MCC are given in Table 3.5.

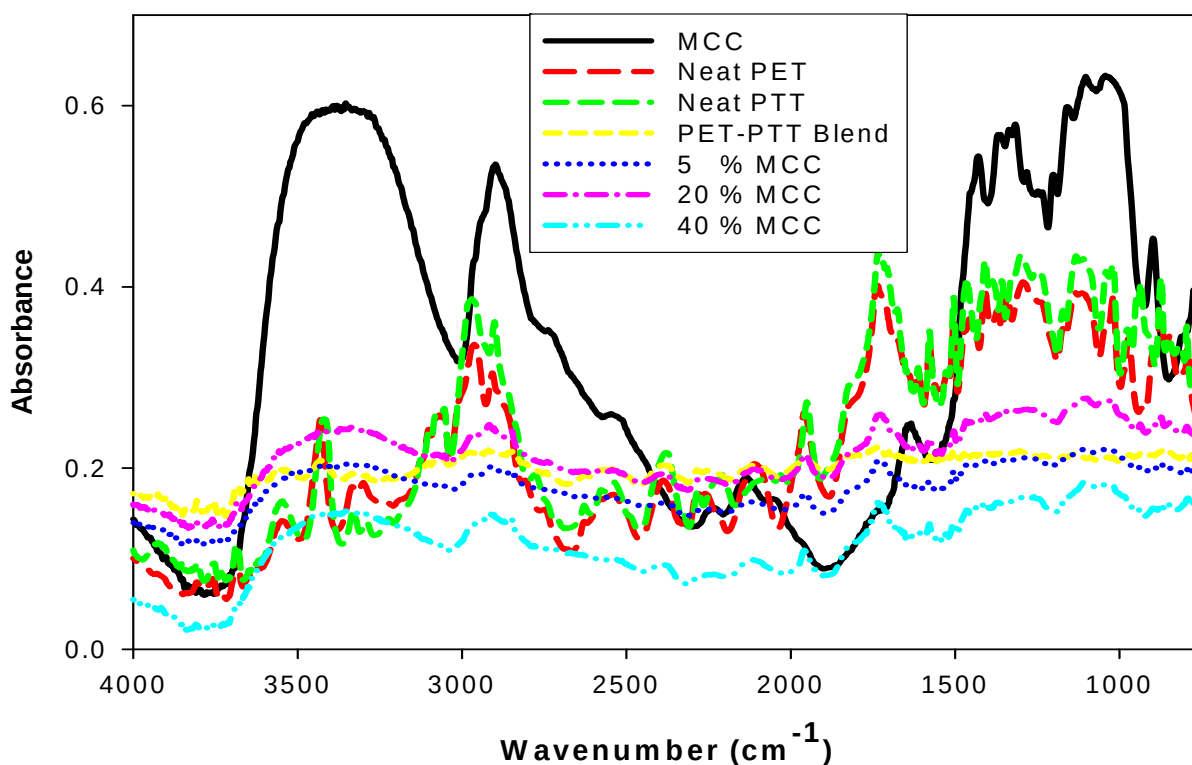


Figure 3.11 DRIFT spectra of MCC, PET, PTT, PET/PTT blend and composites.

Table 3.5 Infrared vibrations and assignments for PET, PTT and MCC.

Major infrared bands of components	
Wavenumber (cm ⁻¹)	Assignment and remarks
PET	
3755	O-H anti symmetric stretching
36839	O-H symmetric stretching
3430	second C=O stretching,
3100-2660	C-H stretching
1735	first C=O stretching
1289	C-C-O asymmetric stretching
1134	O-C-C asymmetric stretching
PTT	
2900	asymmetric stretching vibration of methylene group
2960	symmetric stretching vibration of methylene group
1718	C=O stretching vibration
1504 -1270	stretching vibration of C-O in carboxyl group
1460	vibration of the methylene group
MCC	
2895	C-H symmetric bending
2130	O-H and C-O-O symmetric stretching
1630	O-H symmetric stretching
1330	O-C-O symmetric bending
1000-1200	C-C and C-O stretching (four bands)

3.5. Conclusions

MCC-filled PET/PTT blend composites were prepared by melt compounding followed by compression molding. There were not significant changes in the glass transition (T_g) or melting (T_m) and crystallization (T_c) temperatures of the composites with increasing MCC loading. The degree of crystallinity of composites was quite constant for low loading MCC contents up to 30 wt%, but after 30 wt% crystallinity decreased slightly. The storage modulus (E') of the MCC-filled PET/PTT composite system was higher than that of the neat PET/PTT blend and increased with increasing MCC content, this was attributed to the reinforcement effect of the MCC, and this reinforcing effect is related mainly to the cellulose network and strong interaction among cellulose particles. The $\tan \delta$ peak values are not significantly changed as the MCC content is increased because the viscoelastic properties of the composite were strongly influenced by the matrix polymer. Thermogravimetric analysis indicated that the MCC did not show significant initial degradation under 300°C. Therefore, MCC-filled composites could be used for high temperature circumstances, such like an automobile industry. In this study, no significant changes were observed in the FTIR spectra of the composites.

3.6. References

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DETERMING THE MECHANICAL PROPERTIES OF MCC-FILLED PET/PTT BLEND COMPOSITES

4.1. Chapter Summary

Polymer composite materials consisting of poly (ethylene terephthalate) (PET) – poly (trimethylene terephthalate) (PTT) blends and microcrystalline cellulose (MCC) were prepared by injection molding. The composites were analyzed for tensile, flexural, and impact strength as well as density determinations. There was no statistical difference in terms of mechanical properties between the control PET/PTT blend and 2.5 wt% MCC-filled composites. Because of the better compatibility as well as better stress-transfer properties, the tensile strength of the composites was larger (reaching values from 24.8 to 36.3 MPa with the addition of 20 wt % MCC. Elongation at break of the composites was greater (reaching values from 2.3 to 3.3 % with the addition of 20 wt% MCC. The tensile modulus of MCC-filled composites systemically increased with increasing MCC loading (reaching values from 1.11 to 1.68 GPa with the addition of 30 wt% MCC). The flexural modulus of composites was higher than the control PET/PTT blend. The modulus also increased with increasing MCC loading (reaching values from 2.10 to 3.37 GPa with the addition of 30 wt% MCC). The Izod impact strength of the composites decreased as the MCC loading increased and this observation was expected for filled polymer systems as is commonly observed.

4.2. Introduction

Recently, there has been increased interest in the use of cellulose as mechanical reinforcing phases in polymer matrices because of its lower density compared to inorganic fillers (glass and carbon fibers), renewable character, biodegradability, lower price, lack of abrasion to the processing equipment and a relatively reactive surface (Azizi Samir et al. 2004a; Panaitescu et al. 2007a; Helbert et al. 1996; Bondeson et al. 2006; Ljunberg et al. 2006; Azizi Samir et al. 2004b; Panaitescu et al. 2007b). Wood is a primary resource for cellulose and in addition, contains hemicellulose, and lignin (Seydibeyoglu and Oksman 2008). The thermogravimetric stability of wood component polymers shows that cellulose is more thermally stable than the non cellulosic components such as lignin and hemicellulose (Caulfield et al. 2001a; Xu 2008). Engineering thermoplastics such as nylon (nylon 6 and nylon 66) and polyesters (PET and PTT) have greater mechanical properties and service temperatures than commodity thermoplastics. The automobile and construction industries desire low density and cheap reinforcement for engineering thermoplastics to obtain better mechanical and thermal properties as well as lower density materials. Therefore, cellulose is a good candidate as reinforcement for engineering thermoplastics (Caulfield et al. 2001a; Xu 2008).

MCC is naturally occurring, crystalline cellulose obtained from high quality wood pulp [Azizi Samir et al. 2005; Mathew et al. 2004). MCC has the advantage of high specific surface area in comparison with other conventional cellulose fibers and can used as a cellulosic reinforcement for polymer matrices (Mathew et al. 2004). MCC has been incorporated into a number of different matrices like poly (lactic acid) (Mathew et al.

2004; Petersson and Oksman 2006), polystyrene (Laka and Chernyavskaya 1996) and polyethylene (Panaitescu et al. 2007a; Panaitescu et al. 2007b; Maskavs et al. 1999; Maskavs et al. 2001). MCC-filled poly (lactic acid) composites show that both tensile strength and elongation to break are lower than pure poly (lactic acid) polymer. On the other hand, increased MCC content has a positive effect on composite modulus compared to unfilled poly (lactic acid) (Mathew et al. 2004). Tensile strength at break for a composite containing 40 wt% MCC was two times higher than an unfilled polystyrene matrix (Laka and Chernyavskaya 1996). Addition of 5 wt% MCC in polyethylene contributes to a small increase in tensile strength but higher MCC loadings show no significant tensile strength effect. On the other hand, tensile modulus increases with the increase of MCC loading up to 2.4 times that of unfilled polyethylene for 20 wt% MCC loading (Panaitescu et al. 2007b).

It is thought that higher melting temperature engineering thermoplastics cannot be effectively reinforced with cellulosic fibers because of thermal degradation of cellulose (Caulfield et al 2001a). In recent patent applications, and recently papers demonstrated that this common belief is not true (Caulfield et al 2001a; Sears et al. 2001a; Sears et al 2001b; Sears et al. 2004; Jacobson et al. 2001; Jacobson et al. 2003). In spite of technological interest in engineering thermoplastics, only a few studies of engineering thermoplastic/cellulose polymer composites have been published (Caulfield et al 2001a; Xu 2008; Sears et al. 2001a; Sears et al 2001b; Sears et al. 2004; Jacobson et al. 2001; Jacobson et al. 2003-10; Chen and Gardner 2008; McHenry and Stachurski 2003). However, there is lack of information about MCC-filled engineering thermoplastics in the

peer reviewed literature. Aromatic polyesters including PET, and PTT are important polyesters and high-performance engineering plastics used in industry and are widely used in many areas including the textile, electronics, automotive industries, etc (Liang et al. 2007; Liang et al. 2008; Wei et al. 2005; Son et al. 2003; Chen et al. 2007; Ge et al. 2007; Supaphol et al. 2004). Polymer blending is an attractive alternative to produce a new material with desirable properties such as versatility, simplicity and inexpensiveness without having to synthesize a totally new material (Supaphol et al. 2004). In recent years, many researchers have been interested in blends or copolymers to increase the crystallization rate of PET or improve the mechanical and thermal properties of PTT (Liang et al. 2007; Liang et al. 2008; Wei et al. 2005; Son et al. 2003; Chen et al. 2007; Ge et al. 2007; Supaphol et al. 2004). In this study, PTT was used to reduce the processing temperature and increase the crystallization rate of PET (Liang et al. 2007). There is also lack of information of cellulose fiber-filled polyester composites.

The objective of this study was to investigate the influence of MCC filler loading on the mechanical properties of MCC-filled PET/PTT composites. Microcrystalline cellulose was incorporated over a content range from 0 to 30 wt%. Analyses were conducted using mechanical tests including tensile, flexural and impact tests as well as determining the composite densities.

4.3. Experimental Procedures

The materials used in this work and brabender sample preparation were described in detail in Chapter 3.3.1 and 3.3.2 respectively. The PET/PTT blend- MCC compounds were granulated using a lab scale grinder after brabender. The ground particles were dried at an oven at 105°C for 16 hours before being injection molded into ASTM test specimens. All materials were injection molded using a barrel temperature of 270°C mold temperature of 270°C injection pressure of 2500 psi. The compositions of composites are shown in Table 4.1.

Table 4.1 Composition of MCC-filled PET/PTT composites.

Sample Code	Composition			
	MCC Contents	PET	PTT	Lubricant
Neat PET/PTT	0	63	32	5
PET/PTT – MCC2.5	2.5	61.5	31	5
PET/PTT – MCC10	10	56.5	28.5	5
PET/PTT - MCC20	20	50	25	5
PET/PTT - MCC30	30	43	22	5

Values are percentage by weight (wt. %)

4.3.1. Statistical Analysis

The tensile strength, tensile modulus, elongation at break, flexural modulus, impact strength and density data were compared using a one-way analysis of variance followed by Tukey-Kramer Honestly Significant Differences (HSD) test with JMP statistical analysis program (JMP 2008).

4.3.2. Mechanical Properties

All the tension tests were conducted according to the American Society of Testing and Materials (ASTM) standard D 638-03, "Standard Test Method for Tensile Properties of Plastics". The tensile behaviors of composites were measured using an Instron 8801 with a 10 kN load cell. All tension tests were run at a rate of 0.2 in/min. An extensometer was employed for elongation determinations. At least six specimens were tested for each composition, and the results are presented as an average for tested samples. Tensile modulus of the PET/PTT blend and MCC-filled composites was obtained from the slope of the stress-strain curve. The flexure tests were conducted according to ASTM D 790-03, "Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials", Test Method 1, Procedure A, i.e. three-point loading system utilizing center loading, using an Instron 8801 with a 10 kN load cell. The support span was 2 in., tests were run at a rate of 0.05 in/min. At least six specimens were tested for each composition and the results are presented as an average for tested samples. The impact tests were conducted according to ASTM D 256-06, "Standard Test Methods for Determining the Izod Pendulum Impact Resistance of Plastics." The notches were added using a NotchVIS machine manufactured by Ceast. The specimens were tested on a Resil 50 B impact test machine, manufactured by Ceast. The specimen is clamped in the bottom of the test fixture and the hammer is then released from a specified height. The depth under the notch and the specimen width is entered, and the machine will then record the energy taken to break the specimen. All breaks must be completed breaks to count as a data point. A 2.75 J hammer

was used to impact the specimens. At least seven specimens were tested for each composition. The density profile of the PET/PTT blend and MCC-filled composite specimens was measured using an X-ray densitometer (QMS, Model QDP-01). At least five specimens were tested for each composition. The dimension of density specimens was prepared to be 63.5 mm by 12.5 mm by 3.2 mm. Density determination by the QDP scanning system is based on relationship between X-ray attenuation and density as expressed in the following equation (Jeong 2005; QMS 2001).

$$I/I_0 = e^{-\mu_m \rho t}$$

where I = intensity of radiation beam after passing through the sample, I_0 = intensity of radiation beam without passing through the sample, e = natural logarithm base, μ_m = material mass attenuation coefficient (cm^2/g), ρ = material density (g/cm^3) and t = material thickness (mm).

4.4. Results and Discussion

The tensile behavior of the neat PET/PTT blend as well as the MCC-filled composites reinforced from 2.5 wt% to 30 wt% was performed by tensile testing at room temperature. Figure 4.1 and Figure 4.2 show the tensile strength and elongation at break of the neat PET/PTT blend and MCC-filled composites respectively. The tensile strength and elongation at break were determined from the stress and strain curves and the results are presented in Table 4.2.

Table 4.2 Summary of mechanical properties of PET/PTT Blend and MCC-filled PET/PTT composites.

Sample Code	Tensile Properties		Flexural Properties		Impact Properties	Density
	Strength (MPa)	Modulus (GPa)	Elongation(%)	Modulus (GPa)	Notched (J/m)	g/cm ³
Neat PET/PTT	24.8 (3.1)	1.11 (0.01)	2.34 (0.3)	2.10 (0.4)	47.0 (6.6)	1.25 (0.01)
PET/PTT – MCC2.5	26.8 (6.7)	1.17 (0.07)	2.49 (0.9)	2.12 (0.2)	44.3 (5.9)	1.28 (0.02)
PET/PTT – MCC10	33.6 (3.7)	1.32 (0.06)	3.14 (0.7)	2.65 (0.2)	33.4 (5.3)	1.30 (0.01)
PET/PTT – MCC20	36.3 (2.5)	1.43 (0.15)	3.30 (0.3)	2.96 (0.3)	25.9 (2.6)	1.34 (0.01)
PET/PTT – MCC30	35.6 (1.8)	1.68 (0.13)	2.80 (0.3)	3.37 (0.2)	24.7 (0.5)	1.37 (0.01)

Parenthesis indicates standard deviation.

