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FEATURE ARTICLE

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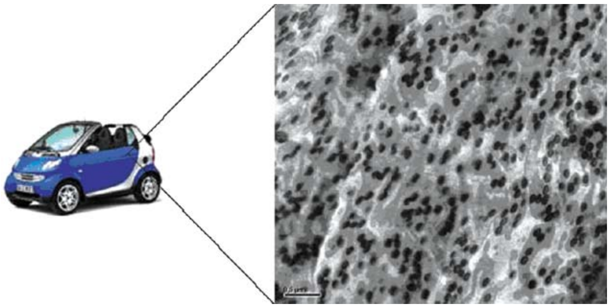
Polymer blends: the PC–PBT case

José M. R. C. A. Santos and James T. Guthrie

Binary polymer alloys represent a fast growing sector of the plastics industry. They can result in new materials exhibiting high degrees of synergism in behaviour and/or materials with optimal cost/performance.



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Polymer blends: the PC–PBT case

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An example of commercially important binary polymer blends is that of PC–PBT composites. The current knowledge of the physical, mechanical and chemical properties of these blends is reviewed and updated in the light of interpretations based on Lewis acid–base intermolecular interactions, as quantified by inverse gas chromatography, carried out under infinite dilution conditions.

1. Introduction

Polymer blends, by definition, are physical mixtures of structurally different homopolymers or copolymers. In polymer blends or polymer alloys, the mixing of two or more polymers provides a new material with a modified array of properties. The constituent polymers are held together through the action of non-covalent forces only. In favourable cases, multiphase systems can display an interesting synergism of properties. The properties of immiscible and partially miscible blends are highly sensitive to their morphology, phase separation, (that is miscibility, connectivity and sizes of the phases, interface thickness) and phase preferences. These, in turn, strongly depend on the interactions between the blend components and on the processing conditions. Most polymers are mutually immiscible from a thermodynamic standpoint since the entropic contribution to the free energy of mixing is negligible.[1,2] Hence, most commercial polymer blends are multiphase systems.

Commercial polymer blends or alloys normally consist of binary systems with partial solubility, thus containing more than two phases. Occasionally, a third component may be added to serve as a compatibiliser or as an impact modifier. Processing conditions play an important role among the factors that influence the degree of solubility of the components and also the morphological structure of a moulded part.[2,3] The morphology also depends strongly on the composition, with bi-continuous morphologies usually observed at near critical compositions.

Blends of thermoplastic polyesters, namely poly(butylene terephthalate) (PBT), with the poly(carbonate) of bisphenol-A (PC), constitute an important type of commercial composite. The semi-crystalline PBT, Fig. 1a), provides chemical resistance and thermal stability. The amorphous PC, Fig. 1b), provides impact resistance, toughness, and dimensional stability at elevated temperatures. Most commercial PC–PBT blends consist of approximately 50/50 (wt%) of a PC and a PBT. An elastomer is usually added to the polymer blend to improve its impact toughness. Inorganic pigments are normally added as 0.1–2.0 wt% of the total blend. Additives such as thermal stabilisers and transesterification reaction inhibitors are also included in the formulations.

The thermal stabiliser is added to prevent thermal degradation, indicated in the chain scission of the PC and of the PBT, and in the crosslinking (oxidative degradation) of poly(methyl methacrylate)–poly(styrene)–poly(butadiene)-based impact modifiers. These deteriorating effects are due to the formation of radicals caused by UV-light, heat and shearing. Heat stabilisers are added to quench the radicals that are formed during melting and during moulding of the material.

In the polymer blend, the PC and the PBT are physically mixed. The occurrence of transesterification, which results in the formation of the PC–PBT copolyester, is avoided by design. A detailed description of transesterification inhibition strategies is given in section 4.1. The degree of chemical resistance of these blends is directly related to the relative percentage of PBT within the blend. In general, the higher the percentage of PBT, the higher is the chemical resistance of the composite material. The alloys, usually with co-continuous morphology, have good processability, heat resistance and chemical resistance, low temperature impact resistance and tensile strength. Most of these blends show high notched impact strength down to −40 °C. From the commercial application point of view, it can be said that the major advantages of PC–PBT alloys are increased stiffness and an improved resistance to chemicals.

PC–PBT blends are mainly processed by injection moulding. However, grades for extrusion, blow moulding, as well as for transfer and compression moulding, solid state processing, and

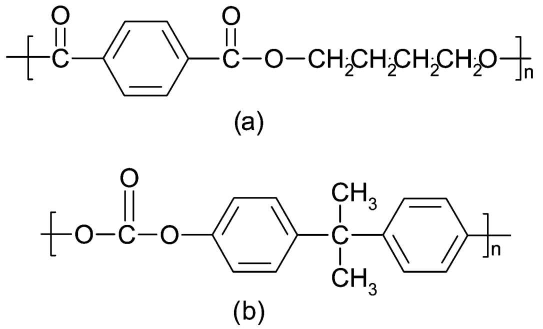

Fig. 1 Repeating unit in (a) poly(butylene terephthalate) and (b) bisphenol A poly(carbonate).

