

Solid-State Carbon-13 NMR Study of Material Composites Based on Sugarcane Bagasse and Thermoplastics Polymers

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ABSTRACT: The composites formed by sugarcane bagasse and thermoplastic polymers, such as polypropylene (PP), polyethylene (PE), and ethylene-co-vinyl acetate (EVA), have been analysed by carbon-13 high-resolution solid-state nuclear magnetic resonance (NMR), employing crosspolarization magic angle spinning (CPMAS); variable contact-time experiment and proton spin-lattice relaxation time in the rotating frame. NMR responses showed that these techniques can be used to observe the degree of compatibility and homogeneity of different polymers composites. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2150–2154, 2001

Key words: solid state NMR; composites; sugarcane bagasse; thermoplastics; polymers

INTRODUCTION

There is a growing interest in the use of natural fibers as a reinforcement for synthetic polymers.^{1,2} Because natural fibers are biodegradable, their composites may offer a new class of materials providing environmental protection.³ The polar nature of reinforcing agents sometimes affects the adhesion to the plastic matrix adversely. Because of it, the fillers are treated with adhesion-promoting agents (stearic acid, etc.).⁴ The treatment of fibers significantly improves the interfacial adhesion and the mechanical properties of the composites.⁵ In fact, natural fibers do not have a very good mechanical performance. They are found in large quantity in Brazil, and are appropriate to low cost applications.^{6,7} There

is a great interest in finding a new application for them, because they are used as fuel in the Brazilian sugarcane industry.⁸ The sugarcane waste fiber is mainly composed by cellulose ($\approx 65\%$), which is a polymer of significant commercial importance.⁹

Objective and Solution

The main purpose of this work was to study the behavior of the composites formed by sugarcane fibers (SC) and thermoplastic polymers. To understand their molecular dynamics, and hence, control the relation between structure and properties of such materials, we employed solid-state nuclear magnetic resonance. NMR is a powerful tool that permits studying samples in different aspects and to obtain response on their dynamic behavior.^{10–19} It is known that solid-state NMR techniques provide good information on chemical structure and sample homogeneity.^{10–16} A comparison between magic angle spinning (MAS) and

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CPMAS spectra shows the existence of different domains or microdomains in a sample^{15,16} as well as to determine its chemical structure. In the case of blends and composites, one can get information on their heterogeneity.^{12,16–24} The distribution form of a series of CPMAS spectra obtained from variable contact-time experiment, permits one to observe distinct regions that have different mobilities, and also if one of the components influences the polarization transfer way of the other one, which occurs as a consequence of the interaction process.^{12,17–24} Proton spin-lattice relaxation time in the rotating frame ($T_{1\rho}^H$) is a parameter that evaluates the blends and composites behavior in terms of sample interactions. Consequently, it provides response on the homogeneity and the degree of distribution of both components.^{11,12} Polymer molecular mobility is also obtained from this parameter, which can be related to the stiffness of the chains, due to the influence of the interaction process between the composites components.

EXPERIMENTAL

Fibers and Polymer

The fibers were obtained directly from the sugarcane industry, and they were only dried in an oven at 80° for 48 h to extract the remaining humidity. After full drying, the fibers were grounded with 5 mm of length. These fibers presented at least 65% of cellulose. The EVA were supplied by Politeno SA, and the contain 19% of vinyl acetate, with the glass transition, $T_g \sim -20$. PP were supplied from Polibrasil S.A., the T_g was $\sim 0^\circ\text{C}$, and PE were supplied from Polialden with $T_g \sim -100^\circ\text{C}$.

Composites Preparation

The fibers and EVA, PP, and PE were mixed in a Haake plastograph (model Rheocord 9000 with Rheomix head), at 200°C for 20 min using the same proportion between both components.

NMR Measurements

All NMR spectra were obtained on a VARIAN VXR 300 spectrometer operating at 299.9 MHz and 74.5 MHz for ^1H and ^{13}C , respectively. All experiments were done at probe ambient temperature, and performed using high-power decoupling. Zirconium oxide rotors of 7-mm diameter

were used to acquire the NMR spectra at spinning rates of 6 kHz. ^{13}C spectra were referred to the chemical shift of methyl group carbons of hexamethyl benzene (17.3 ppm). The ^{13}C runs were carried out in the crosspolarization mode with magic-angle spinning with 2 s of delay and a variable contact-time experiment. A range of contact time was established as 100 to 8000 μs . $T_{1\rho}^H$ values were determined from the intensity of carbon-13 peaks decay with increasing contact times.

