Chemically Modified Cellulosic Materials as Multi-Functional Agents in Polymer Composites

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CHEMICALLY MODIFIED CELLULOSIC MATERIALS AS MULTI-FUNCTIONAL AGENTS IN POLYMER COMPOSITES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The School of Renewable Natural Resources

by

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ABSTRACT

Comparative flame retardancy of micro wood fiber plastic composites (WPCs) with fire retardants (1,2-bis(pentabromophenyl) ethane, metal hydroxides and nanoclay) was studied. The fire additives (1,2-bis(pentabromophenyl) ethane as well as magnesium hydroxide) obviously enhanced the fire retarding properties of WPCs. Especially, 1,2-bis(pentabromophenyl) ethane significantly reduced the total heat release as well as heat release rate. In addition, a synergistic effect of 1,2-bis(pentabromophenyl) and nanoclay was achieved for the enhanced fire retarding performance of WPCs.

A copolymer of cellulose nanocrystals (CNCs) and poly(N-vinylcaprolactam) (PVCL) (PVCL-g-CNCs) for use as thermally-responsive polymers with low critical solution temperatures (LCSTs) was synthesized via atom transfer radical polymerization (ATRP). The rod like morphology of CNCs was well preserved after the grafting modification. The dynamic rheology measurement confirmed the thermally induced phase transition behavior of PVCL-g-CNCs aqueous suspensions (1.0 wt%) with the LCST value at 36 °C.

The surface of CNCs was modified with poly(butyl acrylate) (PBA) and poly(methyl methacrylate) (PMMA) through ATRP technique. The successful grafting modification led to the increased thermal stability of modified CNCs (MCNCs). The increase in Young’s modulus of more than 25-fold and in tensile strength of about 3 times for 7 wt% MCNCs/PBA-co-PMMA nanocomposites was achieved compared to those of neat PBA-co-PMMA. A micro-phase separated morphology (PBA- soft domains, and PMMA- as well as CNCs- hard domains) of MCNCs/PBA-co-PMMA nanocomposites was also observed. In addition, the interfacial miscibility and phase separated morphology of PMMA-g-CNCs (PMCNCs)/PBA-co-PMMA
nanocomposites were further studied. The 10 wt% PMCNCs/PBA-co-PMMA nanocomposites showed increases in Young’s modulus of more than 20-fold and in tensile strength of about 3-fold when compared to those of neat PBA-co-PMMA. Morphological analysis indicated the presence of microphase separation in PMCNCs/PBA-co-PMMA nanocomposites. Therefore, the surface modification of CNCs played a crucial role in reinforcing mechanical performance, controlling interfacial miscibility and tuning phase morphology of the nanocomposites.
CHAPTER 1. INTRODUCTION

1.1. BACKGROUND

Polymer composites with sustainable reinforcing fibers in both micro and nanoscales have been recently developed to utilize vast natural resources (Zhu et al., 2016; Hillmyer, 2017) and to develop environmentally friendly (Fortman et al., 2018; Zhu et al., 2018) and high-performance composites. Natural fibers possess sustainability, low cost and low density, providing opportunities for the development of environmentally friendly microfiber reinforced polymer composites (Lu et al., 2008; Akil et al., 2011). Their excellent properties, i.e., low weight, high stiffness and strength, have proven their value for a variety of industrial applications, such as automotive, construction and other industries (Yu et al., 2006). However, the largely variable length and diameter of microfibers decrease their performance for the composite application, thus compromising their value in use (Lu et al., 2008). Recently, the interest in nano-sized fibers has rapidly grown (Abdul Khalil et al., 2012). The fibers as nano-sized reinforcement elements offer their unique properties never found in traditional microfiber reinforced polymer composites (Siqueira et al., 2009). The dramatically improved mechanical performance with low nanofiber contents is achieved (Yu et al., 2006). They also show the potential to improve thermal endurance and add new functionality and properties of composite materials (Paul and Robeson, 2008).

1.1.1. Micro Wood Fiber Plastic Composites

The environmentally friendly wood plastic composites (WPCs) with wood fibers at the micro size scale have been developed and utilized recently (Zhang et al., 2018). Wood fiber is
relatively cheap and widely available, which could improve the stiffness as well as lower overall costs of WPCs (Arao et al., 2014). Plastics promote the biological resistance, melt processing as well as water barrier property (Zhang et al., 2018). The dimension and shape of WPCs can also be tuned (Nikolaeva and Kärki, 2013). Thus, WPCs have been used in various areas, such as construction (deck boards) and automobiles (interior panels) (Zhang et al., 2017). However, one of the primary concerns for WPCs is the poor fire performance as their components are easy to flame (Zhang et al., 2017). Therefore, the research for the improvement of fire resistant property of WPCs is important, which could contribute to their wider industrial application (Fang et al., 2013).

The incorporation of flame retardants into the polymeric matrix is potential to enhance the fire retarding performance of WPCs. The commonly used fire retardants of WPCs are metal hydroxides (magnesium hydroxide and aluminum hydroxide), boron compounds (zinc borate) and halogenated compound based on chlorine or bromine. Therefore, the research is very important for the comparative study of fire performance of WPCs with various compounds.

Minerals are also highly efficient flame retardants for WPCs. The main advantage of nanofiller incorporation is the decrease of maximum heat release rate, resulted in the reduction of fire spread toward adjacent regions (Paul and Robeson, 2008). The primarily studied nanofiller flame retardant is clay. The clay (montmorillonite) is sandwiched structure with tetrahedral outer layers and octahedral inner layer (Paul and Robeson, 2008). It has been used as the fire retardant for WPC (Xie et al., 2001; Zhao et al., 2006). But the single clay component as fire modifier cannot reach the satisfied fire performance. Therefore, it is an important topic for the study of synergistic effect of clay and halogenated flame retardants on the fire
performance of WPCs, leading to a better understanding of how the synergistic interaction of exfoliated clay and halogenated flame retardants affects the fire performance of WPCs.

1.1.2. Cellulose Nanocrystal - Polymer Nanocomposites

Cellulose nanocrystals (CNCs) as a class of sustainable materials are derived from a variety of renewable bioresources, such as wood fibers, tunicate, and wheat straw (Wohlhauser et al., 2018; Capadona et al., 2008). Various types of acid hydrolysis process have been used to yield CNCs, i.e., sulfuric, phosphoric, and hydrochloric acids (Grishkewich et al., 2017). CNCs extracted from wood fibers via sulfuric acid hydrolysis possess rod-like morphology with widths of several nanometers and lengths of up to hundreds of nanometers (Habibi et al., 2010). The abundant sulfate ester groups on the surface of hydrolyzed CNCs lead to their colloidal stability (Tang et al., 2017). CNCs have many unique properties, i.e., large surface area, high stiffness (elastic modulus up to 140 GPa) (Grishkewich et al., 2017), and abundant hydroxyl groups on the surface for further functionalization. Therefore, CNCs have been used in a variety of fields, such as oil and gas industry (Li et al., 2015), 3D printing (Wang et al., 2018), aerogel (Buesch et al., 2016), energy and battery (Hu et al., 2013). In order to expand the use of CNCs, a feasible strategy is to modify hydroxyl groups on the surface of CNCs because these surface hydroxyl groups are abundant and easily accessible. The surface modification also acts to reduce hydrophilicity while potentially adding hydrophobicity and new chemical functionality (Moon et al., 2011). Surface modifications of CNCs with both covalent and noncovalent bonds have been explored in order to improve the dispersion and compatibility in different solvents and polymer matrices or to impart new properties for various applications (Liang et al., 2012). Grafting polymers onto the surface of CNCs is possible by two methods, namely “grafting to”
and “grafting from” (Majoinen et al., 2011). The “grafting to” strategy involved attaching a pre-synthesized polymer to one of the hydroxyl groups, while the “grafting from” strategy involved initiating the surface of CNCs using an initiator and growing polymers (Moon et al., 2011; Habibi et al., 2010).

Recently, research of CNCs functionalized by responsive polymers, such as temperature (Herbert et al., 2017; McKee et al., 2014), light (Wojtecki et al., 2011; Coulibaly et al., 2014) and pH (Way et al., 2012) have been widely studied. The poly(N, N-diethylacrylamide) (Hufendiek et al., 2014) and poly(N-isopropylacrylamide) (PNIPAM) (Hemraz et al., 2014; Zoppe et al., 2010) as temperature responsive polymers have been utilized for the functionalization of CNCs. The research of poly(N-vinylcaprolactam) (PVCL) as well as its hybrid materials, a new type of temperature responsive polymer, is only limited report in comparison with PNIPAM (Zhang et al., 2017). The unique properties of PVCL include temperature sensitivity, water/organic solvent solubility, biocompatibility as well as its structure with hydrophobic/hydrophilic moieties (Thomassin et al., 2015; Liu et al., 2014; Cortez-Lemus et al., 2016). These unique characters make PVCL widely utilize in the environmental field as well as biomedical area (Rejinold et al., 2011; Schwarz et al., 2012). According to our knowledge, limited work has been made concerning about surface-initiated atom transfer radical polymerization (SI-ATRP) of PVCL based polymers (Kavitha et al., 2014; Karesoja et al., 2013). Therefore, the research on exploration of surface grafted polymerization of CNCs with PVCL via ATRP strategy and further investigation of thermally responsive property will extend the toolbox of thermally-sensitive polymers for the design of versatile
CNC-based temperature responsive hybrid materials. In addition, the ATRP technique is also widely used for the design of thermoplastic elastomers (TPEs).

TPEs are an important class of polymer materials combining elastomer behavior with thermoplastic properties (Dufour et al., 2008). They have been widely used in industry such as adhesives, polymer blending and food packaging (Lu et al., 2018). Although commercial isoprene- or butadiene-containing TPEs are dominant in the market, the presence of unsaturated bonds in the butadiene domain resulted in their lower ultraviolet light degradation (Haloi et al., 2012). Therefore, it is a feasible solution for the development of acrylic based thermoplastic elastomers. Poly (methyl methacrylate) (PMMA), similar to the function of polystyrene (PS) within the styrene-butadiene-styrene block copolymer, was considered as a good alternative for the hard block (Lu et al., 2017). Similarly, poly(n-butyl acrylate) (PBA), similar to the function of poly (isoprene) (PI) of styrene-isoprene-styrene block copolymer, was represented as the substitute for soft domain contributing for the enhanced oxidation stability (Lu et al., 2017). However, acrylic thermoplastic elastomers usually had low initial moduli and stresses at low to intermediate strains (Lu et al., 2018). CNCs have an estimated strength over 10 GPa and a modulus over 150 GPa, which are similar as these of graphene (Pang et al., 2016; Grishkewich et al., 2017; Yin et al., 2016). So CNCs are considered as good reinforced fillers for acrylic thermoplastic elastomers.

However, the dispersion of hydrophilic CNCs into hydrophobic polymers is challenging, resulted in the agglomerates in the polymer matrices (Graham, 2014). Therefore, various approaches (non-covalent and covalent modification) have been utilized for CNC modification for the reduction of aggregation of CNCs in the polymer matrices (Habibi et al., 2010; Moon
et al., 2011). Surface tailoring CNCs through alkyne (Feese et al., 2011), amine groups (Hemraz et al., 2013), living radical polymerizations (Majoine et al., 2011; Zoppe et al., 2010) and azide (Filpponen and Argyropoulos, 2010) have been studied. Regarding the non-covalent approach, cationic polyelectrolytes were utilized for the CNC modification (Salajková et al., 2012). In order to effectively disperse CNCs, the utilization of anionic surfactant has also been reported (Kaboorni and Riedl, 2015). Therefore, the study of surface modification of CNCs and its interfacial miscibility with acrylic copolymer as well as property-morphology relationship of modified CNCs/acrylic copolymer nanocomposites is an interesting and important topic, which will open new opportunities toward a rational design of the CNCs reinforced nanocomposites.

1.2. OBJECTIVES

The objectives for this work are summarized as followings:

Part 1: The objective was to provide a comparative study on mechanical, morphological and fire retarding properties of various compounds for use in WPC;

Part 2: The objective was to study the synergistic effect of flame retardants among nanoclay, 1,2-bis(pentabromophenyl) ethane and ethylene bis(tetrabromophthalimide) on fire performance of WPC;

Part 3: The objective was to functionalize CNCs with PVCL and to elucidate its temperature responsive behavior;

Part 4: The objective was to investigate the mechanical, thermal and morphological property of the CNC-g-(PBA-co-PMMA)/acrylic copolymer nanocomposites;
Part 5: The objective was to explore the interfacial miscibility and phase separated morphology of PMMA-g-CNCs/PBA-co-PMMA nanocomposites.

1.3. ORGANIZATION OF DISSERTATION

Chapter 1 provides an overall introduction of the research documented in this dissertation;

Chapter 2 presents comparative mechanical, fire retarding and morphological properties of high density polyethylene/wood flour composites with different flame retardants;

Chapter 3 presents synergism of nanoclay and halogenated flame retardants on fire retardancy of high density polyethylene and wood flour composites;

Chapter 4 presents thermos-responsive copolymer poly(N-vinylcaprolactam) grafted cellulose nanocrystals: synthesis, structure, and properties;

Chapter 5 presents microphase separated nanocomposites driven by cellulose nanocrystals: enhanced mechanical performance and nanostructured morphology;

Chapter 6 presents surface modified cellulose nanocrystals for tailoring interfacial miscibility and microphase separation of polymer nanocomposites;

Chapter 7 provides an overall conclusion for this dissertation.

1.4. REFERENCES


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CHAPTER 2. COMPARATIVE MECHANICAL, FIRE RETARDING AND MORPHOLOGICAL PROPERTIES OF HIGH DENSITY POLYETHYLENE/WOOD FLOUR COMPOSITES WITH DIFFERENT FLAME RETARDANTS

2.1. INTRODUCTION

Wood-plastic composites, as an emerging class of environmentally friendly materials, have been developed and used in recent years (Arao et al., 2014; Nikolaeva and Kärki, 2013). However, WPCs usually show low fire resistance because plastics and wood are sensitive to flame (Fang et al., 2013).

One strategy used to acquire fire resistance for WPC is the incorporation of fire retardants during processing such as extrusion, compression and injection molding. Much research has been focused on phosphorous compound flame retardants (Arao et al., 2014; Abu Bakar et al., 2010; Aryilmis et al., 2011; Zheng et al., 2014; Zhang et al., 2012). The intumescent char layer was formed on the surface of substrates during the combustion with the addition of flame retardant ammonium polyphosphate (APP), and thus a better fire performance was achieved (Zhou et al., 2011). In addition, APP also promoted esterification, dehydration and char formation for WPCs (Li and He, 2004). Phosphorus compounds are usually combined with other flame retardants to achieve synergistic effects. The synergism of expandable graphite and APP improved fire performance of WPC. The formation of graphite layers blocked the heat and gas transfer between the flame zone and matrix, thus protecting matrix from decomposition (Bai et al., 2014; Seefeldt et al., 2012). However, phosphorous compound flame retardants

release harmful gases upon degradation (Lu et al., 2014). Besides, they are commonly used for polymers with relatively low melting points because they are easily suffered from thermal degradation beyond 200 °C, which deteriorates the fire resistant performance of composites (Morgan and Gilman, 2013).

Boron compounds also play an important role in fire retardancy of WPCs. Zinc borate has been used to retard the thermal degradation of WPCs because of its high thermal stability. It forms a glassy protection layer as a barrier to reduce the heat release rate and thus slow the combustion of composites (Fang et al., 2013; Ayrilmis et al., 2012). In addition, the combination of boron compounds and APP shows synergistic effects for WPCs in flame retardancy (Ayrilmis, 2011). It promotes the formation of char, and also has a positive effect on smoke suppression of composites (Ayrilmis, 2013; Kurt et al., 2012). However, most synergistic effects normally happen at high chemical loading levels. At these levels, mechanical properties of composites decrease sharply owing to the poor compatibility between flame retardants and polymer matrix (Wang et al., 2014).

Metal hydroxides are the most commonly used flame retardants in the industry. The metal hydroxides endothermically decompose to release water when being heated, which reduces heating of the plastic substrate and thereby slows thermal decomposition of the plastics (Gwon et al., 2014; Sain et al., 2004; Stark et al., 2010; Ayrilmis et al., 2012). In addition, metal hydroxides as environmentally friendly flame retardants can significantly decrease the emission of toxic gases such as carbon monoxide because the decomposed residue is nonflammable inorganic compounds. However, high loadings of the metal hydroxides are required to achieve a good fire performance, which deteriorates mechanical properties of
composites (Chen et al., 2013). Moreover, halogenated compound based on chlorine or bromine has also been used as flame retardants for WPCs (Stark et al., 2010). Halogenated flame retardants work in the vapor phase to retard combustion and show highly effective flame retardancy for WPCs (Morgan and Gilman, 2013; Dasari et al., 2013).

The objective of this work is to provide a comparative study on mechanical property, morphology, and fire retardancy of various compounds for use in WPCs. The residual char after complete combustion is further studied using scanning electron microscopy to further understand the reaction of fire retardants in the composites.

2.2. MATERIALS AND METHOD

2.2.1. Materials

High density polyethylene (AD60-007) pellets with a density of 0.963 g/cm³, a melt flow index of 0.73 g/10 min (190 °C, 2.16 kg) and a softening temperature of 127 °C were purchased from ExxonMobile Chemical Co. (Houston, TX, USA). Pine wood flour (WF) (40-mesh particle size) was obtained from American Wood Fiber Inc. (Schofield, WI, USA). Maleic anhydride grafted polyethylene (MA-g-PE) (G2608) with a melt flow index of 8 g/10 min (190 °C, 2.16 kg) was supplied by Eastman Chemical Co. (Kingsport, TN, USA). Aluminium hydroxide (M-ON310), magnesium hydroxide (MAH-5) and 1,2-bis(pentabromophenyl) ethane (SA-8010) were supplied by Albemarle Co. (Baton Rouge, LA, USA). To promote the processing of composites and maintain good composite surface characteristics, a lubricant (TPW 306) from Struktol Co. (Stow, OH, USA) was also used. This plasticizer is a mixture of fatty aliphatic carboxylic derivatives.
2.2.2. Sample Extrusion and Compounding

Before processing, WF was dried in a laboratory oven at 80 °C for 24 h to reduce its moisture content, while HDPE, MA-g-PE and lubricant materials were used directly without further drying. The components were compounded by using a Leistritz Micro-27 co-rotating parallel twin-screw extruder (Leistritz Co., Allendale, NJ, USA). The extruder has 11 heating zones with a screw length-to-diameter ratio of 40:1. For compounding each target formulation, a mixture of HDPE and MA-g-PE pellets was fed upstream with a weight-in-loss pellet feeder, and a mixture of WF, lubricant, and fire-retardant additives was fed downstream by using a weight-in-loss powder feeder through a side-stuffer. The compounding conditions include a screw speed of 50 rpm and a temperature profile of 155 (feeder), 160, 165, 170, 170, 170, 160, 155, 140, 140, and 155 °C (die). The extrudate was continuously pelletized into granules with a BT 25 pelletizer (Scheer Bay Co., Bay City, MI, USA). The pellets were kept in sealed bags based on actual formulations for further processing.

