# Solid-State NMR of Some Cellulose/Synthetic Polymer Blends

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ABSTRACT: Blend films of cellulose with poly(vinyl alcohol), polyacrylonitrile, poly(ϵ-caprolactone), and nylon 6 were prepared from mixed solutions in *N,N*-dimethylacetamide–lithium chloride by coagulation in a nonsolvent. From solid-state NMR relaxation measurements the scale of miscibility of the different blends was evaluated. The values lie in the range from 4 to more than 30 nm. The possible factors affecting the results are discussed.

## Introduction

Several methods have been used to characterize the miscibility of polymer blends,[1,2] including microscopy, scattering techniques, mechanical and thermal measurements, and spectroscopy. Among the spectroscopic techniques, infrared has been used extensively, in particular by Coleman and Painter.[3–6] Another spectroscopic technique that is frequently used is solid-state NMR.[7–20] Changes in line shape and/or frequency of the resonance peaks in the $^{13}C$ CP-MAS NMR spectra of the blends, in comparison to those of the unblended components, have been used as evidence of interaction between the blend components.[7,8,14] In addition, and perhaps more importantly, from NMR relaxation time measurements it is possible to estimate the scale of miscibility of a polymer pair.[7–10,13–16]

The miscibility of binary blends of cellulose (CELL), a natural polymer, with poly(vinyl alcohol) (PVA), polyacrylonitrile (PAN), poly(ϵ-caprolactone) (PCL), and nylon 6 (Ny6) (Figure 1) has been studied by melting point depression analysis and/or glass transition temperature ($T_g$) measurements.[21–23] The CELL/PVA pair was found to be miscible,[21] while CELL and PAN were shown to be miscible only in the blends with more than 50% CELL.[22] In contrast, Ny6 was completely immiscible with CELL, while PCL showed partial miscibility in blends with more than 70% PCL.[23] The purpose of this paper is to provide some insight into the scale of homogeneity that is produced upon blending the above-mentioned polymers with CELL by means of NMR spectroscopy.

## Experimental Section

The cellulose sample used was a dissolving pulp (Tamalfa A) kindly supplied by Tembec (Temiscamingue, Quebec, Canada); the molecular weight was 140 000. Polyacrylonitrile (PAN) was purchased from Polysciences; the nominal molecular weight was 150 000 (Cat. No. 3914). Poly(vinyl alcohol) (PVA) was purchased from Polysciences, Inc.; the nominal molecular weight was 78 000 and the saponification value was 99.7% (Cat. No. 15-129). Poly(ϵ-caprolactone) was purchased from Aldrich Chemical Co., Inc. (Cat. No. 18,160-9); the viscosity-average molecular weight was 36 000 according to ref 24. Nylon 6 (Ny6) was obtained from Du Pont (ZYTEL 211, Lot No. 7-48500). Lithium chloride (LiCl) and *N,N*-dimethylacetamide (DMAc) were both purchased from Aldrich Chemical Co., Inc. (Cat. Nos. 31,046-8 and 27,055-5, respectively).

A stock solution of cellulose in DMAc–LiCl was prepared in the following manner: the cellulose was swollen by subjecting it to several solvent exchanges;[25,26] 12.5 g of dry cellulose was immersed in water for 2 days, filtered, washed with methanol, and then immersed in methanol for 2 days. The cellulose was refiltered and reimmersed in methanol for an additional 2 days. Finally, the methanol was removed, and the cellulose was washed with DMAc and immersed in that solvent for 2 days. The DMAc was exchanged for a fresh aliquot two more times so that the total immersion time in DMAc was 6 days. This swollen cellulose was then immersed in 1 kg of a freshly prepared 5% LiCl solution in DMAc. After a few days of stirring at room temperature a slightly hazy solution resulted. A clear solution was obtained by filtration through a fritted-disk funnel (pore size: 40–60 μm), under full mechanical pump vacuum. From the regeneration of cellulose in an aliquot of the solution, the concentration of the filtered cellulose solution was calculated to be 1.23%. The synthetic polymers PAN, PCL, and Ny6 were dissolved in DMAc at room temperature to give 3% solutions. PVA was dissolved in a 5% DMAc–LiCl solution to give a 3% solution.

