Mechanical Properties in Torsion for Poly(butylene terephthalate) and a Poly(ether ester) Based on Poly(ethylene glycol) and Poly(butylene terephthalate)

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ABSTRACT: The torsional behavior of poly(ether ester)(PEE) thermoplastic elastomer, based on poly(ethylene glycol)(PEG) and poly(butylene terephthalate)(PBT) was studied and compared with that of PBT itself. Two types of experiments were performed: (1) stress relaxation in torsion, and (2) measurement of intermittent couple-twist responses. It was shown that the relaxation of the torsional couple M could be represented as a sum of several exponential terms in the time, rather than as a simple exponential function. This sum might be called a Prony series on the analogy of the usual stress relaxation which occurs after stretching a sample to a certain deformation and holding it constant. The intermittent couple-twist experiments were carried out by analogy with similar experiments in elongation. For PEE the couple rises steadily with the twist, whereas for PBT it rises abruptly and remains constant within the experimental error for high twists. The residual twist, however, showed a similar trend for both PEE and PBT. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 495–502, 1998

Key words: torsion; relaxation; thermoplastic elastomer; poly(butylene terephthalate)

INTRODUCTION

Shortly before 1970 it was found that poly(ether ester)(PEE) thermoplastic elastomers, based on poly(butylene terephthalate)(PBT) and poly(tetramethylene glycol)(PTMG), had outstanding physical properties and processing characteristics.[1] PEE based on PBT and poly(ethylene glycol)(PEG) were also synthesized and were shown generally to have worse characteristics than those containing PTMG as soft segments.[2] Yet the ones based on PEG have some advantages, the most important one being their hydrophilic character, which made them attractive candidates for application in the textile industry.

More recently we investigated the mechanical behavior of the PEG type of PEE.[3,4] It was shown that these polymers orient themselves through necking, which takes place up to several hundred percent strain. All static-mechanical characteristics were found to strongly depend on both the PBT/PEG ratio and the PEG molecular weight.[3,4] In addition, detailed structural and morphological characterization during deformation of the same material was performed.[5,6] Finally, the mechanical characteristics of zone drawn-zone annealed bristles were compared with those of samples which had been annealed with fixed ends.[7] All

these studies dealt with stretching[5–7] or bending[8] deformations of predrawn and annealed polymer bristles. Thus, the PBT/PEG PEE materials were characterized with regard to their Young's modulus, tensile strength, and elongation at break, all measured exclusively in tensile mode.

To better characterize the polymeric materials, one has to know the shear moduli, which can be obtained by measurements in torsion. This deformation is also useful in the very appropriate approach of characterizing mechanical behavior through a number of interconnected quantities.

It is the goal of this article to investigate the torsional behavior of PEE materials based on PBT and PEG. The torsional behavior of PBT homopolymer, homo-PBT, under the same conditions was also studied for purposes of comparison. Both stress relaxation in torsion and intermittent couple-twist experiments were performed. These two approaches differ significantly from those used in other torsion studies,[9,10] which have generally been used to obtain the energetic contribution to the total retractive force (couple).

EXPERIMENTAL

Apparatus

For the torsion experiments we applied the apparatus used in a previous investigation on poly(dimethylsiloxane),[9] which was similar to that of Gent and Kuan, and details may be found in their report.[10] In the present study the apparatus was additionally modified, as shown in Figure 1. The two major improvements were (1) a turnable (rotational) Vernier scale was added at the top in such a way that it could be turned around the rotating table, thus allowing measurements of the residual twist at a couple equal to zero; and (2) the fixed lower clamp was replaced with a rotatable one in order to more precisely adjust the sample at zero couple.

