Physicochemical and Mechanical Properties of Polypropylene-cellulose Nanocrystal Nanocomposites: Effects of Manufacturing Process and Chemical Grafting

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Chemical modifications have been widely adopted for improving the dispersibility of cellulose nanocrystals (CNCs) in nonpolar matrixes. Nonetheless, an engineering design for improving the CNC structure is still challenging due to the differences in the dispersion level of CNCs depending on the modification strategies in a desired matrix. The current study was conducted to find an appropriate functionalization technique for CNCs and an effective manufacturing process for CNC-polypropylene (PP) nanocomposites. The surface structures of CNCs were successfully changed using toluene diisocyanate (TDI) and maleic anhydride grafted PP (MAPP). The tensile properties and thermal stability of the nanocomposites with MAPP grafted CNCs were higher than those of pristine and TDI grafted CNC systems. A melt-extrusion process with predispersion processing exhibited more positive effects on the properties of the nanocomposites in comparison to the systems without pre-dispersion. Scanning and transmission electron microscopes also provided clear evidence of the dispersion levels of unmodified and modified CNCs in the PP matrix.

Keywords: Cellulose nanocrystals; Nanocomposites; Polypropylene; Surface modification; Dispersibility

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INTRODUCTION

Materials combined with nanocellulose in high-tech fields (Korhhonen *et al.* 2011; Chun *et al.* 2012; Anis *et al.* 2014; Choi *et al.* 2014; Spinella *et al.* 2015; Zhang *et al.* 2015; Li *et al.* 2016) have many useful and unexpected properties (Dufresne 2017; Ziaei-Tabari *et al.* 2017), and their potential has attracted much attention from many researchers. In particular, cellulose nanocrystals (CNCs) can be an excellent reinforcement in polymeric nanocomposites due to their intrinsic crystalline structure. CNC nanoparticles are defectfree crystallites that are commonly 5 nm to 70 nm in width and 100 nm to 250 nm in length (Klemm *et al.* 2011). The nanoparticles have unique properties such as low density (1.6 gcm⁻³), high surface area (300 m²g⁻¹) (Majoinen *et al.* 2011), and high performance of mechanical properties (tensile strength and modulus: 7.5 GPa to 7.7 GPa (Moon *et al.* 2011) and 143 GPa (Ljungberg *et al.* 2006), respectively). Due to these appealing properties, studies of nanocomposites reinforced with CNCs have been consistently attempted to improve the physical and mechanical properties of the composites.

Despite gaining popularity for CNC-polymer nanocomposites, studies for polypropylene (PP) as a base matrix have been relatively sparse. Polypropylene as a

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representative of thermoplastic polymer is widely used in many applications due to its low cost, wide spectrum of properties, and easy producibility. Also, it is the world's second most widely produced synthetic plastic after polyethylene. Hence, PP in this study was used as a base matrix for CNC nanocomposites to create commercially extensive usage of CNCs at the industrial level.

Most studies for polymeric nanocomposites reinforced with nanocelluloses have used a solvent casting method rather than a high-throughput melt-extrusion process. The solvent casting method makes it possible to achieve well-dispersed cellulose nanoparticles in reinforced composites at laboratory scale. However, the most meaningful processing technique at the industrial level is melt-extrusion, as it allows for a high production rate (Lee *et al.* 2011; Leite *et al.* 2016). One of the reasons for hesitating to employ the thermal extrusion process could be due to the low thermal stability of CNCs obtained from acid hydrolysis. A sulfate group on the surface of CNCs can act as a catalyst for the degradation of the CNC.

