

NOTES

Solid-State NMR and XPS Studies of EVA/Sugarcane Composites

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Received 6 August 1999; accepted 27 April 2000

INTRODUCTION

Studies^{1,2} have been made in composites formed by blending natural fibers and thermoplastic polymers. One of the possibilities for the use of those composites is in substitution of more expensive polymeric materials with similar properties. In Brasil, we can find waste sugarcane fibers in large quantities, so there is an increasing interest in finding new applications for them.

As sugarcane fibers present different cell arrangements and spatial configurations, and consequently, the ordination and orientation of the chains are different. The bagasse composites with poly(ethylene-co-vinyl acetate) (EVA) have been investigated, and the main purpose of this work was to study the homogeneity at the molecular level of the composites to better understand the behavior, and hence, to control the relation between structure and property of such materials. Therefore, the evaluation of the material surface was also done to obtain response on the polymer distribution.

This study employed solid-state NMR and XPS. Solid-state NMR was used to obtain information on molecular dynamics, and also to evaluate the microscopic homogeneity between composites components by the relaxation times.³⁻⁹ XPS permitted obtaining responses on the surface of these materials.¹⁰ Both data helped us to get information on sample homogeneities and interactions.

EXPERIMENTAL

Composites Preparation

The bagasse used as filler was directly obtained from the sugar cane mills, after being processed to extract sugar and liquor. This "as-received" material was dried at 80°C for 48 h and then was chopped and sieved. Bagasse pieces with lengths of 5 mm were used in this work. The chopped bagasse was dried again at 80°C for 48 h before being incorporated into the EVA matrix. The treated sugarcane bagasse fibers and EVA (19% of vinyl acetate, with a $M_n = 50,000$, $M_w = 216,000$, $M_v = 563,000$ and 4.47 of polydispersity) composites were blended in a Haake plastograph (Rheocord 9000 with a Rheomix head), at 200°C for 20 min. The proportions of sugarcane fibers (SC) was varied up to 60% (by weight).

NMR Measurements

All NMR spectra were obtained on a VARIAN VXR 300 spectrometer operating at 299.9 and 74.5 MHz for ¹H and ¹³C, respectively. All experiments were done at ambient probe temperature and performed using high-power decoupling. Zirconium oxide rotors of 7-mm diameter with Kel-F caps were used to acquire the NMR spectra at spinning rates of 6 kHz. Carbon-13 spectra are referred to the chemical shift of the methyl group of hexamethyl benzene (17.3 ppm). The ¹³C spectra were carried out in the cross polarization mode with magic-angle spinning (CPMAS) using a pulse of 4.8 μs (90°) and 2 s of a pulse interval and a variable contact time experiment (VCT). The contact time was varied from 100 to 8000 μs. Proton T₁^Hρ were determined from the intensity decay of carbon-13 peaks with increasing contact times.

Table I The Surface Elemental Composition of EVA/Sugarcane Fibers Composites

EVA/SC Proportions (%)	Surface Composition (at %)			
	C	O	Si	N
0/100	72	24	3.4	1.1
80/20	87	10	2.7	0.0
70/30	81	14	5.4	0.0
60/40	85	12	3.5	0.0
40/60	86	11	2.4	0.0
100/0	83	12	4.2	0.0

XPS Measurements

The spectra were recorded with a Kratos XSAM-800 spectrometer using a MgK α excitation. Pressure in the sample analysis chamber was 10^{-9} – 10^{-10} Torr. The X-ray gun operated at a moderate power (15 kV, 5 mA) in order not to produce detectable radiation damage to the samples. Charge correction in the binding energy scale was made by setting the lowest binding energy feature of the C1s emission to 285 eV. The surface composition of the blends was calculated from the integral intensities of the C1s, O1s, Si2p, and N1s signals, as described elsewhere.¹⁰ The sampling depth of XPS analysis was about 50 Å.

RESULTS AND DISCUSSION

XPS Results

The results of the quantitative surface analysis of EVA/sugarcane fibers composites are summarized in Table I, which presents the surface atomic concentration of elements C, O, Si, and N, as detected by XPS.

From Table I it can be seen that besides the lines of carbons and oxygen, in spectra of all samples, the silicon line is also detected (102.5 eV), which suggests that there is a siloxane contamination on the surface. The surface concentration of siloxane contamination was about 10–15%. This was expected, because the samples were prepared using commercial materials without any treatment.

At the surface of sugarcane fibers nitrogen is present. The lack of nitrogen on the surface of EVA and all samples allows us to suppose that the surface of sugarcane is covered with EVA. These suggestion can be verified by the analyses of core lines of carbons. Figure 1 shows the C1s core level emission from EVA and the composites. Sugarcane fibers are composed by three features: C₁ = 285.0, C₂ = 286.5, and C₃ = 289.4 eV, reflecting the carbon atoms groups —CH_n, —CO, and —C(O)O, respectively. On the other hand, to better resolve the line of EVA spectrum, the C1s core level of

sugarcane fibers have many unresolved components, whose binding energy range is from 285 to 290 eV. The unique spectral feature is the intense signal at 286.5 eV (\sim 50% of C1s).

