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Phase separated domain structure of poly(vinyl butyral)

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SUMMARY

A morphological study of poly(vinyl butyral) is performed on the thin films prepared by evaporation of polymer solutions. It is shown by transmission electron microscopy that there are many domains of dimensions 0.02 to 1 µm in this amorphous random copolymer. The image contrast of the electron micrographs is improved significantly by RuO_4 staining technique. It is suggested that the domain structure can be mainly attributed to the hetrogeniety of the polymer as a result of microphase separation in the polymer solutions.

INTRODUCTION

Morphology of amorphous polymer is an interesting research topic. Extensive morphological investigations have been reported on block and graft copolymers. However, only very few studies have been made concerning the amorphous random copolymers. Poly(vinyl butyral), a typical amorphous random copolymer, is considered to be homogeneous. A commercial resin of poly(vinyl butyral) (Batvar B-98, Monsanto Company) has been recommended to be used as a support film for electron microscopy (1, 2). Recently, we have found that poly(vinyl butyral) is easy to form islands/sea texture. The RuO_4 staining technique, developed by Trent et al (3), was used for the visualization of phase-separated structure of ether group containing polymeric systems, such as poly(ethylene oxide)/polymethyl methacrylate (4) and polyoxymethylene (5) in this laboratory. Here, we

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present the preliminary results of a study on the phase separated domain structure of poly(vinyl butyral) by using RuO_4 staining technique.

EXPERIMENTAL

Commercially available poly(vinyl butyral) sample (henceforth denoted as PVB) was kindly supplied by Prof. Y. Zhang, Institute of No. 621, Beijing. The compositions of the sample are listed in Table 1. All solvents, tetrahydrofuran, chloroform and butanone were A.R. grade chemicals. Diluted polymer solutions of PVB were prepared by mixing PVB with solvents at room temperature for 24 hrs. or by refluxing the mixture at boiling temperature of solvent for 12 hrs. respectively, then the solutions were filtered through 3# sintered glass filters. The 0.3 % solutions thus prepared were cast into thin films by evaporating the solvent on glass slides at room temperature. The cast film specimens were further dried in vacuo for two days. Staining of the specimens was carried out at room temperature in the vapor of an aqueous solution of RuO_4 (concentration 0.3 g/dl) for a period of time varing between 10 and 100 min. The specimens were floated off from the glass slide and subsequently transferred onto copper grids. Polymer morphology was observed with a Hitachi H-800 electron microscope operating at an accelerating voltage of 200 KV.

Table 1. Chemical Composition of Poly(vinyl butyral)

butyral content, expressed as weight percent poly(vinyl butyral)	81-85
hydroxyl content, expressed as weight percent poly(vinyl alcohol)	14-18
acetate content, expressed as weight percent poly(vinyl acetate)	0.6-0.8

Data supplied by Prof. Y. Zhang, Institute of No. 621.

RESULTS AND DISCUSSION

Fig. 1(a) shows a typical electron micrograph of the RuO_4 stained PVB film cast from 0.3 % tetrahydrofuran solution. As can be seen in the micrograph, the two-phase structure can be characterized as round particles dispersed in a matrix. The average size of the dispersed particles is about 0.2 µm. Generally, the dimensions and volume fractions of the dispersed particles vary from specimen to specimen. Because the difference in the electron densities of the two phase is high enough, the islands/sea texture can also be observed in the unstained specimen, as shown in Fig. 1(b).

Several attempts have been made to visualize the domain structure of PVB films cast from chloroform solution by RuO_4 staining technique. However, the thin films seem to be rather homogeneous. It is difficult to get reliable evidence about phase-separation structure from our experimental observation, i.e., our results are consistent with Baumeister (1) and Handley, Olsen's (2) observations.

In order to investigate the effect of casting solvent on the domain structure, thin films cast from 0.3 % solution in butanone were also examined. Fig. 2(a) and 2(b) show the electron micrographs of RuO_4 stained and unstained PVB films cast from butanone solution respectively. The morphology of the films resembles that cast from tetrahydrofuran solution. In contrast to the domain structure observed in Fig. 1, a phase inversion of islands/sea texture was observed in these films, i.e., the electron density of the dispersed particles is larger than that of the matrix.

