

The Effect of Addition of High-Density Polyethylene on the Crystallization and Mechanical Properties of Polypropylene and Glass-Fiber-Reinforced Polypropylene

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Synopsis

High-density polyethylene up to about 30% by weight was melt-mixed with polypropylene and short-glass-fiber-reinforced polypropylene. The presence of high-density polyethylene and glass fibers in the polypropylene matrix affects its crystallization characteristics, which were studied with the help of differential scanning calorimetry. The blend and composite samples have a large number of polypropylene domains apparently due to an abundance of surface nuclei; as a result, the tensile strength, tensile modulus, and toughness are enhanced. The temperature dependence of shear modulus and logarithmic decrement indicate that high-density polyethylene can have plasticizing effect below the glass transition temperature of polypropylene. The scanning electron micrographs of fractured ends show the presence of dispersed domains in the composite samples.

INTRODUCTION

There have been a number of studies relating to the possible improvement in the impact resistance of polypropylene by melt-blending it with high-density polyethylene, resulting in a number of publications and patents, which have been documented.¹⁻³ Polypropylene (PP) is a semicrystalline polymer with a crystallinity of about 60% and glass transition temperature in the -20 – 0°C range. High-density polyethylene (HDPE) is relatively more crystalline, and its T_g is around -100°C . The tensile modulus and tensile strength of an isotropic HDPE sample at room temperature are lower compared to a PP sample prepared under the same conditions. The HDPE sample will be expected to have higher impact resistance than PP, particularly at low temperatures, in view of its lower glass-transition temperature. Studies on PP/HDPE blends have shown that they are incompatible. It has been reported⁴⁻⁶ that they show a positive synergistic effect in their tensile strength and modulus up to about 20–25% HDPE content. It is thus of interest to understand why synergism is observed at low HDPE content.

Short-glass-fiber-reinforced PP has found wide use as a light, stiff, and strong material having higher temperature resistance than the PP homopolymer. It

was therefore considered appropriate to examine the effect of the addition of small amounts of HDPE to the composite.

Studies reported in this paper relate to nine samples including PP: four samples were PP/HDPE blends containing up to 25% by weight of HDPE, two samples were short-glass-fiber-reinforced PP containing 20% and 30% by weight of short glass fibers and finally two samples were so prepared as to have about 16% by weight of glass fiber and about 9% and 29% of HDPE. The investigations reported include studies on their crystallization behavior, measurement of the temperature dependence of torsional modulus and logarithmic decrement, and finally the tensile strength and tensile modulus of these samples as measured on an Instron tensile tester at room temperature. Structure-property correlations are then attempted.

EXPERIMENTAL

Materials

Shell PP L550 polypropylene and BP Rigidex HDPE R101 were used in the present studies. It has been pointed out⁴ that, for achieving optimum properties in PP/HDPE blends, the molecular weights of these two, as measured by the melt flow index, should not differ a great deal, more specifically, the viscosities must be within a factor of 5 at the blending conditions. The melt flow indices of these two polymers were measured under identical conditions in a Davenport melt flow indexer under standard conditions and were found to be 0.412 g/10 min for Shell PP L550 and 0.784 g/10 min for BP Rigidex HDPE R101. Assuming that the melts were Newtonian, this indicates that their viscosities are in the ratio PP: HDPE = 1:1.8, and these polymer grades are therefore quite acceptable for blending.

Profax PC-072 granules of short-glass-fiber-reinforced PP manufactured by Hercules Chemicals, Belgium, containing 20% and 30% by weight of short glass fibers, were used in the present studies.

TABLE I
Description of Samples

Sample no.	Sample	Weight fraction			Preparation technique
		PP	HDPE	Glass fiber	
1	PP	1.00	—	—	Masticated/ chopped
2	PP/HDPE blends	0.95	0.05	—	Tumble-mixed/ masticated/ chopped
3		0.90	0.10	—	
4		0.80	0.20	—	
5		0.75	0.25	—	
6	PP/glass fiber	0.80	—	0.20	Masticated/ chopped
7	Composite	0.70	0.30	—	—
8	PP/glass fiber/HDPE	0.75	0.09	0.16	Tumble-mixed/ masticated/ chopped
9	Blended composites	0.55	0.29	0.16	—

Compounding of Blend and Composite Samples

PP/HDPE blends having the compositions shown in Table I were prepared as follows. Appropriate quantities of granules of the two polymers were tumble-mixed for 10 min and the tumble-mixed granules were then melt-mixed in a Brabender twin screw extruder, the temperature profile of which was: first zone 190°C, second zone 200°C, and die 210°C. The screw speed was fixed at 10 rpm. The melt-mixed blend came out in the form of a thick continuous strand, which was cut with a knife into small pieces; these pieces were then chopped in a granulator to give a fluffy material which was suitable for injection molding.

For composite blends, also listed in Table I, a similar procedure was used; the starting material being "Profax" glass-fiber-filled PP granules. The PP (sample 1) and Profax (samples 6 and 7) granules were also masticated in the Brabender extruder so that their thermomechanical histories were similar to the other samples. The fiber length distribution in the various composite samples would thus be expected to be similar.

Injection Molding of Test Specimens

The chopped flakes, as obtained above, were dried in an oven and then injection-molded into standard dumbbell test pieces in a Herbert injection moulding machine under the following conditions:

Temperature profile:	rear zone	210°C
	center zone	220°C
	front zone	230°C
	nozzle	240°C
Screw speed:	75 rpm	
Injection cycle:	screw forward time	10 s
	die closed time	15 s
	low pressure closing time	4 s
	dies open time	4 s

The dumbbell test specimens were stored for at least a week before making measurements.

