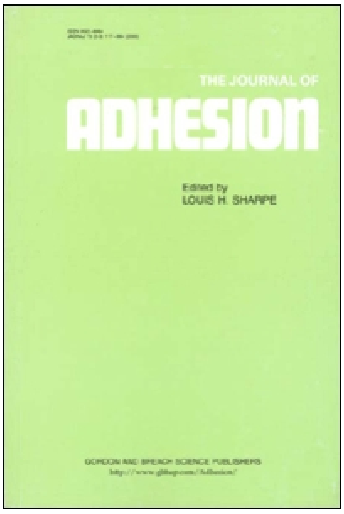

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Confocal Scanning Laser Microscope Image of Gradient Structure Formed in an Acrylate Copolymer/Fluoro-copolymer Blend

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Thin films of poly(2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate)/poly(vinylidene fluoride-co-hexafluoro acetone) [P(2EHA-AA-VAc)/P(VDF-HFA)] of 30/70 (by weight) blends without and with addition of 2 wt% fine silica gel were prepared on poly(ethylene terephthalate) (PET) from 20 wt% THF solution. Gradient domain morphology formed in the 30/70 blend was observed with a confocal scanning laser microscope (CSLM). Separate domains composed of P(2EHA-AA-VAc) phase were found in P(VDF-HFA) matrix at various levels of increasing depth with increasing domain size. Thus, CSLM is quite effective in morphological observation of the gradient structure formed in polymer blends, provided the blends are transparent.

Keywords: Polymer blends; confocal scanning laser microscopy (CSLM); scanning electron microscopy (SEM); gradient structure; morphology; silica gel; domain structure; surface enrichment

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INTRODUCTION

In our previous study [1,2], we were successful in developing a gradient domain morphology in poly(2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate)/poly(vinylidene fluoride-co-hexafluoro acetone) blend thin films, abbreviated as P(2EHA-AA-VAc)/P(VDF-HFA), by casting the blend from THF solution onto a substrate such as poly(ethylene terephthalate) (PET) or poly(dimethyl siloxane) (PDMS). The gradient domain morphology formed in the blend was analyzed by various techniques such as X-ray photoelectron spectroscopy (XPS) [1], attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) [1], step-scan FTIR with photo-acoustic detector (PAS-FTIR) [1], and scanning and transmission electron microscopy (SEM, TEM) [2]. Among these techniques, electron microscopic observation of cross sections of a film was particularly useful to confirm the gradient domain morphology formed in the blends. Addition of micrograin silica into the blends altered the morphology of the gradient structure [2].

Recently, confocal scanning laser microscopy (CSLM) [3,4] was taken note of as a new microscopy for observing cross-sectional images of a sample. Because in CSLM only light coming from a focal point of the sample can be detected but out-of-focus light cannot, the technique is very efficient to obtain a three-dimensional picture of the sample. In fact, CSLM was applied to morphological observation of polymer composites [5] and polymer blends [6, 7].

In this paper we describe the results of CSLM observation of the three-dimensional picture of the gradient domain morphology formed in P(2EHA-AA-VAc)/P(VDF-HFA) blends.

EXPERIMENTAL

P(2EHA-AA-VAc) and P(VDF-HFA) samples were a gift from Mitsubishi Kagaku Co., Ltd. and Central Glass Co., Ltd., respectively. Compositions and molecular weight data of copolymers are summarized in Table I. Micrograin silica (R972) supplied by Nippon AEROSIL Co., Ltd. was utilized as the third component. The particle size and specific surface area of R972 are 15 nm and 170 m^2g^{-1}, respectively.

TABLE I Components and molecular weights* of copolymers

P(2EHA-AA-VAc)	2-Ethylhexyl acrylate/acrylic acid/vinyl acetate $=85/5/10$ (mol%) $Mn=45500$, $Mw=372000$
P(VDF-HFA)	Vinylidene fluoride/hexafluoro acetone $=92/8$ (mol%) $Mn=52000$, $Mw=130000$

*Molecular weight equivalent to that of polystyrene by GPC.

