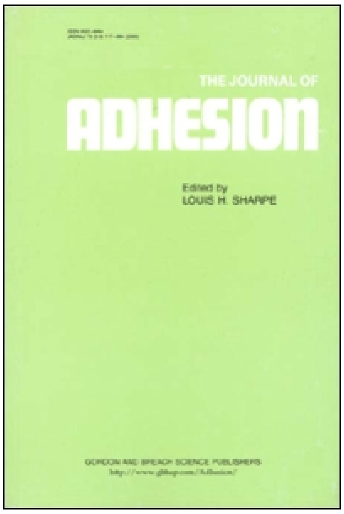

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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John Stuligross[a]; James A. Koutsky[a]
[a] Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin, U.S.A.

To cite this Article Stuligross, John and Koutsky, James A.(1985) 'A Morphological Study of Urea-Formaldehyde Resins', The Journal of Adhesion, 18: 4, 281 — 299

To link to this Article: DOI: 10.1080/00218468508080464

URL: http://dx.doi.org/10.1080/00218468508080464

J. Adhesion, 1985, Vol. 18, pp. 281–299
0021–8464/85/1804–0281 $18.50/0

Printed in the United Kingdom

A Morphological Study of Urea-Formaldehyde Resins

JOHN STULIGROSS and JAMES A. KOUTSKY

University of Wisconsin, Department of Chemical Engineering, Madison, Wisconsin 53706, U.S.A.

(*Revised received February 12, 1985*)

The solid state of a variety of urea-formaldehyde (UF) resins has been characterized by optical and scanning electron microscopy and wide angle x-ray diffraction studies. A first group of resins of various formaldehyde to urea mole ratios (F/U = 1.0, 1.25, 1.5) and solids contents (25%, 45%, 65%) were prepared from oligomeric UF species and cured with NH_4SO_4 catalysts at room temperature for 120 days, and 90°C for 24 hours. Cured samples were dried by vacuum and elevated temperature (160°C). A second group of resins was also prepared by a more standard procedure to obtain F/U = 1.2 and 1.6 and a solids content of 65%. These samples were cured at 160°C for 4 and 5 minutes with NH_4Cl catalyst. The first group of samples showed colloidal character and definite crystallinity especially as F/U decreased to 1.0. The crystals appeared to have high melting points ($T_m > 230°C$) and the formulation of the resin did not appear to vary the crystal structure but only the percent crystallinity. The water content of the cured resins strongly influenced the crystallinity with crystallinity increasing as water is removed. The effect of changing the water content appears to be reversible to a large extent. The second group of samples showed little crystallinity and no obvious colloidal character.

Key Words: Adhesives, Colloids, Crystallinity, Morphology, Multiphasing, Urea-Formaldehyde Resins.

INTRODUCTION

In recent years concern of formaldehyde release from urea-formaldehyde (UF) resins, which are utilized in many bonded wood

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Presented at the 4th Annual International Symposium on Adhesion and Adhesives for Structural Materials, Washington State University, Pullman, WA 99164, U.S.A., September 25–26, 1984.

products, has prompted fundamental investigations into UF resin synthesis, UF chemical structure and hydrolytic stability of the resins. Many past publications on UF resins have been summarized by Meyer.[1]

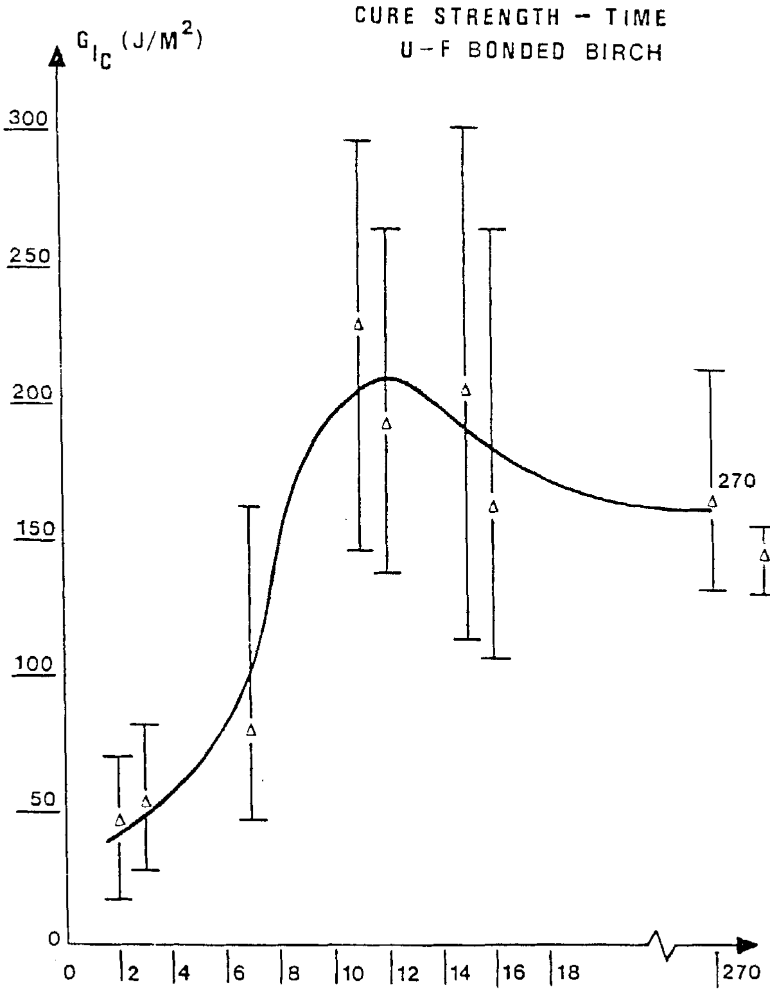

FIGURE 1 Double cantilever beam cleavage fracture energy, G_{I_c}, as a function of cure time for a UF resin bonded to birch substrates. Cure temperature is 25°C. Note large data scatter at intermediate cure times and long times needed for complete cure.

