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A Novel Concept on the Structure of Cured Urea-Formaldehyde Resin

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Condensation of an undefined mixture of water-soluble methylolurea reactants is proposed to proceed through the transient formation of a lyophobic colloidal sol intermediate species that subsequently coalesces to produce gelation during UF resin "cure". An unprotected UF sol dispersion is very unstable, and its brief lifetime may explain why the intermediate sol phase has eluded detection for many years.

Unique characteristics of UF resin behavior observed during preparation, storage and cure are difficult to explain by a conventional mechanism of condensation polymerization. These abnormalities are more logically interpreted by analogy with established colloidal behaviour. Additional support for our coalesced dispersion concept is provided by (i) the known discontinuity in the viscosity of UF resin during cure; (ii) the observed requirement of a minimum threshold concentration of UF resin necessary for gelation to occur and (iii) the SEM of fracture surfaces of cured UF resin which exhibit distinct features that are characteristic of a coalesced sol structure.

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INTRODUCTION

A traditional view of the structure of cured urea-formaldehyde (UF) resins has been arbitrarily assigned a high molecular weight, highly crosslinked structure that is consistent with the observed brittle, insoluble and infusible nature of the cured resin product. Conversely, a tightly associated, small molecule has also been suggested apparently to explain the lack of appreciable viscosity development immediately preceding cure and the retained intractability of cured resin even at sufficiently low formaldehyde to urea (F/U) mole ratios that preclude a high molecular weight, crosslinked structure. Unfortunately, this intractability has prevented definitive characterization by conventional analytical techniques.

Structural arguments based on F/U mole ratios are of questionable validity since the mole ratio of the cured resin has not been demonstrated to be the same as that formulated in the liquid resin precursor. Undefined amounts of formaldehyde are evolved during cure, and conversion of all of the urea or methylolurea reactants to cured resin has not been verified.

Similarly, the lack of appreciable viscosity development during cure does not eliminate the possibility of a high molecular weight species. When a macromolecule is molecularly dispersed in a nonsolvent environment, its contribution to the viscosity of the dispersing medium is negligible. An example of this behaviour is demonstrated by the slow addition of a miscible nonsolvent to a high polymer solution such that the solute polymer is exposed to a gradual change from lyophilic to a lyophobic environment. As the solvent becomes increasingly hostile to the solute polymer, the space or domain occupied by the solute will contract to exhibit substantial reductions in the solution viscosity. The end result of this solvent change is to convert the solute polymer from a true (lyophilic) solution to a colloidal dispersion of a lyophobic sol. If reasonable care is exercised during this process, and the sol particles are stabilized in a sufficiently small particle size range, a pseudostable colloidal dispersion will be obtained that exhibits Tyndall scattering, *i.e.*, a blue opalescence to scattered light with various shades of red to transmitted light.

Although no additional data are presented at this time in support of either the large or small molecule concepts of cured UF structure, we see no need for a crosslinked structure to explain resin behaviour. Logical arguments based on our preliminary data and the

known behaviour of UF resins are presented in support of the transient existence of a lyophobic sol intermediate species that subsequently coalesces to produce UF resin "cure" by gelation. The following discussion will include a brief review of typical small particle behaviour and speculate how this behaviour relates to many unexplained performance characteristics of UF resins during preparation, storage and cure.

BACKGROUND

The initial condensation of urea and formaldehyde to produce methylolureas and higher condensation products is remarkably sensitive to reaction conditions (notably pH and F/U mole ratios). The separation of a white flocculent solid phase of undefined structure is often observed either during resin production, storage or immediately preceding cure. Commercial resin production from the same formulation often results in different products from different production facilities (and many times from the same facility) with no apparent changes in procedures or ingredients.

Typical resin behaviour during storage is to exhibit no significant changes for extended periods. Then, solidification may occur abruptly and without warning. This premature cure in storage is accompanied by evolution of heat and formaldehyde and by pH reduction. Adjustment to a neutral pH is not always a sufficient deterrent to prevent solidification, but mild agitation can be an effective stabilizing technique.

The internal bond strength of UF bonded particleboard seems to be dependent (in some cases) on resin cure rate with the stronger board produced with the faster cure rates. Longer press times for slower curing resins do not significantly improve the board strength. The slower cures resulting from decreased heat transfer into the core of thick particleboards may explain the conventional requirement for increased resin levels to maintain comparable internal bond strengths to that obtained with thinner boards.

It is indeed puzzling to attempt to explain these and other peculiarities of UF resin behaviour by a conventional condensation reaction. It is our position that much of the observed response of UF resins to subtle variations in environment is in better agreement with the temperamental sensitivity of a pseudostable dispersion of a lyophobic sol.

Colloidal terminology is defined as a size description with dimensions between 5 nm and 1 μm . Although a macromolecule may have colloidal dimensions, many colloidal particles are composed of molecular aggregates such that the use of colloidal terminology to describe molecular size can be misleading. A colloidal particle or sol is a separate phase that is thermodynamically unstable. Its behaviour is dominated by its high surface area and energy. The distinction between lyophilic and lyophobic may be one of extent of interaction with the continuous phase.

