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Mechanical and thermal properties of poly(butylene terephthalate)/poly(ethylene naphthalate), and Nylon66/poly(ethylene naphthalate) blends

DYLAN DAE BONG JUNG, D. BHATTACHARYYA*, A. J. EASTEAL
Centre for Composites Research, School of Engineering, The University of Auckland, New Zealand
E-mail: d.bhattacharyya@auckland.ac.nz

The tensile modulus, tensile strength and impact strength of melt blends of (a) poly(ethylene naphthalate) (PEN) and poly(butylene terephalate) (PBT) with 30, 40, 50, 60 and 70 wt% PEN, (b) Nylon66 and PEN with 30, 50 and 70 wt% Nylon66 were measured, and thermal/thermomechanical properties were analysed by differential scanning calorimetry and dynamic mechanical thermal analysis. Scanning electron microscopy was used for examination of the fracture surfaces of the blends.

All PBT/PEN blends show two glass transitions corresponding to the presence of two phases: the glass transition temperature, T_g, of the phase with the lower T_g increases with increasing PEN content, and T_g for the phase with higher T_g decreases with increasing PBT content. The implication is that the two polymers are partially miscible, and scanning electron microscopy of fracture surfaces reveals a very small (sub-micron) domain size. Nylon66/PEN blends also show two phases, but the domain size is of the order of μm and there is no evidence of partial miscibility.

Up to 50 weight proportions PBT does not lower the tensile strength of PBT/PEN blends, and the tensile strength lies between values predicted by the rule of mixtures and a modified rule of mixtures. Incorporation of at least 40% PEN in PBT increases impact strength, but blending with smaller proportions of PEN decreases impact strength. By contrast, blending of Ny66 and PEN results in reduction of tensile strength for all blend compositions. © *2003 Kluwer Academic Publishers*

1. Introduction

Poly(ethylene naphthalate) (PEN) is chemically similar to poly(ethylene terephthalate) (PET) but more temperature resistant [1–5]. It is semicrystalline and colourless, either crystal clear or slightly hazy. Compared to PET, PEN has better long-term electrical properties [6, 7]. Their tensile strengths are similar, but the modulus of PEN films is higher. PEN also has better UV resistance and barrier properties, and is more resistant to hydrolysis in alkaline or very hot aqueous conditions [8–12]. It is, however, more expensive than PET and has a shorter flex life.

Poly(butylene terephthalate) (PBT) is a semicrystalline, high molecular weight polymer that has an excellent balance of properties and processing characteristics [13–15]. Because the material crystallizes rapidly, mould cycles are short and moulding temperatures can be lower than those for many engineering plastics. This thermoplastic polyester has very good dimensional stability. It also exhibits high heat resistance, chemical resistance and good electrical properties. In general, PBT exhibits higher tensile, flexural and dielectric strengths and faster, more economical moulding characteristics compared to many thermosets. PBT has excellent resistance to a broad range of chemicals at room temperature.

In a recent work we have analysed several chemical properties and investigated the miscibility of the Ny66/PEN blend system [16]. The present work has studied the PBT/PEN blend system and found the enhancement of mechanical properties of PBT/PEN blends in contrast to Ny66/PEN blends, which exhibit embrittlement relative to the constituent homopolymers. An interesting feature of this behaviour is that neither Ny66/PEN nor PBT/PEN blends show a new chemical bond coming from interchange reaction between the two constituent homopolymers under the melt processing conditions that we have used [16, 17].

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*Author to whom all correspondence should be addressed.

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However, the domain size in PBT/PEN blends is at least an order of magnitude smaller than that for Ny66/PEN blends.

Previous research [2, 18–21] has reported partial miscibility of PBT/PEN blends using differential scanning calorimetry (DSC), tensile testing and solid-state nuclear magnetic resonance (SS-NMR). Using additional experimental techniques (dynamic mechanical thermal analysis (DMTA), impact strength measurement, and scanning electron microscopy (SEM)), we have reconfirmed that PBT/PEN blends are partially miscible, with very small domain size.

2. Experimental

2.1. Material

Polymers used in this study were PEN from Teijin Ltd (PN-550), Nylon66 (Grilon EMS T300) from EMS—Chemie, and PBT (Arnite T06-202) supplied by DSM Engineering Plastics. In addition, Elvaloy^{R}PTW (Du Pont), an ethylene copolymer containing epoxy functionality (including 1.4 wt% GMA: glycidyl metharylate), was used as a possible compatibiliser for Ny66/PEN blends.

2.2. Mechanical measurement

Ny66, PEN and Ny66/PEN mixtures in the proportions (wt/wt), 70/30, 50/50 and 30/70, and Ny66/PEN (50/50) + Elvaloy^{R}PTW (3% of blend weight) were dried at 70°C for 48 hrs under vacuum. Mixtures were extruded with an Axon (model BX-18-286) single screw extruder and injection moulded using a BOY (model 50M) automatic injection-moulding machine at 280–290°C. PBT/PEN blends with 30, 40, 50, 60 and 70 wt% PEN were prepared using the same procedure, except that because of the lower melting point of PBT the temperature used for injection moulding for PBT/PEN was 250–280°C. Tensile specimens were injection moulded in accordance with ASTM D 638M (*l*: 200 mm, *t*: 4 mm, type 1).

An extensometer was used to determine percentage extension at room temperature with 5 mm min^{-1} crosshead speed. Tensile modulus was calculated as the average gradient of the stress vs. strain curves at 1% initial elongation for nine replicated specimens of each homopolymer and blend. Tensile strengths were measured using an Instron Model 5567 tensile tester.

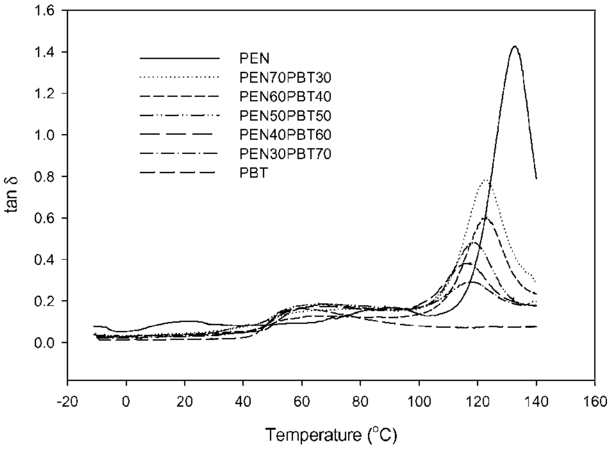


Figure 1 Temperature dependence of tanδ for PBT, PEN and PBT/PEN blends.

