

Synthesis and Properties of PSF/PTMEG Copolyurethanes

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ABSTRACT: A series of polysulfide (PSF)/polyoxytetramethylene glycol (PTMEG) copolyurethanes have been synthesized, which were based on isophorone diisocyanate-terminated liquid PSF, 2,4-toluene diisocyanate-terminated PTMEG, and 2,5-diamino-3,6-dimethylmercaptotoluene (Ethacure-300). Fourier transform infrared spectroscopy spectra have established the formation of PSF polyurea and PSF/PTMEG copolyurethanes. The properties were investigated by DMA, stress-strain, and hardness

analysis. Those results showed that the miscibility of the copolyurethane increases with the increase of PSF polyurea content. With the increase in PTMEG polyurethane content, the tensile strength and elongation increase, whereas the Shore A hardness decreases. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1611–1615, 2007

Key words: polysulfide; PTMEG; copolyurethane; synthesis; properties

INTRODUCTION

Polyurethanes (PUs) consist of hard and soft segments. The soft segment is commonly a polyether or polyester, whereas the hard segment contains an aromatic diisocyanate condensed with a low molecular weight diol.¹ PUs with polyoxytetramethylene glycol (PTMEG) as the soft segments have outstanding dynamic properties, hydrolysis resistance, microbe resistance, resilience, low-temperature flexibility, and abrasion resistance.²

The original polysulfide (Thiokol) rubbers were solid materials. Liquid polysulfide (PSF) polymers were introduced in the 1940s. These liquid PSF polymers are produced by the short-chain dichlorohydrocarbons with sodium polysulfide. Chemical oxidation of the mercaptan groups, by inorganic and peroxide catalysts, leads to the formation of durable, flexible, and adhesive elastomers.³ These elastomers have wide application in industry, particularly as sealants. They adhere to glass, steel, wood, and concrete, and they have a number of very desirable properties, exhibit good low-temperature properties, low water-vapor transmission, especially long-term resistance to solvents and sunlight.⁴ The liquid PSF with thio end-groups can also react with diisocyanates.⁵ A series of PSF-based polyurea have been synthesized via solution polymerization, with based on the liquid PSF as soft segment, and isophorone

diisocyanate (IPDI) and Ethacure-300 as hard segments. The structure and mechanical properties of these elastomers also have been investigated.⁶ Therefore, liquid PSF oligomers can be utilized in the synthesis of PU copolymers as soft segments. Several publications have reported on investigations of structure and properties of liquid PSF-based PU modified with other materials.^{7,8}

The present work was to incorporate the attractive characteristics of the liquid PSF and PTMEG soft segment to obtain new PUs by melt polymerization. The properties of these PUs based on aromatic or aliphatic diisocyanates with Ethacure-300 (chain extender) as hard segment and PSF/PTMEG as soft segments were studied with a variety of techniques.

EXPERIMENTAL

Materials

The materials used and their designations are listed below. LP1000 (liquid PSF, $M_n = 100 \pm 200$; Jinxi Research Institute of Chemical Industry, China), PTMEG2000 ($M_n = 2000 \pm 100$; Jinan Shengquan, China), IPDI (Eq. Wt = 111; CRENDVA Speziaichemie, Germany), 2,4-toluene diisocyanate (TDI) (Eq. Wt = 87; Changshu Yonghua Fine Chemistry, China), Ethacure-300 (2,5-diamino-3,6-dimethylmercaptotoluene; Albemarle, Baton Rouge, LA). Before use, liquid PSF and PTMEG were dewatered under vacuum at 100°C for 3 h and 110°C for 2 h, respectively. Other reagents were used directly without further purification.

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Preparation of PU prepolymer

PU prepolymer was prepared by reacting TDI with PTMEG. TDI (2.1 equiv weight) was poured in a three-neck flask at first. Then proper amount (1 equiv) of PTMEG was poured into the flask. The mixture was vigorously agitated by a mechanical stirrer. The reaction occurred under dry nitrogen atmosphere at 80°C. The isocyanate content of the reaction mixture was determined by using di-*n*-butyl amine titration method.⁹ The reaction was stopped when the isocyanate content reached a theoretical value (all PTMEG prepolymer molecules end-capped by TDI).

Preparation of PSF-based polyurea prepolymer

Polyurea prepolymer was prepared by reacting IPDI with liquid PSF. IPDI (2.1 equiv weight) was poured in a three-neck flask at first. Then proper amount (1 equiv) of PSF was poured into the flask. The mixture was vigorously agitated by a mechanical stirrer. The reaction occurred under dry nitrogen atmosphere at a temperature of ~ 120°C. During the reaction period, samples were drawn for infrared analysis. The reaction was stopped until the absorption peak at 2556 cm⁻¹ disappeared.

