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A solid state ^{13}C high resolution NMR study of raw and chemically treated sisal fibers

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Abstract

The use of natural fibers as reinforcement in composites is a new field of research, which has been growing in the last decades and has been given a great interest by the automotive industry. However, the lack of good interfacial adhesion is a restriction for the use of natural fiber reinforced composites for high performance applications. This problem can be overcome by treating the fibers with suitable chemicals. Mercerization, acetylation, and resorcinol/hexamethylenetetramine (R/H) treatments have been applied to sisal fibers in order to improve their adhesion in composites materials. The effect of chemical modifications on the structure and morphology of the fibers has been studied by ^{13}C VACP-MAS NMR in solid state, and SEM. The results have shown that the best treatment conditions for sisal fibers were mercerization (5% NaOH, 3 h, 50 °C) and acetylation prior to the treatment with 20/10 g/L R/H solution for 15 min.

Keywords: Natural fibers; Fiber modification; Morphology; Solid state NMR; SEM

1. Introduction

The use of natural fibers as reinforcement in composites is an important field of research that has grown in the last decades. However, the interfacial adhesion between fibers and most polymers is a problem which can be solved by treating the fibers with suitable chemicals (Bledzki & Gassan, 1999; Li, Mai, & Ye, 2000; Mattoso, Ferreira, & Curvelo, 1997; Martins & Joekes, 2003).

Among Brazilian natural fibers, sisal is a especially important fiber due to its physico-chemical and mechanical properties. Brazil is its biggest producer and more than a million of people depend on this crop (Mattoso et al., 1997). In the world, sisal is one of the most widely used natural fiber (Li et al., 2000). It is a hard fiber extracted from the leaves of sisal plant. The plant produces roughly 200–250 leaves, each containing 1000–1200 fiber bundles, which is composed of 4% fiber, 0.75% cuticle, 8% dry matter and 87.25% water (Bisanda & Ansell, 1992; Martins, Kiyohara, & Joekes, 2004; Mukherjee & Satyanarayana, 1984). The fiber extraction from the sisal plant is done by cutting and decorticating the leaves and then washing, drying and cleaning the fibers (Mattoso et al., 1997). Their length is between 1.0 and 1.5 m and their diameter is about 100–300 μm (Li et al., 2000).

The fibers are multi-cellular with small individual cells bonded together (Bledzki & Gassan, 1999; Mwaikambo & Ansell, 1999). These ultimate cells are reinforced with spirally oriented cellulose in a hemicellulose and lignin matrix. Then, the cell wall is a composite structure of lignocellulosic material reinforced by helical microfibrillar bands of cellulose. This composition plus the waxy cuticle layers render a poor interaction with the polymer matrix to application in composite materials. Besides, cellulose is a hydrophilic glucan polymer consisting of a linear chain of 1,4-β-bonded anhydroglucose units. This large amount of hydroxyl groups will lead to a very poor interface between the fiber and the hydrophobic matrix, which renders unsatisfactory mechanical properties to composites, and very poor moisture absorption resistance (Bledzki & Gassan, 1999; Li et al., 2000; Martins et al., 2004). If adhesion between cellulose fibers and matrix has to be improved, the interface properties must be modified. Different approaches have been applied to change the fiber-matrix adhesion in natural fiber-reinforced composites: chemical or physical modifications of the fiber, of the matrix, or of both components (Baiardo, Frisoni, Scandola, & Licciardello, 2002; Bledzki & Gassan, 1999; Li et al., 2000; Martins & Joekes, 2003).

Nuclear magnetic resonance (NMR) is a versatile technique to study new materials (Andrew & Szczesniak, 1995). It has

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been extensively applied to study the three major components of lignocellulosic materials—cellulose, lignin and hemicellulose (Newman & Hemmington, 1990; VanderHart & Atalla, 1984; Vignon & Gey, 1998). However, literature shows few examples applying NMR techniques (in solution or solid state) for characterizing natural fibers (Irbe, Andersone, Andersons, & Chirkova, 2001; Mello, Ferreira, Curvelo, Mattoso, & Colnago, 2000). The limitation in using NMR in solution is due to the low solubility of the lignocellulosic materials in organic and aqueous solutions (Mello et al., 2000; Stewart, Azzini, Hall, & Morrison, 1997). However, the solid-state ^{13}C NMR with cross polarization and magic angle spinning (CPMAS) has been proven to be useful to study complex organic solids. This approach overcomes the question of the solubility and eliminates the structural uncertainties associated with the dissolution process. Solid-state ^{13}C CPMAS NMR spectroscopy allows a detailed analysis of a complex organic solid, such as natural fibers, in their natural state (Hatfield, Maciel, Erbatur, & Erbatur, 1987).

