Microscopic Origins of the Normal Force Responses of Glassy Polymers in the Subyield Range of Deformation

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ABSTRACT: Results from torsional stress relaxation experiments in which we measure the torque and normal force responses of two glassy poly(alkyl methacrylate)s are presented. Tests were performed at temperatures ranging from the dynamic glass transition (α-relaxation) to the first sub-glass transition relaxation (β-relaxation) and in the sub-yield range of deformations (strains ranging from 0.02 to 0.045) and at a fixed aging time of 4980 s. We found a significant difference between the relaxation behavior of the normal force response and the torque response of poly(methyl methacrylate) (PMMA). The results provide evidence that the normal force of PMMA is influenced by the β-relaxation. For specimens having a longer side chain length, i.e., poly(ethyl methacrylate) (PEMA), the difference between the normal force and torque relaxation behaviors is less. This is consistent with the less pronounced β-relaxation mechanism in PEMA. Furthermore, an examination of the effect of temperature on the ratio of the normal force modulus to the shear modulus of PMMA provides strong evidence that the normal force modulus relaxes faster than the shear modulus as the β-relaxation is approached. Also, following the scaling law relations of Penn and Kearsley, the derivatives of the strain energy density function with respect to the first and second invariants of the strain tensor were determined. Finally, the departure of the strain energy density function behavior of PMMA and PEMA from the neo-Hookean material behavior is shown.

1. Introduction

The molecular origins of material behavior are important to the ultimate ability to use current materials and to design new materials. In the case of polymeric glasses, there has been considerable work reported in the literature that relates specific molecular mechanisms to linear viscoelastic response. For example, side group motions are often attributed to be the cause of the so-called β-relaxation (the first sub-T_g relaxation) in the *n*-alkyl methacrylates.[1] Similarly, Yee and coworkers have extensively examined the behavior of polycarbonate and polyester.[2−6] They found that the β-relaxation of polycarbonate is due to the cooperative motion of several repeating units along the polymer chain. For polyester, the β-relaxation was attributed to local motion of the ester group.

In the case of nonlinear, but sub-yield, behavior, there have been few investigations of the impact of molecular structure on the response of polymer glasses. On the other hand, knowledge of the molecular origins of the nonlinear (finite) elasticity of cross-linked rubber and the nonlinear viscoelastic response of polymer melts and solutions is of fairly high order, and the models available have led to important progress in both fundamental understanding and practical applications. For example, the development of finite elasticity theory[7−10] and of molecular theories of rubber elasticity[11−14] and the reptation[15] and tube[16] models of melt behavior[17] were major accomplishments. The advances in the understanding of rubber behavior led to many practical advances in the design of rubber in load bearing applications from tires to earthquake isolation bearings for buildings. The reptation and tube models of polymer rheological behavior led to better understanding of molecular effects on, e.g., polymer processing.

Similar models are simply not available for the description of the nonlinear viscoelastic response of glassy polymers, and in fact, little relevant experimental information is available to address the issue. Here we report on new work that investigates the torque and normal force responses of two poly(*n*-alkyl methacrylates) to investigate the importance of the side group motion to the nonlinear response of these materials. In particular, we take advantage of the torsional measurements because to keep the sample at constant length it is necessary to apply not only a torque but also a normal force,[9,18,19] and the combination of torque and normal force responses provides more information about the material behavior than does the torque measurement alone. In the case of the cross-linked elastomers, the origins of the normal force response are understood to arise through a combination of the finite deformation geometry and the action of the molecular network through the strain energy density function[9,18,19] $W(I_1,I_2)$. In fact, molecular theories of rubber elasticity consider that the strain energy density function and the Helmholtz free energy are the same, and molecular models of rubber elasticity derive the latter from statistical mechanical approaches. In finite elasticity theory, this falls in the class of hyperelastic materials.[9] Similarly, the torsional response in a macromolecular melt can be understood in terms of the material functions in large shears or high shear rates through a molecular model such as the Doi−Edwards[17] tube model of reptation, where an equivalent of the strain energy density function is referred to as a damping function $h(I_1,I_2)$.[17,20,21] In both rubber elasticity and the Doi−Edwards models, details of the chemical structure are not considered to dramatically affect W or h, other than through parameters that impact cross-link density or entanglement molecular weights, respectively; i.e., the material behavior is well described by the molecular topology. For glassy materials, no equivalent exists, and we use the