TABLE I Glass transition temperatures of PBT/PEN blends measured using DMTA

wt% PEN	0	30	40	50	60	70	100
T_g/°C (PBT)	59.2	65.5	65.2	65.7	70	76.3	
T_g/°C (PEN)		117.3	117.4	119.2	123.1	123.2	132.6

Impact test specimens were injection moulded in accordance with ASTM D 256 (*l*: 125 mm, *w*: 12.7 mm, *t*: 3 mm). Absorbed energy was measured using a CEAST Impact Tester (RESIL 25) using a 0.5 J hammer according to the Charpy test (ASTM D 256-93a, Test Method B). The impact strength was normalised as the absorbed energy divided by the thickness of the specimen. The recorded result was the average for ten replicate specimens of each homopolymer and blend.

2.3. Rheological measurement

Dynamic mechanical thermal analysis in 3-point bending mode was carried out using a Rheometric Scientific

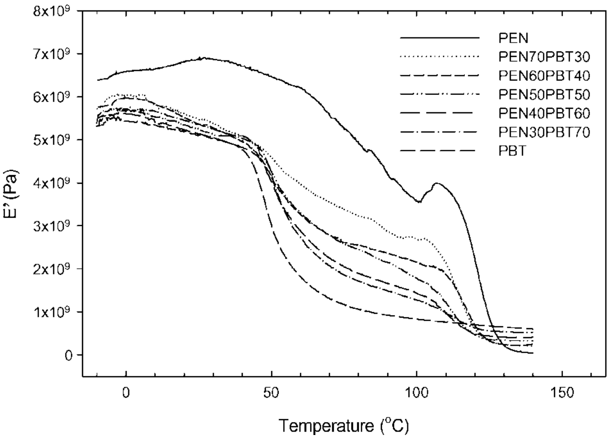


Figure 2 The temperature dependence of the tensile storage modulus (E′) for PBT, PEN and PBT/PEN blends.

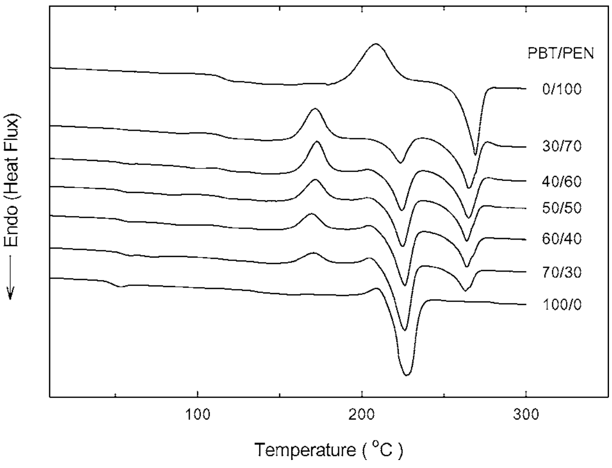


Figure 3 Differential scanning calorimeter scans for PBT, PEN and PBT/PEN blends. The legend gives homopolymer proportions in wt%.

Mark IV instrument, on specimens (l: 35 mm, w: 10 mm, t: 2.5 mm) that were cut from the original moulded samples. The specimens were heated from −10 to 140°C at 1°C min^{-1}, using 0.3 N force at a frequency of 1 Hz.

Differential scanning calorimetry was conducted using a Rheometric Scientific DSP instrument, on approximately 20 mg samples encapsulated in aluminium sample pans and heated and cooled in a nitrogen atmosphere. The samples were cooled to −50°C and maintained at that temperature for 5 minutes to attain thermal equilibrium, then heated at 10°C min^{-1} to 300°C. The glass transition temperatures (T_g), melting temperatures (T_m) and enthalpies of fusion (ΔH_m) of the homopolymers and blends, as well as the crystallisation temperatures (T_c) and enthalpies of crystallisation (ΔH_c) were determined.

2.4. Morphological measurement

A Philips XL 30S(FGG) scanning electron microscope was used for examination of fractured surfaces. For PBT/PEN blends, the fracture surfaces of impact test specimens were examined, and for Ny66/PEN blends, specimens were fractured by impact at liquid nitrogen temperature [16]. All fracture surfaces were gold coated before SEM examination. In the case of PBT/PEN blends, we were unable to find solvents that would readily dissolve the PBT-rich and PEN-rich phases separately; therefore selective leaching experiments were not carried out prior to SEM examination.

TABLE II Transition temperatures and enthalpies for PBT/PEN blends from DSC

wt% PEN	Component	T_g/°C	T_c/°C	ΔH_c/ J g^{-1a}	T_m/°C	ΔH_m/ J g^{-1a}
0	PBT	48.5			227.1	33.9
0	PEN					
30	PBT	54.3			226.3	26.5
30	PEN	115.1	170.8	15	263.2	7.6
40	PBT	54.3			226.3	21.9
40	PEN	115.2	169.6	18	264.1	11.4
50	PBT	53.9			224.9	17.2
50	PEN	115.7	171.8	18	264.0	13.1
60	PBT	53.5			224.5	14.3
60	PEN	116.0	172.8	19.5	265.2	16.0
70	PBT	55.3			223.7	8.9
70	PEN	116.0	171.7	19.5	265.2	18.5
100	PBT					
100	PEN	116.1	208.6	26.2	269.1	21.7

[a] Per unit mass of the component specified.

