

Toughened Electrospun Nanofibers from Crosslinked Elastomer-Thermoplastic Blends

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ABSTRACT: A crosslink-able elastomeric polyester urethane (PEU) was blended with a thermoplastic, polyacrylonitrile (PAN), and electrospun into nanofibers. The effects of the PEU/PAN ratio and the crosslinking reaction on the morphology and the tensile properties of the as-spun fiber mats were investigated. With the same overall polymer concentration (9 wt %), the nanofiber containing higher composition of PEU shows a slight decrease in the average fiber diameter, but the tensile strength, the elongation at

break and tensile modulus of the nanofiber mats are all improved. These tensile properties are further enhanced by slight crosslinking of the PEU component within the nanofibers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2321–2326, 2007

Key words: electrospun nanofibers; elastomeric polymer; thermoplastic; electrospinning; polyacrylonitrile; polyester urethane; effect of crosslinking; tensile properties

INTRODUCTION

Electrospinning has been a promising approach to prepare polymeric nanofibers. This technique typically involves a solution stretching process in which the polymer solution driven by a strong electric field is stretched rapidly into dry or semidry fibers and deposited directly onto a collector, usually in the form of a nonwoven fiber mat.^{1–4} The improved processes have been able to control the fiber alignment,⁵ or to produce multi-component fibers such as core-sheath nanofibers^{6,7} and side-by-side nanofibers.⁸ Because of the high surface-to-volume ratio and inherent porosity structure, electrospun nanofibers have shown a huge potential in areas such as tissue engineering scaffolds,^{9,10} control release,¹¹ filtration,¹² catalysis carrier,¹³ nanocomposites,^{14,15} chemical sensors,^{16–18} and battery separators.¹⁹

The electrospun fiber mats from most polymer materials have a relatively weak mechanical property, which limits their use in practice. Past efforts to improve the mechanical properties included increasing the polymer crystalline within fibers,²⁰ using a polymer material of high strength,²¹ blending two or more polymers of different properties,²² or employing a polymer composite that contains nanostructured materials such as carbon nanotubes^{23–25} and nanoparticles.^{26,27} Crosslinking of polymer could further im-

prove the fiber strength.^{28,29} Although these established techniques have succeeded in improving the fiber strength, the fiber elongation at break is reduced noticeably,^{28,29} which leads to reduced tolerance to deformation. It is not yet established if the fiber strength and the fiber elongation at break can both be improved, so that the nanofiber mat has better toughness.

Elastomer, a polymer having the elastic properties of natural rubber, has been widely used in industry because of its high toughness and long-term durability. The toughness can be reinforced by crosslinking of the polymer chains, alternatively called “vulcanization.” However, most of elastomers are difficult to electrospin into stable nanofibers because of their low glass transition temperature and the viscous surface that make the as-spun nanofibers merge quickly into large fibers or even a continuous film.³⁰ Blending elastomer with a polymer that can be easily electrospun could be a solution, but simple mechanical blending of two or more polymers usually results in poor mechanical properties because most polymers are incompatible. Crosslinking either polymer phase or interlocking both polymers to form a so-called “interpenetrating network” has been an established strategy to compatibilise an immiscible polymer blend.³¹ Also, a slightly crosslinked elastomer has been found to be more effective to toughen a thermoplastic material than its noncrosslinked counterpart.³² Nanofibers from a polymer blend containing an elastomer have been reported;²² however, little is known about the effect of crosslinking the elastomeric component on fiber mechanical properties.

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In this study, we used a crosslink-able elastomeric polymer, polyester urethane (PEU), and a thermoplastic, polyacrylonitrile (PAN) as model compounds to demonstrate that nanofibers from an elastomer-containing polymer blend can be toughened through increasing the composition of elastomer within the nanofibers. We have also found that the fiber strength and elongation at break can be both enhanced if the elastomer component is slightly crosslinked within the fibers.

EXPERIMENTAL

Materials and measurements

Polyacrylonitrile (PAN; M_w 86,200 g/mol) and *N,N*-dimethylformamide (DMF) were obtained from Aldrich. A crosslink-able polyester urethane (PEU, commercial name Impranil CHW) and its crosslinker (Imprafix VP LS 2323) and catalyst (Imprafix TH LSG) were kindly donated by Bayer (Material Science, Germany). The PEU/PAN solutions were prepared by mixing the PEU and PAN in DMF and stirred mechanically at room temperature for 3 days. The crosslinked PEU/PAN fibers were prepared by adding the crosslinker and catalyst (2.5 wt % each based on the weight of Impranil CHW) to the PEU/PAN solutions prior to electrospinning.