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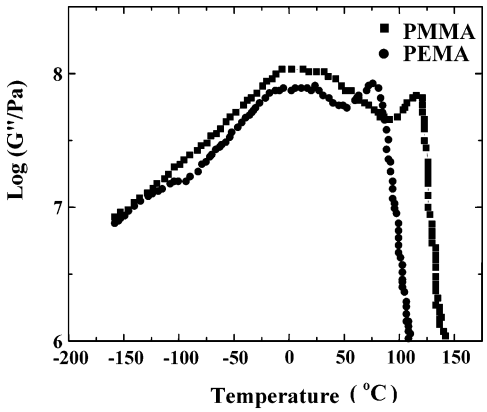

Figure 1. Temperature dependence of G'' at 1 Hz for poly(methyl methacrylate) and poly(ethyl methacrylate) (after Heijboer[1]). Data were digitized.

classical finite deformation framework to show subsequently that molecular level detail has a large effect on the nonlinear viscoelastic material functions.

Our experimental approach of performing torsional experiments arises from the observation that the normal forces that result when a polymeric glass is subjected to a torsional deformation can be very large,[22,23] even for relatively small and sub-yield deformations. There are no molecular or microstructural models to provide insight into the parameters that might affect the nonlinear response in the glassy state, which should be affected primarily by the local or segmental interactions[24] rather than the longer range topological interactions discussed above for melts and elastomers. Nor are there data that explore systematically the chemical structure effects on the normal forces. However, there is some preliminary evidence that they can vary dramatically with the chemical structure of the glassy polymer. In particular, consideration of the limited data available in the literature for the normal force response vs strain for glassy polymers reveals that at ambient temperature the normal force response of poly(methyl methacrylate) (PMMA) can be as much as three times that of polycarbonate. At the same time the torsional moduli of the samples are approximately the same.[22,25] (The measurements are considered at the same strain magnitudes.) An obvious difference between polycarbonate and PMMA at ambient temperature is the large β-relaxation related to side chain motions observed in PMMA.[1] The present work begins with the hypothesis that the strong normal force response of PMMA is a result of its prominent β-process. To investigate this hypothesis, our methodology consists of increasing the length of the methyl side group of PMMA to an ethyl side group, i.e., poly(ethyl methacrylate) (PEMA), which decreases the intensity of the β-peak. We then measure and compare the torque and normal force responses of PMMA and PEMA. In the *n*-alkyl methacrylates, increasing the side chain length not only decreases the intensity of the β-relaxation but also decreases the temperature at which the α-relaxation (glass transition) occurs. This is shown in Figure 1. Interestingly, the temperature location of the β-peak remains unchanged (around 30 °C) when the side chain length varies.[1] Consequently, the effects of two parameters on the normal force are investigated here, i.e., the intensity of β and the closeness or interaction between α- and β-relaxations.

In the following we first present the experimental methods used. This is followed by a description of the theoretical framework used to analyze the torque and normal force data to obtain the strain energy density material functions for both the PMMA and the PEMA as well as considering the deviations of behavior from the classical neo-Hookean response. We then present the results, provide a discussion of their meaning, and end with a set of conclusions.

2. Experimental Methods

2.1. Materials. The PMMA was obtained from Cadillac Plastics in the form of cast rods of 25 mm diameter. PEMA powder was obtained from Aldrich Chemical Co. The average molecular weight of the PMMA is 1×10^6 g/mol, and it is 8.5×10^5 g/mol for the PEMA as reported by the provider. The PEMA powder was molded into rectangular solid plaques using a platen press at a temperature of $T_g + 40$ °C (103 °C) for 5 h and then cooled slowly to below T_g. To facilitate gripping in a special fixture for torsion of solid materials,[22] samples with a gauge section of 25 mm length and 4.8 or 6 mm diameter were machined. The glass transition temperature (T_g) of each material was determined on cooling from DSC measurements at a rate of 10 °C/min and was found to be 116 °C for PMMA and 63 °C for PEMA. The samples were annealed at 4 °C above T_g for 1800 s before being machined and 900 s prior to each experiment in order to remove the effects of mechanical histories.

2.2. Torsional Measurements. The torsional measurements were performed using a Rheometrics RMS 7200 load frame equipped with a digitally controlled servomotor. The torque and normal force responses were measured using the RMS 7200 strain gage transducer that has a 2000 g normal force capacity and a 20 000 g cm torque capacity (original to the equipment). The sample and grips were placed in a heated chamber to control the temperature, allowing experiments to be performed from ambient to 100 °C with an oven stability of ±0.2 °C.

