

High-Resolution Solid-State NMR and SEM Study of the Interaction Behavior of Poly(ethylene-*co*-vinyl acetate)/Poly(vinyl acetate) Blends

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ABSTRACT: Binary blends formed by two types of ethylene-*co*-vinyl acetate (EVA), which have different vinyl acetate contents, and poly(vinyl acetate) (PVAc) were prepared in a Haake Rheocord 9000 plastograph. A series of samples were obtained varying the PVAc amount up to 50%. The studies were carried out employing solid-state nuclear magnetic resonance spectroscopy (NMR) and scanning electronic microscopy (SEM). The xenon-129

(¹²⁹Xe) and carbon-13 (¹³C) NMR response together with the microscopy results showed that the systems are heterogeneous. Therefore, EVA with a higher vinyl acetate content presented some interaction between the polymer blend components. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 116–124, 2002

Key words: NMR; blends; molecular dynamics

INTRODUCTION

The evaluation of the miscibility of binary blends formed by ethylene-*co*-vinyl acetate and poly(vinyl acetate) (EVA/PVAc), prepared in different proportions by melting in a Haake Rheocord plastograph, was investigated by solid-state NMR.^{1–4} The main purpose of this work was to understand the blends' behavior with respect to the structure–mobility–compatibility by characterizing the domains and interaction at the molecular level. For that, we chose solid-state NMR spectroscopy, because it is constituted by several techniques that permit evaluation of the blends' behavior. Changes in the line shapes and/or frequency of the resonance signals in magic angle spinning with cross polarization (CPMAS) ¹³C-NMR spectra of the blends, in comparison to those of the blend components, have been used as evidence of the interaction between blend components.⁵ In addition, the proton ($T_1^H\rho$) and carbon-13 ($T_1^C\rho$) NMR spin-lattice relaxation times in the rotating frame allow estimation of the scale of miscibility of a polymer pair and, consequently, provide information on compatibility.^{6–8}

The cross-polarization experiment has been described as a double rotating frame experiment. Both the proton (abundant) and the carbon (rare) spins need to be spin-locked in an appropriate radio-frequency field, if they are ready to communicate. The time constant for the loss of spin-lock polarization

($T_1\rho$) can be measured in both spin systems.^{6,9} For each spin system, $T_1\rho$ behaves differently. For the proton, the relaxation parameter, $T_1^H\rho$, is sensitive to motion at frequencies around the spin-locking radio-frequency field. Furthermore, $T_1^H\rho$ is subject to spin diffusion. Since this relaxation time can be measured through the carbon spin system, it is possible to detect the heterogeneity of the sample; if different carbons detect different groups of protons, they are not in good communication with each other. Spin diffusion does not operate effectively for carbon nuclei. Carbon may relax directly in the lattice and be sensitive to molecular motion or relax in the proton spin system and sense the strength of the coupling to that system.¹⁰ Each carbon spin relaxes at a rate indicative of its own special environment. So, the carbon relaxation time in the rotating frame, $T_1^C\rho$, is sensitive to motional frequencies near the precession frequency about the radio-frequency field.

¹²⁹Xe-NMR measurements were also carried out to evaluate the domain formations,¹¹ because the local environment in polymer blends can be evaluated by ¹²⁹Xe-NMR; the xenon chemical shift is highly sensitive to the local environment, especially the free volume. Scanning electron microscopy (SEM) has already been used to obtain information on blends' domains and miscibility.^{12,13}

EXPERIMENTAL

Sample preparation

A commercial PVAc and two types of commercial EVA copolymers were used to prepare the blends.

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TABLE I
Materials Used in the Investigation

Sample	Characteristics
EVA1	19% VA content; MFI = 1.03 g/10 min; $d_{25c} = 0.921 \text{ g/cm}^3$
EVA2	31% VA content; MFI = 3.27 g/10 min; $d_{25c} = 0.930 \text{ g/cm}^3$
PVAc	MFI = 1.25 g/10 min; $d_{25c} = 1.169 \text{ g/cm}^3$

They were named EVA1 and EVA2 in relation to the VA content. The characteristics of the materials used are given in Table I. The VA content in EVA1 and EVA2 was determined by solution ^{13}C -NMR in a previous work.¹

The blends were prepared in the melt state at 150°C in a Haake Rheocord 9000 plastograph using a roller-mix rotor, at 60 rpm, for 15 min. The mixed materials were then pressed at 15,000 lb/ft, for 15 min, at 150°C. The blends were named EVA1/PVAc and EVA2/PVAc, and the PVAc content varied from 10 to 50% w/w.

