"Analysis of Phenolic Resins"

by

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Introduction

Organic resins which become precursor matrix systems for carbon-carbon composites must provide very high carbon yields upon pyrolysis. This requirement precludes the use of polyesters and epoxies or any resin where monomers are not bridged by carbon. Ideally, the cured matrix should consist of aromatic monomers linked together with methylene groups both linearly and crosswise. Two systems currently in use are phenolic resins and furfuryl alcohol. While the ladder historically characterizes densification processes of the shuttle's RCC, ACC is molded and densified exclusively with phenolic resin. However, questions have been raised regarding the effective lifetime of phenolic resin in the ACC densification process.

In this investigation, phenolic based matrix systems are evaluated with respect to neat and used resin samples. A discussion of resin chemistry is given in the final section.

Experimental

Neat resin refers to new, unused phenolic resin as received from the vendor and stored at 0°F. Used resin has been employed in the manufacturing densification process for a period of 230 days (about 8 months). Used resin is subjected to 28 inches vacuum and 80psi pressure at room temperature for about 3 hours during each impregnation and then stored at 40°F until the next impregnation run. There were approximately two runs per week giving a total of about 65 impregnations for the 230 day test period.

Resin solids and resin viscosity were monitored throughout the test period. Resin solids data was obtained by curing samples of resin to 325°F at ambient pressure. Resin viscosity was measured with an LVF Brookfield viscometer at room temperature (about 75°F).

Critical resin components were identified and quantified for neat and fully aged resin using an HP-1000 UV detection High Performance Liquid Chromatography system.

Infra-red spectra were obtained for neat and fully aged resin using a Perkin Elmer 983. Also, Gel Permeation Chromatographs were obtained with an HP system.

Finally, impregnations were performed on 4"X4" carbon-carbon panels using neat, fully used and diluted used resin samples.

Results

Graphical representations of changes in resin solids and viscosity for the 230 day test period are shown in Figures 1 and 2 respectively.

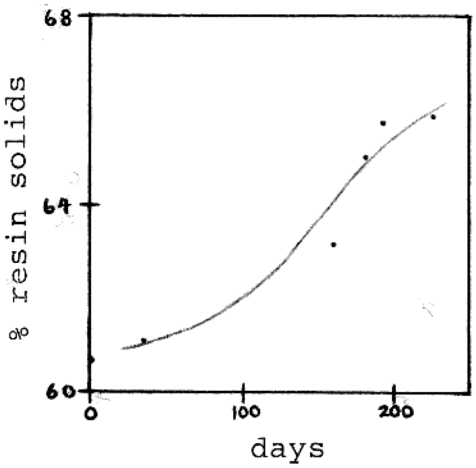


Figure 1. Change in resin solids over time.

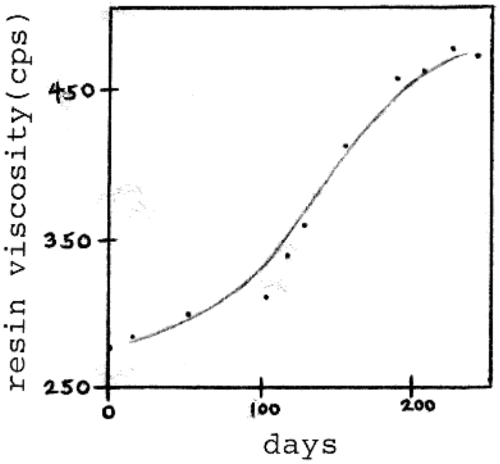


Figure 2. Change in resin viscosity over time.

Assumed to be major components in the resin, HPLC standards were obtained for m-cresol, resorcinol and phenol. Numerous other likely compounds were tested but these three produced strong peaks. Concentrations of each component in neat and used resin samples were determined by using known quantities for the standards. HPLC printouts for neat and fully used resin are shown in Figures 3 and 4 respectively.