The strain is a linear function of the radius r; here γ_R is the nominal strain based on the outer radius:

$$\gamma_R = R\theta/L = \psi R \tag{1}$$

where R is the cylinder radius, θ is the angle of twist, L is the length of the gauge section, and ψ is the angle of twist per unit of length. The strains applied to the sample covered both linear and nonlinear viscoelastic ranges but below the yield point (from 0.02 to 0.045). The standard uncertainty in the torque measurement is 0.03 N m and is 0.8 N in the normal force measurement depending on the applied strain and temperature. In each experiment, the application of the constant strain takes less than 0.08 s. Effects of the finite rate ramp loading on the mechanical responses become negligible for the long relaxation times of these materials after 1 s of time,[26] and we only report data longer than 1 s after the beginning of the step (ramp).

As mentioned previously, prior to each single step stress relaxation experiment, the samples were kept at $T_g + 4$ °C for 900 s to remove the prior mechanical history. They were then quenched in less than 180 s to below T_g (80, 50, and 30 °C for PMMA; 50 and 30°C for PEMA). Because of this isobaric quenching process to below T_g, a nonequilibrium polymer glass was formed. Since nonequilibrium polymer glasses are unstable,[27] the volume of the samples spontaneously evolves toward the equilibrium volume when the samples are tested at constant temperature in the RMS oven. The approach to the equilibrium volume is associated with a change in the mechanical properties, so-called physical aging.[28] Therefore, to account for the changes observed during physical aging, the Struik protocol[28] was adopted. Here, the strains are applied sequentially at aging times that double with each stress relaxation test, and the duration of the stress relaxation test is one-tenth of the aging time (the moment of the quench defining the origin of the aging time). By using this protocol, not only the effect of physical aging during the application of

the strain was minimized but also the effect of the previous loading cycle. The results reported in this paper are for an aging time of 4980 s, and the duration of the stress relaxation tests is 360 s. Remark that this sequence provides "isochronal" aging information vs more difficult to obtain "isostructural" information.[29]

3. Theoretical Considerations

3.1. Torsion of an Incompressible Cylinder. In the present analysis, we assume that torsion is an isochoric motion (constant volume) and use incompressible theory to determine the derivatives of the strain energy density function. Assume a cylinder of length L and radius R subjected to a twist $\psi = \theta/L$ per unit of length. The strain through the cylinder is independent of the length and linearly dependent on the radial position r. The equations describing the torque and normal force as a function of the twist ψ imposed at the end of the incompressible cylinder material whose length is maintained constant were derived by Rivlin[7] as

$$T = 4\pi\psi\int_0^R (W_1 + W_2)r^3\,\mathrm{d}r \tag{2}$$

$$N = -2\pi\psi^2\int_0^R (W_1 + 2W_2)r^3\,\mathrm{d}r \tag{3}$$

where T is the torque, N is the normal force, and W_1 and W_2 are the derivatives of the strain energy density function with respect to the first and second invariants (I_1 and I_2) of the strain tensor, respectively. Using an appropriate change of variables and differentiation of T and N with respect to the limits of the integral in eqs 2 and 3, Penn and Kearsley derived eqs 4 and 5 as the scaling law for incompressible elastic materials:[30]

$$W_1(t) + W_2(t) = \frac{G(t)}{2} = \frac{1}{2\pi\psi R^4}\left[3T(t) + \psi\,\frac{\mathrm{d}T(t)}{\mathrm{d}\psi}\right] \tag{4}$$

$$W_1(t) + 2W_2(t) = \frac{N_\psi(t)}{2} = -\frac{1}{\pi\psi^2 R^4}\left[N(t) + \psi^2\frac{\mathrm{d}N(t)}{\mathrm{d}(\psi^2)}\right] \tag{5}$$

where $G(t)$ is the shear relaxation modulus at strain $\gamma = \psi R$, and we refer to $N_\psi(t)$ as the normal force relaxation modulus in the present work. One point to make here is that the above equations are for elastic materials, but we represent the $W_1(t)$ and $W_2(t)$ as isochronal values. This is consistent with Rivlin's elastic stress relaxing material for which data from isochronal experiments can be treated as elastic data.[31] In addition, McKenna and Zapas[32] showed that identical results are obtained within the framework of the BKZ viscoelastic theory[33] for isothermal, incompressible elastic fluids. By solving simultaneously eqs 4 and 5, the values of $W_1(t)$ and $W_2(t)$ can be determined as a function of twist from isochronal data of torque and normal force at different angles of twist. Note that the method requires good estimates of the slopes $\mathrm{d}T/\mathrm{d}\psi$ and $\mathrm{d}N/\mathrm{d}(\psi^2)$, which respectively make up $^1/_4$ of the total in eq 4 and $^1/_2$ of the total in eq 5 when the responses are linear and quadratic in strain, respectively. We obtained the slopes by performing a fifth-order regression to the isochronal torque data ($a\psi^5 + b\psi^3 + c\psi$) and a sixth-order regression to the isochronal normal force data ($a\psi^6 + b\psi^4 + c\psi^2$).