Chemical structure studies involving FTIR, Laser Raman and solution and solid-state NMR spectroscopies have attempted to establish hydrolytic stability criteria with specific chemical structures in the resin. Formaldehyde release measurements from such resins are presently being made for correlation with the formulation of the resins, their cure procedures, and additives.[2]

Recently, evidence of colloidal behavior during resin prepolymer production has indicated that these systems can be multiphase in nature.[3] Precipitation of water insoluble, low molecular weight, oligomeric species could have great influence on the final cross-linked structure of the cured resin.

It is common knowledge that UF prepolymer resins can be unstable and can lead to poor or irreproducible properties of the final cured adhesive. Evidence of irreproducible behavior has been observed in fracture energy studies involving bonded wood substrates.[4] Figure 1 shows that for a long-term room temperature cure of a typical UF wood bonding resin, reproducibility of fracture behavior is not achieved for many months. This implies that although the resin appears tough and ductile when compared to typical phenolics, the fracture properties are difficult to reproduce, even within one sample. Therefore, accelerated durability studies of such resins are complicated by the fact that the structure of the resin initially is very different from a "fully cured" final stage resin and the durability test itself is not just degrading the bond in a straightforward manner but could actually be curing the resin. Furthermore, if there is evidence that crystallization can occur in such systems, then this would add a complicating factor in understanding their properties and durability since it is well known that crystallization in polymers has profound influence on mechanical properties, as well as chemical properties such as hydrolytic stability.

This paper reports on the morphological structure of UF resins prepared in several ways and especially focusses on preliminary evidence of crystalline order in such resin systems.

EXPERIMENTAL

I. Materials

Two sets of samples were studied. The first series was prepared by Dr. Thomas Pratt of H. B. Fuller Co. A stable UF concentrate,

TABLE I
UF resin synthesis
I. Pratt's method

	1.0	1.25	1.5
UF-85*	180.00	210.00	233.33
water	79.61	66.02	53.43
urea	171.00	149.10	128.33
$(NH_4)_2SO_4$**	3.60	3.50	3.50
Total (gm)	434.21	428.62	418.59
65%	−200 gms	−200.00	−200.00
	234.21	228.62	218.59
water	104.09	101.61	97.12
	338.30	330.23	315.71
45%	−200 gms	−200.00	−200.00
	138.39	130.23	115.71
water	110.64	104.18	92.57
25%	248.94 gms	234.41	208.28

* UF-85 is 60 wt% HCHO, 25 wt% urea, 15 wt% H_2O.
** 40 wt% $(NH_4)_2SO_4$ in water.

II. Forest products laboratory method
F/U

	1.2	1.6
STAGE I		
UF concentrate	301.7	301.7
H_2O	135.7	135.7
urea	105.6	105.6
STAGE II		
urea	25.9	25.9
STAGE III		
urea	94.8	19.4

(UF–85), obtained from Georgia Pacific Corporation, was diluted with water and urea was then added with gentle heating to 70°C to insure rapid urea dissolution. The mixture was then cooled to 25°C. Ammonium sulfate was used as the catalyst and 0.5% was added to the cooled initial mixture. The initial amounts of water and urea added to the UF–85 concentrate, given in Table I, were for the proper F/U ratio and a 65 wt% solids content. The initial mixtures were then diluted after removal of 200 gms of the 65 wt% solids sample. A subsequent water addition produced a 45 wt% solids sample from which 200 gms were removed. The remaining sample was further diluted with water to obtain a 25 wt% solids sample. In all cases deionized water was employed, and the urea was an ACS reagent grade comprising 98% urea.

Two cure temperatures were utilized. Some samples were kept at 25°C for many weeks for comparison with commonly made room temperature curing UF recipes. A second group of samples were heated to 90°C and cured for 24 hours at that temperature in closed sealed glass containers. All samples were left in sealed glass containers and stored at 25°C. All of the samples prepared by Pratt's method had an opaque white appearance. All samples which had 25% solids for any F/U ratio, as well as those of low F/U ratio at a 45% solid content, had physical characteristics of coarse, damp, granular powders. The higher solids content samples (65%) were fused and were increasingly brittle as the solids content, F/U ratio, or cure temperature increased.

A second set of samples was prepared at the Forest Products Lab in Madison, Wisconsin. These were made by a standard method of 3 urea additions.

STAGE I. A UF-concentrate was diluted, and urea was added to bring the F/U to 2.0. A small amount of NaOH was added to maintain a pH between 7.0 and 7.5. This solution was then heated to 95–97°C, and the pH was maintained between 6.8 and 7.2 for 30 minutes. The solution was cooled to 92°C, and the pH was reduced to 5.0–5.2 with formic acid. This allowed the reaction to proceed until a Garner viscosity of "H" was observed.

STAGE II. The mixture was cooled to 85°C and urea added to bring the F/U to 1.75, and the pH was adjusted to 6.2–6.4 with NaOH. When a Gardner viscosity "M" was observed the solution was cooled to 60°C, and the pH was increased to 7.0–7.5 by another small addition of NaOH.

STAGE III. Urea was then added to obtain the desired F/U ratio. This mixture was reacted for 20 min., maintaining the pH at 7.0–7.5 and then was cooled to 25–28°C. The pH was then increased to 7.5–7.8 with NaOH.

This resin was cured at 160°C, under nitrogen, with 0.7% NH_4Cl catalyst. The cured samples were ground, dried under vacuum and stored in glass containers using P_2O_5 as a drying agent. Samples were prepared with $F/U = 1.2$ and 1.6, and cure times of 4 and 5 minutes.

These samples were a fine, dry, white powder and are referred to as FPL resins.

II. Methods

Optical microscopy Optical microscopy was performed on a Zeiss Ultraphot II. Small portions of each sample resin were placed, uncovered, on a glass slide, and then observed with cross polarized light. Magnifications of up to 1000 times were used. No significant change in the specimens was observed.

A *thermolyne* microscope with a heating stage was used to examine temperature effects. The sample was placed on a glass 20 mm cover slip, covered with another cover slip, and then was inserted in the heating stage. Observations were made in the presence of air with cross polarized light, and a magnification of 120 times. The heating rate used was approximately 10 degrees °C per minute.

