Effects of Resole Phenol Adhesives on the Crystallinity of Cellulose

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Synopsis

Resole phenolic resins are widely used for gluing wood structures. Solid state ^{13}C-NMR and wide angle X-ray scattering experiments show that a typical resole adhesive disrupts some of the crystallinity of the cellulose. Several explanations are offered for this observation. It is possible that this effect is connected with the adhesive action of the phenolic polymer. If this is so, then measurements of the type described here could be used to understand the adhesion better and to develop better wood glues.

INTRODUCTION

Resole phenolic adhesives are widely used for gluing wood structures, where they exhibit superior durability under moist conditions. The strength of the adhesive bonds that are produced results from hydrogen bonding and, perhaps, other chemical reactions between the adhesive and cellulose as well as mechanical interlocking following cure of adhesive that has penetrated into the micropores of the wood.[1] Here we report NMR and X-ray evidence that cure of a resole phenolic in contact with cellulose decreases the crystalline character of the latter polymer. This phenomenon may be connected with the mechanism of adhesion of the two materials. If that is the case then measurements such as those described here could be used to understand the adhesion better and to develop superior wood glues.

High resolution solid-state ^{13}C CP-MAS NMR techniques have been employed to study the structures of various kinds of cellulose. The application of these techniques to cellulose chemistry have been reviewed recently.[2] A number of studies have concentrated on the C-4 and C-6 carbons of the β-1,4-anhydroglucose basic structural unit of cellulose. The solid-state ^{13}C CP-MAS spectra of many kinds of natural cellulose show both narrow and broad peaks for C-4 and there are also multiplets found in the narrow component. The origins of these narrow and broad peaks are discussed in the

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original literature.[3-9] Studies of cellulose morphology have been supplemented recently by proton NMR work.[10]

Whatman no. 1 filter paper was used as the source of cellulose in this work to avoid complexity due to the presence of natural impurities, such as lignin, in wood. A fully deuterated resole was prepared. The deuterated resin does not crosspolarize and the deuterium dipolar broadening is not decoupled in the ^{13}C CP-MAS measurement. Therefore, only the signals from the cellulose components will be observed in the CP-MAS spectrum of the deuterated resin and paper composite. By comparing the spectra of the resin-treated composite to that of the blank-treated paper, it is possible to observe changes in the morphology of cellulose after interaction with phenolic adhesive.

EXPERIMENTAL

The fully deuterated resole was prepared according to Steiner[11] with some modifications. All chemicals used were fully deuterated analytical grades (with minimum 98% D). To a 100 mL three-necked flask equipped with a reflux condenser, a thermometer, and a magnetic stirrer, 5 g phenol-d_6, 3.19 g paraformaldehyde-d_2 (formaldehyde/phenol mole ratio = 2), 0.8 mL (1.06 g) 40% sodium hydroxide-d in D_2O (catalyst/phenol mole ratio = 0.2), and 6 g D_2O were added and heated to 60°C in a heating mantle. The reaction is exothermic. The reaction mixture was then kept at 70°C for 2.5 h. As much water as possible was removed at water aspirator pressures and temperatures up to 45°C. The neat, deuterated resole had a pH of 10. Whatman no. 1 filter paper cut to 3 × 5 cm size was soaked in the neat resole at room temperature for 2 min. Excess adhesive was removed from the soaked filter paper with blotting paper. The resole-filter paper was then cured as a thin film (0.3 mm) between polytetrafluoroethylene parting sheets in a press at 160°C under 287 MN/m^2 pressure either for 2 or for 16 min. The cured composite became transparent. The amount of each resin added-on was about 41%. As a reference, another filter paper was blank-treated under identical conditions except for the absence of the phenolic adhesive.

