Studies on the thermal, dynamic mechanical and rheological behaviour of short-glass-fibre-reinforced composites based on poly(butylene terephthalate)/high density polyethylene blends

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Blends of poly(butylene terephthalate) (PBT)/high density polyethylene (HDPE)/ionomer (IONO) polymers, at a blending ratio of 76/19/5 (by weight), were reinforced with short glass fibres (GFs) at levels of 10–30 wt% in order to enhance the mechanical properties for load-bearing engineering applications. The melting and crystallization behaviour of the composites, studied by differential scanning calorimetery (d.s.c.), indicate the presence of an increase in crystallinity in the presence of the glass fibres. Dynamic mechanical thermal analysis (d.m.t.a.) shows that the introduction of glass fibres reduces damping to a greater extent than would be expected theoretically. Incorporation of glass fibres increases the storage modulus, when compared to the unreinforced system, at all temperatures studied. The presence of short glass fibres increased the melt viscosity and decreased the extrudate swell, with the effect being more pronounced at higher temperatures. Rheological data have been analysed on the basis of fibre length (or aspect ratio) and/or distribution of the fibre lengths by using the rheological model proposed by Maron and Pierce.

(Keywords: polymer blends; composites; glass fibre filler)

INTRODUCTION

Blending and alloying of polymers are effective methods for tailor-making materials which possess specific balanced combinations of physical properties, processing characteristics and cost. Reinforcing these polymer blends/alloys with short glass fibres (GFs) can further enhance the mechanical and thermal properties required for load-bearing engineering applications. In our earlier paper[1] it was shown that short-glass-fibre-reinforced composites of poly(butylene terephthalate (PBT)/high density polyethylene (HDPE) blends, suitable for a variety of engineering applications, could be achieved at a comparatively low cost. Furthermore, these composites showed improved mechanical properties, in particular the notched impact strength.

The modification to the crystal morphology promoted by the presence of the fibres is of great interest and has been the subject of several studies[2–7]. Misra and coworkers[2] found that the magnitude and distribution of residual stress and molecular orientation in polypropylene (PP) are modified in the presence of glass fibres, leading to a change in crystal morphology. In most 'pure' homopolymers it is heterogeneous nucleation that primarily prevails in the crystallization process since the degree of supercooling required for spontaneous nucleation is far greater than is observed in practice[3]. The nucleating ability of the heterogeneities can be evaluated by observing their influence on the overall rate of crystallization and the supermolecular structure of the polymer[4].

A knowledge of the dynamic properties of polymeric materials is indispensible in materials design as they are often used under conditions of dynamic stress and strain fields, such as occur in parts of automobiles and aerospace structures. The effect of glass fibres on the dynamic storage (E') and loss (E'') modulus and the damping characteristics of blends/composites based on PBT/HDPE/ionomer (IONO) is analysed in this paper using d.m.t.a.

The rheological behaviour of filled thermoplastics governs their compounding as well as their processing. Shear viscosity and extrudate swell ratios, for example, are important parameters for controlling the flow of the composite melt. The mechanical properties of such composites are influenced by the rheological properties which control fibre migration and orientation, in addition to various other fibre and matrix characteristics. Several studies describing the effects of fibre concentration, fibre length and melt temperature on the rheological behaviour of various fibre-reinforced thermoplastics have been published[8–11].

In this present paper, the role of glass fibres in modifying the thermal, dynamic mechanical, and rheological properties of PBT/HDPE based composites are reported. The heterogenous nucleation of the various

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blend systems is studied by d.s.c. measurements. Dynamic mechanical properties, such as storage modulus, loss modulus and mechanical damping, are reported as functions of the glass fibre content. Rheological properties, such as melt viscosity and melt elasticity, are estimated on the basis of fibre aspect ratio, and are correlated by using a predictive model[12].

EXPERIMENTAL

Materials

The following commercially available polymers were used in this blends/composites study:

1. Poly(butylene terephthalate) (ARNITE T-006), which was obtained from Cenka Plastics Ltd, India. It had a viscosity-average molecular weight, M_v, of 55 000 which was determined by using a 3/5 (v/v) mixture of phenol and tetrachloroethane at 30°C. K_w and a values were taken from the literature[13].
2. High density polyethylene (Hostalen-G of MFI 10), which was obtained from Polyolefin Industries Ltd (PIL), India.
3. Ionomer (Surlyn-8660), which was obtained from DuPont, USA; this was poly(ethylene-*co*-sodium methacrylate), which is a random terpolymer consisting of ~80 wt% PE and 20 wt% methacrylic acid, partially neutralized by sodium[14].
4. Chopped glass fibre (Grade 408) (average fibre length ~4.5 mm), which was obtained from Owens Corning, USA.