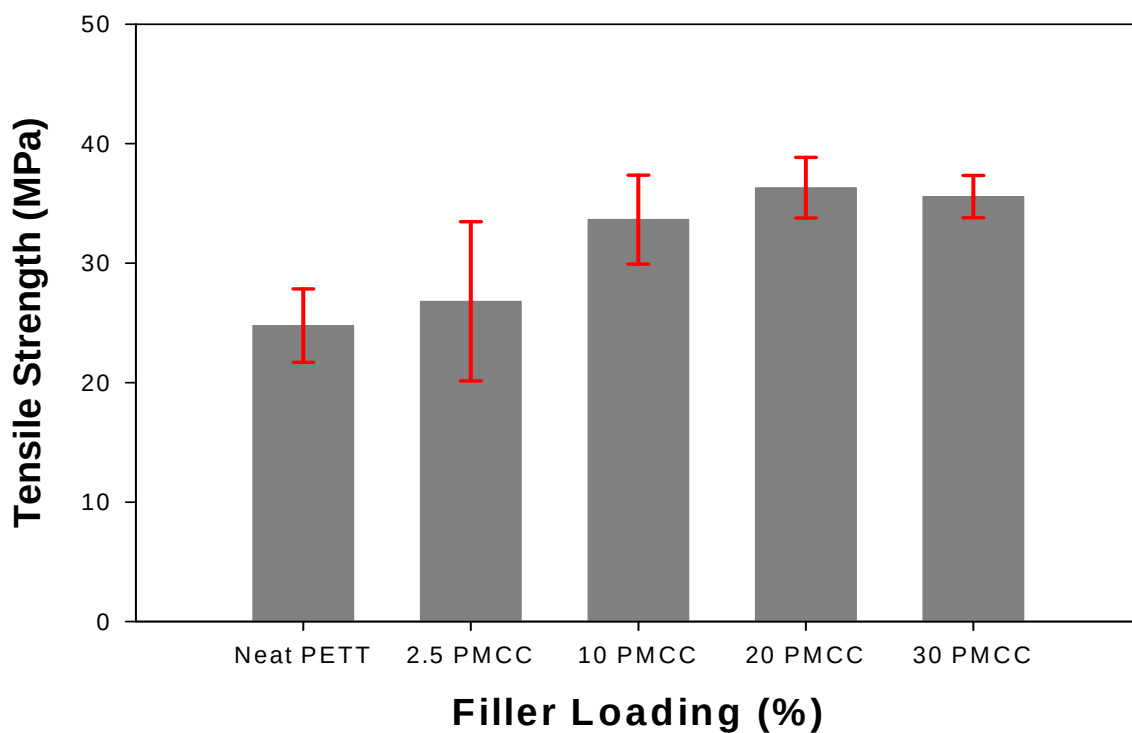


Figure 4.1 Effect of MCC loading on tensile strength of MCC-filled PET/PTT composites.

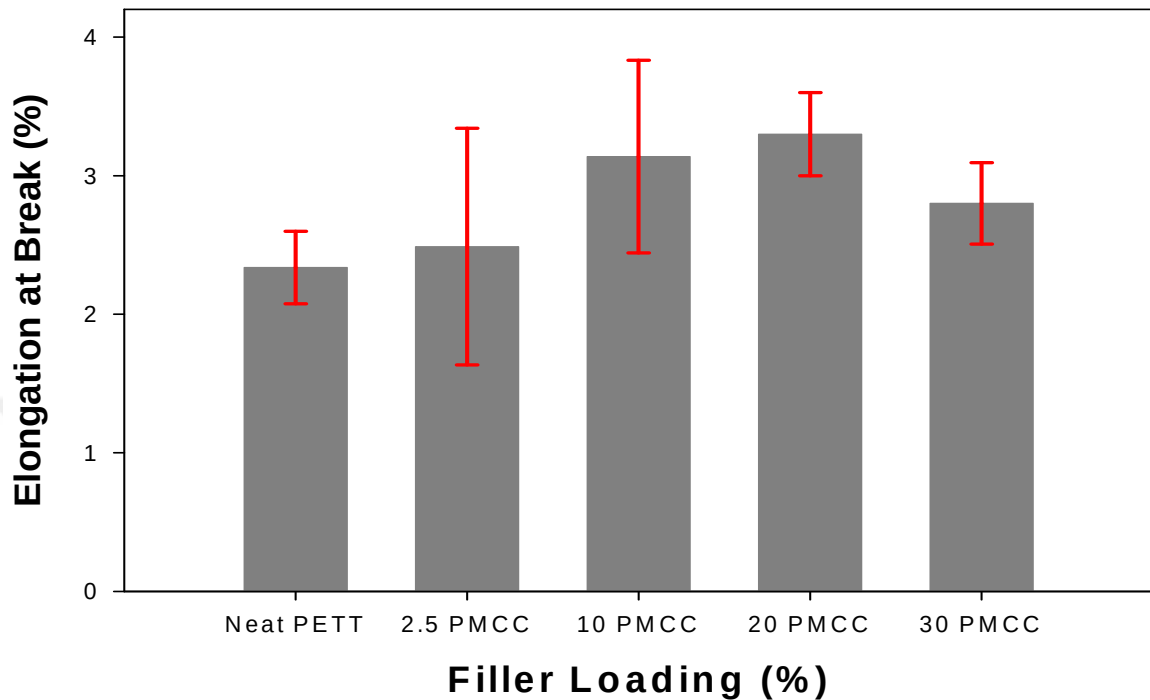


Figure 4.2 Elongation at break as function of MCC loading for MCC-filled PET/PTT composites.

Incorporation of filler into a polymer matrix may increase or decrease the tensile strength of the composite and this phenomenon depends on filler type (Zaini et al. 1996). It was observed that neat PET/PTT exhibits a non linear elastic behavior with a tensile strength of 24.75 MPa and an elongation at break of 2.34 %. None of composites including the neat PET/PTT showed signs of stress yielding. This lack of stress yielding suggests that the mechanism behind the elongation and rupture of the composites was quite similar compared to the neat PET/PTT blend. The composite reinforced with MCC displayed enhanced tensile properties in comparison with the neat PET/PTT blend. Because of better stress-transfer properties, the tensile strength of the composites was greater (reaching values of 36.3 MPa with the addition of 20 wt% MCC. After 20 wt%

MCC addition, the tensile strength decreased but it was greater compared to neat PET/PTT blend. The reason why tensile strength decreased after 20 wt% MCC addition was attributed to very little or no stress-transfer properties in the higher weight percent MCC-filled composite (Ljunberg et al. 2006). In general, almost all filled polymer systems display smaller elongation at break compared to a neat polymer matrix because of deformability of a rigid interphase between the filler and matrix material (Zaini et al. 1996). Figure 4.2 seems to be contradictory to the general observation. In Figure 4.2, elongation at break of composites was greater (reaching values of 3.3 % with addition of 20 wt% MCC. The reason for this, there might be better dispersion below 20 wt% MCC addition. With high filler contents, the degree of MCC-MCC interaction became more prominent and, as a consequence, a reduction in elongation at break was observed (Dikobe et al. 2007).

Figure 4.3 shows the tensile modulus of elasticity of PET/PTT blend and MCC-filled composites. The tensile modulus of elasticity of a polymeric material has been shown to be significantly improved when nano-micro composites are formed with cellulose (Seydibeyoglu and Oksman 2008; Mathew et al. 2004; Petersson et al. 2006). The modulus of elasticity of MCC-filled composites systemically increased with increasing MCC loading (reaching values 1.68 GPa with the addition of 30% MCC). Tensile measurements show that the effect of MCC is more pronounced on the tensile modulus of elasticity than tensile strength and MCC acts as a mechanical reinforcement of the polymer chains. Mathew et al. prepared polylactic acid – MCC composites and they observed similar reinforcement with MCC (Mathew et al. 2004).

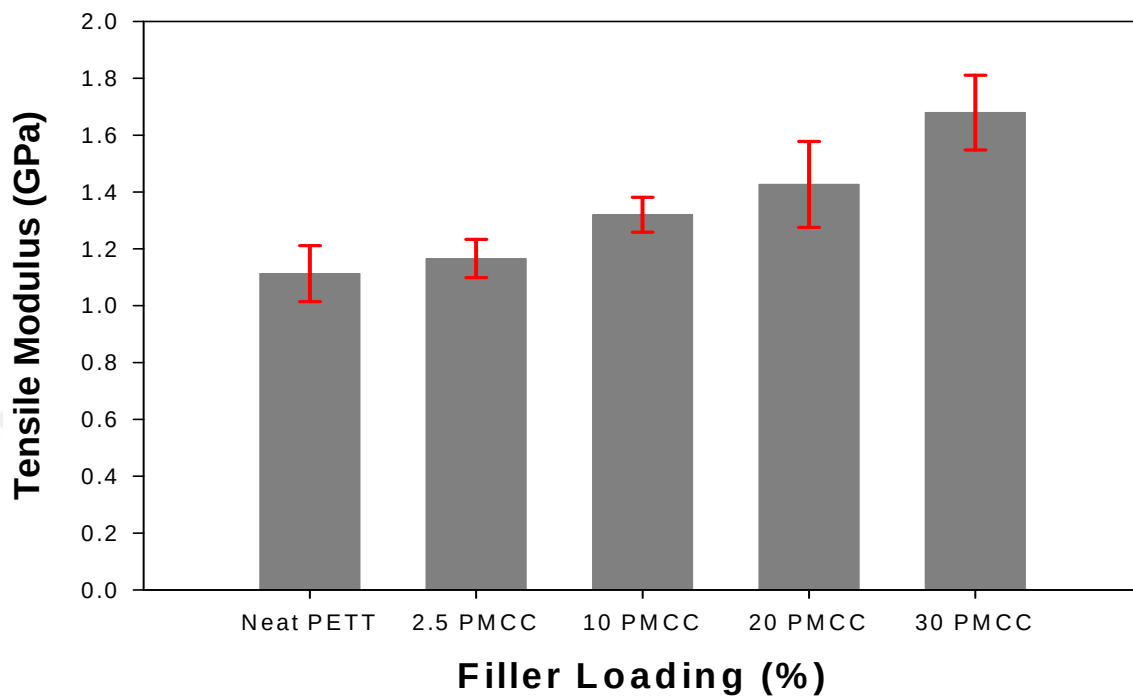


Figure 4.3 Tensile modulus of elasticity of MCC-filled PET/PTT composites.

The flexural behavior of the neat PET/PTT blend as well as the MCC-filled composites reinforced from 2.5 wt% to 30 wt% was performed by flexure testing at room temperature. In Figure 4.4 and Table 4.2 the average values of the flexural modulus of elasticity as a function of MCC are shown. As can be seen in the figure, the flexural modulus of elasticity of composites was higher than the PET/PTT blend. The modulus of elasticity also increased with increasing MCC loading (reaching values 3.37 GPa with the addition of 30 wt% MCC). The flexural modulus of elasticity is strongly affected by MCC loading and MCC orientation and less by the PET/PTT blend–MCC interaction (Bengtsson and Oksman 2006). Caulfield et al., prepared aliphatic polyketone and polyester – cellulose composites and observed similar reinforcements with 33 wt%

cellulose pulp fiber content (Caulfield et al. 2001b). Also Sears et al. used cellulose wood pulps as reinforcement for nylon 6 composites and found that cellulose wood pulps increased flexural modulus compared to neat nylon 6 polymer (Sears et al. 2001b).

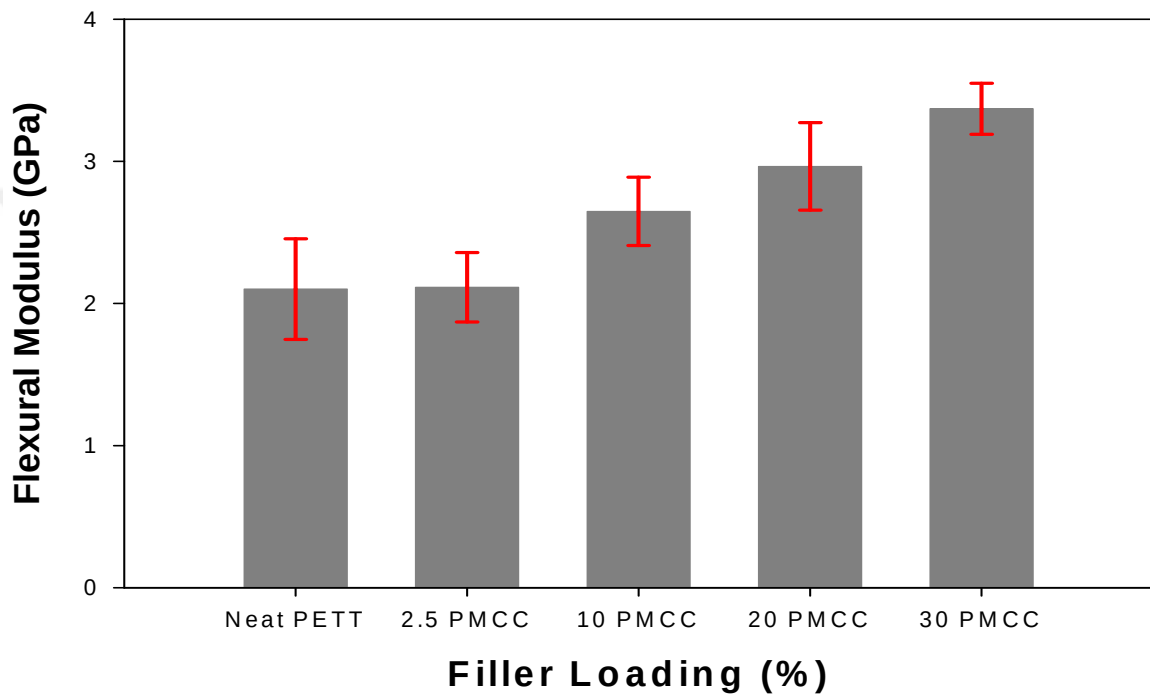


Figure 4.4 Flexural modulus of elasticity of MCC-filled PET/PTT composite.

The impact strength of the composites based on the amount of filler loading and type of testing is dependent on whether the samples were notched or un-notched [38]. The impact behavior of the neat PET/PTT blend as well as the composites reinforced from 2.5 wt% to 30 wt% MCC was performed by notched Izod impact testing at room temperature. Figure 4.5 and Table 4.2 shows the Izod impact strength of PET/PTT and MCC-filled composites. The Izod impact strength of composites decreased as the MCC loading increased and this observation is quite expected for filled polymer systems and

has been commonly observed (Zaini et al. 1996; Bengston and Oksman 2006; Sanadi et al. 1997; Liang 2002; Cui et al. 2008). Because of the possibility of poor wetting of the MCC particles by the PET/PTT blend, poor interfacial adhesion may be created between the MCC and the PET/PTT blend and it contributed to weak interfacial regions (Zaini et al. 1996). This phenomenon might cause lower impact strength with the addition of MCC loading. Another reason for this observation is the untreated filler surface and it caused poor dispersion of the MCC in PET/PTT matrix. In this case, the impact strength decreased quickly although at low filler addition (Zaini et al. 1996; Bengtson and Oksman 2006). On the other hand, a relatively small stress concentration might be formed in the PET/PTT blend because of the smooth rod like shape of the MCC. This phenomenon causes a weak sensitivity of impact strength to filler content (Liang 2002). During the impact tests, cracks travel through the polymer as well as along the weak interfacial regions, which might be caused from poor wetting of the particles by the PET/PTT blend. As a result of crack travel, the latter cannot resist crack propagation as effectively as the polymer region (Zaini et al. 1996) Increasing MCC content only increases the interfacial regions which cause crack propagation. Also, addition of MCC might cause polymer immobility, and that can contribute to lower impact strength. Figure 4.5 also shows that the Izod impact strength of the composites decreased from 47 J/m for the control to 25 J/m for 30 wt% MCC-filled composite. The loss of impact strength of the composite can be improved by providing flexible and strong interfacial bonding in the composite or by using coupling agents or impact modifiers (Zaini et al. 1996; Bengston and Oksman 2006; Sanadi et al. 1997; Liang 2002; Cui et al. 2008).

