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Applications of Porous Urea/Formaldehyde Polymers

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ABSTRACT

Open pore urea/formaldehyde (OPUF) polymers were developed by Usmani and co-workers. They are composed of agglomerated spherical particles (0.1-10 μm in diameter) bonded to one another in a rigid, highly permeable structures. In this paper we describe the applications of OPUF and the development of potential technologies therefrom.

INTRODUCTION

Foamed polymers based on reactive oligomers have recently been reviewed by Shutov [1]. Open pore urea/formaldehyde (OPUF) is not like conventional foams having unit cells but is rather composed of agglomerated spherical particles (0.1-10 μm in diameter) bonded to one another in a rigid, highly permeable structure. The preparation, process of formation, and chemistry of OPUF have been described by us [2-4]. OPUF polymers are formed by solvent (water) evaporation and matrix shrinkage. They contain small (0.1-10 μm) interconnecting pores between randomly packed chains of spheres (0.1-10 μm). OPUF's resiliency, density, porosity, pore size, and sphere size can be controlled by chemistry, composition, and processing.

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A wide range of OPUF products can be made for many worthwhile applications. We shall describe demonstrated and potential applications of OPUF in this paper.

PREPARATION OF OPUF

OPUF was prepared by adding phosphoric acid to an aqueous solution of a nonetherified urea/formaldehyde resin. Nonetherified urea/formaldehyde resin prepolymer was prepared as follows. Urea (7.83 mol) and alcohol-free 50% aqueous formaldehyde (18.0 mol) were refluxed for 30 min at pH 5.9 ± 0.1. After cooling, 248 mL water was removed from the condensate under partial vacuum at 60-80°C. The pH was readjusted to 5.9 ± 0.1 and the mixture was held at 90 ± 2°C for a V-W Gardner viscosity. The flask was rapidly cooled by ice to 50°C. Urea (5.5 mol) and melamine (0.03 mol) were then added under moderate agitation. After complete dissolution, the pH was raised to 7.5. The formed prepolymer (74.0% solids) had a urea-to-formaldehyde combined molar ratio of 0.435 and a cumulative molar ratio of 0.74.

The method for the OPUF preparation is simple. Urea formadehyde prepolymer (345.8 g) was dissolved in deionized water (633.2 g). Phosphoric acid (85%, 21.0 g) was then added and the mixture stirred for 10 s. The mass was allowed to set undisturbed. After 4 min the porous polymer was formed. The solidified mass was allowed to stand for 4 h and then cut into small chunks and washed several times with deionized water until free of phosphoric acid (conductivity of filtrate 50 μmhos). The washed material was dried in a vacuum oven at 50°C for 4 h. The dried mass pulverized easily into a powder.

The copolymerization of urea/formaldehyde with phenol/formaldehyde or melamine/formaldehyde resin increases the range of useful products. An OPUF copolymer was prepared as follows. Pluronic F-68, an 80:20 ethylene oxide/propylene oxide block copolymer of about 8500 molecular weight (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. Phenol/formaldehyde resin was prepared by condensing phenol and formaldehyde at a molar ratio of 0.77, using sodium hydroxide as catalyst to produce a water-soluble resin (65% solids). Phosphoric acid (85%, 22.2 g) was then added to the aqueous solution and the mixture stirred for 10 s. The mass formed at this point was allowed to set undisturbed. Four minutes after the phosphoric acid addition, the clear liquid solidified. The mass was allowed to stand for 4 h and was cut into small chunks with a spatula. OPUF was washe several times with deionized water until the conductivity of the filtrate was ~ 50 μmhos. The washed material was dried, pulverized, and screened to produce a powder.

Properties of OPUF can be regulated by processing and compositional variables, e.g., ratio of urea to formaldehyde in the resin, solid content of the solution, type of catalyst, temperature of polymerization, stirring, presence of surfactant, and presence of phenol/formaldehyde binder comonomer in the formulation.

