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ScienceDirect
Polymer 48 (2007) 5747–5752
polymer
www.elsevier.com/locate/polymer

Effect of hydrostatic pressure on the viscoelastic response of polyurea

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Received 25 May 2007; received in revised form 9 July 2007; accepted 10 July 2007
Available online 15 July 2007

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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0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.07.017

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 $10 \leq P\,(\mathrm{MPa}) \leq 200$ and $299.0 \leq T\,(\mathrm{K}) \leq 386.5$. 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:

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

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

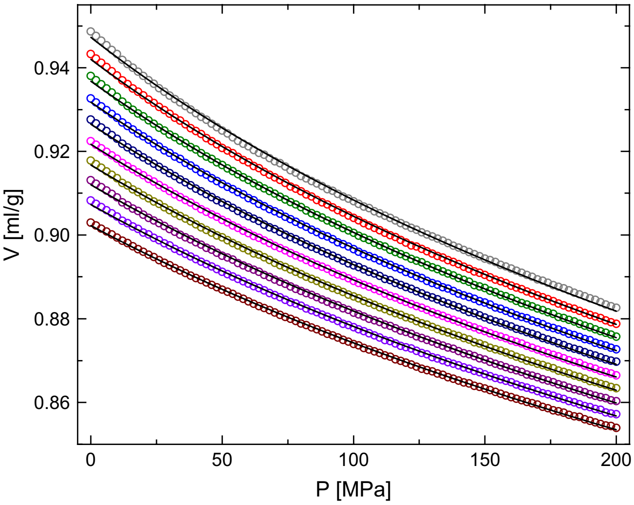

Fig. 1. Specific volume of the polyurea at (bottom to top) $T = 299.2$, 309.3, 318.7, 328.0, 337.8, 347.1, 357.3, 367.0, 376.9, 387.0 K.

2.57 GPa, with $dB/dP = 12 \pm 1$. This is larger than the bulk modulus reported by Chakkarapani et al. [13] from simultaneous shear and volume deformation experiments, $B = 2.10$ GPa. For the ambient thermal expansion coefficient we obtain $\alpha_P = 5.53 \times 10^{-4}\ \mathrm{K}^{-1}$. Amirkhizi et al. [12] cited a much lower value of $2 \times 10^{-4}\ \mathrm{K}^{-1}$, obtained by an unspecified method. We believe the results herein are more accurate, due to the higher accuracy of our measurement technique; however, it should be recognized that the properties of polyurea are very sensitive to chemical stoichiometry [9], so that samples prepared in different labs could show differences.

3.2. Temperature and pressure effects on local segmental relaxation

Dielectric relaxation spectroscopy was carried out on the PU at ambient and elevated pressures, with representative dielectric loss spectra shown in Fig. 2. With decreasing temperature or increasing pressure, the dispersion in the dielectric loss shifts toward lower frequency. We can define a local segmental relaxation time, representing the most probable value, as $\tau = (2\pi f_{\max})^{-1}$, where $f_{\max}$ is the frequency of the peak maximum. The isobaric data, plotted *vs.* inverse T in Fig. 3, show the usual non-Arrhenius behavior. Included in the figure are data for this same PU but with less absorbed water [7]. PU is hygroscopic, so that its moisture content is affected by the ambient humidity. At higher temperatures in Fig. 3, there is no discernible effect, but with cooling the relaxation times for the two samples show some deviation.

Amirkhizi et al. [12] reported mechanical measurements on the PU using a Hopkinson split bar apparatus. These were carried out at a constant strain rate $\sim 3000\ \mathrm{s}^{-1}$ at temperatures down to 273 K. From the data in Ref. [12], the PU remained in the rubbery state during the high strain rate mechanical test, which is consistent with the fact that the time scale of the deformation, 0.3 ms (indicated by the horizontal line in Fig. 3), is longer than the τ measured for the PU; thus, the chain segments can response to the impulse loading. It is only at faster applied strain rates, corresponding to time scales on the order of 6 μs, that the deformation will involve the local segmental dynamics, with the PU transitioning to a glassy state during impact [7].

At constant temperature the relaxation times increase linearly with pressure (Fig. 4). From mechanical experiments at $3000\ \mathrm{s}^{-1}$, Amirkhizi et al. [12] reported a pressure coefficient of the shift factor for the chain (Rouse) modes of this material equal to 7.2 K/GPa. From Fig. 4 we deduce a linear coefficient of 120 ± 14 K/GPa at the frequency of the mechanical experiments. Thus, the segmental modes of PU have a much stronger P dependence than found previously for the chain modes (as noted above, the PU exhibited rubbery behavior in the mechanical experiments [12]). This difference is unsurprising, since similar to the T dependence [16–19], the P dependence of polymer dynamics is stronger for local modes than for chain modes [20,21,23].