The bristle-shaped sample was secured between the lower and the upper clamp, and was surrounded by a water thermostated beaker in order to achieve temperature control. The lower clamp could be moved vertically and also rotated by hand. The upper clamp was attached to the lower end of a thin steel torsion wire, the upper end of which was fixed to a turntable, which was calibrated in degrees. By turning this turntable and twisting the metal wire the initial twist of the sample could be set. A pointer was affixed to
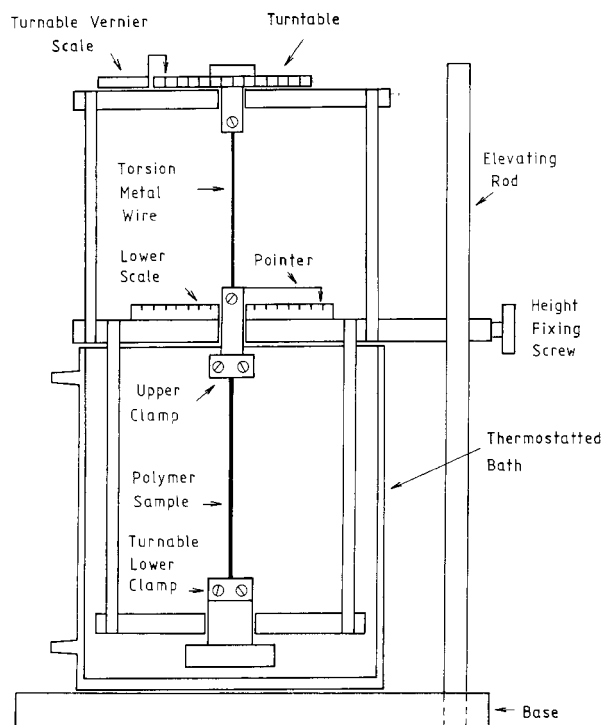

Figure 1   Schematic representation of the torsion apparatus.

the upper clamp and used to read its degree of rotation. The steel torsion wire was changed for different samples in order to achieve appropriate sensitivity.

Samples

The samples used were PEE based on PBT and PEG in a ratio of 75 : 25 wt %, and some homo-PBT. Both the PEE and PBT were synthesized as described elsewhere.[3] The granules obtained after the synthesis of both components were finely milled and put into the barrow of a molecular flow index apparatus MFI-6542 from Donau Electronic, Switzerland, which was used to obtain bristles. The melt was kept in the barrow at 240°C for ~ 10 min and consequently extruded through the nozzle (1 mm in diameter) in ice-cold water by applying a constant force to the plunger.

The bristles obtained were kept unconstrained for 6 h at 140°C in a vacuum oven. This permitted stress relaxation as well as development of higher crystallinity (resulting in a denser physical network in the PEE). The sample length varied in the range of 55–65 mm and the diameter was ~ 0.6 mm.

Procedures

Two types of experiments were performed: stress relaxation in torsion, and intermittent couple-twist experiments.

The stress relaxation in torsion experiments were done at 20, 40, and 70°C. By turning the turntable the initial twist was set to 120° at the moment $t = 0$ and the twist of the upper scale was read. As the stress relaxed, the twist of the polymer bristle changed and was regularly returned to 120° by turning the turntable. The relaxation curve was obtained by taking several readings of the twist of the turntable providing the twist of the upper clamp was 120°. The couple M in g.cm was obtained from the difference between the twist of the turntable and the reading of the lower scale, using the shear modulus of the steel wire. One relaxation curve was normally taken for several hours.

The intermittent couple-twist experiment consisted of several steps: (1) one end of the sample was attached to the upper clamp; (2) the pointer was set to zero by turning the turntable; (3) the setting of the turntable was also placed at zero by turning the Vernier scale; (4) the other end of the sample was attached to the lower clamp and stretched by moving the latter downward; (5) if, after the fourth step the pointer was off the zero setting, then it was reset to zero, this time by turning the lower clamp in order to get the sample into the relaxed state prior the experimental measurements. These measurements were carried out as follows: the twist of the turntable was increased to 180° and the respective couple M was calculated from the twist, read on the lower scale
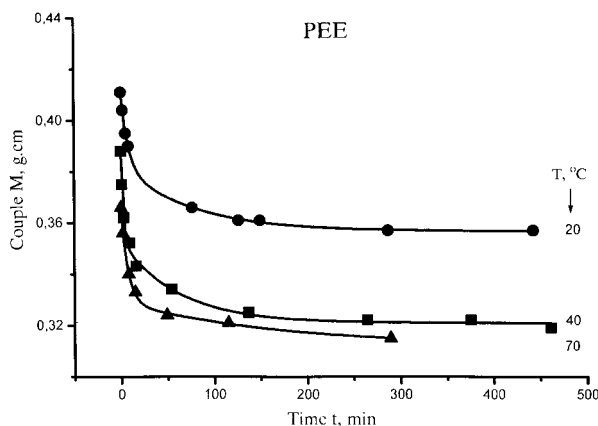

