Fabrication and Characterization of Electrospun Polybutadiene Fibers Crosslinked by UV Irradiation

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ABSTRACT: Crosslinked electrospun polybutadiene (BR) fibers were made using electrospinning and UV curing methods. The crosslinked BR fibers were obtained by irradiating UV light on the electrospun BR fibers containing a photoinitiator and a crosslinker. Although uncrosslinked electrospun BR fibers did not retain the fiber morphology at room temperature due to a cold flow resulting from the very low glass transition temperature (T_g) of BR (below $-80°C$), the crosslinked electrospun BR fibers retained the fiber morphology. The crosslink density increased with increase of the content of crosslinking agent. The crosslinked BR fibers had higher T_g than the raw BR. Tensile strength, modulus, and elongation at break of the electrospun BR fiber mats increased with increase of the crosslinker content. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2333–2337, 2006

Key words: crosslink; electrospun fiber; polybutadiene; UV cure

INTRODUCTION

Electrospinning is a very useful technique to produce submicron–sized organic and inorganic polymer fibers, which can be produced using an electrostatically driven jet of polymer solution.[1–5] Electrospun fibers are generally collected in the form of nonwoven mats and they are of interest for a variety of applications, including semipermeable membranes, filters, composite reinforcements, scaffolding used in tissue engineering, and optical and electronic devices.[6–9] Diameters of electrospun fibers are influenced by the solution concentration, electric field, tip-to-collector distance (TCD), conductivity of solution, and diameter of nozzle.[4,5,7,10]

All of polymer materials dissolved in a proper solvent can be subjected to the electrospinning process. Plastic polymers having higher glass transition temperature (T_g) than room temperature are relatively easy to be made into electrospun fibers, but rubbery polymers are difficult for doing so due to the low T_g. T_gs of elastomers, such as natural rubber (NR), butadiene rubber (BR), and styrene-butadiene rubber (SBR), are far below 0°C. The shape of the fiber can be formed from a rubber solution by electrospinning process, but it tends to be immediately destroyed by cold flow due to the lower T_g than room temperature. In the previous work,[11] we tried to make the electrospun rubber fibers, but it was not successful because the circular fiber shape destroyed soon after the electrospinning. Thus, we attempted to introduce *in situ* crosslinking method during electrospinning to maintain the circular fiber morphology.

Generally, the crosslinking of rubber materials can be made by the sulfur vulcanization,[12–14] peroxide curing,[15] or resole curing.[16] However, these cure systems might be inadequate for the purpose of this study, because they need the elevated temperatures above 100°C and high pressure to attain the reasonable rate of crosslinking reaction. Thus, any cure system available at low temperatures is required for this study.

Based on the requirement mentioned earlier, we selected a UV curing system,[17–21] which has well-defined technology in a variety of industrial applications. Highly crosslinked polymers can be generated within seconds at ambient temperature with the UV cure system. In the system, the UV light produces an initiating species, such as free radicals or cations, by photolysis of radical-type or cationic-type photoinitiators.

In the present work, we attempted to produce the crosslinked-electrospun rubber fibers with circular cross section via *in situ* UV curing at room temperature. Polybutadiene (BR) with extremely low T_g (below $-80°C$) was selected as a rubber. A simple drum-

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type apparatus for electrospinning was modified to make possible for *in situ* UV irradiation onto the electrospun fibers.

EXPERIMENTAL

KBR01 of Korea Kumho Petroleum Co. (Korea) was used as BR (M_w = 520,000). 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (λ_{max} = 310 nm) and tri-methylol-propane 3-mercaptopropionate of Aldrich (USA) were used as the photoinitiator and crosslinking agent, respectively. A UV lamp (306 nm, 8 W) of Sankyo Denki (Japan) was used. Tetrahydrofuran (THF) of Aldrich was used as the solvent. 8 wt % of BR solution was prepared in THF for the electrospinning. The photoinitiator concentration was set to be 1 wt % of BR, and the crosslinker content was varied with 0.5, 1.0, 2.0, and 3.0 wt % of BR.

Figure 1 shows the electrospinning apparatus with UV lamp for curing. A syringe with metal needle (2.0 cm of length and 0.4 mm of diameter) was used as the solution reservoir. A drum-shaped counter electrode was located below the reservoir. The electrospun fibers were collected on the tubular layer. The distance between the capillary tip and the counter electrode (tip-to-collector distance, TCD) was 15 cm, and the applied voltage was 10 kV. The drum was rotated with 50 rpm. The distance between the collector and the UV lamp was 10 cm. The UV was irradiated immediately after the electrospinning. The electrospun fibers were collected on the top of the drum collector and UV light was irradiated on the bottom side of the drum to avoid UV-irradiating the solution reservoir. UV lamp was supplementarily irradiated on the electrospun fibers for 5.0 min after the electrospinning.

