

Solid-State NMR and Morphological Studies of Poly(ethylene-co-vinyl acetate)/Poly(vinyl acetate) Blends

CLÁUDIA M. G. DE SOUZA, MARIA INÊS B. TAVARES

IMA/UFRJ, Centro de Tecnologia, Bloco J, Cidade Universitária, Ilha do Fundão,
C.P. 68525, 21945-970 Rio de Janeiro, RJ, Brazil

Received 15 November 1998; accepted 5 June 1999

ABSTRACT: To obtain a correlation among structure–morphology–mobility–compatibility properties of poly(ethylene-co-vinyl acetate) (EVA)/poly(vinyl acetate) (PVAc) blends, we have used scanning electron microscopy and solid-state nuclear magnetic resonance in our investigations. The results are discussed in terms of blends, component dispersion, plasticization effect, and domain mobilities to acquire a response of the correlation between structural properties. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2990–2996, 1999

Key words: NMR; solid state; EVA/PVAc blends

INTRODUCTION

Polymeric blends with a particular application have been the subject of many research works.^{1–3} As it is known, a new polymer blend must present an improvement of mechanical properties of this new product. The case in point is to increase the VA content in EVA copolymer with low vinyl acetate content (19%) to obtain an EVA/PVAc blend without making a copolymerization. To understand the behavior of these polymer blends, it is necessary to characterize the interaction of the components. There are several techniques that can be used to investigate polymer blends' interactions at different scales, two of which are scanning electron microscopy (SEM)^{4,5} and solid-state nuclear magnetic resonance (NMR) spectroscopy.^{6–11} Combined NMR techniques, such as magic angle spinning (MAS) with cross-polarization (CP), are useful routines to obtain high-resolution solid-state NMR. It is known that, as the

contact time increases, it is easier to detect carbons that belong to mobile regions, as they take longer to be cross-polarized. Mobile carbons are detected in lower chemical shifts, because the chemical environment is different from the rigid phase. The proton spin-lattice relaxation time in the rotating frame ($T_1^{\text{H}\rho}$) is a parameter that can provide direct and detailed information on molecular and segmental motion,^{8–18} as this parameter is a natural function of the carbon nuclei environment and sensitive to the spatial proximity of chains. The $T_1^{\text{H}\rho}$ allows the evaluation of changes of the homogeneity in polymer blends.

Generally, for a compatible blend just one value of this parameter is found. More than one value is a signal that at least two domains with distinct mobilities can be found. However, when proton $T_1\rho$ is measured by the variable contact-time experiment (VCT), this parameter is obtained from the intensity decay for all resolved carbons and a value of proton $T_1\rho$ for all types of hydrogen allows evaluation of the sample's behavior. Generally, all the values of proton $T_1\rho$ do not even change with variations in the samples, such as an addition of other polymer or a plasticizer. There are some types of carbon nuclei that

Correspondence to: M. I. B. Tavares (E-mail: mibt@ima.ufrj.br)

Contract grant sponsor: CAPES.

Journal of Applied Polymer Science, Vol. 74, 2990–2996 (1999)

© 1999 John Wiley & Sons, Inc.

CCC 0021-8995/99/122990-07

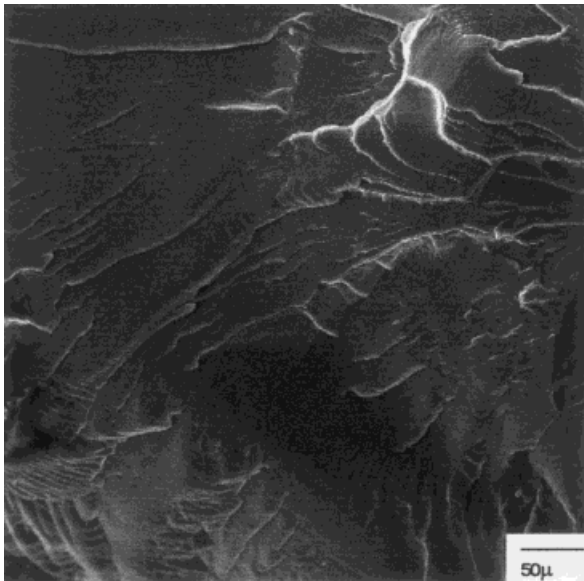


Figure 1 EVA SEM micrograph ($\times 200$).

