Dangling Polymer Networks: Glass Transition of PU Elastomers

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SYNOPSIS

Polyurethane elastomers possessing dangling chains were prepared by partial substitution of the multifunctional polyol with a monohydroxyl alcohol in the reaction with an isocyanate terminated prepolymer. The dynamic mechanical spectroscopy showed that created dangling segments resulted in a broader glass-transition region. This indicated material with potentially good energy absorbing properties might be prepared from a 'dangling polymer' system. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The frequency of sound and mechanical vibration spans from few Hertz to 20,000 Hz, or in terms of the time scale, the range spans from seconds to microseconds. When a polymer is in contact with such a vibrating source, the vibration energy could be absorbed by the polymer if the internal time scales of the relaxation rate of the polymer and the vibration source are of the same order. The absorbed energy by the polymer, eventually dissipated as heat, is the basis for damping with the polymer. This phenomenon resembles electromagnetic wave absorption; an absorption peak is found where the frequency of the waves matches the natural frequency of an involved chemical group.[1]

The absorption of vibration energy by a polymer can be expressed by loss tangent as

$$\tan \delta = \frac{G''}{G'}$$

where G'' is the loss modulus and G' is the storage modulus. The term "loss" is used because part of the energy input is lost by conversion into heat and the energy dissipation property is identified by the term "damping." If the loss tangent is small, damp-

ing will be small, and vice versa. When polymers are at their glass transition, the onset of coordinated chain motion, the time required to complete an average coordinated movement of chain segments, approximates the length of time of the measurement.[2] For dynamic data, the glass-transition temperature (T_g) is frequently defined as the temperature of the loss tangent peak. At that temperature, the conversion of mechanical energy to heat reaches its maximum value. Thus a damping material could be selected by matching its T_g within the region of the service temperature at a specific resonant frequency range. Since the T_g is frequency dependent, a broader glass-transition region is desirable to cover wider vibration frequency damping and therefore sustain a larger temperature variation.

Interpenetrating Polymer Networks (IPNS)[3,4] and polyblending[5] of low and high T_g polymers have been extensively studied in an effort to obtain the desired broad range of mechanical energy absorption property. In the sample preparation, both methods involve the mixing or blending of two semimiscible polymers, thus forming a multiphase or microheterogeneous morphology caused by the well-known thermodynamic incompatibility of polymers. Fortunately, this favors the broadening of sound and vibration damping.[3]

The energy transfer within a coupled system is a well-known physical phenomenon.[6] Consider two identical plane pendula suspended from a nonrigid support; there is a coupling between the pendula

and energy can be transferred from one pendulum to the other. If in a polymeric material, some one-end-free chains are introduced into the polymer networks and suspended from the crosslinked backbones, the energy absorbed by the polymer networks may be transferred to these dangling chains through the coupling of the polymer chains. For the polymer system, a convenient method of modeling the damping behavior is represented by a dashpot, a viscous element. Thus the dangling chains can be treated as viscous fluids and the introduction of one-end-free chains may result in the increasing of damping effectiveness. When polymer is subjected to external vibration force at T_g, cooperative wriggling of macromolecular chains becomes flexing and uncoiling that governs its relaxation. The dangling chains might wriggle into the backbone chains to affect their relaxation rate; this may also broaden the T_g region. These concepts motivated the following research to study the effectiveness of dangling chains in the energy absorption capability.

EXPERIMENTAL

Materials and Sample Preparation

The basic recipe used in this work was the reaction of an octofunctional, sugar-based polypropylene glycol (SP-450, equivalent weight, 125, Chiun Long Co., local supplier) with a difunctional, isocyanate-terminated polypropylene glycol prepolymer (PUR-500, equivalent weight, 1000, Getmore Co., local supplier). The polyol was dried at 110°C for 4 h under vacuum. All other materials were used without further purification. The urethane networks were prepared by mixing 5 g of SP-450 with 42 g of PUR-500. After thoroughly blending, two drops of catalyst, T-12 (dibutyltin dilaurate), was added with stirring. After degassing under vacuum, the mixture was poured into a mold and cured at room temperature for 3 days and then postcured at 70°C for 24 h and conditioned at room temperature for 7 days prior to testing.

