Mechanical Properties of Thermoplastic Elastomers of Poly(butylene terephthalate) and Poly(ethylene glycol) in a Bending Deformation

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SYNOPSIS

Thermoplastic elastomers based on poly(butylene terephthalate) (PBT) and poly(ethylene glycol) (PEG) were studied by bending-creep measurements. The dependence of the creep compliance on the composition of the block copolymer was determined, and the experimental results were compared with calculated results to obtain a better understanding of structure–property relationships for this class of materials. The hard PBT domains in the rubbery PEG matrix make a large contribution to the mechanical strength and hardness, presumably serving as reinforcing fillers as well as cross-links. Relaxation effects were found to decrease significantly with increase in hard-segment content. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Thermoplastic elastomers are special types of block copolymers exhibiting an extraordinary combination of reprocessability, elasticity, toughness, low-temperature flexibility, and strength at relatively high temperatures (frequently ca. 150°C).[1,2] For these reasons, they are now of great commercial importance as engineering materials. The set of unique properties that they exhibit is mainly due to the existence of physical (temporary) cross-links tying the polymer chains into an infinite network. In natural rubber and synthetic elastomers, these cross-links are covalent chemical bonds. In thermoplastic elastomers, however, they are replaced by thermally labile tie points held together by physical forces. These junctions may be glassy, crystalline, or even hydrogen-bonded segments or ionic associations. In any case, they give the material a reprocessability not found in the usual types of elastomers.[1,2]

For a copolymer to behave as a thermoplastic elastomer, the chains must contain two types of blocks (chain sequences): (i) an amorphous, rubbery block (above its glass transition temperature, T_g) referred to as a "soft" segment, and (ii) a block that is much harder, typically because of its being below its T_g or because of the presence of extensive crystallinity. The soft segments impart elastomeric character to the copolymer and are bracketed by the "hard" blocks.[1,2] These hard blocks are capable of intermolecular association to form a phase that is solid within a desired temperature range, thus imparting dimension stability to the material. At elevated temperatures, dissociation of the physical bonds occurs, giving rise to the reprocessability. Although each chain should contain, on the average, at least two hard blocks, the soft and hard blocks may be arranged in various ways, either random or ordered.[1,2] This type of sequential ordering can greatly affect the mechanical properties of the material, as well as its processing characteristics.

The thermoplastic elastomers involved in this investigation are a series of poly(ether/ester)s based on poly(butylene terephthalate) (PBT) and poly(ethylene glycol) (PEG), with PBT forming the hard segments, and PEG, the soft segments. The synthesis and partial characterization of these materials have been reported elsewhere.[3–7] In brief, by

Table I   Compositions and Some Properties of the PBT/PEG Copolymers

PBT/PEG Designation	Wt % PBT	M of PBT (g/mol)	T_m^{PBT} (°C)
49/51	49	1075	182
57/43	57	1480	191
75/25	75	3450	211

changing the segment lengths of soft segments and hard segments in a methodical manner, a series of copolymers with intriguing properties have been obtained.[3,4] In addition, molding conditions and thermal history were found to have large effects on a variety of properties.[5,6]

The influence of the hard-segment lengths at constant length on the soft segments has been studied by NMR, IR, DSC, SAXS, and stress–strain behavior under tension.[3] In the present work, complementary mechanical studies of a similar series of copolymers having different hard-segment lengths were carried out. They involve measurements of creep during bending, which is a type of deformation particularly well suited to materials that are harder than typical elastomers. This information is critically important with regard to their functioning as high-performance materials and serves as a guide in the selection of materials for various applications. The results should also provide a better understanding of the relationships between mechanical properties and polymer structure in this important class of materials.

