Properties of Glass-Filled Thermoplastic Polyesters

B. J. CHISHOLM, P. M. FONG,* J. G. ZIMMER, R. HENDRIX

GE Plastics, One Lexan Lane, Mt. Vernon, Indiana 47620

Received 20 December 1998; accepted 4 January 1999

ABSTRACT: The thermal, mechanical, and rheological properties of glass-filled poly(propylene terephthalate) (GF PPT) were compared to glass-filled poly(butylene terephthalate) (GF PBT). The impetus for this study was the recent commercial interest in PPT as a new glass-reinforced thermoplastic for injection-molding applications. This article represents the first systematic comparison of the properties of GF PPT and GF PBT in which differences in properties can be attributed solely to differences in the polyester matrices, that is, glass-fiber size and composition, polymer melt viscosity, nucleant content and composition, polymerization catalyst composition and content, and processing conditions were kept constant. Under these controlled conditions, GF PPT showed marginally higher tensile and flexural properties and significantly lower impact strength compared to GF PBT. The crystallization behavior observed by cooling from the melt at a constant rate showed that GF PBT crystallized significantly faster than did GF PPT. Nucleation of GF PPT with either talc or sodium stearate increased the rate of crystallization, but not to the level of GF PBT. The slower crystallization rate of GF PPT was found to strongly affect thermomechanical properties of injection-molded specimens. For example, increasing the polymer molecular weight and decreasing the mold temperature significantly increased the modulus drop associated with the glass transition. In contrast, the modulus-temperature response of GF PBT was just marginally influenced by the polymer molecular weight and was essentially independent of the mold temperature. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 889-899, 1999

Key words: polyester; poly(butylene terephthalate); poly(propylene terephthalate); injection molding

INTRODUCTION

Currently, three semicrystalline poly(alkylene terephthalate)s are being utilized commercially to produce injection-moldable, engineering thermoplastics: poly(ethylene terephthalate) [PET; Fig. 1(a)], poly(butylene terephthalate) [PBT; Fig. 1(b)], and poly(cyclohexylenedimethanol terephthalate) [PCT; Fig. 1(c)]. Of these polyesters, PBT possesses the largest market share.¹ The greater

utility of PBT for injection-molding applications can be attributed to its relatively high rate of crystallization which allows for high production rates of molded articles.² In addition, PBT can be successfully molded in water-heated molds, whereas PET, due to its slower crystallization rate and higher T_g , generally requires mold temperatures in excess of 100°C, necessitating the use of oil-heated molds.

The relatively high melting temperature (T_m) of PCT allows for the production of materials capable of serving applications requiring a secondary processing step involving infrared oven soldering.³ While the high T_m is beneficial for withstanding deformation during soldering, it is undesirable from the standpoint of processing ro-

Correspondence to: B. J. Chisholm, General Electric Corporate Research and Development, One Research Circle, Niskayuna, NY 12309.

^{*} *Present address:* Yale University, New Haven, CT. Journal of Applied Polymer Science, Vol. 74, 889–899 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/040889-11

(a) PET: Tg=80°C, Tm=250-265°C



(b) PBT: Tg=50°C, Tm=223°C



(c) PCT: Tg=100°C, Tm=290°C



Figure 1 Chemical structures of commercially available poly(alkylene terephthalates).

bustness since significant levels of decomposition can occur at the temperatures required for injection molding $(\sim 300^{\circ}\text{C}).^{4,5}$

Recently, Shell Chemical Co. announced their intent to commercialize poly(propylene terephthalate) (PPT). This decision was the result of a new process innovation for the production 1,3propanediol at a much lower cost.⁶ While several reports have been published describing the fiber properties of PPT,⁷⁻¹⁰ little has been reported on the properties of injection-molded materials. In fact, the only report describing the properties of injection-molded materials based on PPT was the recent report by Dangayach and coworkers.¹¹ These authors compared the mechanical properties of glass-reinforced PPT to data cited in the literature for glass-reinforced PET, PBT, Nylon 6,6, and polycarbonate. Since factors such as glass-fiber thickness, length, and chemical composition, polymer molecular weight, processing conditions, polymerization catalyst composition and content, and the presence of additives such as nucleants have a significant effect on mechanical properties, the differences in mechanical properties reported for the various materials cannot be attributed solely to the inherent difference in the polymer matrices and their interaction with the glass fiber. The results reported in this study were obtained using controlled conditions allowing for an investigation of the inherent difference in PPT and PBT as a matrix for glass-reinforced,

thermoplastic materials. In addition, the rheology and crystallization behavior, which are extremely important for the processability of an injectionmoldable plastic, were investigated.

