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Effect of hydrostatic pressure on the viscoelastic response of polyurea

C.M. Roland [a,*], R. Casalini [a,b]

[a] *Naval Research Laboratory, Chemistry Division, Code 6120, Washington, DC 20375-5342, United States*
[b] *Chemistry Department, George Mason University, Fairfax, VA 22030, United States*

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Abstract

Dielectric spectroscopy is used to measure the local segmental relaxation times for the soft segments of a polyurea as a function of temperature and pressure. In combination with the equation of state determined for the material, we show that the relaxation times are uniquely defined by the product of temperature times specific volume, with the latter raised to the power of 2.35 ± 0.10. This superpositioning of the relaxation times enables both the local segmental and the global chain dynamics to be calculated for any combination of temperature and pressure, using only measurements at ambient pressure. Since this polyurea finds applications as a coating to mitigate the damage from impact loading, its response to high frequencies and elevated hydrostatic pressure is of some import.

Keywords: Polyurea; Pressure; Viscoelasticity

1. Introduction

Polyurea (PU) is the generic term for the block copolymer formed from reaction of diisocyanates with polyamines. Commercialized in 1989, PU can exhibit a wide range of mechanical properties, from soft rubber to hard plastic depending on the chemistry. The range of properties together with their rapid reaction has led to many applications as coatings, for example on tunnels, bridges, roofs, parking decks, storage tanks, freight ships, truck beds, etc. More recently PU has been used in laminates on buildings and vehicles to impart impact resistance to the structure. For example, building foundations coated with PU are more resistant to damage from a bomb blast and are less likely to fragment (debris propelled by the blast pressure is a leading cause of injury in bombed buildings) [1–3]. PU coatings are also applied to military armor to increase its resistance to ballistic penetration [1,4]. The mechanism of blast and ballistic mitigation from PU laminates is not entirely understood, but contributing factors may include delayed onset of necking of the metal substrate [5], alteration of stress waves through the laminate [6] and substantial energy dissipation within the PU due to a strain-induced transition from the rubbery to the glassy state [7]. The glass transition zone of polymers is the region of greatest energy dissipation and this transition can be induced in rubbers by sufficiently fast deformation [8].

In light of the growing applications of PU for improving impact resistance, there has been substantial effort of late to characterize its viscoelastic behavior, including high strain rate testing in tension [9], compression [10–12], and combined bulk and shear [13,14], as well as modeling [5]. Such efforts are essential for understanding and optimizing the performance of PU coatings. When subjected to impact, the PU coating experiences a locally elevated pressure, in addition to the compressive strain. Since hydrostatic pressure changes the viscoelastic response, an accurate determination of pressure effects is warranted. To date studies addressing this effect have been limited to combined volume and shear deformation experiments, requiring subsequent deconvolution of the pressure effect [13,14] . It is difficult to carry out directly mechanical measurements with hydrostatic pressure as a distinct experimental variable.

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* Corresponding author. Tel.: +1 202 767 1719; fax: +1 202 767 0594.
E-mail address: roland@nrl.navy.mil (C.M. Roland).

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A complicating factor in characterizing the mechanical response of a polymer is that the temperature, T, and pressure, P, dependences depend strongly on the viscoelastic modes that are probed. The chain modes, as described by Rouse, reptation, and various other rheological models [8,15], have a weaker response to thermodynamic variables than do the local segmental modes. The latter arise from intermolecularly cooperative conformational transitions of the polymer backbone and serve as the mechanism of the glass transition, as well as being the precursor to the chain motions responsible for rubbery and flow properties. The difference in temperature dependence of the global and local modes was discovered more than 40 years ago [16] and has been demonstrated for various elastomers, including polyisoprene [17], polyisobutylene [18], and amorphous polypropylene [19]. More recently the different response to pressure of these modes has been reported for polyisoprene [20], polypropylene glycol [21,22], and polyoxybutylene [23]. If the impact of the laminate coating causes transition of the polymer to the glassy state, as has been demonstrated for PU in representative applications [7], accurate characterization of the P dependence of the local segmental dynamics is essential.

