

Characterization of EPDM/Atactic Polypropylene Blends by High-Resolution Solid-State NMR

NAIRA M. DA SILVA and MARIA INÊS B. TAVARES*

Instituto de Macromoléculas Professora Eloisa Mano/Universidade Federal do Rio de Janeiro CP: 68525, Cep: 21945-970, Rio de Janeiro, R.J., Brazil

SYNOPSIS

The study of EPDM/atactic polypropylene blend compatibility was investigated by cross-polarization/magic angle spinning carbon-13 NMR spectra, variation contact time experiment analysis, proton spin-lattice relaxation time in the rotating frame, carbon-13 spin-lattice relaxation time, and a dipolar dephasing experiment. The data are discussed in terms of mobility and compatibility of polymeric blends. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The compatibility study of polymeric blends is one area of polymer science in which high-resolution solid-state NMR has been successfully applied.¹⁻⁵ The first work with blends by solid-state carbon-13 NMR was by Schaefer et al.⁶ using poly(phenylene oxide)/polystyrene blends. They showed that the spin-lattice relaxation time in the rotating frame for protons attached to different carbons can be measured using high-resolution carbon-13 NMR.⁷ These proton spin-lattice relaxation parameters are very sensitive to the short-range spatial proximity of interacting dipole moments of the protons and they can be used to determine the homogeneity of the blend.⁸ The characterization of molecular motion and sample homogeneity may be determined from relaxation data, particularly by proton spin-lattice relaxation time in the rotating frame ($T_1^H\rho$) and spin-lattice relaxation time in the laboratory (T_1^H).^{5,8-10} The spin-lattice relaxation time of carbon-13 also provides information on molecular motion (T_1^{13C}).^{5,9} However, the distribution form of the variable contact time experiment and the behavior of cross-polarization under magic angle spinning with dipolar dephasing (CP/MAS/DD) and proton $T_1\rho$ as well as T_1^{13C} can be a source of information on the samples' homogeneity.

Atactic polypropylene (PPA) is a thermoplastic material that presents good thermal properties.¹¹ Elastomeric EPDMs have a good performance in relation to their mechanical properties which give them special application.¹³⁻¹⁵ PPA can be added to EPDM as an additive to improve mainly their thermal resistance, rupture point, and plasticity range.^{16,17} The PPA behaves differently from isotactic polypropylene. The EPDM/PPA blends have a complex behavior when compared to a system formed by EPDM/PP. This fact makes the EPDM/PPA blends interesting to investigated, especially by NMR at the solid state.

In this study, cross-polarization/magic angle spinning, cross-polarization with variable contact times (to examine local heterogeneities in EPDM/PPA blends under a variety of composition), $T_1^H\rho$, dipolar dephasing carbon-13 spectra, and carbon-13 spin-lattice relaxation time of PPA, EPDMs, and their blends were used to investigate the compatibility range and mobility of these systems.

EXPERIMENTAL

Samples

These samples were prepared using two elastomeric materials (EPDM A and EPDM B) and PPA. The distribution of the molecular weight of the samples was characterized as 2.82 for EPDM A, 11.80 for EPDM B, and 3.65 for PPA. The EPDMs grades are shown in Table I.

* To whom correspondence should be addressed.

Table I EPDM Grades

Physical Properties	EPDM A	EPDM B
Mooney viscosity	47	38
ML ₁₊₄ (100°C)		
Iodine index	19	6
Volatiles (%)	0.5	0.4

Sample Preparation

Blended materials were obtained by processing mixtures of EPDMs with PPA in compositions varying up to 50% in a Brabender plastograph at 140°C. This mixture was also carried out in a Haake plastograph at 120 and 140°C. Thus, the films were pressing at 145°C for 15 min. The samples obtained were stored at room temperature.

NMR Measurements

All NMR spectra were obtained on a Varian VXR 300 spectrometer operating at 299.9 and 75.4 MHz for ¹H and ¹³C, respectively. All experiments were done at ambient probe temperature. All experiments were performed using 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 5 kHz. Carbon-13 spectra are referred to the chemical shift of the methyl group carbons of hexamethyl benzene (17.3 ppm). The ¹³C were carried out in the cross-polarization mode with magic-angle spinning (CP/MAS), variation contact time (VCT), magic-angle spinning (MAS), and dipolar-dephasing (dephasing time of 40 μs). A range of contact time was established as 200–8000 ms. Proton T₁^{Hρ} was determined from the intensity attenuation of carbon-13 peaks with increasing contact times. The carbon-13 spin-lattice relaxation time was measured by focusing the mobile region of the samples using the conventional MAS inversion-recovery method.

