

# CP-MAS NMR Spectra of Polyurethane-Lignin Blends

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## Synopsis

Solid-state high-resolution C-13 NMR spectra of lignin, a polyurethane, and their blend give information about phase structure and interactions in the blend. As the  $T_g$  values indicate, this is an incompatible blend, and values of the spin-lattice relaxation times in the rotating frame confirm that there are two separate phases in the blend. However, buildup of magnetization within the two phases clearly indicates some interactions between the phases, which allow transfer of magnetization from lignin to the polyurethane.

## INTRODUCTION

Most of the literature on polymer blends deals with mixing synthetic polymers with different microstructures and properties. Much less has been published on the polyblends made of synthetic and natural macromolecular compounds. A previous paper<sup>1</sup> reported results on the curing mode and mechanical performance of polyurethane (PU) based sealants blended with Kraft lignin (L) to enhance the mechanical and curing behavior of those blends. In this paper we report the results of a solid-state NMR study of a synthesized PU, Kraft lignin, and their polyblends.

Solid-state high-resolution NMR spectroscopy is a useful tool to investigate compatibility and miscibility in polymer blends.<sup>2</sup> There are many approaches in studying blends, such as measurement of different relaxation times, intermolecular cross polarization (pairs of protonated-deuterated polymers or pairs of protonated-fluorinated polymers), 2-dimensional sequences for spin diffusion studies, etc. The simplest one was proposed in 1981 by Stejskal et al.<sup>3</sup> It consists of measuring one relaxation parameter, proton spin-lattice relaxation time in the rotating frame ( $T_{1\rho H}$ ) for both individual components of the blend and comparing the values found with the  $T_{1\rho H}$  of the blend. If the two components have  $T_{1\rho H}$  values that differ from one another, and an intermediate value is found for the blend, one can assume that there is molecular miscibility within the blend.  $T_{1\rho H}$  is related to spin diffusion within the measured material. Its value can be measured on different carbon signals in the spectrum, and is the same for every carbon when the sample is chemically homogeneous. In a phase-separated blend, with the phases that exceed a few nanometers, one can actually measure two  $T_{1\rho H}$  values, for carbons in the two phases. This can happen even for a blend that is considered technically compatible (for example, having only

one glass transition temperature). Then the result of the NMR study would give evidence of immiscibility at a level lower than that observed by DSC.

There are quite a few studies in the literature already that use this principle of measuring  $T_{1\rho H}$  and obtaining information on the phase structure of different blends. For example, this approach has been used to investigate polymer blends with charge transfer interaction.<sup>4,5</sup> Lignin has been intensively investigated by CP-MAS NMR spectroscopy.<sup>6-8</sup>

## EXPERIMENTAL

All the materials are commercial products and were used as received. To obtain a formulation of a flexible PU with good deformation properties even at low temperature, characteristic for a joint sealant, a two-component PU system was used. The isocyanate component was a solvent-free high-molecular-weight aromatic prepolymer, Desmodur E 14 (Bayer), with an isocyanate content of 3.5% and an equivalent weight of 1200. The polyolic component was a polyether, Desmophen 1920 D (Bayer), with an OH content of 0.85% and an equivalent weight of 2000.

A dynamic calorimetric measurement from 0 to 200°C, with a heating rate of 5°C/min and an isothermal one at 130°C for 60 min, showed that the reaction of the system is very low in terms of curing time. Both measurements are done with a DuPont 1090 thermal analyzer for a mixture of isocyanate-polyol corresponding to an NCO : OH ratio of 1 : 1. Consequently, the curing time was controlled by catalysts (organic metal compounds), a mixture of calcium, and lead octoate. Their concentration was established for a pot life of 20–30 min. In order to increase the flexibility of the system, a plasticizer—an alkyl sulfonic ester of phenol—Mesamoll (Bayer) was also incorporated in the formulation in the proportion of 25–35% by weight. To avoid the reaction of the isocyanate component with atmospheric moisture, a water-absorbent product was added in the mixture. Baylith Paste (Bayer) was used for this purpose in proportion of 5–7% by weight. This paste is an alkali alumino silicate 50% in castor oil.