NMR measurements

All solid-state NMR spectra were obtained on a VARIAN INOVA 300 spectrometer operating at 299.9 and 75.4 MHz for ^1H and ^{13}C , respectively. All experi-

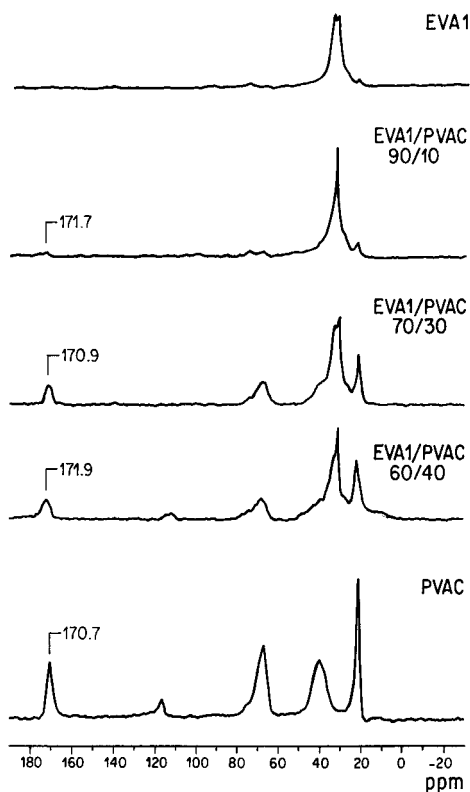


Figure 1 CPMAS ^{13}C -NMR spectra of EVA1, PVAc, and 90/10, 70/30, and 60/40 proportions.

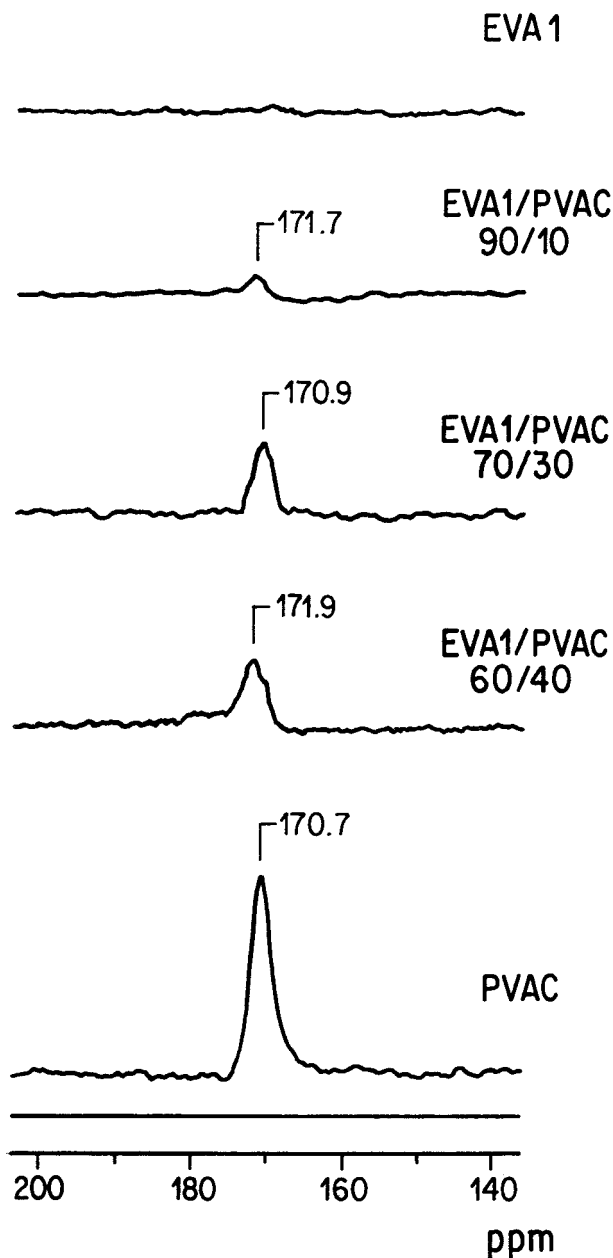


Figure 2 Carbonyl region of CPMAS ^{13}C -NMR spectra of EVA1, PVAc, and their blends (90/10, 70/30, and 60/40).

ments were performed at the probe ambient temperature using gated high-power decoupling. A zirconium oxide rotor of 7-mm diameter with a Kel-F end cap was used to acquire the NMR spectra at rates of 6 kHz. The ^{13}C spectra were referenced to the chemical shift of the methyl group carbons of hexamethylbenzene (17.3 ppm). The ^{13}C was carried out in the cross-polarization mode with magic-angle spinning (CPMAS) with 2 s of delay. A variable contact-time experiment was also recorded and the range of contact time was established as 50–4000 μs . The $T_{1\rho}^{\text{H}}$ values were determined from the intensity decay of the carbon-13 peaks with increasing contact time. The $T_{1\rho}^{\text{C}}$