Composite samples were made with compound pellets by using the Leistritz extrusion machine and a profile die to produce 5 mm thick × 100 mm wide test samples. The material was fed with the weight-in-loss pellet feeder upstream. The extrusion speed was 50 rpm and extruder temperature profile of 155 (feeder), 160, 165, 170, 170, 170, 160, 155, 155, and 150 °C (die). The A0 denotes HDPE/WF composites without flame retardants. The B5, C5 and D5 represent HDPE/WF composites with flame retardant aluminium hydroxide (M-ON310), magnesium hydroxide (MAH-5), and 1,2-bis(pentabromophenyl) ethane (SA-8010) at the loading of 5 wt%, respectively. The B10, C10, and D10 correspond to the HDPE/WF composites with M-ON310, MAH-5, and SA-8010 at the content of 10 wt%, respectively.
2.2.3. Characterization

The modulus of elasticity (MOE) and modulus of rupture (MOR) of composites with and without flame retardants were measured according to ASTM: D790 standard using an INSTRON 5582 Testing Machine (Instron Co., Grove City, PA, USA). The condition for the sample test was at 23 °C and 50% relative humidity. A three-point loading system was utilized with a crosshead speed of 2.3 mm/min. The span length was 127 mm with the sample width of 32 mm. For each formulation, five replicates were tested.

Fire performance was measured with a Stanton Redcroft (Fire Testing Technology Limited, London, UK) cone calorimeter according to the ISO 5660-1 standard using 100 mm x 100 mm test samples. For each test, a test sample was placed on the surface of a piece of aluminum foil inside a corundum crucible (100 mm length × 100 mm width). Subsequently, the crucible was mounted horizontally on the loader and exposed to the heat radiation of 50 kW/m². This heat radiation corresponded to a temperature of 780 °C on the upper surface of the test sample.

After the combustion test, the crucible with sample was removed from the loader and cooled. The top sample surface morphology was taken with a digital camera, and composite residue was collected and stored in plastic bags for further analysis.

The fractured sample surface and residual char after complete combustion for composites with and without flame retardants were examined with a Hitachi S4800 (Hitachi Ltd., Tokyo, Japan) scanning electron microscopy at 20 kV. The fractured samples after mechanical property test were cut into appropriate dimensions and then fixed on the sample plate with conductive adhesive. For the residual powders, they were dispersed on the conductive adhesive. The fractured surfaces and residual powders were then coated with gold to improve the surface
2.3. RESULTS AND DISCUSSION

2.3.1. Mechanical Properties

Table 2.1. MOE and MOR values of the HDPE/WF composites and its composites with different types of flame retardants.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Flame Retardants</th>
<th>MOE (GPa)</th>
<th>MOR (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>None</td>
<td>4.2±0.1</td>
<td>34.5±1.2</td>
</tr>
<tr>
<td>B5</td>
<td>M-ON310</td>
<td>3.9±0.5</td>
<td>33.6±3.5</td>
</tr>
<tr>
<td>C5</td>
<td>MAH-5</td>
<td>4.2±0.1</td>
<td>31.7±1.8</td>
</tr>
<tr>
<td>D5</td>
<td>SA-8010</td>
<td>4.1±0.4</td>
<td>30.1±0.7</td>
</tr>
<tr>
<td>B10</td>
<td>M-ON310</td>
<td>3.9±0.4</td>
<td>32.3±2.8</td>
</tr>
<tr>
<td>C10</td>
<td>MAH-5</td>
<td>4.3±0.5</td>
<td>30.6±1.6</td>
</tr>
<tr>
<td>D10</td>
<td>SA-8010</td>
<td>4.1±0.3</td>
<td>30.2±1.8</td>
</tr>
</tbody>
</table>

MOE values for composites with and without flame retardants are summarized in Table 2.1. For composites with 5 wt% magnesium hydroxide, the MOE value was basically the same as that of control composites without fire retardants. Composites containing flame retardants aluminum hydroxide and 1,2-bis(pentabromophenyl) ethane at 5 wt% loadings retained more than 90% of their original MOE values compared to that of control composites. This result is in agreement with the common trend of wood flour reinforced plastics (Abu Bakar et al., 2010; Aryilmis et al., 2011). This could be attributed to the decrease of compatibility among flame retardants, HDPE and wood flour. As the content of flame retardants (aluminum hydroxide, magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane) increased from 5 to 10 wt%, the MOE value of composites containing aluminum hydroxide had a little decrease. This could be attributed to the poor interaction and compatibility among the flame retardants, wood flour and HDPE (Wu and Xu, 2014). The MOE values for composites with magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane didn’t change much.
MOR values of control composites and composites with flame retardants aluminum hydroxide, magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane are also summarized in Table 2.1. Compared to control composites, the MOR values of composites after the addition of aluminum hydroxide, magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane at the content of 5 wt% were decreased. It was possible that interfacial bonding between wood flour and HDPE decreased after the addition of the flame retardants (Aryilmis et al., 2011; Aryilmis, 2013). As the content of aluminum hydroxide, magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane increased from 5 to 10 wt%, the MOR values of composites were almost constant.

2.3.2. Morphology

The investigation of fractured surface morphology after mechanical property test for composites with different loadings of flame retardants is the basis to further study the fire performance. Compared to flame retardants aluminum hydroxide and magnesium hydroxide, 1,2-bis(pentabromophenyl) ethane showed the best fire performance (discussion in the next part). Therefore, observation of the morphology variation of composites with the addition of 1,2-bis(pentabromophenyl) ethane is very important. So it is necessary to compare the surface morphology of composites without flame retardants and composites with 1,2-bis(pentabromophenyl) ethane.

The morphology of the fractured surface for control composites and composites with 1,2-bis(pentabromophenyl) ethane in the content of 5 and 10 wt% is shown in Figure 2.1. It was seen that the control composites (a-b) showed a ductile fractured surface in some regions with excellent mechanical properties reflected in Table 2.1. The compatibilizer MA-g-PE promoted
the dispersion of wood flour in the HDPE matrix and improved the interfacial adhesion between wood flour and HDPE. However, it was also shown that some apparent cavities existed due to wood fibers pulled out from the HDPE matrix.

Figure 2.1. SEM micrographs of the fractured WPC sample surface: (a) A0-200x, (b) A0-2000x, (c) D5-500x, (d) D5-2000x, (e) D10-500x and (f) D10-2000x.

For composites with 5 wt% (c-d) and 10 wt% (e-f) 1,2-bis(pentabromophenyl) ethane, the heterogeneous dispersion of wood flour and flame retardants in HDPE matrix was observed. Some apparent cavities were presented in the composites with 5 and 10 wt% 1,2-bis(pentabromophenyl) ethane, indicating that the surface adhesion among wood flour, HDPE and flame retardants relatively decreased after the incorporation of flame retardants 1,2-bis(pentabromophenyl) ethane. The brittle fractured surface was also observed, revealing that the wood flour and flame retardants had reduced interfacial adhesion with HDPE matrix, which acted as stress concentrators of failure points of composites (Zhang et al., 2012). This could
lead to the declined mechanical properties.

![Figure 2.2](image.png)

Figure 2.2. A comparison of combustion data for composites at 5 wt% flame retardant loading level as a function of time. (a) Heat Release Rate, (b) Total Heat Release, and (c) Total Smoke Production.

2.3.3. Composite Flammability

Cone calorimetry analysis produced test data on heat release rate (HRR), peak of heat release rate (pHRR), total heat release (THR), and total smoke production (TSP) (Chen et al., 2014). Figure 2.2(a-b) shows the heat release rate and total heat release of control composites and composites with the same amount of aluminium hydroxide, magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane, respectively. Two HRR peaks were observed for all samples. The first peak as the consequence of ignition and the flame spread on the surface of samples (Lu et al., 2014) appeared between 60 and 75 s after ignition. The second peak when the degradation for the surface of samples started, and oxygen got into the inner part of the samples to combustion with high efficiency, and finally a carbonaceous char was formed (Lu et al.,
2014), occurred in the range from 200 to 330 s. The highest peak of 405.78 kW/m² at 280 s was related to the composites with magnesium hydroxide, and the lowest peak of 257.73 kW/m² at 330 s was associated to the composites with 1,2-bis(pentabromophenyl) ethane. The HRR and THR for composites with magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane were reduced compared to that of composites without flame retardants. The best reduction in the THR was achieved by the composites with 1,2-bis(pentabromophenyl) ethane. Bromine radicals released from the 1,2-bis(pentabromophenyl) ethane scavenged the high energy radicals in the combustion zone according to a vapor phase fire retarding mechanism (Dasari et al., 2013). For flame retardant magnesium hydroxide, the flame retarding effect was based on cooling and dilution through endothermic decomposition and water release (Hu et al., 2014; Bee et al., 2014). In addition, decomposed product of nonflammable magnesium oxide insulated the HDPE from heat and produced char that impeded the flow of potentially flammable gases to the flame (Gwon et al., 2014). However, for composites containing aluminium hydroxide, the reduction of the THR was not observed compared to that of control composites, which was in accordance with the HRR as well as pHRR of composites with aluminium hydroxide. It indicated that flame retardant aluminium hydroxide did not show effective flame retardancy for composites. The thermal stability of aluminum hydroxide is around 251 °C. It started to decompose at 251 °C, and then a higher proportion of aluminium hydroxide was decomposed in the early stage of combustion. However, not too much water can be released from aluminium hydroxide during the higher temperature above 300 °C or even more, which resulted in low efficiency of fire retardancy for HDPE substrate.

Figure 2.2(c) shows the total smoke production curves versus time for control composites
and composites with the same amount of fire retardants aluminium hydroxide, magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane, respectively. It was seen that control composites exhibited a relatively low TSP of 11.07 m². Although the incorporation of flame retardant 1,2-bis(pentabromophenyl) ethane into composites showed the high flame retardancy, the total amount of smoke emission was higher than that of control composites. The TSP increased for composites with aluminium hydroxide, which was attributed to the low efficiency in flame retardancy and resulted in the combustion of HDPE to produce volatile gases after the overall decomposition of flame retardants (Gwon et al., 2014). However, the best reduction in the TSP was achieved with magnesium hydroxide compared to the control composites. During degradation of magnesium hydroxide into magnesium oxide and water, it absorbed heat from the HDPE substrate and formed a protective layer for HDPE, which acted as a smoke suppresser (Sain et al., 2004).

The HRR and THR curves for composites with 5 and 10 wt% of different flame retardants are shown in Figure 2.3(a-b). The pHRR values for composites with 10 wt% aluminium hydroxide, magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane were lower than those of the composites with the content of 5 wt%. It indicated that increase in the content of flame retardants had a positive effect in retarding flame. In addition, with the content of flame retardant aluminium hydroxide, magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane increased from 5 to 10 wt%, THR and HRR values of composites were reduced as well. For the composites with aluminium hydroxide and magnesium hydroxide, the formation of dense char layers limited the diffusion of oxygen toward HDPE substrate and protected it from burning. In addition, bromine radicals from the decomposition of 1,2-bis(pentabromophenyl)
ethane were efficient to absorb high energy radicals from the combustion zone and thus reduced the prospect of continued burning (Dasari et al., 2013).

![Figure 2.3. A comparison of combustion data for composites at 5 and 10 wt% flame retardant levels as a function of time. (a) Heat Release Rate, (b) Total Heat Release, and (c) Total Smoke Production.](image)

The TSP curves for composites with 5 and 10 wt% flame retardants are shown in Figure 2.3(c). With the content of flame retardant 1,2-bis(pentabromophenyl) ethane increased from 5 to 10 wt%, a significant increase of TSP was observed. For the composites with magnesium hydroxide, the total smoke production didn’t change much after the loading of flame retardants increased from 5 to 10 wt%. In the case of the composites with aluminium hydroxide, the increase in the content of flame retardants from 5 to 10 wt% led to the reduction of total smoke production. Flame retardant aluminium hydroxide released water into vapor phase and diluted the volatile components from HDPE degradation, and a dense layer of aluminium oxide as a barrier retarded the heat and gas transfer between flame zone and HDPE substrate, which
reduced the release of smoke (Gwon et al., 2014).

Figure 2.4. Photographs of the char residues after cone calorimetry test for selected samples: (a) A0, (b) D5 and (c) D10.

2.3.4. Char Residue Composition and Morphology

Figure 2.4 shows the photographs of the control composites and composites with 5 and 10 wt% 1,2-bis(pentabromophenyl) ethane after cone calorimeter test. It was clearly seen that the residual char was crisp for the control composites (a), and the surface layer was broken into small pieces. Moreover, the residue of the composites tended to aggregate together with many cracks and holes. For the residue of composites with 5 wt% 1,2-bis(pentabromophenyl) ethane (b), the residual char layer was continuous with some holes in the surface. However, the char layer was thin and broken into several big pieces. In contrast, the char of the composites with 10 wt% 1,2-bis(pentabromophenyl) ethane (c) was compact and continuous, which acted as an effective barrier for heat and mass transfer. It suggested that the cohesive and dense char surface blocked the release of internal combustible gases and thus protected the HDPE from combustion (Bai et al., 2014). The barrier effect of the stable char structure could also reduce the HRR and THR, which was corresponding to the heat release curves.
Figure 2.5. SEM micrographs of the char residues after cone calorimetry test: (a) A0-2000x, (b) D5-2000x, (c) D10-2000x and (d) D10-5000x.

As shown in Figure 2.5 for the SEM micrographs of the residual char after combustion, the char layer of control composites (a) was loose and rough with many large holes, so the structure promoted heat transfer and gas diffusion. Thus, the composites were burnt rapidly. However, when 5 wt% 1,2-bis(pentabromophenyl) ethane was incorporated into composites (b), the porous and loose surface changed into a more compact one; the char layer exhibited a continuous structure with fewer cracks and holes. The dense char layer could decrease the transfer efficiency of heat and volatiles and thus provide a good barrier for HDPE. However, this char could not effectively prevent the sample from degradation. The char for composites with 5 wt% 1,2-bis(pentabromophenyl) ethane was brittle and easy to collapse, while the char surface of composites with 10 wt% 1,2-bis(pentabromophenyl) ethane (c-d) was compact, thick and tight. This dense layer reduced the heat and oxygen diffusion into the burning substrate and thereby protected the HDPE from further combustion, which was in agreement with the low pHRR and THR data (Wu et al., 2009).
2.4. CONCLUSIONS

The MOE and MOR values of composites were decreased after the addition of aluminium hydroxide, magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane at the content of 5 wt%. As the content of aluminium hydroxide and magnesium hydroxide increased from 5 to 10 wt%, the MOE and MOR values did not change much. The HRR and THR values were reduced for composites with magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane compared to that of control composites. The composites with 1,2-bis(pentabromophenyl) ethane exhibited the best fire resistance. The THR and HRR values of composites significantly reduced as the content of aluminium hydroxide, magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane increased from 5 to 10 wt%. Morphology analysis of char residues demonstrated that flame retardant 1,2-bis(pentabromophenyl) ethane promoted the formation of continuous and compacted char layer on the composite surface, which acted as an efficient physical barrier to combustion of composites.

2.5. REFERENCES


3.1. INTRODUCTION

WPCs have gained popularity for several fields, including automobiles (e.g., interior panels), construction (e.g., deck boards) and outdoor furniture (Nikolaeva et al., 2013). However, one limitation for the wide application is its poor fire resistance. Thus, it is necessary to improve the fire retarding performance of WPCs (Fang et al., 2013).

Much research has been focused on phosphorous compound-based flame retardants, such as ammonium polyphosphate (APP) (Arao et al., 2014; Abu Bakar et al., 2010; Aryilmis et al., 2011; Zhang et al., 2012; Zhou et al., 2011; Li et al., 2004) and combined expandable graphite and APP (Zheng et al., 2014; Bai et al., 2014; Seefeldt et al., 2012). However, these compounds release harmful gases upon the degradation (Lu et al., 2014) and are limited for fire retardancy of polyolefin (Morgan and Gilman, 2013). Boron compounds, such as zinc borate (ZB) with high thermal stability and easy char formation, are also used for the fire retardancy of WPCs (Avrilmis et al., 2012; Avrilmis, 2011; Avrilmis, 2013; Kurt et al., 2012). Metal hydroxides, such as aluminum hydroxide and magnesium hydroxide, endothermically decompose to release water when being heated, which cools the plastic substrate and thereby slows down thermal decomposition of the plastics (Gwon et al., 2014; Sain et al., 2004; Stark et al., 2010; Avrilmis et al., 2012). However, high loadings of flame retardants are required for the boron compound as well as metal hydroxides to achieve a good fire performance, which deteriorates mechanical
properties (Wang et al., 2014). Halogenated flame retardants are often used as effective flame retardants for WPCs. Halogenated flame retardants work in the vapor phase to retard combustion and show highly effective flame retardancy (Stark et al., 2010). Unfortunately, high level of smoke is released due to its inefficient combustion (Lee et al., 2010). Thus, it is important to reduce its loading for a successful application in WPCs.

Nanoclay with high surface area and aspect ratio is a good candidate to overcome the aforementioned drawbacks in developing fire-resistant WPCs. The addition of a small amount of nanoclay could improve mechanical properties, thermal stability and flame retardancy (Morgan et al., 2013; Guo et al., 2007). The burning rate of HDPE-wood composite was reduced with the addition of nanoclay, and the uniform dispersion of nanoclay generally improved the flame retardancy of composites (Lee et al., 2010). For instance, it has been reported that a better dispersion of montmorillonite promoted the char layer formation and thus reduced the heat release rate of poly(vinyl chloride)/wood composites (Zhao et al., 2006). However, the fire retardancy data of nanoclay in WPCs is generally very limited; nanoclay alone usually could not achieve high fire performance for WPCs. Recent studies mostly concentrated on the combined use of two or more flame retardants in the search for their synergistic effects to reduce heat release, smoke evolution and the burning to give a better balance of flammability and mechanical properties for composites (Zhao et al., 2006).

The objective of this work is to provide a comparative study on the synergistic effect of flame retardants on mechanical, thermal, and fire performance of WPCs. Extruded WPCs with and without flame modifiers were made and analyzed through mechanical testing, scanning electronic microscopy (SEM), thermogravimetry and cone calorimetry. The chemical
component, morphology and structure of residual composite powder after a complete combustion were also studied using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and micromorphology observations. Finally, the fire retardant mechanism was proposed for the composite system.

3.2. EXPERIMENTAL PARTS

3.2.1. Materials

High density polyethylene (AD60-007) pellets (density of 0.963 g/cm³, melt flow index of 0.73 g/10 min at 190 °C/2.16 kg and softening temperature of 127 °C) were purchased from ExxonMobile Chemical Co. (Houston, TX, USA). Pine wood flour (WF-a 40-mesh particle size) was obtained from American Wood Fiber Inc. (Schofield, WI, USA). MAPE (G2608, melt flow index of 8 g/10 min at 190 °C/2.16 kg) was supplied by Eastman Chemical Co. (Kingsport, TN, USA). SA-8010 and SABT-93 were supplied by Albemarle Co. (Baton Rouge, LA, USA). Nanoclay from Nanocor Inc. (Hoffman Estates, IL, USA) was a commercial HDPE based clay masterbatch with a clay content of 50 wt% (25 wt% MA-g-PE and 25 wt% PE). Lubricant (TPW 306) was obtained from Struktol Co. (Stow, OH, USA).

