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Morphology and properties of ASA/PET blends

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This study examines the morphology and mechanical properties of acrylate styrene acrylonitrile (ASA) and polyethylene terephthalate (PET) blends. The morphology of the 60/40 and 40/60 ASA/PET blends reveals a dispersed phase morphology verging on co-continuity, whilst the 50/50 blend appears to be completely co-continuous. Processing temperature has no effect on blend modulus or tensile strength and there is no statistically significant difference in mechanical performance between the three blend ratios. Charpy impact resistance decreases with increasing processing temperature. The fracture surface reveals a similar mushroom fibril morphology found for the ASA/polybutylene terephthalate (PBT) system, but is less extensive. Thermal analysis shows a marked drop in glass transition temperature for the blends compared to the component polymers.

1. Introduction

Over the last twenty years, significant research into blends has produced a number of successful materials such as high-impact polystyrene (HIPS), with properties greater than those of the individual polymers [1]. The growing cost of research and development for intrinsically new homopolymers has made this field more attractive economically, as it is possible to make a blend with the desired properties of each component, at minimal cost and time, using polymers already commercially available [2].

Rigid–rigid blends comprise two thermoplastic components each having a glass transition above room temperature. Rigid–rigid toughening involves the addition of a second rigid phase to an already rigid matrix, to relieve triaxial tension in front of the crack tip and to generate multiple stress concentration sites around the crack tip [3].

Factors which affect the toughness of polymeric materials include the presence of rubber particle inclusions [1, 4], ability to craze [1], shear banding and debonding or cavitation [5], interfacial adhesion [6], interphase adhesion and anisotropy [7]. These factors are all affected by processing conditions and their effect may be studied by mechanical testing and electron microscopy of suitably processed samples.

Wu's theory [8–10] (previously discussed by us [11] in reference to ASA/PBT blends) states that there are three types of polymers, the criteria for which are the polymer chain parameters; entanglement density and characteristic ratio. The first type is that with a brittle matrix, which deforms and fractures mainly by crazing; members are styrene acrylonitrile (SAN), polymethyl methacrylate (PMMA) and polystyrene (PS). The second type is pseudoductile and tends to yield, such as polyamide 6 (PA-6), polycarbonate (PC) and PET. The third type is a subclass of the first two and shows intermediate behaviour. A blend of an SAN-based polymer with PET would be expected to be classified in this third group. Both SAN and PET have good solvent resistance and by combining the impact resistance of ASA with the tensile strength of PET, a toughened blend suitable for engineering applications in a harsh environment may be achievable.

Several blends based on styrene acrylonitrile butadiene (ABS) have been established commercially, including ABS/PC, Terblend B (BASF) and Bayblend (Bayer–Mobay) and ABS/Polyamide, Ultramid-Terluran (BASF) and Triax 1000 (Monsanto). One might consider them comparable with ASA/polyester blends although, despite their chemical similarities, important differences exist. For example, the rubber component of ASA is far more thermally stable than the polybutadiene in ABS. This is significant as particularly high processing temperatures, typically 250 °C, are required for PET. However, the micromechanisms of ASA-based blends are not extensively published and important structural and processing differences exist between the commercial blends and the subject of the present study [12].

PET has been commercially blended with a variety of materials (PC, polypropylene (PP), PA-6) to exploit the solvent-resistant properties of PET [13]. PET also has a high melt temperature (260 °C) which provides advantages of retention of properties at extended service temperatures. PET can be easily moulded and processed with other rigid thermoplastics in ratios not possible with PBT. PET is less vulnerable to degradation than PBT, which can degrade significantly when exposed to high temperatures (280 °C) for short periods. This can be demonstrated by infrared spectroscopy by comparison of –OH peaks of the PBT before and after processing when normalized to the carbonyl peak.

