

# Structure and Oil-Resistant Properties of HTPB-Based Polyurea Modified with Polysulfide

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**ABSTRACT:** A series of hydroxy-terminated polybutadiene (HTPB) polyureas modified with different liquid polysulfide content was synthesized and their structure and oil-resistant properties were studied by attenuated total reflectance–FTIR spectroscopy, dynamic mechanical analysis, isothermal aging and differential scanning calorimetry, stress–strain analysis, oil absorption, and oil-resistance test. The results showed that polysulfide–polybutadiene polyu-

reas retained low temperature flexibility and had lower oil absorption and better oil resistance than that of HTPB-based polyureas. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2672–2675, 2003

**Key words:** polybutadiene; polysulfide; modification; structure; oil resistance

## INTRODUCTION

Polyurethane (PU) containing a hydroxyl-terminated polybutadiene (HTPB) soft segment offers the advantages of low moisture permeability, low glass-transition temperature, and excellent resistance to aqueous acid and bases. HTPB-based PU has been applied for adhesive and electrical potting compounds. The complete hydrocarbon nature of polybutadiene means there is no possibility of hydrogen bonding between the hard and soft segment, which favors phase segregation. There are many publications on HTPB-based PU that deal with the structure and properties,<sup>1–10</sup> such as morphology, thermal transition behavior, crosslinking density, mechanical properties, and thermal stability.

In recent years several publications have reported on investigations of structure and properties of HTPB-based PU modified with other materials. A study by Yang<sup>11</sup> was concerned with modification of HTPB-based PU by the epoxidation method. It was found that the surface properties of modified HTPB-based PU membranes, including the absorption of fibrinogen and albumin onto the surface, were significantly altered by an epoxidation on the membrane surface. Sarkar and Adhikari<sup>12,13</sup> studied synthesis and characterization of lignin–HTPB copolyurethane. They demonstrated that superior tensile strength and thermal stability were observed when 3 wt % lignin was incorporated. A study on pervaporation of aqueous ethanol solution by modified polyurethane membrane

was reported by Lee and coworkers.<sup>14</sup> With chemical-graft polymerization of 2,3-epoxypropylmethacrylate onto the HTPB-based PU membrane, both the hydrophilicity and the permeation rate of modified membrane were improved. Beli et al.<sup>15</sup> reported the effect of different fillers such as carbon black, silica, and aluminum oxide on the thermal properties of HTPB-based PU.

Liquid polysulfide oligomers cured with metal peroxides find wide applications in industry, particularly in sealants.<sup>16,17</sup> They exhibit excellent weatherability and good aging property.<sup>18</sup> Liquid polysulfide oligomers could also react with isocyanates.<sup>19</sup>

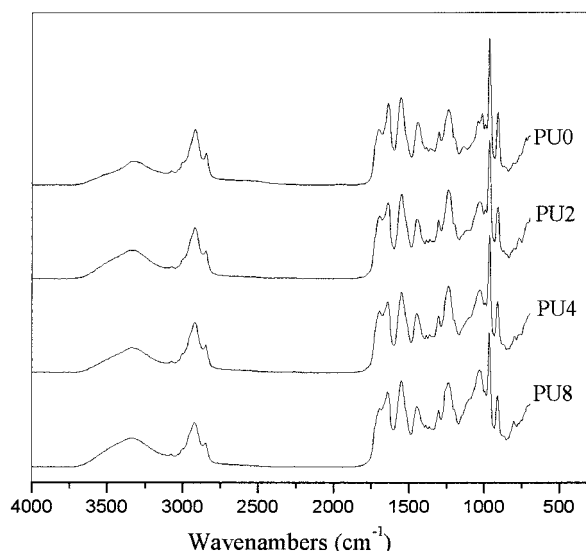
The present work is concerned with HTPB-based PU modified with liquid polysulfide oligomer, the structure and oil-resistant properties of which were studied by attenuated total reflectance (ATR)–FTIR, DMA, DSC, stress–strain analysis, and oil resistance test. The effect of added polysulfide is also reported in this study.