EXPERIMENTAL

Materials

PBT and PPT polymers were produced by the melt polymerization of dimethyl terephthalate (DMT) and the appropriate diol using tetraisopropyl titanate (TPT) as a catalyst. DMT was obtained from Kosa Corp., while 1,4-butandiol and 1,3-propanediol were obtained from BASF and DeGussa Corp., respectively. Both diols and DMT had a purity of 99+%.

A representative polymerization procedure is as follows: 11.7 kg of DMT, 7.35 kg of 1,3-propanediol, and 16.4 ml of TPT were charged to a 10CV Helicone reactor which was preheated to 130°C. The monomer mixture was then heated to 225°C at a rate of 1.5°C/min under atmospheric pressure and most of the methanol by-product removed by distillation. The mixture was then subjected to a gradual reduction in pressure to 175 mmHg at a rate of 50 mmHg/min while the temperature was simultaneously increased to 250°C at a rate of 1.5°C/min. Upon reaching a pressure of 175 mmHg, the pressure was further reduced to 1.5 mmHg at a rate of 25 mmHg/min and held at that pressure for the remainder of the polymerization. The total time under the vacuum was 266 min. This polymerization produced a PPT sample with a melt viscosity at 250°C and shear rate of 100 s^{-1} of 400 Pa s.

The glass fiber used was 183F 14C from Owens-Corning Fiber Glass which has a diameter of 14.0 μ m and length of 4.0 mm. The talc used was Ultratalc 609 from Barretts Minerals and sodium stearate was obtained from Aldrich Chemical. Irganox 1076, a hindered phenol antioxidant, and PEPQ, a phosphite antioxidant, were obtained from Ciba Specialty Chemicals and Clariant, respectively. The compositions of the glass-reinforced materials investigated are shown in Table I.

Characterization

Molecular weight was determined using gel permeation chromatography and poly(methyl methacrylate) standards. The instrument was an

Sample ID	Polyester	MFI (g/10 min)	M_n (g/mol)	M_w (g/mol)	Wt % GF	Nucleant (0.5 wt %)
PH-30%	PPT	40.34	25,100	50,700	30	None
PH-15%	PPT	51.84	26,200	52,400	15	None
PL-30%	PPT	72.03	22,100	43,700	30	None
PL-30%-T	PPT	66.29	21,100	42,600	30	Talc
PL-30%-S	PPT	114.69	18,900	38,000	30	Sodium stearate
BH-30%	\mathbf{PBT}	37.30	21,600	46,100	30	None
BH-15%	\mathbf{PBT}	51.22	22,300	46,100	15	None
BL-30%	\mathbf{PBT}	68.11	17,800	38,800	30	None
BL-30%-T	\mathbf{PBT}	68.33	18,400	38,200	30	Talc
BL-30%-S	PBT	87.28	17,900	36,800	30	Sodium stearate

 Table I
 Composition of the Materials Investigated

All materials contained 0.15 pph. Irganox 1076 and 0.15 pph PEPQ as antioxidants.

HP Model 1050 GPC equipped with a refractive index detector. The column was a Polymer Labs HFIP Plgel, the eluant was 1,1,1,3,3,3-hexafluoro-2-propanol, and the flow rate was 0.5 mL/min.

Crystallization and melting characteristics were investigated using a Perkin–Elmer DSC7 by holding samples in the melt for 3.0 min at 265°C, cooling to 0°C at 100°C/min, holding at 0°C for 5.0 min, and, finally, reheating to 265°C at a specified heating rate. Sample sizes were approximately 3-4 mg.

Processing

Compounding of the PPT and PBT with glass fiber and additives was accomplished using a 2.5in. HPM single-screw extruder with a vacuumvented, double-wave screw, 30:1 L/D, at a barrel and die head temperature of 250°C and 100 rpm screw speed. The extrudate was cooled through a water bath prior to pelletizing.