Mechanical properties of the fiber reinforced composites are mainly influenced by interfacial adhesion between the reinforcements and the base matrix (Gwon et al. 2010). Particularly, in case of using nanoparticles, uniform distribution of the nanoparticles in polymer matrix should be a prerequisite to effectively lead the interfacial interaction between them. In order to take full advantage of nano-sized celluloses as reinforcements, it is essential to achieve a good dispersibility of the hydrophilic nanoparticles in an apolar matrix (Azeredo et al. 2009; Habibi et al. 2010; Gwon et al. 2016b). The difference in surface nature between nonpolar PP and polar CNCs makes it difficult to achieve both good interfacial adhesion and dispersibility of CNCs in a PP matrix. Previous studies for the surface modification of nanocelluloses (Ljungberg et al. 2005, 2006; de Menezes et al. 2009; Lee et al. 2009; Liu et al. 2010; Siqueira et al. 2010; Taipina et al. 2013; Shang et al. 2013; Habibi 2014; Carlsson et al. 2015; Spinella et al. 2015; Tan et al. 2015) have suggested useful solutions in achieving the conditions for successive CNC reinforced PP nanocomposites. The studies also have implied that chemical modifications are one of the most powerful tools for improving compatibility and dispersibility of CNCs in an apolar solvent and matrix. Moreover, the chemical modifications of the CNCs can overcome the drawbacks in the thermal stability, as confirmed in previous studies (Gwon et al. 2016a).

As mentioned above, chemical modifications of CNCs and the control of manufacturing processes can play a key role in obtaining a good dispersion level of CNCs in the PP matrix. In the present study, the major objective was to develop technical information for manufacturing PP-CNC nanocomposite systems. Toluene diisocyanate (TDI) and maleic anhydride grafted PP (MAPP) were employed as the target functionalizations of CNCs, showing differences in molecular lengths and moieties. Achieving good dispersion and interfacial interactions of CNCs in the matrix depends highly on the chemical species applied for the utilization of CNCs. In regards to the preparation process of the nanocomposites, a suitable procedure involving a combined solvent casting and melt-extrusion method for achieving a better dispersion of modified CNCs in the PP matrix were developed. This study explored the physicochemical, morphological, and mechanical properties of the nanocomposites reinforced with the chemically modified CNCs through process combinations. Transmission electron microscopy images (TEM) of the PP-CNC nanocomposites were explored to fully understand the differences in the dispersion levels of CNCs in matrix. In addition, neverdried CNCs with no irreversible aggregations were used through solvent-exchange techniques.

EXPERIMENTAL

Materials

Polypropylene (grade: HJ 700, Samsung Total Co., Ltd., Seosan-Si, Korea) was used as a base matrix. The melt flow index and density of polypropylene were 22 g/10 min at 230 °C and 0.91 g/cm³ at room temperature, respectively. Cellulose powder (grade: W-50, KC Flock) that was used as a source of CNCs was purchased from Nippon Paper Chemicals Co., Ltd., Tokyo, Japan. The average particle size and bulk density was 45 µm and 0.15 g/cc to 0.2 g/cc, respectively. Deionized water (DI-water, resistivity > 18 M Ω) was used for acid hydrolysis. Then, 64 wt.% diluted sulfuric acid was used for the isolation of CNCs. Isolation of the CNCs was performed through hydrolysis, decanting, centrifugation, and predispersion steps, according to established protocols (Siqueira et al. 2010; Costes et al. 2016; Gwon et al. 2016a). Toluene diisocyanate (TDI, 2, 4-TDI: 2, 6-TDI = 80: 20, Alfa Aesar, Haverhill, USA) and maleated polypropylene (MAPP, grade: Adpoly PH-200, Mw = 43,200 Da, grafting level = approximately 4%, Lottechemical Corp., Seosan-Si, Korea) were applied to modulate the surface of CNCs. Acetone, N,Ndimethylformamide, and toluene high performance liquid chromatography (HPLC) grade, Daejung Chemicals Co., Ltd., Siheung-Si, Korea) were used as received. The aqueous CNCs suspension was solvent-exchanged to acetone for chemical modification and nanocomposite preparation.

Surface grafting of CNCs with TDI and MAPP - TDI modification

The TDI grafting on the CNC surface (T-CNCs) in DMF was performed in a similar manner to previously completed studies (Costes *et al.* 2016; Gwon *et al.* 2016a). In brief, the acetone suspension with CNCs was solvent-exchanged to DMF, and TDI with an isocyanate group (NCO) index of 2 (2:1 equivalents ratio of NCO in TDI to total hydroxyl groups in desired CNCs) was added drop wise into the suspension. Subsequently, TDI was grafted onto the CNC surface at 70 °C for 24 h.