Figure 3 Couple M in logarithmic scale versus time t for PEE at 40°C. The least-squares straight line is also shown.

after sufficient time to reach a relatively steady reading, that is, sufficient for the main relaxation to occur. As the next step, the turntable was turned back until its reading coincided with the twist, read on the lower scale, which corresponds to zero couple imposed on the polymer bristle. All procedures were repeated, starting with a higher twist of 360° of the turntable and so on. Measurements were carried out up to the rupture points of the samples.

RESULTS AND DISCUSSION

Figure 2 presents the relaxation curves of PEE for three temperatures. As stated previously, each

Figure 2 Relaxation of the couple M with the time t for PEE at the three indicated temperatures. The lines for $T = 20$, 40, and 70°C are based on eq. (1).
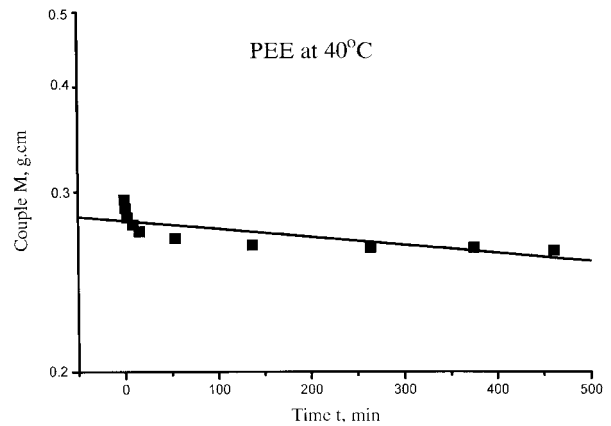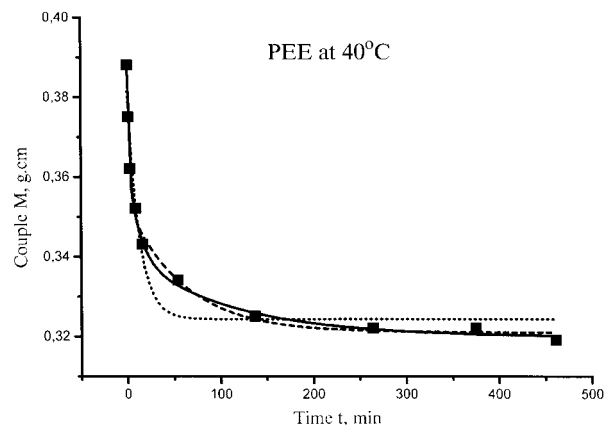

Figure 4 Relaxation of the couple M with the time t for PEE at 40°C. Three different fits of the data according to eq. (1): the dotted line is for $N = 1$; the dashed line for $N = 2$, and the solid line for $N = 3$.
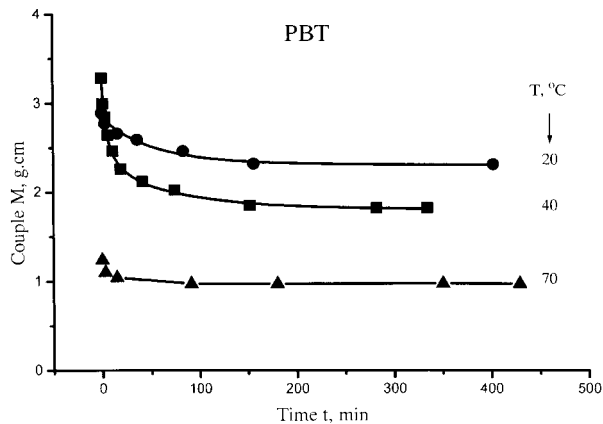
Figure 5 Relaxation of the couple M with the time t for PBT at the three indicated temperatures. The curves for $T = 20$ and 40°C are drawn according to eq. (1), but a series of simple straight lines connecting the points was used for $T = 70$°C.

