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Blends of poly(methyl methacrylate) and polyamides

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The morphology of PMMA blends with different polyamides (PA-6, 6/9 and 12) was investigated by transmission electron microscopy, recognizing PA-6/PMMA as the most miscible pair. Blends of these polymers were prepared from solutions in *m*-cresol and formic acid and the morphology was highly dependent on the solvent. The morphology and the segregation degree of extruded PA-6/PMMA blends was investigated by scanning electron microscopy and dynamic-mechanical analysis. The compatibilization succeeded by the introduction of a block copolymer of polyamide and poly(ethylene oxide). © *1998 Kluwer Academic Publishers*

1. Introduction

The miscibility of polymer pairs depends on specific interactions. Hydrogen bonding, dipolar interactions, phenyl group coupling or ionic interactions may contribute to a negative heat of mixing, making homogeneous polymer blends thermodynamically stable. However, most of the polymer blends are obtained and used at conditions which are far from their thermodynamic equilibrium. The preparation conditions greatly influence their morphology, which determines their final properties.

The properties of polymer blends have been widely revised in the literature [1–5]. Blends have been prepared by many methods, the mechanical mixture having the greater commercial importance. The characteristics of a blend prepared from solution in a common solvent may be totally different from the same mixture obtained by melting the polymer components. When preparing blends by melting, the chain mobility is relatively low and the stress induced in the processing equipment is the dominant aspect, creating a variety of possible morphologies. In solution, the rate of solvent evaporation determines the final morphology.

Most of homopolymer blends are characterized by a phase diagram with lower critical solution temperature. At a temperature range in which the chain mobility is sufficient for processing, the mixtures has two phases. The glass transition temperature, T_g, is usually above the one-phase region of the phase diagram. For these systems, it is impossible to obtain a monophase material starting from the melted polymers. However, for many cases it is possible to obtain a monophase blend of the same components from a solution in a common solvent [6]. The solvent may act in two different ways.

(i) If the enthalpic interactions between the polymer pair are favourable enough to make a homogenous blend thermodynamically stable at a temperature below T_g, the solvent may increase polymer chain mobility, allowing the achievement of the one-phase region of the phase diagram.

(ii) On the other hand, in cases where the polymer pair is immiscible even at the temperature of interest, the solvent may thermodynamically interact with the polymer components as a co-solvent. The presence of the solvent minimizes the unfavourable enthalpic interactions between the polymer components, which otherwise lead to phase separation. If the solvent evaporation is fast enough, an abrupt decrease of the system mobility may occur before demixing and the non-equilibrium monophase situation is maintained.

The morphology of polymer mixtures becomes even more complex if one of the components is able to crystallize. From the thermodynamic point of view, crystallization of this component lowers the total free energy of the system. However, the crystallization kinetics plays a decisive role in determining the morphology. Crystallization of one polymer component may be induced by decreasing the temperature of a melted blend or by evaporating the solvent of a system containing the two polymers. In both cases, if crystallization is fast, a spherullitic structure may embed the multicomponent amorphous phase which is apparently homogenous, although the enthalpic interaction between them would favour demixing. A slow crystallization may be preceded by a liquid–liquid phase separation, which leads to a matrix/domain morphology.

In this work, the influence of preparation conditions is demonstrated for blends containing a crystallizable

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polymer, a polyamide, and an amorphous polymer, poly(methyl methacrylate) (PMMA). Blends were prepared from solution and by extrusion. The compatibilization of the polyamide-6/PMMA blend was investigated, adding a commercial copolymer with poly(ethylene oxide) and polyamide blocks.

2. Experimental procedure

2.1. Sample preparation

2.1.1. Extruded blend

Polyamide-6(PA-6) and poly(methyl methacrylate) (PMMA) ($M_w = 7 \times 10^5 \mathrm{g\,mol}^{-1}$, $M_w/M_n = 1.7$) were mixed in a twin-screw extruder. The temperature range along the screw was 150–210 °C. The die temperature was 30 °C. The melted blend was immediately immersed in water and transformed into pellets. The blend was then dried at 90 °C for 5 h before injection. The mixtures were injected at 215–230 °C into a mould at 70 °C for dumb-bell samples.