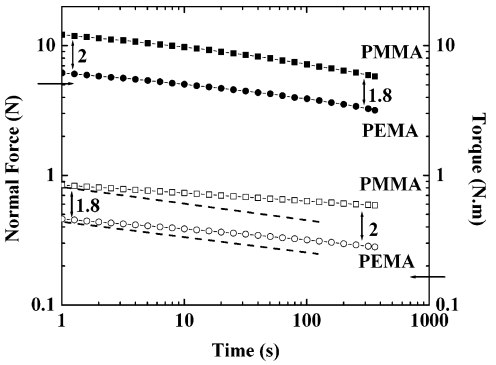

Figure 2. Double-logarithmic representation of the normal force and torque responses vs time for PMMA and PEMA in single-step torsional stress relaxation tests at a value of $\psi_R = 0.04$ and at 30 °C. The dashed lines are the normal forces shifted downwards so that the relaxation rate compared to the shear relaxation rates can be compared directly.

3.2. Neo-Hookean Class of Material. The neo-Hookean theory applies to incompressible materials having the strain energy function in the form $W(I_1)$ ($W_2 = 0$), and this is a common result for early molecular theories of rubber elasticity;[11−14] hence, it is of interest to examine how the behavior of the PMMA and PEMA compare with this model. Using eqs 4 and 5, a universal relation was proposed by Horgan and Saccomandi to describe this class of materials:[34]

$$\psi T(t) + 2N(t) = 0 \tag{6}$$

The above relation was used by Wineman[35] to evaluate the behavior of peroxide vulcanized natural rubber from data reported in torsion. The analysis consists of plotting $2|N(t)|$ as a function of $\psi T(t)$. For the neo-Hookean class of materials, the plot is a straight line with a slope of 1; otherwise, it is not a straight line or the slope differs from unity. Furthermore, for $W_2 > 0$[35]

$$\psi T(t) < 2|N(t)| \tag{7}$$

We remark again that the theoretical considerations presented in this paper use the condition of incompressibility such that the inhomogeneous deformation, in the present case torsion, can be used to measure the strain energy density function derivatives $W_1(t)$ and $W_2(t)$. Because polymer glasses are compressible materials, we recognize this as an approximation. However, volume changes in torsion are small ($\leq 10^{-3}$ cm^3/cm^3),[36−38] and work done by Schultheisz and McKenna suggests that the contribution of the volume change to the normal force is minor.[38]

4. Results

4.1. Time-Dependent Normal Force and Torque Responses. The relaxation data for PMMA and PEMA specimens at the β-peak temperature of 30 °C are presented in Figure 2 for a strain of 0.04. Both specimens have a normal force that relaxes faster than the torque does, though the difference is more pronounced for the PMMA. Also, we see that the torque response for the PMMA is higher and relaxes more slowly than does that of the PEMA. At short times, the torque response for the PMMA is 1.8 times higher than that of PEMA. With increasing time the difference between torque responses increases such that at a test time of 360 s the torque response for the PMMA is 2 times higher than that for the PEMA. This result is in

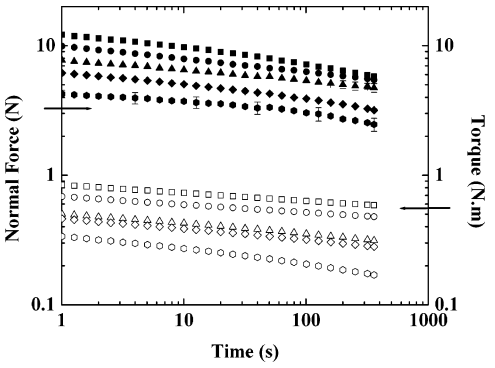

Figure 3. Double-logarithmic representation of the normal force (closed symbols) and torque (open symbols) responses vs time for PMMA and PEMA in single-step torsional stress relaxation tests at a value of $\psi_R = 0.04$ and at different temperatures: (□, ■) PMMA, 30 °C; (○, ●) PMMA, 50 °C; (△, ▲) PMMA, 80 °C; (◆, ◇) PEMA, 30 °C; (⬡, ⬢) PEMA, 50 °C. Error bars representing one standard deviation are smaller than the symbol signs, except at long times and at 80 °C.

agreement with the widely accepted concept that the shear modulus or torque of polymer glasses is mostly related to the experimental temperature compared with the glass transition temperature (α-relaxation). Here the tests were performed at 83 °C below the T_g of PMMA and 33 °C below the T_g of PEMA, and as expected, the torque response of the PMMA is higher than that of the PEMA and relaxes more slowly.

