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Morphology Formation in Mixing of Copolyester Thermoplastic Elastomer (Hytrel) with Poly(vinyl chloride) and Nuclear Magnetic Resonance Relaxation Study on Solid Structures of the Mixture

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ABSTRACT: A mechanical mixing of copolyester thermoplastic elastomer (Hytrel) and poly(vinyl chloride) (PVC) was carried out in an internal mixer, and the morphological changes during mixing were monitored with a scanning electron microscope. It is found that Hytrel formed a continuous phase and PVC was dispersed throughout, first by removal of skins and then gradual disintegration of the particles into the substructures of its unique hierarchy. Proton spin−lattice relaxation times in the rotating frame, $T_{1\rho}$, were evaluated from CP/MAS ^{13}C NMR spectra to determine the solid morphology after the completion of mixing. Pure phases of both Hytrel and PVC microcrystallites were present, dispersed in a mixed matrix. The maximum and minimum domain sizes of the dispersed phases were estimated to be *ca*. 14 and 24 Å, respectively.

Introduction

Copolyester thermoplastic elastomer (Hytrel) is a two-phase material possessing both thermoplastic and rubbery nature; the former results from the crystalline hard segments serving as thermally reversible physical cross-links, and the latter forms the amorphous, soft segments.[1] Mechanical blending of Hytrel with poly(vinyl chloride) (PVC) is the common practice providing improved characteristics of physical/processing properties and optimum cost performance in numerous engineering applications.[2,3] The physical and mechanical properties of such a mixture are primarily dependent on the solid-state structures, which are intimately related to the morphology formed during mixing.

This work is concerned with morphology in the process and upon completion of mixing. The sample was Hytrel/PVC (50/50 mass ratio) mechanically mixed using a Banbury-type internal mixer. As schematically shown in Figure 1, the PVC (suspension grade) is a powder of about 100−150 μm grains which consist of a unique hierarchical structure of skins and tight agglomerates (~10 μm); the agglomerate is composed of primary particles (~1 μm) which in turn consist of domains (~0.1 μm); the domain is made up of microdomains (~10 nm) which are held internally by microcrystallites.[4,5] The mixing is monitored with a scanning electron microscope (SEM) at various stages during the progress of mixing.

The phase structures of the final mixture in the solid state are characterized with a high-resolution, pulsed Fourier-transformed (FT) ^{13}C nuclear magnetic resonance (NMR) spectroscopy capable of magic angle spinning (MAS) and cross-polarization (CP) techniques (shortly, CP/MAS). The CP/MAS not only enhances the sensitivity of carbon signals, otherwise hardly observable, by transferring the magnetization from naturally abundant ^{1}H to rare ^{13}C spins but also enables the resonance of carbons attached to chemically different environments to be resolved.[6,7]

Various methods to characterize the phase structures of a particular mixture have been tried, and their applicability and inherent resolution are shown to differ widely. For example, the T_g measurement by differential scanning calorimetry (DSC) is known to be sensitive to domain structures of the size range between *ca*. 25 and 30 nm.[8−10] A more sensitive dynamic mechanical measurement allows a characterization of domains down to *ca*. 15 nm.[8−10] The CP/MAS ^{13}C NMR measurement of spin−lattice relaxation times permits an analysis of domains with the sizes from a few angstrom to a few tens of nanometers,[11−15] depending on the use of the relaxation times of either in the rotating frame (i.e., $T_{1\rho}$) or in the laboratory frame (i.e., T_1). Furthermore, it is possible to quantify the scale of heterogeneities through the spin-diffusion process.[16] In this paper, the measurement of CP/MAS ^{13}C NMR $T_{1\rho}$ relaxation times is used as a probe to determine the microphase structures and the scale of microheterogeneity of the Hytrel/PVC mixture in the solid state.

