Preparation and Solid-State Nuclear Magnetic Resonance Characterization a Styrene/Butadiene/Acrylonitrile (ABS)/Poly(vinyl chloride) (PVC)/Gypsum Ternary System

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ABSTRACT: Polymer blends were prepared to obtain a new material with specific characteristics. To prepare a miscible polymer blend, it is necessary to evaluate the chemical structure and molecular dynamics of all polymers involved and to thereby establish a structure–property relationship for these materials. In this work, ternary blends for application in plates chromatography were formed with styrene/butadiene/acrylinotrile (ABS), poly(vinyl chloride) (PVC), and gypsum, and were studied by solid-state carbon-13 nuclear magnetic resonance (^{13}C NMR). Magic-angle spinning (MAS), cross-polarization magic-angle spinning (CPMAS), variable contact time (VCT), and proton spin-lattice relation time in the rotating frame ($T_1^H\rho$) were the techniques used to evaluate the miscibility, homogeneity, and compatibility of polymer blends at the molecular level. From the values of $T_1^H\rho$, it was verified that ABS/PVC/gypsum formed good polymer blends with some specific physical interaction at the molecular level. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 293–296, 2003

INTRODUCTION

Ternary blends have a great diversity of applications, for example, plates chromatography, and can be prepared and characterized by several different methods. To establish a relationship between structure and property by evaluating the dynamic behavior of ternary blends and the miscibility of blend components, it is necessary to develop a method of analysis. We chose solid-state carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR) to determine substantial relevant data to interpret the molecular dynamic behavior of polymeric materials. It is known that solid-state NMR gives more information than solution NMR because the rotation effects are pronounced on spectra in the former case and the lineshapes and relaxation parameter reveal the mobility at the molecular level. Solid state NMR also has a wide variety of specialized pulse sequences that allow one to obtain subspectra of components in different domains.[1–7] The magic-angle spin (MAS) ^{13}C NMR technique provides information on different domains of a sample by varying the acquisition conditions to detect only one region; for example, the mobile region.[7–12] This technique generates information on sample molecular mobility. The routine cross-polarization magic-angle spin (CPMAS) ^{13}C NMR technique provides information on changes in the sample environment that depend on the extent of the interaction and the molecular motions because the cross polarization rates depend on the exchange of directly attached or of neighboring protons. It is known that mobile carbons atoms take longer to cross polarize than less mobile carbon atoms.[1, 7–12] Solid-state ^{13}C NMR offers a great variety of relaxation times that provide information on molecular mobility in different time scales.[1–12] The spin-lattice relaxation process is generally dominant in the solid state, and the proton spin-lattice parameter can give direct information about molecular motion. The proton spin-lattice relaxation time can be measured in the laboratory frame with a constant (denoted T_1) and in the rotating frame with a constant (denoted $T_1\rho$). The proton $T_1\rho$ relaxation time ($T_1^H\rho$) is very important and is used to study the segmental dynamics of samples because it is sensitive to molecular motions in the range of kilohertz frequency and also to spin diffusion.[6–16]

The objective of this work was to understand the molecular dynamics of the styrene/butadiene/acrylinotrile (ABS)/poly(vinyl chloride) (PVC)/gypsum (ABS/PVC/gypsum) ternary blend. Solid-state ^{13}C NMR techniques were used to determine the response of the behavior of the samples in relation to homogeneity and compatibility of the componets at the molecular level, with a focus on the use of the blends as chromatography supports.

EXPERIMENTAL

Polymers

Commercial PVC and ABS were characterized by solution ^{13}C NMR. PVC was obtained by suspension

polymerization and presents atactic configurational sequence distributions and a predominance of the syndiotactic microstructure. The glass transition temperature (T_g) is 85°C. The ABS terpolymer composition, evaluated by solution ^{13}C NMR, consists of 60% styrene, 30% butadiene, and 10% acrylonitrile.

Sample preparation

Ternary blends of PVC/ABS/gypsum were prepared in solution with different ratios of ABS to PVC, but a constant ratio of 90/10 between polymer and gypsum.

