Introduction

Recently, considerable effort has been directed toward the cellulose nanocrystals (CNCs), a 'green' nano-size materials, on account of their exceptional high specific strength and modulus, low density, chemical tunability, renewable nature, and relatively low cost. [1-5] Above attractive properties of CNCs allowed the possibility of using nano-reinforcements in the plastic based composites for automobile, aircraft, furniture industries, and sports and leisure items. [6]

However CNCs are still used in a limited industrial extent associated with low dispersibility in polymer matrix and low thermal stability. [6] The large hydroxyl groups of the nanocrystals surface and the nonpolar characteristics of most of the thermoplastics result in difficulties to achieve acceptable dispersion levels of the nanofiller in the matrix, which causes inefficient composites. Moreover, the common method to prepare CNCs from native semicrystalline cellulose is to use sulfuric acid hydrolysis to broken down into its elementary crystalline domains by removing amorphous cellulose segments, [1,6] which results in the introduction of sulfate groups on the surface of CNCs by esterification during hydrolysis as well as a rapid diminish in its degree of polymerization. [7,8] Consequently, the considerable decrease in degradation temperatures was observed as compared to the native cellulose, and this reduction of thermal stability interrupts their use in the composites with thermoplastics typical processed in the temperature of over 200 °C. [6,7]

In this study, CNCs with the thermal stability of native cellulose were obtained by simple sonication method, and composites with PLA were prepared after surface modification.

Experimental

2.1 Materials

PLA was manufactured by Shimadzu Co., Japan with a weight average molecular weight of 1.6×10^5 g/mol. The microcrystalline cellulose powder was purchased from Sigma-Aldrich.

2.2 Preparation of CNCs

The microcrystalline cellulose powder, 10 g, was added in 200 ml di-water. After sonication in a bath for 24 hours using an ultrasonic generator (Kyungill Ultrasonic Co., Korea), 1L of di-water was added and allowed to stand for 24 hours. The supernatant of the suspension was separated and centrifuged for 20 min at 5000 rpm. For the comparison, the CNCs by typical sulfuric acid hydrolysis were prepared. 10 g of microcrystalline cellulose powder were added in 65 wt% sulfuric acid with an acid-to-cellulose ratio of 1:8.75 (g/ml). The solution was stirred continuously at 45 °C for 1 h. The resulting CNCs were collected and purified by repeated centrifugation (9500 rpm, 30 min) and dialysis for 7 days. Both two types of CNCs were re-dispersed in di-water and sonicated for one hour at ambient.

2.3 Surface modification of CNCs

The surface of CNCs was modified by following route reported elsewhere. [9] CNCs in aqueous suspension (100 mg/mL) were solvent exchanged to acetone and then to dry toluene, CNCs were placed in a 500 ml beaker containing a mixture of 108 g of toluene, 105 g of acetic acid and 0.5 ml of 60% perchloric acid. After vigorous stirring for 1 min, 54g of acetic anhydride was added, and the mixture was stirred vigorously for 1 min. The mixture was stood for 1 h at room temperature. After the reaction
of CNCs, modified CNCs was washed thoroughly 3 times with methanol, then 3 times with di-water.

2.4 PLA/CNCs Nanocomposites film

PLA/CNCs nanocomposite films were prepared using a solvent mixture followed by hot pressing. The nanocrystals in aqueous medium were solvent-exchanged to acetone and then to chloroform by centrifuging and re-dispersing steps. To measure the concentration of CNCs, a small amount of the CNCs in chloroform was casted in glass-dish and allowed to evaporate. The CNCs suspension in chloroform was stirred, and PLA was gradually added to the suspension at 55 °C. The ratio of CNCs to PLA was approximately 5 wt%. The mixture was casted and allowed to evaporate by oven vacuum drying at 55 °C for 3 days. After crushing into small pieces, the composite films were obtained by hot pressing at 200 °C.

2.5 Characterization

To confirm the morphology of CNCs, transmission electron microscopy (TEM, CM200, Philips, Netherlands) were used. Thermal stability of the CNCs was obtained by using thermo-gravimetric analyzer (TGA, TA Instruments Q50, U.K.). Fourier transformed infrared spectroscopy (FT-IR, VERTEX 80v, Bruker Optics, Germany) were used for studying the structures of the modified CNCs. Dynamic mechanical measurements (DMA, Q800, TA instruments, U.K.) and differential scanning calorimetry (DSC, Perkin Elmer Jade) were used to study the thermal and mechanical properties of the PLA/CNCs nanocomposites.

3 Results and discussion

3.1 Synthesis of cellulose nanocrystals

The scheme of the preparation of CNCs by simple sonication method is illustrated in Fig. 1. Long time ultra-sonication treatment could allow the creation of fragments from the microcrystalline cellulose. Among the shreds, the small fragments could disperse and float in water. We acquired the CNCs by separation of these floating materials. TEM images of the CNCs produced by sonication method and sulfuric acid treatment are used to confirm the formation of CNCs. In Fig. 2 (b), even the CNCs prepared by sonication method show the appearance of the nanocrystals aggregates and longer length due to less break-down of microcrystalline cellulose, it is clearly shown that the foaming of CNCs by sonication method with a long length and a width of less than 10 nm. Compare with the CNCs by sonication method, the CNCs by sulfuric acid treatment (Fig. 2 (a)) exist more individually due to the negative surface charge of the sulfate group introduced during the acid hydrolysis. [6]

The thermal-degradation of the CNCs obtained by acid treatment and sonication method were measured and plotted in Fig. 3. The thermal analysis showed that the thermal degradation of CNCs from acid treatment (Fig. 3 dot line) was initiated at a much lower temperature (125 °C), while the CNCs prepared by sonication method (Fig. 3 solid line) began at over 250 °C. Also the onset of degradation temperatures (temperature at 5% weight loss) of the CNCs produced by acid treatment and sonication show a great difference (approximately 170 °C and 300 °C). Thus the thermal analysis showed the CNCs prepared by sonication method maintained the thermal stability of native cellulose.

