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Impact modification of poly(butylene terephthalate) by ABS materials

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Poly(butylene terephthalate), PBT, can be impact modified by blending with appropriate ABS materials. The effect of ABS type and processing conditions on the notched Izod impact strength of PBT blends is examined in depth. Of three emulsion-made ABS materials containing 38 to 50% rubber, the one with the highest melt viscosity (50% rubber and a broad rubber particle distribution) proved the least effective for improving the impact strength of PBT when processed at high temperatures (260°C). Blends prepared in twin screw vs a single screw extruder have similar impact behavior. Melt temperatures greater than 240°C used during molding have little effect on the crystalline behaviour of PBT; however, they reduce the effectiveness of some ABS grades for impact modification. Blends moulded at higher temperatures show a coarse phase morphology with large, poorly dispersed ABS domains. PBT/ABS blends can have excellent mechanical properties in the absence of any compatibilizer; however, a compatabilizer would no doubt improve the stability of the morphology of the blends and may lessen their dependence on process conditions. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Impact modification of semi-crystalline thermoplastics such as polyamides and polyesters has received considerable attention in recent years[1-30]. A number of commercial alloys and blends have been developed, based on this class of polymers[1]. The neat polymers are ductile during tensile tests at low strain rates, i.e. with elongations at break above 50%. Usually a stable neck is formed during the extension, with considerable strain hardening occurring as the neck propagates[2]. Even at high deformation speeds, such as in Izod impact tests, both types of polymer can be ductile, depending on testing conditions. Polyamides and poly(butylene terephthalate), PBT, do not break in unnotched Izod impact tests, even at sub-ambient temperatures. On the other hand, both classes of polymer give low notched Izod impact strength[3,4] and break in a brittle fashion when standard notched specimens are tested. The large contrast between unnotched and notched Izod impact strength indicates that polyamides and PBT are fairly resistant to crack initiation but have only modest resistance to crack propagation.

PBT has become an important engineering thermoplastic because of its combination of rigidity, hardness, abrasion resistance, solvent resistance, electric insulation and short cycle times in injection moulding. The strong notch sensitivity of PBT can be eliminated by the incorporation of elastomeric impact modifiers. Several types of rubber have been used, e.g., acrylic, olefinic and dienes[3,4], emulsion-made core-shell impact modifiers[5-10], and functionalized reactive rubbers have been especially useful[11-21]. Core-shell impact modifiers have the advantage of a predetermined particle size and lead to improvement of notched impact strength of PBT, even at sub-ambient temperatures[9,10]. Polycarbonate (PC) has been incorporated as a third component in PBT/core-shell systems[22-28]; the addition of a relatively small amount of PC promotes improved dispersion in these blends by acting[28] as an interphase between the PBT matrix and the impact modifier. This leads to improved impact strength at both ambient and sub-ambient temperatures. For ternary blends containing substantial amounts of PC[23,25,27] the core-shell impact modifier particles promote yielding in the PC phase which transfers to the PBT matrix, resulting in high levels of energy dissipation.

Functionalized elastomers can, in principle, react with the PBT during processing to give a reduced or controlled rubber particle size and an improved interfacial strength. Ethylene/glycidyl methacrylate (EGMA) copolymers have been used for toughening PBT[11,12]. The epoxide group can react *in situ* with the carboxylic and hydroxy end groups of PBT during melt blending to produce grafted PBT–g–EGMA molecules which compatibilize the blend. Other rubbers containing GMA, such as EPDM–g–GMA[14,15] and poly(isoprene–co–GMA)[29], have led to toughened PBT blends by the same mechanism. Maleic anhydride containing reactive rubbers have also been used for *in situ* compatibilization of PBT/olefinic rubber blends. The addition of ethylene/propylene–g–maleic anhydride rubber (EPR–g–MA) improves PBT notched impact strength; however, its

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Table 1 Materials used in this study

		Molecular and structural characteristics							
Designation used here	Supplier designation	Rubber content (wt%)	SAN (free) mol. wt ($g mol^{-1}$)	AN content (wt%)	Graft ratio[a]	Rubber particle size (μm)	Brabender torque[b] (Nm)	Izod impact strength[c] ($J m^{-1}$)	Source
ABS-38[d]	Lustran	38	$\bar{M}_n = 59000$ $\bar{M}_w = 130000$	30	0.57	0.18	13.4	540	Monsanto
ABS-45	Starex	45	$\bar{M}_n = 35000$ $\bar{M}_w = 90000$	25	0.45	0.30	16.5	550	Cheil Industries
ABS-50	BL-65	50	$\bar{M}_n = 44000$ $\bar{M}_w = 167000$	24	0.40	0.05, 0.20[e]	23.5	520	Sumitomo-Naugatuck
PBT	Valox 315		$\bar{M}_n = 35000$			$\bar{M}_w = 100000$	7.0	50	General Electric
Valox 310	Valox 310		$\bar{M}_n = 30000$			$\bar{M}_w = 70000$	6.0	50	General Electric

[a] See Experimental section for definition of graft ratio
[b] Values taken at 250°C and 50 r.p.m., after 10 min
[c] Room temperature notched Izod impact
[d] All the ABS grades were designated by their weight percent rubber
[e] Bimodal particle size distribution

performance depends on processing conditions[19]. It has been shown that there is a critical interparticle distance below which EPR-g-MA promotes toughening of PBT[21]. However, epoxide functionality appears to be more effective in PBT blend modification than anhydride functionality.

Acrylonitrile–butadiene–styrene, ABS, materials have been widely used as impact modifiers for engineering polymers[2,4,30]. The use of ABS for impact modification of PBT has been reported by a number of investigators, with varied success[6,8,9,31,32]. Some PBT/ABS blends are available commercially[1,4]. Recently, Lee and collaborators[32] explored the use of a reactive styrene–acrylonitrile–GMA terpolymer as a compatibilizer for PBT/ABS blends. However, no significant improvement of toughening was achieved. Extremely tough PBT/ABS blends containing no compatibilizer or reactive component have been reported[6,9]. Weatherable analogues of ABS, e.g. acrylonitrile–styrene–acrylate or ASA materials, have also been blended with PBT[33]. It was found that the notched impact strength of PBT/ASA blends significantly decreased as the mixing temperature was increased, presumably due to PBT degradation at elevated temperatures.

Because a wide range of properties has been reported for PBT/ABS blends, it would be instructive to examine carefully the factors that influence the mechanical behaviour of these blends. Accordingly, it is the purpose of this paper to explore the effect of ABS type, concentration, processing conditions and resulting blend morphology on the performance of PBT/ABS blends. It will be shown that very tough blends can be achieved using certain high rubber content ABS materials at well-controlled processing conditions.

EXPERIMENTAL

Table 1 describes the PBT and ABS materials used in this study. The rheological behaviour of each material was characterized by Brabender Plasticorder torque measurements at 50 rpm, using a 50 ml mixing bowl at the temperatures indicated. The two commercial PBT materials were obtained from General Electric and differ primarily in their molecular weight characteristics. Valox 315 was used as the PBT material except where noted otherwise. The three grades of ABS were obtained from different sources and are designated here by their weight percentage of rubber. These materials are synthesized by emulsion polymerization and thus have small rubber particles in the range of 0.05 to 0.3 μm. ABS-50 has a broad particle size distribution, while the other two are substantially monodisperse. These materials are intermediates for producing moulding and extrusion grade ABS by diluting with additional SAN. High-rubber ABS may be used as an impact modifier for a number of engineering thermoplastics.

The graft ratio of the present ABS materials ranges from 0.4 to 0.57, as determined by the supplier. Graft ratio is determined by dispersing a sample of the ABS typically in methyl ethyl ketone and determining the gel fraction that contains all of the rubber and the grafted SAN; the ungrafted SAN polymer remains in solution. The graft to rubber ratio is calculated as follows:

$$\text{Graft ratio} = \frac{\text{wt\% gel} - \text{wt\% rubber}}{\text{wt\% rubber}}$$

From such information the ratio of grafted to ungrafted SAN can be determined.

Table 2 provides information about the processing conditions and equipment used to prepare PBT blends with the various ABS materials. The single screw extruder has an intensive mixing head but generally does not provide as effective mixing as does the twin screw extruder. The range of processing temperatures used represents the extremes of permissible extrusion and moulding temperatures for PBT; the lower temperature limit is fixed by the melting point while the upper temperature is a limit set by thermal degradation as recommended by the supplier. Both absolute and relative viscosities of the components vary significantly with temperature in this range, which affects blend morphology and properties. The temperature profiles for each extruder and the injection moulding machine were kept flat along the barrel. All materials were pre-dried for a minimum of 16 h at 60°C in a vacuum oven before melt processing. The blend components were intensively mixed in powder form prior to the extrusion process. Blends were moulded into dog-bone shaped tensile specimens (ASTM D638, type I) and standard Izod

Table 2 Processing conditions used to prepare PBT/ABS blends

Extrusion conditions			Moulding[c] conditions
Extruder	R.p.m.	Temperature (°C)	Melt temperature (°C)
Twin screw[a]	170	220	240
		220	250
		220	260
		250	240
		260	240
Single screw extruder[b]	30	230	240
		230	250
		230	260
		250	240
		260	240

[a] Baker-Perkins co-rotating, fully intermeshing twin screw extruder ($D = 15\,\mathrm{mm}$), residence time 20 s

[b] Killion single screw extruder ($L/D = 30$, $D = 2.54\,\mathrm{cm}$) outfitted with a high intensity mixing screw, residence time 2 min

[c] Arburg Allrounder injection moulding machine, mould temperature = 50°C, injection and holding pressure = 50 bar, injection time = 3 s

bars of 3.13 mm thickness. The mould temperature was kept constant at 50°C.

Notched Izod impact tests were conducted according to ASTM D256 as a function of temperature to determine the location of the ductile-to-brittle transition. At least five samples each from the gate and far ends of the Izod bars were tested at room temperature and in the temperature region of the ductile–brittle transition; at other temperatures fewer samples were tested, the exact number being dictated by the consistency observed. The standard deviation of impact strength among multiple samples was typically $15\,\mathrm{J\,m^{-1}}$ in the brittle region, $30\,\mathrm{J\,m^{-1}}$ in the fully ductile region, with, of course, higher variability in the transition region. Only gate-end information is reported here, since differences between gate- and far-end specimens were typically insignificant.

