

Phase Relations in Poly(vinyl Chloride)/Ethylene-Vinyl Acetate Copolymer Blends with Low Contents of the EVA Polymer

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Synopsis

A series of polymer blends of commercial poly(vinyl chloride) (suspension-polymerized powder) and an ethylene-vinyl acetate copolymer (EVA with 45 wt % VA) containing 2-10 wt % EVA were prepared by mixing at room temperature (0) and by milling at 160°C for 15 min (I) and then heat treated at 170°C for 20 min (II) and 40 min (III). Wide-line NMR measurements for protons at room temperature show a broad band (assigned to PVC phase) and a superimposed narrow band (assigned to mobile EVA phase). The 0-samples had a narrow band intensity corresponding to the total EVA content; the I-samples had a less intense narrow band than expected, indicating that 2-3% EVA was included in the rigid PVC phase. Heat treatment for 20 min (II) and 40 min (III) increased the narrow band intensity toward the 0-samples showing phase separation except for milled blends containing 2 wt % EVA, which had no separable narrow band and remained so. These results indicate that about 2 wt % EVA is compatible with the PVC phase and in equilibrium, while milled blends with more than 2 wt % EVA are metastable.

INTRODUCTION

The mixed polymer system consisting of EVA (ethylene-vinyl acetate copolymer, with 45 wt % vinyl acetate) and PVC has previously been examined with the aid of NMR.^{1,2} It was thereby found that the polymer components were mixed to an appreciable extent in samples with an EVA content of 7.5 wt %, which is the composition of main technical importance. It was observed that samples prepared by milling and extruding undergo a phase separation under heat treatment at 170°C. This result seems also to be confirmed by further measurements on these samples with DSC.³

The possible partial compatibility of the blends within the low composition range of EVA has been suggested by Rånby et al.^{4,5} At low EVA content of the blends (5 wt %), PVC forms a continuous phase with a fine dispersion of EVA (<0.1 μm). With increasing EVA content, phase inversion takes place, resulting in EVA forming the continuous phase. The fine dispersion of EVA at low contents is attributed to partial dissolution of EVA in PVC, enclosure in voids, or adsorbed on certain surfaces of the PVC.

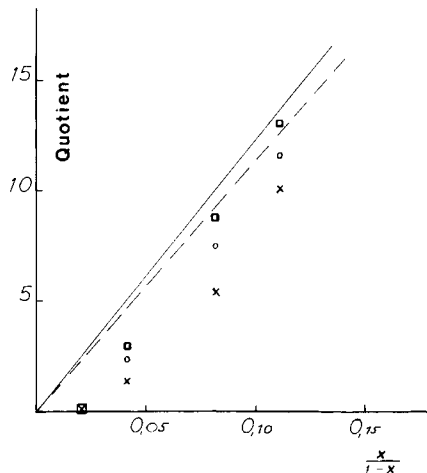


Fig. 1. Quotient between the intensities of the narrow (EVA phase) and the broad line (PVC phase) in the derivative NMR absorption spectra of blends. Full and dashed lines represent blends having the components completely separated in different phases:² (x) milled blends; (O) blends heat treated 20 min at 170°C; (□) blends heat treated 40 min at 170°C.

Two alternate mechanisms are properly applied in interpretation of the phase separation phenomenon. These are the spinodal decomposition mechanism⁶ and the nucleation and growth mechanism.⁷ In the former mechanism, phase separation proceeds spontaneously within the spinodal by negative interface diffusion. The latter mechanism is associated with a metastable equilibrium of the homogeneous system. The system is stable with respect to continuous composition changes, but it is unstable to large composition fluctuations. The large composition fluctuation is called a nucleus. The new phase starts from the nucleus and then grows. The growing follows the ordinary diffusion process, i.e., positive diffusion. Thermodynamically and kinetically, phase separation of multicomponent system can be carried out by heat treatment.

Wide-line and pulsed NMR have been successfully applied to the study of phase separation in polymer blends.^{1,2,8-10} The main principle is that the line contributions can usually be separated for systems with different phases, having sufficient difference between the glass transitions. The temperature variations of the line width observed by wide-line NMR as well as the relaxation times obtained from pulsed NMR can be used for characterizing the compositions of the phases. The relative signal contributions give information concerning the amounts of the phases.

EXPERIMENTAL

In the present work, NMR investigations have been performed on a number of PVC/EVA blends with different EVA contents. All samples have been prepared by milling the polymer components together at 160°C for 15 min. The common stabilizing additives (organic Ba-Cd salts and Pb stearate) have been used in amounts totalling 3 parts per 100 parts of PVC + EVA.

The wide-line NMR measurements have been performed at room temperature. The main bulk of the PVC, which has a glass transition temperature high above



Fig. 2. NMR half-derivative curves for a blend containing 2 wt % EVA in PVC: (---) milled sample; (—) blend heat treated 20 min at 170°C.

this temperature, gives rise to a broad line. The very soft EVA phase with a glass transition temperature much below room temperature produces a very narrow line in the center of the spectrum. The degree of mixing between the polymer components has been determined simply by comparing the intensities between the narrow and the broad line of the investigated blends with blends where the components are known to be quite separated in different phases (Fig. 1). These latter blends have been prepared by evaporation of suspensions of powdered PVC in solutions of EVA in carbon tetrachloride.

DISCUSSION

The experiments show that a considerable part of the EVA polymer is not present as a free phase and may therefore be regarded as being dissolved in the PVC phase. In the sample of lowest EVA content, only 2 wt %, compatibility seems to be almost complete. A considerable growth in the intensity of the narrow line is observed after heat treatment of the blends for 20 and 40 min at 170°C under nitrogen atmosphere. The intensity becomes larger with increasing time of heat treatment. However, for the blend with only 2 wt % EVA, the spectral shape is very little affected by this heat treatment (Fig. 2). It may, therefore, be supposed that the EVA polymer to an extent of about 2 wt % forms a stable solution in PVC. For the sample of 4 wt % EVA, the line intensities are changed considerably by the heat treatment, but the phase separation seems to be incomplete in this case. For the blends with higher EVA content, the separation seems to be almost complete, which also was observed in the earlier results.^{1,2} However, the stabilizing additives present may contribute to the narrow line, making the conclusion of complete phase separation somewhat dubious. Further work will be devoted to this problem.

These results may suggest that the blends containing more than 2 wt % EVA are metastable, with the phase equilibrium being thermodynamically and kinetically a function of temperature, time, and blend composition. The time dependence of the phase separation hints at the spinodal phase separation mechanism, since the level of phase separation is invariant with time in the nucleation and growth mechanism.^{8,9}

The experimental procedure used here illustrates clearly the advantage of using NMR for investigations of mixed binary polymer systems with small amounts

of a soft component. It is probable that the solubility properties between polymer components with low mutual solubility are best investigated in this way by use of a series of blends with decreasing amounts of the soft component. Observations of the phase separation phenomenon after longer times of heat treatment may be less accurate due to thermal decomposition and the disturbances due to the presence of low molecular components. Wide-line NMR may be regarded as a valuable tool in this respect due to the exceedingly high sensitivity obtained for the detection of traces of a soft phase.

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