This advantage can be exploited when processing with ASA. ASA has a saturated acrylate rubber phase which is stable at high temperatures, a distinct advantage over ABS where the butadiene rubber can degrade

0022–2461

at the processing temperatures required for PET. However, there appears to be little compatibility between the SAN and PET phases. Whilst both these phases are considered to be rigid, SAN fractures after crazing and PET fractures after yielding. Both materials have good solvent resistance and combining their fracture mechanisms can lead to a toughened material with good mechanical and solvent properties. A suitable compatibilizer for these two materials is now being investigated.

It was the aim of the present work to examine for the first time, the mechanical and morphological properties of the ASA/PET blends to determine if this potentially rigid–rigid system is suitable for engineering applications.

2. Experimental procedure

2.1. Materials

The samples used in this study were prepared from commercial grades of ASA (Luran S) and PET (Ultradur) supplied by BASF, Melbourne. The two materials were mixed in a volume ratio of 60:40, 50:50 and 40:60 of ASA to PET, as these were recommended by BASF closely to approximate some of their related commercial blends. The mixed blends were processed by either extrusion or injection moulding.

2.1.1. Extrusion

The mixed pellets were processed by a single pass in a Haake Rheocord Systems 90 twin screw extruder ($L/D = 10$). The extruded strip, 30 mm × 3 mm in cross-section, was water quenched and aged at 25 °C for several days before tensile bars were punched in accordance with ASTM D 638, type C. The strip was formed by processing at temperatures ranging from 230–255 °C at 10 °C intervals, the four temperature zones being ramped by 10 °C each. The feed zone was therefore 30 °C lower than the die, with the latter temperature being designated as the processing temperature. Typical screw speeds ranged from 20–30 r.p.m., corresponding to shear rates of 4–8 s^{-1} and residence times of 2–3 min.

2.1.2. Injection moulding

The mixed pellets were processed by a single pass through a Boy 15 S injection moulding machine. A two-cavity mould, consisting of a standard tensile bar and Charpy impact bar (unnotched), was employed using a conventional runner-gate path. The specimens were processed at temperatures ranging from 210–240 °C at 10 °C intervals, with the two temperature zones ramped by 10 °C. Again, the die temperature is used to indicate the temperature of processing. Cooling water was fed at 50 °C to the mould. Temperature measurement was not as accurately achieved as for the extruded samples.

Impact bars were notched in accordance with ASTM D 256 using a standard fly cutter, and broken using a conventional pendulum apparatus, with at least ten repetitions per data point. All tensile bars were tested on an Instron TT-AL universal machine modified with a digital follower/control unit. The crosshead speed was 5 mm min^{-1} and at least five replicates for each material were determined. Errors ranged from 5%–15% for tensile tests (increasing with temperature) and 10%–25% for impact tests (decreasing as temperature increases).

2.2. Microscopy

Sample morphology was studied using a Hitachi 7000 TEM, operating at an accelerating voltage of 75 kV. Samples were prepared by taking sections of the extruded and injection-moulded specimens in all three planes, x, y and z. The samples were glued to a stub and trimmed with a fresh razor blade to around 1 mm square. The samples were then stained with a ruthenium solution as described by Montezinos *et al.* [13] for at least 16 h. The samples were then further trimmed using a fresh glass knife on a Reichert–Jung Ultracut E ultramicrotome, to around 0.1 mm square. The specimens were placed in a freezer for 8 h to allow sectioning to occur below the blend glass transition temperature, T_g. Thin sections were then cut using a diamond knife on the same ultramicrotome.

Fracture surfaces were studied using a Cambridge 360 SEM. Samples were prepared by staining with ruthenium for at least 16 h. The SEM samples were then sputter coated with gold.