Elastomers With Dangling Segments

Forty-two grams of PUR-500 was added with stirring to a mixture of SP-450 and n-propyl alcohol. The formulations are listed in Table I. Since the reaction of isocyanates with the hydroxyl groups of polyol and alcohol were carried out simultaneously, the dangling segments were created when the isocyanate group reacted with the n-propyl alcohol. Then the samples were treated and cured by the same processes as above.

Elastomers With Plasticizer

In order to investigate the possible role of the plasticizing effect of the dangling segments, part of the PUR-500 was blocked by n-propanol on both isocyanate groups and blended into the polyurethane networks as the plasticizer. The plasticizer was prepared by mixing $2 M$ n-propanol with $1 M$ PUR-500 and heated to 70°C overnight. Then 10 ppm T-12 was added and heated at 70°C for another 24 h to ensure that both isocyanates were blocked. After cooling to room temperature, the plasticizer was blended into the basic urethane network recipe according to the formulations listed in Table II and cured by the same preparation method.

Dynamic Tests

The dynamic properties were determined by applying a sinusoidal strain onto the prepared samples by the Rheometrics Dynamic Spectrometer (Model 7700). The measurements were taken from −100°C to 100°C with a heating rate of 1°C/min and a frequency of 1 Hz.

RESULTS AND DISCUSSION

At the T_g, the onset of large-scale motion of polymer chains results in a change in slope of the curve of volume vs. temperature. This motion requires more free volume than the short-range excursions of at-

Table I Formulations for the PU Elastomers with Dangling Segments

Sample No.	SP-450 (g)	n-Propanol (g)	PUR-500 (g)	Equivalent Ratio
1	5.000	0.0	42	8 : 0 : 8
2	4.375	0.3	42	7 : 1 : 8
3	3.73	0.6	42	6 : 2 : 8
4	3.125	0.9	42	5 : 3 : 8
8	10.00	0.0	52.5	8 : 0 : 5

Table II   Formulations for PU Elastomers with Plasticizer Added

| Sample No.	SP-450 (g)	PUR-500 (g)	Plasticizer (g)	Plasticizer (wt %)
5	5	42	0	0
6	5	42	9.4	20
7	5	42	18.8	40

oms in the glassy state. According to the "iso-free-volume" hypothesis, the free volume of a polymer system may be increased by increasing the number of chain ends or inclusion of a compatible compound of lower molecular weight. The large amount of free volume surrounds the branches causing what has been called colloquially the "tent-pole-effect."[7] Therefore the T_g may thus be shifted to a lower temperature. One technique, using a monofunctional alcohol to create chain ends to act as plasticizers, especially in polyurethane systems, has been widely used.[8] In the internally plasticized resin, the plasticization is achieved by branching, and the permanent attachment of these so-called tent-poles along the main polymer chain may cause the resin to be softer. Thus the impact and energy-absorbing

properties of the polyurethane foam can be substantially increased.[9]

