Evaluation of EVA–PVAc Blend Behavior by 1-D and 2-D Solid-State NMR

CLÁUDIA M. G. DE SOUZA,[1] CARLOS R. PACHECO,[2] MARIA I. B. TAVARES[1]

[1] IMA/UFRJ Cidade Universitária, Centro de Tecnologia, Ilha do Fundão, Rio de Janeiro, RJ, CP 68525, CEP 21945-970, Brazil

[2] DIQUIM/CENPES/PETROBRAS, Ilha do Fundão, Rio de Janeiro, RJ, Brazil

ABSTRACT: Ethylene-*co*-vinyl acetate and poly(vinyl acetate) blends were prepared in different proportions by melting in a HAAKE Rheomix mixer. The blends were prepared at a fixed temperature, rotation rate, and processing time. High-resolution solid-state nuclear magnetic resonance was chosen to characterize the blends with respect to structure–mobility–compatibility employing magic angle spinning with cross polarization and high-power hydrogen decoupling and the measurements of the proton spin–lattice relaxation time in the rotating frame ($T_1^H\rho$). The miscibility between polymer chains was also studied by two-dimensional ^{1}H–^{13}C shift correlation (HETCOR). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 221–226, 1999

Key words: EVA; PVAc; NMR; blends

INTRODUCTION

Nowadays, blends are the core of polymeric research. This is due to the low costs of developing new materials allied to the ease of developing new properties in a known polymer just by mixing it with another polymer. However, it is necessary to characterize the blends with respect to the miscibility of the polymer chains to optimize the blending process. There are various techniques available to investigate blend compatibility or miscibility. Such techniques include thermal analysis (differential scanning calorimetry,[1] dynamic mechanical analysis,[2] dielectric analysis[3]), estimation of mechanical properties,[4] and morphological studies using scanning electron microscopy (SEM).[2,5] Solid-state nuclear magnetic resonance (NMR) is also a powerful method.[6–11] Combined techniques, such as CP–MAS, are used to obtain high-resolution solid-state NMR spectra. Proton spin–lattice relaxation time in the rotating frame is measured by a variable contact time experiment through the decay of ^{13}C peak intensities and provide detailed information on molecular and segmental motion[8–13] since this parameter is function of the ^{13}C environment and is also used to obtain a NMR response of polymeric blend compatibility in the solid state.

Polyethylene-*co*-vinyl acetates (EVA) containing 5–40 wt % vinyl acetate are widely used in liquid packing, wrap film heavy-duty shipping sacks, bumper pads, hot-melt adhesives, and so on.[14,15] EVA can be obtained by different methods. Depending on the copolymerization process, one can obtain EVA with different vinyl acetate (VA) content. The properties of each copolymer is dependent on the VA content in the copolymer.[16,17] Copolymerizations are processes of high costs.[17] In Brazil, the processes are restrict to copolymers containing up to 28% of VA.[18] To solve

Figure 1 ^{13}C CP–MAS spectrum of EVA31.

this problem, EVA–poly(vinyl acetate) (PVAc) blends were prepared to obtain EVA with higher VA content. And, consequently, a new product with specific physical properties and new applications were obtained.

The main purpose of this work was to characterize EVA–PVAc blends with respect to structure–mobility–compatibility by solid-state NMR, using both $T_1^H\rho$ measurements and two-dimensional (2-D) heteronuclear shift correlation.

EXPERIMENTAL

Sample Preparation

The materials used in this work were EVA (POLITENO, BA, Brazil) and commercial PVAc. The VA content was measured from solution ^{13}C-NMR, in the EVA CH_3, the ethylene CH_2 (E), and the vinyl acetate C=O. The value found was 31% w/w of VA.[19]

The 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 15 min.

For the sake of clarity, the blends were named CS2-n, where n means the following content of EVA in the blend: 50, 60, 80, and 90.

