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Chemical structure—normal force relationships in polymer glasses

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Abstract

In previous work, we found that the normal force responses in poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) subjected to torsional deformations were strongly influenced by their prominent β-relaxation mechanisms which are related to the *n*-alkyl methacrylate side group motions. Using the concept of an elastic stress relaxing material we were able to extract the derivatives of the strain energy density function with respect to the first and second invariants of the deformation tensor (W_1 and W_2). In the present work, we report results from two materials, polysulfone (PSF) and polycarbonate (PC), with weak β-relaxations that are due to main chain motions. We find that for the two materials, the difference from neo-Hookean behavior is real though very small, contrary to the large deviations from neo-Hookean behavior observed for PMMA and PEMA. The results support the contention that the large normal force responses and the consequent strongly non neo-Hookean behavior of the glassy *n*-alkyl methacrylates is due to the side chain.

Keywords: β-Relaxation; Neo-Hookean; Nonlinear viscoelasticity

1. Introduction

The nature of the molecular motion that underlies the nonlinear (finite) elastic behavior of rubber is well described with the finite elasticity theory [1–4] and the molecular theories of rubber elasticity [5–8]. Similarly, the reptation theory [9] and the tube models [10,11] of melt behavior predict the impact of molecular mechanism on the nonlinear viscoelastic behavior of polymer melts. These molecular theories have made possible important advances in the design and application of polymeric materials including tires and polymer processing. In the case of glassy polymers there are only a few experimental results and no theory addressing the issue of molecular effects on the nonlinear viscoelastic behavior. In this work we exploit the fact that when a twist is applied at the end of a cylinder, the other end being fixed, the cylinder tends to elongate [12]. Therefore, in performing torsional stress relaxation experiments one needs to apply not only a torque but also a normal force to maintain a constant length and deformation [13]. Important information on the nonlinear viscoelastic behavior can be obtained by simultaneously measuring torque and normal force responses [13]. From these values, the derivatives of the strain energy density function with respect to the first and second invariants of the deformation tensor, W_1 and W_2, can be obtained individually within the context of a time dependent modification of Rivlin's finite elasticity model [1,3].

In a previous paper [14], we showed that in the *n*-alkyl methacrylate system, the so called sub-vitreous β-relaxation (located at about 30 °C in the *n*-alkyl methacrylates) and which originates from side group motions [15], influences the behavior of the normal force response. Furthermore, within the framework of finite elasticity [1], the torque is proportional to W_1+W_2 while the normal force is proportional to W_1+2W_2, therefore W_2 can have a large contribution to the normal force [1]. Consistently, we found that the rate of relaxation of W_2 is affected by the β-relaxation. In the present work, we complement the study of the effect of the β-relaxation due to side chain motions on the normal force by investigating the nonlinear viscoelastic behavior of polymers with a weak β-relaxation that is related to the motion of the main chain. To do this, polysulfone (PSF) and polycarbonate (PC) are good candidates because they have weak β-relaxations located at approximately 60 °C [16,17]. Another objective in this work is to provide further insight into how molecular

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structure contributes to the strain energy density function of polymer glasses. Here we examine the influence of a β-relaxation mechanism that is related to a main chain motion on the behavior of W_2 which we found previously to be strongly affected by the side chain motions [14]. It is worth noting that a near neo-Hookean behavior ($W_2=0$) was found previously by one of us in PC [18].

2. Experimental work

In our prior work, the PMMA was obtained from Cadillac Plastics in the form of cast rods of 25 mm diameter and the PEMA powder was obtained from Aldrich Chemical Company. In the present study, the PC and PSF were obtained from General Electric (GE) in the form of cast rods. 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. The weight 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. We do not have information on the molecular weights of PSF and PC. However, alpha (segmental) and beta relaxation processes are related to local motions and therefore, we do not anticipate that molecular weight is an important parameter in the present work. 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, 63 °C for PEMA, 190 °C for PSF and 141 °C for PC. Samples with a gauge section of 25 mm length and 4.8 or 6 mm diameter were machined and gripped in a special torsion fixture for testing [19].