3.2.2. Extrusion and Compounding

Wood flour was dried before compounding in a laboratory oven at 80 °C for 24 h to reduce its moisture content. Other raw materials including HDPE, MAPE and lubricant were used directly without further drying. Compounding was done using a Leistritz Micro-27 co-rotating parallel twin-screw extruder (Leistritz Co., Allendale, NJ, USA). The extruder has 11 heating zones with a screw length-to-diameter ratio of 40:1. For compounding each target formulation, a mixture of HDPE, MAPE and/or clay master batch pellets was fed upstream with a weight-
in-loss pellet feeder, and a mixture of powder wood flour, lubricant and fire retardant additives was fed down-stream using another weight-in-loss powder feeder through a side-stuffer. The compounding was conducted using a screw speed of 50 rpm and a temperature profile of 155 (feeder), 160, 165, 170, 170, 160, 155, 140, 140 and 155 °C (die). The extrudate was continuously pelletized into granules with a BT 25 pelletizer (Scheer Bay Co., Bay City, MI, USA). Composite samples were extruded using the prepared pellets. The Leistritz extrusion machine and a profile die were used to produce 5 mm thick × 100 mm wide test samples.

Table 3.1. Formulations of the composites used in this study.

<table>
<thead>
<tr>
<th>Composite ID</th>
<th>HDPE (%wt)</th>
<th>WF (%wt)</th>
<th>MAPE (%wt)</th>
<th>Lub (%wt)</th>
<th>Clay (%wt)</th>
<th>SA-8010 (%wt)</th>
<th>SABT-93 (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>40.00</td>
<td>50.00</td>
<td>4.00</td>
<td>6.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>B15</td>
<td>33.75</td>
<td>50.00</td>
<td>3.75</td>
<td>5.00</td>
<td>7.50</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>C10</td>
<td>35.25</td>
<td>50.00</td>
<td>2.25</td>
<td>5.00</td>
<td>2.50</td>
<td>5.00</td>
<td>0.00</td>
</tr>
<tr>
<td>C15</td>
<td>32.50</td>
<td>50.00</td>
<td>2.50</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>D10</td>
<td>35.25</td>
<td>50.00</td>
<td>2.25</td>
<td>5.00</td>
<td>2.50</td>
<td>0.00</td>
<td>5.00</td>
</tr>
<tr>
<td>D15</td>
<td>32.50</td>
<td>50.00</td>
<td>2.50</td>
<td>5.00</td>
<td>5.00</td>
<td>0.00</td>
<td>5.00</td>
</tr>
</tbody>
</table>

Designation and composition of composites with fire retardants are listed in Table 3.1. It should be pointed out that the formulation design was based on a constant wood loading (50 wt%) and a constant flame modifier loading (7.5 wt%, except for the control group). The design led to some variation in actual HDPE and MAPE loading in the formulation, especially between the control and treatment groups.

3.2.3. Characterization

The modulus of elasticity (MOE) and modulus of rupture (MOR) for the HDPE/WF composites were measured according to ASTM: D790 standard using an INSTRON 5582 Testing Machine (Instron Co., Grove City, PA, USA). Test samples were conditioned at 23 °C
and 50% relative humidity. Prior to testing, a three-point loading was used with a crosshead speed of 2.3 mm/min and a span length of 127 mm (sample width of 32 mm). For each formulation, five replicates were tested.

Thermogravimetric analysis (TGA) was conducted using a TA Q50 thermal gravimetric analyzer (TA Instruments Inc., New Castle, DE, USA) from 40-600 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Powder samples were performed from composite profile, and weight of the TGA sample was about 10 mg.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to characterize the residual powder of the HDPE/WF composites after the complete combustion. The spectra were collected using the FTIR spectrophotometer (Nicolet Nexus 670-FTIR, Thermo Electron Corporation, Gormley, Canada). The attenuated total reflectance mode was used, and the scanning range of wavenumber was from 4000-800 cm⁻¹.

Fire performance was measured with a Stanton Redcroft (Fire Testing Technology Limited, West Sussex, UK) cone calorimeter according to the ISO 5660-1 standard. For each test, a test sample was placed on the surface of a piece of aluminum foil inside a corundum crucible (100 mm length × 100 mm width). Subsequently, the crucible was mounted horizontally on the loader and exposed to the heat radiation of 50 kW/m². This heat radiation corresponded to a temperature of 780 °C on the upper surface of the test sample.

After the combustion test, the crucible with sample was removed from the loader and cooled. The top sample surface morphology was taken with a digital camera, and composite residues were collected and stored in plastic bags for further analysis.

The fractured surface and residual powder after complete combustion were studied using
Hitachi S4800 (Hitachi Ltd., Tokyo, Japan) SEM at 20 kV. The prepared sample surfaces were coated with gold to improve the surface conductivity before observation.

The crystallographic studied were done by X-ray diffraction (XRD) analysis using a Bruker Siemens D5000 X-ray diffractometer (Bruker AXS Inc., Madison, WI, USA) operated at the Cu Ka radiation (λ of 0.154 nm) with 40 kV and 30 mA in a 2θ range from 5 to 60° at a step size of 0.02°.

3.3. RESULTS AND DISCUSSION

3.3.1. Mechanical Properties

The measured composite MOE and MOR values of HDPE/WF composites are summarized in Table 3.2. It should be pointed out that the composite composition variation among various formulations (Table 3.2) made it difficult to compare exact influence of the material composition on mechanical properties for different composites. Overall, the observed MOE values did not change much among all samples, while the MOR values show a reduction from the control sample A0. The higher MOR value for sample A0 was attributed to the better compatibility between WF and HDPE matrix without the influence of flame modifiers. The esterification reaction for the formation of covalent bond between the maleic anhydride group (COOH group) of MAPE and hydroxyl group of WF promoted the exposed PE molecules entangle with HDPE chains during the compounding (Wu and Xu, 2014). The MOE value of the composite B15 (7.5 wt% clay) was relatively larger than that of the control sample A0 because of the reinforcing effect of the nanoclay, which exhibited much higher Young modulus than that of the HDPE. The MOE values of the composites C10 and C15 were reduced compared to that of the A0 due to the deterioration in the compatibility between HDPE and WF.
with reduced MAPE and the addition of fire retardant SA8010, which is a common phenomenon observed in wood reinforced plastics (Fang et al., 2013; Arao et al., 2014; Aryilmis et al., 2011). The MOE values for the D10 and D15 composite groups with fire retardant SABT-93 were much similar as that of the A0 sample. The results showed that the SABT-93 compound had less negative impact on composite MOE compared with the SA8010.

### Table 3.2. Mechanical and thermogravimetric properties of composite samples.

<table>
<thead>
<tr>
<th>Composites</th>
<th>Mechanical Property</th>
<th>Thermogravimetric Property</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MOE (GPa)</td>
<td>MOR (MPa)</td>
</tr>
<tr>
<td>A0</td>
<td>4.2±0.1</td>
<td>34.5±1.2</td>
</tr>
<tr>
<td>B15</td>
<td>4.5±0.4</td>
<td>24.5±2.2</td>
</tr>
<tr>
<td>C10</td>
<td>3.7±0.5</td>
<td>21.7±1.7</td>
</tr>
<tr>
<td>C15</td>
<td>3.8±0.6</td>
<td>21.8±2.1</td>
</tr>
<tr>
<td>D10</td>
<td>4.6±0.5</td>
<td>22.1±1.8</td>
</tr>
<tr>
<td>D15</td>
<td>4.2±0.3</td>
<td>23.7±2.8</td>
</tr>
</tbody>
</table>

T<sub>1%</sub>: decomposition temperature at 1% mass loss; T<sub>peak1</sub>: the first peak temperature; T<sub>peak2</sub>: the second peak temperature.

The MOR values of the composites B15, C10, C15, D10 and D15 decreased compared to that of the A0. The addition of flame modifiers deteriorated the interfacial adhesion and increased stress concentration, leading to reduced composite strength (Gong et al., 2013; Lee et al., 2009). The MOR values of the composites C15 and D15 were lower compared to those of the C10 and D10, indicating that the presence of compatibilizer MAPE and decrease in the Flame modifier content in the sample group had a positive effect on the MOR values. However, the composite B15 showed a relatively higher MOR value compared with these of the composites C10, C15, D10 and D15. This result was attributed to the fact that without the addition of the fire retardant (SA-8010 or SABT-93), the relatively good dispersion of the nanoclay in the HDPE matrix leads to a better strength property through the stress transfer from
HDPE matrix to WF.

Figure 3.1. SEM micrographs of fractured surfaces: (a) A0, (b) B15, (c) C10 and (d) C15.

3.3.2. Morphology

The morphology of the fractured surface for the composites after bending tests is shown in Figure 3.1. For the control A0 sample (Figure 3.1a), a ductile fractured surface present in some regions implied a better compatibility between HDPE matrix and WF in the present of MAPE without flame modifiers. For the B15 sample (Figure 3.1b), with the addition of nanoclay only, the fractured composite surface became much rougher due to the formation of interacted HDPE-nanoclay structure.

For the C10 sample (Figure 3.1c), with decrease in the contents of the fire retardants and the presence of compatibilizer MAPE, the ductile fractured surface appeared in some areas and the exposed WF disappeared, demonstrating that the addition of the compatibilizer promoted the interfacial interaction among flame retardants, WF and HDPE matrix. For the C15 sample (Figure 3.1d), the increased addition of fire retardant SA-8010 largely weakened the interfacial interaction between WF and HDPE, displaying the largely exposed WF. This observation was
responsible for the decreased MOE and MOR values of HDPE/WF composites with the addition of SA-8010 at high loading levels, as shown in Table 3.2. The composite D10 and D15 show a similar morphology structure as those of the C10 and C15 groups.

![Figure 3.2. TGA (a) and DTG (b) curves of SA-8010 and SABT-93.](image)

### 3.3.3. Thermal Stability

The thermal decomposition of flame modifier SA-8010 and SABT-93 is shown in Figure 3.2. As shown in Figure 3.2, compared to that of SA-8010, the thermally decomposed curve of SABT-93 shifted to a higher temperature. Their peak values are totally different with 400 and 455 °C, respectively. The thermal degradation behavior of the composites is shown in Figure 3.3. The decomposition temperatures at the 1% mass loss and maximum decomposition rate as well as residual material amount are summarized in Table 3.2.

All samples decomposed in two steps corresponding to the decompositions of WF and HDPE, respectively. The peak temperature at the first decomposition step ($T_{peak1}$) corresponded to the decomposition of WF. For the B15 sample (nanoclay only), the $T_{peak1}$ value did not change much compared to that of the A0. However, it was shifted to lower temperatures for the C10, C15, D10, and D15 samples, indicating that the thermal decomposition of WF and char
formation took place earlier with the addition of flame modifiers (i.e., SA-8010, SABT-93, nanoclay) and the compatibilizer MAPE. The esterification, dehydration and crosslinking of hydroxyl group from WF with anhydride carbonyl group from MAPE were responsible for the char formation of WF, supported by FTIR analysis for the char residuals of the composites A0 and C10 shown in Figure 3.4.

Figure 3.3. TGA curves of composites A0, B15, C10, C15, D10 and D15: (a) weight loss from 320 to 380 °C, (b) weight loss from 420 to 480 °C, (c) DTG from 200 to 400 °C, and (d) DTG from 420 to 500 °C.

Figure 3.4. ATR-FTIR spectra of composites A0 and C10.

For the C10 sample, the decrease of peaks at 3671 cm\(^{-1}\) (O-H band stretching vibration)
and 1007 cm\(^{-1}\) (C-OH stretching and deformation) as well as increase of peaks at 1736 cm\(^{-1}\) (C=O band stretching vibration) demonstrated the char formation of WF. The peak temperature at the second degradation step (\(T_{\text{peak2}}\)) associated to the degradation of HDPE had a reversed trend. For the B15 sample with nanoclay only, the \(T_{\text{peak2}}\) value was shifted to a higher temperature compared to that of the A0, indicating that the addition of nanoclay retarded the decomposition of HDPE. For the composites C10 and D10, the synergism of nanoclay and fire retardant SA-8010 and SABT-93 and improved interfacial adhesion by MAPE shifted the \(T_{\text{peak2}}\) values to higher temperatures, especially the C10 sample with the largest \(T_{\text{peak2}}\) value among all the samples. For the composites C15 and D15, the \(T_{\text{peak2}}\) values were lower than that of the A0, possibly due to the aggregation of nanoclay and SA-8010 or SABT-93 at high content levels in the composites and relatively poor insulation layer formation for HDPE during the decomposition. Therefore, WF decomposition and its crosslinking reaction with MAPE for char formation, synergism of nanoclay and fire retardant (SA-8010 or SABT-93) at proper loading level and good interfacial adhesion helped delay thermal degradation of HDPE.

<table>
<thead>
<tr>
<th>Composites</th>
<th>Flame Retardants</th>
<th>pHRR (KW/m(^2))</th>
<th>THR (MJ/m(^2))</th>
<th>TSP (m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>None</td>
<td>371.48</td>
<td>166.85</td>
<td>11.03</td>
</tr>
<tr>
<td>B15</td>
<td>Nanoclay</td>
<td>360.09</td>
<td>174.29</td>
<td>13.50</td>
</tr>
<tr>
<td>C15</td>
<td>Nanoclay/SA-8010</td>
<td>316.79</td>
<td>149.00</td>
<td>23.83</td>
</tr>
<tr>
<td>C10</td>
<td>Nanoclay/SA-8010</td>
<td>351.04</td>
<td>131.11</td>
<td>25.95</td>
</tr>
<tr>
<td>D15</td>
<td>Nanoclay/SABT-93</td>
<td>315.27</td>
<td>151.47</td>
<td>21.81</td>
</tr>
<tr>
<td>D10</td>
<td>Nanoclay/SABT-93</td>
<td>356.62</td>
<td>135.07</td>
<td>23.80</td>
</tr>
</tbody>
</table>

pHRR- peak of heat release rate; THR- total heat release; TSP- total smoke production.
3.3.4. Flammability

The combustion parameters of the HDPE/WF composites from the cone calorimetry test are shown in Figure 3.5 and Table 3.3. For the heat release rate (HRR) curves (Figure 3.5a), all samples had two HRR peaks. The first peak was between 55 and 75 s. The D15 sample exhibited the highest HRR (pHRR) of 356.62 kW/m² at 60 s, and the C15 displayed the lowest pHRR of 277.43 kW/m² at 55 s.

The second peak appeared in the range from 225-305 s. For the second peak, the highest pHRR of 371.48 kW/m² at 235 s was from the A0 sample, and the lowest pHRR of 280.51 kW/m² at 290 s was associated with the sample D10. The A0 sample had the highest HRR value with pHRR value of 371.48 kW/m² among all the samples. In case of the B15 sample, the reduction of HRR and total heat release (THR) values was observed (Figure 3.5a and 3.5b). The improvement of fire performance could be related to good dispersion state and insulation effect of nanoclay. It is well known that nanoclay has a multilayer structure with thin nano-
platelets. The layer structure of nanoclay acted as an effective oxygen and heat barrier during combustion.

For the composites C10 and C15, HRR, THR and pHRR values decreased significantly compared to these of the B15, revealing the synergistic effect of nanoclay and SA-8010. The effective barrier from the multilayer platelets of nanoclay blocked the heat and mass transfer. The bromine radicals released from SA-8010 removed the high energy heat in the gas phase, which largely insulated the HDPE and retarded the mass loss and energy release rate of the decomposed products. However, as the total content of nanoclay and SA-8010 increased from 10 to 15 wt% and the absence of compatibilizer MAPE, a further decrease in HRR and THR values was not observed. For example, the THR value increased from 131.11 to 149.00 MJ/m². This might be attributed to the formation of fire modifier aggregations in the composites with a higher loading as well as the decreased interfacial interaction among flame modifiers, WF and HDPE. The presence of SABT-93 also improved the fire retardancy of HDPE/WF composites. For example, compared to that of the B15, the pHRR values for the D10 and D15 were decreased by 22.1% and 12.4%, respectively. The best fire performances were achieved for the C10 sample, as shown in Table 3.3. It is therefore concluded that SA-8010 had a better fire retardancy than SABT-93 for WPCs, and the combination of nanoclay and SA-8010 showed the synergistic flame retardancy for HDPE/WF composites. Among all samples, the lowest total smoke production (TSP) was observed for the A0 sample (Figure 3.5c). The B15 composite with clay only had a similar TSP curve as the A0 composite. However, significant improvement in the TSP was observed for the composites C15, C10, D15 and D15. When SA-8010 and SABT-93 were burnt, they pyrolyzed to form bromine radicals and volatile organic
(aromatic) compounds, which evolved a large amount of smoke, which led to a large amount of smoke. The overall combustion parameter results demonstrated that SA-8010 exhibited superior fire retardancy compared with SABT-93; the combined use of nanoclay and SA-8010 showed an even better fire retardancy. The compatibilizer MAPE played a critical role in improving the fire performance. Since SA-8010 had a better fire retardancy compared with SABT-93, the combined effect of nanoclay, SA-8010, and compatibilizer MAPE on the fire performance of HDPE/WF composites was further analyzed via the morphology of char residue.

![Char Residual Morphology](figure3.6)

**Figure 3.6.** Photographs of char residues after cone calorimetry test: (a) A0, (b) B15, (c) C10, and (d) C15.

### 3.3.5. Char Residual Morphology

Digital photographs of char residues of the composites A0, B15, C10 and C15 after the cone calorimeter test are shown in Figure 3.6. For the char residues of the A0 sample (Figure 3.6a), it was seen that the char residues were completely collapsed and burnt out in some areas, which implied the poor fire retardancy. For the char residues of the clay-only B15 sample
(Figure 3.6b), the surface layer was quite loose and even burnt out in the center. The char residues had cracks and holes although a continuous char layer was seen. For the char residues of the C10, with the addition of compatibilizer MAPE as well as the decrease in the contents of fire retardants, more compact and continuous surface layer was generated, as shown in Figure 3.6c, indicating the improved fire performance. For the char residues of the C15 sample (Figure 3.6d), the char layer was continuous and compact with small cracks on the surface. These observations confirmed the synergism of SA-8010 and nanoclay in promoting the formation of char layer to protect the HDPE substrate from combustion as well as the contribution of improved interfacial interaction with the addition of MAPE toward the fire performance.

The SEM micrographs of char residues after combustion for the composites A0, B15, C10 and C15 are shown in Figure 3.7. Many big holes and cracks were found in the char residues of the A0, as shown in Figure 3.7a. This structure contributed to fast heat transfer and gas diffusion, and therefore the sample was burnt quickly.

