

STUDY ON THE MORPHOLOGY OF POLYVINYL CHLORIDE/POLYSTYRENE BLENDS BY ELECTRON MICROPROBE ANALYSIS*

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Abstract The morphology of polyvinyl chloride/polystyrene (PVC/PS) blend samples with different mass ratios, prepared by means of solution casting and melt mixing, have been successfully examined by electron microprobe analysis (EMP). This experiment was performed in a scanning electron microscope attached to an energy dispersive X-ray analyzer. Differential scanning calorimetry was also used to investigate the phase separation of the blends. The results show that PVC and PS are incompatible and the blends have sea-islands phase structures. Blends prepared via melt mixing have finer phase-dispersion than those prepared via solution casting.

Keywords Electron microprobe analysis, Polyvinyl chloride/polystyrene blends, Morphology

INTRODUCTION

Morphology investigations play an essential role in the study of polymer blends. Among the commonly used techniques, scanning electron microscopy (SEM) is one of the most frequently used methods. This method is exceptionally suitable for the investigation of the fracture surface of the polymer blends, but unsuitable for the smooth surface. And sometimes it is not easy to identify certain components of the blends.

In this paper, the morphology of PVC/PS blends was examined by electron microprobe analysis (EMP). This technique is performed in a scanning electron microscope with an attached energy dispersive X-ray analyzer. In this method, the measured radiation is a characteristic X-ray generated as a result of transitions between inner atomic electron energy levels, which are stimulated by electron excitation. From the wavelength (or photon energy) and intensity of the lines in the X-ray spectrum, the existing elements can be identified and their concentrations can be estimated^[1-3].

EXPERIMENTAL

Materials

Polyvinyl chloride (PVC, WS-800S) with an average polymerization degree between 750 and 850 is a product of Shanghai Chloralkali Chemicals of China. Polystyrene (PS, 535) with an average molecular weight of 2.24×10^5 g/mol was supplied by Zhangjiang Zhongmei Chemical Limited of China.

Preparation of Blends by Melt Mixing

PVC and its additives (PVC/DOP/3PbOPbSO₄/2PbOPbHPO₃/Stearic acid = 100/10/3/3/1) were compounded

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and mixed in a two-roller mill (front roll 155~160°C, rear roll 145~150°C) for 5 min. PS was then added and mixed for another 10 min. The well-mixed blend was then transferred to a pre-heated compression mould and hot pressed at 170°C under 14 MPa for 15 min to give a blend membrane.

Preparation of Blends by Solution Casting

PVC (without additives) and PS were dissolved in tetrahydrofuran (THF) to form a dilute solution. The solution was then cast on a microscope slide and dried at room temperature for several days.

Characterization

The morphology of the blends was examined by a Hitachi S-570 scanning electron microscope at an accelerating voltage of 20 kV. An EDAX attachment made it possible to analyze the localization of polyvinyl chloride by means of electron microprobe analysis (EMP). Samples were coated with a thin layer of gold to reduce any charge build-up on the surfaces. Two photographs were taken for each sample, one is the original SEM photograph, the other is the EMP photograph that was taken of the same zone. The data were acquired by monitoring the chlorine signal from polyvinyl chloride.

A Perkin-Elmer 7 thermal analyzer was used to measure the glass transition temperature of the blends with a heating rate of 10 K/min.

RESULTS AND DISCUSSION

The solubility parameters of PVC and PS are nearly identical, but a comparison of their bidimensional values (Table 1) shows that these polymers are actually rather incompatible. A simple mechanical blend would have a pronounced tendency to undergo phase separation.

Table 1. Solubility parameters of PS and PVC (from Refs. [4] and [5])

Polymer	δ (J ^{1/2} cm ^{-3/2})	δ_d (J ^{1/2} cm ^{-3/2})	δ_p (J ^{1/2} cm ^{-3/2})
PS	19.5	18.6	0.2
PVC	18.7	15.1	12.5

Figure 1 shows the photographs of PVC/PS blends obtained by solution casting. From the original SEM photos (a~e), we can observe the sea-island structures. From the photo of sample (c), for example, we can perceive three types of phases, designated as I, II and III. Note that region III in fact corresponds to region II. Because the interfacial adhesion is very poor, when the samples were transferred from the glass slides to the sample holder of the microscope, the material of the disperse phase (region II) easily dropped out, leaving voids (region III) in the samples.

