ABSTRACT

We propose new type reinforced polymer composites by electrospinning technique with in situ coffining process. We prepared the reinforced composites that have the structure with one-dimensional polymer fibers (poly(acrylonitrile), PAN, poly(ε-caprolactone), PCL, and Nylon 6,6, Nylon) in situ coffined into the poly(vinyl alcohol) (PVA) matrix by electrospinning technique. The SEM images of the PVA/PAN(es) (PVA/PAN(es) means that the PAN fibers are electrospon on the PVA aqueous solution.) suggested that many PAN fibers spread over the PVA matrix. Similar structure was observed in the PVA/PCL(es) and the PVA/Nylon(es) composite films. Average diameter of the PAN fibers was 1.3 μm, of the PCL fibers was 1.69 μm and of the Nylon fibers was 0.362 μm. The amount of PAN fibers on/in PVA film is lower than those of PCL and Nylon fibers. The fiber density and average diameter of the fibers on the PVA films depend on the electrospun time, the kind of polymer, and the concentration of polymer solution for the electrospinning process. Young’s modulus of PVA/Nylon(es) film was 5.51 GPa, about 3 times higher than that of PVA cast film. The light transmittance of PVA/Nylon(es) composite films was also investigated. The light transmittance of PVA/Nylon(es) composite film at 400 nm was ca. 60%. Our approach for film preparation by electrospinning technique with in situ coffining process is useful for preparing reinforced composite polymer films with high light transmittance.

Keywords: electrospinning, poly(vinyl alcohol), composite, mechanical property, light transmittance

1 INTRODUCTION

A large number of methods are available for preparing a fiber reinforced polymer composite from two or more polymer matrices and fibers. The short fiber reinforced composites are usually made by incorporating reinforcing fibers, such as glass and carbon fibers, into the matrix polymer. Many difficulties (for example, increasing viscosity of processing fluid, homogeneity of fibers in the matrix, and so on) during composite preparation process limit the fiber diameter and length. Some trials that are in situ generation of reinforcing fibers and preparation of the reinforced composites have been reported [1].

We have proposed new type reinforced polymer composites which are prepared by in situ coffining electrospon fibers into polymer matrix [2]. Electrospinning provides a simple and unique technique for preparation of fibers with the diameters ranging from the nano- to micro-scale [3, 4]. The reinforced composites have the structure that one-dimensional various kinds of polymer fibers are coffined into a PVA matrix.

2 EXPERIMENTAL

2.1 Materials

All chemicals were purchased and used without further purification. N,N-dimethylformamide (DMF) was distilled under reduced pressure before use as polymer solvent. Average molecular weight of polymers was 150000 (poly(acrylonitrile), PAN, Aldrich) and 40000 (poly(ε-caprolactone), PCL, Wako). Nylon 6, 6 (Nylon66) was purchased from Aldrich. Poly(vinyl alcohol) (PVA) was supplied as aqueous solution (ca. 10 wt.%, Nihon Gosei Sangyo).

2.2 Preparation of polymer composite with in situ coffining process

Figure 1 shows the electrospinning equipment for our investigation. PVA aqueous solution (ca. 10 wt. %, 2 ml) was spread over the stainless steel plate under the syringe (spread size 6.5 cm x 6.5 cm). Another polymer solution (PAN in DMF, PCL in CH₂Cl₂/DMF, and Nylon in formic acid) was charged in the syringe. Applied voltage was 15 kV, distance between syringe tip and the stainless plate was 10 cm. The stainless steel plate was moved in all directions on the X-Y moving stage to spin the fibers on the PVA solution homogeneously. The composite film is presented as PVA/PAN(es)[n]. This means that one-dimensional polymer fibers (poly(acrylonitrile), PAN) coffin into the poly(vinyl alcohol) (PVA) matrix by electrospinning technique for n minutes.
2.3 Measurements

Observation of the electrospun fibers and the composite films was performed with a digital microscope (VH-5000, VH-Z450, Keyence) and an SEM (VE-9800, Keyence). All the images were recorded "as is" without any filter or image treatment. Their structural characterization was made using an X-ray diffractometer with filtered CuKα radiation (XRD-D1, Shimadzu). Mechanical properties of the PVA cast films and the composite films were measured with a thermal mechanical measurement equipment (EXSTAR6000 TMA/SS, SSI) at 25±5°C. The sample size for the measurement was 20 mm in length and 2 mm in width. The cross-head speed was 4 μm/min and the limit elongation length of the sample was 120 μm. No obvious necking of the sample was observed in the limit length elongation. Young’s modulus of the films was estimated from the slope of the linear part of the stress-strain curves. FTIR spectra of the composite films were recorded with an FTIR spectrophotometer, IRPrestige-21 (Shimadzu) equipped with a DuraSampIR (Smiths Detection). DSC measurements of the composite films were recorded with a DSC3100S (Bulker AXS). Light transmittance of the composite films and PVA cast film was recorded with a UV-visible spectrophotometer (UV-1800, Shimadzu) at room temperature.