Preparation of PSF/PTMEG copolyurethanes

For the synthesis of PSF/PTMEG copolyurethanes, PU prepolymer and PSF-based polyurea prepolymer in various weight ratios were mixed completely using a high-torque stirrer. Following the addition of the Ethacure-300, the viscous solution was degassed to remove trapped bubbles and cast into a poly(tetrafluoroethylene) dish and then left for further reaction. The membrane formed was postcured at 80°C for 24 h.

Characterization

FTIR analysis

The Fourier transform infrared (FTIR) spectra were performed on films cast onto KBr salt plates with a EQUINOX 55 (BRUKER, Germany) spectrometer. The attenuated total reflection (ATR)/FTIR spectra were used to test the copolyurethane films.

Dynamic mechanical analysis

All measurements were performed with a Mark IV Dynamic Mechanical Analyzer. The samples were measured in the tension mode at a fixed frequency of 10 Hz from -100 to 100°C using a heating ramp of 3°C/min. The 1-mm-thick test specimens were cut

into a rectangular shape with 40 × 4 mm² dimensions.

Stress-strain analysis

The tensile properties were determined by using an Instron 4206 universal testing machine (Instron, Canton, MA) at (23 ± 1)°C with a 100-kN load cell at a 5 cm/min cross-head speed. The test bars were dumbbell-shaped with a width and thickness of the narrow section of 6 and 2 mm, respectively. The gauge length was 33 mm. The results were taken as an average from measurements of at least three specimens.

Shore A hardness measurement

Shore LX-A instrument was used to test Shore A hardness. The test was conducted at room temperature (23°C ± 1°C). Hardness values quoted are an average of eight readings taken at random over the entire specimen surface.

RESULTS AND DISCUSSION

FTIR analysis

The FTIR spectra of the PSF, oligomer (NCO-PSF-NCO), and PSF-based thio-polyurea (PSF PU) are shown in Figure 1. The -SH absorption peak at 2556 cm⁻¹ disappeared, and the formation of thiourethane linkages, as indicated by the absorbance peaks at 3300 cm⁻¹ (-NH) and 1676 cm⁻¹ (C=O), confirmed that -SH of PSF entirely reacted with IPDI. The main IR bands for C=O are observed in 1700–1630 cm⁻¹, and no band was found at 1730 cm⁻¹.

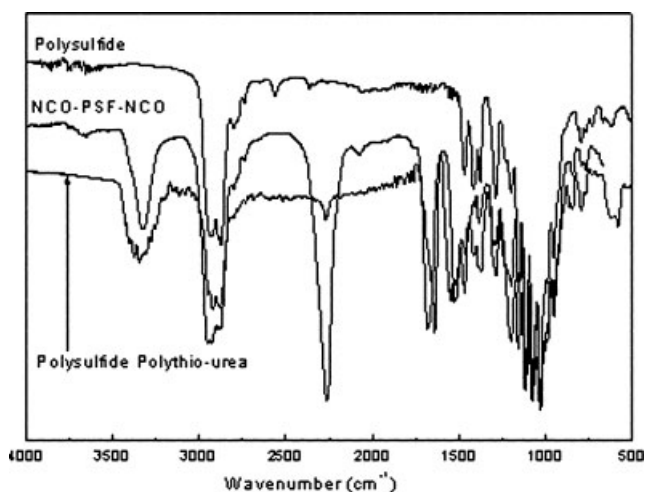


Figure 1 FTIR spectra of liquid polysulfide, NCO-LP-NCO, and polysulfide-based polyurea.

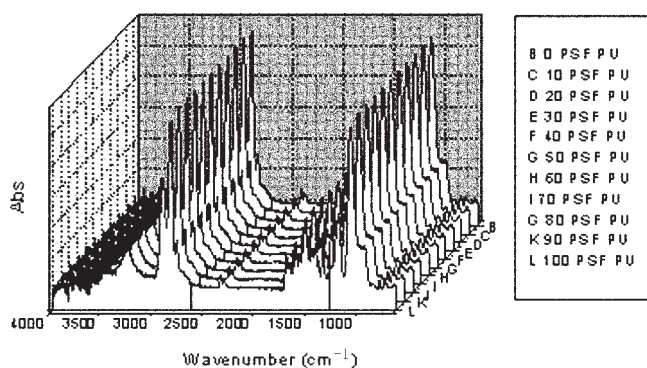


Figure 2 ATR-FTIR spectra of the PSF/PTMEG copolyurethane compositions.

