

Electrosynthesis of Open-Pore Urea/Formaldehyde Structure

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Synopsis

Open-pore urea/formaldehyde (OPUF) structure has been prepared electrolytically at the anode from an aqueous solution of a nonetherified urea/formaldehyde resin. A decrease in pH at the anode due to an electrochemical reaction results in the formation of the open-pore structure. The electrolytically generated OPUF powder has the same characteristics as the chemically prepared OPUF obtained by acidification of urea/formaldehyde resin solution.

INTRODUCTION

In prior work, it was shown that an aqueous solution of a nonetherified urea/formaldehyde resin can be polymerized and converted into a porous structure by phosphoric acid catalyst.¹ This structure consists of a network of entangled spheres about 3 μm in diameter with interconnected pores of 3 μm in cross-sectional diameter. The pores are formed by interstices between the chains of spheres.

Urea/formaldehyde resins are made by condensation polymerization. Urea is reacted with formaldehyde to form dimethylol urea and related compounds. These compounds, highly water soluble, can be reacted at will with elimination of water and/or formaldehyde, to produce medium-sized molecules. The intermediate product is the urea/formaldehyde resin, which is useful in preparation of open-pore structures. Acidification of the medium-sized urea resin molecules results in promotion of their molecular weight via a series of reactions. The increase in molecular weight leads to insolubility and eventual formation of well-defined open-pore structures.

Generally, 7.0% phosphoric acid, based on urea resin solid, is used to make the structure. The structure, when chemically formed, must be extensively washed with water to remove phosphoric acid; this is tedious and time consuming.

This paper describes an electrochemical method for the preparation of open-pore urea/formaldehyde (OPUF) structures which mitigates the extensive washing problem.

EXPERIMENTAL

Preparation of Nonetherified Urea/Formaldehyde Resin

Urea (7.83 mole) and alcohol-free 50% aqueous formaldehyde (18.0 mole) were refluxed for 30 min at pH 5.9 ± 0.1 . After cooling, 248 ml of water was removed from the condensate under partial vacuum at $65^\circ\text{--}85^\circ\text{C}$. The pH was readjusted to 5.9 ± 0.1 , and the mixture was held at $90^\circ \pm 2^\circ\text{C}$ for V-W Gardner viscosity

measurement. The flask was cooled by an ice batch to 50°C. Urea (5.5 mole) and melamine (0.03 mole) were added under agitation. When complete solution occurred, the pH was raised to 7.4. The resulting solution (74.0% solids) had a urea-to-formaldehyde combined molar ratio of 0.435 and a cumulative molar ratio of 0.74.

Electrosynthesis Setup

The setup used for electrosynthesis of the open-pore structure is shown in Figure 1. An ac electrical source was converted to a dc supply by a rectifier. The electropolymerization cell was a 1500 ml beaker. Two 3 × 5 in. stainless-steel electrodes, 3 in. apart, were used. The electrode holder was designed to be versatile so that smaller or larger electrodes or other (e.g., zinc or tin) electrode materials could be used.

Synthesis Conditions

The bath composition and constants are as follows: urea/formaldehyde resin (74% solids), 100.0 g; deionized water, 300.0 g; 0.5*N* sulfuric acid (supporting electrolyte), 1.5 ml; percent resin solid in bath, 18.5; and pH of the bath, 4.5.

Electrosynthesis conditions were as follows: polymerization voltage, 100 V; polymerization current, 0.4 A; time voltage applied with bath, 60 sec; electrode area, 4.5 in.²; and current density, 88.9 mA/in.².

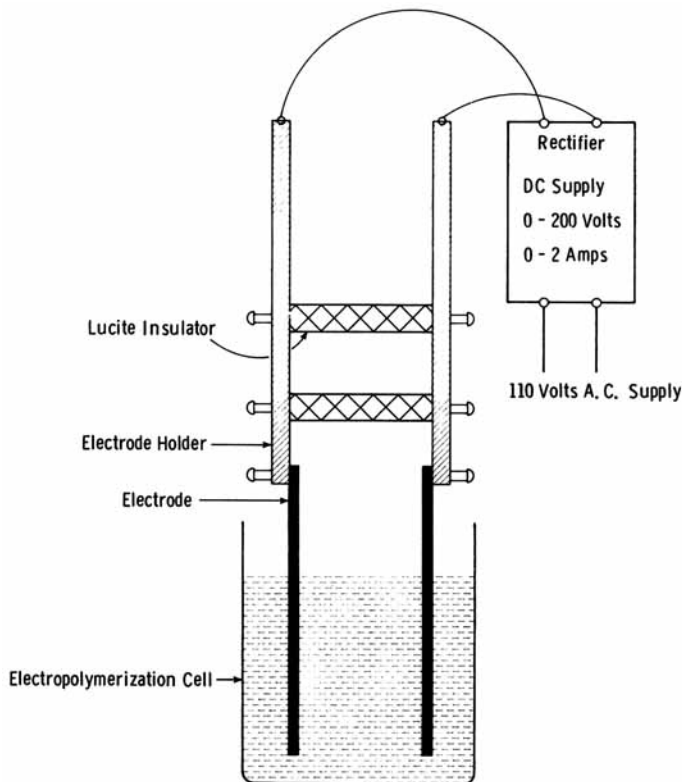
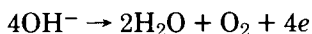


Fig. 1. Setup for electrosynthesis of open-pore urea/formaldehyde structure.