The cured composite and the reference were ground and sieved to pass a 100-mesh screen for ^{13}C CP-MAS and powder X-ray diffraction measurements. All ^{13}C CP-MAS spectra were obtained at 50.3 MHz in a Kel-F spinner with spinning rate of 2.2 kHz. The detailed CP-MAS procedure has been reported elsewhere.[12]

The procedures of powder X-ray diffraction reported by Segal et al.[13] were used to estimate the relative crystallinity of the cellulose. A Philips powder X-ray diffractometer (PW 1050) was operated with focusing technique, with enough sample to fill the sample holder (1 × 15 × 20 mm^3) uniformly.

RESULTS AND DISCUSSION

[13]C CP-MAS

A typical ^{13}C CP-MAS spectrum of the filter paper is shown in Figure 1. According to earlier reports, the sharp and narrow C-4 peak is associated with the crystalline components of the cellulose; the broad shoulder C-4′ probably reflects both the amorphous (disordered regions) and the surface of crystalline
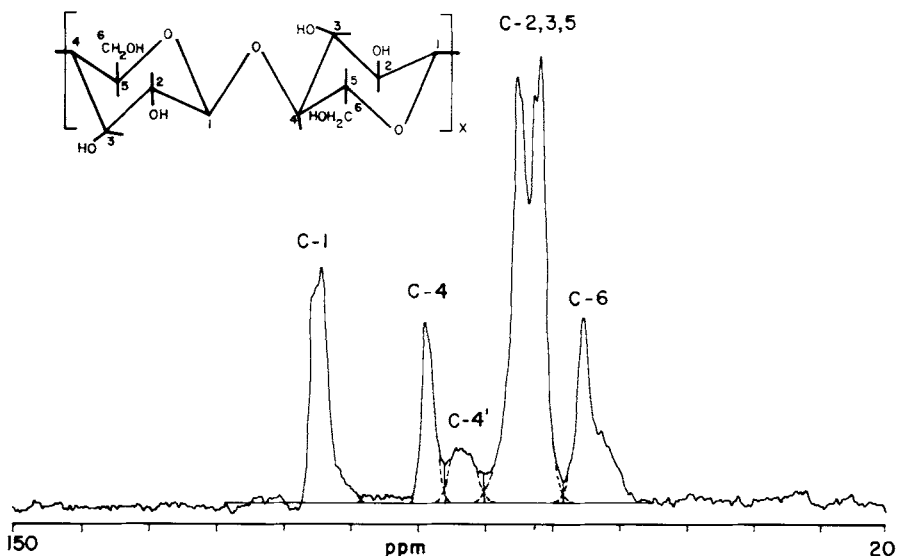
Fig. 1. ^{13}C CP-MAS spectrum of Whatman no. 1 filter paper. The repeating unit of β-1,4-anhydroglucose is shown. Contact time here was 1.5 ms, with a delay time of 10 s, and 1000 scans.

components. To quantify the area of any peak relative to that of C-1, one must resolve the absorbances to the baseline. This can be accomplished as shown by the dashed lines in Figure 1, by assuming Lorentzian curve shapes, or else by dividing the peak areas as shown using solid lines. Experimentally, the results from these two methods were found to be almost the same. Therefore, the latter method was used for all peak area measurements. Areas were estimated with a planimeter.

The optimum cross-polarization contact time for blank filter paper was also determined. The relative intensity of all carbon peaks varies with contact time slightly as shown in Table I. None of the relative intensities agrees perfectly with the expected values. We are less interested here in absolute levels of crystallinity than in changes resulting from interactions with the resole adhesive. Therefore, a single experimental condition for the ^{13}C CP-MAS