Mechanical testing was 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 20 N normal force capacity and a 2 N m torque capacity. Moreover, the sample and grips were placed in a heater chamber to control the temperature, allowing experiments to be performed from ambient to 100 °C.

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

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

where R is the radius of the cylinder, 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 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. Here we report averages of two tests where the uncertainty is small relative to the size of the symbols. Repeat tests were performed on the same sample. However, at each temperature investigated in this work a number of tests were performed, therefore, different samples from the same batch were tested at different temperatures and different strains. The first second of the relaxation data was ignored to account for the finite ramp of deformation [20]. Finally, in the experimental procedure which is described in detail in a previous paper [14], we adopted the Struik protocol [21] in order to minimize the effects of aging and of previous loading histories on the glassy polymers. All results are reported for aging times of 4980 s; i.e. these experiments are isochronal rather than isostructural aging experiments [22].

3. Theoretical considerations

The equations which describe the torque and normal force at large deformations as a function of the twist ψ imposed at the end of the incompressible elastic cylinder of radius R and whose length is maintained constant were derived by Rivlin [1]. These are based on continuum mechanics:

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

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

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 deformation tensor. Penn and Kearsley [23] used an appropriate change of variables and differentiation of T and N with respect to the limits of the integral in the above Eqs. (2) and (3) and showed that torsional measurements could be used to calculate W_1 and W_2 (scaling law). For time dependent materials, McKenna and Zapas [24] used the BKZ theory [25] of isothermal, incompressible elastic fluids to provide a similar relationship for isochronal ($t=$constant) measurements:

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

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

where $G(t)$ is the shear relaxation modulus at strain $\gamma_R=\psi R$ and we refer to $N_\psi(t)$ as the normal force relaxation modulus in the present work. We remark that Rivlin's elastic stress relaxing materials [26] is also described by Eqs. (4) and (5).

As mentioned in Section 1, we want to determine whether a chemical structure effect can be attributed to the strain energy density function behavior. It was previously found that PMMA and PEMA exhibit a $W_2(t)$ which relaxes faster nearer to the β-relaxation demonstrating that the side chain β process does affect the W_2 behavior [14]. We also found that for both PMMA and PEMA, W_2 is not zero, except for the PMMA at long times. In the neo-Hookean theory, materials that have the strain energy density function in the form $W(I_1)$ ($W_2 = 0$) are referred to as neo-Hookean [27]. For these materials, a universal relationship has been derived [28]:

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

For the neo-Hookean type of material, the plot of $2|N(t)|$ as a function of $\psi T(t)$ is a straight line with a slope of 1 [29]. Both the PMMA and PEMA were generally strongly non neo-Hookean in their behaviors [14].

4. Results

4.1. Time dependent normal force and torque responses

The normal force and torque responses of PMMA, PEMA, PSF and PC at the β peak temperature (30 °C for PMMA and PEMA, 60 °C for PSF and PC) are shown in Fig. 1 for a strain of 0.04. We see on the figure that PEMA and PMMA have normal forces that relax faster than the torque responses while for the PSF and PC specimens, the torque and normal force relax slowly and at the same rate. For clarity, in Fig. 2(a) we have replotted the responses for PMMA and PSF obtained at their β peak temperatures (30 and 60 °C, respectively) and at the same strain of 0.04. Very interestingly, at short times the normal force response of PMMA is 1.9 times higher than that of PSF while the torque responses are similar. As time increases the normal force response of the PMMA becomes smaller than the normal force response of PSF because of the faster relaxation rate of the PMMA normal force. The torque responses remain comparable over the full time domain tested. Also for direct comparison, in Fig. 2(b), we replotted the responses for PEMA and PC. At short times, the normal force response of PEMA is 1.5 times higher than that of PC while the torque response of PEMA is lower than the torque response of PC. As time increases, the normal force response of PEMA becomes smaller than that of PC due to the faster relaxation rate of the PEMA normal force. Here the torque response of PEMA also relaxes faster than that of PC. This is expected because here the experiments are performed at 30 °C below the T_g of PEMA and 81 °C below the T_g of PC. Consequently, at long times, the torque response of PEMA is 1.6 times lower than that of PC. Results for the temperature effect on the responses are presented in Fig. 3.