OPUF FORMATION: REACTIONS

The conversion of a urea/formaldehyde that is soluble in water to an insoluble branched OPUF involves the reactions shown in Table 1.

TABLE 1. Reactions Involved in OPUF Formation

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

   $$RNHCH_2OH + H_2NR' \longrightarrow RNHCH_2NHR' + H_2O$$

2. Formation of ether bridges between methylol groups of two neighboring molecules; both inter- and intramolecular reactions are possible:

   $$RNHCH_2OH + HOCH_2NHR' \longrightarrow RNHCH_2OCH_2NHR' + H_2O$$

3. Formation of methylene bridges between two methylol groups: here, the reaction is mostly intermolecular, but intramolecular reaction if also possible:

   $$RNHCH_2OH + HOCH_2NHR' \longrightarrow RNHCH_2NHR' + H_2O + CH_2O$$

PROPERTIES

Depending on the formulation and reaction conditions, OPUF polymers can be prepared in block, thin sheet, rod, or powder form. OPUF can be made into soft, resilient, or hard products. The resiliency of homo-OPUF can be improved by incorporating up to 20% of a phenol/formaldehyde comonomer in the composition. OPUF powders are invariably water white, smooth, and free flowing. The density is generally in the range 0.15-0.4 g/cc. The porosity is generally very high, usually above 80%.

SEM photographs of OPUF (40-80 mesh and -80 mesh powders) at 5100× magnification are shown in Fig. 1.

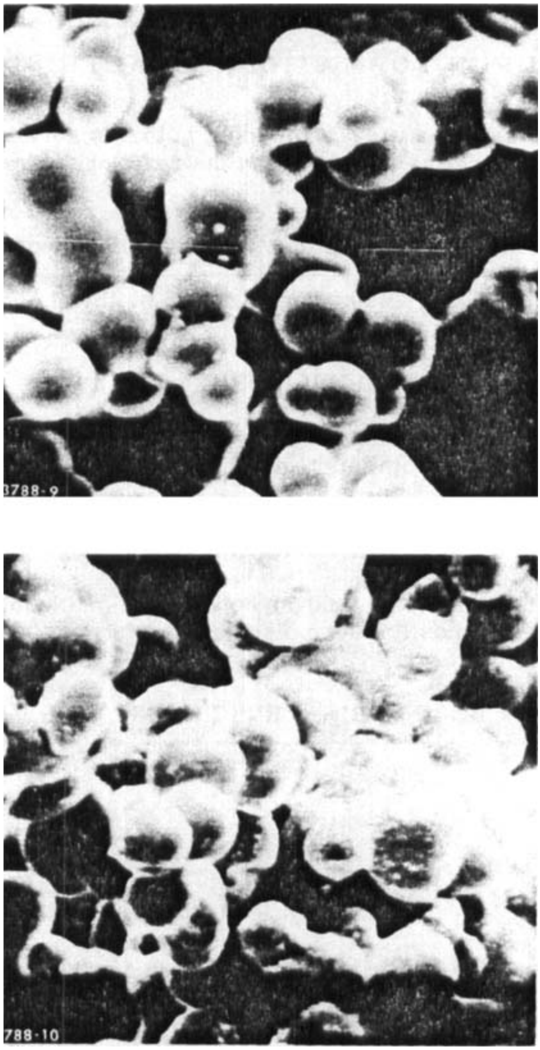

FIG. 1. SEM photographs of OPUF powders [40-80 mesh (top) and -80 mesh (bottom)] at 5100×.

DEMONSTRATED APPLICATIONS

Porous urea/formaldehyde powders of 40 mesh size were found to retain nicotine and tar more effectively than cellulose acetate filters [5]. Powder of -100 mesh size also appeared promising in face powders and other related cosmetic preparations. Dermatological problems have arisen and hence commercial application in face powders will not materialize. Other applications that we reduced to practice are discussed below.