MAPP modification

Acetone suspension, including the CNCs, was added to 200 mL toluene in a threeneck flat-bottomed flask and stirred constantly at 130 °C for 30 min to remove the acetone. Subsequently, a reflux condenser was equipped onto the flask, and the desired amount of MAPP with additional toluene (100 mL) was added and kept for 30 min to graft onto the surface of the CNCs (M-CNCs) under a nitrogen atmosphere. The modified CNC suspensions in toluene or DMF (T-CNCs case) were solvent-exchanged to acetone for preparation of the PP nanocomposites.

Preparation of nanocomposites

Two experimental procedures were examined to find a suitable method for enhancing the dispersibility of the modified CNCs in a hydrophobic PP matrix. One of the procedures was using a general extrusion method (Method 1 in Fig. 1a), which provided a dispersion of the modified CNCs in the PP matrix induced by the high shear force of the kneading block zone. The other was to add a predispersion step to Method 1 (Method 2 in Fig. 1a). In this process, the dispersion of CNCs in the matrix was completed prior to the extrusion step, using polymer swelling in a hot toluene system. The detailed procedures are shown in Fig. 1b. In Method 1, concentrated M-CNC suspension in acetone was simply mixed with powdered PP in a polyethylene bag for 5 min by shaking, and the mixture was fed into the feeding zone of an intermeshing 11-mm co-rotating twin-screw extruder (BA-11, Bautek Co., Pocheon-Si, Korea). The compounding temperature was 100 °C to 180 °C with a 150 rpm screw speed. The strands of composites from the extruder were pelletized and then dried for 24 h at 80 °C. The pelletized materials were extruded again and injection-molded using a HAKKE MiniJet II (Thermo Scientific, Waltham, USA) for further testing. During the injection-mold, the cylinder temperature was 210 °C and the injection pressure was 410 bar.

In Method 2, the desired acetone suspension of M-CNCs was added to the flask with hot toluene (130 °C). The mixture remained for 30 min to eliminate the acetone, and during this time powdered PP (with solution to PP powder ratio = 100:1) was added into the suspension. The polymer dilute system was kept for 3 h under a nitrogen condition to fully achieve homogeneous PP-CNC suspension. The prepared suspension was casted onto a stainless-steel tray, and the evaporation of toluene was completed under a fume hood for 24 h. The obtained powder was extruded and injection-molded, as explained in Method 1.



Fig. 1. Experimental flow scheme (a) and detailed procedures for Method 1 and 2 (b)

Methods

The 64 wt.% acid hydrolyzed CNCs were examined using a transmission electron microscope (JEM 1400, JEOL, Tokyo, Japan) at a 120 kV accelerating voltage. Thirty CNCs from a TEM image were randomly chosen for dimension measurements using Image Pro Plus software (Media Cybernetics Inc., Version 6, Rockville, USA) to calculate the average length and width of the obtained CNCs. The dispersibility of M- or T-CNCs in the PP matrix was observed through TEM (TalosTM F200S, FEI, Thermo Fischer Scientific, Waltham, USA) at a 200 kV accelerating voltage. Thin films with an 80-nm thickness from the PP nanocomposites were prepared using an ultramicrotome (EM UC 6, LEICA Microsystems, Wetzlar, Germany). The thin films were positioned onto a carbon-coated copper grid and then the distribution of the CNC nanoparticles was analyzed.

The surface structures of the pristine and modified CNCs were explored using a Fourier transformed infrared spectroscopy (FTIR, NicoletTMisTM10 FT-IR Spectrometer,

Thermo Scientific, Waltham, USA) with an attenuated total reflectance (ATR) accessory (Thermo Fischer Scientific, Waltham, USA). The FTIR spectra were obtained from an accumulation of 16 scans with a resolution of 4 cm⁻¹ under forced conditions. Pristine CNC and modified CNC (M- and T-CNCs) suspensions in acetone or toluene were fully dried for removal of the solvent at 70 °C for 3 h using a convection oven before testing.