NMR Measurements

The ^{13}C-NMR spectra were obtained on a VARIAN VXR-300 spectrometer operating at 299.9 and 75.4 MHz for ^{1}H and ^{13}C, respectively. All experiments were performed at probe ambient temperature and using high-power proton decoupling. A 7-mm diameter zirconium oxide rotor with Kel-F caps was used to acquire the NMR spectra at rates of 6 kHz. ^{13}C-NMR spectra were referenced to the chemical shift of the methyl carbons of hexamethyl benzene (17.3 ppm). The ^{13}C-NMR experiments were carried out with CP–MAS and CP–MAS with variation of contact time (VCT). A range of contact time was established as 50 to 4000 μs. $T_1^H\rho$ values were determined from the intensity decrease of ^{13}C peaks with increasing contact time. The 2-D HETCOR[20] spectra were obtained on a VARIAN INOVA 300 with a spinning rate of 5.2 kHz, ^{1}H, and ^{13}C 90° pulse of 3.6 ms, 2 s delay, and a range of 250–820 scans. The F1 evolution consisted up to 127 cycles of Blew-12 (012232010032) with $+X = 0$, $+Y = 1$, $-X = 2$, and $-Y = 3$ (43.2 μs F1 dwell). BB-12 ^{13}C decoupling (212012210212) was applied synchronously with BLEW-12. WIM-24 cross-polarization was employed with the sequence (303303101110322332312112 1) for both ^{1}H and ^{13}C. States methods were used to obtain pure absorption data. A Gaussian window was used in both t_1 and t_2 time domains, and their parameters (gf and gfs) were adjusted interactively.

RESULTS AND DISCUSSION

One of the principal advantage of the CP–MAS experiment is a better resolution of the NMR signals. Each ^{13}C has its own optimum contact time,

Figure 2 ^{13}C CP–MAS spectrum of PVAc (asterisk indicates ssb).

t_c, (it is the time chosen to transfer energy from hydrogen to carbons in the cross-polarization mode), which is a consequence of polarization transfer efficiency. Figures 1–6 show the ^{13}C CP–MAS spectra for EVA31, PVAc, and their blends, acquired with the optimum contact time for each one. The EVA31 and PVAc detailed analysis can be found in previous works.[19,21]

From the EVA31 ^{13}C-NMR spectrum (Fig. 1), the following four signals were found: the CH_2 from the ethylene rigid domain (33.4 ppm); CH_2 from the ethylene flexible domain (31.3 ppm); and two signals from VA group, CH—O located at 74.6 ppm and CH_3 at 21.9 ppm.[19] EVA31 was also analyzed by MAS using the conditions to detect the mobile region. And the following five NMR lines were registered: CH_2 from the ethylene mobile region, and the others from the VA group [C=O (167.7 ppm), CH—O (74.6 ppm), CH_2 (38 ppm), and CH_3 (21.9 ppm), which confirms that VA is the mobile region of the copolymer together with the CH_2 group of the ethylene flexible region].

The PVAc ^{13}C CP–MAS spectrum (Fig. 2) presented the following four NMR lines assigned to each ^{13}C present in the chemical structure: 170.7 ppm, carbonyl group; 67.3 ppm, CH—O (C_α); 40.2 ppm, CH_2 (C_β) and 21.5 ppm, CH_3. An important feature is related to the NMR line width of all the carbons: they are larger compared with EVA 31. This was attributed to the amorphous characteristic of the PVAc. In our previous study, it was characterized that PVAc presents distribution of microstructure, and it is highly heterogeneous.[21]

The ^{13}C CP–MAS NMR spectra of the blends showed that each composition has its own contact time, which was related to the amount of PVAc added. For up to 40% of PVAc added to EVA31, no significant difference in the contact time was observed. However, when the amount of PVAc was 50% (CS2-50), the contact time changed to a long value, which is characteristic of elastomeric sam-

Figure 3 ^{13}C CP–MAS NMR spectrum of CS2-50 blend (asterisk indicates ssb).

Figure 4 ^{13}C CP–MAS NMR spectrum of CS2-60 blend (asterisk indicates ssb).

Figure 5 ^{13}C CP–MAS NMR spectrum of CS2-80 blend (asterisk indicates ssb).

Table I $T_1^H\rho$ **Values of the CH$_2$ from the Rigid Rigid Region of EVA (33.4 ppm)**

Sample	$T_1^H\rho$ (ms)
EVA31	—
CS2-90	1.6
CS2-80	1.7
CS2-60	—
CS2-50	2.0

172.2 ppm; this small variation in δ could come from a small decrease in the mobility due to the interaction process between blend components.