Different formulations were prepared by combining preweighed amounts of reactants at room temperature. All the materials were weighed in a dry box to avoid contact with atmospheric moisture. The paste, the plasticizer, and the catalysts were added to the polyolic component, then the polyolic mixture and the isocyanate prepolymer were stirred thoroughly under nitrogen at 1200 rpm for 5 min. The obtained product was cast within 10–20 min. A number of trials were made in order to establish the proper proportion of each component. Each trial product was analyzed after different times of casting for mechanical and adhesion properties. These results will be published in another paper.

For a typical PU formulation with an NCO : OH ratio of 1.02 : 1, L was the base polymer for blending. Polyblends with 30% L were prepared in the same way as described above. Lignin (Domtar, Cornwall, Ontario) was extracted from black liquor (pulp residue from maple, beech, and elm hardwoods) by sulfuric acid precipitation. The pH of the precipitate was adjusted with carbon dioxide to a level between 6 and 7. Lignin, which has a relatively high content of water (3.5–5%), was dried prior to use.

DSC curves for glass transition temperature measurements were obtained on a Mettler TA-3000 system. NMR spectra were recorded on a Bruker CXP-

200 spectrometer at room temperature with the sample spinning in a Doty probe at rates of ca. 4 kHz.  $T_1\rho H$  values were measured using a pulse sequence with variable contact time. This also allows observation of the magnetization buildup for different signals, at very low contact times.

## RESULTS AND DISCUSSION

Figure 1 presents the CP-MAS NMR spectra of: (a) lignin; (b) one blend of polyurethane with 30% lignin by weight; and (c) polyurethane. The spectrum of lignin is assignable according to the literature,<sup>7</sup> the most important signals being those of the aromatic methoxy carbons (56 ppm) and those of carbons 3 and 4 of the aromatic ring, where the methoxy groups are bonded (149 ppm). This is the best spectrum obtained in a series of spectra with different contact times. For the same contact time (2 ms), the polyurethane does not exhibit any carbon spectrum. However, by increasing the contact time, a spectrum is obtained as in Figure 1(c), consisting of two main groups of signals. The quasi triplet at around 75 ppm is assignable to carbons directly bonded to oxygen

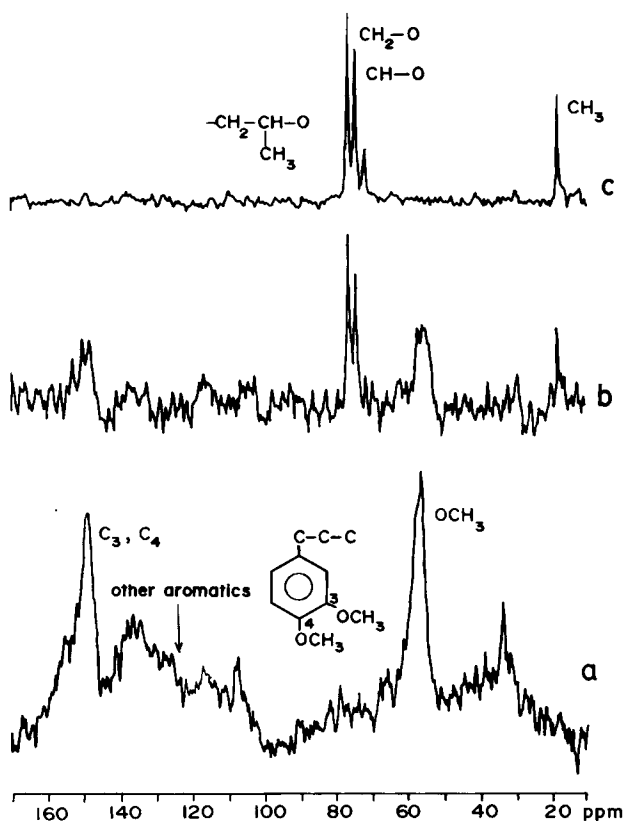


Fig. 1. CP-MAS NMR spectra of: (a) lignin, 100 scans, 2 ms contact time; (b) polyurethane-lignin blend (30% lignin by weight), 200 scans, 10 ms contact time; (c) polyurethane, 1500 scans, 20 ms contact time.