RESULTS AND DISCUSSION

MAS ^{13}C —Analyses and a Qualitative Domains Detection

MAS ^{13}C NMR spectrum of EVA showed signals from vinyl acetate and ethylene amorphous phase (31.2 ppm) showing that this copolymer presents at least two domains that have different mobilities.⁸ For PP three signals referred to CH_3 , CH , and CH_2 were detected at 23.6, 27.9, and 45.9 ppm, respectively. The values of chemical shifts found for this polymers show that the PP presents a large domain constituted by the isotactic sequences and small defects caused by other configurational sequences that were not detected, because they probably are very small. For PE the MAS ^{13}C NMR spectrum one sharp signal at 31.2 ppm was detected, which comes from the amorphous phase, which is large enough to be detected by NMR.

Figure 1 shows the MAS ^{13}C NMR spectrum of EVA/SC (40/60) composite, and from this figure one can see that the mobile domains were mainly formed by the amorphous phases of the ethylene region and vinyl region of EVA, as already detected in the initial polymer. The same behavior was found for the PP/SC and PE/SC composites.

CPMAS ^{13}C —Analyses

The CPMAS ^{13}C NMR spectrum of sugarcane fibers showed three wide resonance lines. The chemical shifts (δ) assignments were based on cellulose lines²³: $\delta = 106.2$ ppm (C—O—C); $\delta = 74.0$ ppm (CH—O) and $\delta = 65.4$ ppm (CH_2).

For the ethylene-co-vinyl acetate (EVA) polymer, with 19% of vinyl acetate (VA) content in weight, the CP/MAS ^{13}C NMR spectrum showed four resonance lines. The carbonyl group (C=O) was detected at 169.4 ppm, the CH—O located at 74.0 ppm, the CH_2 from the ethylene rigid domain

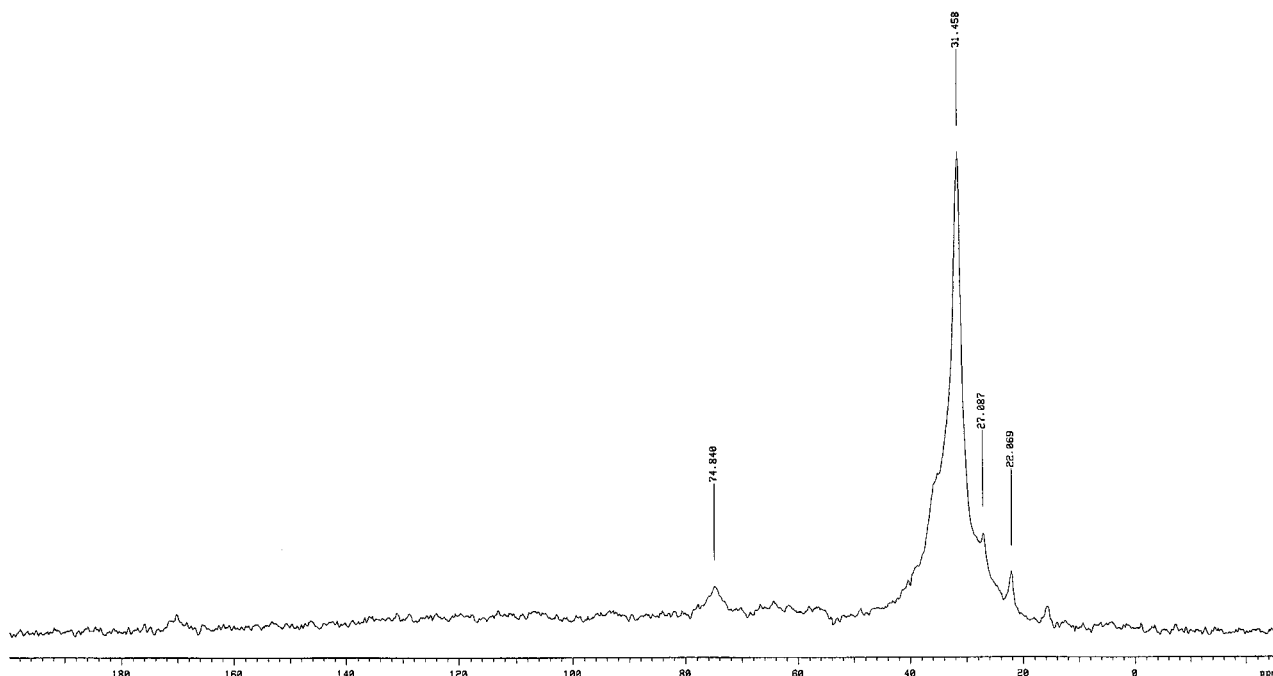


Figure 1 MAS ^{13}C NMR spectrum of EVA/SC (40/60) composite.

