polymer communications

Electron microscopic observation of spinodal decomposition in blends of tetramethyl polycarbonate and polystyrene

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The time development of spinodal decomposition in a blend of tetramethyl bisphenol-A polycarbonate with polystyrene can be followed using permanganic etching and scanning electron microscopy. This method of observation provides a real-space technique for observing the morphology of spinodal decomposition at high resolution.

(Keywords: spinodal decomposition; phase separation; polymer blends; electron microscopy; permanganic etching)

Introduction

Over the past few years there have been an increasing number of studies of polymer miscibility and the kinetics of phase separation in polymer blends, arising from both theoretical interest and commercial exploitation of their special properties[1,2]. The miscibility of tetramethyl bisphenol-A polycarbonate (TMPC) and polystyrene (PS) has been well established[3–5] by several experimental studies, which indicated that the system exhibits a lower critical solution temperature (*LCST*); above the critical point in the phase diagram, spinodal decomposition occurs. This process takes place in the spinodal region of the coexistence curve; a schematic of this can be found in reference 5. In this region, the system is unstable against infinitesimal fluctuations and decomposes into regions which are rich in the polymer species A and those which are rich in species B. Decomposition in this region gives an interconnected morphology which is considered to have potential for good mechanical properties[1].

Spinodal decomposition is most often studied using scattering techniques. In real space, the interconnected morphology has been observed using optical microscopy[6,7], and has been generated using a Monte Carlo simulation[8]. Previous electron microscopic studies of spinodal decomposition[9] have commented on the difficulties involved; these include inherently low contrast in transmission, modification of the segregation and coarsening processes in very thin films, likely bias in fracture surfaces, and limited resolution. To our knowledge, this is the first time that the use of liquid etching techniques on spinodally decomposed bulk samples has been reported. Such techniques enable morphologies to be observed in the electron microscope, on specimens too thick for direct transmission of the electron beam, and without invoking electron beam damage to induce contrast through mass transport[10]. In this paper we present some preliminary results of electron miroscopic studies of TMPC/PS blend using one of the etching techniques developed in this laboratory over the years[10–12].

Experimental

Materials. The materials used in this study and their characteristics are listed in *Table 1*. TMPC is a thermoplastic with a glass transition temperature[5] some 60 K higher than that of conventional polycarbonate, and differs from it in that the benzene rings are substituted with methyl groups in the 2,6 positions, neighbouring the 'phenol' oxygens[5]. The polystyrene was a standard material supplied by the Polymer Supply and Characterization Centre (RAPRA Technology Ltd), who also determined the molecular weights by gel permeation chromatography using tetrahydrofuran as a solvent.

Blend preparation. Films were cast from a solution of equal masses of each polymer in dichloromethane. Several drops of 5% w/v solution of the mixture were placed on a microscope slide contained in a Petri dish. The dish was closed, and the cast films were left at 35°C until most of the solvent had evaporated. (This slow evaporation in confined space avoids blemishes due to uptake of moisture.) After this they were placed in a vacuum oven overnight at approximately 100°C.

Etching and electron microscopy. The prepared film was cut into smaller pieces which were individually phase separated at 260°C for periods of 0.5, 2 and 10 min. The phase-separated specimens, together with an unseparated control, were etched for 1 h in a 1% solution of potassium permanganate in 100% orthophosphoric acid (prepared by boiling off water to 260°C[11]), then washed with hydrogen peroxide solution (~2%) followed by several changes of distilled water, and allowed to dry. The etched surfaces were coated with gold and examined in a Philips SEM 515 scanning electron microscope.

Table 1 Characteristics of the materials

Materials	M_w	M_n	M_w/M_n	T_g(°C)
TMPC	5.26×10^4	1.79×10^4	2.94	200
PS	2.93×10^5	1.07×10^5	2.75	100

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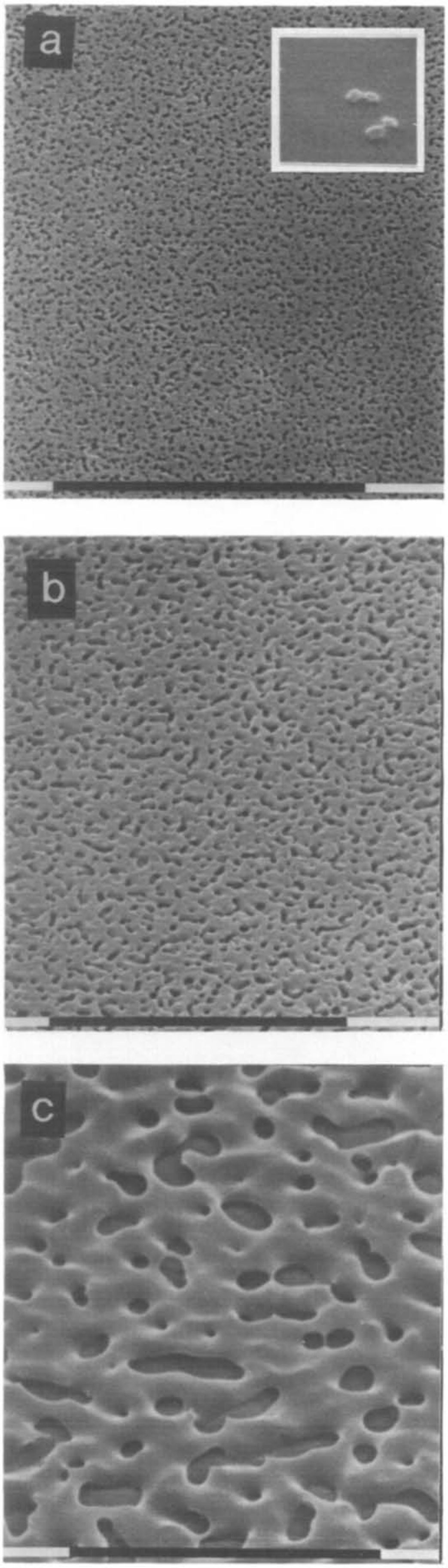

