Characterization of New Type Polymer Composites Prepared by *in situ* Coffining Electrospun Fibers into Polymer Matrixes

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ABSTRACT

A number of methods are available for preparing a fiber reinforced polymer composite from two or more polymer matrixes and fibers. 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. We propose new type reinforced polymer composites by *in situ* coffining electrospun fibers into polymer matrix. The reinforced composites have the structure that one-dimensional poly(vinyl alcohol), PVA, fibers are coffined into the poly(styrene), PSt, matrix.

AFM images of the PVA-PSt composite films prepared by *in situ* coffining method show its fibrous surface with many trenches. The electrospun PVA fibers carve the trenches on the film surface. Film elongation of the PSt cast film and the PVA-PSt reinforced composite film under heating condition was investigated. Both of the PSt-based films started to elongate over 80°C. However, the elongation of the PVA-PSt composite film was smaller than that of PSt cast film. This suggests that the electrospun PVA fibers coffined into the PSt matrix reinforce the composite film.

Keywords: electrospinning, reinforced material, nano-fiber, composite

1 INTRODUCTION

A number of methods are available for preparing a fiber reinforced polymer composite from two or more polymer matrixes 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 propose new type reinforced polymer composites by *in situ* coffining electrospun fibers into polymer matrix. Electrospinning provides a simple and unique technique for preparation of fibers with the diameters ranging from the nano- to microscale [2]. The reinforced composites have the structure that one-dimensional polyvinyl alcohol (PVA) fibers are coffined into the polystyrene (PSt) matrix.

2 EXPRIMENTAL

2.1 Materials

Polystyrene (PSt, Ishizu, average degree of polymerization = 2600) was purchased and used without further purification. Polyvinylalcohol aqueous solution (PVA, Nippon Gohsei) was purchased and used as received. Eosin Y (Ishizu) was also used for dying PVA fibers in the composite film.

2.2 Preparation procedure of reinforced films

Figure 1 shows the electrospinning equipment for our investigation. PVA aqueous solution (*ca*. 10 wt %) was charged into the syringe and PSt-tetrahydrofuran (THF) solution was spread over the stainless steel plate under the syringe. Before the THF evaporated from the PSt solution, we applied high voltage between the syringe and the stainless steel plate and started the electrospinning of PVA. The PVA fibers were spun on the PSt-THF solution. After the electrospinning process the resulted composite films were heated to remove THF and water. Applied voltage was 10 kV, distance between syringe tip and the stainless plate was 10 cm. Typical thickness of the PVA-Pst reinforced film was 88.3 μm. We also prepared PSt and PVA films by solution-casting technique.

2.3 Measurement

AFM images of the cast films and the composite films were recorded with a scanning probe microscope (SPM-9600, Shimadzu, Japan). The typical probe scanning mode was dynamic mode under force constant condition. A commercial silicon tip-cantilever was used and a measured frequency of 1 Hz. Height images were recorded at 0° scanning direction at a given set point and a fixed frequency. All the images were recorded ‘‘as is” without any filter or image treatment. Optical microscopic images of the films were recorded with a digital microscope (VH-5000, VH-Z450, KEYENCE, Japan). Mechanical properties of the PVA-PSt composite films and PVA or PSt cast films were measured with thermal mechanical measurement

equipment (EXSTAR6000 TMA/SS, SSI Co., Japan). The sample size for the measurement was 20 mm in length and 2 mm in width. Typical measurement condition was offset load 40 kPa and sin curve load modulation ±40 kPa, 0.1 Hz, heating rate at 3°C min^{-1}.

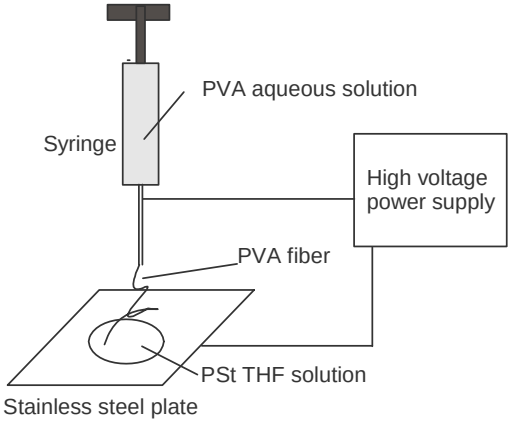

Figure 1: Schematic presentation of electrospinning equipment for this investigation.

3 RESULTS AND DISCUSSION

3.1 Optical microscopic images of composite films

The optimal spread size of the PSt-THF solution on the stainless steel plate was about 3 cm in diameter. When the size was larger than about 3 cm, the PVA fibers were spun around the PSt-THF solution, mainly. The PVA-PSt composite film was flexible and opaque. Figure 2 (a) shows the optical microscopic image of the PVA-PSt composite film. Many PVA fibers in the PSt matrix were observed. The nanofibers were not aligned and their directions were random. The PVA aqueous solution containing Eosin Y was also used as a spinning solution. Figure 2 (b) shows the optical microscopic image of PVA(eo)-PSt composite film. The PVA fibers were stained with Eosin Y. The PVA fibers in the PSt matrix are more clearly observed.

