Rheology of Polycarbonate/Poly(butylene terephthalate) Blends Containing a Core-Shell Modifier and High-Molecular-Weight Acrylic Polymers: Extrusion Blow-Moldable Resins

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SYNOPSIS

Several different polymer modifications are currently used to produce commercial plastic materials, especially engineering resins, that have significantly improved melt strength. However, these modifications rarely produce materials that can be formed into very large parts. This study shows that the melt strength of engineering resins can be enhanced by rubber particles having grafted shells that are compatible with the resin. The melt strength of the engineering resin can be further improved by the incorporation of compatible high-molecular-weight polymers. The melt strength improvements thus obtained facilitate the formation of very large parts requiring 8–10 ft long parisons. The effects of shear rate on complex viscosity indicate that the extent of interaction between the polycarbonate matrix and the core-shell impact modifier decreases with increasing shear rate. Therefore, the impact strength of the part molded from a matrix modified with a core-shell rubber may depend on the process history. Dynamic mechanical measurements may provide a means to evaluate the interaction between the matrix and a core-shell modifier in an actual blend. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Some of the plastics processing methods, especially thermoforming and extrusion blow molding, require that the plastics being formed have sufficient melt strength. Until recently, only commodity plastics such as low density polyethylene could be formed using thermoforming and blow molding. In recent years engineering thermoplastics have been modified to improve their melt strength and make them amenable to thermoforming and blow molding. Several methods of enhancing the melt strength of engineering thermoplastics have been reported including chain branching, cross-linking, or chemical modification through blending with materials of higher melt strength.

In polyesters long chain branching enhances melt elasticity thereby improving melt strength and shear sensitivity of the melt. The modification of linear macromolecules, leading to long-chain branching, has been achieved by incorporation of small amounts of polyfunctional monomers.[1] Polyhydric phenols are used to introduce branching in polycarbonates (PCs).[2-4] The melt strength of polyesters, PCs, and polyamides have also been improved via chemical modification by reactive blending with other polymers.[5-11] Blending PC with ultra high molecular weight PC was another method used to increase the melt strength of the blend for blow molding, especially of large parts.[12]

The effect of inorganic filler on reinforcing polymer melts has been studied.[13,14] Dynamic moduli and complex viscosities were enhanced at low frequencies because of the formation of network structures of agglomerated particles also referred to as particle–particle gel structures. Sun et al.[15] reported on the effects of cross-linked polymeric particles as fillers in polymer melts. These authors found that poor particle dispersion, leading to agglomerates, immobilizes some of the matrix during flow, decreasing the effective volume of the matrix and increasing

the viscosity. The reinforcing effect at low shear rates was not observed when the cross-linked polymeric filler particles, being compatible with the matrix, were well dispersed.

In this work the effect of rubber particles with a grafted acrylic shell (modifier), and high-molecular-weight acrylic polymers on the melt strength of poly(butylene terephthalate)/polycarbonate (PBT/PC) blends was studied. The effect of shear rate on complex viscosity and dynamic modulus was measured and related to the interaction between the PC/PBT matrix and the acrylic shell of the modifier. It should be noted that the grafted acrylic shell on the modifier studied was not cross-linked.

EXPERIMENTAL

Materials

A blend of branched PC (intrinsic viscosity 0.5 dL/g measured in methylene dichloride at 25°C) and PBT (intrinsic viscosity 1.1 dL/g measured in a 60/40 mixture of phenol/tetrachloroethane at 25°C) was used as the matrix. The methyl methacrylate/butadiene/styrene (MBS) core-shell modifier used in this study is essentially made up of a poly(butadiene/styrene) core and poly(methyl methacrylate) (PMMA) shell. The high-molecular-weight-polymers were prepared in the lab using emulsion polymerization methods.

Blend Preparation

The blends containing PBT/PC in the ratio of 43/57 were prepared by first mixing the well-dried components thoroughly, followed by melt mixing in a 25-mm single screw extruder (Killion) at 250°C and 60 rpm. The strand from the extruder was quenched and pelletized. The pellets were dried at 90°C for 12 h prior to molding of parts.

Specimen Preparation

A 30-T Newbury injection molder was used to injection mold the parts for further testing. The melt temperature of 250°C and mold temperature of 65°C was used.

Extrusion Sag Time

The PC/PBT blends containing the additives were melt blended in a 25-mm single screw extruder at a screw speed of 60 rpm, through a 1.59-mm die at the specified temperatures. The strand was cut at the die and the time for the strand to move from the die to a point 1.0 m below the die was measured in seconds. The strand of the material having a higher sag traversed that distance in a shorter interval than the strand of material with lower sag.

Dynamic Mechanical Measurements

These measurements were made using a Rheometrics Dynamic Spectrometer in the parallel plate mode. A sample with a radius of 12.5 mm and approximately 2-mm thickness was placed between the plates, and dynamic torsional shear was applied to the sample at 5% strain. The temperature was held constant when measuring the effect of frequency. The ratio of complex viscosity at 1 rad/s to complex viscosity at 100 rad/s, R^*, provides a measure of melt strength. Higher values of R^* indicate higher melt strength.

Melt Creep Measurements

Melt creep rate and recoverable compliance were measured using a Rheometrics Stress Rheometer. A sample with a radius of 12.5 mm and a thickness of 1 mm was placed between the parallel plates of the instrument and heated to the specified temperature. A constant load of 3×10^4 dyne/cm^2 was applied to the sample. The resulting strain was measured. The melt creep rate is strain divided by the time over which the strain was measured. Once a steady state is reached, the applied load is removed and the sample is allowed to recover. Recoverable strain divided by stress gives the recoverable compliance numbers. Viscosity as a function of time under these low shear conditions is another set of data that is obtained from these experiments.

Other Measurements

Notched Izod measurements were made according to ASTM Standard Method Number D-256. Both number-average and weight-average molecular weights (M_n and M_w) were determined by gel permeation chromatography, using a PMMA reference. Vicat was measured according to ASTM Standard Method Number D-1525. The melt flow rate was measured using a Tinius Olsen Capillary Rheometer at 265°C and 5000-g load.

RESULTS AND DISCUSSION

Most commercial applications of PBT/PC blends require modification to improve the impact strength

1.0 μm

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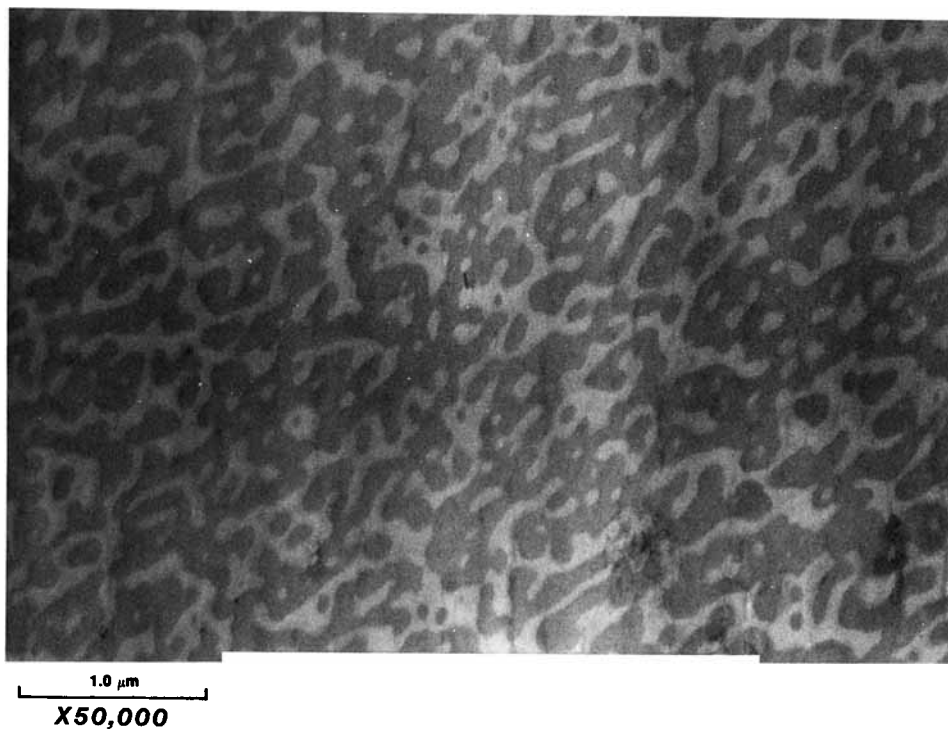
Figure 1   PBT/PC blend without core-shell modifier. PBT is shown as light regions.