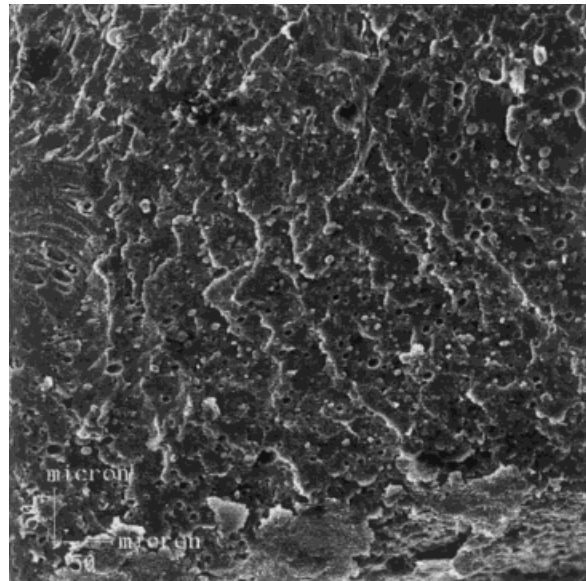


Figure 3 CS90 SEM micrograph ($\times 200$).

do not take part in the interaction process between different polymer blend components. For example, the rigid phase or crystalline phase relaxation time and chemical shifts do not change with the addition of other polymer, because the CP rates of these carbons do not change with the environment. However, a significant change in this parameter and the chemical shift values can be detected where the interaction process occurs. The values of proton $T_{1\rho}$ measured from the VCT

are intimately linked with the process of polarization transfer and to the chemical shift values for the type of carbon to which they are linked. As the proton $T_{1\rho}$ are also sensitive to the proximity of protonated chains to one another, the distance between two protonated chains is directly related to the proton-proton spin diffusion. If the polymer blends' chain components are very close, the spin-spin communication is good; but, if the spa-

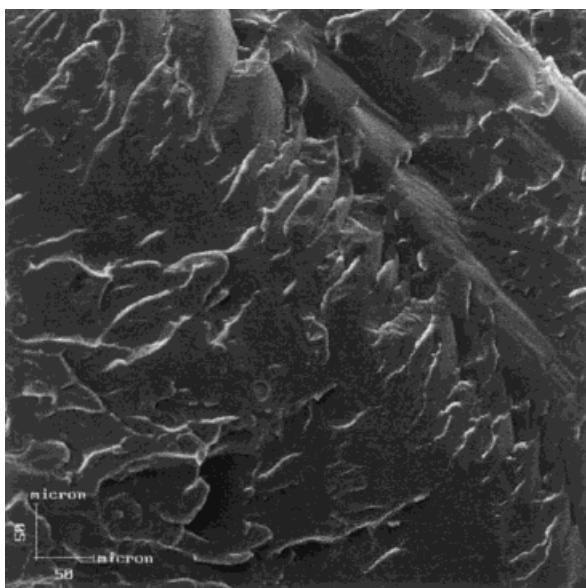


Figure 2 PVAc SEM micrograph ($\times 200$).

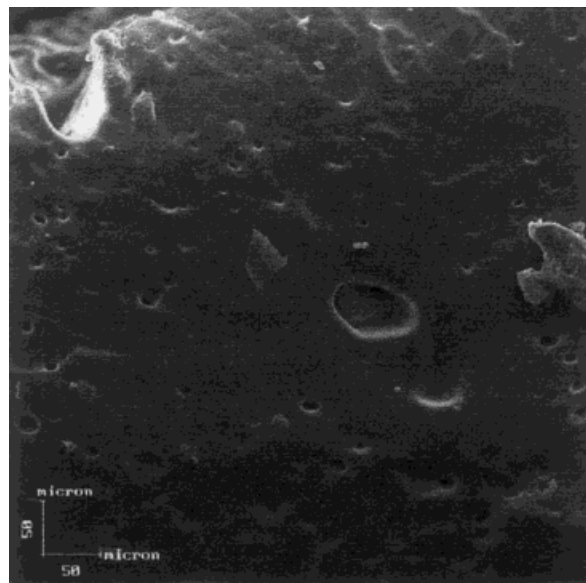


Figure 4 CS90 SEM micrograph after extraction with chloroform ($\times 200$).