2.1.2. Mixer

The samples for the compatibilization experiments were obtained in a mixer (Haake HBI System 90). They were mixed at 240 °C, 45 r.p.m, for 5 min. They were previously dried at 90 °C for 60 min. The samples were pressed at 240 °C. Mixtures were obtained with (i) 50 wt% polyamide-6 and 50 wt% PMMA (non-compatibilized blend), and (ii) 45 wt% polyamide-6, 45 wt% PMMA and 10 wt% copolymer with poly (ethylene oxide) and polyamide-6 blocks, kindly supplied by Elf Atochem with the trade name PEBAX MX 1657.

2.1.3. Blends obtained from solution

For morphological analysis by transmission electron microscopy, 1 wt% solutions of PMMA and polyamides 6, 6/9 and 12, supplied by Aldrich, were prepared in *m*-cresol at 50 °C. Thin films were obtained by casting the solution on a glass surface. Polyamide-6/PMMA blends were prepared in an analogous way using formic acid as a solvent.

2.2. Morphological characterization

2.2.1. Transmission electron microscopy (TEM)

The thin films obtained from solution on glass were floated after immersion in a diluted hydrofluoric acid aqueous solution and collected on a copper grid for microscopy.

Images without staining or any other previous treatment were obtained in a Zeiss CEM 902 transmission electron microscope.

2.2.2. Scanning electrton microscopy (SEM)

For analysis in the scanning electron microscope (Joel T-300) the extruded blends were fractured in liquid nitrogen and covered with gold.

2.3. Dynamic-mechanical analysis

The dynamic mechanical analysis of the extruded/injected samples was performed in a TA Instrument DMA 983 Dynamic Mechanical Analyser. Experiments were performed at 1 Hz with deformation amplitude 0.2 mm. The temperature was increased at 5° C min^{-1} for all samples.

3. Results and discussion

3.1. Blends obtained from solution

The micrographs of (50/50) PMMA blends with PA-6, 6/9 and 12 obtained from solution in *m*-cresol are shown in Fig. 1. A crystalline phase clearly appears in