The morphology and diameter of the electrospun fibers were measured with scanning electron microscope (SEM) of Jeol JSM-5900 (Japan). The crosslink density was measured by swelling method, using toluene. The detail procedure of crosslink density measurement is described elsewhere.[22] Glass transition
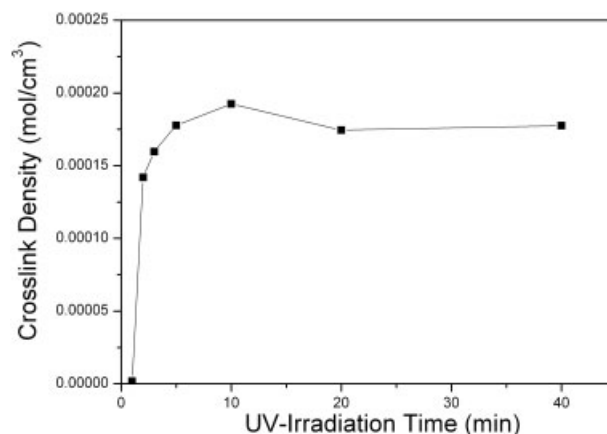
Figure 2 Variation in crosslinking density of 8 wt % BR solution film containing 1 wt % of photoinitiator and 3.0 wt % of crosslinker with UV-irradiation time.

temperatures (T_g) of the electrospun BR fibers were measured with differential scanning calorimeter (DSC) of TA instruments DSC 2910 (USA). For a tensile property measurement, dumbbell-shaped specimens were cut from the electrospun mats. Modulus, tensile strength, and elongation at break were obtained from stress–strain curves by using a tensile tester (Lloyds, UK) at room temperature and at a cross-head speed of 10 mm/min, according to the procedure described in ASTM D412. The tensile stresses were calculated by dividing the measured forces with apparent cross section (i.e., width times thickness of mats, ~60 μm), even though there were lots of free voids made from characteristic structure of mats formed by each fibers. Thus, all the reported values for tensile stresses and moduli in this study are apparent.

RESULTS AND DISCUSSION

To determine an optimum time for UV irradiation, the UV light was irradiated for various time intervals on the BR solution film containing both the photoinitiator and crosslinker. Crosslink densities of the UV-cured films were measured with a swelling method in toluene. The crosslinking density was steeply increased by increasing the UV-irradiation time until 5.0 min and then was leveled-off as shown in Figure 2. This indicates that 5 min of UV irradiation is sufficient for the equilibrium curing.

Since the concentration of polymer solution influences the splaying behavior at the capillary tip, one of the major parameters in fiber morphology, the splaying behavior was investigated for different concentration of polymer solution. At relatively lower solution concentrations of below 4 wt %, the solution jet was splitted into several jets, and beads were formed in the resulting fibers. However, at higher concentrations of
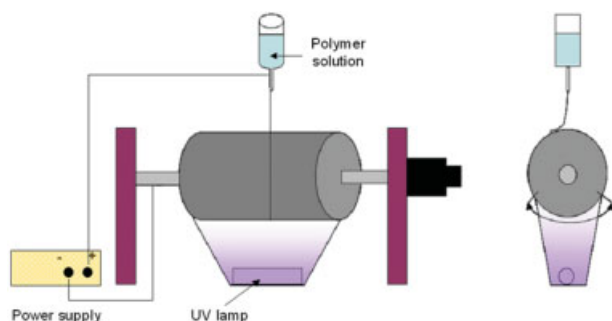