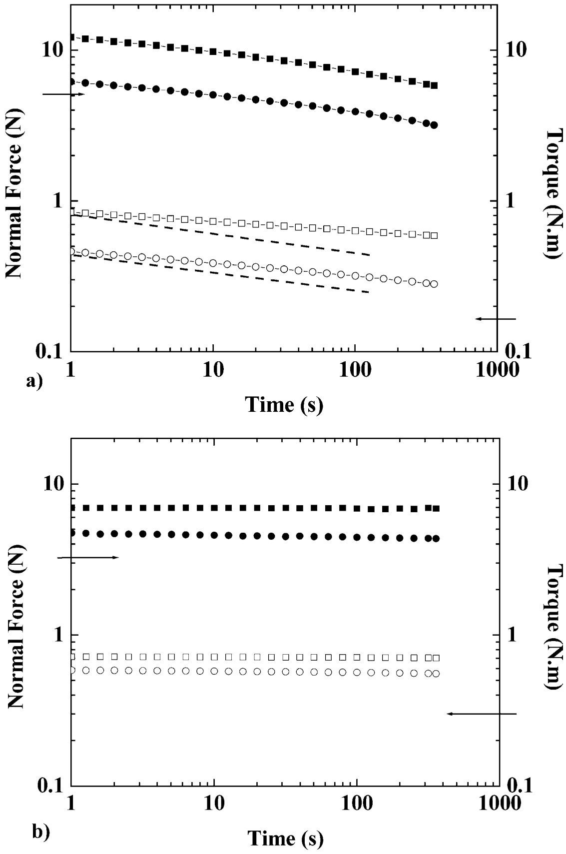

Fig. 1. Double logarithmic representation of the normal force (closed symbols) and torque (open symbols) responses vs. time for (a) PMMA (■) and PEMA (●), and (b) PSF (■) and PC (●) in single step torsional stress relaxation tests at a value of $\psi_R = 0.04$ and at the β peak temperature, i.e. 30 °C (PMMA and PEMA) and 60 °C (PSF and PC).

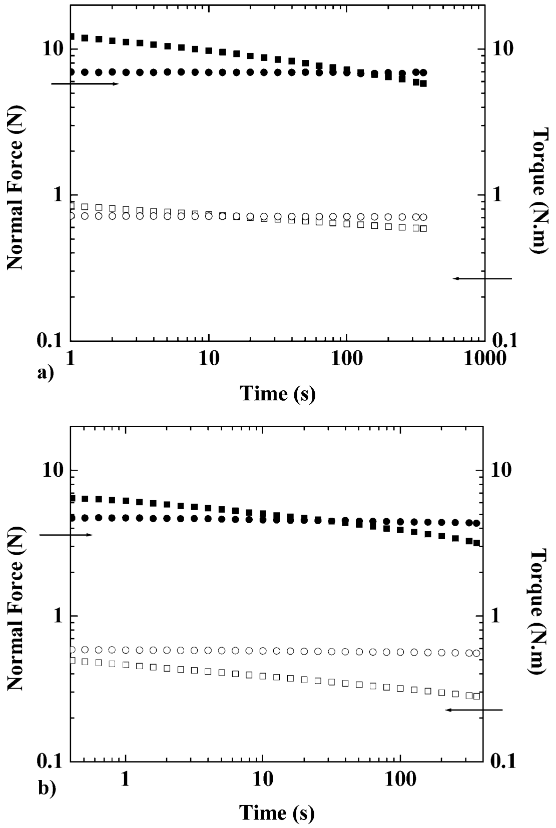

Fig. 2. Double logarithmic representation of the normal force (closed symbols) and torque (open symbols) responses vs. time for (a) PMMA (■) and PSF (●), and (b) PEMA (■) and PC (●) in single step torsional stress relaxation tests at a value of $\psi_R = 0.04$ and at the β peak temperature, i.e. 30 °C (PMMA and PEMA) and 60 °C (PSF and PC).