RESULTS AND DISCUSSION

The CP/MAS carbon-13 NMR spectra are of importance to obtain preliminary information on polymeric blend compatibility. Figure 1(a) and (b) shows the CP/MAS carbon-13 NMR spectra of EPDM A/PPA blends and EPDM B/PPA blends, respectively. Taking into consideration that no strong interaction between polymers in the blends

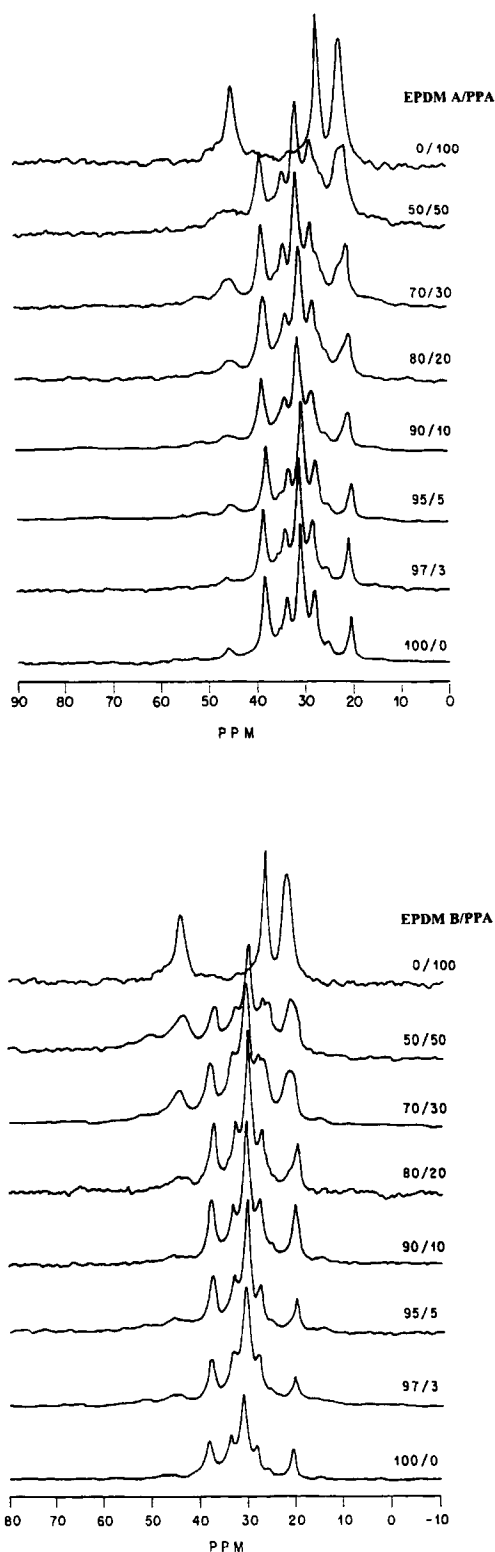


Figure 1 (a) CP/MAS carbon-13 NMR spectra of EPDM/PPA, PPA, and their blends. (b) CP/MAS carbon-13 NMR spectra of EPDM B, PPA, and their blends, at 75 MHz.

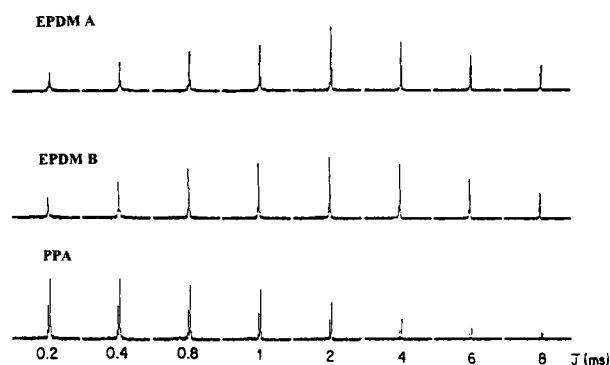


Figure 2 VCT experiment for EPDM A and B and PPA, at 75.4 MHz.

is present, it can be seen that for both systems no change in the chemical shift range was observed. This fact can be an indication of compatibility at the molecular level.² Besides the data mentioned, other information was characterized concerning the methyl resonance. The broadening peak (observed over 5% of PPA) and the change in chemical shift were associated with the methyls, one from EPDMs and the other from PPA.