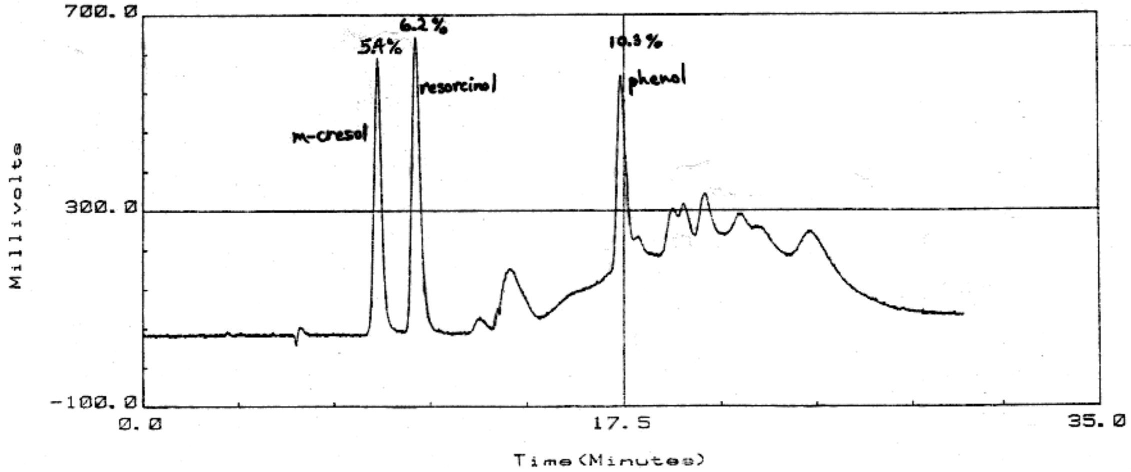


Figure 3. HPLC of neat phenolic resin.

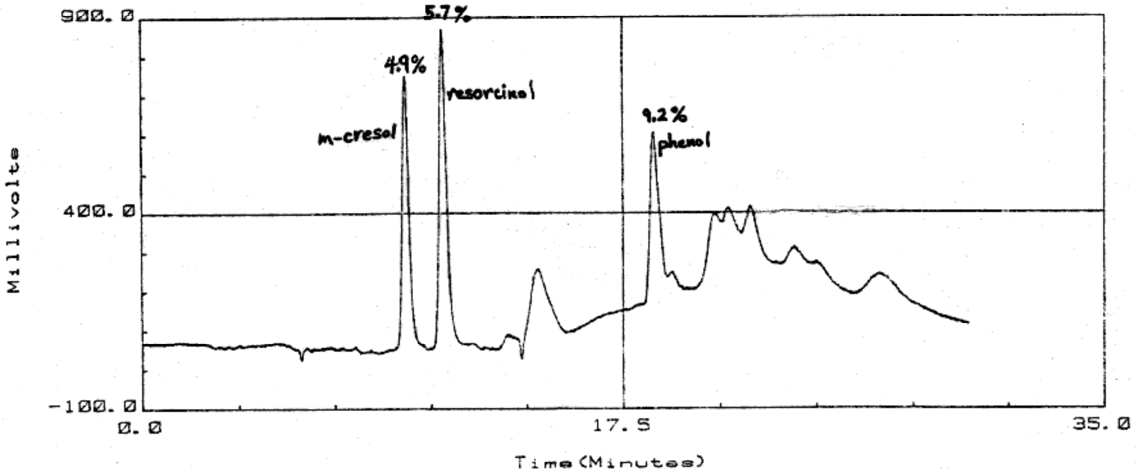


Figure 4. HPLC of fully aged (used) phenolic resin.

Analysis by IR and GPC for neat and fully used resin samples are shown in Figures 5 and 6.