Characterization

Differential Scanning Calorimetry

Crystallization was followed through differential scanning calorimetry (DSC) measurements on a Perkin-Elmer DSC-2. Measurements were made on 10-mg samples in the temperature range 57–177°C under identical settings for all the samples. Thermograms were recorded on four pieces cut from differential parts of each dumbbell. It was observed that the results were significantly reproducible, indicating that the effect of fluctuation in glass fiber content was not significant. The samples were first taken to 177°C (i.e., about 20°C above the melting point of PP) in the instrument and held there for about 5 min, so as to minimize the effect of any previous history on the crystallization. The sample

was then cooled at a rate of 5°C/min. During the cooling cycle, the crystallization exotherms were recorded.

Dynamic Mechanical Properties

The torsional storage modulus (G') and the logarithmic decrement (Δ) were measured with the help of a torsion pendulum of free vibration type. The measurements were made on rectangular strips about 9 cm long cut from the dumbbell test specimens between -80°C and $+80^{\circ}\text{C}$ at a frequency of about 1 Hz. $\tan \delta$ was computed from the relation $\Delta = \pi \tan \delta$ and G' from the standard expression⁷ given below:

$$G' = (\omega_c^2 M/b)(1 + \Delta^2/4\pi^2),$$

where M is moment of inertia of the oscillating system, ω_c is the frequency, and b is the form factor expressed in terms of length h , width c , thickness d , and shape factor μ , as $b = cd^3\mu/16h$. The shape factor $\mu = 5.33(1 - 0.63d/c)$ and was 4.66 for the samples studied.

Tensile Properties

The load elongation characteristics of the dumbbell-shaped specimens were studied on an Instron Tensile Tester at room temperature. The sample had a gauge length of 2.5 in. and cross-sectional area of $1/16$ in.² The crosshead speed was fixed at 0.2 cm/min. A load cell of 500 kg was used. The PP homopolymer had a very large extension at break—it was only taken to above the yield point in most cases, and the highest load recorded was taken for computation of tensile strength.

Scanning Electron Microscopy

The fractured ends of the specimens, as obtained from the Instron tests, were examined on a scanning electron microscope.

RESULTS AND DISCUSSION

Analysis of the DSC Data

The DSC thermograms recorded during the cooling of the samples from melt showed a prominent crystallization exothermic peak centered around 100–120°C for all these samples, viz., the blends (Fig. 1) and the composites (Fig. 2). For the samples containing HDPE (i.e., samples 2–5, 8, and 9), there appear two overlapping exotherm peaks, while in the samples not containing HDPE (i.e., samples 1, 6, and 7) there is only one exotherm peak. The peak which occurs at lower temperature corresponds to the crystallization of HDPE, while the other peak is due to crystallization of PP. Furthermore, the two peaks are better resolved in the thermograms for the composites containing glass fibers (samples 8 and 9) than in the case of blends (samples 2–5). It is also noted that, in the case

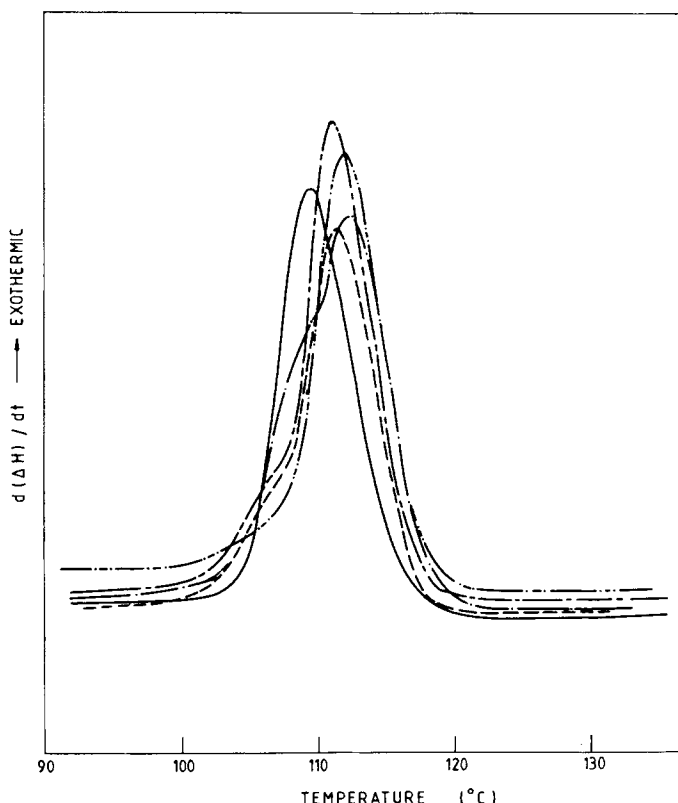


Fig. 1. DSC thermograms recorded during cooling cycle for PP and the various PP/HDPE blends: (1) (—) PP; (2) (-----) 95 PP/5 HDPE; (3) (---) 90 PP/10 HDPE; (4) (- - -) 80 PP/20 HDPE; (5) (- - -) 75 PP/25 HDPE.

of glass-fiber-reinforced PP and the PP/HDPE blends, the peaks shift to higher temperatures.

These results will be discussed in terms of the following quantities:

(i) The temperature where the exotherm shows the peak, denoted as $(T_p)_{PP}$ and $(T_p)_{HDPE}$ for PP and HDPE crystallization peaks. In cases of overlapping peaks, resolution of the peaks was achieved by tracing a mirror image of the nonoverlap part of the PP peak and then by subtracting it from experimental curve in the overlap region, as illustrated in Figure 3, in which the other parameters used in this discussion are also illustrated.

(ii) The temperature of onset of PP crystallization, T_{onset} , which is the temperature where the thermogram initially departs from the base line.

(iii) The initial slope of the PP-crystallization exotherm, S_i , which has been used elsewhere⁸ as a measure of the rate of nucleation.

(iv) The half-width of the PP peak, Δw , which is the width of the PP peak at half-height, determined after normalization of the peak to constant mass of PP component in the sample. This is a measure of crystallite size distribution.

