ELSEVIER

Polymer 40 (1999) 4035–4039

polymer

Conductive IPN based on polypyrrole and silicon crosslinked styrene–isoprene–styrene triblock copolymer

L.H. Gan*, Y.Y. Gan, W.S. Yin

School of Science, Nanyang Technological University, 469 Bukit Timah Road, Singapore 259756, Singapore

Received 3 August 1998; accepted 20 August 1998

Abstract

The conducting interpenetrating polymer network (IPN) is prepared by sequential crosslinking of tetrethyl orthosilicate (TEOS) with acrylic acid grafted styrene–isoprene–styrene triblock copolymer (SIS) and polypyrrole doped with dodecylbenzenesulfonic acid (DBSA). The resulting IPN not only has good conductivity, but also exhibits far superior thermal stability. Various factors affecting the properties of conductive IPNs are investigated. The amounts of water and TEOS used have a profound effect on the conductivity. Significantly, under appropriate experimental conditions, a conductive IPN with conductivity as high as that of pure PPyDBSA has been prepared. Heating the conductive IPNs to 140°C has generally caused the conductivity to decrease. However, samples with conductivity relatively unaffected by the heat treatment can be prepared with proper selections of H_2O/TEOS ratio. The effect of heating on the conductivity is discussed. All the IPNs have excellent thermal stability as clearly shown by the results of thermal gravitational analysis (TGA). The morphologies of the IPN films are investigated using a scanning electron microscope (SEM).

Keywords: Polypyrrole; SIS; Conductive interpenetrating polymer network

1. Introduction

Conducting polymers have attracted much research interest over the past two decades. Today, they remain among the most exciting polymeric materials being constantly investigated, partly motivated by their recent discovered application in the fabrication of light-emitting diodes (LEDs) [1,2]. Composites of conducting polymers have been investigated for some specific practical applications [3–5]. More recently, monomers such as those shown in Scheme 1 have been used successfully to prepare conductive coatings on glass substrates [6,7].

Conducting composites based on silicon oxide have also been reported [8]. The thermal stability of the conducting composite has been greatly improved due to the introduction of silicon oxide into the composite [8]. We now report the synthesis of a new conducting interpenetrating polymer network (IPN) based on silicon crosslinked styrene–isoprene–styrene triblock copolymer (SIS) and polypyrrole (PPy).

2. Experimental section

2.1. Materials

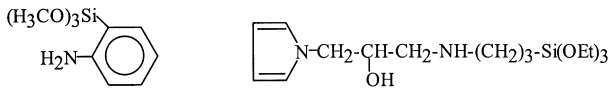
The molar ratio of styrene/isoprene in styrene–isoprene–styrene triblock copolymer (SIS) measured by NMR was 22:78. Acrylic acid (AA) and pyrrole were distilled before use. Benzoxyl peroxide (BPO) was purified by dissolving in chloroform, and precipitated with ethanol and dried under vacuum at room temperature. Tetraethyl orthosilicate (TEOS), dodecyl benzene sulfonic acid (DBSA), ammonium persulfate (APS) and other chemicals were used as received.

2.2. Synthesis of acrylic acid grafted SIS

Here 32 g SIS and 8 g acrylic acid were dissolved in a 480 ml toulene/ethanol mixture (12:1 wt/wt); 1 g of BPO in 40 g of the mixed solvent was added dropwise at 80°C, and the reaction mixture was stirred under a nitrogen atmosphere for 6 h. The graft polymer was precipitated in methanol and the precipitate was dried in a vacuum oven to constant weight. The AA/SIS ratio (wt/wt) in the graft polymer composition was 20:80 as determined by element analysis.

* Corresponding author. Fax: + 65-4698928.
E-mail address: ganlh@nievax.nie.ac.sg (L.H. Gan)

0032-3861/99/$ - see front matter
PII: S0032-3861(98)00624-7



Scheme 1.