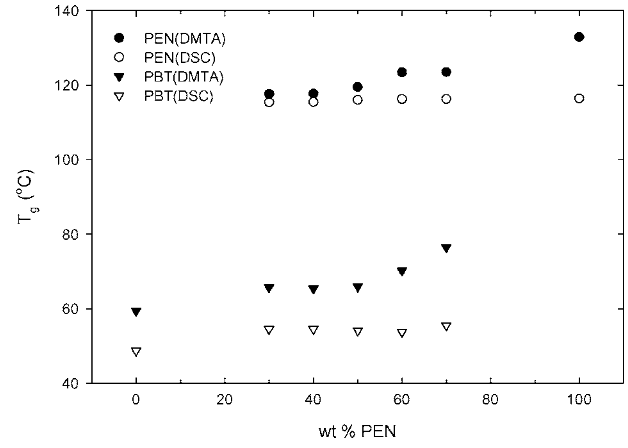


Figure 4 Composition dependence of the $T_g s$ (glass transition temperatures) of PBT and PEN components in the PBT/PEN blends determined using DSC and DMTA.

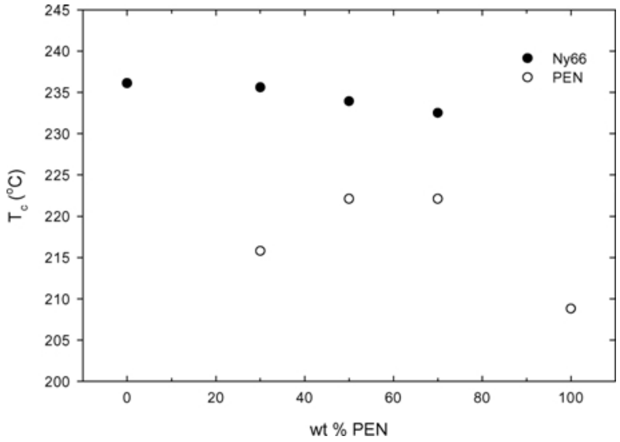


Figure 5 Crystallisation temperatures for the Ny66 and PEN phases of Ny66/PEN blends.

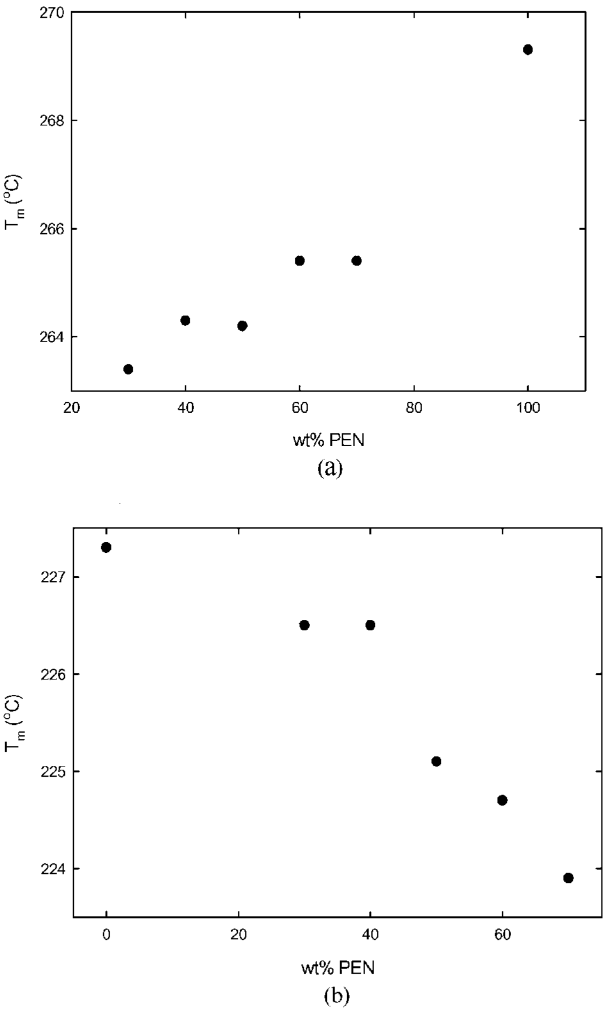
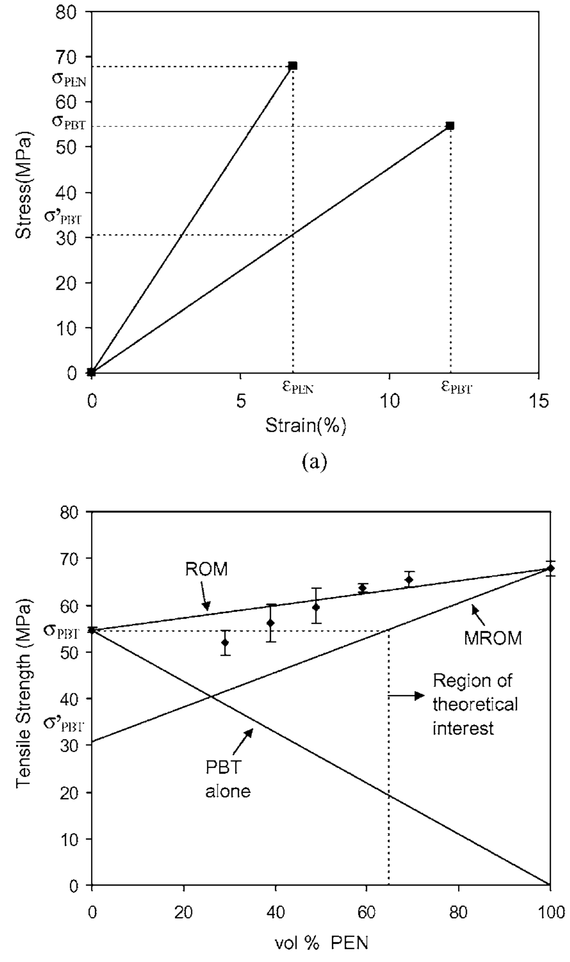


Figure 6 Melting temperatures for (a) the PEN-rich phase of PBT/PEN blends and (b) the PBT-rich phase of PBT/PEN blends.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows tanδ vs temperature curves for PEN, PBT and the PBT/PEN blends. The presence of two maxima in tanδ of the blends shows that the blends contain two discrete phases. The temperature corresponding to the well-defined maximum in tanδ in the vicinity of 120–130°C is taken as the glass transition temperature of PEN or a PEN-rich phase, and the temperature of the less well-defined maximum in tanδ at about 60°C is associated with the glass transition of PBT or a PBT-rich phase. The composition variation of the glass transition temperatures so determined (see Table I) provides a clear evidence for partial miscibility of the two phases: T_g for the PEN-rich phase decreases with increasing proportion of PBT, and T_g for the



(a)

(b)

Figure 7 (a) Stress-strain line of PBT and PEN to the respective yield tensile strengths. (b) Method of relating composite strength (σ_c) to volume fraction of PEN using modified rule of mixtures.