RESULTS AND DISCUSSION

Locus of Polymerization

The locus of polymerization was found to be the anode. The structure was formed on the anode, grew around it, and continued after cessation of the current. In an aqueous solution, the discharge of OH^- leads to



In our case, due to the absence of OH^- , the following reaction occurred²:



This caused a decrease in pH at the anode. This decrease in pH led to formation

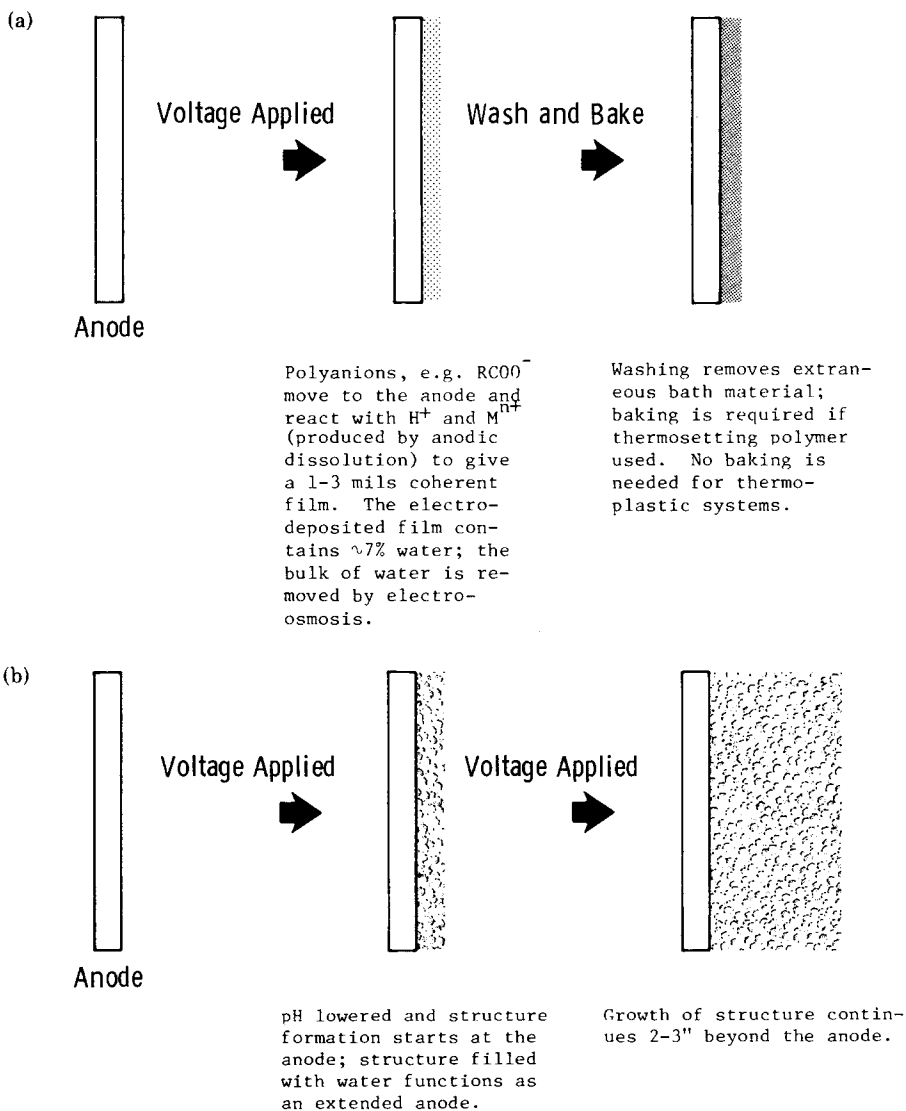


Fig. 2. (a) Events occurring during electrodeposition. (b) Events occurring during electrosynthesis of open-pore urea/formaldehyde structure.