## EXPERIMENTAL

### Material and polymerization conditions

Hydroxy-terminated polybutadiene (HTPB; hydroxyl value: 45.8 mg KOH/g,  $M_n = 3000 \pm 200$ , supplied by Liming Research Institute of Chemical Industry, China) was dehydrated under vacuum at 100°C for 3 h before using. Liquid polysulfide (SH% = 6.2%,  $M_n = 1000 \pm 200$ , supplied by JinXi Research Institute of Chemical Industry, China) was dehydrated under vacuum at 100°C for 3 h before using. IPDI (supplied by CRENDVA Speziaichemie, Germany) was used without purification. Ethacure-300 (E300; supplied by Al-

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**Figure 1** ATR-FTIR spectra of HTPB-based polyureas modified with polysulfide.

bemarle Corp.) was used without purification. Cyclohexanone was distilled before using.

A weighed amount of HTPB, IPDI, and liquid polysulfide oligomer was added into a 150-mL reaction vessel. The mixture was stirred and heated to 120°C in an oil bath for 1 h under nitrogen flow, after which the temperature was lowered to 80°C. After the addition of E300, the reaction was degassed and poured into a poly(tetrafluoroethylene) disc. The films were dried at room temperature for 48 h, and 60°C for 24 h, under vacuum before test.

### Characterization

#### Infrared spectroscopy

ATR-FTIR was performed on films using a Nexus 870FT-IR instrument. The incident angle was 60° and the studied depth of the near surface region was about 1  $\mu\text{m}$ .

#### Differential scanning calorimetry (DSC)

Measurements of the soft-segment glass-transition temperature were made with PYRIS-1 DSC (Perkin

Elmer Cetus Instruments, Norwalk, CT), at a heating rate of 20°C/min, from -100 to +100°C.

#### Dynamic mechanical thermal analysis (DMA)

All measurements were carried out using a DMTA-V apparatus (Rheometric Scientific). The dimensions of the specimens were 7  $\times$  10  $\times$  0.3 mm. The fixed frequency was at 10 Hz. The temperature range was from -90 to +150°C and the samples were heated at a nominal rate of 3°C/min.

#### Stress-strain analysis

The mechanical properties were determined on an Instron 4466 testing machine. The samples were stamped out of solution-cast films (0.4  $\pm$  0.05 mm) using an ASTM 1708 standard die. The samples with gauge length of 1 cm were tested at room temperature using a crosshead speed of 5 cm/min.

#### Oil absorption and oil resistance test

The films were cut into 20  $\times$  20 mm strips, the dry weight ( $W_d$ ) of which was determined, and then immersed in pump oil at room temperature. The wet weight with different immersion times ( $W_t$ ) was determined by wiping off the surface oil with paper. The absorbed oil content was then calculated by

$$\text{Absorbed oil content (W\%)} = \frac{W_t - W_d}{W_d} \times 100$$

In the oil resistance test, the specimens for stress-strain analysis were immersed in pump oil at 50°C. The tensile strength and ultimate elongation were tested after different immersion times.

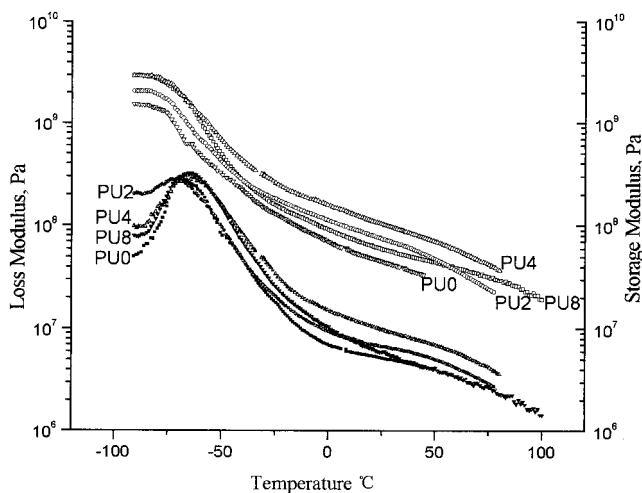
## RESULTS AND DISCUSSION

### ATR-FTIR analysis

Four typical ATR-FTIR spectra of HTPB-based PU modified with polysulfide are shown in Figure 1. The S—H absorption peak at 2556  $\text{cm}^{-1}$  did not appear, which confirmed that all of the polysulfide added in