The bands at about 2270 cm^{-1} , which represent asymmetrical stretching vibration of $-\text{NCO}$ groups, is the most specific bands for isocyanate. The peaks at $1600\text{--}1500\text{ cm}^{-1}$ are the vibration bands of urethane groups. As results from all samples of ATR-FTIR spectra (Fig. 2), the peaks at about 2270 cm^{-1} diminished and the peaks at $1600\text{--}1500\text{ cm}^{-1}$ appeared. Thus the results of ATR-FTIR spectra indicate that the $-\text{NCO}$ groups of prepolymers react with $-\text{NH}_2$ of the chain extender (Ethacure-300).

Dynamic mechanical analysis

The morphology and miscibility of two polymer components greatly influence the mechanical properties of a polymer blend and can be assessed from dynamic mechanical analysis (DMA) data. Two separate loss factor peaks indicate an immiscible system, whereas one peak indicates a high degree of miscibility.¹⁰ The loss factor versus temperature data for the PSF/PTMEG copolyurethanes composition series

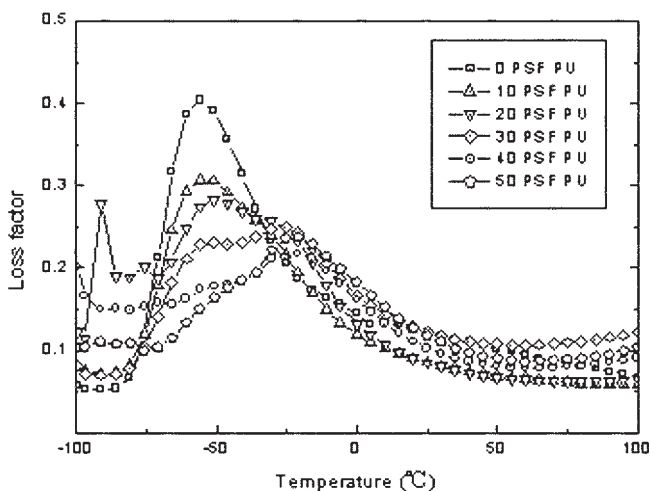


Figure 3 Loss factor ($\tan \delta$) versus temperature for PSF/PTMEG copolyurethane compositions from 0 : 100 to 50 : 50.

are shown in Figure 3. As expected for the immiscible polymer pair, two separate loss factor transitions were observed in the composition series from the PSF polyurea weight fraction from 0 : 100 to 50 : 50. And the loss of intensity in the $\tan \delta$ peaks of the PTMEG PU phase resulted from a decreased weight fraction of the PTMEG PU. Whereas the height of the $\tan \delta$ peaks of the PSF polyurea phase shift slightly as the weight fraction of the PSF polyurea content increases. The PTMEG PU transition slightly shifted to higher temperature with increasing PSF polyurea weight fraction. The increase in the PTMEG PU transition at a little higher PSF polyurea content (PSF polyurea weight from 0 : 100 to 50 : 50) indicates that PTMEG PU segments were less free to move in the copolyurethanes than in pure PTMEG PU network. Reason for this could be an increase in crosslink density through intermolecular interacting between PSF polyurea and PTMEG PU segments.

As Figure 4 shows, as the PSF polyurea content increased to 60% the peak of loss $\tan \delta$ of the sample move to a higher temperature. Similar trends are observed when the PSF polyurea content is 70, 80, and 90%. The transition region is broadened as the PSF polyurea content increased from 60 to 90%. This can be accounted for the small amounts of intermixing by the PTMEG PU segments and PSF polyurea segments when the PTMEG PU contents decrease to below 40%. The PTMEG PU segments and PSF polyurea segments have good miscibility. Only interpenetrating polymer networks (IPNs) can result in broad transition,¹¹ and thus it can be assured there are networks interpenetrating between the PTMEG PU network and PSF polyurea network when the PSF polyurea content increased from 60 to 90%.