![Figure 3.7. SEM micrographs of the char residues after cone calorimetry test: (a) A0, (b) B15, (c) C10 and (d) C15.](image)
The char residues of the B15 (Figure 3.7b) appeared to be aggregated together with holes. This kind of uncontinuous and compact char layer was not effective to prevent the HDPE substrate from degradation under combustion. For the char residues of the C15 (Figure 3.7d), residual char covered on the surface and was continuous with some small holes. This was attributed to the formation of fire retardant aggregations as well as the poor distribution of fire retardants in the composites with a higher loading, as discussed previously. However, in comparison with the A0 and B15, much more compact and continuous morphology was observed for the char residue of the C10 (Figure 3.7c). The char residue of the C10 exhibited more compact surface layer, which was responsible for the improved fire retardancy, indicating the synergistic effect of nanoclay and SA-8010, again. The improved compatibility among fire retardants, WF and HDPE with the presence of MAPE further produced more compact and continuous char residue, which significantly reduced the heat and mass transfer rate, leading to excellent fire performance. These observations were in accordance with the THR and HRR data.

Figure 3.8. XRD patterns of composites B15, C10, C15, D10 and D15.
3.3.6. Char Residual Structure

The X-ray diffractograms of B15, C10, C15, D10 and D15 samples are shown in Figure 3.8. For organically modified nanoclay, the sharp diffraction peak was typically at around 5° (Deka and Makji, 2011). However, the disappearance of typical crystal diffraction peak of nanoclay was observed for C10, C15, D10 and D15 samples as the exfoliation of nanoclay layers in the HDPE matrix (Devi and Maji, 2012). The hydrogen bonding interaction between the oxygen groups of silicates and the maleic anhydride group (or COOH group) as the driving force could promote MAPE molecules enter and penetrate into the gallery between nanoclay layers (Zhao et al., 2006). Subsequently, the HDPE molecular chains could more easily enter the gallery and finally exfoliate layers. All these data suggested that the nanoclay layers were exfoliated, and flame retardants (SABT-93/SA-8010) were dispersed in the wood and polymer matrix.

On the contrary, for the diffractogram of the B15 sample, the broader diffraction peak of nanoclay at around 5° was presented, which implied that the nanoclay was not exfoliated (Kord et al., 2016). The reason is that the size of dispersed nanoclays became larger or even aggregated as the level of nanoclay increased too much. Therefore, the higher clay contents, the higher the MAPE needs to exfoliate the additional clay.

3.3.7. Mechanism Discussion

Flame modifiers in polymer may have an action either in a condensed phase or a gas phase or combined phases. According to the previous reports (Morgan and Gilman, 2013; Dasari et al., 2013; Ahn et al., 2015; Gong et al., 2015), halogenated flame retardants worked in the gas phase, and organo-modified clays acted as a char layer in the condensed phase. Based on the
above analysis, the combustion process during burning for the combination of nanoclay and SA-8010 was schematically proposed (Figure 3.9).

Free radicals were first produced in the thermal degradation of HDPE/WF composites at high temperatures, and accelerated the thermal degradation (Li and He, 2004). For the A0 sample, carbon radicals were produced from the decomposition of the carbon backbone of WF and then attacked hydrogen on HDPE chain to form new long chain radicals at high temperatures (over 400 °C) (Li and He, 2004) indicated in Table 3.2. These new radicals could be broken into volatiles, while much radical formation took place in HDPE, which accelerated the decomposition of HDPE (Gwon et al., 2014).

Figure 3.9. Schematic representation of mechanism for synergistic fire retardancy of nanoclay and SA-8010 in WF/HDPE/MAPE composites.

For the C10 sample, SA-8010 decomposed to produce bromine radicals, which was considered as radical scavengers (Morgan and Gilman, 2013). Therefore, bromine radicals trapped the radicals produced from WF. As a result, SA-8010 reduced the influence of WF on decomposed stability of HDPE. Additionally, the char layer produced from the WF and nanoclay built up on the surface during burning (Shams et al., 2013; Wu and Xiu, 2015). The
stable char layer of nanoclay as an insulation layer prevented further decomposition of HDPE and slowed down the mass loss and energy release rates of the decomposed products (Lee et al., 2010; Guan et al., 2015; Guan et al., 2015). Finally, the presence of MAPE largely improved the interfacial interaction among fire retardants, WF and HDPE, which also contributed to the better fire performance.

3.4. CONCLUSIONS

The MOE values of the composite were reduced after the addition of flame modifiers, and MOR values did not change systematically. The combined addition of fire retardants (SA-8010 or SABT-93) and nanoclay reduced the HRR and THR values of composites, exhibiting the synergism for enhanced char layer formation. The incorporation of compatibilizer MAPE further reduced the HRR and THR values, revealing the effectiveness of MAPE in improving fire performance of HDPE/WF composites. Morphology analysis for char residues revealed that the combined use of SA-8010, nanoclay, and MAPE resulted in much more continuous and compacted char layer, leading to the best flame performance among the formulations tested. Char residual structure analysis indicated that MAPE promoted the exfoliation of nanoclay, and the dispersion of flame retardants SA-8010 and SABT-93 in the wood and HDPE matrix.

3.5. REFERENCES


Properties of Recycled Polyethylene Based Wood Composites via Addition of Polyethylene/Nanoclay Masterbatch. Plastics, Rubber and Composites, 42, 244-255.


Hypophosphite and Improved Flame Retardancy and Mechanical Properties of Flame-Retardant Acrylonitrile-Butadiene-Styrene Composites. RSC Advances, 5, 49143-49152.


CHAPTER 4. THERMO-RESPONSIVE POLY(N-VINYLCAPROLACTAM) GRAFTED CELLULOSE NANOCRYSTALS: SYNTHESIS, STRUCTURE, AND PROPERTIES

4.1. INTRODUCTION

Cellulose nanocrystals, as an inexpensive, renewable and biodegradable nanomaterial, have received an increasing attention in recent years. CNCs possess many attractive properties, such as a large specific surface area, high modulus, unique optical properties and the ability to self-assemble into liquid crystalline phases (Habibi et al., 2010; Tang et al., 2017; Grishkewich et al., 2017). A diverse set of powerful polymerization tools have been used to tailor the surface of CNCs and other nanocellulose materials for creating uniquely surface-functionalized nanomaterials. These techniques include reversible deactivation radical polymerization (atom transfer radical polymerization (ATRP) (Morandi et al., 2009; Zoppe et al., 2016; Majoinent et al., 2011; Wang et al., 2016.), reversible addition-fragmentation chain transfer polymerization (Hufendiek et al., 2014) and nitroxide-mediated radical polymerization (Roeder et al., 2016), ring open polymerization (Habibi et al., 2008; Goffin et al., 2011), olefin metathesis polymerization (ring open metathesis polymerization (Carlsson et al., 2012) and acyclic diene metathesis polymerization (Dong et al., 2016; Meng et al., 2014) and postmodification by click chemistry (copper catalyzed azide-alkyne cycloaddition, Diels-Alder reaction and thiol-ene reaction) (Billiet et al., 2014; Meng et al., 2016). Among these methods, the ATRP technique has emerged as a robust synthesis tool, which is compatible with a wide range of initiators, monomers, and solvents (Matyjaszewski et al., 2009; Matyjaszewski et al, 2014). ATRP is also

a desirable surface functionalization technique as it does not compromise the surface morphology and structure of the substrate (Zoppe et al., 2010). The robustness and versatility of ATRP can lead to a precise control over molecular architecture in term of chain topology, composition, and functionality (Majoinent et al., 2011; Pang et al., 2016). Covalently functionalized CNCs with polymer brushes to tune the hydrophilic surface of CNCs were widely reported in recent years. The functionalized CNCs with polystyrene (PS) by ATRP strategy were firstly published by Yi et al (Yi et al., 2008). Subsequent investigations were reported by Morandi et al concerning the optimizing surface initiated ATRP (SI-ATRP) of polymer brushes from the surface of CNCs (Morandi et al., 2009; Morandi et al., 2012). Different types of polymers have been grafted from CNCs through ATRP method after these developments such as PS (Yin et al., 2016; Huang et al., 2015), poly(methyl methacrylate) (Boujemaoui et al., 2015), poly(methyl acrylate) (Wang et al., 2015), poly(2-aminoethylmethacrylamide) (Rosilo et al., 2014; Yi et al., 2009), (tert-butyl acrylate) (Malho et al., 2016), poly(2-aminoethylmethacrylamide) (Hemraz et al., 2015), poly(butyl acrylate) (Li et al., 2011), soybean amide methacrylate (Wang et al., 2016), poly(2-aminoethylmethacrylate) and poly(6-(4-(4-methoxyphenylazo)phenoxy)hexyl methacrylate (Xu et al., 2008), and poly(methyl methacrylate)-co-butyl acrylate) (Yu et al., 2016).

Recently, the surface functionalized CNCs with responsive polymers, which respond to external stimuli such as pH (Way et al., 2012), light (Biyani et al., 2013; Coulibaly et al., 2014) and temperature (McKee et al., 2014), have been of significant interest. Temperature responsive CNCs have been synthesized with polymers such as poly(N, N-diethylacrylamide) (Hufendiek et al., 2014) and poly(N-isopropylacrylamide) (PNIPAM) (Zoppe et al., 2010; Hemraz et al.,

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and poly(oligoethylene glycol) methyl ether acrylate (POEGMA) (Grishkewich et al., 2016), which possess a well-defined thermal induced phase transition. PVCL as a novel type of thermally responsive polymer has many unique characteristics, such as solubility in water and organic solvents, non-toxicity, biocompatibility, nonionic nature, temperature sensitivity, and the presence of both hydrophilic and hydrophobic groups in its structure (Thomassin et al., 2015; Liu et al., 2014; Cortez-Lemus et al., 2016).

Although an increasing number of studies concerning PVCL appeared recently, cellulose or cellulose nanocrystals (CNCs) based thermoresponsive PVCL hybrid materials were only a few reported up to now. Studies on grafting of PVCL on cellulose (polysaccharide) or its derivatives were reported from the conventional free radical polymerization, such as PVCL grafted cotton fabrics, PVCL grafted dextran, and PVCL grafted sodium alginate copolymers (Grespy et al., 2009; Madhusudana-Rao et al., 2013; Swamy et al., 2013; Shi et al., 2006). Although the synthesis and characterization of PVCL/CNCs nanocomposite hydrogels by the frontal polymerization were reported (Sanna et al., 2013), that particular paper mainly focused on the reinforcement and dispersion of CNCs in the PVCL/CNCs nanocomposite hydrogels through dynamic viscoelastic measurements. However, there was a lack of detailed discussion on the chemical structure of the hydrogels with the frontal polymerization and their thermo-responsive behavior. Compared with the frontal polymerization/conventional free radical polymerization, the controlled radical polymerization could precisely control the molecular structure of grafted PVCL brushes on the surface of CNCs. To our knowledge, there are very few reports dealing with the surface initiated ATRP of NVCL-based polymers. The graphene oxide functionalized with PVCL by the ATRP strategy was reported by Kavitha and co-workers.
(Kavitha et al., 2014). The surface modification of mesoporous silica particles with PEO-b-PVCL copolymers to prepare thermoresponsive hybrid nanoparticles through the ATRP and click reaction were also studied (Karesoja et al., 2013).

The objective of this study is to functionalize CNCs with PVCL and to elucidate its temperature responsive behavior. The initiator modified CNCs (Br-CNCs) were first prepared through esterification reaction. PVCL was then grown from macroinitiator Br-CNCs through SI-ATRP. The chemical structure of Br-CNCs and PVCL-g-CNCs was confirmed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), solid-state NMR spectroscopy and X-ray photoelectron spectroscopy (XPS). The morphology and thermal property were subsequently characterized by transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). The temperature responsive behavior was further investigated through the rheology measurement.

4.2. EXPERIMENTAL SECTION

4.2.1. Materials

Microfibrillated cellulose (Celish KY 100-S grade, 25% solid content) was purchased from Daicel Chemical Industries, Ltd. (Tokyo, Japan). Copper bromide (CuBr, 98%, Acros Organics, Morris Plains, NJ, USA) was purified by stirring in glacial acetic acid, filtering and washing with methanol, followed by drying in vacuum at 30 °C overnight. N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 99%, Sigma-Aldrich, St. Louis, MO, USA), N-vinylecaprolactam (NVCL, 98%, Sigma-Aldrich, St. Louis, MO, USA), triethylamine (TEA, ≥99%, Sigma-Aldrich, St. Louis, MO, USA), 2-bromoisobutyryl bromide (BIBB, 98%, Acros Organics, Morris Plains, NJ, USA) and 4-dimethylaminopyridine (DMAP, 99%, Acros
Organics, Morris Plains, NJ, USA) were used without further purification. Dry N,N-dimethylformamide (DMF) solvent was obtained from the solvent purification system. Other reagents were used as received.

4.2.2. Preparation of CNCs

Microfibrillated cellulose was mixed with sulfuric acid (64 wt%) followed by mechanical stirring at 50 °C for 3 h to allow its hydrolysis. The obtained suspensions were subsequently diluted with excessive deionized water and then dialyzed with deionized water using semipermeable membrane (cutoff molar mass 12000-14000 Da) to remove residual sulfuric acid for 7 days until neutrality was reached. The resultant CNC suspensions were further treated using a high pressure homogenizer (Microfluidizer M-110P, Microfluidics Corp., Newton, MA, USA). CNCs were finally recovered from the resultant suspensions by freeze-drying the suspensions for three days.

4.2.3. Synthesis of Br-CNCs and PVCL-g-CNC Copolymer

Dry CNCs were dispersed in DMF solvent under stirring, and TEA was subsequently added after CNCs were completely dispersed, followed by the addition of DMAP. 2-bromoisobutyryl bromide was then added dropwise to the above CNC suspensions in an ice/water bath. The mixture was stirred at room temperature for 24 h. The resultant mixture was poured into an excess amount of deionized water to remove any residual small molecules and then precipitated as floccules. Purification of the modified CNCs was carried out by redispersing them in DMF and reprecipitating them in deionized water for three times. Yellow powder of Br-CNCs was finally obtained after drying the precipitated materials under vacuum at 30 °C for 24 h to a constant weight.
The formed macroinitiator Br-CNCs then initiated the grafted polymerization of NVCL through a SI-ATRP procedure. The Br-CNCs (0.312 mmol), N-vinylcaprolactam (31.2 mmol) and PMDETA (0.312 mmol) were mixed in DMF in a 25 ml round bottom flask under magnetic stirring. The mixture was then degassed with three freeze-pump-thaw cycles after Br-CNCs was completely dispersed. CuBr (0.312 mmol) was then quickly added into the flask under nitrogen atmosphere, and the flask was degassed again with three freeze-pump-thaw cycles. Thereafter, the flask was immersed into an oil bath preheated at 75 °C. The polymerization was stopped after 12 h by exposing the mixture to air, and DMF was subsequently added to dilute the solution. The product was passed through an activated alumina column to remove copper complex, condensed by rotary evaporation and then precipitated in excess n-hexane. The resulting precipitation was washed with dichloromethane to remove unreacted NVCL monomer and PVCL homopolymer with three times. Finally, the resultant PVCL-g-CNC copolymer was collected and dried under vacuum at room temperature to a constant weight.

4.2.4. Characterization

ATR-FTIR analysis was conducted in the transmittance mode. The scanning range of wavenumbers was from 4000 to 800 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\) and accumulation of 132 scans. The spectra were collected using the FTIR spectrophotometer (Nicolet Nexus 670-FTIR, Thermo Electron Corporation, Gormley, Canada).

Solid-state \(^{13}\)C NMR spectroscopy measurements were performed with a Bruker Avance 400 WB instrument operated at 100.6 MHz at room temperature. The CP/MAS experiments were performed with a relaxation delay of 4.0 s and a contact time of 2.0 ms. Magic angle spinning (MAS) was achieved at a rate of 4 kHz. The chemical shift was in ppm related to an
external sample of tetramethylsilane (TMS).

XPS spectra were recorded using a Specs PHOIBOS-100 spectrometer (SPECS, Berlinm, Germany) with an Al Ka irradiation (1486.61 eV) at 10 kV and 10 mA. Survey scans were conducted from 1200 to 0 eV with pass energy of 40 eV and scan step of 1.0 eV. The high resolution C 1s spectra were recorded at pass energy of 40 eV and scan step of 0.1 eV.

TGA was carried out using a TA Q50 thermo-gravimetric analyzer (TA Instruments Inc., New Castle, DE, USA) from 25 to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

The morphology was observed with a transmission electron microscope (JEM 1400, JEOL, Peabody, MA, USA) at an accelerating voltage of 120 kV. Drops of about 0.001 wt% CNC or PVCL-g-CNC suspension were deposited onto glow-discharged carbon-coated TEM grids. The liquid in excess was absorbed with filter paper, and a drop of 2% uranyl acetate was deposited onto the specimen prior to drying. The stain in excess was blotted, and the remaining thin liquid film was allowed to dry. The TEM grids were allowed to dry at room temperature for 3 hours before imaging.

Rheology measurements were carried out using a TA Instruments Rheometer (AR 2000, TA Instruments Inc., New Castle, DE, USA). A cone and plate geometry with a cone diameter of 40 mm and a 2° truncation angle was employed at a constant shear rate of 150 s⁻¹, and the temperature was controlled by a Peltier plate. The dynamic viscoelastic properties (dynamic storage modulus G’ and loss modulus G”) of the sample were measured by oscillatory shear experiments performed at a fixed frequency of 1 Hz in a temperature ramp of 25 to 90 °C with a heating or cooling rate of 3 °C/min. The 1.0 wt% aqueous suspensions were prepared by
dispersing the powder sample into deionized water with a strong stirring for more than 10 min in order to get a homogeneous suspension as much as possible.

4.3. RESULTS AND DISCUSSION

4.3.1. Chemical Structure

The FTIR spectra of CNCs, Br-CNCs, NVCL and PVCL-g-CNCs as well as digital photographs of CNCs, Br-CNCs and PVCL-g-CNCs are shown in Figure 4.1(a-b).

![FTIR spectra and digital photographs](image)

Figure 4.1. FTIR spectra of CNCs, Br-CNCs, NVCL and PVCL-g-CNC copolymer (a) and digital pictures of CNCs, Br-CNCs and PVCL-g-CNC copolymer (b).

Compared to the spectrum of CNCs, the appearance of C=O group at 1736 cm\(^{-1}\) in Br-CNCs indicated that the bromoisobutyryl ester moiety was bonded onto the surface of CNCs (Pang et al., 2016). In addition, the broad stretching band of –OH groups at 3600-3100 cm\(^{-1}\) in CNCs was significantly decreased, demonstrating that the hydroxyl groups were substituted and converted to ester bonds. The peak of double bond (–C=C-) in the spectrum of NVCL was observed at 1651 cm\(^{-1}\), and vinyl peaks (=CH and =CH\(_2\)) were located at 3104 and 991 cm\(^{-1}\).
(Singh et al., 2012). However, the peaks of double bond disappeared after polymerization. It can be concluded that the polymerization of PVCL was successfully achieved.