Morphology of the fractured surface from tensile tested specimens was taken using a scanning electron microscope (EM-30, COXEM Co., Ltd., Daejeon, Korea) at 30 kV. To prepare clear sample surfaces, all of the samples were dried prior to testing in a convection oven at 80 °C for 24 h. The fractured surfaces of the specimens were coated with gold by an ion sputter coater (KIC-1A, COXEM Co., Ltd., Daejeon, Korea). The sputter coating of the surface was performed at 4 mA with an ionization current for 200 s, and then the samples with a 20 nm coating thickness were achieved.

The tensile properties for the PP-CNC nanocomposites were performed using a universal testing machine (H50KS, Tinius Olsen, Horsham, USA), with a load cell of 5 kN and at a crosshead speed of 10 mm/min, according to ASTM D638 (2003). The samples were 10.0 mm in gauge length and 3.24 mm in width. The mean values from the five composite specimens were taken for each set of samples. The thickness of each sample was re-measured before testing.

Thermal decomposition curves of samples were obtained from thermal gravimetric analyzer (TGA, SDT Q600, TA instruments, New Castle, USA) with scan range from 50 $^{\circ}$ C to 600 $^{\circ}$ C at a heating rate of 10 $^{\circ}$ C min⁻¹ under nitrogen.

RESULTS AND DISCUSSION

CNC Isolation and Functionalization

A TEM image of the sulfuric acid-hydrolyzed CNCs is shown in Fig. 2. The average length and width of the nanocrystals were 154 nm (\pm 23 nm) and 5.8 nm (\pm 1.3 nm), respectively. Some bundles of CNCs were observed. This could be due to an electrostatic attraction induced by negative electrical charges (sulfate groups) onto the surface of the hydrolyzed CNCs (Liu *et al.* 2010; Sacui *et al.* 2014; Li *et al.* 2015).



Fig. 2. TEM image of the cellulose nanocrystals (CNCs)

Figure 3 comparatively presents the changes of the FTIR spectra in the surface structure between the pristine and modified CNCs (a: MAPP, b: TDI). Figure 3a displays the spectra changes after TDI grafting onto the CNCs. There are important differences in the absorption band of the amide region (1800 cm⁻¹ to 1500 cm⁻¹). The peaks at 1710 cm⁻¹ and 1574 cm⁻¹ were attributed to the carbonyl (C=O) stretching in the urethane group that resulted from the grafting reaction of an isocyanate (-NCO) from TDI with the hydroxyl groups of CNCs. The peak at 1600 cm⁻¹ corresponded to the C=C stretching vibration in the aromatic ring of toluene moiety, and the increment of intensity at 1660 cm⁻¹ corresponded to the C-N stretching vibration in the amide (NHCO) group. Figure 3b displays the changes in the characteristic peaks representing the MAPP grafting onto the CNCs surface. A discernible shoulder peak appeared at 1714 cm⁻¹, which indicated the characteristic peak of the maleic anhydride group. The absorption bands near 1730 cm⁻¹ and 1770 cm⁻¹, assigned as symmetric C=O stretching, can be indicative of the ester linkage resulting from the reaction between maleic anhydride and the hydroxyl group (Mohanty et al. 2006; Kim et al. 2007). Consequently, the FTIR results provided clear evidence of MAPP and TDI attachments onto the CNCs surface.



Fig. 3. FTIR spectra of M-CNCs (a) and T-CNCs (b)

A test for dispersibility of the nanocrystals in an apolar solvent is one of the key factors used to assess the change in the surface nature of the nanocrystals. Figure 4 shows the dispersibility of pristine CNCs, T-CNCs, and M-CNCs in the toluene medium. Rapid precipitation of pristine CNCs colloid occurred even after 30 min standing time, but T- and M-CNCs showed better distributions in the solvent. The consolidation in the stability of the modified nanoparticle colloids was contributed to the enhancement of the affinity between the solvent and modified nanoparticles. This result further confirmed the successful changes in the surface structure of the CNCs.



