Morphology and deformation behaviour of toughened blends of poly(butylene terephthalate), polycarbonate and poly(phenylene ether)

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The morphology and properties of blends of poly(butylene terephthalate) (PBT), bisphenol A polycarbonate (PC), poly(2,6-dimethyl-1,4-phenylene ether) (PPE), toughened with styrene–ethylene/butylene–styrene (SEBS) rubber have been found to be strongly affected by spontaneous phase segregation which occurs during melt compounding. In the composition range of interest, such segregation leads to the formation of a unique microstructure in which dispersed particles of rubber-modified PPE are encapsulated by thin envelopes of PC and embedded in a PBT matrix. Electron microscopy and tensile dilatometry studies of partially and fully formulated PBT/PC/PPE/SEBS blends have been used to relate the morphology of these materials to their deformation behaviour.

(Keywords: blends; morphology; toughness; interfacial adhesion; phase segregation)

INTRODUCTION

Polymer blends of increasing complexity continue to be developed in an effort to meet the cost/performance profiles required in many engineering applications. Whereas early systems often consisted of a single resin and rubbery impact modifier (e.g., nylon/EPDM)[1], it has become more and more common to combine one or more glassy or crystalline polymers with several impact modifiers. In such blends, it is critical to establish some level of interfacial adhesion between the components in order to achieve the necessary toughness and delamination resistance. The required bonding is achieved in some commercial blends (e.g., PC/PBT and PC/ABS) as the result of partial miscibility between the blend components[2–6]. In other blends, in which the primary polymers are immiscible (e.g., PPE/nylon), it is necessary to chemically couple the components to produce a satisfactory reduction in dispersed phase size and an adequate increase in interfacial strength[7,8].

Recent work has shown that blends of PBT, PC, PPE and SEBS having an attractive balance of properties including excellent moisture and solvent resistance, high heat distortion temperature and toughness can be prepared by melt compounding without chemically coupling any of the constituents[9],[10]. Significantly, two of the major components (PBT and PPE) appear to be completely immiscible.

In the present paper, it will be demonstrated that this somewhat unusual behaviour can be traced to the way in which the individual polymers segregate during compounding. In analogy with earlier investigations, the process appears to be driven by interfacial energy differences and results in reproducible encapsulation of the dispersed PPE/rubber particles by PC[11]. Tensile dilatometry studies of these multiphase materials indicate that this encapsulation plays a key role in improving the adhesion between the PPE/rubber particles and the PBT matrix resulting in superior toughness.

EXPERIMENTAL

Materials

The four blend compositions investigated in this study are listed in *Table 1*. The PBT, PC and PPE resins were obtained from the General Electric Plastics Business Group. The SEBS rubber was Kraton G-1651 supplied by Shell. The blends were compounded on a Welding Engineers 20 mm twin-screw extruder at 285°C. The components were first dry blended and added simultaneously to the hopper. The extruded strand was quenched in a water bath and pelletized in the usual fashion. The blends were injection moulded into ASTM D256 Izod impact specimens and ASTM D638 tensile specimens.

Microscopy

Samples for transmission electron microscopy (TEM) were sectioned at room temperature using a Reichert Ultracut E ultramicrotome. The sections were stained with RuO_4 to enhance contrast between the phases[3,11]. All observations were carried out on a Hitachi H-600 TEM.

Samples for scanning electron microscopy (SEM) were faced on the ultramicrotome and in some cases etched by brief immersion in diethylene triamine (DETA) (a selective etching agent for PC). Details of the etching experiments may be found in an earlier publication[3]. All surfaces were sputter coated with a thin layer of Au/Pd. Observations were made using a Jeol 840 SEM.

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Table 1 Notched Izod impact strength at 25°C

Blend composition		Notched Izod impact strength ($J m^{-1}$)	Failure mode
PBT/PC/PPE/SEBS	46/10/30/14	600	ductile
PBT/PPE/SEBS	46/30/14	50	brittle
PBT/PC/PPE	46/10/30	50	brittle
PBT/PPE	46/30	30	brittle

Mechanical testing

Tensile dilatometry experiments were performed as described previously[4,8]. The tensile stress–axial strain–volume strain (σ–ε_A–$\Delta V/V_0$) experiments were carried out on an Instron 1350 servo-hydraulic testing machine at an axial strain rate of $1\% s^{-1}$. Volume change measurements were made using nested axial and transverse strain gauges. Notched Izod impact testing was carried out on a Baldwin impact tester according to ASTM D256.