3. Results and discussion

3.1. Mechanical properties

The Young's modulus of ASA/PET blends is constant over the processing temperature range 230–255 °C (Fig. 1). All three blend ratios of ASA/PET have comparable tensile strengths (Table I). This contrasts with

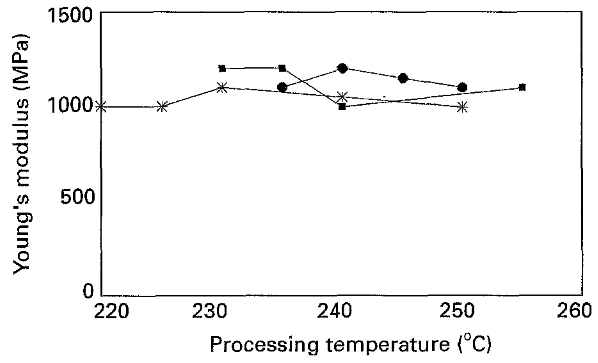

Figure 1 Young's modulus versus processing temperature. (●) ASA 40/PET 60, (*) ASA 60/PET 40, (■) ASA 50/PET 50.

TABLE I Tensile strength data

Processing temperature, °C	ASA/PET blends (MPa)		
	40/60	50/50	60/40
220			23.5
230		29.0	26.5
235	28.0	28.5	
240	30.0	27.5	26.5
245	26.0	27.0	
250		26.0	16.5

blends of ASA with PBT, where mechanical properties increase with processing temperature ([11], BASF). This suggests the ASA/PET blends have a comparable microstructure over the composition range studied, as opposed to the swing in continuity found in the case of the ASA/PBT blends.

The constant tensile strength observed over the wide processing temperature range employed for each blend ratio is accompanied by an essentially constant yield strain, ε_y, for these blends. ε_y was typically 2.7% for the 50/50 and 60/40 PET blends and 4% for the 40/60 blends. The slightly higher elongation is attributed to the higher PET content which is more ductile than the ASA phase. The elongation at break, ε_b, for ASA/PET blends is lower than the ε_b for ASA/PBT. The low ε_b is coupled with high modulus values (almost twice that of ASA/PBT) but is not a true indication of improved performance because the modulus is obtained by dividing the stress by the strain. Hence, high modulus values are obtained due to low elongation, not due to high stress values.

Fig. 2 is a composition diagram comparing the tensile strengths of the experimental values to those expected by averaging the modulus of pure ASA and PET for each blend ratio. The experimental values fall below the average, indicating interaction between the two polymers and changes in the micromechanisms of these relatively incompatible blends. As a result of the interaction, changing factors, such as domain size and interfacial adhesion, are expected to increase the blend modulus towards and possibly above the average. This is considered further below.

The Charpy impact resistance of ASA/PET blends shows a decrease in impact resistance as the processing temperature is increased (Fig. 3), although this is only slight for the 60/40 ASA/PET blend and might be due to a continuous ASA matrix morphology as exists in the ASA/PBT blend. The impact strength changes for other blend ratios may be caused by changes in the crystallinity of the PET phase, which would significantly affect impact behaviour. The drop in impact resistance over the processing temperature may also be due to the ageing of the ester linkage in the PET at the high temperatures of processing. While this is not as significant as the degradation of the PBT phase at these high temperatures, the ageing and hence minor hydrolysis of the ester bond would still cause embrittlement.

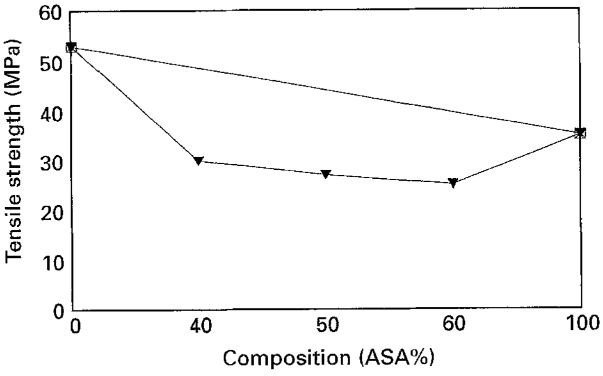

Figure 2 Tensile strength versus ASA% composition (at 240 °C).