EXPERIMENTAL

The three samples employed were multiblock copolymers with a fixed molecular weight of PEG (1000 g/mol) and different values of weight percentage of PBT (49, 57, and 75 wt %). The molecular weights M of the PBT segments and their melt-
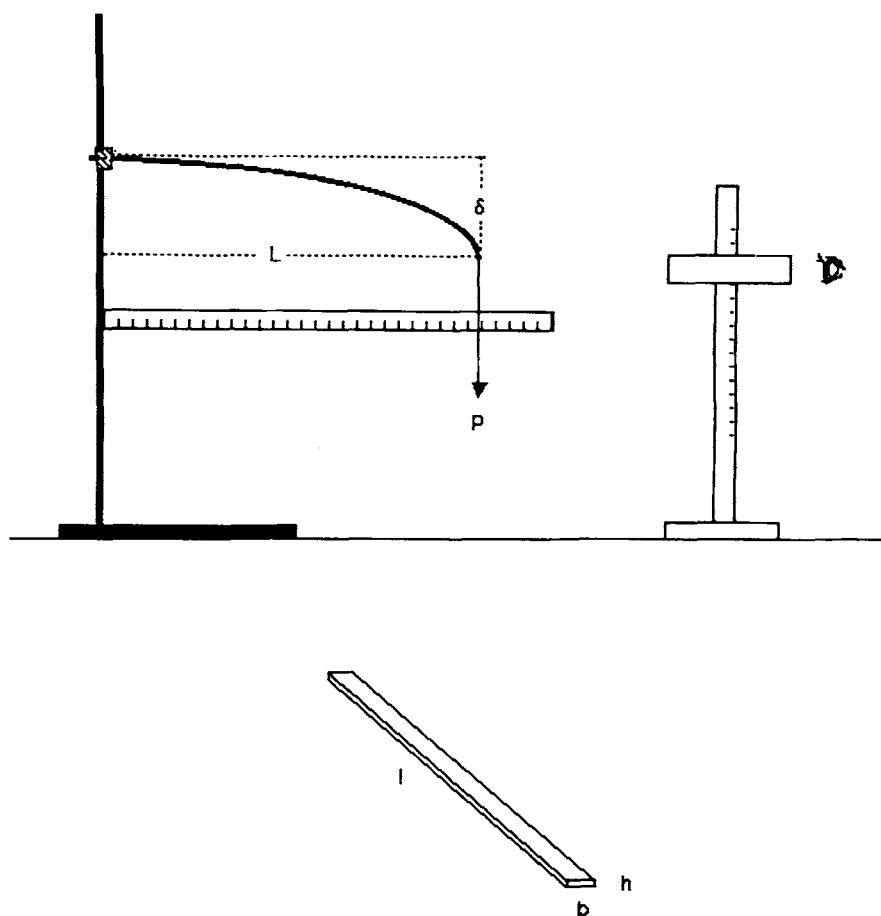

Figure 1   Schematic representation of the apparatus and the specimen employed in the bending measurements.

ing points are given in Table I. A specimen with dimensions of $1 \times 5 \times 90$ mm was obtained from each sample by press-molding (under relatively low pressure) near the melting temperature of the PBT in the copolymer.

The apparatus and the dimensional labeling of the specimens for the bending experiments are shown schematically in Figure 1. The beam was clamped so as to leave about 1 cm inside the clamp. The relationship between the deflection δ of the cantilever beam and the applied load P is

$$\delta = AP/E \qquad (1)$$
$$= 4PL^3/Ebh^3$$

where A is a dimension-related constant; L, the length of the beam (measured from the fixed end to the point of application of the force); E, the modulus of elasticity; b, the width; and h, the thickness of the beam. The deflection caused by the weight of the sample itself was calculated from

$$\delta = 3wL^4/2Ebh^3 \qquad (2)$$

where w is the weight per unit length. This weight was converted to an additional contribution using $P = 3wL/8$, and added to each individual load, thus making the total deflection δ the sum of both contributions.

After a constant load P was applied, a cathetometer was used to measure δ very accurately as function of time. In addition, the distance L was read from the rule, but its change over the range of deformations employed was found to be negligible. The experiments were performed by first applying a small fixed load, measuring $\delta(t)$ for about 24 h, removing the load, and keeping the beam clamped horizontally and then waiting for a somewhat longer time than the loading time for the sample to recover. This procedure was then repeated with increasingly large loads. To check the reversibility, a small load was applied out of sequence. All measurements were conducted at 23°C, which is well below the T_g of PBT (55–56°C) and above the T_g of PEG (−44 to −17°C)

Swelling measurements were carried out on these materials to provide additional information on the effective molecular weight between cross-links. The swelling solvents were chosen to be incompatible with the hard PBT phase, but compatible with the elastomeric PEG phase. They were methanol and benzene, and the swelling measurements were carried out at several temperatures.

RESULTS AND DISCUSSION

Typical curves of deflection vs. time are presented in Figure 2, with each curve labeled by the normalized load AP in N/mm. The line with the filled points is the one taken out of sequence and shows that complete reversibility was not obtained, with some creep clearly in evidence.