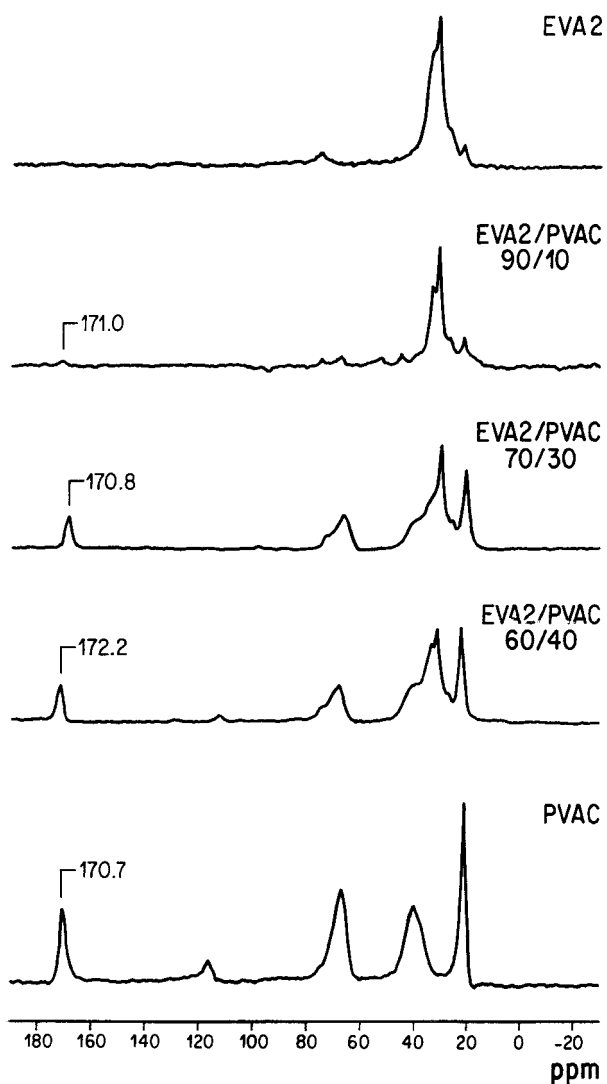


Figure 3 CPMAS ^{13}C -NMR spectra of EVA2, PVAc and 90/10, 70/30, and 60/40 proportions.

measurements were obtained using a spin-lock pulse sequence, at room temperature, using the same conditions for a better CPMAS spectrum (contact time 1 ms) and the range of τ (spin-lock) varied from 200 to 4000 μs . For the ^{129}Xe measurements, the samples were pressurized at 100 psi and conditioned for 24 h. The spectra were carried out in a Bruker AMX 500, at 138.26 MHz, with a 30° pulse.

Microscopy measurements

The fractured surface morphologies of compressed samples of EVA2/PVAc were observed by SEM on a JEOL JMS 5300 microscope at a 20-kV electron accelerating voltage.

RESULTS AND DISCUSSION

CPMAS ^{13}C analysis

Figure 1 shows the CPMAS ^{13}C -NMR spectra of EVA1, PVAc, and their blends (90/10, 70/30, and 60/40). These spectra can provide useful information. For EVA1, a broad signal split into two peaks was detected at 33.2 ppm (CH_2 for the rigid domain) and 31.2 ppm (CH_2 for the mobile domain). A small signal at about 23 ppm (CH_3 from VA) was also assigned. As the EVA has 19% of VA, the carbonyl group was not

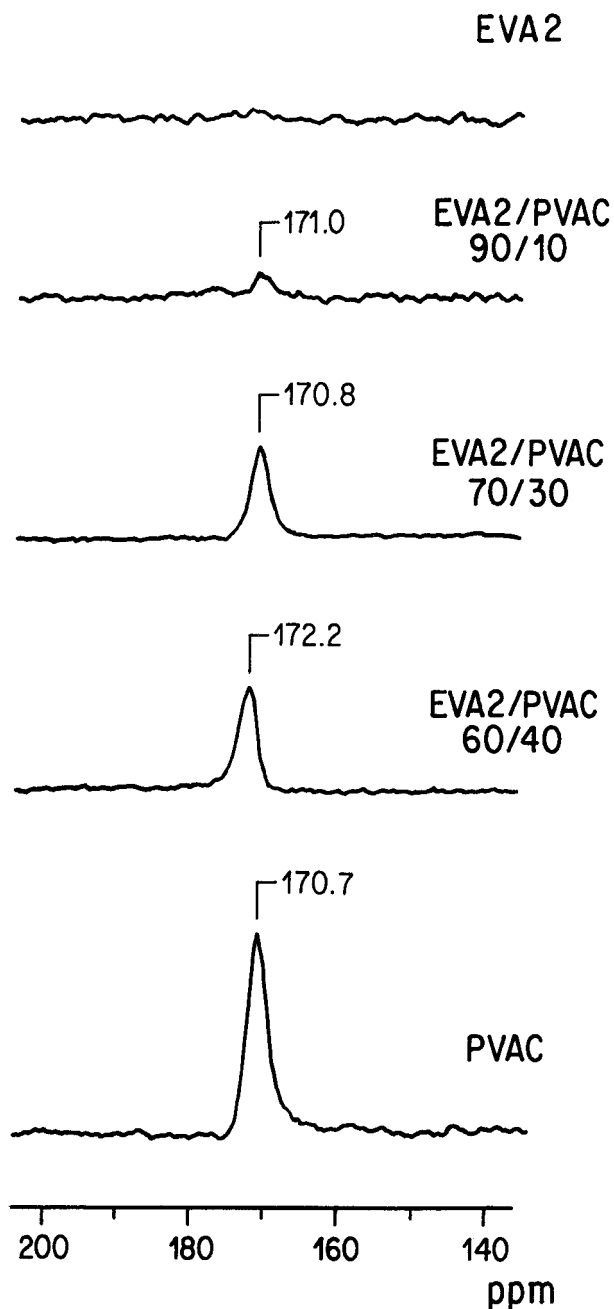


Figure 4 Carbonyl region of CPMAS ^{13}C -NMR spectra of EVA2, PVAc, and their blends (90/10, 70/30, and 60/40).

