Ultraviolet Curing of Liquid Polysulfide Thiourethane Acrylate

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ABSTRACT: A series of liquid polysulfide thiourethane acrylate prepolymers were synthesized by the reaction of liquid polysulfide with isocyanate and hydroxyethyl acrylate. With and without a combination of acrylic monomers, the prepolymers were cured with ultraviolet radiation. The films exhibited a higher soft-segment glass-transition temperature than metal oxide cured polysulfide. With the addition of a diluent, the tensile strength and modulus increased, whereas the ultimate elongation decreased. The polysulfide backbone, combined with the crosslink generated from the photopolymerization of acrylic, produced films with superior oil resistance. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2358–2363, 2004

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INTRODUCTION

Low-molecular-weight polysulfide (PSF) polymers bearing thiol end groups can be cured by metal peroxides and other metal oxy salts, which make use of the reducing properties of the thiol group to cause crosslinking. The main reaction procedures were reported by early researschers.[1,2] These crosslinked elastomers derived from liquid PSF have wide applications in industry, particularly in sealants. They have high resistance to solvents and chemicals.[3] There are many publications on the characterization of metal oxide cured PSF,[4–10] reporting the results of thermogravimetry analysis, dynamic mechanical analysis, tensile strength, and hardness testing.

Considerable interest exists in the photocuring process for liquid oligomers. One feasible approach is to incorporate (meth)acrylic ester into the liquid oligomer, which can then be photocrosslinked to produce networks, combining the properties of rubbers and (meth)acrylic resins. The liquid oligomers can be polyether or polyester mocroglycols,[11] liquid polybutadiene,[12] or other materials.[13,14] These materials combine high abrasion resistance, toughness, and high degree of flexibility (especially at low temperatures) with the weatherability of polyacrylate. Many studies[15–18] have been published on the effects of materials such as reactive diluents (soft-segment and molecular, hard-segment types) on the mechanical and thermal properties.

In this study, liquid PSF was first tipped by IPDI or TDI, and then the oligomer was capped with hydroxyethylacrylate (HEA). With and without a combination of acrylic monomers, the prepolymers were photocrosslinked. Fourier transform infrared (FTIR) spectroscopy, gel fraction by extraction, dynamic mechanical properties, differential scanning calorimetry (DSC), and tensile properties were measured and discussed.

EXPERIMENTAL

Materials

IPDI was supplied by Crendva Speziaichemie (Germany). TDI was purchased from Aldrich. Liquid PSF oligomer (SH = 6.2%, number-average molecular weight = 1000 ± 200) was supplied by the Jin Xi Research Institute of Chemical Industry (China). HEA and methyl methacrylate (MMA) were distilled before being used.

