Reaction Variables and a Proposed Mechanism of Open-Pore Urea/Formaldehyde Structure Formation

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Synopsis

Formation of open-pore urea/formaldehyde structures from nonetherified urea/formaldehyde resins involves reaction of one or more methylol groups with other methylol or amino groups. The structure formation proceeds through particle formation and growth until all the resin is consumed. A strong acid is preferred for achieving a porous structure in urea/formaldehyde resins; weakly ionized acids produce structures with low yield. Colloidal instability is an asset in porous structure formation. An 80:20 polyethylene oxide/polypropylene oxide block copolymer of approximate molecular weight 8500 has been found to be an entropic-type destabilizer in the formation of porous structures.

INTRODUCTION

Open-pore urea/formaldehyde (OPUF) structures can be prepared by adding phosphoric or oxalic acid to an aqueous solution of nonetherified urea/formaldehyde resin. These structures consist of a network of entangled spheres of about 3 μm. The pores are formed by the interstices between the chains of the spheres. The properties of OPUF can be regulated by controlling the composition of the aqueous resin solution and the reaction variables.

Renner[1] has studied the gelation of a melamine/formaldehyde condensation product in the presence of a hydrocolloid which yields crosslinked polymers. In other work, Renner[2] found that a urea/formaldehyde resin above a molar ratio of 0.8 produced a porous structure whereas a polymeric gel was formed when this ratio was below 0.8.

This paper proposes a scheme of the process of OPUF structure formation. The effects of various process variables including catalyst type, presence of phenol/formaldehyde comonomer, and use of a polymeric surfactant were studied. The results obtained were analyzed in terms of the chemical reactions involved and the thermodynamics of the reaction system.

EXPERIMENTAL

Materials

Preparation of Nonetherified Urea/Formaldehyde Resin. Urea (7.83 moles) and alcohol-free 50% aqueous formaldehyde (18.0 moles) were refluxed for 30 min at a pH of 5.9 ± 0.1. After cooling, 248 ml water was removed from the condensate under partial vacuum at 65°–85°C. The pH was readjusted to 5.9 ± 0.1, and the mixture was held at 90° ± 2°C for V-W Gardner viscosity measurement. The flask was cooled by an ice bath to 50°C. Urea (5.5 moles) and melamine (0.03 mole) were then added under agitation. When complete

0021-8995/79/0023-0381$01.00

solution occurred, the pH was raised to 7.4. The resin formed (74.0% solids) had a urea-to-formaldehyde combined molar ratio of 0.435 and a cumulative molar ratio of 0.74.

Preparation of Phenol/Formaldehyde Resin. Phenol and formaldehyde, at a molar ratio of 0.77, were condensed using sodium hydroxide as a catalyst to produce a water-soluble resin (65% solids).

Pluronic F-68 (BASF Wyandotte). This surfactant is an 80:20 ethylene oxide/propylene oxide block copolymer of approximate molecular weight 8500.

Typical Method of OPUF Structure Formation

Pluronic F-68 (20.2 g) was dissolved in deionized water (616.9 g). Urea/formaldehyde (306.5 g) and phenol/formaldehyde (34.2 g) resins were added, and complete solubility was achieved by stirring. Phosphoric acid, 85% (22.2 g), was then added to the aqueous solution and was stirred for 10 sec. The mass formed at this point was allowed to set undisturbed. Four min after the phosphoric acid addition, the clear liquid formed the OPUF structure. The structure was allowed to stand for 4 hr and then was cut into small chunks with a spatula. The structure was washed several times with deionized water until the conductivity of the filtrate was below 60 μmhos. The washed material was dried in a circulatory oven for 48 hr at 120°F, followed by pulverization and particle size screening to produce a powder. Unless otherwise specified, all OPUF structure formation was carried out in a quiescent state.