It can be seen that the temperature affects the normal force and torque responses of both PMMA and PEMA differently. This is not what we observed for PSF and PC, at least for the temperatures investigated here, i.e. 130 and 81 °C below T_g for the PSF and PC, respectively. Remark, however, that for the PMMA at 86 °C below T_g ($T = 30$ °C), there is a strong normal force relaxation.

4.2. Isochronal responses

The isochronal normal force and torque responses vs. strain are presented in Fig. 4 for the range of strain used in the present study. In the low strain region, the data are quadratic for the normal force and linear for the torque, which is in agreement with Eqs. (4) and (5). A deviation from the quadratic and linear behaviors is observed as strain increases but remains below the yield strain.

4.2.1. Normal force and shear moduli

The normal force modulus ($N_\psi(t)$) and shear modulus ($G(t)$) of the four specimens at their β peaks are plotted in Fig. 5. They were obtained by substituting the values of the normal force and torque responses into Eqs. (4) and (5). The normal force moduli of PMMA and PEMA relax faster than those of PSF and PC. Note that the experiments are performed at the β peak temperature which corresponds to the approximately the same distance below the glass transition temperatures for the PMMA and the PC. A similar observation is made for the shear moduli but the differences between relaxation rates of the shear moduli for materials with side chain motions (PMMA and PEMA) and the relaxation rates of the shear moduli for materials without side chain motion (PSF and PC) is less than for the normal force moduli.

In order to compare the magnitude and rate of relaxation

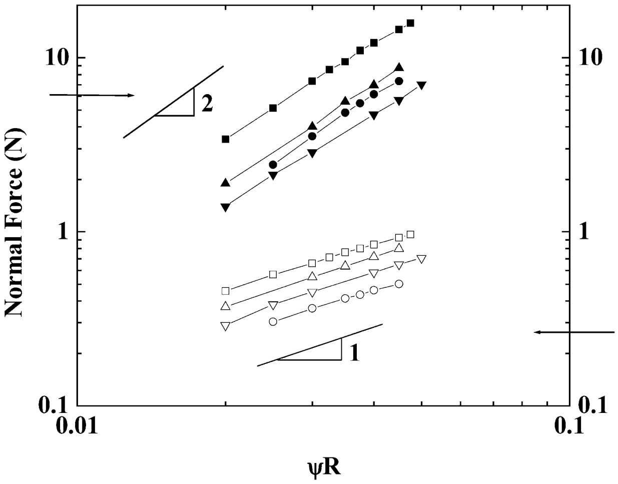

Fig. 4. Double logarithmic representation of the isochronal value of 1 s for the normal force (closed symbols) and torque (open symbols) responses vs. strain for PMMA, PEMA, PSF and PC in single step torsional stress relaxation tests at the β peak temperatures, i.e. 30 °C (PMMA and PEMA) and 60 °C (PSF and PC). ψ_R: [■] PMMA; [●] PEMA; [▲] PSF; [▼] PC.