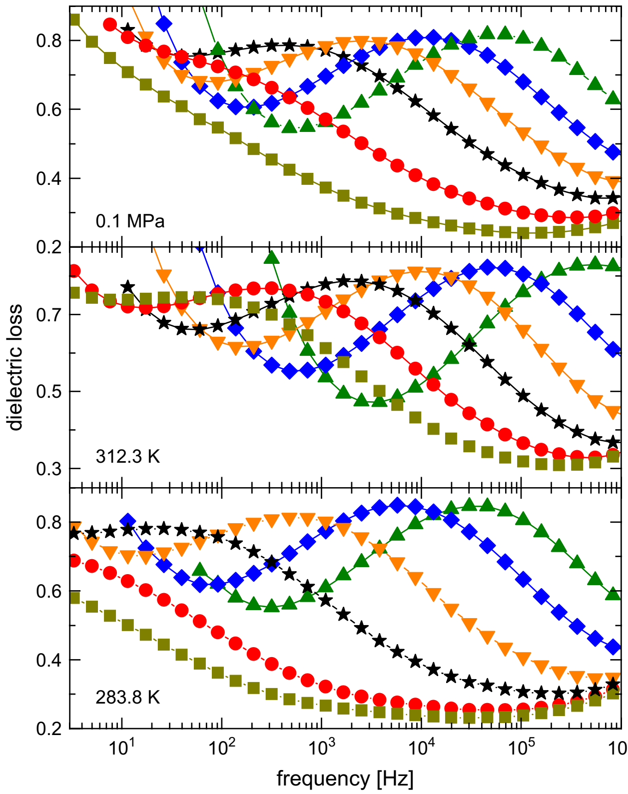

Fig. 2. Representative dielectric loss spectra: (top, from left to right) $T = 232.7$, 242.4, 252.3, 262.4, 273.2, and 288.6 K; (middle, from left to right) $P = 845.0$, 703.1, 517.3, 365.5, 210.9, and 22.3 MPa; (bottom, from left to right) 730.0, 636.3, 430.8, 258.3, 107.1, and 4.9 MPa. The rise toward lower frequency is due to dc conductivity.

The activation volume, $\Delta V^{\#}$, is the usual parameter for quantifying this pressure dependence:

$$\Delta V^{\#} = \frac{RT}{\log(e)} \frac{\partial \log \tau}{\partial \log P}\bigg|_T \tag{2}$$

where R is the gas constant and e is Euler's number. The implied proportionality between $\log \tau$ and $\log P$ describes the data in Fig. 4, but Eq. (2) is not expected to apply at sufficiently high pressures. In the inset of Fig. 4, $\Delta V^{\#}$ is shown for the four measurement temperatures, decreasing by $\sim 1/3$ over the range of T. This inverse variation of $\Delta V^{\#}$ with T is commonly found [27]. The activation volume is often interpreted as a measure of the volume swept out by the relaxing unit; thus, its magnitude is on the order of the repeat unit size.

Table 1
Equation of state parameters for PU above T_g

a_0 (ml/g)	a_1 (ml/g C)	a_2 (ml/g C^2)	b_0 (MPa)	b_1 (C^{-1})	C	$\alpha_P{}^a$ (C^{-1})	B^a (GPa)
0.890	4.90×10^{-4}	1.75×10^{-7}	220	4.03×10^{-3}	0.0776	5.53×10^{-4}	2.57

[a] $T = 298$ K; $P = 0.1$ MPa.

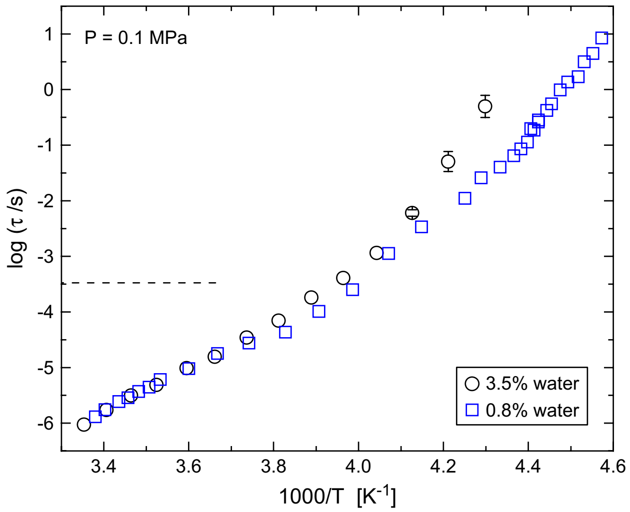

Fig. 3. Temperature dependence of the local segmental relaxation times measured at ambient pressure. Also included are data from Ref. [7] for this same PU but having a lower moisture content. The dashed horizontal line denotes the time scale of high strain rate mechanical tests [12], for which the PU exhibited a rubbery response.