Experimental Variables

The following processing and compositional variables were investigated: (1) ratio of urea to formaldehyde (0.60–0.80); (2) solids content of the structuring solution (15%–40%); (3) type of acid catalyst (e.g., phosphoric, oxalic); (4) polymerization temperature (15–50°C); (5) effect of stirring (0–200 rpm); (6) effect of surfactant on OPUF polymerization (0%–8% Pluronic F-68); (7) level of phenol/formaldehyde polymeric comonomer (0%–30%).

Scanning Electron-Microscopic Analysis

A Cambridge Stereoscan Mark II scanning electron microscope was used to view and photographically record the structure of the OPUF powders at 1020 and 5100X magnifications. The magnifications of the photomicrographs were calibrated using diffraction grating replicas. The OPUF specimens were rendered conductive by vacuum evaporating aluminum onto their surface.

RESULTS AN DISCUSSION

### Mechanism of Structure Formation and Reactions Involved

Urea/formaldehyde resins are built up by condensation polymerization. Urea and formaldehyde are reacted in the absence of alcohol, forming dimethylol urea and other related compounds. These compounds, which are highly water soluble, can be reacted at will, with concurrent elimination of water and/or formaldehyde,

to produce medium-sized molecules. The intermediate condensation product is the nonetherified urea/formaldehyde resin, and it is utilized in preparation of useful structures by acidification. Branched polymers can be produced from the water-soluble intermediate condensation product by simple application of heat.

We propose formation of ether bridges between methylol groups of two neighboring molecules involving a protonated initiating species. OPUF ormation involves initiation, particle formation, particle growth, and termination.

The conversion of a urea/formaldehyde resin that is soluble in water to an insoluble open-pore urea/formaldehyde structure primarily involves the following reactions:

1. Formation of methylene bridges[3] between methylol and amino groups of two neighboring molecules:

$$RNHCH_2OH + H_2NR' \rightarrow RNHCH_2NHR' + H_2O$$
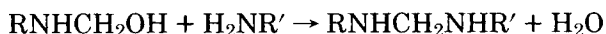
2. The formation of ether bridges between methylol groups of two neighboring molecules; both inter- and intramolecular reactions are possible:

$$RNHCH_2OH + HOCH_2NHR' \rightarrow RNHCH_2OCH_2NHR' + H_2O$$
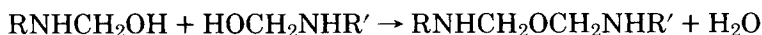
3. Formation of methylene bridges between two methylol groups; here, the reaction is mostly intermolecular but intramolecular reaction is also possible:

$$RNHCH_2OH + HOCH_2NHR \rightarrow RNHCH_2NHR' + H_2O + CH_2O$$
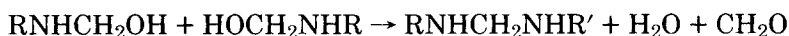
Rate of OPUF Formation

A typical result of conversion at 25°C is depicted in Figure 1. A number of urea/formaldehyde resins with varying molar ratio of urea and formaldehyde were evaluated and their profile of conversion studied. The porous structure was formed fastest when the urea/formaldehyde molar ratio was 0.74. The rate decreased up to about a molar ratio of 0.8. Above a molar ratio of 0.8, the conversion was slow and microporous structures were obtained. This method of controlling particle size has also been studied by Renner.[2]

Generally, resin conversion of OPUF is 74%–80%. In one of the experiments,
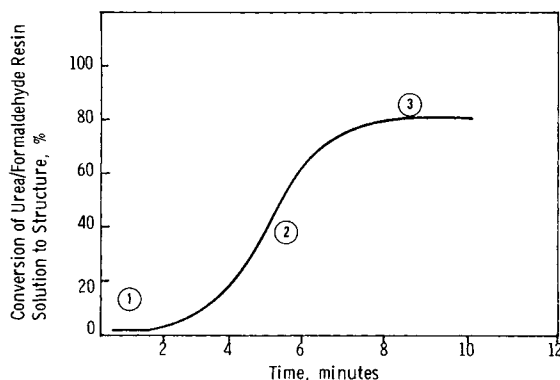

Fig. 1. Profile of conversion in a typical OPUF structure formation: (1) particle formation step; (2) particle growth; (3) disappearance of $p_{aqueous}$; this shows end of reaction.

the structure was formed and allowed to stand for 4 hr. The excess liquid from the structure was removed by aspiration through an inverted sintered funnel and observed over a 48-hr period. The liquid remained clear for 24 hr but turned milky (with particles < 25 μm) after 48 hr. This shows that incomplete conversion is mainly due to the presence of small-sized molecules in the urea resin.