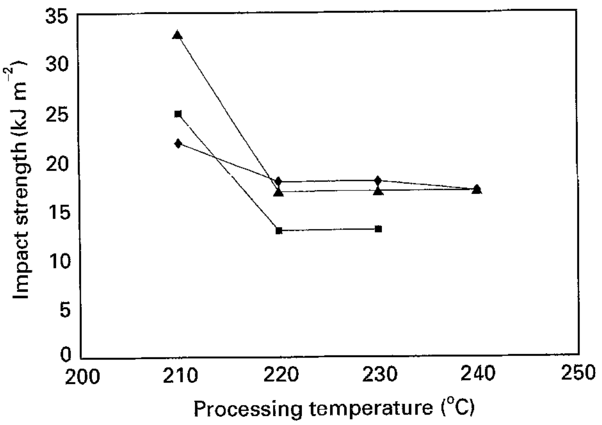

Figure 3 Charpy impact strength versus processing temperature. (▲) ASA 50/PET 50, (■) ASA 40/PET 60, (◆) ASA 60/PET 40.

3.2. Morphology

TEM of the various ASA/PET blend ratios show two distinct and separate phases. The PET phase is the darker of the two phases and ASA is the lighter phase with rubber inclusions (Fig. 4).

Fig. 4a shows the co-continuous structure of the 50/50 ASA/PET blend. In this context, co-continuous refers to a two-phase immiscible system. Each phase forms an interlocking half of the network, for example an interpenetrating network (IPN). This often occurs for blends in a 50/50 ratio [14]. The advantage of co-continuous morphology is the possibility of combining the mechanical behaviour of each of the blended materials, provided there is good adhesion between the phases. In this case, it combines the crazing/yielding behaviour of the ASA with the yielding behaviour of the PET. Fig. 4b and c show the morphology of the 60/40 and 40/60 blends. While there are areas of the minor phase being dispersed in the major phase matrix, the structure appears to be on the verge of changing from co-continuous to dispersed morphology.

The droplet break-up theory adapted by Utracki and Shi [15] to explain the break up of a non-Newtonian polymer in a non-Newtonian matrix, can be used suitably to describe these blends. The large dispersed phase is broken into smaller domains during melt processing when it is exposed to an extensional force. Fig. 4b shows the dispersed PET phase broken into various sizes, from 0.5–15 μm. The greater the extensional force and difference in interfacial tension, the greater is the degree of break up, causing smaller domains to form. It is the smaller domains (0.5–3 μm) that are thought to cause the mushroom morphology during fracture.

Fig. 4d shows a transmission electron micrograph of the interface between ASA and PET. There appears to be some slight penetration of the acrylate rubber phase into the PET phase, but whilst resolvable, it is only of the order of a few nanometres deep and we do not consider it to be the major factor in imparting improvement in mechanical properties.

The rigorous sectioning procedure described in Section 2.2 was followed to distinguish between orientation effects due to the processing or to artefacts

