

Thermal Stability of Substituted Phenol-Formaldehyde Resins

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Synopsis

A variety of crosslinked phenol-, or derivatized phenol-formaldehyde polymers have been synthesized. The phenol derivatives included *o*- and *p*-cresol, *p*-nonylphenol, *m*-pentadecylphenol, and raw and distilled cashew nutshell liquid. The derivatives were copolymerized with phenol and formaldehyde using sulfuric acid as catalyst to yield novolak-type prepolymers, which were then cured with hexamethylenetetramine. Thermogravimetric analysis was used to evaluate the thermal stability of the cured resins. It was found that the thermal stability of the resins decreased with increasing amounts of cashew nutshell liquid, with distilled cashew resins being slightly more thermally stable than raw cashew resins. The thermal stability of resins containing substituted phenols with alkyl chains was observed to increase from *n*-pentadecylphenol to cresol to phenol. The trend in thermal stability of the resins may be explained on the basis of alkyl groups being less thermally stable than aromatic rings. The amount of hexamethylenetetramine used to cure the prepolymers also influences the thermal stability of the resin. It appears that a level of 10 to 15% hexamethylenetetramine maximizes the thermal stability of the resin.

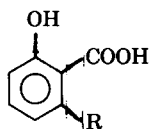
INTRODUCTION

Phenol-formaldehyde polymers are of great importance as materials^{1,2} and were discovered over seventy years ago.^{3,4} The synthesis⁵ and characterization of these polymers by gel permeation chromatography (GPC)^{6,7} and ¹³C nuclear magnetic resonance (NMR)⁸⁻¹¹ have been well documented. In many cases, however, the mechanical properties and/or cost of straight phenol-formaldehyde resins make them less desirable than other modified phenolics with alkyl side chains. In many cases, the effect of the alkyl substituents on the thermal stability of these materials is not known. In this study, the synthesis and thermal degradation of several modified phenolic resins is reported. These were copolymers of phenol and formaldehyde with: raw and distilled cashew nutshell liquid (CNSL); *o*-cresol, *p*-cresol, *p*-nonylphenol, and *m*-pentadecylphenol.

Cashew nutshell liquid (CNSL) is isolated from cashew nutshells usually grown in Brazil or India. The major components of CNSL have been characterized by a number of techniques including proton NMR, ultraviolet (UV), infrared (IR), and chromatography.¹²⁻¹⁵ The major component of CNSL is

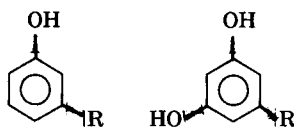
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anacardic acid (I):



I

where R can be: $(\text{CH}_2)_{14}\text{CH}_3$; $(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_5\text{CH}_3$; $(\text{CH}_2)_7\text{CH}=\text{CH}-\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{CH}_3$; or $(\text{CH}_2)_7\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}_2$. Even though a variety of R groups are possible, all have *m*-substitution and a 15-carbon chain length. Tyman and Jacobs¹⁵ showed that the relative proportions of the unsaturated components of anacardic acid from CNSL were monoene, 38.7%; diene, 16.3%; and triene, 45.1%. Some minor components of CNSL include cardanol (II) and cardol (III):



II

III

where the R groups are also 15 carbons long and possibly unsaturated. Upon heating, anacardic acid will decarboxylate to yield cardanol, a raw material used in the manufacture of synthetic resins.

In order to probe the effect of the side chain on the thermal stability of phenolic resins, cashew liquids and other substituted phenols were copolymerized with phenol and formaldehyde under acid catalysis to yield novolak-type prepolymers. The resins were subsequently cured with hexamethylenetetramine to give crosslinked polymers which were characterized by thermogravimetric analysis. In this case, the species chosen were to test both the effect of the type of substitution (*ortho* vs. *para*) and the chain length (1 to 15 carbons) on thermal stability.

EXPERIMENTAL

Two types of decarboxylated cashew liquid were used in this study. The first is raw cashew liquid which is dark brown viscous liquid. The second is distilled cashew liquid (from vacuum distillation of the raw cashew liquid) which is an oily, amber-colored liquid. The cashew liquids were used as received from Cardolite Corporation, Newark, NJ. Paraformaldehyde, hexamethylenetetramine, *m*-pentadecylphenol, and *p*-nonylphenol were also from Cardolite and used as received. *O*-cresol and *p*-cresol obtained from Fisher, Fairlawn, NJ and Aldrich, Milwaukee, WI, respectively.