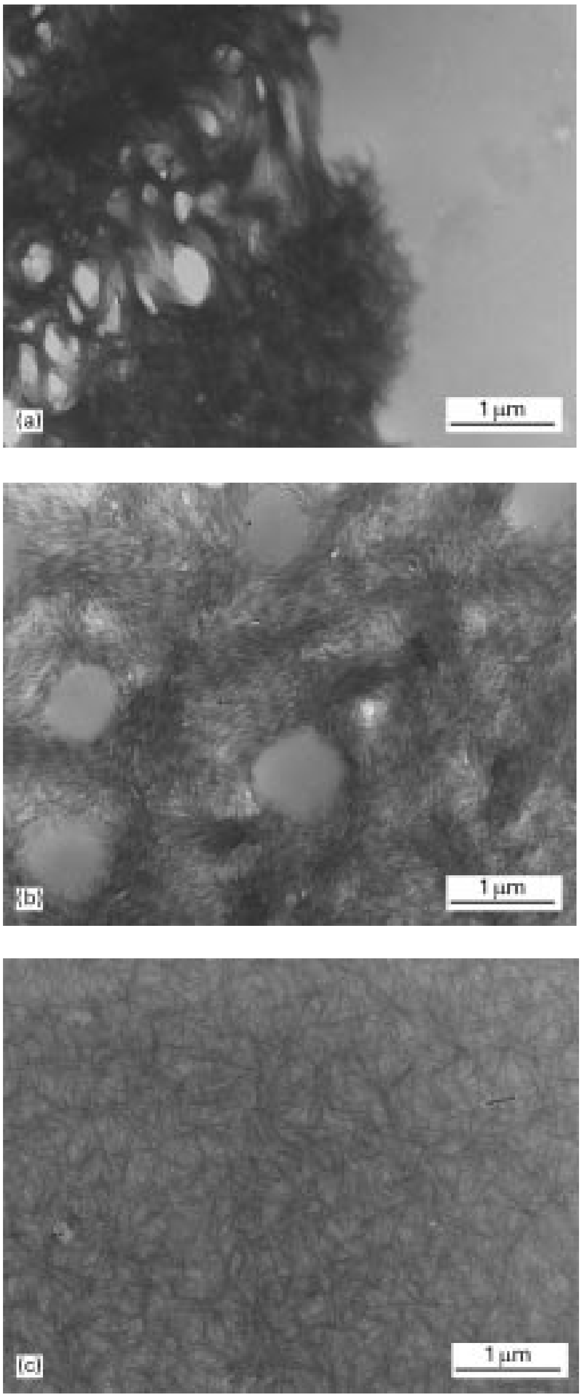

Figure 1 Transmission electron micrographs of 50/50 blends of (a) PA-12 (b) PA-6/9 and (c) PA-6 with PMMA 50/50, prepared from solution in *m*-cresol.

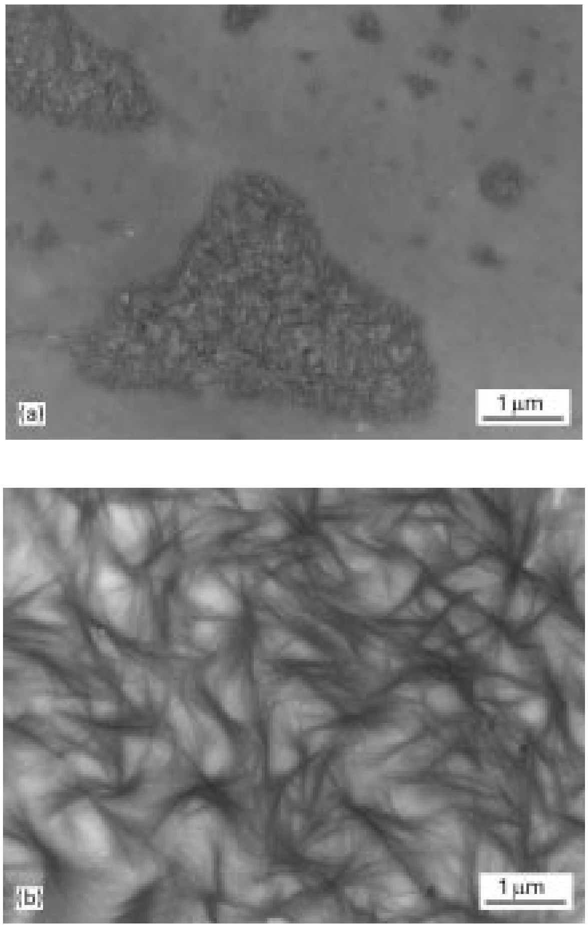

Figure 2 Transmission electron micrographs of (a) 80/20 and (b) 20/80 PA-6/PMMA blends prepared from solution in *m*-cresol.