point represents the couple M necessary to maintain the twist of 120° at the moment t. A relatively fast relaxation in the first few minutes takes place at all three temperatures. For times of 300 min and higher the couple remains relatively constant and is further marked M_∞. In order to check whether there is a simple exponential decrease of M versus t, the curves were replotted using a log scale for M. The results obtained are very similar for all three temperatures and for this reason only one curve (for $T = 40$°C) is shown in Figure 3, together with a straight line, drawn using the least-square method. Since the points obviously deviate from a straight line, the relaxation process is more complex, as may be expected.[11] An attempt was made to represent each of the curves

in the form of the so-called Prony series,[12] but in terms of $M(t)$ instead of $E(t)$:

$$M(t) = \sum_{i=1}^{N} M_i \exp(-t/\tau_i) \qquad (1)$$

where τ_i is the ith relaxation time.

The next representation, Figure 4, shows the results of fitting the experimental points of the PEE relaxation at 40°C with the function in eq. (1) for $N = 0, 1, 2,$ and 3. As expected from Figure 3, fitting with only one exponential term (dotted line in Fig. 4) is unsatisfactory. On the other hand, fitting with two (dashed line) or three terms (solid line) [i.e., $N = 2$ or 3 in eq. (1)], is seen to give quite satisfactory results. For this reason fitting with more than three exponential terms was not attempted. The picture is quite similar for temperatures 20 and 70°C; in fact the three curves in Figure 2 were not drawn through the experimental points, but represent lines based on eq. (1) for $N = 3$.

The relaxation curves for PBT at the same temperatures are shown in Figure 5. This figure is very similar to Figure 2 except for the higher couples (by an order of magnitude), since PBT is much more brittle than PEE. The points were again fitted by eq. (1), with $N = 2$ corresponding to $T = 20$ and $N = 3$ to 40°C, whereas attempts to fit the data for $T = 70$°C failed for all three values of N. For this reason the longer time points in Figure 5 for $T = 70$°C are connected with a straight line. The results from the fitting are shown in Tables I and II in the case of PEE and PBT, respectively. As can be seen from Table II,

Table I   Parameters Obtained from Fitting the Points in Figure 2 with Equation (1)

Parameter	M_∞ (g.cm)	A_1 (g.cm)	A_2 (g.cm)	A_3 (g.cm)	τ_1 (min)	τ_2 (min)	τ_3 (min)
$T = 20$°C							
$N = 1$	0.360	0.0500	—	—	15.0	—	—
$N = 2$	0.357	0.0288	0.0255	—	7.6	74.9	—
$N = 3$	0.354	0.0328	0.0170	0.0064	8.6	67.7	294.0
$T = 40$°C							
$N = 1$	0.324	0.0571	—	—	12.5	—	—
$N = 2$	0.321	0.0347	0.0318	—	2.6	60.7	—
$N = 3$	0.320	0.0245	0.0234	0.0203	1.6	12.2	112.6
$T = 70$°C							
$N = 1$	0.320	0.0448	—	—	11.0	—	—
$N = 2$	0.312	0.0366	0.0170	—	7.2	170.2	—
$N = 3$	0.310	0.0289	0.0100	0.0179	5.5	16.6	242.7

Table II   Parameters Obtained from Fitting the Points in Figure 5 with Equation (1)

Parameter	M_∞ (g.cm)	A_1 (g.cm)	A_2 (g.cm)	A_3 (g.cm)	τ_1 (min)	τ_2 (min)	τ_3 (min)
$T = 20°C$							
$N = 1$	2.31	0.525	—	—	54.9	—	—
$N = 2$	2.30	0.439	0.097	—	46.1	116.4	—
$N = 3$: cannot be fitted							
$T = 40°C$							
$N = 1$	1.90	1.23	—	—	14.2	—	—
$N = 2$	1.82	0.765	0.644	—	4.8	58.0	—
$N = 3$	1.80	0.527	0.439	0.466	3.2	14.0	81.7
$T = 70°C$							
$N = 1, 2, 3$: cannot be fitted							

in some cases fitting was not possible for any of the three values of N.

