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Structure and Dynamics of Starch Cross-Linked with Urea–Formaldehyde Polymers by ^{13}C CP/MAS NMR Spectroscopy[†]

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ABSTRACT: Solid-state ^{13}C CP/MAS studies of starch cross-linked with urea–formaldehyde prepolymer (St–UF) have been conducted to elucidate its structure and dynamics. ^{13}C NMR spectra and spin–spin relaxation times (T_2) were obtained for various St–UF samples having different degrees of cross-linking. Line width and T_2 measurements of starch carbons show that a maximum degree of cross-linking is obtained at a urea to starch (w/w) ratio of 0.6. Increasing the urea to starch ratio beyond 0.6 leads to competing self-condensation of dimethylolurea. These results also establish that chemical cross-linking occurs through the primary hydroxyl groups located at the C-6 position of starches.

Introduction

Starch is an important naturally occurring polymer which finds wide application in diverse areas of polymer science.[1–6] Frequently starch is chemically modified to confer additional properties such as hydrophobicity, porosity, functionality, formability, and mechanical integrity. One of the common chemical modifications of starch is cross-linking, achieved using the hydroxyl functionality and suitable cross-linking agents.

The structure of carbohydrates has been studied by ^{13}C NMR in solution.[7,8] They include inositols, aldopyranoses, and methyl glucoside, and continuous-wave magnetic resonance has been used to study aryl glucosides, glucobioses, and oligosaccharides. More recently, Gidley and Brociek[9] reported a study of starch and related compounds in the solid state using high-resolution ^{13}C CP/MAS NMR spectroscopy. They observed that the C-1 and C-4 carbons (i.e., sites involved in glucosidic linkages) show large chemical shift displacements between amorphous and crystalline materials including substantial conformational differences. The former is a single chain whereas the latter is a double-helical conformation.

Solid-state NMR is a powerful tool for the study of the structure and dynamics of cross-linked polymers.[10] In view of our current interest in the application of chemically cross-linked starch as an encapsulating matrix for controlled-release applications,[11] we undertook a detailed ^{13}C CP/MAS NMR study of urea–formaldehyde (UF) resin cross-linked starch. Although ^{13}C CP/MAS studies of UF resins have been previously reported,[12] there have been no prior reports on the structure and dynamics of cross-linked starch in the literature.

Experimental Section

Materials. Maize starch powder received from Anil Starch Products, India, containing 72% amylopectin and 28% amylose was used. Urea (extra pure), formaldehyde as a formalin solution (37–40%) (S. D. Fine Chemical Pvt. Ltd., India), and formic acid (Loba Chemie Industrial Co., India) were used as received. Samples of starch cross-linked with urea-formaldehyde (St–UF) were synthesized with different degrees of cross-linking.[11] Degree of cross-linking (X) was expressed as the ratio (w/w) of urea to starch (U/S). The urea to formaldehyde mole ratio in all cases was kept at 1:1.5. Dried granules of mesh size −10+25 were ground in an analytical mill, and a fraction −100+170 was generally used for NMR analysis. Prior to analysis, St–UF samples (U/S = 0.2 and 0.8) and UF resin alone were refluxed in 50% methanol–water mixture for 4 h to extract any low molecular weight material. Samples used for NMR studies are listed in Table I.

Measurements. ^{13}C CP/MAS NMR spectra were measured with a Bruker MSL-300 NMR spectrometer (75.5 MHz) with a CP/MAS accessory at room temperature (25 °C). The sample (ca. 200 mg) was placed in a cylindrical ceramic rotor and spun at 3 kHz. Contact time and repetition time were 2 ms and 5 s, respectively. Spectral width and data points were 27 kHz and 8 K, respectively. The ^1H field strength was 2.0 mT for both the CP and decoupling processes. The number of accumulations were 160–200. ^{13}C chemical shifts were calibrated indirectly with reference to the higher field adamantane peak (29.5 ppm relative to tetramethylsilane ($(CH_3)_4Si$). The Hartmann–Hahn condition was matched using adamantane in each case. The experimental error for the chemical shifts was within ±0.1 ppm for the broad peaks as described.

The spin–spin relaxation times (T_2) were obtained using the $90°–\tau–180°$ pulse sequence, the amplitude of the spin echo (occurring at 2τ) being measured as a function of pulse separation. Care was taken to ensure that there arose no contribution to the T_2 decays from self-diffusion in the field gradient caused by inhomogeneities in the static magnetic field. Again, plotting $A(t)/A(0)$ versus delay time τ, the slope $-1/T_2$ was calculated by using a least-squares method.