Figure 1 Electrospinning apparatus with *in situ* UV irradiation system. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
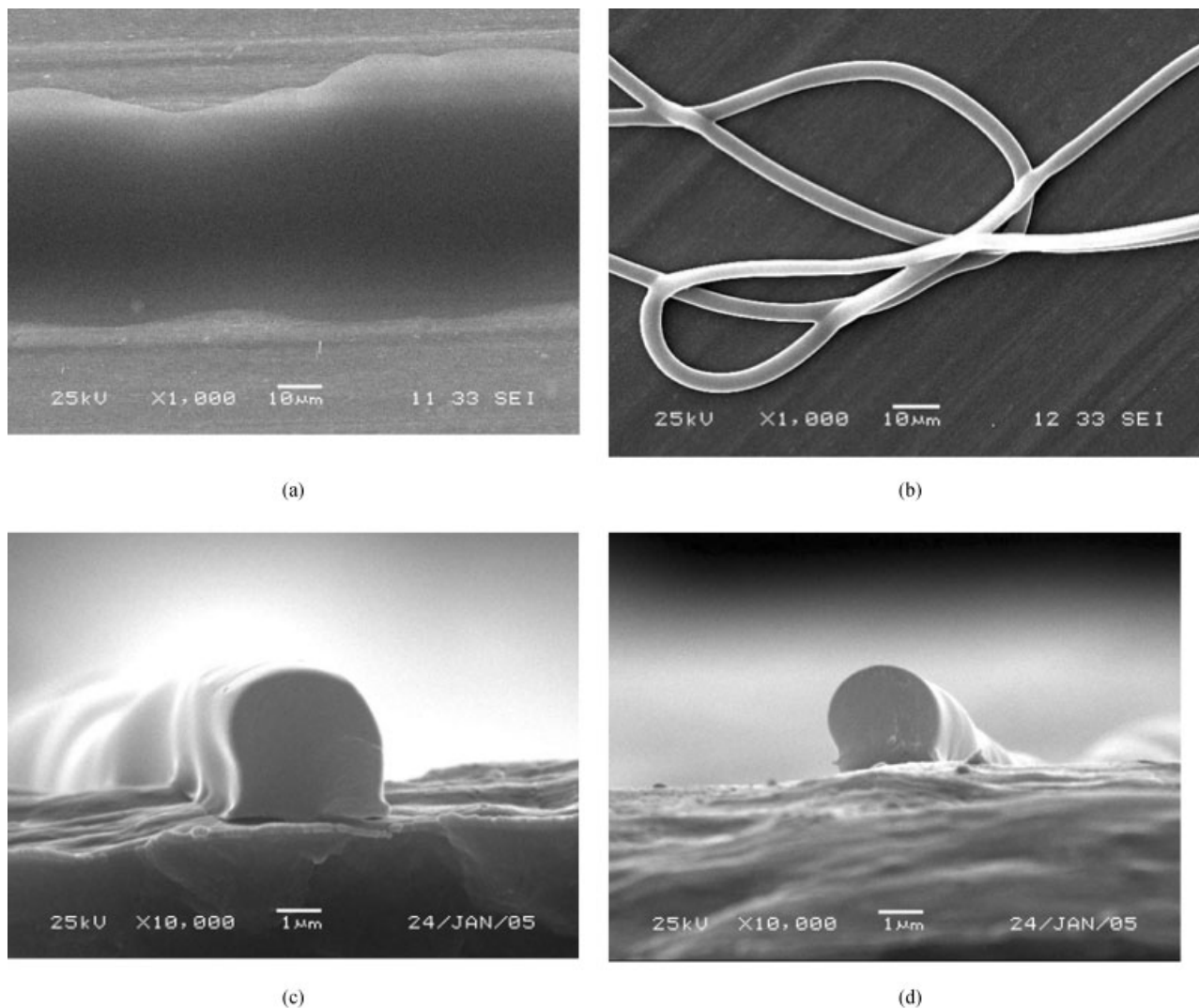
(a)

(b)

(c)

(d)

Figure 3 SEM images of electrospun BR fibers: (a) uncrosslinked BR fiber(0 wt % crosslinker), (b) crosslinked BR fiber(3 wt % crosslinker), (c) cross-sectional view of crosslinked BR fiber (0.5 wt % crosslinker), and (d) cross-sectional view of crosslinked BR fiber (3 wt % crosslinker).

above 5 wt %, the solution jet was not splitted, and it turned to become a single filament, and the spinning behavior became very stable. Therefore, the solution concentration was kept to be 8 wt % for making electrospun fibers reported in this study.

Figure 3 shows the SEM images of the electrospun BR fibers. The diameter of the cured-electrospun fibers was found to be 1–4 μm. The observed diameter is somewhat thicker than the usual values of submicrons for common plastic polymer materials, possibly due to the single filament formation described earlier. As shown in Figure 3(a), the uncured electrospun fibers tended to deform to become flat and finally lost their initial circular fiber morphology due to a viscous cold flow coming from its low T_g. However, the UV-cured electrospun BR fibers show circular fiber morphology as shown in Figures 3(b)–3(d). Figures 3(c) and 3(d) are the cross-sectional view of the UV-cured electro-

spun fibers at two different crosslinker levels: 0.5 and 3.0 wt %, respectively. The cross section of the less-cured fibers with 0.5 wt % of crosslinker showed a severe deviation from a circular shape. But, the highly-cured fibers showed the circular fiber morphology. Thus, the crosslinking seems to be successfully taken place in the route reported in literatures.[17–21] Radicals formed from the photoinitiator by UV irradiation first react with the crosslinker, trimethylolpropane 3-mercaptopropionate, to form sulfide radicals. The sulfide radicals then attack allylic sites of rubber molecules to form crosslinks. Since the crosslinker used in this study has three thiol (—SH) groups, one crosslinker molecule can bond two or three BR molecules.