2.3. Preparation of polypyrrole (PPy)

In this case, 0.075 mol of DBSA and 0.15 mol of pyrrole were dissolved in 250 ml of distilled water with vigorous stirring. Then 0.03 mol of APS in 50 ml of distilled water was slowly added to the above solution maintained at 0°C. The reaction was allowed to proceed for 40 h and then terminated by pouring into methanol. The resultant PPy powder was filtered and washed sequentially with distilled water, methanol and acetone several times, and dried in a vacuum oven at 25°C for 12 h.

2.4. Preparation of PPyDBSA chloroform solution

The PPy powder obtained (1 g) was completely dissolved with ultrasonification in 50 ml of chloroform, aided with the addition of 1 g of DBSA. This is referred to as PPyDBSA chloroform solution.

2.5. Synthesis of conductive IPN based on PPy and silicon crosslinked AA-g-SIS

A fixed amount of TEOS, 0.8 g AA-g-SIS and a small amount of distilled water were dissolved in 12 g of tetrahydrofuran (THF). The mixture was refluxed for 1 h and cooled. Then 10 g of PPyDBSA chloroform solution was added, and the mixture was stirred for about 24 h at room temperature. The mixture was cast onto a substrate plate (teflon or glass) which was then placed in open air at room temperature for the solvent to evaporate off. The free-standing films obtained were washed several times with distilled water, pressed between glass plates, and dried in vacuum for more than 12 h.

2.6. Measurement

The electrical conductivity of the composite films was measured at room temperature by the standard four-probe method. The phase morphological characteristics of the samples were studied by using a Cambridge S-360 scanning electron microscope (SEM). The tensile testing was performed with an Instron Testing Instrument (model 4302) at room temperature with a cross-head speed of 20 mm/min. Thermal degradation of the samples was examined by using a Perkin-Elmer 7 system with TGA thermogravimetric analyzer. The sample size was about 10 mg and was analyzed from 40 to 600°C with a heating rate of 40.0°C/min under a nitrogen atmosphere.

3. Results and discussion

Table 1 lists the conductivity of PPyDBSA/AA-g-SIS silicon crosslinked conducting IPNs. It can be seen that under a constant amount of H_2O, increasing TEOS from 0.1 (Y10) to 0.5 g (Y9) caused little change in conductivity. However, by increasing the water content from 0.01 (Y10) to 0.1 g (Y11), the conductivity increases from 2.1×10^{-1} to 1.2 S/cm which is as high as that of the pure PPyDBSA. These results suggest that the conductivity is strongly dependent upon the silicon network structure and the nature of the residue active groups within the network. As the amount of distilled water increases, more Si–OH is produced through the hydrolysis of TEOS. Condensation reaction among Si–OH groups leads to the formation of Si–O–Si networks. It is believed that the residue Si–OH groups in the network could interact strongly with PPyDBSA, causing the PPy polymer chain to be more extended, thus producing a better conductive phase structure. Thus the higher H_2O content in sample Y11 has resulted in the generation of more Si–OH groups, and hence better conductivity.

Table 1 also shows the change of conductivity after the samples are subjected to the heat treatment at 140°C. It can be seen that the heat treatment has no effect on the conductivity of the pure PPyDBSA (Y7). However, the conductivity of samples Y10 and Y11 decreases by more than one order of magnitude for the air surfaces, whereas for the bottom surfaces, the conductivity became too low to be measured. As it has already been established that the PPyDBSA is unaffected by the heat treatment, the decrease

Table 1
Conductivity of PPyDB/AA-g-SIS silicon crosslinked conducting IPN

Code	IPN	H_2O (g)	TEOS (g)	PPy/AA-g-SIS (wt/wt)	Conductivity (S/cm)		Conductivity (S/cm)[a]	
					Air surface	Bottom surface	Air surface	Bottom surface
Y7	PPyDBSA	0	0	100/0	1.2×10^{0}	1.2×10^{0}	1.7×10^{0}	1.7×10^{0}
Y10	PPyDBSA/AA-g-SIS	0.01	0.1	20/80	5.1×10^{-1}	2.0×10^{-1}	1×10^{-2}	—[b]
Y9	PPyDBSA/AA-g-SIS	0.01	0.5	20/80	2.1×10^{-1}	3.1×10^{-1}	2.3×10^{-1}	4.4×10^{-1}
Y11	PPyDBSA/AA-g-SIS	0.1	0.1	20/80	1.2×10^{0}	3.1×10^{-1}	9×10^{-2}	—
Y16	SIS-g-AA	0.01	0.1	0/100	Insulating			

[a] After treatment of samples by heating to 140°C at 3.5°C/min and cooling down to room temperature naturally in vacuum oven.
[b] Unable to measure.