The viscosity and conductivity were measured with a digital rotational viscometer (D443 Rheology International) and a conductivity meter (LF330 Merck), respectively. The morphology of the as-spun PEU/PAN fibers was observed under a scanning electron microscope (SEM, LEO 1530 microscope), and the average fiber diameter was calculated based on the SEM images with the aid of computer software (ImagePro plus 4.5). The ATR-FTIR spectra were recorded with a FTIR spectrophotometer (Bruker Optics). The differential scanning calorimetry (DSC) analyses were conducted on a Mettler Toledo 821 with "Star Software" version 9. Samples of between 5 and 10 mg were encapsulated in lightweight aluminum pans (13 mg) and were run in alternating DSC mode with an underlying heating rate of 10°C/min. The tensile properties of the nanofiber mats were determined using a Universal Testing Machine (Lloyd Tensile Tester) according to Australian standard AS1145 (crosshead speed 10 mm/min, gauge length 50 mm).

Electrospinning

A purpose-made electrospinning apparatus³³ was used in this study. The polymer solution was put into a 5 mL plastic syringe and connected to a high voltage power supply (ES30P, Gamma High Voltage Research) through a metal syringe needle (21 G). The as-spun fibers were collected on a knitted polyester

fabric wrapped around a grounded and rotating metal drum, 15 cm away from the tip of the needle. The flow rate of the polymer solution was controlled by a syringe pump (KD scientific). All electrospinning processes were conducted with an applied voltage of 20–24 kV and a polymer flow rate of 1.5 mL/h.

RESULTS AND DISCUSSION

Electrospinning a PEU-DMF solution could not produce stable fibrous product. The as-spun PEU fibers rapidly merged into larger filaments and finally formed a continuous film even when the PEU concentration was very high. By contrast, electrospinning a PAN-DMF solution can have different fiber morphologies, including individual beads, beads-on-string structure and, uniform fibers, depending on the PAN concentration used. Our previous research³⁴ has revealed that individual beads were produced when the PAN concentration was low (smaller than 2 wt %), the beaded fibers were electrospun from a solution having higher PAN concentration (3–6 wt %); further increasing the PAN concentration would lead to uniform fibers.

Electrospinning a PEU/PAN polymer blend solution was able to produce fibrous structure. When the overall concentration of PEU/PAN blend was kept at the same value (9 wt %), the ratio between the PEU and the PAN affected the fiber morphology. As illustrated in Figure 1, three different PEU/PAN ratios (PEU/PAN = 2 : 1; 1 : 1; 1 : 2 w/w) resulted in different fiber morphology. When the PEU/PAN ratio was 2 : 1, the PEU concentration was 6% (wt). Electrospinning such a polymer solution resulted in a fibrous product, though the fibers tended to stick together to form an interconnected web structure. This suggests that the addition of PAN to the PEU solution has facilitated the formation of nanofibers in electrospinning. When the PEU concentration was reduced to 4.5% (wt) (PEU/PAN ratio = 1 : 1), individual fibers containing a small amount of fiber beads were produced. Further reduction of the PEU concentration to 3% (wt) (PEU/PAN ratio = 1 : 2) led to nonsticky and uniform fibers.

The average fiber diameter of the as-spun PEU/PAN fibers is listed in Table I. The fiber diameter from the different PEU/PAN ratios is in the range of 200–300 nm. By comparison, the pure PAN nanofibers electrospun with the same overall concentration have a fiber diameter range of 354 ± 64 nm [Fig. 1(a)]. The PEU/PAN ratio also influenced the fiber diameter. The fiber diameter decreased slightly with an increase in the PEU component, even though the same overall polymer concentration was used. The change in the fiber diameter can be attributed to the effect of the PEU/PAN ratio on the solution properties. As listed in Table I, the solution viscosity and conductivity both decreased with the increase in PEU concentra-