![Solid-state CP/MAS $^{13}$C NMR spectra of CNCs (a), Br-CNCs (b), NVCL (c), and PVCL-g-CNC copolymer (d).](image)

The solid state $^{13}$C NMR spectra of CNCs, Br-CNCs, NVCL and PVCL-g-CNC copolymer are displayed in Figure 4.2. By comparison of CNCs and Br-CNCs, the new peaks in Br-CNCs at 56 ppm (C7), 31 ppm (C8) and around 170 ppm (C9) were assigned to the quaternary carbon, methyl groups and carbonyl carbon of the attached 2-bromoisobutyryl ester groups, which indicated that the 2-bromoisobutyryl ester moiety reacted with the hydroxyl groups of CNCs. In addition, no substantial modifications were observed for CNC backbone in the 60-110 ppm region, indicating that the esterification reaction did not remarkably affect the backbone structure of CNCs. For PVCL-g-CNC copolymer, the peaks for CNC backbone were clearly observed. The characteristic peaks belonging to vinyl groups in NVCL shifted to the range of 38-45 ppm (C10 and C11) in the PVCL-g-CNC copolymer. The above analysis
confirmed the successfully grafted polymerization of PVCL onto the surface of CNCs.

The solid-state $^{13}$C NMR spectroscopy is not only used for structural identification, but also used for the determination of degree of substitution (DS) (Xiao et al., 2012; Yue et al., 2015). The DS value of Br-CNCs was determined by the amount of 2-bromoisobutyryl bromide grafted, and calculated according to:

$$DS = \frac{I_{CH_3}}{2I_{O-CH-0}}$$  \hspace{1cm} (1)

where $I_{CH_3}$ represents the integral area of the carbon peak of methyl group from the grafted 2-bromoisobutyryl ester moiety, and $I_{O-CH-O}$ denotes the integral area of the carbon peak of C1 in the backbone of CNCs. The DS value was calculated to be 0.78. The relatively low DS may be explained by the fact that most hydroxyl groups in CNCs were not available for the reaction due to the crystalline character and hydrogen bonding (Ifuku et al., 2008).

![XPS spectra](image)

Figure 4.3. XPS full survey spectra of CNCs, Br-CNCs and PVCL-g-CNC copolymer (a) and deconvolved curves of C 1s in the high resolution spectrum of CNCs (b), Br-CNCs (c) and PVCL-g-CNC copolymer (d).

The XPS spectra of CNCs, Br-CNCs and PVCL-g-CNC copolymer are shown in Figure
4.3. For Br-CNCs, bromine element as new peaks at around 182 eV (3p) and 70 eV (3d) was observed except for the same peaks in CNCs. In addition, a new peak for the C=O (288 eV) bond appeared in the high resolution spectrum of Br-CNCs. As shown in Table 4.1, the value for the O/C ratio in Br-CNCs was slightly reduced compared with that of CNCs. These results indicated the immobilization of 2-bromoisobutyryl ester moiety onto the surface of CNCs. For the PVCL-g-CNC copolymer, the presence of distinctive nitrogen signal was a further indication that PVCL chains were presented on the surface of CNCs.

<table>
<thead>
<tr>
<th>Samples</th>
<th>O 1s (%)</th>
<th>C 1s (%)</th>
<th>N 1s (%)</th>
<th>Br 3d (%)</th>
<th>O/C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNCs</td>
<td>42.64</td>
<td>57.36</td>
<td>—</td>
<td>—</td>
<td>74.34</td>
</tr>
<tr>
<td>Br-CNCs</td>
<td>26.50</td>
<td>49.58</td>
<td>—</td>
<td>23.92</td>
<td>53.44</td>
</tr>
<tr>
<td>PVCL-g-CNCs</td>
<td>16.78</td>
<td>69.70</td>
<td>6.91</td>
<td>6.62</td>
<td>24.07</td>
</tr>
</tbody>
</table>

It should be pointed out that the molecular weight of grafted PVCL chains is not available here as the process for sufficiently cleaved PVCL chains did not succeed. PVCL-g-CNCs were attempted for hydrolysis to cleave PVCL grafting chains from the CNC backbones for gel permeation chromatography test as the ester bond between CNCs and PVCL chains was the obvious site to hydrolyze (Zoppe et al., 2010; Hemraz et al., 2014). It is possible that CNC backbones were tightly wrapped around by the grafted PVCL chains, resulting in the ester linkage less accessible. Similar issues were also reported for the hydrolysis of cellulose or CNCs based grafted polymer brushes (Castelvetro et al., 2007; Sui et al., 2008; Lacerda et al., 2013).
4.3.2. Morphology

The TEM images of CNCs and PVCL-g-CNCs are shown in Figure 4.4. The particle lengths of CNCs were between 100 and 300 nm. The particle widths were fairly uniform in the range of 15-20 nm. These measurements are in close agreement with the dimensions of CNCs derived from microcrystalline cellulose, as observed in literature (Habibi et al., 2010). For PVCL-g-CNCs, the particle lengths and widths were about 172 and 32 nm, respectively. Compared to CNCs, PVCL-g-CNCs had similar shape and size with well-preserved nanorod-shaped morphology (except width increase). These results also indicated that the morphology of CNCs after grafting polymerization of PVCL was not apparently destroyed. On the other hand, CNCs had a relatively smooth surface, while a rough surface for the grafting PVCL layers was observed. These results indicated that the grafted PVCL brushes were covered on the surface of CNCs.

Figure 4.4. TEM images of CNCs (a-b) and PVCL-g-CNCs (c-d).
4.3.3. Thermal Stability

Thermogravimograms of CNCs, Br-CNCs and PVCL-g-CNC copolymer are shown in Figure 4.5. The CNCs showed two separated pyrolysis within a wider temperature range rather than one pyrolysis because trace residue of sulfuric acid in the CNCs reduced the degradation temperature. The decomposition ranges were from 150 to 230 °C and from 250 to 375 °C with a maximum decomposition rate at 301 °C and a residual weight of 6.4 wt%. The Br-CNCs showed an initial pyrolysis at 169 °C with a maximum decomposition rate at 264 °C and a higher residual weight of 22.0 wt%. The decomposition shifted to lower temperature due to the lower thermal stability of grafted initiator (2-bromoisobutyryl ester moiety) on the surface of CNCs. The decomposition of PVCL-g-CNCs displayed two stages with the first stage from 200 to 400 °C for CNCs and the second stage from 450 to 577 °C for grafted PVCL (Kozanoglu et al., 2008). The maximum decomposition rate of PVCL-g-CNC copolymer was about 281 °C, and its residual weight was 1.64 wt%.

![Figure 4.5. Thermal stability (TG (a) and DTG (b)) of CNCs, Br-CNCs and PVCL-g-CNC copolymer.](image)

4.3.4. Thermally Responsive Behavior

The viscoelastic properties (storage modulus $G'$ and loss modulus $G''$) as a function of
temperature for 1.0 wt% aqueous suspensions of CNCs and PVCL-g-CNCs are shown in Figure 4.6.

![Viscoelastic properties (G' and G'') for 1.0 wt% aqueous suspensions of CNCs and PVCL-g-CNCs from oscillatory shear experiments at a frequency of 1 Hz, a strain amplitude of 1.0 and a heating rate of 3 °C/min.](image)

For CNCs, the values of G' and G'' were nearly constant as the temperature raised from 25 to 60 °C. However, in the case of PVCL-g-CNC copolymer, below its low critical solution temperature (LCST, 36 °C determined at the point, G' > G''), the PVCL chains were extended due to their hydrophilic nature, and it had low G' and G''. The LCST of 36 °C was relatively higher than that of the PVCL homopolymer reported in the literature (32 °C) (Liu et al., 2014; Prabaharan et al., 2008). The slightly higher LCST observed in PVCL-g-CNCs may be due to the solubility issues. The PVCL-g-CNCs was not soluble in water and appeared in the suspensions at room temperature although both CNCs and PVCL are hydrophilic polymers. The heterogeneous suspensions should have somewhat influence on the performance of rheology test. Similar situation was found for the PNIPAM-g-CNCs reported in the reference
(Ifuku et al., 2008). Above the LCST, PVCL chains collapsed into a thin hydrophobic layer on the CNC surface, and hence $G'$ and $G''$ significantly increased. The proposed mechanism for temperature induced phase transition behavior of PVCL-g-CNCs is as follows. At temperature below the LCST, the hydrophilic PVCL chains were extended. Entropic repulsive interactions between particles made the aggregation or connection between particles unfavorable (Azzam et al., 2016). Therefore, they had low $G'$ and $G''$ as confirmed by the dynamic rheology measurement. Upon heating above the LCST, the hydrophobic nature of the PVCL globules dominated the inter-particle attractions among CNC particles, and the absence of any electrostatic repulsion formed coagulation of PVCL-g-CNCs with evidence of the increased $G'$ and $G''$ in the dynamic rheology measurement (Hemraz et al., 2014).

4.4. CONCLUSIONS

The peaks of double bond as well as the vinyl group disappeared in the spectrum of CNCs-g-PVCL copolymer by the ATR-FTIR spectroscopy and solid-state $^{13}$C NMR spectroscopy measurement confirmed grafting polymerization of PVCL on the surface of CNCs. A new signal of nitrogen element observed in the spectrum of PVCL-g-CNC copolymer by the XPS measurement also supported the grafting polymerization. The nanorod-shaped morphology of CNCs before and after polymerization was well-preserved. The dynamic rheology measurement confirmed the temperature responsive behavior for aqueous suspensions of PVCL-g-CNCs (1.0 wt%). The temperature sensitivity of the aggregation properties provides the polymer-decorated CNCs as an opportunity for preparation of advanced CNC-based functional materials.
4.5. REFERENCES


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5.1. INTRODUCTION

Acrylic-based thermoplastic elastomers (TPEs) are combined of polyacrylate soft block with polymethylacrylate hard block (Haloi et al., 2012; Lu et al., 2017). However, acrylic based TPEs usually have relatively low initial Young’s moduli and tensile strength (Muppalla et al., 2012). Therefore, improvement of the mechanical performance of acrylic based TPEs is an important issue.

The addition of nanofillers is a feasible strategy to improve the performance of acrylic copolymer. Currently, CNCs, the crystalline form of cellulose, consisted of stiff, closely-packed cellulose chains with strong intermolecular forces (Pang et al., 2016; Grishkewich et al., 2017), are commercially available, inexpensive, renewable and biodegradable, and easy-to-modify nanomaterials. The nanoscale dimensions and high Young’s modulus (above 100 GPa) (Pei et al., 2011; Phua et al., 2012) make them idea candidates for the improvement of the mechanical properties of acrylic copolymers. The reinforced effect of CNCs was first reported by Favier et al. resulted from the formation of a hydrogen bonded three-dimensional (3D) network within the poly(styrene-co-butyl acrylate) matrix (Favier et al., 1995). The 3D network of CNCs can also act as a barrier for the enhanced thermal stability of nanocomposites (Ferreira et al., 2018). These properties (e.g., mechanical and thermal property) are also affected by other factors such as dispersion of CNCs within the polymeric matrix and intermolecular interactions between the above two components (Habibi et al., 2010). However, achieving homogenous dispersion of CNCs in the acrylic based matrices as nanoscale
reinforcements has been a major challenge since the hydrophilicity of CNCs makes their dispersion difficult in these hydrophobic matrices (Lyer et al., 2015; Noshirvani et al., 2018; Rajisha et al., 2014). In addition, multiple hydroxyl groups at the surface promotes the agglomeration of CNCs via hydrogen bonding limiting the extent of mechanical reinforcement. In order to circumvent this problem, it is necessary to introduce appropriate interactions between the acrylic matrix and CNCs. According to the study of poly(methyl methacrylate) (PMMA)/CNCs nanocomposites, the improved mechanical performance and thermal property are resulted from the interaction of hydroxyl groups of CNCs and ester groups of PMMA (Kiziltas et al., 2015). Similar work for the hydrogen bonding interactions for the increased glass transition temperatures was also reported (Pan et al., 2012). Therefore, it is important to chemically modify the surface of CNCs to further enhance the interfacial interactions so that it can be well mixed with the polymer matrix.

Many strategies regarding the modification of CNCs for their dispersion have been reported. Silylation modification, grafting polymerization and adsorption of macromolecular surfactant on the surface of cellulose are the most successful strategies to tune the hydrophobicity and hydrophilicity (Moon et al., 2011; Habibi et al., 2010). In addition, quaternary ammonium salts (such as stearyl trimethyl ammonium chloride and epoxypropyl trimethyl ammonium chloride) as well as imidazolium salt have been used to modify CNCs to render their surface hydrophobicity (Salajková et al., 2012; Kaboorani et al., 2015; Hasani et al., 2008; Eyley et al., 2011). The hydrophobic polymers grafted from CNC backbones via a controlled radical polymerization process have been widely reported as well (Matyjaszewski et al., 2009; Matyjaszewski et al., 2014). A large number of functional polymers have been
used for the hydrophobic surface modification of CNCs (Yi et al., 2008; Morandi et al., 2012; Yin et al., 2016; Wang et al., 2015; Boujemaoui et al., 2015; Hemraz et al., 2014). After the surface modification of CNCs, the transformation of electrostatic to steric stabilization was achieved (Hemraz et al., 2015; Xu et al., 2008; Yu et al., 2016).

Although CNCs reinforced polymer nanocomposites has been widely studied, including poly(L-lactide) (Kargarzadeh et al., 2017), polypropylene (Khoshkava et al., 2014; Agarwal et al., 2012; Wang et al., 2017), and polyurethane (Rueda et al., 2013; Saralegi et al., 2013), few CNC/acrylic based copolymer nanocomposites have been reported. The first CNCs reinforced acrylic copolymer nanocomposite work was published about 20 years ago. The moduli of acrylic copolymer latexes were indeed enhanced after blending with the CNCs attributed to the strong hydrogen bonding interactions among CNCs (Favier et al., 1995). Subsequent efforts for the reinforcement of the copolymer latexes were done with CNCs derived from different sources (wheat straw and starch, etc.) (Dufresne et al., 1996; Helbert et al., 1996; Dufresne et al., 1997; Angelier et al., 2005). However, the direct blend strategy for the manufactured nanocomposites was only explored at the relatively low contents of CNCs. Recently, the CNCs reinforced acrylic copolymer latex nanocomposites were further investigated in term of various CNC contents (Dastjerdi et al., 2018; Vatansever et al., 2015). However, the high contents of CNCs incorporated resulted in the unstable suspensions of polymer latexes and CNCs although low contents of CNCs contributed to the polymer particle stabilization through absorption of CNCs on the copolymer latexes (Kedzior et al., 2017). Therefore, the nonhomogeneous dispersion or aggregation of CNC nanoparticles were presented in ensuing nanocomposites with the negative influence on the mechanical performance although in situ or novel emulsion
polymerization strategies were explored (Dastjerdi et al., 2017; Mabrouk et al., 2011). The formation of three-dimension network of CNCs at the high loadings caused the coalescence of the polymer latexes (Elmabrouk et al., 2009; Zhang et al., 2017). So the challenging issue of miscibility of CNCs and hydrophobic acrylic copolymer latexes has not been well addressed. However, CNCs incorporated at much low contents could not ensure the satisfied mechanical performance of resulting nanocomposites. The compatibility of bacterial cellulose and acrylic copolymer latexes was further studied for the contents of cellulose up to 10 wt%, but the elongation at break values were significantly reduced at the high contents although other mechanical performance (tensile strengths or elastic moduli) was obviously enhanced (Trovatti et al., 2010). The reduced mechanical properties were resulted from the weak miscibility between the acrylic copolymer matrix and cellulose. Subsequently, surface modification of bacterial cellulose membrane by n-butyl acrylate (BA) as well as methyl methacrylate (MMA) was studied, but its mechanical properties were not provided (Lacerda et al., 2013). The acrylic copolymer grafted from the rigid cellulose backbone as a novel type of TPEs was also reported. The composites showed a largely enhanced tensile strength, while the improvement of elastic moduli is still possible (Jiang et al., 2013). Subsequently, the CNC reinforced acrylic based nanocomposites from the in-situ polymerization approach indicated an improved elastic modulus and tensile strength (Yu et al., 2016). However, the elongation at break values much declined compared to these of the pristine acrylic based TPEs as the strong intermolecular hydrogen bonding and high crystalline structures of CNCs restricted the development of CNCs grafted acrylic copolymer. Therefore, improvement in elastic moduli of CNCs/acrylic copolymer composites while maintaining its elongation at break is still difficult. To further
develop the composites with tunable Young’s modulus as well as strain at break, it is necessary to explore the influence of varied CNC loadings on the properties of acrylic copolymer. However, it is challenging to get high content of grafted polymer from the surface of CNCs and thus to quantitatively tune the loadings of modified CNCs in the acrylic copolymer matrix in one pot approach as the relatively low initiation efficiency as well as the aggregation of CNCs during the polymerization, which are obviously different from other nanoparticles, such as silica (Kong et al., 2004; Maeda et al., 2016). We envision that the variation of loadings of modified CNCs enables the fabrication of CNCs reinforced acrylic copolymer nanocomposites not only exhibiting tunable elastic modulus but also retaining elongation at break.

Herein, we report our study on the hydrophobically modified CNCs (MCNCs)/acrylic based copolymer nanocomposites. The MCNCs as well as acrylic based copolymer were first prepared through the controlled radical polymerization process. Its chemical structure as well as morphology was then confirmed by spectroscopy techniques and transmission electron microscope (TEM). Subsequently, thermal and mechanical properties as well as morphology of the MCNCs/PBA-co-PMMA nanocomposites were explored via static and dynamic mechanical tests, thermal and morphological analysis.

5.2. MATERIALS AND METHODS

5.2.1. Materials

Ethyl 2-bromo-2-methylpropionate (98%, EBiB), methyl methacrylate (>99%, MMA), N,N,N',N'',N''-pentamethyldiethylenetriamine (99%, PMDETA), butyl acrylate (>99%, BA), and trimethylamine (>99%, TEA) were supplied by sigma-Aldrich (St. Louis, MO, USA). Dry N,N-dimethylformamide was obtained from solvent purification system. Copper bromide
(98%) with purification treatment (acetic acid and methanol), 4-(dimethylamino) pyridine (99%, DMAP) and 2-bromoisoctylbromide (98%, BIBB) were supplied by Acros Organics (Morris Plains, NJ, USA). Other solvents were utilized as received. Microfibrillated cellulose was provided by Daicel Chemical Industries, Ltd. (white solid product, Tokyo, Japan).

5.2.2. Isolation of CNCs

Cellulose Nanocrystals were prepared by the sulfuric acid hydrolysis. Commercial CNFs were slowly added to the sulfuric acid (64 wt%) under the mechanical stirring. After the reaction at 45 °C for 30 minutes, the resulting viscous suspensions were poured to a glass beaker and then diluted with deionized water. The sediments of hydrolyzed products at the bottom of the glass beaker were collected after the removal of the supernatant on the top carefully. Repeated washing was made for the removal of excess sulfuric acid. The diluted suspensions were then dialyzed in the deionized water for the further removal of the residual sulfuric acid. The cutoff molar mass of the semipermeable membrane for the dialysis was from 12000 to 14000 Da. After the pH value approached to neutral, the CNC suspensions were further treated with a high-pressure homogenizer from the Microfluidics Corp. (Microfluidizer M-110P series, Newton, MA, U.S.A) for the reduction of the size of CNCs. Finally, the concentration of CNC suspensions was tuned to 1.0 wt% by the deionized water (dilution or evaporation treatment). A certain amount of CNCs suspensions (1.0 wt%) was freeze-dried for 3 days to get the CNC powder samples.