An Instron was used for tensile testing in accordance with ASTM D638 at a crosshead speed of $5.08\,\mathrm{cm\,min^{-1}}$. An extensometer strain gauge with a 5.08 cm gap was used to obtain the modulus and yield stress values. A Perkin-Elmer DSC-7 equipped with a thermal analysis data station was used to measure the thermal properties of the samples. The samples were first heated from −10°C up to 250°C and then cooled to −10°C, followed by a second heating. All runs were made at a rate of $20\,^{\circ}\mathrm{C\,min^{-1}}$.

The morphology of selected blends was examined using a JEOL JEM 200 CX transmission electron microscope (TEM) at an accelerating voltage of 120 kV. Ultrathin sections were obtained by cryo-microtoming samples from moulded Izod bars, using a Riechert-Jung Ultracut E microtome at −45°C. No significant differences in morphology were observed between sections taken from the gate vs far ends, the centre vs near the surface, or those oriented perpendicular vs parallel to the flow direction. To be consistent, all photomicrographs shown here correspond to sections taken from the centre of the gate end of the Izod bar and perpendicular to the direction of flow. Thin sections (15–20 nm thick) were stained with RuO_4 vapour for a maximum of 20 min. The ABS and rubber phases of ABS are stained under these conditions and appear as dark domains in the TEM images.

RESULTS AND DISCUSSION

Effect of ABS type on impact behaviour

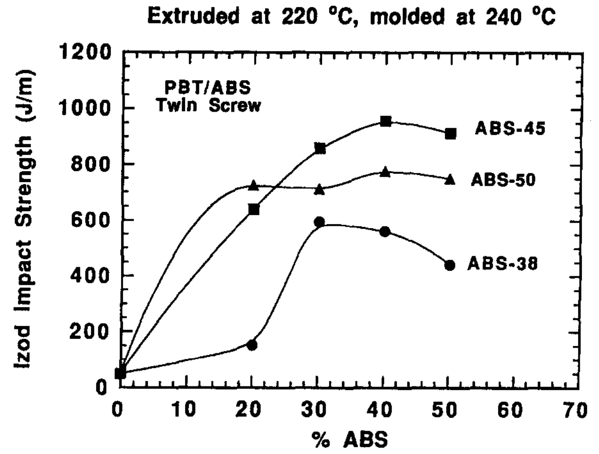


Figure 1 Room temperature notched Izod impact strength as a function of ABS type and content for blends with PBT prepared in a twin screw extruder at 220°C and moulded at 240°C

Table 3 Tensile properties of PBT/ABS blends[a]

PBT/ABS blend (wt/wt)	Tensile modulus (GPa)	Yield strength (MPa)	Elongation at break (%)
100/0	2.4 ± 0.21	48 ± 0.3	165 ± 58
PBT/ABS-38			
80/20	2.1 ± 0.16	41 ± 0.2	48 ± 21
70/30	2.1 ± 0.08	39 ± 0.1	59 ± 28
60/40	1.7 ± 0.03	36 ± 0.3	114 ± 45
50/50	1.7 ± 0.08	34 ± 0.1	35 ± 21
PBT/ABS-45			
80/20	1.9 ± 0.09	39 ± 0.1	76 ± 35
70/30	1.7 ± 0.10	36 ± 0.1	110 ± 59
60/40	1.5 ± 0.09	31 ± 0.1	300 ± 97
50/50	1.3 ± 0.06	28 ± 0.2	248 ± 69
PBT/ABS-50			
80/20	1.9 ± 0.36	39 ± 1.1	110 ± 62
70/30	1.8 ± 0.30	36 ± 0.2	176 ± 1.28
60/40	1.5 ± 0.08	33 ± 0.2	62 ± 21
50/50	1.4 ± 0.06	29 ± 0.3	65 ± 17

[a] All blends were prepared in the twin screw extruder at 220°C and molded at 240°C. Five specimens of each sample were tested at $5.08\,\mathrm{cm\,min^{-1}}$

The room-temperature notched Izod impact strength of PBT (Valox 315) blends with the three ABS materials is shown in *Figure 1* as a function of weight percentage of ABS. The blends were mixed in the twin screw extruder at 220°C and moulded at 240°C. All three grades of ABS lead to significantly improved impact strength; above 30 wt% ABS all blends consistently failed in a ductile manner. The ABS material with the lowest rubber content, ABS-38, gives lower impact strength at all compositions studied. However, ABS-50, which has the highest rubber content, does not show the highest impact strength for these blends. Issues other than rubber content of the ABS material appear to affect the impact strength. It has been shown[24,26,34] that the main toughening mechanism for blends of PBT with impact modifiers involves cavitation of rubber particles which triggers extensive shear yielding in the PBT matrix. Rubber particle size and its distribution plus the morphology of the ABS/PBT mixture all can affect the level of toughening achieved.

Table 3 shows the tensile properties for the various PBT/ABS blends. The presence of ABS reduces tensile modulus and yield strength of PBT. Blends based on

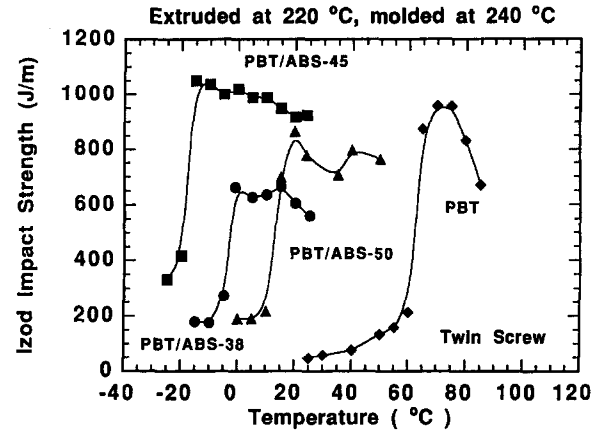


Figure 2 Effect of temperature on notched Izod impact strength for blends containing 40 wt% ABS. The blends were prepared at 220°C in a twin screw extruder and moulded at 240°C. Results for PBT are shown for comparison

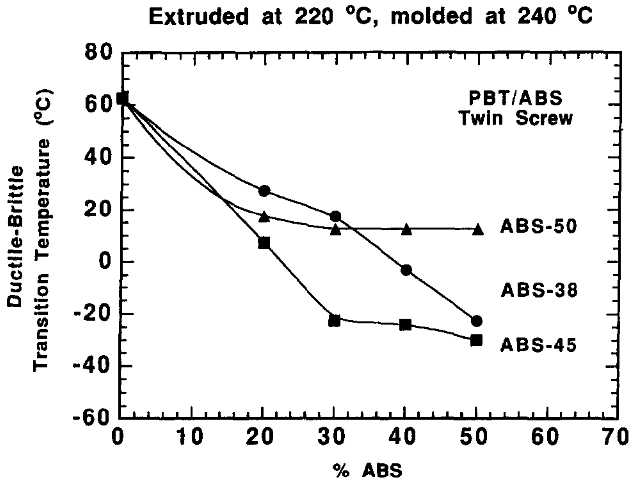


Figure 3 Effect of ABS content and type on the ductile–brittle transition temperature of PBT/ABS blends prepared in the twin screw extruder at 220°C and moulded at 240°C

ABS-38 exhibit the highest tensile modulus and yield strength; however, their elongation at break is the lowest which is consistent with the lower impact strength of their blends. Blends based on ABS-45 and ABS-50 have similar tensile behaviour; however, blends based on ABS-45 have significantly higher elongation at break for some compositions.

The effect of temperature on the impact behaviour is of great practical concern since many applications of engineering thermoplastics require high ductility at subambient temperatures. *Figure 2* shows impact strength as a function of temperature for blends containing 40 wt% ABS. The impact behaviour of pure PBT is included to show that this material becomes supertough just above its T_g. Blends based on ABS-45 are supertough down to −20°C; even below this temperature, the impact strength of these blends is considerably higher (~200 J m^{-1}) than that of PBT at room temperature. Blends with the high rubber content ABS-50 lose their supertough character just below room temperature. The ductile–brittle transition temperatures for PBT/ABS blends are shown in *Figure 3*. Blends based on ABS-38 show a continuous decrease in the ductile–brittle temperature as a function of ABS content, while blends based on ABS-50 have ductile–brittle temperatures just below room temperature for all compositions. Blends based on ABS-45 exhibit low ductile–brittle transition temperatures for all compositions (8°C to −30°C), which are only slightly influenced by ABS concentrations above 30 wt%.

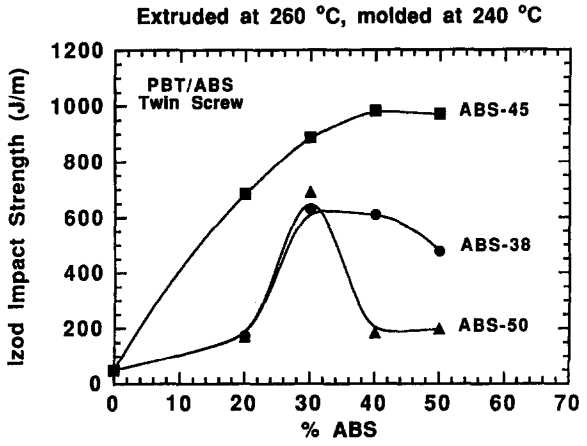


Figure 4 Notched Izod impact strength as a function of ABS content and type for PBT/ABS blends prepared in a twin screw extruder at 260°C and moulded at 240°C

Effect of processing conditions

Processing conditions during compounding and moulding may be important factors affecting the resulting performance of polymer blends. Phase morphology can be significantly influenced by rheological characteristics and shear conditions during both mixing and moulding, particularly for non-compatibilized systems. Various modes of interfacial reactions and degradation of the components may also be caused by excessively severe processing conditions. The performance of toughened PBT has been shown to be especially affected by changes in fabrication temperature[19,31].

