Formation of gradient phase structure during annealing of a polymer blend*

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The phase morphology of ethylene–vinyl acetate copolymer (EVAc) and polypropylene (PP) blends was studied. It was observed that a 70/30 blend of PP and EVAc having 33 wt% vinyl acetate formed a gradient phase structure in the cross-section by annealing. In other words, the particle size of the EVAc dispersed phase increased gradually along the direction perpendicular to the sample surface from the centre to the surface. The longer the annealing time, the more the particle size of the dispersed phase grew. The vertical distribution of the EVAc component was analysed using an image processor analyser and found to be inhomogeneous. The component increases along the vertical direction of the sample from the centre to the surface. This corresponds to the result of the particle size of the EVAc dispersed phase growing uniquely.

(**Keywords: ethylene–vinyl acetate copolymer; polypropylene; blends; dispersed phase; gradient phase structure; SEM**)

Introduction

The morphologies of two-component polymer blends have become a very important subject and been discussed extensively in the literature over the past 10 years. The blending or mixing of polymers is an inexpensive route to the modification of various polymer properties. The effective property modification was carried out for totally miscible and partially miscible polymer blends in many cases[1,2]. However, most polymer blends are immiscible. For these systems containing a distinct dispersed phase, the properties are strongly influenced by the morphology of the dispersed phase. Thus, the control of morphology is crucial to obtain the desired polymer blend performance.

On the other hand, in the fields of metallic and ceramic materials, so called functionally gradient materials have been actively developed for improving the properties of heat distortion, impact resistance and fatigue behaviour[3,4]. For the functionally gradient material, its performance changes with a continuous concentration change of a component from the inside to the surface for multiphase and compound systems.

However, is it possible to design functionally gradient polymer materials? In this study, we have investigated the two-phase morphology of immiscible ethylene–vinyl acetate/polypropylene (EVAc/PP) blends by using scanning electron microscopy (SEM). This paper illustrates how unique gradient dispersed phase morphologies can be obtained for a PP/EVAc 70/30 blend by annealing. The blend can be used in applications for improving mechanical and surface properties such as heat distortion, impact resistance, coating and adhesive. The results not only provide a new way to design the phase morphology and the functional properties of the polymer blend but also yield a new problem of how to understand the formation of the two-phase morphology of the blend itself.

Experimental

The PP resin used was a homopolymer, with a melt flow rate of 7.2 g per 10 min. The EVAc was a random copolymer containing 33 wt% vinyl acetate and had a melt flow rate of 9.4 g per 10 min. Both polymers were made by Showa Denko Co.

A 70/30 blend of PP and EVAc was compounded on a Brabender Plasti-Corder equipped with a 50 cm^3 sample chamber at 170°C, and at a rotor speed of 35 rev min^{-1}. The components were first dry blended. A mixing time of ~5 min was required for complete dispersion of the blend. The torque was continuously recorded during the mixing.

The sheets used were prepared by the following procedure. The appropriate blend samples were put in a mould and melt-pressed between two polyimide films after preheating for 10 min to mould a sheet at 200°C. Then the moulded sheet was maintained at that temperature and annealed as a function of time. After annealing, the moulding was rapidly quenched in ice-water. The moulded sheets were ~1 mm thick.

The phase morphologies of the moulded sheets were examined by SEM. The sections were obtained with a Reichert-Nissei Ultracut N type ultramicrotome under a liquid nitrogen atmosphere. Then the sections were stained by exposure to the vapour of an aqueous solution of 0.5% ruthenium tetroxide (RuO_4) for 4 h to enhance contrast between the phases, and subsequently carbon plated using a Jeol JEE-3X vacuum evaporator. All observations were carried out on a Jeol JSM-T330A scanning electron microscope.

Furthermore, the image analysis technique was used to obtain quantitative morphology information. The average particle size, the particle size distribution and the occupied areas of the EVAc dispersed phase were evaluated along the direction vertical to the surface in the section. A Nireco Luzex III U image processor analyser was used.