5.2.3. Synthesis of CNCs-g-(PBA-co-PMMA)

CNCs based macroinitiators (CNCs-Br) were synthesized by homogeneous esterification reaction of CNCs and 2-bromoisoctyl bromide. CNCs (0.50 g) were first dispersed in DMF
solvent (15.0 ml). 2-bromoisobutyryl bromide (1.20 ml, 9.71 mmol) was then dropwised into the suspension. The suspension was precipitated after the reaction for 24 h, and then floccules were filtered and dried under vacuum.

The surface grafting of PBA-co-PMMA chains from the CNCs based macroinitiator was performed through the atom transfer radical polymerization (ATRP). BA (4.95 ml, 34.5 mmol), MMA (3.02 ml, 28.2 mmol), and CNCs based macroinitiators (17.5 mg) were first dispersed in DMF solvent (8.0 ml), and then PMDETA (13.1 µL, 0.0627 mmol) was injected into the flask under stirring. The resulting suspensions were degassed with freeze-pump-thaw cycles for three times after the quick addition of catalyst CuBr (9.0 mg, 0.0627 mmol). After reaction at 90 °C for few hours, the schlenk flask was open to air and then placed in the ice container to stop the polymerization. The polymerized products were centrifuged for 5 min, and then the precipitation was subsequently separated from DMF solutions. The precipitated product was diluted with THF solvent again, and then repeatedly centrifuged for three times to further wash away homopolymers, and the precipitation of CNCs-g-(PBA-co-PMMA) was obtained. The CNCs-g-(PBA-co-PMMA) was further purified with chloroform solvent. Finally, the purified CNCs-g-(PBA-co-PMMA) was collected and dried to a constant mass after purification.

5.2.4. Synthesis of PBA-co-PMMA

In a typical ATRP process, EBiB (9.2 µL, 0.0627 mmol), MMA (3.02 ml, 28.2 mmol), BA (4.95 ml, 34.5 mmol), CuBr (9.0 mg, 0.0627 mmol), PMDETA (13.1 µL, 0.0627 mmol) and DMF (8.0 ml) were dispersed in the schlenk flask. The resulting mixture was degassed. And then the polymerization was started at 90 °C under stirring. After 7 hours, the polymerization was stopped. The resulting products were precipitated in the methanol solvent. The precipitated
polymer was then diluted with THF and subsequently precipitated in methanol again. These purified steps were repeated for few times to remove the unreacted monomer. Finally, the precipitation was dried to constant mass.

5.2.5. Preparation of Modified CNCs/PBA-co-PMMA Nanocomposites

PBA-co-PMMA/MCNCs nanocomposites were prepared through casting. PBA-co-PMMA copolymer was first dissolved in THF solvent by magnetic stirring. MCNCs dispersed in THF were then mixed with PBA-co-PMMA solution under stirring. The resulting homogeneous suspensions were casted on the glass petri-dishes and dried at room temperature until the constant mass.

5.2.6. Characterization

The Fourier transform infrared spectroscopy measurement with the mode (attenuated total reflectance) was carried out, and a spectrophotometer (Thermo Electron Corporation, series of Nicolet Nexus 670, Gormley, Canada) was utilized to record the spectra. The range for the wavenumbers from 4000 to 800 cm\(^{-1}\) was recorded. Solid state nuclear magnetic resonance measurement was performed with Bruker Avance 400 MHz equipment, and the test was at the ambient temperature. The spectra were recorded at 100.6 MHz, and the chemical shift from 0 to 200 ppm was collected. Thermal stability was evaluated by the thermogravimetric analyzer (TA Instruments Inc., series of TA Q50, New Castle, DE, USA) with a constant N\(_2\) flow environment. The parameters for the heating rate and temperature range were 5 °C/min and from 40 to 600 °C, respectively. DSC tests were performed at inert atmosphere using an analyzer (TA Instruments Inc., TA Q2000, New Castle, DE, USA). Temperature first increased from 25 to 200 °C, and then equilibrated for 5 min for the removal of thermal history. The
temperature subsequently reduced to -55 °C with 10 °C/min, and finally increased to 200 °C at the same rate (10 °C/min). Transmission electron microscope (Peabody, JEOL JEM 1400 series, MA, USA) was utilized for the morphological observation. The accelerating voltage was 120 kV. The suspensions of CNC or CNCs-g-(PBA-co-PMMA) (0.01 wt%) were first prepared and then deposited onto the TEM grids with glow-discharged treatment. Few drops of uranyl acetate (2%) was deposited on the sample surface, and then the liquid film was dried under room temperature for 2-3 hours. In the case of nanocomposite specimens, the samples were first embedded in the epoxy resin, and then ultramicrotome was utilized for the preparation of thin slices in the thickness of 80 nm. A slice of specimen was subsequently loaded on the TEM grid after stained treatment (osmium tetroxide (OsO₄)). The mechanical performance was evaluated by the universal tester (Instron Co., INSTRON 5582 series, Grove City, PA, USA) at 50% relative humidity and 23 °C. The cross-head velocity was 25 mm/min. The dumbbell-shaped samples following the ASTM standard D 638- V were utilized for the evaluation of tensile strength and strain at break. The load cell used for the tensile test was 5 kN, and the sample dimensions for the length, width and thickness were 9.53, 3.18 and 0.30 mm, respectively. The elastic modulus was calculated from the slope of stress-strain curve within 2% strain. For each polymer sample, three replicated specimens were tested. Dynamic mechanical test was carried out in tension mode. Dynamic mechanical analyzer (Q800, TA Instruments Inc, DE, USA) was utilized to record the thermos-mechanical data. The heating rate at 3 °C/min and temperature range from -50 to 200 °C were used. The parameters for the stain amplitude as well as frequency were 0.1% and 1 Hz. The fractured morphology was observed through scanning electron microscopy (Hitachi S4800, Hitachi Ltd., Tokyo, Japan) operating at 20 kV.
Before observation, the coating treatment with gold was conducted in order to enhance the conductivity. The morphology of nanocomposites was determined by atomic force microscopy (Bruker Nanoscope VIII Multi-Mode, Billerica, MA, USA). The tapping mode was utilized for morphological observation. Samples were first dispersed in N,N-dimethylformamide solvent at the concentration of 1.0 mg/ml. The homogeneous suspensions were then spin-coated on the mica surface, and then dried at the ambient temperature. The samples were subsequently scanned through the variation of cantilever. The parameters for the tip radius and spring constant were 2 nm and 20-80 N/m, respectively.

5.3. RESULTS AND DISCUSSION

5.3.1. Chemical Structure and Thermal Property

The FTIR and solid state NMR spectra of CNCs-g-(PBA-co-PMMA) are shown in Figure 5.1(a-b), the acrylate functionality can be confirmed due to the peak at 1726 cm\(^{-1}\) (carbonyl group) in Figure 5.1(a). In addition, the peak for double bonds of BA and MMA monomers disappeared in the spectrum of CNCs-g-(PBA-co-PMMA). The results above confirmed the successfully grafting polymerization of CNCs with PBA and PMMA. The chemical structure of CNCs-g-(PBA-co-PMMA) was further characterized from the solid state NMR spectrum (Figure 5.1(b)). The peaks at C3 (α-CH\(_3\)), C2 (quaternary C), C5 (OCH\(_3\)), C1 (CH\(_2\)) and C4 (C=O) were associated to the PMMA segment. The peaks at C12 (CH\(_3\)), C10 (CH\(_2\)-CH\(_2\)-CH\(_3\)), C11 (CH\(_2\)-CH\(_2\)-CH\(_3\)) and C8 (C=O) confirmed the structure of PBA (Castelvetro et al., 2007). The profiles of CNCs in CNCs-g-(PBA-co-PMMA) were also observed, and the weak intensity was resulted from the sensitivity limit of solid state NMR and low content of macro-initiator (Br-CNCs) used in the polymerization, for which other related research published also met this
issue (Lacerda et al., 2013).

Figure 5.1. Chemical structure and thermal properties of CNCs-g-(PBA-co-PMMA): FTIR (a), solid state NMR spectrum (b), DSC (c) and TGA (d) curves.

The thermal properties of CNCs and CNC-g-(PBA-co-PMMA) are shown in Figure 5.1(c-d). The pristine CNCs didn’t have glass transition temperature ($T_g$) because of the mobility restriction of rigid CNC chains (Navarro and Edlund, 2017), while a clear $T_g$ at 27.15 °C was observed after grafting of PBA and PMMA, which also provided an evidence of grafting polymerization onto the surface of CNCs (Figure 5.1(c)). The thermal decomposition behavior of CNCs and CNCs-g-(PBA-co-PMMA) is shown in Figure 5.1(d). The thermal decomposition of pristine CNCs started at 90 °C. And then a large degradation until 240 °C was observed. Finally, the full degradation was at about 500 °C. The decomposition at about 200 °C was resulted from the sulfate groups on the surface of CNCs (Lin and Dufresne, 2014). The weight loss at 400 to 500 °C was associated to the decomposition of crystalline domains of CNCs. In
addition, the thermal decomposition behavior was also associated to the content of sulfate groups (Liu et al., 2010). The main degradation temperature was improved for CNCs-g-(PBA-co-PMMA) compared to that of CNCs, which indicated random copolymers (PBA and PMMA) grafted on the surface of CNCs.

The temperature values associated with weight loss at 10, 20, 40 and 60% are 209, 274, 306, 329 °C for neat CNCs, and 349, 365, 379 and 387 °C for CNCs-g-(PBA-co-PMMA), respectively. It can be seen that the thermal degradation behavior of modified CNCs was significantly different from neat CNCs. The covered hydrophobic PBA and PMMA contributed to less thermal degradation at low temperature in comparison with that of CNCs. In addition, the major degradation step was shifted to higher temperatures (300 °C) compared to that of neat CNCs, and this might be due to the grafted copolymer that covered the surface sulfate groups (Yu et al., 2015). Furthermore, no weight loss can be seen below or around 100 to 150 °C as the absence of absorbed water in the modified CNCs. Similar phenomenon has been reported for hydrophobic polymers modified cellulose (Azouz et al., 2012). The presence of sulfate groups significantly reduced the onset decomposition behavior of CNCs as discussed above, and then the sulfuric acid produced during the thermal decomposition catalyzed the degradation process (Roman and Winter, 2004). However, water as a primary factor is required during this acid catalyzed decomposition process (Rinaldi and Schüth, 2009). Therefore, the hydrophobic surface modification of CNCs with PBA and PMMA blocked the water adsorption from hydroxyl groups, which stabilized it during decomposition steps, although the sulfate groups were still present (Rosilo et al., 2013; Nagalakshmaiah et al., 2016). Therefore, the thermal decomposition behavior as an indirect evidence demonstrated the CNCs grafted PBA
and PMMA copolymer.

Figure 5.2. TEM micrographs of CNCs (a) and CNCs-g-(PBA-co-PMMA) (b).

5.3.2. Morphology

Morphology of pristine CNCs and CNCs-g-(PBA-co-PMMA) is further characterized by TEM (Figure 5.2(a-b)). The rod-like nanocrystals can be clearly observed for the pristine CNCs. The lengths and widths as shown in Figure 5.2(a) were about 213 and 18 nm, respectively. The measured lengths and widths of CNCs were within the range of sizes reported (Habibi et al., 2010). The widths and lengths of CNCs-g-(PBA-co-PMMA) in Figure 5.2(b) were around 25 and 250 nm, respectively. The rod-like morphology was also well-preserved except the variation in widths, which indicated no damage for its morphology after the grafting polymerization of PBA-co-PMMA copolymer. The CNCs-g-(PBA-co-PMMA) had a rough surface, while a smooth surface for the pristine CNCs can be clearly seen. These analyzes above
also demonstrated the grafting polymerization.

Figure 5.3. Typical stress-strain curves of the neat PBA-co-PMMA and its nanocomposites (a), and photo of tensile test samples (PBA-co-PMMA/MCNCs nanocomposites) (b).

5.3.3. MCNCs/PBA-co-PMMA Nanocomposites

5.3.3.1. Static Tensile Data

The stress-strain curves for neat PBA-co-PMMA and MCNCs/PBA-co-PMMA nanocomposites are shown in Figure 5.3(a). At very low stresses and strains, all samples behaved as a linear elastic solid, and a plastic regime was observed for high level of stresses. It appeared clearly that these materials exhibited elasto-plastic deformation. The representative MCNCs/PBA-co-PMMA nanocomposite sample is shown in Figure 5.3(b). It is a transparent and flexible material.

The values of mechanical properties including Young’s modulus, tensile strength as well as strain at break are summarized in Table 5.1. The improvement in the Young’s modulus and tensile strength was observed when MCNCs were introduced into the PBA-co-PMMA matrix compared to that of neat PBA-co-PMMA. The increase of Young’s modulus as well as tensile strength was observed when the loadings of MCNCs increased. These results indicated that
MCNCs could reinforce the PBA-co-PMMA matrix as the good interfacial compatibility and improved chain entanglements between MCNCs and PMMA-g-PBA matrix.

Table 5.1. Mechanical properties of PBA-co-PMMA and MCNCs/PBA-co-PMMA composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s Modulus (MPa)</th>
<th>Strain at Break (%)</th>
<th>Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% MCNCs</td>
<td>2.3±0.2</td>
<td>2099.2±104.5</td>
<td>2.6±0.6</td>
</tr>
<tr>
<td>1% MCNCs</td>
<td>3.8±0.6</td>
<td>1869.0±182.9</td>
<td>3.3±0.5</td>
</tr>
<tr>
<td>5% MCNCs</td>
<td>7.5±0.6</td>
<td>1608.2±65.2</td>
<td>6.3±0.6</td>
</tr>
<tr>
<td>7% MCNCs</td>
<td>53.5±2.1</td>
<td>980.1±66.2</td>
<td>9.9±1.0</td>
</tr>
<tr>
<td>10% MCNCs</td>
<td>65.9±0.7</td>
<td>278.9±52.5</td>
<td>6.8±0.5</td>
</tr>
</tbody>
</table>

It was striking to see that PBA-co-PMMA nanocomposites with 7 wt% MCNCs exhibited not only obviously enhanced Young’s modulus but also much increased strength than these of pristine PBA-co-PMMA. By incorporating 7.0 wt% of MCNCs into the PBA-co-PMMA matrix, the Young’s modulus was increased by more than 25 times over that of neat PBA-co-PMMA, and the tensile strength had a more than 3-fold increase compared to that of pure PBA-co-PMMA. This prominent increase of mechanical performance was attributed to the reinforcement effect of the CNC nanofibrils, and better compatibility for the stress transfer. Additionally, the increase in Young’s modulus as well as tensile strength after the addition of MCNCs also caused a considerable decrease in the strain at break, when compared to that of the PBA-co-PMMA matrice counterpart. This phenomenon, improvement of strength at the cost of reduction in strain, was resulted from the suppression of plastic deformation in the
matrix caused by the rigid phase (Yao et al., 2014; Rahimi et al., 2017; Xu et al., 2013). Concerning the composites with 10 wt% MCNCs, the strain at break was obviously decreased although further improvement for the elastic modulus was observed compared to these of the pure PBA-co-PMMA. It was likely that MCNCs did not establish full interface binding with the PBA-co-PMMA matrix, possibly due to CNC aggregation at high loading levels (Yin et al., 2016; Xiao et al., 2012). Based on the analysis above, the 7 wt% MCNCs/PBA-co-PMMA nanocomposites displayed the obviously increased tensile strength and Young’s modulus as well as decent strain at break among all samples, showing the overall best performance property.

![Figure 5.4. DMA curves (storage moduli (a) and tanδ (b)) of PBA-co-PMMA and MCNCs/PBA-co-PMMA composites.](image)

5.3.3.2. Dynamic Thermomechanical Data

The storage moduli and alpha transition temperatures (tanδ, associated to $T_g$) of the pristine PBA-co-PMMA and MCNCs/PBA-co-PMMA nanocomposites are shown in Figure 5.4 and Table 5.2. They both showed typical amorphous thermoplastic behavior. In the glass to rubber transition region, the modulus was significantly reduced, and it further decreased in the range of rubbery region as the temperature increased because of the thermoplastic character of
the nanocomposites.

Table 5.2. Thermo-mechanical properties of PBA-co-PMMA and MCNCs/PBA-co-PMMA composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E’ (MPa)</th>
<th>Tanδ peak (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt%</td>
<td>2391.21a</td>
<td>4.82b</td>
</tr>
<tr>
<td>1 wt%</td>
<td>2420.48a</td>
<td>5.84b</td>
</tr>
<tr>
<td>5 wt%</td>
<td>2238.26a</td>
<td>6.04b</td>
</tr>
<tr>
<td>7 wt%</td>
<td>3081.60a</td>
<td>22.60b</td>
</tr>
<tr>
<td>10 wt%</td>
<td>3122.73a</td>
<td>27.61b</td>
</tr>
</tbody>
</table>

a: storage modulus values at -10 °C; b: storage modulus values at 42 °C.

The MCNCs/PBA-co-PMMA nanocomposites had relatively larger value for the storage moduli in comparison with pristine PBA-co-PMMA below T_g. This behavior common to nanocomposites was explained by a fairly small distinction in the modulus for the glassy matrix and CNC networks taking into account the low filler content. However, the storage moduli of MCNCs/PBA-co-PMMA nanocomposites were significantly higher than these of pristine PBA-co-PMMA above T_g. For example, the storage modulus of 7 wt% MCNCs/PBA-co-PMMA nanocomposites at 42 °C was 22.60 MPa, about 4 times larger compared to the value of the neat PBA-co-PMMA (4.82 MPa). The significant reinforcement of nanocomposites above T_g was attributed to the well dispersed rigid nanofiller in the matrix. Also, considering the presence of PBA and PMMA on the surface of MCNCs, further chain entanglement interactions between MCNCs and PBA-g-PMMA matrix could also facilitate the reinforcement (Pei et al., 2011; Cao et al., 2007).
The peak of tan\(\delta\) data also shifted to the higher temperature. The effect of MCNCs on \(T_g\) of PBA-co-PMMA was attributed to a reduction in polymer chain mobility. The ability of entanglements between MCNCs and PBA-co-PMMA matrix resulted in stronger interfacial interactions between the nanofiller and matrix, which created addition barriers that restricted chain motion.

Figure 5.5. DSC curves of PBA-co-PMMA and MCNCs/PBA-co-PMMA composites.