at 33.4 ppm and the CH_3 group—from the VA group at 21.7 ppm.²⁴

The CPMAS ^{13}C NMR spectrum of polypropylene (iPP) showed 3 NMR lines: one located at 45.9 ppm (CH_2), another one at 28.1 ppm (CH), and the last one at 23.6 ppm (CH_3). The values of chemical shifts are due to highly isotactic PP.²⁵

The CPMAS ^{13}C NMR spectrum of high density polyethylene (HDPE) showed a large signal located at 33.4 ppm, which was attributed to the CH_2 group from the ethylene rigid domain.^{8,25}

To obtain a first indication of the compatibility at molecular level, all composites polymer/fibers containing the same proportion of polymer/fibers (40/60), have been investigated by the CPMAS ^{13}C spectra recorded at the same conditions: contact time (1 ms), time delay 2 s, and number of transients 3200. Figure 2 shows the CPMAS ^{13}C NMR spectrum of EVA/SC (40/60) composite. The NMR signals detected were from both sugarcane fibers and EVA, which confirms the composite homogeneity in the MHz

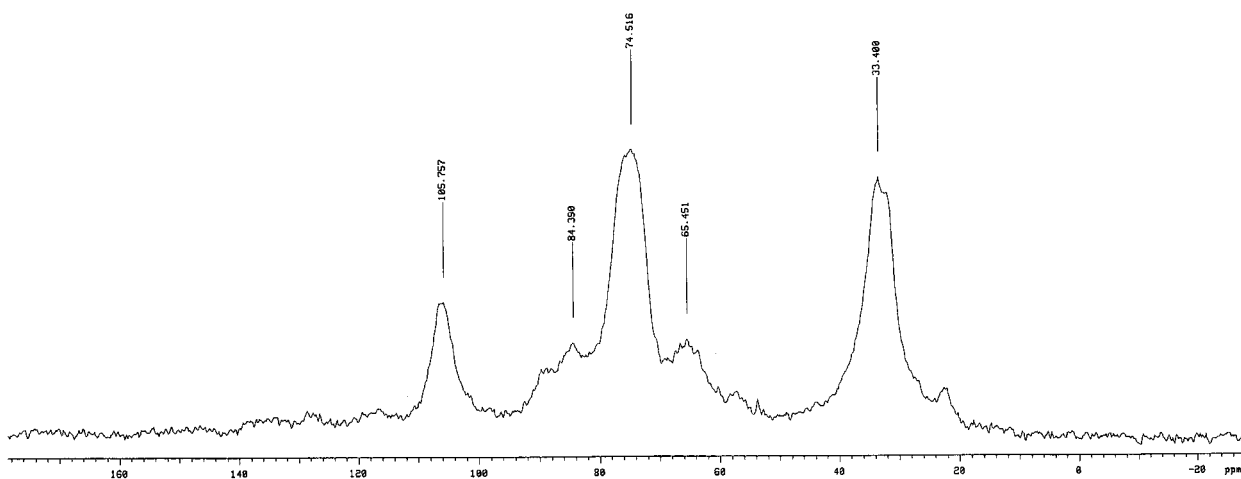


Figure 2 CPMAS ^{13}C NMR spectrum of EVA/SC (40/60) composite.

frequency. The same behavior was found for the two others composites.

Variable Contact-Time Experiments

The distribution form of a series of CPMAS ^{13}C spectra during the variable contact time (ct) which is the time chosen to transfer energy from ^1H to ^{13}C in the crosspolarization mode) can show the presence of domains with different mobilities. It is known that rigid domains appear at short contact times (μs) and mobile domains, which need more time to be polarized, have their signals concentrated at long contact times (ms).

Analyzing the variable contact time, the EVA copolymer presents one decay with the signals located at short contact time, one optimum contact time was detected at $200 \mu\text{s}$, which is a consequence of low VA content and because the ethylene phase dominates the relaxation process.

It was observed through the variable contact-time experiment decay that PP presents just one domain, which confirms that this polymer is highly ordered as already detected by MAS technique, whose optimum contact time was $800 \mu\text{s}$.