atoms, and in the soft segment they will be the methylene and the methine carbons. At 18 ppm, the signal can be assigned to the carbon-bonded methyl group of the polyether. This spectrum has been obtained with a contact time of 20 ms. Such values for the contact time are typical for elastomeric materials. Their carbon atoms tend to cross-polarize very slowly from the attached protons, due to vigorous chain motion at room temperature. There are no visible aromatic signals in this spectrum, and the explanation for this absence is a combination of low concentration of aromatic isocyanate residue in the polymer and a spread in the expected aromatic chemical shifts, which essentially buries the signals into the noise.

It is worth noting that the plasticizer also does not show any signal in the spectra. A combination of factors could account for this. First, it is assumed that the plasticizer forms a continuous phase with the "hard" segment of the polyurethane and there is little, if any, information about this phase in the spectrum. This could be due to a different cross-polarization pattern, but no signals are observed for contact times between 0.25 and 150 ms—a very wide range. A second possible explanation is similar to the one used for the isocyanate residues—a spread in chemical shifts combined with a relatively low content in the polymer. It is not clear which explanation is more appropriate, or if a combination of the two is needed. The fact is that the plasticizer is not seen in either the polyurethane or in the blend; therefore, all changes observed are due to the components that can be seen. The DSC curve indicates two glass transitions for this polyurethane, both of them well below room temperature ( $-58$  and  $-30^{\circ}\text{C}$ ). According to the DSC data, this is not a "classical" two-phase polyurethane, because the phase separation involves two elastomer regions. Lignin, with a glass transition of  $147^{\circ}\text{C}$ , will mix with this polyurethane elastomer to form a "real" two-phase system, in which one of the phases has a high glass transition temperature. The blend presents three  $T_g$ 's ( $-52$ ,  $-21$ , and  $143^{\circ}\text{C}$ ), showing a slight tendency of all values to come toward each other. This is called by some authors miscibility enhancement.<sup>9</sup> The spectrum of this blend, presented in Figure 1(b), has been obtained with a contact time of 10 ms, and shows signals for both components of the blend.

The relaxation behavior of the samples analyzed here is quite different. For lignin, the best spectrum is obtained at a contact time of 2 ms, and the signals practically disappear at contact times longer than 25 ms. The polyurethane has the maximum signal at 20 ms contact time, and the decay is not complete even after 100 ms. As the DSC curves show, the blend is a phase-separated system, and therefore one expects that the components will retain their relaxation behavior even in the blend. This can be demonstrated by the spectra of the blend. At low contact times, only the lignin signals are visible. Above 2 ms, the lignin signals start decaying, while the polyurethane signals start appearing. One can see them together at 10 ms contact [Fig. 1(b)]. Above ca. 25 ms, only the polyurethane signals are present in the spectra. Figure 2 shows the evolution of magnetization for the polyurethane signals as a function of contact time. From the slope of this curve at longer contact time<sup>10</sup> one can reasonably conclude that  $T_1\rho H$  remains constant at 70 ms for both the polyurethane and the blend (there is a higher scatter of data in the blend spectra). However, there is quite a difference in the cross polarization behavior of the polyurethane as such and in the blend. The slopes at lower contact times clearly indicate that in the

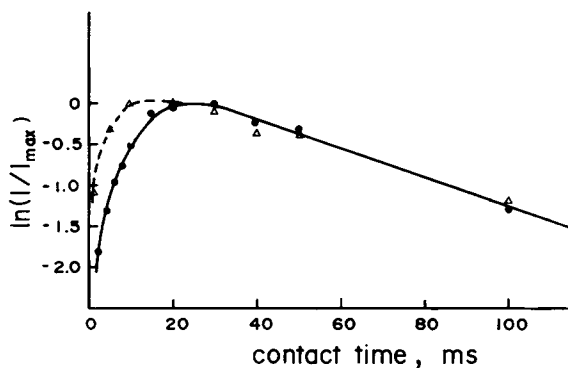


Fig. 2. Signal intensity at 76 ppm for the polyurethane as such (●) and in the blend (Δ) against contact time.

