

## Impact-induced glass transition in elastomeric coatings

R. B. Bogoslovov and C. M. Roland<sup>a)</sup>

Naval Research Laboratory, Chemistry Division, Code 6120, Washington, DC 20375-5342

R. M. Gamache

Naval Surface Warfare Center, Research and Technology Department, Indian Head, Maryland 20640

(Received 16 April 2007; accepted 8 May 2007; published online 31 May 2007)

Polybutadiene (PB) has a low glass temperature  $T_g$  and exhibits rubbery behavior during mechanical perturbation. The corresponding PB-based polyurea (PU) has a higher  $T_g$  and fails in a brittle mode for high strain rates. However, unlike in glasses, this brittle failure is accompanied by large energy dissipation. Dielectric relaxation measurements demonstrate that whereas the PB segmental dynamics are faster than the strain rate during impact loading, for PU these motions are on the order of the strain rate,  $\sim 10^5 \text{ s}^{-1}$ . Consequently, impact induces a transition to the glassy state, with the accompanying response markedly different from that of a rubber. © 2007 American Institute of Physics. [DOI: 10.1063/1.2745212]

Although high elasticity is the defining characteristic of rubber, elastomers are also used because of the substantial mechanical hysteresis and energy loss accompanying their deformation. Applications of rubber relying on this inelasticity include<sup>1</sup> dampers, anechoic coatings for sound absorption, wet-skid-resistant tire treads, shock absorbers, and vibration isolation systems (although damping is not always the main purpose of the latter two). Some applications involve high rates of strain, for which the response of the elastomer may differ appreciably from typical rubbery behavior. In particular, if the loading imposes a strain rate sufficiently high that the material response extends to frequencies beyond the rubbery plateau regime of the viscoelastic spectrum, rearrangements of the polymer chains over a significant length scale are precluded. The polymer exhibits a “leathery” behavior as it begins to transition to a glassy state; this glass transition zone is associated with large energy dissipation.<sup>2</sup> To exploit this effect requires rubbers having relatively high glass transition temperatures, although  $T_g$  must be lower than the use temperature. The exact value depends on the relevant strain rate.  $T_g$  is conventionally defined as the temperature at which the heat capacity or thermal expansivity changes abruptly. However, the glass transition temperature is rate dependent<sup>3</sup> (“dynamic glass transition”), so that in the present context a more useful definition of  $T_g$  is the temperature at which the material response becomes significantly slower than the experimental time scale (i.e., Deborah number  $\gg 1$ ). When this condition prevails during impact loading, the rubber transitions to a glass, with consequent high levels of mechanical energy absorption.

Two polybutadiene-based elastomers were studied: 1,4-polybutadiene (PB), reacted with 0.05% organic peroxide to form a lightly cross-linked network (for shape retention), and a polyurea (PU) formed by the reaction of amine-terminated 1,4-polybutadiene (1.2 kg/mol molecular weight) with an isocyanate. The PU has a partially phase-separated structure, with rigid isocyanate domains embedded within the compliant polybutadiene. It was measured by thermal gravimetric analysis to have a water content equal to 0.8%, reflecting the absorption of ambient humidity. The important distinction

between the two rubbers is that  $T_g$  (measured calorimetrically) of the polybutadiene is about 32° lower than  $T_g$  of the polybutadiene phase of the polyurea (see Table I). (Note that the  $T_g$  of the PU hard segment domains is much higher,  $>400 \text{ K}$ , and not relevant herein.) Dielectric relaxation measurements of the local segmental dynamics were carried out using a Novocontrol alpha analyzer. From these data we determine the frequency of the local segmental relaxation process, which gives rise to a prominent dispersion in the dielectric loss spectrum. The local segmental dynamics involve correlated conformational transitions of a couple of backbone bonds and, along with all chain motions over larger length scales, become “frozen out” upon vitrification. Dielectric spectroscopy has the advantage over mechanical measurements because dielectric data can be routinely obtained at high frequencies ( $\leq 10^6 \text{ Hz}$ ). Room temperature impact tests were also carried out on the two elastomers. The impact tests involved accelerating a metallic projectile through the rubber, with the latter affixed to a steel substrate. High speed video was used to determine the projectile velocity, and thus the strain rate imposed on the elastomer coating. Prior mechanical characterization of this PU has been limited to strain rates below  $10^4 \text{ s}^{-1}$ .<sup>4-6</sup>

The dielectric loss curve for the PU at 296 K is shown in the inset to Fig. 1. The absorption peak corresponds to the segmental dispersion, reflecting the local motion of dipoles oriented transverse to the chain contour (this process is also seen in the spectra of polar, glass-forming liquids and is commonly referred to as the  $\alpha$  relaxation<sup>7</sup>). The PU exhibits a broad dispersion, more than two decades half-width at half maximum on the low frequency side (the measurements were limited to frequencies  $< 10^7 \text{ Hz}$  due to cable impedance). The breadth of the PU peak is a consequence of the material’s morphology, with rigid isocyanate domains dispersed within the polybutadiene matrix, and the extensive intermolecular coupling engendered by the hydrogen bonding.<sup>8</sup>

The frequencies of the maximum in the dielectric loss,  $f_{\text{max}}$ , for both polymers are plotted in Fig. 1. The data for the PU span temperatures from approximately the calorimetric  $T_g$  to above room temperature. The dielectric strength of the PB is too weak (at least a factor of 25 lower than for the PU)

<sup>a)</sup>Electronic mail: [mike.roland@nrl.navy.mil](mailto:mike.roland@nrl.navy.mil)

TABLE I. Segmental relaxation parameters for the two elastomers.