In the variable contact time experiment, from the distribution form of the ^{13}C spectra decay, one can observe the homogeneity and/or 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, hence, have their signals located at long contact times. The $T_1^H\rho$ was measured from the variable contact time experiment. As this parameter is sensitive to a short-range spatial proximity, it can be interpreted in terms of blend mobility/compatibility. The $T_1^H\rho$ of EVA31 in the blends were measured for the CH$_2$ groups in the rigid and flexible regions and are listed in Tables I and II, respectively. The VA content in EVA31 caused an increase in the mobility of the copolymer, and the $T_1^H\rho$ value was only detected for the CH$_2$ group of the mobile region. As for the blends, the $T_1^H\rho$ parameter was measured for both regions, and one could not observe changes in the $T_1^H\rho$ values for the NMR signal at 33.4 ppm; as this signal comes from the ethylene rigid domain, it was a response that this domain did not take part in the interaction process. As a consequence, it was an indication that there was not an effective influence of PVAc in the rigid domains of EVA. However, for the flexible region, one could see, as expected, that the $T_1^H\rho$ values were higher

ples and could be a first indication of the PVAc plasticization effect in the EVA31. Also, for this same proportion, the ^{13}C spectrum was better resolved, and two carbonyl chemical shifts (δ) were detected, one at 170.7 ppm (due to PVAc), and the other one at 177.7 ppm. The second carbonyl could be attributed to the interface with strong interaction between both the polymers in the blend, in spite of being a signal of phase separation. Therefore, this interaction seemed to appear when the amount of PVAc was 40% (CS2-60). Only one carbonyl chemical shift was detected at higher frequency in relation to PVAc,

Figure 6 ^{13}C CP–MAS NMR spectrum of CS2-90 blend (asterisk indicates ssb).

Table II $T_1^H\rho$ **Values of the CH$_2$ from the Flexible Region of EVA (31.3 ppm)**

Sample	$T_1^H\rho$ (ms)
EVA31	3.2
CS2-90	4.1
CS2-80	3.3
CS2-60	2.8
CS2-50	3.9

Table III $T_1^H\rho$ Values of EVA–PVAc Blends for the Carbonyl Groups at 170.7 ppm

Sample	$T_1^H\rho$ (ms)
EVA31	—
CS2-90	66.4
CS2-80	39.7
CS2-60	42.7
CS2-50	47.8
PVAc	3.6

than the rigid one. Analyzing the CS2-90 blend, the $T_1^H\rho$ value was the highest, and it was an indication that this blend was intimately mixed and also highly plasticized.

For the other proportions, no significant difference was found for this parameter, and they are very similar to the EVA 31; this can be attributed to a phase separation. Therefore, CS250 showed a small increase in the $T_1^H\rho$, due, probably, to the VA plasticization effect.

To obtain further information on the compatibility of the blends, the $T_1^H\rho$ parameter for the carbonyl group at 170.7 ppm from the PVAc was also measured (Table III). Considering the values of $T_1^H\rho$ for CS2-80 to CS2-50 blends, an increase of that parameter with the increase of PVAc amount was observed, which could be related to a VA amount effect. But the value of this parameter is still higher than the PVAc, so it is an indication that there is phase separation. Therefore, this phenomena was not completed, and an interface of communication between both blend components at a molecular level still exists. CS2-90, however, showed a particular behavior: the highest value of $T_1^H\rho$ confirmed the plasticization effect of PVAc in the blend and also showed the compatibility effect, which corroborated with the response obtained from the CH_2 group of ethylene for the flexible region.

To better investigate the behavior of blend domain communication, a 2-D HETCOR experiment was acquired, and the principal information obtained from spectra was related to the carbonyl groups. The chemical shifts observed for the pure polymers were 167.5 ppm for EVA31 and 170.7 ppm for PVAc. For the CS2-60 (Fig. 7), three

Figure 7 Two-dimensional $^{13}C–^1H$ HETCOR spectrum of CS2-60 blend. ^{13}C and ^1H projections are shown above and to the left of the plot.

carbonyl signals were detected. Two of them were due to noninteracting fractions of the polymer blend components (168.4 and 172.0 ppm, for EVA31 and PVAc, respectively). However, the third signal located at 164 ppm was an indication that a fraction of the polymers was mixed at the molecular level. The difference of approximately 4 ppm from the value of EVA31 could be evidence that the EVA–PVAc interaction changed the carbonyl group to a lower frequency, as a consequence of plasticization effect. These results corroborated the data observed by CP–MAS experiments.

CONCLUSION

The results showed that ^{13}C CP–MAS NMR (one-dimensional and 2-D) provided a good methodology to obtain information on the compatibility and plasticization effect on polymer blends. In this particular study, we could also extract information on the interface of EVA31 and PVAc blends.

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