

# NOTE

## The Effects of Molecular Weight on Polycarbonate–Polybutylene Terephthalate Blends

### INTRODUCTION

Polycarbonate–polyester blends have attracted both commercial and academic interest for over 10 years.<sup>1</sup> In particular, the blending of BPA polycarbonate (PC) with polybutylene terephthalate (PBT) results in an alloy that has both improved chemical resistance compared to PC and better impact and heat-distortion temperature than that typically associated with PBT. This material, along with further blend modifications, has found wide use as an engineering thermoplastic alloy. However, certain precautions must be taken in preparing these blends. First among these is addressing the chemical reactivity of these materials owing to the presence of titanium residues in the PBT. The titanium is introduced as a transesterification catalyst in the manufacture of the polyester. The high reactivity of this catalyst is of great benefit in the manufacture of PBT, but the very same reactivity leads to the catalysis of transesterification of PC and PBT. Even during the relatively short contact times typical of commercial plastic processing operations, transesterification is observed in unstabilized blends, leading to the formation of PC–PBT copolymer. Initially, this may improve certain properties, but, ultimately, it will lead to an amorphous random copolymer without the desired chemical resistivity or heat distortion of a phase-separated blend. In addition, thermal instability resulting in carbon dioxide generation is observed due to the formation and subsequent degradation of alkyl carbonates. A yellow color is developed due to the presence of aryl titanate residues. Consistent performance of PC/PBT blends can be achieved only through control of melt transesterification. If this reaction is not controlled, the properties of the blend will change with each heat history.

The miscibility of PC and PBT in cases of both controlled and uncontrolled reactions have been previously investigated.<sup>2</sup> However, the effect of the molecular weight of the blend components on the viscosity and miscibility under conditions where transesterification has been controlled has not been reported. This paper details the effect of PC and PBT molecular weights upon these properties.

### EXPERIMENTAL

The PC and PBT materials studied are shown in Tables I and II, respectively, and are all products of GE Plastics with the exception of PBT1, a PBT made by the Mitsubishi Rayon Co. Polycarbonate GPC molecular weights are calibrated with PC standards. Polybutylene terephthalate GPC molecular weights are calibrated with polystyrene standards.

All formulations were prepared from 50 phr PBT pellets and 50 phr PC pellets. All materials were undried prior to extrusion. In all cases, materials were extruded at 250°C on a 30 mm twin-screw extruder at 300 rpm using a good mixing screw. Each formulation was stabilized by the addition of 0.10 phr of aqueous 45% phosphorous acid solution.

Standard samples were molded from dried pellets (> 3 h at 125°C) on an 80 ton, 6 oz molding machine. Melt temperature was 250°C and mold temperature 65°C, with a cycle time of 30 s. Abusive molding conditions used a melt temperature of 285°C with a 2 min cycle time.

Glass transition temperatures were measured by DMA using a  $\frac{1}{8}$  in. bar molded under standard conditions. The heating rate was 2°C/min from 40 to 200°C. Viscosity measurements were obtained on a Tinius Olsen viscometer using a 21.5 kg load, a 0.42 in.  $\times$  0.615 in. orifice. Samples were dried for > 2 h at 115°C before measurement. Vicat analyses were performed as described in ASTM test 1525 using a 1 mm<sup>2</sup> circular probe.

DSC analyses were performed on 10 mg samples using a Perkin-Elmer System 7 thermal analysis system. Abusive DSC analyses involved holding the sample at 290°C for 15 min followed by rapid cooling and a second heating to record both the  $T_m$  and the  $\Delta H$  of the PBT melt endotherm (see Table III).

**Table I** Molecular Weights of PC Materials

	$M_n$	$M_w$
PC1	8,000	18,000
PC2	10,500	24,500
PC3	12,000	28,500
PC4	13,000	34,000

Table II Molecular Weights of PBT Materials

	$M_n$	$M_w$
PBT1	25,000	52,000
PBT2	30,600	70,500
PBT3	45,900	105,500

## RESULTS AND DISCUSSION

In the years since the development of PC/PBT blends, many additives have been used as stabilizers to prevent the melt reaction. Phosphites, as a class, have gained the widest acceptance in this role.<sup>2,3</sup> Other materials that have been used include phosphates and phosphorus-containing acids. In this study, 45% aqueous phosphorous acid was selected as the stabilizer due to its lack of organic by-products during the passivation of the titanium residue.

Table IV shows the viscosities of different PC/PBT 50 : 50 blends stabilized by 0.1% phosphorous acid solution and demonstrates that at this ratio the viscosity is determined primarily by the PBT. This is probably due to PBT being the continuous phase in the blend of this composition. For a given PBT viscosity, increasing the PC viscosity increases the blend viscosity, but this increase does not reflect the full range of PC viscosities used.

