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Enhancement of the mechanical property of poly(ε-caprolactone) composites with surface-modified cellulose nanofibers fabricated via electrospinning

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Abstract

Poly(ε-caprolactone) (PCL) is one of the leading biocompatible and biodegradable polymers. However, the mechanical property of PCL is relatively poor as compared with that of polyolefins, which has limited the active applications of PCL as an industrial material. In this study, to enhance the mechanical property of PCL, cellulose nanofibers (C-NF) with high mechanical property, were employed as reinforcement materials for PCL. The C-NF were fabricated via the electrospinning of cellulose acetate (CA) followed by the subsequent saponification of the CA nanofibers. For the enhancement of the mechanical property of the PCL composite, the compatibility of C-NF and PCL was investigated: the surface modification of the C-NF was introduced by the ring-opening polymerization of the ε-caprolactone on the C-NF surface (C-NF-g-PCL). The polymerization was confirmed by the Fourier transform infrared (FTIR) spectroscopy. Tensile testing was performed to examine the mechanical properties of the C-NF/PCL and the C-NF-g-PCL/PCL. At the fiber concentration of 10 wt%, the Young's modulus of PCL compounded with neat C-NF increased by 85% as compared with that of pure PCL, while, compounded with C-NF-g-PCL, the increase was 114%. The fracture surface of the composites was analyzed by scanning electron microscopy (SEM). From the SEM images, it was confirmed that the interfacial compatibility between PCL and C-NF was improved by the surface modification. The results demonstrated that the effective surface modification of C-NF contributed to the enhancement of the mechanical property of PCL.

INTRODUCTION

Poly(ε-caprolactone) (PCL) has been studied as a potential biomaterial targeting wide-ranging applications such as biomedical devices, biodegradable packaging, and agricultural areas because of the low-cost and the excellent processability of PCL [1]. However, the mechanical property of PCL is relatively low compared to that of polyolefins. In order to enhance the mechanical property of PCL, compounding nanofibers into the polymeric matrix is considered as an effective method [2]. Among the fabrication processes of nanofibers, electrospinning is one of the promising methods because electrospun nanofibers have extremely high aspect ratios and specific surface. Containing such electrospun nanofibers, a new composite with high mechanical property was produced [3, 4]. The high mechanical property of cellulose nanofibers (C-NF) was due to a lot of hydrogen bonds in their chemical structure. Especially, the C-NF fabricated via electrospinning process could gain a relatively high mechanical property (the Young's modulus could reach ~30 GPa), which were considered as an effective reinforcement material for composites. However, naturally-derived cellulose has a highly crystalline nature. The crystallinity gives rise to the insolubility, for which naturally-derived cellulose cannot be dissolved in normal organic solvent, inhibiting electrospinning. In fact, ionic liquid could be considered as an effective solvent, but the liquid is difficult to adjust the condition for the fabrication process [5]. Therefore in this study, C-NF was not fabricated directly from naturally-derived cellulose, but instead cellulose acetate (CA), a derivative material of cellulose, was used. The C-NF were thus fabricated via the electrospinning of CA followed by the subsequent saponification of the CA nanofibers [6, 7]. However, the compatibility at the interface between C-NF and PCL matrix has yet to be investigated, for the sufficient reinforcing effects in the composites. To achieve the high reinforcing effect, improvement of the compatibility between nanofibers and polymer matrix is necessary [8]. For the improvement of the compatibility, surface modification using the matrix monomers grafted on the nanofiber surface has been considered to be an effective method [9]. In this study, the molecular PCL chains were grafted on the surface of C-NF to improve the interfacial compatibility between C-NF and PCL matrix. Subsequently, the PCL-grafted C-NF were compounded into PCL, and the mechanical properties of the PCL composites were investigated.

MATERIALS AND METHODS

Materials

Cellulose acetate (CA) with the molecular weight (M_n) of 3.0×10^4 g/mol and the acetyl content of 39.8% was used. The molecular weight (M_n) of polycaprolactone (PCL) was 4.5×10^4 g/mol. These materials and tin(II)

2-ethylhexanoate ($Sn(Oct)_2$) were all purchased from Sigma Aldrich (Tokyo, Japan). ε-caprolactone (ε-CL) with the molecular weight (M_w) of 114.14 g/mol was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Acetone, *N*,*N*-dimethylacetamide (DMAc), dichloromethane, and super-dehydrated toluene were purchased from Wako Pure Chemical Industries Co. (Osaka, Japan).