Experimental Section

Materials, Mixing Procedures, and Microscopic Examination. Hytrel (E.I. DuPont de Nemours & Co.), grade 4056, is a multiblock random copolymer of alternating soft and hard segments. The soft segments are amorphous poly(tetramethylene ether) glycol terephthalate blocks with a molecular weight of about 1000.[1,17,18] The hard segments are polytetramethylene terephthalate blocks which are at least 10 units long and capable of crystallization. They consist of *ca*. 30 wt % polymer.[1,17,18] The soft segments have the glass transition temperature of about −50 °C, and the hard segments melt at about 150 °C.[1,17,18] The number-average molecular weight is about 30 000. PVC resin was Geon 103 EP F-76 (Geon Co.) with number-average molecular weight of 40 000 and weight-average molecular weight of 89 000.[19]

The two polymers were mixed in a batch, nonintermeshing, counter-rotating two-wing rotor internal mixer (1.57 L Farrel Banbury mixer); the mass ratio was 50/50, and 1 phr of thermal stabilizer (Therm-Chek 1872 from Ferro Corp.) for PVC was incorporated. Before mixing, the Hytrel was first masticated until the temperature reached 135 °C. PVC was then charged into the mixer, and the mixing time was measured from this moment. The mixing continued for 450 s with the rotor speed of 80 rpm, and the fill factor was about 0.7.

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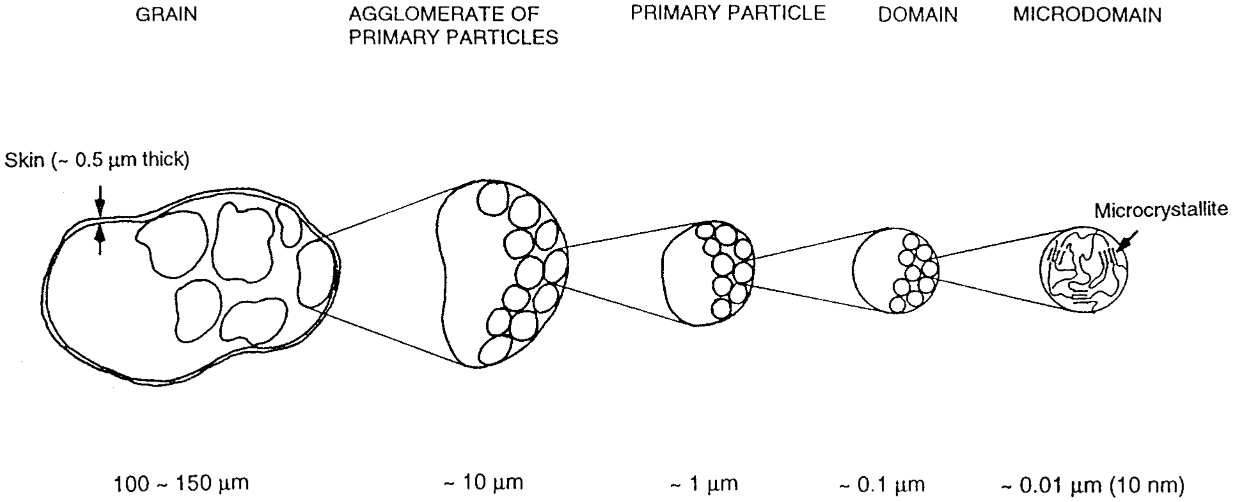

Figure 1. Structural hierarchy of suspension-polymerized PVC.

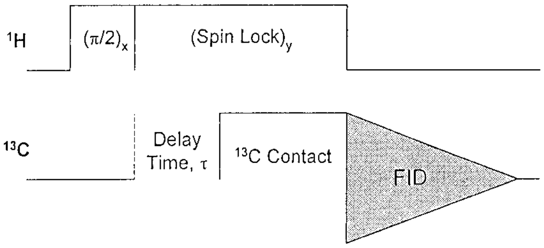

Figure 2. Pulse sequence employed to measure proton $T_{1\rho}$ relaxation times.

At various stages during the progress of mixing, the machine was stopped and the samples were removed for the microscopic examination of morphology formation. The microscopic examination was performed with a scanning electron microscope, ISI Model SX-40. For the SEM experiments, the samples removed from the mixer were cut into appropriate sizes, immersed in liquid nitrogen, and freeze-fractured. The fracture surfaces were coated with silver by a sputter-coating machine and then inspected.