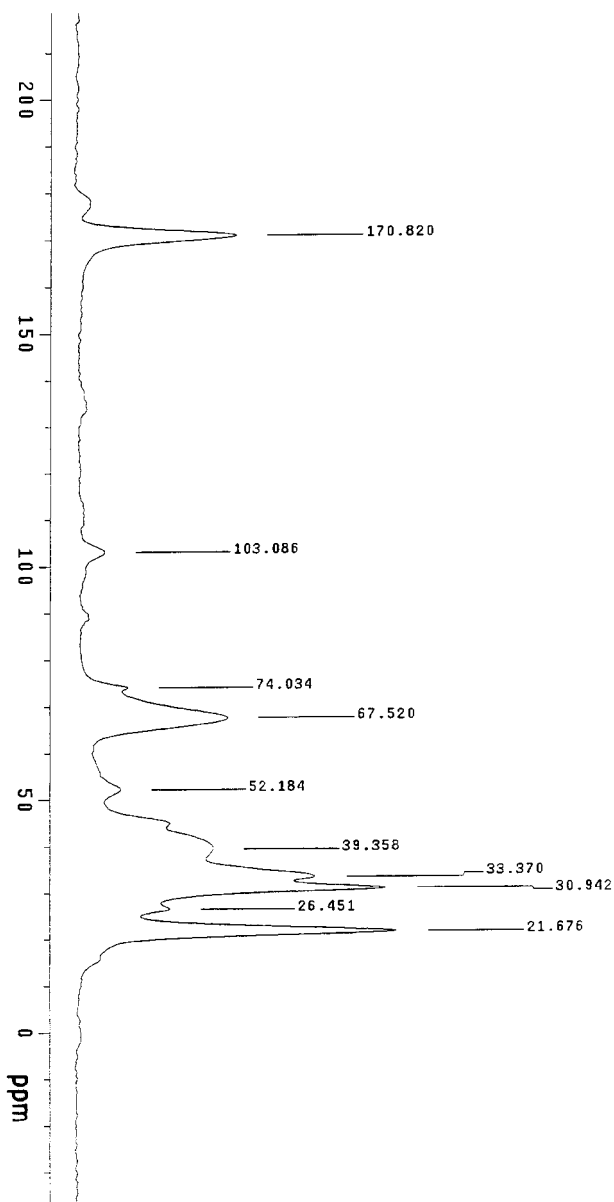


Figure 5 CPMAS ^{13}C -NMR spectra of EVA2/PVAc 50/50.

easily detected. In focusing on the carbonyl groups (Fig. 2) in the blends, this group presents an increase in the relative intensities as the PVAc content increases, and their line widths become broad as well. Knowing that, if an interaction of blend components

TABLE II
 ^{13}C Chemical Shifts of Carbonyl Carbon
Obtained by HETCOR

EVA2/PVAc	δ (ppm)
100/0	167.5
	164.2
60/40	168.4
	172.0
0/100	171.5

TABLE III
 $T_1^{\text{H}\rho}$ and Chemical Shift Values of the Carbonyl
of EVA1, PVAc, and Their Blends

EVA1/PVAc	δ (ppm)	$T_1^{\text{H}\rho}$ (ms)
90/10	170.9	9.8
80/20	172.0	15.2
70/30	170.9	5.0
60/40	171.9	5.0
50/50	170.8	4.3
0/100	170.8	3.6

occurs, it can cause changes in the line widths and/or the ^{13}C chemical shift frequencies in the NMR spectra of the blend components, in comparison to the spectra of pure components. For the case in point, there is some possibility of interaction between the carbonyl from the PVAc and the hydrogen of the methane (CH) that comes from the VA group of the EVA. So, in this figure, a small change in the carbonyl resonance frequency and line width occurred when the PVAc content increased, as a consequence of the interaction or/and phase separation. In looking at the PVAc spectrum, the signals located at 40 ppm (CH_2), referred to VA-VA linkage in the copolymer, 75 ppm ($\text{CH}\alpha$), to all types of linkage in the copolymer, and 120 ppm (spinning side band, ssb) are decreased considerably with increase in the EVA content, because these signals only come from the VA group in the copolymer, and as the copolymer proportion decreases in the blends, those intensity signals also decrease.

The CPMAS ^{13}C -NMR spectra of EVA2, PVAc, and their blends (90/10, 70/30, and 60/40), recorded at the same contact time (1 ms), are shown in Figure 3. EVA2 has 31% of VA. The assignment of EVA2 showed that the CH_2 signal from the ethylene monomer comes from the mobile domain, which is located at 31.2 ppm with a shoulder at 33.2 ppm from the rigid domain. Small changes in the carbonyl chemical shifts (Fig. 4) were also detected for these blends. In focusing on the 60/40 composition, the carbonyl group was detected at 172.2 ppm; this small shift (~ 1 ppm) in the carbonyl absorption frequency of the PVAc sample can be derived from the changes in the molecular dynamics of EVA/PVAc, which probably is a consequence of phase separation.