Fabrication of cellulose acetate nanofibers and saponification

CA-NF were fabricated by electrospinning. The spinning solution was prepared by dissolving CA in acetone/DMAc (6/4, wt/wt) mixture solvent. The concentration of CA was set at 20 wt%, and the flow rate of solution was controlled at 0.6 mL/h. CA-NF fabricated by electrospinning were dried under vacuum at 50°C for 24 h and hydrolyzed in a 0.05 M NaOH/ethanol solution at room temperature for 24 h to obtain cellulose nanofibers (C-NF).

Ring-opening polymerization (ROP) for the surface modification of C-NF

A typical procedure for the grafting of PCL was as follows: pre-dried C-NF, 5×5 cm^2, was put into a flame-dried flask after three vacuum/argon cycles. To remove the residual water on the C-NF, super-dehydrated toluene was added to the flask to remove the remaining water by warming the flask under vacuum. Thereafter $Sn(Oct)_2$, a commonly used catalyst for the polymerization of monomers, ε-CL, and super-dehydrated toluene were all added to a flask under argon atmosphere in a glovebox. Then, the flask was set into an oil bath and the polymerizations began in the flask at 130°C for 1 h. After the procedure, to stop the polymerization, the flask was immersed in an ice bath and the C-NF were washed with dichloromethane and dried under vacuum at room temperature for 24 h to obtain C-NF-g-PCL.

Fabrication of C-NF/PCL composites

C-NF/PCL and C-NF-g-PCL/PCL composite films were prepared by inserting synthesized C-NF or C-NF-g-PCL between two compression-molded PCL sheets, which were thermally compressed at the pressure of 8 MPa by a hydraulic press at 80°C. The melted PCL percolated into C-NF. All compressed and compounded samples were immediately immersed in ice water at 0°C directly after the compression molding.

FT-IR spectra of C-NF

To confirm the synthetic success in the surface modification of C-NF, the chemical structures of the C-NF and the C-NF-g-PCL were analyzed by the Fourier transform infrared (FTIR) spectroscopy (ALPHA-E Platinum, BRUKER Ltd.). The infrared spectra were constructed through the wavenumber range from 400 to 4000 cm^{-1} at the resolution of 2 cm^{-1}.

Tensile testing of composites

Tensile testing was performed to examine the tensile mechanical properties of the C-NF/PCL composites. Each composite film was cut into a dog-bone shape (16.5 mm × 3 mm × 0.1 mm) before the tensile testing. The tensile testing was carried out at room temperature using a universal testing machine (AG-50NIS MS, SHIMADZU Co., Ltd., Tokyo, Japan), measuring the stress by changing the strain at the strain ratio of 1.0×10^{-2} s^{-1}. The stress-strain behavior of each specimen was measured three times to determine the Young's moduli of the samples. Additionally, in order to investigate the compatibility between C-NF and PCL, the fracture surface of the C-NF/PCL composites by the scanning electron microscopy (SEM) was analyzed.

RESULTS AND DISCUSSION

Chemical structure of C-NF

To investigate the chemical structures of C-NF and C-NF-g-PCL, the Fourier transform infrared (FTIR) spectroscopy was used. Figure 1 shows the FTIR spectra of C-NF and C-NF-g-PCL. In the chemical structure of C-NF, the peak due to the -OH hydroxyl group appeared at 3350 cm^{-1}. This peak could also be due to the structure of C-NF-g-PCL. Additionally, the band at ~1720 cm^{-1} was due to the C=O carbonyl group from C-NF-g-PCL. This indicated that the surface modification by ROP was successfully performed and PCL was actually grafted on the surface of C-NF.

Mechanical property of composites

The tensile testing of the C-NF/PCL composite films was performed to investigate the effects of the surface modification and the compounding of C-NF on the mechanical properties of PCL. Figure 2 shows the Young's modulus of the pure PCL, C-NF/PCL, and C-NF-g-PCL/PCL composite films at the C-NF concentration of 10 wt%. The Young's modulus of PCL was 227 MPa, and that of C-NF/PCL was found to increase by 85%. The Young's modulus of C-NF-g-PCL/PCL was increased by 114% compared to PCL, indicating that the surface modification of C-NF had a significant effect on the mechanical enhancement of PCL composites.