CP/MAS ^{13}C NMR $T_{1\rho}$ Relaxation Measurements. The ^{13}C NMR experiments were performed with a Chemagnetic Inc. Model CMX-300 spectrometer equipped with a magic angle probe at a ^{1}H frequency of 299.6 MHz. For NMR experiments, the batch of the mixture after the completion of mixing was sheeted using a two-roll mill and the sheets were cut into pieces of squares of about 1 mm × 1 mm. Then, they were packed inside the rotor, being positioned at the center of the magnet, and spun at a rate of about 3.5 kHz. A ^{1}H 90° pulse width of 4.25 μs was employed with free induction decay (fid) signal accumulations. Proton spin–lattice relaxation times in the rotating frame, $T_{1\rho}$, were measured at 21 °C by monitoring and analyzing the changes of the peak intensities in the series of ^{13}C NMR spectra obtained with a ^{1}H matched spin–lock–τ pulse sequence followed by CP, as seen in Figure 2. The CP Hartmann–Hahn contact time of 1 ms was taken.

Measurements of $T_{1\rho}$ relaxation times for the pure component polymers, Hytrel and PVC, were performed with a Brucker Model MSL-200 spectrometer under the same experimental conditions as done for the mixture with a Chemagnetic CMX-300 spectrometer.

Results and Discussion

Figures 3–5 represent the SEM micrographs of morphology during mixing of Hytrel and PVC. At a mixing time of 15 s, Figure 3 (top), the skins of most PVC grains were removed and incorporated into Hytrel matrix. At 30 s, Figure 3 (bottom), the skins no longer existed and the grains were broken down to much smaller sizes. Hytrel is shown to form a continuous phase and PVC a dispersed phase. For further mixing to 50 s, Figure 4 (top), the breakdown of PVC grains was progressed much more, a large number reaching the size of agglomerates (~10 μm). With 70 s mixing, PVC grains were disintegrated into the primary particles (~1 μm), and at 90 s, they were further reduced to the domains (~0.1 μm), finely dispersed throughout Hytrel matrix [Figures 4 (bottom) and 5].

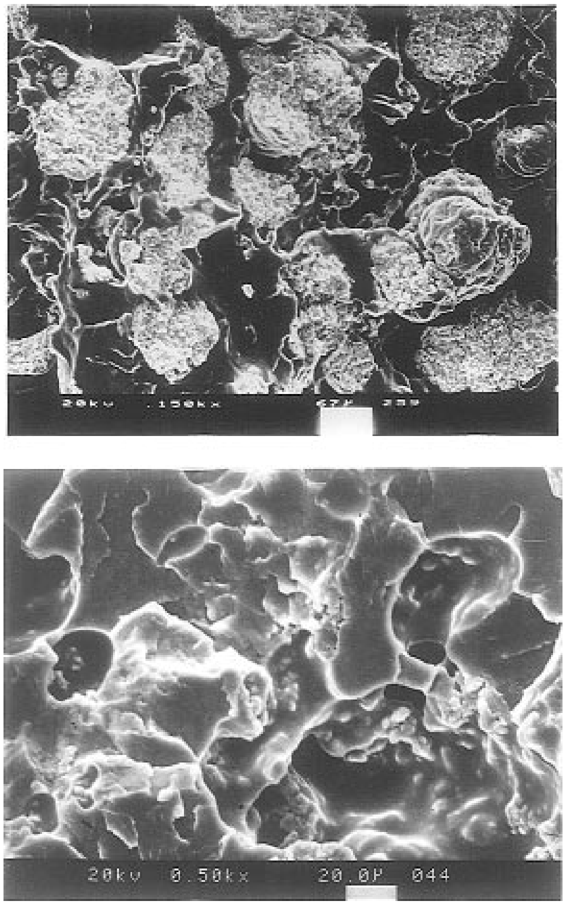

Figure 3. SEM micrographs of Hytrel/PVC mixture at a mixing time of 15 s and a magnification of 150× (top) and at 30 s and 300× (bottom) (reproduced at 65% of original size).