X-ray diffraction patterns were obtained using nickel-filtered Cu Kα radiation on a Philips X-ray unit (Philips PW 1730 generator).

Results and Discussion

Structure of Pure and Gelatinized Starch. The ^{13}C CP/MAS spectra of pure and gelatinized starch are shown in Figure 1a,b. The chemical shifts were assigned on the basis of previous findings[13,14] (Table II). The peaks at 98.7, 99.7, 100.9, and 102.3 ppm for pure starch are assigned as C-1. The C-1 carbon of pure starch is the only carbon with two directly attached oxygen atoms and hence resonates at lower field relative to the other five carbons. The observed multiplicity in the pure starch may arise from the symmetry of packing of the double helixes in the A type structure.[9] In A type starch, C-1 splits into a triplet of identical intensity. This is not observed here due to the contribution from crystalline and amorphous material in native maize starch. The sharp peak at 100.9 ppm is due to the crystalline component of the C-1 line, while the downfield shoulder at 102.3 ppm and upfield shifts at 99.9 and 98.7 ppm are both assigned to amorphous components.

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Table I
NMR Samples

no.	sample desig	U/S (w/w)	no.	sample desig	U/S (w/w)	no.	sample desig	U/S (w/w)
1	B0[a]		5	B2	0.4	9	B4A[d]	0.8
2	B0G[b]		6	B2A[d]	0.4	10	B4(E)[c]	0.8
3	B1	0.2	7	B3	0.6	11	UF[c]	
4	B1(E)[c]	0.2	8	B4	0.8			

[a] Pure starch. [b] Gelatinized starch. [c] Extracted in MeOH–H_2O. [d] Particle size −40+100.

The crystalline part arises from the amylopectin and amorphous regions from branch points of amylopectin and long chains of linear amylose. This observation is supported by XRD (Figure 3a), which indicates 63% amorphous character. The major signal intensities in the spectrum (Figure 1a) of pure starch in the range 68.0–78.0 ppm are due to the C-2, C-3, and C-5 carbons. The peak obtained at 81.2 ppm is assigned to the C-4 carbon. It is a very sharp peak and may provide direct evidence for the presence of a glucosidic linkage.[13] Furthermore, the C-6 carbon appears at 61.4 ppm and is more efficiently cross-polarized than the other five carbon resonances; i.e., T_{CH} is shorter, presumably because C-6 is a methylene carbon whereas the others are methine carbons.[9]

The chemical shifts obtained for gelatinized starch in Figure 1b are consistent for all carbons except C-1. The C-1 of gelatinized starch shows a broad peak at 102.2 ppm which is due to its amorphous nature. Apparently, loss of crystallinity occurs during the process of gelatinization. XRD of gelatinized starch (Figure 3b) also supports this observation.

Structure of Extracted Urea–Formaldehyde. The spectrum of extracted UF resin is shown in Figure 1x. The peaks are assigned on the basis of literature data[12] and are listed in Table II. The spectrum shows a number of sharp peaks (47.0–80.0 ppm region) which arise from the methylene resonances in different environments. The carbonyl peak appears at ~159.0 ppm. The signal for low molecular weight compounds was found to be absent, indicating that the extraction was efficient.

^{13}C CP/MAS of Cross-Linked St–UF. Figure 1c–f shows ^{13}C CP/MAS NMR spectra of St–UF polymers with varying degrees of cross-linking, namely, $X = 0.2$, 0.4, 0.6, and 0.8. The assignments of chemical shifts are given in Table II. To observe whether any overlapping of sidebands with chemical shift signals in the ^{13}C CP/MAS spectrum occurred, two spectra of sample B1 were obtained at different rates of magic angle spinning (i.e., 4.5 and 5.0 kHz). It was confirmed that in all cases no overlapping of sidebands were signal due to chemical shifts occurred. Samples B2A and B4A with a particle size −40+100 mesh (Figure 2m,n) show chemical shifts similar to those of samples B2 and B4 (particle size −100+170 mesh), indicating practically no effect of particle size in the ^{13}C CP/MAS NMR spectrum.