Preparation of composites

All composites were prepared by a melt-mixing technique using a single-screw extruder (Windsor SX 30) with a screw speed of 10–15 rev min^{-1}, at temperatures ranging from 250–260°C. The PBT/HDPE/ionomer ratio was fixed at 76/19/5, by weight. Glass fibre content varied from 10–30 wt%. PBT and HDPE were dried in a vacuum oven for 3 h at 100°C and 80°C, respectively. The granules were dry blended, along with the glass fibre and ionomer (as required), to various compositions before feeding into the extruder. The thick strands leaving the extruder die were water cooled, dried and then chopped into granules for further processing.

Preparation of test specimens

Test specimens were prepared by the use of a Windsor SP-1 screw-type injection moulding machine using carefully dried granules. Moulding was carried out in the temperature range 250–260°C, at a screw speed of 30 rev min^{-1} and an injection pressure of 14.7 MPa. The mould that was used had a rectangular edge gating design. Test specimens for dynamic mechanical analysis were in the shape of rectangular bars machined from injection moulded dumb-bell shaped specimens, according to the specification prescribed for the instrument. For thermal studies (d.s.c.), a mixture of powder collected from different cross-sections of the blend specimens was used.

Measurements and analysis

Thermal characterization was carried out on a DuPont 1090 differential scanning calorimeter using a Mettler FP85 TA cell in a nitrogen atmosphere. The samples were first heated to 250°C and then held at this temperature for 10 min in order to eliminate any previous thermal history; they were subsequently cooled to 50°C at a rate of 10°C min^{-1} to obtain the cooling curves. The samples were next reheated to 250°C (at the same heating rate) to obtain the heating curves.

The dynamic mechanical properties were studied with a Polymer Laboratories Dynamic Mechanical Thermal Analyser, at a heating rate of 5°C min^{-1}, over the temperature range −50 to 100°C. Samples were scanned with an imposed frequency of 5 Hz in the bending mode, and E', E'' and tan δ values were recorded as a function of temperature.

A Rheograph 2001 (Göttfert, Germany), with a cylindrical die of diameter 1 mm and L/D ratio of 30 was used to generate rheological data at temperatures of 250, 260, and 270°C. The comparison interval was 8 s, with an initial melting time of 1 min. The instrument was set at a constant speed/shear rate mode. A maximum of 8 piston speeds, in the range 0.04–2.4 mm s^{-1}, were used to give a shear rate range of 40–3000 s^{-1}. Melt viscosity and melt elasticity parameters were evaluated by using the RABKOR program (Version 9.3), according to the instrument manual[15–17].

RESULTS AND DISCUSSION

Differential scanning calorimetry

The d.s.c. heating scans (*Figure 1*) were used to determine the melting behaviour of the components in the blend, such as the onset of melting (T_1), the melting peak temperature (T_2), and the completion of melting (T_4), plus the melting temperature range and the heat of fusion. The onset of crystallization (T_5), the crystallization peak temperature (T_6), and the completion of crystallization (T_7), plus the heat of crystallization, were determined from the cooling scans (*Figure 2*). The thermal data are summarized in *Tables 1* and *2*.

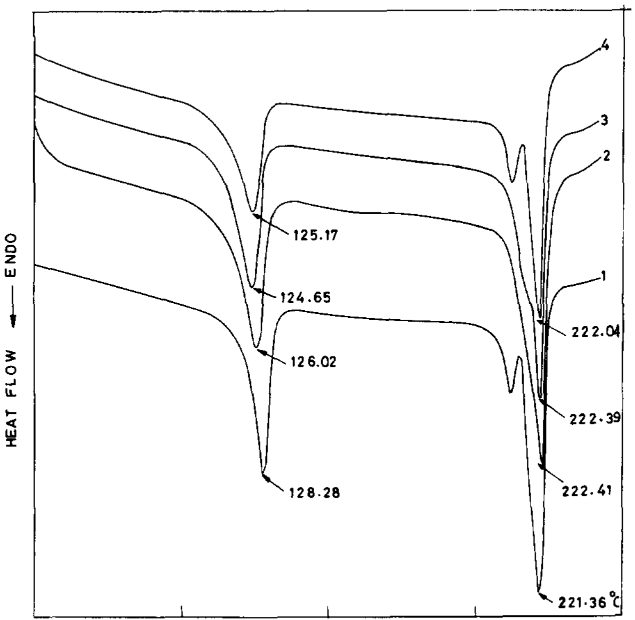


Figure 1 D.s.c. thermograms (heating cycle) of PBT/HDPE/IONO/GF composites: (1) PBT/HDPE/GF (20 wt%); (2) PBT/HDPE/IONO/GF (10 wt%); (3) PBT/HDPE/IONO/GF (20 wt%); (4) PBT/HDPE/IONO/GF (30 wt%)

Melting behaviour

The mechanical behaviour of composites is primarily influenced by the state (length distribution, orientation) of fibres and the matrix morphology (crystallinity, molecular orientation etc.). In fibre reinforced composites, there is a direct influence of the fibres on the morphology of the surrounding matrix[18,19]. Ramos and Belmontes[20] studied the effect of glass fibres on a PP low density polyethylene (LDPE) blend and found that in the presence of fibres the spherulite size decreases. This was attributed to the restrictions caused by the glass fibres in the development of a spherulitic structure in injected materials. The onset of melting of both PBT and HDPE does not change significantly on the addition of glass fibre, either in the case of pure PBT or in the PBT/HDPE blends (see *Table 1*), indicating that there is no change in the crystallite size of PBT in the presence of GF. This may be due to the very fast crystallizing nature of PBT.