^{13}C NMR measurements

All solid-state ^{13}C NMR spectra were obtained on an INOVA 300 spectrometer, operating at 75.4 MHz. All solid-state ^{13}C NMR experiments were conducted at ambient probe temperature and with gated high decoupling. A zirconium oxide rotor of 7 mm diameter was used to acquire the ^{13}C NMR spectra at 6 kHz. The MAS ^{13}C NMR spectra were acquired with a short delay time (0.3 s) between 90-degree pulses. CPMAS ^{13}C NMR spectra were determined with variable contact time (VCT), with a range of contact times of 0.2 to 8 ms and with a 2-s delay time. The $T_1^H\rho$ values were determined from the intensity decay of ^{13}C peaks with increasing contact times during the VCT, and also by the delayed contact time experiment, with a spin-locking range of 0.2 to 8 ms.
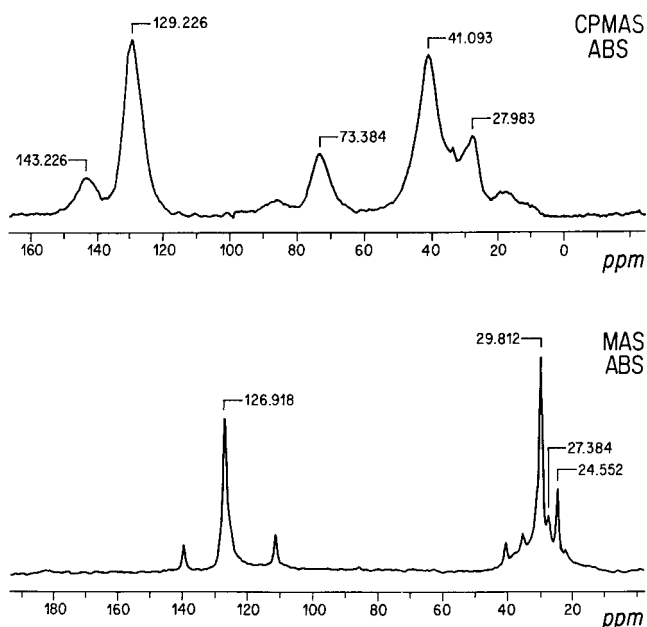
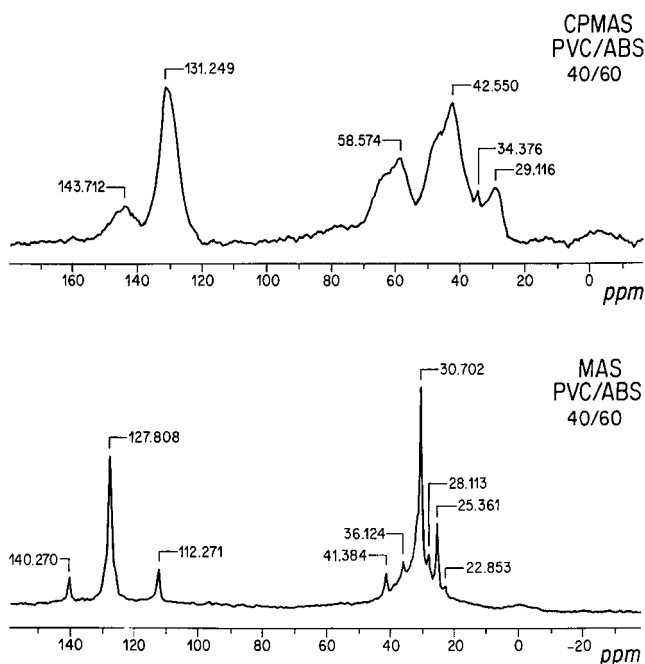**Figure 1** Comparison of CPMAS and MAS ^{13}C NMR spectra of ABS.
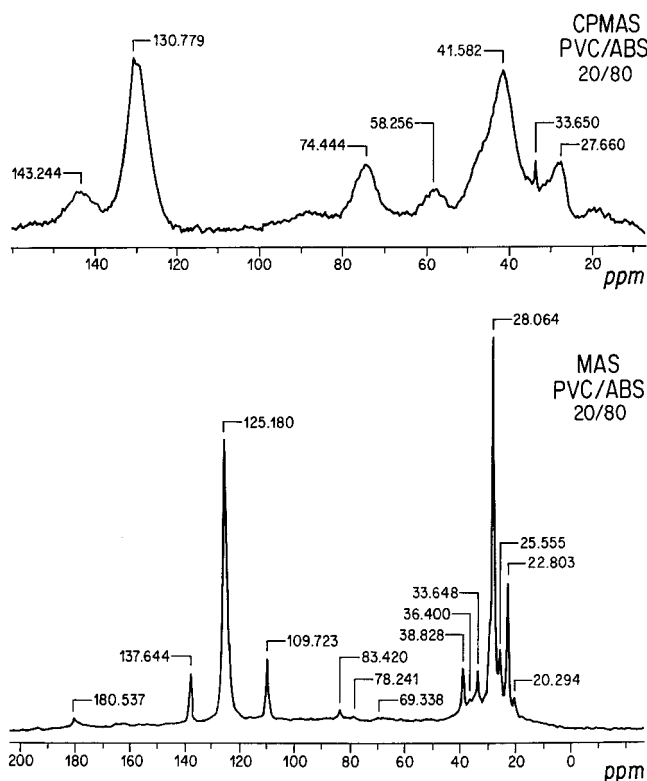
Figure 2 Comparison of MAS and CPMAS ^{13}C NMR spectra for the ternary system formed by PVA/ABS at 80/20.