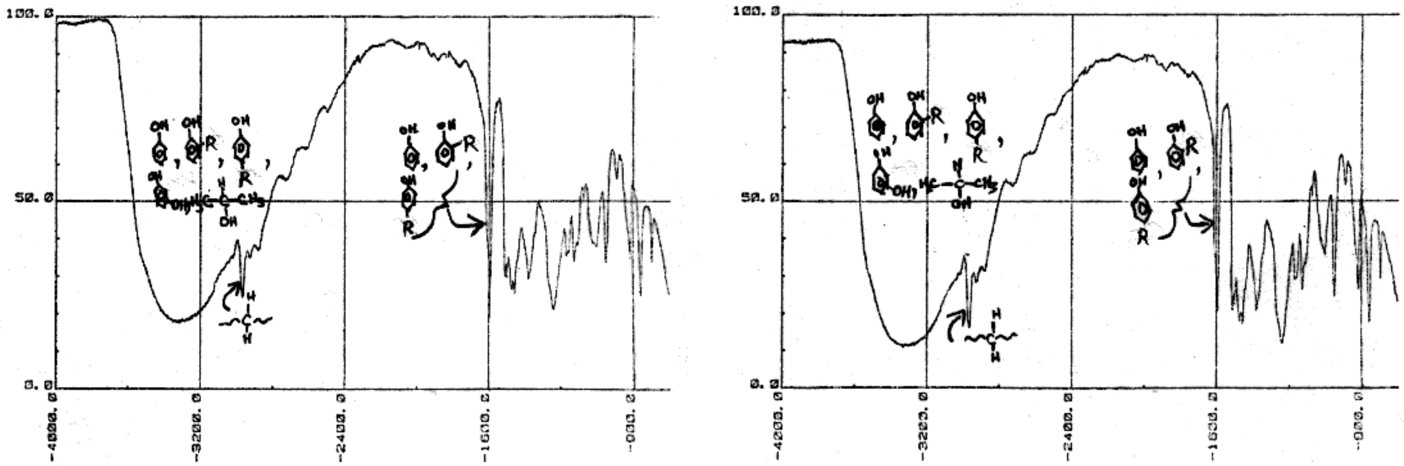


Figure 5. IR of neat and fully aged phenolic resin.

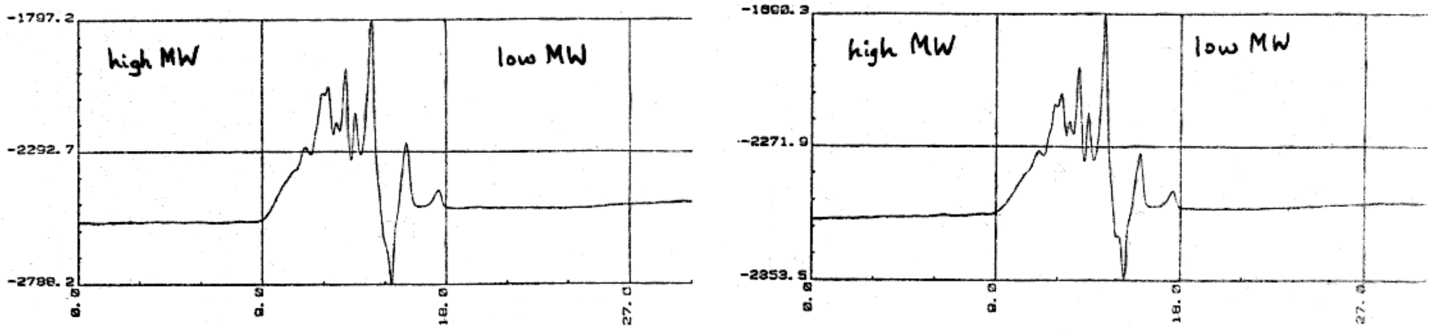


Figure 6. GPC of neat and fully used (aged) phenolic resin.

Impregnation and cure (325°F) of carbon-carbon samples was performed with neat resin, fully used resin and fully used resin after dilution with isopropyl alcohol back to 'neat' viscosity. Resin solids, viscosity, substrate weight gain from impregnation/cure and weight loss from subsequent pyrolysis were measured as shown in Table 1.