Figure 3 illustrates the histogram showing the diameter distribution of PVA fibers in the PVA-PSt composite film. The average diameter of the PVA fibers was 411 nm and standard deviation was 24 nm. The distribution of the diameter of the PVA fibers was very sharp as shown in Figure 3. The typical size of PVA fibers prepared by electrospinning technique is in the range of 200 to 600 nm in diameter in various molecular weight of PVA. [3]. It indicates that the PSt solution on the stainless steel plate do not affect the size of the PVA fibers.

3.2 Surface morphology of composite films

Optical microscopic images suggest that the electrospun PVA fibers are incorporated in the PSt matrix.

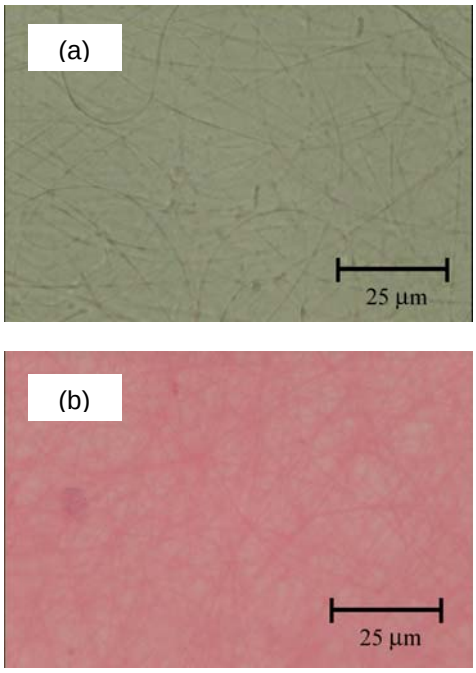

Figure 2: Optical microscopic images of PVA-PSt composite film (a) and PVA(eo)-PSt composite film.

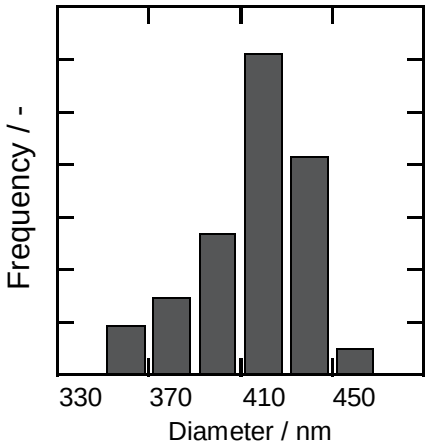

Figure 3: Histogram showing the diameter distribution of PVA fibers in the PVA-PSt composite film. Average diameter is 411 nm, standard deviation is 24 nm.

Surface morphology of the composite films is not obvious with the optical microscopic observation. We analyzed surface morphology of the composite films and the cast films with AFM technique. Figure 4 shows AFM images of the PSt cast film and the PVA-PSt composite film prepared by *in situ* coffining method. The surface of the PSt cast film is smooth. No obvious structure is observed. Some fibrous structures and trenches are observed on the surface of the PVA-PSt composite film. The PVA fibers existed in and on

NSTI-Nanotech 2008, www.nsti.org, ISBN 978-1-4200-8504-4 Vol. 2

the PSt matrix. Some PVA fibers bedded on the surface of the PSt film. Figure 5 shows the results of the length measurement of the fibers and the trenches. The average width of the trenches (*ca.* 390 nm) is almost equal to the average diameter of the fibers (*ca.* 411 nm). This suggests that the electrospun PVA fibers carve the trenches on the film surface. Many crossovers of the PVA fibers were observed on the composite film surface.

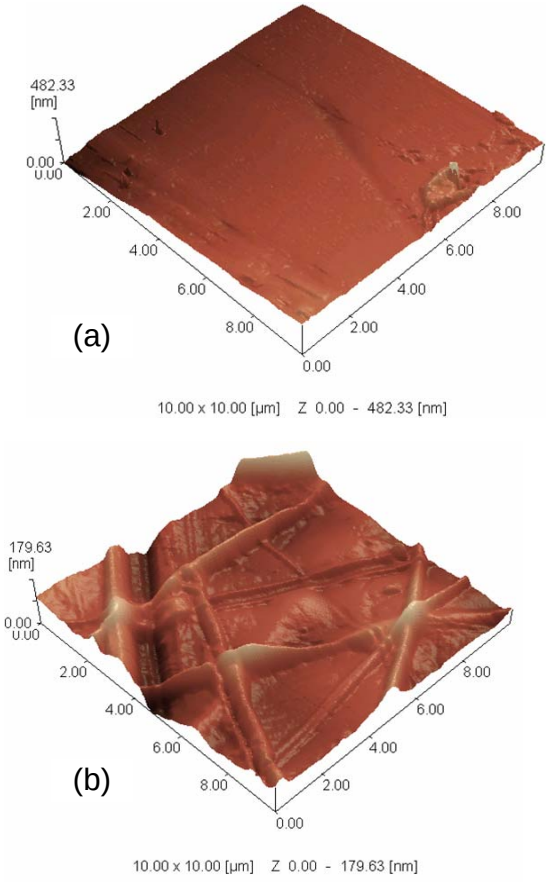

Figure 4: AFM image of surface of the polystyrene cast film (a) and the polyvinylalcohol-polystyrene composite film (b).