5.3.4.3. Thermal Properties

DSC curves of pristine PBA-co-PMMA and PBA-co-PMMA nanocomposites with 1, 5, 7 and 10 wt% MCNCs are shown in Figure 5.5. The \(T_g\) values of MCNCs/PBA-co-PMMA nanocomposites were 12.41, 17.91, 23.73 and 21.12 °C at 1, 5, 7 and 10 wt% MCNC loadings, respectively, while that of PBA-co-PMMA copolymer was 10.70 °C. The \(T_g\)s of MCNCs/PBA-co-PMMA nanocomposites were obviously increased compared to that of neat PBA-co-PMMA. It is believed that MCNCs acted as physical interlocking points in the PBA-co-PMMA matrix restraining chain mobility and caused \(T_g\) to shift to higher temperatures. For the 10 wt%
MCNCs/PBA-co-PMMA nanocomposites, the $T_g$ value was a bit lower than that of 7 wt% MCNCs/PBA-co-PMMA as it is probably that the uneven distribution of MCNCs in the PBA-co-PMMA matrix due to its higher loadings. In addition, the $T_g$s derived from DSC were relatively lower in comparison with these from DMA because of the different measuring mechanisms. DSC recorded the change in thermal enthalpy, while DMA measured the change of mechanical modulus although both the DSC and DMA could be used to characterize the glass transition temperature of materials. Therefore, the $T_g$ data collected from the DSC and DMA could not be compared directly.

![Figure 5.6. SEM micrographs of fractured surfaces: neat PBA-co-PMMA (a), and MCNCs/PBA-co-PMMA nanocomposites with the content of MCNCs at 1 wt% (b), 5 wt% (c), 7 wt% (d) and 10 wt% (e).](image)

5.3.4.4. Morphology

SEM micrographs of fractured surfaces of neat PBA-g-PMMA and its nanocomposites with 1, 5, 7 and 10 wt% of MCNCs are shown in Figure 5.6. The pristine PBA-g-PMMA in the
Figure 5.6(a) showed a clean and homogeneous surface due to the MMA and BA in the random polymerization. For PBA-co-PMMA nanocomposites with 1 wt% MCNCs (Figure 5.6(b)), the magnification image showed the ductile fractured surface, the rod-like CNCs were still bonded with the matrix during pulling out. In the case of the 5 wt% MCNCs/PBA-co-PMMA nanocomposites, the bi-continuous ductile fractured morphology was also present in Figure 5.6(c), and the irregular fractured surface of CNCs during the pulling out can be clearly seen. These results indicated that the hydrophobic modification of CNCs indeed enhanced their miscibility with hydrophobic matrix and even interfacial interactions (entanglement and hydrogen bonding interactions) (Kiziltas et al., 2015; Pei et al., 2011). For the 7 wt% MCNCs/PBA-co-PMMA nanocomposites (Figure 5.6(d)), the increased numbers of CNCs pulled out during the fracture and partial embed CNCs scattered in the matrix can be observed as well, and the surface of CNCs was coated with some polymer blocks as shown in the enlarged image, which were considered to be the grafted polymers. These evidences implied that the much enhanced chain entanglement and hydrogen bonding interactions facilitated the better interfacial compatibility of MCNCs with PBA-co-PMMA matrix (Habibi et al., 2010; Yao et al., 2014), leading to the homogeneity of the 7 wt% MCNCs/PBA-co-PMMA nanocomposites. By contrast, heterogeneity was obviously observed for 10 wt% MCNCs/PBA-co-PMMA nanocomposites shown in Figure 5.6(e). Large agglomerates of MCNC particles were clearly observed for the 10 wt% MCNCs/PBA-co-PMMA nanocomposites, indicating uneven dispersion of MCNCs in PBA-co-PMMA matrix and declined compatibility between the composite components.

The typical TEM micrographs of 7 wt% MCNCs/PBA-co-PMMA nanocomposites are
shown in Figure 5.7. The CNCs with rod like shape had a homogeneously dispersion in the matrix shown in Figure 5.7(a), also observed in the SEM above, demonstrating that the hydrophobic modification of CNCs could promote the dispersion and compatibility in the PBA-co-PMMA matrix. The TEM image of PMCNCs/PBA-co-PMMA nanocomposites shown in the Figure 5.7(b) also showed the microphase separation morphology. The morphological phenomenon further revealed the increase of MCNC/PBA-co-PMMA nanocomposites in the mechanical and thermal properties.

Figure 5.7. TEM micrographs of MCNCs/PBA-co-PMMA nanocomposites (a-b).

The morphology of the microdomain structure of 7 wt% MCNCs/PBA-co-PMMA nanocomposites is further studied by AFM as shown in Figure 5.8. The micro-phase separated morphology of the MCNCs/PBA-co-PMMA nanocomposites was clearly observed. The bright regions of the phase image represented the worm-like stiff domains, CNCs and PMMA (Dufour et al., 2008; Young and Lovell, 2011; Heshmati et al., 2018). The dark zones represented the soft domains, PBA. The proposed micro-phase separation of MCNCs/PBA-co-PMMA nanocomposites is shown in the Figure 5.9. For the PBA-co-PMMA matrix, PBA and PMMA components tend to segregate (phase separation) for the formation of PBA and PMMA domains due to the mutual repulsion of chemically distinct domains (da Silva et al., 2018). Since the
two components are covalently connected to each other, they display the micro-phase separation (Vatankhah-Varnosfaderani et al., 2018). For MCNCs, the grafted short chains (PBA and PMMA) on the surface of CNCs tend to entangle with the polymer matrix due to the miscibility (Ilčíková et al., 2014). Therefore, the hydrogen bonding and molecular chain entanglement interactions between MCNCs and PBA-co-PMMA matrix facilitate the miscibility on the molecular level (Kiziltas et al., 2015). The strong hydrophilicity of CNCs in CNCs-g-(PBA-co-PMMA) imparted by the presence of multiple hydroxyl groups drives the segregation of CNCs from these hydrophobic domains (PBA and PMMA in both the grafted short chains and polymer matrix) (Lin et al., 2011; Cushen et al., 2012). The micro-phase separation behavior is further enhanced by the rigid and rod-like nature of CNCs (Noronha et al., 2017). Thus, the hard domains of PMMA as well as polar and rigid CNC components acts as the physically crosslinking points to connect the soft rubbery domains of PBA for the formation of micro-phase separated nanocomposites (Hasanabadi et al., 2017; Wang et al., 2015).

Figure 5.8. AFM height (a) and phase (b) images of MCNCs/PBA-co-PMMA composites.

The presence of these micro-phase separated morphology provided unique mechanical
properties of MCNCs/PBA-co-PMMA nanocomposites (Chu and Hsiao, 2001; Odian, 2004; Zhou et al., 2016; Yu et al., 2013). The homogeneous dispersion for CNCs as well as its miscibility with PBA-co-PMMA contributed to the increase of mechanical performance due to the easy stress transfer from PBA-co-PMMA matrix to CNCs (Wang et al., 2018).

![Figure 5.9. Microphase separation of MCNCs/PBA-co-PMMA nanocomposites.](image)

**5.4. CONCLUSIONS**

The successfully grafting polymerization of CNCs with PBA-co-PMMA changed the hydrophilic surface of CNCs into the hydrophobic one. The rod-like morphology of CNCs was preserved after the polymerization. The grafting modification also improved the thermal stability of CNCs. The homogeneous distribution and micro-phase separation of the MCNCs significantly improved the tensile strength and elastic modulus of PBA-co-PMMA thermoplastic elastomers. PBA-g-PMMA/MCNC nanocomposites also showed the much increased storage modulus and glass transition temperature. Therefore, the hydrophobic surface modification of CNCs is shown to be a feasible strategy to impart the reinforcement effect at nanoscale for the hydrophobic polymer matrices.
5.5. REFERENCES


6.1. INTRODUCTION

Thermoplastic elastomers combined with thermoplastic and elastomeric property are considered important functional materials (Dufour et al., 2008). They have been utilized in the industry for many years in polymer blending, adhesives, wire insulation and food packaging. However, many of them show unsatisfactory mechanical performance with low initial stress as well as modulus (Lu et al., 2018).

Thermoplastic elastomeric nanocomposites have become popular recently, in which the reinforcement fillers are at nanoscale. Cellulose nanocrystals (CNCs), comprising crystalline domains of nanocellulose, have an estimated strength over 10 GPa and a modulus over 150 GPa (Pang et al., 2016; Grishkewich et al., 2017). CNCs are considered good candidates as reinforcement fillers. Several CNC-reinforced thermoplastic elastomeric nanocomposites have been reported during the past decade (Yadav et al., 2018; Amin et al., 2016; Neto et al., 2016; Kargarzadeh et al., 2015). However, the mechanical performance, especially strain at break, was not optimal. The reasons were probably due to the immiscibilities in the CNCs/polymer system. Thus, the insufficient interactions between CNCs and matrix at the molecular scale could not produce a satisfactory improvement in the mechanical performance (Rosilo et al., 2013). In addition, the high polarity of CNCs, which easily led to aggregation, resulted in unsatisfactory miscibility within thermoplastic elastomeric matrices (Kanoth et al., 2015). Therefore, the attainment of enhanced mechanical performance and miscibility of CNCs in the thermoplastic elastomer nanocomposites remains to be a challenging issue.
To further increase the mechanical properties and compatibilization of CNCs/acrylic thermoplastic elastomeric nanocomposites, it is essential to create strong interactions at the interface (Phua et al., 2012), such as van der Waals forces, entanglement of molecular chains and electrostatic attractions (Miao et al., 2013). One strategy to tune the performance of nanocomposites is to use a suitable compatibilizer (Eagan et al., 2017). The basic principle is that the repeat units of block copolymer (A-b-B) or grafting copolymer (A-g-B) should be miscible with both CNCs and polymer matrices (Zhang et al., 2013). For example, for a copolymer compatibilizer containing polyethylene (PE) and methacrylates, the domains of [(poly(2-hydroxyethyl methacrylate) and poly(lauryl methacrylate)] in the block copolymer are not only miscible with PE matrix but are also interactive with cellulose, thereby contributing to the effectively dispersed cellulose nanofibrils in the hydrophobic PE matrix (Sakakibara et al., 2016; Sakakibara et al., 2017; Nagalakshmaiah et al., 2016). Another strategy is the utilization of block or graft copolymer (A-g-C or A-b-C) with one domain identical with polymer matrices and the other domain miscible with CNCs. For instance, poly(L-lactic acid) (PLA) grafted xyloglucan enhanced the compatibility of PLA/cellulose composites (Marais et al., 2012; Chen et al., 2017).

In addition, physical or chemical modification strategies have been utilized as well to promote their compatibility (Pinheiro et al., 2017). Surface modifications such as adsorption of surfactants (Rojas et al., 2009), TEMPO-mediated oxidation (Batmaz et al., 2014), esterification (Mariano et al., 2014) and polymer grafting (Mangalam et al., 2009) have been studied. However, absorption of a modifier onto CNC surface gave relatively weak durability that resulted in low-efficiency modifications. These drawbacks can be addressed through graft
copolymerization with covalent bond linkages. The surface-initiated atom transfer radical polymerization (SI-ATRP) was initially reported for CNC modification in 2008 (Xu et al., 2008). Following this work, surface grafting modification for CNCs with the ATRP technique has emerged quickly (Hemraz et al., 2015; Wang et al., 2015; Boujemaoui et al., 2015; Yu et al., 2016), and the typical grafted polymers included poly(N-isopropylacrylamide) (Hemraz et al., 2014), polystyrene (Morandi et al., 2012) and poly(2-aminoethylmethacrylate) (Hemraz et al., 2015).

There are only few reported studies of CNCs and acrylic-based thermoplastic elastomeric nanocomposites (Dufresne et al., 1997; Angellier et al., 2005; Elmabrouk et al., 2009). The acrylic copolymer latex reinforced with CNCs at relatively low contents was first studied about 20 years ago (Favier et al., 1995; Dufresne et al., 1996; Helbert et al., 1996). Subsequent studies of its reinforcement at varying CNC content were reported (Dastjerdi et al., 2018; Vatansever et al., 2015). Yet, aggregation of CNCs in the nanocomposites was observed at high loading levels (Dastjerdi et al., 2017; Mabrouk et al., 2011). Interfacial compatibility was further explored, but the mechanical performance of the resulting nanocomposites from bacterial cellulose and acrylic latexes was significant reduced (Trovatti et al., 2010; Shamsabadi et al., 2017; Dastjerdi et al., 2017). As ways to counteract the miscibility issue, surface grafting modification and in-situ polymerization methods were utilized (Lacerda et al., 2013; Jiang et al., 2013). Interestingly, microphase separation associated with the rigid celluloses resulted in enhanced mechanical performance of nanocomposites (Yu et al., 2016; Wang et al., 2015). In addition, the saccharide-base and sugar-base hybrid copolymers with organized morphology (lamellar, cylinder, body-centered cubic and gyroid) were reported as a fascinating approach.
for the design of carbohydrate-base block copolymers with high Flory–Huggins interaction parameter and microphase-separated nanostructures (sub-10 nm scale) (Isono et al., 2013; Otsuka et al., 2013; Isono et al., 2018; Sinturel et al., 2015; Stoykovich et al., 2005). A new type of elastomers has been reported with adaptive coloration and excellent mechanical performance that was attributed to the microphase separation of linear domain and bottlebrushes-like segment (Vatankhah-Varnosfaderani et al., 2018; Vatankhah-Varnosfaderani et al., 2017).

Inspired by the above publications, we anticipated that the rigid rod-type CNCs, after surface modification, should enhance the interfacial miscibility and even influence the microphase separation. First, CNCs were chemically decorated with poly (methyl methacrylate) (PMMA) to subsequently minimize the aggregation of modified CNCs (PMCNCs) in the hydrophobic matrix (Panganiban et al., 2018; Warren et al., 2008). The targeted PMCNCs/PBA-co-PMMA nanocomposites were then used to study interfacial miscibility and microphase-separated morphology (Ilčíková et al., 2014; Daga et al., 2011).

For characterization, the chemical structure and thermal properties of PMMA-g-CNCs (PMCNCs) synthesized via ATRP were confirmed via spectroscopic techniques and thermal analysis. The mechanical and morphological studies of PMCNCs/PBA-co-PMMA nanocomposites were conducted through the tensile testing and microscopic analysis.

6.2. MATERIALS AND METHODS

6.2.1. Materials

4-(dimethylamino) pyridine (99%, DMAP) and 2-bromoisobutyrylbromide (98%, BIBB) were supplied by Acros Organics (Morris Plains, NJ, USA). CNC preparation and copper
bromide purification (Across Organics, 98%, Morris Plains, NJ, USA) were according to the past procedures (Zhang et al., 2017). Dry N,N-dimethylformamide (DMF) solvent was from solvent purification system. Ethyl 2-bromo-2-methylpropionate (98%, EBiB), methyl methacrylate (≥99%, MMA), N,N,N',N'',N''-pentamethyldiethylenetriamine (99%, PMDETA), butyl acrylate (≥99%, BA), and trimethylamine (≥99%, TEA) were supplied from the Sigma-Aldrich (St. Louis, MO, USA). All chemicals were utilized as received.

6.2.2. Synthesis of CNCs-g-PMMA

The esterification reaction was performed for the preparation of CNCs based macroinitiators (Zhang et al., 2017). The typical procedure for The PMMA-grafted CNCs is given here. Catalyst CuBr (9.0 mg, 0.0627 mmol) and ligand PMDETA (13.1 µL, 0.0627 mmol) were quickly added into a flask after MMA (6.71 ml, 62.7 mmol) and CNCs based macrorinitiators (17.5 mg) were homogeneously dispersed in DMF (8.0 ml) solvent. The reaction was started at 90 °C after degassing. After a few hours of reaction, the schlenk flask was open to air and then placed in the liquid nitrogen container to stop the polymerization. The polymerized products were diluted with DMF solvent, and then centrifuged at 7000 rpm for 5 min at 20 °C. The precipitate and DMF solution were subsequently separated. The precipitate was dilute with THF solvent again, and repeatedly centrifuged for three times to further wash away the PMMA homopolymer, and only the precipitate of PMMA-g-CNCs was obtained. The PMMA-g-CNCs powder was further purified with chloroform to remove the MMA (monomer) and PMMA (homopolymer). Finally, the purified PMMA-g-CNCs sample was collected and dried to a constant mass.
6.2.3. Synthesis of PBA-co-PMMA

In a typical polymerization process, EBiB (9.2 µL, 0.0627 mmol), MMA (3.02 ml, 28.2 mmol), BA (4.95 ml, 34.5 mmol), CuBr (9.0 mg, 0.0627 mmol), PMDETA (13.1 µL, 0.0627 mmol) and DMF (8.0 ml) were dispersed in the schlenk flask. The resulting mixture was degassed. The polymerization was initiated at 90 °C with stirring. After 7 hours, the polymerization was stopped. The resulting products were precipitated in the methanol solvent. The precipitated polymer was then diluted with THF and subsequently precipitated in methanol again. These purified steps were repeated for a few times to remove the unreacted monomer. Finally, the precipitate was dried to constant mass.

6.2.4. Preparation of Modified CNCs/PBA-co-PMMA Nanocomposites

For the preparation of PBA-co-PMMA/PMCNCs nanocomposites, PBA-co-PMMA and PMCNCs were stirred in THF solvent separately overnight and then mixed together with further stirring. The homogeneous suspension was casted on the glass petri-dishes and dried at the ambient temperature until a constant mass was achieved.

6.2.5. Characterization

Fourier transform infrared (IR) spectroscopy in the ATR mode (attenuated total reflectance) and solid state nuclear magnetic resonance (NMR) were utilized for chemical structural analysis. The ATR spectra were recorded on a Nicolet Nexus 670 spectrophotometer from Thermo Electron Corporation (Gormley, Canada). The spectral range from 4000 to 800 cm⁻¹ was collected. Solid state NMR measurements were carried out in the CP/MAS mode on a Bruker Avance 400 MHz instrument. The ¹³C spectra were taken at 100.6 MHz at ambient temperature, covering a spectral width from 0 to 200 ppm.
Thermal decomposition behavior was analyzed by the thermogravimetric analyzer (TGA), using a TA model Q50 instrument (TA Instruments Inc., New Castle, DE, USA) in a nitrogen flow environment. About 5 mg of samples was used for each test at a heating rate of 5 °C/min and temperature range of 40 - 600 °C. Differential scanning calorimetry (DSC) analysis was performed with 4-6 mg of samples at a nitrogen atmosphere using a model TA Q2000 analyzer (TA Instruments Inc., New Castle, DE, USA). The temperature was ramped from 25 to 200 °C, and held at 200 °C for 5 min to remove the sample’s thermal history. The temperature was cooled to -55 °C and then increased to 200 °C at 10 °C/min.

For transmission electron microscopy (TEM), the accelerating voltage of the microscope (JEOL JEM 1400 series, Peabody, MA, USA) was 120 kV. An ultramicrotome was used for the sample preparation (each thin slice having a thickness of 80 nm) after embedded in the epoxy resin. After treatment with osmium tetroxide (OsO₄), the sample was loaded on a copper grid for observation. Scanning electron microscopy (SEM) was used for surface morphological analysis. The instrument (Hitachi S4800, Hitachi Ltd., Tokyo, Japan) was operated at 20 kV. The samples were sputtered with a gold coating in order to allow electron conductivity. For atomic force microscopy (AFM) (Bruker Nanoscope VIII Multi-Mode, Billerica, MA, USA), the tapping mode was utilized. The homogeneous suspension of a sample was dispersed with N,N-dimethylformamide solvent and spin-coated on a mica surface. The sample (after drying) was observed at the ambient temperature with a tip radius of 2 nm and a spring constant of 20-80 N/m.