Scanning electron microscopy A JEOL JSM 35C Scanning Electron Microscope (SEM) was employed. Resolution limits of 30 Angstroms are attainable with this instrument. The samples were vacuum dried and then mounted on aluminum stubs with double-stick tape. A drop of silver paint was used to ensure good contact between sample and stub. Then a layer of gold was evaporated onto the sample surface in a vacuum metallizing unit. A 15 kv source was used in the microscope, with magnification of up to 30,000 times.

X-ray diffraction X-ray diffraction analysis was performed *via* a Picker x-ray diffractometer employing a rotating goninometer. A copper target was used with a source voltage of 38 kv and 15 milliamps of current. The radiation was filtered by a Nickel foil to give the a 1.54 angstrom wavelength characteristic of the Copper K_α line. Slit collination was employed with a final slit width of 1 mm. Scan speeds of 1°/min were employed for this analysis and angles 5° to 50° were examined.

Approximately 100 mg of each sample was mounted on a glass slide by a spatula. The samples, which were moist and granular, or powdered, would remain affixed to the slide due to residual moisture when the slide was placed vertically in the goiniometer. The samples which were fused were first powdered in a mortar and pestle, then slightly moistened with a few drops of water before being mounted. That water was allowed to evaporate before the diffraction was taken.

In addition to being run immediately after the above procedure, the effects of a number of treatments were examined. The mounted samples were vacuum dried at 200 millitorr pressure for 20 minutes. A diffraction scan was recorded. The same sample was then heated for between 10 minutes and 1 hour, at either 90°C or 160°C, and the diffraction re-recorded. Then the samples were placed in a 100% humidity environment for 11 days. The x-ray diffraction pattern was recorded again. Finally two to three drops of distilled water were placed directly on the sample, and the x-ray diffraction analysis was repeated to see if any difference in the pattern resulted from 100% humidity vapor contact or direct liquid water contact. These treatments were performed both in successive steps on the same sample and as individual tests on different samples.

RESULTS

Microscopy

Optical microscopy indicated birefringence of all samples except the FPL resins (see Figure 2). Birefringence remained until 210°C for a 10°C/min rate in temperature rise when samples were exposed in air. At ~235°C the samples turned amber color and appeared to be liquid-like. Upon cooling, however, the birefringence returned, although not with as much intensity as the original samples. The FPL resins had no birefringence and remained colorless until 200°C, when a yellow color was first observed.

SEM results show spherical particles for all resins except those at higher F/U ratios and higher solids content. This indicates a colloidal character for resins. The implication is that UF at these low solids content polymerized and precipitated as colloidal particles which appeared to grow by agglomeration. For samples of low F/U values cured at low temperatures (room temperature), colloidal behavior was observed at both low and high solids content. (See Figures 3A and 4A). For samples having high F/U values cured at low temperatures, only low solids samples showed distinct colloidal character (See Figures 3B and 4B).

When higher cure temperatures were used, colloidal character was generally observed for low solids content recipes. Higher solids contents show fused glassy behavior, however, with low F/U samples some exceptions were observed. At higher F/U ratios some colloidal struc-

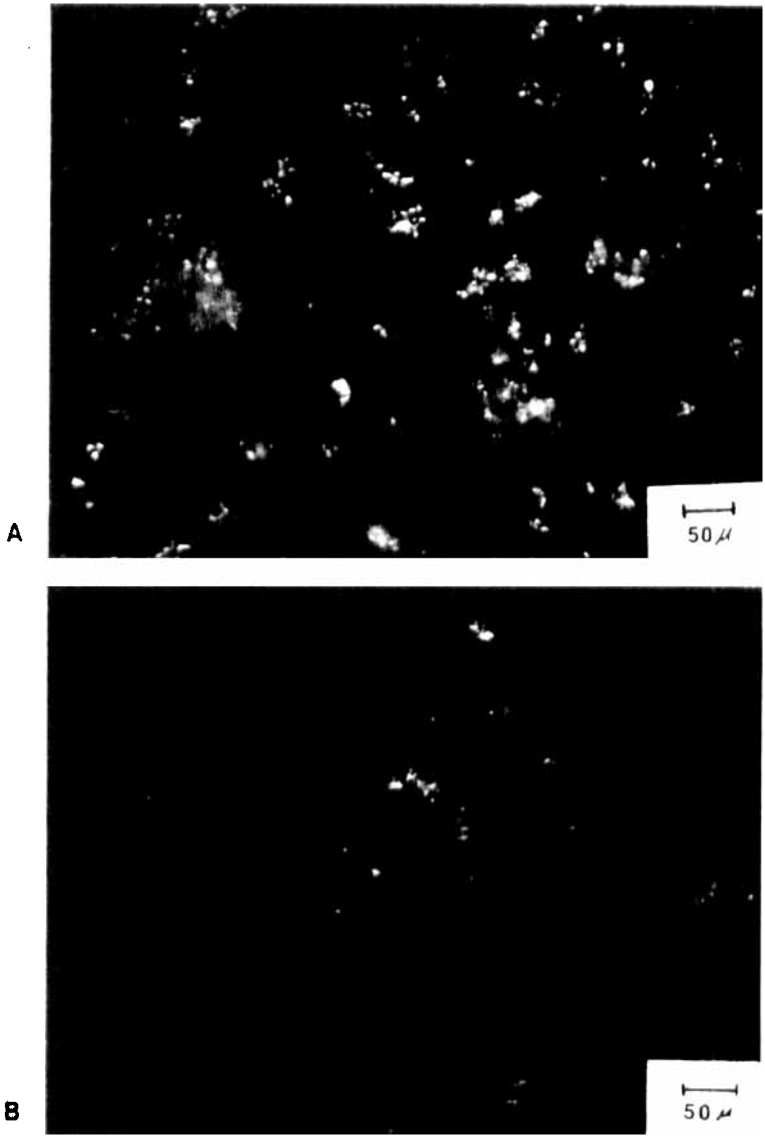

FIGURE 2 Optical Microscopy of UF resins under crossed polarizers at room temperature A—Pratt's UF: (0.5% NH_4SO_4 catalyst based on total dry solids content) F/U = 1.25, 25% solids, 25°C cure temperature. B—FPL resin: F/U = 1.2. (0.7% NH_4Cl catalyst based on total dry solids content)