Figure 6 is the CP/MAS ^{13}C NMR spectrum of the Hytrel/PVC mixture after the completion of mixing for 450 s. The assignments of the resonance peaks are as follows:[20] the peak at about 165 ppm (peak 1) is assigned to the carbonyl carbons (C=O) of the Hytrel chain in

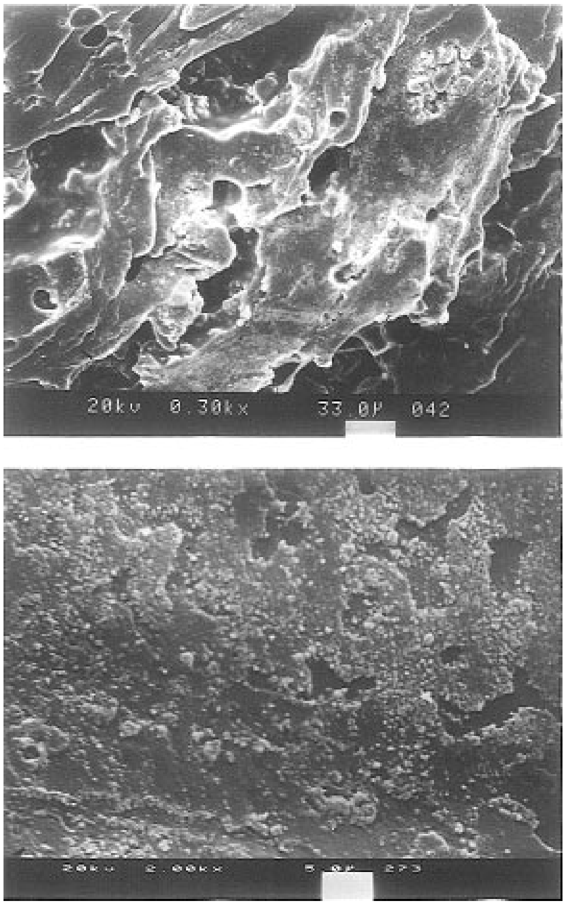

Figure 4. SEM micrographs of Hytrel/PVC mixture at a mixing time of 50 s and a magnification of 500× (top) and at 70 s and 2000× (bottom) (reproduced at 65% of original size).

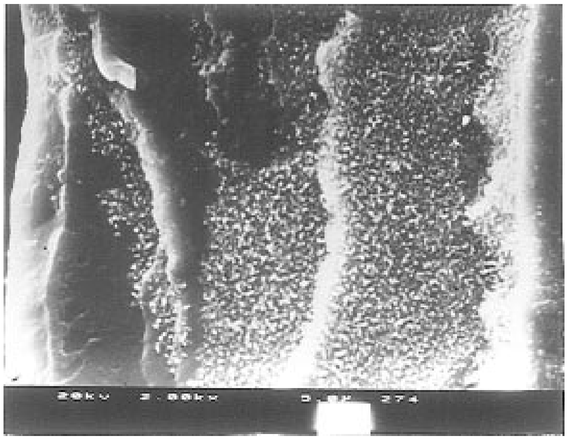

Figure 5. SEM micrograph of Hytrel/PVC mixture at a mixing time of 90 s and a magnification of 2000× (reproduced at 65% of original size).

the mixture; the two peaks, 2 and 3, at 135 and 130 ppm are assigned to nonprotonated and protonated aromatic carbons of Hytrel, respectively; the peaks at 70 and 65 ppm (4 and 5) arise from the OCH_2 carbons in the soft segments and those in the hard segments of Hytrel, respectively; the two peaks, 6 and 7 are designated to methine (CH) and methylene (CH_2) carbons of PVC in the mixture, respectively; the peak positioned at 25 ppm (8) is due to overlapping central CH_2 carbons in the soft and hard segments of Hytrel.

Among the peaks in the spectrum, the two peaks assigned for CH_2 carbons of Hytrel fraction and of PVC fraction in the mixture were selected to measure proton