Injection molding of the ASTM test specimens was done using an 80-ton Van Dorn molding machine with a barrel set temperature of 250° C, mold temperature of 60° C, unless specified otherwise, and cooling time of 20 s. The pellets were dried for 3–4 h at 120°C in a forced-air-circulating oven prior to injection molding.

Mechanical Property Determination

The tensile strength (TS), flexural strength (FS), and flexural modulus (FM), unnotched Izod impact strength (UNI), and heat-distortion temperature (HDT) were determined according to ASTM methods D638, D790, D256, and D648, respectively. Dynamic mechanical analysis (DMA) was used to measure the storage modulus (E') of materials as a function of temperature. The analyzer was a TA Instruments Model 2980 dynamic mechanical analyzer equipped a dual cantilever fixture operating at a heating rate of 3°C/min, frequency of 1.0 Hz, and vibration amplitude of 20 mm. All specimens were injection-molded and were approximately 6.5 cm long, 1.27 cm wide, and 3.175 mm thick.

Rheology

The melt-flow index was determined at 250°C for PBT-based materials and at 255°C for PPT-based materials using a Tinius Olsen rheometer and the procedure described in ASTM D1238. Apparent viscosity was measured as a function of shear rate at 250°C for PBT-based materials and 255°C for PPT-based materials using a Goettfert Model 2002 capillary rheometer.

RESULTS AND DISCUSSION

A description of the materials investigated is shown in Table I. The scheme used for sample identification is as follows: (1) The first letter of the sample designation indicates the polymer composition, with "B" and "P" signifying PBT and PPT, respectively; (2) the second letter represents the relative magnitude of the melt viscosity/molecular weight, with "H" and "L" indicating relatively high melt viscosity/molecular weight and relatively low melt viscosity/molecular weight, respectively; (3) the numerical value expressed as a percentage, represents the weight percent of glass fiber in the material; and (4) the last letter indicates the composition of the nucleant, if present in the material, with "T" indicating the presence of 0.5 wt % talc and "S" indicating the presence of 0.5 wt % sodium stearate.

Rheology

This study was designed to compare the properties of GF PBT to GF PPT at an equivalent melt viscosity. The decision to compare the materials at the equivalent melt viscosity, as opposed to the equivalent polymer molecular weight, was based on the fact that the melt viscosity of an injectionmoldable material generally needs to be tightly controlled for a given application. The recommended molding temperature for commercial GF PBT materials such as GE Plastics' Valox[®] products or Ticona's Celanex® products is about 250°C which is 27°C above the nominal melting temperature that we measured for PBT using DSC.¹² A barrel set temperature of 250°C generally ensures a fully molten material, even for very short residence times, and does not cause substantial thermal degradation of the polymer.¹³ Taking these facts into account, it was decided to characterize the rheology of GF PBT using a temperature of 250°C.

Since the nominal melting temperature measured for PPT was 228°C, the temperature used to characterize the rheology of GF PPT was 255°C which was 27°C above the polymer's melting temperature, allowing for a comparison of the rheology of the materials at a constant ΔT , where ΔT



Figure 2 Apparent viscosity versus shear rate for 30 and 15% GF materials. GF PBT and GF PPT samples were measured at 250 and 255°C, respectively.



Figure 3 Apparent viscosity versus shear rate for 30% GF materials, illustrating the effect of molecular weight on shear sensitivity. GF PBT and GF PPT samples were measured at 250 and 255°C, respectively.

 $T_p = T_p - T_m$ and T_p is the processing set temperature and T_m is the polymer melting temperature.

Typically, measurements such as melt-flow index or melt-volume rate, which measure weight and volume, respectively, of molten material expelled from a capillary per unit time under a constant applied weight, are used to describe the flow properties of commercial injection-moldable materials.¹⁴ Thus, the melt viscosities of the polymer samples were precisely controlled, allowing for the production of GF PBT and GF PPT materials with a similar MFI. The MFIs of the materials produced were representative of commercially available GF PBT materials and are listed in Table I. In addition to measuring the MFI, the apparent viscosities of the materials were measured at various shear rates to determine shear sensitivity.