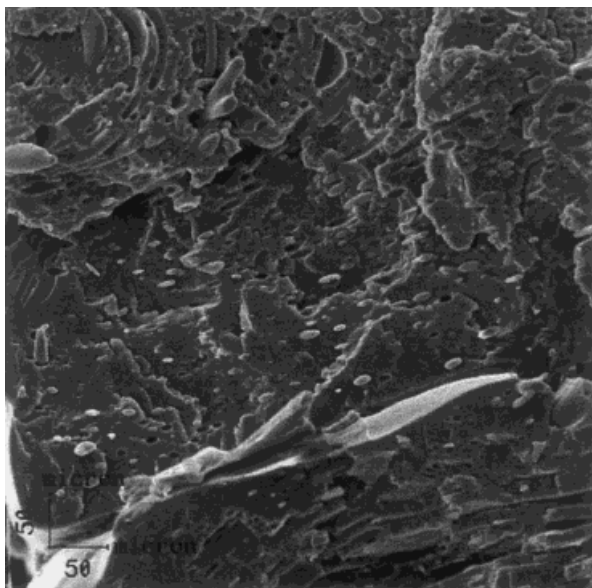


Figure 5 CS80 SEM micrograph ($\times 200$).

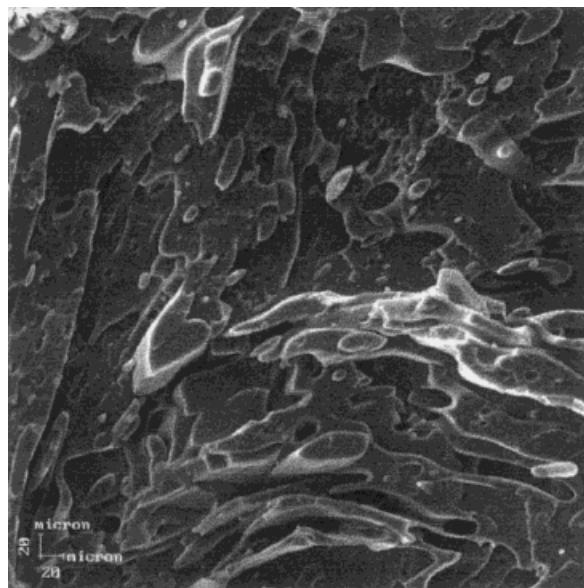


Figure 7 CS60 SEM micrograph ($\times 200$).

tial proximity of chains is not close enough, the spin-spin communication cannot be detected.⁸⁻¹⁸

In summary, the main purpose of this work was to obtain EVA with high VA contents by blending this copolymer with poly(vinyl acetate), focusing its application in the shoe industry; and also to characterize EVA/PVAc blends with respect to structure-morphology-mobility-compatibility, using solid-state NMR and SEM.

EXPERIMENTAL

Sample Preparation. The materials used in this work were EVA (POLITENO, BA, Brazil) and commercial PVAc. Blends were prepared in the melt state at 150°C with a Rheomix HAAKE (Rheocord 9000) for 15 min. The blends were compression-molded under 15,000 lbf at 150°C. For a better understanding, the blends were named as CS-*n*, where *n* is related to EVA content in the

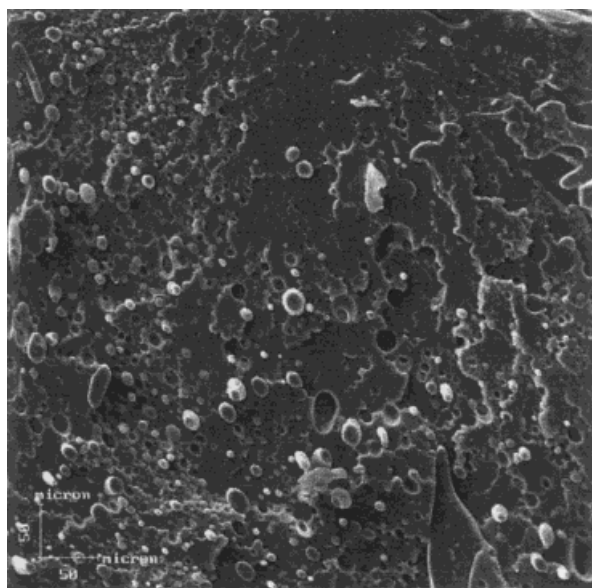


Figure 6 CS70 SEM micrograph ($\times 200$).