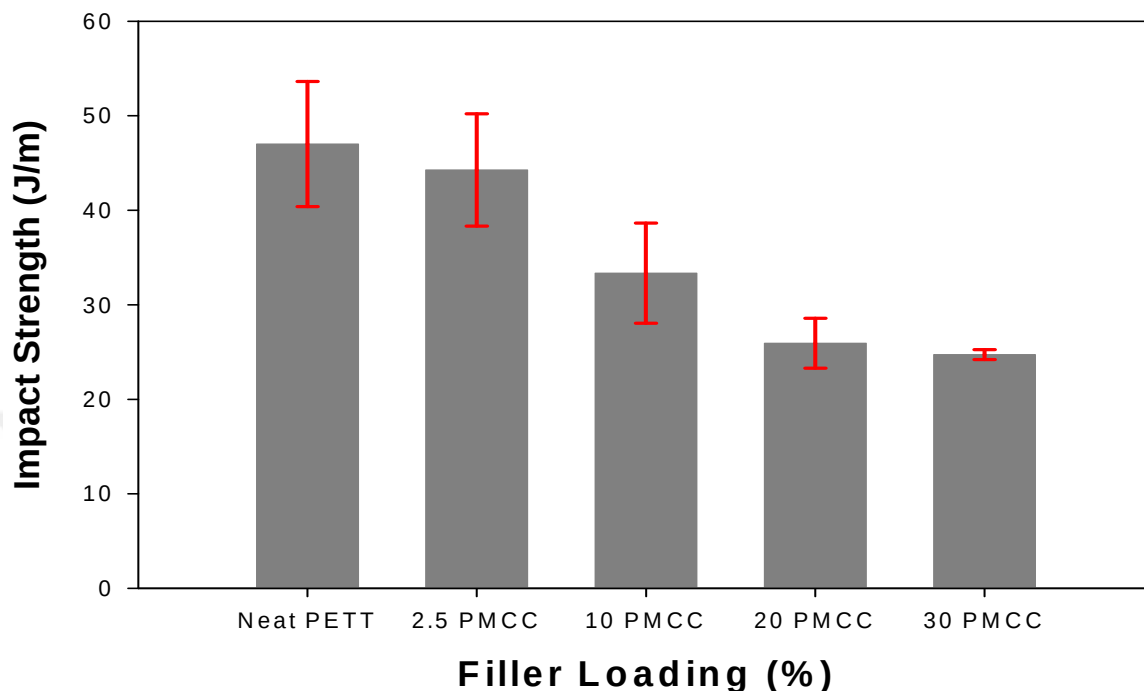


Figure 4.5 Effect of MCC loading on impact strength of PET/PTT blend and MCC-filled composites.

Figure 4.6 and Table 4.2 shows the density of PET/PTT and MCC-filled composites. The density of the composites increased slightly as a function of MCC loading. This was expected since MCC has a greater density compared to the PET/PTT blend. Generally, there is a certain correlation between density and mechanical properties such as flexural strength and modulus of elasticity (Klyosov 2007). Figure 4.6 seems to be contradictory to the general observation. There was not a strong correlation between density and tensile modulus of elasticity ($R^2 = 0.74$) or density and flexural modulus of elasticity ($R^2 = 0.80$). It was assumed that these large improvements in the mechanical properties would come from the MCC itself. The strong hydrogen bonding between the MCC molecules, which leads to strong interactions between fibers and fibrils, might

contribute to better mechanical properties in comparison with the PET/PTT blend (Seydibeyoglu and Oksman 2008). As a result from density study, it can be said that MCC provided the reinforcement (flexural and tensile modulus) with a smaller increase in density which could be important for low weight applications, especially in the automobile industry (Caulfield et al 2001b).

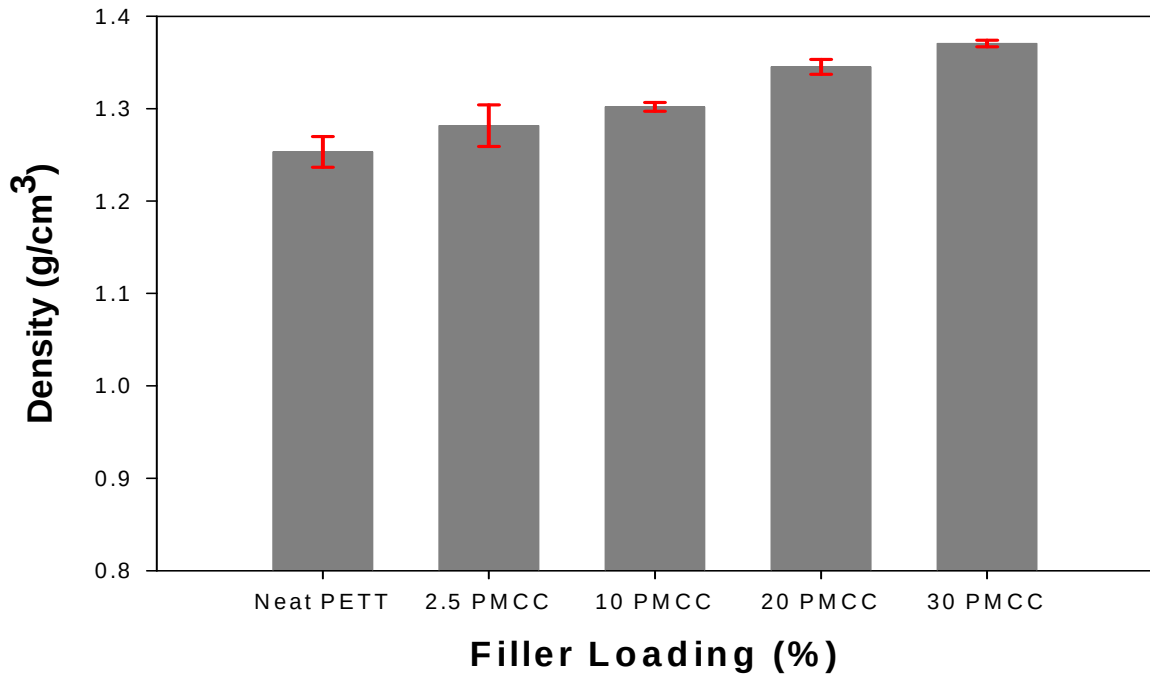


Figure 4.6 Density as function of MCC loading for MCC-filled PET/PTT composites.

As expected, the PET/PTT blend and MCC-filled composites manufactured by injection molding had highly uniform density distribution through their thickness as shown in Figure 4.7. Table 4.3 shows summary of the effect of MCC loading on the mechanical properties of composites in terms of statistical analysis.

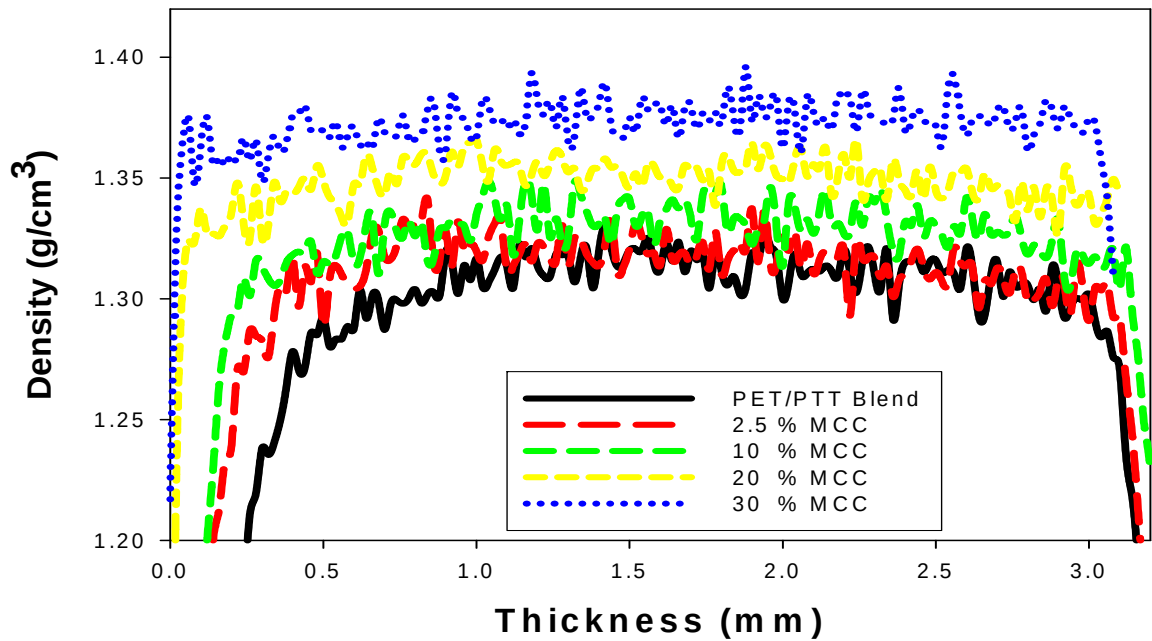


Figure 4.7 Average density profile of PET/PTT blend and MCC-filled composites.

Table 4.3 Results of Tukey-Kramer HSD comparison at $\alpha = 0.05$ for PET/PTT blend and MCC-filled composites.

Sample Code	Tensile Properties		Flexural Properties		Impact Properties	Density
	Strength (Mpa)	Modulus (GPa)	Elongation(%)	Modulus (GPa)	Izod Notched (J/m)	g/cm ³
Neat PET/PTT	B	C	B	C	A	C
PET/PTT – MCC2.5	B (NC)	C (NC)	AB (NC)	C (NC)	A (NC)	BC NC)
PET/PTT – MCC10	A (+36%)	B (+19%)	A (+34%)	B (+26%)	B (-29%)	B (+4%)
PET/PTT – MCC20	A (+47%)	B (+28%)	A (+41%)	AB (+41%)	BC (-45%)	A (+7%)
PET/PTT – MCC30	A (+44%)	A (+51%)	AB (NC)	A (+60%)	C (-47%)	A (+9%)

The same letters indicates no statistical difference between properties of composites and those around it. NC is no significant change upon the addition of MCC ($\alpha=0.05$) and parenthesis show that effect of MCC loading on the mechanical properties of composites in comparison with the PET/PTT blend.

4.5. Conclusions

MCC-filled PET/PTT blend composites were prepared by melt compounding followed by injection molding. The following conclusions are reported.

There was no statistical difference in terms of mechanical properties between the PET/PTT blend and 2.5 wt% MCC-filled composites in Table 4.3. The composite reinforced with high filler loading MCC displayed enhanced tensile properties in comparison with the neat PET/PTT blend. Because of better compatibility as well as better stress-transfer properties, the tensile strength of MCC-filled composites, compared to that of the control ranged from 36 to 47 %. Tensile modulus of elasticity under tensile load increased from 19 to 51% when MCC was added to the PET/PTT blend. Elongation at break of composites was greater (reaching values 3.3 % with the addition of 20 wt% MCC. Elongation at break increased compared with the controls from 34 to 41 % when MCC was added to the PET/PTT blend. The flexural modulus of elasticity increased with increasing MCC loading (reaching values 3.37 GPa with the addition of 30 wt% MCC). Flexural modulus of the MCC-filled composites compared to that of the control increased from 36 to 47 %. Izod impact strength decreased compared with the control from 29 to 47 % when MCC was added to the PET/PTT blend. The density of the composites increased slightly as a function of MCC loading. This was expected since MCC has a greater density compared to the PET/PTT blend. There was not a strong correlation between density and tensile modulus of elasticity ($R^2= 0.74$) or density and flexural modulus of elasticity ($R^2= 0.80$). It was assumed that large improvements in the mechanical properties arose from the MCC itself.

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DYNAMIC MECHANICAL BEHAVIOUR AND THERMAL PROPERTIES OF MCC-FILLED NYLON 6 COMPOSITES

5.1. Chapter Summary

The dynamic mechanical behavior and thermal properties of nylon 6 composites containing from 2.5 wt.% to 30 wt.% MCC were investigated using dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The DSC results indicated that there was not a significant change in the glass transition (T_g) or melting temperature (T_m) of the nylon 6 with the addition of MCC. The DSC results also indicated that the crystallinity (X_c) decreased with increasing MCC level because of the inability of polymers chains to be fully incorporated into growing crystalline lamellae. With increasing MCC content, viscoelastic properties improved because of the reinforcing effect of the MCC. The $\tan \delta$ peak values from the dynamic mechanical thermal analysis were not significantly changed as the MCC content increased. DMTA also indicates that the magnitude of the loss factor ($\tan \delta$) of MCC filled composites was significantly decreased around the glass transition temperature. Thermogravimetric analysis indicated that the onset temperature of rapid thermal degradation decreased with increasing MCC content. The TGA data also show that as the MCC filler loading increased, the thermal stability of the composites decreased slightly because of the lower thermal stability of MCC compare to neat nylon 6.

5.2. Introduction

Over the past several decades, interest in the development of new composite materials derived from wood fiber and thermoplastic polymer matrices has received considerable attention in the marketplace. Wood fiber-filled thermoplastic composites are lightweight, low cost, offer high strength to weight ratios, less abrasive to processing equipment than mineral or glass fillers and can be recycled (Chen and Gardner 2008; McHenry and Stachurski 2003). In spite of these attractive properties, the processing temperature of these composites is restricted to about 200°C because the hemicellulose component of wood fibers degrades above 180°C and the melting temperature of selected plastics should not be over 200°C, which restricts the use of engineering thermoplastics such as nylon and polyethylene terephthalate (Chen and Gardner 2008; McHenry and Stachurski 2003; Azizi Samir et al. 2005; Jacobson et al. 2001; Sears et al. 2001; Sears et al. 2004). Thermogravimetric analysis studies show that the purified cellulosic component is thermally more stable than other wood component polymers (Jacobson et al. 2001). Because of greater thermal stability compared to wood fibers, microcrystalline cellulose can be used with engineering thermoplastics. Figure 5.1 shows that MCC is thermally more stable and has less weight loss in comparison with a similar sized wood flour material at 250°C.

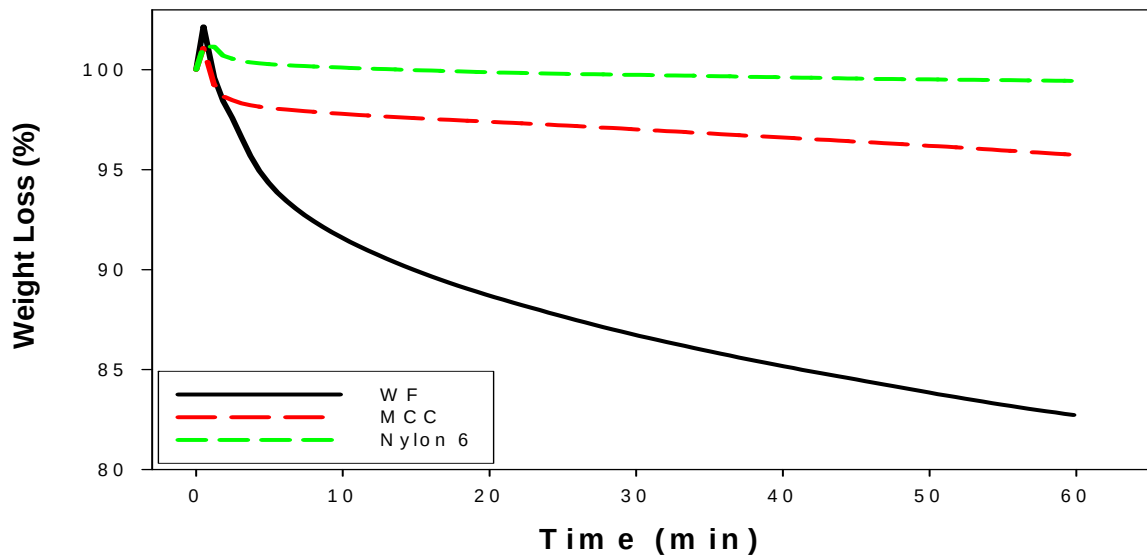


Figure 5.1 Weight Loss in % vs. time of MCC, wood flour and Nylon 6 by isothermal TGA.

Natural and synthetic polymers are exposed to thermal degradation reactions under the effect of increased temperatures (Wielage et al. 1999). Because of the higher processing temperatures of engineering thermoplastics, cellulose might be degraded and its mechanical properties decreased during melt processing. Therefore, it is extremely important to have information about the impact of processing temperatures during the manufacturing of cellulose reinforced composite materials with engineering thermoplastic matrices (Wielage et al. 1999). Essential statements regarding the processing temperatures and thermal stability of natural and synthetic polymers are obtained from thermal analysis techniques including dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). These techniques measure the thermal behaviors and interfacial characteristics of composite materials as a function of temperature (Miri et al. 2008; Kim et al. 2005; Kim et al. 2006; Yang et al. 2005). DMTA has been used extensively and is

an important technique in terms of determining the viscoelastic properties of composite materials as a function of temperature. DSC which can be used to determine melting temperature (T_m), glass transition temperature (T_g), crystallization temperature (T_c) and crystallinity (X_c) of composite materials, is a widely used thermal analysis technique. TGA can be used to determine the moisture content, mass change, thermal degradation temperature and thermal stability of composite materials (Kim et al. 2005; Kim et al. 2006; Yang et al. 2005).