Figure 2 shows the viscosity-shear rate profiles for 30% GF and 15% GF materials. Interestingly, GF PPT was slightly more shear thinning than was GF PBT. Decreasing the molecular weight of the polyesters reduced the difference in shear sensitivity between GF PPT and GF PBT over the range of shear rates investigated, as illustrated in Figure 3. Rheological characterization of the neat polyesters (no glass fiber) also showed that neat PPT was somewhat more shear thinning than was neat PBT, suggesting that the difference in shear sensitivity shown in Figures 2 and 3 was inherent to the polyester matrices. In general, the shear sensitivity of a linear polymer is primarily dependent on the average number of entanglements per chain. Since it is the entanglements that resist deformation, an increase in entanglement density results in an increase in shear thinning character. Considering the similarity in molecular weight and molecular weight distribution for the GF PPT and GF PBT materials described in Figure 2, it was not obvious why GF PPT would possess a higher entanglement density and, therefore, greater shear sensitivity. Further work is required to understand the origin of the difference in the shear-thinning character observed for GF PPT and GF PBT.

Crystallization and Melting Behavior

As previously stated, crystallization speed is a very important property for semicrystalline, thermoplastic materials designed for injection-molding applications. For PBT and PET, nucleating agents such as talc or sodium stearate have been successfully used to increase the crystallization rate.^{15,16} Nonreactive, nonmelting nucleants such as talc have been termed heterogeneous nucleants, while reactive, soluble nucleants such as sodium stearate have been termed chemical nucleants. Nucleation by heterogeneous nucleants occurs by molecular interactions between the polymer and the surface of the nucleant, resulting in a reduction in the free energy needed to form a stable nucleus.¹⁷ Chemical nucleation of condensation polymers such as PET was described by Legras et al.^{18,19} as occurring by the reaction of alkali metal salts of organic acids with the polymer to produce chains with ionic end-groups. Due to strong electrostatic interactions, these ionic end groups form clusters that reduce the local mobility of the chain, thereby facilitating the formation of stable nuclei.



Figure 4 Crystallization exotherms obtained by cooling the materials from the melt at 100°C/min using DSC.

Table II	Nonisothermal Crystallization Data
Illustratii	ng the Effect of Talc and
Sodium S	tearate as a Nucleant

	T_c Onset	T_c Peak	
Sample	(°C)	(°C)	$\Delta H_c ~(\mathrm{J/g})$
BL-30%	180	164	-38.4
PL-30%	164	150	-35.3
BL-30%-T	189	174	-40.3
PL-30%-T	165	154	-36.5
BL-30%-S	182	170	-40.5
PL-30%-S	170	157	-36.8

In the process of injection molding, crystallization occurs under nonisothermal conditions in which the cooling rate varies with cooling time. At an early stage of the cooling process, cooling rates in excess of 1000°C/min may be experienced.²⁰ The crystallization characteristics of various GF PPT and GF PBT samples were compared by cooling the materials from the melt at a cooling rate of 100°C/min using DSC; 100°C/min was the fastest cooling rate that allowed for temperature control between the reference oven and the sample oven over the range of temperatures in which crystallization was observed to occur.

Figure 4 shows the cooling curves for both GF PPT and GF PBT and derivatives containing either talc or sodium stearate as a nucleating agent. Table II lists the temperature of the onset and peak maximum of the exotherms. The data showed that the crystallization exotherm obtained for GF PBT began and reached a maximum at temperatures about 15°C higher than that of GF PPT, illustrating faster crystallization for GF PBT. The presence of talc and sodium stearate resulted in a further shift in the crystallization exotherm to higher temperature for both GF PBT and GF PPT, demonstrating their nucleating ability. However, nucleated GF PPT still crystallized slower than did unnucleated GF PBT. For PBT, talc appeared to be a more efficient nucleant than was sodium stearate when compared at an equivalent nucleant weight of 0.5 pph. In contrast, the presence of sodium stearate produced the higher-temperature crystallization exotherm for GF PPT.