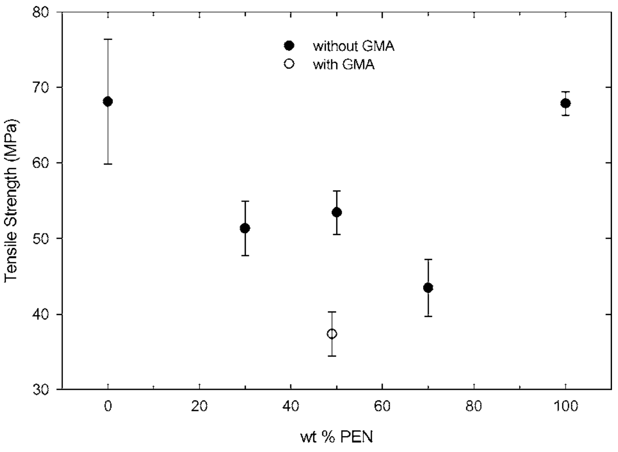


Figure 8 Tensile strength of Ny66/PEN blends with and without compatibiliser.

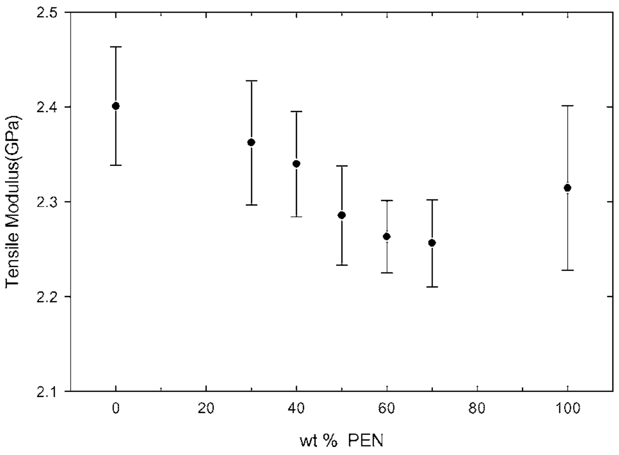


Figure 9 Tensile modulus of PBT, PEN and PBT/PEN blends.

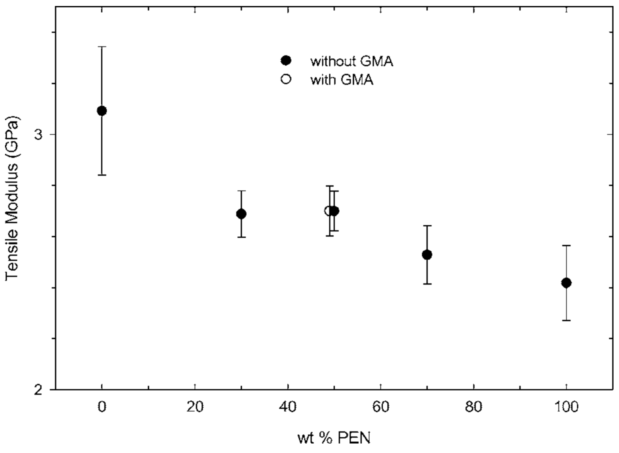


Figure 10 Tensile modulus of Nylon66, PEN and Nylon66/PEN blends.

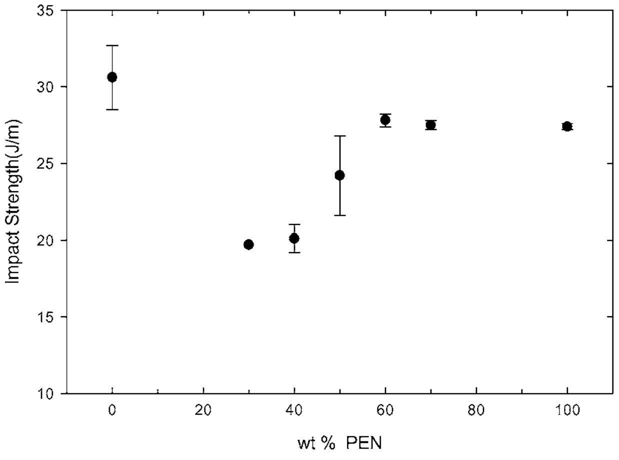
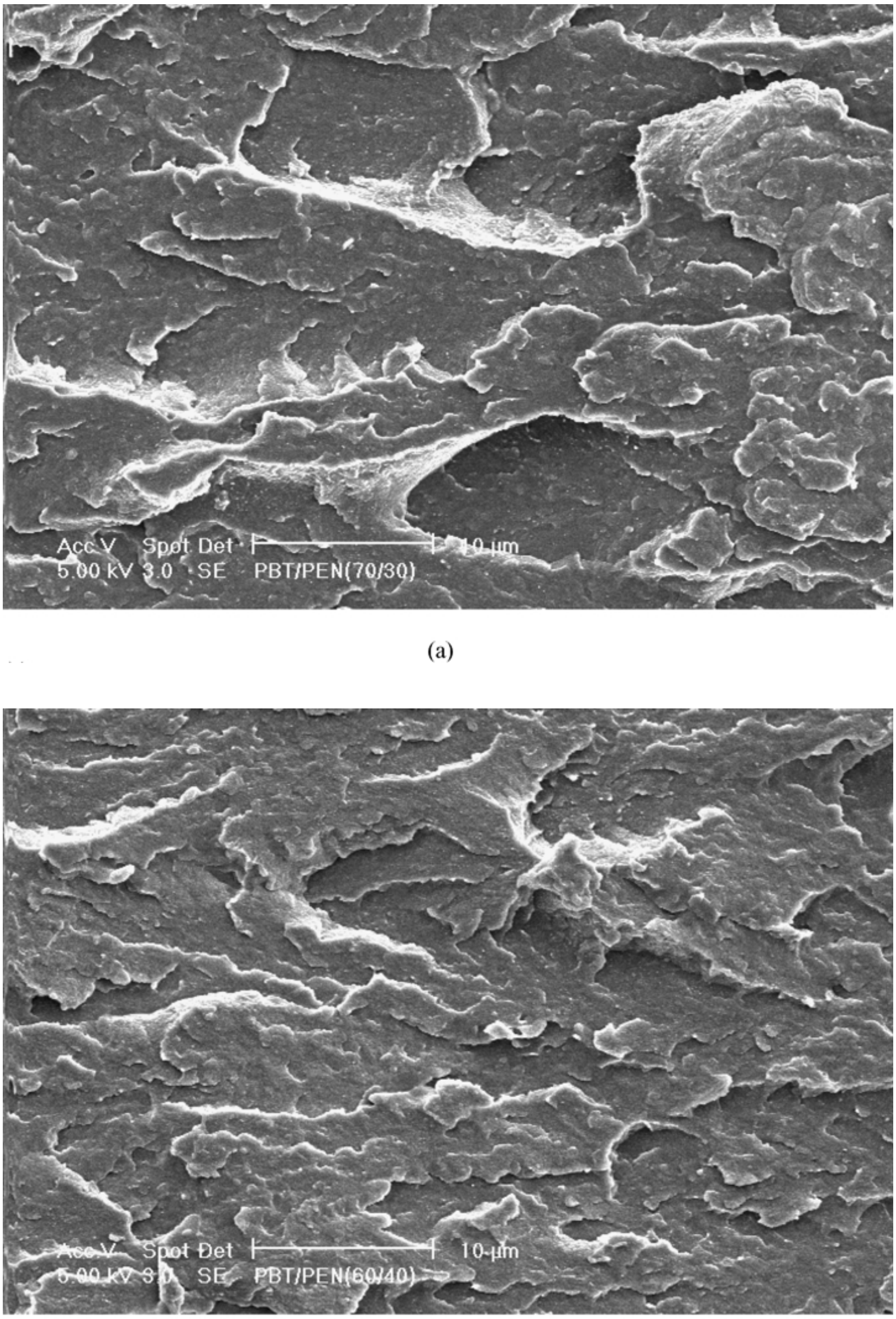