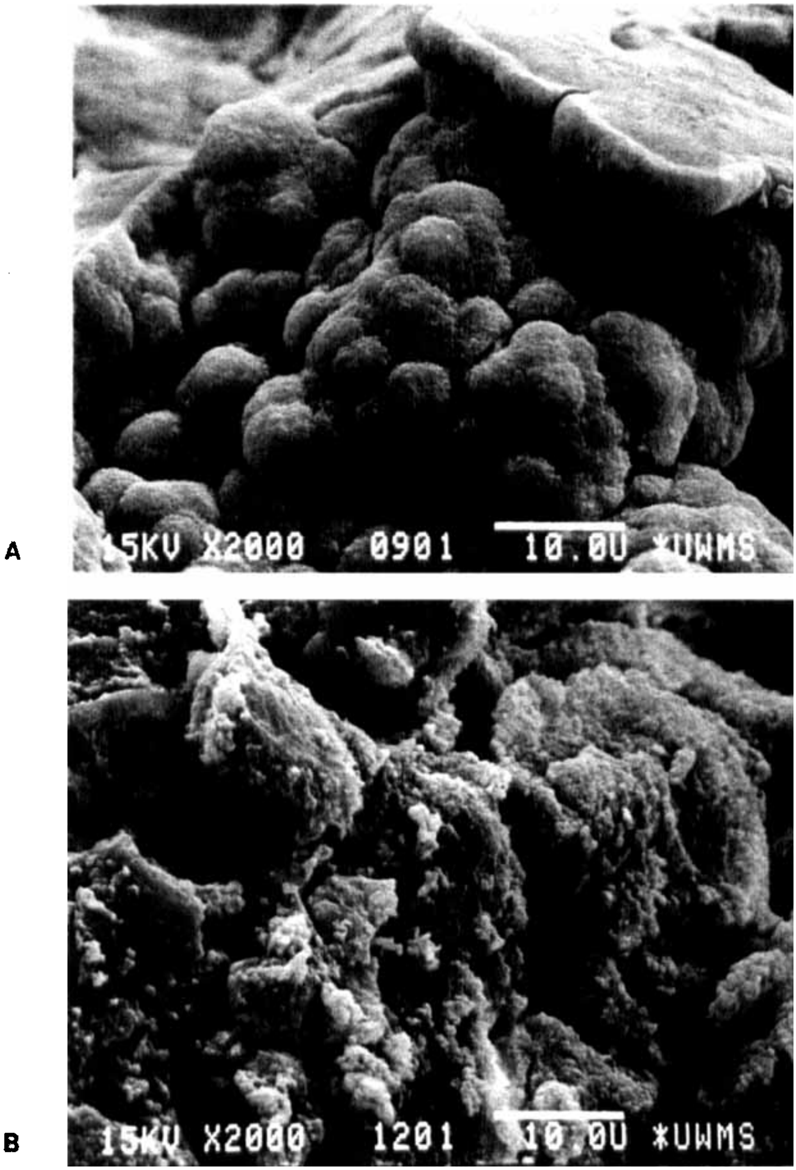

FIGURE 3 Scanning electron micrograph (SEM) of solution cured UF at two F/U ratios for high solids content oligomers (65%). Temperature of cure was 25°C for 120 days. (0.5% NH_4SO_4 catalyst based on total dry solids content.)
A F/U = 1.0
B F/U = 1.5

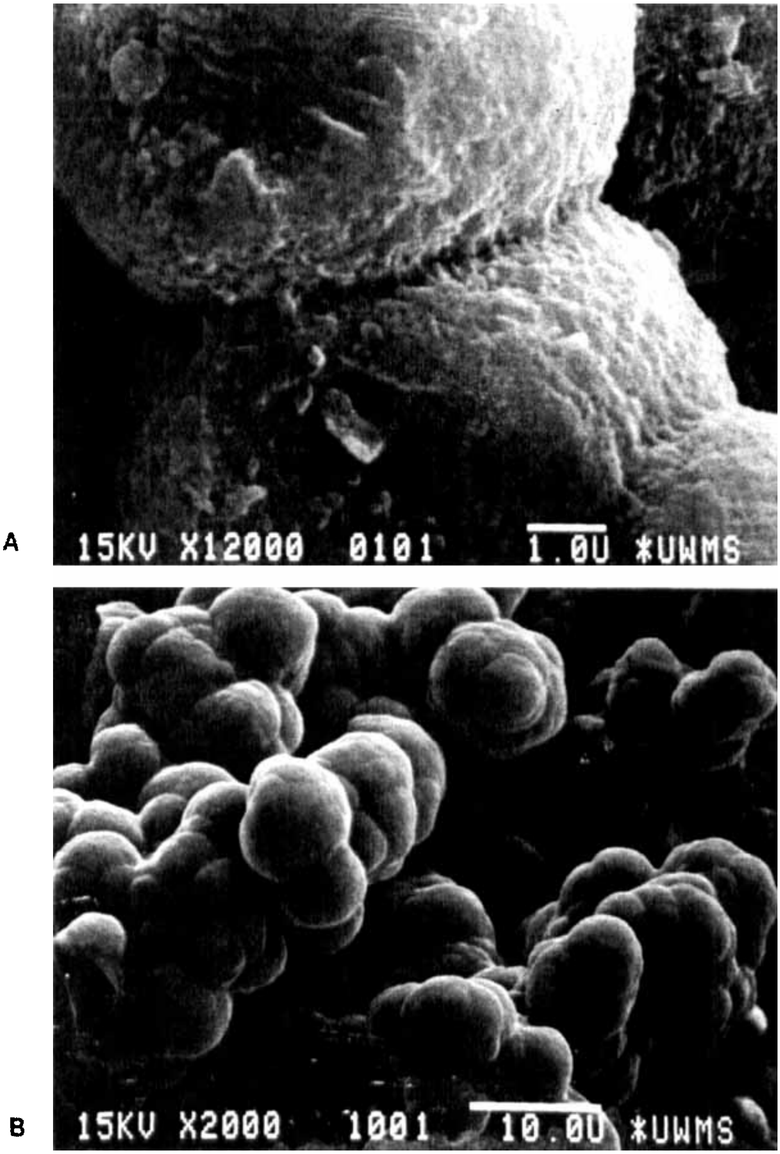

FIGURE 4 SEM of solution cured UF for low solids content oligomers (25%). Temperature of cure was 25°C for 120 days (0.5% NH_4SO_4 catalyst based on total dry solids content).
A F/U = 1.0
B F/U = 1.5

