Characteristics of Elastomeric Nanofiber Membranes Produced by Electrospinning

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Abstract

This study examines the feasibility of co-electrospinning vapor grown carbon nanofibers (VGNF) within thermoplastic elastomer. The reinforcement effect was studied. The diameter of the thermoplastic elastomer was found to range from 0.5 to 3 μm . The mechanical properties of the electrospun fibrous structure were found to be similar to that of cast elastomeric films. However, the electrospun fibrous membranes have superior tactile properties. The addition of VGNF significantly increases the bulkiness of the fibrous elastomeric membranes.

Key Words: Elastomer, Polymeric resin, Fiber reinforcement, VGCF

1. Introduction

The electrospinning process has been rediscovered in recent years as an attractive and convenient technique for the fabrication of submicron level fibers. Most of the polymers that have been successfully electrospun are crystalline polymers having a molecular weight over 100,000 [1]. Only a few studies have been reported on elastomers. We reported on the nanofiber making from the thermoplastic elastomer in 2003 [2]. Afterwards, there were some reports by polyurethane rubber [3], SIS [4] and BR [5] etc. On the other hand, Viriyabanthorn et al. [6, 7] report the electrospinning of the heat curing elastomer. Generally, it is difficult to spin nano-scale fibers from non-crystalline polymers. Not only the nano-order but also a lot of micron orders are included as for the fiber diameter. In addition, it is also difficult to obtain dissolution of crosslinking agents such as sulfur and peroxide within the solvent. Accordingly, it is our objective to examine the feasibility of producing nanofibers by electrospinning a thermoplastic elastomer using polymer blending. By using a sulfur free thermoplastic elastomer, this material system may be applicable to electronic components and devices. There is peculiar advantage to the following nano elastomeric fibers, too.

The observation of phase separated structure of the thermoplastic elastomer in which the direct observation was only possible in thin section by the microtome.

Nanofilter that can adjust the mesh size in proportion to the draw ratio can be made.

Also the separation of the chemical substance becomes possible by imparting the functionality to the nanofiber.

We also specifically investigate the feasibility of improving the conductivity and mechanical properties by adding carbon nanofiber to this elastomer. There are a lot of reports concerning the electroconductive improvement of the resin that uses VGCF [8-11]. However, there is little electrical conductivity measurement of a nano elastomeric fiber with VGCF.

2. Experimental

As shown by Ko's group [1, 12], nanofibers can be produced by electrospinning. Electrospinning the crystalline polymer, polylactic acid, poly acrylic nitrile, and the polyethylene oxide can produce nanofibers relatively easily. However, it is not easy to make nanofibers from an elastomer whose polymer chain is flexible in the amorphous state. In this study, we examined the condition of the electrospinning using the polybutadiene and SBS elastomer.

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2.1 Materials

Thermoplastic syndiotactic 1–2 butadiene elastomer (BR830, Mw100,000, JSR Co. Ltd.) with 30% crystal component by weight and polystyrene (PS, Mw120,000, Aldrich) were used for this study. Styrene butadiene styrene block co-polymer (SBS-TR2000, Mw100,000, JSR Co. Ltd) was also selected. This SBS co-polymer consisted of 40% styrene and 60% butadiene by weight. To improve the conductivity and the mechanical properties of this elastomer, carbon nanofiber was blended in this material. Vapor grown carbon fibers (VGCF, fiber diameter 150 nm, length 2 μ m, Showa Denko Co. Ltd.) is cheap (50,000 yen/kg) and has excellent in the dispersibility in the elastomer. The production capacity of Showa Denko Ltd. will improve from 40 tons to 100 tons during 2007. In order to overcome the dispersibility issues of VGCF, it was stirred in a ball mill for 4 hours prior to being introduced into the solution. Dispersion was further promoted by sonication for 4 hours in the solution.

2.2 Processing

These elastomer and polymer (BR, SBS and, PS) were dissolved in chloroform (Aldrich) and this solution placed in a glass syringe. High voltage was applied to the needle (16–22-gauge) made of the stainless steel mounted on the glass syringe. The voltage was 15–25 kV, and the distance from the point of the syringe to the negative electrode target was 5–20 cm. The negative electrode (ground) was a plate of copper plate 15 cm² in size. The sample was made with an atmospheric humidity of 40% and a temperature of 20–25°C. Detailed experimental conditions are shown below. The polymer solution is retained in a syringe (3 ml). It is then spun from the tip of the needle (16 G) of the syringe. The angle of the syringe was held constant at 45 degrees. A high positive voltage was applied to the needle, where the voltage and current were respectively 25 kV and 10 μ A. The elastomer spun from the tip of the syringe was sprayed in the form of a very fine fiber on the copper plate that located 15 cm away.