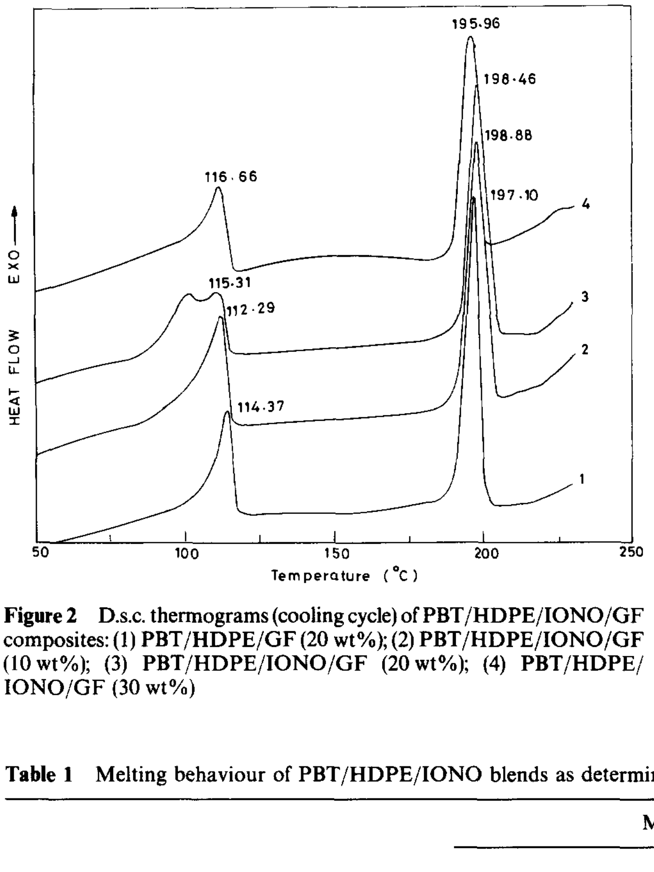


Figure 2 D.s.c. thermograms (cooling cycle) of PBT/HDPE/IONO/GF composites: (1) PBT/HDPE/GF (20 wt%); (2) PBT/HDPE/IONO/GF (10 wt%); (3) PBT/HDPE/IONO/GF (20 wt%); (4) PBT/HDPE/IONO/GF (30 wt%)

Values of the parameter A/M, which is a measure of the degree of crystallinity, are also shown in *Table 1*. A/M is the area under the exotherm of the PBT phase, divided by the mass of the PBT component in the sample. It is seen that the value of A/M increases for the glass-fibre-filled systems containing only pure PBT as well as for its blends (alloys) with HDPE. The value increases as the GF content increases from 10 to 20 wt% and then decreases for a 30 wt% GF content system. This decrease may be due to a very high nucleation density, provided by the glass fibre at this level, leading to imperfect crystals. Therefore, it is seen that there is an overall increase in crystallinity in the presence of glass fibres, which can be attributed to the heterogeneous nucleation provided by this component[3]. An increased heat of fusion for the constituents of the blends in the reheating scans further supports this argument.

Non-isothermal crystallization

It can be seen from *Table 2* that both the onset (T_5) and peak (T_6) temperatures of crystallization have shifted to higher values for all of the systems containing glass fibres, except for the composition without any ionomer (No. 4). This means that the presence of the glass fibre facilitates the crystallization of PBT as well as HDPE in the blends. This is evident from the decreased degree of supercooling in the presence of glass fibre for both polymer components (see *Table 2*). The heats of fusion for the constituents in the blends, as calculated from the areas under the melting peaks, are higher than those obtained by using the additivity rule (*Table 1*). This is due to an overall increase in crystallinity which can be explained on the basis of the heterogeneous nucleation provided by the glass fibres *versus* the homogeneous nucleation in the unfilled system.

The calculated heats of fusion for the composites were computed by using the proportional additivity rule on the basis of the actual weight percentages of the polymers (excluding glass fibres), as given below.