RESULTS AND DISCUSSION

The CPMAS and MAS ^{13}C NMR spectra of ABS, compared in Figure 1, show the chemical and dynamic behavior of ABS. The difference in the chemical shifts, linewidth, and number of detected signals is a response of the molecular dynamic of the terpolymer due to the different components present in the polymer chains.

Analyses of the ternary blends by MAS and CPMAS ^{13}C NMR (Figures 2 and 3, respectively showed that the mobile region of these systems consists mainly of ABS. Comparison of both spectra (Figures 2 and 3) shows the presence of at least two domains; one formed by plasticized PVC and the other one by ABS. Signals from ABS and PVC were detected under the conditions used, which indicates that ABS is plasticizing PVC in this time scale.

Analyses of the CPMAS ^{13}C NMR series of spectra shed light on the signal distribution. Only signals from PVC were detected up to 20% ABS in the ternary blends, which is a consequence of domain formation and also ABS dispersion in the PVC matrix. The PVC matrix is too large to permit detection of small domains. When the ABS content was ~30%, signals from both polymers were detected in all contact times. These results indicate that both polymers present some miscibility and/or ABS is plasticized PVC (Figure 4). Furthermore, the distribution form of the sig-

Figure 3 Comparison of MAS and CPMAS ^{13}C NMR spectra for the ternary system formed by PVA/ABS at 60/40.

nals also indicates that the samples show miscibility. Therefore, for a higher quantity of ABS (80%) and for long contact times, only signals from ABS were detected. However, some plasticized PVC was also detected, indicating that a phase separation could be occurring.