(v) The area under the peak divided by the mass of the specific component in the sample, A/m . In the case of blends and composites, the mass m of the specific component, viz., PP, was calculated by taking into account the presence

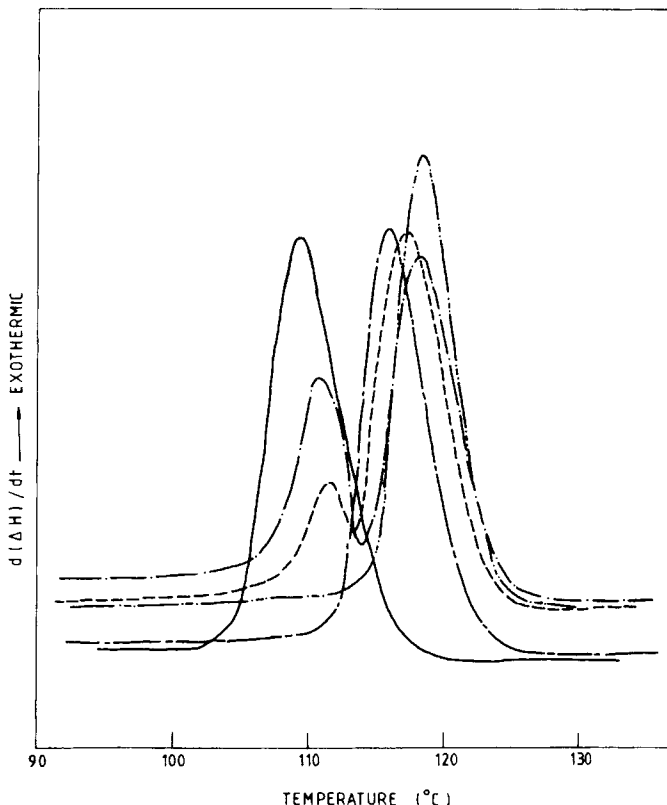


Fig. 2. DSC thermograms recorded during cooling cycle for PP, the PP/glass-fiber composites and PP/glass-fiber composites containing HDPE: (1) (—) PP; (6) (---) 80 PP/20 GF; (7) (-·-·-) 70 PP/30 GF; (8) (···) 75 PP/16 GF/9 HDPE; (9) (- - -) 55 PP/16 GF/29 HDPE.

of other components. Since measurements for all samples were done under identical settings of the instrument, A/m is hence proportional to the heat of crystallization of the given sample and thus to its degree of crystallinity.

Values of these parameters for the various samples obtained from these DSC thermograms are summarized in Table II and plotted in Figures 4–6. The following points emerge from these results:

(1) The PP-peak temperature $(T_p)_{PP}$ is about 6–7°C higher than HDPE-peak temperature $(T_p)_{HDPE}$ in the blends (samples 2–5) as well as the composite samples containing HDPE (samples 8 and 9). For the composites (samples 6–9), both $(T_p)_{PP}$ and $(T_p)_{HDPE}$ are about 5–8°C higher than their respective values for the blends and the PP sample. For composites without HDPE (samples 6 and 7), $(T_p)_{PP}$ is higher by 2°C for 30% compared to 20% glass-fiber composite sample. However, for the composites with HDPE (samples 8 and 9), which have identical glass fiber content, such a shift in $(T_p)_{PP}$ with variation in HDPE content is not observed. For the PP/HDPE blends the shift in $(T_p)_{PP}$ is quite small, i.e., 1–3°C only.

(2) T_{onset} , which is 121°C for PP sample, increases by about 1°C for the blends, almost independently of the HDPE content. For the composites with and without HDPE, T_{onset} is about 6–8°C higher than that for the PP sample.

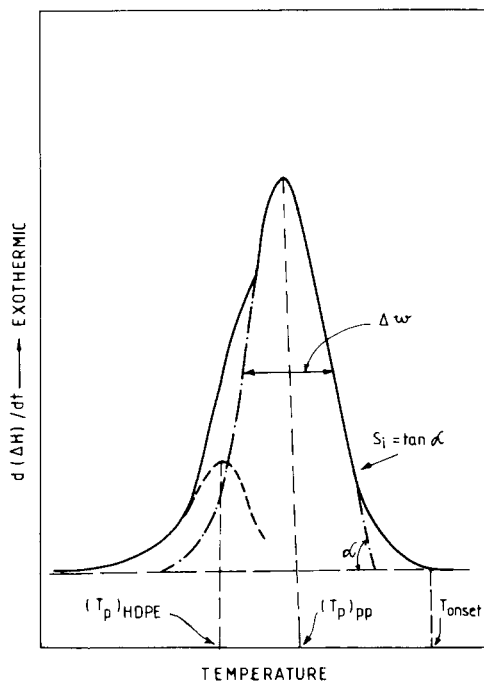


Fig. 3. Typical resolution of the PP and HDPE crystallization peaks from the DSC thermogram showing overlapping peaks. The various other parameters used in the text are also represented.

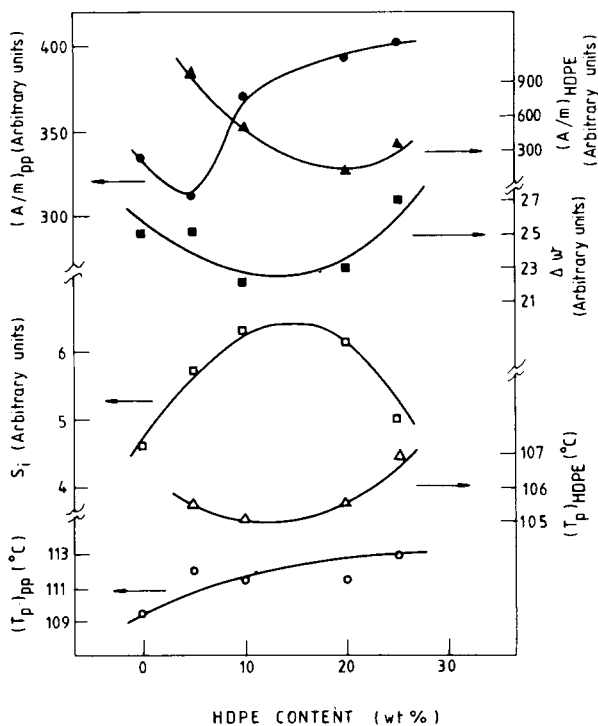


Fig. 4. Variation of $(T_p)_{PP}$, $(T_p)_{HDPE}$, initial slope S_i of crystallization exotherms, half-width Δw of PP crystallization peak, $(A/m)_{PP}$, and $(A/m)_{HDPE}$ with HDPE content for the PP/HDPE blends.