An alternative to mechanical measurements of the local segmental dynamics is dielectric spectroscopy. The local dynamics measured dielectrically are identical to the segmental motions underlying the dynamic mechanical properties in the glass transition zone. Although dielectric relaxation times are somewhat longer than mechanical relaxation times [17,24,25], their variation with thermodynamic conditions is expected to be the same. Dielectric spectroscopy has three advantages over mechanical experiments in this regard: (i) the resolution of the local modes from the chain modes is unambiguous; (ii) the frequency range of dielectric measurements is broader, routinely covering 9 or more decades; and (iii) the absence of moving parts in the dielectric experiment facilitates measurements at elevated pressure. Of course, the dielectric experiment probes only the linear response. In the present work we measured dielectrically the local segmental dynamics of the soft segments of a PU of interest as a coating for blast and ballistic mitigations. The measurements extended over a range of $232 < T\,(\mathrm{K}) < 299$ and pressures up to almost 1 GPa. The calorimetric glass transition temperature of the soft segments is *ca*. 182 K, whereas T_g of the PU hard segment is higher than 400 K, and thus not relevant herein [7]. We also report the equation of state (EOS) for the material, obtained from static PVT measurements. Using the latter, we show that the relaxation times for the PU superpose as a function of the product variable, temperature times specific volume with the latter raised to the power of 2.35. This master curve enables the dynamics to be obtained for any combination of T and P for relaxation times in the range from less than 1 μs to ~1 s.

2. Experimental

The polyurea was formed by reaction of Isonate 143L (Dow Chemical) and Versalink P1000 (Air Products), in the ratio of 1:4 isocyanate to amine. Prior to measurements the sample was annealed to a water content of 3.5%, as determined by thermogravimetric analysis.

Dielectric spectroscopy was done using a parallel plate geometry with the sample in the form of a disk (16 mm diameter, 2 mm thick). Spectra were obtained as a function of T and P using a Novocontrol Alpha analyzer (10^{-2}–10^{6} Hz). For measurements at ambient and elevated pressure, the sample capacitor assembly was contained in a Manganin cell (Harwood Engineering), with pressure applied using an Enerpac hydraulic pump in tandem with a pressure intensifier (Harwood Engineering). Pressures were measured with a Sensotec tensometric transducer (resolution = 150 kPa). The sample assembly was contained in a Tenney Jr. temperature chamber (±0.1 K precision at the sample).

Changes in volume as a function of pressure at fixed temperature were obtained with a Gnomix instrument [26], utilizing mercury as the confining fluid. The experimental range was $10 \le P\,(\mathrm{MPa}) \le 200$ and $299.0 \le T\,(\mathrm{K}) \le 386.5$. Samples with ~1 ml volume were cut from the same PU sheet used for dielectric samples. The differential volume data were converted to specific volumes using the value of $V = 0.9052$ g/ml, determined at 295.9 K and ambient pressure by the buoyancy method.

3. Results and discussion

3.1. Equation of state

The specific volume change was measured over a temperature range from $299 < T\,(\mathrm{K}) < 387$ as a function of pressure up to 200 MPa (Fig. 1). The Tait EOS [26] describes well the behavior of liquids and polymers above the glass transition:

$$V(T,P) = \left(a_0 + a_1 T + a_2 T^2\right)\left[1 - C\ln\left(1 + P/b_0\exp(-b_1 T)\right)\right] \tag{1}$$

Fitting the experimental data we obtain the Tait parameters in Table 1. At ambient conditions the bulk modulus, B, equals

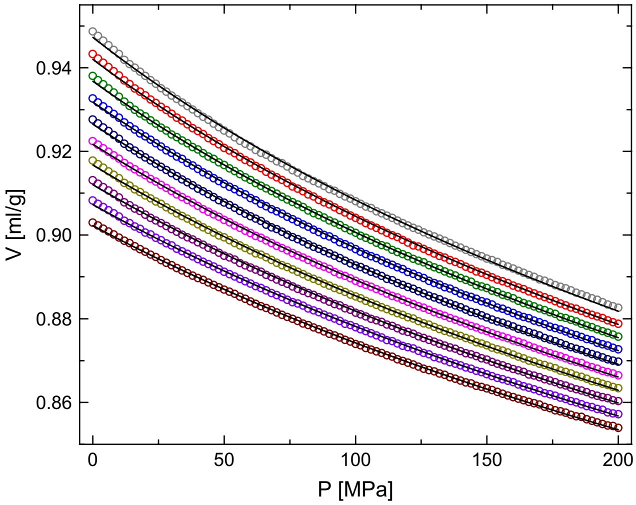

Fig. 1. Specific volume of the polyurea at (bottom to top) $T = 299.2$, 309.3, 318.7, 328.0, 337.8, 347.1, 357.3, 367.0, 376.9, 387.0 K.