Solid-State Nuclear Magnetic Resonance Study of Polyurethane/Natural Fibers Composites

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ABSTRACT: In the present study, fiber-reinforced plastics (FRP) were prepared with sisal and the sugarcane waste material. The composites of these fibers with polyurethanes were obtained by processing these materials in a Haake plastograph, and their homogeneity was characterized by nuclear magnetic resonance (NMR) measurements. The results are discussed in terms of composites interaction, homogeneity, and compatibility. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1465–1468, 2002

Key words: solid-state nuclear magnetic resonance spectroscopy; polyurethane; natural fibers; composites

INTRODUCTION

Natural fibers have been attractive waste materials with which to obtain composites using two different type of polymers, one with thermoplastic properties and the other one with elastomeric characteristics, because they are of low cost and have low density, flexibility, a rough surface, and civil engineering applications.[1] A great advantage of natural fibers is related to the fact that they are biodegradable and are obtained from renewable sources. These fibers consist mainly of cellulose and, therefore, can be used as reinforcing filler. But, the application of natural fibers depends on fiber orientation, chain packing, and fiber matrix adhesion. In this work we have chosen to obtain a composite involving sisal and sugarcane waste fibers, which are lignocellulosic materials extracted from the plants, with polyurethane. The incorporation of sisal or sugarcane waste fibers into plastics and elastomers, as a reinforcement, has been reported.[2–4] In these studies, the feasibility of developing composites was considered to improve their physical, mechanical and dielectric properties, surface behavior, and fracture morphology. However, few researchers[4, 5] have reported the use of sisal or sugarcane waste fibers for reinforcement of polyurethanes. In Brazil there is a lot of sisal and sugarcane waste fibers, some of which is used in utensils and as a fuel in industry. But the great majority is burned. To find a better use for these types of fibers, because of their cellulose content, we prepared a compos-
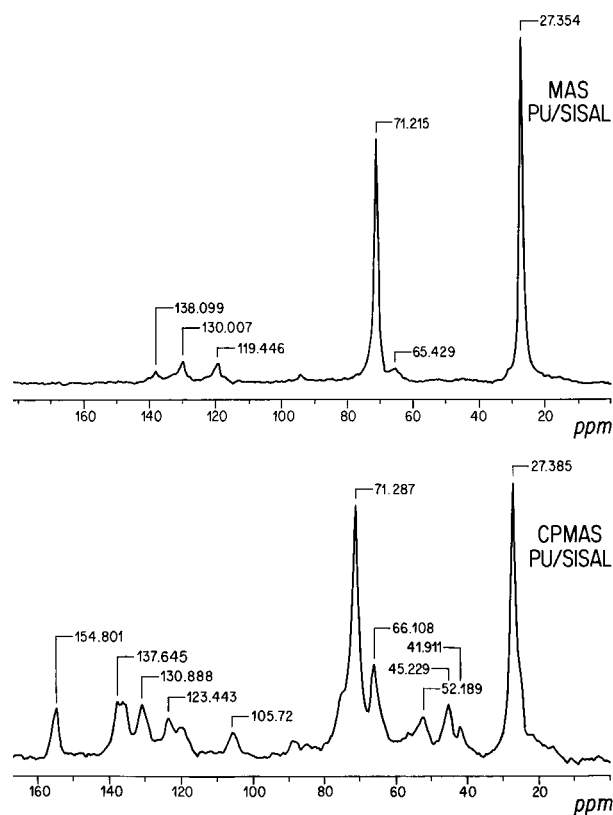

Figure 1 Comparison of CPMAS and MAS ^{13}C NMR spectra for PU/sisal composite.

ite with polyurethane. The main purpose of the present work was to study the dynamic behavior of the composites formed by polyurethanes and sisal or sugarcane waste fibers. The materials obtained were characterized, focusing on interaction, homogeneity, and compatibility between composite components using solid-state nuclear magnetic resonance (NMR) techniques.[3, 6–8] The solid-state NMR techniques employed were magic angle spinning (MAS), cross-polarization/magic angle spinning (CPMAS), variable contact-time experiments, and the proton spin-lattice relaxation time in the rotating frame ($T_1^H\rho$),[4, 5, 8–10] which was used as a parameter to identify the influence of the fiber in the polyurethane to obtain information on composite compatibility.