The pseudostability of a colloidal dispersion of a lyophobic sol results from a combination of attractive (destabilizing) and repulsive (stabilizing) forces between sol particles. The relative magnitude of these opposing forces determines the sol stability and lifetime which can range from seconds to years. The shape of a typical curve of energy dependence on sol separation often exhibits a double minimum separated by an energy barrier. The secondary (shallow) minimum holds the sol particles in a loose association that is shear reversible. Thermal transition to the primary minimum is accompanied with considerable shrinkage (sintering) and is normally irreversible.

The attractive forces are primarily due to the dominant contribution of London dispersion forces to the Van der Waals interactions between particles. These forces result from a fluctuating dipole caused by instantaneous electron perturbations and are essentially independent of external (solvent) conditions. The repulsive forces result from a combination of electrostatic repulsion of the ionic double layers, a steric effect produced by a nonionic protective colloid adsorbed at the sol surface, and an entropy loss creating an osmotic pressure exerted by a solute species or segment trapped between the approaching sol particles. Considerable latitude is available to vary sol stability by medium effects on repulsive forces.

The types of products ultimately formed due to sol instability are generally those that reduce the surface energy or area of the particle. Ostwald ripening is a spontaneous process where small particles are consumed with a corresponding growth of larger particles. Monodisperse (uniform particle size) sols are known to associate into an ordered array¹ that parallels molecular crystallization. The colors of many natural products and some synthetic polymer emulsion films are believed to originate from visible light diffraction of an ordered sol structure in an analogous manner to the Bragg x-ray scattering by crystals.² Coalescence of a polydisperse sol can produce either a

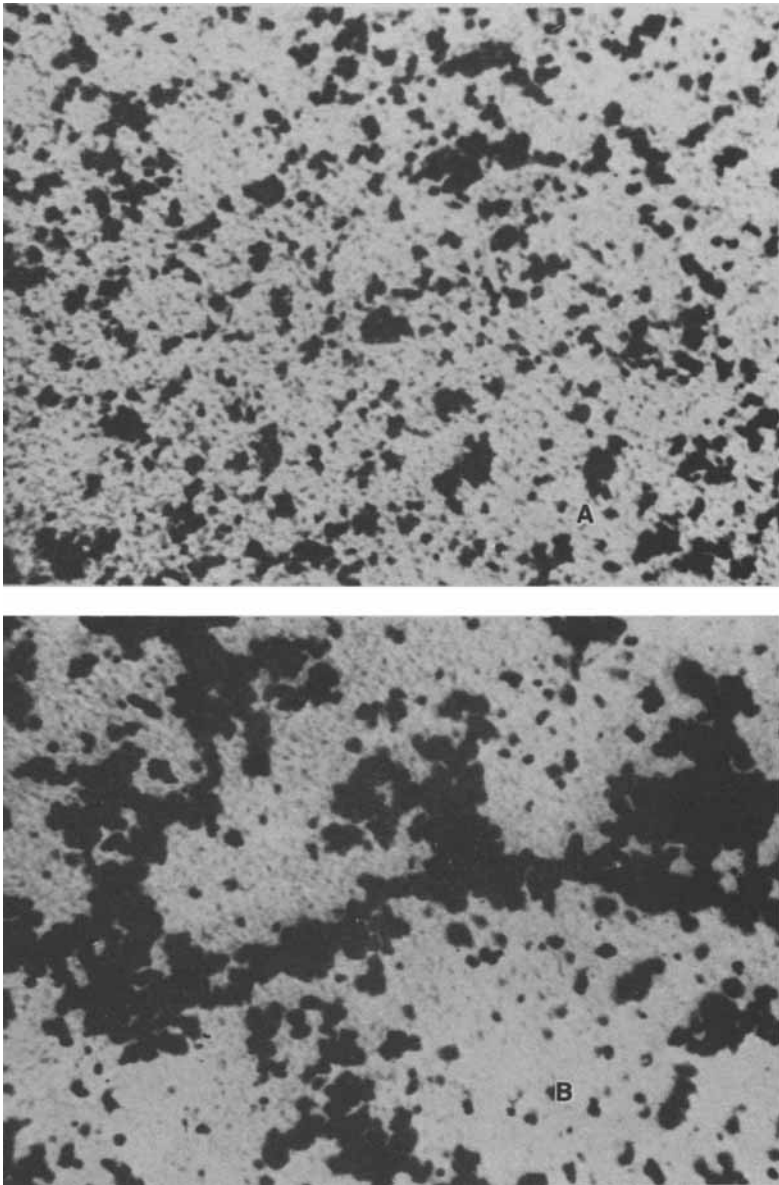


FIGURE 1 Tungsten particles in molten silica; (a) dispersed as discrete particles, (b) development of fibrous structure (reference 3).

