

## Polyurethane Elastomers from Post-Grafted Polymer-Polyol Systems

WILLIAM C. KURYLA and ROBERT D. WHITMAN,  
*Research and Development Department, Chemicals Division,  
Union Carbide Corporation, South Charleston, West Virginia 25303*

### Synopsis

Certain homopolymer-polyol mixtures, after treatment with a free-radical generating agent or ionizing radiation, will produce polyurethane elastomers of nearly twice the stiffness and tensile properties compared to control elastomers made with untreated mixtures. Specific examples of these mixtures include the homopolymers of acrylonitrile and vinyl chloride with a poly(oxypropyl) triol of about 3000 molecular weight as the polyol in each case. The marked improvement in the stiffness and tensile properties of elastomers made with the treated mixtures over those of the untreated controls indicates a grafting process occurring between the polyol and homopolymer upon the generation of free radicals. In the present work, grafting could occur by a chain-transfer hydrogen-abstraction mechanism, whereby a free-radical site is generated on both the homopolymer and polyol chains. Coupling of these two free-radical sites would thus result in the establishment of a polymer-polyol graft bond.

As part of the continuing study in the synthesis of polymer-polyols as intermediates for polyurethanes,<sup>1</sup> we have discovered that certain homopolymer-polyol mixtures, after treatment with a free-radical generating agent or ionizing radiation, will produce polyurethane elastomers of nearly twice the stiffness and tensile properties compared to control elastomers made with untreated mixtures. Specific examples of these mixtures include the homopolymers of acrylonitrile and vinyl chloride, with a poly(oxypropyl triol) of about 3000 molecular weight as the polyol in each case. The free-radical generating agents employed in this study were either benzoyl peroxide or azobisisobutyronitrile; <sup>60</sup>Co (22.6 × 10<sup>6</sup> r) was the source of the ionizing radiation. All composition, treatment, and elastomer data are summarized in Table I.

### EXPERIMENTAL

#### Mixing and Treatment

The polyol and polymer (composition and percentage specified in Table I) were charged to a Papanmeier intensive mixer (Model TL-8) and the mixture purged with dry nitrogen for about 30 min. The polyol-polymer mixture was then stirred at 1800 rpm at a time and temperature specified

TABLE I  
 Post-Grafted Polymer-Polyol Systems: Composition, Treatment, and Polyurethane Elastomer Data

| Compo-<br>sition<br>no. | Polymer              | Polymer,<br>% in<br>mixture | Polyol,<br>% in<br>mixture <sup>a</sup> | Treatment              |                         |                       | Hydroxyl<br>no. of<br>mixture<br>after<br>treatment | Polyurethane elastomer data |                 |                    |
|-------------------------|----------------------|-----------------------------|---|------------------------|-------------------------|-----------------------|---|-----------------------------|-----------------|--------------------|
|                         |                      |                             |   | Mixing<br>time,<br>hr. | Mixing<br>temp.,<br>°C. | Catalyst <sup>b</sup> |   | Stiffness,<br>psi           | Tensile,<br>psi | Elonga-<br>tion, % |
| 1                       | None (control)       | 0                           | 100                                     | None                   | None                    | None                  | 56.5  | 300                         | 120             | 60                 |
| 2                       | None (control)       | 0                           | 100                                     | None                   | None                    | G                     | 58.4  | 260                         | 50              | 47                 |
| 3                       | Polyacrylonitrile    | 11                          | 89                                      | 5.0                    | 45                      | None                  | 50.2  | 350                         | 174             | 90                 |
| 4                       | Polyacrylonitrile    | 11                          | 89                                      | 5.0                    | 45                      | A, 2%                 | 50.7  | 623                         | 222             | 67                 |
| 5                       | Poly(vinyl chloride) | 20                          | 80                                      | 5.0                    | 45                      | None                  | 44.8  | 91                          | 160             | 375                |
| 6                       | Poly(vinyl chloride) | 20                          | 80                                      | 5.0                    | 45                      | B, 2%                 | 44.8  | 670                         | 290             | 100                |
| 7                       | Poly(vinyl chloride) | 20                          | 80                                      | 5.0                    | 45                      | G                     | 63.0  | 680                         | 347             | 100                |
| 8                       | Poly(vinyl chloride) | 20                          | 80                                      | 1.5                    | 105                     | A, 1%                 | 49.8  | 439                         | 330             | 155                |

<sup>a</sup> Polyol LG-56 = NIAX polyol LG-56; a poly(oxypropyl) triol having an average molecular weight of 3000, made by the Union Carbide Corp. used in all cases.

<sup>b</sup> Catalyst A = azobisisobutyronitrile (VAZO catalyst, made by E. I. du Pont de Nemours & Co.); Catalyst B = benzyl peroxide (technical grade catalyst, made by the Lucidol Division of Wallace and Tiernan, Inc.); Catalyst G =  $22.6 \times 10^6$  r of  $\gamma$ -radiation from a <sup>60</sup>Co source.

in Table I, during which time the nitrogen purge was continuously maintained. The mixture was then cooled to room temperature and a portion of this simple mixture evaluated as such in a polyurethane cast elastomer. Treatment of the polyol-polymer mixture was then carried out with 1-2 wt.-% (based on the weight of the mixture) of either azobisisobutyronitrile or benzoyl peroxide (see Table I) by heating to 120°C. for 1 hr. (under nitrogen), followed by vacuum stripping. Alternately, treatment of the polyol-polymer mixture was accomplished by subjecting a nitrogen purged sealed glass bottle of the mixture to ionizing radiation from a  $^{60}\text{Co}$  source.

