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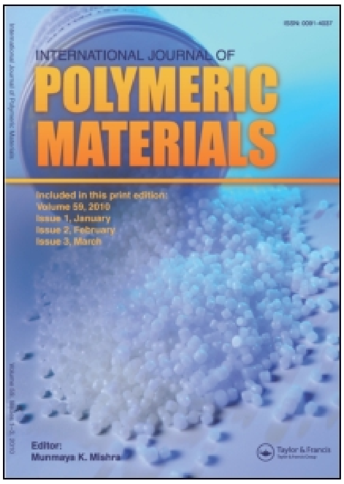

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Maria Iněs B. Tavares[a]; Carla R. De Araújo[b]; Cheila G. Mothé[b]
[a] IMAIUFRJ, Cidade Universitária, Centro de Tecnologia, Ilha do Fundo, Brasil [b] EQ da Universidade Federal do Rio de Janeiro, Brasil

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Solid State NMR Study of Natural Fibres

MARIA INÊS B. TAVARES[a,]*, CARLA R. DE ARAÚJO[b]
and CHEILA G. MOTHÉ[b]

[a]IMA/UFRJ, Cidade Universitária, Centro de Tecnologia, Ilha do Fundão, Rio de Janeiro, CP 68525, CEP 21945-970; [b]EQ da Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, CP 68522, CEP 21949-900, Brasil

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The investigation of natural fibres by nuclear magnetic resonance (NMR) showed that the sugarcane fibres are more rigid than coconut and sisal fibres. This can be explained in terms of the changes in the chemical compositions and in the chains molecular packing of the distinct natural fibres.

Keywords: Natural fibres; Solid state NMR; Carbon-13

INTRODUCTION

Natural fibres are interesting materials [1], and they have been used in composites with thermoplastic polymers [2, 3]. Generally, these fibres are found in large quantity in Brazil and their employment is not suitable, since they have been used as an industry fuel and in some kind of manufacture. Focusing the employment of these fibres as a substrate to obtain new materials with specific application, it is necessary to provide information on both chemical structure and molecular dynamic to understanding their behaviour. The main purpose of this work was to obtain a link between the chemical structure and molecular dynamic of natural fibres, like: sugarcane, sisal,

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*Corresponding author.

coconut and cotton. According to the purpose of this work, solid state nuclear magnetic resonance was chosen as an analytical method, because NMR is constituted by several techniques that have different pulse sequences, which permit to evaluate the chemical structure and molecular dynamics [4–7]. The techniques chosen were: magic angle spinning (MAS), with respect to the mobile region; cross-polarization/magic angle spinning (CPMAS); CPMAS with dipolar dephasing (CPMASDD); variable contact-time experiment and the proton spin lattice relaxation time in the rotating frame ($T_1^H\rho$), to obtain further information on molecular mobility [8–11].

EXPERIMENTAL

NMR measurements: All NMR spectra were obtained on a VARIAN INOVA 300 spectrometer operating at 75.4 MHz for ^{13}C. All experiments were done at ambient probe temperature and were performed using gated high decoupling. A zirconium oxide rotor of 7 mm diameter with Kel-F caps were used to acquire the NMR spectra at rates of 6.2 kHz. ^{13}C 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 magic angle spinning. For the dipolar dephasing, a dephasing time, τ, was 40 μs. As for the variable contact-time $T_1\rho$ values were determined from the intensity decay of ^{13}C peaks with increasing contact-times, using a computer program.

RESULTS AND DISCUSSION

The MAS ^{13}C NMR was carried out using an appropriated delay to observe the mobile region only, and no resonance signals were detected for all fibres investigated. The high-resolution CPMAS ^{13}C NMR spectra of all fibres studied are presented in Figures from 1 to 4. The assignments were done based on the cellulose lines [1, 2], because this spectra are similar. The sugarcane fibres presented four wide resolved NMR lines located at: 105.3 ppm (C1); 84.9 ppm (C4) from the crystalline region; 73.3 ppm (C2,3,5) from the amorphous