blend the polyurethane acquires magnetization much faster than in the pure state. This indicates that there must be some "communication" between the two phases of the blend, maybe at the interface, that allows the polyurethane carbons to receive magnetization from the lignin carbons.

As pointed out before, the magnetization buildup change in the polyurethane signals cannot be explained by the presence of the plastifier. This would require a change in the magnetization buildup of the plastifier and, besides, would be present even in the nonmixed polyurethane.

That lignin is the source of magnetization in polyurethane at low contact times can be demonstrated by the same magnetization curves registered for lignin (Fig. 3). Again, the  $T_{1\rho}H$  value does not change from pure lignin to the blend (16.3 ms), but the cross-polarization time (associated with the slope of the curve at low contact times) clearly indicates slower magnetization in blend lignin. This means that part of the magnetization that would normally have been used for the lignin carbons goes to the polyurethane carbons in the blend.

## CONCLUSIONS

CP-MAS NMR spectra show that in a polyurethane-lignin blend the individual components present an unchanged  $T_{1\rho}H$  value, indicating phase sep-

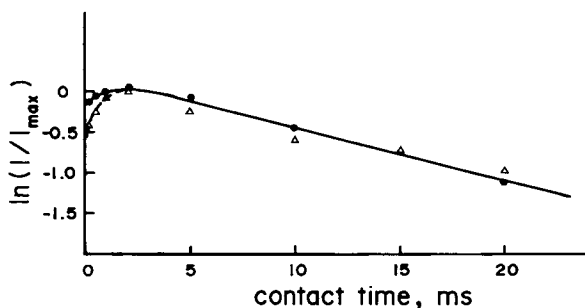


Fig. 3. Signal intensity at 56 ppm for lignin as such (●) and in the blend (Δ) against contact time.

aration. This is the same conclusion that can be drawn from the DSC measurements. However, measurements of the magnetization buildup in the two components of the blend suggest that there is some form of "compatibilization," with some carbons of the polyurethane being cross-polarized by the lignin protons. This is an ideally suited system for such studies, because one of the components is an elastomer and the other is rapidly cross-polarized under the experimental conditions. One of the conclusions of this work is that any phase-separated system (thermoplastic elastomers, for instance) could be the subject of similar investigations.

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### References

1. D. Feldman, M. Lacasse, and R. St. J. Manley, *J. Appl. Polym. Sci.*, **35**, 247 (1988).
2. V. J. McBrierty, in *Comprehensive Polymer Science*, Vol. 1, Pergamon, New York, 1988, Vol. 1.
3. E. O. Stejskal, J. Schaefer, M. D. Sefcik, and R. A. McKay, *Macromolecules*, **14**, 275 (1981).
4. A. Natansohn and A. Simmons, *Macromolecules*, **22**, 4426 (1989).
5. A. Natansohn, in *Contemporary Topics in Polymer Science*, Plenum, New York, Vol. 6, to appear.
6. J. Schaefer, M. D. Sefcik, E. O. Stejskal, R. A. McKay, and P. L. Hall, *Macromolecules*, **14**, 557 (1981).
7. W. Kolodziejski, J. S. Frye, and G. E. Maciel, *Anal. Chem.*, **54**, 1419 (1982).
8. J. J. Lindberg and B. Hortling, *Adv. Polym. Sci.*, **66**, 1 (1985).
9. P. Smith and A. Eisenberg, *J. Polym. Sci. Polym. Lett. Ed.*, **21**, 223 (1983).
10. D. E. Axelson and K. E. Russell, *Progr. Polym. Sci.*, **11**, 221 (1985).

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