**TABLE I**  
Characterization of HTPB-Based Polyurea Modified with Polysulfide

Sample	Weight composition HTPB/JLY121/IPDI/E300	DMA $T_g$ (°C), from $E''_{\text{max}}$	DSC $T_g$ (°C)
PU0	10/0/4/1.5	-70.0	-74.7
PU2	10/0.2/4.1/1.5	-69.5	-74.2
PU4	10/0.4/4.2/1.5	-66.8	-73.5
PU8	10/0.8/4.3/1.5	-65.0	-73.2



**Figure 2** Temperature dependency of the storage modulus and loss modulus for HTPB-based polyureas modified with polysulfide.

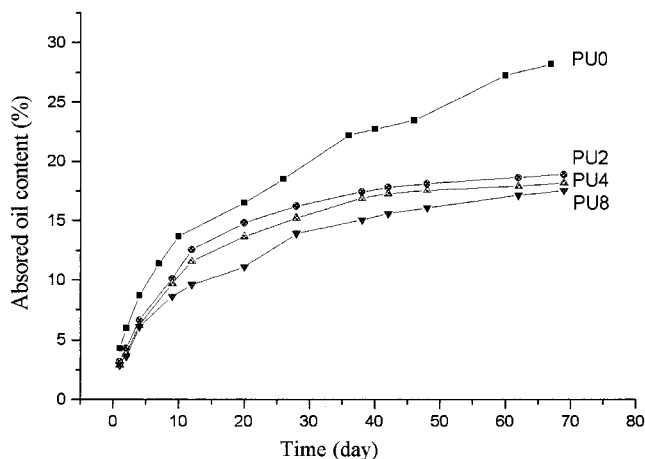
the system was incorporated into the copolymer. With the increase of the polysulfide content in polyurethane from PU0 to PU8, the intensity of the peaks at  $910\text{ cm}^{-1}$  ( $1,2 =\text{CH}_3$  out-of-plane def.) and  $968\text{ cm}^{-1}$  (*trans*  $=\text{CH}$  out-of-plane wag.) decreased, whereas the intensity of the peaks at  $1330\text{ cm}^{-1}$  ( $-\text{C}-\text{O}-\text{C}-$  stretching) increased simultaneously.

### Thermal analysis

The DSC and DMA results for HTPB-based PU modified with polysulfide are summarized in Table I. Figure 2 shows DMA analysis for modified materials. The samples showed the soft-segment  $T_g$  values of  $-65$  to  $-70^\circ\text{C}$  by DMA and about  $-73.2$  to  $-74.7^\circ\text{C}$  by DSC, both very close to that of the free HTPB, indicating that the soft and the hard segments of these polyureas were well separated. The slightly different  $T_g$  values by DMA and DSC account for the different heating rates. Generally, a decrease in  $T_g$  is associated with a higher degree of phase separation. The polysulfide segments were expected to have a slight compatibility with HTPB. With an increase of polysulfide content, the  $T_g$  of the soft segment increased slightly. This result is confirmed by both DSC and DMA analyses.

**TABLE II**  
Mechanical Properties of HTPB-Based Polyurea Modified with polysulfide

Sample	Tensile strength (MPa)	Ultimate elongation (%)	Young's modulus (MPa)
PU0	15.3	503	13.7
PU2	14.4	385	20.4
PU4	13.4	254	30.9
PU8	12.6	234	26.2