MCC is a naturally occurring substance obtained from purified, partially depolymerized cellulose, prepared by treating alpha-cellulose, obtained as a pulp from fibrous material with mineral acids and it is used extensively in the pharmaceutical, food, paper and composite manufacturing industries (Azizi Samir). MCC-filled polyethylene and polystyrene polymer composites have been studied (Panaitescu et al. 2007; Laka and Chernyavskaya; Maskavs et al. 1999; Maskavs et al. 2001). However, there is lack of information about MCC-filled engineering thermoplastics. Aliphatic polyamides are well known engineering plastics in industry (Fornes and Paul 2003). Nylon 6 is in a major class of aliphatic polyamides and has several advantages including good chemical resistance, good abrasion resistance, and good mechanical and thermal properties (Jang and Kim 2000). Because of these advantages, nylon 6 is widely used in many areas such as automobile and textile industries (Jang and Kim 2000). A variety of inorganic materials such as clay minerals, glass fiber, talc and kaolin have been used in nylon 6 composites (Unal et al. 2003; Cho and Paul 2001). In spite of the technological interest in nylon 6, only a few studies of nylon 6/ cellulose polymer composites have been

published. Most were concerned with mechanical properties and there is not enough information related to thermal properties of nylon 6/cellulose composites in the literature.

The objective of this study was to investigate the effect of microcrystalline cellulose on the dynamic thermomechanical behavior and thermal properties of nylon composites. Microcrystalline cellulose was incorporated over a content range from 0 to 30 wt. %. Analyses were conducted using thermal tests including DMTA, DSC, and TGA. The thermal stability, DTGmax, viscoelastic behavior (storage modulus and Tan (δ)) T_m , T_g , T_c and X_c of the neat nylon 6 and MCC-filled nylon 6 composites were compared. In the present study, the nylon 6 composites were prepared with microcrystalline cellulose as the filler phase by injection molding.

5.3. Experimental Procedure

5.3.1. Materials

The nylon 6 used as the thermoplastic matrix polymer, was supplied by Entec Co., USA. Nylon 6 has a density of 1.13 g/cm³ and has reported mold shrinkage of 0.015 in/in. The lubricant (TPW 113) used as an additives to improve processing conditions, was supplied by Struktol Co. The same brand MCC used as a reinforcing agent for Nylon 6 composites. The MCC was described in detail in Chapter 3.3.1.

5.3.2. Sample Preparation

The MCC and nylon 6 were dried to moisture contents less than one percent using an oven at 105°C for 16-hours. The nylon 6 was mixed with the MCC by compounding using a Brabender Prep-mixer® equipped with a bowl mixer and the process temperature and torque changes were measured in real time. Melt temperature and torque changes for every run were recorded to determine optimum processability for the nylon 6-MCC composites. The basic processing parameters are listed in Table 5.1. The temperature was set to 250°C and rotor speed to 60 rpm. MCC was added to the mixer when the polymer melt appeared well mixed. After addition of the MCC, the melt temperature dropped sharply to 200° C. and increased again as the mixing progressed. The melt mixture was released from the mixture immediately after the temperature reached 230° C. These temperature ranges and MCC residence times were recognized as a relatively safe temperature range to prevent severe thermal degradation with a guarantee of composite processability. The resulting nylon 6-MCC compounds were granulated using a lab scale grinder. The ground particles were dried at an oven at 105°C for 16 hours before being injection molding into ASTM test specimens. All materials were injection molded using a barrel temperature of 250°C mold temperature of 250°C injection pressure of 2500 psi. The compositions of composites are shown in Table 5.2.

Table 5.1 Basic operating parameters of the Brabender rheomixer for the nylon 6 and MCC-filled nylon 6 composites.

Stage Level	Operating Parameters				
	Set Temp.	Melt Temp.	RPM	Mix Melt Temp.	Reaction Time
1 st stage (Nylon 6)	250	240	60-70	-	8 min
2 nd stage (with MCC)	230	200-240	50	Cont. under 240	2 min

Table 5.2 Composition of the MCC-filled nylon 6 composites.

Sample Code	Composition		
	MCC Content	Nylon 6	Lubricant
Neat Nylon 6	0	95	5
Nylon 6 – MCC2.5	2.5	92.5	5
Nylon 6 – MCC10	10	85	5
Nylon 6 – MCC20	20	75	5
Nylon 6 – MCC30	30	65	5

Values are percentage by weight (wt. %)

5.3.3. Thermal Properties

DSC analysis was carried out using a Perkin Elmer Instrument Pyris DSC with a sample weight of 8 to 10 mg. Each sample was scanned from -10 to 250°C at a heating rate of 20°C/min and then cooled at the same rate under a nitrogen atmosphere to observe the T_m taken as the peak temperature of the melting endotherm, T_g taken as the inflection point of the specific heat increment at the glass-rubber transition and crystallization behaviors of the composites. In addition, melting temperature and glass transition temperature were determined from a second scan.

The specimens' relative degree of crystallinity (X_c) was calculated according to the following equation (Azizi Samir et al. 2004).

$$X_c = (\Delta H_f \times 100) / (\Delta H_f^\circ \times \omega)$$

where, ΔH_f is the heat of fusion of the nylon blend and composites, ΔH_f° the heat of fusion for 100% crystalline nylon 6 ($\Delta H_{100}=190$ J/g) and ω is the mass fraction for nylon 6 in the composites (Wu et al. 2001). At least three randomly picked specimens from ground samples were tested for each composition, and the results are presented as an average for tested samples. The viscoelastic properties of the composites were determined with a Rheometric Scientific DMTA IV. The experiments were conducted in three point bending mode under isochronal conditions at a frequency of 1 Hz. The strain amplitude was fixed at 0.01% to be in the domain of the linear viscoelasticity of the composites. The samples were rectangular with dimensions about 42 mm x 3.2 mm x 3 mm. The temperature range was from 0 to 150°C at a scanning rate of 5°C/min. The storage modulus (E'), loss modulus (E'') and loss factor ($\tan \delta$) of the samples were measured as a function of temperature. At least three specimens were tested for each composition, and the results are presented as an average for tested samples. TGA measurements were carried out using a Mettler Toledo analyzer on samples of about 10 mg. Each sample was scanned over a temperature range from room temperature to 500°C at a heating rate of 10°C/min under nitrogen with a flow rate 20 ml/min to avoid sample oxidation. The samples used for the TGA measurement were randomly picked 5 individual samples from ground sample.

5.4. Results and Discussion

5.4.1. Differential scanning calorimetry (DSC)

The effect of the microcrystalline cellulose on the thermal properties of the thermoplastic polymer composites was examined in non-isothermal DSC experiments. All samples were held at 20°C for 1 min, heated at a rate of 20°C/min to 250°C, subsequently held for 1 min, then cooled at a rate of 20°C/min to -10°C, subsequently held for 1 min and heated again at a rate of 20°C/min to 250°C. The values of glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c) and corresponding melting enthalpies (ΔH_m) and crystallization enthalpies (ΔH_c) are presented in Table 5.3. The DSC thermograms of heating and cooling the neat nylon 6 and MCC-filled composites are presented in Figure 5.2. The DSC measurements indicate that the presence of MCC does not affect the T_g of the nylon 6 matrix, which occurs approximately at 42°C in Figure 5. 3.

Table 5.3 Summary of T_g , T_m , T_c , ΔH_m (J/g), ΔH_c (J/g), and X_c for the MCC-filled nylon 6 composites.

Sample Code	Composition					
	T_g (°C)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	ΔH_c (J/g)	X_c (%)
Neat Nylon 6	41.3 (0.8)	222.7 (1.3)	189.4 (0.8)	52.6 (1.4)	-67.3 (0.4)	27.7 (0.8)
Nylon 6 – MCC2.5	41.4 (0.9)	221.6 (0.3)	189.3 (0.4)	52.2 (1.1)	-66.2 (0.6)	28.2 (0.6)
Nylon 6 – MCC10	43.3 (1.4)	222.4 (1.2)	189.4 (0.3)	49.5 (1.5)	-60.3 (1.6)	28.9 (0.9)
Nylon 6 – MCC20	41.7 (2.4)	221.2 (0.8)	188.6 (0.7)	44.1 (2.1)	-57.9 (1.3)	29.1 (2.6)
Nylon 6 – MCC30	42.8 (1.4)	221.5 (0.6)	188.8 (0.4)	36.2 (0.3)	-50.1 (0.2)	27.2 (0.2)

Parenthesis indicates standard deviation.

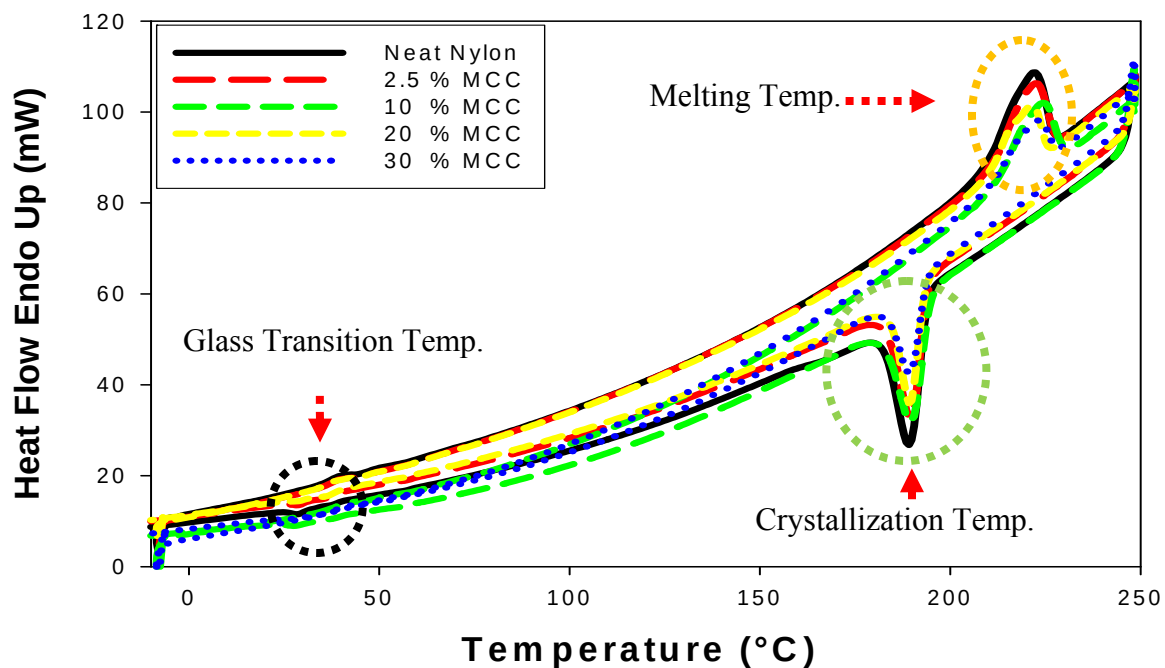


Figure 5.2 The DSC thermograms of heating and cooling courses of Nylon 6 and MCC filled Nylon 6 composites .

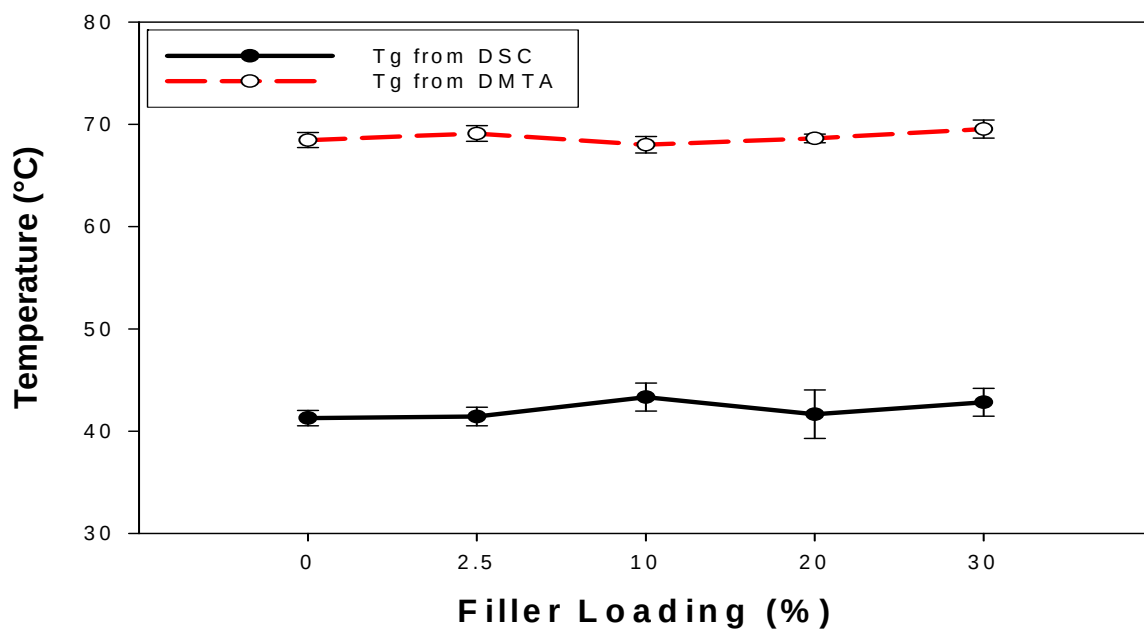


Figure 5.3 Tan $\delta_{\max}$ peak temperatures from DMTA and glass transition temperatures from DSC of the Nylon 6 and MCC-filled Nylon 6 composites at different filler loadings.

A similar behavior was observed in glass fiber, montmorillonite and organoclay-filled nylon 6 composites (Cho and Paul 2001; Goitisolo et al. 2008). Figure 3 also shows that there was not a good correlation between T_g obtained from DSC and DMTA. T_g by DMTA, loss factor ($\tan \delta$) measurements can differ by up to 25°C from DSC measurements. In addition, a 10 to 20 °C difference from DSC measurements is also seen in many different materials (Wunderlich 2005).

Figure 5.4 shows the crystallization temperature of neat nylon 6 and MCC-filled composites. Figure 5.4 illustrates that adding MCC does not change the crystallization temperature of the composites or it has a slight effect at most. (Table 5.3). Similar phenomena were also observed for the addition of nontreated silica in nylon 6 composites (Racz et al. 2004). However, increasing the MCC content in the composite, in all cases, results in smaller crystallization enthalpies (ΔH_c) and melting enthalpies (ΔH_m). A reason for this is that polymer chain mobility is hindered in highly filled composites. The melting point was taken as the main peak of the endothermic curve. The melting point of neat nylon 6 is 223°C. The effect of MCC on T_m of the composites is presented in Figure 5.4. It can be seen in Figure 5.4 that the melting points of composites were between 221°C and 223°C. The addition of the MCC to the nylon 6 has only a marginal effect on the melting temperature and no correlation of the results with the MCC loading can be established. This result suggests that the presence of MCC does not affect the T_m of the nylon 6. From these results, it can be concluded that the T_g and T_m values of the MCC-filled nylon 6 composites were strongly influenced by the matrix polymer. Furthermore, the T_m of the matrix polymer plays an important role in determining their processing

temperature and thermal properties (Kim et al. 2005; Kim et al. 2006). The degree of crystallinity of composites was calculated using the heat of fusion determined from DSC measurements and the one corresponding to a 100% crystalline nylon 6 reported by Wu et al. 2001. These values are reported in Table 5.3. For low loading levels of MCC up to 20 wt%, increasing the MCC content results in a minor change in percent crystallinity as seen in Table 3. For high loading contents above 20 wt%, increasing the MCC content results in a small decrease in percent crystallinity. The lower percent crystallinity seen in the composites is because of the inability of polymers chains to be fully incorporated into growing crystalline lamella (Fornes and Paul 2003). A similar effect was reported by Wu et al. 2001, Fornes and Paul 2003, for nylon 6/clay composites.