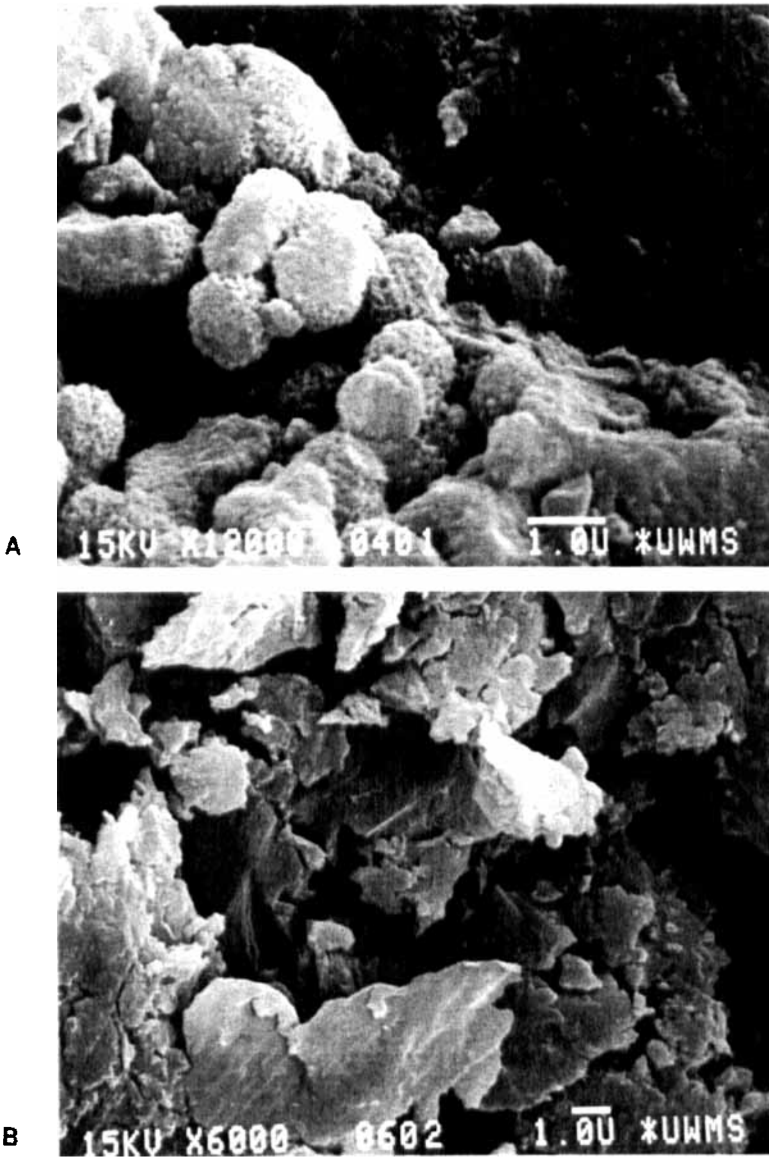

FIGURE 5 SEM of solution cured UF at two F/U ratios for high solids content oligomers (65%). Temperature of cure was 90°C for 24 hours. (0.5% NH_4SOH_4 catalyst based on total dry solids content.)
A F/U = 1.0
B F/U = 1.5

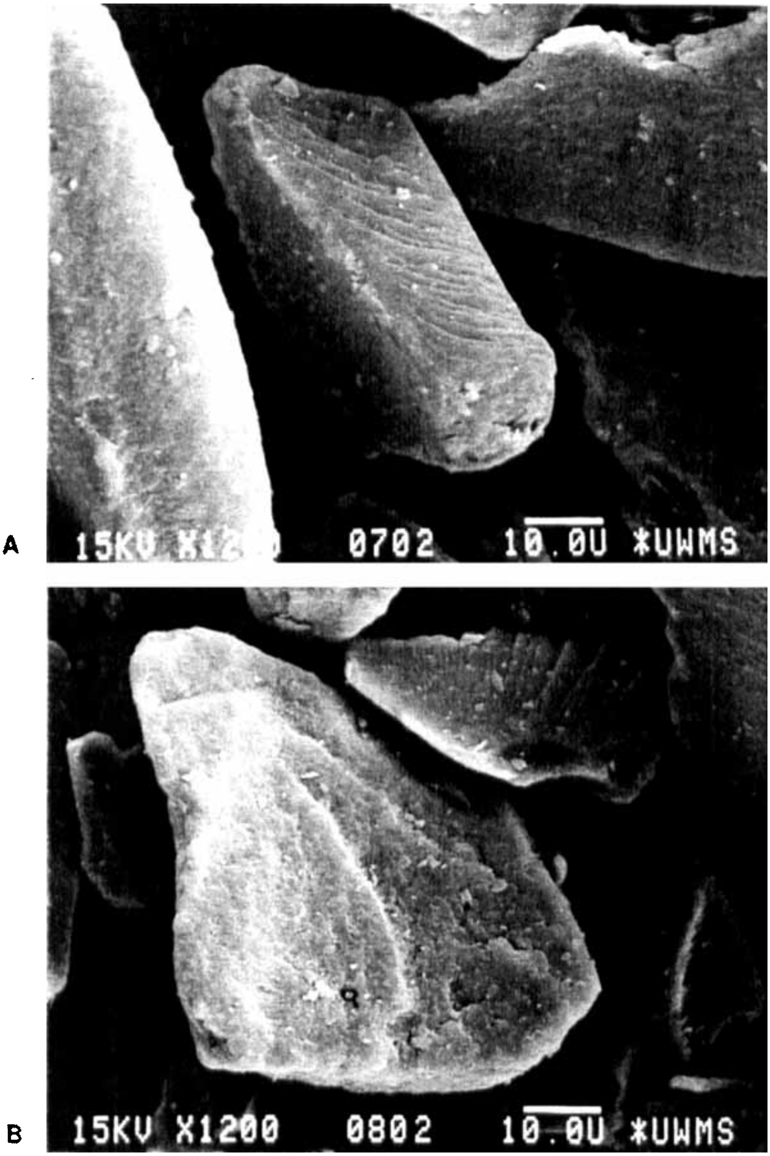

FIGURE 6 SEM of cured FPL UF resins at two F/U ratios. These samples were cured at 160°C for 4 minutes and then milled at low temperatures to obtain small particles of approximately 80 mesh sizes. (0.7% NH_4Cl catalyst based on total dry solids content.)
A F/U = 1.2
B F/U = 1.6

ture was observed however at higher temperatures of cure (90°C) all colloidal particles appeared to be pocked, smaller and more fused (See Figure 5).