The loss modulus temperature plots of the PSF/PTMEG copolyurethanes composition series are

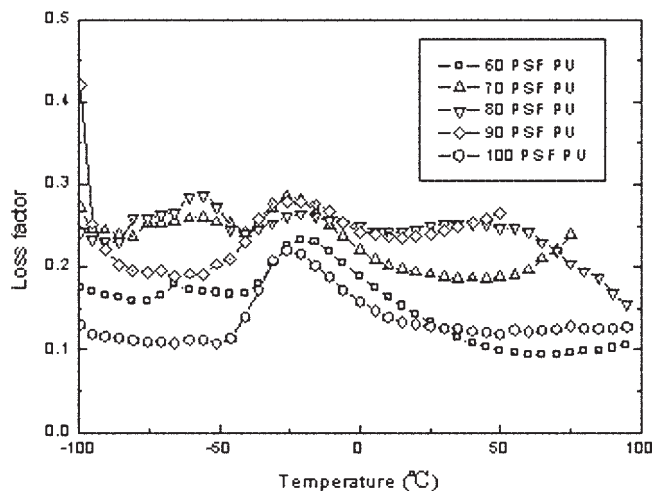


Figure 4 Loss factor ($\tan \delta$) versus temperature for PSF/PTMEG copolyurethane compositions from 60 : 40 to 100 : 0.

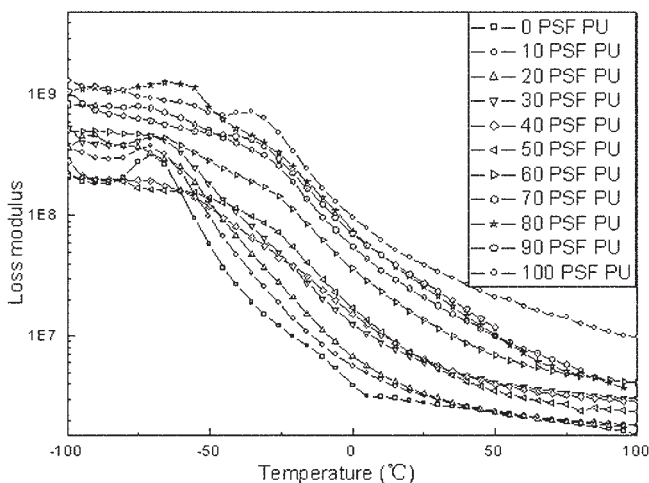


Figure 5 Loss modulus versus temperature for PSF/PTMEG copolyurethane compositions.

shown in Figure 5. A pronounced drop in modulus occurred at the PSF polyurea and PTMEG PU transition with increasing weight fraction of PTMEG PU. But the modulus of PSF polyurea content at 80% is not accordance with this order. Similar trend is found in Figure 6. This could be due to the changing of microphase structure¹¹ at 80:20 PSF/PTMEG copolyurethanes.

Stress–strain analysis

The mechanical properties of the composition series were investigated by tensile testing and Shore A hardness measurements. Plots of the stress and strain at break versus copolyurethane composition are shown in Figure 7. Stress at break values were low (10 MPa) for the 20 : 80 and 80 : 20 PSF/PTMEG copolyurethanes, but they increased with increasing PSF polyurea content to 20 MPa for the 40:60 PSF/

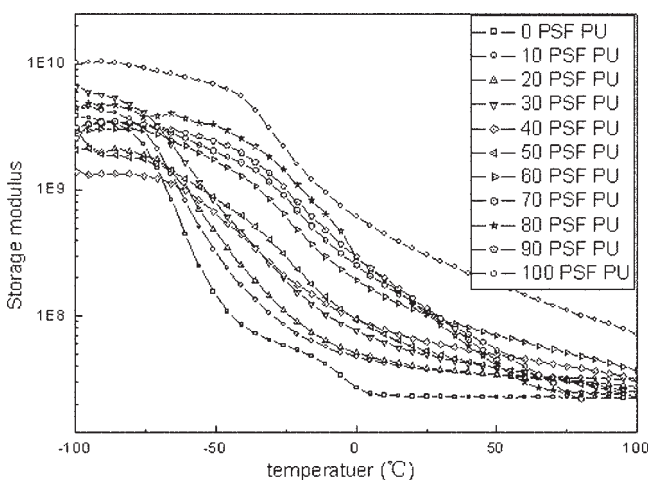


Figure 6 Storage modulus versus temperature for PSF/PTMEG copolyurethane compositions.