3 RESULTS AND DISCUSSIONS

3.1 Structure of PVA/polymer composite films

Figure 2 shows the SEM images of the PVA-PAN(es)[1], PVA/PCL(es)[10], and PVA-Nylon(es) [10] composite films. Average diameter of the fibers in the PVA matrix is 1.3 μm (PAN), 1.69 μm (PCL), and 0.36 μm (Nylon). Density of the fibers in the PVA matrix depended on kind of polymer and electrospinning time. We also prepared the PVA/PAN(es)[5] and PVA/PAN(es)[10]. However, SEM observation of the films brought fine images. The films are covered with many PAN fibers and their images are not clear.

Figure 1: Schematic presentation of electrospinning equipment for this investigation.

Figure 2: SEM images of PVA/polymer composite films, (a) PVA/PAN(es)[1], (b) PVA/PCL(es)[10], and (c) PVA/Nylon(es)[10] films.
Figure 3 shows the expanded FTIR spectra of the PVA cast film, PVA/PAN(es)[1], [5], and [10] films. The absorbance of the peak at 2245 cm⁻¹ which is attributed to the band of CN stretching vibration increases with the electrospun time. This indicates that the total amount of PAN fibers in the PVA matrix increases with the electrospun time. Elongation of electrospun time provides the PVA/polymer composite films with larger amount of fibers in case of PCL and Nylon.

Figure 3: Expanded FTIR spectra of PVA (a) and PVA/PAN(es)[n] composite films, (b) n = 1, (c) n = 5, and (d) n = 10.

3.2 Mechanical properties of PVA/polymer composite films

Mechanical properties of fiber reinforced materials draw to our interest. We recorded stress-strain curves of the PVA/polymer(es) composite films at room temperature. Figure 4 shows the strain-stress curves of PVA/Nylon(es)[n] (n = 1, 5, and 10) composite films at room temperature. All samples show the linear elongation about 3%, before the yield load step. Estimated Young’s modulus of the PVA/Nylon(es)[n] is 1.93 GPa (n = 1), 2.43 GPa (n = 5), and 5.51 GPa (n = 10). The Nylon fibers in the PVA matrix reinforce the PVA film. Young modulus values of the PVA/polymer(es) composite films are listed in Table 1. The Young modulus of the PVA/polymer(es) films is larger than that of PVA cast film. Young’s modulus is increased from 104 % to 319 %, as compared to PVA film.

Figure 4: Stress-strain curves of PVA cast film and PVA/Nylon(es)[n] composite films, n = 1, 5 and 10.

<table>
<thead>
<tr>
<th>Composite films</th>
<th>Young’s modulus / GPa</th>
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<tr>
<td>PVA/PAN(es)[1]</td>
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<td>2.43</td>
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<tr>
<td>PVA/Nylon(es)[10]</td>
<td>5.51</td>
</tr>
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</table>

Table 1 Young’s modulus of PVA/polymer(es) composite films.

(a) Young’s modulus of PVA cast film is 1.73 GPa.

3.3 Optical properties of PVA/polymer composite films

Optical properties, especially, transmittance of polymer composite films are of great interest in the manufacture of
transparent and robust panels for bendable displays, windows, and light transmitting electromagnetic wave shielding material. Liu et al., has reported about preparation and characterization transparent PVA-based composites with electrospun fibers (cellulose nano-fiber) [5]. We checked light transmittance of the PVA/polymer(es) composite films. Figure 5 shows appearance of the cast PVA film and PVA/Nylon(es)[n] film, n = 1, 5, and 10. Light transmittance of PVA/Nylon(es) films is almost similar as that of PVA cast film. Appearance of other PVA/polymer(es) films is very similar as that of the results of PVA/Nylon(es) films.

Figure 6 shows light transmittance of PVA/Nylon(es) films in the light wavelength range from 200 nm to 900 nm. Light transmittance of all films under 220 nm is very low. Transmittance of PVA/Nylon(es) films over 400 nm is over 50%. Visible light may theoretically pass nanofibers whose diameters are less than 400 nm, without the occurrence/refraction at the fiber/matrix interface, because light is a magnetic wave [6]. Therefore, the high light transmittance of the PVA/Nylon(es) composite films is high. However, the light transmittance of the PVA/PAN(es) and PVA/PCL(es) composite films is lower than that of the PVA/Nylon(es) films. The average diameter of the included fibers in both PVA/polymer(es) films is very larger than that of PVA/Nylon(es) films, over 1 mm, longer than length of visible light.

We prepared PVA/polymer composites by in situ confining electrospun nano-fibers into PVA matrix. The PVA/nano-fiber composites show about 3 times higher Young’s modulus than the PVA cast film and high light transmittance with even high content of many fibers to reinforce the film.

Figure 5: Appearance of the PVA cast film (a) and PVA/Nylon(es)[n] film, (b) n = 1, (c) n = 5, and (d) n =10.

Figure 6: Light transmittance of the PVA cast film and the PVA/Nylon(es)[n], n = 1, 5, and 10, composite film. The thickness of the film is PVA 37 μm, PVA/Nylon(es)[n] film, n = 1, 54 μm; n = 5, 50 μm; and n = 10, 41 μm.

REFERENCES