### Elastomer Preparation

Elastomer samples for this study were based on a formulation consisting of 200 g. of polyol, 0.025 g. of *N,N,N',N'*-tetramethyl-1,3-butanediamine, 0.025 g. of *N*-ethylmorpholine, 0.6 g. of stannous octoate (M. and T. catalyst T-9) and tolylene diisocyanate (80/20 ratio of 2,4 and 2,6 isomers) in the amount of 1% excess of the stoichiometric quantity for the polymer/polyol. These ingredients were mixed vigorously for 10 sec. and then poured into a 5 $\frac{1}{4}$ -in. diameter closed mold. The mold was heated to 50°C., after which a pressure of 2000 psi was applied to the mold. Heating was continued until the mold reached 150°C., and this temperature was maintained for a period of 5 min.; thereafter, the mold was cooled to room temperature and the elastomer plaque was removed from the mold. The elastomer plaque was then cured in a nitrogen-purged oven for 2 hr. at 150°C. before testing.

### Elastomer Evaluation

Test specimens were cut from each elastomer plaque with the use of a standard "dogbone" tensile die. The tensile specimens produced in this manner were  $\frac{1}{4}$  in. in width, 1 in. in length (linear part of the specimen), and 0.04-0.06 in. in thickness. An Instron tensile tester was used to measure tensile properties of the elastomers; an extension rate (initial) of 1%/min. was used in determining stiffness modulus, and an extension rate (initial) of 100%/min. was used for tensile strength and elongation measurements. The data are found in Table I.

## RESULTS

The marked improvement in the stiffness and tensile properties of elastomers made with the treated mixtures over the untreated controls seems to indicate a grafting process is occurring between the polyol and homopolymer upon the generation of free radicals.

In the present work, grafting could occur by a chain-transfer hydrogen-abstraction mechanism, whereby a free-radical site is generated on both the homopolymer and polyol chains. Coupling of these two free-radical sites would thus result in the establishment of a polymer-polyol graft bond.

While a chain-entanglement concept cannot be ruled out as an explanation for the improvement in elastomer physical properties, we nevertheless believe the following observations lend support for the grafting postulate. First, irradiation of polyol LG-56 has essentially no effect on elastomer properties. Secondly, a simple dispersion of poly(vinyl chloride) in LG-56 appears to reduce the effective functionality of this polyol as evidenced by the low stiffness modulus and high elongation in the elastomer derived from this mixture. Both treatments, chemical and irradiation of the LG-56-poly(vinyl chloride) polymer-polyol mixture, gave substantial improvements in elastomer properties—which would be difficult to explain on the basis of chain-entanglement.

### Reference

1. W. C. Kuryla, F. E. Critchfield, L. W. Platt, and P. Stamberger, *J. Cell. Plastics*, **2**, 84 (1966).

### Résumé

Certains mélanges homopolymère-polyol après traitement avec des agents générateurs de radicaux libres ou de radiations ionisantes produisent des élastomères de polyuréthanes de rigidité environ double et de propriétés de tension supérieures aux élastomères de contrôle préparés avec des mélanges non-traités. Des exemples spécifiques de ces mélanges comportent des homopolymères d'acrylonitrile et de chlorure vinylique, avec le polyoxypropyltriol d'environ un poids moléculaire de 3,000 comme polyol dans chaque cas. La remarquable amélioration de dureté et de propriétés de tension des élastomères obtenues par les mélanges de traitement par rapport aux échantillons de contrôle non-traités indiquent un processus de greffage qui se passe entre le polyol et le polymère par génération de radicaux libres. Dans le présent travail le greffage pourrait résulter d'un mécanisme de transfert de chaîne par abstraction d'hydrogène suite auquel le site radicalaire est formé à la fois sur l'homopolymère et sur la chaîne polyolique. Le couplage de ces deux sites de radicaux libres pourrait résulter dans la formation d'un lien greffé polymère-polyol.

### Zusammenfassung

Gewisse Homopolymer-Polyolmischungen sind befähigt nach Behandlung mit einem radikalbildenden Agens oder mit ionisierender Strahlung Polyurethan-Elastomere mit nahezu der doppelten Steifigkeit und den doppelten Zugeigenschaften als die mit der unbehandelten Mischung erhaltenen Vergleichssubstanzen zu erzeugen. Charakteristische Beispiele für diese Mischungen sind die Homopolymeren von Acrylnitril und Vinylchlorid mit einem Polyoxypropyltriol vom Molekulargewicht von etwa 3000 als Polyolkomponente. Die merkliche Verbesserung der Steifigkeit und der Zugeigenschaften der mit den behandelten Mischungen erhaltenen Elastomeren gegenüber den unbehandelten Vergleichsprodukten spricht für einen zwischen dem Polyol und dem Homopolymeren Radikalbildung auftretenden Aufpfropfprozess. In der vorliegenden Arbeit kann die Aufpfropfung durch eine Kettenübertragung eintreten. Es wird so am Homopolymeren und an der Polyolkette ein radikalisches Zentrum erzeugt und eine Kombinationsreaktion zwischen diesen beiden Radikalen würde zur Bildung einer Pfropfungsbindung zwischen Polymeren und Polyol führen.

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