Figure 11 Impact strength of PBT, PEN and PBT/PEN blends.

PBT-rich phase increases as the PEN content of the blends increases.

In Fig. 1 the β transition, the highest temperature glassy-state relaxation at around 90°C and the γ transition, bending and stretching of the segment at around 21°C were to be revealed in pure PEN curve because the previous articles [22–24] reported that the β process extends approximately from -30 to $+100$ °C—hence it is very broad and is visibly overlapping with the α or glass transition process. The inflection points in modulus around 60°C at PBT region and around 130°C at PEN region in homopolymers indicate the $T_g's$ of PBT and PEN components of the PBT/PEN blends in Fig. 2 plotting the temperature vs. E' (storage modulus) curves, and the inflection points of curves approach each other according to the variation of weight proportions the PBT/PEN blends.

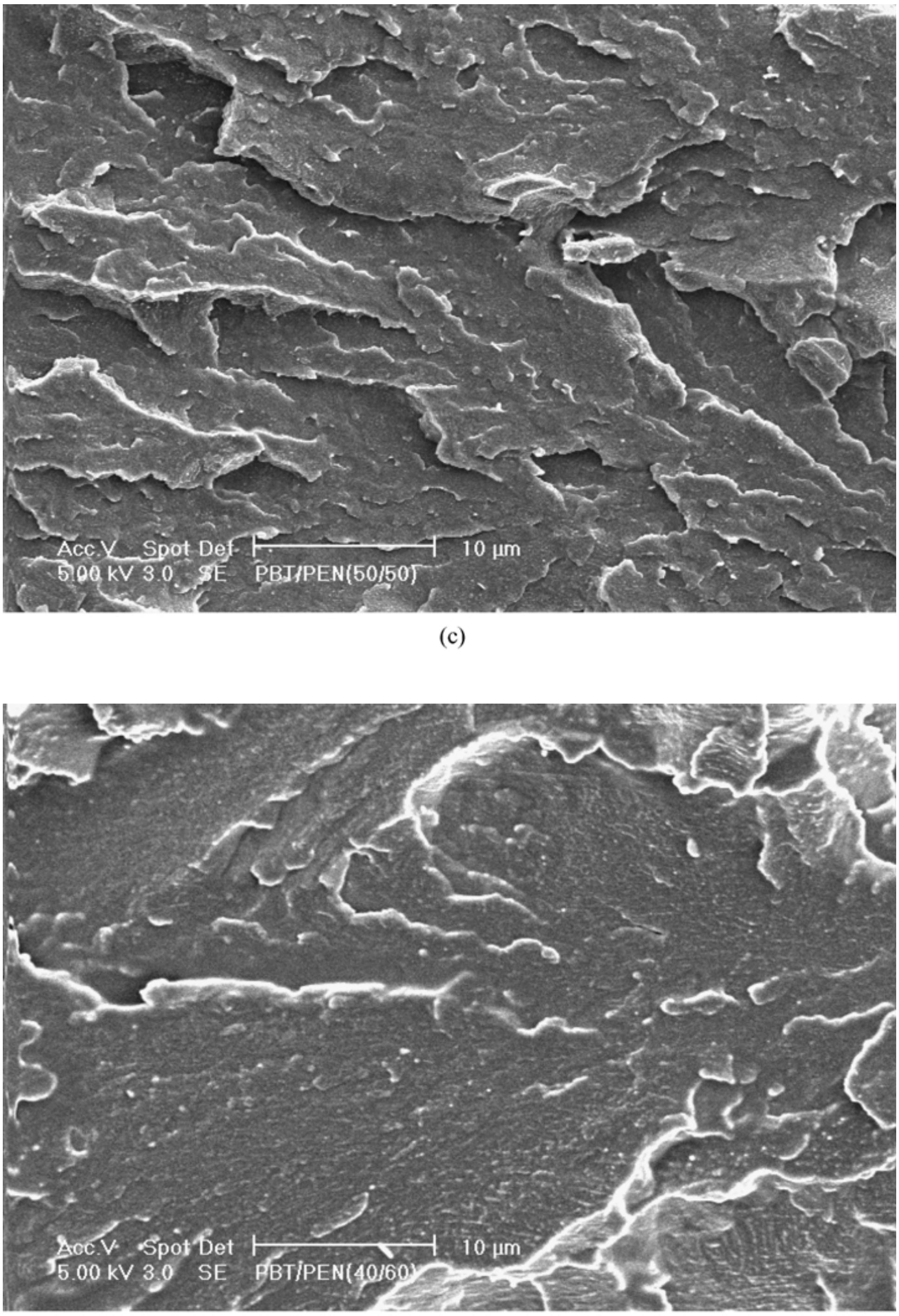
Fig. 3 shows differential scanning calorimeter (DSC) scans of PEN, PBT and the PBT/PEN blends. The glass transitions of the pure homopolymers are well defined and, as expected, are smaller than the values obtained from DMTA. For the blends, the glass