A water-soluble phenol/formaldehyde resin does not form a porous structure with a reasonable degree of acidification in the same way that a urea/formaldehyde resin does (see Fig. 2). This was demonstrated for a phenol/formaldehyde resin of 0.77 molar ratio at the level of 7% phosphoric acid based on resin solids. However, the introduction of a small amount of phenol/formaldehyde resin into an acidified urea/formaldehyde formulation leads to copolymerization. The effect of incorporation of the phenol/formaldehyde units in the structure was checked by physical characteristics, such as a comparison of resiliency and compressive strength of a structure based on 100% urea/formaldehyde with a structure containing 80:20 urea/formaldehyde and phenol/formaldehyde.

Precipitating Acids Studied

A Brϕsted acid such as H_3PO_4 with a pK_a in the range of 1 to 2 produces fast particle formation and particle growth steps. Weakly ionized acids, such as acrylic acid or poly(acrylic acid), at 7% acid based on resin solids also produce microporous structures, but the conversion is low (see Fig. 3).

Thus, selective precipitation of the higher molecular weight water-soluble urea/formaldehyde occurs with the weakly ionized acids. Medium-sized and small-sized molecules, even after molecular weight promotion, remain water soluble, and hence the extent of conversion is low.
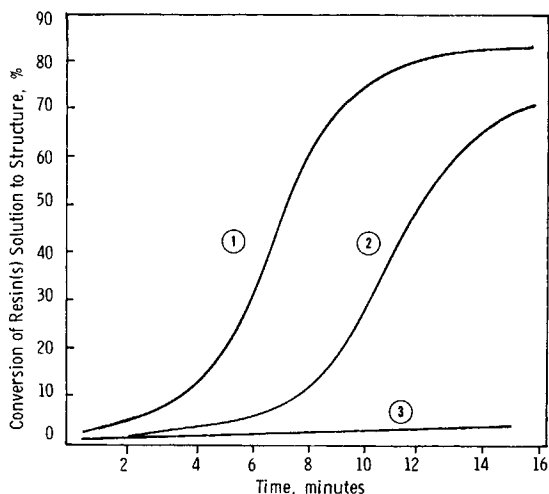

Fig. 2. Comparison of urea/formaldehyde and phenol/formaldehyde resin solution in regards to structure formation: curve 1, 100% urea/formaldehyde; curve 2, 80:20 urea/formaldehyde: phenol/formaldehyde; curve 3, 100% phenol/formaldehyde.
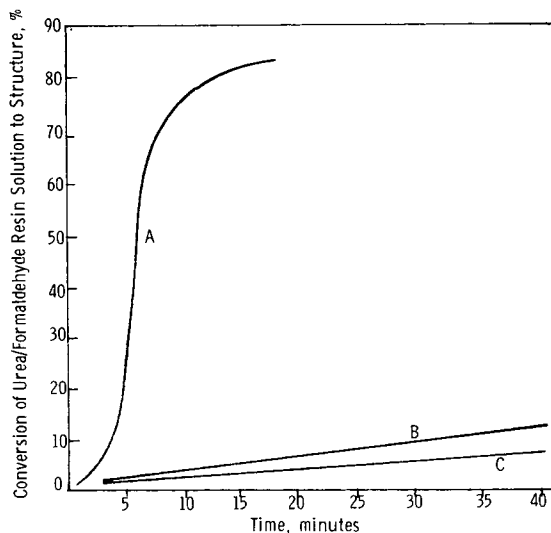
Fig. 3. Gelation of urea/formaldehyde resin by acids: curve A, phosphoric acid; curve B, acrylic acid; curve C, poly(acrylic acid).