The molecular dynamic of PE was also evaluated through the variable contact-time experiment decay, and this polymer presented just one domain concentrated at short contact times, which was referred to a crystalline region; the optimum contact time was $800 \mu\text{s}$. Therefore, at long contact times the value of chemical shift (31.2 ppm) was the same already registered by MAS technique, with specific conditions to assign the mobile region, which confirms the presence of other domain with high mobility.

CPMAS ^{13}C spectra, obtained from variable contact-time experiments, for the EVA/SC, PP/SC, and PE/SC composites at 40/60, are presented in Figure 3. From the decays, one can see that all composites are well mixed, because for the series of CPMAS ^{13}C spectra one can find signals from both composite components, which is an indication of the sample homogeneity at the molecular level, and the domain size are around 200 \AA .

$T_1^{\text{H}}\rho$ Measurements

To evaluate the behavior of the composites, in relation to each other, $T_1^{\text{H}}\rho$ parameter was measured through the variable contact-time experiment. The $T_1^{\text{H}}\rho$ values for the homopolymers EVA, PP, and PE and their composites with SC are listed in Table I.

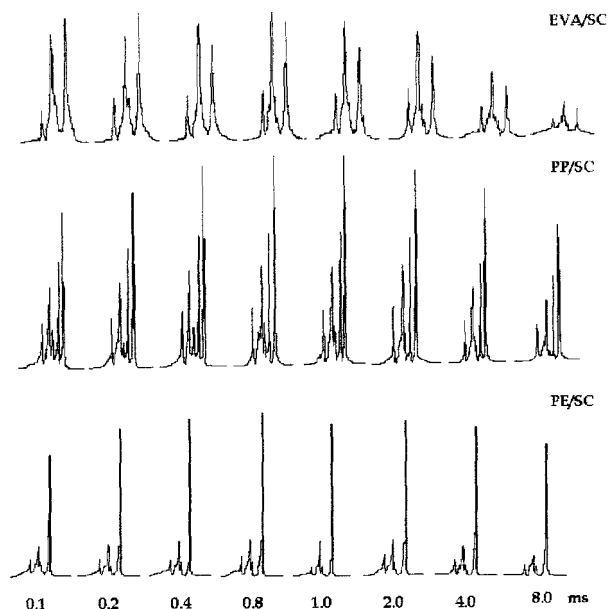


Figure 3 Variable contact-time experiment for EVA/SC, PP/SC, and PE/SC composites at 40/60 proportions.

Comparing the composites from the values of the $T_1^{\text{H}}\rho$ parameter, it can be observed that EVA/SC composite presents a better physical interaction between the fiber and polymeric matrix at molecular level, due to the decrease in the $T_1^{\text{H}}\rho$ values in relation to SC. This interaction can come from the polar groups randomly distributed in the EVA macromolecular chains. This good interaction between EVA/fibers tells us that the fibers are acting as a reinforcement. The increase in the $T_1^{\text{H}}\rho$ values, in comparison to the initial components, indicates that in PE/SC and PP/SC composites present phase separation, showing that these fibers can only be acting as a filler, because they are not interacting with the polymers. The difference of physical interaction and fibers dispersity among the three composites is basically constituted by the chemical structures of the polymers and molecular packing of both composites components.

CONCLUSION

NMR spectroscopy is a powerful technique for characterizing the molecular motion of the composites. Proton $T_1\rho$ relaxation parameter showed the compatibility at the molecular level, and ^{13}C spectra obtained from both MAS and CPMAS show that they are relevant to obtain a good com-

Table I $T_1^H \rho$ Values for the Homopolymers EVA, PP, and PE and Their Composites with SC, Using the Same Fiber Size (Medium) and Proportion 40/60

Composites $\delta(^{13}\text{C})$	$T_1^H \rho$ (ms)							
	105.2	74.0	65.4	44.4	33.4	31.9	26.4	22.0
SC	2.7	2.5	2.0	—	—	—	—	—
EVA/SC	0.9	—	0.8	—	—	1.3	—	1.3
EVA	—	—	—	—	1.0	—	—	—
PP/SC	5.1	4.3	2.6	9.4	—	—	11.7	14.7
PP	—	—	—	2.9	—	—	3.1	4.0
PE/SC	5.6	6.0	—	—	—	19.4	—	—
PE	—	—	—	—	2.6	—	—	—

posite. In our opinion, we can see that NMR spectroscopy can be used to evaluate the behavior of the composites at the molecular level.

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