Another possibility to compare the relaxation data for PEE and PBT is to obtain the continuous relaxation spectrum $H(\ln t)$, also called distribution of relaxation times.[13] It can be estimated from a relaxation curve plotted on a $\log(t)$ scale[13]:

$$H(\ln t) = -\frac{1}{2.303} \cdot \frac{d[M(t)]}{d \log t} \qquad (2)$$

Equation (2) can be used to obtain quick estimates and to visualize the responses of the polymer system under investigation. Curves for PEE and PBT in $\log(t)$ scale are shown in Figure 6. In the case of PEE the slopes are approximately the same for all three temperatures, whereas in the case of PBT the slopes differ significantly with temperature (Fig. 6). In both cases, however, representation of the results with a straight line is very good, as documented by the values of the
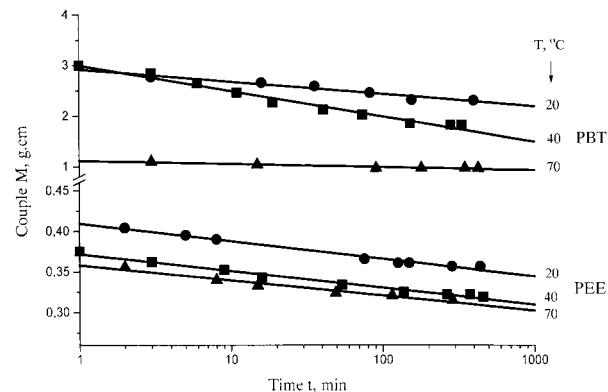

Figure 6 Couple M versus time t in logarithmic scale for PEE and PBT at the indicated temperatures. Least-square straight line fits of the data are also shown.

correlation coefficient R. These coefficients are shown in Table III, together with the values of the distribution of relaxation times $H(\ln t)$ and the parameters for fitting the data with a straight line (values of the intercept A and slope B).

As seen in Table III, the values of $H(\ln t)$, A, and B for PEE are approximately the same order of magnitude at different temperatures. In the case of PBT, however, these parameters differ significantly with temperature, especially for $T = 70°C$, where the lowest magnitudes were obtained. Since PBT is not an elastomer, raising the temperature above its glass transition temperature T_g (ca. 55°C) causes a significant change in its behavior. In PEE the elastic behavior is due to the existing physical network, the junctions of which are crystallites (melting point ca. 210°C). Their structure does not depend on the PBT glass transition temperature. On the other hand, the PEG chains, which impart elastic behavior to PEE, are in these experiments far above T_g of PEG (which is below 0°C). As a result, this sample has the same behavior regardless of temperature.

Stress relaxation was also characterized by the difference (ΔM) between the couple taken immediately after the setting of the initial twist and the couple close to elastic equilibrium (M_∞). Figure 7 shows the values of ΔM of PBT and PEE for three sample temperatures. The dashed lines between the points provide some guidance, but hardly represent the real trend of ΔM. This is particularly the case around the T_g of PBT (ca. 55°C), where a steep decrease of ΔM is to be expected in connection with the increase of segment mobility.

The curves in Figure 7 illustrate the importance of the soft PEG blocks occurring in PEE. Since these blocks are flexible, they do not trans-

Table III   Distribution of Relaxation Times $H(\ln t)$, Intercepts A and Slopes B of the Straight Lines Used to Fit M versus $\ln(t)$ Data in Figure 6, and the Corresponding Correlation Coefficients R

Temp. (°C)	$H(\ln t)$	A (g.cm)	B (g cm min^{-1})	R
PEE				
20	0.00936	0.409	−0.0216	−0.99
40	0.00894	0.372	−0.0206	−0.99
70	0.00803	0.358	−0.0185	−0.98
PBT				
20	0.104	2.92	−0.24	−0.97
40	0.217	2.99	−0.50	−0.99
70	0.027	1.12	−0.06	−0.96

form the torsional strain to the adjacent molecules and the relaxation in PEE does not lead to a significant rearrangement of the molecules at the relatively low twist of 120°. In the case of homo-PBT, however, the PBT crystallites are connected with PBT tie molecules, which are not as flexible as the PEG ones. The inner friction in this case is higher, which results in (1) high absolute values of M (compare Figs. 2 and 5), and (2) larger drops in ΔM for $T > T_g^{\mathrm{PBT}}$ (see Fig. 7).