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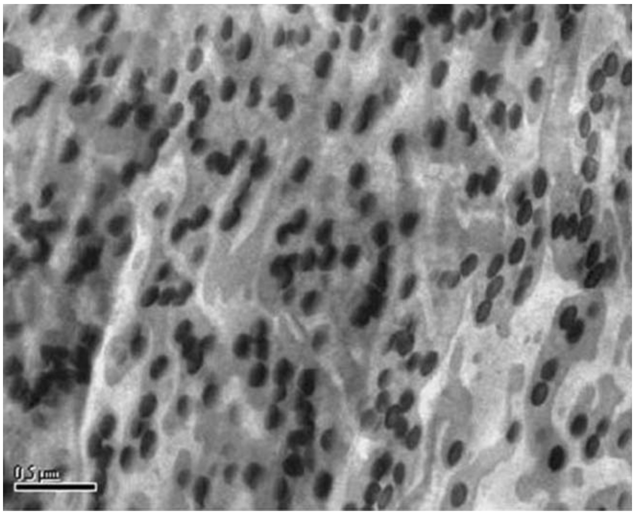

Fig. 2 TEM image of the PC–PBT–MBS blend corresponding to the unpigmented blend.

thermoforming are available. The moulded parts can be painted, hot stamped, metalised and plated. These blends are mainly used in the automotive industry for body panels that require toughness at low temperatures, chemical resistance, heat resistance and dimensional stability.[4] Commercial blends of PC and of PBT include Xenoy®, from General Electric Plastics, Makroblend®, from Bayer, Sabre® 1600 from the Dow Chemical Company, Stapron® E from DSM and Ultrablend® KR from BASF.

Fig. 2 gives a typical TEM image of a PC–PBT blend that includes MBS rubber as the impact modifier. This impact modifier consists of a core of poly(styrene), an inner layer of poly(butadiene) and a shell of poly(methyl methacrylate). A schematic representation of the characteristic morphology observed in a typical TEM image of these bends is presented in Fig. 3. The TEM image corresponds to the cross-section of a tensile bar that was processed as an unpigmented blend. In Fig. 2, the PC domains can be identified as the darker areas and the PBT phase as the lighter areas. The impact modifier (MBS rubber) particles are seen in the PC phase as small dark particles. In blends that are stabilised against transesterification, PC and PBT are only partially miscible (less than 10%).

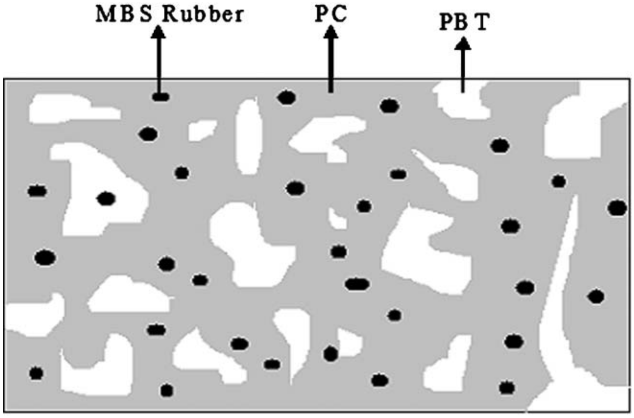

Fig. 3 Schematic representation of the characteristic morphology observed in a typical TEM image of the PC–PBT–MBS blends.

2. Impact modification of PC–PBT blends

Controlling of the transesterification reactions is critical because the crystallinity of the PBT decreases with increasing transesterification extent, reducing the mechanical performance as well as solvent resistance, chemical resistance and thermal stability. On the other hand, if the extent of the transesterification reactions is too limited, the interphase adhesion will be poor, leading to brittleness. Therefore, the introduction of impact modifiers, compatibilisers, and glass fibres into the composition is preferable to the use of the transesterification reaction in the improvement of the impact resistance.

Among the additives used, MBS impact modifiers have demonstrated a significant impact-modifying effect at low temperatures[5–7] and are used normally as 15–20 wt%.[4,7] The PMMA-shell of this impact modifier gives "good adhesion" with the polycarbonate, in which the impact modifier is to be dispersed. The poly(butadiene) is the component that causes the higher impact strength. The poly(styrene) layer has an aesthetic function. It is used in the impact modifier to ensure the proper reflection of light.

Functional MBS impact modifiers for PC–PBT blends are also reported in the literature. Tseng and Lee[5] grafted three different kinds of functional group containing monomers in the outer layer of the MBS: glycidyl methacrylate, acrylamide, and methacrylic acid. The introduction of a functional group to improve the adhesion between the MBS rubber and the PC–PBT alloy and, thus, to have a beneficial effect on the impact strength of these blends, has been realized. The adhesion was improved by enhancing the intermolecular forces interaction strength (namely Lewis acid–base interactions) between the surface modified MBS particles and the polymeric matrix. The impact strength was observed to improve if the amount of functional monomer was between 4 and 6 wt%, thus allowing a smaller amount of impact modifier to be used.

The mechanical properties, the chemical resistance and the impact resistance of PC–PBT blends incorporating butadiene based and butyl acrylate based impact modifiers have been studied by Lyu.[8] It was concluded that the butyl acrylate based impact modifier resulted in blends showing slightly greater impact strength than that of the butadiene based impact modifier blends, for temperatures above 0 °C. Yet, the butadiene based impact modifier blends showed considerably higher impact strength than the butyl acrylate based impact modifier blends for temperatures below 0 °C.