A comparison of Figure 1a with Figure 1b–f shows that the chemical shifts obtained upon gelatinization and cross-linking of starch with UF are similar to those of pure starch except for the C-1 and C-6 carbons (Table II). The signal at 100.9 ppm for C-1 transforms from a multiplet to a broad singlet with an upfield shoulder as in the case of gelatinized starch and cross-linked St–UF samples. The shoulder is more pronounced in B4. During gelatinization intra- and interhelical hydrogen bonds rupture, causing dissociation of double helixes and disturbing the closely packed ordered double-helical structure. The maize starch retrogrades very slowly because of the presence of highly branched amylopectin as one of its major components as well as the presence of dimethylolurea. Therefore, the broadening of the C-1 resonance is due to the opening of the double-helical structure to a random coil.

The chemical shift of the C-6 carbon decreases from 61.4 to 60.2 ppm as the U/S ratio is increased. The line width of the C-6 peak initially broadens, from 226 (B0) to 604 Hz (B3), but becomes narrower for sample B4 (528 Hz). The line widths of C-1 to C-5 remain unchanged for all samples. This indicates that the C-6 carbon of starch participates in a chemical reaction forming $-CH_2OCH_2-$ and $CHCH_2NH-$ linkages, resulting in cross-linking of the starch. Similar line broadening has been observed for divinylbenzene-cross-linked poly[(chloromethyl)styrene].[15,16] It has also been shown that the reactivity of the methylol derivative of urea with glucose is higher compared to that of other carbohydrates.[17] The major products from St–UF cross-linked polymers (B1–B3) are C, D, and E, respectively, along with some minor products A, B, F, G, and H (Schemes I and II). The self-condensation of urea–formaldehyde is suppressed in the presence of a large excess of hydroxyl groups of starch in acid-catalyzed condensation.[18] As expected, the primary hydroxyl group of C-6 is more reactive than the secondary hydroxyl groups of starch. As the degree of cross-linking increased, (B0–B4), the C-6 carbon showed an upfield chemical shift from 61.4 (B0) to 60.4 ppm (B3). Parfondry and Perlin[19] have observed downfield shifts from 62.4 to 70.5 ppm for C-6 of α-D-glucose with simple substitutions such as carboxymethyl and hydroxyethyl groups. In the present study C-6 showed an upfield chemical shift, indicating that cross-linking causes a shielding effect at the C-6 carbon in contrast to simple substitution. The reason for this observation is not apparent at the present time.

The spectra of all the St–UF samples (Figure 1c–f) show the carbonyl peak at ~159.0 ppm. The sharpness and intensity of this peak as calculated from the peak area increase with increase in U/S ratio. The increase in intensity presumably arises due to the increasing number of C=O functionalities in cross-linked starch ascribed to the field-dependent environmental effect of ^{14}N, as reported in the literature of ^{13}C CP/MAS NMR.[12]

As shown in Schemes I and II, reaction between starch and dimethylolurea takes place along with self-condensation reactions (G, H, I, and J). Sample B1 shows two distinct additional peaks at 47.2 and 54.5 ppm which are due to the methylene peak in different environmental conditions (shown in Scheme II as G and I). However, the peak at 54.5 ppm disappears in the case of B1(E) (Figure 1z), indicating that the low molecular weight products formed in sample B1 were extracted out in the methanol–water solvent.

Figure 1d–f shows spectra similar to that of Figure 1c with the following notable exceptions. The upfield shoulder at 99 ppm becomes more pronounced from B1 to B4 as the U/S ratio increases, which is absent in B0. In sample B4, the C-1 peak almost appears like a doublet. The peak at C-6 of sample B3 (Figure 1e) shows a weak downfield shoulder, which is more clear in sample B4. The upfield shoulder of C-1 in samples B1–B4 can be ascribed to C-1 of starch molecules having low molecular weight.[20] The splitting of C-6 into a doublet pattern may be due to two states of exocyclic conformation of the hydroxymethyl groups.[21] The signal at 64.5 ppm can be ascribed to the methylene in the methylol group ($NHCH_2OH$) of unreacted mono- (A) and dimethylolurea (B) or of low molecular weight of UF resin molecules (J). The peaks at 99.9 and 64.5 ppm are due to low molecular weight compounds, which was confirmed by the disappearance