A comparison of Fig. 1(a), 2(a) with 1(b), 2(b) indicates that the image contrast of the micrographs of the RuO_4 stained specimens is improved significantly. This means that RuO_4 staining technique was proved to be a useful method for studying the complex morphology of this copolymer. As RuO_4 reacts preferably with some of functional groups in PVB, the enhencement of image contrast provides an evidence that functional group heterogeneity exists in this phase separation structure.

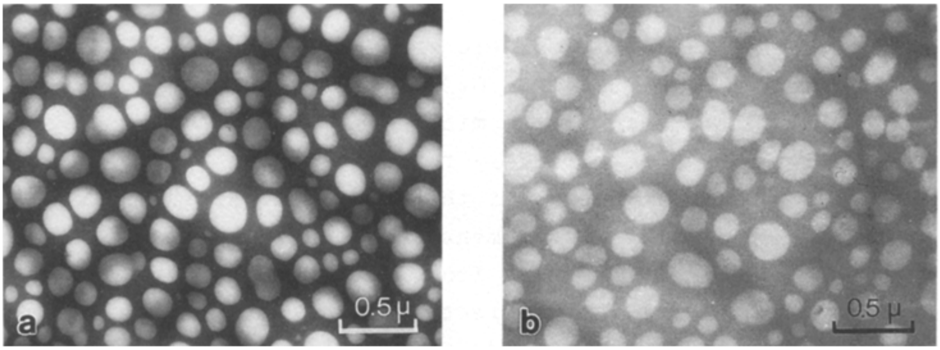

Fig. 1, Electron micrograph of poly(vinyl butyral) films cast from 0.3 % tetrahydrofuran solution. (a), stained by RuO_4 vapor. (b), unstained.

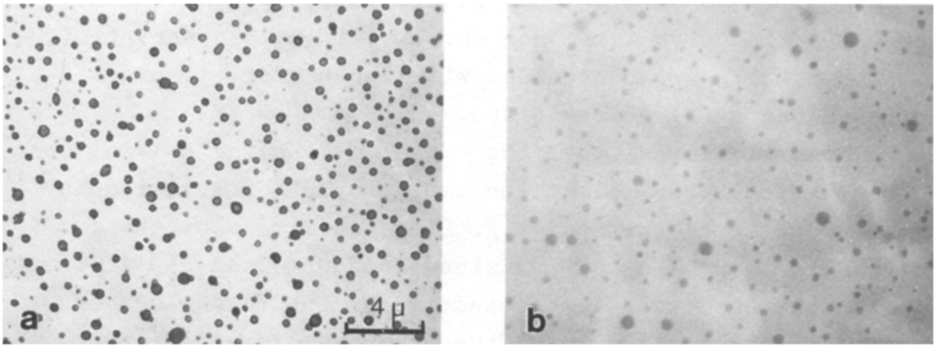

Fig. 2, Electron micrograph of poly(vinyl butyral) films cast from 0.3 % butanone solution. (a), stained by RuO_4 vapor. (b), unstained.

It is of great interest to compare the characteristic features of different films cast from different solvents for the same polymer sample (for example, see Fig. 1 and Fig. 2). Since the volume fraction and the electron density of the dispersed domain are very sensitive to the casting solvent and other experimental conditions, the phase separation appears to be independent of the average functional groups percentage of the copolymer as shown in Table 1. In other words, the domain formation mechanism of PVB from solutions seems to be rather different from common block copolymers with incompatible sequences, such as styrene-butadiene di- or triblock copolymers. It is known that inhomogeneity in composition always exists in poly(vinyl butyral) and the solubility of the copolymer in solvent can be expected to be dependent on chemical composition of individual molecules. It is suggested that segregation of different species may occur in some concentrated solutions. The globular shape of the dispersed domains and the RuO_4 staining experiments are also consistent with the liquid-liquid phase separation mechanism of the domain structure formation.

ACKNOWLEDGEMENTS

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