Blends of PEEK and PET–PHB 60: a preliminary study on thermal and morphological aspects

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The system poly(ether ether ketone) (PEEK)/PET–PHB 60 has been studied by differential scanning calorimetry and scanning electron microscopy (SEM). The thermal analysis data, especially the glass transition temperatures, indicate that the blends are compatible. The SEM analysis seems to confirm this, showing a mostly homogeneous structure. When the two phases are still evident, a good adhesion is shown; this is of interest in terms of the mechanical properties, results for which are not yet available.

(Keywords: blends; PEEK; PET–PHB 60)

Introduction

The class of thermoplastic engineering materials referred to as 'superpolymers' is the subject of increasing interest, because they are characterized by very high mechanical properties, good flame retardance and high temperature applications. Among these materials, the most commonly used are polysulfone (PS), poly(ether imide) (PEI) and poly(ether ether ketone) (PEEK). However, these polymers are difficult to process. The inclusion of a low viscosity second phase could be a good method to improve the processing conditions; owing to their unique physical properties[1], the thermotropic liquid crystalline polymers (TLCPs) seem to represent a class of materials suitable for this. In fact the structure of TLCPs has domains including fairly parallel chain molecules which are randomly oriented in the absence of an external field; however, in the presence of an orienting flow field, and in the temperature range of mesophase existence, they are mostly oriented along the flow direction. As a consequence, there is evidence of a decrease in viscosity in such cases[2], while in the solid state the blends show an increase in mechanical properties.

Owing to the high cost of TLCPs, small percentages are usually added, especially when the main aim of their use is to improve processability[3].

Experimental

The thermoplastic matrix used was PEEK 450G, kindly provided by ICI, while the TLCP was PET–PHB 60, produced by Eastman Kodak Company. According to Jackson and Kuhfuss[4], the PET–PHB 60 is a copolymer with a random distribution of the PHB (parahydroxybenzoic acid) as seen by n.m.r., showing a very slight indication of PET (poly(ethylene terephthalate)) or of PHB crystallinity. The materials were vacuum dried at 105°C for 24 h before mixing. The blending procedure was performed by means of a Brabender Plasticorder equipped with a mixing chamber at 30 rev min^{-1} and at 365°C, which is within the temperature range of mesophase existence for PET–PHB 60[5] and is higher than the melting temperature of PEEK[6]. Mixing was performed in the presence of nitrogen to avoid oxidation. Blends were prepared with compositions ranging from 10 to 30% w/w of TLCP in PEEK, and are referred to as PEEK/PET–PHB 60 90/10, PEEK/PET–PHB 60 80/20 and PEEK/PET–PHB 60 70/30.

A differential scanning calorimetry (d.s.c.) system (Mettler TA4000) was used to evaluate the transition temperature of the pure polymers and of the blends. The temperature range investigated was -50 to 460°C at a heating rate of 10°C min^{-1}, in the presence of nitrogen.

Scanning electron microscopy (SEM), using a Philips model 501, was used to evaluate the morphology of the blends.

Results and discussion

The d.s.c. thermograms of unfilled PEEK and PET–PHB 60 are shown in *Figure 1*.

The PEEK shows the usual glass transition at about 152°C and melting at around 345°C (ref. 6). The PET–PHB 60, as already reported[5,7], shows a glass transition at about 60°C corresponding to the PET portion of the copolymer, and a second glass transition at about 175°C, which can be attributed to the PHB-rich phase; the peak at 245°C corresponds to the crystal phase of PET and the peak at 385°C to the isotropization temperature. In *Figure 2* the d.s.c. thermograms of the PEEK/PET–PHB 60 90/10, PEEK/PET–PHB 60 80/20 and PEEK/PET–PHB 60 70/30 blends are also reported.