For interpretation of the creep experiments, it is better to define the creep compliance by

$$Y(t) = 1/E(t) \qquad (3)$$

From eq. (1), we have

$$E(t) \propto P/\delta(t) \qquad (4)$$

and, therefore,

$$\delta(t) \propto PY(t) \qquad (5)$$

The dependence of creep compliance on time can be obtained as shown in Figure 3(a)–(c). Specifically, $Y(t)$ may also be obtained from the expression

$$Y(t) = Y(0)$$
$$+ [Y(\infty) - Y(0)][1 - e^{-\alpha t}] + t/\eta \qquad (6)$$
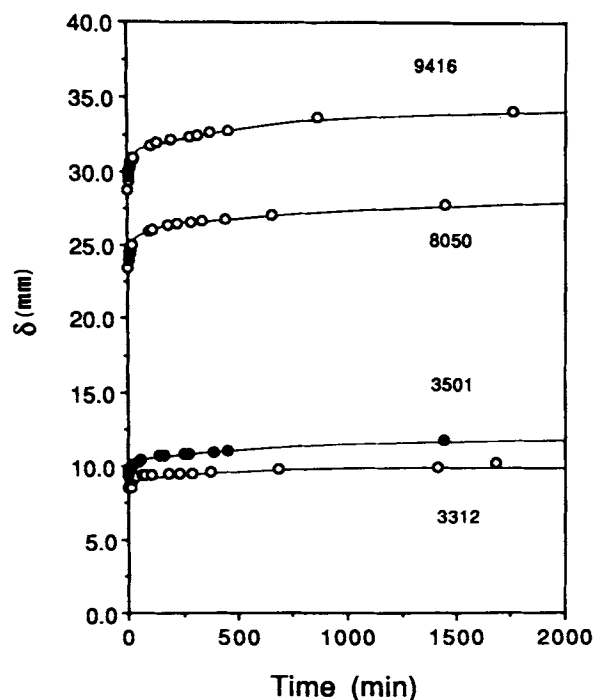

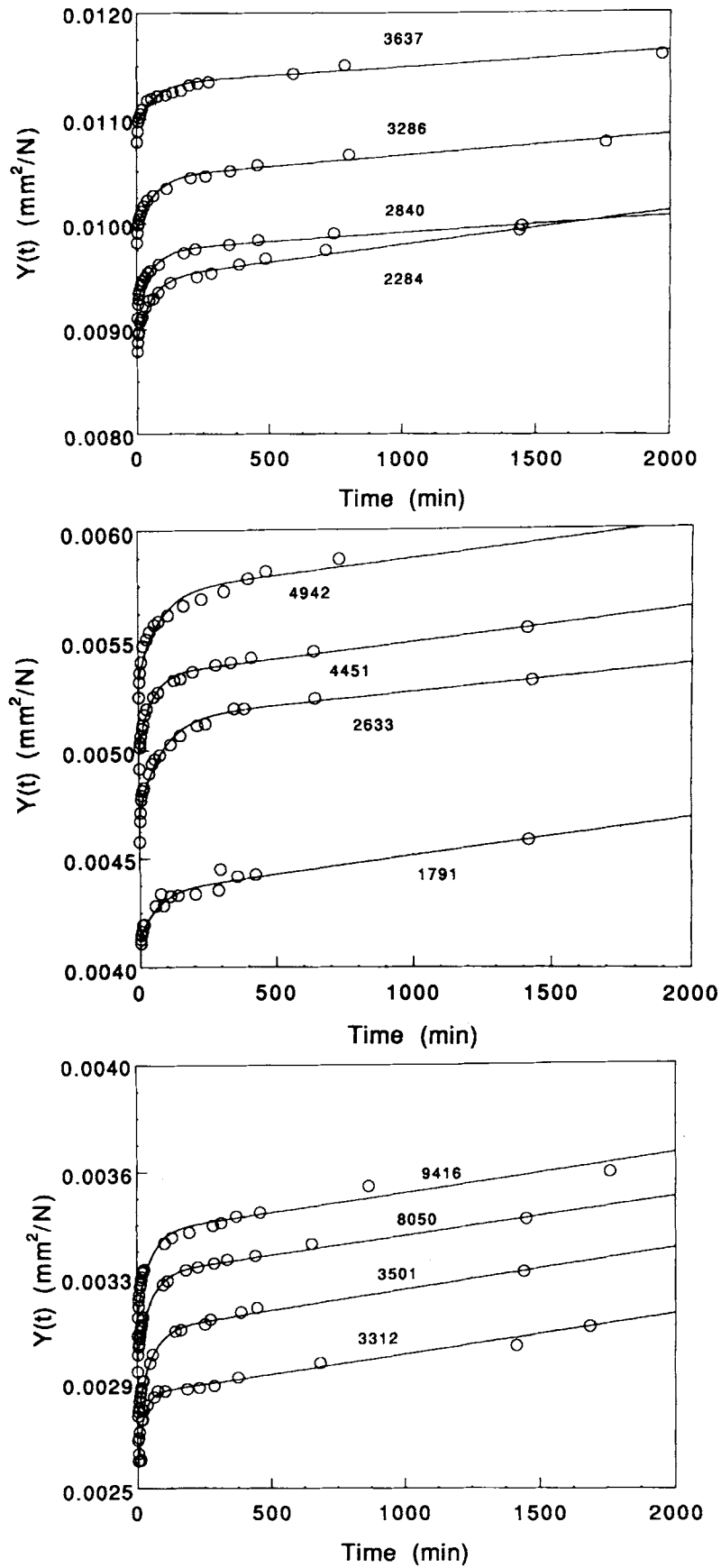**Figure 2** Typical deflection vs. time behavior for sample PBT/PEG (75/25).