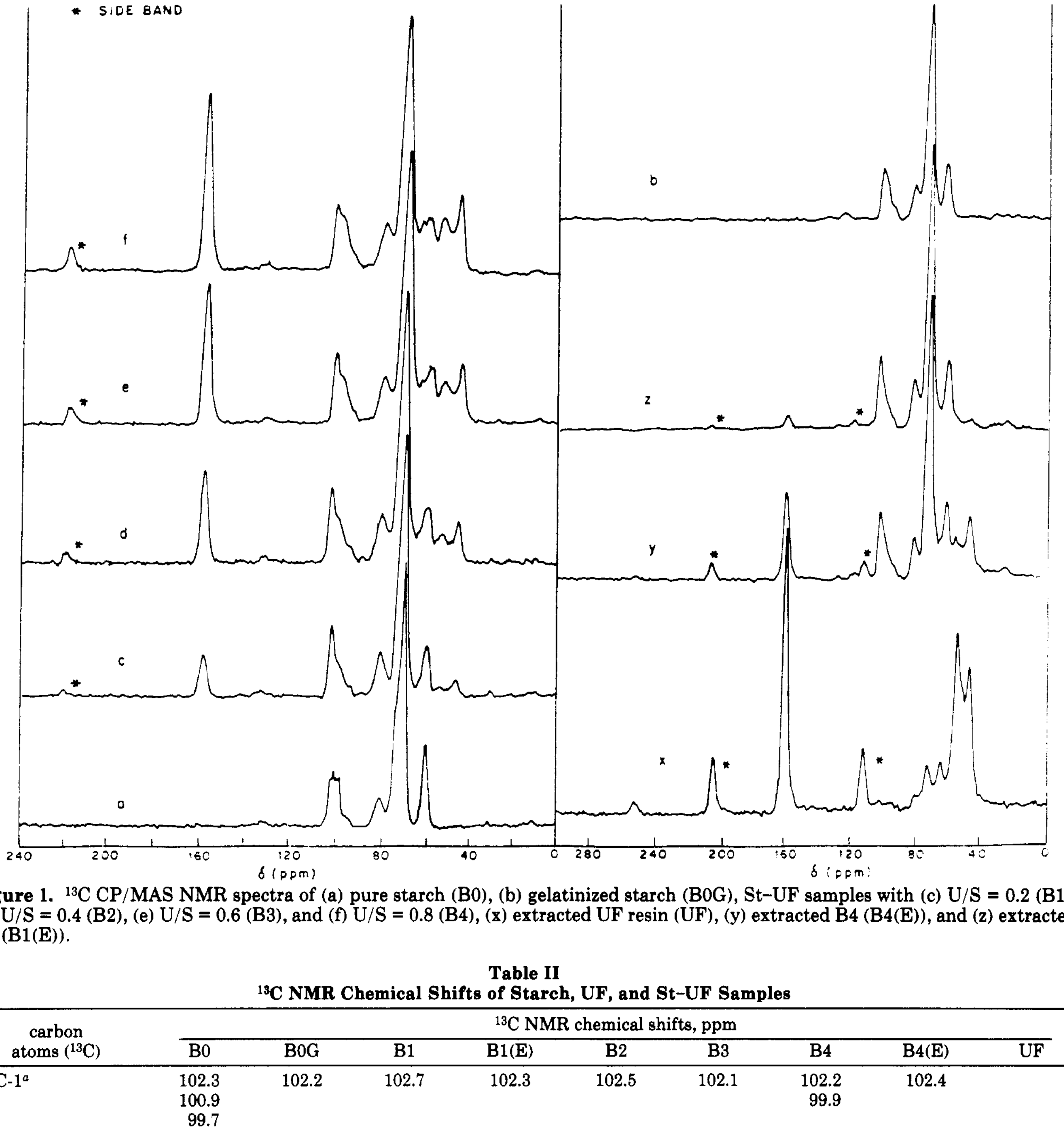


Figure 1. ^{13}C CP/MAS NMR spectra of (a) pure starch (B0), (b) gelatinized starch (B0G), St–UF samples with (c) U/S = 0.2 (B1), (d) U/S = 0.4 (B2), (e) U/S = 0.6 (B3), and (f) U/S = 0.8 (B4), (x) extracted UF resin (UF), (y) extracted B4 (B4(E)), and (z) extracted B1 (B1(E)).