However, it is impossible to determine whether a certain phase is PVC or PS if we do not have additional information. Thus, electron microprobe analysis (EMP) was performed for this purpose. The X-ray spectrum is recorded in energy dispersive spectroscopy (EDS) mode. From the wavelength (or photon energy) and intensity of the lines in the X-ray spectrum, the existing elements can be identified and their concentrations can be estimated. However, this method is not sensitive enough to analyze light elements. Only those that have an atomic number larger than 11 (sodium) could be determined.

In this study, data were acquired by monitoring the chlorine signal originating from polyvinyl chloride. From EMP measurements (Fig. 1 a'~e'), it is easy to affirm that region I is the PVC-rich phase and region II is the PS-rich phase, because the white spots give the localization of chlorine atoms and hence the PVC molecules. Pure PVC sample (a') gives a picture with dense white spots, and pure PS (e') gives a black photo with few white spots which might be caused by the background. For PVC/PS (70/30) sample (b, b'), PVC constitutes the matrix and PS constitutes the domain with a diameter of ca. 0.1 mm. Conversely, for PVC/PS (30/70) sample (d, d'), PS constitutes the matrix and PVC constitutes the domain. For PVC/PS (50/50) sample (c, c'), PVC constitutes the matrix and PS constitutes the domain, although the volume fraction of PS is higher than PVC due to their difference in density. We think this is due to the fact that PVC has a higher solubility in THF than PS. Hence, PS is easier to precipitate than PVC during the solution casting process^[6, 7].