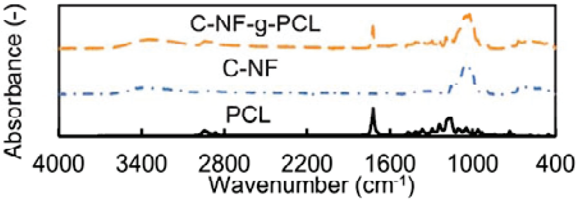

Figure 1. Chemical structures of PCL, C-NF, and C-NF-g-PCL

Fracture surface of composites

To determine the morphology and the structure of the composites, the fracture surface of pure PCL, C-NF/PCL, and C-NF-g-PCL/PCL composite films was characterized by SEM before and after tensile testing. The results were presented in Figure 3 (a), (b), (c), (d), (e), and (f). The fiber concentrations of C-NF/PCL and C-NF-g-PCL/PCL in Figure 3 (b), (c), (e), and (f) were all kept constant at 10 wt%. It was found that the pure PCL film had a smooth fracture surface without fibrous structures. On the other hand, there existed fibrous structures in C-NF/PCL. These results indicated that C-NF were successfully compounded into PCL by maintaining the original fiber shape. Additionally, from Figure 3 (b) and (e), it was also found that nanofibers were pulled out of the matrix after tensile testing. Moreover, by analyzing Figure 3 (c) and (f), such pullout of the nanofibers in C-NF-g-PCL was not observed, suggesting the improvement of the interfacial compatibility between the nanofibers and the matrix [10].

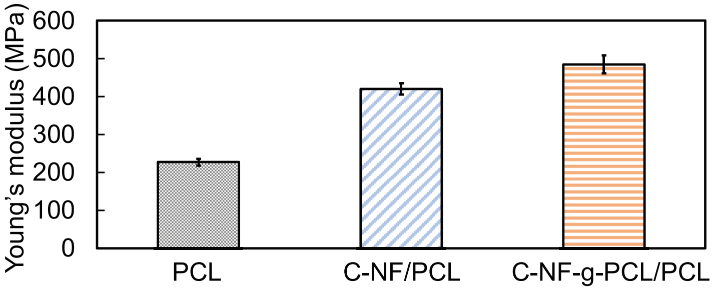

Figure 2. Young's moduli of PCL and composites

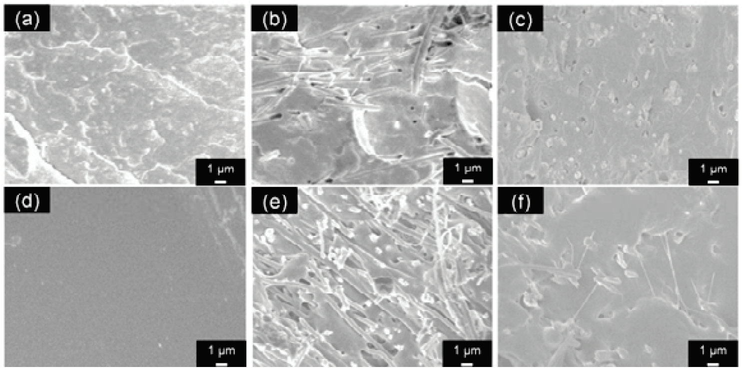

Figure 3. Fracture surface: before tensile testing (a) PCL, (b) C-NF/PCL, and (c) C-NF-g-PCL/PCL and after tensile testing: (d) PCL, (e) C-NF/PCL, and (f) C-NF-g-PCL/PCL

CONCLUSIONS

By electrospinning cellulose acetate (CA) and subsequent saponification of the CA nanofibers, C-NF were successfully fabricated. C-NF were then surface-modified by the ROP method to graft molecular chains of PCL. The FTIR analysis of the surface-modified C-NF confirmed the successful surface modification of the C-NF. It was found by the tensile testing that, at the fiber concentration of 10 wt%, the Young's modulus of PCL compounded with neat C-NF increased by 85% compared to that of PCL, while, compounded with C-NF-g-PCL, the ratio reached 114%. The results indicated that the surface-modified C-NF had greater effects on the improvement of the mechanical property of the PCL composites. The SEM analysis of the fracture surface of the composites also revealed that the interfacial compatibility between C-NF and PCL was substantially improved by the surface modification.

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