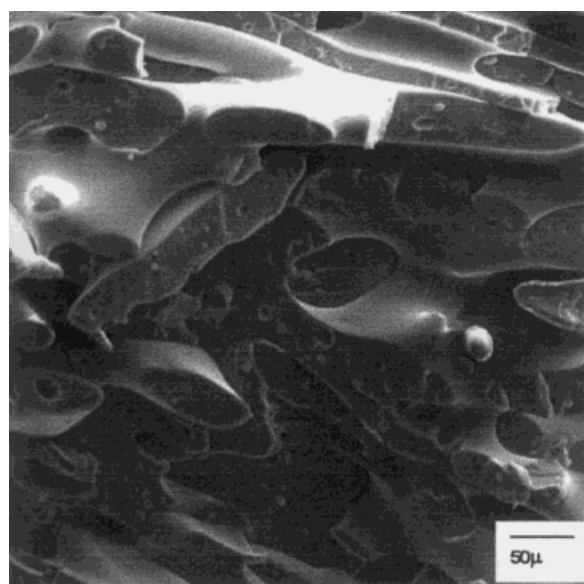


Figure 8 CS50 SEM micrograph ($\times 200$).

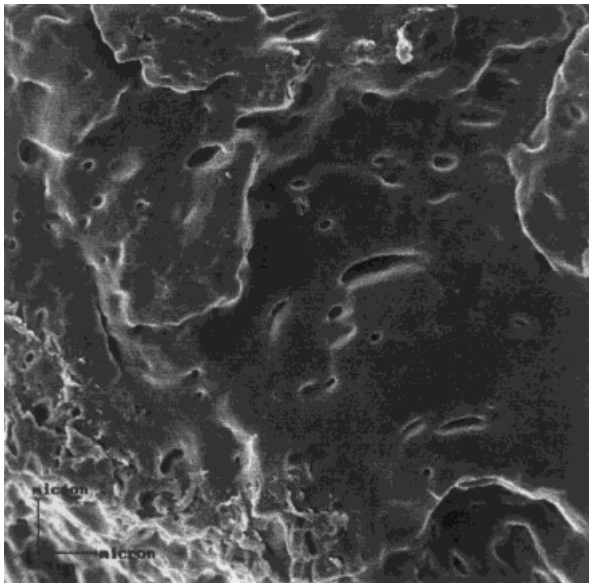


Figure 9 CS80 SEM micrograph after extraction with chloroform ($\times 200$).

blend: 90, 80, 70, 60, and 50. The VA content in EVA copolymer was determined by solution ^{13}C -NMR.¹⁹ The value found was 19% (w/w) of VA.

Microscopy Measurements. The fracture surfaces morphology of compressed samples was observed by SEM (JEOL JMS 5300) at 20 kV electron accelerating voltage. The samples were also etched

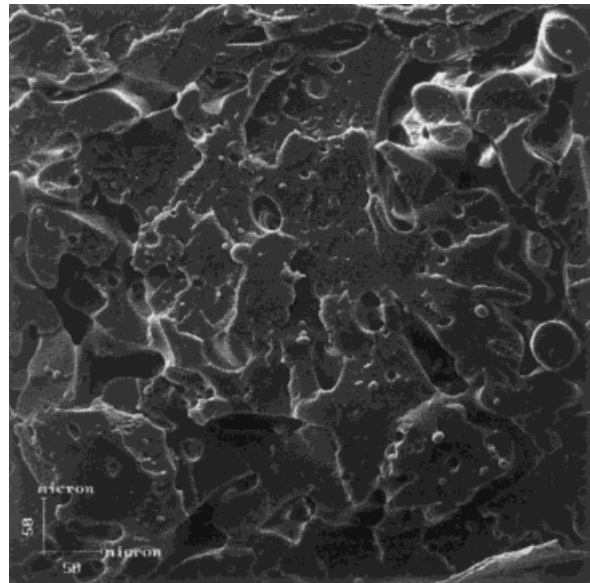


Figure 11 CS60 SEM micrograph after extraction with chloroform ($\times 200$).

with chloroform for 12 h to extract the PVAc and dried.