Figure 1 Electron micrographs of the TMPC/PS blend (50/50) after phase separation at 260°C for (a) 0.5 min (inset, not phase separated), (b) 2 min and (c) 10 min. Scale bar = 10 μm (horizontal dimension; verticals foreshortened by cos 45°)

Results and discussion

From earlier experiments[5] it was known that the cloud point for this particular TMPC/PS blend is around 240°C. This was confirmed in our study by observation of the phase-separated texture under the optical microscope. The electron micrographs show the texture of the phase-separated specimens at 260°C for periods of 0.5, 2 and 10 min (note that the surfaces are tilted at 45° away from the observer in order to enhance contrast, so the vertical dimension is foreshortened). There are evident similarities between the micrographs here and the pictures generated by Monte Carlo simulations[8]. In *Figure 1* the black parts are the PS-rich regions which are eaten away by the etchant, while the white regions are the TMPC-rich areas. No texture was observed in the unseparated control, except for a few isolated areas where small sheaf-like structures were seen (inset, *Figure 1a*). These small objects are so similar to the 'axialites' observed in semicrystalline polymers, that they are most likely to be axialites of TMPC produced by solvent-induced crystallization during the final stages of drying the film. However, the control specimen appears mostly bland like the background of the inset figure; moreover, in treated specimens, any axialites would be rapidly melted during heating up to the decomposition temperature. The morphology of the phase-separated specimens shows the interconnected structure expected for spinodal decomposition, which contrasts with the morphology formed by nucleation and growth, which is known to be one of almost spherical domains. The observed textures are very homogeneous, with no major variation from place to place.

Studies of early stages of the spinodal decomposition in this blend[5] indicate that the Cahn–Hilliard theory[13] well describes the initial behaviour of phase separation of this blend, in which the domain size remains constant. Here, however, we are observing the later stages, where the non-spherical domain size increases with time of treatment. Over the range studied, the rate of growth appears to be linear (*Figure 2*), as found by previous observers[9]; however, the time dependence of coarsening

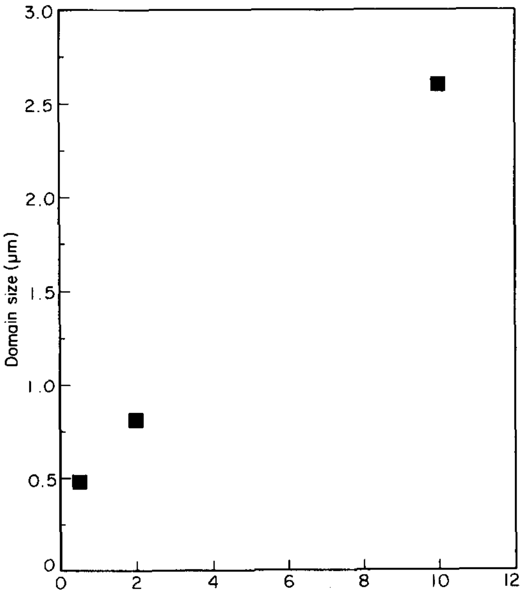

Figure 2 Diagram of the domain size (as obtained from the micrographs) plotted against the phase separation time

is not necessarily expected to obey a simple relationship, since several mechanisms (Ostwald ripening, coalescence, viscous flow, and possibly others) may be operating simultaneously[14]. The domain size of the interconnected structure in the earlier stages of phase separation is about 0.5 μm, which agrees well with the size scale obtained via light scattering experiments[5]. In addition, the observed morphology suggests that the interphase boundaries are sharp (to within 15 nm) but the mechanism of etching would need to be studied further to confirm that they have not been sharpened during etching by preferential solvent action. Moreover, the real-space technique reveals directly the statistics of domain size and shape.

Conclusion

In this communication we have introduced an electron microscopic technique which allows bulk specimens of phase-separated blends to be examined at enhanced resolution. Preliminary micrographs show the interconnected structure of the TMPC/PS blend after spinodal decomposition. It is found that the actual real-space morphology corresponds to previously expected forms suggested by scattering results and numerical modelling, but in addition, the distribution of domain size and shape is directly accessible. The etching technique should be applicable to the study of decomposition in many different blend systems; however, the composition of etchant used will have to be tailored to the chemistry of each set of two or more components.

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