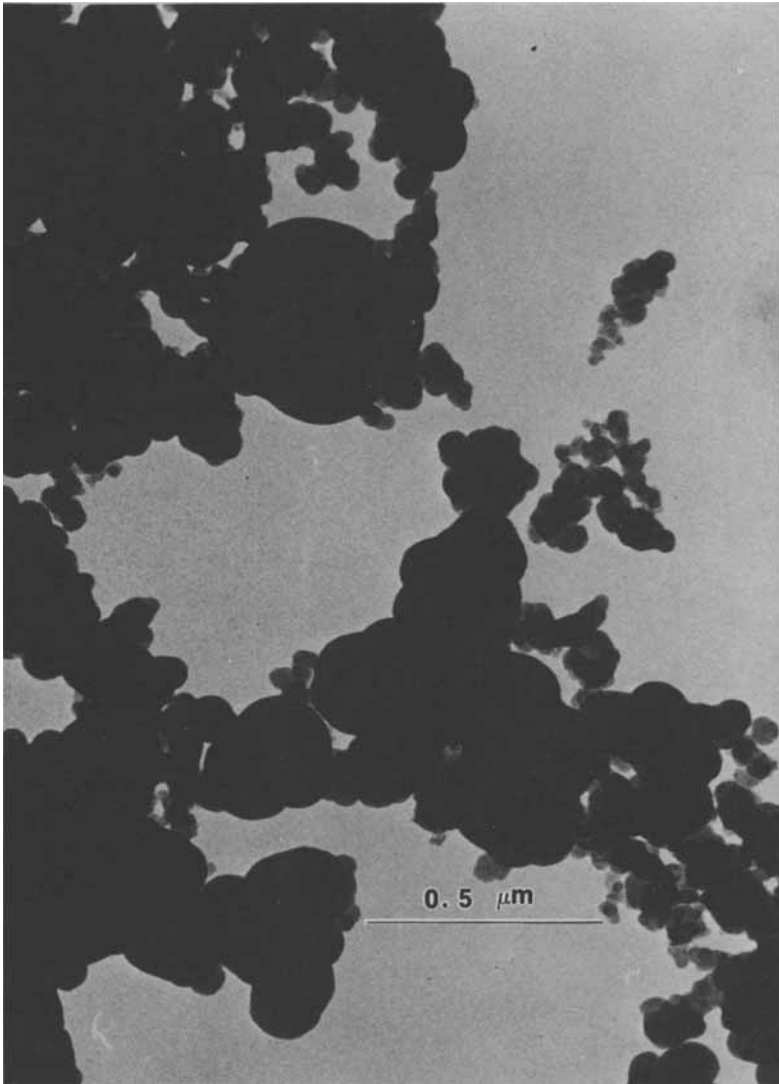
fibrous type structure or large spherical aggregates. Fibre growth is accompanied with large increases in viscosity that ultimately produce gelation to a homogeneous (bicontinuous) structure containing occluded dispersing medium within the sponge type network. Aggregate formation results in sufficiently large clusters to produce gravitational settling. Combinations of aggregate interconnected by fibrous structure can also be formed by appropriate conditions during coalescence.

An example of fibrous structure development is shown in Figure 1a where 2.78 volume per cent of 50 nm tungsten particles are dispersed in molten silica.³ Accompanying the time dependent development of structure (Figure 1-b), the viscosity of the molten silica dispersion was observed to increase by many orders of magnitude.

A conventional technique for compounding elastomers with a reinforcing carbon black filler is first to disperse the black (aggregate) under high shear conditions to produce discrete, primary sol particles of 10–50 nm particle size. (Particles larger than 50 nm are generally not reinforcing but merely act as extenders). The refined stock is then allowed to “rest” during which time the black structure forms, and the viscosity increases. The effect of particle size on structure development is illustrated in Figure 2-a and b. Figure 2-a is a relatively large particle size, extending filler and shows the larger particles as discrete entities. Figure 2-b is a highly reinforcing (*ca* 20 nm particle size) super abrasion furnace black that exhibits substantial fibrous structure. The critical effect of filler particle size on tensile strength⁴ is shown in Figure 3.

The contribution of filler structure development to viscosity and reinforcement is further illustrated in Figure 4. Patel and Byers⁵ have plotted the observed viscosity (as a reinforcing factor) *versus* the volume loading of various fillers (particle size is increasing from left to right) in a standard elastomer masterbatch. By compounding the filler loading necessary to produce a constant reinforcement factor into a standard masterbatch recipe, the cured elastomers will exhibit similar mechanical strength properties.

Of specific interest to the general topic of small particle behavior is their observation that the onset of structure development (the departure of the observed viscosity from that calculated by Guth⁶ for discrete particles) is dependent on concentration, surface area (particle size) and surface energy of the particle. Figure 4 shows that a minimum threshold concentration must be reached prior to the development of structure, *i.e.*, the onset of coalescence.



(a)

FIGURE 2 Carbon black particles; (a) relatively large size carbon black as discrete particles.



FIGURE 2(b) Smaller carbon black particles demonstrating structure development (electron micrographs courtesy of Ashland Chemical Company).

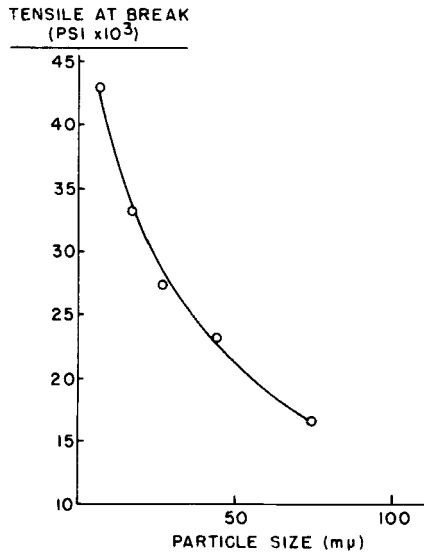


FIGURE 3 Effect of particle size on tensile strength (reference 4).

This threshold concentration requirement for coalescence predicts that if UF resin cure does indeed proceed through formation and coalescence of a lyophobic sol intermediate species, a resin concentration should exist below which there should be no gelation. We have observed a minimum threshold concentration of UF resin below which gelation does not occur.