Figure 5 displays the thermograms obtained when the samples crystallized using a cooling rate of 100°C/min were reheated at 20°C/min. All the PPT-based samples as well as BL-30% showed a small exotherm just before the melting



Figure 5 Melting endotherms of GF PPT and GF PBT samples crystallized from the melt using a cooling rate of 100°C/min. The endotherms were obtained using a heating rate of 20°C/min.

endotherm, while the nucleated GF PBT samples, BL-30%-T and BL-30%-S, showed what appeared to be two melting endotherms. Double melting peaks such as those observed for BL-30%-T and BL-30%-S have been previously reported for PBT. Initially, it was thought that the two melting endotherms were the consequence of the existence of two different crystal structures.^{21,22} However, later, it was shown that double melting was due to a partial melting and recrystallization process taking place in the calorimeter in which crystallites with a low degree of perfection melt and recrystallize to form thicker, more perfect crystallites.^{23,24} Thus, the expected melting endotherm described by Kim et al.²⁵ as consisting of a distribution having a single maximum skewed toward higher temperature ($\sim 223^{\circ}$ C) and a tail extending to low temperature is observed as a bimodal distribution.

To understand the difference in melting behavior observed for the nucleated and unnucleated materials described in Figure 5, the melting behavior of BL-30%, PL-30%, BL-30%-S, and PL-30%-S crystallized from the melt at 100°C/min was observed as a function of the heating rate. As shown in Figure 6, samples BL-30% and BL-30%-S showed double melting with the area and peak temperature of the low-temperature endotherm increasing with an increasing heating rate until, at a heating rate of 80°C/min, the lowtemperature peak became a shoulder on the hightemperature endotherm. For both materials, the overall heat of fusion (integrated over both peaks) remained fairly constant with the heating rate and was similar to the heat of crystallization obtained upon cooling from the melt. These results were consistent with the results of Hobbs and Pratt²³ and indicated that a fraction of the crystallites formed on cooling from the melt at 100°C/ min were metastable such that they underwent partial melting and recrystallization during heating in the calorimeter. The increase in the area of the low-temperature endotherm at the apparent expense of the high-temperature endotherm with increasing heating rate was a consequence of there being less time available for the metastable crystallites to undergo the partial melting–recrystallize process.

Comparing the melting behavior of BL-30% to BL-30%-S at a given heating rate, it could be seen that the area and peak temperature of the lowtemperature endotherm for BL-30%-S was higher than that for BL-30%, indicating that the presence of the nucleant, sodium stearate, allowed for the production of crystallites with a higher degree of stability. This result seemed logical since the presence of the nucleating agent increased the onset temperature for crystallization upon cooling from the melt, allowing thicker, more perfect crystallites to be formed.

The presence of a melting-recrystallization process was also observed for GF PPT (Fig. 7); however, the stability of the metastable crystals was much lower compared to GF PBT as indicated by the absence of a distinct low-temperature endotherm and the lower temperatures of the recrystallization process. Obviously, the slower crystallization rate of PPT resulted in the production of more unstable crystallites when cooled from the melt at 100°C/min.



Figure 6 Melting endotherms obtained at various heating rates for GF PBT samples crystallized from the melt using a cooling rate of 100°C/min.

Mechanical and Thermomechanical Properties

Tables III and IV show the mechanical properties of materials produced from relatively high viscosity/high molecular weight polymers and relatively low viscosity/low molecular weight polymers, respectively. In addition, Table IV describes the properties of materials containing talc or sodium stearate as a nucleating agent.

Since the polymer matrix viscosity and processing conditions were kept constant, the glassfiber size, size distribution, and degree of dispersion should be similar for GF PBT and GF PPT samples of comparable composition. Thus, differences in the mechanical properties should be due to the inherent differences in the properties of the polymer matrices and the degree of interaction between the polymer and fiber.

The UNI impact strength of the GF PPT samples was found to be significantly lower than that of the GF PBT samples. The similarity in chemical structure between PBT and PPT should result in a similar level of fiber-matrix adhesion for GF PBT and GF PPT. Therefore, the lower UNI obtained for GF PPT was thought to be the result of an inherently lower ductility of the PPT matrix as compared to the PBT matrix. Measurement of the impact strength of neat PPT and neat PBT confirmed the lower ductility of PPT when compared at similar melt viscosity/molecular weight.