Bai *et al.*[9] have recently reported the use of ethylene–butylacrylate–glycidyl methacrylate (PTW) as a toughening modifier for PC–PBT blends. The blends were characterized by DMTA, DSC, and SEM. Their results show that the addition of PTW leads to great increases in the impact strength, in the elongation at break and in the Vicat softening temperature. The tensile strength and the flexural properties show a reduction. Also, the relation between the impact resistance and the phase morphology is discussed, and the critical ligament size for PBT–PC is determined. The critical ligament thickness below which ductile behaviour occurs was determined to be around 0.4 mm for these blends. The fracture surfaces of the toughened PBT–PC–PTW blends showed extensive yielding of the matrix.

3. Mechanical properties of PC–PBT blends

In general, both for homopolymers and for polymer blends, the molecular weight influences the impact toughness and the viscoelastic properties such as the tensile modulus and, thus, the toughness of the material. The degree of crystallinity determines the impact resistance and the viscoelastic properties such as the strain at break and the extendibility of the material. Also, the miscibility level in polymer blends, both inherent and due to transesterification reactions, influences the impact resistance, the creep resistance and the aforementioned viscoelastic properties.

It has been shown that the toughness of 50/50 wt% PC–PBT blends lies on the additive line between the toughness of bulk PC and PBT, except when tested under non-plane strain condition (*e.g.* using thin samples or at high temperatures).[10,11] The introduction of rubbery particles into the PC domains has been suggested as a means of eliminating the crack bridging effect of the PC phase, as the yield strength of this polymer will be strongly diminished by the rubbery particles.

Pompe and coworkers[12] studied the notched impact toughness of PC–PBT blends in which the copolyester content could not be detected within the limits of the analytical methods utilised. They concluded that the composition is not the main factor for the notched impact toughness and that, in the amorphous state, the modulus, strength, elongation at failure and notched Izod impact toughness are nearly linearly dependent on the composition.

Wu *et al.*[13–15] found that, for PC–PBT–MBS rubber blends, the increase in impact toughness with temperature is a consequence of the relaxation processes of the rubbery zones and the parent polymers, in a relatively low-temperature range and the thermal blunting of the crack tip at higher temperatures. The mechanisms suggested for the excellent impact resistance of this blend are multiple crazing, shear yielding, crazing with shear yielding and rubbery particle stretching and tearing. Wu and Mai[14,16] found that massive plastic deformation of the matrix occurred after rubber particle cavitation. This plastic deformation, shear yielding, was responsible for the drastic enhancement in fracture toughness, although the widespread cavitation did also absorb a considerable amount of energy.

Under an applied stress, rigid particles, such as inorganic pigments, induce tensile stress concentrations in the matrix. They become readily debonded from the matrix as they are unable to deform to any significant degree. Since there is limited adhesion between the rigid particulates and the matrix, the inorganic particles are not particularly effective craze or crack terminators, resulting in poorer toughening performance when compared to that achieved with well-bounded rubber particles.[17]

The effect of PBT–PC interfacial strength on the fracture and tensile properties of the PBT–PC blends has been addressed by Wu *et al.*[18] To this end, a series of PBT–PC blends with different contents of *in situ* formed PBT–PC copolymers were prepared by melt blending. The existence of the PBT–PC copolymer was investigated by means of DSC. The characterisation of the blends' microstructure showed that the domain sizes of the PBT and PC decrease and that the PBT–PC interfacial strength increases with the copolymer content. The transesterified PC–PBT blends had higher yield strength, elongation at break and tensile modulus than the control samples. The fracture toughness of the blends increases with the copolymer content. The impact toughness of the transesterified PBT–PC blends was found to decrease with the increase of the blends' interfacial strength.

The role of interphase interactions in the impact strength of PC–PBT and PC–PET blends has also been studied by Pesetskii *et al.*[19] The major conclusion was that phase separation phenomena can cause variations in properties of both the amorphous and crystalline phases. The effects of PBT contents on the blends' crystallinity and T_g were assessed. The DMTA results showed strong adhesion between phases in the blends over the temperature range from the beta-transition observed for PC and the T_g of PBT. The adhesion strength decreases in the temperature range from the T_g of PBT to that of PC. It was observed that over the temperature range where interphases interactions are strong, and the two components are in the glassy state, the impact resistance of the blends is weak. Over the temperature range between the T_g of the PBT and the T_g of the PC the impact resistance of the blends increases. This behaviour was attributed to dissipation of the energy of crack propagation in the PBT amorphous phase.

Our results,[20] Fig. 4, show that the impact energy absorption (notched Izod impact testing at 23 °C) of unpigmented PC–PBT blend (50/50 wt%) containing 12 wt% of MBS rubber is closer to that of the PC phase than to that of the PBT phase. The PBT-based samples and the PC-based samples were formulated so as to emulate the corresponding phases in the PC–PBT–MBS blends. Thus, the PC-based samples also comprise MBS rubber. The impact resistance was concluded to be influenced mainly by the molecular mass of