Fig. 4. Differences in the dispersion level among pristine, T-CNCs, and M-CNCs in dried toluene

Processing Effects

Figure 5 and Table 1 present the tensile properties of the PP nanocomposites reinforced with pristine CNCs and M-CNCs through Method 1. With the increased MAPP or CNC loading levels, there are no positive effects on the properties of the composites applied with Method 1. The decrease in the tensile properties of composites can be generally explained by two main reasons: 1) the occurrence of severe agglomeration between the nanoparticles in the matrix and 2) the disharmony in the compatibility between the nanoparticles and the matrix. Pristine CNCs in the PP matrix led to adverse effects as well as a decrease in the tensile strength of the nanocomposites. The tensile response of the composites with MAPP-grafted CNCs also showed similar trends with that of the pristine CNCs in spite of the enhanced compatibility of CNCs with the PP chains. Previous research (Kim et al. 2007) has shown that a MAPP addition to the PP composites reinforced with micro-sized bio-fibers effectively led to an improved mechanical strength of the composites. This was attributed to the dispersibility and compatibility of the micro-sized particles, modified with the MAPP in the PP matrix, which were sufficiently achieved through a simple extrusion process. Hence, it was assumed that CNCs (if they are chemically modified) as well as the bio-fiber could be fully dispersed in the matrix through the use of a kneading block in the extruder. However, the results shown in Fig. 5 implied that using only the use of Method 1 would make it hard to anticipate the improvements for the dispersibility and compatibility of even modified CNCS in matrix. Therefore, further efforts were needed to obtain PP nanocomposites with the reinforcing potentials of CNCs.



Fig. 5. Tensile strength of CNCs-PP composites by the extrusion method (M1) as functions of MAPP and CNC contents

CNC (wt. %)	MAPP (wt. %)	Modulus (MPa)	Elongation at break(%)
0	0	5175.8(±221.6)	1.52(±0.25)
	1	5224.8(±78.0)	1.54(±0.42)
	3	5159.9(±283.7)	1.23(±0.15)
1	0	5376.4(±323.8)	1.24(±0.12)
	1	4988.3(±306.8)	1.41(±0.26)
	3	4801.9(±246.7)	1.18(±0.12)
5	0	5179.9(±333.5)	1.21(±0.22)
	1	4846.3(±148.3)	1.25(±0.15)
	3	4994.4(±279.1)	1.18(±0.13)
10	0	5260.0(±221.5)	1.53(±0.38)
	1	4788.4(±300.7)	1.02(±0.11)
	3	4900.3(±408.9)	1.07(±0.07)

Table 1. Tensile Responses (modulus and elongation at break) of CNCs-PI	C
Nanocomposites by the M1	

To overcome the limitation in Method 1, Method 2 (M2) was designed to include a predispersion step using polymer swelling in a hot toluene system. A comparison of the tensile strengths of PP-CNC nanocomposites prepared by M1 and M2 is presented in Fig. 6. The tensile strengths of the composites by M2 were mostly higher than those by M1, with an increased CNC loading level. The increase in the strength of nanocomposites applied with chemically modified CNCs can be attributed to the better dispersibility of the modified CNCs (Gwon *et al.* 2016b). Polymer chains in a good solvent (miscible solvent) are swollen such that the number of chains per cm³ decreases (de Gennes 1993). The increase in the free volume between the polymer chains makes the nanoparticles move freely through the solvent medium.

Other tensile responses (modulus and elongation at break) for the processing effect are shown in Fig. 7. Both the modulus and elongation at break of the nanocomposites by M2 manufacturing process had higher values than those of the nanocomposites by M1. Differently from the results in Table 1, these increments in the modulus and elongation at break can be due to the uniformly distributed CNCs acting as hard domains in continuous PP matrix by M2. Therefore, the predispersion step using polymer swelling can be effective in improving the dispersibility of the modified CNCs and further increasing the tensile properties of the extruded nanocomposites. Also, enhanced dispersibility of modified CNCs can improve the thermal stability of its nanocomposites.