of these blends. Core-shell impact modifiers that consist of a rubber core and a PMMA shell are generally used for this purpose. The effect of one of these core-shell impact modifiers on the rheological properties of PBT/PC blends was studied. It was also decided to determine how the rheological be-

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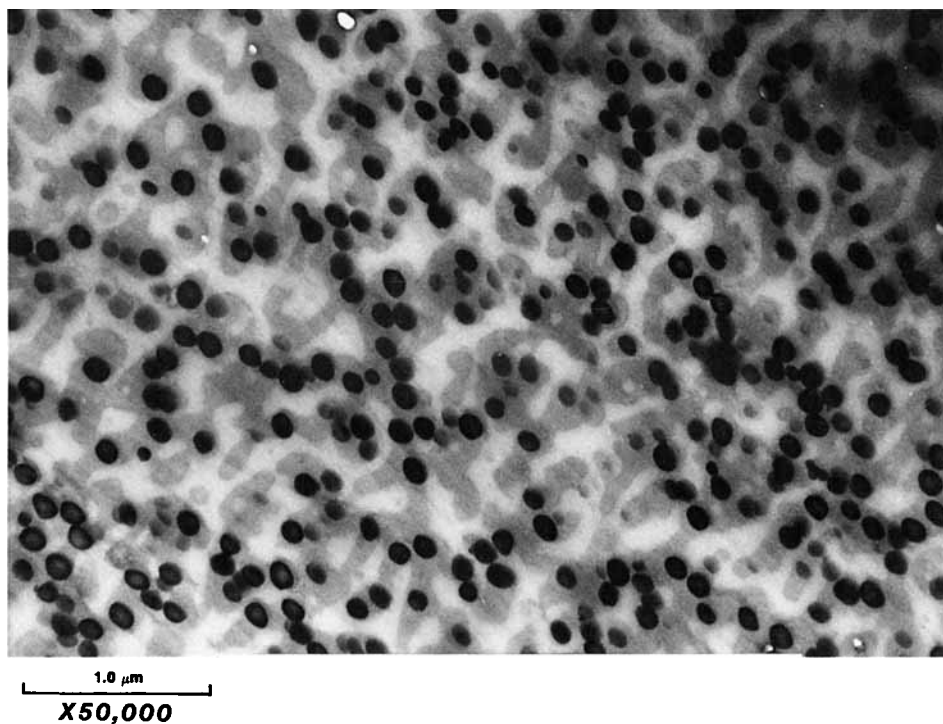
Figure 2   PBT/PC blend with 15% core-shell modifier. Core-shell modifier in PC phase.

Table I   Effect of Core-Shell Modifier in PC/PBT Blends

| Modifier Level (%)	Notched Izod (ft-lb/in)	Vicat (°C)	Melt Flow Rate (g/10 min)	R^*	Melt Creep Rate (s⁻¹)	Steady-State Low-Shear Viscosity (P)	Recoverable Compliance (cm²/dyne)
0	1	169	15.4	3.2	0.79	3.5×10^4	1.87×10^{-5}
15	13[a]	156	7.9	7.4	0.09	3.2×10^5	2.02×10^{-5}

[a] Ductile breaks.

havior of PBT/PC blends containing core-shell rubber modifier can be further modified with the incorporation of high-molecular-weight acrylic polymers.

Effect of Core-Shell Modifier

The transmission electron micrograph (Fig. 1) of PBT/PC blend shows a co-continuous phase of PBT and PC. The micrograph in Figure 2 shows that the core-shell modifier is present only in the PC phase and in that phase the core-shell modifier is well dispersed. There are no obvious agglomerates. The good dispersion of the modifier results in significantly

improved impact strength as reflected by high notched Izod values (Table I). The dispersion of the modifier is attributed to the compatibility of the acrylic shell of the modifier with PC.[16] PC and PMMA are not thermodynamically miscible, however, their interaction parameter is positive and small. It is therefore the PC phase that is modified by the core-shell modifier.

Figure 3 provides the data on complex viscosity as a function of frequency at 245°C for PBT/PC blend and for PBT/PC blend containing 15% by weight of the core-shell modifier. The complex viscosity is significantly higher for the modified blend at low frequencies. The increased complex viscosity
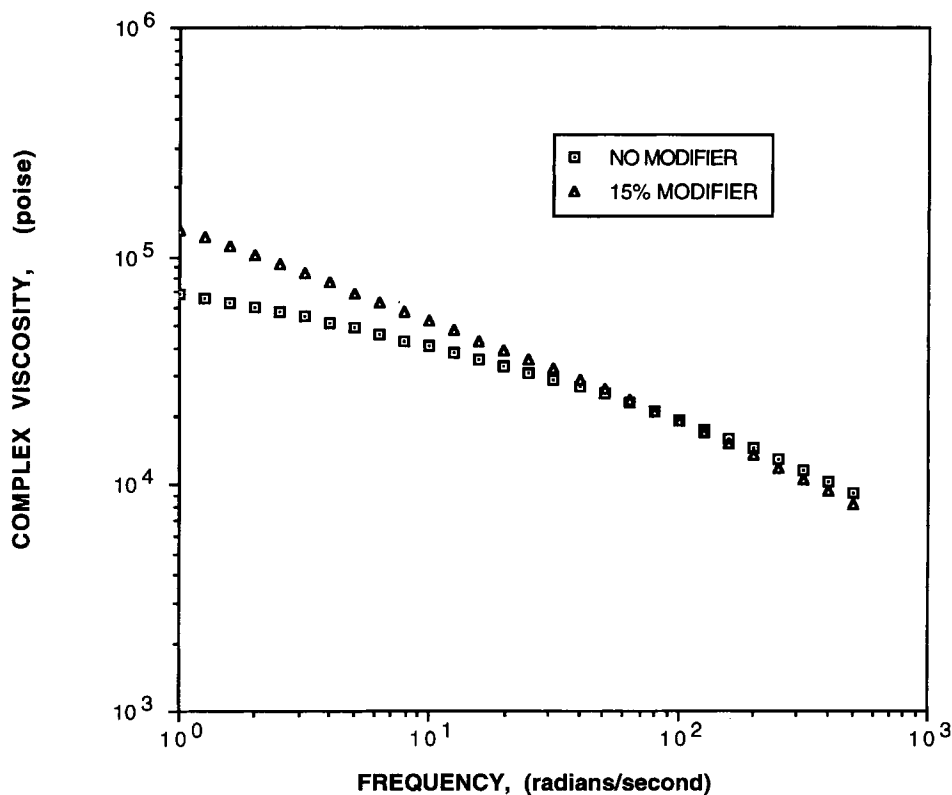
Figure 3   Effect of core-shell modifier on viscosity of PBT/PC blend at 245°C.