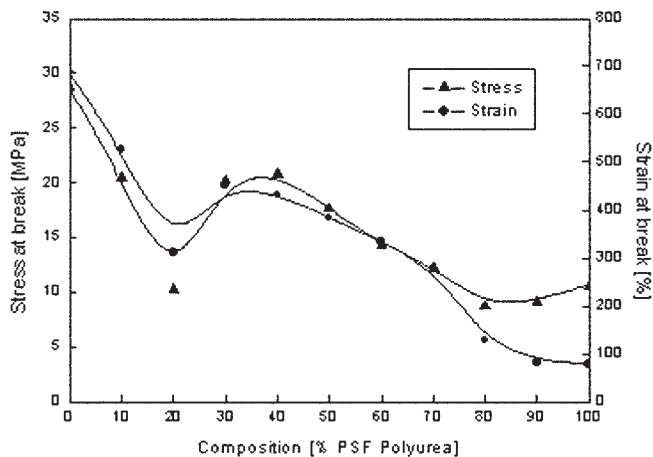


Figure 7 Stress and strain at break versus PSF/PTMEG copolyurethane composition.

PTMEG copolyurethane. After that, they fell again to a value of 8 MPa for the 80 : 20 composition before increasing from the 80 : 20 composition onwards. This trend can be explained by looking at phase continuity of the IPNs, as the continuous phase is known to have a large influence on the mechanical properties of IPNs. From the DMA data, it was believed that phase inversion took place between the 20 : 80 and 80 : 20 PSF/PTMEG copolyurethanes. This is similar to the result of Hourston et al.'s,¹² in which he found that the phase inversion took place in the IPN compositions, and result in a lower stress value at that composition at which phase inversion took place. The increasing stress at break values up to 60% PTMEG PU composition could be explained by the reinforcing effect of the PSF polyurea by the PTMEG PU. In creasing the PTMEG PU content further would lead to larger PTMEG PU domains and, as a consequence, a decreased phase continuity of the PSF polyurea network. This weaker PSF polyurea network would lead to lower stress at break values.

The strain at break versus copolyurethane composition exhibited a similar trend (Fig. 7). But this trend is different with Hourston et al.'s result. The strain at break showed lower values at the 20 : 80 and 80 : 20 PSF/PTMEG copolyurethane compositions. And no strain values were higher than pure PTMEG PU. This could be explained by the formation of tightly bound between the two components, thus leading to break at lower elongations than pure PTMEG PU.

The plot of Shore A values against PSF/PTMEG copolyurethanes composition is shown in Figure 8. A slightly lower than expected increase in Shore A hardness occurred at 20 : 80 and 80 : 20 PSF/PTMEG compositions, possibly indicating a change in the phase continuity. The Shore A hardness increases with the increasing of the PSF PU content. The

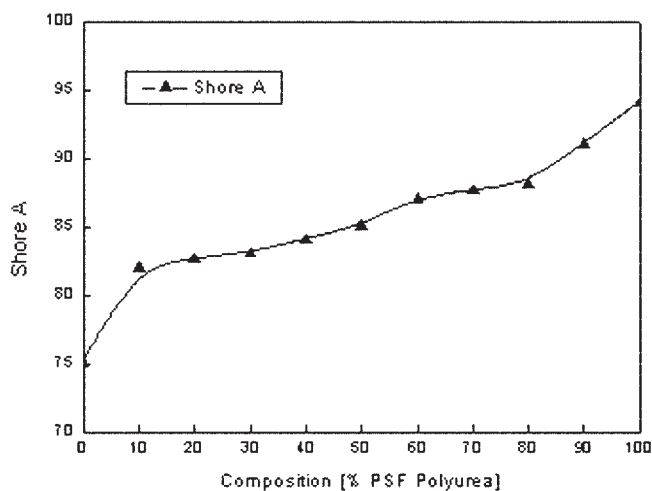


Figure 8 Shore A hardness versus PSF/PTMEG copolyurethane composition.

behavior is not surprising since hardness is directly related to modulus and strength.¹³

CONCLUSIONS

The PSF/PTMEG copolyurethanes have been synthesized based on IPDI-terminated PSF oligomer, TDI-terminated PTMEG, and Ethacure-300. The copolyurethanes were investigated by FTIR, DMA, stress-strain, and hardness analysis. The FTIR spectroscopy indicates the formation of copolyurethanes and IPNs. Two separate loss factor transitions were observed in the composition series from the PSF polyurea weight fraction from 0:100 to 40:60. The $\tan \delta$ values of the PTMEG PU decreased simultaneously. When the PSF polyurea content are more than

60, the loss factor ($\tan \delta$) peaks of the samples move to a higher temperature and the transitions are also broadened. Those are accounted for by intermixing between the PTMEG PU segments and PSF polyurea segments, and IPN formation between the PTMEG PU network and PSF polyurea network. With the increase in PTMEG PU content, the tensile strength and elongation increase, whereas the Shore A hardness decreases.

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