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Fig. 7. Effects of the predispersion step on tensile modulus and elongation of CNC-PP composites by extrusion at the 1 wt. % MAPP treatment

Figure 8 shows thermal decomposition behaviors of PP nanocomposites with modified CNCs by M1 and M2 manufacturing processes. The graph of mass loss rate (derivative weight loss, Fig. 8b) for CNCs-PP nanocomposites had two pyrolysis steps. Modified CNCs were decomposed in the first step (about 250 °C ~ 300 °C), and the degradation of PP occurred in the second step (about 300 °C to 500 °C). Degradation of modified CNCs started at a similar temperature (about 250 °C). However, the onset degradation temperature of PP in the nanocomposites prepared with a predispersion step was higher than that without the step. This may be because the modified CNCs effectively act as thermal barriers due to the CNCs with better dispersibility induced by the predispersion step.



Fig. 8. TGA results of CNC-PP nanocomposites (with 5 wt. % CNC and 1 wt. % MAPP) manufactured by M1 and M2 process

Figure 9 shows SEM images of fractured surfaces of nanocomposites incorporated with 5 wt.% CNCs (pristine or MAPP-treated). The red arrows indicate aggregated CNC particles distributed within the matrix. As can be expected, unmodified CNCs (Fig. 9a) showed higher agglomeration than the MAPP-treated CNCs (Figs. 9b and c) in the PP matrix. In addition, the fractured surface of the nanocomposites applied with the predispersion step (Fig. 9c) showed a clear surface and had minimally agglomerated CNC particles compared to that without the step (Fig. 9b). These morphological differences are consistent with the finding of increased tensile properties and TGA results shown in Figs. 5 to 8.



Fig. 9. Fractured surfaces of PP-based nanocomposites with 5 wt.% CNCs: (a) by M1 with pristine CNCs, (b) by M1 with M-CNCs, and (c) by M2 with M-CNCs

Chemical Modification Effects

The tensile responses of PP nanocomposites with pristine CNCs, MAPP-grafted CNCs (M-CNCs), and TDI-grafted CNCs (T-CNCs) are shown in Figs. 10 and 11. The pristine CNC system showed a considerable reduction in the tensile properties compared with the chemically-modified CNC (M- and T-) systems. This can be due to severe self-agglomerations of hydrophilic CNCs in a hydrophobic PP matrix as explained above (Fig. 9a). In comparison to T-CNCs with M-CNCs, the expectation was that long chain

molecules of MAPP could hinder M-CNC mobility in the PP matrix due to an anchoring effect of the long chain to the PP backbone in the dilute solvent system. Therefore, the dispersion level of M-CNCs would be lower than the CNCs covered with short TDI molecules. Thus, the strength of the nanocomposites with M-CNCs would be lower than that with T-CNCs. However, as shown in Figs. 10 and 11, the M-CNCs system had higher tensile properties than those from the T-CNCs system.



Fig. 10. Tensile strength of PP-CNCs nanocomposites with 5 wt.% pristine, M-CNCs, and T-CNCs



Fig. 11. Tensile modulus and elongation at break of PP-CNCs nanocomposites with 5 wt.% pristine, M-CNCs, and T-CNCs

TEM observations were conducted to explore the dispersion level of M- and T-CNCs in the base matrix, and the results are shown in Fig. 12. Interestingly, the M-CNC system (Fig. 12a) showed a better distribution state in the matrix than that of the T-CNC system (Fig. 12b). Hence, based on the TEM result, the anchoring effect of long chain functionality on the mobility of M-CNCs can be determined as negligible in the very dilute solvent system. In addition, the long chain grafted surface structure of M-CNC improved the interfacial bonding strength between the CNCs and the PP backbone. Interfacial interactions between chemically modified CNCs and the PP backbone are shown in Fig. 13. The T-CNC system (Fig. 13a) can have only non-covalent interactions, such as hydrogen bonding and Van der Waals forces, while the M-CNC system can have chain entanglement effects as well as non-covalent interactions, as shown in Fig. 13b. Therefore, the nanocomposite reinforced with M-CNCs had higher the mechanical properties than that from the T-CNC system due to a better dispersion state and the additional interaction forces of M-CNCs in the PP matrix.