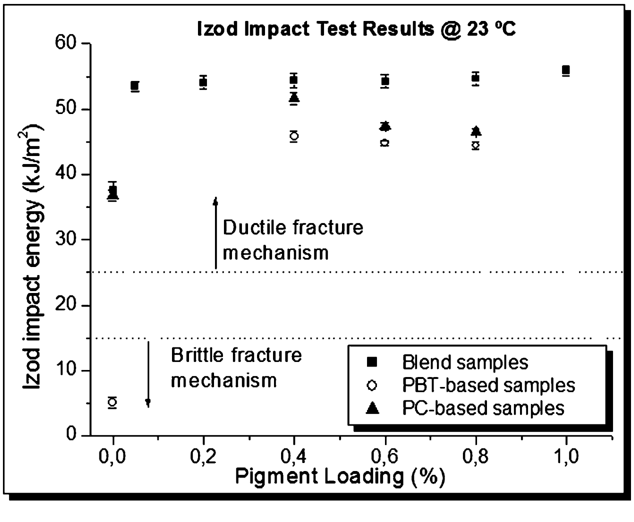

Fig. 4 Variation of the notched Izod impact energy absorption for PC–PBT–MBS blend samples, PBT-based samples and PC-based samples, as a function of C. I. Pigment Blue 28 loading.

the amorphous polymer and by the crystallinity degree. These influences increase in importance as the average molecular weights of the PC and of the PBT decrease. The greater the molecular weight of the PC, the better is the impact energy absorption. However, when C. I. Pigment Blue 28 (an inorganic pigment: $CoAl_2O_4$) is included in the formulation, the impact resistance of the blend is greater than that of the pigmented PC-based samples and than that of the pigmented PBT-based samples. The C. I. Pigment Blue 28 also enhances the impact resistance of the PC-based samples and of the PBT-based samples. The pigment both indirectly (due to its influence on the transesterification reactions and on the crystallisation properties of the blends) and directly (due to alterations to the mechanisms of impact energy absorption) influences the impact resistance of the blend. It was also concluded that the pigment particles present good adhesion to the PC phase and to the PBT phase, in accord with expectation from evaluation, by means of inverse gas chromatography (IGC), of the intermolecular forces interaction potential between the pigment, the PC, the PBT and the MBS rubber,[21] as explained below.

4. Phase separation and phase preferences in impact-modified PC–PBT blends

Blends of PC and PBT represent an excellent example of the complex interplay between phase separation and phase preferences, crystallisation properties, thermal degradation and transesterification reactions.

In approximately 50/50 wt% PC–PBT blends, partial miscibility exists both in the melt and after melt blending, with phase separation occurring during PBT crystallisation.[6,22–28] The solubility of PBT in PC is better by a factor of 2 than the solubility of PC in PBT.[29] Conversely, Cheng *et al.*[30] concluded that PC is more miscible in PBT than the opposite. Moreover, completely immiscible PC–PBT blends have been reported.[12,31–33] These disagreements arise from the complex behaviour of PC–PBT blends during melt processing, in which there is competition between liquid–liquid phase separation, interfacial transesterification reactions, crystallisation of PBT and reduction of the molecular weights of PC and of PBT.

The partial miscibility of the amorphous phases (amorphous PBT and amorphous PC) in this polymer blend has been attributed to various factors such as the morphology of the crystalline phase,[28,32] transesterification reactions resulting in PC–PBT copolyesters[12,23,25,32,34] and the closeness of the solubility parameters of PC and PBT.[35] Most of these studies have been based on:

(a) Thermal analysis of the influence of the miscibility of PC and PBT on the T_g of PC and of PBT, and on the T_m, the crystallisation temperature (T_c) and crystallinity degree of PBT (DSC,[23,26,30,32,35–38] DMTA,[16,26,28,30,37,39–41] TGA[28,30,38]);

(b) Microscopic assessment of the influence of the miscibility of PC and PBT on the morphology of the blends (SEM,[11,16,37] TEM[10,11,16,19,36,37] and OM[11,23,35]);

(c) Spectroscopic assessment of the influence of miscibility of PBT and PC on characteristic bands of PC, PBT and PC-PBT copolymer (FTIR[23,37,38] and NMR[23]);

(d) Other techniques such as solvent extraction methods[42] and density measurements.[38,43]

Evaluations based on the Lewis acidic/basic properties of the major components of these polymeric systems, as determined by IGC, and consequences to the establishment of specific intermolecular interactions and phase separation/preferences phenomena, have been published.[21]

4.1 The transesterification reaction between PC and PBT

Interchange reactions in step-growth polymers at elevated temperatures are well known, especially with polyesters. Delimoy *et al.*,[44] Birley and Chen,[42] Bertilsson *et al.*,[43] Hamilton *et al.*,[40] Hobbs *et al.*,[45] Kim and Burns,[29] Kong and Hay,[46] Montaudo *et al.*,[47] Pellow-Jarman and Hetem,[48] Tattum and coworkers,[37] Wilkinson and colleagues,[25,34,36] and Pompe and coworkers[12,23,31,32,49,50] studied in detail the interchange reactions in PC–PBT blends.

This PC–PBT blends may undergo three types of exchange reactions during melt processing:[48,49] acidolysis (reaction between the carboxyl end-groups of PBT with the carbonate groups of the PC), alcoholysis (reaction between the hydroxyl end-groups of PBT with the carbonate groups of PC) and direct transesterification (reaction between the ester groups of PBT with the carbonate groups of PC). The main process is that of direct transesterification.[24,31] As a consequence of this, copolymers act as compatibilisers in these blends, making it difficult to characterise the inherent miscibility of PC and PBT in melt blends. Delimoy *et al.*[44] reported that IR spectroscopy and NMR gave a very coherent picture of the PC–PBT copolyester structure that resulted from an exchange reaction of the aliphatic ester sequences and the aromatic carbonate sequences.