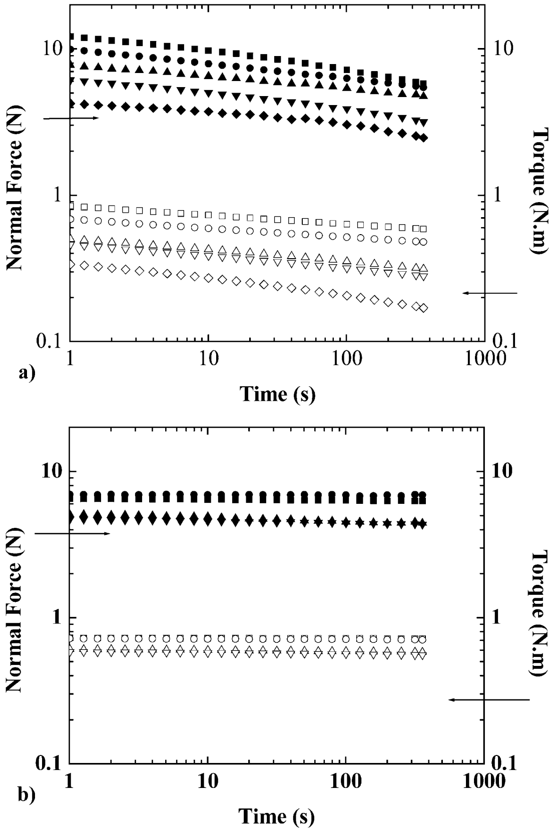

Fig. 3. Double logarithmic representation of the normal force (closed symbols) and torque (open symbols) responses vs. time for (a) PMMA, PEMA and (b) PSF and PC in single step torsional stress relaxation tests at a value of $\psi_R = 0.04$ and at different temperatures. (a) [■] PMMA at 30 °C; [●] PMMA at 50 °C; [▲] PMMA at 80 °C; [▼] PEMA at 30 °C; [♦] PEMA at 50 °C; (b) [■] PSF at 30 °C; [●] PSF at 60 °C; [▲] PC at 30 °C; [▼] PC at 60 °C.

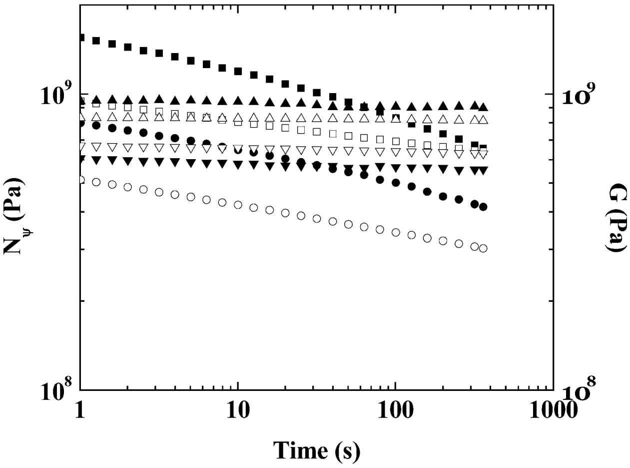

Fig. 5. Double logarithmic representation of the normal force modulus, N_ψ (closed symbols) and the shear modulus G (open symbols) vs. time for PMMA, PEMA, PSF and PC in single step torsional stress relaxation tests at $\gamma = 0.04$. Tests are performed at the β transition temperatures, i.e. 30 °C (PMMA and PEMA), 60 °C (PSF and PC). [■] PMMA; [●] PEMA; [▲] PSF; [▼] PC.

of the two moduli, we calculated the ratio of the normal force modulus to the shear modulus, ($N_\psi(t)/G(t)$). The result is presented in Fig. 6. For PMMA and PEMA, the ratio $N_\psi(t)/G(t)$ is greater than unity, 1.6 and 1.5, respectively, at the shortest time, and it decreases with time though the decay is faster for PMMA. For PSF and PC, the ratios are 1.1 and 0.9, respectively, and they remain relatively constant with time. Note that by examination of Eqs. (4) and (5) one sees that a ratio of 1 corresponds to a neo-Hookean type of material ($W_2=0$).

4.2.2. Derivatives of the strain energy density function—deviation from the neo-Hookean class of material

The behaviors of W_1 and W_2 vs. time are shown in Figs. 7 and 8, respectively, for the four different materials and at different temperatures. At the β peak, it can be seen that PC and PSF exhibit the same W_1 behavior. It is greater in magnitude than that of PMMA and PEMA and it remains relatively constant with time. For PMMA, W_1 increases with time while for PEMA it remains relatively constant with a lower magnitude than that of PMMA. For PC and PSF, W_2 is close to zero at all times (almost neo-Hookean). For PMMA, the magnitude of W_2 is high at the shortest time of 1 s (0.3 GPa) but it decreases rapidly to zero as time increases. The same observation is made for PEMA except that the decay of W_2 is lower than it is for PMMA.