While the presence of talc as a nucleating agent was found to have essentially no effect on impact strength, the chemical nucleant, sodium stearate, significantly reduced the impact strength for both GF PPT and GF PBT. This reduction in impact strength can be attributed to a reduction in molecular weight resulting from reaction of the polymer with sodium stearate as described by Legras et al.^{18,19} As shown in Table I, the addition of sodium stearate reduced the M_n of PPT and PBT by 14.5 and 17.0%, respectively.

The HDT of GF PPT was also lower than that of GF PBT and was significantly affected by PPT molecular weight. The lower HDT observed for GF PPT was thought to result from a lower level of crystallinity originating from the slower crystallization rate of PPT as compared to PBT. Since HDT represents the temperature at which a specimen softens sufficiently to produce a 0.25-mm deflection under an external load, a lower level of crystallinity would result in a higher rate of specimen deflection due to greater creep, which would ultimately result in a lower HDT.²⁶ To compare



Figure 7 Melting endotherms obtained at various heating rates for GF PPT samples crystallized from the melt using a cooling rate of 100°C/min.

the relative level of crystallinity in molded specimens of GF PPT and GF PBT, specimens were analyzed using DMA (Fig. 8). According to Khanna,²⁷ the storage modulus drop between the beginning of the T_g and the beginning of the T_m [$\Delta \log E'(T_g - T_m)$] can be utilized to estimate the level of crystallinity of a polymer using the expression

% Crystallinity

$$= \{1 - [\Delta \log E'(T_g - T_m)]/2.46\} \times 100 \quad (1)$$

where the value of 2.46 represents $\Delta \log E'(T_g - T_m)$ of a totally amorphous material. This value

of 2.46 was experimentally determined by measuring the modulus drop associated with the glass-to-rubber transition of a wide range of wholly amorphous polymers. Considering this expression, the larger modulus drop observed for PH-30% ($\Delta \log E'_{\rm PH-30\%}$) as compared to BH-30% ($\Delta \log E'_{\rm BH-30\%}$) indicated a lower level of crystallinity for the former. The "dip" in the modulus curve for PH-30% just after the T_g was indicative of crystallization during the DMA experiment and results in an overestimate of the level of crystallinity in the molded sample based on the value of $\Delta \log E'_{\rm PH-30\%}$.²⁷ Unfortunately, eq. (1) is not in a form that can be directly used to calculate the level of crystallinity of the GF PPT and

Table IIIMechanical Properties of 30 and 15 Wt % GF Materials Based on Relatively HighMelt Viscosity/Molecular Weight Polymers

Property	PH-30%	BH-30%	PH-15%	BH-15%
UNI (J/m)	$454~\pm~87$	$738~\pm~40$	$278~\pm~25$	$395~\pm~34$
HDT (°C)	$167~\pm~15$	$198~\pm~2$	$152~\pm~9$	$165~\pm~5$
TS (MPa)	$125~\pm~3$	$117~\pm~1$	$98~\pm~1$	$94~\pm~0.5$
FS (MPa)	$179~\pm~3$	$177~\pm~0.5$	$146~\pm~2$	$135~\pm~0.4$
FM (GPa)	$6.66 ~\pm~ 0.05$	$6.62 ~\pm~ 0.05$	$4.82 ~\pm~ 0.09$	$4.29 ~\pm~ 0.03$

Property	PL-30%	BL-30%	PL-30%-T	BL-30%-T	PL-30%-S	BL-30%-S
UNI (J/m)	$523~\pm~54$	683 ± 30	$523~\pm~52$	$619~\pm~32$	$336~\pm~22$	$550~\pm~31$
HDT (°C)	$186~\pm~5$	195 ± 2	196 ± 2	$203~\pm~2$	197 ± 2	202 ± 2
TS (MPa)	$132~\pm~1$	119 ± 1	$136~\pm~2$	$121~\pm~2$	119 ± 2	$120~\pm~1$
FS (MPa)	$189~\pm~4$	$177~\pm~3$	187 ± 3	$179~\pm~2$	$163~\pm~2$	$177~\pm~2$
FM (GPa)	$7.58~\pm~0.05$	$6.90~\pm~0.05$	$7.81 ~\pm~ 0.05$	$7.23 ~\pm~ 0.04$	$7.85 ~\pm~ 0.05$	$6.96~\pm~0.03$

Table IVMechanical Properties of 30 Wt % GF Materials Based on Relatively LowMelt Viscosity/Molecular Weight Polymers

GF PBT materials investigated since they contain glass fiber. Nonetheless, a comparison of $\Delta \log E'_{\rm PH-30\%}$ to $\Delta \log E'_{\rm BH-30\%}$ does provide a means for comparing the relative difference in the crystal-linity of the materials and supports the hypothesis that the lower HDT observed for PH-30% was due to a lower level of crystallinity in the molded specimen.