Figure 8 shows the dependence of the couple M on the twist in the intermittent couple-twist
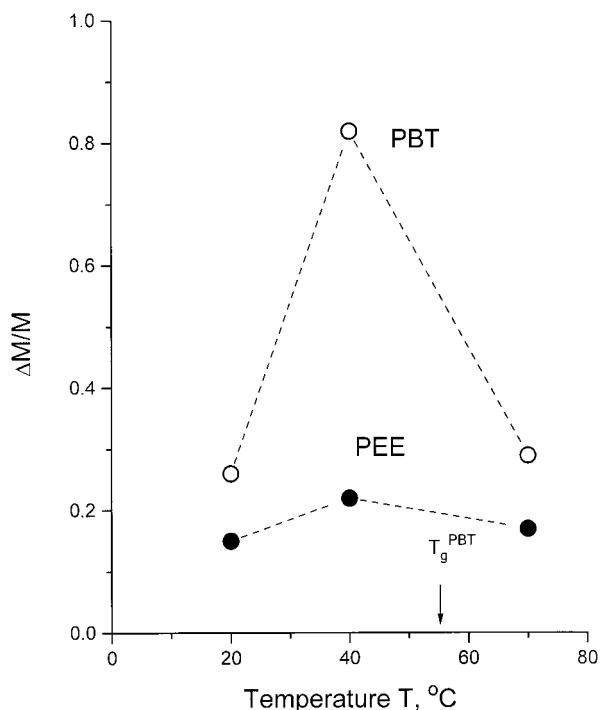

Figure 7   Values of the couple change ΔM for PEE and PBT at three temperatures. The PBT glass transition temperature is also shown.

experiment. Figures 8(a) and (b) correspond to PEE and PBT, respectively. These results were obtained using a sequence of stepwise increasing values of twist, as already described. Since the shearing stress is proportional both to the bristle radius r and to the angle of rotation per unit length Ψ,[14] the torsional strain is expressed in terms of the parameter Ψr corresponding to n turns of twist in the total length of the sample.[14] These results should be close to elastic equilibrium, since the couple readings were taken after sufficient time had been allowed for the stress relaxation, with this time varying from minutes to several hours, depending on the twist. In the case of PEE [Fig. 8(a)], a value of $\phi = 360°$, which corresponds to a step of the twist of 0.0249 rad, was taken as an increment. Since PBT is much more rigid than PEE, the increment of the twist was taken equal to 180°. The full circles in Figure 8(a) marked 2, 3, 4, and so on represent positive couples, whereas the open circles marked 2′, 3′, 4′, and so on were obtained from the respective points at zero couple and represent the residual twists. A steady increase of the couple with the twist can be seen, up to the rupture point $\Psi r = 0.245$ rad, at about $n = 11$ rounds of the 50 mm long PEE bristle.