In this study, sisal fibers have been submitted to mercerization, acetylation, and resorcinol/hexamethylenetetramine (R/H) solution treatments with the aim to modify the fibers surface and to increase the adhesion with a polymer or rubber matrices in composite materials. Variable-amplitude cross-polarization (VACP-MAS) ^{13}C solid state NMR (Peersen, Wu, Kustanovich, & Smith, 1993), and scanning electron microscopy (SEM) have been used to study the effect of chemical modification on the structure and morphology of the fibers.

2. Experimental

2.1. Materials

Sisal fibers, *Agave sisalana*, were harvested from the first crop. The density of the fibers was measured in a Micromeritics 1305 helium picnometer, as 1.31 ± 0.03 g/cm^3, and the diameter was measured on 150 fibers using a Mitutoyo micrometer, as 124 ± 26 μm. The chemical composition of this variety of the Brazilian sisal fibers was determined as cellulose: $75.2 \pm 0.3\%$, hemicellulose: $13.9 \pm 0.1\%$, lignin: $8.0 \pm 0.1\%$, ash: $0.87 \pm 0.01\%$ (Martin, 2001).

Analytical grade sodium hydroxide and acetic anhydride were purchased from Mallinckrodt, sulfuric acid and glacial acetic acids were purchased from Synth and J.T. Baker, respectively. Resorcinol and hexamethylenetetramine were purchased from Acros Organics. All reagents were used as received.

2.2. Chemical treatments

Prior to the chemical treatments, samples of sisal fibers were washed in distilled water at 80 ± 2 °C for 1 h. The washed sisal fibers were mercerized with 5 or 10% sodium hydroxide (NaOH), at room temperature (26 ± 2 °C), 50 or 80 °C, for a period of 1, 3 and 5 h. The fibers were rinsed and neutralized with acetic acid and dried. For the acetylation treatment, raw and mercerized sisal fibers were immersed in glacial acetic acid for 1 h at room temperature (26 ± 2 °C). They were separated and immersed in acetic anhydride containing concentrated sulfuric acid for 5 min, according to the methods reported by Chand, Verma, and Khazanchi (1989). The fibers were filtered, rinsed and dried.

The resorcinol/hexamethylenetetramine solutions (80/40, 40/20, 20/10 g/L) were prepared at room temperature. Samples of raw, mercerized and mercerized/acetylated fibers were immersed into the solution for 15 min, 1 or 2 h at room temperature, and dried in oven at 80 °C.

2.3. NMR and SEM analysis

The NMR spectra were acquired in a Varian Inova 400 spectrometer (9.4 T). The high-resolution solid-state ^{13}C spectra were obtained through the VACP-MAS technique (Peersen et al., 1993). We used a 4-μs $\pi/2$ pulse; 12.8 ms of acquisition time, 1 ms of contact time, 3 s of recycle time and a 60 kHz decoupling bandwidth. The samples were packed into zirconia type rotors of 5 mm, and spun at 8 kHz. All spectra were filtered by an exponentially decaying function (lb = 10).

For the scanning electron microscopy, the fibers were glued on the proper stub and covered with gold in a Sputter Edward S 150 B. The samples were analyzed in a JEOL scanning electron microscope, model JSM 840 A, operating at 25 kV. The fibers treated with resorcinol/hexamethylenetetramine solution were studied in a Zeiss DSM 960 instrument, operating at 20 kV.

3. Results and discussion

The ^{13}C VACP-MAS NMR spectra of the raw and treated (mercerized and mercerized/acetylated) sisal fibers are shown in Fig. 1. In the raw fiber (Fig. 1(A)), it can be seen that the most intense signals are those from cellulose carbons, that appear between 60 and 110 ppm. The signals from 60 to 70 ppm are assignment to C6, from 70 to 80 ppm to C2, C3, and C5, from 80 to 90 ppm to C4, and from 98 to 110 ppm to C1. Hemicellulose, the second major constituent of sisal fibers, is a heterogeneous group of polymeric carbohydrate, and in these samples the signal of methyl and carboxylic carbons of acetyl groups attached to hemicellulose resonate at 21 and 174 ppm, respectively. The carbohydrate signals of the xylans should be at 103 ppm (C1), 84 ppm (C4), 72 to 75 ppm (C2, C3), and 65 ppm (C5), but these lines are overlapped by the strong cellulose signals (Sterk, Sattler, & Esterbauer, 1987). The signal at 89 ppm corresponds to C4 of the highly ordered cellulose of the crystallite interiors, whereas the signal at 84 ppm is assigned to the C4 of disordered cellulose (Wikberg & Maunu, 2004). The less intense signals observed at 56 ppm, from 130 to 138 ppm, and from 156 to 159 ppm, are assigned to methoxyl and aromatic groups of lignin. The other structural elements of lignin, e.g. CHOH, CH_2OH, and C–O–C groups, are overlapped by the carbohydrate signals from cellulose (Sterk at al., 1987). These observations are in agreement with the literature (Mello et al., 2000; Newman & Hemmington, 1990; VanderHart & Atalla, 1984; Wikberg & Maunu, 2004).