In this work, a large molecule, isocyanate-terminated, difunctional prepolymer, instead of small diisocyanate molecule, for example, MDI or TDI, was used in the reaction with a polyol of high functionality. The larger molecule of the dangling segments may reduce the tent-pole-effect and the chance of a shift of the T_g. In the reaction of the basic recipe as sample #1, all functional groups are used to form the crosslinked networks. In samples #2, #3, and #4, part of the octofunctional polyol is substituted by monofunctional alcohol. When the isocyanate reacts with the n-propanol, the polymer chain will stop growing and thus segments will dangle between two crosslinking joints. When more n-propanol is added, more dangling segments are created. The dynamic mechanical properties for these elastomers are shown in Figures 1 and 2. Figure 1 shows that the storage modulus at the rubbery state decreases as the added n-propanol increases. This result may be caused by the decrease of crosslinking density as the dangling segments increase. Figure 2 shows the loss-tangent data of the dangling elastomers. It is noted that neither the peak position nor the peak height have any significant change as the dangling segments increase. This means that the larger number of dangling segments causes little in-
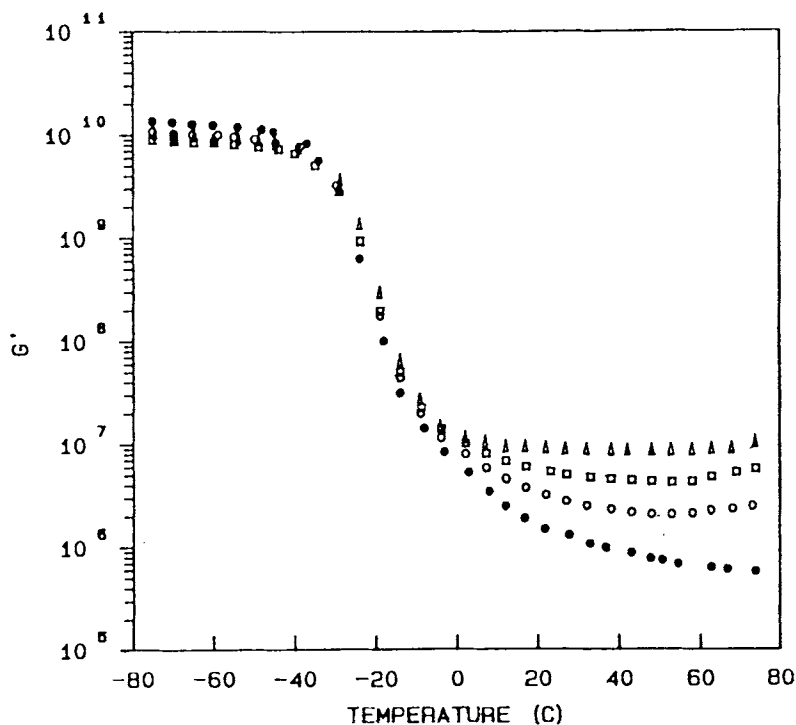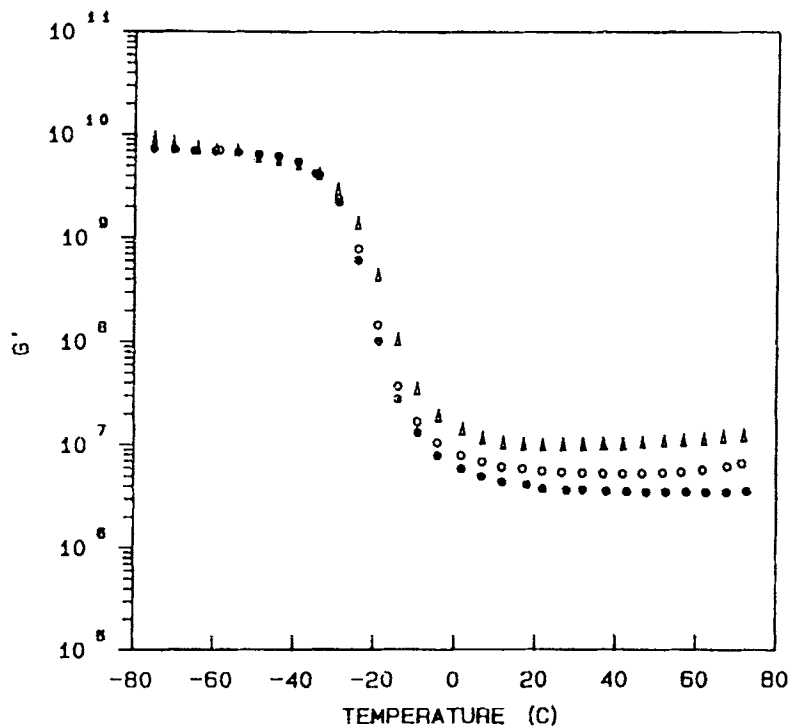