at low frequencies for PBT/PC blends containing the core-shell modifier could result from entanglement of PC chains with the acrylic shell of the core-shell modifier forming a particle of much larger effective volume. The effect of this interaction between PC and the core-shell modifier is a reduction in free PC chains that can flow readily. This structure would create a drag on the flow of PC chains causing an increase in viscosity. As the shear rate increases the PC chains would become increasingly disentangled from the acrylic shell of the core-shell modifier and as a result the complex viscosity of the modified blend decreases and approaches that of the unmodified blend. In fact it seems that at a frequency of 500 rad/s the complex viscosity of the modified blend is lower than that of the unmodified blends. This indicates that under high shear conditions it is likely that the PC chains are no longer entangled with the shell of the modifier and the modifier particles will rotate under such conditions to reduce viscosity. The action of the modifier under high shear conditions is similar to that proposed for "temporarily crosslinked clusters" by Busse.[17]

This effect of shear rate on core-shell modifier/matrix interaction may have important implications

regarding the use of impact modified resins molded under very high shear conditions and where the molded parts are thin and cooled very rapidly. The molding of resins containing core-shell impact modifiers under these conditions may result in the modifier remaining sufficiently disentangled from the matrix during solidification of the melt and cause significantly lower efficiency of the impact modifier.

The effect of the modifier on dynamic and loss moduli as a function of frequency is depicted in Figures 4 and 5. These data also point to a strong interaction between the core-shell modifier and the PC phase of the matrix under low shear conditions.

A summary of data obtained for modified and unmodified PBT/PC blends is provided in Table I. The data show that, as expected, the modifier improves the impact strength and reduces the heat distortion temperature. The parameters, melt flow rate, R^*, melt creep rate, and steady-state low shear viscosity, are positively affected by the presence of the core-shell modifier. Therefore, the blend with the modifier will have higher melt strength compared to the blend without the modifier. The effect on recoverable compliance is marginal suggesting that under these conditions the relaxation time of the
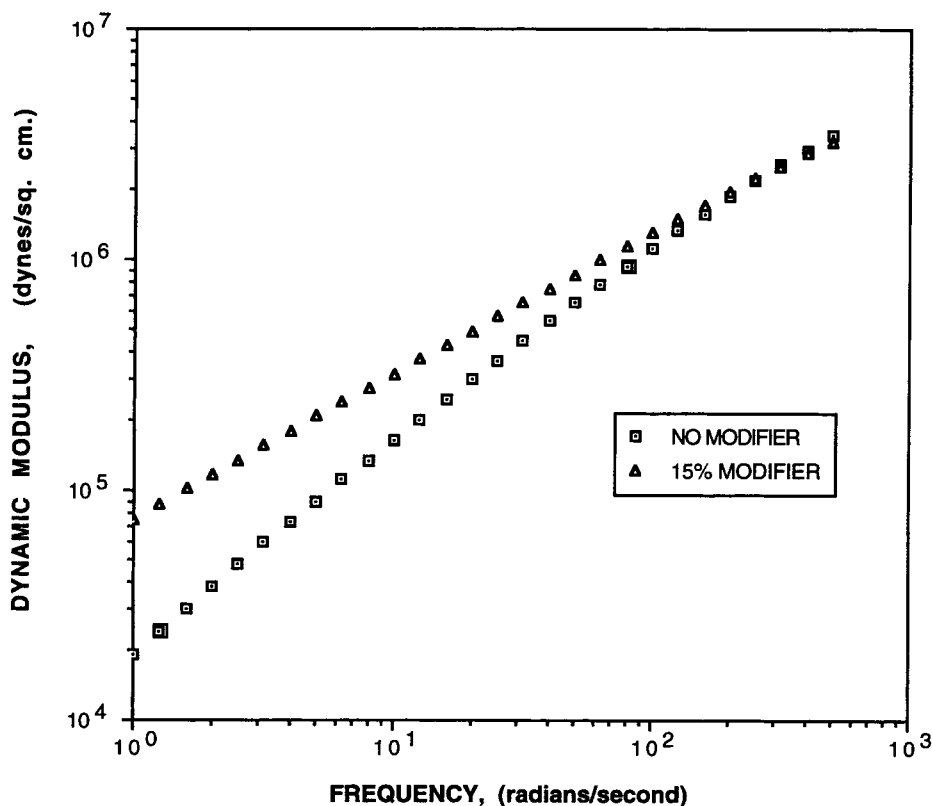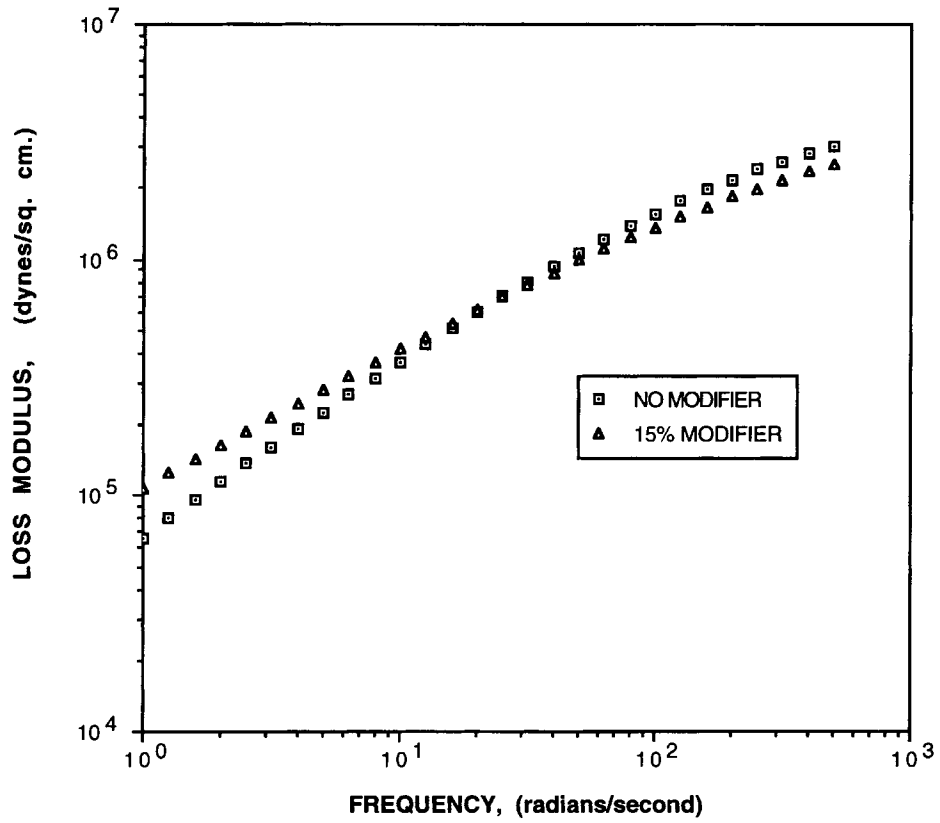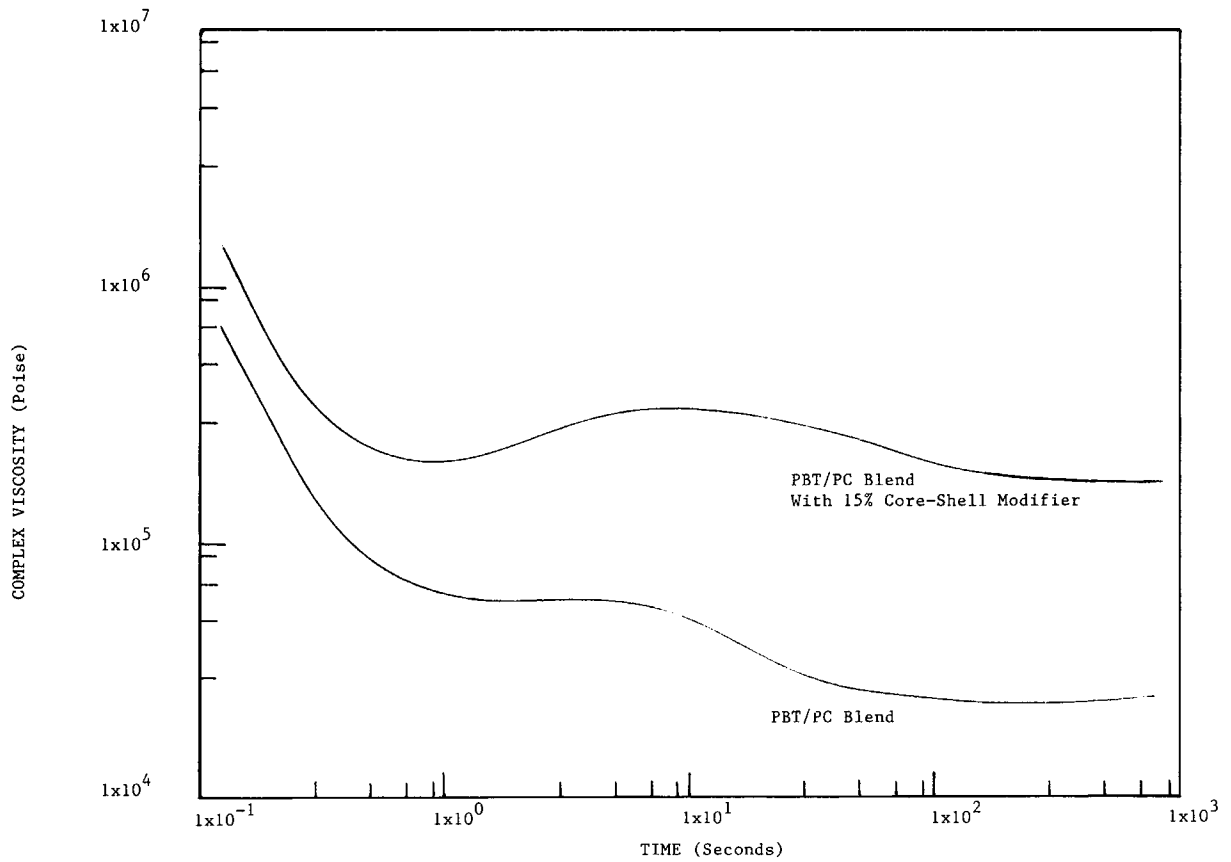