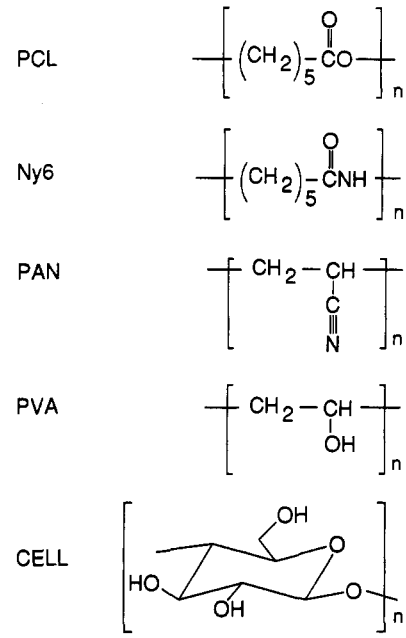


**Figure 1.** Structure of the polymers used in this study: poly(ϵ-caprolactone) (PCL), nylon 6 (Ny6), polyacrylonitrile (PAN), poly(vinyl alcohol) (PVA), and cellulose (CELL).

Blend solutions with compositions of 25:75, 50:50, and 75:25 (w/w) were prepared by mixing the appropriate amounts of the CELL solution with either the PVA, PAN, PCL, or Ny6 solutions. The blend solutions were then stirred at room temperature for 24 h. The solid homopolymer and blend samples were obtained by coagulating the homopolymer or blend solutions with absolute ethanol as described by Nishio et al.[21–23] The resulting gelatinous films were then washed several times with a fresh aliquot of ethanol. To ensure the complete removal of LiCl and DMAc from the films, the blends were steeped overnight in water (CELL/PAN, Ny6, PCL blends) or methanol (CELL/PVA blends). The

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films were then washed with methanol and cut into squares of ca. 1 mm². Finally, the samples were dried in vacuo at room temperature.

NMR spectra were obtained on a Chemagnetics, Inc., M-100 instrument with a dedicated solids accessory. Measurements of proton spin–lattice relaxation times in the rotating frame ($T_{1\rho}$) were obtained from a computer-generated best fit of the intensity of the $^{13}C$ NMR spectra to the single-exponential equation $M(t) = M(0)\exp(-\tau/T_{1\rho})$. The pulse sequence employed was $^1H\ 90°_x$–$90°_y$–$\tau$ followed by a 1-ms $^{13}C$ and $^1H$ spin-lock and acquisition of the $^{13}C$ magnetization with $^1H$ decoupling. The delay times $\tau$ ranged from 1 to 15 ms depending on the blend under investigation. At least five $\tau$ values were taken to determine each relaxation time. Proton spin–lattice relaxation times ($T_1$) were obtained from a computer-generated best fit of the intensity of the $^{13}C$ spectra to the equation for saturation recovery, $M(t) = M(0)\ [1 - \exp(-\tau/T_1)]$. The pulse sequence was $^1H\ 90°$–$\tau$–$90°$ followed by a 1-ms $^{13}C$ and $^1H$ spin-lock and acquisition of the $^{13}C$ magnetization with $^1H$ decoupling. At least 10 $\tau$ values, ranging from 100 ms to $7T_1$, were used to determine the $T_1$ of the specimens. Each plot used to obtain $T_1$ or $T_{1\rho}$ was a single exponential. All NMR measurements were performed at room temperature with 200–300 mg of sample in a Zirconia rotor with Kel-F end cap. A 90° pulse of 5 μs was employed with 800–1000 FID signal accumulations. Spinning rates were 3.5–4.0 kHz, and the Hartmann–Hahn match was adjusted before each accumulation with hexamethylbenzene.