Filtration Structures

We prepared many filtration structures based on porous urea/formaldehyde. Activated charcoal and other similar materials can be coherently made by means of nonetherified urea resin solutions into convenient shapes, e.g., cylinders. Both charcoal filled and unfilled porous urea/formaldehyde cylinders (Fig. 2) recycled spent dry cleaning liquid extremely efficiently.

Chromatographic Columns

Chromatographic columns can be made from nonetherified urea/formaldehyde solutions. Columns were also coated with porous urea/formaldehyde polymer for use in liquid chromatography.

Brightening and Opacifying Pigments

Initially, polymerization of styrene with urea/formaldehyde powders in a quiescent state was attempted. Invariably, phase separation occurred and therefore polymerization was conducted in a bottle polymizer with tumbling capability. Styrene catalyzed by 0.01% di-t-butyl peroxide was polymerized containing 1, 5, 10, and 20% open pore urea/formaldehyde powder (-80 mesh of about 3 μm spheres and pores). A programmed polymerization cycle of 90, 120, and 150°C each for a 24-h period was used. This polymerization cycle produced homogeneous and well-dispersed high molecular weight polystyrene. All resins were converted into 40-mil thick film by compression molding. Film containing 5% open pore urea/formaldehyde was opaque. Use of urea/formaldehyde will, however, limit the molding temperature to below 190°C. Above 190°C, urea/formaldehyde powder will decompose to give slightly yellowish brown to black films. Thus the microvoids of the porous urea/formaldehyde powder can be utilized for opacifying. In a similar way, a white paint was prepared from urea/formaldehyde powder at 200 lb/100 gal paint concentration. Some hiding was observed. We did not optimize the microvoid to produce maximum scattering.

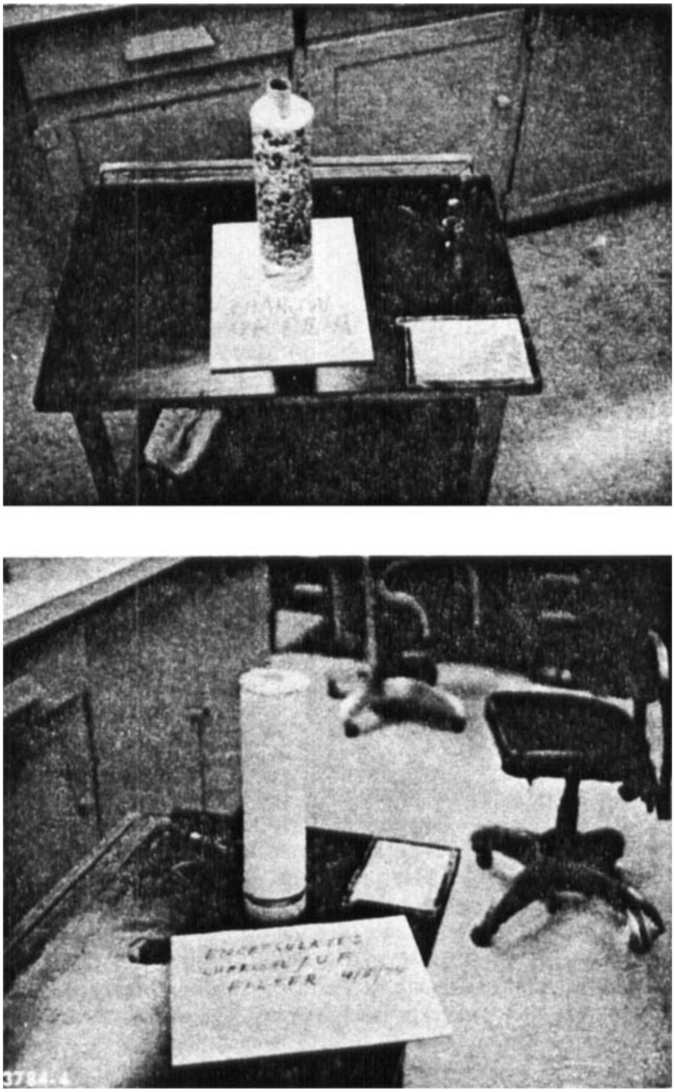

FIG. 2. Charcoal and encapsulated charcoal urea/formaldehyde filters. Activated charcoal must be soaked in deionized water prior to structuring. Basicity of activated charcoal slows the structure formation.