Figure 4 Effect of core-shell modifier on modulus of PBT/PC blend at 245°C.

Figure 5 Effect of core-shell modifier on loss modulus of PBT/PC blend at 245°C.

Figure 6 Effect of core-shell modifier on melt creep behavior of PBT/PC blends.
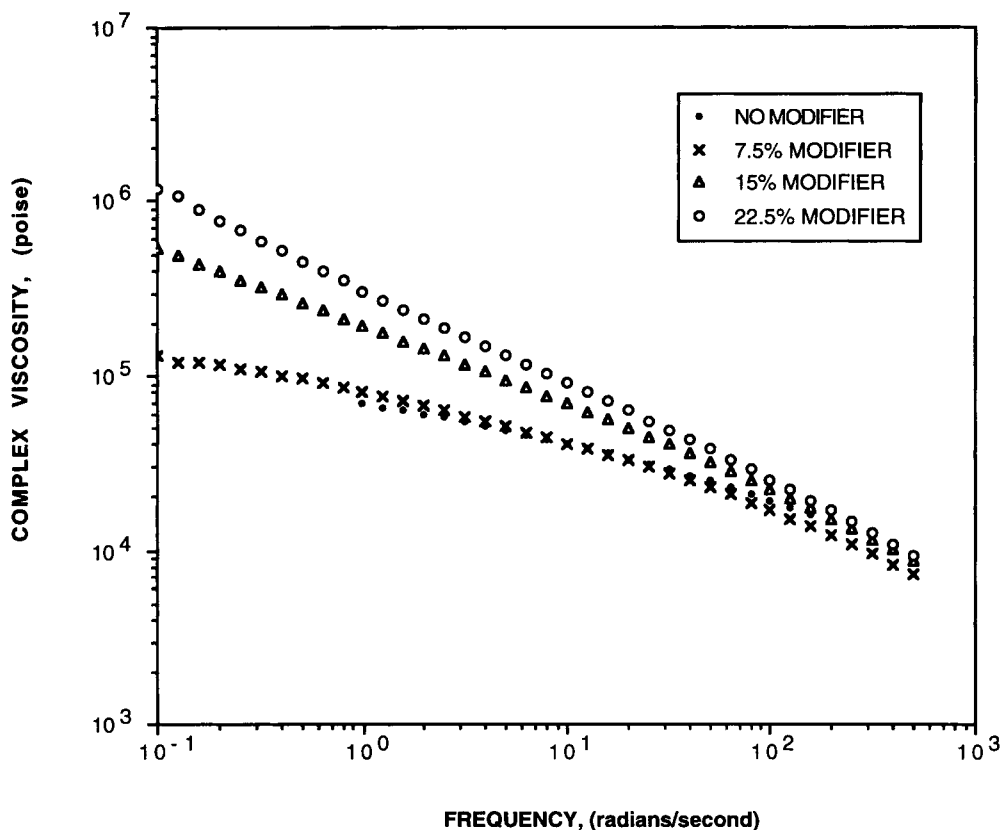
Figure 7   Effect of core-shell modifier level on viscosity of PBT/PC blend at 245°C.

entangled chains is comparable to the inverse shear rate. The low shear rate in this experiment does not produce large elastic deformations of the entangled coils.

The data from the melt creep experiment on the stress rheometer can be depicted in the form of complex viscosity as a function of time under a small constant load. This is shown in Figure 6. Under low shear conditions, because the modifier shell is sufficiently entangled with PC chains, the modifier acts to restrict flow of the melt. The modifier particles seem to behave as tie-down points similar to the way hard domains function in ABA block copolymer elastomers.[18]

Effect of Modifier Loading

The data discussed so far provide an understanding of the changes in the rheological properties as result of the presence of the modifier particles in the blend. These experiments were expanded to study the effect of different modifier levels on rheological properties at frequencies of 0.1–500 rad/s. The data on complex viscosity as a function of frequency for these blends is provided in the conventional log–log plot in Figure

7. The behavior is similar to that obtained with fillers and cross-linked particles. In the case of fillers[13,14] and cross-linked plastic particles[16] the effect at low shear conditions is ascribed to particle–particle agglomerates that break up at higher shear rates. As pointed out previously, the transmission electron micrograph in Figure 2 shows that the blends of this study do not have visible particle–particle agglomerates.