TABLE IV
 $T_1^{\text{H}\rho}$ Values for Carbonyl Carbons (170.7 ppm)
of EVA2/PVAc Blends

EVA2/PVAc	$T_1^{\text{H}\rho}$ (ms)
90/10	66.4
80/20	39.7
70/30	9.1
60/40	42.7
50/50	47.8
0/100	3.6

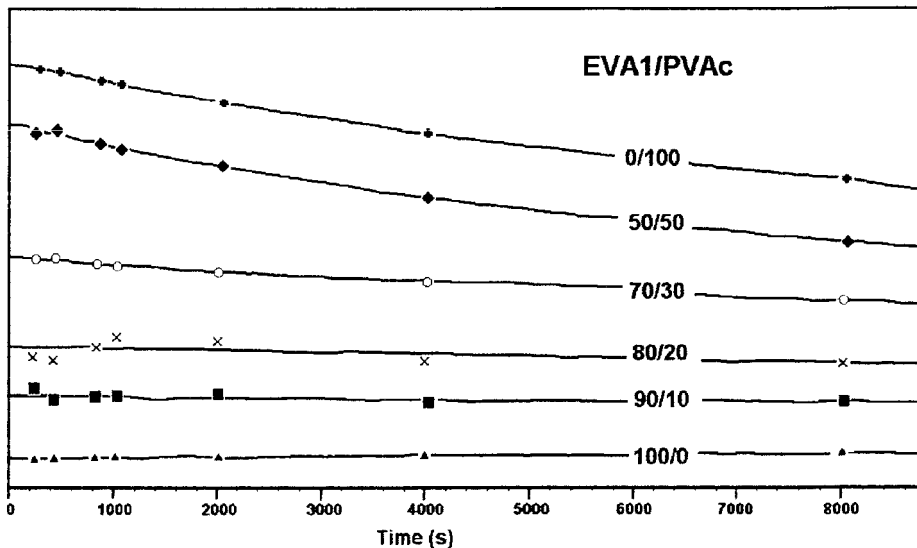


Figure 6 Carbonyl $T_{1\rho}^C$ decays of EVA1/PVAc blend systems.

When the amount of PVAc in blends was 50%, the optimum contact time changed, which could be an indication that a higher amount of PVAc promotes a kind of plasticization in EVA2. The ^{13}C spectrum for the 50/50 composition showed two carbonyl groups, one located at 170.7 ppm from a mobile domain and the other at 177.7 ppm from a rigid domain (Fig. 5), as a consequence of phase separation. In our opinion, the second carbonyl (which is not a feature) can be attributed to the interface that presents some interaction between both components.

The formation of an interfacial interaction can result in a change of chemical shifts of the groups involved. In

particular, in exploiting the chemical shift of the carbonyl carbon in the two-dimensional (2D) HETCOR,³ some evidence was found in relation to the formation of an interfacial interaction between EVA2 and PVAc, due to the detection of a third carbonyl group at 164.2 ppm (Table II), which also showed that PVAc plasticized EVA2 and confirmed that both components presented an interaction at the molecular level.

$T_{1\rho}^H$ analysis

According to the distribution form of the average signals of the ^{13}C spectra, obtained by the variable con-

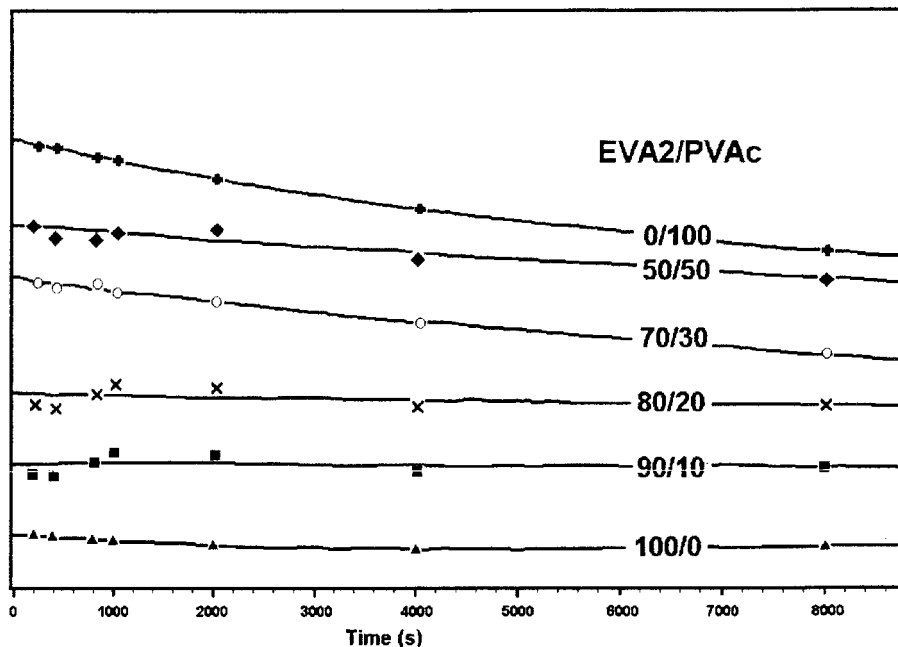


Figure 7 Carbonyl $T_{1\rho}^C$ decays of EVA2/PVAc blend systems.