TABLE I
Effect of Contact Time in the ^{13}C CP-MAS Experiment on the Relative Intensity
of All Carbon Peaks of Blank-Treated Filter Paper

| Contact time[a] | Relative intensity | | | | Relative crystallinity $\left(\dfrac{C\text{-}4}{C\text{-}4 + C\text{-}4'} \right) \times 100\%$ |
	$\dfrac{C\text{-}4}{C\text{-}1}$	$\dfrac{C\text{-}4'}{C\text{-}1}$	$\dfrac{C\text{-}2,3,5}{C\text{-}1}$	$\dfrac{C\text{-}6}{C\text{-}1}$	
1 ms	0.56	0.37	3.31	0.89	60%
1.5 ms	0.57	0.31	3.14	1.03	65%
2.5 ms	0.62	0.28	3.17	0.92	69%
(Expected value)	(1.00)[b]	—	3.00	1.00	60–90%

[a] Delay time 10 s, number of scans 1000, line broadening 10.
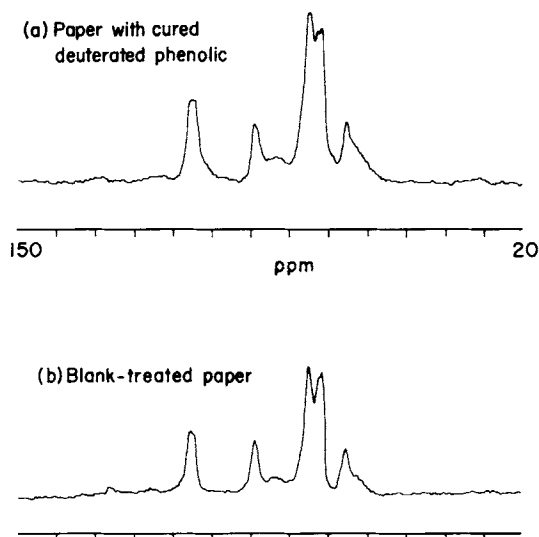[b] Sum of (C-4/C-1) and (C-4'/C-1).

Fig. 2. ^{13}C CP-MAS spectra of blank-treated cellulose and that cured with a deuterated phenolic resin.

measurements was used; i.e., contact time 1.5 ms, delay time 10 s, and number of scans 1000.

The ^{13}C CP-MAS spectra of both deuterated resin-treated and blank-treated papers are shown in Figure 2. Firstly, it is immediately evident that the intensity of C-4 peak decreases while that of C-4′ peak increases in the resin-treated paper. Secondly, all carbon peaks are generally broadened in the resin-treated paper as shown in Table II from the half-height peak width data. The replicate measurements recorded in this table were made about 1

TABLE II
Summary of the ^{13}C CP-MAS Results on the Relative Crystallinity
of Deuterated Phenolic-Treated and Blank-Treated Filter Papers

Sample	Half-height peak width (Hz)			Relative intensity				Relative crystallinity
	C-1	C-4	C-6	$\dfrac{\text{C-4}}{\text{C-1}}$	$\dfrac{\text{C-4}'}{\text{C-1}}$	$\dfrac{\text{C-2,3,5}}{\text{C-1}}$	$\dfrac{\text{C-6}}{\text{C-1}}$	
Blank-treated (2 min cure)	165	127	178	0.57	0.31	3.14	1.03	65%
Phenolic-treated (2 min cure)	180	150	258	0.45	0.40	3.09	0.84	53%
Phenolic-treated (16 min cure)	171	133	230	0.62	0.48	3.13	0.81	56%
Replicate experiment								
Blank-treated (2 min cure)	148	104	118	0.57	0.35	2.96	0.90	62%
Phenolic-treated (2 min cure)	163	133	184	0.49	0.43	2.93	0.89	54%
Phenolic-treated (16 min cure)	163	126	178	0.53	0.35	2.85	0.76	60%

month apart; therefore, the instrument broadening and measurement errors might account for the differences in the half-height peak width for repeated measurements.

In ^{13}C NMR of solids, one expects to observe narrow resonances for crystalline regions of polymers, while amorphous or paracrystalline regions will exhibit broader peaks. Both pieces of evidence—peak areas and half-height peak widths—clearly indicated a significant difference in the crystallinity of blank-treated and resin-treated cellulose. Because of the limited data and uncertainty in the optimum CP contact time, it is not possible to draw firm conclusions about the effect of curing time on this change of morphology.