Table II   Effect of Core-Shell Modifier Level on Complex Viscosity at Different Frequencies

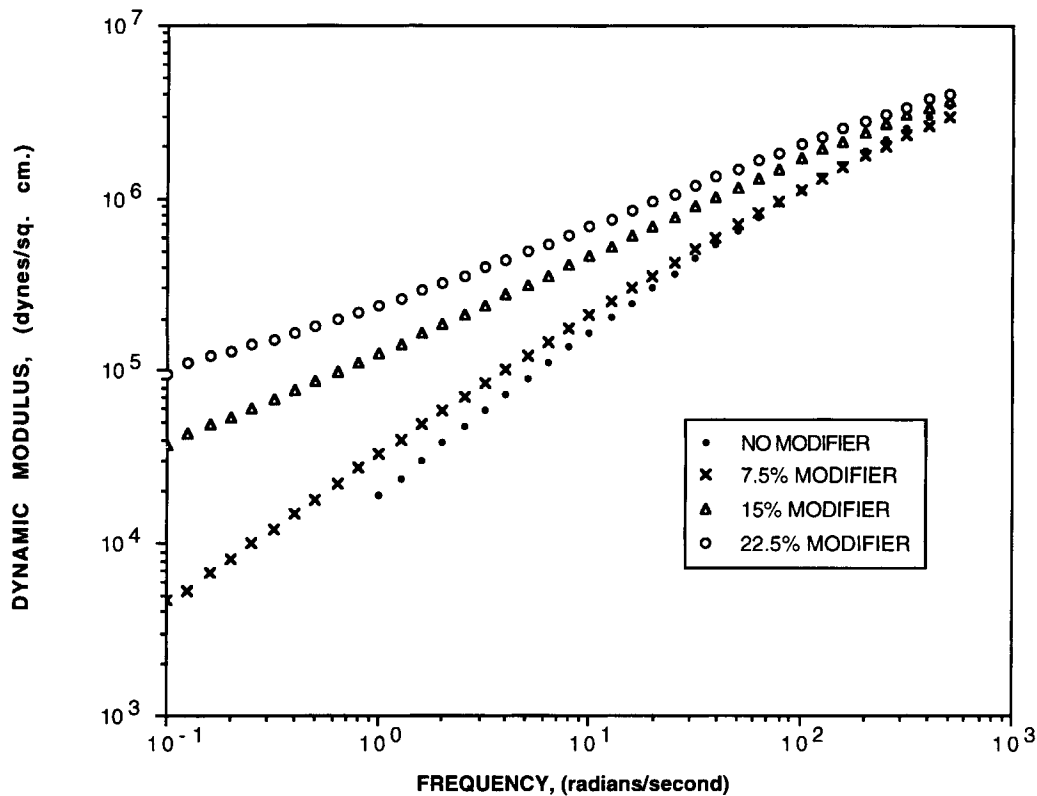| Modifier Level (%)	Slope of Complex Viscosity vs. Frequency Plot (P/rad/s)		
	Frequency Range (rad/s)		
	0.1–0.25	1.0–10.0	100–500
0	—	-3.2×10^3	-2.5×10^1
7.5	-1.2×10^5	-4.4×10^3	-2.4×10^1
15.0	-1.2×10^6	-1.4×10^4	-3.4×10^1
22.5	-3.3×10^6	-3.4×10^4	-4.0×10^1

Figure 8   Effect of core-shell modifier level on modulus of PBT/PC blend at 245°C.
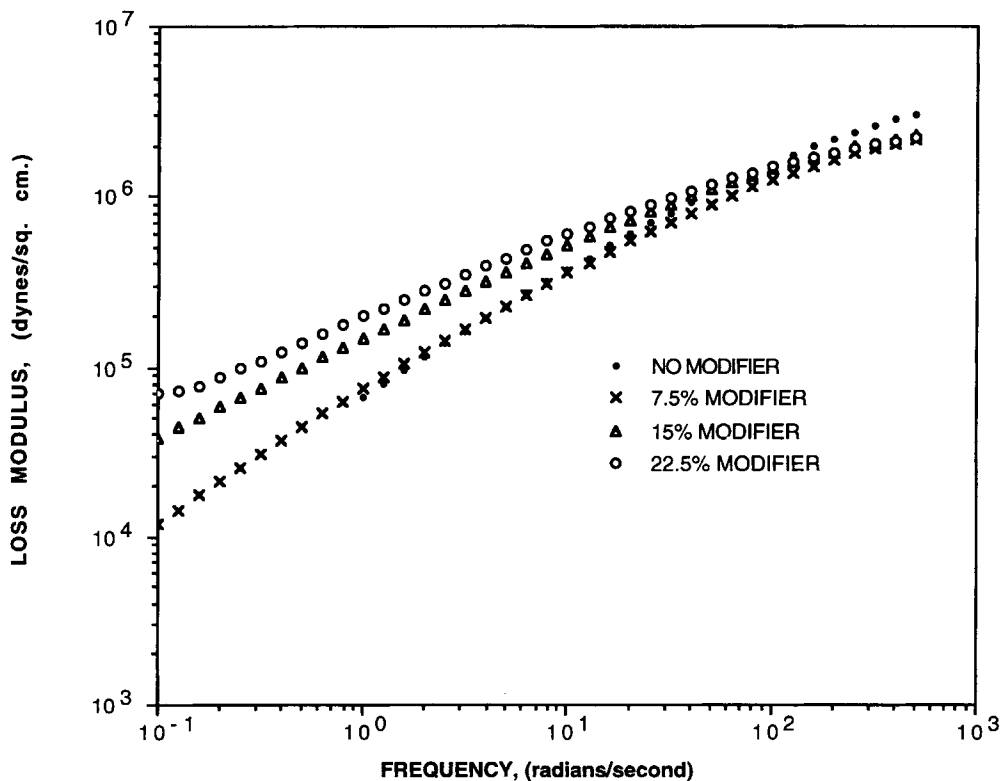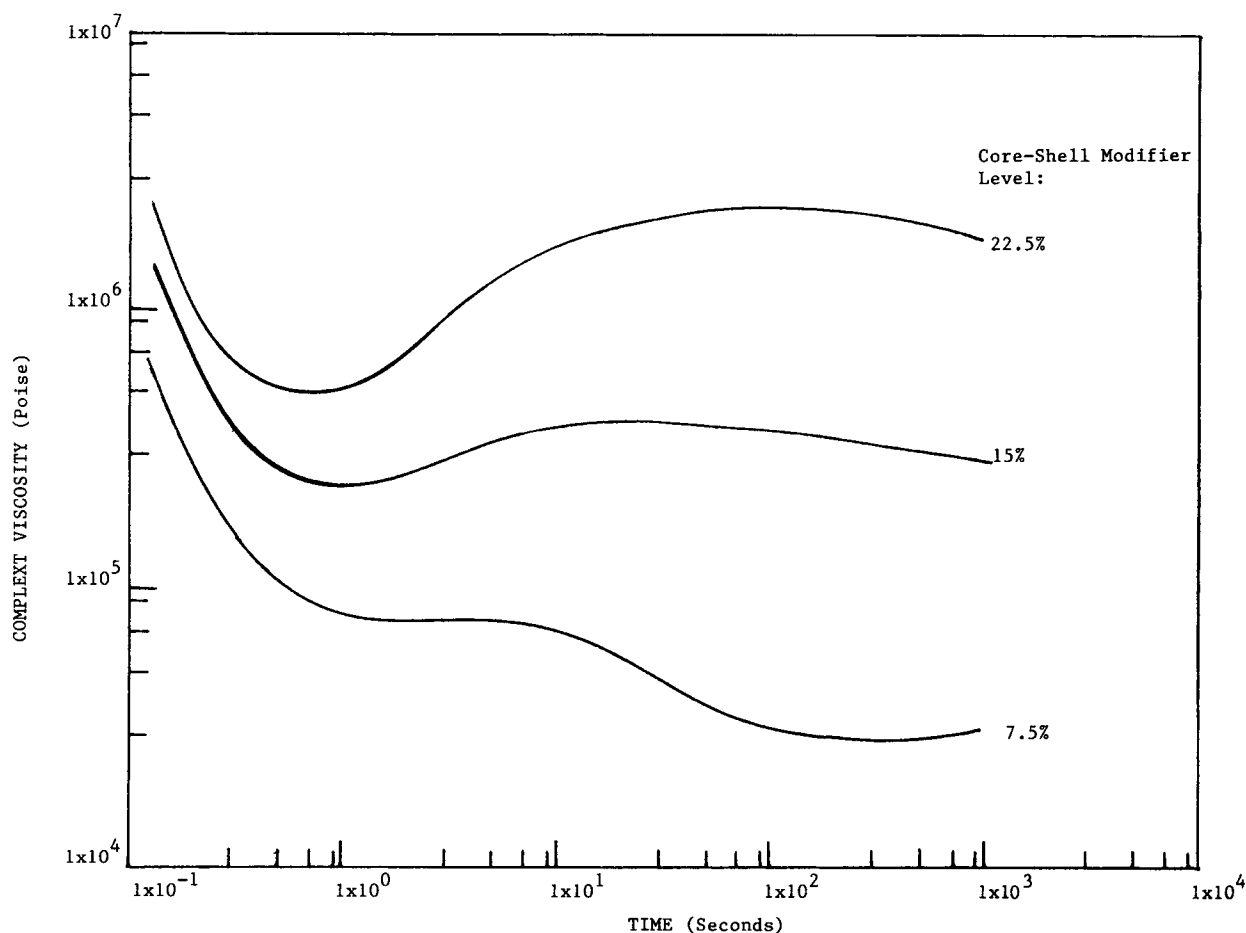