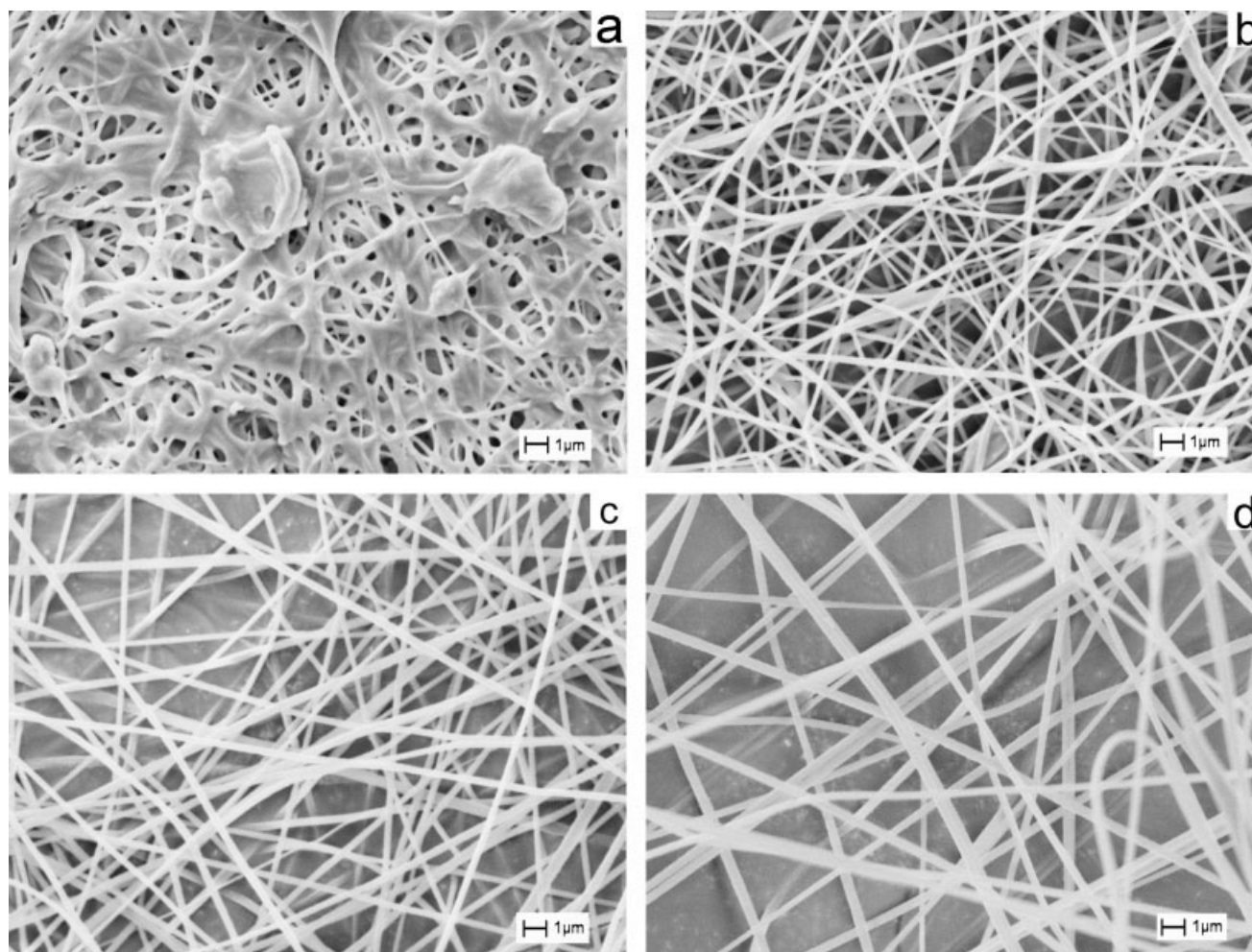


Figure 1 SEM images of noncrosslinked nanofibers: (a) PEU 6 wt % and PAN 3 wt % (PEU/PAN ratio = 2 : 1); (b) PEU 4.5 wt % and PAN 4.5 wt % (PEU/PAN ratio = 1 : 1); (c) PEU 3 wt % and PAN 6 wt % (PEU/PAN ratio = 1 : 2); and (d) PEU 0% and PAN 9 wt %.

tion. A lower solution viscosity would make the filaments easier to stretch, but the decrease in the solution conductivity weakened the fiber stretching in

electrospinning.³³ The contradicting effects on the fiber stretching resulted in a relatively small difference in fiber diameter.