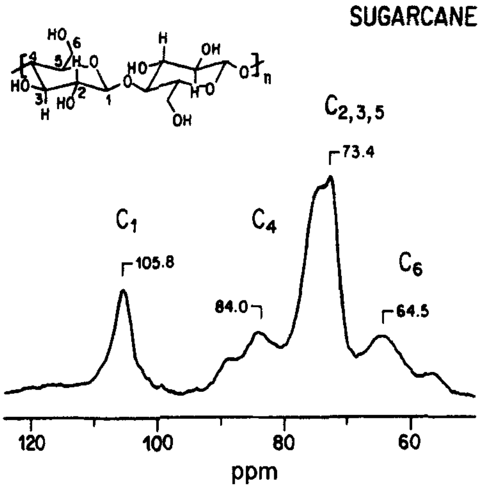

FIGURE 1 CPMAS ^{13}C spectrum of sugarcane fibre.

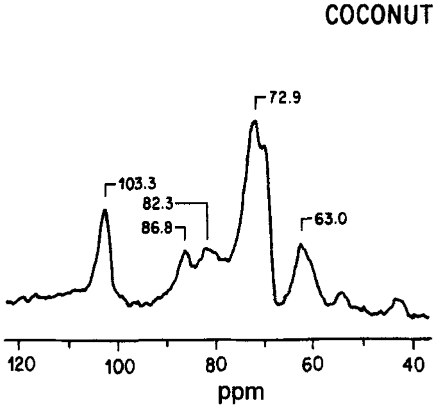

FIGURE 2 CPMAS ^{13}C spectrum of coconut fibre.

region and 64.5 ppm (C6) from the crystalline region. The sisal showed six resolved NMR resonance lines at: 105.7 ppm (C1); 89.4 ppm – 84.5 ppm (C4); 75.4 ppm – 72.9 ppm (C2,3,5) and 65.4 ppm (C6). The coconut presented five wide NMR resonance lines 103.3 ppm (C1); 85.8 ppm – 82.3 ppm (C4); 73.0 ppm (C2,3,5) and 63.0 ppm (C6). As for cotton six well resolved resonance lines were detected: 105.6 ppm

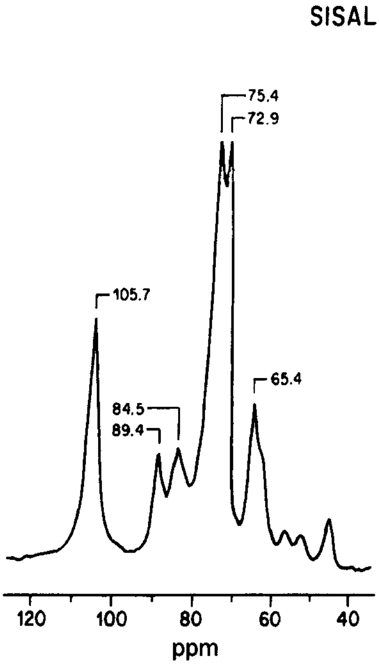

FIGURE 3 CPMAS ^{13}C spectrum of sisal fibre.

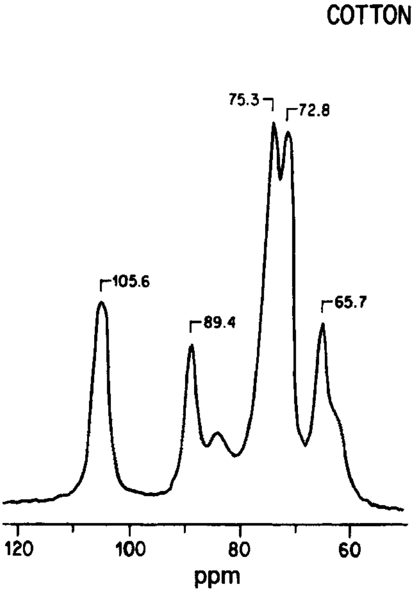

FIGURE 4 CPMAS ^{13}C spectrum of cotton fibre.

(C1); 89.4 ppm – 85.8 ppm (C4); 75.5 ppm – 73.0 ppm (C2,3,5); 65.9 ppm (C6), the resonance lines were also wide and the CH_2-O (C6) line showed a tendency to split, which can come from the mixture of conformation. The comparison of CPMAS ^{13}C NMR spectra of distinct fibres shows that each one presents a particular spectrum in spite of the basic structure be the same, due to the chains packing and molecular dynamic. It was observed that the CPMASDD ^{13}C spectra obtained were similar to registered by CPMAS technique comparing each type of natural fibre, which shows that these fibres can be homogeneous, but they are also predominantly amorphous.