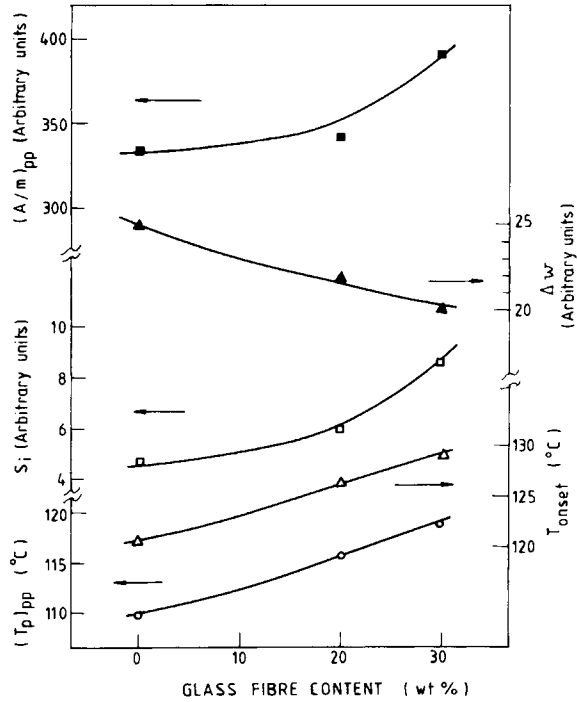


Fig. 5. Variation of $(T_p)_{PP}$, T_{onset} , initial slope S_i of crystallization exotherms, half-width Δw of PP crystallization peak, and $(A/m)_{PP}$ with glass-fiber content for the PP/glass-fiber composites.

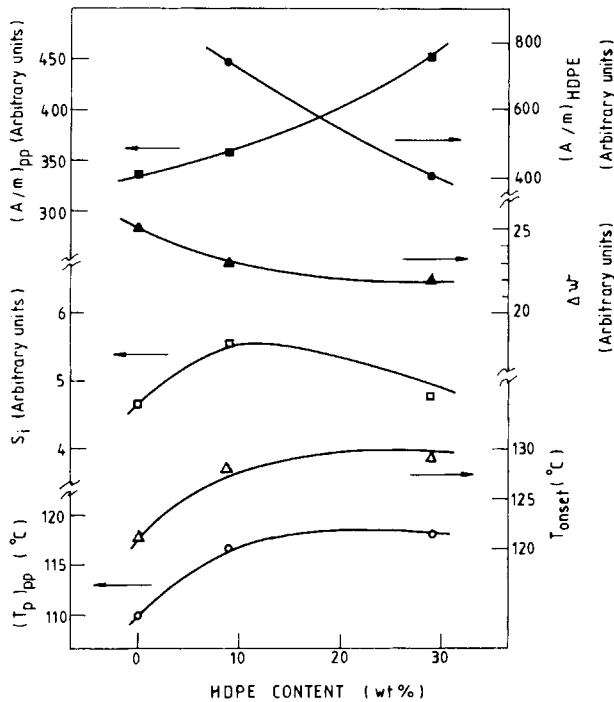


Fig. 6. Variation of $(T_p)_{PP}$, T_{onset} , initial slope S_i of crystallization exotherm, half-width Δw of PP-crystallization peak, $(A/m)_{PP}$, and $(A/m)_{HDPE}$ with HDPE content in PP/glass-fiber composites containing HDPE.

TABLE II
DSC Data

Sample	Crystallinity		Peak temp (°C)		T_{onset} : temp of onset of crystalli- zation (°C)	S_i : initial slope of PP crys- tallization exotherm (arbitrary units)	Δw : Half-width of PP crystalli- zation peak (arbitrary units)
	$(A/m)_{\text{PP}}$ (arbitrary units)	$(A/m)_{\text{HDPE}}$ (arbitrary units)	$(T_p)_{\text{PP}}$	$(T_p)_{\text{HDPE}}$			
	1	335.7	—	109.5			
2	311.5	975.5	112.0	105.5	122.0	5.76	25
3	372.2	495.0	111.5	105.0	122.0	6.33	22
4	393.5	93.6	111.5	105.5	122.5	6.13	23
5	401.8	354.5	113.0	107.0	122.0	5.00	27
6	341.2	—	116.0	—	127.5	5.94	22
7	391.8	—	118.5	—	128.0	8.64	20
8	361.3	740.0	117.0	112.0	128.0	5.59	23
9	452.9	401.7	118.0	110.5	129.0	4.75	22

Variation in glass fiber content and HDPE content does not show any appreciable variation in T_{onset} .

(3) The initial slope of the PP crystallization exotherm for the blends is higher than that for the PP sample; its variation with HDPE content shows a maximum in the region of 10–20% HDPE content (Fig. 4). Composites with HDPE have a higher value of the initial slope than the composites without HDPE, its value being higher for 30% than 20% glass fiber content. For the composites with HDPE, the value of the initial slope is only slightly higher than that for PP sample, its value being lower for higher HDPE content.