For common industrial recipe formulations (FPL resins) no colloidal behavior in the fully cured state was observed (See Figure 6). Fracture of such high cure temperature and short cure time resins gave glass-like fracture surfaces showing ridges.

X-Ray Diffraction

All of the resins prepared by Pratt showed the same diffraction pattern except for varying intensities (See Figures 7 and 8). A

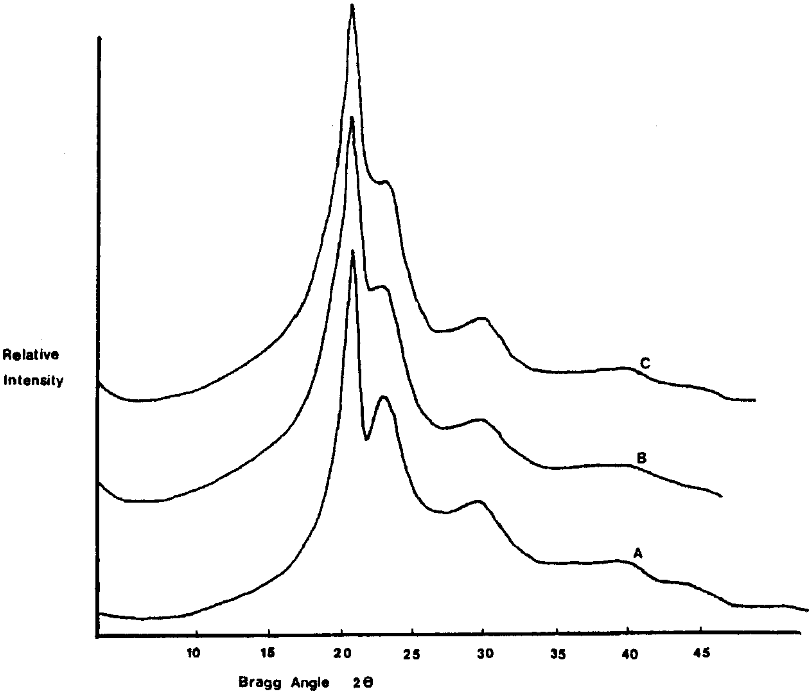

FIGURE 7 X-Ray diffraction of 25% solids content cured UF resin. F/U = 1.0. Cure temperature was 25°C for 120 days. (0.5% NH_4SO_4 catalyst.)

A Original sample dried on glass slide at 25°C at relative humidity of 40% for 20 minutes.

B Sample A exposed to 160°C for 10 min in air.

C Sample A exposed to 160°C for 1 hour in air.

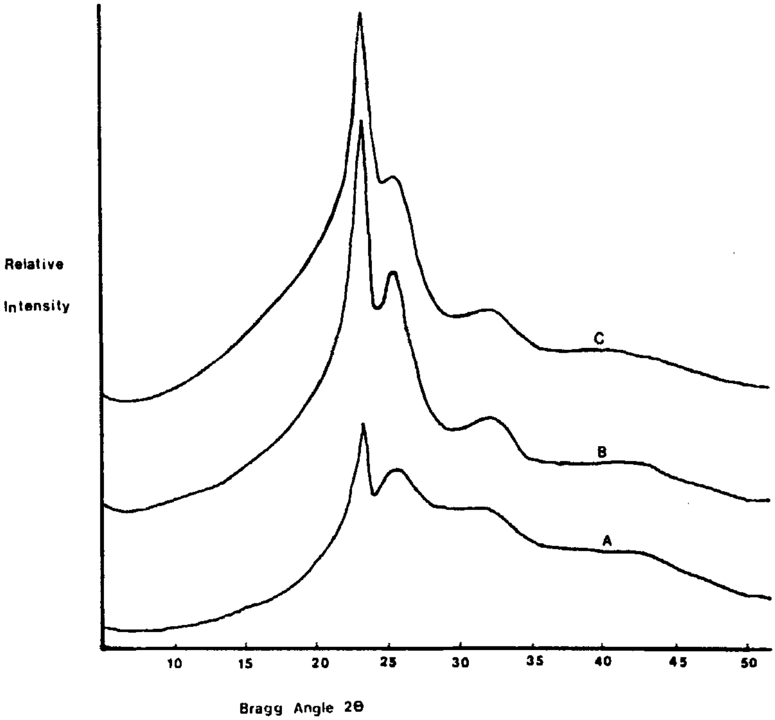

FIGURE 8 X-Ray diffraction of 25% solids content cured UF resin. F/U = 1.5. Cure temperature was 25°C for 120 days (½% NH_4SO_4 catalyst).

A Original sample dried on glass slide at 25°C at relative humidity of 40% for 20 minutes.
B Sample A vacuum dried at 25°C for 20 minutes.
C Sample B exposed to 160°C for 15 minutes in air.

major peak was seen at 2θ of 22.75°, and successively less pronounced peaks at 25°, 32°, and 42°. These reflections correspond to repeat distances 3.91, 3.56, 2.80 and 2.15 angstroms respectively. There appeared to be minimal difference between the samples of 1.25 and 1.5 F/U ratios, but for F/U = 1.0 a much higher degree of crystallinity was observed.

The FPL resins showed a fairly broad peak which had its maximum at $2\theta = 23°$ (See Figure 9). There was no noticable difference between FPL resins of different F/U ratio.