20 (wt%) THF solutions of P(2EHA-AA-VAc)/P(VDF-HFA)/R972 blends of 30/70/0 or of 28/70/2 by weight were spread on PET using a hand coating bar and the films were prepared by evaporating THF from the solution in a well-controlled manner. In practice, the coated films were allowed to stand at room temperature for at least 24 h, and further dried in vacuum at 40°C for 7 days. The specimens obtained were about 20 μm thick.

The (30/70/0) and (28/70/2) blend films were observed with a confocal scanning laser microscope (CSLM) (Lasertec. Co., 1LM21) [8] at ambient temperature. A He–Ne gas laser of wavelength 632.8 nm was used as a light source.

RESULTS AND DISCUSSION

Figure 1 shows scanning electron microscope (SEM) photographs of cross-sectional layers of the 30/70/0 and 28/70/2 blends [2]. As seen in Figure 1, the 30/70/0 blend exhibits a gradient domain morphology [2]. The size of the ellipsoidals corresponding to the P(2EHA-AA-VAc) phase increases as they go from the surface (the air/blend interface) to the bottom (the blend/substrate interface), and a pure P(2EHA-AA-VAc) layer of 10 μm thickness is seen at the bottom.

In our previous paper [2], we reported that adding a small amount of R972 into the P(2EHA-AA-VAc)/P(VDF-HFA) blend moderated its gradient domain morphology. We explained this moderation as the result of the fact that R972 was preferentially enriched near the surface [9] and presumably the affinity of P(2EHA-AA-VAc) to R972 is stronger than that of P(VDF-HFA) to R972, thus enriching the former's content near the surface. In other words, preferential surface enrichment with R972 with stronger affinity towards P(2EHA-AA-VAc) moderated the gradient structure of the blends.

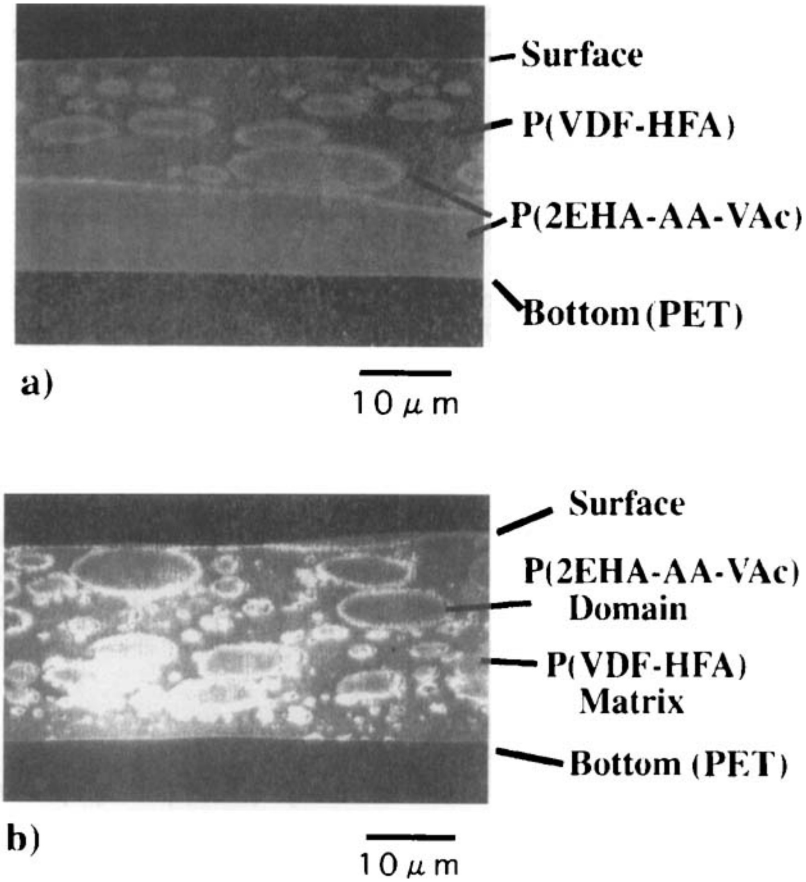

FIGURE 1 SEM photographs of cross-sectional layers for P(2EHA-AA-VAc)/P(VDF-HFA)/R972 blends: (a) 30/70/0, (b) 28/70/2.