For PBT/HDPE/GF in the weight ratio of 64/16/20:

$$\Delta H_f = 0.80(\Delta H_f(\text{PBT})) + 0.20(\Delta H_f(\text{HDPE}))$$

Table 1 Melting behaviour of PBT/HDPE/IONO blends as determined from d.s.c. studies

		Melting parameters from heating scans						
						Heat of fusion (J g^{-1})		
No.	Sample	Onset T_1 (°C)	Peak T_2 (°C)	Completion of melting T_4 (°C)	Peak width T_4-T_1 (°C)	Found	Calcd	A/M
1	PBT	216.1	222.4	236.6	20.4	26.0	–	796.6
2	PBT/GF (20 wt%)	218.8	222.6	233.3	14.5	42.3	–	996.5
3	PBT/HDPE	220.5 122.8	227.6 129.0	240.7 144.8	20.2 22.0	24.8 138.9	20.8 83.8	689.0
4	PBT/HDPE/GF (20 wt%)	214.8 121.5	221.4 128.3	234.7 143.0	19.9 21.6	42.6 102.9	40.9 83.8	880.7
5	PBT/HDPE/IONO (5 wt%)	219.6 123.8	226.7 129.1	237.8 140.7	18.2 16.9	24.6 98.1	20.7 83.8	863.6
6	PBT/HDPE/IONO/GF (10 wt%)	215.8 144.3	222.4 124.7	231.1 139.0	14.9 24.7	44.3 94.8	46.0 70.2	921.9
7	PBT/HDPE/IONO/GF (20 wt%)	216.2 114.3	222.4 124.7	231.1 139.0	14.9 24.7	48.8 104.3	46.0 70.2	1038.0
8	PBT/HDPE/IONO/GF (30 wt%)	216.3 114.1	222.0 125.2	232.5 136.2	16.2 22.1	48.3 97.4	46.0 70.2	894.8

Table 2 Non-isothermal crystallization behaviour of PBT/HDPE/IONO blends as determined from d.s.c. studies

		Crystallization parameters from cooling scans					
No.	Sample	Onset T_5 (°C)	Peak T_6 (°C)	Completion of crystallization T_7 (°C)	Peak width T_5-T_7 (°C)	Degree of supercooling $T=T_2-T_5$ (°C)	Heat of crystallization ΔH_c ($J\,g^{-1}$)
1	PBT	199.3	195.3	179.7	19.7	23.1	37.1
2	PBT/GF (20 wt%)	201.6	197.5	180.6	21.0	21.0	50.5
3	PBT/HDPE	197.8 119.1	193.7 117.5	170.9 88.9	26.9 30.1	29.8 9.9	38.7 163.0
4	PBT/HDPE/GF (20 wt%)	199.8 117.0	197.1 114.4	183.4 87.1	16.4 29.9	21.5 11.2	56.1 118.7
5	PBT/HDPE/IONO (5 wt%)	199.05 118.6	194.6 116.8	177.1 77.32	21.9 41.3	32.3 10.6	37.7 150.5
6	PBT/HDPE/IONO/GF (10 wt%)	203.1 115.4	197.8 112.3	182.9 82.5	20.1 32.9	19.3 10.6	43.1 88.5
7	PBT/HDPE/IONO/GF (20 wt%)	203.2 115.3	198.5 114.3	184.9 80.1	18.9 35.2	19.1 9.3	47.6 87.9
8	PBT/HDPE/IONO/GF (30 wt%)	204.0 115.7	196.0 111.7	188.3 79.7	14.7 36.0	18.0 9.5	43.6 71.8

and for PBT/HDPE/IONO/GF in the weight ratio of 60.8/15.2/4/20

$$\Delta H_f = 0.76(\Delta H_f(\mathrm{PBT})) + 0.19(\Delta H_f(\mathrm{HDPE})) + 0.05(\Delta H_f(\mathrm{Surlyn})).$$

Dynamic mechanical thermal analysis

D.m.t.a. traces, as shown in *Figure 3* for the PBT/HDPE based composites, show that introduction of the filler has not shifted the temperature location of the peaks but has reduced their magnitude. Fillers, such as glass fibres, decrease the damping of the composite. If the mechanical damping of a filled polymer results only from the inherent damping of the constituents[21], then

$$\tan\delta_c = V_f \tan\delta_f + (1 - V_f)\tan\delta_m \qquad (1)$$

and as the glass damping is effectively zero, equation (1) reduces to

$$\frac{\tan\delta_c}{\tan\delta_m} = (1 - V_f) = V_m \qquad (2)$$

where $\tan\delta_c$, $\tan\delta_f$ and $\tan\delta_m$ are the damping values of the composite, the fibre and the polymer respectively, and V_f and V_m are, respectively, the volume fraction of the fibre and the matrix.