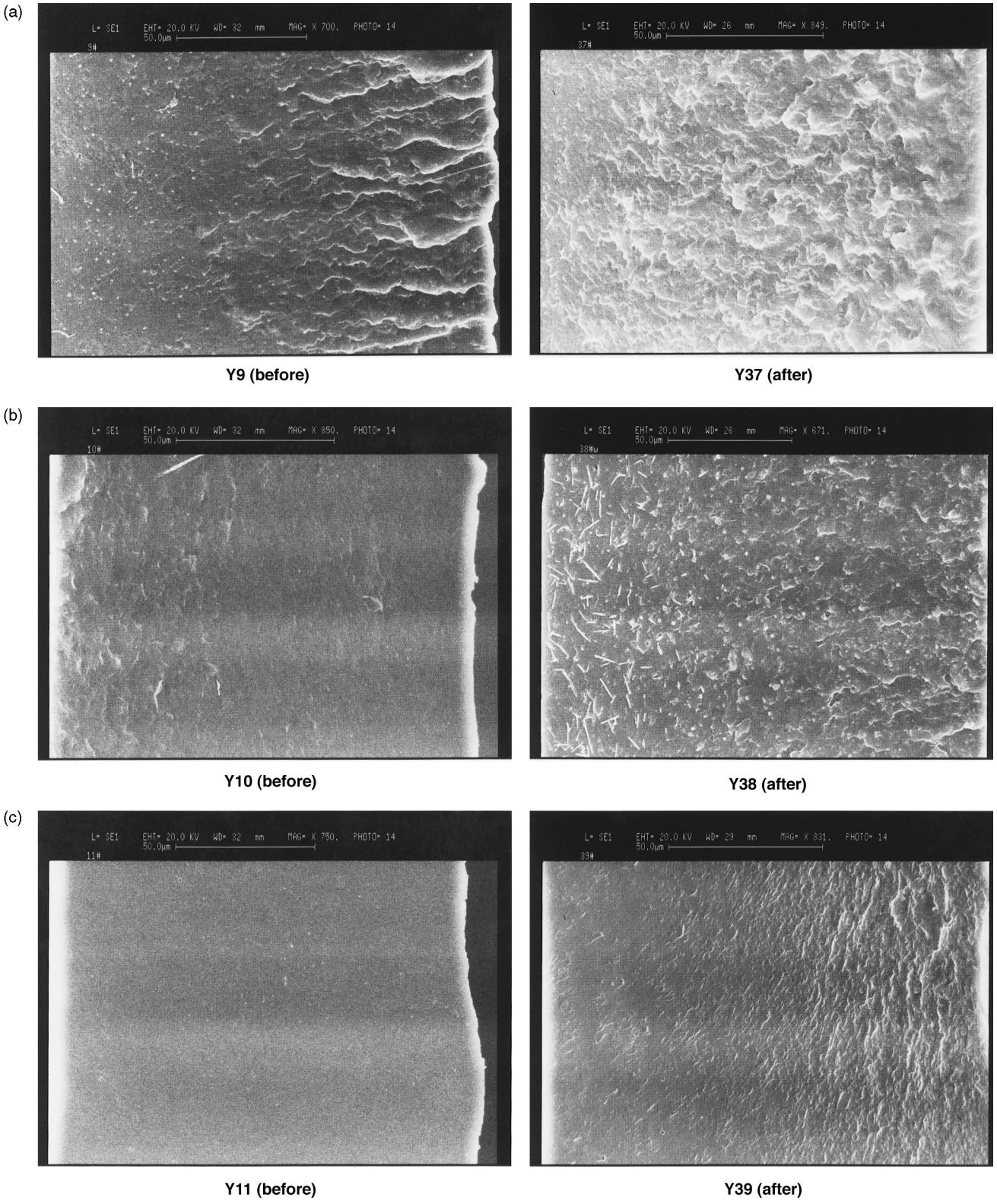
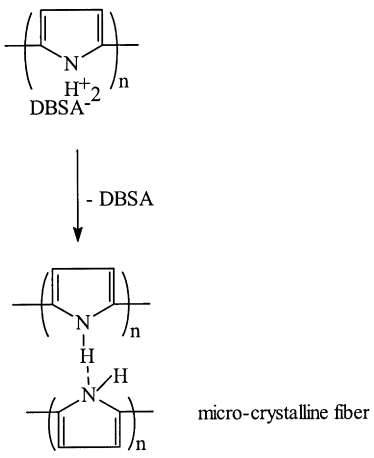