Figure 2 shows CSLM images obtained in the regions (a) near the surface, (b) the center, and (c) the bottom of the P(2EHA-AA-VAc)/P (VDF-HFA) (30/70) blend. In the former two regions, we see in P(VDF-HFA) P(2EHA-AA-VAc) spherical domains with diameter ranging approximately from 1 to 6 μm. In Figure 2(a) for the near-surface region, the smaller domains look brighter than the larger domains, while in Figure 2(b) for the central region, the larger domains are brighter. In principle, for CSLM the image in the focal plane should be the brightest. Thus, this fact suggests that the domains

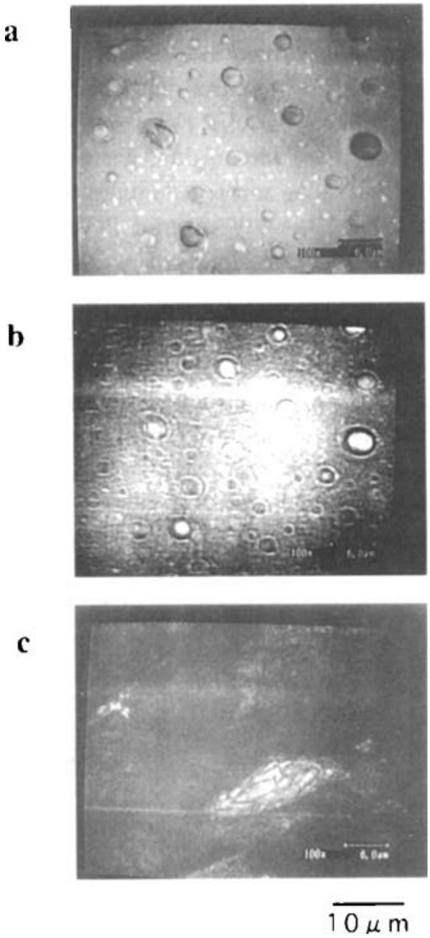

FIGURE 2 Confocal laser scanning microscope images of P(2EHA-AA-VAc)/P(VDF-HFA) (30/70) blend with three different depth regions: (a) Surface, (b) Central and (c) Bottom.

of 1 μm in diameter are most abundant in the near-surface region, whereas the domains having 6 μm diameter are most abundant in the central region of the blend. By comparing with the SEM micrograph of the cross-section of the blend [2], we may conclude that the domains having 1 μm diameter exist in the layer of 3 μm in depth from the surface and the domains of 6 μm diameter, in the layer of 5 to 10 μm in depth. As anticipated from the SEM picture, we see no domain structure in the bottom region because a P(2EHA-AA-VAc) layer having 10 μm thickness is formed in the bottom layer of the blend [2]. The CSLM images suggest that the gradient domain morphology is formed in the P(2EHA-AA-VAc)/P (VDF-HFA) (30/70) blend.

P(2EHA-AA-VAc) phase having low glass transition temperature (Tg:−70°C) is very sticky at ambient temperature and the interfacial strength between P(2EHA-AA-VAc) and P(VDF-HFA) phases may be weak because of their immiscibility. For SEM observation we had to perform complex sample preparations such as embedding in epoxy resin, cutting at −120°C, and staining with ruthenium tetraoxide. On the other hand, we carried out no sample preparation for CSLM observation. Therefore, we judge that CSLM is a powerful technique for determining the gradient domain morphology formed in the polymer blend, if it is transparent towards the laser beam.

Figure 3 shows the CSLM image of silica gel in the P(2EHA-AA-VAc)/P(VDF-HFA)/R972(28/70/2) blend. We brought the object