RESULTS

Morphology

TEM photographs of the PBT/PPE/SEBS 46/30/14 blend and the PBT/PC/PPE/SEBS 46/10/30/14 blend are presented in *Figures 1* and *2*. Phase assignments are based on independent staining studies of two- and three-component blends and supported by SEM observations of etched samples described below. In both cases PPE completely encapsulates the SEBS rubber and forms a composite dispersed phase in the PBT matrix. When PC is added to the blend it becomes segregated as a thin envelope around the dispersed PPE/rubber particles rather than forming a separate dispersed phase in the PBT. This feature is even more obvious in the photomicrograph of the PBT/PC/PPE 46/10/30 blend where the SEBS rubber has been omitted (*Figure 3*). The PC envelope formation is reproducible and is believed to be dictated by interfacial energies differences among the components as reported earlier[11]. In analogy with other blends showing envelope formation, changes in the ratios of the dispersed components were found to affect the thickness and uniformity of the enveloping PC layer but did not alter the basic microstructure of the system.

Further evidence for PC encapsulation of the PPE phase is provided by DETA-etched samples in the SEM. *Figure 4* shows a microtomed surface of the PBT/PC/PPE 46/10/30 blend exposed to DETA for 15 s. Although there is relatively little surface relief, the domains of PPE are readily visible as the result of removal of PC from the interfacial region.

It is noteworthy that in the blends containing PC, no debonding of the dispersed and matrix phases is observed during microtomy. When PC is eliminated from the blend, however, a significant amount of interfacial cracking is visible on the faces of the microtomed blocks examined in the SEM. An example of this difference between blends with and without PC is shown in *Figure 5*. The facile debonding observed in these samples without PC suggests that interfacial adhesion is poor. This observation is consistent with the known immiscibility of PBT and PPE as well as the low toughness of blends containing no PC. A more quantitative comparison of blends with and without PC is presented in the discussion of tensile dilatometry results presented below.

Mechanical properties

Table 1 shows the notched Izod impact strength of the four blends under investigation. The fully formulated four component PBT/PC/PPE/SEBS blend is a very ductile material; however, omission of either PC or SEBS or both leads to severe brittleness.

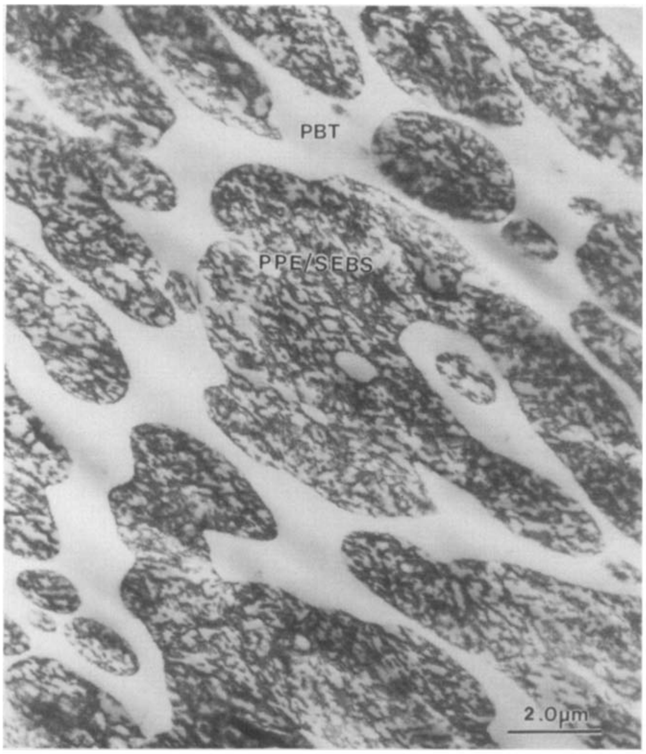

Figure 1 TEM photograph. Thin section of PBT/PPE/SEBS 46/30/14 blend stained with RuO_4