## Results and Discussion

**CP-MAS NMR.** The interaction of blend components by hydrogen bonding has been shown to cause changes in line shape and/or shifts in the $^{13}C$ resonance frequencies in the NMR spectra of the blend components, in comparison with the spectra of the unblended components.[7,8,14] In the present blends, there is the possibility of interaction between the hydroxyl groups of CELL and the hydroxyl, nitrile, ester, or amide groups of PVA, PAN, PCL, and Ny6, respectively. If enough functionalities of the respective blend components interact to produce homogeneous mixing on a molecular scale (ca. 1 nm) and cause the electron density around the carbons bearing the interacting groups to be perturbed, then the $^{13}C$ resonance peak of these carbons will show changes in line shape and/or a chemical shift. However, for the blends that we are concerned with, no changes in line shape or frequency shifts are observed. The $^{13}C$ spectra of these blends are mere weighed superpositions of the unblended CELL and synthetic polymer $^{13}C$ spectra. As an example, Figure 2 shows the $^{13}C$ CP-MAS NMR spectrum of CELL, PVA, and the 50:50 CELL/PVA blend. On the basis of the dynamic mechanical analysis (DMA), which was summarized earlier, it is not surprising to find no change in the $^{13}C$ spectra of the CELL/Ny6 and CELL/PCL blends in comparison to those of the unblended constituents. This is because from DMA the homogeneity is monitored on a scale of 15 nm,[27] whereas it is monitored at the scale of ca. 1 nm by CP-MAS, as previously noted. On the other hand, DMA has shown that the CELL/PVA and CELL/PAN pairs are miscible over a major portion of their composition spectrum. The fact that no changes are observed in the CP-MAS spectra of these blends suggests that their scale of homogeneity is between those monitored by DMA and CP-MAS.

**Relaxation Measurements.** Neighboring protons in a molecule usually relax at identical rates because of dipolar coupling. In contrast, protons far apart or in different environments relax independently of one another. It is thus possible, from the relaxation rates of protons belonging to two different polymers, to measure the homogeneity of mixing in a polymer blend. For example, in polyblends homogeneous on the scale characterized by the relaxation time, the measured proton relaxation rate is an average of the proton relaxation rates of the constituent polymers.[8,9,13] The relaxation measurement method is complementary to DMA and CP-MAS since relaxation times are sensitive to homogeneity scales different from the scale to which the DMA or CP-MAS is sensitive.

The measured spin–lattice relaxation time ($T_1$) and spin–lattice relaxation time in the rotating frame ($T_{1\rho}$) for the pure polymers and various CELL blends are shown in Tables I–III, as well as the expected $T_1$ and $T_{1\rho}$ values for the blends as calculated from a linear relaxivity model.[13] For the unblended CELL and PVA the $T_1$ values are 1.0 and 1.8 s, respectively (Table I). In the three blends investigated, the $T_1$ values of both components are effectively the same and these values are essentially those that are expected from the linear relaxivity model. This denotes homogeneous mixing on the scale over which diffusion can take place in a time $T_1$. This scale of mixing

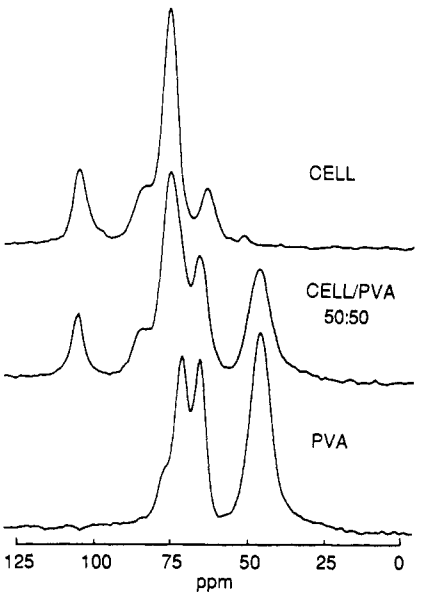


**Figure 2.** $^{13}C$ CP-MAS NMR spectra of CELL, PVA, and the 50:50 CELL/PVA blend.

**Table I**
**Proton $T_1$ and $T_{1\rho}$ Relaxation Time for CELL, PVA, and Their Blends**

| | $T_1$,[a] s | | | $T_{1\rho}$,[b] ms | | |
|---|---|---|---|---|---|---|
| blend | CELL | PVA | theory[c] | CELL | PVA | theory[c] |
| 0:100 | | 1.8 | 1.8 | | 4.3 | 4.3 |
| 25:75 | 1.6 | 1.7 | 1.5 | ND[d] | ND | 4.4 |
| 50:50 | 1.3 | 1.2 | 1.3 | ND | ND | 4.5 |
| 75:25 | 1.1 | 1.1 | 1.1 | ND | ND | 4.7 |
| 100:0 | 0.96 | | 0.96 | 4.9 | | 4.9 |