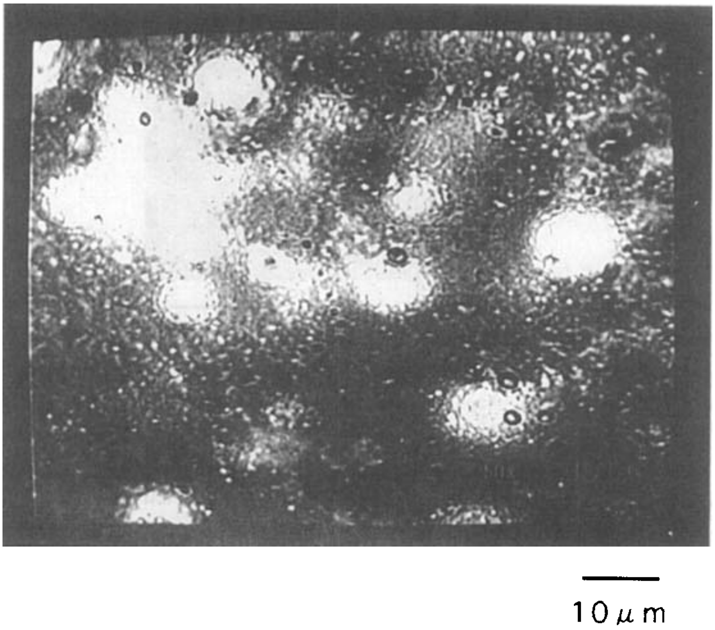

FIGURE 3 Confocal laser scanning microscope image of P(2EHA-AA-VAc)/P(VDF-HFA)/R972 (28/70/2) blend.

existing at 8 μm depth from the surface into focus. We see P(2EHA-AA-VAc) spherical domains in P(VDF-HFA) matrix with the diameter varying approximately from 1 to 10 μm. The shape of P(2EHA-AA-VAc) domains for the 30/70/2 blend is similar to that for the 30/70 blend. However, the brightness of the small domains is the same as that of the large domains. This means that the gradient domain morphology formed in the 30/70 blend is moderated by loading with only a small amount of R972. The CSLM result is consistent with the result of cross-sectional layers observed with the SEM [2]. Thus, the difference of morphology between the gradient structure formed in the 30/70 blend and the moderated gradient structure formed in the R972-loaded system was confirmed with CSLM.

For the (30/70) blend, combining a top view revealed with CSLM and a side view of the gradient domain morphology with SEM, we have drawn a model view of the gradient domain morphology in three dimensions, as shown in Figure 4. P(2EHA-AA-VAc) spheroidal

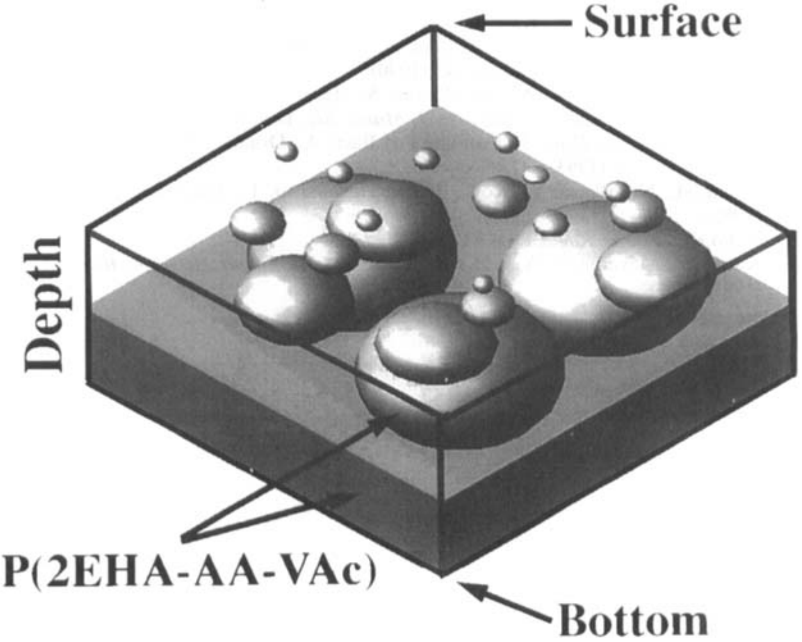

FIGURE 4 Three-dimensional modeling picture of gradient domain morphology *formed in* P(2EHA-AA-VAc)/P (VDF-HFA) 30/70 blend.

domains exist in P(VDF-HFA) matrix. The domain size increases from the surface to the bottom and a P(2EHA-AA-VAc) layer is formed on the bottom side. This modeling picture is presumably the image of the real gradient domain morphology expected in the 30/70 blend. In the future, a computer stacking of these images [7] should provide us a three-dimensional picture of the gradient structure formed in the blend. Moreover, the CSLM technique will allow us to observe directly the real-time forming process of gradient domain morphology under solvent evaporation.

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