If one assumes that the size of the resole molecules prevents penetration of the resin inside the microfibrils of cellulose, the increase of the C-4′ must be associated with the disruption of the surface of the crystalline regions by the phenolic adhesive. This observation agrees very well with the earlier findings by other researchers.[5,6]

An attempt was made to identify the nature of the cellulose-resole reaction by using CP-MAS techniques with a conventional (undeuterated) phenolic resin. This was not successful because of the plethora of carbon resonances within the possible range of chemical shifts.

Powder X-Ray Diffraction

In X-ray diffraction, Ruland's method[14] has been widely accepted in the determination of crystallinity from the diffractogram. Although the quantitative value of crystallinity determined by the simpler method of Segal et al.[13] may be highly criticized, the method is adopted here, since we are more interested in the change in crystallinity rather than the absolute levels of crystallinity. The results are shown in Figure 3 and Table III. In order to correct the intensity for the presence of amorphous phenolic resin, it is necessary to subtract the corresponding intensity contributed by the resin from the intensity of the paper. Thus, the amount of resin added-on must be known for this correction. For instance, taking the data from Table III with samples cured for 2 min:

the relative crystallinity of blank-treated paper

$$= \frac{I_{cr} - I_{am}}{I_{cr}} \times 100\% = \frac{(43.5 - 2)}{43.5} \times 100\% = 95.4\%$$

where I_{cr} is the maximum intensity related to crystalline regions of the paper (peak height in arbitrary unit) at $2\theta = 22.5°$ and I_{am} is that of noncrystalline regions in the same unit at $2\theta = 18°$. The intensity of the resin added-on on the paper would be

$$14.3 \times 0.408 = 5.8$$

(intensity of the resin-treated paper at $2\theta = 18°$)

$$= \text{(intensity of the resin-treated paper composite at } 2\theta = 18°)$$

$$- \text{(that of the resin at } 2\theta = 18°)$$
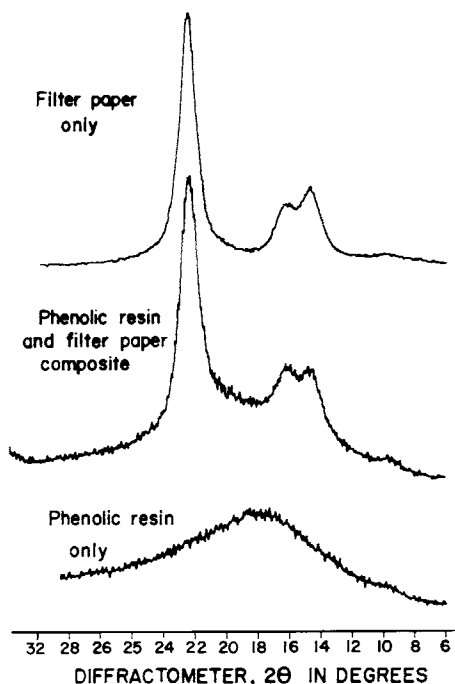
$$= 16 - 5.8 = 10.2$$

Fig. 3. Typical powder X-ray diffraction traces on resin-treated and blank-treated papers, along with that of the cured resin alone. (All patterns are not to the same scale.)

Similarly, the intensity of the resin-treated paper at $2\theta = 22.5°$

$$= 62 - 4.1 = 57.9$$

Therefore, the relative crystallinity of resin-treated paper that has been cured for 2 min is