Fig. 1. (a) SEM micrographs of samples Y9 (before heat treatment) and Y37 (after heat treatment). (b) SEM micrographs of samples Y10 (before heat treatment) and Y38 (after heat treatment). (c) SEM micrographs of samples Y11 (before heat treatment) and Y39 (after heat treatment).



Scheme 2.

in the conductivity for samples Y10 and Y11 must have been caused by the change in the structure of the network. The decrease in the conductivity is attributed to the decrease in the Si–OH groups due to further condensation reactions forming more Si–O–Si networks. In addition, the decrease in conductivity is found to be associated with a change in morphology of the sample (see the discussion later). Interestingly, the heat treatment has little effect on the conductivity of Y9. It should be noted that sample Y9 has a much lower H_2O/TEOS ratio. It is believed that under this condition, less residue Si–OH groups remain in the network. The higher content of TEOS in sample Y9 has yielded a network with higher crosslinked density. As a result, the sample is thermally more stable. The above results have demonstrated that thermally stable conductive polymer network can be produced if the experimental conditions are correctly chosen.

The SEM micrographs of the IPNs are shown in Fig. 1. With increasing ratio of H_2O/TEOS, it can be seen that the sample morphology changes from rough for Y9 to very smooth for Y11. The high H_2O/TEOS ratio for Y11 has generated more Si–OH groups which have strong interaction with PPyDBSA, yielding a very homogeneous phase with high conductivity. On the other hand, the rough surface of Y9 is caused by the relatively high content of TEOS. In fact, SiO_2 particles are visible in this sample. After heat treatment, the surfaces of all three samples Y9, Y10 and Y11 become coarser as a result of further condensation reaction of Si–OH groups, as shown by SEM micrographs Y37, Y38 and Y39, respectively. Interestingly, micro-crystalline fibres are found to form at the bottom surface of Y10 after heating to 140°C (micrograph Y38). The micro-crystalline fibres of about 10 μm in length are non-conducting as the bottom surface of Y10 is insulating. The formation of the micro-crystalline fibres is believed to result from the de-doping of DBSA from the conducting polymer (PPyDBSA) as shown in Scheme 2.

The fact that the de-doping of DBSA is found only in the conducting IPNs but not in the pure PPyDBSA suggests that DBSA is more labile in the IPNs. The residue –COOH and –OH groups in the IPNs could replace DBSA in the doping of PPy, causing the easier release of DBSA on heating.

Fig. 2 shows the TGA curves of Y7, Y9, Y10, Y11 and Y16 (matrix without PPyDBSSA). Pure PPyDBSA (Y7) is least stable. At about 300°C it begins to decompose rapidly. The conductive IPNs, on the other hand, show superior thermal stability. Furthermore, samples Y9, Y10 and Y11 are even more stable than Y16. These samples show significant weight loss occurring only at temperatures above 400°C. Apparently, the presence of silicon oxide has enhanced the thermal stability of the matrix. The TGA thermograms also show that there are only small weight losses at temperatures of around 140°C, due mainly to the losses of H_2O and perhaps some DBSA as well. This is in line with the earlier suggestion that the decreases in the conductivity of Y10 and Y11 are caused by the continuous reaction of Si–OH in the network matrix.