DISCUSSION OF RESULTS

Perhaps the most common and most revealing indication of a coalesced sol mechanism for UF cure is the abrupt discontinuity in viscosity observed during cure. This established behaviour is quantified in Figure 5 where the log viscosity is plotted *versus* time during cure. The shape of this curve is more representative of crystallization of a super-saturated solution (or freezing of a supercooled liquid) than to that expected for a condensation polymerization. The apparent change in cure rate is attributed to attainment of the minimum threshold concentration of UF sol required to produce structure development and gelation.

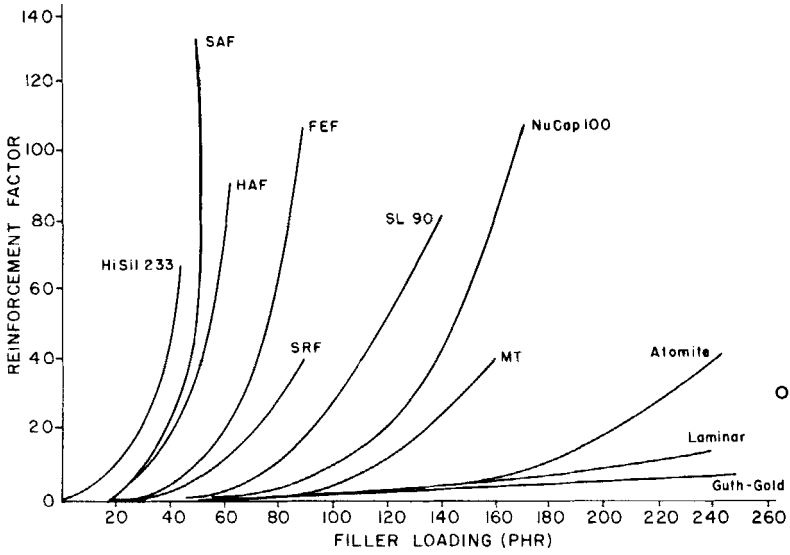


FIGURE 4 Effect of various fillers on reinforcement factor (reference 5).

LOG VISCOSITY

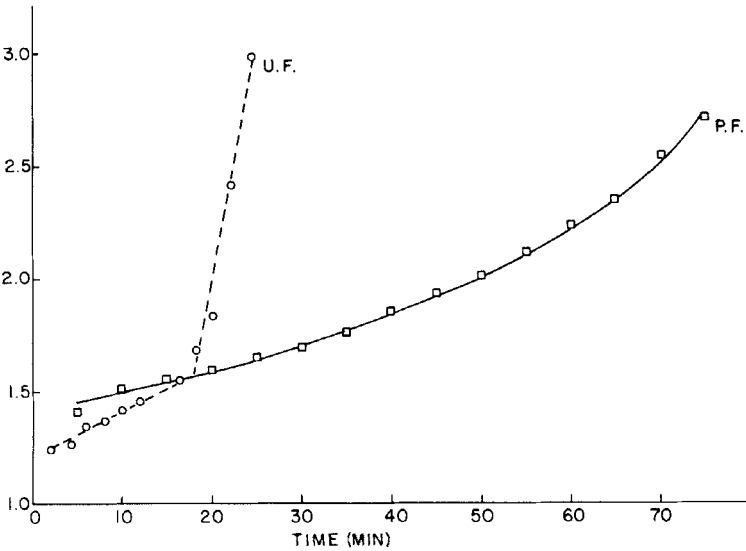


FIGURE 5 Log viscosity as a function of time during resin cure.

Although this discontinuous viscosity behaviour is predicted by Flory⁷ for condensation of reactants having a functionality greater than two, we do not believe this explanation is applicable to UF resin cure. The Flory theory also predicts that at gelation (formation of an infinite network), a substantial part of the reaction mixture will not be gelled. The existence of a soluble phase by exhaustive extraction of a cured UF resin could not be detected.⁸

The continuous dependence of viscosity with time observed during cure of the phenolic control resin (Figure 5) merits further discussion. If this system is truly a condensation of trifunctional phenol with difunctional formaldehyde, a sharp break in viscosity would be expected at the point of infinite network formation. This point is calculated to occur at 50% completion of reaction.⁷ The extent of reaction during cure of this high solids phenolic resin is unknown. Even qualitative attempts to relate degree of cure or molecular weight with high solids solution viscosities can be very misleading.

Alternatively, phase separation of a colloidal PF sol that is sufficiently stabilized or immobilized to delay coalescence would also predict the observed viscosity behavior. In support of this interpretation, Koutsky⁹ has observed submicron sized spherical particles at both the fracture surface and from the residue obtained by evaporation of a hot solvent extract of the fracture surface of a cured phenolic resin. Formation of a colloidal sol or nodules of high crosslink density during cure of epoxy resins has been the topic of considerable interest. Battista¹⁰ describes the preparation by attrition of "microcrystalline" sols of colloidal dimensions from cellulose, collagen, amylose, silicate, polyamide, polyester, and polyolefins.

Immediately preceding the break in viscosity during UF resin cure, the solution typically becomes increasingly turbid as the proposed sol particles form and coalesce or aggregate to sufficiently large size to be visible. In formulations containing high F/U mole ratios, turbidity is often delayed until sometime after gelation. This observation is attributed to stabilization of the sol particles by solvation with formaldehyde in a size range that is too small for visibility. Although we have no definitive evidence to verify a formaldehyde solvated sol, the concept does explain the established improvement in clarity and stability of high F/U mole ratio resins. Evolution of substantial amounts of formaldehyde during cure of UF resins may originate from release of the proposed solvating layer of formaldehyde during coalescence.