As expected, the M versus Ψr dependence for PBT [Fig. 8(b)] differs significantly from that of PEE [Fig. 8(a)]. For low twist the couple increases steeply, then for Ψr of ~ 0.045 rad the increase becomes gradual, and for $\Psi r > 0.09$ rad M remains constant within experimental error. The rupture point is $\Psi r = 0.214$ rad, which is a little lower than the corresponding value for PEE, as shown in Figure 8(a). This rupture took place at about $n = 7$ turnings of the 50 mm long PBT bristle. The residual twist [Figs. 8(a) and (b), open circles] can be taken as a measure of the
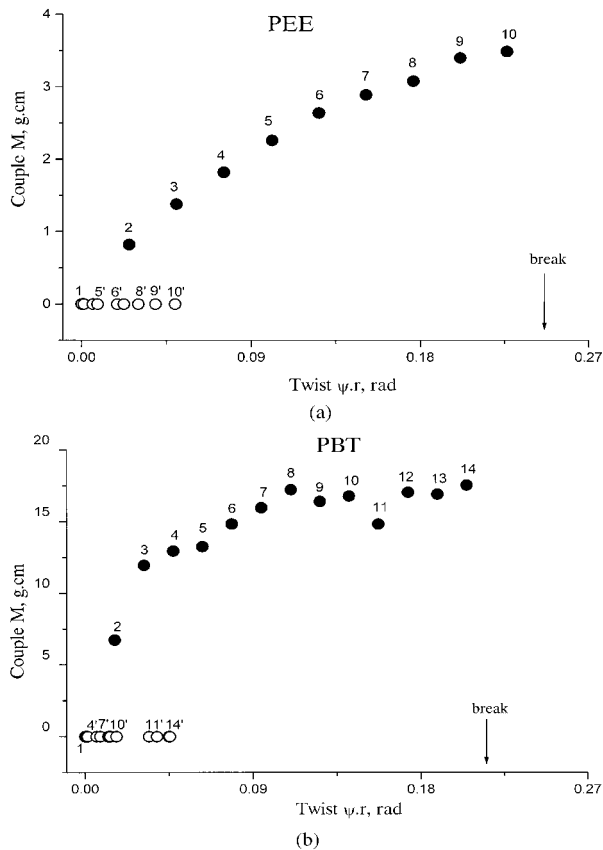
Figure 8 (a) Dependence of the couple M on the twist for PEE, and (b) dependence of the couple M on the twist for PBT. The full circles represent the positive couple M necessary to maintain a certain twist, whereas the open circles represent the residual twist (i.e., taken at $M = 0$).

reversibility of the deformation. This quantity is plotted as a function of the overall (preset) twist for both PEE and PBT in Figure 9. This figure is
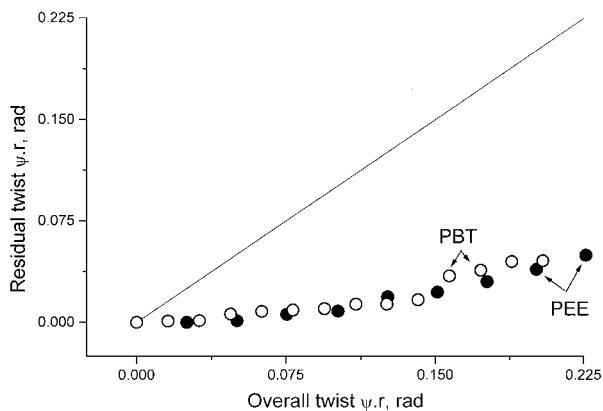

Figure 9 Dependence of the residual twist on the overall twist for PEE and PBT, as indicated. The line representing totally irreversible torsion is also shown.

analogous to similar figures in the case of elongation.[15] The line in Figure 9 represents totally irreversible torsion, whereas the abscissa itself (Ψr = 0.0 rad) represents the totally reversible case. Surprisingly, there is not a significant difference between the behavior of PEE and PBT in this regard. If we take the ratio of the residual twist to the overall twist for a specific value of the latter, for example for Ψr = 0.2 rad, it is 0.19 for PEE and 0.22 for PBT. Since these values are close to one other, it may be concluded that PEE with this composition, although being drawn, does not behave as a typical elastomer in torsion experiments. This is probably due to the high (75 wt %) PBT content in this particular PEE, whereas typically elastomeric PEEs contain ∼ 40–70 wt % PBT.[16]

In order to obtain the dependence of the shear modulus G on the twist,[17,18] the following well-known relation was used:

$$G = \frac{2M}{\pi \Psi r^4} \qquad (3)$$

The dependences of the modulus G on the twist Ψr as calculated from eq. (3) for both PEE and PBT are shown in Figure 10. There is a striking difference in the trend of G with twist. For PEE the initial value of G is small and decreases steadily down to half of its initial value with increase in the twist to the highest value of Ψr. For PBT the initial value of G is about sevenfold higher than that of PEE, but decreases very rapidly down to approximately one-sixth of its initial value with increase in the twist to the highest value of Ψr.