(a)

(b)

Figure 12 SEM image of the fracture surfaces of the PBT/PEN (wt/wt%) blends from impact test: (a) (70/30), (b) (60/40), (c) (50/50), (d) (40/60), and (e) (30/70). (*Continued on next page.*)



(c)

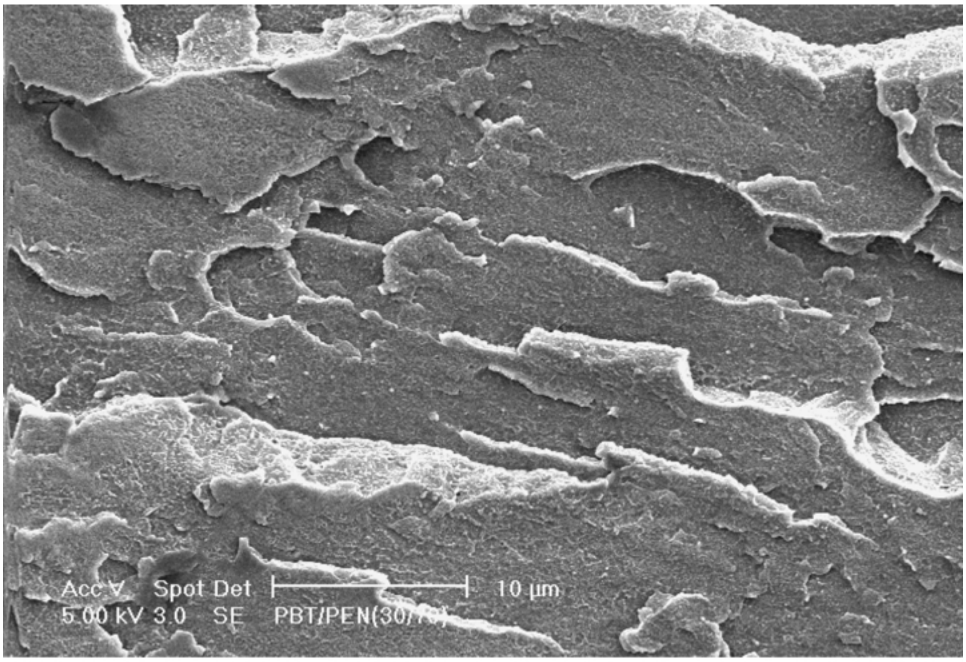
(d)

Figure 12 (*Continued*)

transitions are less well defined, and the values of T_g for the two phases are more uncertain. Notwithstanding the uncertainties in T_g, the glass transition temperatures measured using DSC (see Table II) are more composition invariant than the values determined by DMTA.

A graphical comparison of the glass transition temperatures determined using DSC and DMTA is shown in Fig. 4. It is apparent that the trend in the composition dependence of T_g for each phase is method-independent for blends with up to about 50 wt% PEN, in those blends a PBT-rich phase should form the matrix, and a PEN-rich phase is the dispersed phase. For blends with more than 50 wt% PEN, in which a PBT-rich phase should be dispersed in a PEN-rich matrix, $T_g s$ determined by DSC and DMTA diverge increasingly with increasing PEN content.

In addition, for blends with up to 50 wt% PEN $T_g s$ for the PEN-rich phase, determined by DMTA, are only a few degrees larger than the values measured using DSC. The small difference implies that for small PEN domains the frequency dependence of T_g from DMTA is small and the associated structural relaxation has a small activation energy. For pure PEN, by contrast, the more typical value of ΔT_g ($=T_g$(DMTA) $-$ T_g(DSC)) indicates an activation energy of the order



(e)

Figure 12 (*Continued*).

that is commonly found for homopolymers. It is interesting to note that in PEN-rich blends ΔT_g for the PBT-rich dispersed phase becomes larger as the proportion of PBT diminishes: in those domains the activation energy for the structural relaxation is relatively large in the 70 wt% PEN blend.

The crystallization temperature (T_c) and enthalpy of crystallization (ΔH_c) of PEN, and the glass transition temperatures (T_g), melting temperature (T_m) and heat of fusion (ΔH_m) of each component in the blends, determined using DSC, are listed in Table II. The crystallisation temperature of PEN is dramatically reduced by addition of 30 wt% PBT, but is essentially unchanged by further incorporation of PBT. It is interesting to note in passing, that the processing window ($T_m - T_c$) is almost constant and about 50% larger for the blends than for PEN homopolymer.

In contrast to the PBT/PEN system, for Ny66/PEN blends the crystallisation temperatures of the two phases (Fig. 5) show very different behaviour, assuming that as for the pure homopolymers the Ny66 phase crystallises at a higher temperature than the PEN phase. The behaviour of the PEN phase is complex, in that incorporation of Ny66 as a dispersed phase in PEN allows the PEN to crystallise at a higher temperature than in pure PEN. Furthermore, when PEN is the dispersed phase the crystallisation temperature is still greater than for pure PEN.