The theoretical curve, obtained using this equation, is plotted, along with the experimental values for the transition of PBT in *Figure 4*. All experimental points lie below the theoretical curve, indicating that the presence of a 'reinforcement' has led to a greater reduction in $\tan\delta_c$ than would be expected theoretically from equation (2). This additional reduction could be due to a shell of immobilized polymer surrounding the individual reinforcing elements, as shown in *Figure 5*. The shell thickness should be independent of V_f, but it was found, however, to decrease from 0.580 to 0.208 μm as V_f increased from 0.051 to 0.173. The shell thickness was calculated using the equation shown in *Figure 5*. The decrease could be due to fibre agglomeration at higher levels of loading. A recent publication[22] has claimed that this immobilized shell is the 'interphase', i.e. a region surrounding the fibre where the properties differ from the bulk matrix. The d.m.t.a. results from this present work support this hypothesis and also are in agreement with the results of similar work carried out by Morgon[23].

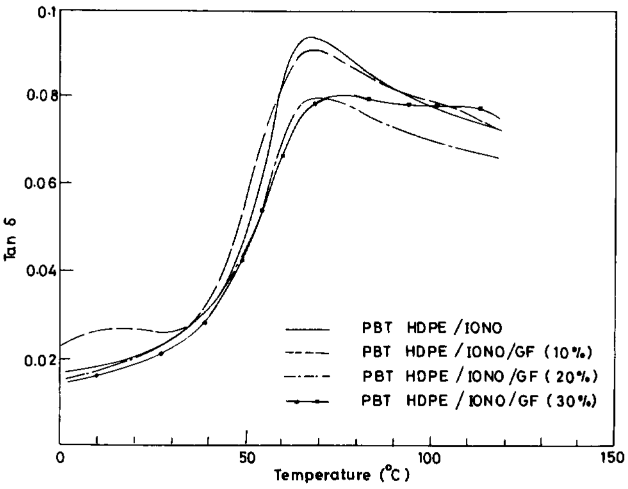


Figure 3 D.m.t.a. traces tan δ vs. T) for the blend and composites based on the PBT/HDPE system

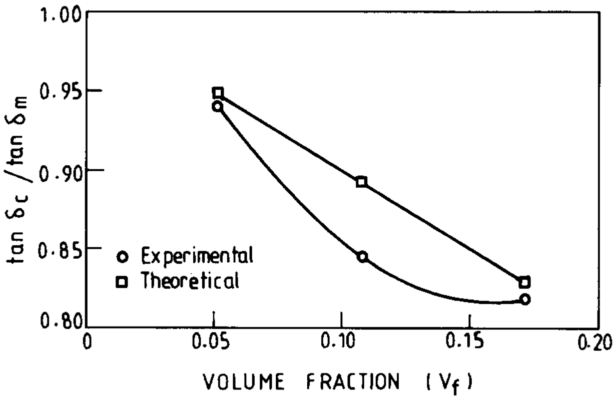
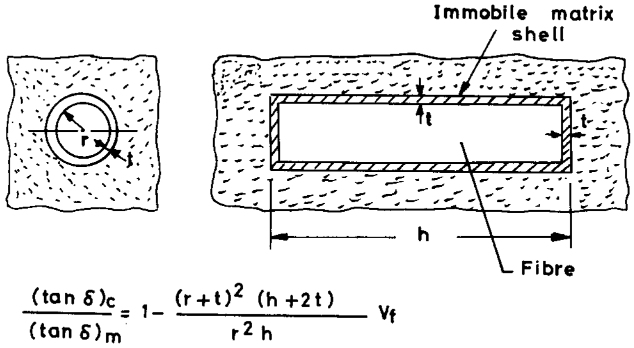


Figure 4 Plot of $\tan\delta_c/\tan\delta_m$ vs. V_f for the PBT/HDPE/IONO/GF composites as obtained from d.m.t.a.

The relative modulus, E'_c/E'_m, of this system is plotted in *Figure 6* as a function of temperature for different volume fractions. It is seen that the incorporation of glass



$$\frac{(\tan\delta)_c}{(\tan\delta)_m} = 1 - \frac{(r+t)^2\,(h+2t)}{r^2 h}\,V_f$$

Figure 5 Schematic diagram of the immobilized shell model

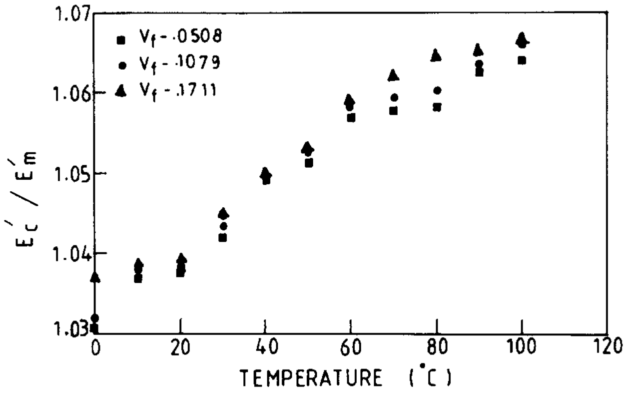


Figure 6 Relative storage modulus E'_c/E'_m vs. temperature for the PBT/HDPE/IONO/GF composites at three different volume fractions of GF

fibres has increased the modulus at all temperatures, when compared to the unfilled system (see *Figure 7*). At the same time, the drop in the modulus on passing through the glass transition temperature (T_g) is comparatively less for reinforced composites than for unreinforced blends. In other words, glass fibres have a larger effect on the modulus above T_g than below it (*Figure 7*). A higher relative modulus at higher temperatures can be due to the fact that the glass fibre reduces the flexibility of these materials by introducing constaints on the segmental mobility at the transition regions, a phenomenon which is more pronounced at higher temperatures.