[a] Accuracy is ±10%. [b] Accuracy is ±5%. [c] Expected values based on theoretical model.[8,9,13] [d] ND: not determined.

**Table II**
**Proton $T_1$ and $T_{1\rho}$ Relaxation Time for CELL, PAN, and Their Blends**

| | $T_1$,[a] s | | | $T_{1\rho}$,[b] ms | | |
|---|---|---|---|---|---|---|
| blend | CELL | PAN | theory[c] | CELL | PAN | theory[c] |
| 0:100 | | 2.0 | 2.0 | | 15.1 | 15.1 |
| 25:75 | 1.2 | 1.3 | 1.5 | 5.4 | 15.1 | 9.5 |
| 50:50 | 0.90 | 1.0 | 1.2 | 5.0 | 15.2 | 7.1 |
| 75:25 | 0.50 | 0.60 | 1.1 | 4.6 | 15.2 | 5.7 |
| 100:0 | 0.96 | | 0.96 | 4.9 | | 4.9 |

[a] Accuracy is ±10%. [b] Accuracy is ±5%. [c] Expected values based on theoretical model.[8,9,13]

**Table III**
**Proton Relaxation Time $T_1$ (s) for CELL, PCL, Ny6, and the Respective CELL Blends[a]**

| | CELL/PCL | | | CELL/Ny6 | | |
|---|---|---|---|---|---|---|
| blend | CELL | PCL | theory[b] | CELL | Ny6 | theory[b] |
| 0:100 | | 0.54 | 0.54 | | 0.59 | 0.59 |
| 25:75 | 0.71 | 0.47 | 0.59 | 0.84 | 0.60 | 0.64 |
| 50:50 | 0.77 | 0.43 | 0.66 | 0.94 | 0.60 | 0.70 |
| 75:25 | 0.95 | 0.43 | 0.78 | 0.98 | 0.61 | 0.80 |
| 100:0 | 0.96 | | 0.96 | 0.96 | | 0.96 |

[a] Accuracy of measurement is ±10%. [b] Expected values based on theoretical model.[8,9,13]

can be readily calculated with the equation[28]

$$L^2 \approx L_0^2 t/T_2 \quad (1)$$

where $L_0$ is the distance between protons, typically 0.1 nm, $t$ the measured relaxation time, and $T_2$ the spin–spin relaxation time which, below $T_g$, is ca. 10 μs.[28] Hence, from the $T_1$ values measured for the CELL/PVA blends it is estimated that the pair is homogeneous on a scale of ca. 36 nm or less. Because $T_{1\rho}$ values are shorter than $T_1$ values, it is possible to have a measure of the blend homogeneity on a scale that is better than that given by $T_1$ measurements. Unfortunately in the present case, the respective $T_{1\rho}$ values for unblended CELL and PVA are equal within experimental error. An estimation of the scale of homogeneity in CELL/PVA blends is thus not possible from proton $T_{1\rho}$ measurements.

In contrast to the CELL/PVA pair, the $T_1$ and $T_{1\rho}$ values for unblended PAN and CELL are sufficiently different to permit an estimation of the homogeneity of the blends based on both relaxation times (Table II). In each blend the $T_1$ values of CELL and PAN are effectively the same, indicating that the blends are homogeneous on a scale of 23–35 nm as calculated with eq 1 using the $T_1$ values for the 25:75 and 75:25 blends. The $T_{1\rho}$ values of CELL and PAN in the blends were essentially equal to the values of the unblended homopolymers. There is thus no mixing on the scale over which diffusion proceeds in times characterized by the measured $T_{1\rho}$ of PAN, e.g., ~4 nm. Therefore, from the $T_1$ and $T_{1\rho}$ values, it is estimated that CELL and PAN mix on a scale between 4 and 35 nm.