A comparison of the HDT of BH-30% and PH-30% to that of BL-30% and PL-30%, respectively, illustrates the effect of molecular weight on HDT. This comparison shows that a reduction in M_n from 25,100 to 22,100 resulted in an increase in HDT of almost 20°C for GF PPT while a similar reduction in M_n for GF PBT resulted in about a 5°C increase in HDT. The increase in HDT obtained by decreasing M_n was consistent with the modulus-temperature behavior displayed in Figures 9 and 10. A higher HDT for the lower molecular weight materials was the result of their faster crystallization rate, allowing for greater extents of crystallinity to be obtained during the molding process. Similarly, the presence of nucleating agents also allowed for an increase in HDT for both GF PPT and GF PBT by increasing the crystallization rate.

Since thermomechanical properties such as HDT are influenced by the level of crystallinity obtained during the molding process, it was of interest to study the effect of molding conditions on the modulus-temperature response of the materials. Figures 11 and 12 show the modulus-temperature curves of PL-30% and BL-30%, respectively, injection-molded using a range of mold temperatures. For BL-30%, the modulus-temperature profile was essentially independent of the mold temperature, while the modulus-temperature profile of PL-30% varied with the mold temperature. The PL-30% molded using a mold temperature of 40°C showed a much larger drop in the modulus upon heating through the T_g as compared to specimens molded using a 65 or 93°C mold temperature, indicating a lower level of crystallinity for the former condition. These results suggest that mechanical properties, especially the thermomechanical properties such as HDT,



Figure 8 Storage modulus-temperature profile for 30% GF materials produced from relatively high viscosity/high molecular weight polyesters.



Figure 9 Influence of molecular weight on the storage modulus-temperature profile of injection-molded GF PPT.

would be less dependent on the molding conditions for BL-30% as compared to PL-30%. In addition, the apparent insensitivity of the level of crystallinity to mold temperature exhibited by GF PBT suggests that shrinkage and, therefore, the molded part dimensions should be quite uniform even if fluctuations in mold temperature were encountered.

The tensile strength, flexural strength, and flexural modulus of GF PPT was found to be slightly higher than that of analogous GF PBT materials. Figure 13 shows a representative stress-strain curve for GF PBT and GF PPT. All materials showed very low elongation to break and the absence of a yield point. Since the same glass fiber was used for all materials, and the glass-fiber size, size distribution, and level of fiber orientation were believed to be approximately the same, the marginal difference in mechanical properties observed was probably due to the in-



Figure 10 Influence of molecular weight on the storage modulus-temperature profile of injection-molded GF PBT.



Figure 11 Influence of mold temperature on the storage modulus-temperature behavior of PL-30%.

herent differences in the properties of the polyesters. Higher tensile strength for injection-molded samples of neat PPT (58.9 MPa) as compared to neat PBT (55.9 MPa) was previously reported in a patent by Yoshitsugu and coworkers.²⁸ In addition, Ward and coworkers¹⁰ reported markedly different stress–strain behavior of oriented fibers of PPT and PBT, with the yield stress of PPT being higher than that of PBT. Since PPT possesses a somewhat stiffer backbone than that of PBT, as illustrated by its 5°C higher T_g , it was not surprising that greater stress was needed to deform the material in the low-strain, elastic region.

CONCLUSIONS

GF PPT was found to possess higher strength and modulus, but lower impact strength compared to GF PBT of similar melt viscosity. An investigation of crystallization characteristics clearly



Figure 12 Influence of mold temperature on the storage modulus-temperature behavior of BL-30%.