Figure 8 shows the plot of the loss modulus (E'') as a function of temperature for the PBT/HDPE/IONO system with three different loadings of glass fibre. It is seen that the most pronounced effect of the rigid filler is the broadening of the transition region as the fibre concentration increases. The matrix surrounding the glass fibres is in a different physical state to the rest of the matrix, thus hindering the molecular motion. This may be one of the possible reasons for the observed broadening of the transition region in filled systems.

Rheological studies

Flow curves for the PBT/HDPE/IONO/GF composites with various glass fibre loadings are shown in *Figure 9*. Fibre-filled polymer melts usually obey the power law equation, in which the power law exponents decrease on addition of glass fibre, when compared to unfilled systems, thus showing a higher pseudoplasticity (see *Table 3*).

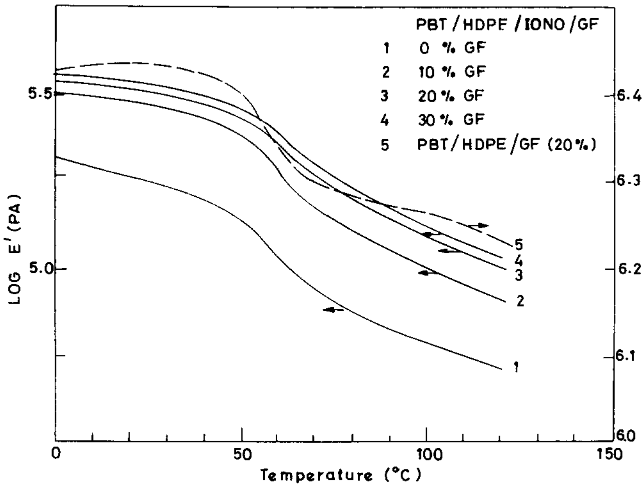


Figure 7 D.m.t.a. traces (lof E' vs. T) of the PBT/HDPE/IONO/GF composites

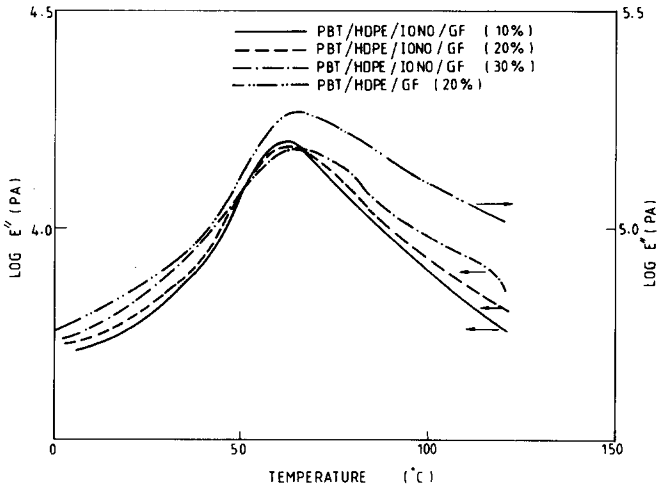


Figure 8 D.m.t.a. traces (log E'' vs. T) of the PBT/HDPE/IONO/GF composites

Table 3 Rheological parameters of the PBT/HDPE/IONO/GF composite system

No.	Sample	Power law exponent n	Activation energy (kg kg^{-1} mol^{-1})	Shift factor a_T
1	PBT/HDPE/IONO/0 wt% GF	0.73	25.6	0.90
2	PBT/HDPE/IONO/10 wt% GF	0.48	40.1	0.84
3	PBT/HDPE/IONO/20 wt% GF	0.46	46.6	0.82
4	PBT/HDPE/IONO/30 wt% GF	0.43	41.8	0.81

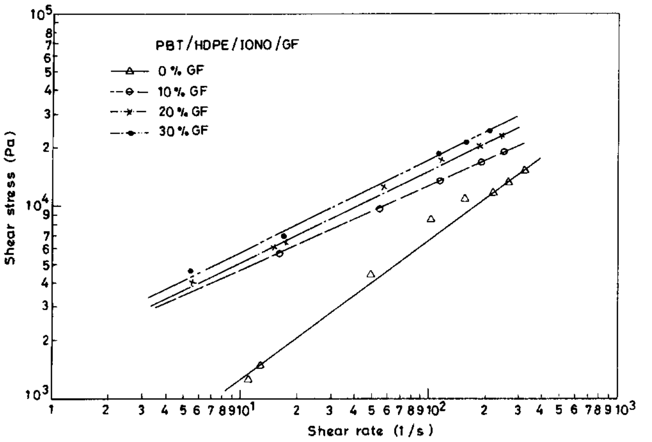


Figure 9 Shear stress vs. shear rate plots for the PBT/HDPE/IONO/GF composites with varying GF contents