Returning to the $T_1$ values of the CELL/PAN blends, it can be noted that the trend shown by the $T_1$ values for CELL in that system reveals a minimum. This is reminiscent of the relationship between the relaxation time and the rate of motion (or correlation time) described by the BPP equation[28,29] (Figure 3). Two curves represent the $T_1$/rate of motion relationship for CELL and PAN, one for each polymer. In the figure, the rate of motion increases from left to right so that the polymer with the highest $T_g$ will have the slowest rate of motion. Consequently, for CELL and PAN, the point relating the measured $T_1$ of CELL to the rate of motion characteristic of this $T_1$ will be to the left of the corresponding point of PAN since CELL has a considerably higher $T_g$ (and therefore lower rate of motion) than PAN. The two points are placed on either side of the minimum on their respective curves, with CELL closer to the minimum than PAN, because of the minimum shown by the measured $T_1$ values for CELL. In this way, as the two polymers are blended, their respective rates of motion are averaged so that the measured $T_1$ of CELL is lowered by the addition of a relatively small amount of PAN and then increases again when the proportion of PAN in the blend becomes more important; at the same time the measured $T_1$ of PAN decreases along the curve describing its motion as it is blended with CELL. The trends of the measured $T_1$ for CELL and PAN are shown schematically in Figure 3. It is seen that the representation reflects well the trend of the measured data. This suggests that the relaxation rate of CELL decreases (or correlation time increases), when CELL is added to PAN until a composition in the range between 50:50 and 75:25 in CELL/PAN is reached, and then the relaxation rate decreases. This sudden decrease appears to be consistent with the trend in $T_g$ which rises rapidly in the composition range of 60:40 to 100:0 CELL/PAN;[22] i.e., the motions become more restricted as $T_g$ increases. To arrive at a more detailed understanding of these effects, further experimental work will be required.

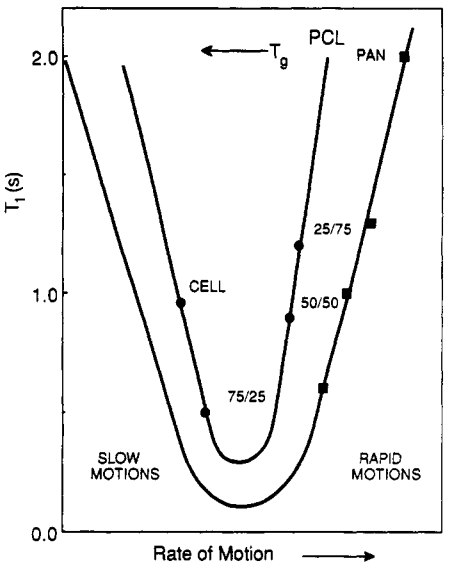


**Figure 3.** Schematic representation of the theoretical dependence between $T_1$ and the rate of motion for CELL (circles) and PAN (squares). The points and the curves are positioned to agree with experimental data.

The $T_1$ relaxation times for PCL, Ny6, CELL, and their blends are displayed in Table III. For the two types of blends, CELL/Ny6 and CELL/PCL, the miscibility is poor as indicated by the fact that there is little variation in the $T_1$ values of CELL or Ny6 in the CELL/Ny6 blends in comparison with the $T_1$ values of the respective pure components. Each polymer in the blend thus relaxes independently of the other, so that no mixing takes place on a scale lower than ca. 32 nm (based on the $T_1$ value of CELL in the 25:75 CELL/Ny6 blend). On the other hand, the $T_1$ values of PCL in its blended and unblended states are essentially the same, while the $T_1$ of CELL is slightly lowered by the increasing amount of PCL. This slight depression of the $T_1$ of CELL is an indication of mixing, but the fact that no averaging between the $T_1$ values of CELL and PCL takes place is a sign that the miscibility of the two polymers is poor, although it is slightly better than for the CELL/Ny6 pair, i.e., ~27 nm, as calculated with the $T_1$ of CELL in the 25:75 blend.