$$\frac{57.9 - 10.2}{57.9} \times 100\% = 82.4\%$$

TABLE III
Summary of Powder X-Ray Diffraction Results

Curing time	Blank-treated paper intensity (arbitrary unit)			Phenolic resin intensity (arbitrary unit)		% Added on	Resin-paper composite intensity (arbitrary unit)			Change of CI
	I_{cr}	I_{am}	CI	I_{cr}	I_{am}		I_{cr}	I_{am}	CI	
2 min	43.5	2	95.4%	10 (4.1)[a]	14.3 (5.8)[a]	40.8%	62 (57.9)[b]	16 (10.2)[b]	82.4%	13.0%
Repeat experiment	40	1.5	96.3%	10 (4.1)	14.8 (6.0)		66 (61.9)[b]	16.5 (10.5)[b]	83.0%	13.3%
16 min	42	2.5	94.0%	10 (4.1)	15.5 (6.4)	41%	50 (45.9)[b]	12 (5.6)[b]	87.8%	6.2%
Repeat experiment	42.5	2.7	93.6%	10.5 (4.3)	15.5 (6.4)		49.5 (45.2)[b]	11 (4.6)[b]	89.8%	3.8%

[a] Intensities corrected with the corresponding resin added-on %.
[b] Intensities corrected for resin contribution.

Since the ^{13}C CP-MAS NMR and powder X-ray diffraction techniques depend on different physical phenomena, the relative crystallinities obtained by the methods are different. It is clearly shown in Table III that the relative crystallinity is significantly very different for the resin-treated and blank-treated cellulose. This evidence supports the results from ^{13}C CP-MAS measurements that the phenolic adhesive disrupts some of the cellulose crystallinity.

Phenol–Cellulose Interactions

The crystallinity of cellulose has been shown to be affected by the presence of the amount of water present.[15-19] This effect has been studied by DSC,[16,17,19] NMR,[15,18] and X-ray.[17,19] CP-MAS NMR results[18] show that, with increasing water contents, resonance lines narrow and clearer splitting of the C-4 and C-6 into crystalline and noncrystalline components is observed. This has been attributed to the ordered noncrystalline chains undergoing distortion upon drying and relaxation or rearrangement back to the ordered state upon absorbing water. X-ray diffraction study[19] gives similar results. The increase in crystallinity with increase in water content has also been attributed to the transformation of the molecular chains in the amorphous region into a more ordered state upon absorbing water.

In the preparation of resole–cellulose composites, during curing at 160°C, water (free and bound) is expelled from the cellulose. Upon completion of the reaction and cooling, the crosslinked thermoset may form an impervious surface barrier encapsulating the cellulose and preventing reabsorption of water by the cellulose. This could result in a decrease in crystallinity for the resin-treater paper compared to the blank-treated cellulose.

Celluloses undergo transformation from cellulose I to cellulose II readily in the presence of alkali.[20,21] NaOH concentration as low as 2% ethanolic system results in significant difference in the CP-MAS NMR, with broadening and flattening of peaks. However, WAXS patterns may indicate a cellulose I lattice without a significant difference in supermolecular order. The resole prepared under alkaline conditions may have most of the NaOH in the form of sodium phenoxide, but the high pH of 10 may itself be sufficient to cause alkaline transformation of cellulose I to cellulose II. At short curing time of 2 min, this transformation may not be significant. With increasing curing time, transformation together with recrystallization may occur. Hence for short curing time, a decrease of crystallinity, as observed here, could be due to the effect of exclusion of water. However, with longer curing times, transformation/recrystallization due to the alkaline nature of the phenolic resin could result in an increase in overall crystallinity compared to the composite cured with shorter time.

CONCLUSIONS

Both the ^{13}C CP-MAS and powder X-ray diffraction measurements have shown the resole adhesive disrupting some of the cellulose crystallinity when the resin is cured at high temperature under pressure. This could be due to the exclusion of absorbed water on the crystalline cellulose and transforma-

tion and/or recrystallization of cellulose I and cellulose II in the presence of the alkaline phenolic resin. Alternatively, the observed description of crystalline order could be connected with the adhesive action of the phenolic resin. Further studies are underway on the effect of water content, alkalinity, and resole structure on the cellulose crystallinity, and the relationship of this phenomenon with the mechanical properties of the cured composites.

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