NMR Measurements. All NMR solid-state spectra were obtained on a VARIAN VXR 300 spectrometer operating at 299.9 and 75.4 MHz for ^1H and ^{13}C , respectively. All experiments were performed at probe ambient temperature and performed us-

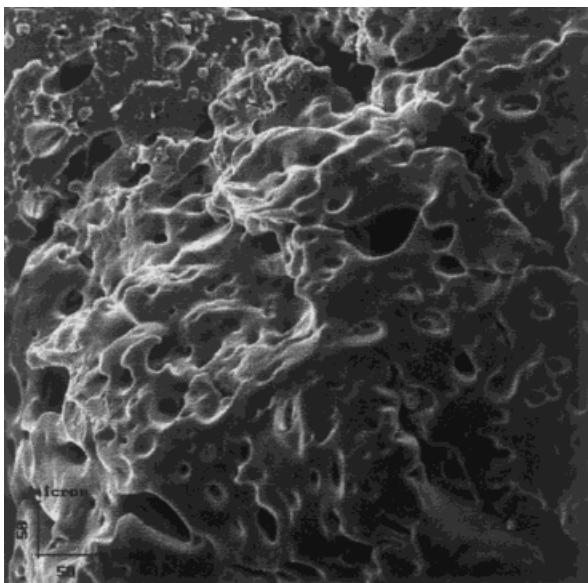


Figure 10 CS70 SEM micrograph after extraction with chloroform ($\times 200$).

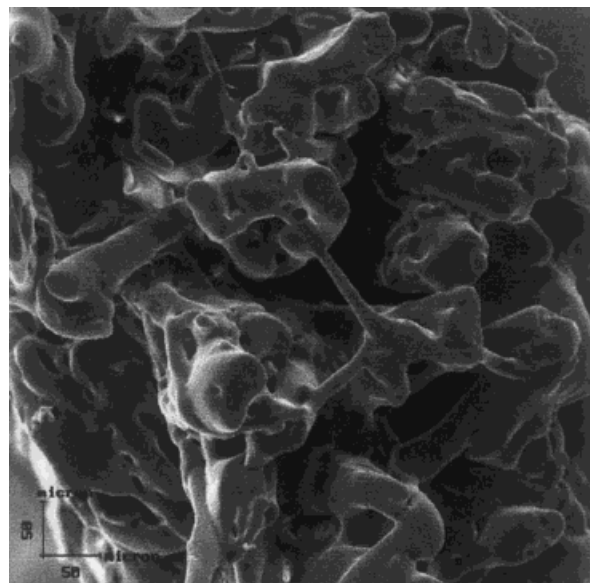


Figure 12 CS50 SEM micrograph after extraction with chloroform ($\times 200$).