Effect of Stirring on Particle Geometry

Process research was conducted on a 100% urea/formaldehyde powder polymer. Four powders were generated from an aqueous solution of a nonetherified urea/formaldehyde resin with a molar ratio of 0.74 at an operating solid level of 18.0%. Phosphoric acid at a level of 1.6% based on the total formula was used as precipitating agent. The processing variations are listed in Table I, together with the results obtained. SEM photographs of the four samples described in Table I are presented in Figures 4–7, at magnifications of 1020 and 5100X. Table II summarizes the results of examination of these photographs.

Colloidal Stability and Instability

Colloidal stability is important in microporous suspensions and, to a lesser degree, in porous structures. For colloidal dispersions to be stable, it is imperative to provide a repulsion barrier between the particles so that the London and van der Waals attractive energies do not overcome the energy of thermal motion, which is 3/2 kT. Dispersions of neutral colloidal particles flocculate rapidly as a direct consequence of the long-range attractive forces. In particle dispersions, the total potential is the sum of the energies of attraction (London and van der Waals) and the energies of repulsion. When the potential energy maximum is quite large as compared to the thermal energy, then dispersions of such particles display long-term stability. In order to achieve a potential energy maximum, it is necessary to provide a repulsive potential energy between particles. This is achieved by electrostatic or steric stabilization.

Electrostatic Stabilization. Interparticle repulsion due to coulombic forces[4] between two particles is a function of the dielectric constant of the continuous medium. The surface potential develops by methods such as adsorption and ionization of potential determining ions. If particles approach a point where attractive forces overcome electrostatic forces, flocculation will occur.

Steric Stabilization. The term steric is not used in an organic chemical sense

TABLE I
Urea/Formaldehyde Powder Polymers

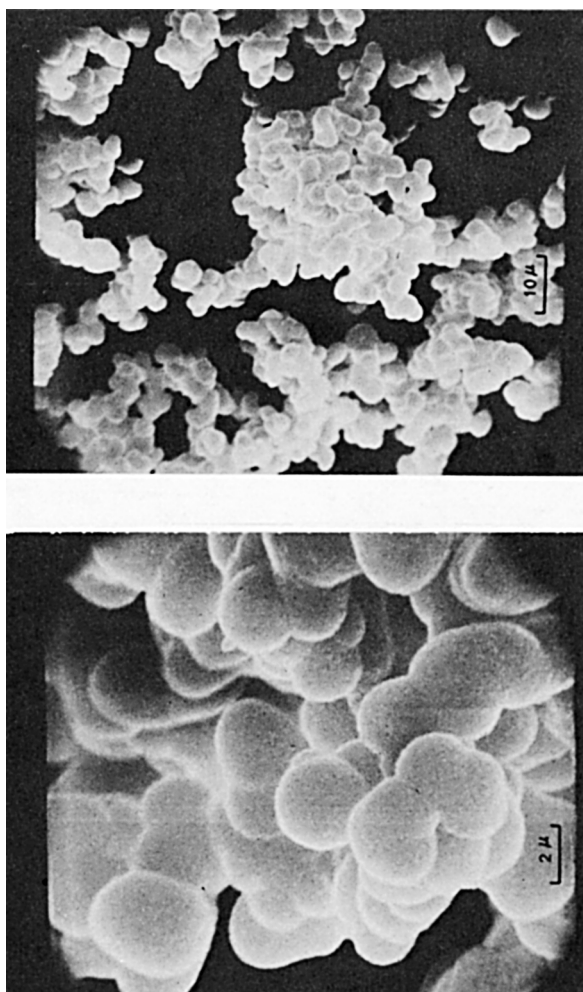|	Sample 172904	Sample 172908	Sample 172909	Sample 172910
Method of preparation	make block; pulverize while wet; wash with water; dry and screen	add phosphoric acid to the resin solution with constant stirring by a high shear blade at ~200 rpm; total reaction time 30 min	add phosphoric acid; stir for 10 sec; allow to set to yogurt stage ~4 min, then stir 200 rpm for 10 min; total reaction time 30 min	slow precipitation by phosphoric acid over a 20-min period with constant stirring; total reaction time 30 min
Power yield, %	74.2	75.7	82.8	63.5
Apparent density, g/cm^3	0.300	0.358	0.214	0.397
Screen analysis, %				
Particle size				
>420 μm (40 mesh)	0.0	0.5	0.6	1.1
>177 μm (80 mesh)	2.0	2.0	6.2	0.4
>149 μm (100 mesh)	0.0	0.5	74.9	0.0
<149 μm	98.0	97.0	18.3	98.5