Table III Abusive DSC Conditions

First scan	Heat 40°–290°C at 20°C/min Hold at 290°C for 15 min Cool 290°–40°C at 80°C/min
Second scan	Heat 40°–290°C at 20°C/min

Table V shows the  $T_g$  of the PC phase of several PC/PBT blends. These data indicate that the use of lower viscosity PBT results in a lower  $T_g$  of the PC phase that is due to the increased solubility of the PBT phase in the PC. The PBT  $T_g$  is also present but is generally only a shoulder on the PC peak. Increasing the molecular weight of the PC phase generally results in a decrease in miscibility between the two phases as the  $T_g$  of the PC phase shows. A representative DMA is shown in Figure 1.

In the study of PC/PBT blends, it is important to have analytical tools that can readily distinguish stable from unstable blends. One such tool that the authors have used is abusive DSC.  $T_m$  and  $\Delta H_m$  are recorded during a normal scan. After a hold period at high temperature, the drop in  $T_m$  and  $\Delta H_m$  is recorded. The lack of stabilization is indicated by a drop in  $T_m$  and  $\Delta H_m$  on the second scan (see Table VI). This drop may be caused by the titanium-catalyzed ester/carbonate exchange leading to copolymer

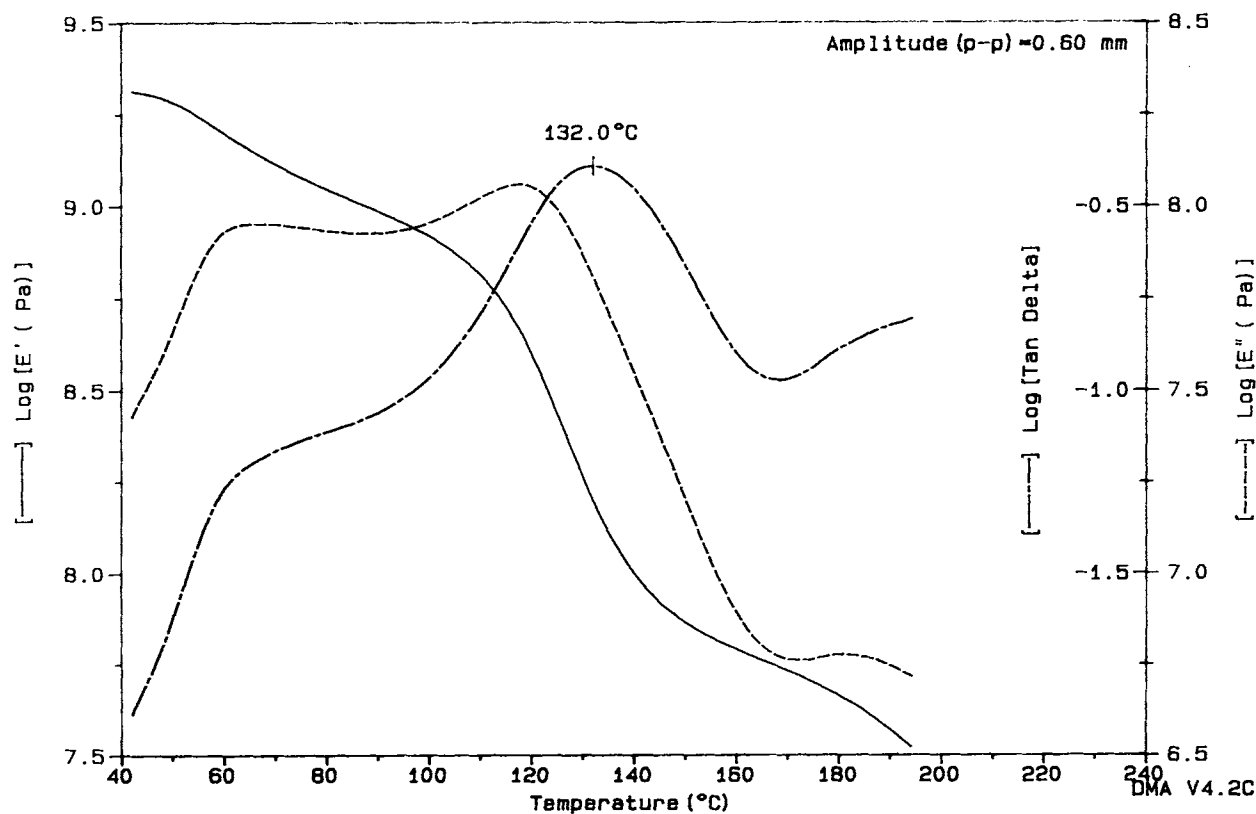


Figure 1 DMA of a 1 : 1 Blend of PC4/PBT2.

**Table IV Viscosities of 50 : 50 PC/PBT Blends**

	PBT1 (Poise)	PBT2 (Poise)	PBT3 (Poise)
PC1	801	1725	5,040
PC2	2353	3824	10,985
PC3	2251	4073	11,766
PC4	3022	5213	13,022

**Table V  $T_g$  of PC in 50 : 50 PC/PBT Blends**

	PBT1 (°C)	PBT2 (°C)	PBT3 (°C)
PC1	90.6	116.3	127.1
PC2	122.7	127.8	136.0
PC3	124.3	129.1	134.3
PC4	127.1	132.0	138.6

formation. As this process continues, the PBT block length gets shorter, resulting in the drop in  $T_m$  and  $\Delta H_m$  that is observed. Eventually, all crystallinity is lost as a random copolymer is formed. All the samples used in this study showed no significant changes ( $> 20^\circ\text{C}$ ,  $> 14 \text{ J/g}$ ) on abusive DSC analysis, indicating little, if any, transesterification.