This interpretation suggests that the source of formaldehyde emissions from UF bonded particleboard may not be completely due to resin degradation but in part to hydrolytic depolymerization of low molecular weight paraformaldehyde that is spontaneously formed during resin cure. If resin degradation is not the primary source of formaldehyde emissions, and since formaldehyde is known to dissolve (or redisperse) cured UF resins,¹¹ perhaps formaldehyde is a source of resin degradation. This logic predicts that formaldehyde emissions from UF bonded board should precede strength losses due to resin degradation. An accelerated aging study of boards with various levels of formaldehyde emissions would be informative.

The addition of salt to UF resins is a standard industry practice to both reduce the resin cost and to increase the rate of resin cure. Questionable attempts to explain the faster cure rates have ranged from increased ionic strength of the solvent to competition for solvent creating an effective increase in resin solids. An alternate interpretation of increased UF resin cure rates by salt that is based on colloidal behavior is suggested from Figure 6. Although these data were generated with colloidal silica,¹² the principle of sol destabilization by reducing the thickness of the stabilizing double layer applies to other colloidal dispersions.

The pH behavior during salt addition to UF resins initially exhibits a pH drop followed by a slow recovery that is accompanied by an increase in viscosity. (Similar behavior was observed during salt addition to a colloidal silica dispersion.) This observation is attributed to adsorption or ion exchange of the sodium ion into the double layer surrounding the sol to produce the initial pH drop. The pH recovery and viscosity increase may then be due to salt destabilization of the sol causing partial coalescence to produce an increase in viscosity and release of the sodium ion back to solvent. A similar phenomenon could explain the pH drop and formaldehyde release observed during inadvertent resin solidification in storage. Thus, a hydronium ion double layer and a solvating formaldehyde protective colloid (or a protonated formaldehyde double layer) is released to solvent during sol coalescence.

The exponential dependence of gel time on surface area of colloidal silica (Figure 6) indicates that the larger aggregates are relatively inert to further coalescence. The reluctance of large particles other than silica to coalesce is shown in Figure 4 where the threshold concentration required for structure development increases with increasing particle size.

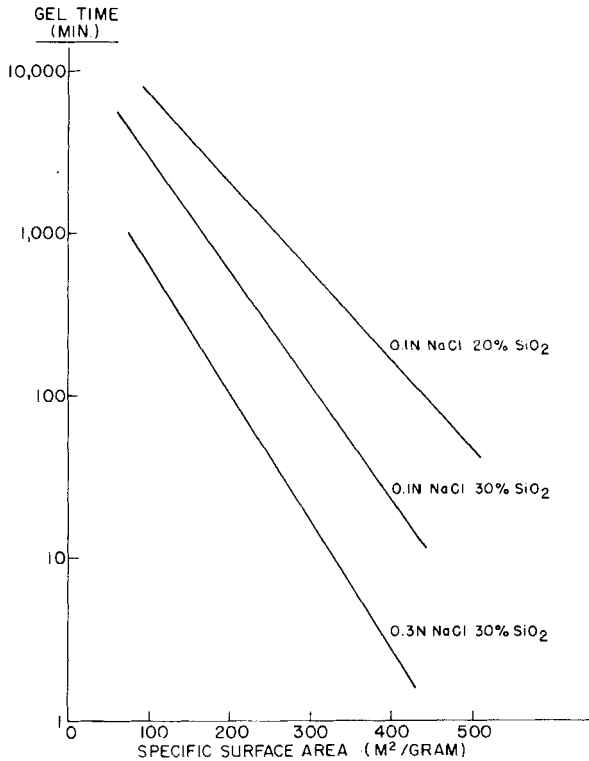


FIGURE 6 Effect of salt and surface area on gel time of colloidal silica (reference 12).

These observations encourage a speculative reinterpretation of UF resin behavior during cure. If curing conditions during coalescence are such that aggregate formation competes with fibrous structure development, or if fibrous structure is converted to spherical aggregates, then much of the observed low strengths and strength degradation of UF bonded particleboard (traditionally attributed to precure, overcure, low mole ratio, etc.) may be due to excessive formation of large inert aggregates that provide a minimal contribution to board strength. A similar strength loss is observed with carbon black reinforcement of elastomers if the compounded stock is not sufficiently refined to disrupt the black aggregate and allow fibrous structure formation.