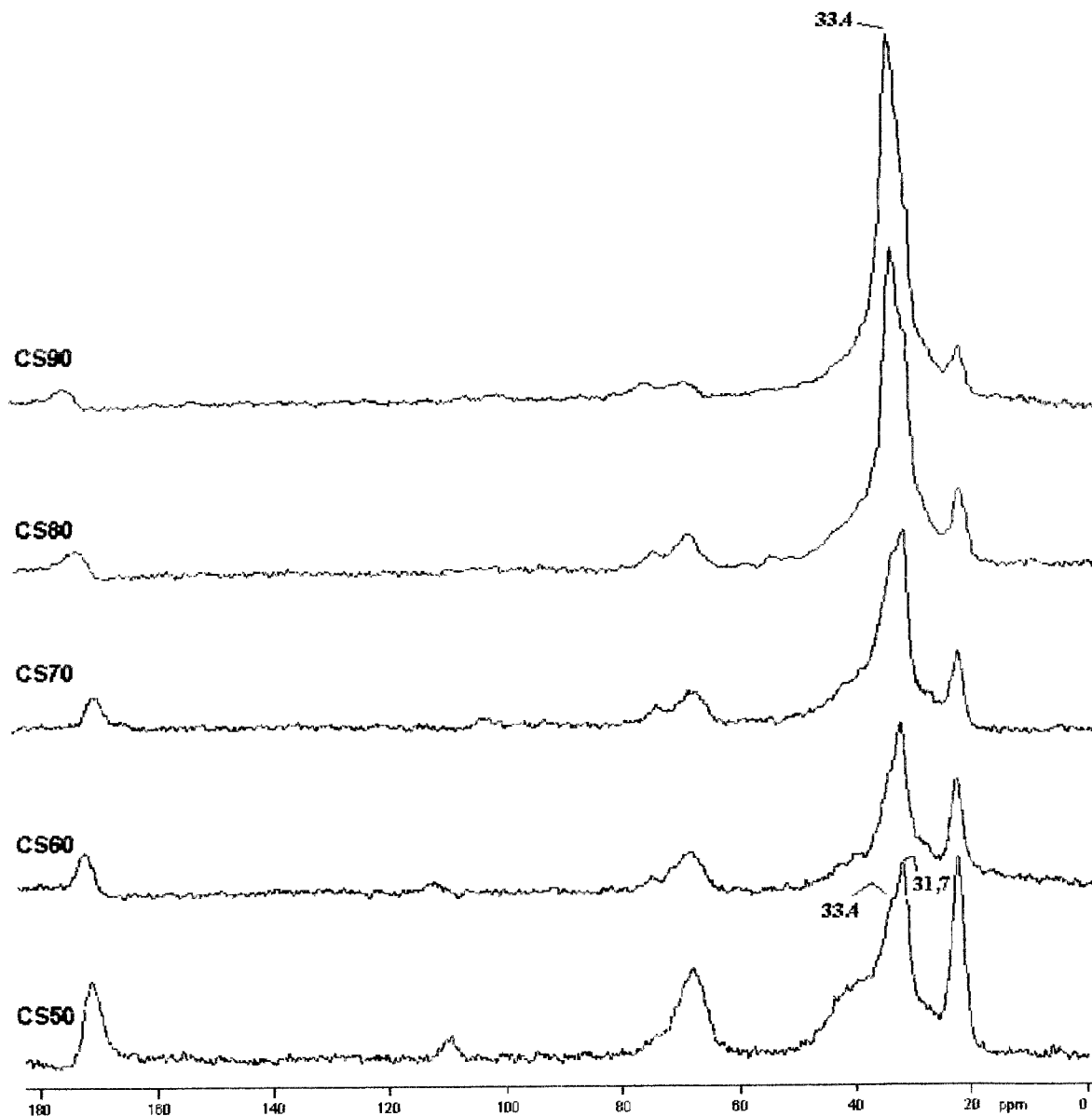


Figure 13 CP/MAS ^{13}C -NMR spectra of blends at the same contact time (1 ms).

ing gated high-power decoupling. A zirconium oxide rotor of 7 mm diameter with Kel-F caps was used to acquire the NMR spectra at rates of 6 kHz. ^{13}C -NMR spectra are referenced to the chemical shift of the methyl group carbons of hexamethyl benzene (17.3 ppm). The ^{13}C spectra were carried out in the cross-polarization mode with magic-angle spinning (CP/MAS) with 2 s of delay and variable contact time; the experiment was also recorded and the range of contact time was established as 50 to 4000 μs . Proton $T_1^{\text{H}\rho}$ values were determined from the intensity decay of ^{13}C peaks with increasing contact time.

RESULTS AND DISCUSSION

Morphology

To study the blends' morphology, the molded samples were cryogenically fractured and etched with chloroform for 4 h to extract the poly(vinyl acetate) phase, and dried for 6 h. The SEM micrographs of the EVA and PVAc are shown in Figures 1 and 2, respectively. The SEM micrograph of CS90 blend shows a typical morphology of an incompatible blend (see Fig. 3). From this figure, a very fine and homogeneous dispersion of the

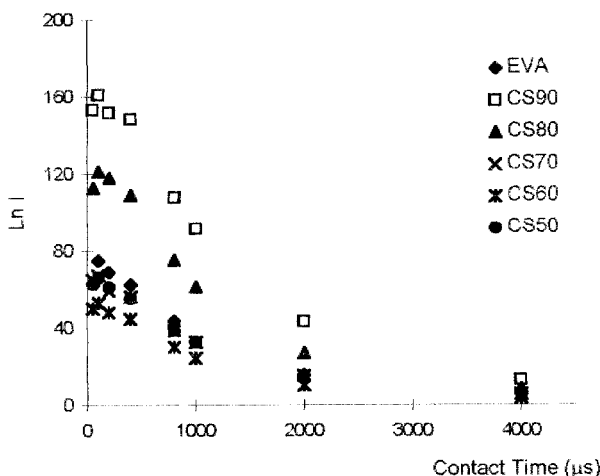


Figure 14 Intensity decay versus contact time for the methylene groups.