2.3 Mechanical testing and SEM observation

Tensile measurements of the elastomer nonwoven fabric sheet produced by the electro-spinning process were carried out using a KESG1 (Kato-tech, Japan) tensile tester. The detection force limit of this device is 1.0×10^{-4} N. However, the strength of a single nanofiber is smaller than this. Therefore, the measurement was done with the nonwoven mat of the nanofiber. The sectional area of the nonwoven is calculated by Ayutsede's techniques [12]. That is, the

sectional area of the nonwoven mat is calculated from the density of polymer, the volume of the appearance, and weight. The diameter of the fiber was measured using a scanning electron microscope (XL-30, Philips). The fiber diameter was measured only in the fiber part where the bead area was not included. That is, when the bead existed together to the fiber, the size of it was disregarded. The diameter of the fiber part of 50 places of each sample was measured by using the Sion Image picture processing software. When the section area was an oval, the extended shaft side was assumed to be a fiber diameter.

2.4 Conductivity of membrane

Conductivity of the electrospun membrane and cast film were measured using an MCP-HT450 and MCP-T600 (Dia-instruments Co. Ltd.). This device carries out measurements for various shapes of samples in the measurement range (10^4 – 10^{13} Ohm). The supplied voltage was 1,000 V. The surface resistance was measured by the double ring probe (UR-SS) technique on the basis of JIS-K6911.

2.5 Measurement of intrinsic viscosity

The viscosity measurement was performed in a temperature controlled bath of 20°C using an Uberorde type viscosimeter. An average of ten measurements was used.

3. Result and discussion

3.1 Effect of polymer concentration

Figure 1 shows the relationship between the solution concentration of RB830 and the average diameter of the fiber obtained by electrospinning. In a solution concentration of 6 wt% or less, a nonwoven membrane

Fig. 1 Effect of polymer concentration (1-2 polybutadiene, RB830). Electrospinning condition; 25 kV, 15 cm distance, 16 G needle.

consisting of elastomer nanofibers was obtained. However, the samples contain many beads. On the other hand, the diameter of the fiber increases rapidly using solution concentrations above 6 wt%. In a solution concentration of 7.5 wt%, no bead formation was found and the deviation of the fiber diameter was smaller. We were not able to suppress bead generation using solutions of 6 wt% or less.

3.2 Production of a droplet free nanofiber nonwoven membrane using a low concentration polymer solution

The most important point is the distance from the tip of the needle to the target. Figure 2 shows the relationship between the distance to target and average fiber diameter. We did not observe a significant correlation between distance and fiber diameter. There was no droplet formation when the distance to the target was very short. When the solution concentration is low, the liquid tends to form droplets easily in order to reduce surface tension. However, if a large shearing force, which overcomes the surface tension, acts on the solution, a nanofiber nonwoven membrane without droplet can be obtained. Note that the voltage for each unit length increases as the distance between the nozzle and the target is reduced. That is, high voltages and small nozzle diameters are therefore needed. It is also necessary to satisfy the following requirements so that a non-crystalline polymer can become fibrous; (1) entanglement of polymer chains in the solution, (2) the use of a large charge to draw the polymer chain, (3) use of the solvent with the best vapor rate.

The fiber diameter increases when the vapor rate of the solvent is too high. If the solvent evaporation rate is low, it becomes fibrous with the solvent, and many holes are found on the fiber surface. However, this is not observed when the fiber diameter is one micrometer or less. Polybutadiene was

Fig. 2 Effect of distance between needle and target (1-2 polybutadiene, RB830). Electrospinning condition; 25 kV, 5.25 wt%.

able to form nanofibers without beads using a distance of 5 cm, solution concentration of 5.25 wt% and a voltage 25 kV. It was even possible to bring the distance as close as 3 cm. However, if a discharge occurs between the needle and the target, then electrospinning is not possible.