A minimum threshold concentration required for UF gelation is

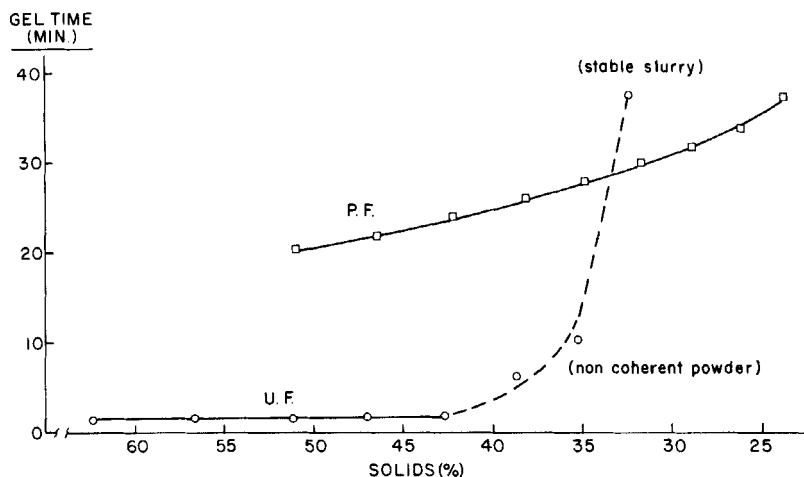


FIGURE 7 Effect of resin concentration on gel time.

illustrated in Figure 7 where gel time was monitored *versus* resin solids. Below a concentration of about 40% solids, the cured UF resin was obtained as a noncoherent, particulate solid slurry that would not solidify (gel) even when heating was continued for several hours. In agreement with Figure 4, this threshold concentration required for gelation of UF resins was observed to decrease with decreasing sol particle size. Filtration of the stable slurry obtained from dilute solution cures gave finely divided, spherical particles believed to result from agglomeration of smaller primary sol particles.

The phenolic control resin (Figure 7) under dilute solution cure conditions showed no indications of discontinuity or slurry formation. Although a discrete nodular (sol) particle has been observed⁹ on the surface of a cured phenolic resin, apparently this heterogeneous phase is either highly stabilized, or it separates from solution after resin immobilization, since no indications of sol coalescence were observed under our reaction conditions. The shape of the gel time *versus* solids curve for the phenolic resin appears as a classic example of a condensation polymerization. The apparent linearity at high solids is indicative of pseudozero order kinetics where the decrease in

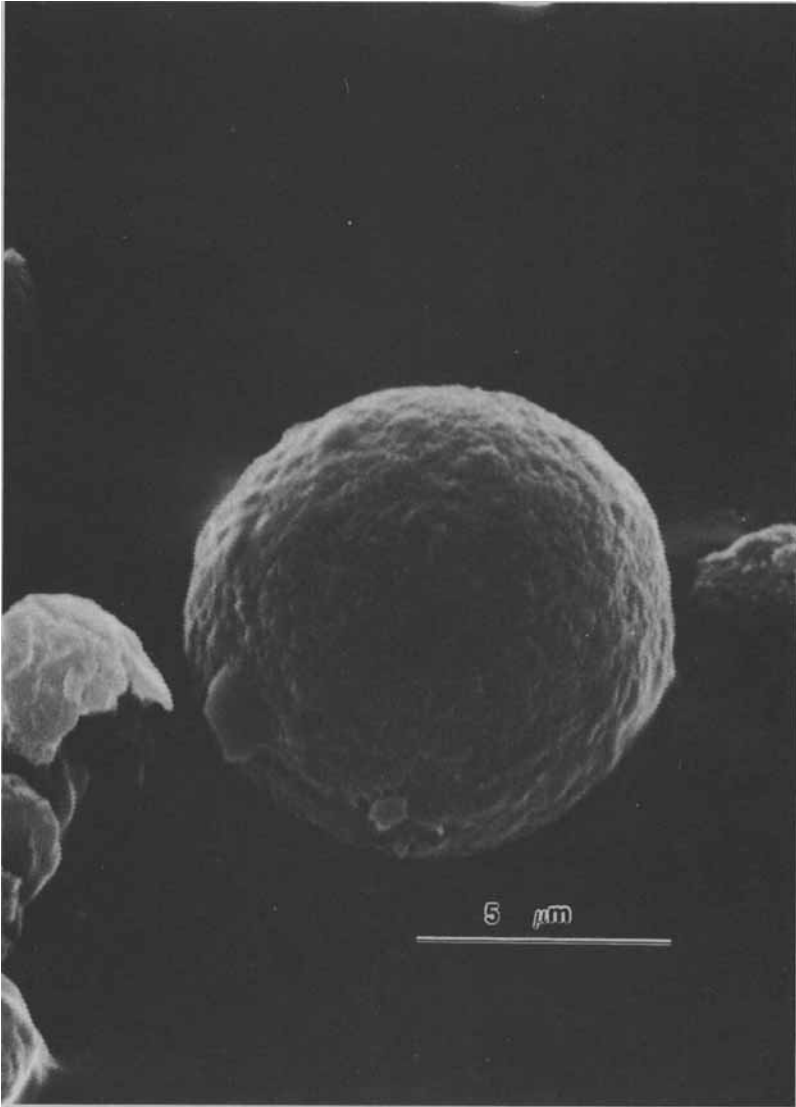


FIGURE 8a Scanning electron micrographs of particles obtained from dilute solution cures of UF resins.