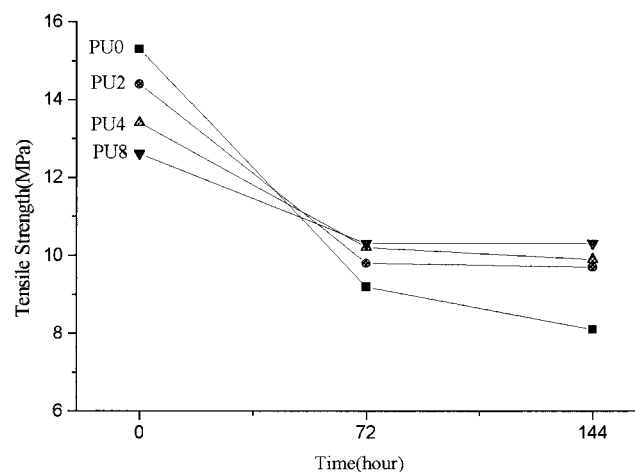


**Figure 3** Oil absorption of HTPB-based polyureas modified with polysulfide.

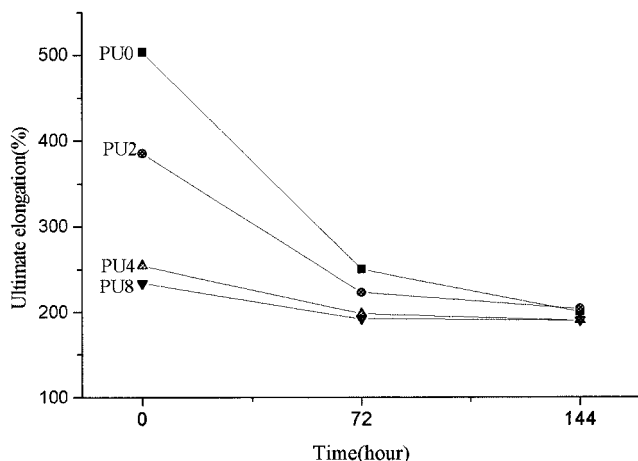
Figure 2 also shows that PU4 had the greatest storage modulus. When the polysulfide content was increased to 8%, the storage modulus decreased again.

### Stress-strain analysis

The data of the Young's modulus, tensile strength, and ultimate elongation are summarized in Table II. After 4% polysulfide modification, the tensile strength and ultimate elongation of copolymers decreased from 15.3 to 13.4 MPa and from 503 to 254%, respectively, but the Young's modulus increased from 13.7 to 30.9 MPa. HTPB-based PU had better ultimate elongation than that of polysulfide-based PU. The sample was a multisegment copolymer and the ultimate elongation was determined by polysulfide-based PU. On the other hand, polysulfide-based PU had greater rigidity and modulus than that of HTPB-based PU. The copolymers had greater Young's modulus than that of HTPB-based polyurea.



**Figure 4** Effect of oil on tensile strength at elevated temperature ( $50^\circ\text{C}$ ).



**Figure 5** Effect of oil on ultimate elongation at elevated temperature (50°C).

### Oil absorption and oil resistance test

Figure 3 shows curves of the percentage increase in mass after immersing in pump oil at room temperature. From Figure 3, it appears that pure HTPB-based PU absorbed more oil than did materials with mixed soft-segment copolymer. The materials with greater polysulfide content showed lower oil absorption. When the content of polysulfide was increased to 4–8%, there was a 50% decrease in oil absorption because polysulfide has a higher resistance to oil.

The mechanical properties of samples before and after some days of oil immersion are summarized in Figures 4 and 5. For the dry sample, HTPB-based PU showed better tensile strength and ultimate elongation than that of mixed soft-segment composition. After a 72-h immersion in oil at 50°C, with the addition of polysulfide, the material showed better resistance to oil. The HTPB-based PU sustained a significant reduction in mechanical properties, retaining less than 60% of its initial value in tensile strength and 50% in ultimate elongation. Meanwhile, PU8 retained more than 81% of its initial value in tensile strength and 81% in

ultimate elongation. After 144 h, the mechanical properties of HTPB-based PU sustained subsequent damage, whereas the mechanical properties of PU4 and PU8 were virtually unchanged.

### CONCLUSIONS

By means of the modification with polysulfide, the HTPB-based polyurea produced superior resistance to oil. Upon addition of the polysulfide, there was a slight increase in  $T_g$  and all samples exhibited  $T_g$  values well below 0°C. With the increase of polysulfide content, the HTPB-based polyurea had better resistance to oil.

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