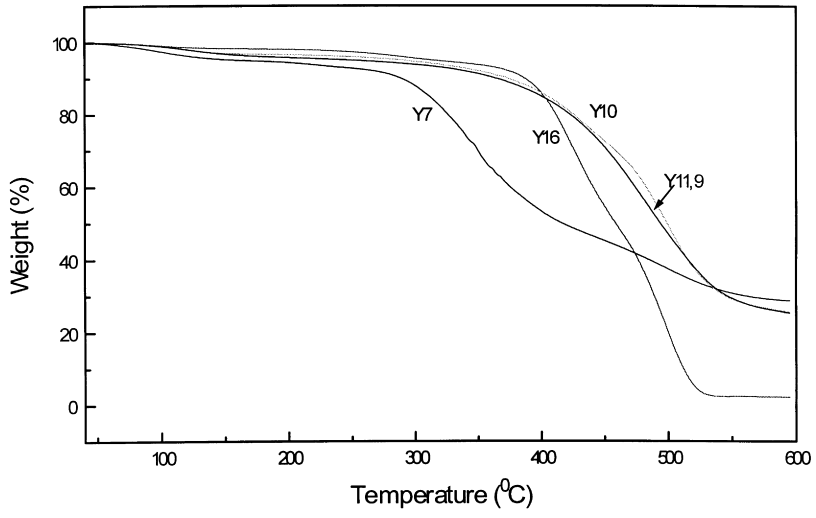


Fig. 2. TGA thermograms of PPy/SIS-g-AA-silicon conducting IPNs.

Table 2
The mechanical properties of PPyDBSA/AA-g-SIS silicon crosslinked conducting IPNs

Code	Elongation yield (%)	Tensile strength (MPa)	Young modulus (MPa)
Y9	114	8.64	27.2
Y11	115	8.9	24.5
Y16	733	5.73	30.1

Table 2 shows the mechanical properties of PPyDBSA/AA-g-SIS silicon crosslinked conducting IPN films. The mechanical properties of these conductive IPN films are good. For example, the elongation yield, tensile strength and Young's modulus of sample Y11 are 115%, 8.9 MPa and 24.5 MPa, respectively. Compared to the pure silicon crosslinked network matrix, Y16, the conductive IPNs Y9 and Y11 have lower elongation yield and higher tensile strength.

4. Conclusion

A series of PPyDBSA/AA-g-SIS silicon crosslinked conducting IPNs have been successfully synthesised. These conductive IPNs exhibit good conductivity and mechanical properties. The conductivity and its stability are strongly affected by the presence of the active Si–OH groups in the silicon network. Under suitable synthetic conditions, the conductivity of the IPN prepared is as high as that of the pure conducting polymer, PPyDBSA. Heating of the IPN samples at 140°C has caused the conductivity to change significantly, depending on the experimental conditions used in the sample preparation. Interestingly, formation of insulating micro-crystalline fibres is observed in sample Y10 after heat treatment at 140°C. The thermal stability of the conductive IPNs is far superior when compared to that of the pure PPyDBSA.

Acknowledgements

LHG thanks NTU for research grants ARC 1/97 GLH and WSY thanks NSTB for the post-doctoral fellowship, respectively.

References

[1] Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, Burns PL, Holmes AB. Nature 1990;347:539.
[2] Gustafsson G, Cao Y, Treacy GM, Klavetter F, Colaneri N, Heeger AJ. Nature 1992;357:477.
[3] Liu G, Freund MS. Macromolecules 1997;30:5660.
[4] Bergeron H-Y, Dao LH. Macromolecules 1992;25:3332.
[5] Ryder KS, Morris DG, Cooper JM. J Chem Soc Chem Commu 1995:1471.
[6] Cattery H, Audebert P, Attias AJ. Synth Met 1998;93:127.
[7] Faverolle F. Thesis, University of Paris 6, 16 May 1994.
[8] Yin WS, Liu HW, Gan LH. J Appl Polym Sci 1998, in press.