Extrusion temperature. Figure 4 shows the Izod impact strength of PBT/ABS blends compounded in the twin screw extruder at 260°C, which may be compared with the same compositions extruded at 220°C (*Figure 1*); the moulding temperature was kept constant at 240°C for all blends. The change from 220 to 260°C during melt extrusion does not significantly affect the impact strength for blends based on ABS-38 and ABS-45; however, blends containing 20, 40 and 50 wt% ABS-50 show significantly lower impact strength compared to the same blends prepared at 220°C. Surprisingly, such a decrease is not seen for blends containing 30 wt% ABS-50. As seen in *Figure 5*, these impact strength results correlate well with blend morphology changes due to changes in blending temperature for two selected blend compositions. Blends containing 40 wt% ABS-50 show better dispersion of the ABS phase when mixed at 220°C, *Figure 5c*, than at 260°C, *Figure 5d*. However, for blends containing 30 wt% ABS-50 the morphologies are quite similar at the two mixing temperatures. As seen in *Figure 6*, a low extrusion temperature leads to lower ductile–brittle transition temperatures for 40 wt% ABS-50 blends. At 260°C the ductile–brittle temperature is just above room temperature. The proximity of the ductile–brittle transition to room temperature for 260°C blends may be why the small morphology differences shown in *Figures 5c* and *d* for 40 wt% ABS apparently have such a large effect on room-temperature toughness.

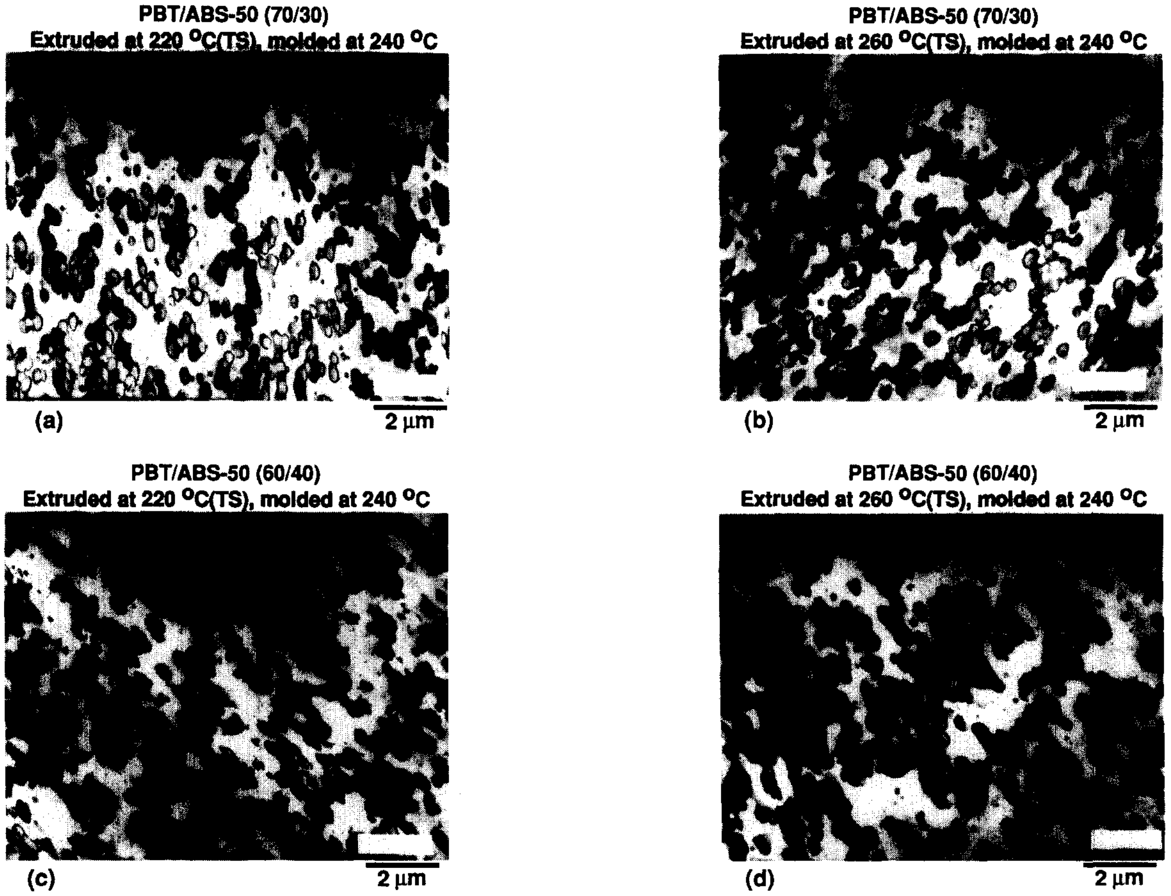


Figure 5 TEM photomicrographs of PBT/ABS-50 blends prepared at different temperatures in a twin screw extruder and moulded at 240°C: (a) 30% ABS at 220°C; (b) 30% ABS at 260°C; (c) 40% ABS at 220°C; (d) 40% ABS at 260°C. The ABS phase is stained dark by RuO_4

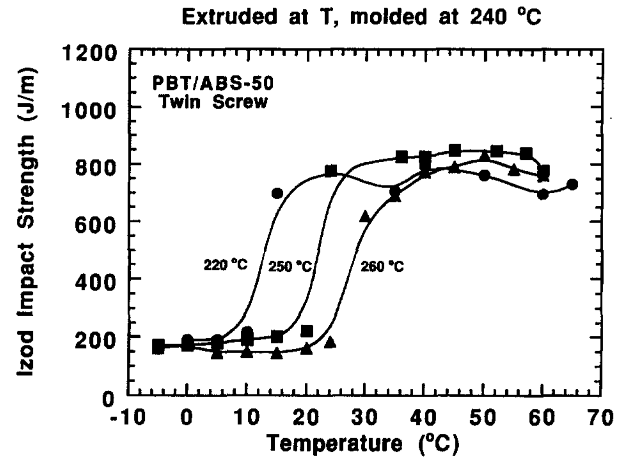


Figure 6 Effect of temperature on notched Izod impact strength of PBT/ABS-50 blends (60/40). Blends were prepared in a twin screw extruder at various temperatures and moulded at 240°C

Extruder type. Twin screw extruders are frequently preferred for compounding polymer blends because they generally can provide more effective mixing than single screw extruders. Furthermore, twin screw extruders are more versatile since their screw design can be conveniently altered to optimize mixing for a given system. On the other hand, single screw extruders are generally less expensive and more readily available for commercial purposes. Thus, it is important to know to what extent extruder type affects blend morphology and performance.

Figure 7 shows impact strength as a function of ABS content for PBT blends prepared in the single screw extruder at low (230°C) and high (260°C) melt mixing temperatures. These results can be compared with data for the same compositions prepared in the twin screw extruder at low (*Figure 1*) and high (*Figure 4*) melt extrusion temperatures. The effects of both extruder type and extrusion temperature depend significantly on which ABS materials are being compared. For ABS-38 and ABS-45, the toughness is nearly independent of extrusion temperature when the blends are prepared in the twin screw extruder. At the low extrusion temperature, the results for these materials are very similar regardless of whether the blends are prepared in the twin or single screw extruder. At the high extrusion temperature, more ABS material must be added to obtain toughness when using the single screw extruder compared to the twin screw extruder. For ABS-50, the best results are obtained using the low extrusion temperature in the twin screw extruder and the poorest results are seen at the high extrusion temperature in the single screw extruder. The performance of PBT blends with this material is more sensitive to processing conditions than is observed for the other two ABS materials.

Figure 8 shows the effect of extrusion temperature on the morphology of PBT/ABS-50 blends prepared in the single screw extruder. At the low extrusion temperature, ABS-50 is relatively well dispersed in the PBT matrix; the ABS-50 domains are sufficiently small that only a few rubber particles are located in each domain. At the high extrusion temperature the dispersion is poorer; the ABS-50 domains are considerably larger and contain many

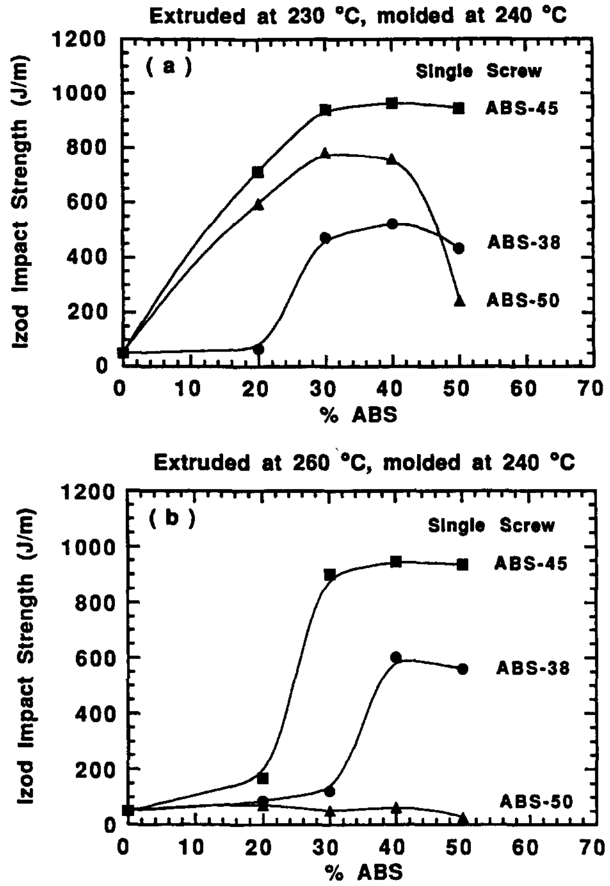


Figure 7 Notched Izod impact strength of PBT/ABS blends prepared in a single screw extruder at (a) 230°C and (b) 260°C and moulded at 240°C

rubber particles. At high ABS-50 contents there is a tendency for cocontinuity of both phases. This effect of the temperature of extrusion compounding on morphology is entirely consistent with the observations on toughness discussed above. When the mixing intensity is held constant, the size of the dispersed phase in a blend is influenced primarily by the absolute viscosity of the matrix phase and the ratio of the viscosity of the dispersed phase to that of the matrix[35]. The degree of dispersion is the poorest when the matrix viscosity is low and the viscosity ratio is far from unity. Brabender torque measurements are used here to compare the melt viscosities of PBT and the different grades of ABS materials.