(4) The half-width of the PP-crystallization peak, in the case of blends (Fig. 4), has a minimum value in the region of 10–20% HDPE content. For composites without HDPE (Fig. 5), the peak width decreases with increasing glass fiber content. For composites with HDPE (Fig. 6), the peak width decreases with increasing HDPE content. Furthermore, the peak width for the composites is lower than that for the PP sample as well as the blends, suggesting that the presence of glass fiber lowers the width of the PP-crystallization peak in PP/glass fiber as well as in PP/glass fiber/HDPE samples. This decrease in peak width is further confirmed by the fact that a better resolution of PP and HDPE peaks is observed in the samples containing glass fiber (samples 8 and 9) than in the blends (samples 2–5), where the peak temperatures of PP and HDPE peaks differ by an almost equal amount in both cases.

(5) Crystallinity, as represented by area/mass (A/m), broadly shows an increase for PP and decrease for HDPE with: (i) increasing HDPE content in blends (Fig. 4), (ii) increasing glass fiber content in composites without HDPE (Fig. 5), and (iii) increasing HDPE content in composites with HDPE (Fig. 6). However, in the blends there appears a minimum in A/m for PP containing around 5% HDPE; no suitable explanation for this can be offered. The decrease in crystallinity of HDPE component up to 20% HDPE content (Fig. 4) could be attributed to the fact that, in the blends, the PP crystallizes first and the crystallization of HDPE is consequently likely to be impeded by the constraints imposed by the crystallized domains of PP. It must, however, be remembered that the peak area for HDPE peaks in the blend samples was calculated after

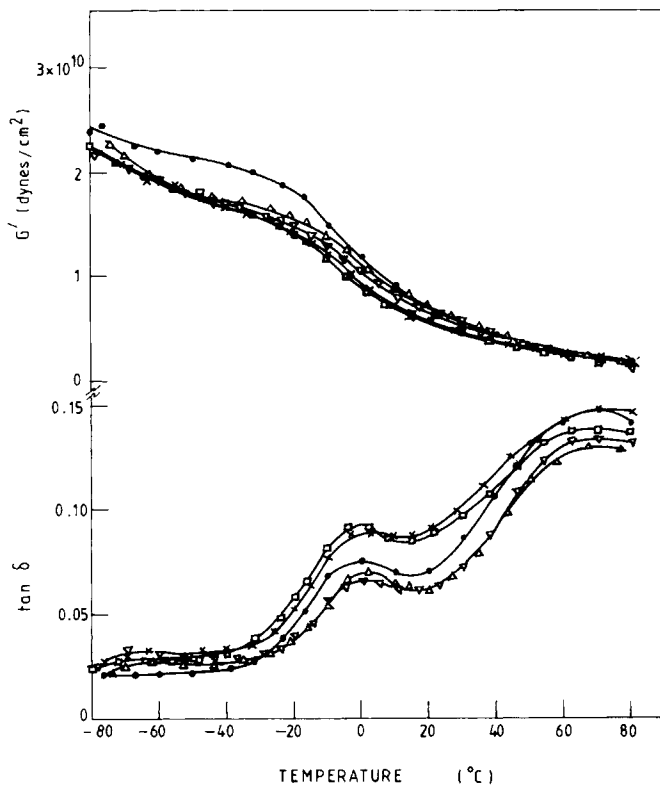


Fig. 7. Dynamic mechanical data (G' and $\tan \delta$) for PP and PP/HDPE blends: (●) sample 1: PP; (□) sample 2: 95 PP/5 HDPE; (▽) sample 3: 90 PP/10 HDPE; (△) sample 4: 80 PP/20 HDPE; (X) sample 5: 75 PP/25 HDPE.

curve resolution from the shoulder in the exotherm peak and the crystallinity values, therefore, cannot be considered to be very accurate.

Thus the addition of HDPE to PP (Fig. 4), the addition of glass fiber to PP (Fig. 5), and the addition of HDPE to glass fiber/PP composites (Fig. 6) produce the following broad effects:

- enhancement of the rate of nucleation of PP as evidenced by the variations of $(T_p)_{PP}$, T_{onset} , and the initial slope of the exotherm;
- reduction of the size distribution of PP crystallites as evidenced by the decrease of half-width of the crystallization peak;
- higher crystallinity of PP;
- lower crystallinity of HDPE in the samples containing HDPE.

The increase in crystallinity accompanied by a faster rate of nucleation and a narrower distribution of crystallite size implies a larger number of small domains of PP in the structure.

Dynamic Mechanical Properties

The dynamic mechanical data are presented in Figures 7 and 8, where the storage torsional modulus G' and $\tan \delta$ are shown as functions of temperature for the various samples. While G' decreases with increasing temperature, \tan

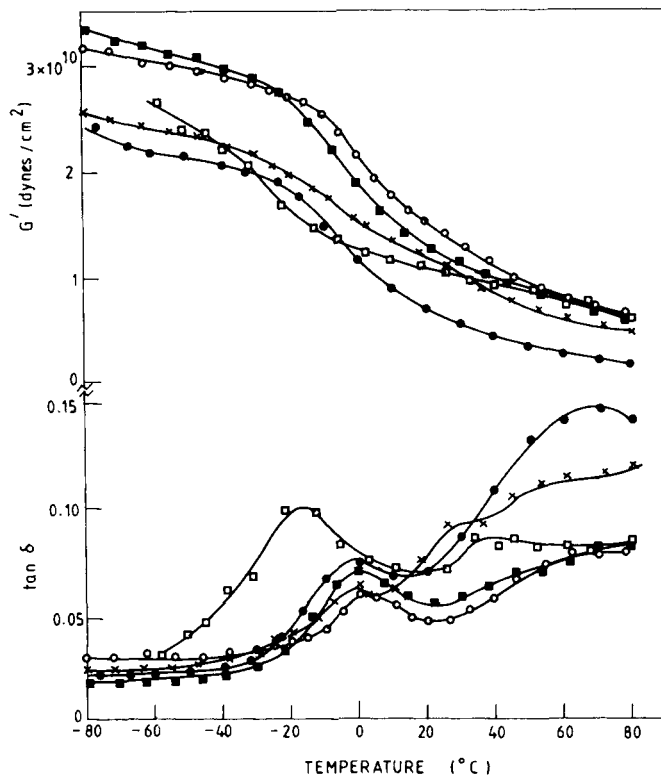


Fig. 8. Dynamic mechanical data (G' and $\tan \delta$) for PP, PP/glass-fiber composites and PP/glass-fiber composites containing HDPE: (●) sample 1: PP; (○) sample 6: 80 PP/20 GF; (■) sample 7: 70 PP/30 GF; (□) sample 8: 75 PP/16 GF/9 HDPE; (X) sample 9: 55 PP/16 GF/29 HDPE.