Fig. 12. TEM images for dispersibility of M-CNCs (a) and T-CNCs (b) in the PP matrix



Fig. 13. Schematic of interfacial interactions between the PP backbone and modified CNCs (a: T-CNC, b: M-CNC)

Randomly aggregated particles can cause local stress concentrations, leading to a reduction in the mechanical properties (Li *et al.* 2016). Pristine CNCs with inherent hydrophilicity were easily agglomerated in the hydrophobic PP matrix. The T-CNC nanoparticles can also form heterogeneous dispersion states in the matrix despite an enhanced hydrophobicity. Considering the predispersion step of CNCs in hot toluene (130 °C), further reactions between T-CNC particles could have occurred. The reactivity of the secondary NCO group in the T-CNC particles is stable at room temperature due to the electron releasing effect of the primary NCO group (Lonescu 2005). However, the high

thermal condition can render T-CNCs susceptible to additional grafting with the other T-CNC particles due to increased inherent isocyanate reactivity. The T-CNCs agglomeration in the PP matrix took place through dimerization of isocyanate groups and urethanization of T-CNCs, as shown in Fig. 14. These explanations also support the reason for why the mechanical properties of PP nanocomposites reinforced T-CNCs decreased compared with that of the M-CNCs system.



Fig. 14. Possible reaction schemes of T-CNCs under high thermal conditions: (a) dimerization and (b) urethanization

The effect of chemically modified CNCs on the thermal stability of the PP nanocomposites is shown in Fig. 15. PP nanocomposites reinforced with M-CNCs had a higher onset degradation temperature than T- and pristine CNC cases. It could be also due to the discrepancy in dispersion level of CNCs among types (pristine, TDI, MAPP) of chemical modification in PP matrix, as explained above.



Fig. 15. TGA results of PP nanocomposites reinforced with pristine, T-, and M-CNCs

Figure 16 shows the tensile strength of PP-CNC nanocomposites as a function of the MAPP content. The tensile strength of the composites reinforced with M-CNCs increased with MAPP content, and decreased over the optimum MAPP content (5 wt.%), obtaining the maximum tensile strength at approximately 39 MPa; a 30% increment compared with the composites filled with pristine CNCs. Tensile modulus had a similar trend with the strength case, and elongation at break was gently reduced with increasing MAPP content. The long aliphatic chains of previously grafted MAPP molecules onto the

CNC surface could have blocked the pathway of the other MAPP molecules to active sites over the optimum loading level. Therefore, the fluctuation phenomenon in the strength and modulus could be due to limitations of the MAPP grafting induced by the geometric hindrance of the aliphatic chains.



Fig. 16. Tensile strength of PP nanocomposites as a function of the MAPP content



Fig. 17. Tensile modulus and elongation at break of PP nanocomposites as a function of the MAPP content

CONCLUSIONS

- 1. The PP-based nanocomposites reinforced with TDI and MAPP-grafted CNCs were manufactured using a melt-extrusion method with or without the use of a hot toluene based-solvent casting step. The SEM images established that adding a solvent casting step before the melt extrusion step, which allowed for a better dispersion level of the modified CNCs in the PP matrix compared with the simple extrusion method, resulted in an increase of the tensile properties and thermal stability of the nanocomposites.
- In comparison to M-CNCs with T-CNCs, the tensile properties and thermal stability of PP nanocomposites reinforced with M-CNCs were higher than that of the T-CNC system. The TEM results showed a heterogeneous distribution state of T-CNCs in the PP matrix due to the creation of irreversible agglomerations between the T-CNC

particles under high thermal conditions. The tensile strength of the composites reinforced with M-CNCs showed a fluctuating trend with increased MAPP content having the maximum strength (30% increment in comparison to the pristine CNC system).

3. As a result, the modified melt-extrusion process combined with the predispersion step can be a good approach to producing well-dispersed CNCs-PP nanocomposites at an industrial scale. In addition, a long chain grafting strategy can be an effective way to enhance the interfacial interactions between CNCs and PP chains.

ACKNOWLEDGMENTS

The authors are grateful for the support of National Institute of Forest Science, Korea.

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Article submitted: July 20, 2017; Peer review completed: September 17, 2017; Revised version received and accepted: January 14, 2018; Published: January 18, 2018. DOI: 10.15376/biores.13.1.1619-1636