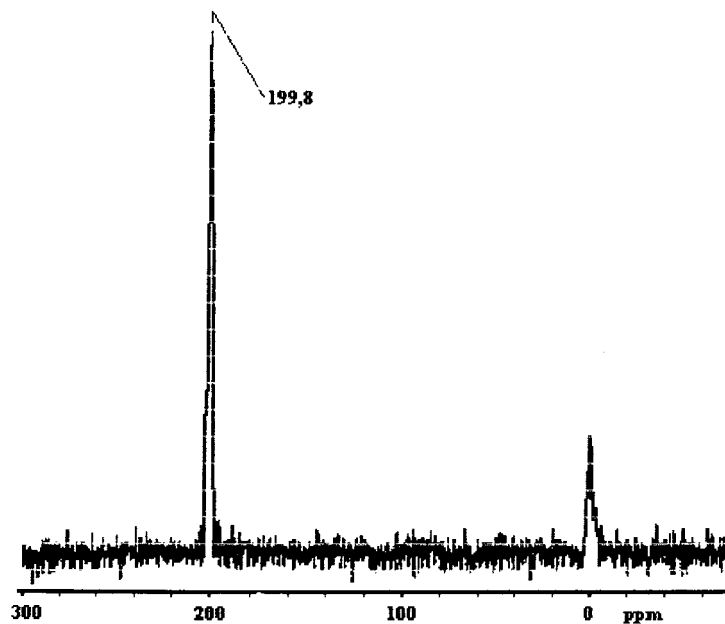


Figure 8 ^{129}Xe -NMR spectrum of EVA2 and PVAc.

tact-time experiment, one can observe the homogeneity and mobility of the sample. Rigid samples have signal intensities concentrated on short contact times. Flexible samples, on the other hand, need more time to polarize, and, thus, they have their signals located at long contact times. From the carbon-13 intensity decays, it is possible to measure the T_1^H .^{9,12-15}

In analyzing the EVA1/PVAc blends, no changes in the slope of the curves and in the $T_1^H\rho$ values for the rigid domains for the blends up to 50/50 were observed, because these domains did not take part in the interaction process. So, it is clear that there was no influence of PVAc in the rigid domains of EVA1. Therefore, for the blends, as the PVAc content in-

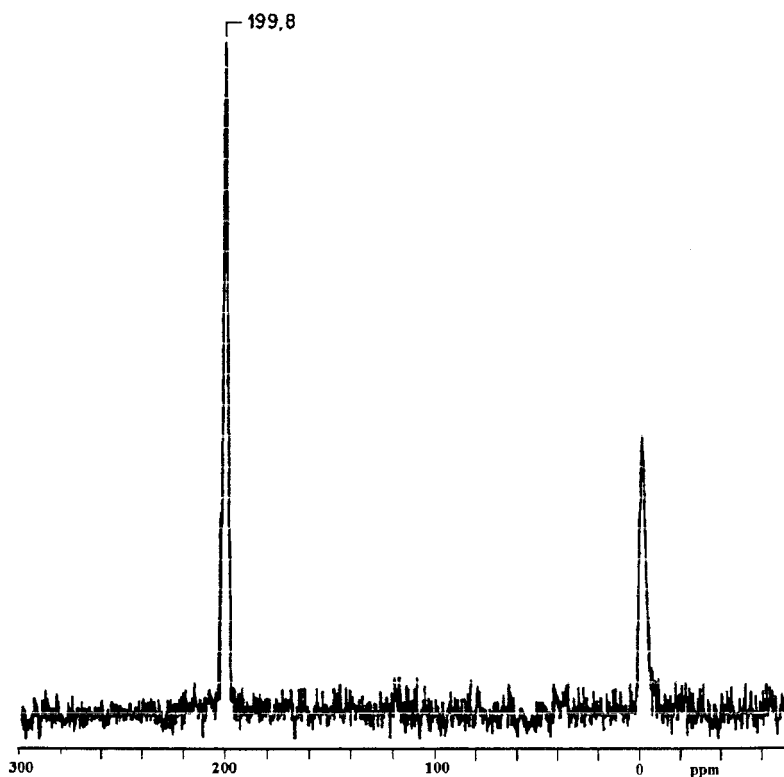


Figure 9 ^{129}Xe -NMR spectrum of EVA2/PVAc 60/40 blend.