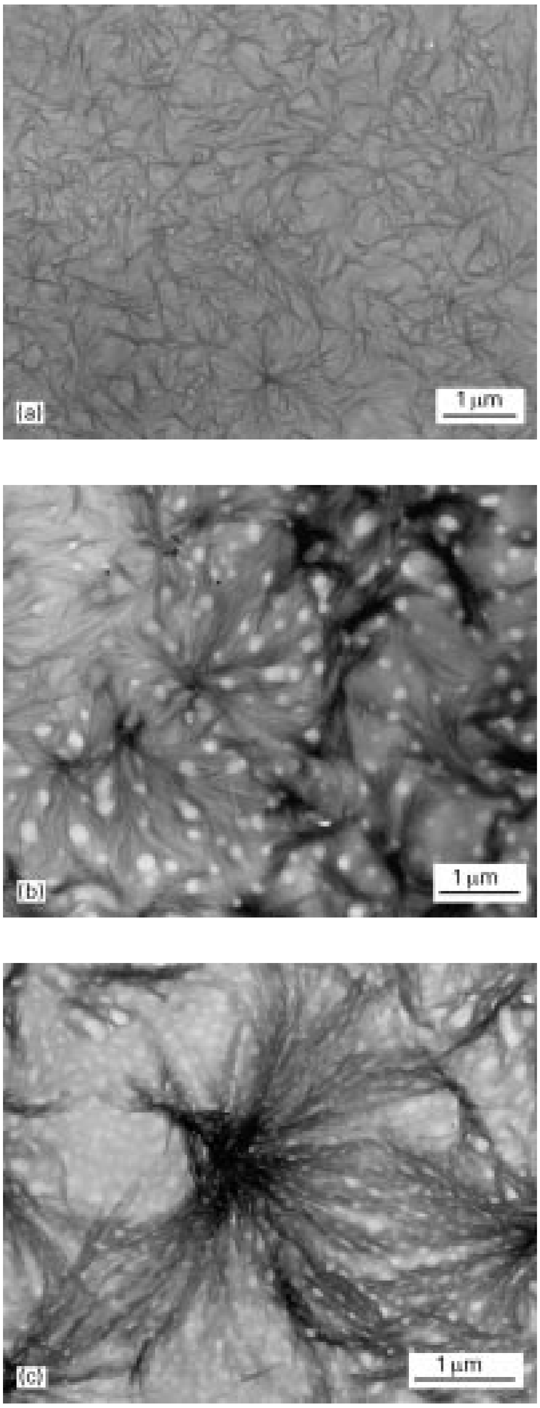

Figure 3 Transmission electron micrographs of (a) 20/80, (b) 50/50 and (c) 80/20 PA-6/PMMA blends prepared from solution in formic acid.

each mixture. A liquid–liquid phase separation led to quite different morphologies when different polyamides were used. Blends with PA-6/9 and PA-12 had large dispersed domains, while for blends with 50 wt% PA-6 (Fig. 1c) domains could not be detected.

The interactions between PMMA and PA-6 are much more favourable than with other polyamides. The miscibility of the polymer pair is probably enhanced by hydrogen bonding between the carbonyl group of PMMA and the amide groups. Considering the monomeric structure of each polyamide, PA-6 has the highest ratio of amide groups to $-CH_2-$ units (1: 5), which make it more available to interact with PMMA. PA-6/9 has one amide group to six $-CH_2-$ and PA-12 has one amide to eleven $-CH_2-$. Therefore, most of the experiments were further performed with the system PA-6/PMMA.

In blends with 50 or 80 wt % PA-6 obtained from solutions in *m*-cresol (Figs 1c and 2b) no domains could be observed. However, blends with 20 wt % PA-6 (Fig. 2a) have large domains of a crystalline phase dispersed in an amorphous matrix.

Fig. 3 shows transmission electron micrographs of thin films of 20/80, 50/50 e 80/20 PA-6/PMMA blends, obtained from solution in formic acid. The morphology is quite different than that of films obtained from *m*-cresol. The 20/80 PA-6/PMMA blend is more homogeneous and amorphous domains dispersed in a crystalline matrix can now be observed in films of 50/50 and 80/20 PA-6/PMMA blends.

The solvent has a clear influence on the morphology of PA/PMMA blends. The different morphologies can be explained, considering thermodynamic and kinetic aspects. From the thermodynamic point of view, there is a co-solvency effect both in the case of *m*-cresol as well as formic acid. The ternary solutions are homogeneous in a wide composition range. The polymer–polymer miscibility in the final binary blend is a function of the Flory–Huggins interaction parameter, χ_{23}, which does not vary with the solvent. However, the morphology ususally represents a non-equilibrium situation. It depends on interaction

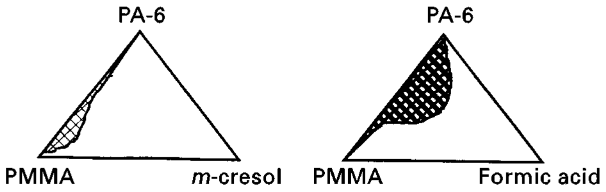

Figure 4 Hypothetical ternary phase diagrams for PA-6, PMMA and (a) *m*-cresol or (b) formic acid.

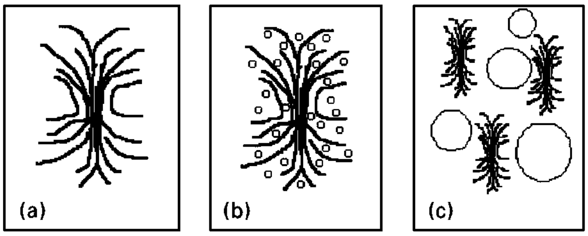

Figure 5 Morphologies obtained with different relative rates of crystallization v_c, and liquid–liquid phase separation, v_{l-1}: (a) $v_c > v_{l-1}$; (b) $v_c = v_{l-1}$; (c) $v_c < v_{l-1}$.