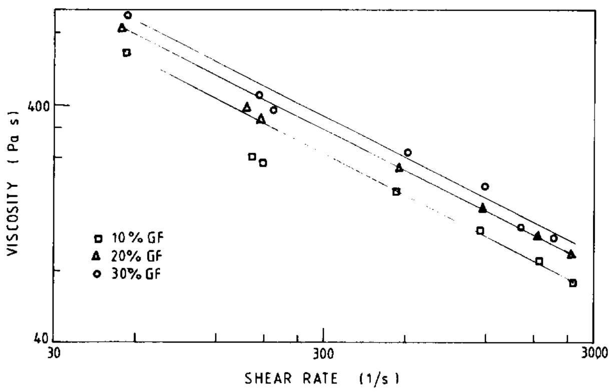


Figure 10 Viscosity vs. shear rate plots for the PBT/HDPE/IONO/GF composites with varying GF contents

Figure 10 shows the variation of viscosity with shear rate for samples with varying glass fibre contents. Incorporation of fibres results in a viscosity increase over the whole shear-rate range that was studied. The viscosity curves tend to converge at higher shear rates, which means that the viscosity tends to be independent of the fibre loading at very high rates of shear.

Extrudate swell measurements

Figure 11 shows the variation of extrudate swell ratio with glass fibre content at three different temperatures. The extrudate swell ratio values that are reported here are calculated using the normal stress difference (σ) and shear stress (τ), according to the following equation[15]:

$$\text{extrudate swell} = \left(\frac{D}{d}\right)^2 = (1 + d/L)^2\left(1 + \frac{\sigma^2}{2\tau^2}\right)^{1/3} \qquad (3)$$

where d is the diameter of the die, L is the length of the die, and D is the diameter of the extrudate after emerging from the die.

It is seen that as the glass fibre content and temperature increases, the extrudate swell ratio decreases. This reduction with fibre concentration was attributed to a lower polymer concentration in the filled extrudate[10]. The presence of glass fibre inhibits the elastic recovery of the matrix melt since, in contrast to the behaviour of macromolecules, the glass fibres have only a small tendency to disorient upon removal of the shear field when emerging from the capillary. This reduction in extrudate swell on adding glass fibre is of some advantage from the processing point of view, i.e. it compensates for the increase in extrudate swell on adding ionomer to the PBT/HDPE blend[1].

Analysis of rheological data using the Maron and Pierce model

Metzner[24] reviews in detail the flow behaviour of concentrated suspensions based on polymeric melts, where a substantial variety of equations have been suggested for the description of the viscosity concentration behaviour of these suspensions. However, the best empirical expression is probably the very simple relationship originating from the work of Maron and Pierce[12], which was further carefully evaluated by Kitano *et al.*[25]:

$$\eta_r = [1 - (\phi/A)]^{-2} \qquad (4)$$

where η_r is the relative viscosity, ϕ is the volume fraction of the fibres and the empirical constant A describes the packing geometry of the filler, with a value of 0.680 being used for suspensions of smooth spheres in a liquid. This equation has been employed to evaluate the data generated in this work.

Figure 12 shows the plot of relative viscosity as a function of the volume fraction of the fibres at three different shear rates. It is seen that the relative viscosity increases as the volume fraction of the fibres increases, and decreases as the shear rate increases. This is expected, since the increase in viscosity on adding increasing amounts of glass fibre is less pronounced at higher shear rates, as shown earlier.

Using the Maron and Pierce relationship (equation (3)), the values of A were calculated taking the η_r values at the lowest shear rate (46.7 s^{-1}). Since the samples used for these rheological studies were in the form of extruded granules and also that during the extrusion process extensive fibre damage was found to occur, thus giving a range of fibre lengths, the L/D ratio taken for these