TABLE I
Solution Properties, Fiber Diameter, and Mechanical Properties of Nanofiber Mats^a

Properties	PEU/PAN (2 : 1)	PEU/PAN (1 : 1)	PEU/PAN (1 : 2)
Noncrosslinked PEU/PAN			
Solution viscosity (cP)	241.0	358.5	403.0
Solution conductivity ($\mu\text{S}/\text{cm}$)	18.1	24.9	30.9
Fibre diameter (nm)	204 ± 63	212 ± 49	292 ± 60
Tensile strength (MPa)	3.69	2.03	1.55
Elongation at break (%)	54.5	51.5	48.6
Tensile modulus (MPa)	41.0	24.4	15.7
Crosslinked PEU/PAN			
Solution viscosity (cP)	248.6	360.3	520.1
Solution conductivity ($\mu\text{S}/\text{cm}$)	18.2	26.2	33.2
Fibre diameter (nm)	224 ± 45	221 ± 51	247 ± 38
Tensile strength (MPa)	6.64	3.12	2.45
Elongation at break (%)	70.5	62.0	50.5
Tensile modulus (MPa)	48.1	35.8	24.0

^a All overall polymer (PEU + PAN) concentrations were kept at 9 wt %.

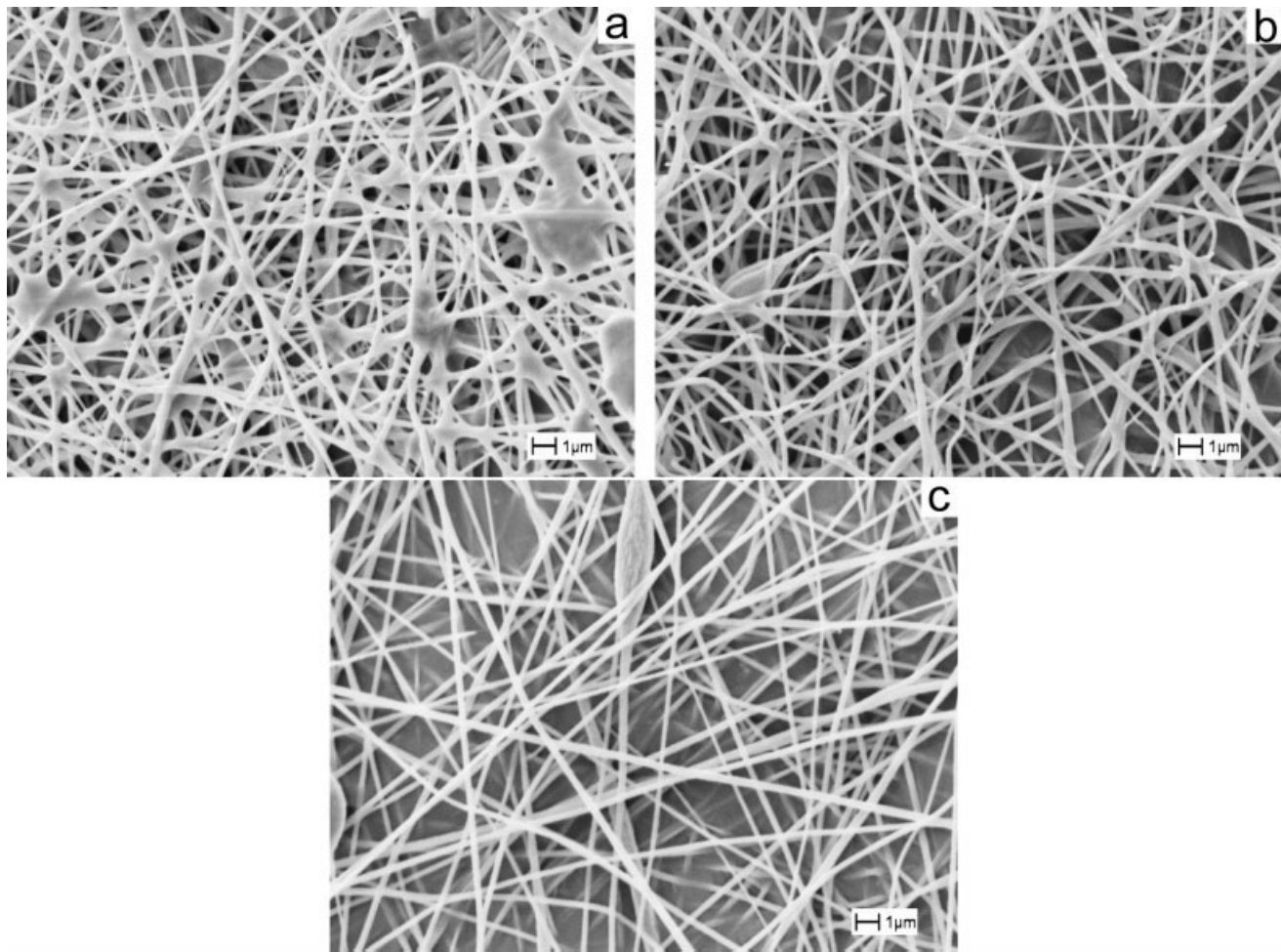