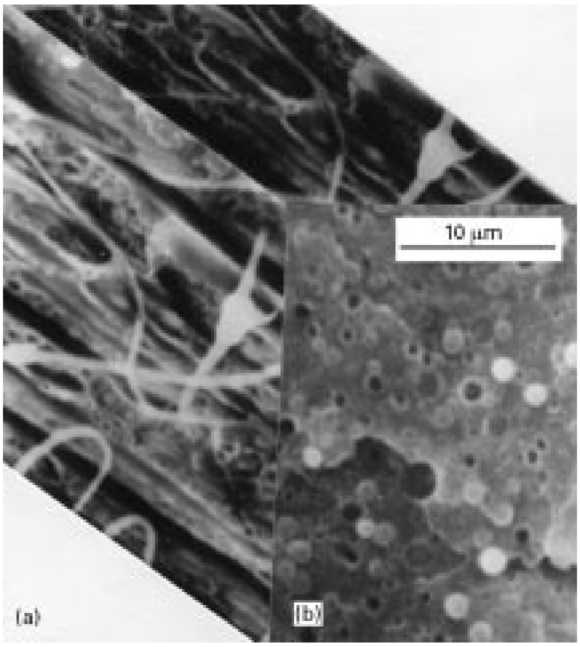

Figure 6 Scanning electron micrographs of 20/80 PA-6/PMMA blend in (a) a parallel and (b) an orthogonal direction to the injection direction.

parameters between the solvent and each of the polymers (χ_{12} and χ_{23}) and also on the evaporation path chosen for the film preparation. Three main situations have to be considered:

(i) in a relatively good common solvent, the polymer coils will be expanded and the interaction between chain segments of different polymers will be favoured. A non-equilibrium homogeneous blend may be obtained after solvent evaporation;

(ii) in a bad solvent, the polymer coils will contract and the contact between segments of different molecules will be disfavoured;

(iii) on the other hand, a very good solvent may dissolve the molecules to an extent which inhibits the contact between different polymer chains and the final blend becomes heterogeneous [6].

Hypothetical ternary phase diagrams are considered in Fig. 4 for each system with the respective solvent evaporation paths. The starting point was always the same: a diluted solution in a homogeneous region of the phase diagram. The final equilibrium condition was independent of the solvent: a binary PA-6/PMMA mixture probably immiscible in any composition. However, the ternary phase diagram with *m*-cresol has only a narrow two-phase region at high PA concentrations. Considering the kinetic aspects, the mobility of the polymeric chains near the two-phase region is probably very low, due to the low solvent content. If the solvent evaporation is fast enough, the final blend is obtained before any demixing occurs. For systems with formic acid, the two-phase region is larger, especially when the polyamide content is higher than 50 wt %. In this case, when the solvent is evaporated, the two-phase region is reached when the mobility is still high (high solvent content) and phase separation is allowed to proceed. The phase diagrams in Fig. 4 also explain why demixing is more evident at higher polyamide contents in films obtained from solutions in formic acid, in contrast to *m*-cresol.

Because one of the blend components is able to crystallize, kinetic aspects are even more important. In blends obtained from solution the spherullitic structures are much better formed, because the viscosity is lower, favouring an ordered arrangement of the polymer chains. During the solvent evaporation, a competition between two processes occurs. (i) liquid– liquid phase separation, and (ii) crystallization, according to Fig. 5. If the crystallization is fast, the spherullites may embed a homogeneous amorphous phase between lamellae or the crystallites which form the secondary structure (Fig. 5a). In an intermediate situation, a phase separation may start with a simultaneous crystallization. Small domains of a PMMA-rich phase will be embedded inside the spherullites (Fig. 5b). If the liquid–liquid phase separation is much faster, the domains are expelled from the spherullites (Fig. 5c) which are being formed. If the phase separation starts much earlier than crystallization, a morphology similar to that of Fig. 2a, for 20/80 PA-6/PMMA from solutions in *m*-cresol, can be observed. PA-6-rich domains are first formed in the PMMA-rich matrix, followed by crystallization inside the domains.