3.3 Mechanical properties of composite films

Mechanical properties of the PVA-PSt composite films were tested with a thermal mechanical analysis. Figure 6 shows the relationships between temperature and the length of the PSt cast film, the PVA cast film and the PVA-PSt reinforced composite film under same load condition (offset load 40 kPa and sin curve load modulation ±40 kPa, 0.1 Hz) and heating rate at 3°C min^{-1}. There is no thermal change at an initial region (low temperature range from -40°C to 80°C), then is followed by a linear behavior which is the main deformation region. Both of the PSt-based films started to elongate over 80°C. The grass transition temperature (T_g) of polystyrene is 80 - 117 °C and T_g of

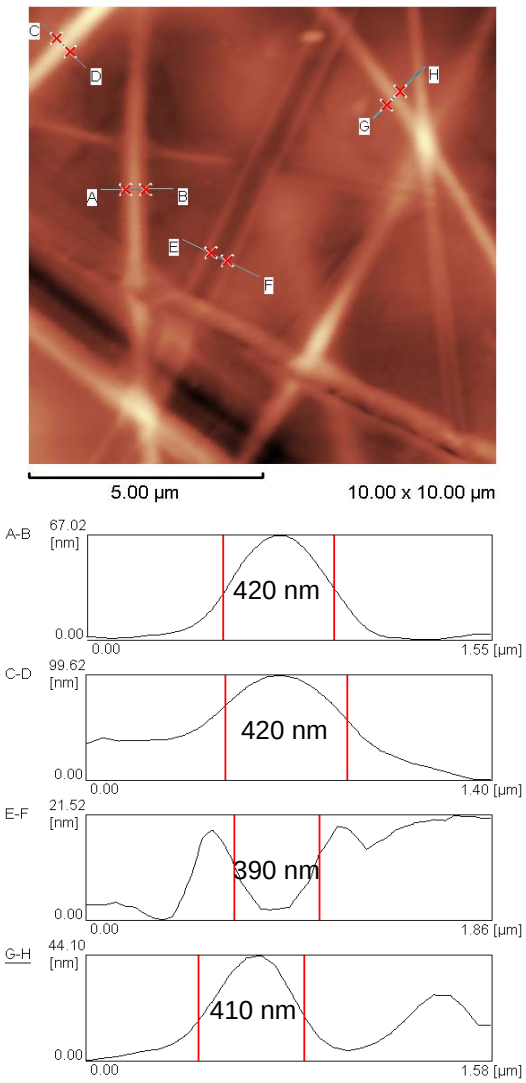

Figure 5: Surface morphology profiles of PVA-PSt composite film.

polyvinyl alcohol is 70 - 99°C [4-6]. The elongation temperature almost equals to the T_gs. However, the elongation of the PVA-PSt composite film was smaller than that of PSt cast film. This suggests that the electrospun PVA fibers coffined into the PSt matrix reinforce the composite film. The improvements in the thermal and dimensional stability of PVA-PSt composite film can be resulted from the interaction between the PSt matrix and the PVA fiber under nano-scale hybridization.

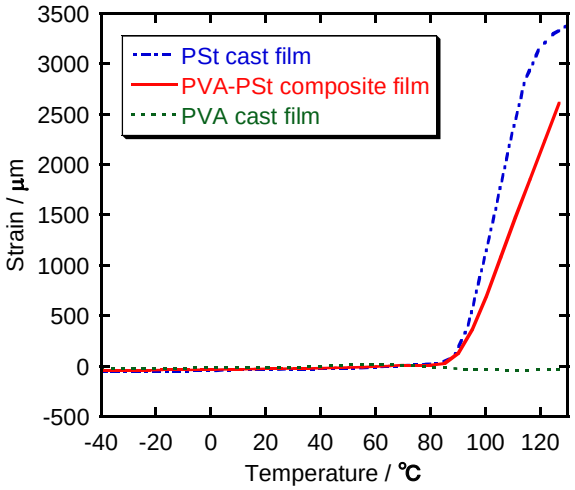

Figure 6: Variation of the length of the polymer film with temperature, PSt cast film, PVA cast film and PVA-PSt composite film. Load condition: offset load 40 kPa, sin curve load modulation ± 40 kPa, frequency 0.1 Hz, and heating rate at 3°C.

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