Figure 9 shows torque as a function of fluxing time in the Brabender for each ABS grade and PBT at 235°C and 260°C. As time increases, the torque decreases as the materials are fluxed and approach the set temperature of the Brabender mixing bowl, and then tends to level off at around 10 min. *Table 4* shows the torque values taken at 10 min for all materials at different temperatures. As the melt temperature goes up, the melt viscosity of PBT decreases significantly and the difference between PBT and ABS viscosities becomes larger. The significant drop in the Brabender torque for PBT at 260°C may reflect some thermal degradation, mainly because the torque curve does not seem to level off after 10 min in comparison with the ABS materials; see *Figure 9b*. The ABS/PBT torque ratio is also shown in *Table 4* to quantify the effect of temperature on the ratio of ABS and PBT melt viscosities. For all melt temperatures the ratio of torques (or melt viscosities) for ABS/PBT rank as follows:

ABS-50 > ABS-45 > ABS-38

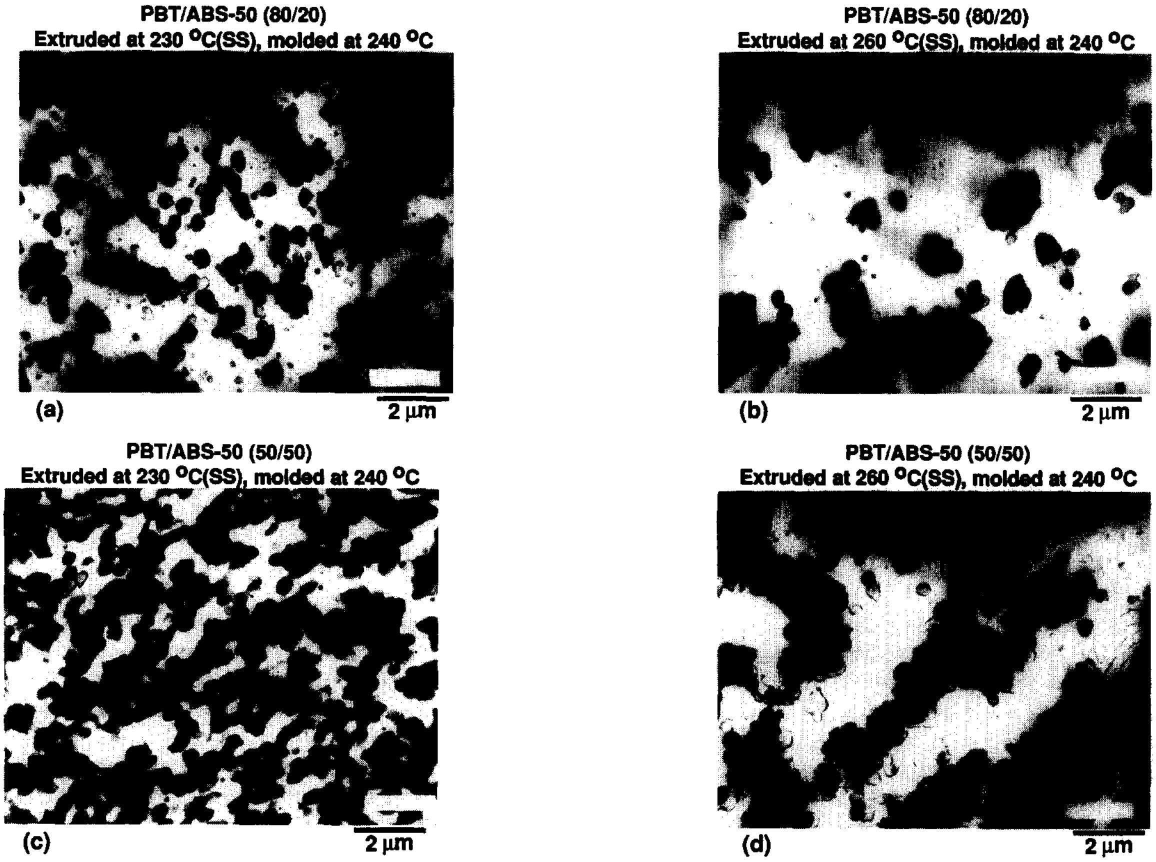


Figure 8 TEM photomicrographs of PBT/ABS-50 blends prepared in a single screw extruder at different temperatures and moulded at 240°C: (a) 20% ABS at 230°C; (b) 20% ABS at 260°C; (c) 50% ABS at 230°C; (d) 50% ABS at 260°C. The ABS phase is stained dark by RuO_4

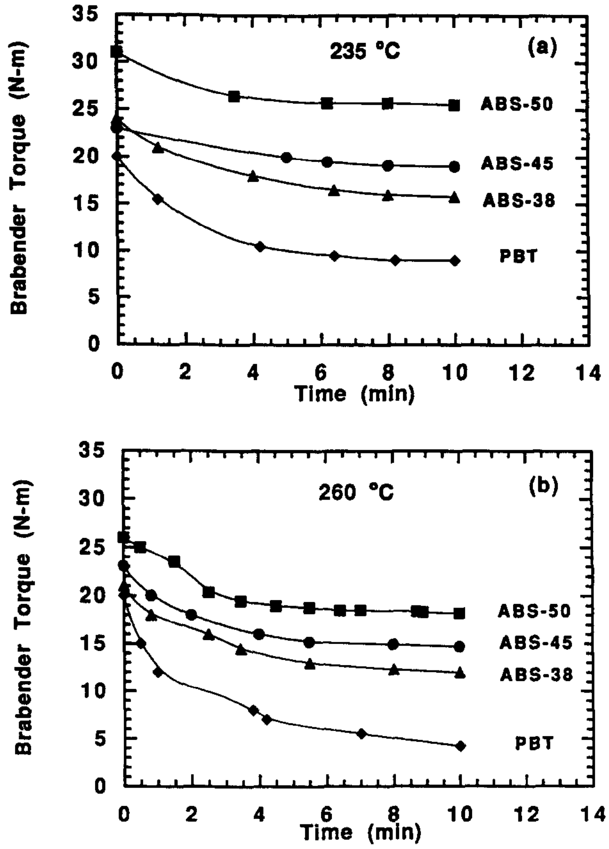


Figure 9 Brabender torque at 50 r.p.m. of PBT (Valox 315) and ABS materials as a function of time at (a) 235°C and (b) 260°C

Table 4 Brabender torque for PBT and ABS at 50 r.p.m.[a]

	Torque[a] (Nm)			ABS/PBT torque ratio		
	Temperature (°C)			Temperature (°C)		
	235	250	260	235	250	260
PBT	9.0	7.0	4.2	–	–	–
ABS-38	15.8	13.4	12.0	1.8	1.9	2.7
ABS-45	19.0	16.5	14.7	2.2	2.4	3.3
ABS-50	25.5	23.5	18.2	2.8	3.4	4.5

[a] Brabender torque measurements taken after 10 min

which coincidentally corresponds to the same order as the rubber content of these ABS materials. Since the viscosity of PBT decreases and the ABS/PBT viscosity ratio increases with increasing melt temperature, one can expect that the ABS dispersion in the PBT matrix will become poorer as the extrusion temperature goes up. The mixing conditions in a twin screw extruder diminish the effects of these rheological changes relative to what is found in a single screw extruder. The higher viscosity of ABS-50 indicates that it should be the most difficult to disperse in PBT. However, it is important to note that a variety of other factors can contribute to how blend performance varies among these ABS materials; e.g. rubber content, rubber particle size, particle size distribution, extent of SAN grafting to the rubber, SAN molecular weight, etc.

As seen in *Figure 10*, blends containing 40 wt% of ABS-38 and ABS-45 show similar morphologies at low and high extrusion temperatures when prepared in the twin screw extruder. On the other hand, similar blends based on ABS-50 have a coarser disperse phase morphology, as seen in *Figures 5c* and *d*. Clearly, rheological characteristics are a contributing factor but may not be the only issue, as mentioned above.

Moulding conditions. The mechanical properties of injection moulded semicrystalline thermoplastic polymers may depend on moulding conditions. For example, melt temperature affects flow properties during mould filling and to some extent the crystallization process, for a fixed mould temperature, during cooling. Moulding conditions can influence the crystalline microstructure and the percentage of crystallinity; as a result, mechanical behaviour can be altered. The tensile properties of PBT have been shown to be affected by melt temperature during injection moulding[36]. As the melt temperature is increased for a constant mould temperature, the elongation at break is reduced and its characteristic double yielding behaviour[37,38] disappears. In addition to the obvious changes in the mechanical behaviour that can result when PBT is blended with another polymer, the second component can affect the PBT crystallization process and the properties of the PBT phase. In addition, melt temperature can also affect the blend phase morphology and, thus, the blend mechanical properties. A lack of stability of the phase morphology generated during mixing can lead to major morphological changes during injection moulding. An increase in melt temperature during the moulding process may accelerate the change in blend morphology prior to and during mould filling.

Figure 11 compares the notched Izod impact strength as a function of ABS content for various PBT/ABS blends prepared in the twin screw and single screw extruders at 220°C and 230°C, respectively, and moulded at 260°C; in most cases, the properties of the blends prepared in the twin screw extruder are slightly better. Increasing the moulding temperature from 240°C—see *Figures 1* and *7a*—to 260°C leads to a significant reduction in toughness for some compositions and especially those based on ABS-50. The latter blends show low impact strength with brittle failure for all compositions. *Figure 12* shows the ductile–brittle transition behaviour for PBT/ABS blends prepared in the twin screw extruder at 220°C and moulded at 260°C. The curves show similar trends as in *Figure 3* for the same blends moulded at 240°C; however, the high moulding temperature shifts the ductile–brittle transition temperatures to higher values, as seen in *Table 5*. The shift in the ductile–brittle transition temperature is of the order of 5 to 25°C depending on ABS type and blend composition. Therefore, some PBT/ABS blends may have their impact behaviour changed from ductile to brittle at room temperature by increasing the moulding temperature from 240°C to 260°C.