The major effect seems to be on the glass transition temperature (T_g). A decrease in the T_g of the PEEK is clearly evident, and the decrease is larger the larger the amount of PET–PHB 60 present. The T_g values are reported as a function of concentration in *Figure 3*, and for comparison the theoretical curve corresponding to the usual mixture rule for compatible blends is also reported. From such a comparison it seems that the two polymers are mostly compatible.

A plasticizing effect, as seen from the T_g decrease, has recently been found by other authors for a similar system[8].

The melting transition temperature data also show a slight decrease in the presence of TLCP; it thus

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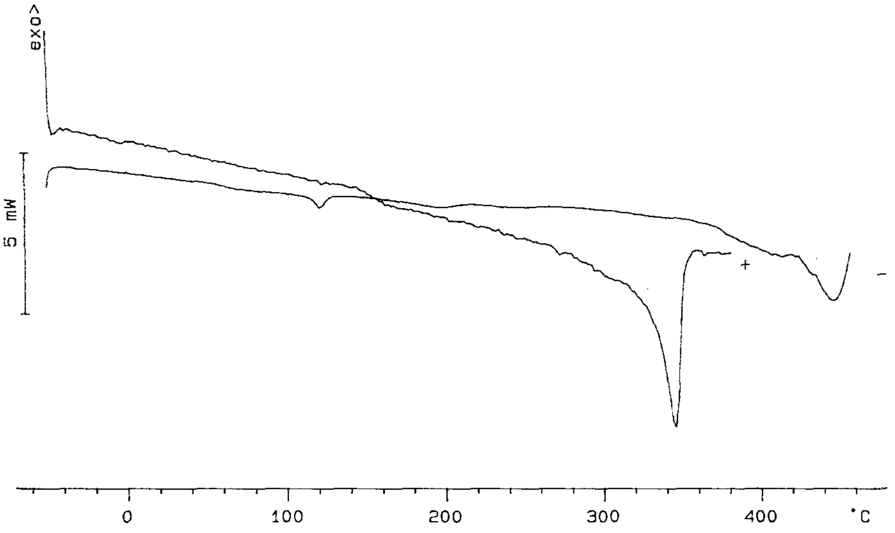

Figure 1 D.s.c. thermograms of PEEK (+) and PET–PHB 60 (–)

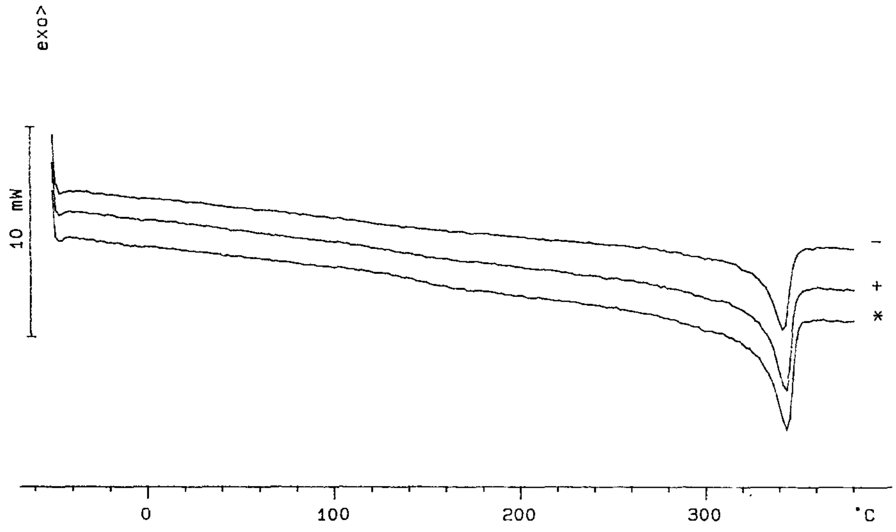

Figure 2 D.s.c. thermograms of PEEK/PET–PHB 60 90/10 (*), PEEK/PET–PHB 60 80/20 (+) and PEEK/PET–PHB 60 70/30 (–)