PVAc phase in the EVA matrix can be seen as small spherical domains. Figure 4 exhibits the micrograph of CS90 after PVAc has been extracted by chloroform. The EVA matrix presents small cavities, which confirms that PVAc was homogeneously dispersed in the EVA matrix, although this does not mean compatibility. Therefore, this observation suggests a poor adhesion between the PVAc phase and EVA matrix. As the PVAc content of CS80 and CS70 blends increases, the domain size becomes bigger and not dispersed in the matrix, as can be seen in Figures 5 and 6, respectively, due to the phase separation. For CS60 and CS50 blends, the PVAc domain appears as fibers completely separated from EVA matrix (Figs. 7 and 8, respectively). For blends containing from 20 to 50% PVAc, the etched SEM micrographs show big holes in the EVA matrix (Fig. 9–12), which confirms the component incompatibility of blends.

NMR Analysis

Analyzing the CP/MAS ^{13}C spectra for all blends at the same contact time (1 ms), when the PVAc content increases, the NMR signals of the methylene units, provided from the EVA rigid region located on 33.4 ppm, became large; and the signal at 31.7 ppm for the methylene units from the EVA mobile region appeared. The change in the chemical shifts can be an indication that PVAc caused an increase in the EVA mobility, in spite of the phase separation (Fig. 13). Therefore, some interfacial interaction can be promoting the plasticization effect.

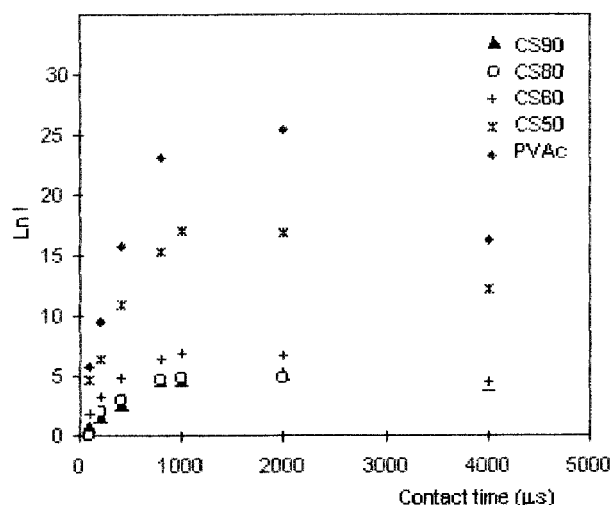


Figure 15 Intensity decay versus contact time for the carbonyl groups.

From the distribution form of the ^{13}C spectra, obtained by variable contact time (VCT) experiment, one could observe the homogeneity and mobility of the sample. Two regions were studied by VCT experiments: the CH_2 units from the rigid phase of EVA (located on short contact times) and the carbonyl group, which we believe is taking part of the interaction process. Figures 14 and 15 show the ^{13}C intensity decay versus contact-time plots for those two regions: CH_2 ($\delta = 33.4$ ppm) and the carbonyl ($\delta = 170.8$ ppm) groups. There were no changes in the slope of curves at short and long contact times for CH_2 groups; as a consequence, no change was observed in the $T_1^{\text{H}\rho}$

Table I Correlation Between the Chemical Shifts and $T_1^{\text{H}\rho}$ of EVA/PVAc Blends and Pure Polymers Focusing on the Methylene Rigid Phase

Sample	δ (ppm)	$T_1^{\text{H}\rho}$ (ms)
EVA	33.4	1.1
CS90	33.0	1.5
CS80	33.0	1.2
CS70	33.4	1.2
CS60	33.4	1.1
CS50	33.4	1.1

For CS70, CS60 and CS50 blends, the phase separation was clearly defined by the changes in the $T_1^{\text{H}\rho}$ values. Focusing CS60 blend an increase in the chemical shift allied to a decrease in the $T_1^{\text{H}\rho}$ shows that from this proportion a phase separation process was marked. Those data corroborated the observation extracted from SEM micrographs analysis.