Acrylated liquid PSF prepolymer

As depicted in Scheme 1, the prepolymer was synthesized with a two-step reaction. First, the oligomer was prepared with a reaction of a 2:1 molar ratio of IPDI and PSF at 80°C for 3 h. Then, the oligomer was capped by HEA at room temperature for a week, the molar ratio of the oligomer to HEA was 1:2. The reaction was performed at room temperature to avoid thermal polymerization of the vinyl group. The oligomer was allowed to stand a week to complete the reaction before ultraviolet (UV) curing. The comple-
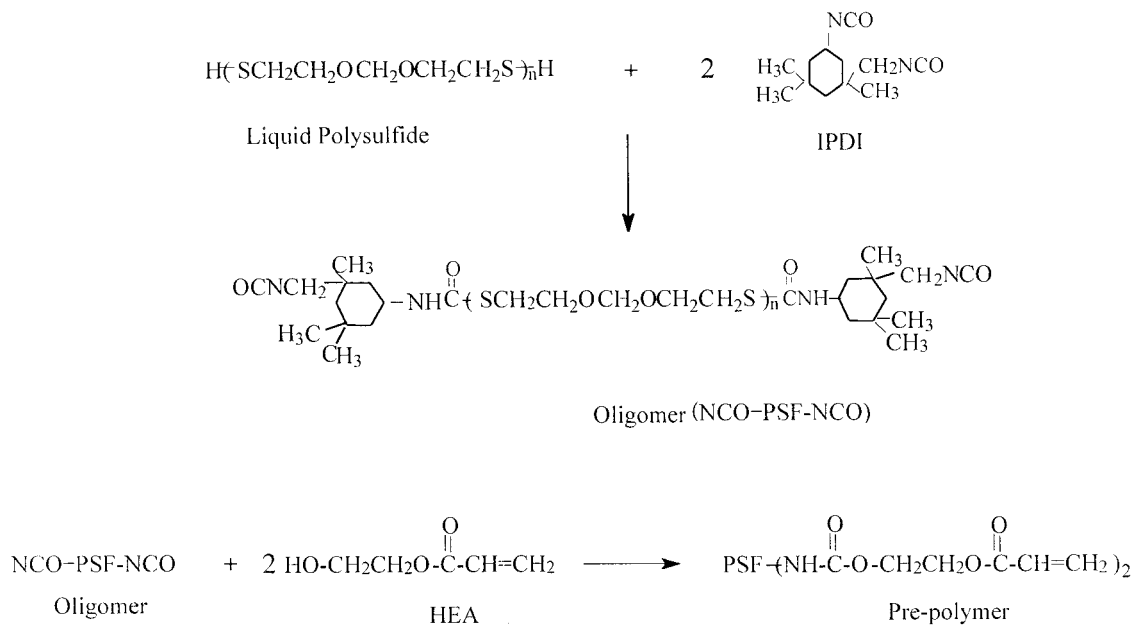
Scheme 1 Synthesis of acrylated liquid PSF prepolymer.

tion of the reaction was confirmed by the disappearance of the NCO peak with FTIR.

UV curing

UV curing coatings were formed by the blending of the prepolymer with or without MMA. After the addition of 0.6 wt % 2-phyenyl-2,2-dimethoxy-acetophenone as a photoinitiator and 0.6 wt % triethanol amine as a synergist to reduce O_2 inhibition, the coatings were applied to glass plates as 200-μm liquid films and cured with a 20-W mercury lamp for 10 min. The distance between the lamp and the samples was 20

cm. An irradiation time of 10 min was found to completely cure the samples.

Characterization methods

The FTIR-TX spectrum was performed on films cast onto KBr salt plates with a Nicolet 170SX FTIR spectrometer. The Fourier transform infrared/attenuated total reflection (FTIR-ATR) spectrum was tested with a Nexus 870 FTIR instrument; the incident angle was 45°, and the studied depth of the near-surface region was about 1 μm.
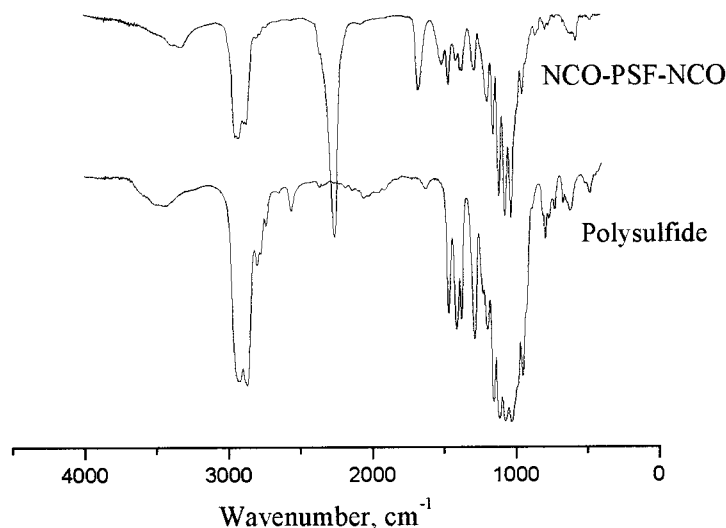
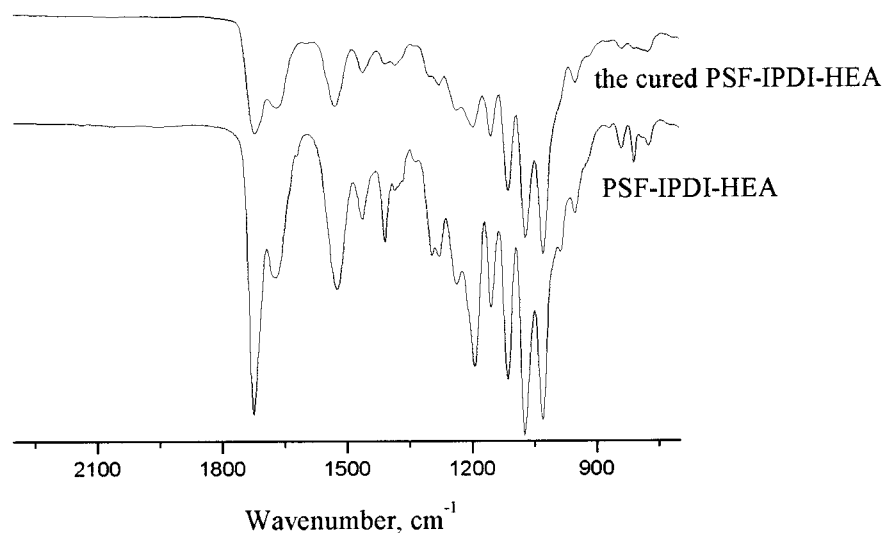**Figure 1** FTIR-TX spectra of liquid PSF and NCO–PSF–NCO.