Figure 2 SEM images of crosslinked PEU/PAN fibers: (a) PEU/PAN = 2 : 1; (b) PEU/PAN = 1 : 1; (c) PEU/PAN = 1 : 2.

As long as the crosslinker and catalyst were added to the PEU/PAN solutions, the PEU chains started to crosslink. There was no sediment or murky product occurring in the solution, indicating a low degree of crosslinking. The presence of the crosslinker and cata-

lyst had a little effect on the fiber morphology. As shown in Figure 2, the crosslinked PEU/PAN fibers have similar fiber morphology to the noncrosslinked

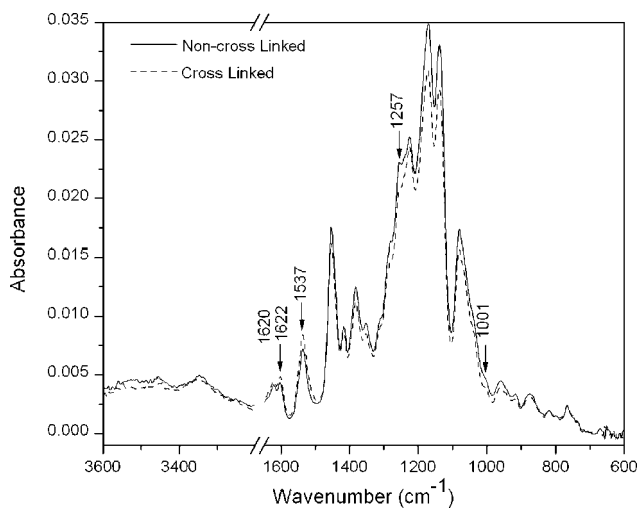


Figure 3 FTIR spectra of PEU/PAN nanofiber mats.

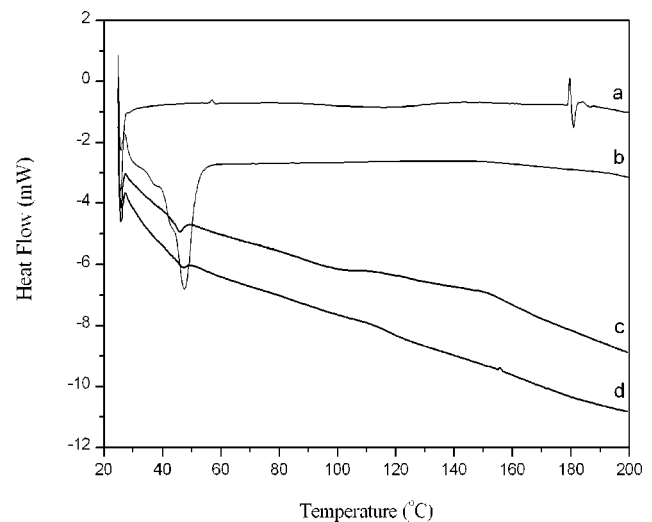


Figure 4 DSC thermograms: (a) PAN powder; (b) PEU powder; (c) noncrosslinked PEU/PAN nanofibers (PEU/PAN = 1 : 1); (d) crosslinked PEU/PAN nanofibers (PEU/PAN = 1 : 1).