δ shows a peak between 0°C and -10°C. As Nielsen has pointed out⁹ and also suggested from the WLF equation,¹⁰ the $\tan \delta$ peak at 1 Hz generally appears at a temperature 5–15°C above the glass transition temperature as measured by dilatometry or DTA.

The PP sample has higher torsional modulus compared to the blends in the low temperature region up to about -10°C, i.e., up to the T_g of PP, while at higher temperatures the torsional moduli for all the samples of the blend are almost equal to that of PP (Fig. 7). In the lower temperature region, PP is in the glassy state while the HDPE component would be expected to be in the rubbery state. This might account for the lower modulus of the blends in this temperature range. Compared to the PP sample, $\tan \delta$ peak amplitude is lower for the blends containing 10–20% HDPE and higher for the blends containing 5% and 25% HDPE. On the basis of the present studies, it is not possible to explain this, but it is noteworthy that there are some similarities between these results and those reported by Plochocki¹¹ for PP/HDPE blends.

For composites without HDPE the torsional modulus is higher than that for PP sample by a factor of 1.5–4, depending on the temperature (Fig. 8). $\tan \delta$, in the temperature region about T_g of PP, is lower for the composites without HDPE than the composites with HDPE.

The loss peak attributable to the glass transition of PP occurs for all the samples close to 0°C, indicating that the matrix is essentially unaffected, except in the case of the composite containing 9% HDPE. The height of the loss peak, however, decreases in samples 3, 4, 6, 7, and 9, which may be partly due to the lower fraction of amorphous phase, as it is apparently accompanied by the increase in crystallinity of PP in that sample. The other factor which contributes to the lowering of the loss peak height is the restricted mobility of PP segments in the presence of glass fiber and the presence of a large number of small domains in the blends.

Data on composites with HDPE (Fig. 8) show that torsional storage moduli (G') for these composites are of the same order as for the composites without HDPE in the higher temperature region, but differ considerably in the lower temperature region. At lower temperatures G' is higher for composites without HDPE than the composites with HDPE. The observed difference in G' does not seem attributable to the difference in glass fiber content, since the glass fiber content in the latter class of composites is only slightly lower than in the former, particularly the sample containing 20% glass fiber. The presence of HDPE appears to lower the torsional stiffness at low temperatures; this was also the case with the blends (Fig. 7). As stated earlier, in this low temperature region, although the PP is in the glassy state, the HDPE component will be expected to be in the rubbery phase.

Furthermore, the composite sample containing 9% HDPE shows greater damping ($\tan \delta$) than the PP sample and also a shift of the T_g peak to a lower temperature. This seems to indicate that 9% HDPE has a more pronounced plasticizing effect in shear at around 0°C but not at higher temperatures. The composite sample containing 29% HDPE does not show this effect. While an explanation of this effect will require a more detailed study, the discussion of tensile properties in the next section will consider some aspects of this problem.

Tensile Properties

In the present investigations, the PP/HDPE blends have been prepared containing upto 25% by weight of HDPE, and it is observed that their tensile strength and tensile modulus show positive synergism. Since, for similar blends, this effect has already been reported by various earlier workers,⁴⁻⁶ the results are not reproduced here. The short-glass-fiber-reinforced polypropylene composite samples containing HDPE also show a similar synergistic effect in their tensile modulus and tensile strength, as shown in Figure 9. The extension at break increases with increasing HDPE content, and the area of the load elongation curve, which may be taken as an index of low frequency toughness, also increases.

The data thus indicate that the presence of small amounts of HDPE in PP results in improvement of mechanical properties not only in PP/HDPE blends but also in the PP/glass fiber/HDPE composite system. As noted from the DSC studies reported above, crystallization commences at a higher temperature and proceeds at a faster rate in the presence of HDPE and, more noticeably, in the presence of glass fibers, suggesting that the number of sites on which crystallization can occur has increased because of the very large interfacial surface that

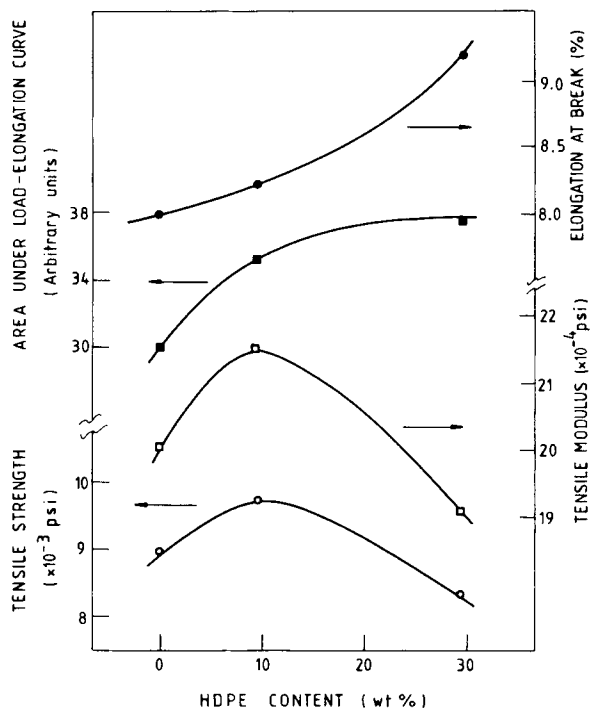


Fig. 9. Variation of the various tensile properties with HDPE content for the PP/glass-fiber composites containing HDPE.