It should be noted that the miscibility of the synthetic polymers with CELL, as obtained from NMR relaxation measurements, follows the order PAN, PVA > PCL > Ny6. The miscibility of PAN and PVA with CELL cannot be readily differentiated because we could not measure the $T_{1\rho}$ values for the CELL/PVA blends; nonetheless, the order of miscibility agrees well with the one deduced from the comparison of the dynamic mechanical analysis (DMA) of the different blends.[21–23] This suggests that the two methods are equally valid to establish an order of miscibility and that they can be used independently. However, by combining NMR and DMA results it is

**Table IV**
**Scale of Homogeneity of the Various CELL Blends Based on CP-MAS, Relaxation Measurements, and DMA[a]**

| composition | domain size in blend, nm | | | |
|---|---|---|---|---|
| | CELL/PVA | CELL/PAN | CELL/PCL[e] | CELL/Ny6[e] |
| 25:75 | 15–39[b] | 15–35[b] | ~27 | >31 |
| 50:50 | 15–36[b] | 15–31[b] | ~27 | >31 |
| 75:25 | 1–15[c] | 4–15[d] | >28 | >31 |

[a] Dynamic mechanical analysis.[21-23] [b] Based on $T_1$ and DMA. [c] Based on CP-MAS and DMA. [d] Based on $T_{1\rho}$ and DMA. [e] Based on $T_1$ and CELL in the blend.

possible to estimate more precisely the domain size produced upon blending two polymers; hence, blends can be looked at on a scale of ~1 nm (CP-MAS), ~4 nm ($T_{1\rho}$), 15 nm (DMA), and 25–40 nm ($T_1$). The estimations of the domain size in the 25:75, 50:50, and 75:25 CELL/synthetic polymer blends are shown in Table IV.

It is interesting to consider the possible sources of the disparity in the miscibility behavior of the synthetic polymers used in this study, all of which are capable of forming hydrogen bonds with CELL. The degree of polymer self-association is certainly one important factor; CELL, possessing an abundance of hydroxyl groups, is self-associating, as are Ny6 and PVA, while PCL and PAN are not self-associating. Coleman and Painter et al.[30,31] have pointed out that miscibility is favored when a polymer strongly self-associating through hydrogen bonding is blended with a weakly self-associating polymer capable of engaging in hydrogen bonding. This aspect is recognized when the miscibility of the CELL/Ny6 pair is compared to that of the CELL/PCL pair. The mixing scale produced upon mixing the two self-associating polymers CELL and Ny6 is larger than 32 nm. This is not a sign of good miscibility. When Ny6 is replaced with PCL in the CELL blends the miscibility is somewhat enhanced; these two polymers are semimiscible on a scale of ~27 nm. The miscibility with CELL is thus improved by removing the possibility of self-association in the synthetic polymer, i.e., replacing the N–H group of the amide by an oxygen. Self-association is, however, one among other factors that can possibly influence the miscibility of synthetic polymers with CELL; PVA, which is also self-associating, shows much better miscibility with CELL than both Ny6 and PCL. It is thus possible that the number of interacting groups per methylene unit in the repeat unit of the synthetic polymer may be important. This would explain why PAN and PVA, which possess more interacting groups per methylene unit than PCL or Ny6, show better miscibility with CELL than the latter polymers. If this is true, then it would be expected that polyesters and nylons with a higher number of interacting groups per methylene unit would show better miscibility with CELL than PCL or Ny6. A similar hypothesis has been tested for a series of homologous polyesters blended with various polymers,[32-34] where it was found that the miscibility state of the blends varied appreciably with the number of ester groups per methylene unit in the polyester. Therefore, it would be interesting to compare the miscibility behavior of synthetic polymers such as nylon 4, nylon 46, poly(ethylene adipate), poly(ethylene succinate), and poly(butylene adipate) with CELL.

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**Registry No.** PAN (homopolymer), 25014-41-9; CELL, 9004-34-6; PVA (homopolymer), 9002-89-5; PCL (homopolymer), 24980-41-4; PCL (SRU), 25248-42-4; Ny6, 25038-54-4.