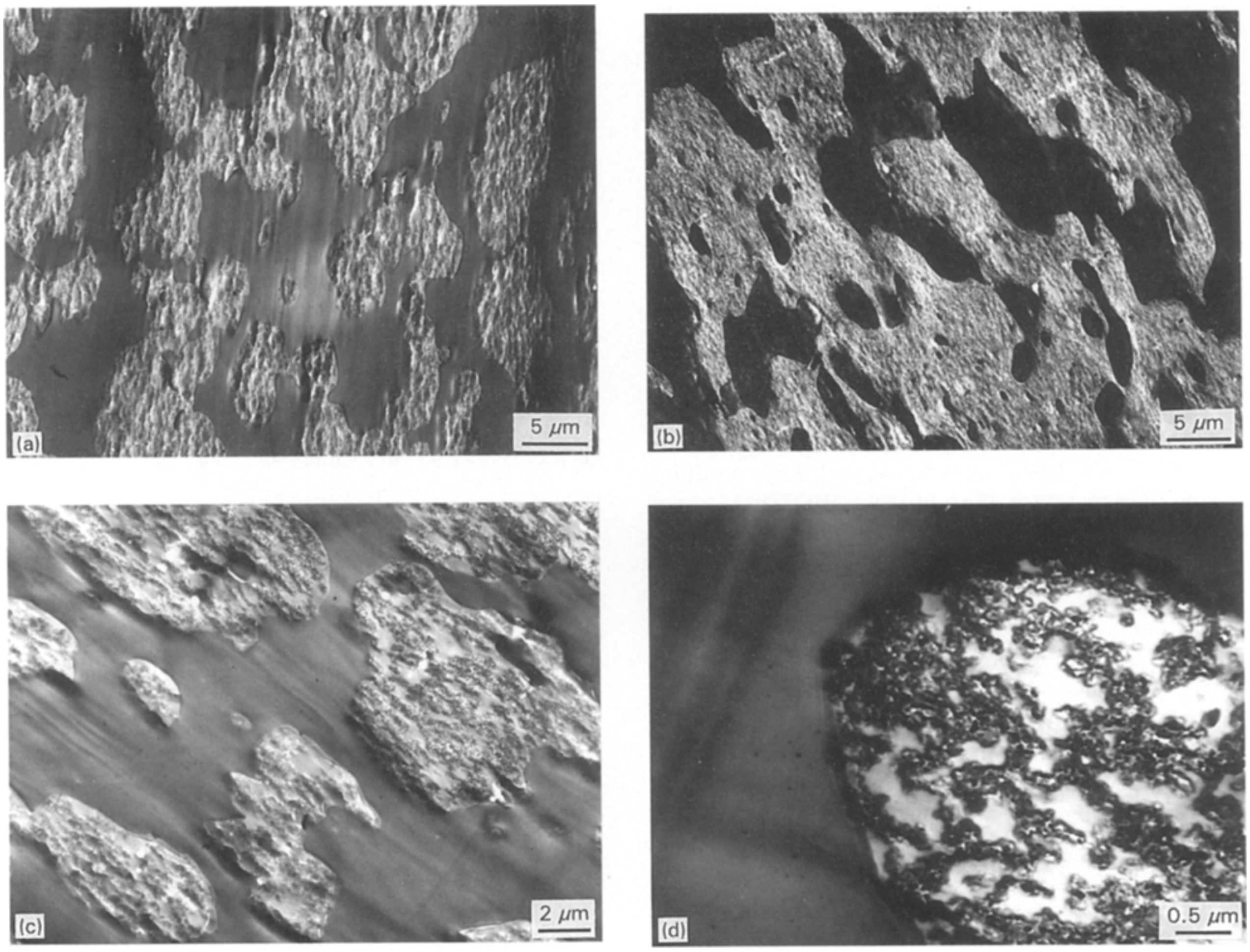

Figure 4 Transmission electron micrographs of (a) a 50/50 blend of ASA/PET showing co-continuous morphology, (b) a 60/40 ASA/PET blend showing areas of continuous and dispersed PET phases, (c) a 40/60 ASA/PET blend showing large ASA domains dispersed in a PET matrix, and (d) the interface between ASA (right) and PET (left) with minor penetration of the rubber phase to the PET.