3.3 The formation of nanofibers using a multi-cone spray system

One interesting method for making nanofiber is to form a multi-cone by the tip of the needle. The spray from a noncrystalline polymer solution forms multiple branches easily. However, this multi spray is unstable and droplets can still form because the drawing force on the multi cone-jet becomes weak amongst several branches. It was previously described that this problem could be solved by decreasing the nozzle diameter and shortening the distance between the nozzles to the target. A thick nozzle diameter and spinning to a wide area will be efficient for the multi spray, however, the fiber diameter is larger than from a single spray. That is, electro-spinning can be carried out with branches at the tip of the nozzle. These cones are shown in Fig. 3. At the tip of the nozzle, the positively charged polymer solution forms a multi-cone shaped like a crown. The appearance of the spray from this multi cone looks like the movement of a jellyfish's tentacle. The following two conditions are necessary in order to form this multi cone: a high voltage and wide target area. This multi-cone technique has not been reported before. The formation mechanism of this technique will be examined in detail in the future.

3.4 Effect of VGCF to elastomer

Figure 4 shows the relationship between the solution concentration and fiber diameter for polybutadiene. We added 1 wt% of VGCF to the polybutadiene. In spite of the higher concentration of polymer solution, the fiber diameter was thin and droplets were observed. VGCF improves the flowability of the polymer solution. This is because VGCF

(a) Single cone spun

(b) Multi-cone spun

Fig. 3 Photograph of single cone and multi cone spinning.

Fig. 4 Effect of the VGCF (VGCF 1 wt% for BR830, 25 kV, 15 cm distance).

Fig. 5 Stress strain curve of tensile test (RB830 concentration is 7.5 wt%).

aligns in the direction of flow. It also improves the electric conductivity of the polymer solution.

Figure 5 shows the stress-strain curve of the nonwoven membrane made by electrospinning of the polybutadiene elastomer. The elastic modulus of the membrane increased 3 times when 5 wt% VGCF was added to the elastomer. However this improvement in the modulus was not observed when only 2 wt% of VGCF was added. When the change in modulus with the addition of VGCF is calculated using the simplest mixing rule, it becomes the following [13].

$$E_c = ((E_1\phi_1 + E_2(1 - \phi_1))a)^b \quad (1)$$

E_1 (VGCF): 500 GPa [14, 15], E_2 (PB): 0.022 GPa

ϕ (VGCF): volume fraction of VGCF

a : Coefficient of composites model (unidirectional model is 1.0, nonwoven mat model is 3/8)

b : Power coefficient

This is a predictive equation for the modulus of a composite material in which continuous fiber is series aligned. The $a = 3/8$ factor was applied to account for the random orientation of the fiber. The model equation and the

Fig. 6 Tensile modulus for the VGCF reinforced nonwoven membrane.

experimental data are corresponding well the amount of VGCF is 1.5vol% (2.8 wt%) or more (Fig. 6). It will be necessary to improve interfacial adhesion of VGCF and elastomeric in the future. Through SEM observation, we did not observe a change in fiber diameter with the addition of VGCF. The breaking elongation decreased greatly when the added amount of VGCF was 4 wt% or more, e.g. the breaking strain when 5 wt% VGCF was added was 100% or less. The membrane's color changes from a white to a dark gray with increasing of the amount of VGCF. Therefore, it is appears that VGCF was contained in the nanofiber.

3.5 SBS (polystyrene-polybutadiene alloy elastomer, TR2000)

For the SBS alloy elastomer, we observed the geometrical arrangement of the fibers in the nonwoven membrane and the diameter of the electrospun fibers by SEM. The diameter of the electrospun SBS fibers ranged from 2 to 22 μm . Droplet formation was observed in fabrics spun with an SBS concentration of 15% or less. Spinning was not possible with a SBS percentage over 20% because of the solutions high viscosity. Figure 7 shows photographs of electrospun SBS elastomer fiber from different concentration solutions. The fiber diameter of the SBS elastomer was larger than that of polybutadiene. Polybutadiene contains the crystal part though SBS originates from a complete amorphous structure. Figure 8 shows the photographs of electrospun polystyrene fiber. The fiber diameter of polystyrene was larger than that of the SBS elastomer.