	$T_g$ (K)	$\log(f_0/s)$	$B$	$T_0$	$\log(f_{\max}/s)$ at $T=296$ K
PB	182	$11.1 \pm 0.2$	$349 \pm 15$	$152 \pm 1$	$8.7 \pm 0.5$
PU	213	$11.0 \pm 0.3$	$694 \pm 68$	$160 \pm 4$	$5.95 \pm 0.3$

to obtain results above 204 K. The solid curves in the figure are fits to the Vogel-Fulcher equation<sup>2,7</sup>

$$\log f_{\max} = \log f_0 - \frac{B \log(e)}{T - T_0}, \quad (1)$$

in which  $B$  and  $T_0$  are constants and  $f_0$  is the asymptotic, high temperature value of  $f_{\max}$ . The parameter values obtained for the polymers are listed in Table I. The  $T$  sensitivity decreases strongly with temperature; for example, the apparent activation energy for the PU segmental dynamics changes from 186 kJ/mol at the lowest temperatures in Fig. 1 to 83 kJ/mol at the highest temperatures. From the data we determined the  $f_{\max}$  for 296 K listed in Table I. This quantity defines the frequency for the transition to the glassy state under ambient conditions of temperature and pressure. Note that the segmental dynamics of the PB are almost three orders of magnitude faster than for PU.

A layer of each rubber (thicknesses systematically varied from 0.64–1.9 cm) was applied to 5.1 mm thick steel plates using a cyanoacrylate adhesive for the PB and relying on the inherent adhesion of the PU to the steel surface. (The use of mechanical fasteners for the PB instead of chemical adhesion had no discernible effect on its response.) A 13 g cylindrical projectile (flat face with a cross-sectional area of 1.3 cm<sup>2</sup>) impinged at normal incidence on the rubber-coated surface of the laminate at room temperature, with the response of each polymer shown in Fig. 2. The PB deforms in a typical rubbery fashion—a high level of strain, with the deformation very delocalized. The PU behavior is quite different. There is minimal stretching of the rubber; rather, it shatters in a brittle fashion upon impact. A measure of the energy dissipated to

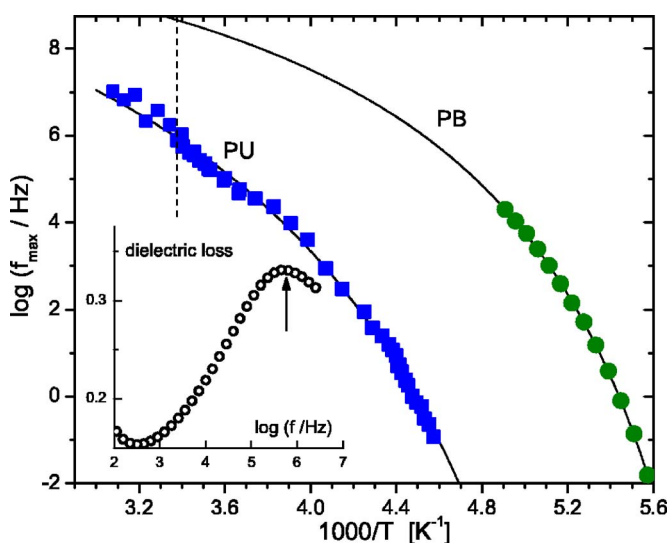


FIG. 1. Frequencies of the maximum in the dielectric loss peak. The solid lines are fits to Eq. (1) (see Table I). The inset shows the loss spectrum of the polyurea at 296 K (corresponding to the vertical dashed line in the main figure), with the peak frequency indicated by the arrow. The measurement terminates on the high frequency side due to cable inductance.