Some researchers believe that the transesterification reaction in PC–PBT blends occurs only at temperatures that are greater than the T_m of PBT, approximately 220 °C.[30,42,47] Pompe[12,31] has shown, nevertheless, that transesterification also occurs after "thermal treatment" at 200 and 210 °C (lower than the T_m of PBT).

The transesterification reaction is catalysed by Ti residues that are present in the PBT,[12,23,25,44] which can, furthermore, lead to the development of a yellow colour in the blend.[40] Consistent performance of PC–PBT blends can be achieved only through control of melt transesterification. If this reaction is not controlled, the properties of the blend will change with each thermal history. The transesterification process can be suppressed by added stabilisers,[25,44] but complete suppression cannot be proven.[12,31] The problem is that the analytical detection of a very small, *in situ* formed copolymer content is limited by the sensitivity of methods such as NMR and FTIR,[12,31,35] which is reported to be restricted to copolymer concentrations above 1 mol%.[44] Even very low contents of block copolymers are known to influence the morphology of immiscible blends.[31,44] Furthermore, a correct estimation of the copolymer content is impossible, because the transesterification is influenced by many parameters. Additionally these parameters have an interaction. On this basis, Pompe and coworkers[12,31] concluded that PC and PBT are inherently immiscible and that the partial miscibility referred to in the literature by analysis of the glass transition behaviour is caused by the compatibilisation of both components by a small, virtually undetectable copolymer content. They also concluded that the transesterification is at first faster than the reaction between the stabiliser and the residual catalyst. In summary, the direct proof of the complete absence of a copolyester is virtually impossible.

Many additives have been used as stabilisers to prevent-transesterification. These include phosphates and phosphorus-containing acids.[30,40] Stabiliser systems based on phosphoric acid can lead to a decrease of the hydrolytic stability of the blend. Di-*n*-octadecyl[44] and triphenyl phospite[35] are widely used as efficient transesterification inhibitors. However, Birley and Chen[42] found that, even in commercial PC–PBT blends (Xenoy® CL-100), that were stabilised against transesterification, small but significant reactions occurred after 3 min at 240 °C. Large structural changes were observed after 30 min at 270 °C.

The transesterification rate increases with decreasing molecular weight of the PC.[12] Therefore, the reported increased miscibility with lower molecular weight species can also have contributed to the greater transesterification rate.

In what concerns the influence of transesterification reactions on surface composition and chemical structure, little information can be found in the literature. Auditore *et al.*[51] have used time-of-flight secondary ion mass spectrometry (ToF-SIMS), in the so called "static-SIMS" mode, in order to follow the surface evolution caused by thermal processing of PC–PBT and PC–PET blends at 270 °C. The ToF-SIMS spectra obtained from the surface of PBT–PC and PET–PC blends at increasing melt mixing times successfully allowed to follow the evolution of peaks related with the products of the reactions inside the melt blend. The authors concluded that the surface composition at the early stages of the process is dominated by segregation of polycarbonate chain segments. This phenomenon becomes increasingly less pronounced as the transesterification reactions evolve.

4.2 Crystallisation properties of PC–PBT blends

The presence of a second component, either in the molten state or in the solid state, influences both the nucleation and the crystal growth of semicrystalline polymers.[52] Usually, the presence of the second component physically restricts the movement of the crystallising polymer molecules and, thus, constrains the crystal growth. The extent of this effect is controlled by the blend composition, by the relative melt viscosities of the polymers involved, and by their miscibility. The effect of blending on nucleation is more complex, especially in the presence of the melt of the second component, namely with regard to the formation of critical size nuclei.

The crystallisation temperature of PBT is approximately 180 °C.[19] The crystallinity of the PBT in PC–PBT blends has been determined by Hanrahan *et al.*[30] and by Cheng *et al.*[30] to be 26 to 38%. A maximum degree of PBT crystallisation of 40% in these blends was observed by Ratzsch *et al.*[28] The overall degree of crystallinity is greater in cold-crystallised blends than in melt crystallised blends.[30] The formation of PBT crystals from within the PC-rich phase, as well as within the PBT-rich phase, leads to greater overall crystallinity, in the case of cold-crystallised blends.

With high T_g PC, the PBT crystallisation from the melt depends strongly on the "crystallisation window"[26] and on the cooling rate.[12] The "crystallisation window" of the blend is determined by the melting temperature (T_m) and the T_g of the PC phase, upon cooling.[50] The crystallisation rate is at its maximum at the crystallisation temperature (T_c). This temperature for PBT is strongly dependent on the cooling rate.[26] The T_g of PC and that of PBT are slightly dependent on the cooling rate. The crystallisation of PBT in a partially miscible PC blend can occur from the PBT-rich phase or from the PC-rich phase.[24] The crystallisation from the PBT-rich phase is hindered by the presence of dissolved PC that has a higher T_g.[12,52] The chain mobility is reduced and the crystallisation rate is slowed down. The rate of crystallisation from the PC-rich phase is strongly hindered by the high T_g of this phase. Here, the "crystallisation window" is small and the rate of crystallisation very slow.