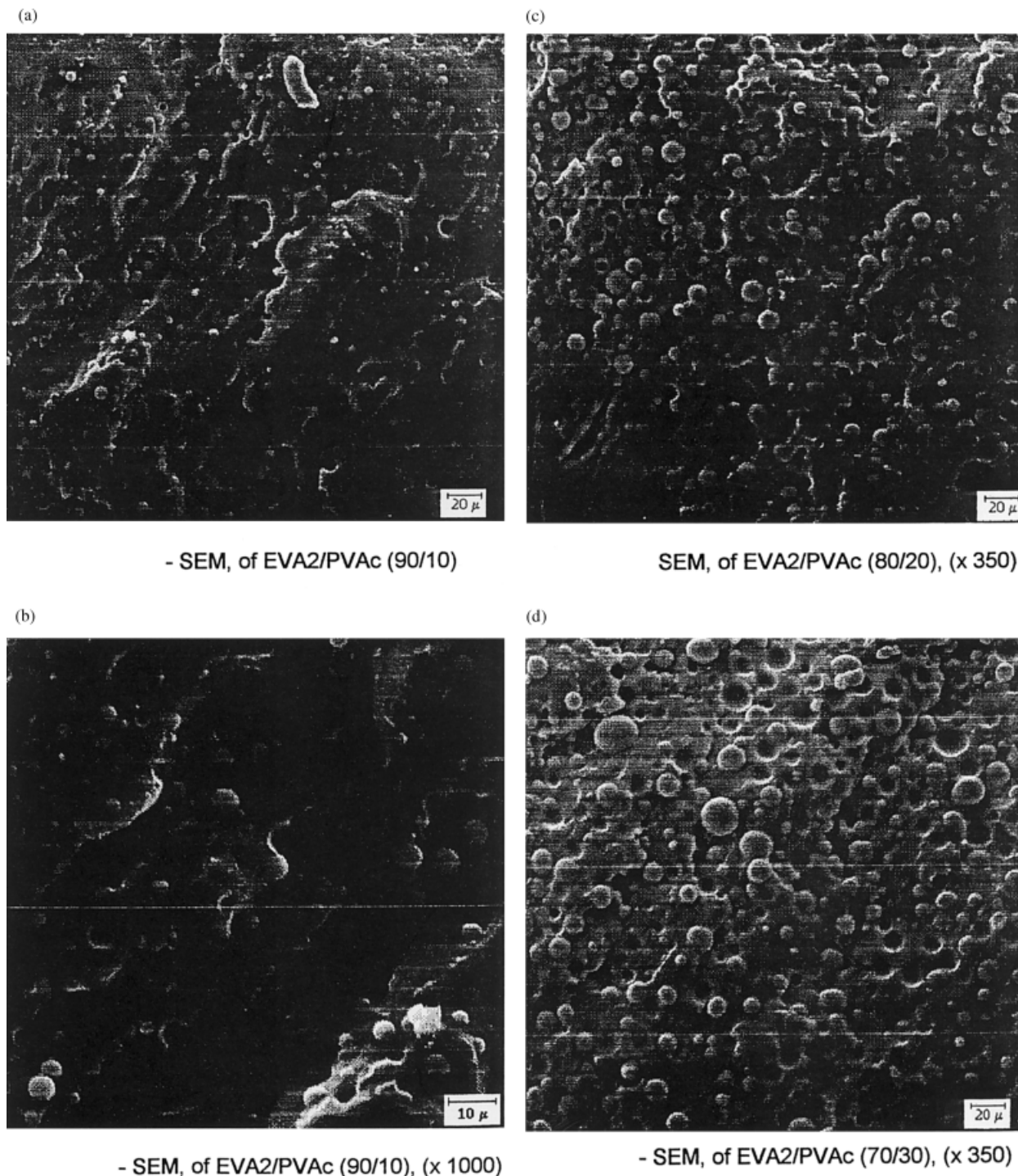
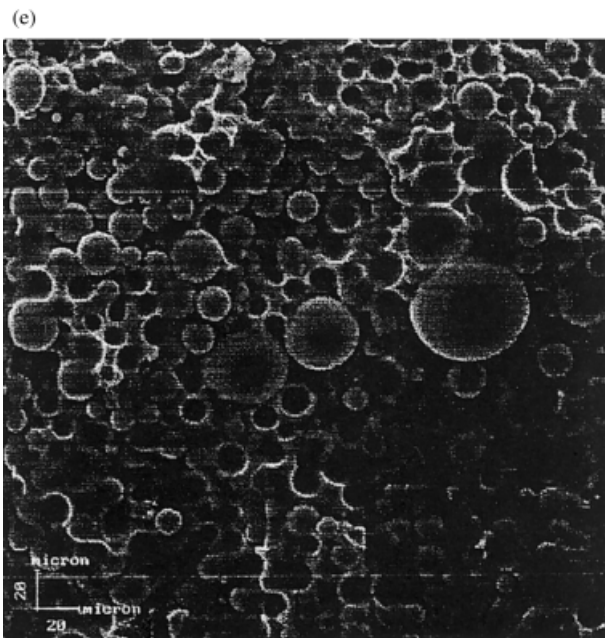


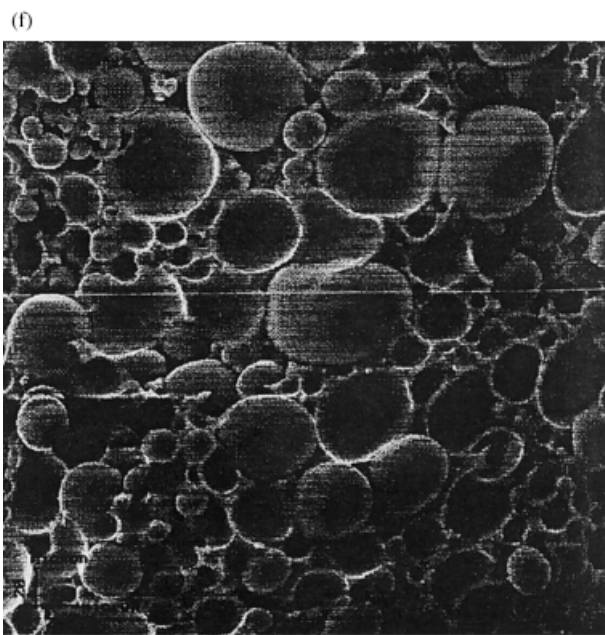
Figure 10 (a) SEM of EVA2/PVAc (90/10); (b) SEM of EVA2/PVAc (90/10), magnification 1000 \times ; (c) SEM of EVA2/PVAc (80/20), magnification 350 \times ; (d) SEM of EVA2/PVAc (70/30), magnification 350 \times ; (e) SEM of EVA2/PVAc (60/40), magnification 350 \times ; (f) SEM, of EVA2/PVAc (50/50), magnification 350 \times .