Figure 1   The storage modulus for dangling PU elastomers: ($\triangle$) #1; ($\square$) #2; ($\bigcirc$) #3; ($\bullet$) #4.
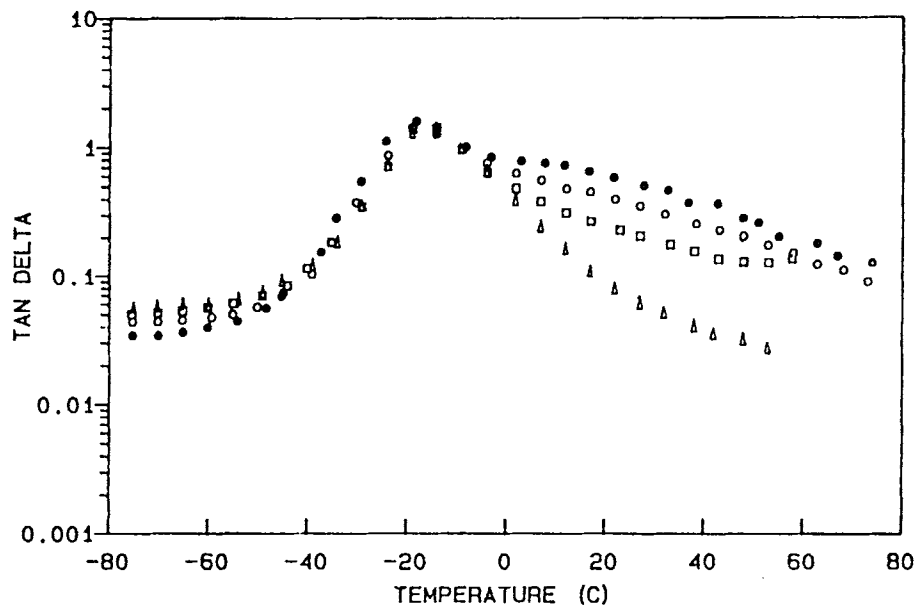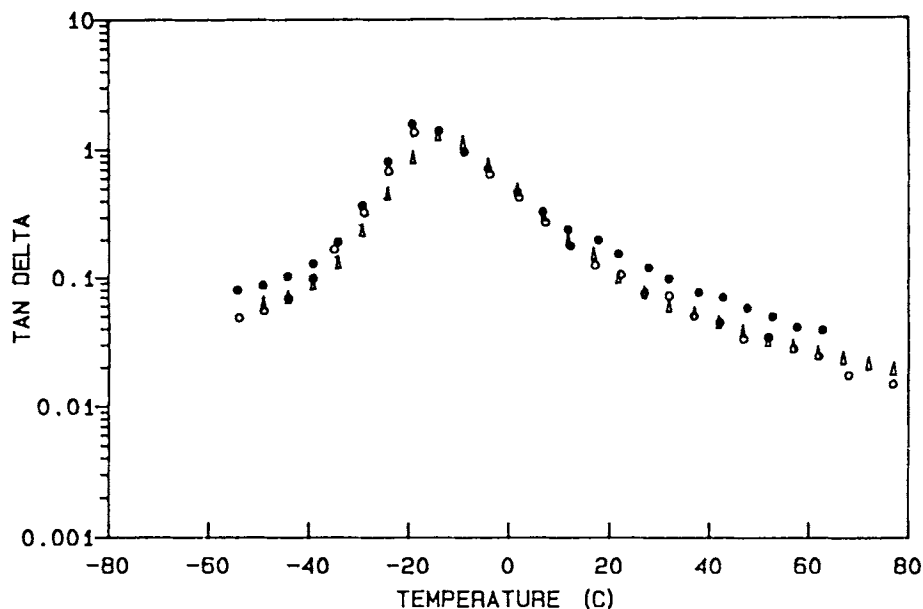
Figure 2 Temperature dependence of tan δ for dangling PU elastomers: (△) #1; (□) #2; (○) #3; (●) #4.

fluence on the T_g as previously assumed. But the loss tangent magnitude at a temperature higher than T_g increases as the number of dangling segments increase. With the onset of large-scale motion of polymer chain above the T_g, the energy loaded on polymer chain above the T_g, the energy loaded on the polymer networks may transfer to the dangling chains by the chain coupling mechanism and finally dissipates as heat. Thus, the loss tangent curve vs. temperature stays high over a broader temperature range above T_g, but does not change below T_g.