Table II Correlation Between the Chemical Shifts and $T_1^H\rho$ of EVA/PVAc Blends and Pure Polymers Focusing on the Carbonyl Group

Sample	δ (ppm)	$T_1^H\rho$ (ms)
CS90	170.9	9.8
CS80	172.0	15.2
CS70	170.9	5.0
CS60	171.9	5.0
CS50	170.8	4.3
PVAc	170.8	3.6

values (Table I) for all blends compositions. As this signal comes from the ethylene rigid domain, this was a response that this domain did not take part in the interaction process; and it confirmed that there was not an effective influence of PVAc in the rigid domains of EVA, because the EVA is dominating the relaxation process. The same behavior was observed for the EVA/PVAc blends with higher VA content (31%) in the copolymer, studied in another work.²⁰ Therefore, the slope of curves changed dramatically for carbonyl groups when compared with PVAc. Observing the $T_1^H\rho$ values for the carbonyl group (Table II), one can see that the value of $T_1^H\rho$ for CS90 is higher than PVAc and a change in the mobility for this blend could be considered as a plasticization effect. The increase in the $T_1^H\rho$ values was an indication that PVAc was acting as a polymeric plasticizer to EVA, in spite of the phase separation process. Therefore, for CS80 blend, an increase in both chemical shift and $T_1^H\rho$ shows that two situations could be occurring at the same time: one was related to the plasticization effect of PVAc on EVA matrix, as the $T_1^H\rho$ increases, and the second one was attributed to the detection of the carbonyl group from the blend interface. If both phenomena could be taking place, they are related to a phase-separation process.

For CS70, CS60, and CS50 blends, the phase separation was clearly defined by the changes in the $T_1^H\rho$ values. Focusing on the CS60 blend, an increase in the chemical shift allied to a decrease in the $T_1^H\rho$ shows that from this proportion a phase-separation process was marked. Those data corroborated the observation extracted from SEM micrograph analysis.

CONCLUSIONS

Comparing the NMR and SEM data we could see that a small PVAc amount (up to 10%) in the

blends was well dispersed. As the PVAc content increased, it caused a phase separation, but an interfacial interaction was still observed, which could be attributed to a partial blend compatibility. Another interesting observation was related to the PVAc plasticization effect to all compositions. Both NMR and SEM responses showed that these two techniques were a complementary source to obtain a correlation among structure–morphology–mobility–compatibility properties.

The authors thank PETROBRAS/CENPES/DIQUIM for the use of the NMR spectrometer and POLITENO INDUSTRIA E COMÉRCIO S.A. for the EVA samples. Thanks to CAPES for the financial support.

REFERENCES

- MacKnight, W. J.; Karasz, F. E. *Polymeric Blends*, Vol. 1; Academic Press: London, 1978.
- Ohnaga, T.; Sato, T. *Polymer* 1996, 37, 3729.
- Schenk, W.; Reichert, D.; Schneider, H. *Polymer* 1990, 31, 329.
- Ray, I.; Khastgir, D. *Polymer* 1993, 34, 2030.
- Amorim, M. C. V.; Oliveira, C. M. F.; Tavares, M. I. B. *J Appl Polym Sci* 1996, 61, 2245.
- Bovey, F. A.; Mirau, P. A. *NMR of Polymers*; Academic Press: New York, 1996.
- Stejskal, E. O.; Memory, J. D. *High Resolution NMR in the Solid State*; Oxford University Press: New York, 1994.
- Simmons, A.; Natanshon, A. *Macromolecules* 1991, 24, 3651.
- Tavares, M. I. B.; Castro, W. P.; Costa, D. A. *J Appl Polym Sci* 1995, 55, 1165.
- Silva, N. M.; Tavares, M. I. B. *J Appl Polym Sci* 1996, 60, 663.
- Tavares, M. I. B.; Monteiro, E. E. C. *Polym Testing* 1995, 15, 273.
- Feng, H.; Feng, Z.; Shen, L. *Polymer* 1993, 34, 2516.
- Cheng, H. N.; Lee, G. H. *Macromolecules* 1988, 21, 3164.
- Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* 1977, 10, 384.
- Sefcik, M. D.; Schaefer, J.; Stejskal, E. O.; McKay, R. A. *Macromolecules* 1980, 13, 1132.
- English, A. D. *Macromolecules* 1985, 17, 2182.
- Gabriëlse, W.; Gaur, H. A.; Feyen, F. C.; Veeman, W. S. *Macromolecules* 1994, 27, 5811.
- Takegoshi, K.; Tsuchiya, K.; Hikichi, K. *Polym J* 1995, 27, 284.
- de Souza, C. M. G.; Tavares, M. I. B. *Polym Testing* 1998, 17, 533.
- de Souza, C. M. G.; Tavares, M. I. B. *J Appl Polym Sci* to appear.