A different scenario is observed for the normal force responses of these materials. At short times the normal force for the PMMA is 2 times higher than that of the PEMA. Because of the faster relaxation rate of the PMMA normal force, at a test time of 360 s the PMMA's normal force is 1.8 times higher than that of the PEMA. The fast normal force relaxation rate of PMMA at 83 °C below the glass transition (where one might expect a slow relaxation process) suggests that the behavior is influenced differently at the molecular level than simply by the α-relaxation. Moreover, this result agrees with the hypothesis that the normal force response for PMMA is related to the prominent β-peak relaxation present at 30 °C. For PEMA specimens that have a weaker β-relaxation, one can expect the intensity of the normal force to be smaller and to relax more slowly. This is what is observed here.

4.2. Influence of Temperature on the Time-Dependent Normal Force and Torque Responses. On the basis of the present hypothesis that the normal force response is more strongly affected by the β-relaxation than is the torque response, we would expect that as we go far from and above the temperature of the β-relaxation maximum and therefore approach T_g, the intensity of the normal force should decrease. From the data presented in Figure 3, we see that this is the case for both the PEMA and PMMA. Also, as we approach T_g from below, the magnitude of the torque response decreases as expected. For both materials, the temperature influences the normal force and torque responses differently. This is elaborated upon subsequently.

4.3. Isochronal Responses. In Figures 4 and 5, isochronal plots of normal force and torque vs nominal strain for both materials are shown for data at times of 1, 10, and 100 s and at various temperatures. As expected in the low-strain region, the data are quadratic for the normal force and linear for the torque (see eqs 2 and 3). The responses show a nonquadratic and non-

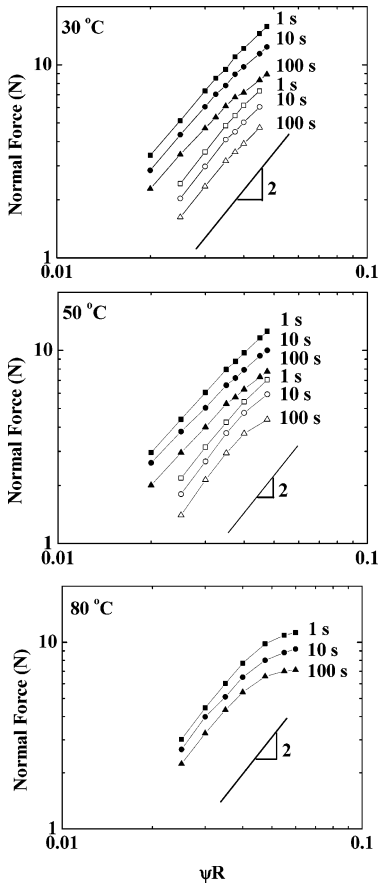

Figure 4. Double-logarithmic representation of the isochronal values of the normal force responses vs strain for PMMA (closed symbols) and PEMA (open symbols) in single-step torsional stress relaxation tests at various temperatures. Isochronal times and temperatures are indicated in the figure.

linear behavior, respectively, as the strain increases (>0.03), showing that the nonlinear response regime is reached above this deformation. An interesting point here is that these results show that the strain at which the nonlinear regime is reached decreases with increasing temperature.

4.3.1. Normal Force and Shear Moduli. From eqs 4 and 5 we determined the normal force modulus ($N_\psi(t)$) and the shear modulus ($G(t)$) for PMMA and PEMA. The results are shown in Figure 6 for 30 °C. The relaxation rate of the normal force modulus for PMMA is faster than that for PEMA while the opposite is observed for the relaxation rate of the shear moduli.