The effect of moulding temperature on the melting and crystallization behaviour of PBT is shown in *Table 6*. No major differences are observed in the melting and crystallization parameters of PBT as the melt temperature is increased; there is a slight increase in the percentage of crystallinity of PBT observed in the first heat, for samples moulded at 260°C. This change might be expected due to the larger difference between the melt and the mould temperatures for moulding at 260°C, as compared to moulding at 240°C; this allows more time for the PBT to crystallize during cooling. Another possibility for the slight increase in PBT crystallinity

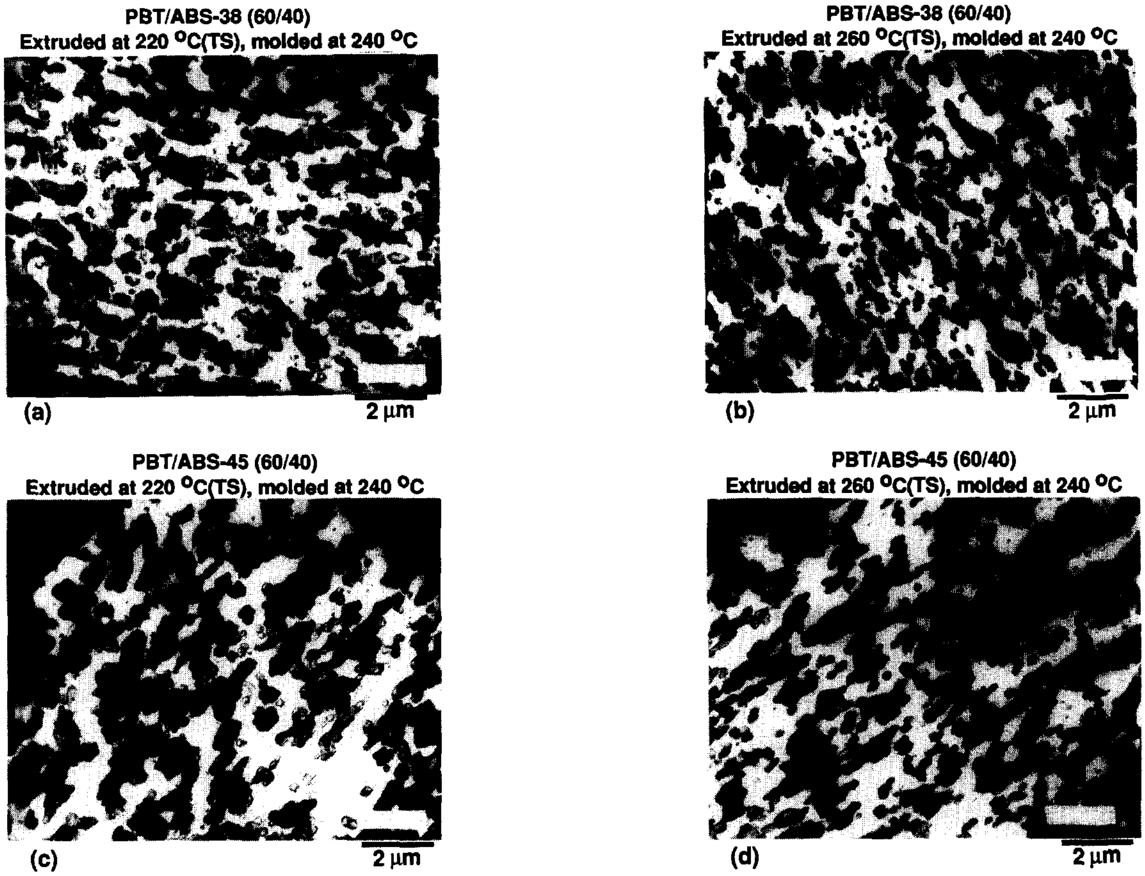


Figure 10 TEM photomicrographs of PBT/ABS blends containing 40% ABS prepared in a twin screw extruder at different temperatures and molded at 240°C: (a) ABS-38 at 220°C; (b) ABS-38 at 260°C; (c) ABS-45 at 220°C; (d) ABS-45 at 260°C

Table 5 Ductile–brittle transition temperatures for PBT/ABS blends prepared in the twin screw extruder and moulded at different temperatures

PBT/ABS blend[a] (wt/wt)	Ductile–brittle transition temperature (°C)[b] Moulding temperature 240°C	260°C
PBT/ABS-38		
80/20	28	38
70/30	18	33
60/40	−3	18
50/50	−13	3
PBT/ABS-45		
80/20	8	23
70/30	−23	3
60/40	−24	−18
50/50	−30	−23
PBT/ABS-50		
80/20	13	33
70/30	18	43
60/40	13	27
50/50	13	38

[a] Blends prepared in the twin screw extruder at 220°C

[b] The ductile–brittle transition temperature was taken as the mid-point of the step-like change in the Izod impact strength vs temperature curve

may be a reduction in the molecular weight of PBT due to some thermal degradation at the higher moulding temperature. A decrease in the molecular weight of PBT should increase the rate of crystallization, thereby leading to a higher degree of crystallinity.

The presence of different grades of ABS has no significant effect on the main melting peak temperature during first and second heats for both moulding temperatures. PBT usually shows a minor melting peak for samples crystallized in the DSC at specific cooling rates[10], as can be seen in *Figure 13*. The minor melting peak temperature of the PBT phase was slightly affected for blends based on ABS-45. All ABS types promote a reduction in the crystallization peak temperature for the blends during cooling, compared to neat PBT. This may be an indication that ABS delays PBT crystallization in the blends. However, the proposed delay does not suppress the PBT crystallinity, as can be observed during the second heat in *Table 6*. The most significant change in PBT crystallization was found for blends based on ABS-50. A large increase in PBT crystallinity is observed for blends with high ABS-50 contents. This effect is more accentuated for higher moulding temperatures. Considering that all processing parameters were held constant, the presence of the highly viscous ABS-50 may have generated thermal degradation of the PBT phase during the compounding and moulding processes. As mentioned earlier, a reduction in the molecular weight of PBT would be expected to increase both the rate of crystallization and the final degree of crystallinity.

Figure 14 shows TEM photomicrographs for PBT/ABS blends moulded at 260°C. By comparing *Figure 14a* with *Figure 10a*, and *Figure 14b* with *Figure 10c*, it can be concluded that the melt temperature during moulding, within this range, has no significant effect on morphology for blends based on ABS-38 and ABS-45. This observation is consistent with the lack of change found in

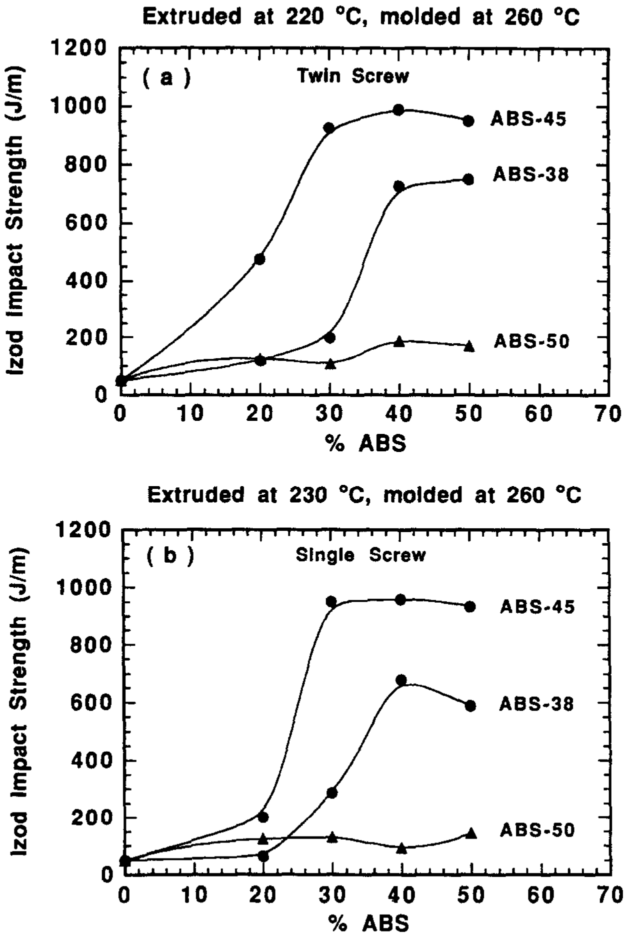


Figure 11 Notched Izod impact strength as a function of ABS content and type for blends with PBT prepared in (a) the twin screw extruder at 220°C and (b) the single screw extruder at 230°C and moulded at 260°C

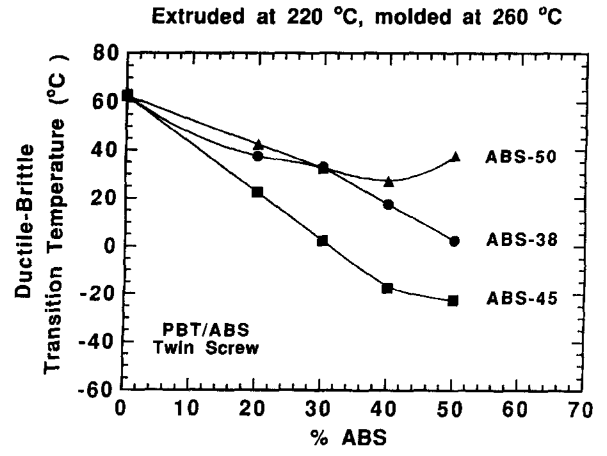


Figure 12 Effect of ABS content and type on the ductile–brittle transition temperature for PBT/ABS blends prepared in the twin screw extruder at 220°C and moulded at 260°C