EXPERIMENTAL

Sisal and sugarcane waste fibers were supplied by Brazilian textile and sugarcane industries, respectively. The length of both fibers is random

because they are waste materials. The fibers were used as received.

Sample Preparation

Commercial polyurethane polymer and sisal or sugarcane waste fibers (SCF) in different proportions (i.e., 5, 10, 20, and 40%) by weight of fibers were prepared in a Haake rheometer at 100 °C for 15 min at 80 rpm. The composites were cured in a Carver press at 140 °C and 10,000 lb/in^2.

NMR Measurements

All NMR spectra were obtained on a VARIAN INOVA 300 spectrometer operating at 299.9 and 75.4 MHz for ^{1}H NMR and ^{13}C NMR, respectively. All experiments were done at ambient probe temperature and were performed using gated high decoupling. A zirconium oxide rotor of 7-mm diameter was used to acquire the NMR spectra at rates of 5.5 kHz. ^{13}C NMR spectra are referenced to the chemical shift of the methyl group carbons of hexamethylbenzene (17.3 ppm). The ^{13}C NMR spectra were carried out in the cross-polarization mode with MAS, using a 90° pulse. For the variable contact time, a range of contact time was established from 200 to 8000 μs. Proton $T_1\rho$ values were determined from the intensity attenuation of ^{13}C peaks with increasing contact time, employing the delayed contact-time
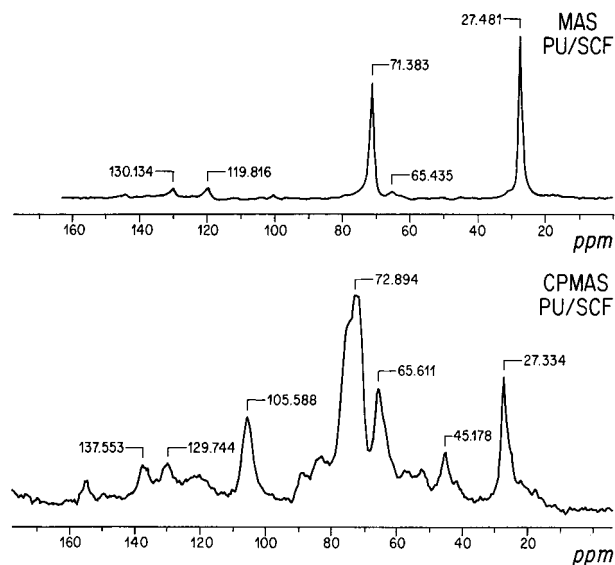

Figure 2 Comparison of CPMAS and MAS ^{13}C NMR spectra for PU/SCF composite.
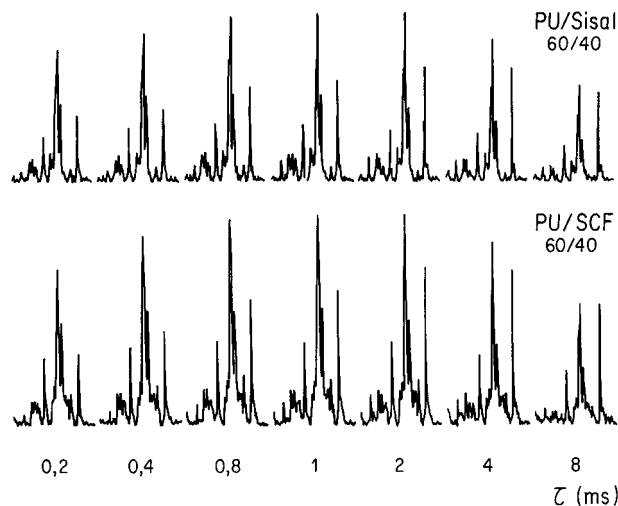
Figure 3 CPMAS ^{13}C decay of a series of NMR spectra for both PU/natural fibers composites.

experiment, and with the spin-locking range varied from 1000 to 12,000 μs.