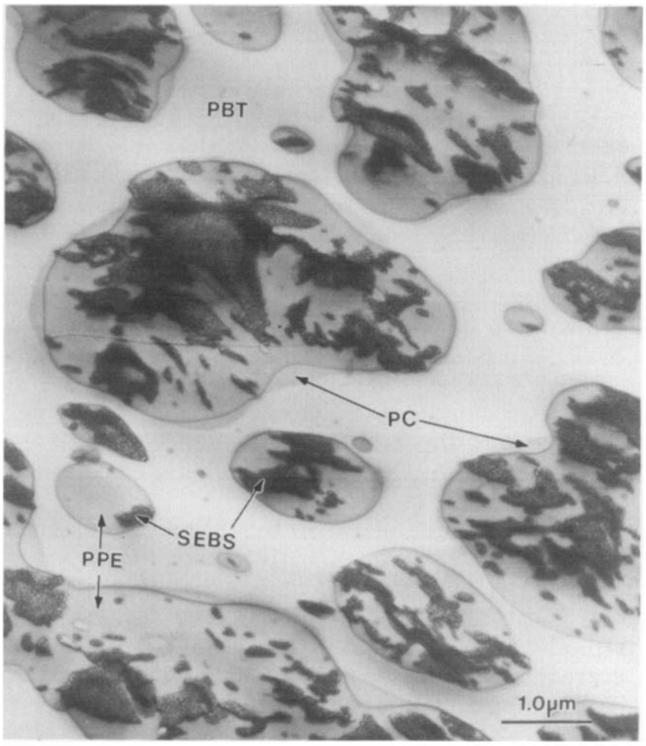

Figure 2 TEM photograph. Thin section of PBT/PC/PPE/SEBS 46/10/30/14 blend stained with RuO_4

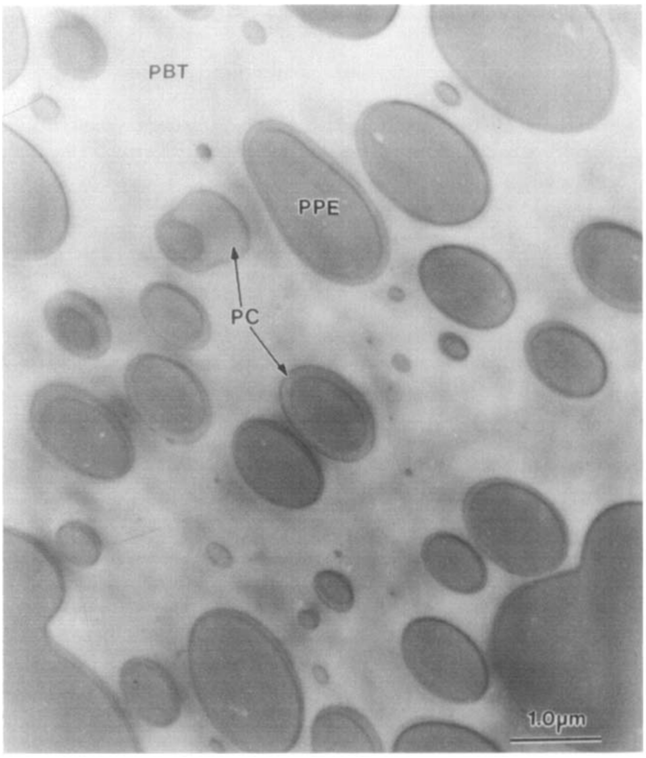

Figure 3 TEM photograph. Thin section of PBT/PC/PPE 46/10/30 blend stained with RuO_4

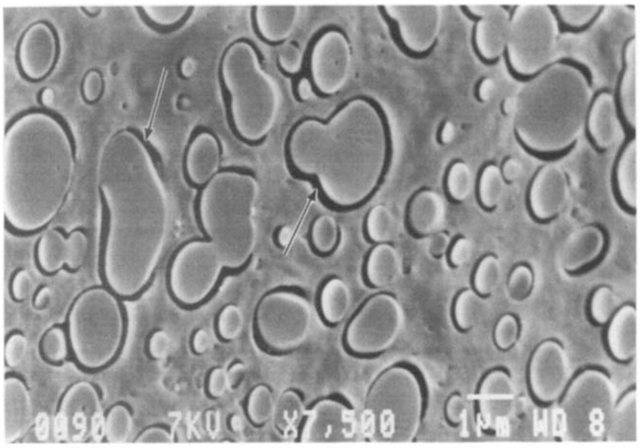

Figure 4 SEM photograph. Microtomed surface of PBT/PC/PPE 46/10/30 blend etched with DETA to remove PC (see arrows)

The fact that omission of SEBS rubber leads to brittleness is not surprising. Encapsulation of the rubber by PPE produces a composite dispersed phase whose effective modulus is significantly lower than that of the PPE resin alone[7,8]. As a result, the local stress fields around the dispersed particles are enhanced and microscopic deformation mechanisms (principally shear deformation) are facilitated.