Table II
^{13}C NMR Chemical Shifts of Starch, UF, and St–UF Samples

carbon atoms (^{13}C)	^{13}C NMR chemical shifts, ppm								
	B0	B0G	B1	B1(E)	B2	B3	B4	B4(E)	UF
C-1[a]	102.3	102.2	102.7	102.3	102.5	102.1	102.2	102.4	
	100.9						99.9		
	99.7								
	98.7								
C-2,3,5[a]	71.8	72.1	72.2	71.8	71.9	71.9	71.9	71.8	
C-4[a]	81.2	81.6	81.8	81.6	81.5	81.5	81.2	81.0	
C-6[a]	61.4	61.6	61.3	60.7	60.5	60.4	60.2	60.8	
							62.0		
=NC(O)N=[b]			159.4	159.0	159.1	159.0	159.0	159.0	159.2
$-NHCH_2NH-$[b]			47.2	47.1	46.8	46.7	46.9	46.5	47.8
$>NCH_2NH-$[b]			54.5		54.1	54.3	54.5	54.7	55.4
$-NHCH_2OH$[b]						64.6	64.5		65.0
$>NCH_2OH$[b]									72.1
$>NCH_2N<$[b]									61.0

[a] Chemical shifts of all carbons of starch are assigned from refs 13 and 14. [b] Chemical shifts of carbonyl and methylene groups of UF are assigned from ref 12.

of these peaks in the extracted B4(E) sample (Figure 1y).

The cross-linking of starch with UF resin (Schemes I and II) is also accompanied by other concurrent reactions leading to different types of UF condensates which appear at ~47, ~54, and ~64.5 ppm. As the U/S ratio increases, additional $-NHCH_2NH-$ and $>NCH_2NH-$ linkages are formed. The low molecular weight products containing $>NCH_2NH-$ linkages (54.5 ppm) are present in B1 but absent in B1(E) (Figure 1z). The low molecular weight products containing $>NCH_2NH-$ linkages are soluble and can be extracted out. However, B4 shows the peak for $>NCH_2NH-$ linkages even after extraction, indicating the higher molecular weight nature of this product.

The line width plot of the C-6 carbon in hertz vs U/S ratio is shown in Figure 4. The ^{13}C line widths have been measured in organic solids by means of high-power proton

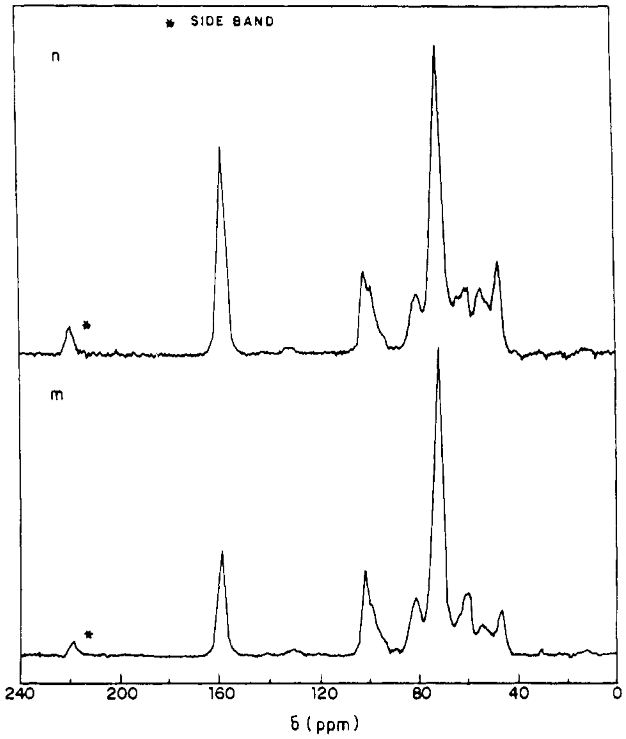


Figure 2. ^{13}C CP/MAS NMR spectra of B2A (m) and B4A (n) samples with particle mesh size −40+100.