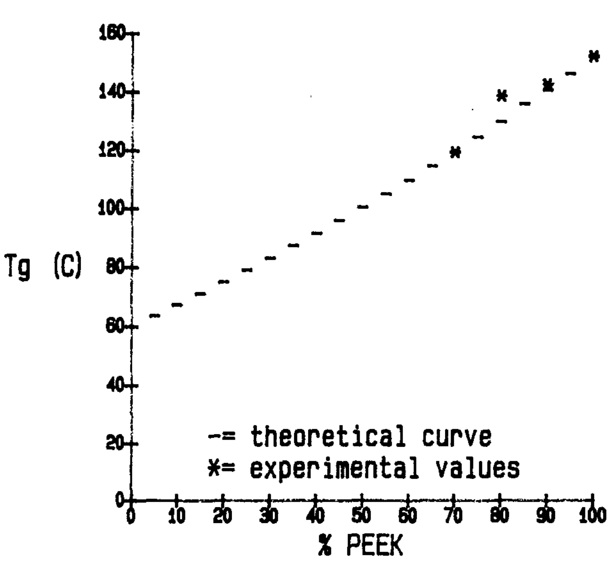

Figure 3 Glass transition temperature *versus* percentage PEEK

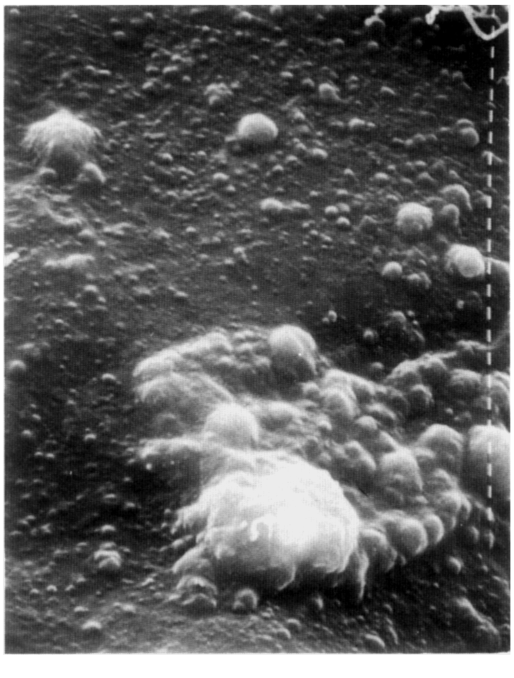

Figure 4 Micrograph of PEEK/PET–PHB 60 70/30 blend

seems that less perfect crystals grow in such cases. Further studies on the degree of crystallization and the crystallization kinetics are perhaps needed.

Figure 4 shows a micrograph of the PEEK/PET–PHB 60 70/30 blend, which confirms the good adhesion between the different materials of the blend and indicates homogeneous structure.

More accurate analyses are in progress, together with a study on mechanical properties. It is worth mentioning that this seems to be one of the first cases in which TLCPs show some compatibility with a thermoplastic matrix.

References

1 Stupp, S. I. *Chem. Eng. Prog.* 1987, **83**, 17
2 Nobile, M. R., Acierno, D., Incarnato, L. and Nicolais, L. *J. Rheol.* 1990, **34** (7), 1181
3 Williams, D. J. *Adv. Polym. Technol.* 1990, **10** (3), 173
4 Jackson, W. J. and Kuhfuss, H. F. Jr *J. Polym. Sci., Polym. Chem. Edn* 1976, **14**, 2043
5 Nobile, M. R., Amendola, E., Nicolais, L., Acierno, D. and Cerfagna, C. *Polym. Eng. Sci.* 1989, **29** (4), 244
6 Blundell, D. J. and Osborn, B. N. *Polymer* 1983, **24**, 953
7 Frigione, M. E. 12th International SAMPE European Conference, Maastricht, 28–30 May 1991
8 Metha, A. and Isayev, A. I. *Polym. Eng. Sci.* 1991, **31** (13), 963