The critical role of PC in this blend system can be elucidated by tensile dilatometry studies. *Figure 6* shows the σ–ε_A–$\Delta V/V_0$ curves for the PBT/PC/PPE/SEBS 46/10/30/14 blend tested at 25°C. The σ–ε_A curve is a typical curve for a ductile material. In *Figure 6* the σ–ε_A curve is shown only up to $\varepsilon_A = 14\%$ but the actual strain at break is about 50%. Shortly after yielding, the sample shows distinct neck formation. When a neck forms, volume strain measurements become impossible because of the non-homogeneous transverse contraction. The interesting part of *Figure 6* is the $\Delta V/V_0$–ε_A curve. After the initial volume increase, the volume strain curve levels off and becomes flat at the axial strain at which the yield point in the σ–ε_A curve is reached ($\mathrm{d}\Delta V/V_0/\mathrm{d}\varepsilon_A \approx 0$ at $\mathrm{d}\sigma/\mathrm{d}\varepsilon_A = 0$). This behaviour indicates that cavitation processes do not occur and that shear deformation is the only non-Hookean deformation process[12]. The volume increase of the sample is entirely due to elastic deformation (Poisson effect).

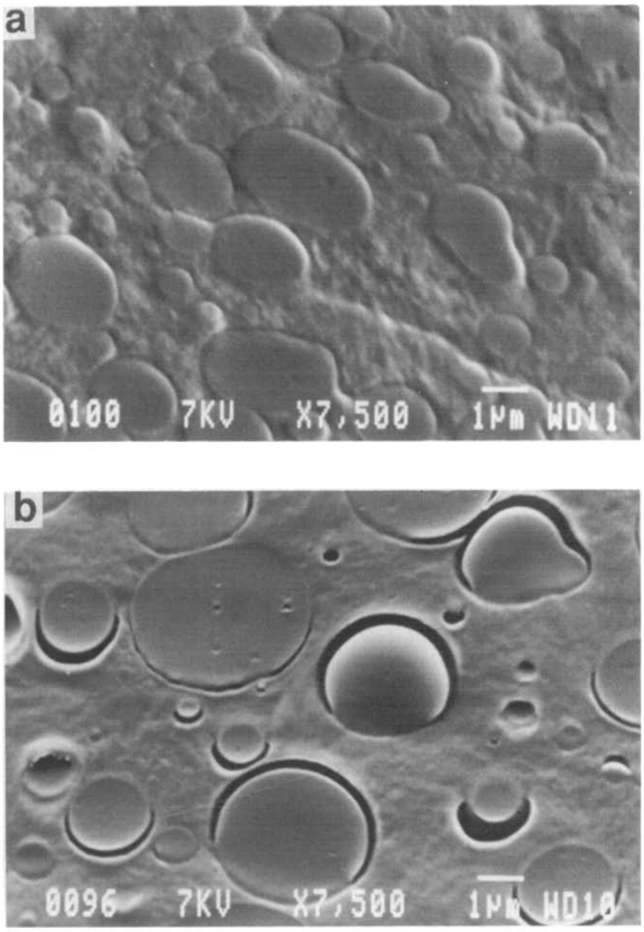

Figure 5 SEM photographs. Microtomed surfaces of (a) PBT/PC/PPE 46/10/30 and (b) PBT/PPE 46/30. The latter photograph clearly shows debonding of the PPE domains produced during microtoming