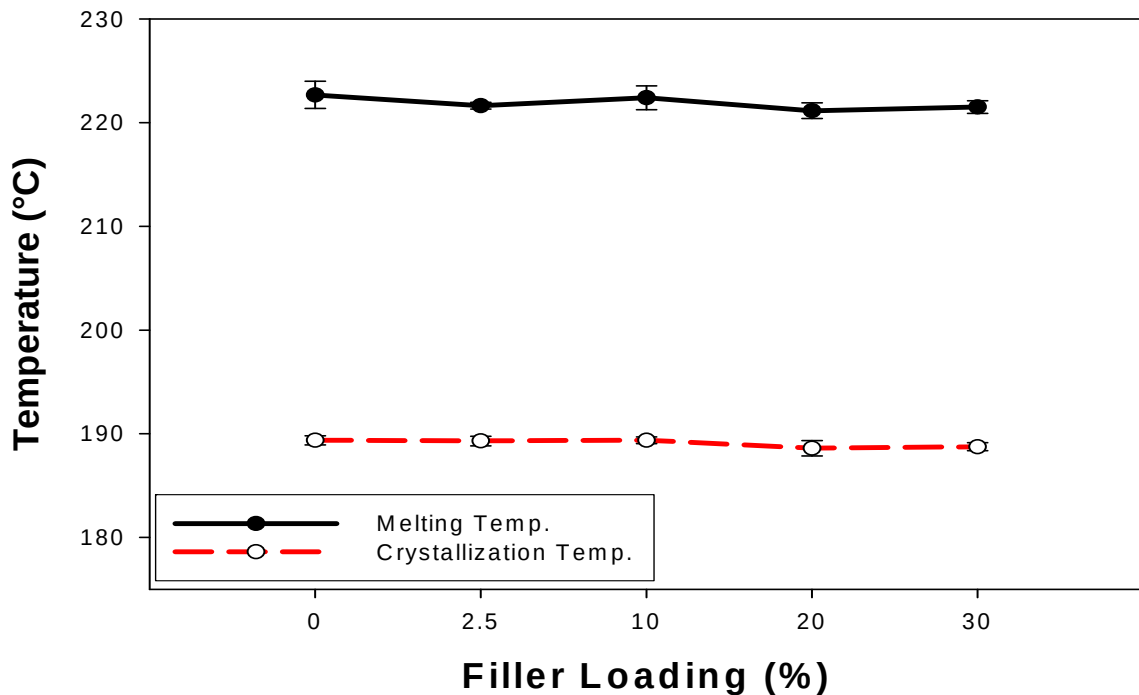


Figure 5.4 The effect of MCC loading on the melting and crystallization temperatures for Nylon 6 and MCC-filled Nylon 6 composites.

5.4.2. Dynamic mechanical thermal analysis (DMTA)

Figure 5.5 shows the temperature dependence of the storage modulus (E') and loss factor ($\tan \delta$) of nylon 6 and MCC-filled nylon 6 composites. The neat nylon 6 shows a typical behavior of semi crystalline polymer with three distinct regions that could be identified as glassy, glass transition and rubbery regions. In the glassy region (temperature is smaller than 25°C), the storage modulus remains roughly constant. Around 30°C, the modulus decrease is related to the glass transition region of the nylon amorphous phase. The magnitude of this storage modulus decrease is small due to high degree crystallinity of the nylon 6. At higher temperatures after the glassy region (temperature is higher than 35°C) the storage modulus decreases sharply because of the decreased viscosity and polymer chain mobility (Kim et al. 2005; Kim et al. 2006; Petersson et al. 2007). The sharp decrease in the storage modulus is continued until the rubbery region. MCC-filled nylon 6 composites show a similar behavior and have a higher modulus for the all temperature ranges compared to unfilled composites except the addition of 2.5 % MCC. The higher modulus for the composites could be a result of the highest degree of crystallinity of nylon 6 in the composite formulations, but DSC measurements show that the degree of crystallinity of the composites decreases with the high level addition of MCC (Xie et al. 2005). It is hypothesized that the increase of the modulus should be related to a reinforcing effect of MCC. A similar observation was reported for nylon 6 /clay nanocomposites (Miri et al. 2008, Xie et al. 2005]. Also, it can be seen that for Figure 5.5 the composites with MCC except the 2.5% MCC level exhibit much better temperature stability than neat nylon 6 in the rubbery region due to the percolating network effect (Seydibeyoglu and Oksman 2008).

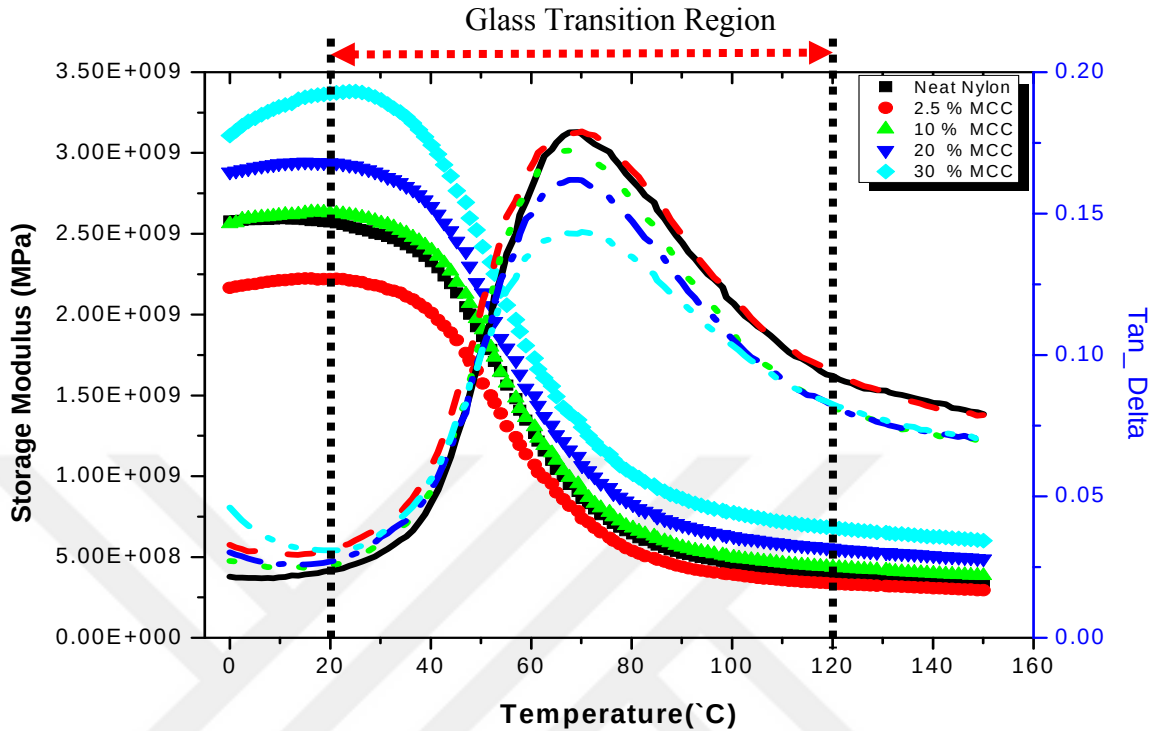


Figure 5.5 Storage modulus and Tan (δ) of Nylon 6 and MCC-filled Nylon 6 composites from -50 to 150°C as a function of temperature.

Figure 5.6 shows that the storage modulus of the MCC-filled nylon 6 composites increased with increasing MCC percent at high filler loading both at room (20°C) and glass transition temperatures. At 30 wt% percent MCC loading, the storage modulus increased significantly. As the MCC loading increases, the stress is more evenly distributed throughout the composite and therefore the modulus increases with the addition of MCC compared to the neat nylon 6. In addition, strong interactions, which arise from the hydrogen bonds between cellulose molecules and fibers and fibrils, lead to much a greater storage modulus (Seydibeyoglu and Oksman 2008).

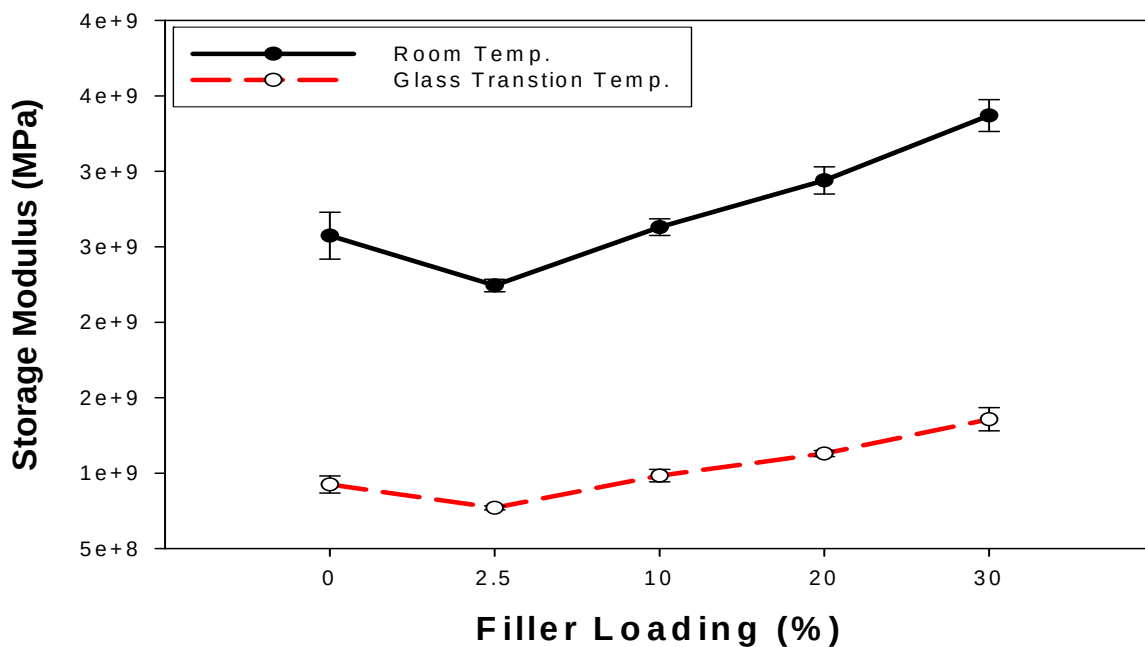


Figure 5.6 The storage modulus of Nylon 6 and MCC-filled Nylon 6 composites at the room temperature and glass transition temperature.

The temperature dependence of $\tan \delta$ (loss factor) versus for the MCC-filled nylon composites as a function of temperature at a frequency of 1 Hz is presented in Figure 5.5. The shift in $\tan \delta$ peak temperature can provide information about molecular interactions between nylon 6 and MCC (Seydibeyoglu and Oksman 2008). The main mechanical relaxation associated with the glass transition of the nylon 6 in composites is quite similar to and in agreement with several reports regarding nylon 6/ clay nanocomposites (Miri et al. 2008; Xie et al. 2005; Masenelli-Varlot et al. 2007). Incorporation of MCC does not significantly affect the glass transition temperature of the composite, but it does have a significant effect on the magnitude of $\tan \delta$ values in Table 5.4. This means that the overall chain mobility is not sensitive to the presence of MCC despite the high filler loading (Miri et al. 2008). The $\tan \delta_{\max}$ peak temperatures

correspond to the glass transition temperature and these values are not significantly changed as the MCC content is increased because the viscoelastic properties of the composite are strongly influenced by the matrix polymer. The neat nylon 6 presents a $\tan \delta_{\max}$ peak temperature of about 68°C and the composites present $\tan \delta$ peak temperatures between 68 and 69 °C. Figure 5.5 indicates that the $\tan \delta$ peak did not experience a temperature shift which indicates that there are no molecular interactions between the polymer matrix and MCC. As a result, we can see that the reinforcing effect is related to mainly with the cellulose network and strong interaction of cellulose particles (Kim et al. 2005; Kim et al. 2006; Seydibeyoglu and Oksman 2008). Figure 5.7 shows that the magnitude of the $\tan \delta$ peak of the MCC-filled composites were significantly decreased around the glass transition temperature because of the restriction in the chain segment mobility in the amorphous region of nylon 6 brought about by the incorporation of MCC (Kim et al. 2006; Xie et al. 2005; Chow and Mohd Ishak 2007).

Table 5.4 Tg Temperatures from Storage Modulus and Tan (δ) for neat nylon 6 and MCC-filled composites.

Sample Code	Tg Values		
	T_g Onset Temperature	T_g	T_g Offset Temperature
Neat Nylon 6	17.6 (1.5)	68.5 (0.7)	120.1 (1.1)
Nylon 6 – MCC2.5	22.1 (2.1)	69.1 (0.8)	120.5 (0.7)
Nylon 6 – MCC10	22.3 (2.4)	68.0 (0.8)	120.9 (1.5)
Nylon 6 – MCC20	22.0 (2.9)	68.6 (0.4)	123.8 (0.1)
Nylon 6 – MCC30	25.4 (0.7)	69.5 (0.9)	123.9 (1.3)

Parenthesis indicates standard deviation

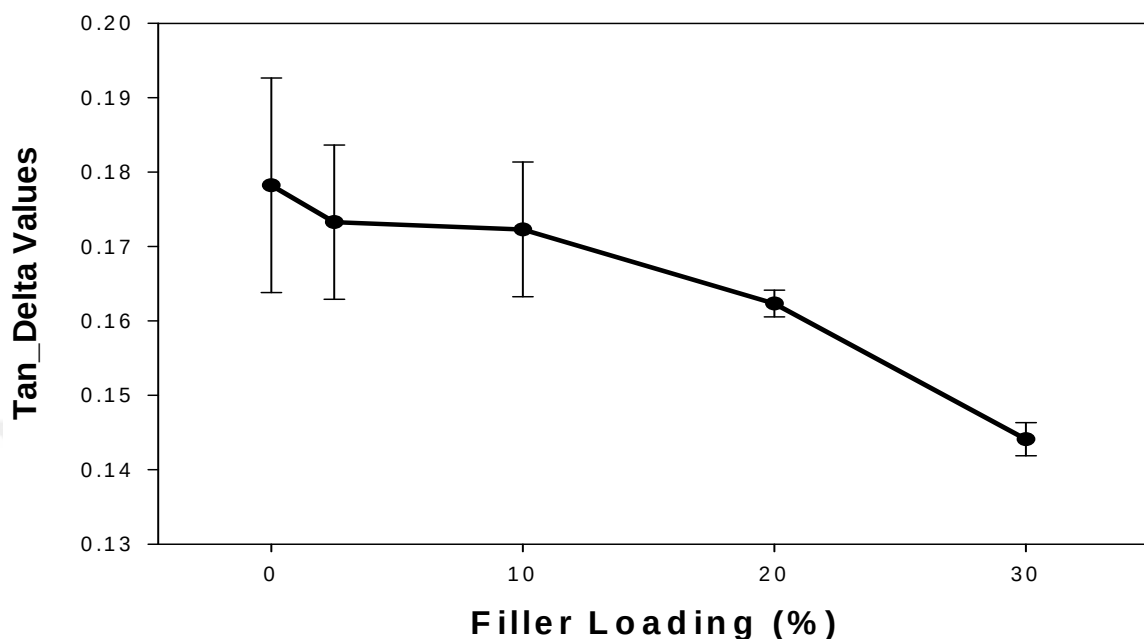


Figure 5.7 The effect of MCC loading on Tan δ peak values for Nylon 6 and MCC-filled Nylon 6 composites.

5.4.3. Thermogravimetric Analysis

The TGA and DTGA curves for nylon 6 and MCC-filled nylon 6 composites are shown in Figure 5.8. The onset temperature of rapid thermal degradation of composites decreases with increased MCC loading level in Figure 5.8. As the filler loading increased, the thermal stability of the composites slightly decreased, whereas the final ash content monotonically increased from around 2 % to 13% for the 30 wt% MCC addition. The degradation temperatures of neat nylon 6 and MCC-filled nylon 6 composites are different. The nylon 6 exhibited a single stage degradation with a peak at 452°C whereas MCC-filled nylon 6 composites show two degradation peaks in the range of 372 to 450°C.