It is interesting to note that the melting temperatures of the PEN (or PEN-rich) and PBT (or PBT-rich) phases are shown as a function of blend composition in Fig. 6a and b. It is apparent that the melting temperatures are smaller, for each phase, when that phase is dispersed. Moreover, there appears to be a discontinuous change in T_m in the vicinity of the phase inversion point around 50 wt% of PEN.

3.2. Mechanical analysis

The forgoing results show that PBT/PEN blends may be treated as composite materials with a partial miscibility. Therefore, it would be interesting to examine whether the tensile strength of PBT/PEN blend can be approximated by rule of mixtures (ROM) or the modified rule of mixtures (MROM) [25, 26]. In Fig. 7 ROM and MROM predictions of the tensile strengths of PBT/PEN blends are depicted; the volume fractions were obtained from weight fractions using the density of each polymer (PBT: 1300, PEN: 1360 kg m^{-3}). All error bars shown represent $\pm 1\ \sigma$ (standard deviation) of the data. In Fig. 7a, if the smallest yield strain of PEN is extended to stress-strain line of PBT and then the largest stress ever experienced by PBT would be σ'_{PBT} rather than σ_{PBT}. In essence the full stress capacity of matrix cannot be utilised. Fig. 7b indicates the region of practical interest where the MROM line, which connects the tensile strength of PEN with σ'_{PBT}, lies above the dotted line indicating the same tensile strength of PBT alone.

The tensile strengths of the PBT/PEN blends lie between the ROM and MROM lines, and particularly for blends with more than 50% volume fraction of PEN the tensile strengths are close or greater than the ROM predictions. The tensile strengths of the Ny66/PEN blends are shown in Fig. 8, where the ROM or MROM is not applicable because of lack of miscibility that was discussed previously [16]. It is clear from Fig. 8 that GMA compabiliser did not improve the miscibility of the Ny66/PEN (50/50 wt%) blend.

The tensile moduli of PBT/PEN blends are shown in Fig. 9. The tensile modulus increases with addition of PBT to PEN, the variation of tensile modulus with PBT content is highly non-linear, and incorporation of over 60% PBT in PEN increases a material with tensile modulus that exceeds that of PEN. The tensile modulus of Ny66/PEN blends with and without GMA is shown in Fig. 10: in this case the tensile modulus increases almost linearly with PBT content, and the compatibiliser has no effect.

The impact strength of PBT/PEN blends is plotted in Fig. 11, and again shows highly non-linear variation with PBT content of the blends; the trend is very similar to that of the tensile strength (Fig. 7b). In the composition region where PEN is the disperse phase the toughness of the blends is reduced by up to about 30%, whereas dispersion of PBT in PEN enhances toughness.

3.3. Morphological analysis

SEM pictures of the fracture surface of PBT/PEN blends with different weight fractions by impact test are shown in Fig. 12a–e. The domain size decreases as the proportion of PEN increases from 30 to 50 wt% of PEN (Fig. 12a–c), which is consistent with increasing miscibility. This fact could explain the peculiar behaviour of the impact strength of PBT/PEN blends; the increase of fine domains in accordance with high proportions of PEN gives better adhesions of two interphases and consequently high impact strengths of PBT/PEN blends at higher proportions of PEN, even in the contradiction with lower impact strengths of PBT/PEN blends at