Figure 7 shows a comparison of the magnitude and rate of relaxation of the normal force modulus with the shear modulus as the ratio ($N_\psi(t)/G(t)$) for both PMMA and PEMA. Here we have plotted $N_\psi(t)/G(t)$ as a function of time and at different temperatures. Note that from eqs 4 and 5 a value of $N_\psi(t)/G(t) = 1$ corresponds to a neo-Hookean type of material ($W_2 = 0$). At the β-peak maximum (30 °C) the ratio $N_\psi(t)/G(t)$ for PMMA is greater than unity and decreases with time. This indicates that the normal force modulus is higher than the torque modulus and that $N_\psi(t)$ decreases faster than $G(t)$. For PEMA, the ratio $N_\psi(t)/G(t)$ is also greater than 1, but it decreases more slowly with time than it does for PMMA. For PMMA, as the temperature increases the rate of relaxation of N_ψ approaches the rate of relaxation of G ($N_\psi(t)/G(t)$ tends to be a constant). For PEMA, for which the β-relaxation

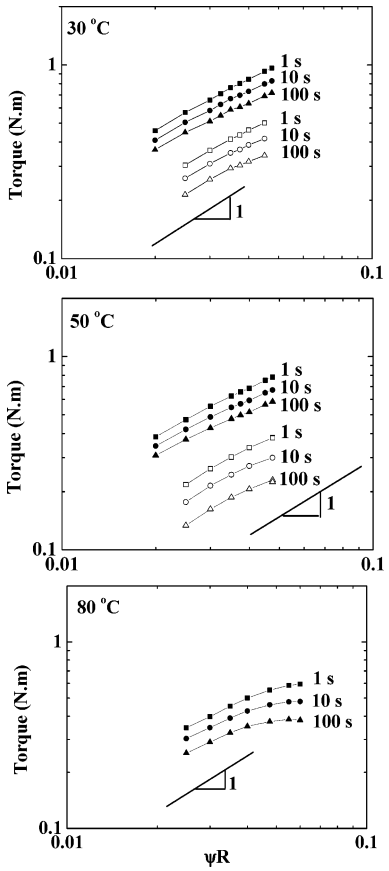

Figure 5. Double-logarithmic representation of the isochronal values of the torque responses vs strain for PMMA (closed symbols) and PEMA (open symbols) in single step torsional stress relaxation tests at various temperatures. Isochronal times and temperatures are indicated in the figure.

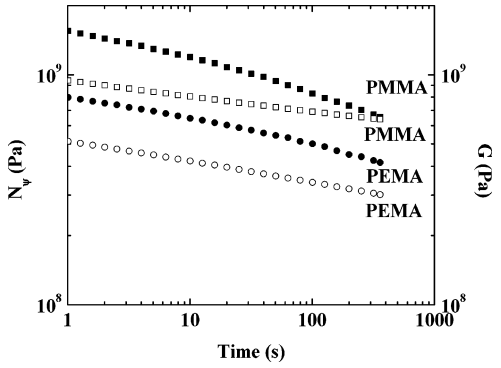

Figure 6. Double-logarithmic representation of the normal force modulus (N_ψ, eq 5) (closed symbols) and shear modulus (G, eq 4) (open symbols) vs time for PMMA (squares) and PEMA (circles) in single-step torsional stress relaxation tests at $\gamma = 0.04$ and at 30 °C.

is less intense, the ratio $N_\psi(t)/G(t)$ is less affected by the temperature than for the PMMA, at least for the two temperatures investigated here. Interestingly, for the PMMA at 80 °C, $N_\psi(t)/G(t)$ is nearly constant with time, and although the absolute magnitude of $N_\psi(t)$ is lower than at 30 and 50 °C, the ratio $N_\psi(t)/G(t)$ is itself higher than for the other temperatures.

4.3.2. Derivatives of the Strain Energy Density Function. Figures 8 and 9 depict $W_1(t)$ and $W_2(t)$, respectively, vs time and at different temperatures. For PMMA, at 30 °C (β-peak maximum), W_1 is positive and increases with time while W_2 is positive and becomes zero or negative as time increases. For PEMA, at 30 °C

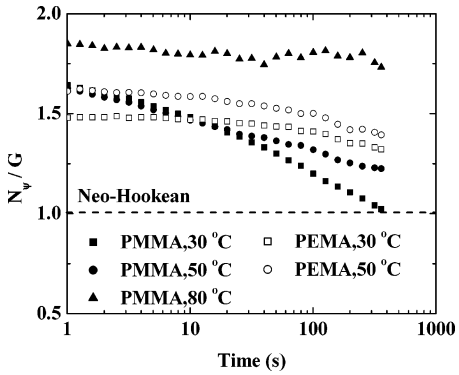

Figure 7. Semilogarithmic representation of the ratio of the normal force modulus to the shear modulus ($N_\psi(t)/G(t)$) vs time for PMMA (closed symbols) and PEMA (open symbols) in single-step torsional stress relaxation tests at $\gamma = 0.04$ and at various temperatures.