is available having a large number of nuclei. For this reason the blend and composite samples have a much greater number of small domains. This observation, made in the case of the samples under investigation on the basis of DSC studies, is supported by the findings of a number of authors^{2,5,12-15} using other techniques. It has been observed⁵ that the presence of HDPE results in heterogeneous nucleation in the PP/HDPE blends which give rise to a large number of small spherulites of PP; at low HDPE content, small islands of HDPE of 1–2 μm size are present, while, at higher concentrations, islands of HDPE of 2–10 μm size are dispersed in the continuous matrix of PP in the blend. Alle et al.⁶ have made similar observations and have noted that the size of the dispersed droplets was 0.7–1.7 μm for 75 PP/25 HDPE blend and 2.76–4.80 μm for 25 PP/75 HDPE blend. These latter authors have also found that at PP/HDPE = 75/25, phase inversion takes place which switches the HDPE from the continuous to the discontinuous phase. They, however, add that in the 75/25 blend, both PP and HDPE appear to form cocontinuous phases and phase interconnections.

A large number of small morphological units impose more restraints on the mobility of the matrix polymer than a small number of large units. Friedrich¹⁶ has shown that coarse spherulitic morphologies in PP exhibit the lowest values in respect of yield or fracture stress and fracture toughness. He attributes this to the fact that plastic deformation is mainly concentrated on the small volume of the weak spherulite boundaries. Optimum values of fracture stress and fracture toughness were obtained from fine spherulitic polypropylene. Similar

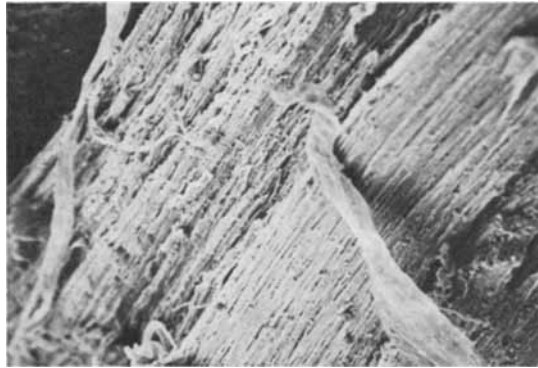


Fig. 10. Micrograph of the fractured end of a polypropylene sample ($\times 280$).

observations have been made by others for impact strength,¹⁷ ultimate tensile strength,¹⁸ and elongation at break.¹⁹ The second phase domains not only enhance yielding but can also disturb the fracture path and enhance toughness.

The fractured ends of the various samples were studied on the scanning electron microscope. In the blends, fracture involves a high amount of plastic deformation, and hence the original morphology of the injection-molded blend sample will be considerably changed by the large amount of stretch that the sample undergoes before fracture. It may be emphasized that at room temperature both PP and HDPE will deform inhomogeneously and there are considerable differences in their draw potential. As Paul has pointed out,²⁰ each component has a maximum draw ratio that can be achieved without breaks. In the absence of interaction between the components, damage will occur to one of the phases of a blend with a parallel-phase arrangement if the draw ratio used exceeds the limit for this polymer although the limit for the other polymer is not exceeded. In the composite sample, the average extension at break is of the order of 7–10%, and these samples will therefore not undergo significant structural and morphological changes on being stretched to the breaking point.

The PP fractured sample end shows, as expected, a clear cut coarse fibrillar morphology as shown in Figure 10, which is a typical micrograph. The fractured

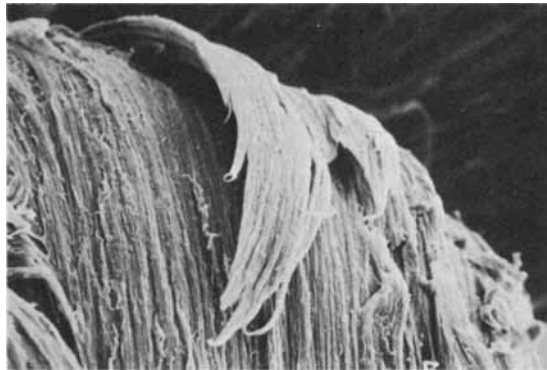


Fig. 11. Micrograph of the fractured end of a 90 PP/10 HDPE blend sample ($\times 280$).

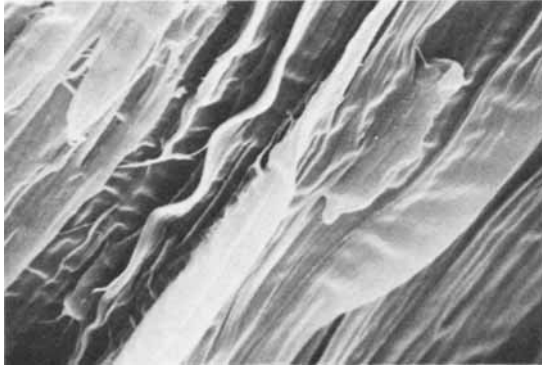
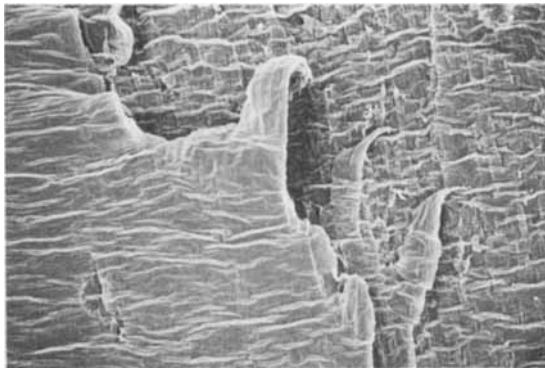
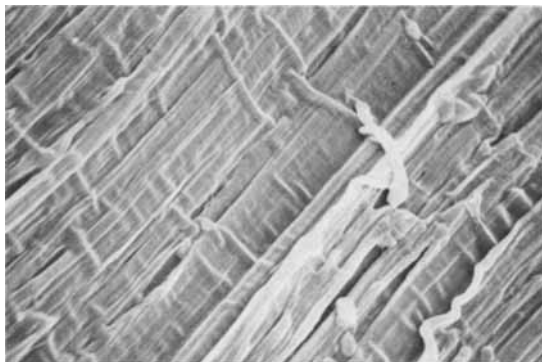