As the temperature increases, W_1 of PMMA and PEMA decrease. For PSF and PC no remarkable changes are observed for the two temperatures investigated in this work. Furthermore, for PMMA W_1 becomes nearly independent of time at 80 °C (far from the β-peak maximum). Examination of the values of W_2 for the PMMA and the PEMA reveals that W_2 decreases faster at the β peak temperature (30 °C) while for PSF and PC it remains very close to zero and time independent with increasing times for the temperatures examined.

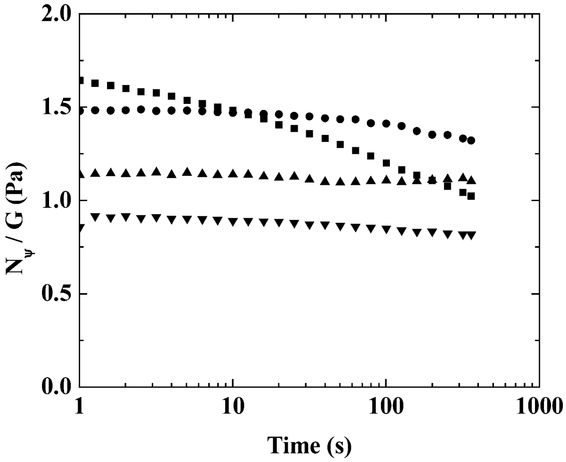

Fig. 6. Representation of the ratio of the normal force modulus to the torsional modulus ($N_\psi(t)/G(t)$) vs. logarithmic of time for PMMA, PEMA, PSF and PC in single step torsional stress relaxation tests at $\gamma=0.04$ and at β transition temperatures, i.e. 30 °C (PMMA and PEMA), 60 °C (PSF and PC). [■] PMMA; [●] PEMA; [▲] PSF; [▼] PC.

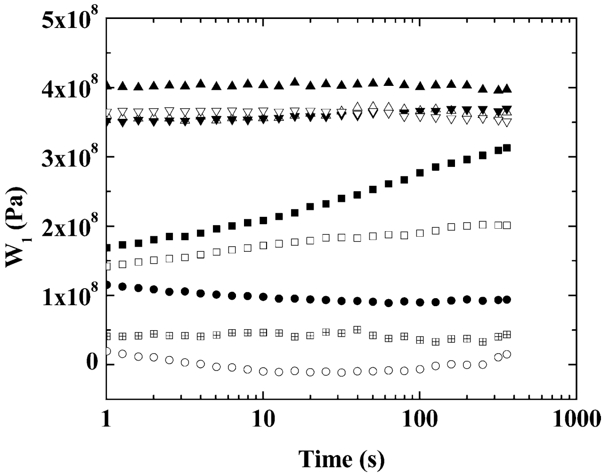

Fig. 7. Representation of W_1 vs. logarithmic of time for PMMA, PEMA, PSF and PC in single step torsional stress relaxation tests at $\gamma=0.04$ and at different temperatures. Closed symbols are for tests at 30 °C, open symbols are for tests at 50 °C and crossed symbol is for 80 °C. [■] PMMA; [●] PEMA; [▲] PSF; [▼] PC.

In order to examine the deviation from neo-Hookean behavior of the four glassy polymers studied in this work, we plot $2|N(t)|$ as a function of $\psi T(t)$ (Section 3). The results are shown in Fig. 9 for the 1 s isochrone. The results confirm that for PSF and PC, the difference from neo-Hookean behavior exists but is small. This is contrary to the strongly non neo-Hookean behaviors observed for the PMMA and PEMA.