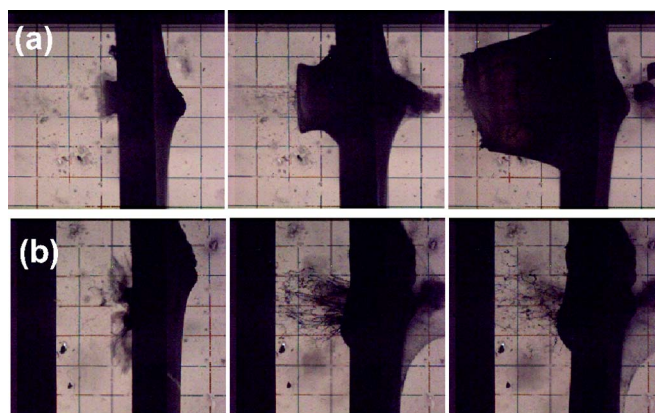


FIG. 2. (Color online) High speed photographs of the impact response of (a) polybutadiene (rubbery behavior) and (b) polyurea (induced glass transition). The projectile arrives from the left (speed  $\sim 900$  m/s), making an initial contact with the rubber-coated side. The grid lines are spaced 25 mm apart. The preexisting protrusions evident in the substrate are from previous impacts.

the rubber can be estimated from the change in kinetic energy of the projectile after traversal of the coating, calculated from the velocities with and without the rubber in place on the steel substrate. For the PU these were measured to be 899.2 and 586.7 m/s, respectively. The energy loss to the rubber is then 3 kJ, which corresponds to a strain energy density of about 4 GJ/m<sup>3</sup>, assuming no delocalization. (This assumption is consistent with the absence of any visual perturbation to the PU away from the immediate locus of the impact.)

The ratio of the projectile velocity to the rubber thickness defines the mean strain rate for the impact loading,  $= (1.4 \pm 0.1) \times 10^5$  s<sup>-1</sup> for the 0.64 cm coatings. This is more than 3.5 orders of magnitude less than the frequency of segmental relaxation of the polybutadiene; thus, the PB chains can accommodate the imposed strain and respond in a rubbery mode. However, the strain rate is within a factor of 6 of  $f_{\max}$  for the PU at this temperature, causing its response to traverse the glass transition zone of the viscoelastic spectrum. The consequence is the glassy, brittle mode of failure seen in Fig. 2.

Mechanical characterization of the PU was reported previously for strain rates as high as  $\sim 9 \times 10^3$  s<sup>-1</sup>, through which there was no qualitative change in the nature of the stress/strain curves,<sup>4</sup> indicating the material remains in the rubbery state during the tests. For the highest strain rate, the energy density of the PU was only about 0.04 GJ/m<sup>3</sup>;<sup>4</sup> that is, the strain energy for a rubbery response is two orders of magnitude smaller than the value observed herein for impact loading. This corroborates our conclusion that the high strain rate of the impact test induces a transition of the PU to the glassy state, with the appearance of brittle failure yet concomitant large energy dissipation.

In summary, a change of  $\sim 30$  K in the glass transition temperature of an elastomer can cause a qualitatively different response to impact loading. When the local segmental dynamics of the polymer become slower than the mechanical strain rate, a transition to the glassy state is induced by the impact, resulting in brittle failure. However, this failure is accompanied by substantial energy dissipation, unlike such failure in glassy materials. The essential requirement is that a transition to the glassy state occur during the deformation.

These results demonstrate the effectiveness of high  $T_g$  elastomers for damping applications involving a rapid application of mechanical stress. Of course, the resistance to penetration of a laminate likely entails other factors beyond direct energy dissipation, such as impedance matching, mode conversion, and strain delocalization. Mechanical coupling between the polymer and the steel substrate is expected to affect the distribution of the impact pressure and thus influence the response of the laminate. However, such ballistic performance is beyond the scope of the present study.

This work was supported by the Office of Naval Research. One of the authors (R.B.B.) thanks the American Association of Engineering Education / Naval Research Laboratory for a postdoctoral fellowship. The authors thank

Dave Owen of NSWC-Caderock for preparing the polyurea samples and Riccardo Casalini of NRL for assistance with the dielectric experiments.

<sup>1</sup>C. M. Roland, *Rubber Chem. Technol.* **79**, 429 (2006).

<sup>2</sup>E. Riande, R. Diaz-Calleja, M. G. Prolongo, R. M. Masegosa, and C. Salom, *Polymer Viscoelasticity* (Dekker, New York, 2000).

<sup>3</sup>C. M. Roland, S. Hensel-Bielowka, M. Paluch, and R. Casalini, *Rep. Prog. Phys.* **68**, 1405 (2005).

<sup>4</sup>S. S. Sarva, S. Deschanel, M. C. Boyce, and W. Chen, *Polymer* **48**, 2208 (2007).

<sup>5</sup>J. Yi, M. C. Boyce, G. F. Lee, and E. Balizer, *Polymer* **47**, 319 (2006).

<sup>6</sup>C. M. Roland, J. N. Twigg, Y. Vu, and P. H. Mott, *Polymer* **48**, 574 (2007).

<sup>7</sup>*Broadband Dielectric Spectroscopy*, edited by F. Kremer and A. Schönhalz (Springer-Verlag, Berlin, 2003).

<sup>8</sup>K. L. Ngai and C. M. Roland, *Macromolecules* **26**, 6824 (1993).