The molecular weight of PBT is the determining factor as far as crystallinity is concerned. The PBT degree of crystallinity increases with decreasing molecular weight of PBT, and of PC, due to increased molecular chain mobility. For samples that are effectively stabilised against transesterification, it has been suggested[43] that processing temperatures that are higher than 260 °C might have resulted in a higher degree of crystallisation due to lowering of the PC and PBT molecular weight by thermal degradation. Also, the molecular chain length decreases by eventual, non-detectable, transesterification. However, if the molecular chain is shorter than the critical length, that is necessary for crystallisability, the PBT crystallinity decreases. This is the reason why some authors, *e.g.* Hopfe *et al.*,[23] report decreased crystallinity with decreased molecular weight. Hamilton and Galluci[40] showed that if low molecular weight PC and PBT are used in transesterification stabilised blends, the improvement of miscibility is also sufficient to reduce the rate of crystallisation.

The mechanical properties of polymers are strongly influenced by an induced molecular orientation occurring under various polymer processing operations. This is particularly important in semi-crystalline/amorphous, partially miscible, polymer blends. The orientation and orientation relaxation in PBT–PC blends has been the subject of study of Kalkar *et al.*,[53] by means of rheo-optical FTIR spectroscopy. Among other aspects, the effect of increasing amount of amorphous content in the blend on the orientation behaviour of the crystallisable component was studied. The authors concluded that the molecular orientation and the deformation mechanism are consistent with the resulting PBT spherulitic morphology and with the temporary network formed by the elongated PBT and PC chains inside the interlamellar regions. Another important conclusion is that structural transformation in the semi-crystalline PBT is the dominant process during stretching of the PBT–PC blends, as encountered in uniaxially drawn solution-cast films.

4.3 Phase separation in PC–PBT blends

The most commonly used method for establishing miscibility or partial phase mixing in polymer–polymer blends is the analysis of the behaviour of glass transition temperatures (T_g).

This characteristic temperature is dependent on blend composition. A homogenous blend of two miscible polymers will exhibit a single glass transition between the T_g values of the components with a sharpness of the transition that is similar to that of the components. In the case of limited miscibility, two phases exist and two separate glass transitions between those of the constituents are observed. The difference between the glass temperature of the partially mixed phase and that of the corresponding pure component gives information concerning the level of partial miscibility. It is important to note that a single T_g does not necessarily mean that miscibility exists on a molecular level. A single T_g also appears if the components are separated in phases the size of which is smaller than a critical value. This critical value ranges from $\leqslant 5$ µm to 30–50 nm.[12] Other commonly used methods to assess miscibility in polymer blends include the melting point depression method,[12,26,30,36,52,54–59] light scattering studies and X-ray scattering studies.[30]

Delimoy *et al.*,[35,44] Bertilsson and colleagues[60] and Abdeyev and Chalykh (cited by Cheng[30]) reported UCST behaviour in PC–PBT blends, suggesting that the mixture is miscible at temperatures above a critical temperature that depends on the composition. On the other hand, Okamoto and Inoue[61]found LCST behaviour in a PC–PBT (50/50 wt%) blend, by means of a time-resolved light-scattering study. A spinodal temperature of 198 °C was determined.

Phase mixing is in kinetic competition with the crystallisation of the PBT (initiated at temperatures below T_m). This polymer has one of the highest rates of crystallisation of common polymers and, although some retardation occurs, due to the presence of the PC in the PBT-rich phase, the crystallisation kinetics of the PBT-rich phase is still fast in most PC–PBT blends.[34,37] Finally, the reductions of the molecular weight of the PC and of the PBT due to thermal degradation[6,62] and the occurrence of transesterification also contribute to miscibility of PC and PBT. Summarising, it can be established that the construction of a phase diagram of the PC–PBT blend system from the thermodynamic point of view would be very difficult, if at all possible.

Ratzsch *et al.*[28] found that, in DMTA and DSC studies of blends prepared by melt processing in an extruder, followed by injection moulding, shifts of the PC T_g occur, indicating a certain degree of miscibility. They concluded that PC and PBT are miscible if both components are liquid or completely amorphous.

The immiscibility of PC and PBT found by Pompe[12] is in agreement with the results of Hanrahan *et al.*[33] and Hobbs *et al.*,[45] obtained on solution-cast blends. Nevertheless, as pointed out by Pompe,[12] these results can be influenced by the kinetics of evaporation of the solvent and, therefore, cannot be used as providing conclusions concerning inherent properties such as the miscibility of PC and PBT. Liquid–liquid phase separation during evaporation of the solvent can lead to different phase behaviour as in a quasi-equilibrium state.[12,45] In this way, it is not clear whether the observed behaviour represents the inherent immiscibility or a special state of phase segregation.

Cheng and co-workers[30] studied blends of PBT and PC, for a range of molecular weights and blend compositions. The molecular weight of the PBT is determinant as far as the crystallinity and miscibility is concerned. The degree of crystallinity of PBT increases with the decreasing molecular weight of the PBT, and of the PC, agreeing with other researchers.[49] The T_g of the PC-rich phase was lower in blends that had a lower molecular weight of PC than in blends that had a higher molecular weight, but more pronounced lowering was seen when low molecular weight PBT was used. The investigated blend states were completely crystallised. Also, it was observed that the T_g of the PBT-rich phase shifts to higher temperatures if low molecular weight PBT is used. The authors concluded that the compatibility would be better if the molecular weight of the PC, and of PBT, is smaller. Furthermore, in 40/60 wt% PBT–PC blends, the molecular weight of PBT affects the amorphous phases more than does the molecular weight of PC.