3.2. Extruded blends

The morphology of the extruded blends was highly dependent on the processing conditions. When two immiscible polymers are extruded, the interfacial tension is of the same order of magnitude as the shear tension during processing. The mixing process starts by melting the two blend components. Shear and elongational flow during processing give rise to threads and droplets. According to the viscosity rate between the polymer components, interfacial tension and the shear stress involved, threads may break or remain stable for some compositions [1, 2, 7–9]. The instability of threads in a viscous medium has been the subject of mathematical models, which were not originally described for polymers. Theories and discussions on the sinusoidal distortion of threads, leading to droplet formation, were developed earlier by Tomotika [10] and Rayleigh [11] and accepted for polymer systems [7, 12]. For the 20/80 PA-6/PMMA, threads can be clearly seen in Fig. 6a obtained by SEM, in a direction parallel to the extrusion. The stability of spherical domains is higher for higher viscosity ratios between domain and matrix [1]. For higher shear rates and lower interfacial tension, smaller domains are obtained.

Composition has an obvious influence on the morphology. Under the same processing conditions, dispersed domains are smaller for very low and very high contents of one component and are larger for intermediate composition, as shown in Fig. 7.

A 80/20 PMMA/PA-6 blend has smaller domains with higher adhesion between phases. All the morphologies presented here correspond to the centre of the sample. As reported for other systems in the literature [13], the domain size decreases from the centre to the surface.

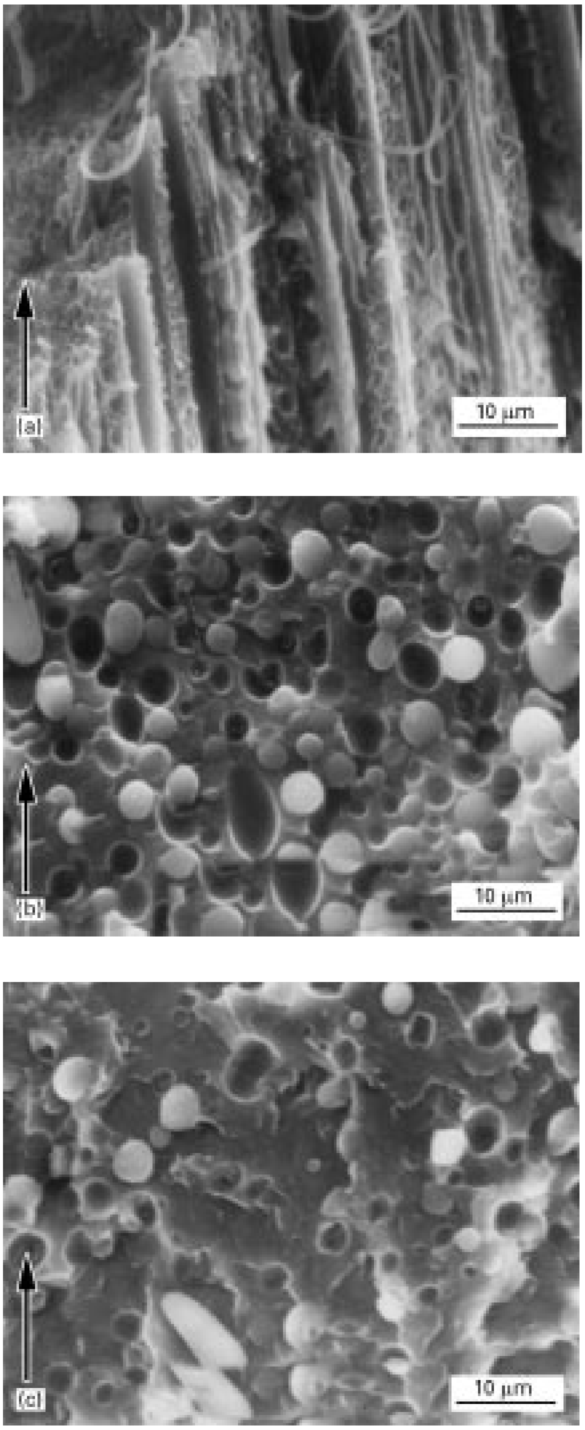

Figure 7 Scanning electron micrographs of (a) 20/80, (b) 50/50 and (c) 80/20 PA-6/PMMA blends. The arrows indicate the injection direction.