Figure 2 FTIR-TX spectrum of PSF–IPDI–HEA and FTIR-ATR spectrum of cured PSF–IPDI–HEA.

The gel fraction of the cured samples was evaluated by extraction with methyl ethyl ketone; the insoluble materials were dried *in vacuo* for 24 h at 60°C and weighed to determine the gel fraction.

The dynamic mechanical thermal analysis (DMTA) was carried out with a DMTA-V instrument (Rheometric Scientific) at a fixed frequency of 10 Hz from −90 to 150°C at a nominal rate of 3°C/min.

DSC was performed on a Pyris-1 differential scanning calorimeter (PerkinElmer) at a heating rate of 20°C/min from −100 to 100°C.

The tensile properties were determined on an Instron 4466 tensile testing machine at a strain rate of 20 mm/min.

In the oil absorption test, the films were cut to 20 mm ×20 mm, their dry weight (W_d) was determined, and they were immersed in double-distilled pump oil at room temperature. The wet weight with a different immersion time (W_t) was determined after paper was used to wipe off the surface oil. The absorbed oil content was then calculated from the oil content: W (%) = (W_t − W_d) ×100/W_d.

In the oil resistant test, the specimens for stress–strain analysis were immersed in 50°C pump oil. The

tensile strength and ultimate elongation were tested after different immersion times.

RESULTS AND DISCUSSION

IR and gel fraction analysis

The FTIR-TX spectra of the PSF and oligomer (NCO–PSF–NCO) are shown in Figure 1. The S—H absorption peak at 2556 cm^{-1} disappeared, and the formation of thiourethane linkages, as indicated by the absorbance peaks at 3300 (N—H) and 1676 cm^{-1} (C=O), confirmed that PSF reacted with IPDI. Figure 2 shows the FTIR-TX spectrum of PSF–IPDI–HEA and the FTIR-ATR spectrum of UV-cured PSF–IPDI–HEA. As expected, the peaks at 1620 (C=C stretching) and 1408 cm^{-1} (C=CH$_2$) disappeared, indicating that the acrylate double bond was incorporated into the polymer. All of the samples used in this study had gel fractions extracted by methyl ethyl ketone greater than 93 wt % (shown in Table I); this also indicated a nearly complete reaction of vinyl groups. The addition of MMA did not affect the polymerization of the acrylate function.

TABLE I
Gel Fractions of UV-Cured Acrylated Liquid PSF by Methyl Ethyl Ketone Extraction

Sample	Gel fraction (%)
PSF–IPDI–HEA-0	94.8
PSF–IPDI–HEA–MMA20	94.2
PSF–IPDI–HEA–MMA40	94.1
PSF–IPDI–HEA–MMA60	93.9
PSF–TDI–HEA-0	95.2
PSF–TDI–HEA–MMA40	94.9
PSF–TDI–HEA–MMA60	93.5