Table 1

	LVF viscosity 77°F (cps)	resin solids (%)	weight gain from impregnation/cure (%)	weight loss from pyrolysis (%)
neat phenolic resin	258	59	2.4	1.8
fully used phenolic resin	454	66	2.6	1.8
fully used diluted phenolic resin	273	60	2.3	1.8

Conclusions

(1) Increases in resin solids and viscosity over the 230 day test period appear to be a result only of solvent loss from evaporation.

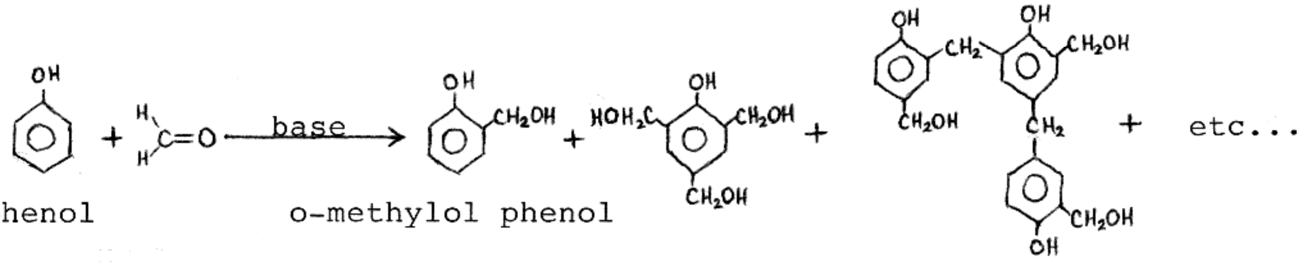
(2) Results of HPLC show expected and insignificant consumption of primary resin reactants after 230 days of use and aging.

(3) IR and GPC indicate no noticeable change in resin chemistry over 230 days of shop use and aging.

(4) Finally, data obtained from impregnation/cure/pyrolysis of substrate samples indicate no significant change in the effectiveness of phenolic resin as a substrate densifier during normal processing. Furthermore, dilution of used processing resin with isopropanol to 'neat' viscosity is acceptable for at least 8 months after removal from 0°F storage.

Discussion

Phenolic resins undergo three stages of condensation polymerization from the reaction of phenol with formaldehyde to the formation of an infusible, highly crosslinked network. Stage A resole-type phenolic resins are produced by reacting excess formaldehyde with phenol in alkaline solution to yield complex mixtures of pre-polymer methylol phenols:



phenol

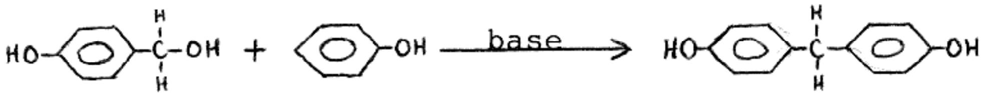
formaldehyde

o-methylol phenol

trimethylol phenol

tri-nuclear methylol phenol

Phenol directs electrophilic substitution of the acyl group predominantly to the ortho and para positions. Exact composition of the resole mixture depends on reaction conditions and the phenol-formaldehyde ratio. Reactions of methylol phenols with phenol produce diphenol methanes:

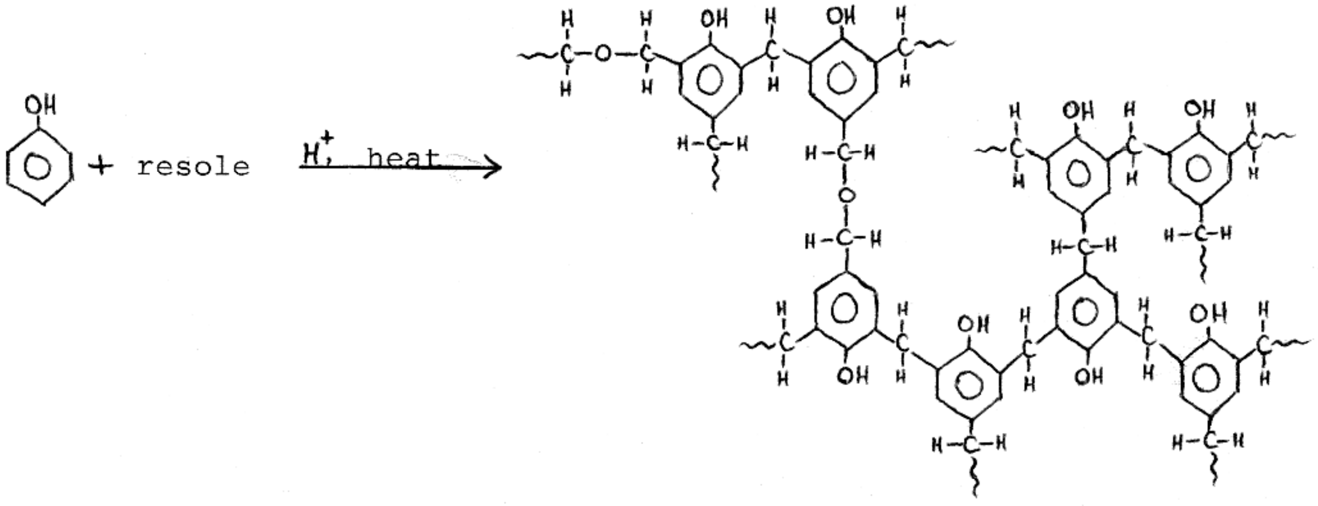


p-methylol phenol

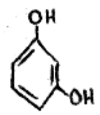
p,p-diphenol methane

The resole mixture is generally soluble in organic solvents and is fusible under heat and pressure.

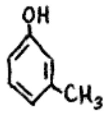
Prior to B-stage polymerization, the mixture is overneutralized and excess phenol is added. B-staging may be carried out by the manufacturer or the user with the application of heat. During heat staging, phenol may react with itself, formaldehyde or any number of polynuclear methylol phenols producing a network of benzene rings crosslinked by methylene and ether bridges:



Resorcinol and m-cresol are more reactive than simple phenol during ortho and para substitution. They are used to affect structural characteristics of the growing polymer as well as the overall rate of polymerization.