For mechanical testing, an Instron model 5582 universal tester (Instron Co., Grove City, PA, USA) was used with a cross-head velocity of 25 mm/min. The load cell used for the tensile
test was 5 kN, and the sample dimensions for length, width and thickness were 9.53, 3.18 and 0.30 mm, respectively. The samples were at 50% relative humidity and 23 °C. The mechanical evaluation (elastic modulus, tensile strength and strain at break) followed the ASTM standard D 638- V method with three dogbone specimens tested for each sample. The slope in the stress-strain curve (at less than 2% strain) was calculated for the elastic modulus.

6.3. RESULTS AND DISCUSSION

6.3.1. Structure-Property of PMCNCs

The FTIR spectra are shown in Figure 6.1 (a-b). In the case of PMCNCs, the peak for the double bonds of monomers at 1639 cm⁻¹ disappeared compared to that of MMA monomer; the peak (1726 cm⁻¹) that corresponded to carbonyl group (strong and narrow) indicated the presence of methacrylate functionality. The peaks at 3300 and 1100 cm⁻¹ corresponded to characteristic bands of cellulose (OH and C-O-C groups).

![Figure 6.1. FTIR and solid state NMR spectra of MMA (a), CNCs (c) and PMCNCs (b, d).](image)
The chemical structure was further characterized by solid state $^{13}$C NMR (Figure 6.1 (c-d)). The presence of PMMA domain in PMCNCs (Figure 6.1d) was confirmed by the following peaks: quaternary C at 44.8 ppm, -CH$_3$ in the range of 15.7 to 22.7 ppm, -OCH$_3$ at 51.7 ppm and C=O group at 177.7 ppm (Souto-Maior et al., 2005). The peaks for CNCs in PMCNCs were also present in the spectrum, and the weak intensities compared to that of neat CNCs (Figure 6.1c) resulted from the low content of macro-initiator (Br-CNCs) used in the polymerization. The same issue was previously reported for the solid state NMR spectra of bacterial cellulose-grafted-PMMA materials (Lacerda et al., 2013). Therefore, the overall evidence from the $^{13}$C solid state NMR and FTIR confirmed that the PMMA was grafted onto the surface of CNCs.

![Figure 6.2. Thermal properties (DSC (a) and TGA (b)) of CNCs and PMCNCs.](image)

The thermal properties of neat CNCs and PMCNCs are shown in the Figure 6.2 (a-b). In the DSC curve of PMCNCs (Figure 6.2a), a clear glass transition temperature at 124 °C for grafted PMMA chains was observed. In the case of TGA data (for studies of thermal stability of CNCs and PMCNCs) shown in Figure 6.2b, the major degradation of PMCNCs was shifted to higher temperatures compared to that of neat CNCs due to the grafted PMMA that replaced
the sulfate groups near the surface of the nanocellulose.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elastic Modulus (MPa)</th>
<th>Strain at Break (%)</th>
<th>Tensile Strength (MPa)</th>
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<td>0% PMCNCs</td>
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<td>2099.2±104.5</td>
<td>2.6±0.6</td>
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<td>1% CNCs</td>
<td>19.4±2.6</td>
<td>1595.0±72.3</td>
<td>5.3±0.3</td>
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<tr>
<td>1% PMCNCs</td>
<td>28.4±1.5</td>
<td>1327.6±95.5</td>
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<tr>
<td>10% CNCs</td>
<td>20.6±1.7</td>
<td>1112.4±21.4</td>
<td>1.8±0.2</td>
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<tr>
<td>10% PMCNCs</td>
<td>63.5±3.3</td>
<td>754.8±21.3</td>
<td>8.2±1.0</td>
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</table>

6.3.2. PMCNCs/PBA-co-PMMA Nanocomposites

6.3.2.1. Mechanical Properties

The stress-strain plots of neat PBA-co-PMMA and PBA-co-PMMA composites with CNCs and PMCNCs are shown in Figure 6.3. The values of mechanical properties (tensile strength, strain at break as well as Young’s modulus) are showed in Table 6.1. The elastic modulus as well as tensile strength of nanocomposites notably increased with CNC loadings. For the unmodified CNCs, the Young’s modulus as well as tensile strength only showed modest increases. Tensile strength with an eightfold increase and elastic modulus with a twofold improvement were observed for the nanocomposites loaded with 1 wt% CNCs. Further increase in the elastic modulus was seen when the loading of CNCs was at 10 wt%. The reason is that the rigid CNC backbones with high aspect ratio and moduli could indeed act as
reinforcing nanofillers for PBA-co-PMMA copolymer matrices. On the contrary, the strain at break as well as tensile strength was significantly reduced at 10 wt% CNC loading. The reason is that the CNCs displayed an obviously aggregation in the matrix, and the interfacial miscibility of CNCs and PBA-co-PMMA was significantly reduced. As is already known, the CNCs as polar rigid chains were immiscible with PBA-co-PMMA matrices. So a high content of hydrophilic CNC nanoparticles within the hydrophobic PBA-co-PMMA matrices certainly resulted in the aggregation of CNCs. The aggregation of CNCs led to weak hydrogen bonding interactions with the PBA-co-PMMA matrix, which resulted in the poor chain entanglements among the CNCs and the matrix. As a result, the CNCs tended to interact with each other through strong hydrogen bonding and then interconnected and formed CNC networks rather than to entangle with the chains of PBA-co-PMMA matrix. The stress transfer was less efficient from the matrix to the CNC nanoparticles. Thus, the low energy dissipation during the fracture resulted in the low mechanical performance, especially the strain at break.

Figure 6.3. Representative stress-strain curves of PBA-co-PMMA, CNCs/PBA-co-PMMA and PMCNCs/PBA-co-PMMA nanocomposites.
In contrast, the PMCNCs/PBA-co-PMMA nanocomposites displayed relatively larger increases in the elastic modulus as well as the tensile strength when compared to those of CNCs/PBA-co-PMMA nanocomposites. The Young’s modulus and the tensile strength for the 1 wt% PMCNCs/PBA-co-PMMA nanocomposites showed over 10 and 5 times increase, respectively, while the corresponding values for 10 wt% PMCNCs were improved much more. The obviously enhanced mechanical performance (tensile strength and elastic modulus) of PMCNCs/PBA-co-PMMA nanocomposites resulted from good interfacial miscibility and improved chain entanglements between PMCNCs and PMMA-co-PBA matrix (Lu et al., 2015; Neto et al., 2016). However, after the addition of PMCNCs, the values of strain at break were also reduced, in accordance with past experience with composites (Yu et al., 2015; Huang et al., 2017). This phenomenon regarding the strength increase at the expense of strain at break was at least partly due to the reduction in the plastic deformation region (Xu et al., 2013; Rahimi et al., 2017).

6.3.2.2. Thermal Properties

Figure 6.4 displays DSC curves for PBA-co-PMMA as well as its composites with different levels of CNCs and PMCNCs. The T_g value increased by about 9 °C for 1 wt% CNCs/PBA-co-PMMA composites, while the PMCNC/PBA-co-PMMA nanocomposites exhibited relatively larger increase in T_g, especially at 10 wt% compared to that of PBA-co-PMMA. The variation of CNC content on the change in T_g of PBA-co-PMMA was attributed to a reduction in polymer chain mobility. It is believed that CNCs act as physical interlocking points in the matrix that restrain chain mobility. In the case of CNCs/PBA-co-PMMA nanocomposites, CNC agglomeration limited this “restriction effect”. On the contrary, the
ability of entanglements between PMCNCs and PBA-co-PMMA matrix resulted in strong interfacial interactions, which created additional barriers that restricted chains motion and caused $T_g$ to shift to higher temperatures. For the 10 wt% CNCs/PBA-co-PMMA nanocomposites, the $T_g$ value was lower than that of 1 wt% CNCs/PBA-co-PMMA nanocomposites and PMCNCs/PBA-co-PMMA nanocomposites. As reduced interfacial adhesion between PBA-co-PMMA matrix and CNCs at high loading caused increased CNC-CNC interactions and reduced the intermolecular interactions among CNCs and PBA-co-PMMA, the weak chain entanglements among CNCs and PBA-co-PMMA matrices significantly compromised the barrier effects of CNCs on the chain mobility of PBA-co-PMMA.

Figure 6.4. DSC curves of PBA-co-PMMA, CNCs/PBA-co-PMMA, and PMCNCs/PBA-co-PMMA nanocomposites.

6.3.2.3. Morphology

The morphologies of neat PBA-co-PMMA and its composites containing 1 wt% CNCs
and PMCNCs are shown in Figure 6.5. A smooth surface was observed for the neat PBA-co-PMMA in Figure 6.5(a-b). On the contrary, a rougher fractured surface was detected for the 1 wt% CNCs/PBA-co-PMMA composites (Figure 6.5(c-d)). The brittle fractured surface as well as the obvious cavities in the interfacial boundary were clearly observed, indicating that the neat CNCs did not have good interfacial adhesion with the PBA-co-PMMA matrix, which resulted in mediocre mechanical performance. However, as shown in Figure 6.5(e-f), PMCNCs were embedded into the PBA-co-PMMA matrix. They also showed better interfacial adhesion with the PBA-co-PMMA matrix, which might be attributed to the PMMA grafted on the surface of CNCs, thereby leading to better miscibility and enhanced interactions with the PMMA domains in the PBA-co-PMMA matrix. The enhanced interfacial boundary was crucial for the increase of mechanical property (Trovatti et al., 2010; Cao et al., 2007).

Figure 6.5. Micrographs of PBA-co-PMMA (a-b), 1 wt% CNCs/PBA-co-PMMA (c-d) and 1 wt% PMCNCs/PBA-co-PMMA (e-f) nanocomposites.
The AFM images of PMCNCs/PBA-co-PMMA nanocomposites are shown in Figure 6.6 (a-b). In the case of the phase image, the bright areas represented stiff domains (CNCs and PMMA), while dark zones represented soft domains (PBA). Therefore, the microphase separated morphology of PMCNCs/PBA-co-PMMA nanocomposites could be visualized (Panganiban et al., 2018; Ilčíková et al., 2014), which was also supported by the TEM image for the same nanocomposites shown in Figure 6.6 (c).

The proposed mechanism for the formation of microphase separated morphology of PMCNCs/PBA-co-PMMA nanocomposites is illustrated as follows. For the PBA-co-PMMA matrix, PBA and PMMA components are thermodynamically immiscible on the molecular level and tend to segregate (microphase separation), resulting in the formation of PBA and PMMA domains (Vatankhah-Varnosfaderani et al., 2018). For PMCNCs, the grafted short PMMA chains (PMCNCs) are effectively entangled with the PBA-co-PMMA matrix due to the improved miscibility and hydrogen bonding interactions with hydroxyl groups of CNCs (PMCNCs) and carbonyl groups in PBA-co-PMMA matrix (Kiziltas et al., 2015). However, the strong hydrophilicity from the hydroxyl groups of CNCs contributes to the segregation of CNC segments in PMCNCs from the hydrophobic PBA-co-PMMA matrix (Cushen et al., 2012; Sinturel et al., 2015). The microphase separation is further driven by the incompatibility among the rigid CNC backbone and hydrophobic domains (PBA and PMMA) (Crawford and Sita, 2015; Otsuka et al., 2013), resulting in the formation of microphase separated structures (hard PMMA and rigid CNC components as physical crosslink points connected to soft rubbery PBA components), which contributed to the enhanced mechanical properties of PMCNCs/PBA-co-PMMA nanocomposites (Daniel et al., 2016).
6.4. CONCLUSIONS

The enhanced interfacial compatibility among PMCNCs and PBA-co-PMMA contributed to the significantly increased mechanical properties (tensile strength and elastic modulus) and glass transition temperature. Morphological analysis further indicated the enhanced interfacial miscibility between PMCNCs and PBA-co-PMMA, which resulted in the enhanced interfacial adhesion of PMCNCs and PBA-co-PMMA matrix. PMCNCs/PBA-co-PMMA nanocomposite morphology exhibited microphase separation with PBA as the soft domains and PMMA/CNCs as the hard domain. Therefore, not only can surface-tailored CNCs be utilized as effective reinforcing agents, but they can also influence the microphase-separated morphology.
6.5. REFERENCES


CHAPTER 7. OVERALL CONCLUSIONS

7.1. MAIN CONCLUSIONS

This work was carried out to study properties of micro-size wood fiber plastic composites and cellulose nanocrystal - thermoplastic elastomeric nanocomposites as influenced by chemical additives and/or fiber surface chemical modification. The following conclusions are reached from the study.

Part 1: The MOE and MOR values of composites retained more than 90% of their original values after the addition of 5 wt% aluminium hydroxide, magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane. The MOE and MOR values have no further decrease as the content of aluminium hydroxide and magnesium hydroxide increased from 5 to 10 wt%. Cone calorimeter test results indicated that the HRR and THR values were reduced for composites with magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane compared to those of control composites. The composites with 1,2-bis(pentabromophenyl) ethane exhibited the best fire performance. The significantly reduced pHRR, THR and HRR values of composites were observed as the contents of aluminium hydroxide, magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane increased from 5 to 10 wt%. For the morphology analysis of char residues, a continuous and compacted char layer was formed for WPCs with the fire additive 1,2-bis(pentabromophenyl) ethane, which acted as an efficient physical barrier to suppress the combustion of composites.

Part 2: The addition of flame retardants resulted in the reduced MOE values, and MOR values did not change systematically. The synergism of nanoclay and 1,2-bis(pentabromophenyl) ethane/ethylene bis(tetrabromophthalimide) and improved interfacial
miscibility by MAPE contributed to the thermal degradation of the composites toward higher temperature. The reduced HRR and THR values of composites were observed with the combined addition of fire additives (nanoclay and 1,2-bis(pentabromophenyl) ethane/ethylene bis(tetrabromophthalimide)), revealing the synergistic effect of nanoclay and 1,2-bis(pentabromophenyl) ethane/ethylene bis(tetrabromophthalimide) for char layer formation. For the morphology analysis of char residues, the combined use of nanoclay, 1,2-bis(pentabromophenyl) ethane and MAPE contributed to the formation of much more continuous and compacted char layer.

Part 3: Temperature responsive PVCL-g-CNC copolymer was synthesized through SI-ATRP. The grafting polymerization of PVCL on the surface of CNCs was confirmed via the ATR-FTIR and solid-state ¹³C NMR spectroscopy measurement. The rod like morphology of CNCs before and after polymerization were well maintained. The aqueous suspensions of PVCL-g-CNCs (1.0 wt%) showed the temperature responsive phase transition behavior confirmed by the dynamic rheology measurement. The proposed mechanism for temperature responsive phase transition was that the hydrophilic PVLC chains transformed into hydrophobic ones upon its LCST, and then collapsed into a thin hydrophobic layer on the surface of CNCs.

Part 4: The grafting polymerization of CNCs with PBA and PMMA imparted their hydrophobic traits. The grafting modification also led to an increased thermal stability of MCNCs. The 7 wt% MCNCs/PBA-co-PMMA nanocomposites had an increase in Young’s modulus of more than 25-fold and in tensile strength at about 3 times compared to these of neat PBA-co-PMMA. The large increase in the storage moduli and glass transition temperature of
PBA-g-PMMA/MCNC nanocomposites was also observed compared to those of neat PBA-co-PMMA. The microphase separated morphology of MCNCs/PBA-co-PMMA nanocomposites was also observed from the AFM and TEM measurement, which will open new opportunities toward a rational design of the CNC reinforced nanocomposites with the micro-phase separation morphology and better mechanical performance.

Part 5: The improved thermal stability was observed for the surface-tailored CNCs. The mechanical properties (tensile strength and elastic modulus) and glass transition temperature of PMCNCs/PBA-co-PMMA nanocomposites were largely improved compared to those of neat PBA-co-PMMA and CNCs/PBA-co-PMMA nanocomposites resulted from the better interfacial compatibility among PMCNCs and PBA-co-PMMA. The 10 wt% PMCNCs/PBA-co-PMMA nanocomposites had an increase in Young’s modulus of more than 20-fold and in tensile strength at about 3 times compared to these of neat PBA-co-PMMA copolymer. The improved interfacial miscibility of PMCNCs and PBA-co-PMMA matrix was observed from the morphological analysis. The PMCNCs/PBA-co-PMMA nanocomposite also exhibited the microphase separation behavior with PBA as the soft domains and PMMA/CNCs as the hard domain. Therefore, the surface modification of CNCs is a feasible strategy to improve interfacial miscibility and even drive a phase segregation morphology.

7.2. FUTURE WORK

For the flame retardancy of wood flour and high density polyethylene composites, the obviously enhanced fire retarding performance was achieved after the addition of fire additive nanoclay and bromide based compounds (SA-8010 and SABT-93), but their mechanical performance was obviously decreased. The largely decreased mechanical performance was
attributed to the decline in the interfacial miscibility among the fire additives (bromide based compounds and nanoclay), wood flours, high density polyethylene and compatibilizer MA-g-PE. The continued work in the future could focus on the balance of their mechanical and fire retarding properties by optimizing the content of MA-g-PE in the system. In addition, the detailed mechanism for the synergistic effect of bromide based compounds and nanoclay in the fire retardancy of WPCs is still not clearly understood although the proposed mechanism is given. Thus, the future work could continue to study how the gas and condensed phase interaction contributes to the better fire performance through the analysis of pyrolysis products. The characteristic functional groups can be determined from the Fourier transform infrared spectrometry (FTIR), while the information related to the decomposed products can be analyzed with the thermogravimetric analysis (TGA) and mass spectrometry (MS). Therefore, the TGA coupled with FTIR or TGA coupled with MS for the time resolved measurement of the decomposed products could give more evidences for the analysis of synergistic effects of fire retardants to further understand the flame retardancy mechanism.

For the surface modification of CNCs with ATRP technique, the freeze drying treatment of CNCs caused the obvious aggregation of CNC powder samples and led to a restriction of the accessibility of surface hydroxyl functionalities during the following esterification modification. Thus, the resulted CNCs based macroinitiators had relatively low degree of substitution (bromide content). Subsequently, in the surface-initiated ATRP step, the relatively low bromide content and unwanted interparticle aggregation via hydrogen bonding interaction during the polymerization resulted in a low grafting density. Thus, a few polymer chains were grafted onto the surface of freeze-dried CNCs. Therefore, the reduction of aggregation of CNCs
and enhanced available sites (hydroxyl groups) for the increased degree of substitution in the step of esterification reaction will be the further work. The solvent exchange treatment is a feasible solution to reduce the aggregation of CNCs and then increase the bromide content in the following substitution reaction.
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Synergistic influence of halogenated flame retardants and nanoclay on flame performance of high density polyethylene and wood flour composites

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Thermoresponsive Copolymer Poly(N-Vinylcaprolactam) Grafted Cellulose Nanocrystals: Synthesis, Structure, and Properties

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