RESULTS AND DISCUSSION

MAS is routinely employed in solid-state NMR as a line technique that suppresses the broadening introduced by chemical shift anisotropy and dipolar coupling. MAS also can be used to generate simplified spectra. So, in this work, the MAS technique was used with a short delay between 90° pulses to investigate the mobile region. All MAS ^{13}C NMR spectra showed only sharp signals related to the polyurethane part, located at 27.4 ppm (CH$_2$); 71.3 ppm (CH—O); 119.6 ppm (C=C); 130.0 ppm (C=C); 137.9 ppm (C=C), as expected, is the mobile. CPMAS ^{13}C PU spectrum present the lines located at 27.3 ppm (CH$_2$); 45.1 ppm (CH$_2$); 65.6 ppm (CH$_2$—O); 105.6 ppm (C—O—C);

119.4 ppm (C=C); 137.5 ppm (C=C), and 154.5 ppm (C=O).

The CPMAS ^{13}C NMR spectra were obtained by recording the variable contact time; the optimum contact time was determined as 1 ms and signals from both components were detected. The CPMAS ^{13}C NMR spectrum of PU/SCF exhibits lines located at 27.3; 45.1; 65.7 (CH$_2$—OH of SCF); 71.6 (CH—OH of both PU and SCF); 75.4 (CH—OH of SCF); 84.5 (CH—OH of SCF); 89.4 (CH—OH of SCF); 105.6 (C anomeric of SCF); 119.6; 123.1; 131.0; 137.2, and 154.5 ppm (C=O of PU). The comparison between CPMAS and MAS ^{13}C NMR spectra, for both composites (Figures 1 and 2), showed that the composites presented at least two domains with different mobilities, because the number, line width, and frequency of the signals are different. It is known that the presence of specific intermolecular interaction causes changes in the line width.

Another interesting point obtained from variable contact-time experiment was the distribution form of the ^{13}C decays that permitted evaluation of the mobility tendency of the composites after the fibers were incorporated. The ^{13}C decays for both PU/sisal and PU/SCF are shown in Figure 3. Both decays show the optimum contact time at 1 ms, which is not common for elastomeric materials like polyurethanes. The behavior of PU/natural fibers composites can be easily observed from the values of proton $T_1\rho$, which were measured for all resolved carbons and were determined by ^{13}C decays listed in Table I.

In the polyurethane/natural fibers composites, the polyurethane component influenced the molecular mobility of the SCF more than the sisal. The polyurethane/SCF and polyurethane/sisal changed the chemical shifts of C anomeric to low frequency compared with fibers, and the $T_1^H\rho$ values are higher compared with fiber values. Even

Table I $T_1^H\rho$ **Values for the Natural Fibers and Their Composites (40% fibers) as a Function of Chemical Shifts**

Sample	$T_1^H\rho$ (ms)				δ (^{13}C ppm)
	106.3	105.7	75.5	65.4	
SCF	4.1	—	3.1	3.6	
Polyurethane/SCF	—	9.3	6.6	4.4	
Sisal	—	6.8	6.6	6.6	
Polyurethane/sisal	—	10.6	5.7	5.5	

though the value of this parameter is a little higher for the polyurethane/sisal composite, the values determined for CH—OH and CH_2—OH are increased for polyurethane/SCF compared with SCF and decreased for polyurethane/sisal compared with sisal. These behaviors show that polyurethane/SCF presents a better interaction between both components. Furthermore, as the relaxation parameter values increased, the polyurethane can be acting as a plasticizer as well. This change can be caused by some modifications in the molecular packing and chains fibers ordination.

CONCLUSION

It is clear form the proton spin-lattice relaxation time in the rotating frame that the composites exhibited some interaction. The polyurethane/SCF composite showed more changes; probably as a consequence of better physical interaction between composite components at the molecular level. This pysical interaction can promote changes in the molecular mobility due to the plasticization effect in the lattice.

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