Figure 3 The storage modulus for plasticizing PU elastomers: (△) #5; (○) #6; (●) #7.

Figure 4 Temperature dependence of tan δ for plasticizing PU elastomers: ($\triangle$) #5; ($\bigcirc$) #6; ($\bullet$) #7.

Plasticizers are either monomeric or low-molecular-weight polymeric liquids that are added to high-molecular-weight polymers to reduce their rigidity or improve their flexibility. Thus, plasticizers are highly efficient in lowering the stiffness of polymers and T_g. They also tend to broaden the transition region.[10,11] The increasing loss tangent magnitude of dangling elastomers might be caused by the plas-

ticizing effect of nonreacted prepolymer. In order to distinguish the possibility of plasticizing effect from the dangling effect, both-end-blocked PUR-500, prepared by reacting PUR-500 with n-propanol, was blended into the crosslinked polyurethane elastomers as plasticizer. The formulations are listed in Table II and the dynamic spectroscopy is shown in Figures 3 and 4. It is noted that the inclusion of
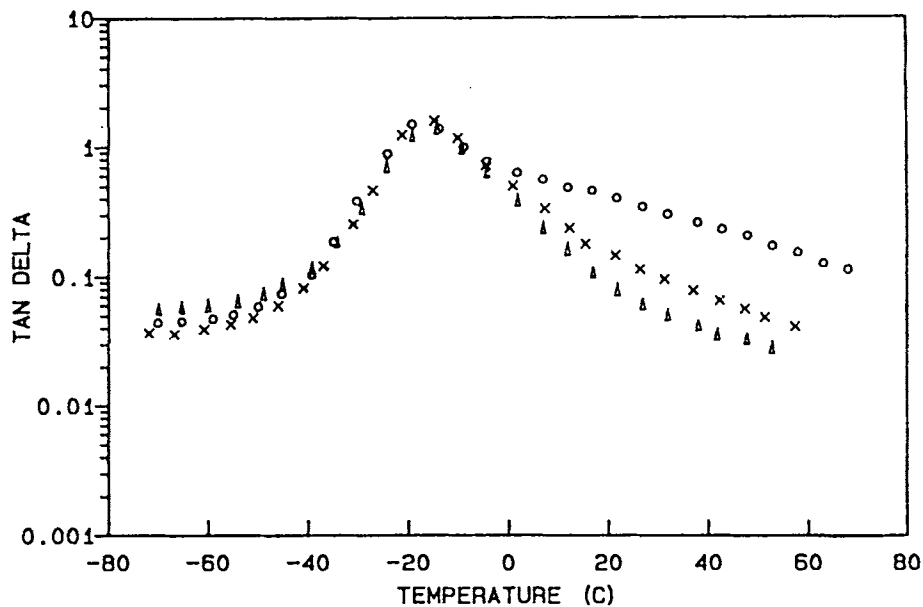
Figure 5 Temperature dependence of tan δ for PU elastomers: ($\triangle$) #1; ($\bigcirc$) #3; ($\times$) #8.

both-end-blocked PUR-500 gave little enhancement in loss-tangent magnitude or broadening of tan δ peak. In addition the T_g does not have any significant change (shift from $-14°C$ to $-18°C$). These results prove that the dissipation of energy loaded on the dangling elastomers is caused by the energy transfer through the coupling system to the dangling segments and not caused by the plasticizing effect of nonreacted prepolymer.

In general, the crosslinking density has a dramatic effect on the dynamic mechanical properties above T_g. At temperatures above T_g, the damping effect decreases with the increase of crosslinking density.[12] In the preparation of dangling elastomers, the crosslinking density decreases as part of the polyol is substituted by propanol. The influence of the decrease of crosslinking density on the damping effect is checked by preparing a sample with 3/8 equivalent hydroxyl group of octol unreacted with isocyanate. The formulation is listed in Table I as sample #8. The dynamic spectroscopy is shown in Figure 5 along with the dynamic curves of samples #1 and #3 for comparison. It shows that the decrease of crosslinking density does not result in much of an increase of damping magnitude above T_g as compared with that caused by dangling segments of sample #3.

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