resorcinol

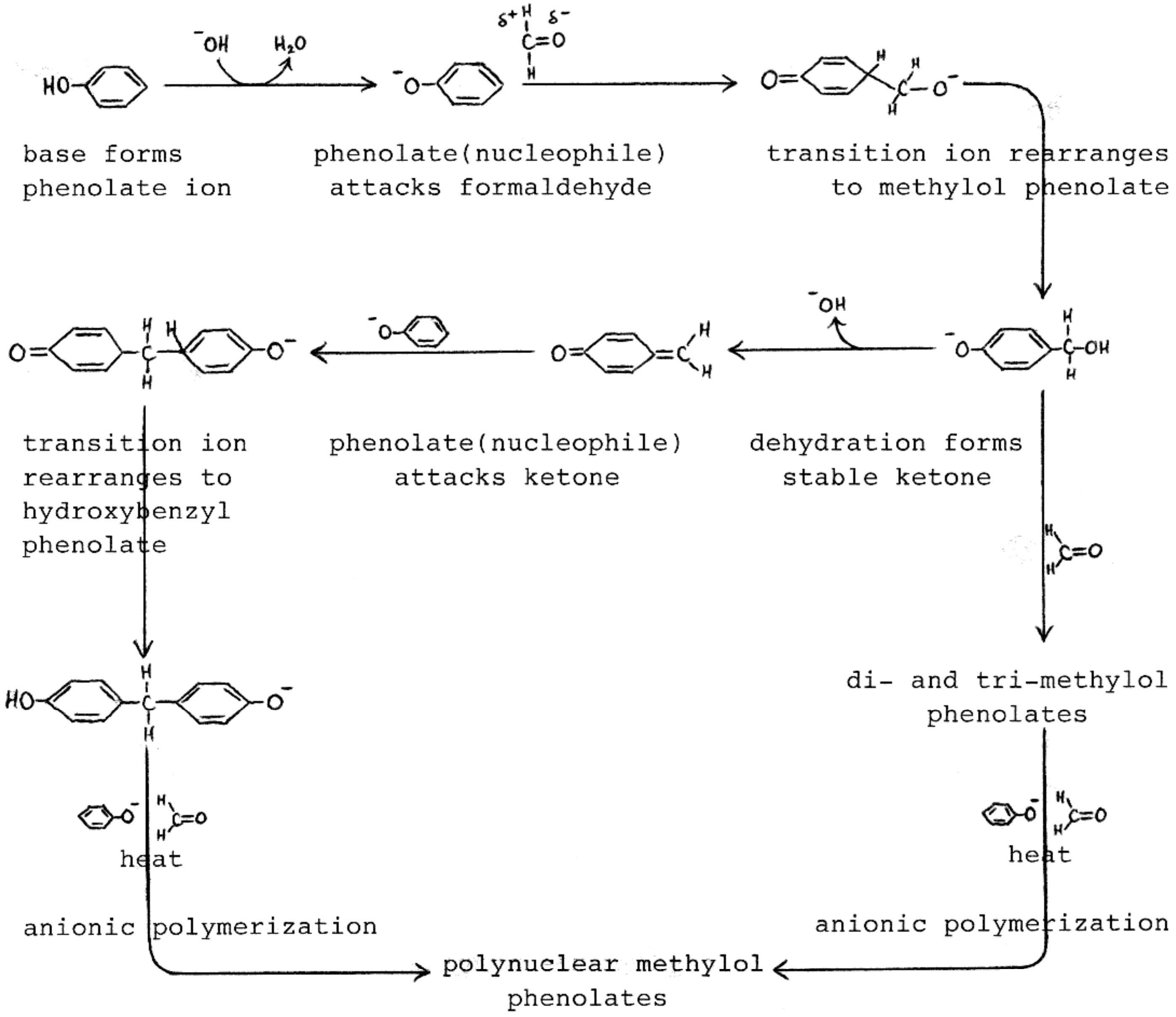


m-cresol

C-staging of phenolic resins is accomplished by heat curing to 350-400°F. While the B-staged resole is slightly soluble and fusible, the C-staged product represents an almost fully polymerized and crosslinked network.

The mechanism for this system proceeds by reduction of phenol under acid or base catalysis according to the following scenerio.

By base catalysis:



base forms phenolate ion

phenolate(nucleophile) attacks formaldehyde

transition ion rearranges to methylol phenolate

dehydration forms stable ketone

phenolate(nucleophile) attacks ketone

transition ion rearranges to hydroxybenzyl phenolate

di- and tri-methylol phenolates

heat

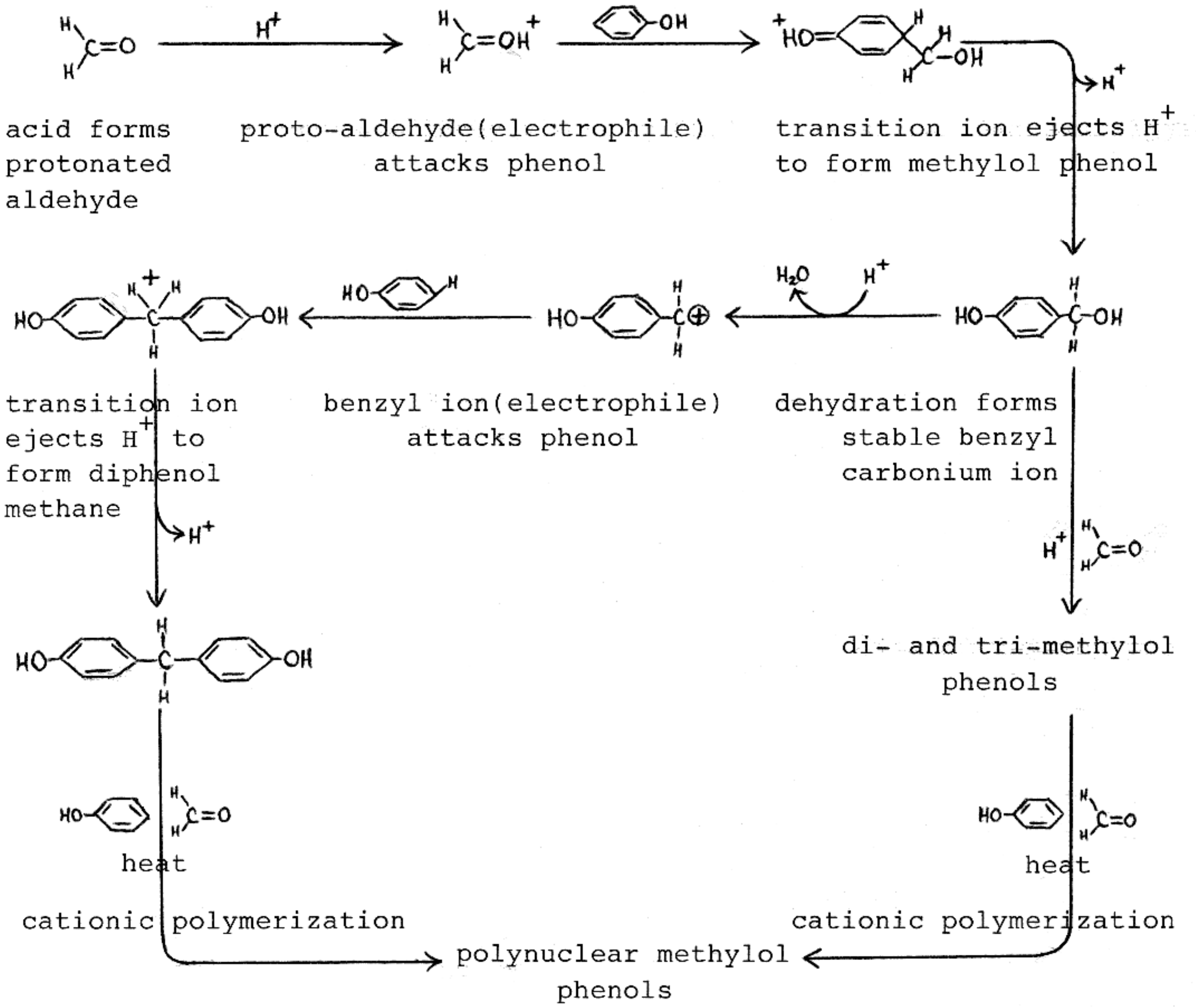
anionic polymerization

heat

anionic polymerization

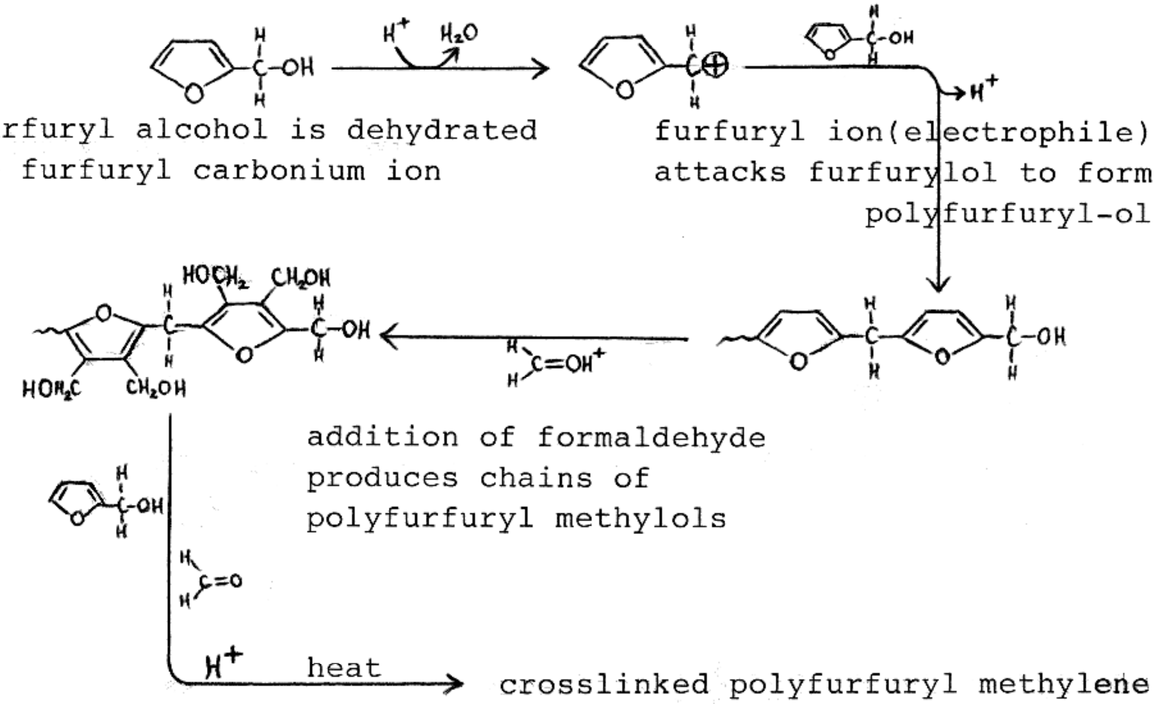
polynuclear methylol phenolates

By acid catalysis:



Furfuryl alcohol has been the densification resin for carbon-carbon on the space shuttle since the late 70's. Neat resin is acid catalyzed just prior to use. Catalyzed furfuryl alcohol has a short lifetime and must be cured to 300-350°F immediately after impregnation of panels. The user must add acid prior to the specific application. Furfuryl alcohol is less desirable to work with but appears to be a more effective impregnation fluid than phenolic resin. Safety characteristics favor the use of phenolics.

The monomer is acid catalyzed to produce linear chains of furan joined by methylene bridges through condensation. The solution is then neutralized and formaldehyde is added. After the user mixes oxalic acid into the resin and begins the curing process, crosslinking occurs between polymer chains by substitution with formaldehyde. The cured product is insoluble and infusible. A likely scenario for these reactions is illustrated below:



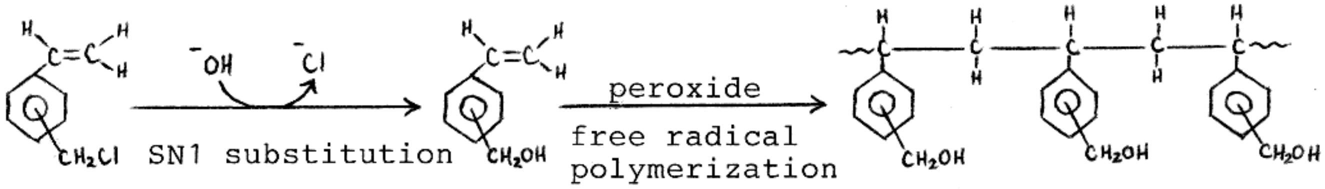
furfuryl alcohol is dehydrated to furfuryl carbonium ion

furfuryl ion(electrophile) attacks furfurylol to form polyfurfuryl-ol

addition of formaldehyde produces chains of polyfurfuryl methylols

crosslinked polyfurfuryl methylene

Studies have been performed integrating furfurylol and phenolic systems. Catalyzed furfurylol can be blended with phenolic resin to produce a unique composite matrix. Advanced composite resins can be formed from polymer and pre-polymer systems based on numerous available monomers such as divinyl benzene and vinyl benzyl chloride. In the ladder case, vinyl benzyl chloride is first converted into the corresponding alcohol and then subjected to conditions for free radical polymerization:



vinyl benzyl chloride

vinyl benzyl alcohol (methylol styrene)

polyvinyl benzyl alcohol (polymethylol styrene)

This process produces polymethylol styrene which provides alcohol groups available for reaction with formaldehyde, phenol or furfurylol. Polymethylol styrene can be blended with phenolic and furfuryl alcohol resins to give advanced crosslinked matrixes.