4.4 Phase preferences in PC–PBT blends

Another aspect of the polymer blend studied that is of interest is the preferential presence of the impact modifier (MBS rubber) in the PC phase,[6,19,27,39,44,60] although not to such an extent as was found for the studies relating to the partial miscibility of PC and PBT. This phase preference is thought to be caused partially by the expulsion of the impact modifier particles from the crystallising PBT. Thus, "bad" interaction of the shell of the modifier with the molten matrix during blending, especially with the PC is thought to occur,[36] by mechanical stripping and partial dissolution of the PBT in the surrounding PC[19] and by the values for the spreading coefficients of the blend components.[19,63]

The PC and the PMMA (the shell component of the MBS rubber) are not thermodynamically miscible, their interaction parameter being positive and small.[39] The preferential location of the MBS particles in the PC phase is, thus, not justifiable solely by its interaction capability with PC.

Dekkers *et al.*[19] concluded, from TEM evidence, that in PC–PBT–MBS blends in which the MBS rubber is precompounded with PBT, spontaneous migration of the MBS rubber particles into the PC phase is observed during mixing with PC. Furthermore, it is observed that migration and subsequent retention of the MBS in the PC phase is driven by the positive spreading pressure of the PC on the MBS, and facilitated by the partial solubility of the PBT phase and the PC phase.

The use of spreading coefficients is based on the definition of surface tension. However, the study of surface Lewis acidic/basic properties of PC, PBT and MBS rubber, and consequences to the effectiveness of intermolecular forces needed to be undertaken to explain this phase preference. Furthermore, the phase preference of insoluble colorants in polymer blends, and the consequences thereof for the physical properties, for the mechanical properties and for the colour properties of these systems was considered to be worthy of attention.

5. Intermolecular interactions in pigmented PC–PBT–MBS blends

Inverse gas chromatography, carried out at infinite dilution, was used by the authors to study the surface Lewis acid/base properties, and the dispersive component of the surface tension, of the major components of pigmented PC–PBT–MBS blends.[20,21] The materials characterized were C. I. Pigment Blue 28 ($CoAl_2O_4$, Sicopal® Blue K6310, from BASF), an impact modifier (MBS rubber from the Rohm and Haas Company), a PC (Lexan® from GE Plastics) and a PBT (Valox® also from GE Plastics).

The IGC experimental and data reduction procedures used were based on use of the approach of Fowkes, for the determination of the dispersive component of the surface tension, and on the Guttmann's electron acceptor and donor numbers, for the determination of the surface Lewis acidity and basicity constants.[21,64–66]

These analyses provided basis for an interpretation of the phase separation and the phase preferences that exist in these polymer blends and of the consequences to their physical properties and to their mechanical properties. The IGC characterisation of the major materials involved allowed for an evaluation of the interaction potential of C. I. Pigment Blue 28 with the remaining components of the pigmented composites.[21,66]

Controlled surface modifications of the pigment were achieved by means of a photo-sensitised grafting procedure.[20] Methacrylic acid–based units were successfully fixed onto the surface of C. I. Pigment Blue 28. This was confirmed using TGA, EDXA, IGC, SEM and pH value measurements of dispersions of the pigments.

Several analytical techniques, and mechanical tests, were used in the physical and chemical characterisation of the pigmented blends prepared by extrusion. Moreover, the influence of the pigments (C. I. Pigment Blue 28, unmodified version and surface-modified versions) on their physical properties, their mechanical properties, and their morphology has been studied.

With regard to the analysis of the Lewis acid–base interaction potential between the components of complex polymeric systems, the interaction parameters currently in use do not take into account the relative presence of each material in the polymeric system, the accessibility of the Lewis acidic and Lewis basic sites in relation to the Lewis acidic and Lewis basic sites available for interaction on the interactive species, and an appropriate balance of the contribution of the Lewis acid–acid and Lewis base–base repulsions to the overall Lewis acid–base interaction potential. Thus, a semi-quantitative analysis of the Lewis acid–base interaction potential between the major components of these blends was the approach used.[20,21]

The specific intermolecular forces are known to dominate over dispersion intermolecular forces and dipole–dipole intermolecular forces, and to determine, to a large extent, the useful properties of multicomponent polymeric systems. The values determined[21] for the surface Lewis acidity constant, K_a, and for the surface Lewis basicity constant, K_b, of the PBT, the PC, the unmodified C.I. Pigment Blue 28 and the MBS rubber (Table 1), show that:

(1) The PBT and the MBS rubber are the most interactive materials and PC is significantly less interactive that the remaining materials;

(2) The MBS rubber has the greater predominance of basic sites, and C. I. Pigment blue 28 the lower predominance;

Table 1 Values of K_a and K_b determined for the materials studied

	K_a	K_b
PC	0.09	0.48
BASF Sicopal® K6310	0.33	0.60
MBS rubber	0.10	1.14
PBT	0.49	0.96

(3) The MBS rubber, and the PBT are the more basic materials, and PBT and C. I. Pigment Blue 28 are the more acidic materials.