5. Discussion

Both PSF and PC have normal force moduli of the same

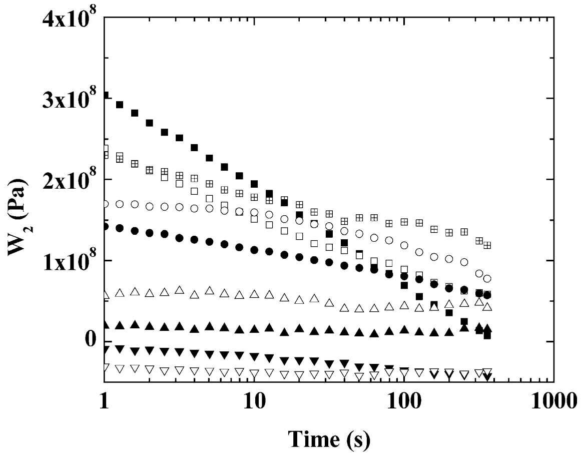

Fig. 8. Representation of W_2 vs. logarithmic of time for PMMA, PEMA, PSF and PC in single step torsional stress relaxation tests at $\gamma=0.04$ and at different temperatures. Closed symbols are for tests at 30 °C, open symbols are for tests at 50 °C and crossed symbol is for 80 °C. [■] PMMA; [●] PEMA; [▲] PSF; [▼] PC.

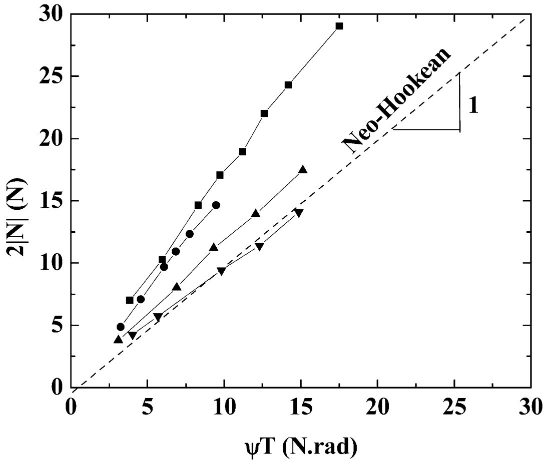

Fig. 9. Representation of $2|N(t)|$ as a function of $\psi T(t)$ for PMMA, PEMA, PSF and PC in single step torsional stress relaxation tests performed at β transition temperatures. Results are for isochronal time of 1 s. [■] PMMA at 30 °C; [●] PEMA at 30 °C; [▲] PSF at 60 °C; [▼] PC at 60 °C.

magnitude as the shear modulus at the weak β-transition temperature. Moreover, these two moduli relax at the same rate ($N_\psi(t)/G(t) \cong 1$). This is not what we observed for PMMA and PEMA [14]. At their prominent *β* peaks, the two *n*-alkyl methacrylates have normal force moduli higher than their shear moduli. Furthermore, both PMMA and PEMA have normal force moduli that relax faster than their shear moduli. Therefore, there is a clear indication that the weak main chain motion β-mechanisms of PSF and PC have little effect on the normal force relaxation behavior unlike the prominent side chain motion β-mechanisms of PMMA and PEMA. In Figs. 7 and 8 we reported results found in our previous work on the derivatives of the strain energy density function of PMMA and PEMA [14]. It was found that W_2 decreases with increasing times though the decrease is faster for the sample with the more prominent β-mechanism, i.e. PMMA. It was also found that W_2 is greater than W_1, except for the PMMA at long times and at the β-transition temperature (actually due to the fast relaxation rate of W_2). Here we found that the PSF and PC exhibit different behaviors than the PMMA and PEMA for the strain energy density function. In fact, for PSF and PC W_1 has small time dependence and values of W_1 are greater than values of W_2. Also, for PSF and PC, $W_2(t)$ is almost zero, i.e. they exhibit an almost neo-Hookean behavior. Interestingly, a comparison of the behavior of W_2 for the different samples provides evidence that W_2 is indeed influenced by the prominent side chain induced β-relaxation. It is also interesting to note that there is a consistency in the behaviors of W_1 for the PSF and PC which is not the case for the PMMA and PEMA. For PMMA, W_1 increases with time at the β-transition temperature while for PEMA it is relatively constant.