Figure 9   Effect of core-shell modifier level on loss modulus of PBT/PC blend at 245°C.

The examination of complex viscosity data for these blends containing different modifier levels shows three distinct behaviors as a function of frequency. These behaviors can be described by examining the rates of change of complex viscosity within different frequency ranges. The slope values at frequency ranges of 0.1–0.25, 1.0–10.0, and 100–500 rad/s for different modifier levels are provided in Table II. The data show that in the high frequency range of 100–500 rad/s the slope values are low and do not change significantly with the modifier loading. This points to very little, if any, interaction between the modifier and the matrix in this frequency range. In the middle frequency range of 1.0–10.0 rad/s the slopes are significantly higher (approximately a factor of 200) than those at the higher frequency range. Also, the slope increases with increasing modifier level. These observations support the earlier argument that the acrylic shell of the modifier is entangled with the PC chains. This results in par-

ticles of larger effective volume that restrict the flow of matrix polymer chains resulting in higher viscosity values. At low frequencies, 0.1–0.25 rad/s, the particle effective volumes become so large that the "effective" particle boundaries now touch. This would result in "agglomerates" of these effective particles and cause very high complex viscosities. At modifier levels of 0–15% the reinforcement of the melt increases with increasing modifier loading. However, as the modifier loading increases further the viscosity increase tends to level off because the formation of new agglomerates decreases after a certain modifier loading is reached. The dynamic modulus and loss modulus data presented in Figures 8 and 9 support the interpretation of the complex viscosity data.

The data presented in Figure 10 show the change in complex viscosity as a function of time measured under low shear conditions on the Rheometrics Stress Rheometer. The data demonstrate that the

Figure 10 Effect of different levels of core-shell modifier on melt creep behavior of PBT/PC blend.

Table III Effect of Core-Shell Modifier Loading in PC/PBT Blends

| Modifier Level (%)	Notched Izod (ft-lb/in)	Vicat (°C)	R^*	Melt Creep Rate (s^{-1})	Steady-State Low-Shear Viscosity (P)	Recoverable Compliance (cm^2/dyne)
0	1	169	3.2	0.79	3.5×10^4	1.87×10^{-5}
7.5	15[a]	164	4.8	0.27	8.1×10^4	1.7×10^{-5}
15	13[a]	156	7.4	0.09	3.9×10^5	1.9×10^{-5}
22.5	13[a]	150	12.2	0.02	2.2×10^6	1.4×10^{-5}

[a] Ductile breaks.

melt is reinforced by the modifier particles and this reinforcement can be attributed to the agglomerates of the effective particles and the drag provided by these effective particles of larger effective volume formed by the entanglement of the modifier shell with PC chains.

The effect of modifier loading on the melt strength of the blend is summarized in Table III. The data show that at low shear conditions the melt viscosity of these blends, as measured by different parameters, increases significantly as the shear rate decreases. This indicates an increase in melt

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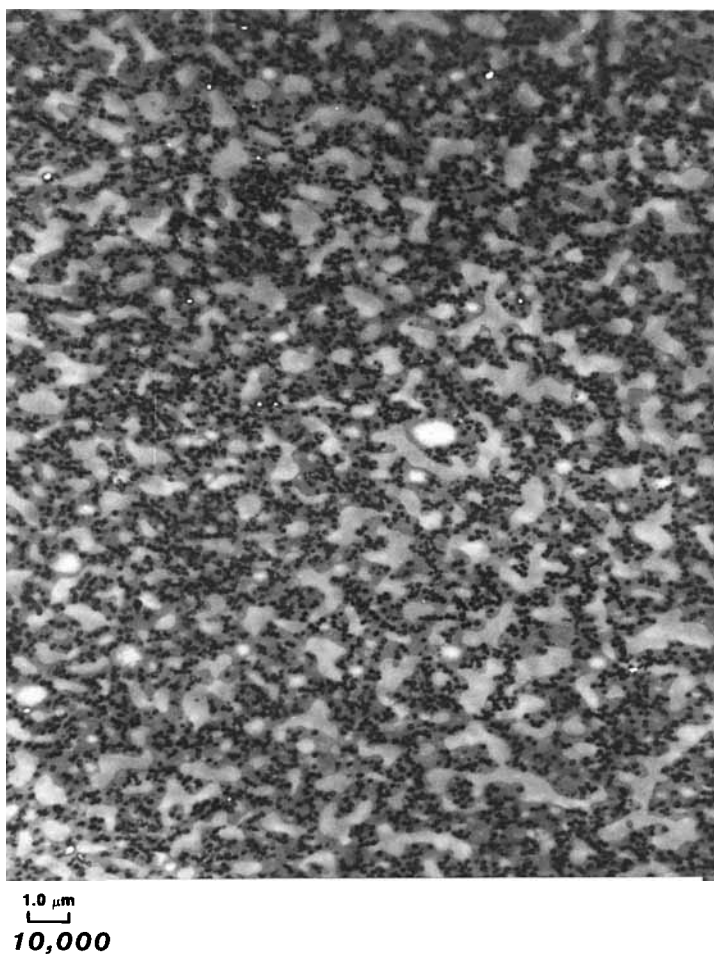
Figure 11 PBT/PC blend with 15% core-shell modifier and 5% high-molecular-weight acrylic polymer. Core-shell modifier and high-molecular-weight acrylic polymer in PC phase.
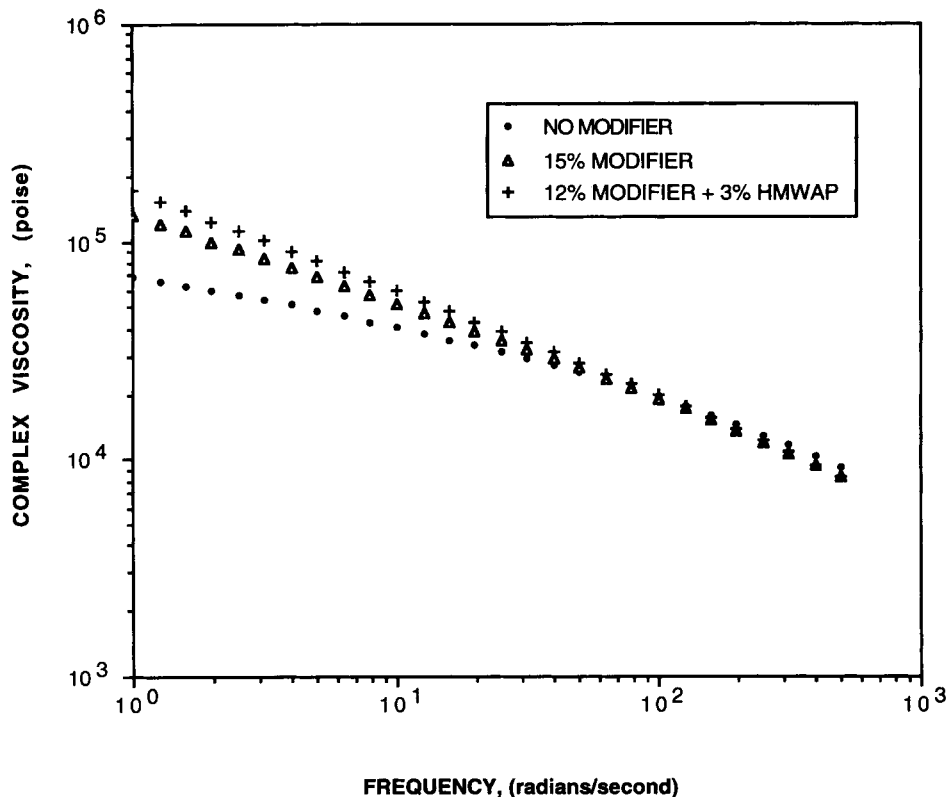
Figure 12 Effect of high-molecular-weight acrylic copolymer on viscosity of PBT/PC blend at 245°C.