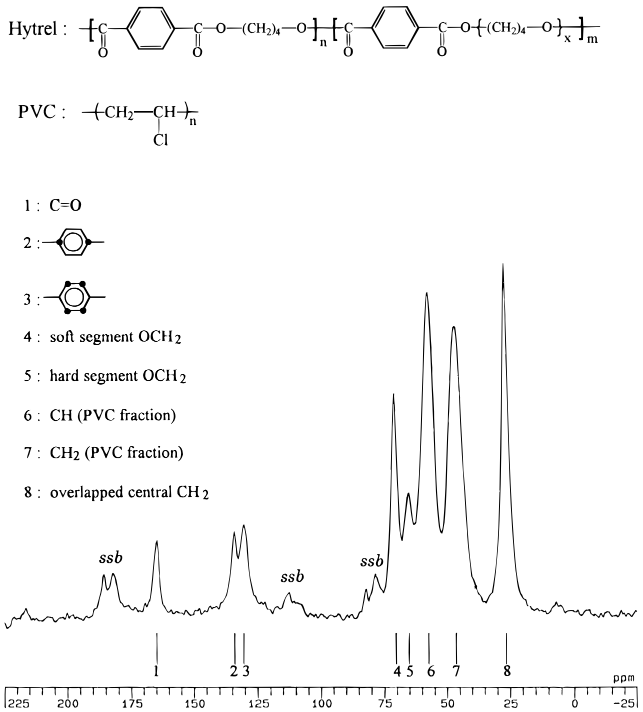

Figure 6. CP/MAS ^{13}C NMR spectrum of Hytrel/PVC mixture. The spinning side band is labeled ssb.

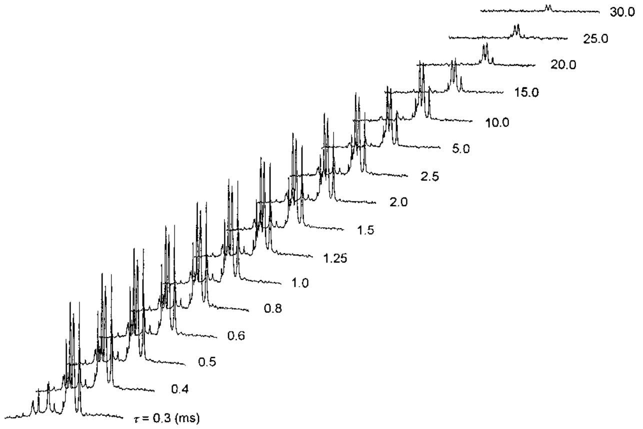

Figure 7. ^{13}C NMR stack spectra of Hytrel/PVC mixture for determination of proton $T_{1\rho}$ relaxation times.

$T_{1\rho}$ relaxation times. The $T_{1\rho}$ values can be determined by monitoring the decay of peak intensities of the specific carbons in a series of spectra (called stack spectra) obtained from introducing various delay times (τ) between the 90° pulse and the CP in the $T_{1\rho}$ pulse sequence shown in Figure 2. Figure 7 is the stack spectra of the mixture, and analysis of the decay in the heights of magnetization intensities, $M(\tau)$, of Hytrel and PVC CH_2 carbons in the mixture as a function of delay times, τ, permits a determination of $T_{1\rho}$ relaxation times. Because the $T_{1\rho}$ relaxation process follows the exponential function, $M(\tau) = M_o \exp(-\tau/T_{1\rho})$, the slopes in the plot of logarithmic $M(\tau)$ against τ, Figure 8, are the $T_{1\rho}$ values, and the results are summarized in Table 1. From Figure 8 and Table 1, a double-component $T_{1\rho}$ relaxation behavior for the mixture was clearly observed as indicated by the slope change in both CH_2 carbon signals. This observation implies that there must exist microseparated phases interfering an efficient spin diffusion across mixed phase to average out the $T_{1\rho}$'s.

In order to have a better interpretation and understanding of the microstructure in the mixture, the $T_{1\rho}$

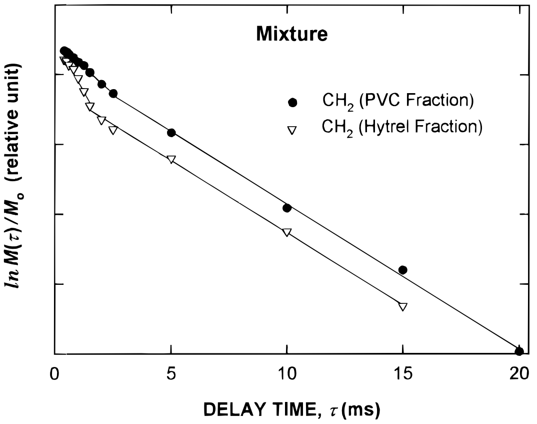

Figure 8. Logarithmic plots of ^{13}C magnetization intensity vs delay time for Hytrel/PVC mixture.