Fig. 4. Urea/formaldehyde powder polymer prepared via a block sample 172904.

of the restriction of movement; rather, it has thermodynamical implications. Interpenetration of particles due to Brownian motion results in compression of the nonionic hydrocolloid polymer or its chain segments (see Fig. 8). This compression produces a change in the free energy, given by the Gibbs-Helmholtz equation[5]

$$\Delta F_R = \Delta H_R - T\Delta S_R$$

There are three possibilities regarding the change of free energy ΔF_R. Case 1: $\Delta F_R = 0$; if no nonionic hydrocolloid is present. Case 2: $\Delta F_R = +$; hydrocolloid stabilizes the particles and does not sensitize them. Case 3: $\Delta F_R = -$; hydrocolloid sensitizes the particles and destabilizes them.

For OPUF structures such as those represented in Figure 3, curves B and C, a positive ΔF_R is important for stability during formation. However, a less
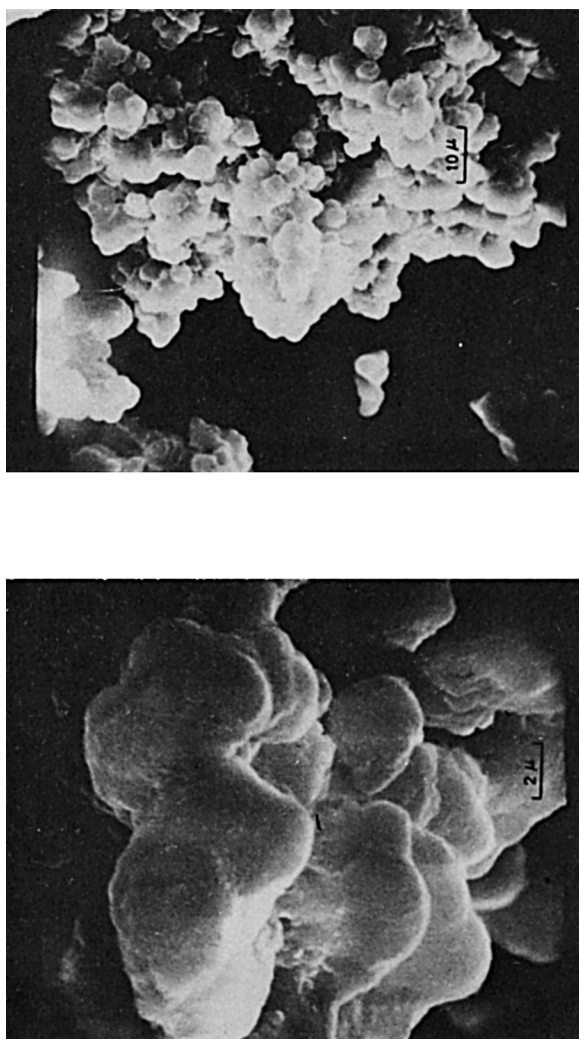
Fig. 5. Urea/formaldehyde powder polymer prepared under constant high shear stirring, sample 172908.

positive or a negative ΔF_R is needed for recovery of the polymer and better coagulation during porous structure formation (see curve A, Fig. 3).