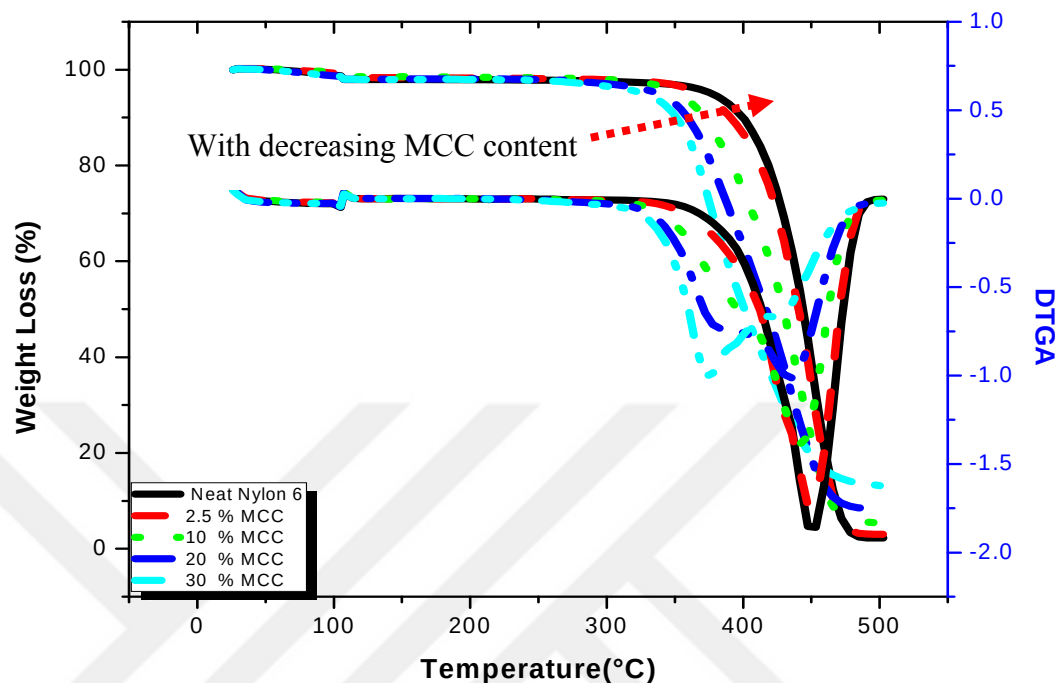


Figure 5.8 TGA and DTGA curves of Nylon 6 and MCC-filled Nylon 6 composites.

The temperature at 10% weight loss (T_{10}) and the temperature at 50% weight loss (T_{50}) for the neat nylon 6 and the MCC-filled nylon 6 composites are shown Figure 5.9. Both T_{10} and T_{50} values for the composites decreased monotonically from neat nylon 6 to the 30 wt% MCC addition. It is also obvious from Figure 5.10 that the percentage of weight loss for composites decreased monotonically from around 98% for neat nylon 6 to 87% for 30 wt% MCC additions. The results also show that as the filler loading increased, the thermal stability of the MCC-filled nylon 6 composites decreased slightly as the MCC content increased because of lower thermal stability of MCC compared to the neat nylon 6. A summary of weight loss (%), peak temperature and residual weight after 500°C of the composites is given in Table 5.5.

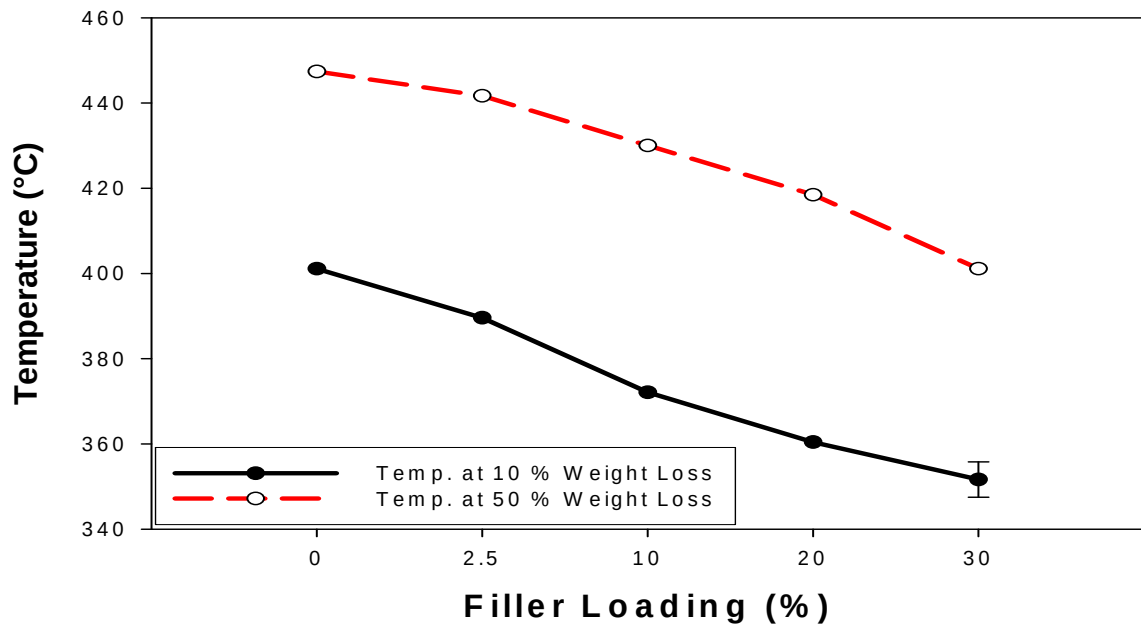


Figure 5.9 Temperatures at 10% and 50% weight loss for Nylon 6 and MCC-filled Nylon 6 composites

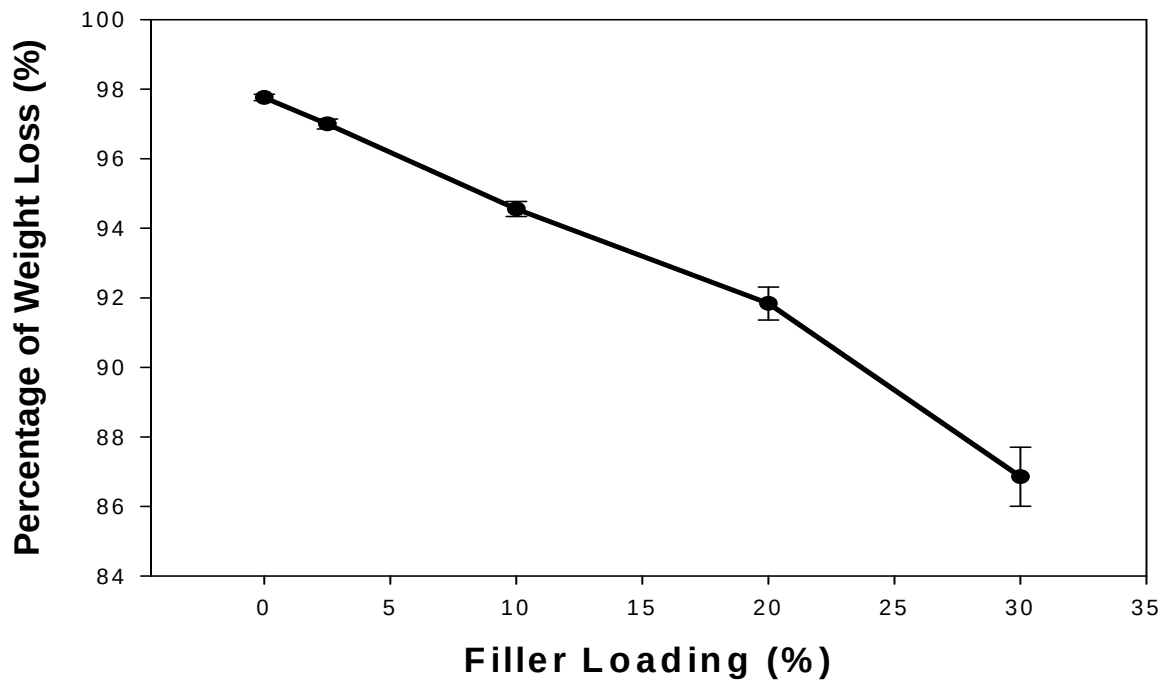


Figure 5.10 Ultimate percentage of weight loss for Nylon 6 and MCC-filled Nylon 6 composites.

Table 5.5 Thermogravimetric data for the MCC-filled nylon 6 composites.

Sample Code	DTGA Temp. (°C)		W.L. (%)		Residue (%)	
Neat Nylon 6	451.2 (0.9)		56.3 (0.3)		2.2 (0.1)	
Nylon 6– MCC2.5	450.5 (0.4)		60.9 (0.5)		3.1 (0.4)	
	1 st Peak	2 st Peak	1 st Peak	2 st Peak		
Nylon 6– MCC10	385.1 (0.5)	441.9 (0.2)	15.5 (0.4)	65.8 (0.1)	5.5 (0.2)	
Nylon 6- MCC20	380.6 (0.7)	434.9 (1.1)	20.5 (0.6)	68.1 (1.4)	8.2 (0.5)	
Nylon 6- MCC30	375.9 (2.2)	431.3 (2.6)	24.4 (0.1)	71.1 (1.9)	13 (0.9)	

Parenthesis indicates standard deviation

5.5. Conclusions

There was not a significant change in the glass transition (T_g), crystallization (T_c) and melting (T_m) temperatures of the composites with increased MCC loading. The degree of crystallinity of the nylon 6-MCC composites decreased after 20% MCC loading because of the inability of polymers chains to be fully incorporated into the growing crystalline structure of the matrix. The storage modulus (E') of the MCC-filled nylon 6 composite system was higher than that of neat nylon and increased with increasing MCC content except for the 2.5 wt% MCC loading. This is because the reinforcement effect of the MCC and is primarily related to the cellulose network and strong interaction of cellulose particles. The $\tan \delta$ peak values were not significantly changed as the MCC content increased because the viscoelastic properties of the composite are strongly influenced by the matrix polymer. Composites with MCC except the addition of 2.5 % MCC exhibit much better temperature stability than neat nylon 6 in the rubbery region. Thermogravimetric analysis indicated that the onset temperature of rapid thermal

degradation decreased with increasing MCC content. As the filler loading increased, the thermal stability of the composites slightly decreased, whereas the final ash content monotonically increased from around 2 % for the neat nylon 6 to 13% for the 30 wt% MCC addition.

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MECHANICAL PROPERTIES OF MCC-FILLED ENGINEERING THERMOPLASTICS

6.1. Chapter Summary

Microcrystalline cellulose (MCC) is thermally stable compared to other wood constituents and has the advantage of high specific surface area in comparison with conventional cellulose fibers. Because of these properties, MCC can be used as filler in polymer matrices. This study shows that it is possible to produce MCC-filled engineering thermoplastics with melt compounding followed by injection molding without the need for compatibilizers and other additives. Tensile, flexural, Izod impact and density tests were used to determine the material properties of the MCC-filled engineering composites. In general, the tensile and flexural properties increased with increasing MCC content. The Izod impact strength of composites decreases as the MCC loading increases and this observation is quite expected for filled polymer systems and has been commonly observed. There was not a strong correlation between density and tensile ($R^2 = 0.89$) and flexural modulus ($R^2 = 0.81$). MCC-filled composites manufactured by injection molding had a uniform density distribution throughout their thickness. MCC could be a good source for engineering thermoplastic applications such as in automobile manufacture.

6.2. Introduction

Engineering thermoplastic composites have attracted much interest over the past several decades as a result of its properties (excellent chemical resistance, high thermal stability, low creep compliance and high tensile, flexural and impact strength) and wide range of industrial and consumer applications including automotive, electrical and aerospace (Field 2003). Aliphatic polyamides are well known engineering thermoplastics in industry (Field 2003; Fornes and Paul 2003). Nylon 6 is in a major class of aliphatic polyamides and has several advantages including good chemical resistance, good abrasion resistance, thermal and weather resistance and good mechanical properties (Field 2003; Jang and Kim 2000). A variety of inorganic materials such as clay minerals, glass fibers, talc, calcium carbonate and kaolin have been used in nylon 6 composites as additives or reinforcement to improve mechanical and thermal properties of nylon 6 (Unal et al. 2003; Cho and Paul 2001; Racz et al. 2004; Avella et al. 2006). In spite of technological interest in nylon 6, only a few studies of cellulose filled or reinforced nylon 6 composites have been published in literature (Xu 2008; Caulfield et al. 2001; Jacobson et al. 2001; Sears et al. 2001; Jacobson et al. 2003; Chen and Gardner 2008; McHenry and Stachurski 2003; Snijder et al. 1997).

Earlier research related to cellulose-filled engineering thermoplastics did not provide encouraging results. Cellulose-filled engineering thermoplastics exhibited severe discoloration and pronounced pyrolytic degradation because of the high processing temperatures of polymer matrix (Caulfield et al. 2001; Jacobson et al. 2001; Sears et al. 2001; Snijder et al. 1997). Based on initial research, scientists believed that the use of

cellulose as a reinforcement or additive in engineering thermoplastics could not be effective because cellulose thermal degradation occurs at temperatures needed to process engineering thermoplastics (Xu 2008; Caulfield et al. 2001; Jacobson et al. 2001; Sears et al. 2001). The automobile and construction market requires low density and cheap reinforcement for engineering thermoplastics. Because of this demand, researchers have recently looked again at cellulose-filled engineering thermoplastics (Xu 2008).

Jacobson et al. developed a unique compounding method called low temperature compounding to produce cellulose pulp fiber-filled nylon 6 composites. They found that mechanical properties for the 33 percent cellulose fiber-filled nylon 6 composites were approximately twice as stiff as neat nylon composites and had better strength properties than the neat nylon. Mechanical properties of the 33 percent cellulose fiber reinforced nylon 6 composites were also intermediate between glass fiber and wollastonite, which are extensively used in the automobile industry as filler, reinforced nylon 6 composites. They also found that the density, color and surface appearance of these injection-molded materials appeared to be suitable for some automobile applications (Jacobson et al. 2001). In another study, Misra et al. 2004 used small quantities Lithium chloride (LiCl) during melt extrusion processing to decrease melting temperature of nylon 6. They realized that the addition of LiCl to nylon 6 also decreased the crystallization temperature and degree of crystallinity. They also exhibited that both tensile modulus and strength increased with reinforcement of modified nylon 6 with 40% hemp fiber (Xu 2008; Misra et al. 2004. Xu [2008] studied cellulose filled-engineering thermoplastics with different production methods and found that for cellulose fiber/nylon 6 composites, extrusion-injection

molding gave better mechanical properties than extrusion-compression molding and low temperature extrusion exhibited better properties than high temperature extrusion. Xu also found that modulus and strength increased with an increase in fiber content (Xu et al. 2008).

MCC is highly crystalline cellulose obtained from high quality wood pulp (Azizi Samir et al. 2005; Mathew et al. 2004). MCC has the advantage of high specific surface area in comparison with other conventional cellulose fibers and can be used as a cellulosic reinforcement for polymer matrices (Mathew et al. 2004). MCC has been incorporated into a number of different matrices like poly (lactic acid) (Mathew et al. 2004; Petersson and Oksman 2006), polystyrene (Laka and Chernyavskaya 1996) and polyethylene (Maskavs et al. 1999; Maskavs et al. 2001; Panaitescu et al. 2007a; Panaitescu et al. 2007b). However there is lack of information about MCC-filled engineering thermoplastics.

The objective of this study was to investigate the influence MCC filler loading on mechanical properties of MCC-filled nylon 6 composites. Microcrystalline cellulose was incorporated over a content range from 0 to 30 wt. %. Analyses were conducted using mechanical tests including tensile, flexural and impact test as well as determination of composite densities.

6.3. Experimental Procedures

The materials used in this work and sample preparation were described in detail in Chapter 5.3.1 and 5.3.2 respectively. The statistic programs also used in this work described in detail in Chapter 4.3.1.

6.3.1. Mechanical Properties

The same mechanical tests used in this work and described in detail in Chapter 4.3.2.

6.4. Results and Discussion

The tensile behavior of the neat nylon 6 as well as the MMC-filled composites from 2.5 wt% to 30 wt% was performed by tensile testing at room temperature and 50% R.H. Figure 6.1 and Figure 6.2 show tensile strength and elongation at break of the neat nylon 6 and MCC-filled composites. The tensile strength and elongation at break were determined from stress and strain curves and the results are presented in Table 6.1.