Smog Disposal

In large industrial and population centers of the world, fog and smog are a big problem. Fog and smog enveloping a populated area for an extended time create both health and transportation (e.g., airport closing) problems. We have demonstrated in a simulated experiment that porous urea/formaldehyde is an effective fog and smog dispersal agent. In actual practice, porous powder can be sprayed by a dusting plane to lift the smog. A jet approaching a fogged-up runway can electronically detonate small canisters containing porous powder along the runway, thus improving visibility and ensuring safe landing.

Moisture Retentive Fertilizers

Porous urea/formaldehyde polymers in the form of slabs can find use in agriculture. The fabricated slab, when buried in the soil, will retard the evaporation of water. Farmers in low precipitation areas of the world can utilize this concept. Urea/formaldehyde slabs will eventually biodegrade in the soil and produce desirable nitrogen and phosphorus fixation. Alternatively, the farmer can cover the plot with a sparse urea/formaldehyde solution. The solution will convert into porous solid. This in situ preparation will furnish water, nitrogen, phosphorus, and the retentive property of the structure.

Fruit Coating

Due to unexpected freeze, some fruit crops such as apple and citrus perish. During prolonged and unexpected weather, the citrus orchards are heated in California. Expensive energy is expended to save the fruits from freezing. However, a fruit coating based on urea/formaldehyde solution has been developed. When a warning of a freeze is issued, this solution can be applied by spray or dipping. After the freezing spell is over, the growth of the fruit will rupture the protective shell. Alternatively, the coating can be washed down after the freeze is over.

POROUS POLYMER BOUND MULTICOMPONENT CORROSION INHIBITOR: A POTENTIAL APPLICATION

An improved novel nontoxic multicomponent corrosion inhibitor for aircraft and ship primers can be developed based on porous urea/formaldehyde. The porous polymer will serve as carrier and control release agent. In Fig. 3, corrosion and corrosion inhibitors are schematically shown.

CORROSION

ANODIC REACTIONS | CATHODIC REACTIONS

CORROSION CONTROL

- ANODIC
- RETARD ANODIC PROCESS
- ANODIC INHIBITORS

  CrO_4^-, $PO_4^{\equiv}$ } WIDELY USED

  NO_3^-

  NO_2^-

  MnO_4^-

- CATHODIC
- ENHANCE CATHODIC PROCESS
- CATHODIC INHIBITORS

  MO_4^{n-}, NO_3^- } IN ACID MEDIA

  MULTIVALENT CATION

- ANODIC/CATHODIC

OTHER INHIBITORS

- CHELATING AGENTS (NH_2/COOH) CONTAINING, E.G., SARCOSINE-TYP
- PHOSPHONOCARBOXYLIC ACID COMPOSITIONS
- POLYPHOSPHATE-PHOSPHONIC-POLYACRYLIC AID COMPOSITIONS
- PHOSPHONOMETHYL AMINO CARBOXYLATES
- NITRITE-PHOSPHORIC/BORIC ESTERS
- NITRATE, PHOSPHATE, BENZOTRIAZATE, BORATE, AND SILICATE COMPOSITIONS
- TETRABUTYLAMMONIUM CHLORIDE AND OTHER QUARTERNIZED COMPOUND
- MIXED: 0.35% $Na_2B_2O_4$, 0.1% $NaNO_3$, 0.05% $NaNO_2$, 0.01% Na_2SiO_3 20 PPM $(NaPO_3)_6$, AND 10 PPM MERCAPTOBENZOTHIAZOLE.

FIG. 3. Corrosion and corrosion inhibitors.