An 80:20 block copolymer of polyethylene oxide and polypropylene oxide, Pluronic F-68, produces a negative free energy change in our formulations. This is based on the experimental finding that incorporation of this hydrocolloid reduced the particle size of the structures. Furthermore, Pluronic F-68 contributes to instability in curves B and C of Figure 3. There are three methods of achieving a negative ΔF_R, these are indicated in Table III. An increase in temperature produced smaller-sized particles in our formulations. This is also true in open-pore polyurethane systems.[6] Pluronic F-68 functions, therefore, as an entropic-type destabilizer in the formation of open-pore urea/formaldehyde structures.
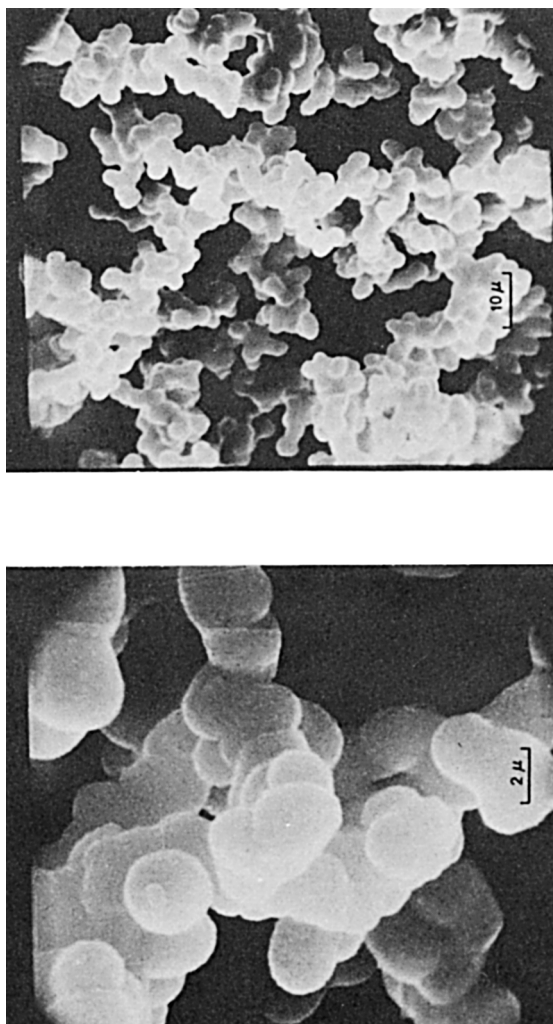
Fig. 6. Urea/formaldehyde powder polymer prepared under constant high shear stirring after allowing to set for 4 min, sample 172909.

CONCLUSIONS

Urea/formaldehyde resins and open-pore urea/formaldehyde structures are both built up by condensation polymerization. A scheme for formation of these structures has been presented. The mechanism of the conversion of the water-soluble, medium-sized urea/formaldehyde resin to a porous structure involves formation of methylene bridges by reaction of methylol or amino groups. The formation of the structure involves a particle formation step, a particle growth step, and, finally, the disappearance of the resin in the aqueous phase.