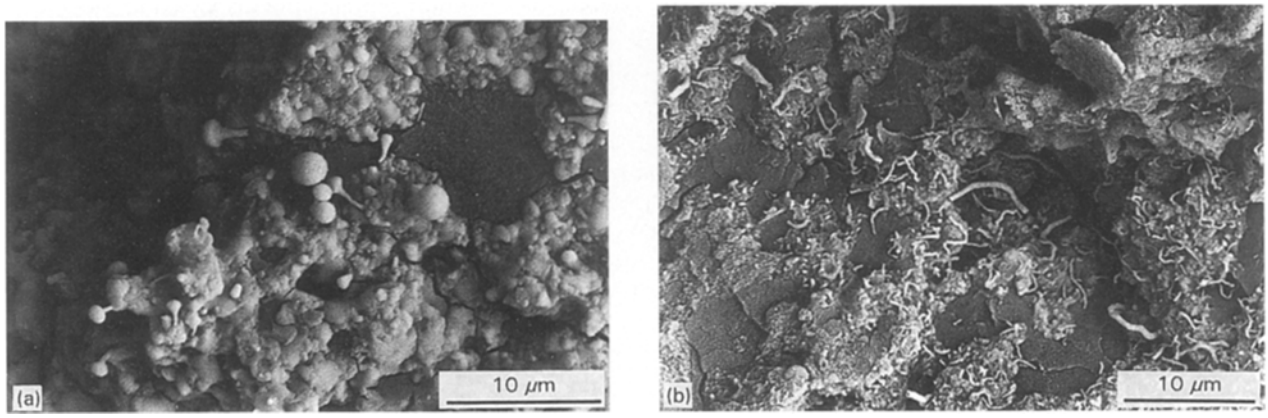

Figure 5 Scanning electron micrographs of typical fracture surfaces (a) near the crack tip (region I) showing mushroom fibrillar morphology, and (b) showing region III, fibril morphology at the end of the specimen.

imparted during sectioning. There appears to be some very minor orientation of the morphology, in the direction of cutting during sectioning. This is because the sections stretch as they are cut, due to their softness, despite the glass transition of each polymer being well above room temperature (ASA being 113 °C and PET 86 °C). The fact that a polymer nominally has a high T_g does not necessarily indicate that ambient sectioning is practicable.

3.3. Fracture surface

When the entire fracture surface is scanned, three distinctive regions were observed in the fracture surface of ASA/PET blends, the first being near (within 100 μm) the crack tip (Fig. 5a) where dispersed areas of fibril and mushroom morphology are observed. The fibril morphology, as described previously [11], is attributed to the drawing of the smaller polyester domains (less than 3 μm) during fracture when