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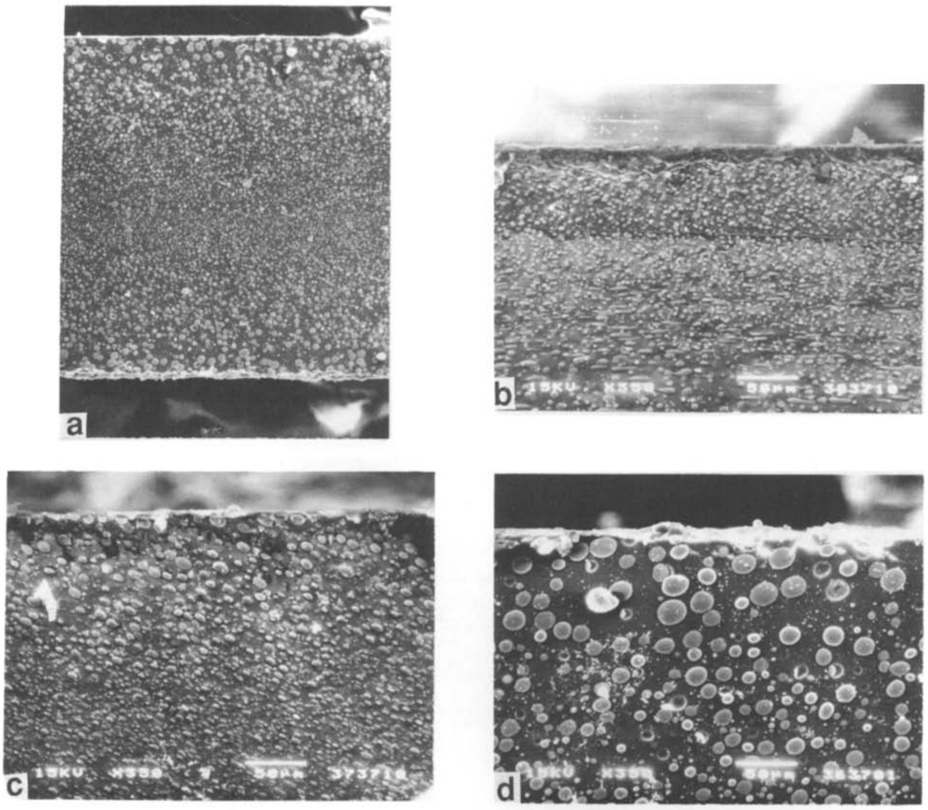

Figure 1 SEM micrographs of a cross-section of a 70/30 PP/EVAc blend annealed at 200°C for: (a) 70 min; (b) 12 min; (c) 20 min; (d) 70 min

Results and discussion

SEM micrographs of microtomed cross-sections of 70/30 PP/EVAc blends annealed at 200°C are shown in *Figure 1*. In this system the matrix polymer is PP appearing as the dark matrix, with RuO_4 staining the PP phase in preference to the EVAc phase. One can see that the particle size in the EVAc dispersed phase increased gradually along the direction vertical to the free surface from the centre to the surface as shown in *Figure 1a*, namely, gradient morphology was formed which had not been observed prior to annealing. This means that gradient polymer materials can only be obtained through simple processes.

The changes in the phase morphology with changing annealing times at 200°C are shown in *Figures 1b–d*. For a short annealing time, the EVAc particles of the dispersed phase in the PP matrix are small and distribute uniformly as shown in *Figure 1b*. For a longer annealing time, the particle size increased in the vicinity of the sample surface and the gradient morphology of the dispersed phase was formed as shown in *Figure 1c*. This is caused by coalescence of the particles of the dispersed phase, with interfacial tension providing the driving force. This mechanism contributes to the reduction in interfacial contact for a discrete system. The longer the annealing time, the more the particle size of the dispersed phase grew from the inside to the surface as shown in *Figure 1d*. We have not yet been able to explain why the nearer the dispersed phase to the surface, the more the size increased. In our latest work[5], we have found that a uniform distribution of the initial dispersed phase in the matrix is a necessary condition for the formation of the gradient phase morphology, and that melt viscosity and surface tension of the polymer are involved in the formation.

Further, in order to obtain quantitative phase morphology information of the PP/EVAc 70/30 blend, the SEM micrograph of the microtomed section was put in an image analyser and divided into eight equal regions from the centre to the surface. The average particle size, the particle size distribution and the occupied area of the dispersed phase in each region were calculated, respectively.

Figure 2a shows the dependence of the average diameter of the EVAc particles on the distance from the various regions to the surface. The diameter was calculated from the area of an equivalent circle for the EVAc particles. The average diameter in the respective region increases with decreasing distance from the region to the surface. The average diameter of the nearest region to the surface is 12 μm, being 3.5 times that in the centre. The largest diameter is $\sim$24 μm, in contrast to the minimum diameter which is <1 μm. Most of the particles have diameters distributed in the range of 4–6 μm, amounting to 70% as shown in *Figure 2b*.

The EVAc component change in the section was determined by a two-dimensional morphology analysis of the blend. The occupied area of the EVAc dispersed phase in each region was calculated, and the occupied area ratio of the dispersed phase to the matrix is illustrated as a function of the distance from the region to the surface in *Figure 3*. The occupied area ratio of the EVAc dispersed phase in the whole section was found to be equal to the EVAc volume fraction of the compound. However, the ratio is lower than the EVAc volume fraction of the compound in the vicinity of the sample centre, and increases gradually from the centre to the surface as shown in *Figure 3*. In the vicinity of the sample surface, the ratio shows a drastic increase and is much higher than the EVAc volume fraction of the compound.