Domain formation and compatibility were evaluated using the $T_1^H\rho$ results. The values for this relaxation parameter were measured by two techniques; they are, VCT, which reveals chain spatial proximity, domain size, and consequently miscibility at the molecular level, and delayed contact time (DCT), which generates information on homogeneity of chains due to the distribution of the components of the polymer blends in the materials. The $T_1^H\rho$ values for the PVC signals, obtained by a VCT experiment, for PVC and PVC/ABS/gypsum are listed in Table I. These data indicate that the ternary system presented higher mobility compared with pure PVC. However, a higher quantity of ABS (from 60%) promotes a phase separation, which is indicated by the changes in the values of $T_1^H\rho$. As the quantity of ABS increases (60%) the values found for this parameter are almost the same as those found for pure PVC, which confirms the phase separation. When the quantity of ABS is 80%, the values of $T_1^H\rho$ found for the methylene carbon of PVC increases but it is still continuous, indicating the phase separation. The mixtures that contain 60 and 80% ABS do not present good homogeneity. The increase in the ABS proportion causes a formation of at least two domains (size, ~50 nm), one rich in PVC and the other one rich in ABS. However, a domain formed by PVC/ABS probably exists.
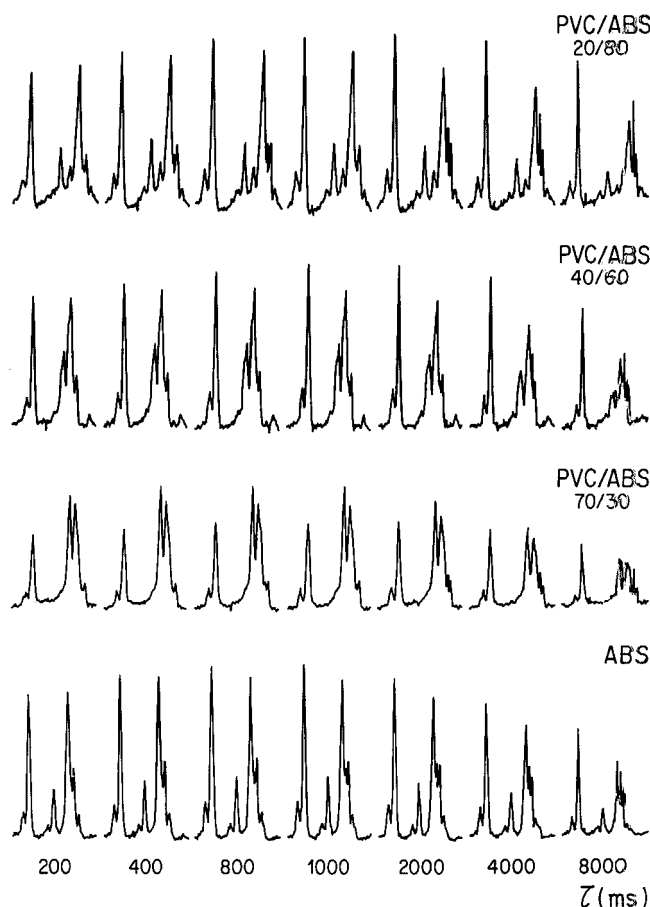
Figure 4 Distribution form of the ^{13}C signals decay during the VCT experiment for PVC/ABS/gypsum at different proportions.

For comparison with the $T_1^H\rho$ results measured by VCT, this parameter was determined from results of a DCT experiment. The $T_1^H\rho$ values were determined for the sample with higher quantity of ABS (80%) and are listed in Table II. These $T_1^H\rho$ values clearly indicate that at least two domains were the formed, and that these domains do not present a homogeneous distribution. Thus, the system can be characterized as het-

TABLE I
$T_1^H\rho$ **Values for PVC Signals, Measured by Variable Contact Time, for PVC and PVC/ABS/Gypsum**[a]

PVC/ABS/Gypsum	$I_1^H\rho$ (ms)[a]	
	57	47 δ (^{13}C)
100/0/0	2.3	2.6
90/0/10	4.0	4.1
80/20/10	4.9	8.2
60/40/10	7.3	8.0
40/60/10	3.0	3.2
20/80/10	nd[b]	5.7

[a] Determined as a function of chemical shift.
[b] Not determined.

TABLE II
$T_1^H\rho$ **Values for the PVC Signals, measured by Delayed Contact Time, for PVC and PVC/ABS/Gypsum (80/20/10)**

PVC/ABS/gypsum	$T_1^H\rho$ (ms)[a]	
	57	47 $\delta(^{13}C)$
100/0/0	2.3	2.6
90/0/10	4.0	4.1
80/20/10	3.2	6.4

[a] Determined as a function of chemical shift.

erogeneous, but an interfacial physical interaction probably also exists.

CONCLUSION

Based on the main purpose of this work, the solid-state ^{13}C NMR techniques used were able to provide substantial information on the dynamics of the ternary blend. With this information, a better proportion (60/40) of both polymer components was determined.

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