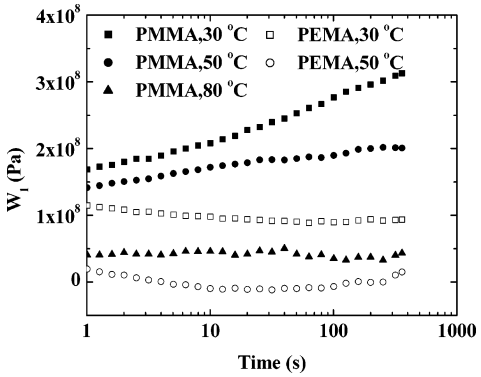

Figure 8. Semilogarithmic representation of W_1 vs time for PMMA (closed symbols) and PEMA (open symbols) in single-step torsional stress relaxation tests at $\gamma = 0.04$ and at various temperatures.

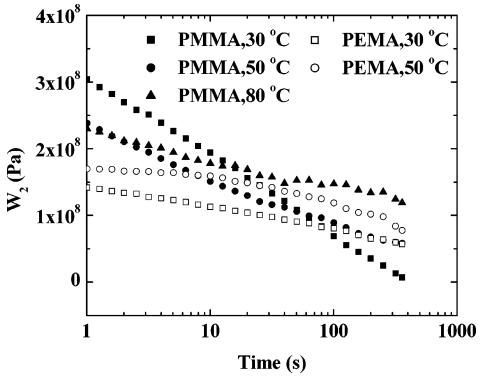

Figure 9. Semilogarithmic representation of W_2 vs time for PMMA (closed symbols) and PEMA (open symbols) in single-step torsional stress relaxation tests at $\gamma = 0.04$ and at various temperatures.

(β-peak maximum), W_1 is positive and nearly independent of time while W_2 is positive and decreases with increasing time. As the temperature increases, W_1 for both PMMA and PEMA decreases. Furthermore, for PMMA, W_1 tends to become independent of time as temperature increases, especially at 80 °C. At the same time, both PMMA and PEMA show somewhat faster relaxation rates for $W_2(t)$ at 30 °C, where the β-relaxation is strongest, than at the higher temperatures.

4.3.3. Deviation from the Neo-Hookean Behavior. In Figure 10 we plot the values of $2|N(t)|$ as a function of $\psi T(t)$ for PMMA and PEMA at 30 °C and for 1 and 100 s. The data do not fall on the neo-Hookean

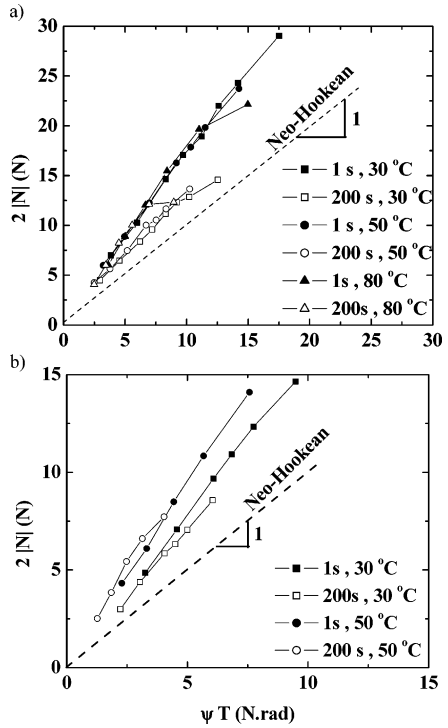

Figure 10. Plot of $2|N(t)|$ as a function of $\psi T(t)$ for (a) PMMA and (b) PEMA in single-step torsional stress relaxation tests performed at different temperatures. Isochronal times and temperatures are indicated in the figure.

line of slope unity (see eq 6), or the value of $2|N(t)|$ falls above that line. It may be that the PMMA response begins to look neo-Hookean at long times and at 30 and 50 °C. This is consistent with the value of W_2 approaching zero for PMMA at long times for these temperatures (see Figure 9) and that the ratio $N_\psi(t)/G(t)$ relaxes at the lower temperatures but not at 80 °C for the PMMA.