Figure 2 illustrates the carbon-13 NMR variable contact time (VCT) experiment for EPDM A, EPDM B, and PPA. EPDMs showed the maximum intensity signals of carbon-13 peaks located at long contact times, which is expected of elastomeric materials. Otherwise, PPA decay shows a predominant rigid domain. A comparison of the VCT experiment of EPDM A, EPDM B, PPA, and their blends gave further useful information. The distribution of signal intensity from the VCT can also be a primary indication of the compatibility of blends. Figure 3 exhibits the form of the intensity distribution of

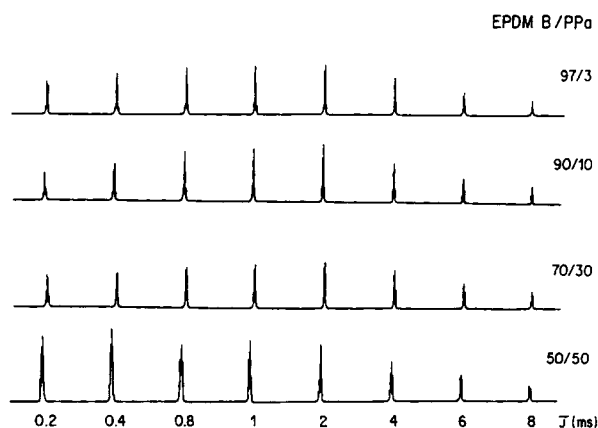


Figure 3 VCT experiment for EPDM A/PPA blends.

Table II $T_1^H\rho$ Values for EPDM B/PPA System

System EPDM B/PPA (phr)	$T_1^H\rho$ (ms)
100/0	5.7
97/3	4.8
95/5	4.1
80/20	4.9
75/25	4.3
70/30	4.5
65/35	4.3
60/40	4.1

EPDM B/PPA systems. It revealed that in mixtures of over 45% of PPA two domains were observed (the first one located at short contact time from PPA and the other one of EPDM). Proton spin-lattice relaxation time in the rotating frame was determined from the decay of carbon-13 signal intensity by VCT. Table II shows the values of $T_1^H\rho$ measured only for the carbon-13 peaks ($\delta = 30.7$ ppm) of EPDM

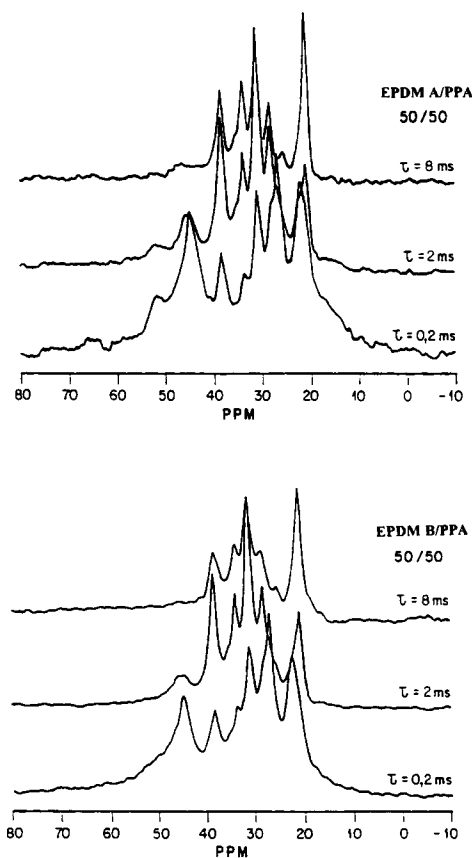


Figure 4 Carbon-13 NMR spectra of (a) EPDM A/PPA blends 50% of PPA and (b) EPDM B/PPA blends 50% of PPA.