The analyses of the distribution form of the decay, obtained from the variable contact-time experiment, for each type of natural fibre showed a first indication that the fibres presented different molecular mobilities, besides the basic chemical structure be similar to the cellulose. This observation corroborates with the information obtained by the routine CPMAS ^{13}C spectra. From the variable contact time experiment, the ^{13}C NMR line decays with an increase in the contact times, one can determine the proton $T_1\rho$ relaxation parameter for all resolved carbons, and their values are listed in Table I.

From the NMR relaxation data listed in Table I one can see that sisal presents a homogeneous dispersion of fibres or a better ordination and molecular chains packing. The coconut fibres presented lower chemical shifts for the ^{13}C and higher values of $T_1^H\rho$, which indicated that these fibres are packing in different way, and as the $T_1^H\rho$ parameter is sensitive to the spatial chains proximity, in this case the chains are more separated. The sugarcane fibres present higher chemical shifts and low values of $T_1^H\rho$, which confirm that these fibres are more rigid than the others and consequently their packing are also distinct. So, the values of $T_1^H\rho$, measured for all resolved carbons, for the different types of natural fibres, following the sequence described as: **$T_1^H\rho$ coconut fibre > $T_1^H\rho$ sisal fibre > $T_1^H\rho$ sugarcane fibre**. These results shows an interesting behaviour: the molecular mobility

TABLE I $T_1^H\rho$ values for the resolved ^{13}C of the natural fibres

Fibres	$T_1^H\rho(ms)$							
$\delta(^{13}Cppm)$	106.3	105.7	103.3	84.9	75.5	73.0	65.4	63.0
Sugarcane	4.1	–	–	3.0	3.1	–	–	–
Sisal	–	6.8	–	–	6.6	–	6.6	–
Coconut	–	–	7.9	–	–	8.1	–	9.0

of these fibres are different, regardless of having the same basic structure. The NMR relaxation response indicates that the packing and ordination of fibres are different and it is dependent on the nature of the fibre.

CONCLUSIONS

The responses of high resolution solid state NMR techniques show that the chain ordination and molecular packing of the fibres chains are different. This seems to be a function of the fibre nature and it is independent of the chemical structure.

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References

[1] Darveniza, M., Hill, D. J. T., Le, T. T. and Withittaker, A. K., In: *Proceedings of the 4th International Conference on Properties and Applications of Dielectric Materials*, Brisbane, Australia, July, 1994.

[2] Stael, G. C., D'Almeida, J. R. M., De Menezes, S. M. C. and Tavares, M. I. B. (1998). *Polymer Testing*, **17**, 147.

[3] Stael, G. C. and Tavares, M. I. B. (2000). *Polymer Testing*, **19**, 251.

[4] Stejskal, E. O. and Memory, J. D., In: *High Resolution NMR in the Solid State*, Oxford University Press, New York, 1994.

[5] Feng, H., Feng, Z. and Shen, L. (1993). *Polymer*, **34**, 2516.

[6] Cheng, H. N. and Lee, G. H. (1988). *Macromolecules*, **21**, 3164.

[7] Schaefer, J., Stejskal, E. O. and Buchdahl, R. (1977). *Macromolecules*, **10**, 384.

[8] Stael, G. C. and Tavares, M. I. B., Carbon-13 NMR study of the homogeneity of sugarcane fibres and poly(ethelene-co-vinyl acetate) composites, *38th ENC*, Orlando, Florida, USA, 22–27 March, 1997.

[9] Tavares, M. I. B., Castro, W. P. and Costa, D. A. (1995). *J. Appl. Polym. Sci.*, **55**, 1165.

[10] Silva, N. M. and Tavares, M. I. B. (1996). *J. Appl. Polym. Sci.*, **60**, 663.

[11] Silva, E. P. and Tavares, M. I. B. (1998). *J. Appl. Polym. Sci.*, **67**, 449.