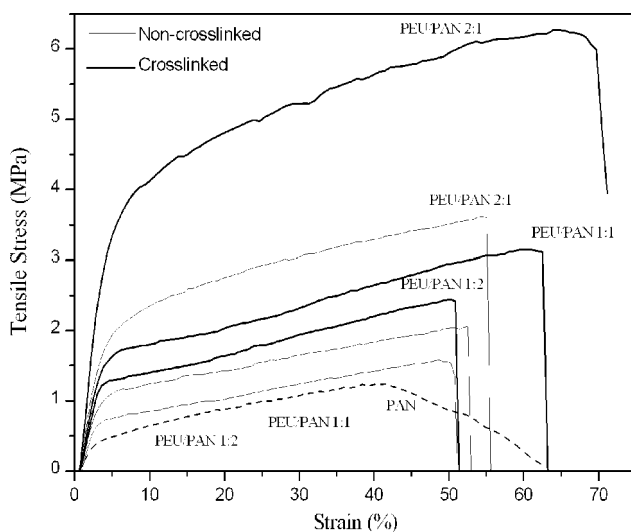


Figure 5 Tensile stress–strain curves of PEU/PAN nanofiber mats.

fibers, except that the crosslinked fibers from the 2 : 1 of PEU/PAN solution are less interconnected than the noncrosslinked fiber mat. The presence of the crosslinker led to a fiber diameter increase when the solution contained a higher composition of PEU (PEU/PAN, 2 : 1 and 1 : 1), but the fiber diameter was observed to decrease slightly when the PEU composition was low (PEU/PAN = 1 : 2). The crosslinker led to a slight increase in the solution viscosity and conductivity. With the same PEU/PAN ratio, the effect of the crosslinker on the solution viscosity was greater than on the conductivity.

The crosslinking reaction suggests the formation of new chemical bonds in the polymer. The ATR-FTIR spectra of PEU/PAN nanofibers are shown in Figure 3. The main difference in FTIR between the noncrosslinked and the crosslinked fibers is at 3200–3600,

1530–1620, and 1257 and 1001 cm^{-1} . Slight decreases in the vibration range of 3200–3600 and 1257 cm^{-1} can be attributed to the decrease in O–H/N–H stretching and asymmetric C–C–OH stretching vibrations, respectively. The increase in the vibration bands of 1622, 1620, and 1537 cm^{-1} correspond to higher C=C stretching and N–H bending vibrations due to the addition of an aromatic isocyanate crosslinker. A slight increase in the vibration at 1001 cm^{-1} indicates the formation of a C–O–C bond. These results confirm that chemical reactions have taken place between the crosslinker and the PEU polymers.

The crosslinking reaction can be further confirmed by a DSC test.²⁸ As shown in Figure 4, the DSC curve of the noncrosslinked nanofibers showed an exothermic peak at $\sim 154^\circ\text{C}$. However, such a peak disappeared when the crosslinker was involved in the electrospinning process. It clearly shows no further reaction taking place in the system with crosslinker.

The stress–strain curves under tensile loading for the noncrosslinked and the crosslinked electrospun fiber mats with different PEU/PAN ratios are shown in Figure 5, and the tensile properties obtained from these curves are listed in Table I. For both types of the fiber mats, the tensile strength, the elongation at break, and the tensile modulus are all increased with an increase in the PEU composition. The largest tensile strength, elongation at break and tensile modulus were 6.64 MPa, 70%, and 48 MPa respectively, which were all found from the crosslinked PEU/PAN nanofiber mats with the PEU/PAN ratio at 2 : 1. The improvement in tensile properties was due to the changes in material composition and nanofiber mat morphology. It was also noted that, with the blend of a high PEU composition (PEU/PAN ratio = 2 : 1), the fibers are interconnected together that effectively prevented the interfiber slippage under tensile loading,