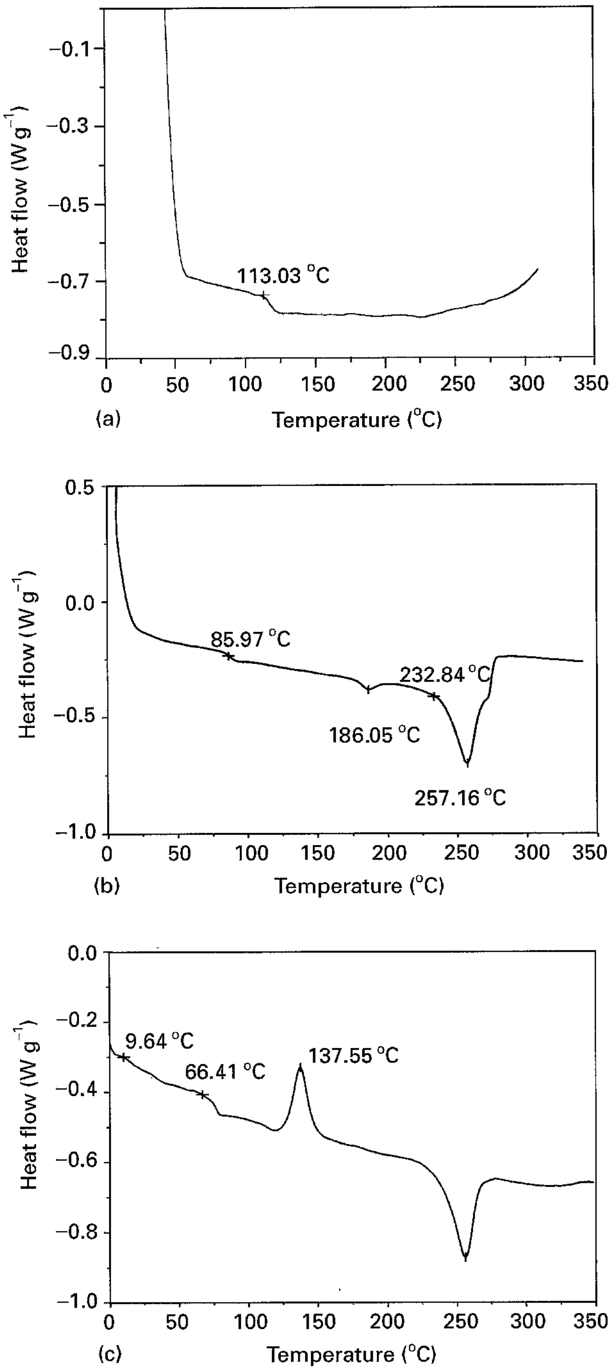

Figure 6 DSC traces of (a) ASA, (b) PET and (c) a 50/50 blend showing the marked drop in T_g.

competition between adhesion and cohesion occurs. As only small areas of this morphology are observed (small compared to ASA/PBT blends), it can be concluded that there is little adhesion between the SAN and PET phases. PET is more rigid and less ductile than PBT and would be expected to undergo less drawing during fracture.

The second region extends from 100 μm from the crack tip to about 50 μm from the end of the sample and is largely flat with no observed polyester fibrils. There appear to be no shear bands or other signs of toughening in this region. The third region (50 μm from the end of the sample) also contains dispersed areas of thin polyester fibrils (Fig. 5b). This is the first time that this morphology has been observed in this region. It is attributed to the same geometrical conditions of plane strain occurring here as at the crack tip.

These three regions correspond to areas of fast and slow crack growth, as will be discussed in future work. At the crack tip, energy is being absorbed during crack initiation and maximum deformation occurs: region I. The crack propagates at high speed with little deformation (region II) before being arrested at the end of the specimen (region III) where the speed is again slow and deformation high.

3.4. Thermal behaviour

The thermal behaviour of ASA/PET blends is quite different to what is expected. The glass transition temperature of ASA used in this study is 113 °C, and the glass transition of the PET used is 86 °C (Fig. 6a, b). However, the glass transition of the blends is quite different. A typical DSC trace of a 50/50 blend is shown in Fig. 6c. The peak at 136 °C is due to the recrystallization of the PET (due to processing) and may mask a minor transition of ASA at 113 °C. The main transition observed is at 65 °C, almost 20 °C lower than for the T_g of PET. This is a remarkable drop in the T_g of PET for the blends and is a further indication of interaction between the two constituent polymers. The melt transitions and recrystallization transitions are not shifted to the same extent as the T_g.

4. Conclusions

1. The mechanical and morphological data indicate little interfacial adhesion between the SAN matrix of the ASA phase and PET phase. Without good adhesion, there is no benefit obtained by blending these two materials.
2. Blend modulus falls below that expected by simple averaging of the two constituent polymers, indicating interaction between them. This evidence of interaction can be exploited by increasing the adhesion and changing the domain sizes to toughen this system significantly.
3. TEM shows the co-continuous morphology of the three blend ratios.
4. TEM also shows the break up of the PET phase during processing and the size and shape of these small domains serve to confirm the hypothesis that the mushroom and fibril morphology observed on the fracture surface is due to the drawing of these domains during fracture.
5. The DSC traces show a reduction in the glass transition temperatures for these blends, which is below the T_g for both the constituent polymers.

This system differs from the ASA/PBT system previously studied, in that the modulus and morphologies of the different blend ratios are similar and the interaction between the ASA and PET is more pronounced as reflected by both modulus and thermal analysis data.

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