It is concluded that PBT molecules are preferentially involved in intramolecular and intermolecular interactions with other PBT molecules, because PBT is characterised by both strong Lewis basic functionality and strong Lewis acid functionality. It should also be noticed that no steric hindrance, due to bulky side-groups, is expected and, thus, the basic sites, and the acidic sites, are easily accessible to interaction through intermolecular forces and intramolecular forces. Nevertheless, it can then be said that, although naturally phase-separated, PC and PBT may be miscible to a certain, low, extent, as a consequence of Lewis acid–Lewis base attraction between these molecules and of Lewis base–base repulsion between PBT molecules (repulsion effect).[21]

The MBS rubber interacts preferentially with the PC rather than with the PBT molecules. This is due to two factors: (1) The preference of the PBT molecules to interact with other PBT molecules, and (2) The Lewis base–base repulsion between the PBT molecules and the MBS rubber particles. The second effect, *i.e.* a predominant repulsion effect, is due to the fact that the PBT molecules and the MBS rubber particles are very strong bases and the Lewis acidity of the MBS rubber is low. Therefore, the impact modifier interacts mainly through the basic sites. As the PC has the weakest Lewis basicity and weakest Lewis acidity, the base–base repulsion with the MBS rubber will not be as significant as is that between the impact modifier and the PBT. Thus, acid–base attraction is thought to dominate in the MBS rubber/PC pairing. Also, the PBT and the PC are used in an approximately 1 : 1 proportion, meaning that the interaction opportunities between the MBS rubber and the PC are substantial. The interaction between PC and the shell component of the MBS rubber (PMMA) has been shown by Nishimoto *et al.*[67] to be weak but slightly favourable. Good adhesion between the PC and the MBS rubber has also been reported by Dekkers and colleagues.[7] The fast crystallisation of PBT also contributes to the expulsion of the MBS rubber from the PBT domains.

The results presented in Table 1 also allows one to predict that C. I. Pigment Blue 28 interacts preferentially with the PBT molecules and then with the PC molecules. This is due to the fact that the pigment is a strong Lewis acid and the PBT is strong Lewis basic. Also, the PBT molecules are strongly Lewis acidic and the pigment is moderately Lewis basic. Nevertheless, as the PBT molecules prefer to interact with other PBT molecules, it is expected that some acid–base interaction between the pigment and the PC would occur. Based on the above thermodynamic analysis of the interaction potential between the pigment and the polymers, a predominantly Lewis basic pigment would be expected to locate itself preferentially in the amorphous PC phase, as is the case with the MBS rubber. A pigment with predominant surface Lewis acidity would be expected to be preferentially located in the PBT phase, due to the strong Lewis basic character of this polymer. The above-mentioned surface modifications of C. I. Pigment Blue 28 provided two pigments, one with dominant surface Lewis acidity and the other with dominant surface Lewis basicity.

C. I. Pigment Blue 28 has both direct influences and indirect influences on the physical and mechanical properties of the pigmented PC–PBT–MBS blends. The direct influences stem from the physical properties and from the chemical properties of the pigment (particle size and particle size distribution, surface area, surface chemical composition), and from its preferential location in the characteristic morphology of these blends. The indirect consequences arise from the influence the pigment has on the occurrence of transesterification reactions between the PC and the PBT, on the crystalline properties of the PBT, and on the molecular weights of the PC and of the PBT.[20]

At low pigment loadings, the unmodified pigment enhances the thermal degradation (molecular weight) of the polymers, mainly that of the PBT. The decrease in the molar mass of the PC and of the PBT at lower pigment loadings is also thought to have a contribution from the transesterification reactions that occurring between PC and PBT. At greater pigment loadings, the pigment particles act as an inhibitor of the transesterification reactions and of the thermal scission of the polymeric chains. The decrease in the molecular weight of the PBT, at low pigment loadings, caused by the use of C. I. Pigment Blue 28, was eliminated after the surface treatments. The molar mass of the PC and of the PBT in the blends was greater and the molar mass change with pigment loading was more consistent, when compared to the situation where the unmodified pigment was used. Transesterification reactions are importantly decreased upon the surface modifications of the pigment, especially at the lower pigment loadings. These differences result from changes in the preferential location of the modified pigments and from improved adhesion of these pigments with the polymeric matrix.

When the surface modified pigments are used, the impact resistance of the blends is slightly reduced, a consequence of the increased crystallinity degree. In addition, the dependence of the impact resistance on temperature is less pronounced, a consequence of changes to the impact toughening mechanisms and of better adhesion between the pigments and the polymers.

6. Conclusions

The current scientific knowledge relating to the technology and properties of the commercially important PC–PBT blends has been reviewed.

The interpretation and prediction of intermolecular interactions occurring in complex multicomponent polymeric systems, and the interpretation of consequences of such interactions to the physical and mechanical properties of these systems, has been shown to be facilitated by the use of the Lewis acid–base interactions concept and by quantification of these specific forces through inverse gas chromatography. Lewis acid–base interactions have proven to be determinant to the physical properties and to the mechanical properties of pigmented PC–PBT–MBS blends as they influence phase separation and phase preference phenomena.

The importance of the PBT-rich phase and of the PC-rich phase to the physical properties and to the mechanical properties of the PC–PBT–MBS blends depends on the magnitude of the molecular weights of the PC and of the PBT.

Pigments (*e.g.* C. I. Pigment Blue 28) can influence significantly the physical properties and the mechanical properties of the PC–PBT–MBS blends by affecting the thermal degradation of the polymers, the transesterification reaction and the crystalline properties of PBT. Direct contributions arise from the physical properties and from the chemical properties of the pigment.

The control of the surface Lewis acid–base properties of additives such as inorganic pigments has been shown to be an efficient method of controlling the useful properties of these blends, by means of adjusting the phase preference and the adhesion level of these particles in relation to the polymeric matrix.

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