At the present time, we see two possible causes for these divergences. One is the assumption made here that torsion of glassy polymers is isochoric which allows us to use a framework based on incompressibility for PMMA and PEMA. This was done because results reported on the torsional stress relaxation of epoxy glass show a very small volume change during torsion ($\leq 10^{-3}$) [30]. Results from constant rate of strain in torsion on PMMA also give very small volume changes [31]. Furthermore, it would be surprising that the same framework would be perfectly adequate for PSF and PC and not for the other two polymers. We are currently measuring the volume change during the torsion of the different materials investigated in this work. Second, theories available to analyze the strain energy density behavior of glassy polymers, are based on continuum mechanics, i.e. they do not contain any information related to the molecular or chemical structure of the polymer. Such theories might not be sufficient to describe the strain energy function behavior of glassy polymers and models which contain details of molecular structure or other heterogeneous/non-continuum structure in these materials may be required.

6. Conclusions

In the present work, we have provided the first data that compares the normal force and torque responses of polysulfone and polycarbonate and combines these with comparisons of the behaviors of PMMA and PEMA that were reported in a previous study [14]. We have shown that the normal force response in torsional measurements is influenced by the large β mechanism caused by the side chain motion while the weaker β mechanism related to the main chain motion does not influence the normal force behavior. Very importantly, our analysis to obtain the derivatives of the strain energy density function indicates that both PSF and PC, which have weak β relaxations have a behavior that does not deviate much from neo-Hookean while the two *n*-alkyl methacrylates, which have strong β relaxations, exhibit a strongly non neo-Hookean behavior.

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References

[1] Rivlin RS. Philos Trans R Soc 1948;A241:379.
[2] Treloar LRG. Proc Phys Soc 1948;60:135.
[3] Green AE, Adkins JE. Large elastic deformations. Oxford: Oxford University Press; 1970.
[4] Mooney M. J Appl Phys 1940;11:582.

[5] Flory PJ, Rehner J. J Chem Phys 1943;11:455.
[6] James HM, Guth E. J Chem Phys 1943;11:455.
[7] Hermans JJ. Trans Faraday Soc 1947;43:591.
[8] Mark JE, Erman B. Rubberlike elasticity: a molecular primer. New York: Wiley; 1988.
[9] De Gennes P-G. Scaling Concepts in Polymer Physics. Ithaca: Cornell University Press, 1979.
[10] Doi M, Edwards SF. J Chem Soc, Faraday Trans 1978;II.
[11] Larson RG. Constitutive equations for polymer melts and solutions. Boston: Butterworths; 1988.
[12] Poynting TH. Proc R Soc London 1909;A82:546.
[13] McKenna GB, Zapas LJ. J Rheol 1979;23:151.
[14] Flory A, McKenna GB. Macromolecules, 2005;38:1760.
[15] Heijboer J. In: Prins JA, editor. Physics of non-crystalline solids. New York: Wiley; 1965.
[16] Fried JR, Letton A. Polymer 1990;14:54.
[17] Yee AF, Smith SA. Macromolecules 1981;14:54.
[18] Pesce JJ, McKenna GB. J Rheol 1997;41:929.
[19] McKenna GB, Kovacs AJ. Polym Eng Sci 1984;24:1138.
[20] Flory A, McKenna GB. Mech Time-Depend Mater 2004;8:17.
[21] Struik LCE. Physical ageing in amorphous polymers. Amsterdam: Elsevier; 1978.
[22] Cerrada ML, McKenna GB. Macromolecules 2000;33:3065.
[23] Penn RW, Kearsley EA. Trans Soc Rheol 1976;20:227.
[24] McKenna GB, Zapas LJ. Rheology. In: Astarita G, Marruci G, Nicolais L, editors. Applications, vol. 3. New York: Plenum; 1980. p. 289.
[25] Bernstein B, Kearsley EA, Zapas LJ. Trans Soc Rheol 1963;VII:83.
[26] Rivlin RS. Q Appl Math 1956;14:83.
[27] Macosko CW. Principles, measurement and applications (advances in interfacial engineering). New York: Wiley; 1994.
[28] Horgan CO, Saccomandi G. J Elasticity 1999;56:159.
[29] Wineman AS. Int J Non-linear Mech, 2005;40:271.
[30] Duran RS, McKenna GB. J Rheol 1990;34:813.
[31] Wang TT, Zupko HM, Wyndon LA, Matsuoka S. Polymer 1982;23.