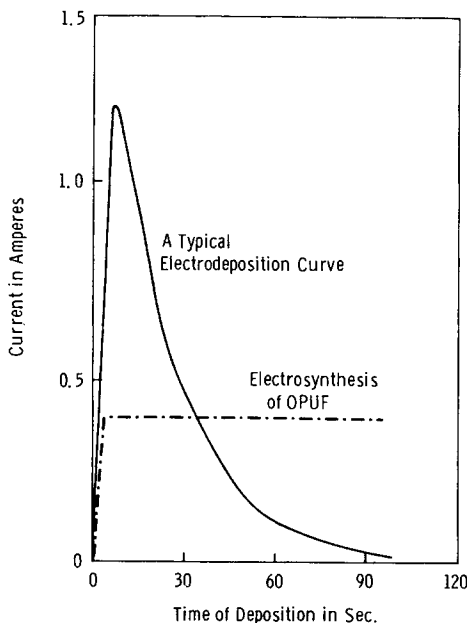
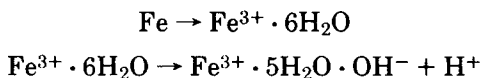


Fig. 3. Time current relationship in electrodeposition of polymers and electrosynthesis of open-pore urea/formaldehyde structure (OPUF).

of the OPUF structure. Use of zinc as an electrode material was initially tested and resulted in the anodic dissolution.³ Accordingly, stainless-steel electrodes were used throughout the remainder of the research. The electrode reactions are believed to be as follows:



The first dissociation constant is high,⁴ in the order of 10^{-1} . This strong acidity results in OPUF structure formation electrolytically.

Events Occurring During Electrolytic Preparation of OPUF

The electrolytic process uses solid, nonporous, and impermeable electrodes to convert a water-soluble urea/formaldehyde resin into water-insoluble and highly branched powders that have the unique features of being open-pore and spherical. As noted earlier, the decrease in pH at the anode initiates the polymerization and structure formation on and around the anode. Because of the open pores in the resulting structure, the anode in effect extends, and this extended anode functions as a porous electrode (see Fig. 2). If a continuous film were to form on the anode as in the electrodeposition⁵ of base-neutralized acid polymer, RCOO^- , the electrical resistance offered by the 1–3 mil electrodeposit would impede the current, resulting in the termination of the resin deposition and completion of the electrodeposition (see Fig. 3).

The urea/formaldehyde resin that was converted electrolytically into the open-pore structure using a stainless-steel anode was recovered by washing twice with deionized water and drying. Figure 4 compares scanning electron micrographs (SEM) of this product with a powder prepared from the same urea/

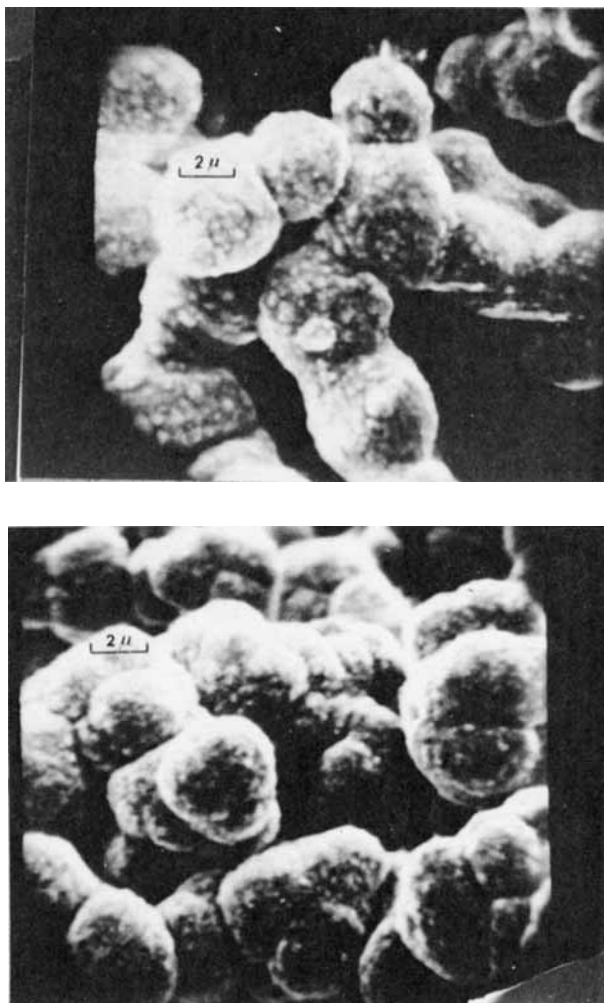


Fig. 4. SEM of chemically made open-pore urea/formaldehyde (OPUF) structure (top) and electrolytically prepared (OPUF) (bottom), both at $\times 5100$ magnification.

formaldehyde resin by acidification with phosphoric acid. Note that the particles are nearly identical in shape and size (average $\sim 3 \mu\text{m}$ in diameter).

CONCLUSIONS

Urea/formaldehyde resins and electrolytically prepared open-pore urea/formaldehyde structures are both built up by condensation polymerization. The locus of electropolymerization was the anode, and structure formation resulted from a lowering of pH at the anode. The electrolytically generated OPUF powder has the same characteristics as one made chemically by acidification.

References

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