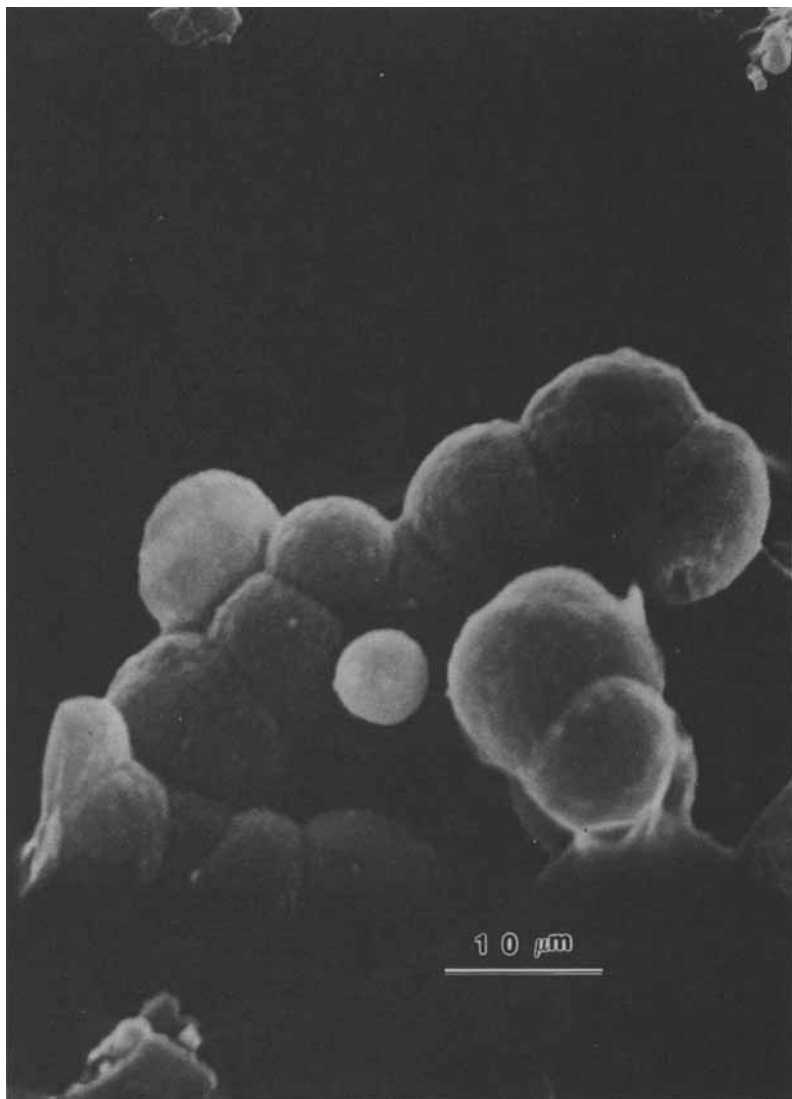


FIGURE 8b Scanning electron micrographs of particles obtained from dilute solution cures of UF resins.

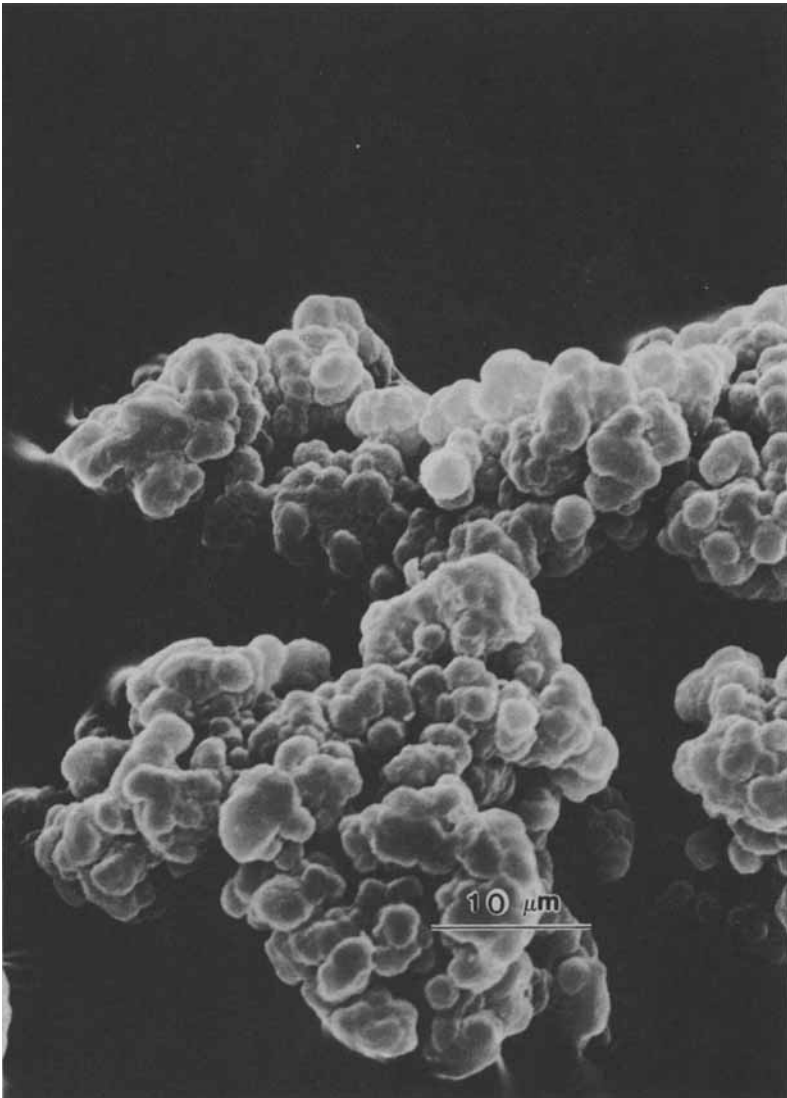


FIGURE 8c Scanning electron micrographs of particles obtained from dilute solution cures of UF resins.