The activation volume concept implies that volume governs the segmental dynamics, but this is not the case for the PU. To show this we use the EOS (Eq. (1)) to calculate the specific volume for each measurement condition, and plot in Fig. 5 the τ vs. V. It is clear that the relaxation times are not solely defined by V; rather changes in thermal energy amplify the variation of τ with V. Thus, a full accounting of the segmental behavior requires quantifying the relative contribution of T and V to the dynamics.

3.3. Thermodynamic scaling

There are various approaches to extract the distinct effects of T and V on τ. We have recently shown very generally for non-associated liquids and polymers that the structural or local segmental relaxation times are a single function of a product variable [28–30]:

$$\tau = f(TV^{\gamma}) \tag{3}$$

where γ is a material-specific constant. This means that the relaxation times measured for various T and P yield a master curve when plotted versus the quantity TV^{γ}. The exponent is constant with respect to T, P, and V, and for different materials varies over a broad range $0.14 \leq \gamma \leq 8.5$ [27]. We apply this scaling procedure herein to the polyurea data, adjusting the value of the exponent to obtain superpositioning of the τ (Fig. 6). The deduced value of $\gamma = 2.35 \pm 0.10$ is rather small, reflecting a weak influence of volume. The magnitude of the scaling exponent is related to the steepness of the intermolecular repulsive potential [31,32], with the low value for PU in keeping with the associated

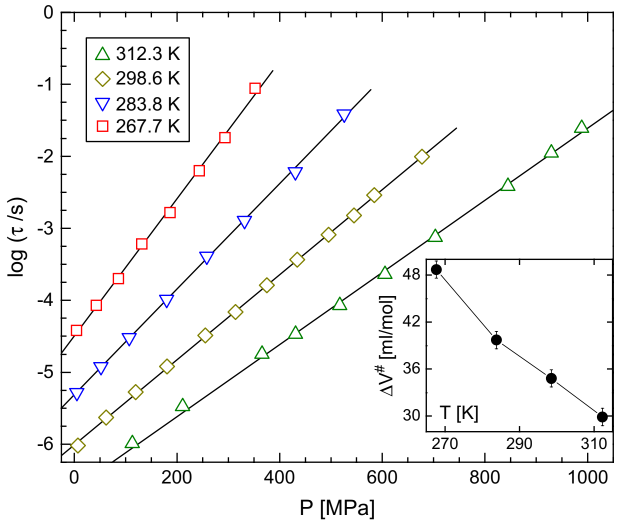

Fig. 4. Pressure dependence of the local segmental relaxation times at the indicated temperatures. The slopes of the fitted lines yield the activation volumes (Eq. (2)) displayed in the inset.

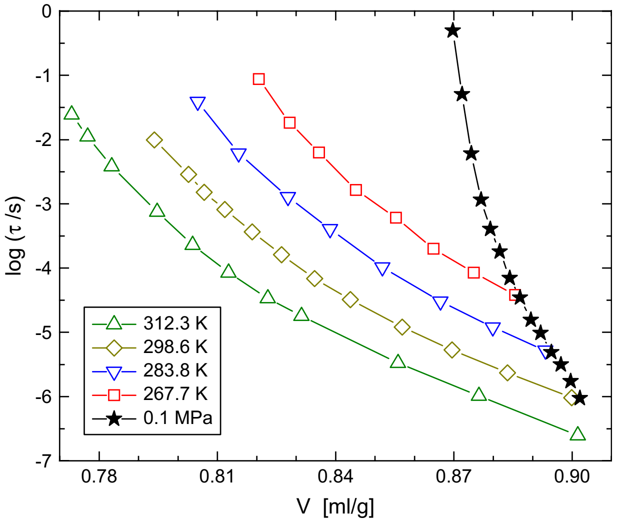

Fig. 5. Local segmental relaxation times plotted versus the specific volume.

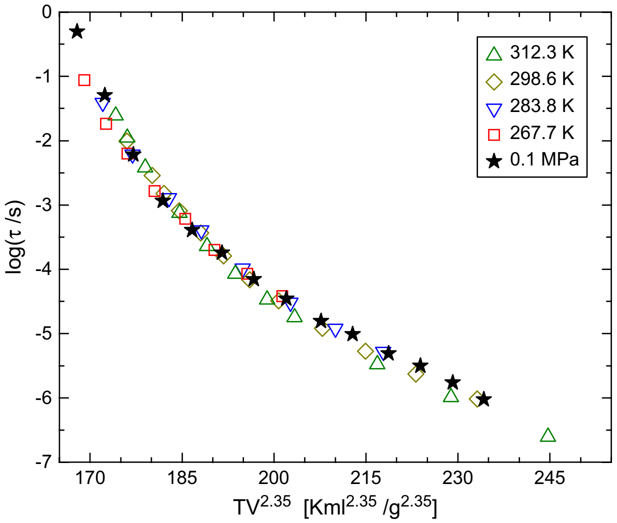

Fig. 6. Local segmental relaxation times plotted according to Eq. (3) with $\gamma = 2.35$.