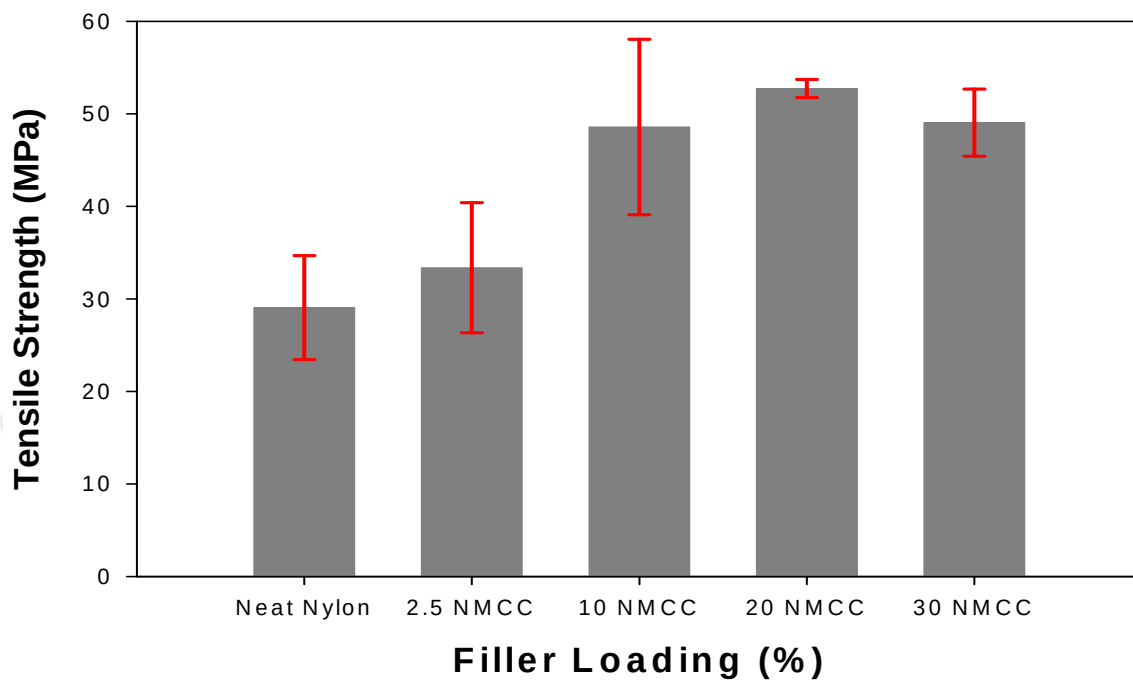


Figure 6.1 Effect of MCC loading on tensile strength of MCC-filled nylon 6 composites.

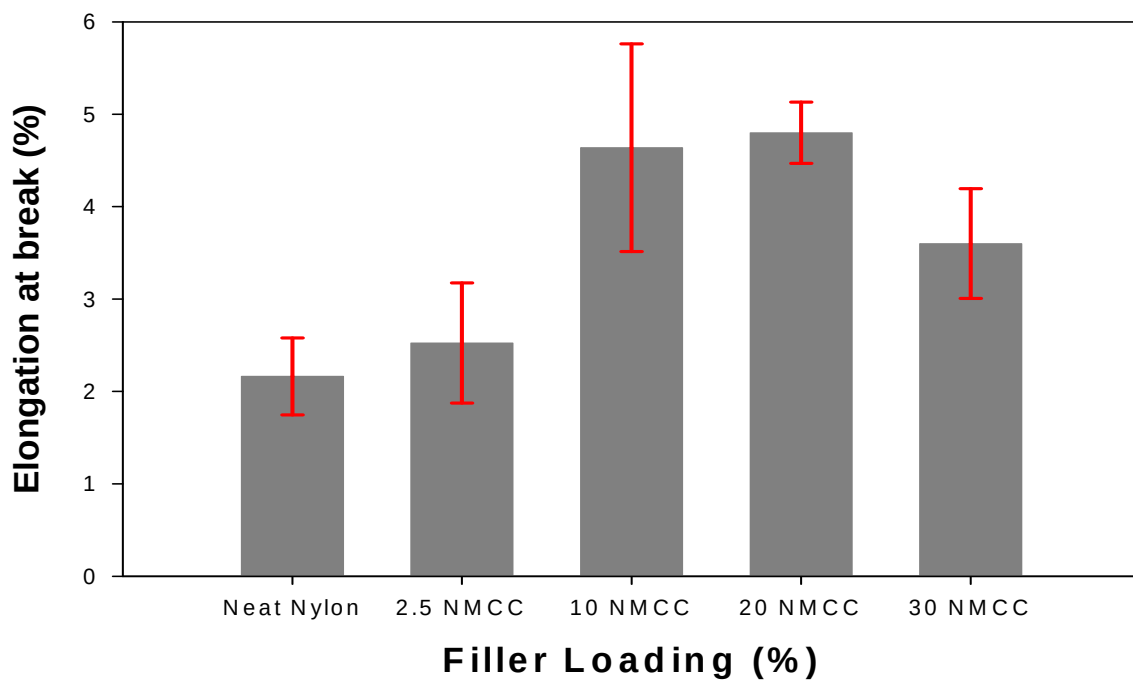


Figure 6.2 Tensile modulus of elasticity of neat nylon 6 and MCC-filled composites.

Table 6.1 Summary of mechanical properties of neat nylon 6 and MCC-filled composites

Sample Code	Tensile Properties		Flexural Properties		Impact Properties	Density
	Strength (Mpa)	Modulus (GPa)	Elongation(%)	Modulus (GPa)	Izod Notched (J/m)	g/cm3
Neat Nylon 6	29.1 (5.6)	1.41 (0.05)	2.16 (0.4)	2.56 (0.1)	41.3 (2.5)	1.09 (0.01)
Nylon 6 – MCC2.5	33.4 (7.0)	1.38 (0.05)	2.53 (0.6)	2.75 (0.2)	42.6 (3.8)	1.10 (0.02)
Nylon 6 – MCC10	48.6 (9.5)	1.46 (0.05)	4.64 (1.1)	2.97 (0.1)	31.6 (5.2)	1.13 (0.01)
Nylon 6 – MCC20	52.7 (1.0)	1.69 (0.04)	4.80 (0.3)	3.76 (0.3)	24.3 (4.1)	1.17 (0.01)
Nylon 6 – MCC30	49.1 (3.6)	1.86 (0.06)	3.60 (0.6)	3.74 (0.3)	19.8 (4.8)	1.21 (0.01)

It was observed that neat nylon 6 exhibits a non linear elastic behavior with a tensile strength of 29.06 MPa and an elongation at break of 2.16%. None of composites including the neat nylon 6 showed signs of stress yielding. This result suggests that the mechanism behind the elongation and rupture of the composites was similar to that of neat nylon 6. The composite reinforced with MCC displayed enhanced tensile properties in comparison with the neat nylon 6. Because of better compatibility as well as better stress- transfer properties, tensile strength of composites was larger (reaching values of 52.7 MPa with the addition of 20% MCC). Tensile strength increased by 81% with 20% MCC addition. After 20% MCC addition, tensile strength decreased but it was greater compared to neat nylon 6. The reason why tensile strength decreases after 20%MCC addition could be very little or no stress-transfer properties in this highly filled composite (Lijunberg et al. 2006). This behavior is also mainly because of the high MCC content, which contributes to material brittleness. Xu [2008] observed similar reinforcements with cellulose fiber in nylon 6 composites. The tensile strength increased up to 20% addition of cellulose fiber and beyond 20% MCC addition tensile strength decreased but was higher than neat nylon 6. The tensile strength also increased by 23% with 20 wt% cellulose fiber addition using an extrusion-injection molding method (Xu 2008]. In

general, almost all filled polymer systems display smaller elongations at break compared to the neat polymer matrix because of deformability of a rigid interphase between filler and the matrix material (Zaini et al. 1996). Figure 6.2 seems to be contradictory to this observation. In our case, elongation at break of composites was longer (reaching values 4.8% with addition of 20% MCC). Like tensile strength, the elongation at break also decreased beyond a critical MCC loading (20% MCC). A possible explanation for this result might be attributed to better particle dispersion below 20 wt% MCC additions. At high MCC contents, the degree of filler-filler interaction becomes more prominent and, as a consequence, a reduction in elongation at break was seen in the MCC-filled composites. (Dikobe and Luyta 2007). Based on the above results, it clearly shows that there is an optimal amount of MCC needed in a composite to achieve the greatest improvement in tensile properties.

Figure 6.3 shows the tensile modulus of neat nylon 6 and MCC-filled composites. The tensile modulus of a polymeric material has been shown to be significantly improved when nano-micro composites are formed with cellulose (Mathew et al. 2004; Petersson and Oksman 2006; Seydibeyoglu and Oksman 2008). The tensile modulus of elasticity of neat nylon 6 was 1.41 GPa. The tensile modulus of elasticity was first seen to decrease with 2.5 wt% MCC addition, however this value (1.38GPa) was not significantly different from neat nylon 6. The tensile modulus of elasticity of MCC-filled composites after 2.5 wt% MCC addition systemically increased with increasing MCC loading (reaching values of 1.86 GPa with the addition of 30 wt% MCC). Xu observed similar phenomena. Tensile modulus of elasticity of the composites increased with increasing

cellulose fiber content (Xu 2008). A similar effect was also reported by Caulfield et al. for Nylon 66/hardwood and softwood fiber composites (Caulfield et al. 2001).

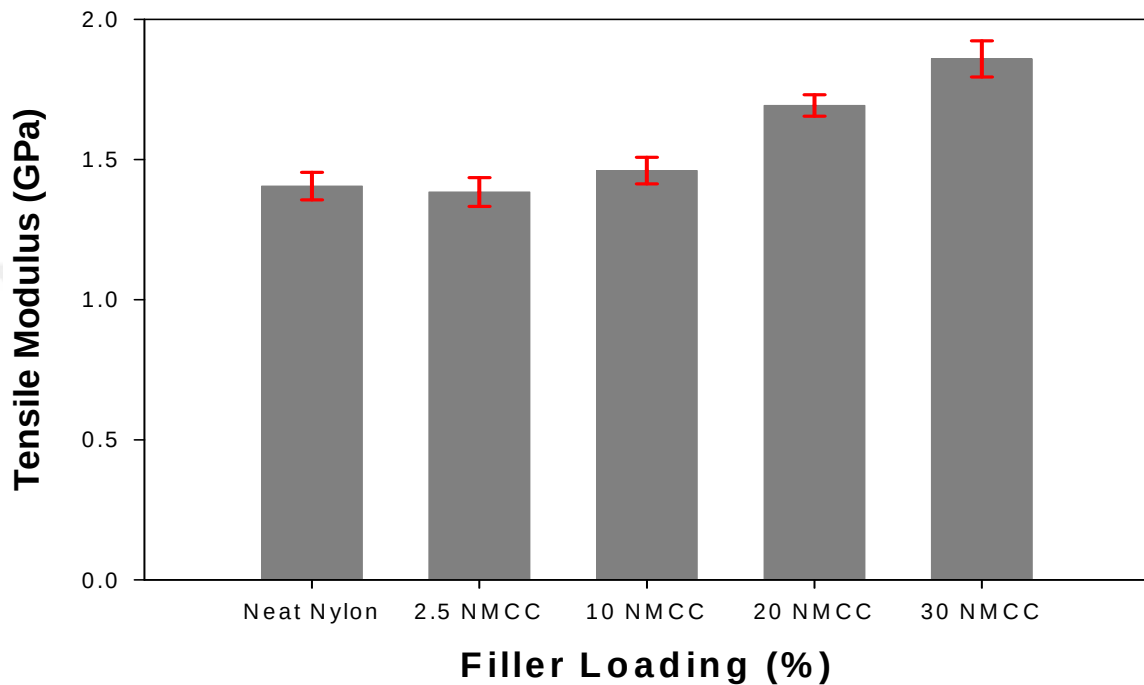


Figure 6.3 Tensile modulus of elasticity of neat nylon 6 and MCC-filled composites.

The flexural behavior of the neat nylon 6 as well as the composites reinforced from 2.5 wt% to 30 wt% MCC was performed by flexure testing at room temperature and 50% R.H. In Figure 6.4 and Table 6.1, the average values of the flexural modulus as a function of MCC are shown. As can be seen in the figure, the flexural modulus of composites was higher than neat nylon 6. Flexural modulus of elasticity of neat nylon 6 was 2.56 GPa. The modulus also increased with increasing MCC loading (reaching values of 3.76 GPa with the addition of 20 wt% MCC). There was no statistical difference in terms of flexural modulus of elasticity between 20 wt% MCC and 30 wt% MCC-filled composites. Flexural modulus of elasticity increased by 47% with 20 wt%

MCC addition. The flexural modulus is strongly affected by MCC loading and MCC orientation and less by neat nylon 6 –MCC interaction (Seydibeyoglu and Oksman 2008). A similar effect was also reported by Xu for nylon 6/cellulose fiber composites (Xu 2008). Also Sears et al., used cellulose wood pulps as a reinforcement for nylon 6 composites and found that cellulose wood pulps increased flexural modulus compared to neat nylon 6 composites (Sears et al. 2001).

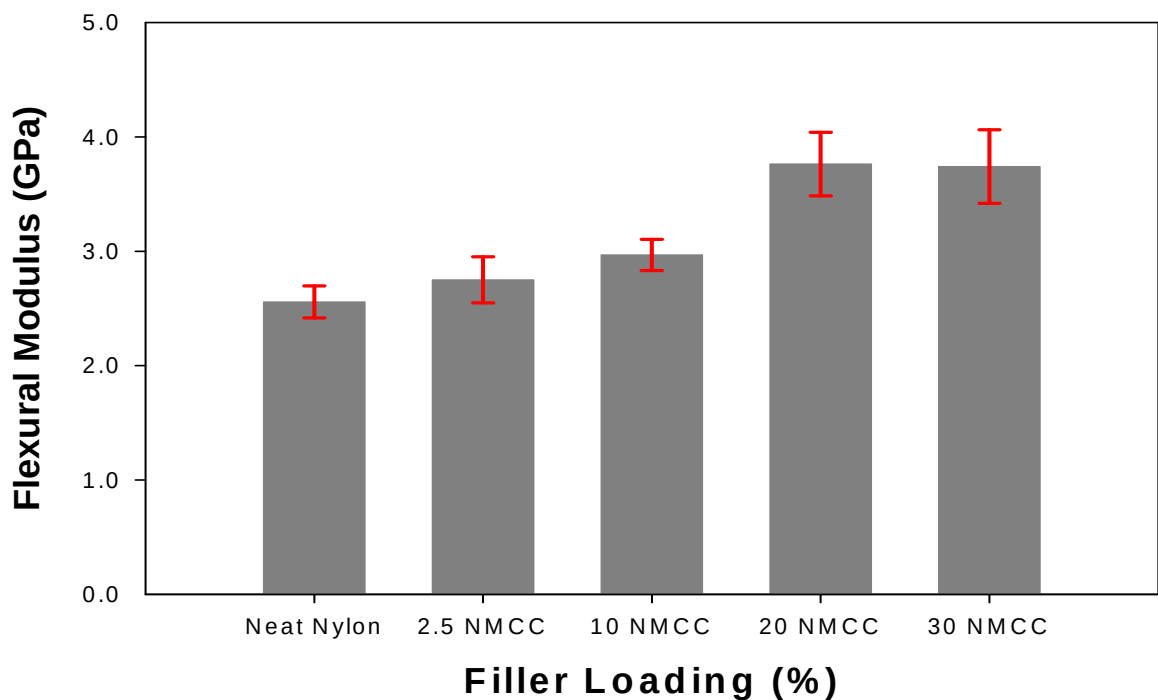


Figure 6.4 Flexural modulus of elasticity of neat nylon 6 and MCC-filled nylon 6 composites

The impact strength of the composites can be attributed to the amount of filler loading and the type of testing whether the samples were notched or un-notched (Zaini et al. 1996). The impact behavior of the neat nylon 6 as well as the composites reinforced from 2.5 wt% to 30 wt% MCC was performed by notched Izod impact testing at room

temperature and 50% R.H. Figure 6.5 and Table 6.1 show the Izod impact strength of neat nylon 6 and MCC-filled composites.