Figure 3 Dependence of creep compliance on time. The open circles are the experimental data, and the solid lines are the fitting curves. Each curve is labeled with the corresponding load. The compositions were (a) PBT/PEG (49/51), (b) PBT/PEG (57/43), and (c) PBT/PEG (75/25).

Table II   Parameters from Curve Fitting for PBT/PEG Copolymers

PBT/PEG (Wt/Wt)	AP (N/mm)	$A \times 10^{-5}$ (mm^{-1})	$Y(0) \times 10^3$ (mm^2/N)	$Y(\infty) \times 10^3$ (mm^2/N)	$Y(\infty) - Y(0) \times 10^3$ (mm^2/N)	$\alpha \times 10^3$ (min)	$1/\eta \times 10^7$ (mm^2/N min)
49/51	2284	2.097	8.888	9.475	0.587	1.83	3.28
	3286	1.705	9.942	10.45	0.508	1.52	2.05
	3637	1.397	10.95	11.34	0.390	1.45	1.55
	2840	1.974	9.247	9.751	0.504	1.67	1.67
57/43	1791	1.819	4.132	4.342	0.210	1.54	1.73
	4451	1.503	5.005	5.343	0.338	2.07	1.53
	4942	1.375	5.332	5.723	0.391	1.28	1.53
	2633	1.819	4.707	5.145	0.438	1.17	1.23
75/25	3312	1.757	2.581	2.838	0.257	4.59	1.42
	8050	1.558	2.967	3.263	0.296	2.06	1.36
	9416	1.405	3.109	3.412	0.303	2.14	1.39
	3501	1.757	2.753	3.062	0.309	2.07	1.47

where $Y(0)$, $Y(\infty)$, α, and η may be obtained by curve fitting the experimental data. The three terms in eq. (6) are the contributions from Hookean deformation, elastic relaxation, and Newtonian flow, respectively. The results are shown in Table II. Figures 4 and 5 show the relationship between the stress–strain behavior and the compositions of the copolymers. Again, the filled points obtained for checking reversibility indicated that these materials were not totally reversible in this time scale. $Y(t)$ was found to depend on the degree of deformation for all three samples, particularly Sample 49/51.

This is perhaps due to the nonlinearity of the samples, an issue that could be addressed in later studies.

With increase of the hard-component content, the stiffness increases, as can be seen from the values of $Y(0)$ and $Y(\infty)$. The increase in elastic modulus results from the hard domains, which function in three ways: (1) increase in effective network cross-linking, from bonding at the domain surface (and possibly from entanglements that are trapped because of chain ends being anchored in the domains); (2) stiffening of the domains acting as hard filler particles; and (3) stiffening of the network because
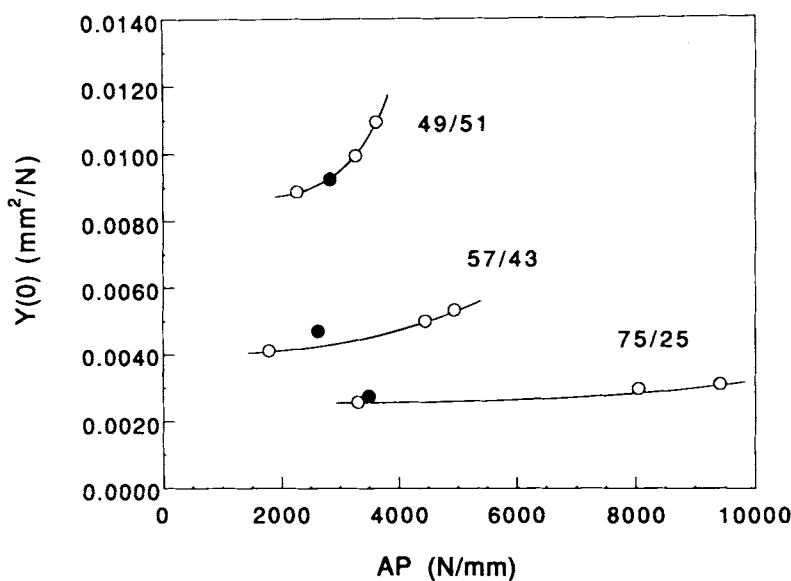