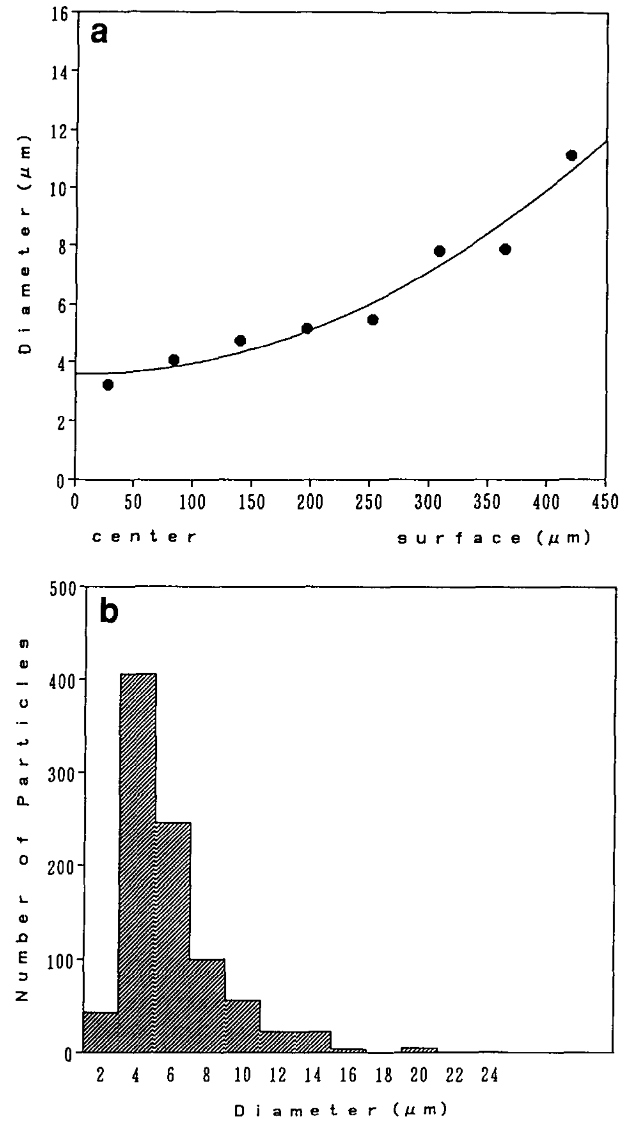

Figure 2 Diameter calculated from the area of an equivalent circle for EVAc particles. (a) Plot of average diameter *versus* distance from each region to the sample surface and (b) diameter distribution

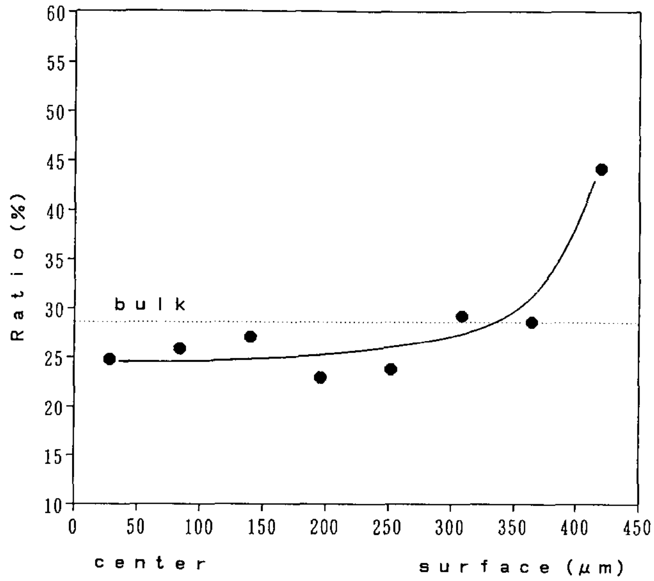

Figure 3 Plot of the occupied area ratio of EVAc particles to the PP matrix *versus* distance from each region to the sample surface

The concentration of EVAc in the sample surface has been evaluated to be higher than that of the bulk by Fourier transform infra-red spectroscopy and electron spectroscopy for chemical analysis[6]. This means that the EVAc component increases along the perpendicular direction of the sample from the centre to the surface, which corresponds to the particle size of the EVAc dispersed phase growing uniquely.

The formation of the gradient phase structure should be a thermodynamic phenomenon and a dynamic process. It may be possible to suppose that the EVAc molecules in the blend near the sample surfaces in contact with the polyimide films are mainly active because of the effect of minimization of the interfacial energy. If the thermal energy of the molecules is sufficiently high to overcome a barrier to diffusion, the diffusion must occur in the blend system and consequently the EVAc particles of the dispersed phase in the matrix of PP will coarsen[7,8]. The nearer to the surface, the more coalescence takes place easily. Since the smaller particles will be absorbed by larger particles when two particles collide[8], so the nearer the dispersed phase particles were to the surface, then the more the particles grew and the component increased.

However, further investigations are necessary. The mechanism of the formation of the gradient phase structure is currently being investigated, and the results will be reported in due course.

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