creased, an increase in the amorphous region mobility occurred, indicating that PVAc could be acting as a plasticizer. Therefore, the slope of the carbonyl curves changed greatly compared with PVAc. In analyzing the $T_1^H\rho$ values for the carbonyl group listed in Table III, a variation in the mobility of the EVA1/PVAc 90/10 blend could be considered. The increase in the

$T_1^H\rho$ values confirmed that PVAc was acting as a polymeric plasticizer to EVA and also that phase separation phenomena were occurring. However, for the EVA1/PVAc 80/20 blend, an increase in both the chemical shift and $T_1^H\rho$ showed that a phase separation occurred, but it could also indicate the formation of an interfacial interaction. A deep decrease in the $T_1^H\rho$ or



SEM, of EVA2/PVAc (60/40), (x 350)



SEM, of EVA2/PVAc (50/50), (x 350)

Figure 10 (Continued from the previous page)

the 70/30 proportion confirmed the phase separation. For EVA1/PVAc 60/40 and 50/50 blends, an incompatibility was clearly defined by the changes in the chemical shift and $T_1^H\rho$ values, which might be a consequence of the VA content in the EVA copolymer.¹³

Table IV shows the $T_1^H\rho$ values of the carbonyl of EVA2, PVAc, and the EVA2/PVAc blends. In analyzing the values of this parameter, we can see that the 90/10 blend showed a particular behavior: The highest value of $T_1^H\rho$ for this composition confirmed the

plasticization effect of PVAc and also showed some interfacial interaction, because the chemical shift is the same as for PVAc. For the EVA2/PVAc 80/20, there is a deep decrease in the relaxation-time parameter, which can be an indication of phase separation. In looking at the 70/30 proportion, the value of $T_1^H\rho$ is the lowest. In our opinion, it is the limit of phase separation, but some interfacial interaction does exist. The EVA2/PVAc 60/40 and 50/50 blends presented another range of increase in the $T_1^H\rho$ value, which is clear, because of phase separation and increase in the PVAc content.

$T_1^C\rho$ measurements

Figures 6 and 7 show carbonyl $T_1^C\rho$ decays for EVA1/PVAc and EVA2/PVAc, respectively. From these figures, it was observed that the $T_1^C\rho$ relaxation process did not change when the PVAc content varied up to 20%, which suggested that, in both systems, EVA dominated the relaxation process. Therefore, for higher PVAc contents, from 30 to 50%, the carbonyl $T_1^C\rho$ relaxation decays presented a similar behavior to the PVAc, which indicated that, in those proportions, PVAc controls the relaxation process. Hence, one could conclude that these systems presented phase separation.

$^{129}\text{Xe-NMR}$

Knowing that $^{129}\text{Xe-NMR}$ is an important tool to reveal the local environment in polymer blends, we chose to apply this technique to obtain further information on the blends in our study. The ^{129}Xe spectrum obtained for the two pure polymers simultaneously, not blended, is shown in Figure 8, with only one resonance line, at the same chemical shift (199.8 ppm), detected, showing that both polymers presented a large amorphous domain, constituted by the VA groups, which have the same molecular mobility. The ^{129}Xe spectrum for EVA2/PVAc 60/40 is presented in Figure 9 and, again, one signal at 199.8 ppm was detected, which could also be derived from the same large domain, indicating that this blend has some interaction at the molecular level, but, at the same time, showed a phase separation as well.

Morphology

To obtain more information on the correlation among structure–morphology–mobility of EVA2/PVAc blends, SEM qualitative studies were done. The molded samples were cryogenically fractured and the SEM micrographs of those blends are shown in Figure 10(a–f). In the 90/10 blend, a homogeneous dispersion of the PVAc phase in the EVA matrix as small spherical domains can be seen. As the PVAc content increased,

the size of the spherical morphology increased as well the PVAc and did not disperse well in the EVA matrix. Those blends present a typical morphology of partial miscibility.

CONCLUSIONS

The CPMAS technique was effective in the studies related to the influence of PVAc on EVA. According to the relaxation data, one can conclude that EVA1/PVAc did not present an interaction between the blend components; in our opinion, this was attributed to the lower VA content in the EVA1 copolymer. Therefore, for the EVA2/PVAc system, an interfacial interaction was detected. As for lower PVAc content (up to 10%) in the EVA2/PVAc, a partial miscibility was also detected. In comparing both systems, one can see that EVA2/PVAc showed a better miscibility and compatibility at the molecular level, as a consequence of the high VA content in the EVA2 copolymer.

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