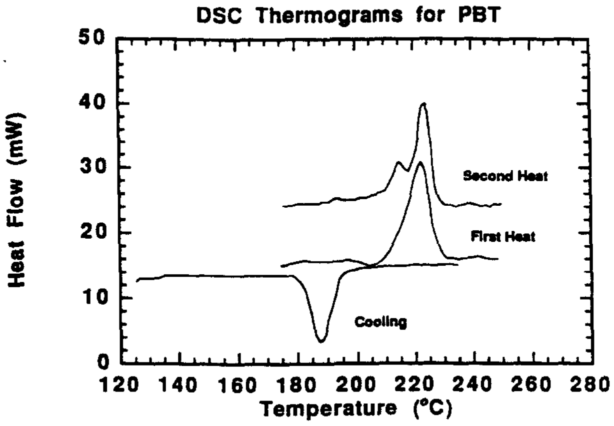
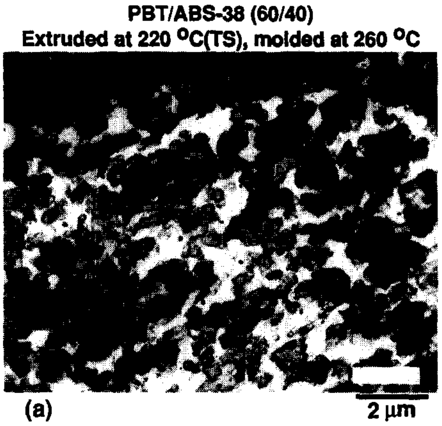


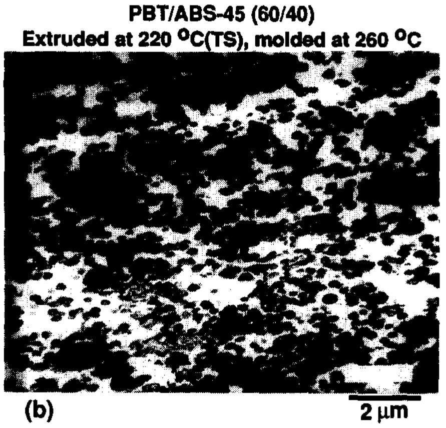
Figure 13 Typical d.s.c. thermograms for PBT during first heat, cooling and second heat

Table 6 Effect of moulding conditions on PBT/ABS thermal properties

PBT/ABS blend (wt/wt)	First heat: Peak temp. (°C) A[a]	First heat: Peak temp. (°C) B[b]	First heat: PBT[c] cryst. (%) A	First heat: PBT[c] cryst. (%) B	Cooling: Peak temp. (°C) A	Cooling: Peak temp. (°C) B	Cooling: Heat[d] of crystallization ($J g^{-1}$) A	Cooling: Heat[d] of crystallization ($J g^{-1}$) B	Second heat: Main peak (°C) A	Second heat: Main peak (°C) B	Second heat: Minor peak (°C) A	Second heat: Minor peak (°C) B	Second heat: PBT cryst. (%) A	Second heat: PBT cryst. (%) B
100/0	223	223	28	30	186	186	44	45	224	223	214	214	24	25
PBT/ABS-38														
80/20	223	222	27	30	181	182	43	44	223	222		211	23	25
60/40	222	223	28	31	183	180	43	44	223	224	213	212	23	25
50/50	222	223	29	31	179	179	40	42	222	223	211	211	25	24
PBT/ABS-45														
80/20	222	223	29	32	187	187	44	46	222	224	215	213	26	25
60/40	222	222	26	31	181	182	43	44	223	223	217	211	23	24
50/50	222	223	27	32	180	180	44	47	222	223	216	210	25	26
PBT/ABS-50														
80/20	223	223	31	32	183	183	46	46	223	223	212	212	27	25
60/40	223	223	32	34	182	182	47	46	223	223	212	211	27	27
50/50	223	223	35	39	182	182	49	51	223	223	212	210	29	30

[a] Blends prepared at 220°C and moulded at 240°C
[b] Blends prepared at 220°C and moulded at 260°C
[c] Heat of fusion of $142 J g^{-1}$ for 100% crystalline PBT was used to calculate the percentage of crystallinity of PBT in the blends
[d] Heat of crystallization for PBT in the blends





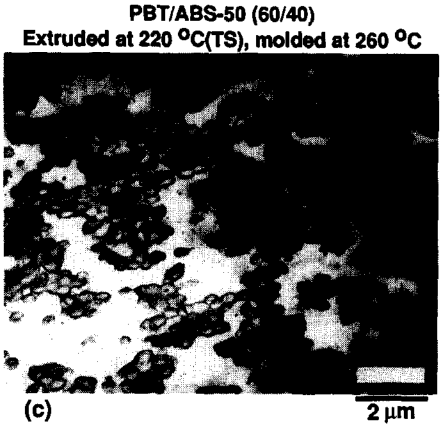


Figure 14 TEM photomicrographs of PBT/ABS blends prepared in the twin screw extruder at 220°C and moulded at 260°C containing: (a) 40% ABS-38; (b) 40% ABS-45; (c) 40% ABS-50

impact behaviour with moulding temperature. However, for ABS-50-based blends an increase in the moulding temperature leads to poorer dispersion of the ABS phase in the PBT matrix. This behaviour can be easily seen by comparing *Figure 14c* with *Figure 5c*; this may be attributed to a lack of stability of phase morphology for PBT/ABS-50 blends prepared at 220°C. PBT blends containing 40 wt% of ABS moulded at 240°C show no significant change in the degree of dispersion of the ABS phase in the PBT matrix, as seen in *Figures 5c*, *10a* and *10b*. However, blends of PBT with 40 wt% ABS-50 moulded at 260°C show large ABS domains due to coalescence, as seen in *Figure 14c*. The coarsening of morphology for this blend leads to a significant change in its impact behaviour, as seen in *Figure 11*.

The effect of poor morphology stability for PBT/ABS blends can be clearly observed for all ABS grades at lower contents. *Figure 15* shows TEM photomicrographs for blends of PBT containing 20 wt% ABS moulded at low and high temperatures. Even for blends based on ABS-45, whose properties are not much affected by processing conditions, a decrease in the degree of dispersion of ABS in the PBT matrix can be observed, as seen in *Figures 15c* and *d*. The coarsening of phase morphology due to lack of stability is more evident for blends based on ABS-50, as seen in *Figures 15e* and *f*. For these blends, a more stable morphology might be achieved by using some compatibilization process during compounding.

Evidence for degradation. Chemical reactions of components in some polymer blends, particularly at extreme processing conditions, can have a detrimental influence on properties. This can be quite a serious issue for blends of ABS with polycarbonate (PC)[39,40]. For example, polycarbonate blends with the same ABS-50 used in this work[41] were found to have poor mechanical properties, and the cause was traced to rapid degradation of the PC matrix during melt blending. The PC molecular weight was estimated by exposing the blend to methylene chloride, recovering the soluble portion (mostly PC), and determining its intrinsic viscosity. The intrinsic viscosity of the recovered PC was reduced by 40% due to melt blending with ABS-50. It was disclosed by the manufacturer that ABS-50 is not recommended for blending with PC because of its high alkaline electrolyte and residual chemical content that can cause PC to degrade at high melt temperatures.

Of the three ABS types used here, blends of PBT and ABS-50 appear to have the least desirable properties. It was postulated that the contaminants in ABS-50 from its manufacturing process that cause degradation of PC may lead to analogous reactions for PBT/ABS-50 blends. The limited solvent choices for PBT made solvent extraction and subsequent intrinsic viscosity determination an unattractive option for exploring this hypothesis. As an alternative, Brabender torque rheometry was used to examine the rheological behaviour of certain blends in some detail. Blends of PBT/ABS 70/30 at 260°C (the highest processing temperature) were prepared in the Brabender to examine how each ABS type affects the torque response. Additionally, previously extruded and moulded tensile bars of PBT/ABS 60/40 blends were ground and fluxed in the Brabender mixer at 235°C to assess the effect of the prior extrusion and moulding history on blend rheology.

Figure 16a shows the torque behaviour for a PBT/ABS-50 70/30 blend. Responses for pure PBT and ABS-50 are shown for reference. The blend torque approaches that of the PBT. Comparing these data with similar experiments for the other two ABS materials in *Figures 17a* and *18a*, it is evident that ABS-50 causes a greater reduction in blend torque, relative to pure PBT, than any of the other ABS materials. This could be taken as evidence of greater degradation in molecular weight of the PBT matrix. *Figure 16b* shows the torque behaviour of regrind from test bars of PBT/ABS-50 60/40 blends as a function of process conditions used originally to produce these materials. In this figure it is clear that higher temperatures during the original processing reduces the blend torque, suggesting a reduction in PBT molecular weight. Comparing *Figure 16b* with