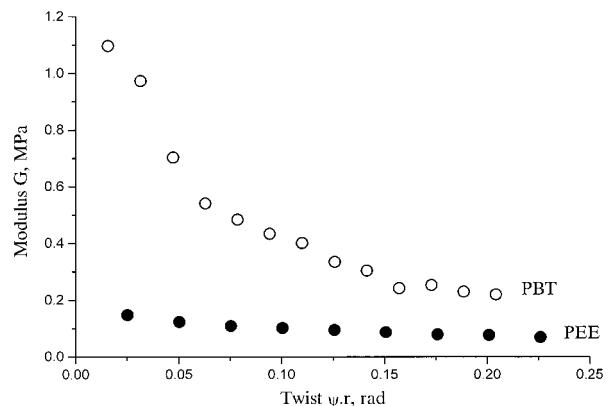As can be concluded from Figures 2 and 5, PEE and PBT behave similarly with regard to relax-

Figure 10 Dependence of the shear modulus G on the twist for PEE and PBT.

ation of the couple in torsion. The only difference is that the main relaxation in PEE is much faster (the order of minutes) than the relaxation in PBT (the order of tens of minutes). PEE and PBT behave rather differently in the couple-twist experiments [compare Figs. 8(a) and (b)], although the residual twist is of the same order of magnitude for both polymers and rises gradually with the twist itself (Fig. 9). It is also worth mentioning that the shear modulus of PBT, measured at low twist, exceeds sevenfold the one for PEE, whereas the Young's modulus of PBT is only three-fold higher than that of PEE.[7]

REFERENCES

1. R. K. Adams and G. K. Hoeschele, in *Thermoplastic Elastomers: A Comprehensive Review,* N. R. Legge, R. K. Adams, and G. K. Hoeschele, Eds., Carl Hanser Verlag, New York, 1987, p. 164.
2. R. Wolfe, *Rubber Chem. Technol.,* **50,** 691 (1977).
3. S. Fakirov and T. Gogeva, *Makromol. Chem.,* **191,** 603 (1990).
4. S. Fakirov and T. Gogeva, *Makromol. Chem.,* **191,** 615 (1990).
5. S. Fakirov, C. Fakirov, E. W. Fischer, and M. Stamm, *Polymer,* **33,** 3818 (1992).
6. S. Fakirov, C. Fakirov, E. W. Fischer, M. Stamm, and A. A. Apostolov, *Coll. Polym. Sci.,* **271,** 811 (1993).
7. A. A. Apostolov, S. Fakirov, B. Sezen, I. Bahar, and A. Kloczkowski, *Polymer,* **35,** 5247 (1994).
8. S. Wang, J. E. Mark, B. Erman, and S. Fakirov, *J. Appl. Polym. Sci.,* **51,** 145 (1994).
9. J. Wen and J. E. Mark, *Polymer J.,* **26,** 151 (1994).
10. A. N. Gent and T. H. Kuan, *J. Polym. Sci., Polym. Phys. Ed.,* **11,** 1723 (1973).
11. F. W. Billmeyer, Jr., *Textbook of Polymer Science,* Wiley-Interscience, New York, 1984, p. 319.
12. L. E. Nielsen and R. F. Landel, *Mechanical Properties of Polymers and Composites,* Marcel Dekker, Inc., New York, 1994, p. 72.
13. L. E. Nielsen and R. F. Landel, *Mechanical Properties of Polymers and Composites,* Marcel Dekker, Inc., New York, 1994, p. 71.
14. P. L. Gould, *Introduction to Linear Elasticity,* Springer-Verlag, New York, Berlin, 1983, p. 85.
15. U. Eisele, *Introduction to Polymer Physics,* Springer-Verlag, Berlin, New York, 1990, p. 155.
16. R. K. Adams and G. K. Hoeschele, in *Thermoplastic Elastomers: A Comprehensive Review,* N. R. Legge, R. K. Adams, and G. K. Hoeschele, Eds., Carl Hanser Verlag, New York, 1987, p. 166.
17. L. R. G. Treloar, *The Physics of Rubber Elasticity,* Oxford University Press, Clarendon, 1975.
18. B. Erman and J. E. Mark, *Structures and Properties of Rubberlike Networks,* Oxford University Press, New York, 1997.