

Experiment 2

Preparation of Urea-formaldehyde Resin

Introduction

One classification of polymers divides them into thermoplastic and thermosetting resins. Most amorphous linear polymers (e.g. polystyrene, polyethylene, poly(ethylene terephthalate)) are thermoplastics. The mobility of the polymer increases as the temperature increases. If a linear polymer is cross-linked, a three-dimensional network is formed, and translational motion is inhibited or even prohibited. Cross-linkable polymers are generally referred to as thermosets, or thermosetting resins. From a processing point of view, the above distinction of thermoplastic and thermoset implies that the former can, in principle, be extruded and molded many times, while the latter can be processed at high temperature only once before cross-linking reactions render the polymer hard and solid. The shape of the polymer is thermally set.

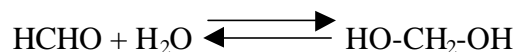
Thermosets are generally insoluble, even when the degree of cross-linking is low (~ 2%). For example, natural rubber (gutta percha, all *cis*-1,4-polyisoprene) is normally used as a thermoplastic. Cross-linking with about 2% sulfur produces an insoluble, swellable elastic material. At 10-15% cross-linking density, the polymer becomes stiffer, and can be used to make articles such as combs. At higher (25-35%) cross-link density, the rubber becomes extremely hard, and is used to make bowling balls.

An important group of thermosetting resins is the aminoplasts, or amino resins, of which about 80% are urea-formaldehyde (UF) resins, and 20% are melamine-formaldehyde (MF) resins. A small proportion of amino resins contain other aldehydes or other amines. Amino resins are water soluble before curing, colourless (which allows unlimited colourability), have excellent solvent resistance once cured, outstanding hardness and abrasion resistance, and good heat resistance. A drawback of these materials is the potential release of formaldehyde during and after cure, and poor weatherability. Melamine mouldings have somewhat better weatherability than the urea mouldings.

A major application of amino resins is in the area of adhesives, primarily for the plywood, chipboard, and sawdust board markets. Amino resins are also used in textile processing (to impart wash and wear quality), automobile tires (to improve adhesion between rubber and tire cord), and paper processing (to improve the wet strength).

Reaction chemistry

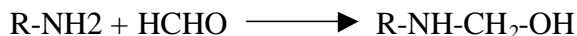
The raw materials for amino resins are urea, melamine, and formaldehyde. Formaldehyde is generally marketed as a 37% aqueous solution known as formalin. Gaseous formaldehyde dissolves readily in water, and reacts to form methylene glycol,



The other major form of formaldehyde is solid (flake or powder) paraformaldehyde, which is a mixture of poly(oxymethylene glycols), $\text{HO}(\text{CH}_2\text{O})_n\text{H}$, where $n = 8 - 10$. These chains readily regenerate formaldehyde when mixed with water.

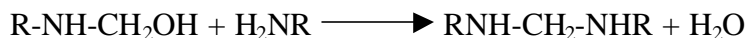
There are two main reactions in UF and MF condensations. The first one, hydroxymethylation, can be catalyzed by either acid or base.

Hydroxymethylation



This is generally the first step in UF polymer formation, and these methylol compounds are prepared under neutral or alkaline conditions. The second important reaction is methylene bridge formation, and is only catalyzed by acid.

Methylene bridge formation

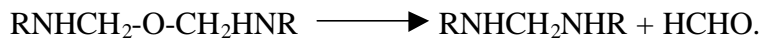


This reaction results in dimer, polymer chain, or network formation. Thus, the stable resin intermediate formed in hydroxymethylation can be converted to solid cross-linked polymer by addition of an acid catalyst.

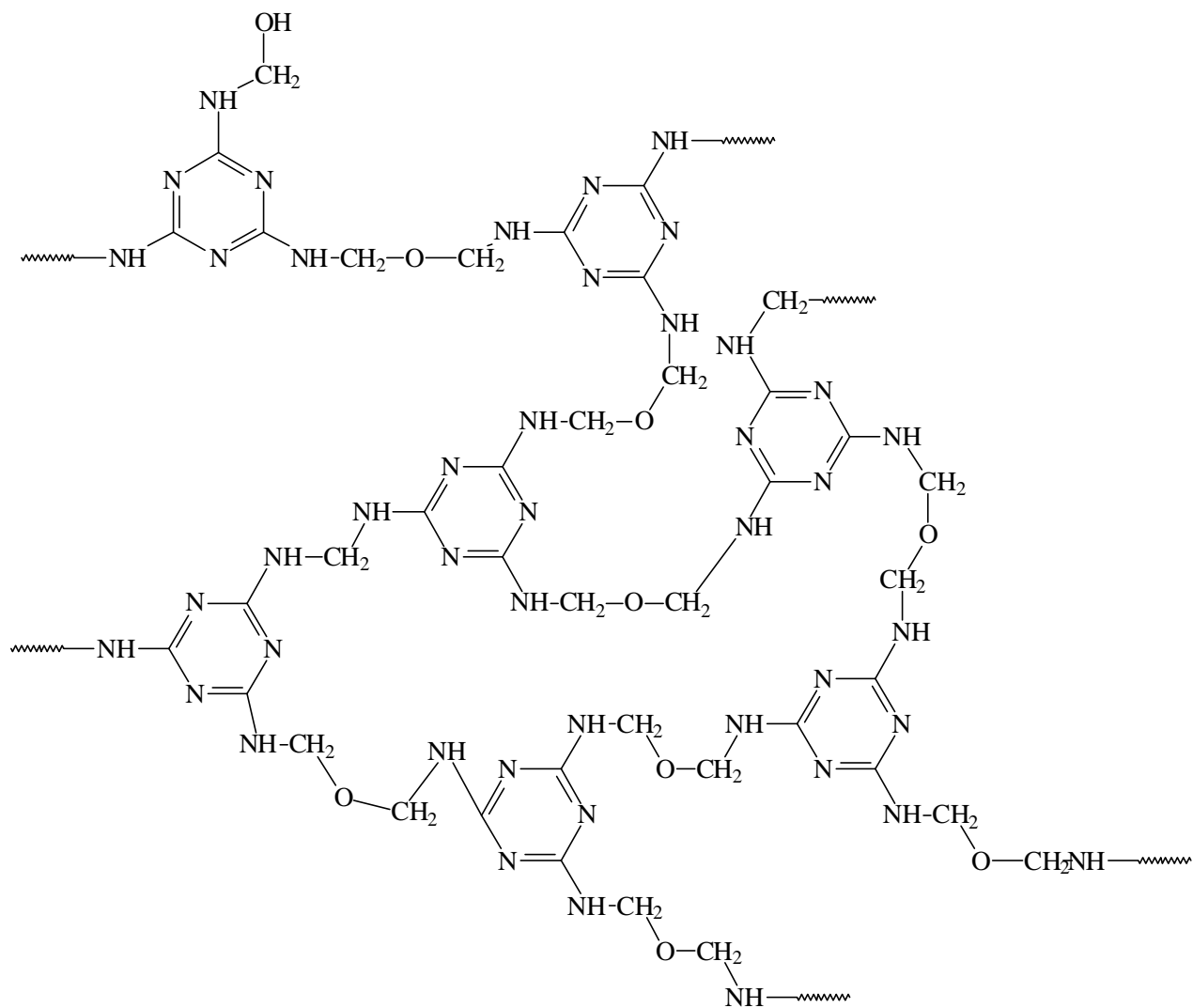
During crosslinking, two main reactions are believed to occur. The first involves the formation of dimethylene ether linkages,