3.3. Dynamic-mechanical analysis of extruded blends

For all the extruded blends investigated here, two glass transition temperatures were observed, T_g, due to the presence of more than one phase. By analysing the tan δ curves, a shift of T_g value, a change in the height of the T_g peaks and/or the occurrence of a third peak, indicate that the phase segregation is not complete and there is partial miscibility. Lipatov [14] proposed an empirical equation (Equation 1) for calculating segregation degrees, α, in IPNs of amorphous polymers. Although the system investigated here is a blend containing a crystalline phase, the same equation was used to estimate α values

$$\alpha = \left[h_1 + h_2 - \frac{(l_1 h_1 + l_2 h_2 + l_m h_m)}{L} \right] \Big/ (h_1^o + h_2^o) \quad (1)$$

h_1^0 and h_2^0 are the height of tan δ peaks for the pure components, L is the initial difference between T_g. The other parameters are shown in Fig. 8.

Fig. 9 shows tan δ as a function of T curves for blends obtained by extrusion/injection. From these curves, using Equation 1, a segregation degree of 0.06 was estimated for a 80/20 PA-6/PMMA blend, 0.11 for 50/50 and 0.40 for 20/80. These results follow the morphology shown in Figs 6 and 7. A 20/80 blend has a fibrous structure of breaking threads which correspond to higher segregation. On the other hand, a 80/20 blend has small spherical domains with diffuse

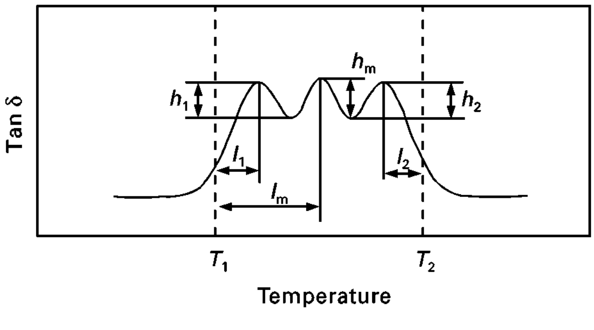

Figure 8 Parameters for Equation 1.