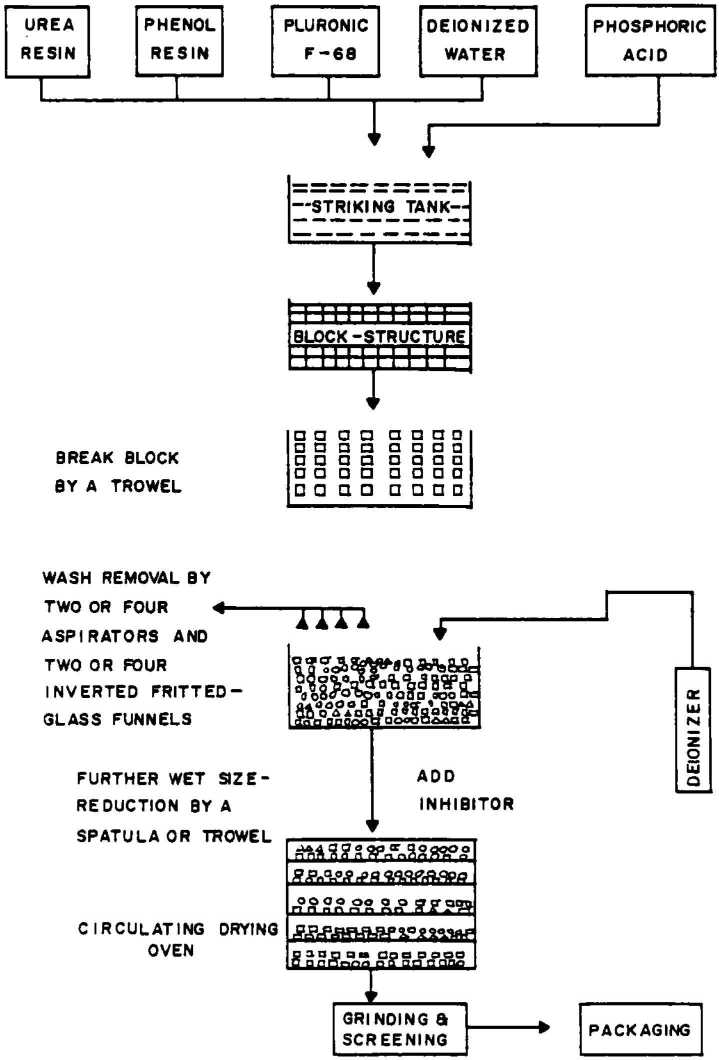

FIG. 4. Open pore urea/formaldehyde bound inhibitor system.

The suggested methodology for inhibitor formulation loading (adsorption) and release (desorption) is now described. Postloading is preferred since porous urea/formaldehyde polymers are processed from aqueous solutions. Prepare the porous polymer to which the aqeuous inhibitor formula is added and milled for uniform distribution. The treated structure should be dried to remove water. Alternatively, water-soluble inhibitor formula can be added at a suitable place in processing (see Fig. 4).

The release study can be conducted by conductivity measurement of inhibitor formula-bound structure in water. The rate of release can be conducted using high voltage electrophoresis, thin-layer chromatography, or liquid chromatography techniques, for example.

The aircraft primer is used to provide corrosion protection and adhesion promotion. Its components are resin, cross-linker, pigments and extenders, state-of-the-art corrosion inhibitor pigment (or new porous polymer-bound multicomponent inhibitor), additives, e.g., silane-type adhesion promoter, and solvent.

CONCLUSIONS

Open pore urea/formaldehyde structures have unique properties and their spherical and pore sizes can be controlled at will to make them suitable for many applications. Filtration structures, chromatographic columns, porous urea/formaldehyde pigmented polystyrene, smog dispersal agent, moisture retentive fertilizers, fruit coatings, and porous polymer-bound multicomponent corrosion inhibitors were prepared and their utility shown. Development of technologies based on open pore urea/formaldehyde structures is a distinct possibility.

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