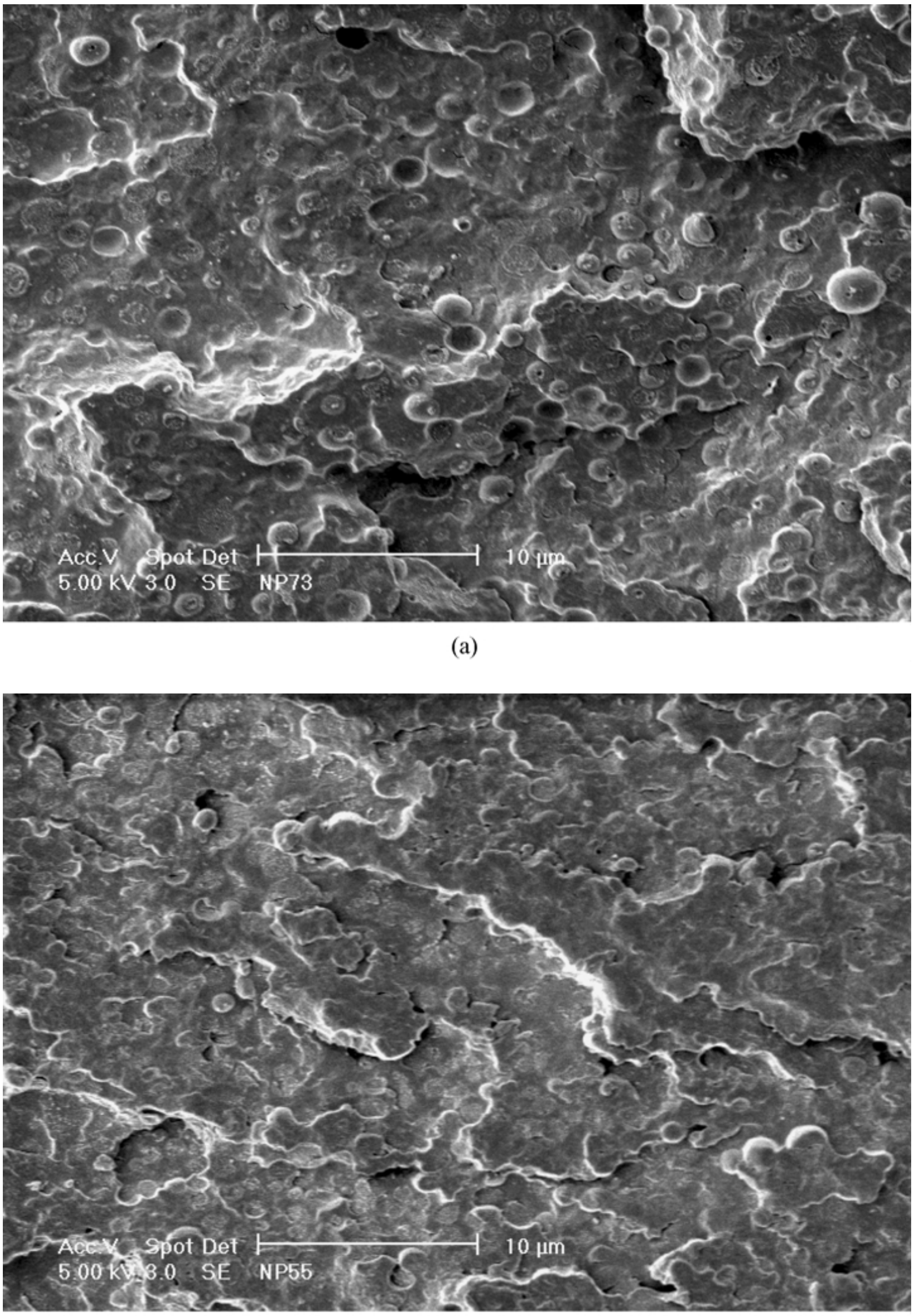
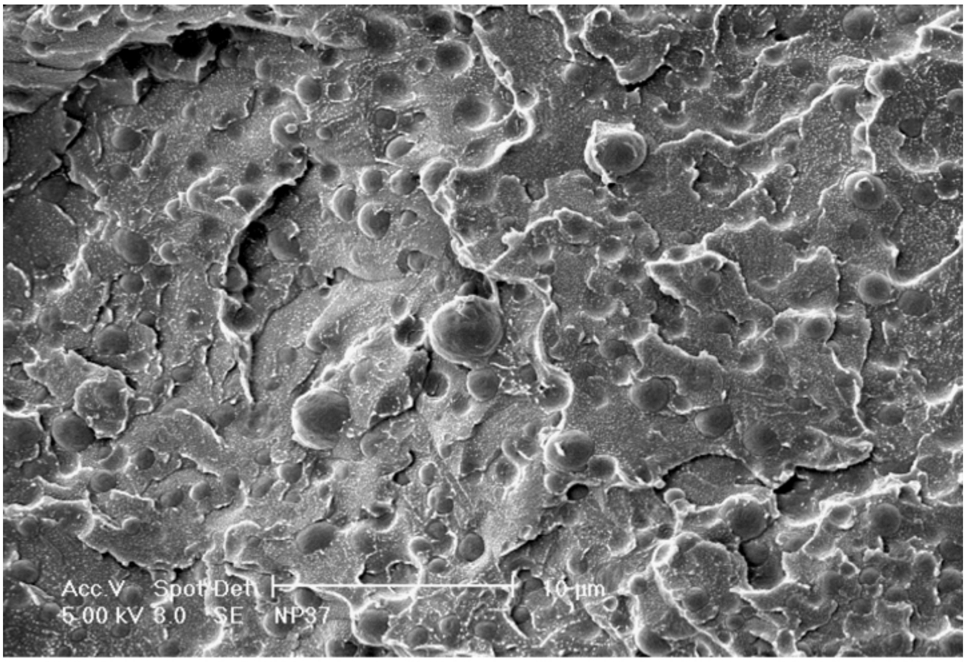


Figure 13 SEM image of the fracture surfaces of Ny66/PEN (wt/wt%) blends by cryoscopic method: (a) (70/30), (b) (50/50), and (c) (30/70). (*Continued on next page.*)



(c)

Figure 13 (*Continued*).

higher content of PBT that has a higher impact strength than PEN does.

At proportions of PEN larger than 50 wt%, where PEN forms the matrix (Fig. 12d and e), the morphology is distinctly different: the domain size is smaller and there are more adhesions between the dispersed and matrix phases, which is consistent with the affect of addition of PBT on strength and toughness.

For comparison micrographs of fracture surfaces (produced by cryoscopic fracture) of Ny66/PEN blends are shown in Fig. 13a–c. The domain size in these blends is much larger and the phase boundaries are sharp, indicating very low miscibility of the homopolymers.

4. Conclusions

Under the melt processing conditions that have been used, the PBT/PEN and Ny66/PEN blend systems have the common feature that there is no direct evidence of chemical interactions, which have been investigated by NMR and reported elsewhere [16, 17]. This implies that there is no formation of covalent bonds between the constituent homopolymers. In neither case are the blends fully miscible, but whereas Ny66 appears to be almost completely immiscible with PEN, PBT shows partial miscibility that is reflected in a much smaller domain size.

The microdispersed PBT phase in blends with up to 40 wt% PBT seems to act almost as a reinforcing element and toughener, by increasing the impact strength of PEN to some extent while not significantly reducing the tensile strength. At the same time the crystallisation temperature is reduced by nearly 40°C, which should make the blends processable at a much lower temperature than for pure PEN, although that aspect of the properties has yet to be confirmed by melt viscosity measurements. In addition, the improvement of the mechanical properties of PBT/PEN blends with addition of up to 50 wt% PBT to PEN gives much benefit economically without a significant loss of other properties because of low cost of PBT.

It is generally agreed that transesterification reaction gives improved miscibility, i.e., chemical reaction is a necessary condition for miscibility. However, in the absence of chemical bonding interactions [27] in the interphase regions of the blends with dispersed PBT, we attribute the improved mechanical properties of the PBT/PEN blends to physical interactions occurring over the interfacial areas that are orders of magnitude larger, per unit mass of blend, than those in the corresponding Ny66/PEN blends, which have poor mechanical properties.

In some respects the difference in properties of the two blend systems is contrary to expectations. Ny66 and PBT have similar, relatively low glass transition temperatures, but Ny66 chains have abundant hydrogen bond donor (—NH) groups that might be expected to form hydrogen bonds to acceptor groups (—C=O and —O—) in PEN chains, which should promote miscibility of Ny66 and PEN. The lack of apparent miscibility implies that polyamide-polyamide interactions are much stronger than polyamide-polyester interactions. In the PBT/PEN system (as in PET/PEN blends, which are miscible in some proportions) the properties cannot be ascribed to chemical bonding interactions or to specific interactions such as hydrogen bonding. However, the similar structures (both PEN and PBT have ester groups, aliphatic chains and aromatic rings) may give some affinities to the PBT/PEN system.

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