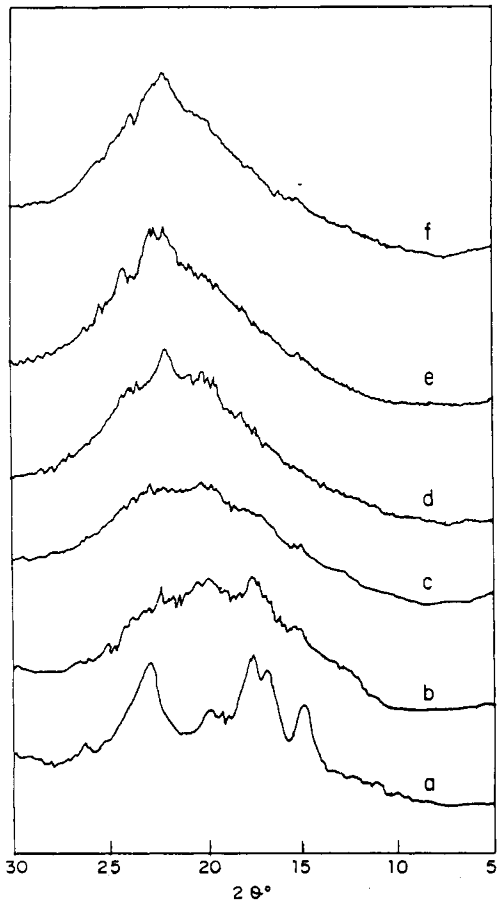
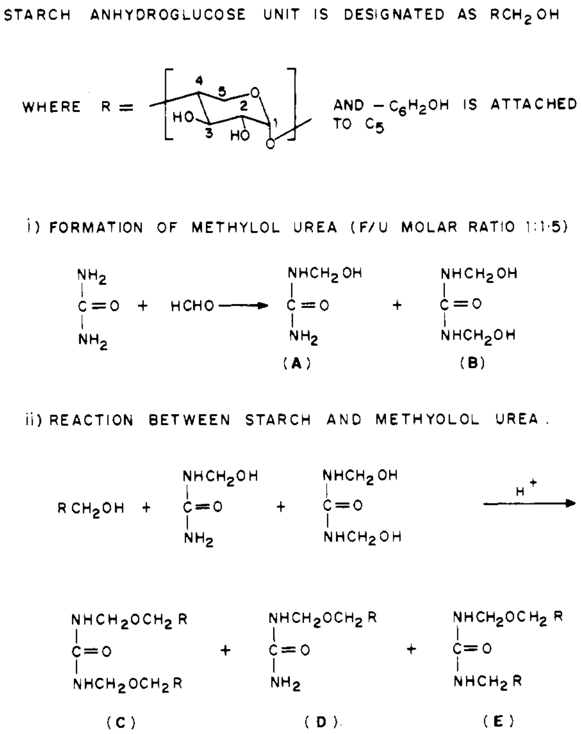
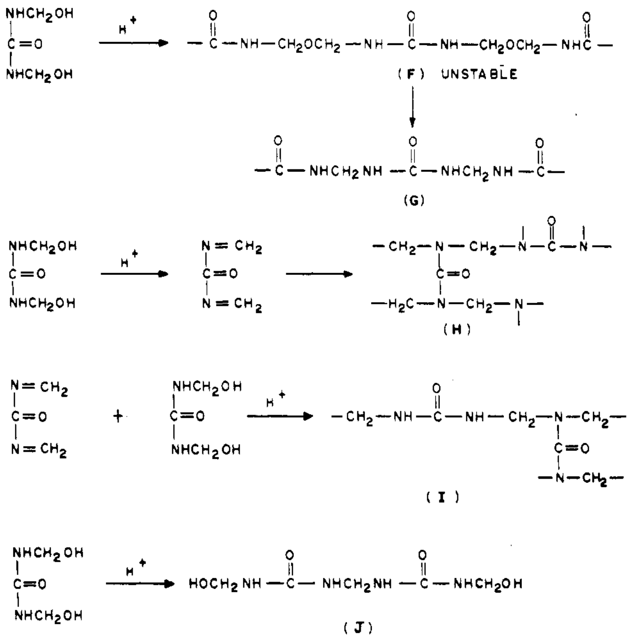


Figure 3. X-ray diffraction patterns of (a) pure starch (B0), (b) gelatinized starch (B0G), and St–UF samples with (c) U/S = 0.2, (d) U/S = 0.4, (e) U/S = 0.6, and (f) U/S = 0.8.

Scheme I
Reaction Scheme Leading to St–UF Cross-Linked Polymer



Scheme II
Self-Condensation Reactions of Dimethylolurea



decoupling and magic angle sample spinning. VanderHart et al.[22] have identified the importance of the ^{13}C line-broadening mechanism in solid polymers. They have suggested that ^{13}C line widths are usually expressed in hertz, a linear dependence on magnetic field B_0 which corresponds to equivalent resolution at different static fields. The ^{13}C line width broadening occurs in solid polymers due to factors such as insufficient proton decoupling fields, off-resonance decoupling, imperfections in magic angle spinning, and motional modulation of both the carbon–proton dipolar coupling and carbon shift anisotropy. In the present study, the line broadening arising out of above factors was eliminated by high-power proton decoupling and magic angle spinning. Thus, the line broadening observed can be attributed only to chemical reactions occurring at the C-6 carbon. The plot (Figure 4) shows an essentially linear relationship except for B4.