TABLE II
DSC Data for UV-Cured Acrylated Liquid PSF

Sample	T_g (°C)	Heat-capacity change (J/GK)
PSF–IPDI–HEA-0	−34.8	0.14
PSF–IPDI–HEA–MMA20	−30.3	0.057
PSF–IPDI–HEA–MMA40	−30.0	0.039
PSF–IPDI–HEA–MMA60	−30.2	0.024
PSF–TDI–HEA-0	−33.0	0.17
PSF–TDI–HEA–MMA40	−24.0	0.058
PSF–TDI–HEA–MMA60	−22.2	0.034

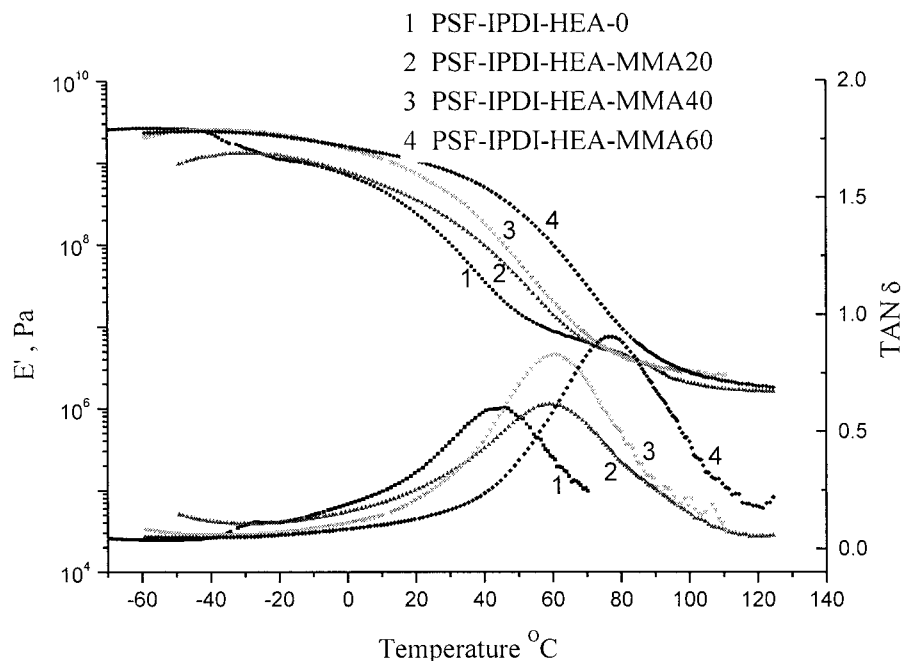**Figure 3** Temperature dependence of E' and tan δ for PSF–IPDI–HEA–MMA-x.

DSC analysis

DSC traces showed a soft-segment glass-transition temperature (T_g) at about −30°C, but there was no evident hard-segment glass transition in the DSC traces. The results were similar to those of other UV-cured polyurethane or poly(urea acrylate) studied by earlier researchers.[16] The DSC data are given in Table II. Consistent with the soft-segment phase fraction decreasing, the heat-capacity change decreased as the diluent content increased. The diluent either was forming its own phase or was partitioning into the hard-segment phase. For the PSF–IPDI materials, the addition of the diluent caused only a slight increase in the soft-segment T_g, whereas the soft-segment T_g of PSF–TDI materials moved from −33 to −22°C with the added diluent.

DMTA

The DMTA results are shown in Figures 3 and 4. Generally, T_g of PSF cured by metal oxide is about −40