As seen from Figure 1, all EVA/SC composites showed an ideal coincidence of C1s lines with C1s lines of EVA, which indicates that EVA forms a continuous overlayer on the surface of the sugarcane fibers.

NMR Results

The CPMAS ¹³C NMR spectrum of sugarcane fibers showed three wide NMR lines. The chemical shifts (δ) assignments were based on cellulose lines¹: δ = 106.2 ppm (C—O—C); δ = 74.0 ppm (CH—O) and δ = 65.4 ppm (CH₂—O).

For the ethylene-*co*-vinyl acetate (EVA), with 19% of vinyl acetate (VA) content in weight, the CPMAS ¹³C-NMR spectrum showed four resonance lines. The carbonyl group (C—O) detected at 169.4 ppm, the CH—O located at 74.0 ppm, the CH₂ from the ethylene rigid domain at 33.4 ppm, and the CH₃ group—from the VA group at 21.7 ppm.

CPMAS ¹³C spectra with a contact time of 1 ms for different proportions of EVA/SC composites were recorded as a first indication of homogeneity at the molecular level. For all of them we could see characteristic signals from the fiber and EVA, indicating a microscopic homogeneity in the composites.

The distribution form of a series of CPMAS ¹³C spectra obtained varying contact times showed the presence of different domains. Therefore, rigid domains appear at short contact times (μ s), while mobile ones, which need more time to be polarized, showed their signals at long contact times (ms). Analyzing the series of spectra, it could be observed that the signals of EVA

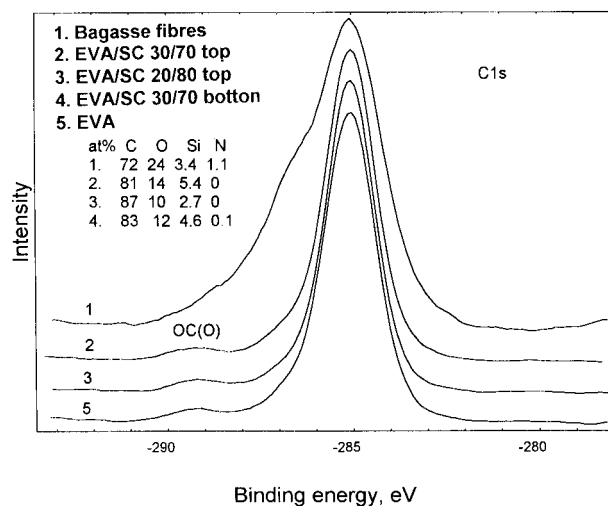


Figure 1 C1s core level emission from EVA and the composites.

Table II $T_1^H\rho$ Values for the Two NMR Signals, One from SC (106.2 ppm) and the Other for EVA (33.4 ppm) for the Pure Polymers and Their Composites

Composites EVA/SC	$T_1^H\rho$ (ms)	
	106.2	33.4
0/100	2.7	—
80/20	—	1.4
60/40	1.3	1.2
40/60	0.9	0.8
30/70	1.7	1.1
100/0	—	1.0

showed maximum polarization transfer at a short contact time (200 μ s). This is due to the low VA content in the copolymer being the ethylenic phase responsible for the relaxation process. The VCT experiments confirmed the homogeneity of the samples, as in all spectra of the series it could be observed signals from both composite components.

$T_1^H\rho$ parameter was used to understand the behavior of the composites and the interactions between components. $T_1^H\rho$ values for the two NMR signals, one from SC (106.2 ppm) and the other for EVA (33.4 ppm), were measured for the pure polymers, and their composites from variable contact-time curves. The results are listed in Table II.

All composition presented only one value for the $T_1^H\rho$, and it is known that a single value for this parameter means that a dipolar coupling exists between protons, and the spin diffusion is efficient. Comparing the $T_1^H\rho$ data, it can be observe that the 40/60 sample presented a better physical interaction between the fiber and polymeric matrix at the molecular level, due to the decrease in the $T_1^H\rho$ values of the SC carbon in the composite when compared with $T_1^H\rho$ of the same carbon of the pure fiber and EVA. As $T_1^H\rho$ is dependent on the spatial proximity of the chains at the EVA/SC (40/60) composite, it can be conclude that fibers and EVA chains are close.

CONCLUSION

NMR and XPS were used to investigate the homogeneity of EVA/SC composites. XPS data showed that EVA is covering the surface of SC fibers homogeneously. NMR $T_1^H\rho$ measurements indicated that the samples are homogeneous at the molecular level, and that the 40/60 ratio presented a better physical interaction between fibers and polymer matrix, as it showed the shortest $T_1^H\rho$ values for both carbons of SC and EVA when compared with values obtained for the pure components. Both methods permitted us to understand the mechanical properties of these composites.

The authors would like to thank CNPq for the financial support, and to DIQUIM/CENPES/PETROBRAS for the use of the NMR spectrometer.

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