and the second is a rearrangement reaction, leading to diaminomethylene bridge formation,



The resulting matrix is depicted below for melamine-formaldehyde. These four basic reactions account for much of the reaction chemistry of UF and MF resins, and their precise control is still the subject of intense industrial and academic research.



Experimental

1. *Preparation of monomethylolurea*

During the laboratory period two weeks prior to performing this experiment, add 5 g urea and 6 mL formalin to a small flask. Adjust the pH of the mixture between 7 and 8 (indicator paper), and stir the mixture until solution is effected. Let the flask stand at room temperature for 2 - 4 hours, and then store it in the refrigerator until the next laboratory period.

After two weeks, remove the flask from the fridge, and filter the mixture by suction. Wash the residue with ethanol and dry it in an oven at 50°C. Determine the melting point and the water solubility of the crude product. (T_m of monomethylolurea = 110°C).

2. *Preparation of a urea-formaldehyde adhesive*

Sixty grams (1 mole) of urea and 137 g (1.7 mole) formalin are charged into a 500-mL reaction kettle equipped with a mechanical stirrer and a reflux condenser. The pH of the mixture is adjusted with 2M NaOH to between 7 and 8 as determined by universal indicator paper, and the mixture is refluxed for 2 hours using a heating mantle as the heat source.

After the mixture has been refluxed for 2 hours, a Barrett receiving trap is introduced between the flask and the reflux condenser. The distillation is continued until about 40 mL of water is distilled into the trap and discarded. [See Senior Demonstrator or TA for assistance]. The solution is acidified with 5 drops of glacial acetic acid; 44 g of furfuryl alcohol and 0.55 g triethanolamine are introduced into the reaction mixture, and the solution is heated at 90 °C for 15 minutes.

The mixture is then cooled to room temperature. A 15-g sample of the resin is removed and is mixed with a hardener composed of 1 g of wood flour, 0.05 g calcium phosphate, and 0.2 g ammonium chloride. The mixture is set aside to harden at room temperature. The remaining resin to which the hardener has not been added is placed in a vial.

3. *Preparation of UF resin under acidic conditions*

In order to demonstrate the rapidity of the reaction of urea with formaldehyde under acidic conditions, mix 5 g of urea with 6 ml of formalin in a test tube, and shake the test tube until the urea has dissolved. Adjust the pH of the solution to 4 by addition of 4 drops of 0.5N H_2SO_4 , and observe the time required for precipitation to occur. Remove part of the precipitate and compare its solubility in water with the sample of monomethylolurea prepared in Part 1 above.

Discussion

In your report, describe the materials that you prepared, and compare them to each other. Also, answer the following questions.

1. Describe, with reactions, the formation of formaldehyde from poly(oxymethylene glycol) under acidic and basic conditions, respectively.
2. What role do the furfuryl alcohol and triethanolamine play in the preparation of the UF adhesive?

References

- S. R. Sandler, W. Karo, *Polymer Syntheses*, Volume II, Second Edition, Academic Press, Inc. 1992.
- B. Meyer, *Urea-Formaldehyde Resins*, Addison-Wesley Publishing Company, Inc. 1979.

Apparatus

500-mL reaction kettle	1
4-neck lid	1
clamp	1
glassrod stirrer	1
jacketed collar for stirrer	1
heating mantle	1
overhead stirrer	1
50-mL Erlenmeyer flasks	2
125-mL Erlenmeyer flasks	2
250-mL Erlenmeyer flasks	2
condenser with tubing	1
Buchner funnel	1
Barrett distillation trap	1
250-mL beaker	2
600-mL beaker	2

Chemicals

Urea, formalin (37%)

ethanol

NaOH solutions

0.5N H₂SO₄

wood flour

calcium phosphate

ammonium chloride

furfuryl alcohol

triethanolamine