strength as the modifier loading increases. The data on recoverable compliance suggest that at these shear rates the modifier does not affect elastic deformation and relaxation rate.

The data presented in this section suggests that incorporation of the modifier with an acrylic shell would result in increased melt strength of PC and its blends. Also, there is strong dependence of the extent of interfacial interaction between the modifier and the matrix polymer on the shear rate. Therefore, the process history (shear rate and cooling rate in the mold) may determine the efficiency of the modifier in systems with core-shell impact modifiers.

Effect of High-Molecular-Weight Acrylic Polymers

As discussed in the previous section the core-shell impact modifier enhances the melt strength of PBT/PC blends. However, it is still difficult, if not impossible, to thermoform or extrusion blow mold large parts such as bus body panels and truck bumpers from PBT/PC blends containing the core-shell impact modifier. The effect of high-molecular-weight acrylic polymers was studied in PBT/PC blends containing core-shell impact modifier to determine

if such modification will result in formulations that could be formed into large parts. Again, the effect of shear rate on the melt viscosity was used as the main criteria to determine if the blends had sufficient melt strength. In addition, the measurement of extrusion sag time was used to determine the resistance of different formulations to sag in the melt state.

Figure 11 shows a transmission electron micrograph of a PBT/PC blend containing 15% modifier and 5% of high-molecular-weight acrylic copolymer. As shown before the modifier is in the PC phase. The high-molecular-weight acrylic copolymer domains of different sizes are also randomly distributed in the PC phase. At the interface the boundary is diffuse suggesting intermixing and entanglement of acrylic and PC chains in this region.

Figure 12 compares the behavior of the PBT/PC blend containing 15% core-shell modifier with the blend containing 12% modifier and 3% high-molecular-weight acrylic copolymer. The composition of the copolymer used was MMA/butyl MA/ethyl acrylate (80/13/7) with a M_w of 4×10^6. The data show that the high-molecular-weight copolymer is more effective in increasing the complex viscosity

Table IV   Melt Strength of PBT/PC Blends; Effect of Core-Shell Modifier and High-Molecular-Weight Acrylic Copolymer

Modifier Level (%)	High M_w Acrylic Copolymer[a] (%)	R^*	Melt Creep Rate (s^{-1})	Steady-State Low Shear Viscosity (P)	Recoverable Compliance (cm^2/dyne)
0	0	3.2	0.79	3.5×10^4	1.87×10^{-5}
15	0	7.4	0.09	3.2×10^5	2.0×10^{-5}
12	3	8.7	0.06	4.9×10^5	2.3×10^{-5}

[a] P(MMA/BMA/EA) (80/13/7); $M_w = 4 \times 10^6$.

at the lower shear conditions. This effect results from the dispersion of the high-molecular-weight copolymer in PC to form a large number of domains of different sizes. These domains are fluid at the conditions of the test but, because of high molecular weight, form highly entangled acrylic networks that are resistant to flow under low shear conditions. At the interface the acrylic networks are entangled with the PC chains and, thus act as tie-down points at low shear rates. As the shear rate increases the acrylic network becomes progressively disentangled and is less resistant to flow. Also, the entanglements between PC chains and the acrylic network decrease resulting in higher flow at higher shear rates.

The data on blends containing both the modifier and the high-molecular-weight acrylic copolymer are summarized in Table IV. The data on melt creep rate, R^*, and steady-state low shear viscosity indicate that the high-molecular-weight acrylic modifier is more efficient at improving the melt strength of the blend. However, the high-molecular-weight acrylic copolymer does not seem to affect the recoverable compliance under the conditions used in this study.

Table V   Melt Strength of PBT/PC Blends: Effect of Different Levels of High-Molecular-Weight Acrylic Copolymer

Modifier Level (%)	High M_w Acrylic Copolymer[a] (%)	R^*	Melt Creep Rate (s^{-1})	Extrusion Sag Time (s)
0	0	3.2	0.79	—
15	0	7.4	0.09	20
15	3	9.8	0.04	29
15	5	10.4	0.03	34

[a] P(MMA/BMA/EA) (80/13/7); $M_w = 4 \times 10^6$.

The data in Table V show the effect of different levels of high-molecular-weight acrylic copolymer on the melt strength of the blends that contain the same loading of the modifier. The melt strength increases rapidly as the level of high-molecular-weight acrylic copolymer increases from 0 to 3%, but the effect starts to level off as the loading of high-molecular-weight acrylic copolymer increases to 5%. The complex viscosity vs. time data presented in Figure 13 also suggest that under low shear conditions the high-molecular-weight acrylic polymer reinforces the melt.

Extrusion Blow Molding

In the previous sections the effect of the impact modifier and that of the high-molecular-weight acrylic copolymer on the melt strength of PBT/PC blends was described in terms of rheological parameters. These findings were confirmed by extrusion blow molding a 12 × 25 in panel (36-in long parison) from the compositions containing the impact modifier and the high-molecular-weight acrylic copolymers of two different compositions. The data, in the form of parison hang time (Table VI) support the conclusions reached based on rheological data presented. The longer parison hang times indicate decreased sag of the parison and significant improvement in the processing window. A 60 × 15 in part was successfully molded from a PBT/PC blend containing 15% core-shell modifier and 5% high-molecular-weight acrylic polymer.