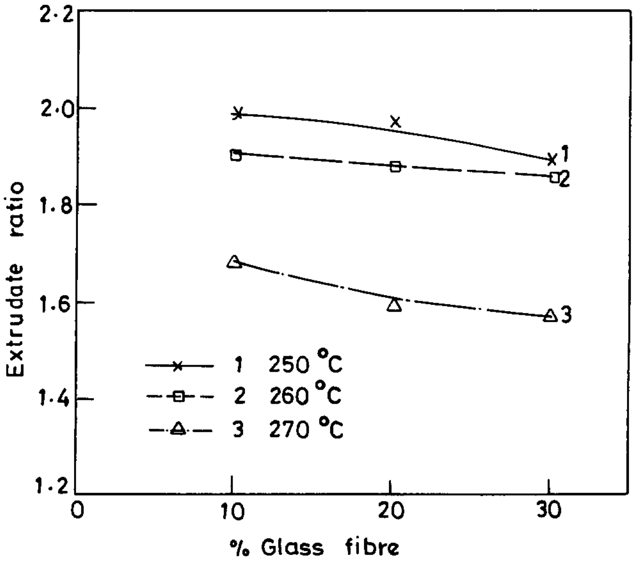


Figure 11 Extrudate swell ratio vs. GF content for the PBT/HDPE/IONO/GF composites, measured at different temperatures with a constant shear rate

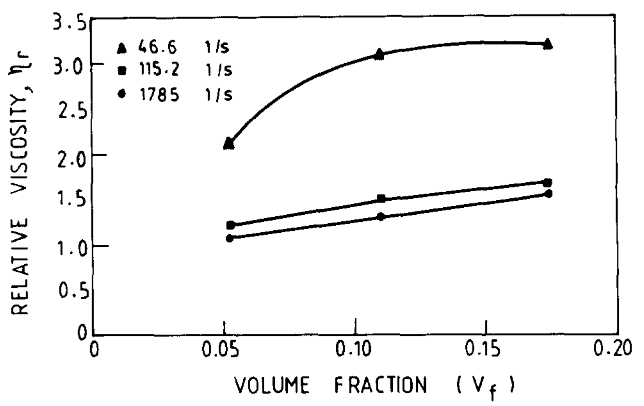


Figure 12 Relative viscosity vs. volume fraction for the PBT/HDPE/IONO/GF composites at different shear rates

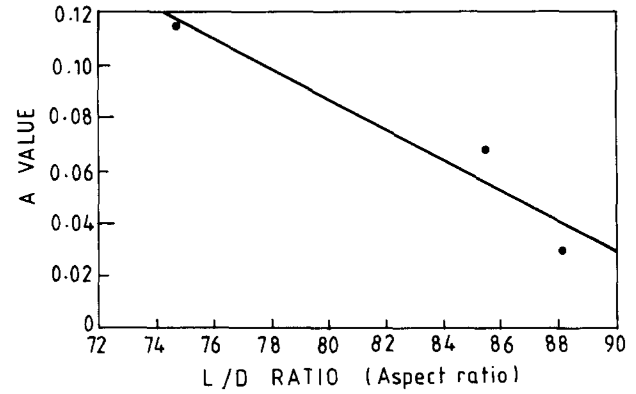


Figure 13 Values of the 'A' parameter (derived from the Maron and Pierce model) vs. aspect ratio for the PBT/HDPE/IONO/GF composites

fibres is given as an average:

$$\frac{L}{D} \simeq \frac{\text{number average fibre length } (\bar{L}_n) \text{ after extrusion}}{\text{diameter of fibre}} \quad (5)$$

Values of $\bar{L}_n$ for the composite samples have been determined as described in our earlier paper[1]. *Figure 13* shows the variation of the value of A as a function of the aspect ratio of the fibres. It is seen that this parameter increases as the aspect ratio decreases. This is consistent with the relationship given by Kitano *et al.*[25], as described by Metzner[24]:

$$A = 0.54 - 0.0125L/D \quad (6)$$

where L/D is the aspect ratio of the fibres. Although these authors have used this equation for fibres with a maximum aspect ratio of 27, Chan *et al.*[10] have employed the same equation for suspensions of fibres with L/D values of 80 ($\phi = 0.19$) and 160 ($\phi = 0.08$). Since there is a distribution of the aspect ratios in extruded samples, curves with a concave downward shape are obtained for the relative viscosity *versus* volume fraction plots of the PBT/HDPE/IONO/GF composite system, as seen in *Figure 12*.

CONCLUSIONS

The main conclusions drawn from these studies are as follows:

1. The melting behaviour of the composites, as determined from the d.s.c. measurements, indicates both a faster crystallization rate and an increased degree of crystallinity in the presence of glass fibres. This may be due to heterogeneous nucleation, which is brought about by the presence of the fibres. A lowering of the degree of supercooling for the glass-fibre-containing systems further supports this hypothesis.
2. D.m.t.a. results show that the presence of glass fibres decreases the mechanical damping of the composites and also expands the transition region. The incorporation of glass fibre increases the modulus at all temperatures, but the drop in modulus on passing through T_g decreases in the case of the filled systems.
3. Rheological studies show an increase in viscosity with increasing glass fibre content, with this effect being less pronounced at higher temperatures. However, the extrudate swell decreases on the addition of glass fibre. The rheological data has fitted well to the Maron and Pierce model for describing the rheology of certain suspensions[12,25].

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