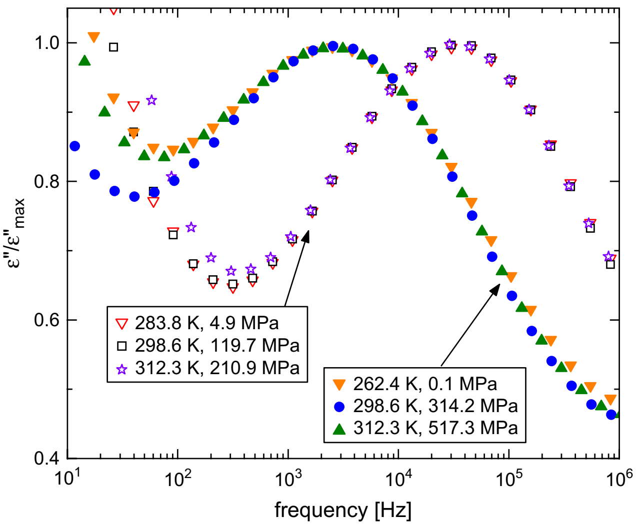

Fig. 7. Dielectric loss (normalized by the peak value) measured under conditions (as indicated) for which the peak frequency is equal to a constant value of: (solid symbols) 2560 Hz or (open symbols) 29,040 Hz. The spectra were shifted slightly along the abscissa to superpose the peaks.

nature of its chain segments. For strongly hydrogen-bonded liquids such as water, the thermodynamic scaling breaks down entirely with γ approaching unity (i.e., volume changes *per se* do not affect the dynamics) [32].

3.4. Isochronal superpositioning

Usually a decrease in temperature or increase in pressure (i.e., longer τ) causes the relaxation function (distribution of relaxation times) to systematically broaden. By judicious selection of P and T, combinations can be found for which the peak frequency for local segmental relaxation is constant; that is, higher pressure and higher temperature compensate to give constant τ. When this is the case, it has been shown quite generally that the peak shape (breadth) is constant [33,34]. This means that the relaxation function of a material at fixed τ is constant, independent of temperature and pressure.

We assess conformance of the PU to this temperature—pressure superpositioning of the segmental dispersion at constant τ. In Fig. 7 the dielectric loss peak is shown for 6 measurement conditions, for which $f_{\max}$ is equal to one of two values. The loss peak for a given $f_{\max}$ remains the same, except for the slight rise toward lower frequency due to dc conductivity. Thus, for PU the relaxation time determines the breadth of the segmental dispersion (but not the converse, since the breadth may be sensibly invariant to small changes in T or P). This peak breadth in turn is correlated with other relaxation properties, such as the "dynamic crossover" [35,36] and the "fragility", or T_g − normalized temperature dependence of τ [37].

4. Summary

The soft-segment local segmental relaxation times and the EOS were measured for a PU of special interest for ballistic and other impact applications. Both temperature and pressure affect the dynamics, with the product variable $TV^{2.35}$ yielding superposition of the τ. Using the obtained master curve, the relaxation time can be calculated for any thermodynamic condition; that is, if τ is known for any T and P, via Eq. (3) it can be calculated for any other T and P. Since as shown herein the shape of the relaxation function is a function of τ, this means that γ also uniquely defines the relaxation function. Thus, at least in the linear viscoelastic regime, the most important properties of the local segmental relaxation process − τ and its distribution − are governed entirely by the material constant γ. Although no normal mode was observed herein for the PU, we note that it has been found that the normal model relaxation times, reflecting the global chain dynamics, have been found to superpose as a function of TV^{γ}, with the exponent identical to the value yielding superpositioning of the local segmental relaxation times (although the dependence *per se* is weaker) [23,38,39]. This means that the chain relaxation times, obtained from rheological measurements at ambient pressure as a function of T, can be calculated for any arbitrary pressure, by making use of the scaling relationship, Eq. (3). Consideration of the effect of hydrostatic pressure can be quite important for blast and ballistic mitigation applications.

Acknowledgements

This work was supported by the Office of Naval Research. We thank D.P. Owen of NSWC-Caderock for preparing the polyurea sample, K.J. McGrath for assistance with the PVT measurements, and R.B. Bogoslovov of NRL for fruitful discussions.

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