CONCLUSIONS

Several strategies have been used in recent years to improve the melt strength of engineering resins with some success. However, the use of engineering resins to extrusion blow mold or thermoform very large
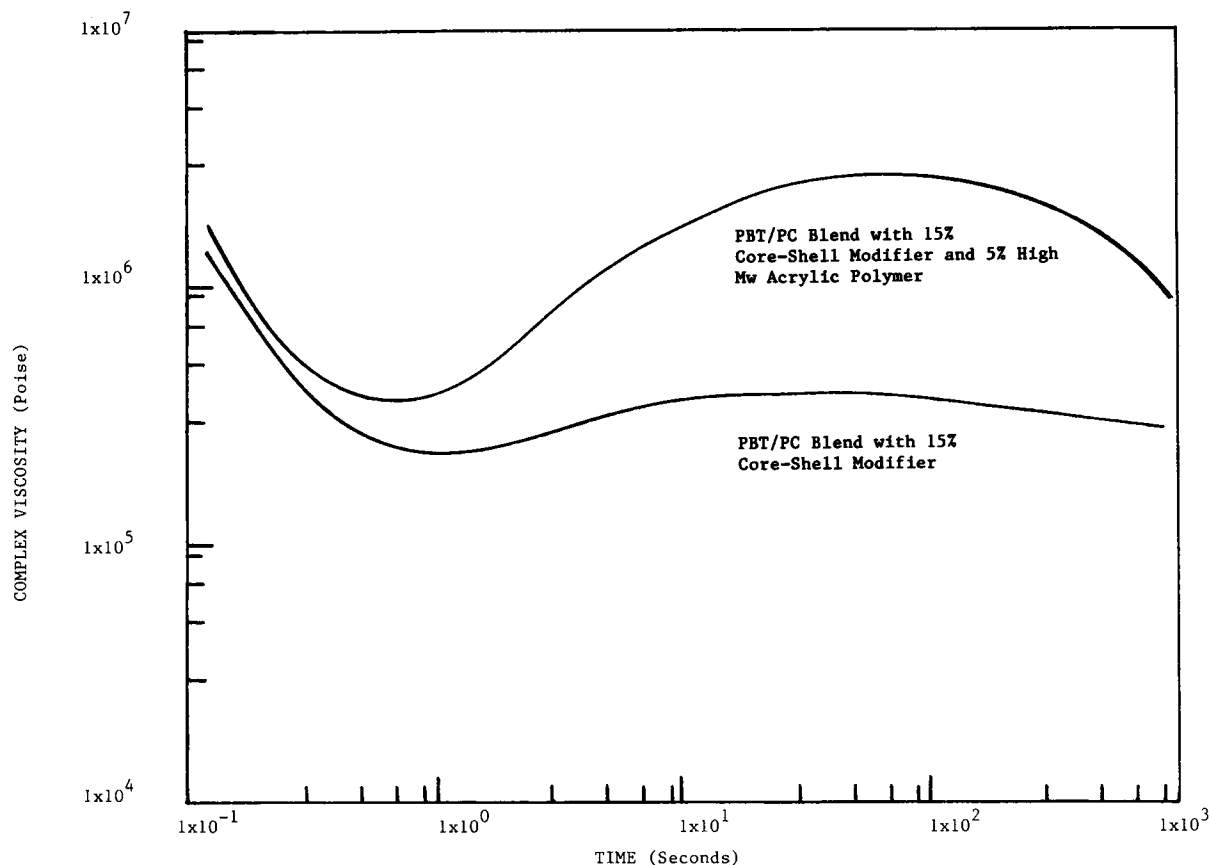
Figure 13 Effect of high-molecular-weight acrylic polymer on melt creep behavior of PBT/PC blend.

parts is limited due to inadequate melt strength. It has been shown that the incorporation of a core-shell modifier in combination with a high-molecular-weight acrylic polymer in PBT/PC blends would result in resins that can be successfully extrusion blow molded into very large parts requiring 8–10 ft long parisons. The rheological measurements such

as R^*, melt creep rate, extrusion sag time, and steady-state low shear viscosity do provide a means to study the relative melt strength of plastic materials. The dynamic mechanical measurements to study the effect of frequency on viscosity, dynamic modulus, and loss modulus may be correlated with the extent of interaction of the modifier shell with

Table VI Melt Strength of PBT/PC Blends: Extrusion Blow Molding Effect of High-Molecular-Weight Acrylic Copolymers of Different Compositions

Modifier Level (%)	Composition High M_w Acrylic Copolymer	High M_w Acrylic Copolymer[a] (%)	R^*	Melt Creep Rate (s^{-1})	Extrusion Sag Time (s)	Parison Hang Time(s) @ 248°C	@ 260°C
0	None	None	3.2	0.79	—	—	—
15	None	None	7.4	0.09	20	2.5	—
15	a	5	10.4	0.03	34	6.3	3.7
15	b	5	10.6	0.03	38	11.0	5.8

[a] P(MMA/BMA/EA) (80/13/7); M_w = 4 × 10^6
[b] P(MMA/BMA/BA) (87/10/4); M_w = 4.7 × 10^6.

the matrix. This implies that the shear conditions during the molding process and the rate of cooling of the part in the mold may have significant consequences related to the interaction of the modifier with the matrix. In the parts molded under high shear/rapid cooling conditions the interfacial interaction between the impact modifier and the matrix may not be adequate to provide the required impact strength improvement.

REFERENCES

1. L. W. Fisher, G. H. Pearson, and P. D. Yacobucci, *Am. Chem. Soc. Polym. Chem.*, (Preprint), **20**, 130 (1979).
2. H. O. Krabbenhoft and E. P. Boden, Eur. Pat. Appl. EP 400,478 (1990).
3. H. O. Krabbenhoft and E. P. Boden, U.S. Pat. 5,021,521 (1991).
4. M. K. Laughner, PCT Int. Appl., WO 9,010,675 (1990).
5. L. K. Howe, PCT Int. Appl., WO 9,119,766 (1991).
6. M. Joshi, A. Misra, and S. N. Maiti, *J. Appl. Polym. Sci.*, **43**(2), 311 (1991).
7. K. L. Howe, PCT. Int. Appl., WO 9,119,767 (1991).
8. D. J. Patterson, U.S. Pat. 4,788,263 (1988).
9. N. W. Thomas, F. M. Berardinelli, and R. Edelman, U.S. Pat. 4,071,503 (1978).
10. E. C. Szamborski, *Am. Chem. Soc. Div. Org. Coat. Plast. Chem.* (Preprint), **37**, (1977).
11. M. P. Subramanian, U.S. Pat. 4,966,941 (1990).
12. N. Namanishi and K. Hashimoto, Eur. Pat Appl. EP 498,406 (1992).
13. H. Tanaka and J. L. White, *Polym. Eng. Sci.*, **20**, 949 (1980).
14. L. Li and T. Masuda, *Polym. Eng. Sci.*, **30**, 841 (1991).
15. L. Sun, M. Park, J. J. Aklonis, and R. Salovey, *Polym. Eng. Sci.*, **32**, 1418 (1992).
16. D. R. Paul, M. Nishimoto, and H. Keskkula, *Polymer*, **32**, 272 (1991).
17. W. F. Busse, *J. Polym. Sci.*, **5**(A-2), 1261 (1967).
18. N. A. Memon and H. L. Williams, *J. Appl. Polym. Sci.*, **17**, 1361 (1973).