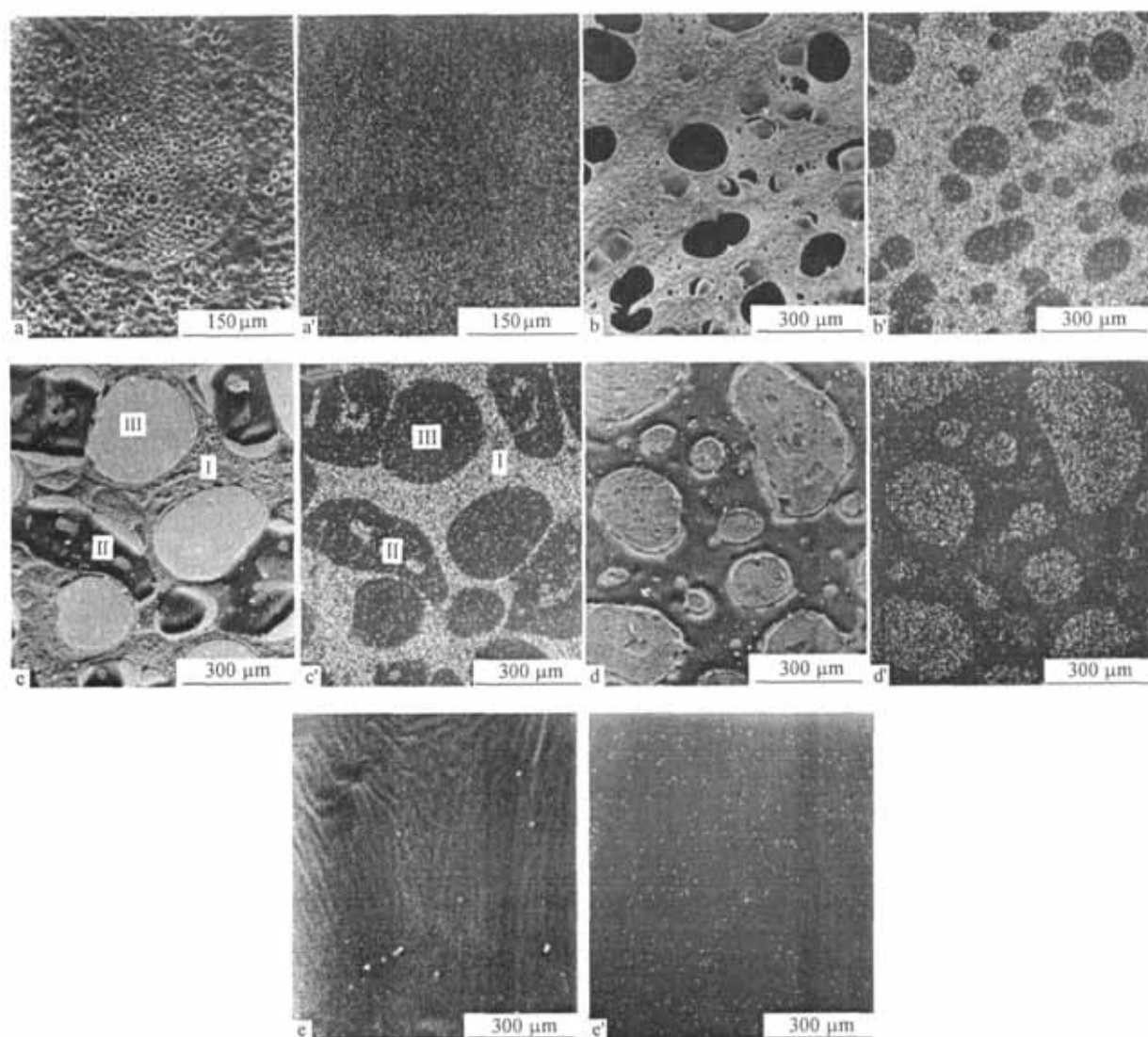


Fig. 1 SEM (a~e) and EMP (a'~e') photographs of the membranous surface of PVC/PS blends prepared by solution casting

Composition: a), a') 100/0; b), b') 70/30; c), c') 50/50; d), d') 30/70; e), e') 0/100

In addition, a part of the PVC is present in PS phases, as shown by a few areas with dense white spots in the black regions (e.g., region II of sample c), at least in PVC/PS (50/50) blend.

Figure 2 shows the photographs of PVC/PS blends obtained by melt mixing. The white spots become less concentrated as the PVC content decreases but their distribution remains uniform, showing finer phase dispersion patterns than solution casting blends. This is due to the fact that the phase separation of melt mixing sample is not as complete as that of solution casting sample. During the melt mixing process, the two components were forced to disperse into each other to form a finer phase dispersion pattern, and it became stable when the sample was cooled.

Figure 3 shows the DSC scans of PVC, PS and PVC/PS (1/1, mass ratio) blend obtained by melt mixing. The glass transition temperature of PS is 100°C while that of the plasticized PVC is 58°C. The DSC curve of PVC/PS (1/1, mass ratio) blend shows two glass transitions at 72°C and 82°C, respectively, revealing the existence of the two phases (although it is not easy to find phase separation in Fig. 2). Note there is a shift in the

two T_g which is caused by the migration of part of the DOP (the plasticizer for the PVC) from the PVC phase to the PS phase.