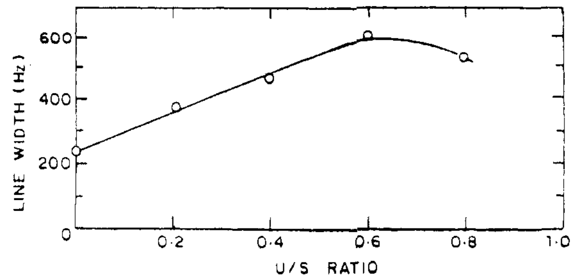


Figure 4. Effect of degree of cross-linking on line width of the C-6 carbon of starch.

This is attributed to the occurrence of a maximum degree of cross-linking at the U/S ratio 0.6 with complete reaction between the $-CH_2OH$ group of starch with the HOH_2CNH- and $-H_2N$ groups of the UF polymer. In the case of B4, self-condensation of the UF prepolymer appears to be predominant rather than condensation between starch and UF. As the degree of cross-linking is increased, the glucosidic linkages of starch in the cross-linked network become more strained, causing the breaking of these chains to smaller fragments. This is confirmed by the upfield shoulder of the anomeric carbon (~99 ppm).[20] The absence of the peaks at ~99 and 64.5 ppm in B4(E) suggests that these are low molecular weight compounds which do not participate in cross-linking but become entrapped in the St–UF cross-linked network.

In the case of B1 and B2, the major products are C, D, and E (Schemes I and II) as stated earlier along with G and I as minor products. In B3, the self-condensation reaction begins, which is observed by the significant increase in intensities at ~47.0, ~54.0, and a small signal at 64.6 ppm. The self-condensation reaction becomes more predominant in B4 compared to St–UF condensation, leading to UF condensates as the major products. Figure 1f shows a marked increase in intensities at ~47.0 and ~54.0 ppm and a significant signal at 64.9 ppm. There is a decrease in intensity of peaks at ~47.0 and ~54.0 ppm in B4(E), which confirms that B4 contains two products G and I (Scheme II) having both high and low molecular weights. Further the upfield shoulder of the anomeric carbon peak at ~99 ppm appears more pronounced, presumably due to fragmentation of the polysaccharide chains (glucosidic linkage) in the presence of high molecular weight UF condensates.[20]

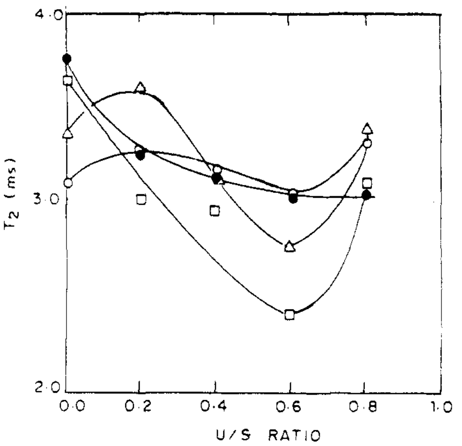


Figure 5. Effect of degree of cross-linking on the spin–spin relaxation times T_2 of starch carbons C-1 (○), C-2,3,5 (●), C-4 (△), and C-6 (□).

Table III
Spin–Spin Relaxation Times T_2 (μs) of Starch Carbons at Various Degrees of Cross-Linking

sample	C-1	C-4	C-2,3,5	C-6 exptl[a]	C-6 actual
B0	3100	3300	3800	1800	3600
B1	3300	3600	3300	1500	3000
B2	3200	3100	3100	1500	3000
B3	3000	2800	3000	1200	2400
B4	3300	3400	3000	1600	3200

[a] Experimentally observed.

Dynamics of Cross-Linked St–UF Polymers. The physical and chemical properties of polymers are profoundly modified by cross-linking. An objective of the study of the dynamics of cross-linked polymers is to understand the influence of cross-linking on the motion of chain segments both in its close proximity and away from it. T_1 (spin–lattice relaxation time) measurements reflect the fast motions in the megahertz region while $T_{1\rho}$ (spin–lattice relaxation in the rotating frame) is sensitive to the kilohertz region. The spin–spin relaxation time T_2 is much more sensitive to the low-frequency motion.