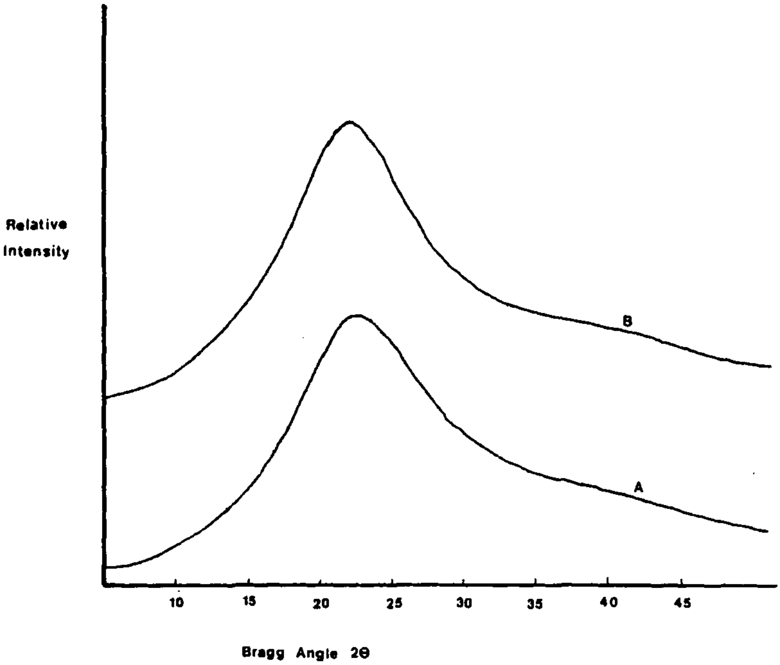

FIGURE 9 X-Ray diffraction of FPL resins for F/U = 1.2.
A Cured sample (160°C—4 minutes in air; 0.7% NH_4Cl catalyst).
B Cured sample of A exposed to 90°C for 10 minutes in air.

Upon heating and/or vacuum drying a very marked increase in the degree of crystallinity was observed for all samples synthesized by Pratt's method. However, there was minimal change in diffracted intensity after the initial treatment of either vacuum drying or heating at 160°C for 10 min (See Figure 8 and compare data B and C). The samples did show additional increases in the degree of crystallinity when a sample, which had been heated at 90°C, was subsequently heated at 160°c. Some line broadening was observed after prolonged heating at 160°C when compared to short heating times or vacuum drying. Without exception the exposure to a humid environment had no noticeable effects on the x-ray diffraction patterns. However, the direct application of liquid water did dramatically reduce the crystallinity. For the high solids content samples, it was reduced to below the level of the original samples (See Figure 10).

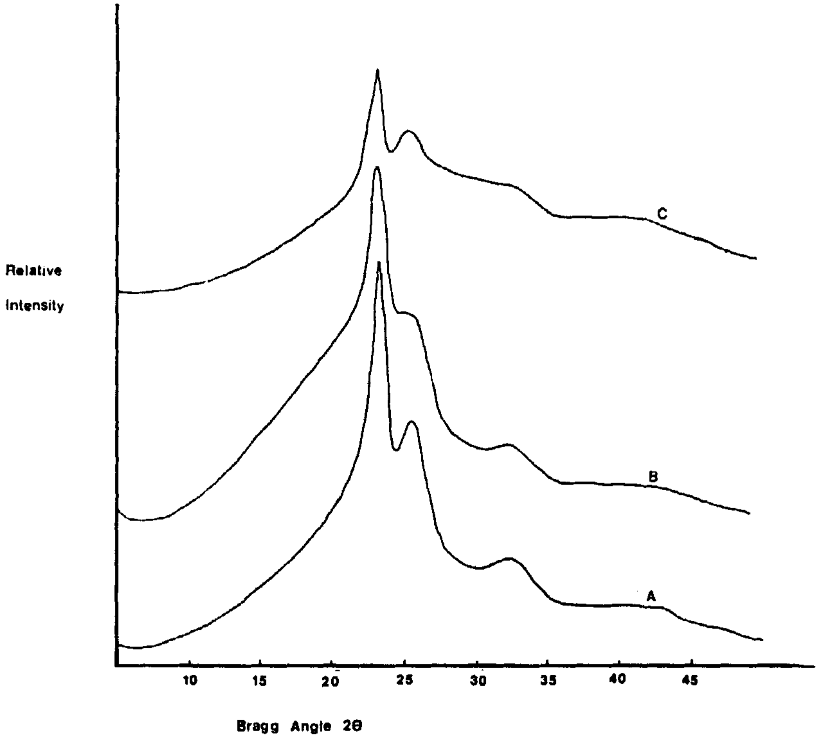

FIGURE 10 X-ray diffraction of 45% solids content cured UF resin. F/U = 1.5. Cure temperature was 25°C for 120 days.
A Original sample dried on glass slide at 25°C at 40% RH for 20 minutes.
B Sample A heated at 160°C for 15 minutes.
C Sample B contacted with liquid water at 25°C for 20 minutes.

DISCUSSION AND CONCLUSIONS

The data obtained in this study supports the following conclusions and observations.

1) Crystallinity can exist for UF polymers in both uncured, prepolymer state and in the "cured" state.

2) From optical microscopy, crystallinity appeared to be due to high melting point crystals where $T_m > 230°C$. For a variety of formulations the crystal structure did not appear to vary. Degradation in air for these crystals began rapidly at 200°C.

3) Colloidal precipitates of high crystallinity were obtained in dilute solution polymerization. As the F/U ratio increased, crystallinity decreased. The size of the colloid appeared to be smaller at higher solids content.

4) Water content of the "cured" resin strongly influenced its crystallinity. The crystallinity changed by a large extent when the resin was exposed to liquid and appeared to be reversible to a major extent.

It appears reasonable that during the formation of oligomers of UF resin in water solutions a precipitate is formed due to the increased hydrophobicity of the oligomers and their strong inter or intra molecular hydrogen bonding. The crystals formed have a high melting point and therefore when polymerization proceeds there is a large driving force in terms of supercooling to nucleate and grow crystallites.