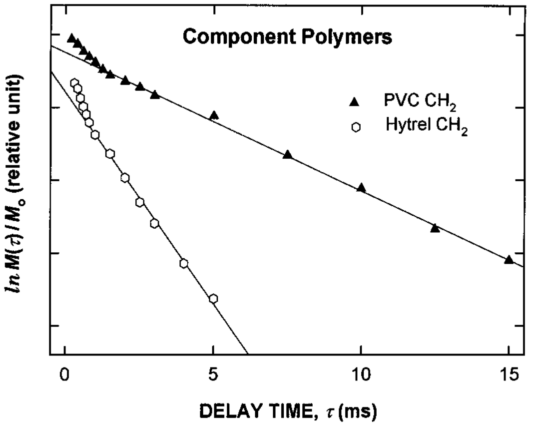

Figure 9. Logarithmic plots of ^{13}C magnetization intensity vs delay time for pure component polymers, Hytrel and PVC.

Table 1. $T_{1\rho}$ Times and Estimated Phase Sizes in Hytrel/PVC Mixture

carbon	$T_{1\rho}$ (ms)	estimated size (Å)
CH_2 (Hytrel) short-component	3.3	14.1
long-component	9.7	24.1
CH_2 (PVC) short-component	6.7	20.1
long-component	9.6	24.0

relaxation behavior of Hytrel and PVC in their respective pure state is represented in Figure 9. For Hytrel, a double-component $T_{1\rho}$ decay process is observed by the slope change in the ln $M(\tau)/M_0$ vs τ plot. The slope at the shorter delay times yields a $T_{1\rho}$ value of 3.4 ms for a hard phase, while that at the longer times results in $T_{1\rho}$ of 5.5 ms for an amorphous soft phase. A double-component $T_{1\rho}$ relaxation also occurred in PVC: The shorter $T_{1\rho}$ (6.7 ms) belongs to the microcrystallites, and the longer one (10.7 ms) indicates the amorphous chains. Thus, the short components of both CH_2 carbons in the mixture indicate the Hytrel microcyrstalline hard segments and PVC microcrystallites, respectively. The long ones are for the mixed phase and intermediate in the value as compared to the pure components, where the $T_{1\rho}$'s of both CH_2 carbons are identical considering an experimental uncertainty. Therefore, the mixture retains the morphology of three phases consisting of two separated microcrystalline domains dispersed in the matrix of the mixed phase. By comparing the $T_{1\rho}$ values for a mixture to those for the pure component polymers, it is possible to estimate the maximum scale of the microseparated domains with single-component decay and the minimum domain sizes with double-component decay[21] through the following approximate equation[11,22] based on spin diffusion:

$$\langle L^2 \rangle \approx 6DT_{1\rho} \qquad (1)$$

where L is the maximum path length over which the spin diffusion is effective and D is the spin-diffusion constant typically taken for solid polymers to be 10^{-12} cm^2/s. From the short-component $T_{1\rho}$ value of Hytrel, the minimum scale of the microcyrstalline dispersed phases is calculated to be *ca.* 14 Å. Based on the identical value of the $T_{1\rho}$'s for the component fractions in the mixture, the upper limit of the domain sizes was estimated to be *ca.* 24 Å. The above size estimates are approximate because they depend on the choice of the value of D in eq 1.

Conclusions

The scanning electron microscopy revealed that the dispersion of PVC occurred in the sequences of (i) removal of skins, (ii) breakdown of the agglomerates (~10 μm), (iii) disintegration down to the primary particles (~1 μm), and (iv) further breakdown to the domains (~100 nm) and possibly to a size smaller than the domains.

The CP/MAS ^{13}C NMR analysis with proton $T_{1\rho}$ relaxation times revealed the existence of three phases consisting of Hytrel and PVC microcrystallites and a completely mixed amorphous region. The minimum sizes of the microcrystalline domains in the mixture were *ca.* 14 Å. The maximum scale of the phase separation in the mixture was estimated to be *ca.* 24 Å so that no mixing occurred in the scale lower than 24 Å.

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