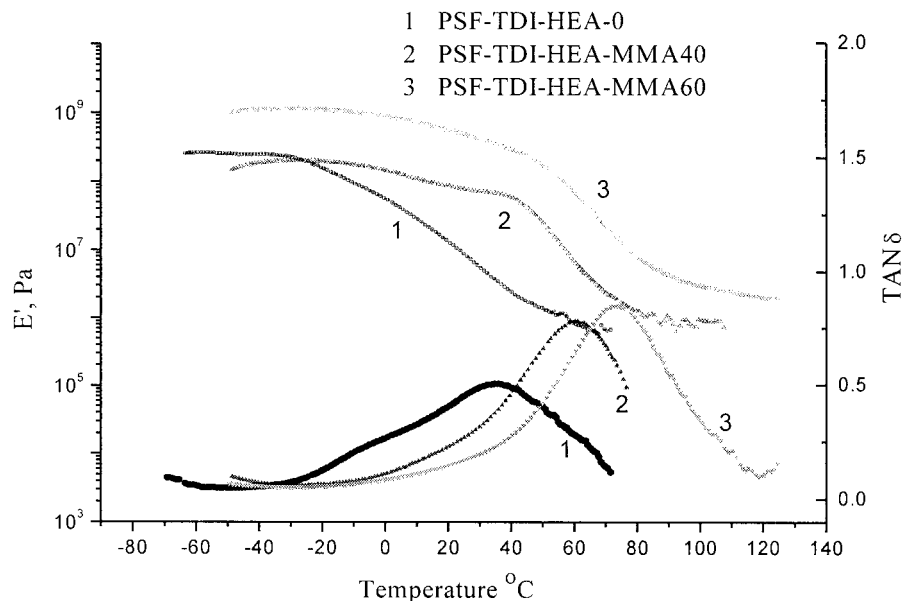**Figure 4** Temperature dependence of E' and tan δ for PSF–TDI–HEA–MMA-x.

TABLE III
Mechanical Properties of UV-Cured Acrylated Liquid PSF

Sample	Tensile strength (Mpa)	Ultimate elongation (%)	Young's modulus (MPa)
PSF–IPDI–HEA-0	6.2	118	26.3
PSF–IPDI–HEA–MMA20	9.6	94	81.1
PSF–IPDI–HEA-MMA40	12.9	81	239.5
PSF–IPDI–HEA-MMA60	18.7	20	459.6
PSF–TDI–HEA-0	5.4	65	35.4
PSF–TDI–HEA–MMA40	7.4	32	266.1
PSF–IPDI–HEA–MMA60	14.5	15	569.2

to −45°C.[8] Figures 3 and 4 show that the soft-segment T_g of UV-cured PSF thiourethane acrylate moved to a higher temperature (ca. −15 to 0°C). The tan δ peak of the soft segment was overlapped by that of the hard segment. Near this temperature area, there was the obvious drop change in the storage modulus (E'). With the addition of the diluent, the rapid drop change of E' turned to a higher temperature after the increase in the soft-segment T_g, and this was consistent with the results of the DSC analysis. The loss of intensity in the tan δ peak of the soft segment resulted from a decreased weight fraction of the soft segment.

As the diluent content increased, the hard-segment T_g also occurred at a higher temperature for both PSF–IPDI and PSF–TDI materials. The diluent preferentially segregated to the more polar hard phase, while more or less changing the soft-segment phase purity; this resulted in a certain increase in T_g of the soft segment. This conclusion disagreed with the results of other polyurethane and poly(urea acrylate)s.[16]

Mechanical properties

The results of tensile testing are summarized in Table III. The PSF–IPDI materials showed higher tensile strength and ultimate elongation than the PSF–TDI materials. With an increase in the diluent content, the modulus and tensile strength at break improved, whereas the ultimate elongation decreased. The increased modulus could be attributed to the fact that the cured diluent became part of a glassy phase and may have been acting as a filler. This result was consistent with other UV-cured liquid oligomers.[15,16]

Oil absorption and oil resistance

Figure 5 shows the percentage increase in mass after different days of immersion in pump oil at room temperature for PSF–IPDI–HEA-0 and PSF–IPDI–HEA–MMA20. PSF–IPDI–HEA-0 had a little lower oil absorption than PSF–IPDI–HEA–MMA20. On the whole, it appeared that all the materials based on PSF absorbed no more than 1.2% oil. This important property resulted from the presence of the PSF linkage, which provided good resistance to hydrocarbon flues.