The properties of the urea/formaldehyde structure can be modified by introducing a water-soluble phenol/formaldehyde resin. Generally, the phenol/formaldehyde resin retards the particle formation and particle growth steps. A strong acid structures the urea/formaldehyde resins effectively. Weakly ionized acids produce structures with low yield.
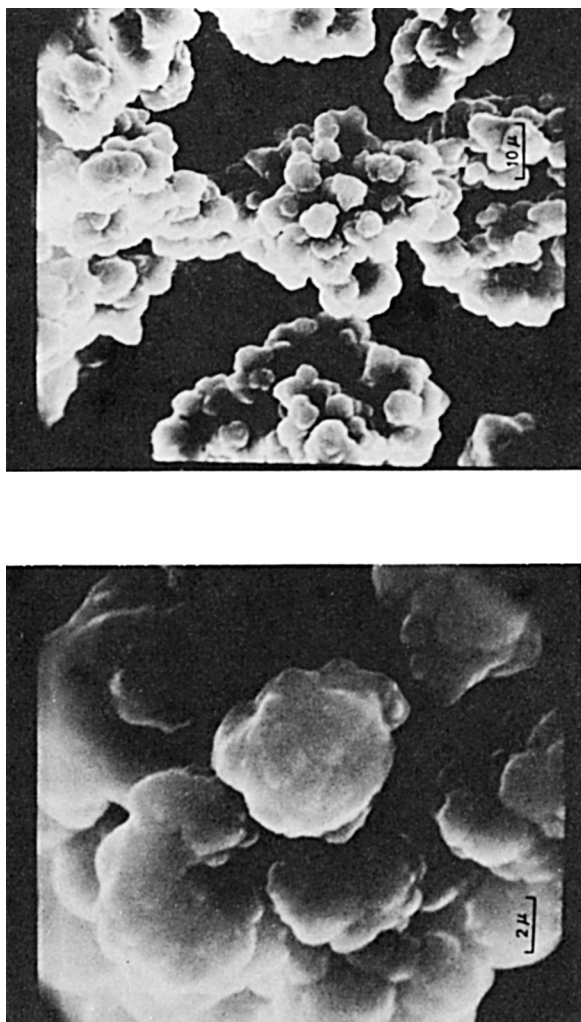
Fig. 7. Urea/formaldehyde powder polymer prepared with slow precipitation under constant high shear agitation, sample 172910.

Colloidal instability is an asset in formation of porous structures. The formation of such structures involves steric destabilization. Pluronic F-68 has been found to be an entropic-type destabilizer in the formation of porous structures. The degree of conversion of the resin from the aqueous phase to the porous structure is approximately 75%. This is due to the presence of small molecules in the urea resin. These small molecules are not promoted sufficiently, after acidification, to become insoluble.

The polymer particles obtained by allowing the aqueous urea/formaldehyde resin solution to set undisturbed to the structure were the most spherical. The OPUF particles prepared under constant high stirring were irregular in shape. Powder prepared under high shear stirring, after being allowed to set for 4 min, produced the highest yield, and the particles were nearly monodisperse and spherical.
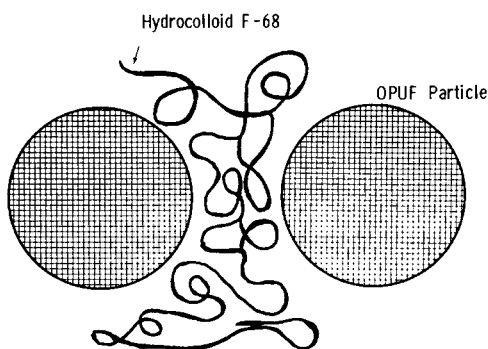
Fig. 8. Compression of a hydrocolloid due to interparticle penetration resulting in a change of free energy.

TABLE II
Summary of SEM Photographs, Figures 4 Through 7

Powder sample	Approximate primary particle size, μm	Degree of dispersity	Remarks
172904	3	nearly monodisperse	particles are nearly spherical
172908	$\frac{1}{2}$–3	high dispersity	particles are spherical but irregular in size
172909	3	nearly monodisperse	particles are nearly spherical
172910	3–5	medium dispersity	particles are spherical but irregular in size

TABLE III
Schemes for Negative Change in Free Energy During Formation of Open-Pore Urea/Formaldehyde Structures

ΔH_R	ΔS_R	$T\Delta S_R/\Delta H_R$	Type	Temperature effect
−	−	>1	enthalpic	if temperature increases, less negative ΔF_R and less instability
−	+	<1	entropic	if temperature increases, more negative ΔF_R and more instability
±	±	$\gtrless 1$	hybrid	increase of temperature can produce either stability or instability

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