It has been previously reported from kinetic measurements that the formaldehyde addition on the primary amine of urea is approximately 100 times faster than the addition of formaldehyde on a secondary amine of urea.[5] These kinetic data and the possibility of crystallization during synthesis, which would further inhibit secondary amine addition, implies that linear UF molecules are more readily formed than previously suspected. Figure 11 shows a simple schematic of what could happen when forming a "cured" UF resin, particularly for a low solids content recipe. The agglomeration of these microcrystals will be very dependent on the solids content of the recipe and the ability of the solution to stabilize the microcrystals. In a traditional recipe (FPL method) the crystallites appear to be very small or nonexistent since the x-ray diffraction pattern is nearly diffuse for such systems. This is not surprising since high mole ratios of F/U and high initial pH values, which are always maintained for these recipes, would give greater degree of secondary amine substitution and formation of methylene-ether links between urea moities.

Although the diffraction data on conventional UF resins do not show extensive crystallinity, it is possible by other suitable synthesis procedures to produce crystalline, linear UF molecules. For instance, acid catalysis and the maintenance of low F/U ratios during polymerization could possibly give highly crystalline linear molecules. These polymers could have properties approximating the "Nylons" and have unique application as adhesives.

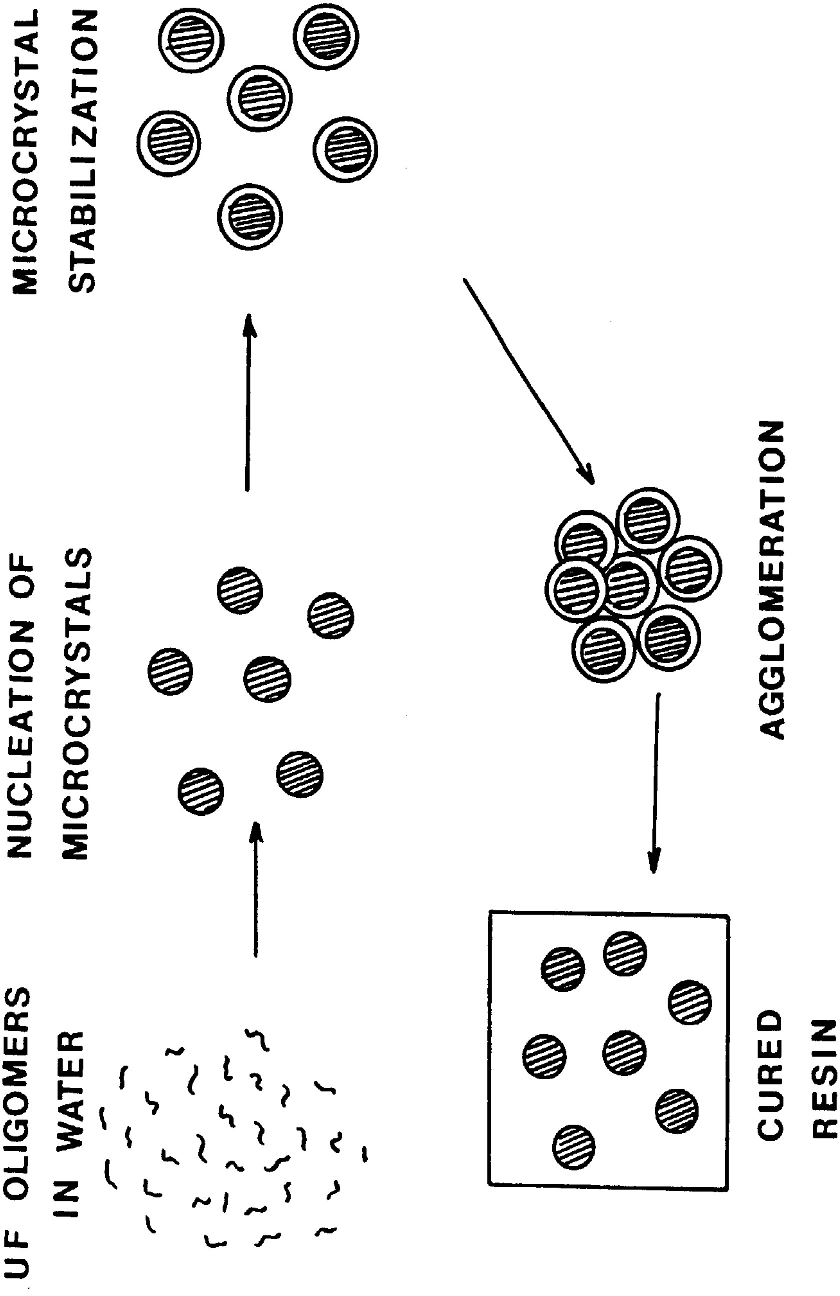

FIGURE 11 Proposed model of urea-formaldehyde crystallization and cure.

Acknowledgements

The authors would like to thank Dr. Thomas Pratt of the H. B. Fuller Corporation and Dr. George Myers and Mr. Ralph Schaefer of the Forest Product Laboratory–Madison for supplying the resins analyzed by this paper. They also want to thank Rick Noll of the Materials Science Department, University of Wisconsin, for helping in the scanning electron microscopy studies. Finally, they would like to thank the Forest Products Lab, and the Formaldehyde Institute for providing funds for this study.

References

1. B. Meyer, *Urea-Formaldehyde Resins* (Addison Wesley Publishing, New York, 1979).
2. G. Myers, "Formaldehyde Emission Studies" Forest Products Laboratory–Madison, Department of Agriculture, Sponsor: Formaldehyde Research Institute (1983).
3. T. J. Pratt, W. E. Johns, R. M. Rammon and W. L. Plagemann, "A Novel Concept on the Structure of Cured Urea-Formaldehyde Resin," 3rd Annual International Symposium on Adhesion and Adhesives for Structural Materials, Pullman, Washington, September (1983); *J. Adhesion* **17**, 275 (1985).
4. C. T. Scott and J. A. Koutsky, "Evaluation of Durability of Performance via Fracture Mechanics," 3rd Annual International Symposium on Adhesion and Adhesives for Structural Materials, Pullman, Washington, September (1983).
5. J. I. de Jong and de Jonge, *J. Rec. Trav. Chim.* **71**, 643, 661, 890 (1952).