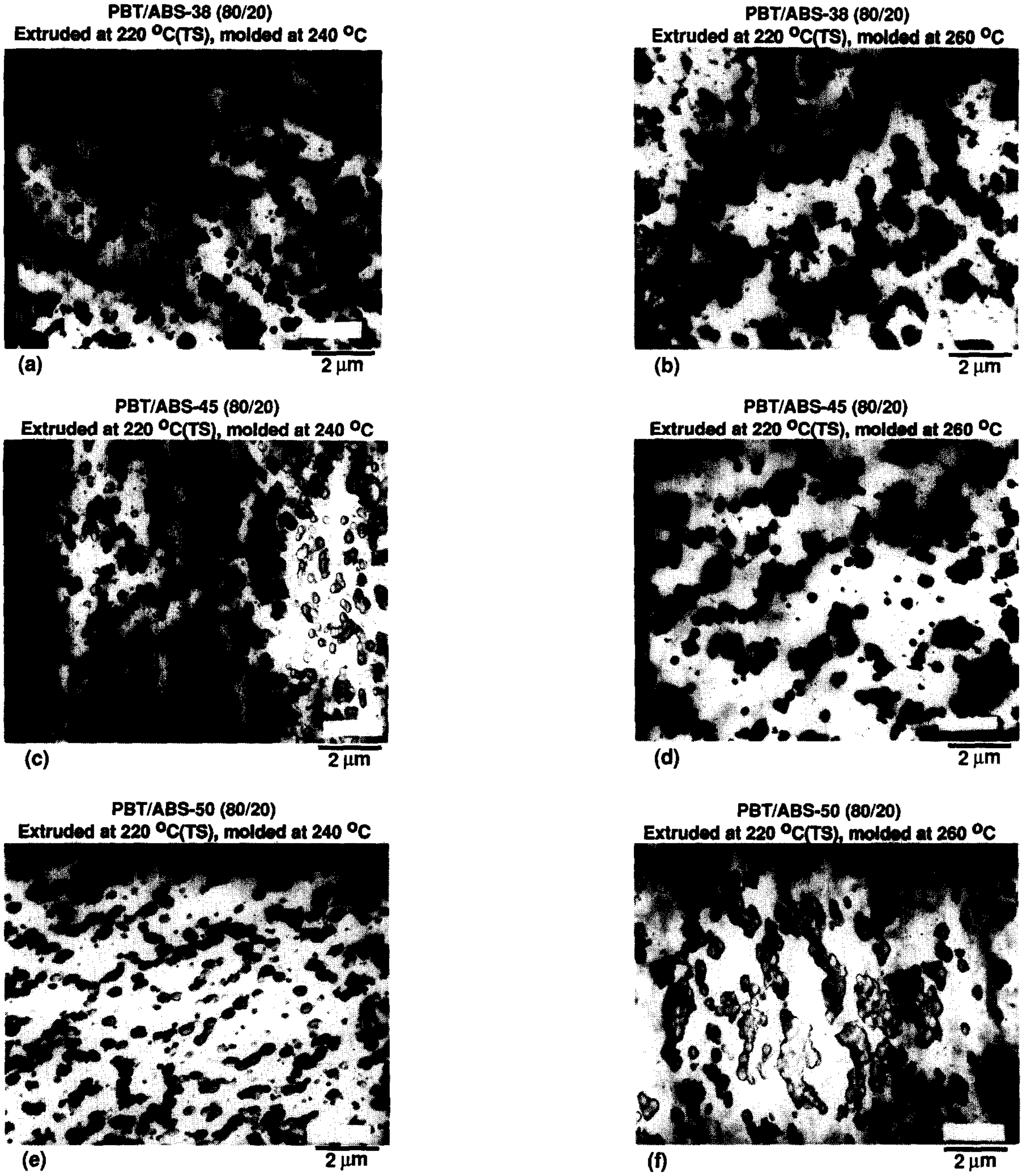


Figure 15 TEM photomicrographs of PBT/ABS blends prepared in the twin screw extruder at 220°C containing 20% ABS-38 and moulded at (a) 240°C and (b) 260°C; containing 20% ABS-45 and moulded at (c) 240°C and (d) 260°C; containing 20% ABS-50 and moulded at (e) 240°C and (f) 260°C

Figures 17b and *18b*, one can see that the reduction in torque is most exaggerated for blends based on ABS-50. These results suggest that the somewhat poorer properties of PBT/ABS-50 blends may be due in part to melt degradation of PBT, presumably influenced by impurities in ABS.

Effect of PBT type on impact behaviour

It has been shown already that the ABS type affects the impact behaviour of PBT/ABS blends to a degree that depends on processing conditions. Blends of PBT (Valox 315) with ABS-50 are strongly affected by extrusion and moulding conditions. The effect of PBT grade is examined here briefly. *Figure 19* compares the toughness of blends of two PBT grades (Valox 315 and Valox 310) with ABS-50 prepared in the twin screw extruder at 220°C and moulded at 240°C. Both PBT grades lead to tough blends above 30 wt% ABS. The molecular weight differences between the two PBT grades do not lead to large differences in impact behaviour of their blends when prepared in the twin screw extruder and moulded at low temperatures. Valox 315 seems to lead to slightly tougher compositions. However, completely different responses were observed for both types of blends when prepared at high temperature, as can be seen in *Table 7*. Blends based on Valox 310 show low impact strength for all compositions tested, whereas an increase in extrusion temperature does not affect impact strength for blends based on Valox 315 at contents above 30 wt% ABS.

Similar comparisons are made in *Table 8* for blends prepared in the single screw extruder at 230°C and 250°C. The extruder type strongly affects the impact

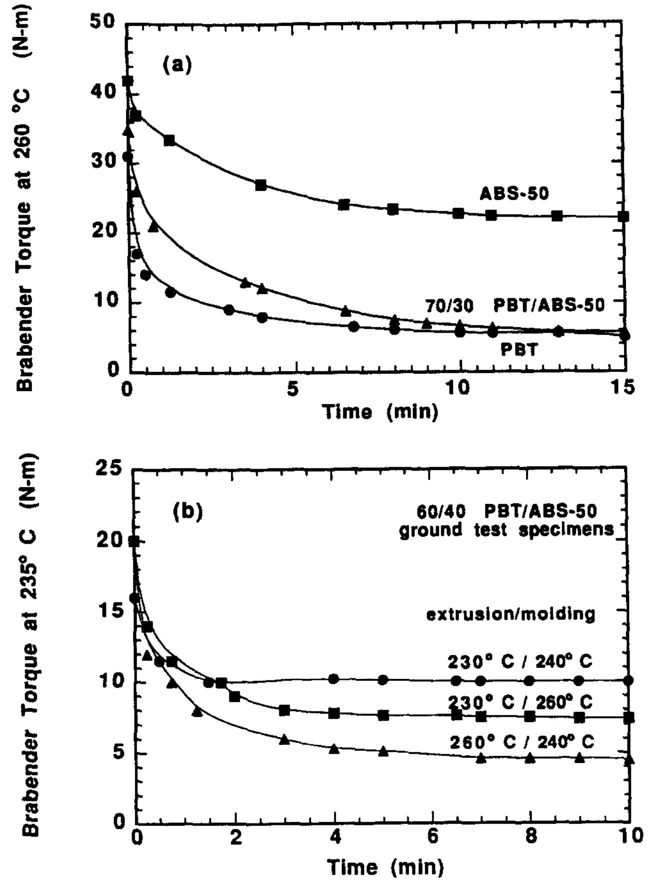


Figure 16 Brabender torque at 260°C of 70/30 PBT/ABS-50 blend and components (a); and at 235°C of regrind of 60/40 PBT/ABS-50 test specimens from several fabricating procedures (b)

Table 7 Effect of PBT type on notched Izod impact strength for PBT/ABS-50 blends prepared in the twin screw extruder at different temperatures

PBT/ABS blend (wt/wt)	Notched Izod impact strength ($J m^{-1}$) Valox 310/ABS		Valox 315/ABS	
	A[a]	B[b]	A	B
80/20	303	153	711	210
70/30	773	234	725	746
60/40	849	226	777	776

[a] A—Blends prepared at 220°C and moulded at 240°C
[b] B—Blends prepared at 250°C and moulded at 240°C

behaviour of blends based on Valox 310. These blends show lower impact strength than the same blends prepared in the twin screw extruder at equivalent extrusion temperatures. The extruder type has no significant effect on the impact behaviour for blends based on Valox 315 when prepared at low temperature. However, as the extrusion temperature is increased, all blends with both PBT materials show low impact strength and brittle failures. *Table 1* shows that at 250°C Valox 310 has a slightly lower Brabender torque than Valox 315. This difference may affect the degree of dispersion of the ABS phase in the PBT matrix established in either extruder. In addition, blends based on Valox 310 show more sensitivity to extrusion temperature than blends based on Valox 315. Therefore, to some extent, these differences in molecular weight characteristics of the two grades of PBT affect the impact behaviour of certain PBT/ABS blends.

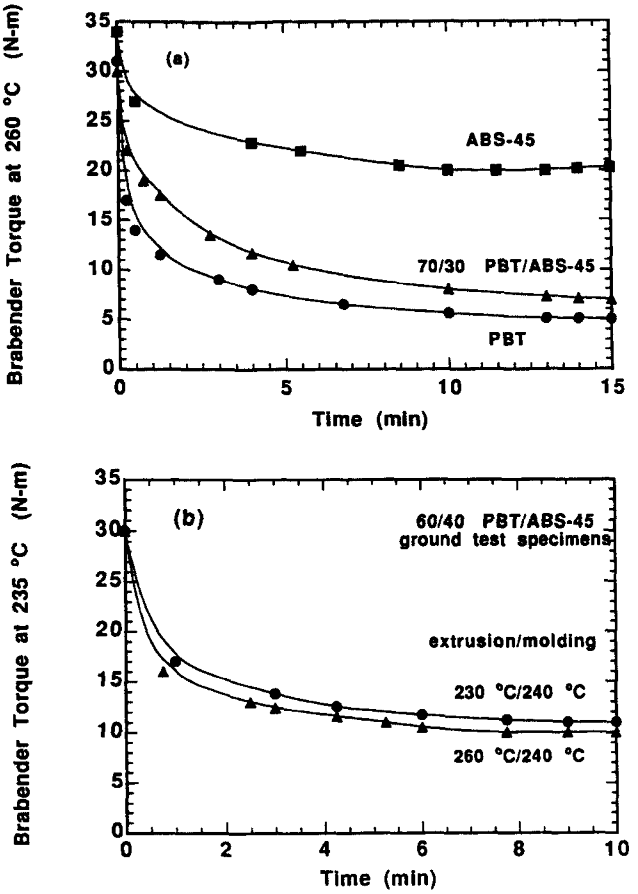


Figure 17 Brabender torque at 260°C of 70/30 PBT/ABS-45 blend and components (a); and at 235°C of regrind of 60/40 PBT/ABS-45 test specimens from several fabricating procedures (b)

Table 8 Effect of PBT type on impact behavior of PBT/ABS-50 blend, prepared in the single screw extruder at different temperatures

PBT/ABS blend (wt/wt)	Notched Izod impact strength ($J m^{-1}$) Valox 310/ABS		Valox 315/ABS	
	A[a]	B[b]	A	B
80/20	118	60	597	104
70/30	161	68	781	118
60/40	164	78	759	101

[a] A—Blends prepared at 220°C and moulded at 240°C
[b] B—Blends prepared at 250°C and moulded at 240°C

CONCLUSIONS

Extremely tough PBT blends with appropriate ABS materials can be achieved without the addition of a compatibilizer. The very high impact strength generated by addition of ABS to PBT can extend to sub-ambient temperatures of −30°C and lower. However, the extent of improvement in toughness is strongly dependent on the ABS type and moderately influenced by the PBT grade.