Muncie et al.[23] measured $T_{1\rho}(H)$ at 64 and 15 kHz to investigate the slow motions of cross-linked *cis*-polybutadiene above T_g. The results showed the insensitivity of $T_{1\rho}(H)$ to M_c (molecular weight between cross-links) except for the M_c = 14 m (m = monomeric unit) sample. It has been shown[23,24] that $T_2(H)$ is sensitive to long-range chain motions affected by entanglements and cross-links at elevated temperatures. These proton relaxation times are insensitive to cross-links below T_g. ^1H NMR studies of the thermoset system containing the diglycidyl ether of Bisphenol A (DGEBA), *N,N'*-dimethyl-1,6-diaminohexane (DDH), and 1,4-diaminobutane (DAB) at various proportions of DDH and DAB have been made.[25] It was observed that the ^1H NMR spin–spin relaxation plateau around T_g in the epoxy thermoset resins increases linearly with the average number of bonds between cross-links, even in the most highly cross-linked systems.

In a complementary way, CP/MAS NMR seems to be ideally suited to probe molecular motion below the T_g of polymers. Chien et al.[26] have shown that the spin–lattice relaxation of ^{13}C nuclei is sensitive to cross-links below T_g whereas the spin–spin relaxation is insensitive in this temperature region. They have also demonstrated the distribution of correlation times for network systems with short segmental lengths between cross-links. The short relaxation component attributed to the backbone carbon is proximate to the cross-link. Solid-state ^{13}C NMR has been used to determine cross-linking sites in sulfur vulcanized natural rubber.[27] Peroxide[28] and γ-irradiation-cured elastomers[29] have also been studied. However, more recent studies on relaxation time measurements with a variety of cross-linked elastomers indicate their sensitivity to cross-link levels. Curran et al. observed that changes in $T_2(C)$ are influenced by long-range low-frequency motions in the case of cross-linked polybutadienes.[30] $T_2(C)$ values are also affected by the high-frequency motions. But $T_1(C)$ relaxation times, which are influenced only by high-frequency motions, showed no dependence on cross-linking. Thus it was confirmed that the change in T_2 arises due to low-frequency motions.

We therefore undertook a study of $T_2(C)$ measurements of St–UF cross-linked polymers at different degrees of cross-linking.

Figure 5 illustrates the plot of T_2 values against various U/S ratios for all carbons. T_2 values of all carbons are computed and are shown in Table III. As the C-6 carbon possesses two protons, the experimentally observed T_2 values should be multiplied by a factor of 2 for comparison with the ring carbons.[31]

The T_2 values of the C-6 carbon of starch decrease monotonously as the U/S ratio is increased to 0.6. However, T_2 increases at a U/S ratio of 0.8 (Figure 5). This implies that the mobility of the C-6 carbon (CH_2OH) decreases continuously because of the increased cross-linking up to a U/S ratio of 0.6. The increase of T_2 at U/S = 0.8 implies a free C-6 (CH_2OH) group of starch and predominant self-condensation of urea and formaldehyde. Moreover, the T_2 value of C-6 at U/S = 0.8 is less when compared to that of pure starch, indicating that part of the hydroxymethyl group takes part in the cross-linking reaction. In the case of the C-2, C-3, and C-5 carbons, the T_2 values decrease from that of pure starch to a polymer wherein the U/S ratio is 0.2 and thereafter remain constant. Apparently, the motion of the secondary hydroxyl groups decreases only initially. The T_2 values of C-1 and C-4 increase up to a U/S ratio of 0.2, remain constant up to U/S = 0.6, and thereafter increase again. This is understandable in terms of the motions of the C-1 and C-4 carbons, which are mobile up to U/S = 0.2 as a result of the change in structure from crystalline to amorphous. Upon going to a U/S ratio of 0.6, there is a restriction to motion of the C-1/C-4 carbons as a result of cross-linking at the C-6 carbon. Further increase in the T_2 value at U/S = 0.8 arises due to the presence of unreacted starch as well as fragmentation of the polysaccharide chains in the presence of high molecular weight UF condensates.

Conclusion

^{13}C CP/MAS NMR spectra of cross-linked St–UF polymers have been studied in terms of the chemical shift displacement, line width, and T_2 measurements. Pure starch loses its crystallinity upon gelatinization and cross-linking and is evidenced by the disappearance of the multiplicity of the anomeric carbon of starch. The primary hydroxyl group on C-6 on starch takes part in the cross-linking reaction. The cross-linking reaction between starch and UF predominantly suppresses the self-condensation of UF resin up to a U/S ratio of 0.6. The line width of the C-6 peak of starch linearly increases with degree of cross-linking. At a U/S ratio of 0.8 self-condensation reactions of UF resins become more important than condensation with starch. The spin–spin relaxation time (T_2(C)) of C-6 is more influenced by cross-linking compared to other ring carbons of starch. T_2(C) is affected by both short-range and long-range frequency motion.

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