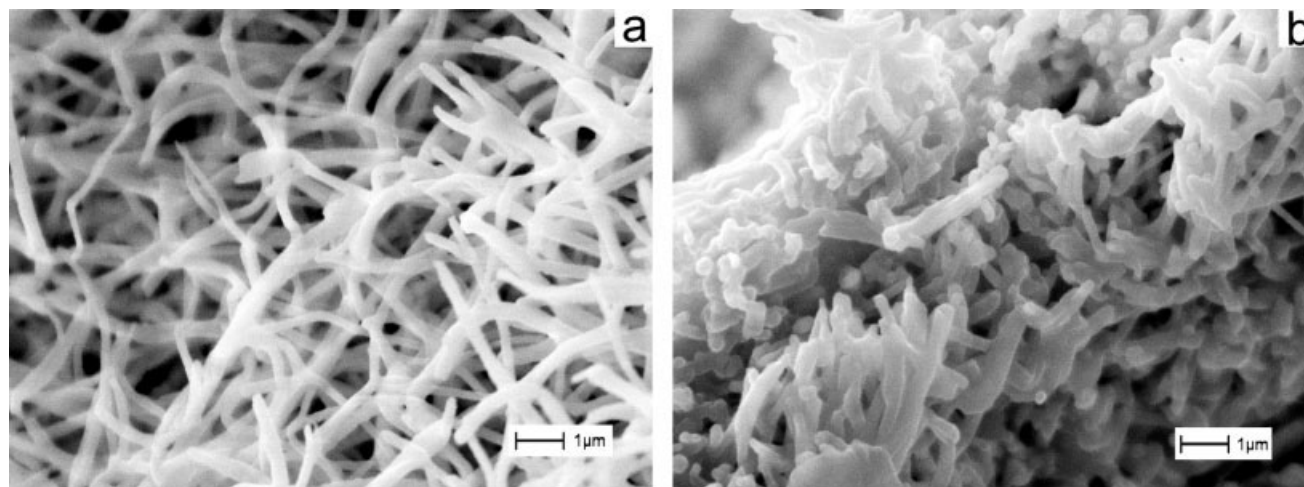


Figure 6 SEM images of fractured section of (a) noncrosslinked and (b) crosslinked PEU/PAN fiber mats (PEU/PAN = 1 : 1).

thereby leading to improved toughness. A similar result was also found from other electrospun polymer system.²²

With the same PEU/PAN ratio, the tensile strength of the crosslinked fiber mats is more than 50% greater than that of the noncrosslinked fiber mats, but the crosslinked fiber mats have a higher elongation at break than the noncrosslinked ones. At the highest concentration of PEU (PEU/PAN ratio = 2 : 1), the crosslinking led to 79% increase in the tensile strength and 29% increase in the elongation at break. These results indicate that the crosslinking reaction could enhance the interaction between PEU and PAN chains.

Compared to the PEU-containing nanofiber mat, the pure PAN fiber mat has a lower tensile strength (1.24 MPa). During the tensile test, the PAN fiber mat started to fall apart at 41.6% of strain and further extension led to the fiber slippage and then breakage (Fig. 5).

The SEM images of the fracture section of the nanofiber mats (PEU/PAN ratio = 1 : 1) are shown in Figure 6. For the noncrosslinked fiber mat, some fibers became slightly thinner at the fractured sections. However, the fractured fiber section in the crosslinked nanofiber mat tends to maintain its original morphology.

CONCLUSIONS

This study has demonstrated that the electrospun nanofiber mats from an elastomer-containing polymer blend can be toughened significantly by increasing the composition of the elastomeric polymer (e.g., PEU), and that the mechanical properties of nanofiber mats can be further improved by the formation of a lightly crosslinked elastomeric network in the polymer blend. The improvement in toughness can be attributed to the elastomeric network that restricts the motion of polymer chains during tensile loading, and also the interconnected fiber web which effectively prevents interfiber slippage in the mat. This concept should be applicable to other electrospun elastomeric polymer systems.