5. Discussion

We began this work with the view that the normal force response in polymeric glasses is strongly influenced by the side chain motion driven β-relaxation. In fact, the results described above support this hypothesis. The difference in the relaxation rates for the normal force modulus and shear modulus for PMMA indicates that the normal force and torque responses depend differently on the α- and β-relaxations. We find that the magnitude of the ratio $N_\psi(t)/G(t)$ is generally greater than unity for both PMMA and PEMA. For PMMA at the β-peak maximum (30 °C), the ratio decreases rapidly because of the fast relaxation rate of the normal force modulus N_ψ. As we go above the β-peak maximum and approach the α-relaxation, the ratio $N_\psi(t)/G(t)$ becomes a constant. These results are a clear indication of the influence of the β-relaxation on the normal force behavior. For the PEMA, which has a less intense β-relaxation, the difference between the normal force modulus and shear modulus relaxation rates is low; i.e., $N_\psi(t)/G(t)$ changes slowly with time at and above the β-peak. Because of the fact that the α- and β-relaxations are very close to each other ($T_g - T_\beta = 33$ °C) in PEMA, it is difficult to separate the contribution of these two relaxation mechanisms to the normal force modulus and shear modulus. The effect of temperature on the ratio $N_\psi(t)/G(t)$ is not very strong.

In looking at the definitions of $N_\psi(t)$ and $G(t)$, it is possible that we can obtain further insight into the behaviors of the materials by examining the individual components of the strain energy density function derivatives, $W_1(t)$ and $W_2(t)$. Since $N_\psi(t)$ depends on $W_1(t) + 2W_2(t)$ and $G(t)$ depends on $W_1(t) + W_2(t)$, it is clear that $W_2(t)$ has a larger contribution to the normal force response than it does to the shear response. Hence, the observation that the rate of relaxation of $W_2(t)$ is faster at the β-peak (30 °C) for the PMMA adds an additional perspective to the influence of this side-group mechanism on the nonlinear response of the material. In fact, examination of Figures 8 and 9 shows that the short time values of $W_2(t)$ are generally larger than for $W_1(t)$. This is certainly unexpected, though observed by McKenna and Zapas for PMMA previously[19,31] and without interpretation. What is important here is that the behavior of $W_2(t)$ seems to determine the relaxation rate of the normal force and its relation to that of the torque when it is large relative to $W_1(t)$. When a material is neo-Hookean, such differences in relaxation rates would not occur. However, even when the PMMA shows relaxation rates that are the same for $N_\psi(t)$ and $G(t)$ ($N_\psi(t)/G(t)$ is constant), the value of $W_2(t)$ is large, it simply relaxes at a slower rate. Hence, it appears that the β-relaxation affects the rate of relaxation of $W_2(t)$, but not its short-time magnitude.

The large values of $W_2(t)$ show up in the observation that both the PMMA and PEMA were found to be non neo-Hookean. As a comparison, this is unlike polycarbonate for which a small value of $W_2(t)$ compared with $W_1(t)$ was reported.[25] The observation of the weak $W_2(t)$ for polycarbonate may be related to its weak and main-chain β relaxation and requires further investigation.

A note of caution here is that we did use an incompressible analysis, and some of the differences in normal force could arise from the volume changes in the material upon twisting.[39] Another consideration may be the limits of working with continuum models to interpret the behavior of inherently heterogeneous materials. For example, Beiner et al.[40] found evidence of dynamic and structural nanoheterogeneities in the *n*-alkyl methacrylates due to the difference in motion of the side group and the main chain. It may, therefore, be of importance to consider that the macroscopic normal force and torque responses of *n*-alkyl methacrylates might be influenced by such nanoheterogeneity, which also influences the β- and α-relaxations.

Finally, we note that further work should consider materials with different molecular mechanisms for the β-relaxation. For example, a more extensive study of the behavior of polycarbonate would be warranted because it has a main-chain β-process, and as discussed above, it has a near to neo-Hookean behavior. In addition, examination of different tacticity PMMA may provide further information because the intensity of the β-relaxation is dependent on tacticity.[41,42] Regardless, it is clear that there is a molecular structure effect on the normal force response of glassy polymers. The work here shows that the relative relaxation rates of the shear and normal stress responses change as one moves toward or away from the β-relaxation.

6. Summary and Conclusions

Simultaneous measurements of normal force and torque responses in torsion of cylinders made of glassy PMMA and PEMA have been performed in stress relaxation at deformations below yield. We find that the subvitreous β-relaxation, which is related to a side-chain

motion, influences the relaxation behavior of the normal force response of both PMMA and PEMA. In both of these materials the strain energy function derivatives indicate strongly non-neo-Hookean behavior, which does not go away upon moving away from the β-relaxation. However, it does appear that the rate of relaxation of the normal force modulus relative to that of the shear modulus is significantly affected by proximity to the β-relaxation. In PMMA, where the β-relaxation is particularly intense, the normal stress modulus relaxes much faster than does the shear modulus. In both materials the results also show that the strain energy function derivatives and their relaxations are strongly influenced by the proximity to the β-relaxation.

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