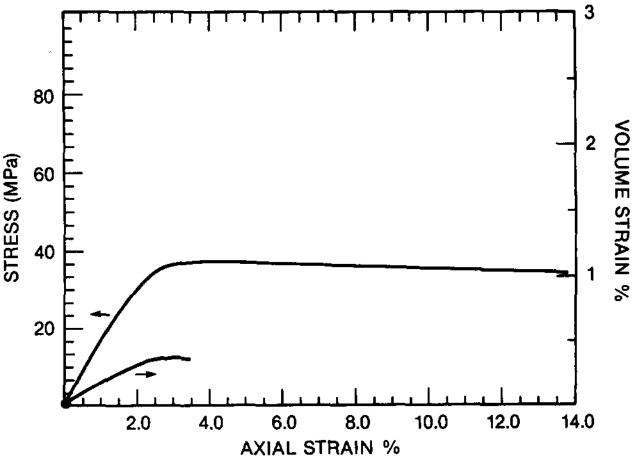

Figure 6 PBT/PC/PPE/SEBS 46/10/30/14;25°C; axial strain rate $1\%\,s^{-1}$

Figure 7 shows the σ–ε_A–$\Delta V/V_0$ curves for the PBT/PPE/SEBS 46/30/14 blend. This blend does not contain PC and is brittle. The σ–ε_A curve does show a yield point but shortly after yielding, the sample breaks in a brittle manner at an axial strain of about 3.5%. It is interesting to compare the volume strain curves of *Figures 6* and *7*. After the initial volume increase, the volume strain in *Figure 7* does not level off but continues to rise up to the point of brittle failure. This feature indicates that in this blend without PC considerable cavitation takes place. This cavitation must be attributed to debonding at the interface between the PPE/rubber particles and the PBT matrix, as a result of poor interfacial adhesion. The debonding leads to the development of flaws of critical size which in turn lead to the premature brittle failure. The fact that no cavitation is observed in the fully formulated blend with PC (*Figure 6*) indicates that in that case the encapsulation of the PPE/rubber particles by PC provides a sufficient level of adhesion between the PPE/rubber particles and the PBT matrix.

Figure 8 shows σ–ε_A–$\Delta V/V_0$ curves for the PBT/PC/PPE 46/10/30 blend. This blend does not contain SEBS rubber and breaks at a low axial strain of about 4.5%. The volume strain behaviour is similar to the blend with rubber (*Figure 6*); the volume strain curve becomes flat when the sample begins to yield. This means that also in the blend without rubber the interfacial adhesion provided by PC is sufficient to prevent cavitation processes from occurring.