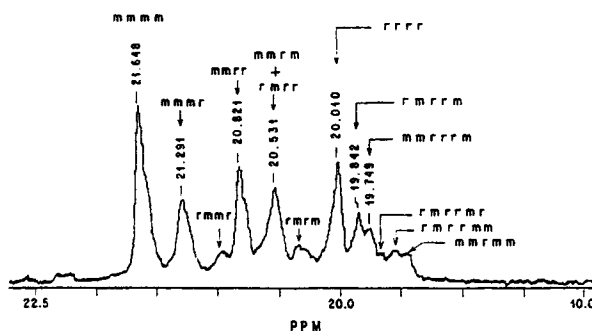
Table III Correlation Among Contact Time, Microstructure of PPA, and Mobility

Contact Time (ms)	Sequence	Mobility
0.2	Isotactic	Rigid
2	Heterotactic	Intermediate
8	Syndiotactic	Flexible

B and their blends with PPA. The $T_1^{H\rho}$ value of PPA was measured considering all the peaks. Just one value of this parameter was found as 2.6 ms.

It is known that the proton spin-lattice relaxation time in the rotating frame is a function of the environment and the nature of the carbon as well as the extent of molecular motion. From Table II it is observed that for all compositions studied there was just one high value of $T_1^{H\rho}$, which is an indication that these compositions show only one high flexible domain, which can be a consequence of compatibility, due to the plasticizer effect of PPA.

Other interesting information can be extracted for the CP/MAS array of contact times. There was a change observed in the chemical shift of methyl resonance for compositions over 30% of PPA, when distinct contact times were recorded in an array (Fig. 4). In our opinion, this occurs due to the PPA microstructure (Fig. 5), taking into consideration that these systems do not have a strong interaction (hydrogen bond) and that the EPDMs studied do not present any spread either, as a consequence of the sequence configurational distribution. Therefore, during the polymerization process, the length of propylene and ethylene unities do not form any

**Figure 5** Methyl region of PPA, in $CDCl_3$ 20% (wt/vol), at 60°C and 75.4 MHz.

stereoregularity. In accordance with Figure 4, it was possible to make a correlation between region mobility and PPA microstructure, as can be seen in Table III.

The dipolar dephasing (DD) experiment was carried out to confirm the distinct mobility of methyl, due to the response of the sample when a dephasing time is applied in the cross-polarization/magic angle spinning technique. The CP/MAS/DD of PPA showed only the methyl resonance split into two peaks, assigned as heterotactic and syndiotactic sequences, respectively, which are linked to high mobility. Both EPDMs did not present any split in the methyl region, which confirms no configurational sequence distribution at all. The spectrum obtained from this experiment was equal to both MAS and CP/MAS spectra, which still confirms the high mobility of both EPDMs. As for blends up to 30% of PPA, no difference was observed in relation to mobility or even to methyl resonance. Therefore, for blends over 40%, a splitting in the methyl peak

Table IV Measurements of Spin-lattice Relaxation Time for Carbon-13 Nuclei of the EPDM B/PPA System

System EPDM B/PPA (phr)	$T_1^{13}C$ (s)						
	$\delta(^{13}C)$ ppm						
	46.4	38.8	34.4	31.5	28.8	26.0	21.3
0/100	0.75				0.76		0.75
100/0		0.16	0.25	0.25	0.26	0.18	0.45
97/3		0.17	0.27	0.25	0.20		0.42
70/30	0.21	0.19	0.30	0.30	0.29	0.29	0.43
55/45	0.47	0.49	0.16	0.26		0.13	0.26
50/50	0.23	0.19	0.27	0.25	0.34		0.46

was detected. Also, the values found for the lines were the same as those assigned to PPA. The results were corroborated by the response obtained from the VCT experiment, with respect to the presence of different regions which present distinct mobilities.

The results of carbon-13 spin-lattice relaxation time measurements by the inversion-recovery technique, considering the mobile region, are listed in Table IV. It is interesting to note that the recovery of magnetization of carbons in the blends varying up to 30% of PPA added has a similar value (or form) as that of pure EPDM. Although for the compositions of 45 and 50% of PPA added, a change in the values can be attributed to phase separation. Therefore, we may conclude that the addition of PPA into EPDM has a definite effect on the mobility behavior of EPDM. This conclusion is in agreement with the results obtained by other NMR measurements.

CONCLUSION

With regard to the techniques employed, it can be affirmed that EPDM/PPA blends are miscible at the molecular level up to 45% of PPA added. The results of the ^{13}C -CP/MAS technique, variation contact time, proton $T_{1\rho}$, dipolar dephasing experiment, and carbon-13 spin-lattice relaxation time gave very much detailed information on the compatibility and mobility of blends.

The authors are very grateful to PETROBRÁS/CENPES/DIQUIM for the NMR facilities and to CAPES and CNPq for the financial support of this research.

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Received June 2, 1995

Accepted November 2, 1995