Fig. 12. Fractured end of a 75 PP/25 HDPE blend sample ($\times 4900$).

ends of the blend also show a similar fibrillar morphology (Fig. 11), but there is a tendency to form a layered structure. The fractured layer tips of a PP/HDPE blend containing 25% HDPE by weight shown in Figure 12 indicate the considerable plastic deformation at the tips and also some amount of microbuckling leading to a corrugated appearance. Striations perpendicular to the stretch

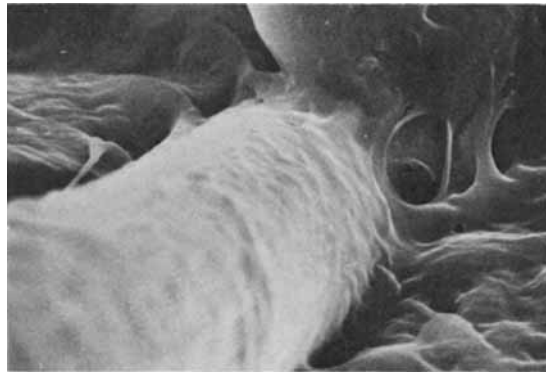


(a)

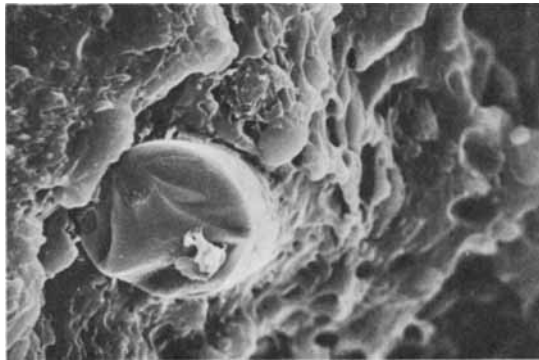


(b)

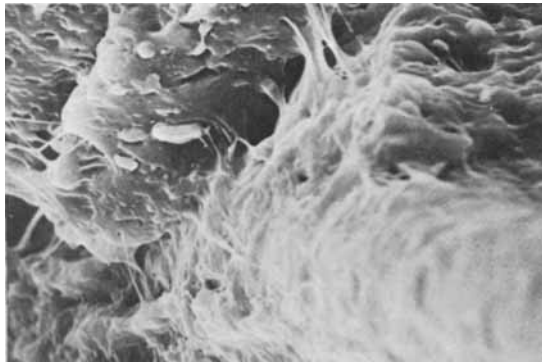
Fig. 13. Fractured ends of a 95 PP/5 HDPE blend sample: (a) $\times 490$; (b) $\times 2100$.



(a)



(b)



(c)

Fig. 14. Micrographs of fractured ends of glass-fiber-reinforced polypropylene samples containing HDPE: (a) 9% HDPE ($\times 3500$); (b) 29% HDPE ($\times 2100$); (c) 29% HDPE ($\times 2100$).

direction are also seen, and two typical micrographs are reproduced in Figures 13(a) and (b) as illustrations. Though an explanation of the mechanism of formation of these striations will require more detailed and systematic study, there would appear to be an interconnection between the corrugated layers and the presence of striations. This effect could be related to the difference in the draw ratios of the two polymers. The one which draws less will collapse while the other will continue to stretch. The micrograph shown in Figure 12 is a good illustration of inhomogeneous drawing with considerable undrawn domains.

The work of Alle et al.⁶ on PP/HDPE blend of 75/25 composition provides useful information on the possible origin of the layered structure. During melt-mixing, these authors observed that the structure was "microscopically homogeneous" while flowing through the capillary, but it formed a two-phase structure after leaving the capillary exit. Their optical micrographs show⁶ clear evidence for phase segregation along layers. In the present case, since the melt flows into a rectangular mold, the stress field and the velocity profile will be laminar, and, therefore, the laminar memory can lead to phase segregation along layers.

In the case of the glass-fiber-filled composite, the dispersed domains do not undergo large deformation, and in typical micrographs [Figs. 14(a)–(c)] they can be seen as dispersed domains or as holes from which apparently these inclusions have been plucked out. These domains have the dimensions of 1–5 μm . In the glass-fiber-reinforced polypropylene samples without HDPE, such domains are not seen.

On the basis of the DSC data and the SEM micrographs, it may be stated that in the blends and the composites containing upto 30% HDPE, a large number of HDPE domains of small size are present resulting in considerable restraints on mobility. The higher tensile strength and tensile modulus lead to higher impact strength. These studies do not include work on samples with HDPE content greater than 30%, but apparently in that case, the phase reversal is likely to occur, as pointed out by Alle et al.⁶ and the properties will then be principally governed by the HDPE which is less stiff and less strong than PP at room temperature. The synergism will thus occur only at low HDPE content.

CONCLUSION

The addition of small amounts of HDPE, glass fibers, and HDPE/glass fiber to PP results in enhancement of the rate of nucleation of PP, reduction of the size distribution of PP crystallites, and increase in crystallinity of PP. In the samples containing HDPE, the crystallinity of HDPE is reduced.

Small amounts of HDPE have a plasticizing effect on PP and PP/glass fiber systems below the glass-transition temperature of PP; the PP/HDPE and PP/HDPE/glass fiber systems show a synergistic effect in their mechanical properties at low HDPE content. The scanning electron micrographs of fractured ends of the PP/HDPE/glass fiber systems show the presence of dispersed domains in the composite samples.

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