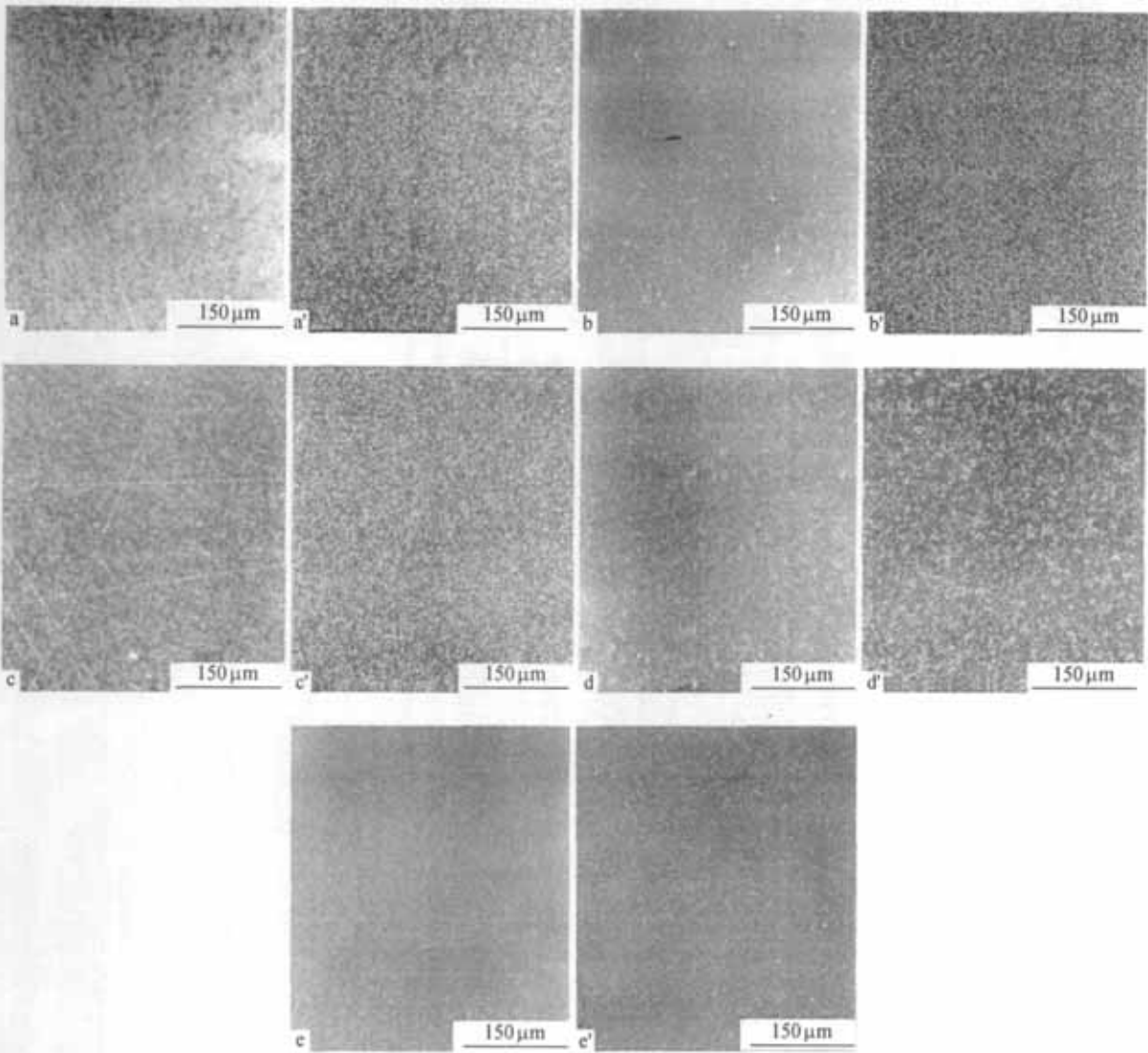


Fig. 2 SEM (a~e) and EMP (a'~e') photographs of membranous surface of PVC/PS blends prepared by melt mixing
Composition: a), a') 100/0; b),b') 70/30; c), c') 50/50; d), d') 30/70; e), e') 0/100

CONCLUSION

Electron microprobe analysis (EMP) was successfully used to study the morphology of polyvinyl chloride/polystyrene blends with different mass ratios. Result shows that PVC and PS are incompatible and the blends have sea-islands phase structures. Blends prepared via melt mixing have a finer phase dispersion than those prepared via solvent casting.

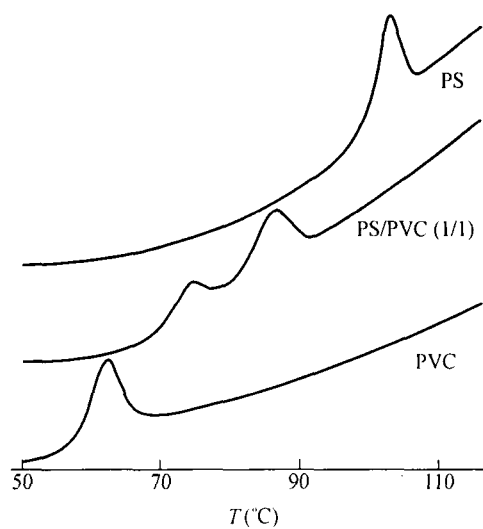


Fig. 3 DSC thermograms of PVC, PS and PVC/PS (1/1) blends

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