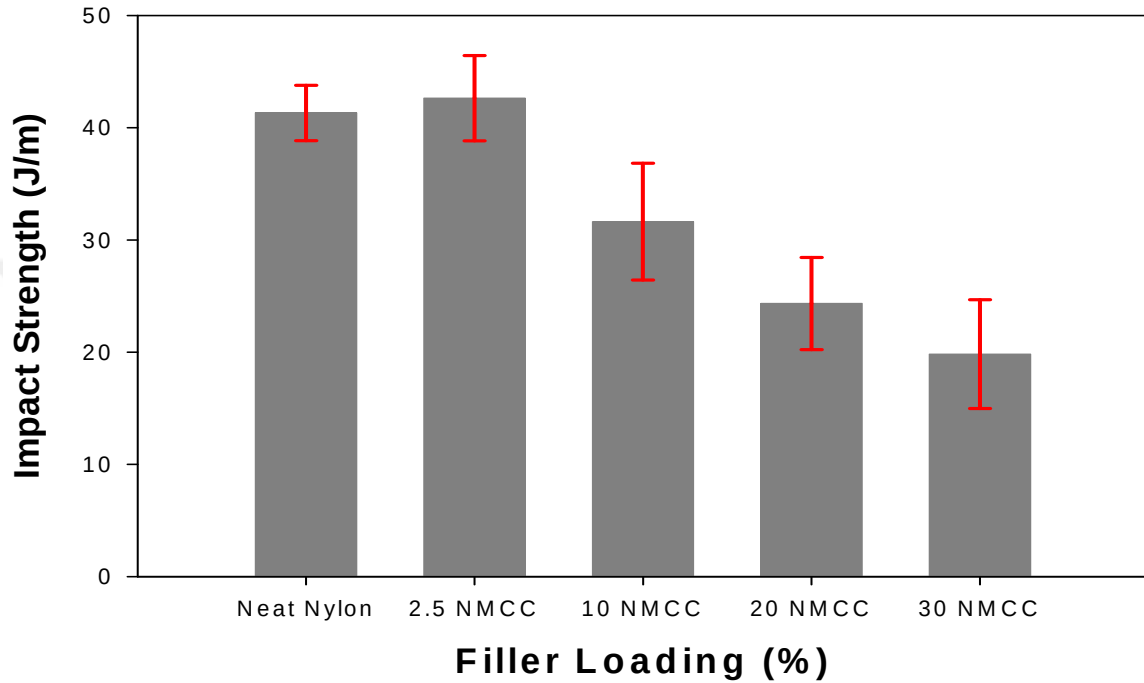


Figure 6.5 Effect of MCC loading on impact strength of neat nylon 6 and MCC-filled composites.

The Izod impact strength of composites decreased as the MCC loading increased and this observation was expected for filled polymer systems and has been commonly observed (Zaini et al. 1996; Bengtsson and Oksman 2006; Sanadi et al. 1997; Liang 2002; Cui et al. 2008). Because of the possibility of poor wetting of the particles, by the matrix polymer, poor interfacial adhesion between the MCC and the neat nylon 6 can cause weak interfacial regions (Zaini et al. 1996). This phenomenon might explain the lower impact strength with the increase in MCC loading. Another reason for this observation was the unmodified cellulose surface which was not optimized for dispersion in the nylon 6 matrix. In this case, the impact strength can decrease quickly at low filler

additions (Zaini et al. 1996; Bengtsson and Oksman 2006). During the impact tests, cracks travel through the polymer as well as along the weak interfacial regions, which might be attributed to poor wetting of the particles by the nylon 6. As a result of crack travel, the latter cannot resist crack propagation as effectively as in the polymer matrix regions; therefore lower impact strengths are observed (Zaini et al. 1996). Increasing MCC content increases the interfacial regions which contribute to crack propagation. Also, the addition of MCC might cause polymer immobility which can result in lower impact strength. Fig. 5. also shows that the Izod impact strength of composites decreased from 41 J/m for neat nylon 6 to 20 J/m for the 30 wt% MCC-filled composite. A similar effect was also reported by Xu for nylon 6/cellulose fiber composites [8]. The impact strength of the composite can be improved by providing flexible and strong interfacial bonding in the composite or by using coupling agents or impact modifiers (Zaini et al. 1996; Sanadi et al. 1997; Liang 2002; Cui et al. 2008).

Figure 6.6 and Table 6.1 shows the densities of neat nylon 6 and MCC-filled composites. The density of the composites increased slightly with increased MCC loading. This was expected, since MCC has a greater density compared to neat nylon 6. Generally, there is a certain correlation between density and mechanical properties such as flexural strength and modulus of elasticity (Klyosov 2007). Our results seem to be contradictory to this general observation. There was not a strong correlation between density and tensile ($R^2 = 0.89$) and flexural modulus of elasticity ($R^2 = 0.81$). It was hypothesized that the large improvements in mechanical properties come from the MCC itself. The strong hydrogen bonds between MCC molecules, which lead to strong

interactions between fibers and fibrils, might contribute to better mechanical properties in comparison with neat nylon 6 (Seydibeyoglu and Oksman 2008).

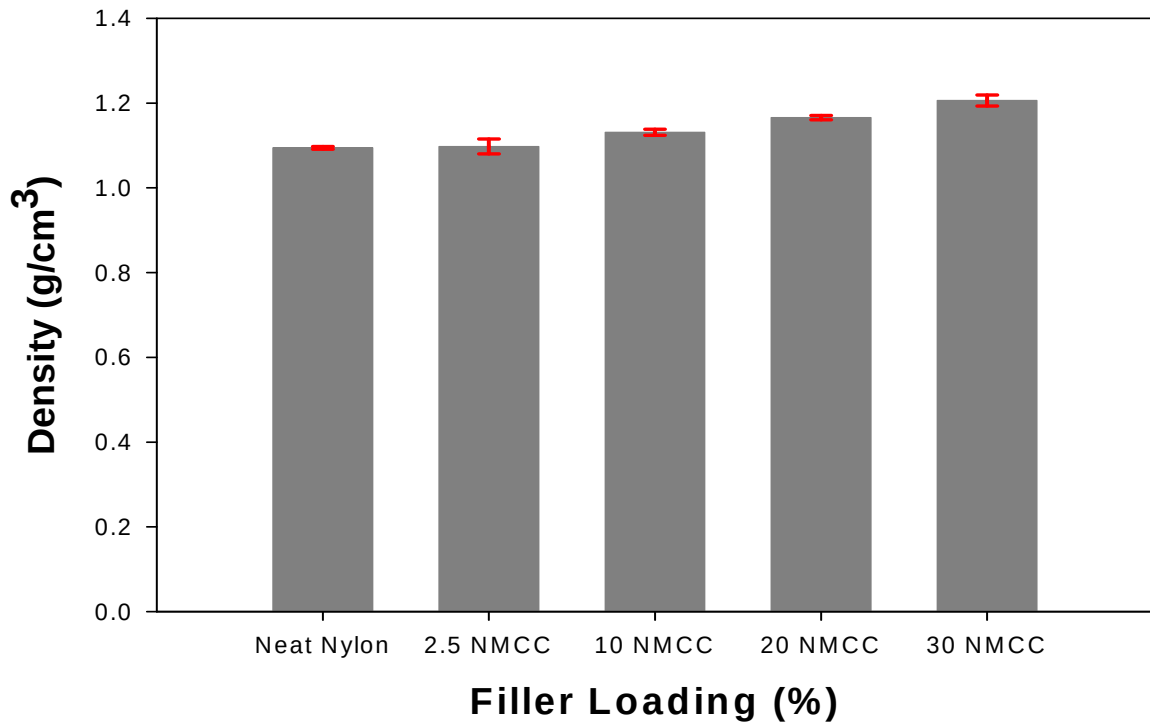


Figure 6.6 Density as function of MCC loading for MCC-filled nylon 6 composites.

As a result of the density study, it can be confirmed that MCC provides the reinforcement (flexural and tensile modulus) effect for composites with a smaller increase in density, which should not be discounted, especially for automobile applications (Caulfield et al. 2001b). As expected, neat nylon 6 and MCC-filled composites manufactured by injection molding had a highly uniform density distribution throughout the sample thickness Figure 6.7. Table 6.2 also shows that the effect of MCC loading on the overall mechanical properties of composites in terms of statistical analysis.

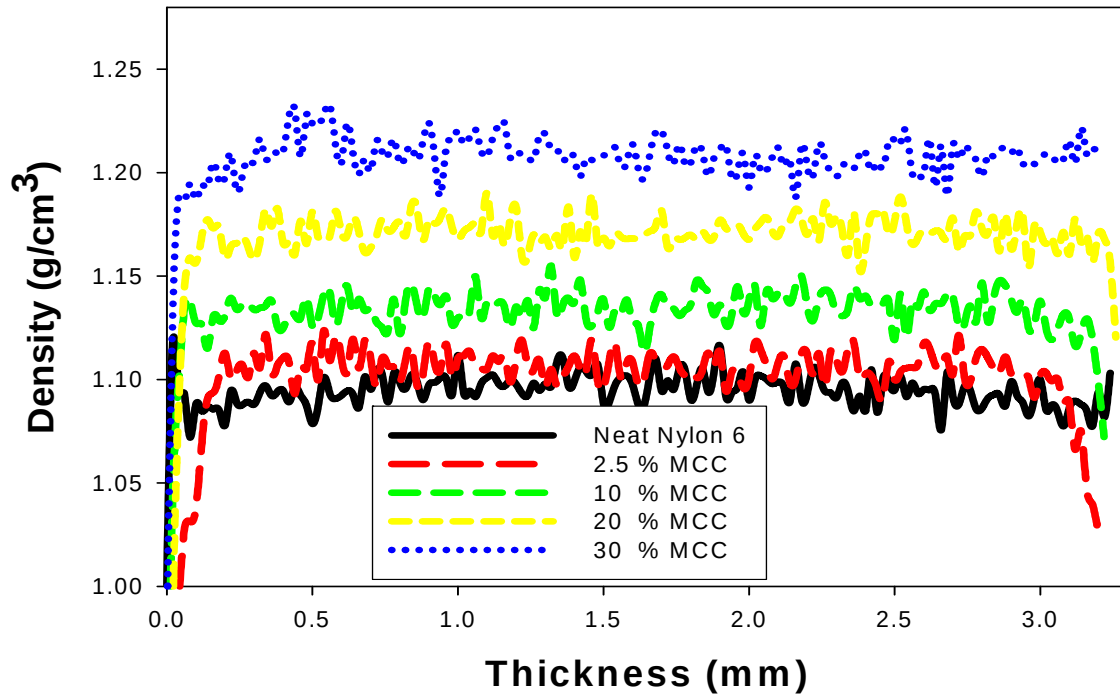


Figure 6.7 Average density profile of neat nylon 6 and MCC-filled composites.

Table 6.2 Results of Tukey-Kramer HSD comparison at $\alpha = 0.05$ for nylon 6 and MCC-filled composites

Sample Code	Tensile Properties			Flexural Properties	Impact Properties	Density
	Strength (MPa)	Modulus (GPa)	Elongation(%)	Modulus (GPa)	Izod Notched (J/m)	g/cm ³
Neat Nylon 6	B	CD	B	B	A	D
Nylon 6– MCC2.5	B (NC)	D (NC)	B (NC)	B (NC)	A (NC)	D (NC)
Nylon 6– MCC10	A (+67%)	C (NC)	A (+214%)	B (NC)	B (-23%)	C (+4%)
Nylon 6– MCC20	A (+81%)	B (+20%)	A (+222%)	A (+47%)	C (-41%)	B (+7%)
Nylon 6– MCC30	A (+69%)	A (+32%)	AB (166%)	A (+46%)	C (-52%)	A (+10%)

The same letters indicates no statistical difference between properties of composites and those around it. NC is no significant change upon the addition of MCC ($\alpha=0.05$) and parenthesis show that effect of MCC loading on the mechanical properties of composites in comparison with neat nylon 6.

6.5. Conclusions

The results of this study verify that MCC can be utilized to produce engineering thermoplastic composites. There was no statistical difference in terms of mechanical properties between neat nylon 6 and 2.5 wt% MCC-filled composites. The composites reinforced with higher MCC filler loadings displayed enhanced tensile and flexural properties in comparison with the neat nylon 6. The results also appear to be contradictory to the general observations that elongation at break of the composites was greater (reaching values 4.8 % with the addition of 20 wt% MCC). Izod impact strength decreased in comparison with the controls from 23 to 52 % when MCC was added to nylon 6. The density of the composites increased slightly with increased MCC loading. It was hypothesized that the large improvements in mechanical properties come from MCC itself. In general, MCC-filled composites showed comparable or higher mechanical properties compared to neat nylon 6.

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CONCLUSIONS AND RECOMENDATIONS

7.1. Conclusions

The overall objective of this study was to investigate the influence of MCC filler loading on the mechanical and thermal properties of MCC-filled engineering thermoplastic composites. Microcrystalline cellulose (MCC) and engineering thermoplastics (nylon 6 and PET-PTT blend) were chosen as the filler/matrix combinations. The results of this study verify that MCC can be utilized to produce engineering thermoplastic composites. Following are a summary of findings:

- 1) There was not a significant change in the glass transition (T_g), crystallization (T_c) and melting (T_m) temperatures of the composites with increased MCC loading. The degree of crystallinity of the MCC-filled composites changed slightly after 20% MCC loading.
- 2) The storage modulus (E') of the MCC-filled engineering thermoplastic composite system was higher than that of the control samples and increased with increasing MCC content, this was attributed to the reinforcement effect of the MCC, and this reinforcing effect is related mainly to the cellulose network and strong interaction among cellulose particles. The $\tan \delta$ peak values were not significantly changed as the MCC content increased because

the viscoelastic properties of the composite are strongly influenced by the matrix polymer.

- 3) Thermogravimetric analysis indicated that the onset temperature of rapid thermal degradation decreased with increasing MCC content. As the filler loading increased, the thermal stability of the composites decreased slightly.
- 4) There was no statistical difference in terms of mechanical properties between the control samples and 2.5 wt% MCC-filled composites. The composite reinforced with high filler loadings of MCC displayed enhanced tensile and flexural properties in comparison with the control samples.
- 5) The results also appear to contradict to the general observations that elongation at break of the composites was greater. Izod impact strength of the composites decreased in comparison with the control samples.
- 6) The density of the composites increased slightly as a function of MCC loading. This was expected since MCC has a greater density compared to the control samples. There was not a strong correlation between density and tensile modulus of elasticity or density and flexural modulus of elasticity. It was assumed that large improvements in the mechanical properties arose from the MCC itself.

- 7) Overall, MCC-filled composites showed comparable or better mechanical properties compared to control samples without compatibilizers.

7.2. Recommendations for Future Work

1. The state of dispersion and structure of engineering composites need to be studied with X-ray scattering and transmission electron microscopy (TEM). Crystallinity also needs to be measured from X-ray diffraction.
2. The filler-matrix interface and interphase are important factors in terms of mechanical properties of the composites. It is expected that with continuing research on crosslinking agents such as silanes and corona discharge treatments that significant improvements in mechanical properties can be achieved (Oksman Niska and Sanadi 2008)
3. Accelerated aging testing studies should provide information for predicting long term performance of the composites. For that purpose, characterization of the temperature-dependent and time-dependent dynamic mechanical properties of the engineering thermoplastic composites needs to be studied (Marcovich and Aranguren 2008).
4. Recycled carpet is a good source for polyamides. MCC can be used to reinforce polyamides from recycled carpet to make low cost, high

performance composites. The effect of thermal degradation on the mechanical properties of engineering thermoplastic composites also needs further study (Xu 2008).

5. Lower melting temperatures are very important during the processing of engineering thermoplastic polymers with lignocellulosics in the extrusion process. Lower melting temperatures of engineering thermoplastic polymers by adding inorganic salts needs to be studied.
6. Understanding the melt rheology of composite materials can give much important information such as design of dies, processing profiles, dispersion properties and interfacial properties between the natural fiber, thermoplastic polymers and processing and performance additives. For that purpose, melt viscosity of composites need to be studied (Englund and Wolcott 2008).

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