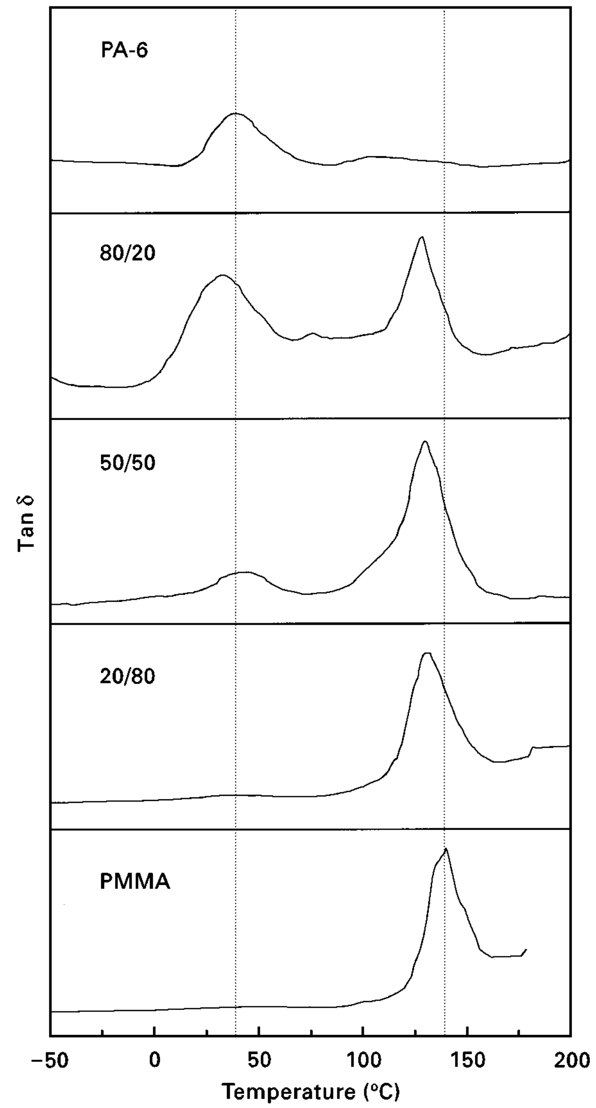

Figure 9 Tan δ curves for PA-6/PMMA extruded blends and homopolymers.

interfaces and low segregation degree, which justify the appearance of the third peak in the tan δ curves.

3.4. Compatibilization of PA-6/PMMA blends

The extruded 50/50 PA-6/PMMA blend is clearly a two-phase system, with dispersed domains. Impact modifiers for polyamide with core–shell structures have an increasing application. It is usually formed by a rubber core enveloped by an acrylic shell [15–17]. The development of compatibilizing agents, to increase the adhesion between the acrylic shell and the polyamide matrix, is highly desired. The compatibilization of 50/50 PA-6/PMMA blends was investigated, adding 10 wt % copolymer with poly(ethylene oxide) (PEO) and polyamide-6 blocks. The PEO blocks have a favourable interaction with the PMMA-rich phase [18, 19]. The results can be seen in Fig. 10 in blends prepared in a mixer. Compatibilized mixtures had a smooth fracture surface, in contrast to non-compatibilized blends where domains could be clearly seen.

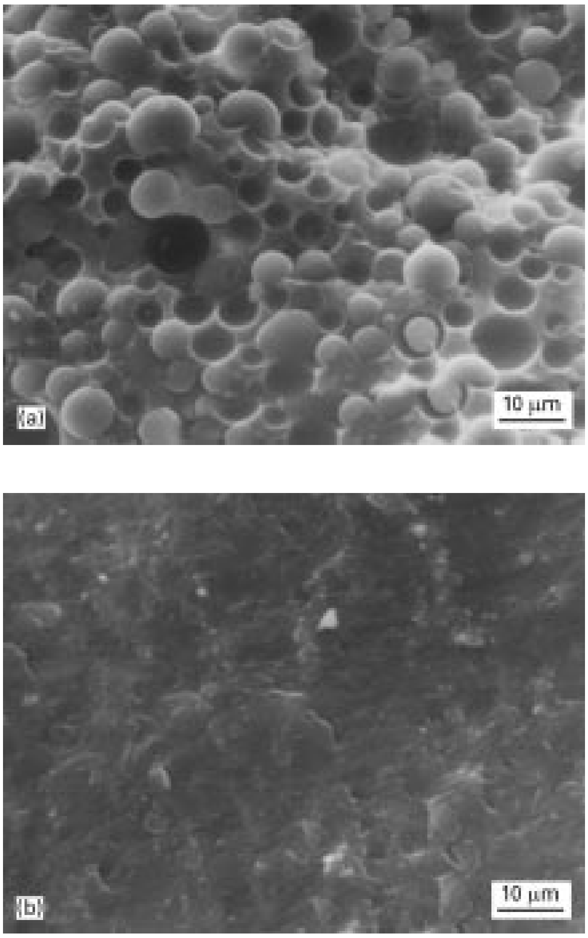

Figure 10 Scanning electron micrographs of 50/50 PA-6/PMMA 50/50 blends (a) with, and (b) without 10 wt% PEBAX.

4. Conclusion

Among the PMMA blends with different polyamides (PA-6, 6/9 and 12), PA-6/PMMA has the higher miscibility due to the large number of amide groups which are available for hydrogen bonding. The morphology of PA-6/PMMA blends obtained from solution is highly dependent on the solvent used. Crystallization and liquid–liquid phase separation compete during film formation.

The segregation degree of extruded blends increased in the following sequence: 80/20 < 50/50 < 20/80 PA-6/PMMA, as observed by morphological and by dynamic-mechanical analysis. Blends could be compatibilized through the introduction of a copolymer with polyamide and poly(ethylene oxide) blocks.

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