The changes in the tensile strength of PSF–IPDI–HEA-0 and PSF–IPDI–HEA–MMA20 before and after oil immersion are shown in Figure 6. After 72 h of immersion in pump oil at 50°C, the films based on UV-cured PSF experienced little change in their tensile strength. After 288 h, PSF–IPDI–HEA-0 retained 90.3% of its initial value, and PSF–IPDI–HEA–MMA20 retained 88.5% of its initial value. This was consistent with oil absorption, which accounted for the excellent resistance to the oil by PSF.
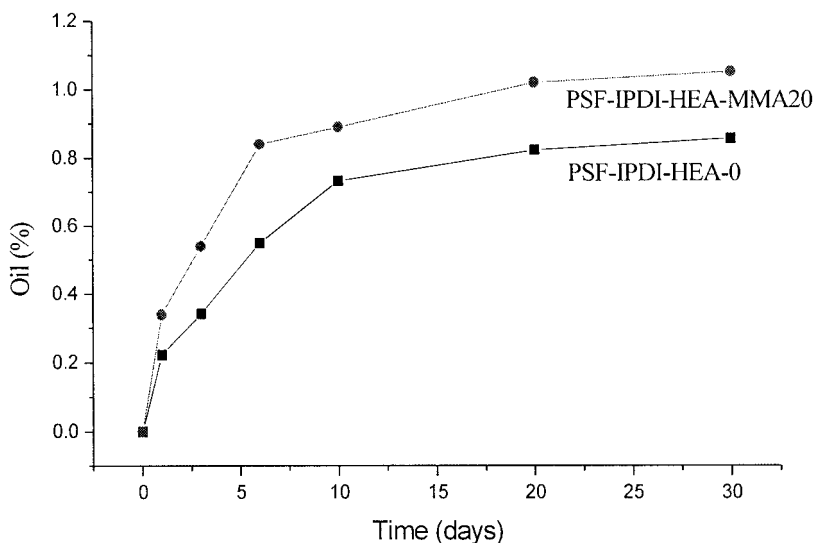
Figure 5 Oil absorption of UV-cured acrylated liquid PSF at room temperature.
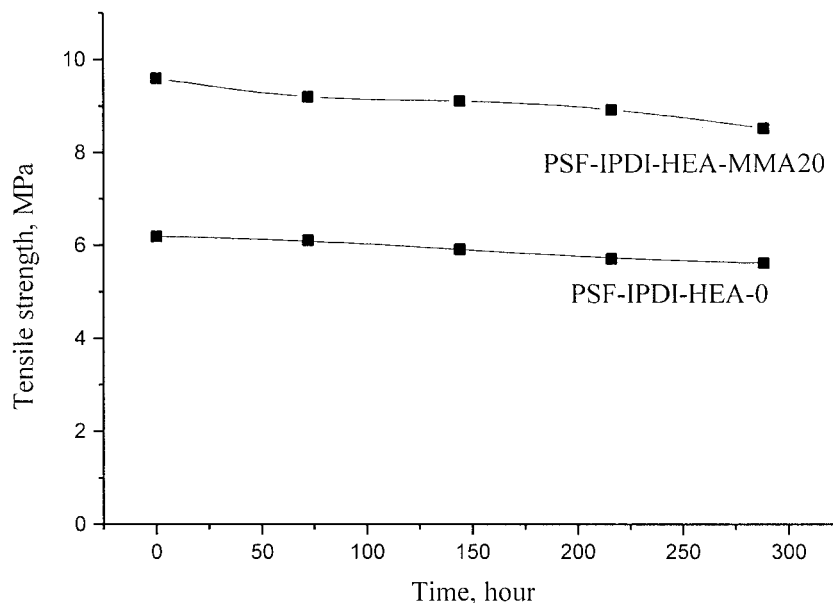
Figure 6 Effect of oil on the tensile strength of UV-cured acrylated liquid PSF at an elevated temperature (50 °C).

CONCLUSIONS

PSF thiourethane acrylate underwent photochemically induced polymerization. A diluent effectively caused a decrease in the viscosity of the prepolymer. With the addition of an MMA diluent, the modulus and tensile strength of the UV-cured materials increased, whereas the ultimate elongation decreased. The films exhibited a higher soft-segment T_g than metal oxide cured PSF, especially for PSF–TDI materials; the addition of the diluent resulted in an apparent increase in T_g of the soft segment. The testing of the oil resistance and oil absorption showed that the PSF backbone, combined with the crosslink generated from the photopolymerization of acrylic, produced films with superior resistance to oil and low oil absorption. The oil resistance of the UV-cured samples containing MMA was as good as that of an MMA-free sample. UV-curable PSF thiourethane acrylate offers another way of applying PSF.

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