Figure 4   Relationship between stress expressed as AP and compliance $Y(0)$ for PBT/PEG copolymers with different compositions. Filled circles are used for checking reversibility.
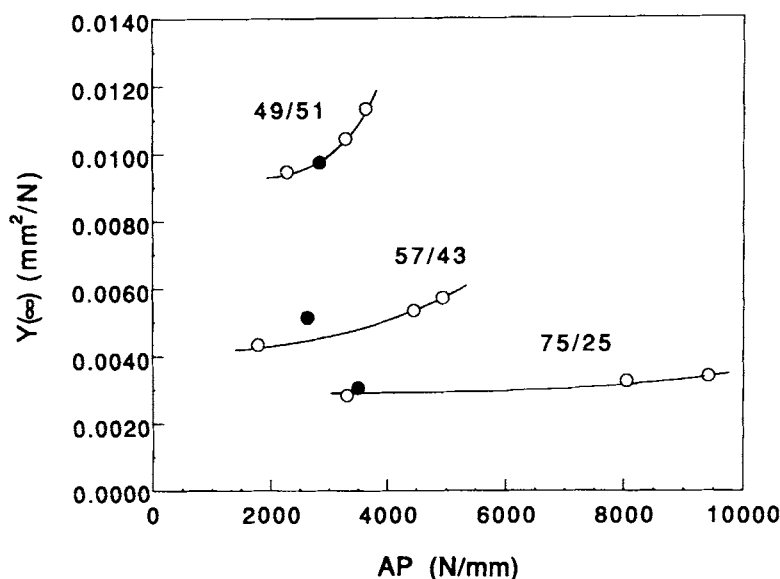
Figure 5   The relationship between stress expressed as AP and compliance $Y(\infty)$ for PBT/PEG copolymers with different compositions. Filled circles are used for checking reversibility.

of the constraints at the domain surfaces arising from domain–network bonding. The bonding of the network to the domains may also enhance the tensile strength in a manner similar to that of reinforcing filler particles in conventional vulcanizates.

The quantities $Y(0) - Y(\infty)$ and α characterize the relaxation, which results from the long-range translational motions in an entangled rubbery mass. These relaxations should increase with molecular weight. Although the values of molecular weight of the PEG soft blocks for the three samples are the same, the molecular weights between cross-links M_c may be different and much more complicated. The swelling results listed in Table III show a decrease in the degree of swelling with increase in the hard-block component. Because of the high weight percentage of hard blocks in the network, which act not only as cross-links but also as reinforcing filler particles of nonnegligible volume, a quantitative correspondence between the degree of swelling and M_c should not be expected.[8] However, qualitative comparisons should be reasonable. Decrease in the volume fraction v_1 of the solvent corresponds to a decrease in the degree of swelling, which corresponds to a decrease in the effective molecular weight between cross-links. The results thus indicate that the molecular weight between cross-links decreases with increase in the amount of the hard component. The maxima in the relaxation $Y(0) - Y(\infty)$ are generally smaller in the samples with a larger hard-

component content, giving larger values of α (which is an indication of relaxation rate). These qualitative conclusions are based on the assumptions that the molecular motions in the hard domains are negligible and that only the contributions from the rubbery matrix are important in this regard.

The quantity $1/\eta$ from the Newtonian-flow region depends on all motions of the polymer chains, both in the soft blocks and the hard blocks. It plays a dominant role in large time scales and generally decreases with increase of hard-segment content.

Additional work is underway to further characterize the physical properties of these thermoplastic elastomers, over a wider range of composition and structure.

Table III   Swelling Behavior of PBT/PEG Copolymers Represented as the Volume Fraction of Solvent in the Swollen Network

PBT/PEG	49/51	57/43	75/25
Benzene, 24°C	0.399	0.251	0.156
Benzene, 50°C	0.532	0.317	0.190
Methanol, 24°C	0.159	0.118	0.074

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