References

1. Reneker, D. H.; Chun, I. *Nanotechnology* 1996, 7, 216.
2. Theron, S. A.; Zussman, E.; Yarin, A. L. *Polymer* 2004, 45, 2017.
3. Li, D.; Xia, Y. *Adv Mater* 2004, 16, 1151.
4. Subbiah, T.; Bhat, G. S.; Tock, R. W.; Parameswaran, S.; Ramkumar, S. S. *J Appl Polym Sci* 2005, 96, 557.
5. Li, D.; Wang, Y.; Xia, Y. *Adv Mater* 2004, 16, 361.
6. Sun, Z.; Zussman, E.; Yarin, A. L.; Wendorff, J. H.; Greiner, A. *Adv Mater* 2003, 15, 1929.
7. Li, D.; Xia, Y. *Nano Lett* 2004, 4, 933.
8. Lin, T.; Wang, H.; Wang, X. *Adv Mater* 2005, 17, 2699.
9. Bhattarai, S. R.; Bhattarai, N.; Yi, H. K.; Hwang, P. H.; Cha, D. I.; Kim, H. Y. *Biomaterials* 2004, 25, 2595.
10. Kim, K.; Luu, Y. K.; Chang, C.; Fang, D.; Hsiao, B. S.; Chu, B.; Hadjiargyrou, M. *J Controlled Release* 2004, 98, 47.
11. Abidian, M. R.; Kim, D.-H.; Martin, D. C. *Adv Mater* 2006, 18, 405.
12. Ma, Z.; Kotaki, M.; Ramakrishna, S. *J Memb Sci* 2005, 256, 115.
13. McCann, J. T.; Marquez, M.; Xia, Y. *J Am Chem Soc* 2006, 128, 1436.
14. Bergshoef, M. M.; Vancso, G. J. *Adv Mater* 1999, 11, 1362.
15. Shao, C.; Yang, X.; Guan, H.; Liu, Y.; Gong, J. *Inorg Chem Commun* 2004, 7, 625.
16. Wang, X.; Drew, C.; Lee, S. H.; Senecal, K. J.; Kumar, J.; Samuelson, L. A. *J Macromol Sci* 2002, A39, 1251.
17. Zhang, D.; Liu, Z.; Tang, C.; Liu, X.; Han, S.; Lei, B.; Zhou, C. *Nano Lett* 2004, 4, 1919.
18. Ding, B.; Kim, J.; Miyazaki, Y.; Shiratori, S. *Sens Actuators* 2004, B101, 373.
19. Kim, J. R.; Choi, S. W.; Jo, S. M.; Lee, W. S.; Kim, B. C. *J Electrochem Soc* 2005, 152, 295.
20. Yao, L.; Haas, T. W.; Guiseppi-Elie, A.; Bowlin, G. L.; Simpson, D. G.; Wnek, G. E. *Chem Mater* 2003, 15, 1860.
21. Huang, C.; Chen, S.; Heneker, D. H.; Lai, C.; Hou, H. *Adv Mater* 2006, 18, 668.
22. Lee, K. H.; Kim, H. Y.; Ryu, Y. J.; Kim, K. W.; Choi, S. W. *J Polym Sci Polym Phys* 2003, 41, 1256.
23. Ko, F.; Gogotsi, Y.; Ali, A.; Naguib, N.; Ye, H.; Yang, G.; Li, C.; Willis, P. *Adv Mater* 2003, 15, 1161.
24. Sen, R.; Zhao, B.; Perea, D.; Itkis, M. E.; Hu, H.; Love, J.; Bekyarova, E.; Haddon, R. C. *Nano Lett* 2004, 4, 459.
25. Ge, J. J.; Hou, H.; Li, Q.; Graham, M. J.; Greiner, A.; Reneker, D. H.; Harris, F. W.; Cheng, S. Z. D. *J Am Chem Soc* 2004, 126, 15754.
26. Mack, J. J.; Viculis, L. M.; Ali, A.; Luoh, R.; Yang, G.; Hahn, H. T.; Ko, F. K.; Kaner, R. B. *Adv Mater* 2005, 17, 77.
27. Hong, J. H.; Jeong, E. H.; Lee, H. S.; Baik, D. H.; Seo, S. W.; Youk, J. H. *J Polym Sci Polym Phys* 2005, 43, 3171.
28. Ding, B.; Kim, H.-Y.; Lee, S.-C.; Shao, C.-L.; Lee, D.-R.; Park, S.-J.; Kwag, G.-B.; Choi, K. J. *J Polym Sci Polym Phys* 2002, 40, 1261.
29. Wang, X.; Chen, X.; Yoon, K.; Fang, D.; Hsiao, B. S.; Chu, B. *Environ Sci Technol* 2005, 39, 7684.
30. Choi, S.-S.; Hong, J.-P.; Seo, Y. S.; Chung, S. M.; Nah, C. *J Appl Polym Sci* 2006, 101, 2333.
31. Brown, S. B. In *Polymer Blends Handbook*; Utracki, L. A., Ed.; Kluwer Academic: London, 2002.
32. Lee, W. H. In *Polymer Blends and Alloys*; Folkes, M. J.; Hope, P. S., Eds.; Blackie Academic & Professional: London, 1993.
33. Lin, T.; Wang, H.; Wang, H.; Wang, X. *Nanotechnology* 2004, 15, 1375.
34. Lin, T.; Wang, H.; Wang, H.; Wang, X. *J Mater Sci Technol* 2005, 21, 9.