The toughness of PBT/ABS blends depends strongly on the extrusion and moulding conditions. An increase in melt temperature leads to a higher ABS/PBT viscosity ratio. Blends prepared at temperatures where this ratio is

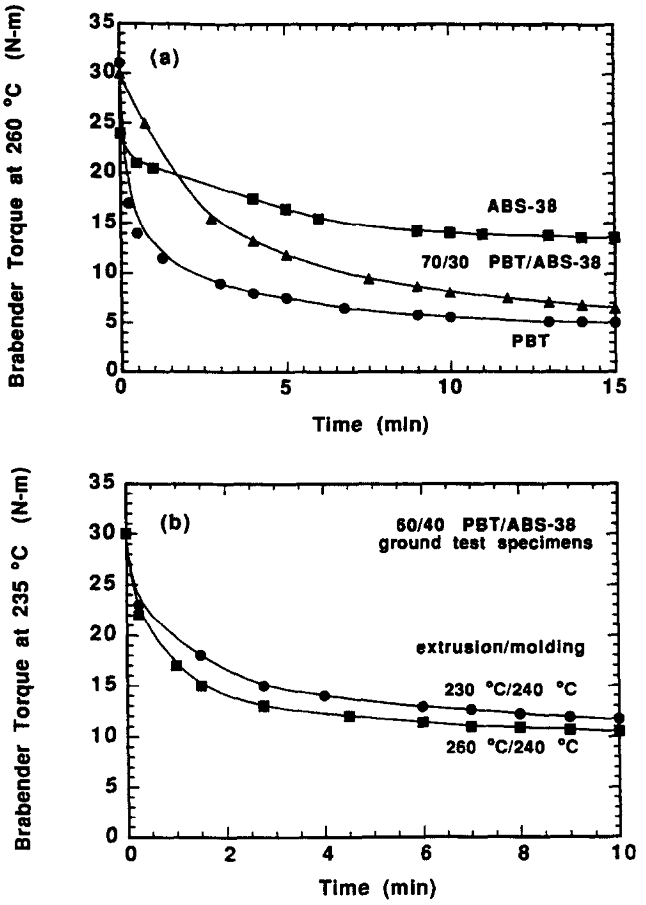


Figure 18 Brabender torque at 260°C of 70/30 PBT/ABS-38 blend and components (a); and at 235°C of regrind of 60/40 PBT/ABS-38 test specimens from several fabricating procedures (b)

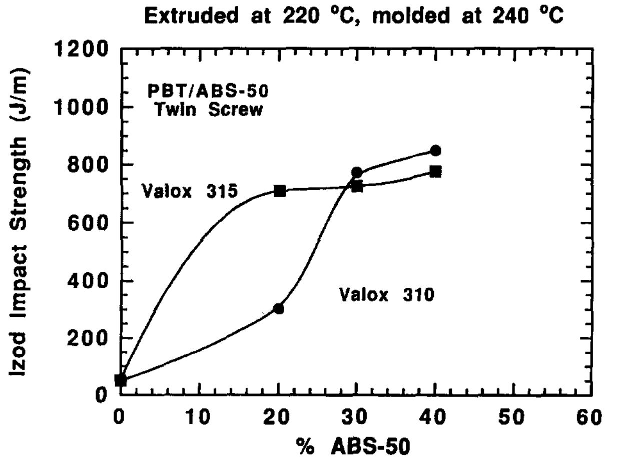


Figure 19 Effect of PBT type on notched Izod impact strength of PBT/ABS-50 blends prepared in a twin screw extruder at 220°C and moulded at 240°C

most elevated have low impact strength due to poor dispersion of the ABS in the PBT matrix. This behaviour is more evident when the blends are prepared in a single screw extruder at high temperatures. The melting or crystallization behaviour of PBT in these blends is not significantly affected by the moulding temperature. However, high melt temperatures during injection moulding lead to a coarsening in phase morphology, a reduction in the impact strength and an increase in the ductile–brittle transition temperature. These phenomena are most evident when the melt viscosity ratio of ABS to PBT is large, as in the case of ABS-50. For such cases, high melt temperatures during moulding lead to low impact strength and high ductile–brittle temperatures. In addition to its high melt viscosity, the relatively low graft ratio and broad rubber particle size distribution inherent to ABS-50 may also be factors in the blend behaviour. Residual chemicals from emulsion synthesis of ABS-50 may cause degradation of PBT and may contribute to the poorly dispersed rubber phase, resulting in low toughness of the blend. However, the other two ABS materials, particularly ABS-45, gave rise to toughened PBT with excellent properties.

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REFERENCES

1. Utracki, L. A., *Polym. Eng. Sci.*, 1995, **35**, 2.
2. Flexman, E. A., *Am. Chem. Soc., Adv. Chem. Ser.*, 1993, **233**, 79.
3. Flexman, E. A., *Polym. Eng. Sci.*, 1979, **19**, 564.
4. Hourston, D. J. and Lang, S., in *Rubber Toughened Engineering Plastics*, ed. A. A. Collyer, Chapman & Hall, London, 1994.
5. Lane, C. A. (Rohm and Haas), US Pat. 4 034 013, 1977.
6. Binsack, R., Rempel, D., Humme, G. and Ott, K.-H. (Bayer), US Pat. 4 292 233, 1981.
7. Lindner, C., Binsack, R., Rempel, D. and Ott, K.-H. (Bayer), US Pat. 4 417 026, 1983.
8. Binsack, R., Rempel, D., Lindner, C. and Morbitzer, L. (Bayer), US Pat. 4 535 124, 1985.
9. Wang, I.-C. W. (General Electric), US Pat. 4 753 986, 1988.
10. Cruz, C. A., Havriliak, S. J. and Slavin, S., in *Proceedings of Additives '95: Advances in Additives and Modifiers for Polymers and Blends*, Executive Conference Management, Clearwater Beach, FL, 22–24 Feb. 1995.
11. Deyrup, E. J. (E. I. Du Pont de Nemours), US Pat. 4 034 013, 1988.
12. Hert, M., *Angew. Makromol. Chem.*, 1992, **196**, 89.
13. Holsti-Miettinen, R. M., Heino, M. T. and Seppala, J. V., *J. Appl. Polym. Sci.*, 1995, **57**, 573.
14. Pratt, C. F., Phadke, S. V. and Oliver, E. (General Electric), US Pat. 4 965 111, 1990.
15. Phadke, S. V. US Pat. 5 008 342, 1991.
16. Greco, R., Musto, P., Rogosta, G. and Scarinzi, G., *Makromol. Chem., Rapid Commun.*, 1988, **9**, 129.
17. Laurienzo, P., Malinconico, M., Martuscelli, E. and Volpe, G., *Polymer*, 1989, **30**, 835.
18. McCready, R. J. (Arco), US Pat. 4 931 502, 1990.
19. Cecer, A., Greco, R., Ragosta, G. and Scarinzi, G., *Polymer*, 1990, **31**, 1239.
20. Kanai, H., Sullivan, A. and Auerbach, A., *J. Appl. Polym. Sci.*, 1994, **53**, 527.
21. Kanai, H., Auerbach, A. and Sullivan, V., *Soc. Plast. Eng., ANTEC* 1994, 2817.
22. Hobbs, S. Y., Dekkers, M. E. J. and Watkins, V. H., *J. Mater. Sci.*, 1988, **23**, 1219.
23. Dekkers, M. E. J., Hobbs, S. Y. and Watkins, V. H., *J. Mater. Sci.*, 1988, **23**, 1225.
24. Wu, J., Yee, A. F. and Mai, Y.-W., *ACS Polym. Prepr.*, 1992, **33**, 626.
25. Okamoto, M., Shimodu, Y., Kojima, T. and Inoue, T., *Polymer*, 1993, **34**, 4868.
26. Wu, J., Mai, Y.-W. and Cotterel, B., *J. Mater. Sci.*, 1993, **28**, 3373.

27. Wu, J. and Mai, Y-W., *J. Mater. Sci.*, 1993, **28**, 6167.
28. Brady, A. J., Keskkula, H. and Paul, D. R., *Polymer*, 1994, **35**, 3665.
29. Modic, M. J. (Shell Oil Co.), US Pat. 5 300 567, 1994.
30. Kulich, D. M., Kelly, P. D. and Pace, J. E. Acrylonitrile–butadiene–styrene polymers, in *Encyclopedia of Polymer Science and Engineering*, ed. H. F. Mark, N. M. Bikales, C. G. Overberger and G. Menges, Vol. 1. Wiley–Interscience, New York, 1988, p. 388.
31. Benson, C. M. and Burford, R. P., *J. Mater. Sci.*, 1995, **30**, 573.
32. Lee, P.-C., Kuo, W-F. and Chang, F.-C., *Polymer*, 1994, **35**, 5641.
33. Hourston, D. J., Lane, S. and Zhang, H. X., *Polymer*, 1995, **36**, 3051.
34. Hourston, D. J., Lane, S. and Zhang, H.-X., *Polymer*, 1991, **32**, 2215.
35. Wu, S., *Polym. Eng. Sci.*, 1987, **27**, 335.
36. Moginger, B., Lutz, C., Polsak, A. and Muller, U., *Colloid. Polym. Sci.*, 1991, **269**, 535.
37. Muramatsu, S. and Lando, J. B., *Polym. Eng. Sci.*, 1995, **35**, 1077.
38. Bopp, R. C. and deTorres, P. D., *Soc. Plast. Eng. Tech. Pap.*, 1978, **24**, 315.
39. Gaines, G. L., Jr, *Polym. Degrad. Stab.*, 1990, **27**, 13.
40. Lee, M. S., Kao, H. C., Chiang, C. C. and Su, D. T., *Adv. Polym. Blends Alloys Tech.*, 1989, **2**, 25.
41. Lombardo, B. S. Master's thesis, University of Texas at Austin, 1994.