Fiber diameter depends greatly on polymer viscosity. We found that the multiplication of the intrinsic viscosity with the concentration of polymer solution (Berry number [16]) is an important factor for electrospinning. Figure 9 shows the relationship between the Berry number and the diameter of the fiber obtained by electrospinning. This result shows that the fiber diameter of an amorphous or slightly

Figure 7 Electorspinning of SBS elastomer (TR000, 25 kV, 15 cm distance, 16 G needle).

Figure 8 Electorspinning of Polystyrene (15 kV, 15 cm distance , 16 G needle).

Fig. 9 Effect of B ($[\eta] \times c$) on fiber diameter; c : concentration (g/dL) $[\eta]$: Intrinsic viscosity (dL/g), SBS (TR2000) 0.3114, Polybutadiene 0.5234, Polystyrene 0.184 [17].

crystallized polymer greatly depends on the Berry number. The slope of these three kinds of polymers was found to be almost equal. Where do these coefficients originate? They are probably related to the molecular weight, radius of gyration of molecular chains and entanglement of the molecular chains. The molecular weight of each polymer is nearly identical. Polystyrene is 120,000, polybutadiene is 100,000 and SBS is also 100,000. It is thought that the α is related to molecular weight. It is very useful that the gradient is almost the same in order to guess the conditions for producing nanofibers from electrospraying of an elastomeric polymer. That is, we can predict the polymer concentration necessary to obtain the nanofibers can be

Fig. 10 SEM photograph of electrospraying membrane from Polystyrene/Polybutadiene mixed solution (4:6), 15 kV, 15 cm distance, 16 G needle, average fiber diameter is 1.55 μm .

predicted using this relationship.

Also, electrospraying was possible from a solution that consisted of polystyrene mixed with polybutadiene. Figure 10 is the SEM photograph of the membrane made from the solution of mixed polybutadiene and polystyrene in 4:6 (weight ratios). The concentration of the polymer solution was 16 wt%. The mean fiber diameter of the fiber was 1.55 μm , and it was thinner than that spun from SBS. Though fiber diameter is dominated by polybutadiene, the obtained membrane is brittle and the polystyrene dominates its mechanical properties.

3. 6 Tensile property of electrospun fiber

Figure 11 shows the results of tensile measurements on the SBS elastomer. The stress-strain curve of the nonwoven

Fig. 11 Tensile property of electrospun nanofiber (SBS elastomer).

mat containing fibers with a diameter of $2.34\ \mu\text{m}$ was almost the same as a cast film. If these fibers are oriented along the loaded direction, a higher strength will be expected for the nonwoven mats. The electrospun fibrous membranes have superior tactile properties. This cross section of the nonwoven mats considers the voidage. It gives a very soft hand and the feeling like leather.

3.7 Electrical conductivity

The conductivity of the nanofiber nonwoven that contains VGCF is higher than that of the cast film. (Fig. 12). Conductivity may be proportional to the number of contact points of VGCF. Therefore, it is thought that VGCF containing nanofiber may also be conductive. But the conductivity of the nano elastomeric fiber nonwoven was only two digits though VGCF was added. It has been known so far that conductivity improves rapidly by existing of several vol% VGCF. The conductivity of the expectation in our research is not obtained. This cause seems the agglomeration of VGCF by the voltage. When we applied a high voltage to the ethanolic solution in which VGCF dispersed, we confirmed VGCF agglomerated. VGCF might

Fig. 12 Conductivity of the VGCF reinforced electro-spun BR elastomer.

agglomerate in the nozzle charged in a high voltage of the plus as well as electrodeposition to the anode of CNT in the organic solution.

4. Summary

The preparation of a nanofiber membrane from an elastomer was successfully performed using the electrospinning process. The diameter of the resulting fiber is highly dependent on the solution concentration, voltage and polymer viscosity. Beadless nanofiber membrane produced from polybutadiene were obtained under the conditions of 5.25 wt%, 25 kV, and 5 cm. The mean diameter of the fiber was $0.46\ \mu\text{m}$. In addition, it was possible to produce fibers without beads by growing a multi-cone at the needle tip. It was possible to co-electrospin VGCF with the elastomer. The viscosity and electrical conductivity of the polymer increased with the addition of VGCF. The tensile strength of the elastomeric nanofiber membrane was similar to that of the film. However, a soft feeling elastomer nonwoven membrane was obtained.

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