FIGURE 8d Scanning electron micrographs of particles obtained from dilute solution cures of UF resins.

reactive monomer concentration is insignificant compared to the large reservoir in solution. The gradual departure from linearity at lower concentrations supports a predicted kinetic behavior of first (or higher) order in reactive monomer.

Examination by SEM of the polydisperse spherical particles obtained from dilute solution cures of various UF resins are shown in Figure 8-a through d. The mottled surface features on the larger spheres (5–10 μm) suggests their formation is by aggregation of much smaller sols. Sufficient resolution to resolve this possibility was not obtainable at this time.

The fibrous type structure depicted in Figure 8-b is not understood. The relatively large particle size (5–10 μm) predicts an inert species that should not coalesce. Perhaps the apparent deformation of these spheres is due to collapse of fibrous structure to form a loosely associated spherical aggregate with occluded solvent that exhibits a similar reactivity to coalescence as the smaller sols. Alternatively, the high surface energies of an unprotected, low formaldehyde UF sol may be sufficient to induce coalescence of larger sols. Stabilization of a low formaldehyde UF sol dispersion is extremely difficult, and its transient existence may explain why the sol phase has gone unnoticed for many years. The characteristic blue haze of a stable UF colloidal sol has been previously reported¹³ in an excessively high (2.5:1) F/U mole ratio resin formulation.

The fracture surface of a high solids (65%) cured UF is shown in Figure 9. The coalesced sol structure appears as an almost monodisperse sol of *ca* 300 nm particle size with the voids (dark areas) attributed to occupation by solvent. We believe that even this smaller size sol is not the primary sol, but that it results from either Ostwald ripening or coalescence of a smaller sol. This reasoning is based on visual observations of a characteristic blue haze (that typify a 20–50 nm sol) from a stabilized UF sol dispersion. Determinations of particle size and dispersity of the primary sol are currently in progress.

SUMMARY

Although our preliminary data and tentative conclusions require the scrutiny of additional studies for acceptance, we contend there is considerable merit for the transient formation of a lyophobic UF sol intermediate species that subsequently coalesces to produce gelation during

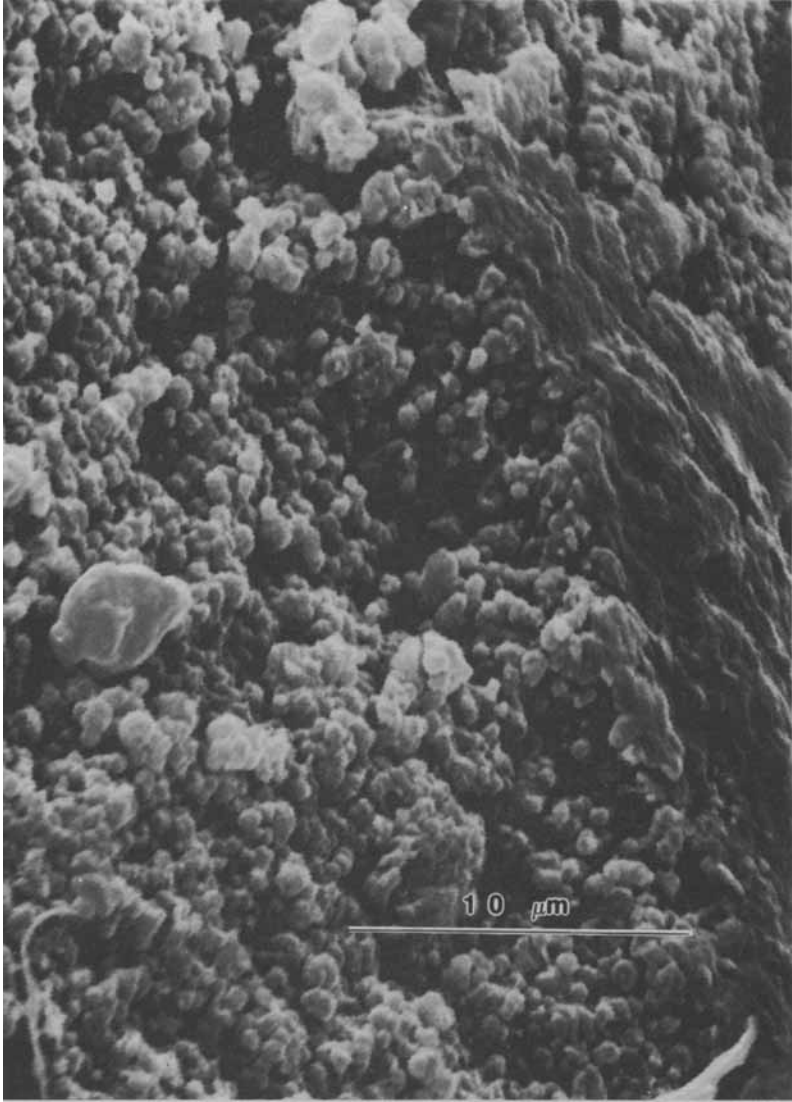


Figure 9 Scanning electron micrograph of the fracture surface of (65% solids) cured UF resin.

UF resin cure. We submit that this colloidal dispersion model better explains many of the peculiarities inherent to UF resin behaviour and may have significant practical application for increasing performance and reducing formaldehyde emissions from cured UF resin products. The extension of the coalesced sol concept to other polymeric systems has exciting potential.

Acknowledgements

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