Figure 13 Representative stress–strain curve for GF PBT and GF PPT.

showed that GF PPT materials crystallized slower than did similar GF PBT materials. The addition of talc or sodium stearate as a nucleating agent increased the rate of crystallization of GF PPT, but not to the level of GF PBT. The slower crystallization rate of GF PPT resulted in an increase in the sensitivity of thermomechanical properties to molding conditions and polymer melt viscosity/molecular weight. For example, increasing polymer molecular weight significantly reduced the HDT. In addition. injection-molded specimens of GF PPT had a tendency to undergo cold crystallization when heated above the T_g . In contrast, GF PBT showed a modulus-temperature response that was just marginally influenced by the polymer molecular weight and essentially independent of the mold temperature. These results suggest that GF PBT would provide shorter cycle times during injection molding and greater processing tolerance.

The authors would like to thank Alan Tenison, Steve Dickens, and Susan Eaton of GE Plastics, Mt. Vernon, Indiana, for the preparation of PBT and PPT samples, and William D. Richards and Hongyi Zhou of GE Corporate Research and Development for revising the manuscript.

REFERENCES

- 1. Research report R-233/96, Fleck Research, 1996.
- 2. Morton-Jones, D. H. Polymer Processing; Chapman and Hall: London, 1989; Chapter 8.

- 3. Ishida, T. Jpn. Patent 10 065 318 A2, 1996.
- Gregory, D. R.; Watson, M. T. Polym Eng Sci 1972, 12, 454.
- Wampler, F. C.; Gregory, D. R. J Appl Polym Sci 1972, 16, 3253.
- Chuah, H. H.; Brown, H. S.; Dalton, P. A. Int Fiber J 1995, Oct.
- Brown, H. S.; Chuah, H. H. Chem Fibers Int 1997, 47, 72.
- Traub, H. L.; Hirt, P.; Herlinger, H. Chem Fibers Int 1995, 45, 110.
- 9. Traub, H. L.; Hirt, P.; Herlinger, H. Angew Makromol Chem 1995, 230, 179.
- Ward, I. M.; Wilding, M. A.; Brody, H. J Polym Sci Polym Phys. Ed 1976, 14, 263.
- Dangayach, K.; Chuah, H.; Gergen, W.; Dalton, P.; Smith, F. Annu Tech Conf-Soc Plast Eng 1997, 55, 2097.
- 12. GE Plastics Processing Guide, 1998.
- Passalacqua, V.; Pilati, F.; Zamboni, V.; Fortunato, B.; Manaresi, P. Polymer 1976, 17, 1044.
- 14. DeLaney, D. E.; Reilly, J. F. Plast Eng 1998, June, 45.
- Groeninckx, G.; Berghmans, H.; Overbergh, N.; Smets, G. J Polym Sci Polym Phys Ed 1974, 12, 303.
- Biebuyck, J. J.; Mercier, J. P.; Nield, E.; Legras, R. M. H.; Griffin, B. P. Eur. Patent Appl .21 648, 1981.
- Dovbreva, A.; Alonso, M.; Gonzalez, M.; De Saja, J. A. J Appl Polym Sci 1997, 63, 349.
- Legras, R.; Mercier, J. P.; Nield, E. Nature 1983, 304, 432.
- Legras, R.; Bailly, C.; Daumerie, M.; Dekoninck, J. M.; Mercier, J. P.; Zichy, V.; Nield, E. Polymer 1984, 25, 835.
- Okamoto, M.; Shinoda, Y.; Kinami, N.; Okuyama, T. J Appl Polym Sci 1995, 57, 1055.
- 21. Roberts, R. C. Polymer 1969, 10, 113.
- 22. Roberts, R. C. Polymer 1969, 10, 117.
- 23. Hobbs, S. Y.; Pratt, C. F. Polymer 1975, 16, 462.
- Yeh, J. T.; Runt, J. J Polym Sci Polym Phys Ed 1989, 27, 1543.
- Kim, H. G.; Robertson, R. E. J Polym Sci Polym Phys Ed 1998, 36, 133.
- 26. Takemori, M. T. Polym Eng Sci 1979, 19, 1104.
- 27. Khanna, Y. P. J Appl Polym Sci 1989, 37, 2718.
- Yoshitsugu, N.; Takatoshi, K.; Takeo, K. Jpn. Patent 52 056 154 A, 1977.