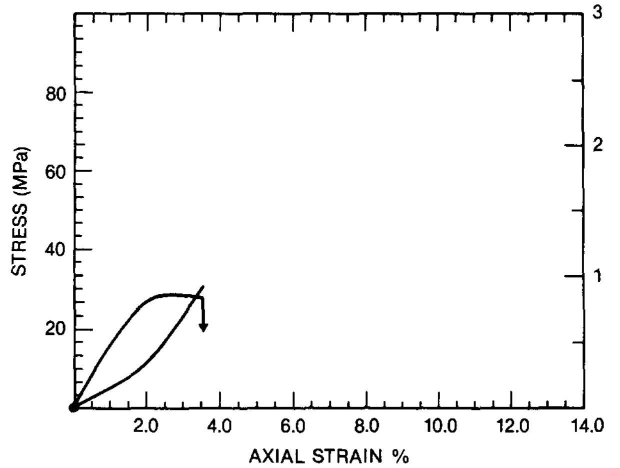

Figure 7 PBT/PPE/SEBS 46/30/14; 25°C; axial strain rate 1% s^{-1}

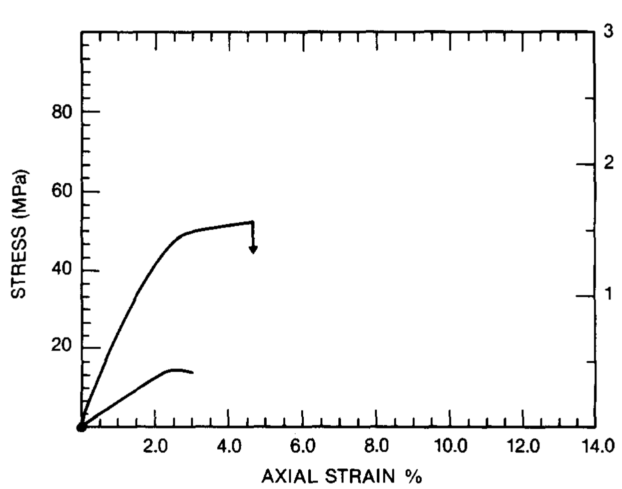

Figure 8 PBT/PC/PPE 46/10/30; 25°C; axial strain rate 1% s^{-1}

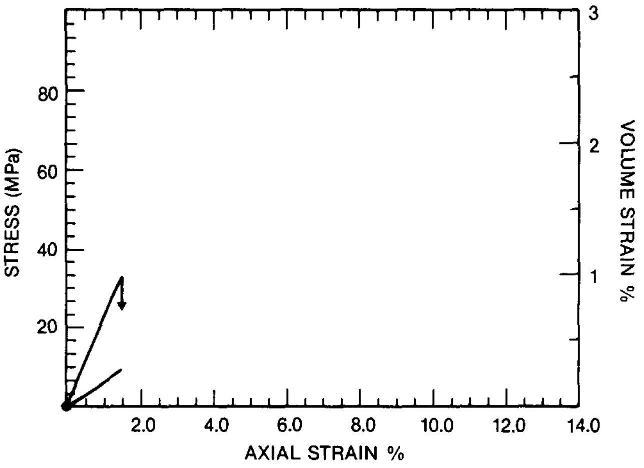

Figure 9 PBT/PPE 46/30; 25°C; axial strain rate 1% s^{-1}

Figure 9 shows σ–ε_A–$\Delta V/V_0$ curves for the PBT/PPE 46/30 blend. This blend is so brittle that the sample breaks at an axial strain of 1.5%, with no significant deviation of linear elastic behaviour. The behaviour is directly analogous to that of PPE/nylon blends having low copolymer levels and is attributed to catastrophic cracking initiated at the surface of the relatively hard and poorly bonded PPE inclusions.

DISCUSSION AND CONCLUSIONS

The previous results demonstrate that the properties of complex blend systems depend largely on how the individual polymers segregate during compounding. This segregation is believed to be driven by interfacial energy differences as discussed elsewhere[11]. In the present case of PBT/PC/PPE/SEBS blends, the presence of PC envelopes around the PPE/SEBS particles appears to be critical for good ductility. The PC envelopes enhance the interfacial adhesion in this blend by forming a 'bridge' between the PPE/SEBS particles and the PBT matrix.

The adhesion between the PC envelopes and the PBT matrix is not surprising. Earlier differential scanning calorimetry studies have shown that melt blends of PC and PBT exhibit significant partial miscibility[2]. Also, tensile dilatometry studies of impact modified PC/PBT blends have indicated good interfacial adhesion between the PC and PBT phases[4]. The bond formation between PC and PBT has been more extensively investigated recently[13]. The adhesion between the dispersed PPE phase and the PC envelopes, however, is somewhat surprising. Differential scanning calorimetry studies on melt blends of PC and PPE do not show clear-cut shifts of the glass transition temperatures of the individual components, indicating that there is very little, if any, miscibility between PC and PPE[14]. Nevertheless, the present study shows that there appears to be sufficient interaction between PPE and PC to achieve a level of adhesion adequate for good mechanical properties. This is consistent with the fact that segmental penetration leading to adhesion is predicted for non-miscible polymer pairs[15] and with other experimental observations of adhesion between non-miscible pairs[16].

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REFERENCES

1 Flexman, E. A. *Polym. Eng. Sci.* 1979, **19**, 564

2 Hobbs, S. Y., Groshans, V. L., Dekkers, M. E. J. and Shultz, A. R. *Polym. Bull.* 1987, **17**, 335

3 Hobbs, S. Y., Dekkers, M. E. J. and Watkins, V. H. *J. Mater. Sci.* 1988, **23**, 1219

4 Dekkers, M. E. J., Hobbs, S. Y. and Watkins, V. H. *J. Mater. Sci.* 1988, **23**, 1225

5 Keitz, J. D., Barlow, J. W. and Paul, D. R. *J. Appl. Polym. Sci.* 1984, **29**, 3131

6 Mendelson, R. A. *J. Polym. Sci., Polym. Phys. Edn* 1985, **23**, 1975

7 Hobbs, S. Y., Dekkers, M. E. J. and Watkins, V. H. *J. Mater. Sci.* 1989, **24**, 2025

8 Hobbs, S. Y. and Dekkers, M. E. J. *J. Mater. Sci.* 1989, **24**, 1316

9 Brown, S. B. and Yates, J. B. *US Patent* 4 806 297, 1989

10 Brown, S. B. and Yates, J. B., manuscript in preparation

11 Hobbs, S. Y., Dekkers, M. E. J. and Watkins, V. H. *Polymer* 1988, **29**, 1598

12 Dekkers, M. E. J. and Heikens, D. *J. Appl. Polym. Sci.* 1985, **30**, 2389

13 Hobbs, S. Y., Watkins, V. H. and Bendler, J. T. *Polymer* 1990, **31**, 1663

14 Shultz, A. R., personal communication

15 Helfand, E. and Tagami, Y. *Polym. Lett.* 1971, **9**, 741

16 Fowler, M. E., Barlow, J. W. and Paul, D. R. *Polymer* 1987, **28**, 2145