The crosslink density of the UV-crosslinked electrospun fibers was measured using the solvent swelling method to confirm the effect of crosslinker content. The crosslink density of the cured electrospun BR

Concentration of crosslinker (wt %)	0.0	0.5	1.0	2.0	3.0
Crosslink density (g mol/cm^3)	–	1.65×10^{-3}	1.76×10^{-3}	2.11×10^{-3}	2.23×10^{-3}
T_g (°C)	−84.35	−84.31	−83.16	−81.05	−80.07

fibers continuously increased with increase of the crosslinker level as given in Table I. It is believed that the crosslinking reaction occurs well cross the fibers since the diameter of fibers is thin enough for the UV light to penetrate. Variation of T_gs of the crosslinked electrospun fibers with the crosslinker concentration was also given in Table I. T_g increased from −84.35 to −80.07°C as the crosslinker level was raised from 0 to 3.0 wt %. This also supports the increased crosslink density. When the crosslink density is increased, the molecular motions of BR are more restricted, and thus more energy is required for the polymer chains to move. The difference of T_g between uncrosslinked- and crosslinked fibers (3 wt %) was found to be more than 4°C.

In the case of bulk rubber specimen, the crosslink density greatly affects various physical properties, such as modulus, hardness, resilience, elongation at break, heat build-up, and so forth. [12] Generally, the tensile modulus increases, while the elongation at break decreases with increasing the crosslink density. It is interesting to see whether the general trend can also be applicable to the tensile behavior of nonwoven rubbery fiber mats. Figure 4 shows the stress–strain curves for UV-cured electrospun fiber mats having different crosslinker level. The tensile behavior for all the mats resembles that of typical bulk rubber sheets or films, especially at relatively lower elongation regions. At extremely higher elongation regions before breaking, rubber films generally show a typical stress-hardening behavior due to strain-induced crystallization.[23] But, the fiber mats did not show such a stress-hardening behavior. The tensile properties, such as tensile strength, modulus, and elongation at break, considerably improved with increasing the degree of cure. In our previous study, based on electrospun polyurethane fiber mats, it was found that the tensile behavior was greatly affected by both the number and type of netting points among fibers.[24] For instance, the tensile deformation was mainly governed by both the slippage of crossing fibers and the breaking of fibers of permanently bonded junctions (or netting points). Thus, the improved tensile performance in this study can be explained by the increased number of permanently bonded junction points between by cocuring between netting fibers, as well as by the increased stiffness of the fiber themselves by curing of BR molecules inside the fibers. Several representative tensile properties are summarized in Table II. The modulus and tensile strength of highly cured fiber mat (3 wt %) were about two times higher than those of less-cured fiber mat (0.5 wt %). Thus, it can be concluded that the type and number of netting points is one of the major controlling factors in the tensile behavior of nonwoven fiber mats.

CONCLUSIONS

Crosslinked BR fibers were successfully fabricated through electrospinning process, followed by UV curing. The BR solution containing the photoinitiator and crosslinker was electrospun, and UV light was irradiated on the electrospun BR fibers immediately after the electrospinning. The crosslinking was confirmed by several methods. The crosslinked electrospun BR fibers retained the fiber morphology and were not dissolved in toluene. The crosslink density and glass-
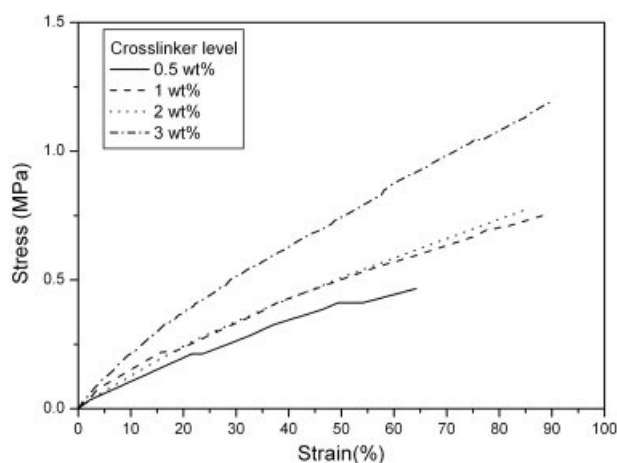
Figure 4 Stress–strain curves for UV-cured electrospun BR fiber mats.

TABLE II
Physical Properties of the UV-Cured Electrospun BR Fiber Mats

Concentration of crosslinker (wt %)	0.5	1.0	2.0	3.0
30% Modulus (MPa)	0.27	0.34	0.34	0.52
50% Modulus (MPa)	0.39	0.50	0.51	0.75
Tensile strength (MPa)	0.47	0.76	0.77	1.19
Elongation at break (%)	64	90	85	90

transition temperature, T_g, increased by increasing the crosslinker content. Tensile properties, including modulus, tensile strength, and elongation at break, improved by increasing the crosslinker content. The suggested *in situ* UV-curing method in electrospinning process can be a promising way to obtain nanoscales of rubbery nanofiber mats.

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