3.2 Surface modification of cellulose nanocrystals

FT-IR analysis was performed to monitor modification of CNCs. In the Fig. 4 (b), the IR spectra of acetylated CNCs showed a significant decrease in the O-H band (3338 cm$^{-1}$) and increases in three major bands of cellulose triacetate, i.e. the C=O band (1740 cm$^{-1}$), the C-O band (1231 cm$^{-1}$) and the C-CH$_3$ band (1371 cm$^{-1}$). [10] The optical image of the CNCs and modified CNCs dispersion in chloroform shows the improvement of dispersion in hydrophobic organic solvent. Though these analyses, it is confirmed that the surface acetylation of CNCs were successfully performed. Thus, the number of hydrophilic hydroxyl groups decrease and hydrophobic groups of CNCs increased, which may introduce CNCs to good adhesion with polymer matrix.

3.3 PLA/CNCs nanocomposite

The visual optical image of neat PLA and PLA nanocomposite films with different types of CNCs is presented in Fig. 5. As shown in Fig. 5 (b), the PLA composite film with the CNCs produced by sulfuric acid treatment shows lots of black spots, the traces of the CNCs pyrolysis, due to their low thermal stability while no thermal degradation of the CNCs by sonication method. (Fig. 4 (c) and (d)) As seen in
Fig. 4 (C), some spots are visible in the PLA/CNCs film due to aggregation of CNCs in the PLA matrix. However, the PLA/modified CNCs film shows good and similar transparency almost same as the neat PLA film. It is seems to increase of dispersibility of CNCs in the PLA matrix by surface modification of the CNCs.

Fig. 6 shows the thermograms of DSC for neat PLA and its nanocomposites with CNCs acquired by sonication method. In the cooling scan, the thermograms of neat PLA and PLA/modified CNCs composite show a peak of melt crystallization temperature ($T_{mc}$). However the peak of PLA/unmodified CNCs composite id shown faintly, which indicates that the unmodified CNCs prevent nucleation and crystallization of PLA. As a result, the thermogram of glass transition ($T_g$) and cold crystallization peaks still exhibits in the second heating. The thermogram of the PLA/modified CNCs composite shows the similar trend as neat PLA, but the $T_{mc}$ of composite (103.7 °C) is higher than that of neat PLA (100.4 °C). Furthermore $T_g$ and cold crystallization temperature ($T_{cc}$) are almost absent, which indicates that the PLA/modified CNCs composite was highly crystalline after the cooling scan. Consequentially the modified CNCs could act as nucleating agent on the crystallization of PLA. Similar observation was studied in microcrystalline cellulose reinforcements. [11]

DMA analysis provides information of the mechanical properties and molecular relaxations that occur in polymer nanocomposites during heating. Fig. 7 shows the storage modulus and tan delta as a function of temperature of the PLA nanocomposites with unmodified and modified CNCs. In the Fig. 7 (a), the storage modulus of the PLA/modified CNCs composites shows higher storage modulus compared to neat PLA and PLA/CNCs composites in the glassy region. The increase of storage modulus in the glassy region supported the reinforcing effect of highly dispersed in polymer matrix and formed network of nanocrystals. As can be seen from Fig. 7 (b), the tan delta peak is shifted to higher temperature and decreased the intensity according to the addition of CNCs. This indicates that fewer polymer chains are participating in this transition. The increase in storage modulus and positive shift in tan delta peak position could be attributed to physical interaction between the polymer and reinforcements that restrict the segmental mobility of the polymer chains.

3.3 Conclusions

The simple method was developed to prepare the CNCs with high thermal stability as compared to the CNCs obtained from sulfuric acid hydrolysis. TEM and TGA analysis supported the formation and high thermal stability of CNCs. Without thermal degradation of CNCs, the nanocomposites with PLA were accomplished in high temperature. DSC and MDA analysis revealed the improvement of thermal and mechanical properties of PLA composite with surface modified CNCs. This novel method to acquire CNCs is expected to scale-up and broadly applicable in the plastic based composites industry.

References


Figure Captions

Fig.1. Schematic illustration of the preparation of CNCs by sonication method.

Fig.2. TEM images of the CNCs prepared by sulfuric acid hydrolysis (a) and sonication method (b).

Fig.3. TGA curves of CNCs prepared by sulfuric acid hydrolyzed (dot line) and sonication method (solid line).

Fig.4. FTIR spectra of (a) CNCs and (b) modified CNCs obtained by sonication treatment. The optical image shows the dispersion of CNCs and modified CNCs in chloroform.

Fig.5. Image showing the appearance of the nanocomposites. (a) neat PLA, (b) PLA/CNCs by acid treatment, (c) PLA/CNCs by sonication method, (d) PLA/modified CNCs by sonication method.
Fig. 6. DSC curves obtained by cooling (left) and second heating (right) scans of (a) neat PLA and PLA nanocomposite films reinforced with (b) unmodified CNCs and (C) modified CNCs obtained by sonication method.

Fig. 7. DMA analysis of neat PLA and PLA nanocomposites; (a) storage modulus and (b) tan delta curves