An additional measure of the morphological stability of a blend is its Vicat temperature. The Vicat temperature is proportional to the degree of crystallinity in PC/PBT blends. The comparison of Vicat temperatures during "normal" and "abusive" injection molding is another measure of the melt stability of a PC/PBT blend. A large drop in the Vicat temperature during abusive molding often indicates the formation of PC-PBT copolymer. Table VII shows that blends made with higher molecular weight pairs show higher Vicat values. Surprisingly, the blends made with PBT1 were transparent and had low abusive Vicat values despite the addition of 0.10 phr of a stabilizer to stop transesterification.

When titanium-catalyzed transesterification takes place, abusive processing results in molded parts that are both transparent (due to loss of crystallinity) and orange-

**Table VII Vicat of Abusively Molded 50 : 50 PC/PBT Samples**

	PBT1 Vicat/ Abusive Vicat (°C)	PBT2 Vicat/ Abusive Vicat (°C)	PBT3 Vicat/ Abusive Vicat (°C)
PC1	73.9/65.0	110.5/87.8	131.7/129.4
PC2	114.8/71.5	127.9/119.1	136.1/128.6
PC3	121.6/71.4	130.9/121.6	137.3/130.8
PC4	121.7/74.3	131.8/123.5	138.9/132.8C

yellow (due to the formation of titanium phenolate complexes) and exhibit reduced  $T_m$  and  $\Delta H_m$  in the abusive DSC. In addition, gas generation is observed from the molten polymer due to the decomposition of alkyl carbonates formed by transesterification. The PBT1/PC blends, in contrast, while transparent after abusive molding, were water white and did not show reduced  $T_m$  and  $\Delta H_m$  in the abusive DSC. Also, during molding, gas evolution was not observed. It appears that in the case of low molecular weight pairs, miscibility, unaided by transesterification, is sufficient to reduce the rate of crystallization. Abusive processing, which can further reduce the molecular weight through degradation, enhances miscibility to the point where transparent parts are produced.

To further test this hypothesis, a low molecular weight PBT was extruded separately with the phosphorous acid stabilizer. This would allow complexation of the titanium catalyst before any reaction could take place with the PC. This material was then blended with PC and extruded. A blend of the same composition was prepared in the normal way by combining all ingredients together (see Table VIII). The preextruded material again showed transparency after abusive molding while remaining water white and no gas evolution was observed. Thus, titanium catalysis is not a necessary condition for the formation of transparent parts. Very low molecular weight, nonreactive pairs of PC and PBT will form blends with sufficient miscibility to reduce the normal crystallinity seen in higher molecular weight pairs where better phase separation is observed.

**Table VI Comparison of Stabilized and Unstabilized PC2/PBT3 Blends**

	Abusive DSC <sup>a</sup> First Scan		Abusive DSC <sup>a</sup> Second Scan	
	$\Delta H_m$	$T_m$	$\Delta H_m$	$T_m$
PC2 + PBT3 (50:50)	23.6	222.5	7.8	191.2
PC2 + PBT3 + 45% phosphorous acid sol <sup>n</sup> (49.95 : 49.95 : 0.1)	18.9	222.9	22.0	222.8

<sup>a</sup> See Table III for DSC program.

Table VIII Effect of Preextrusion upon Stability

	Preextruded Formulation	Single Extrusion Formulation
PBT1	—	50
PBT1 + 0.2 phr H <sub>3</sub> PO <sub>3</sub> 45% sol <sup>a</sup>	50.1	—
PC2	50	50
H <sub>3</sub> PO <sub>3</sub> 45% sol <sup>a</sup>	—	0.1
Viscosity	2028 poise	2157 poise
PC Tg	127.1°C	125.2°C
Vicat	116.9°C	123.2°C
Abusive vicat	74.6°C	77.8°C
Abusive DSC T <sub>m</sub> (°C)/ΔH <sub>m</sub> (J/g)	218.8/31.5	218.7/30.5

### CONCLUSION

The melt stability of PC/PBT blends can be measured by either DSC or Vicat methods. In the absence of any stabilizer, the blend components may react to give copolymers. This reaction results in materials with reduced Vicat temperatures and lower crystallinity.

It has been demonstrated in stabilized systems that the miscibility of a PC/PBT blend increases with decreasing weight of the component resins. If sufficiently low molecular weight pairs are used, miscible, transparent blends are obtained even in well-stabilized systems. Low molecular weight pairs can be combined intentionally or may arise from the degradation of the homopolymer components under abusive processing conditions.

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