Phenol, substituted phenol, and sulfuric acid (46 wt%) were charged into a three-neck reaction kettle equipped with an overhead mechanical stirrer,

TABLE I
Compositions of Phenol-Cashew-Formaldehyde Resins

Resin #	Raw cashew liquid (mol)	Distilled cashew liquid (mol)	Phenol (mol)	<i>Para</i> -formaldehyde (mol)	Sulfuric acid (mol)	Cashew as percent of phenolic
1	—	—	0.26	0.180	0.0033	0
2	0.198	—	—	0.138	0.0019	100
3	0.159	—	0.040	0.138	0.0019	80
4	0.199	—	0.080	0.138	0.0019	60
5	0.080	—	0.119	0.138	0.0019	40
6	0.040	—	0.159	0.138	0.0019	20
7	—	0.198	—	0.138	0.0019	100
8	—	0.159	0.040	0.138	0.0023	80
9	—	0.119	0.080	0.138	0.0023	60
10	—	0.080	0.119	0.138	0.0019	40
11	—	0.040	0.159	0.138	0.0019	20

TABLE II
Composition of Resins with Substituted Phenolic Compounds

Resin	Phenolic compound	Phenolic (mol)	<i>Para</i> -formaldehyde (mol)	Sulfuric acid (mol)
12	<i>o</i> -cresol	0.50	0.35	0.0033
13	<i>p</i> -cresol	0.50	0.35	0.0033
14	<i>p</i> -nonylphenol	0.50	0.35	0.0033
15	<i>m</i> -penta-decylphenol	0.20	0.14	0.0023

thermometer, and reflux condenser. The contents were stirred and heated with an oil bath to 77°C at which time paraformaldehyde and mineral spirits (15 mL) were added. The reaction temperature was raised to 95°C and maintained for 30 min. At that time isopropanol was added and the isopropanol-water azeotrope was distilled off. The resin was allowed to cool to room temperature then poured off and stored. The compositions of the resins are summarized in Table I and II.

The novolak prepolymers listed in Tables I and II were cured with hexamethylenetetramine for 1 h at 105°C and then postcured for 3 h at 180°C. The weight of curing agent used was 6.5% of the weight of the dry resin except where otherwise noted. The cured resins were ground to fine powders. The duPont 990-950 thermogravimetric analysis (TGA) units were used to perform TGA experiments. The heating rate used was 20°C per min and the runs were from room temperature to at least 700°C.

RESULTS AND DISCUSSION

TGA traces were obtained for a cured phenol-formaldehyde novolak (resin #1). The atmosphere under which the polymer is heated has a marked effect on the thermal behavior. When heated under an atmosphere of nitrogen a residue of 53% remains after heating to 700°C. When heated under a flow of air, total oxidation of the material has occurred by 700°C. This result is

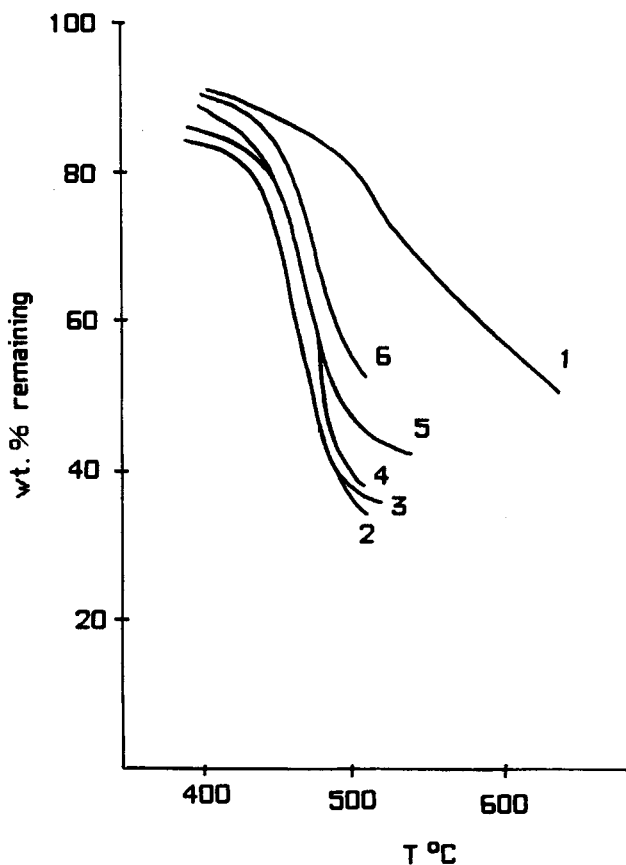


Fig. 1. TGA traces for cured resins produced from raw cashew liquid and phenol. The TGA curves were recorded while the polymers were under air with no flow. The numbers in the figure correspond to the resin numbers from Table I.

consistent with TGA curves reported phenol-formaldehyde resins¹⁶ and for polybenzimidazoles under nitrogen and under air.¹⁷

The TGA traces for resins produced from raw cashew liquid (resins 2–6) are shown in Figure 1. The TGA curves were recorded while each polymer was under air but without any flow of air. The general trend in thermal stability of the resins is clear. The higher the amount of phenol in the resin, the higher its thermal stability. The main degradation of the raw cashew resins occurs between 450 and 500°C.

Shown in Figure 2 are the TGA traces for the resins made from distilled cashew liquid (resins 7–11). Again samples were heated under air with no flow. The same trend in thermal stability is observed with the highest phenol content resins having the greatest thermal stability. Figure 3 compares the TGA traces of the resins from the raw cashew liquid with the resins from the distilled cashew liquid. It appears that the resins derived from the raw cashew liquid start to degrade at lower temperatures than do the resins from the distilled cashew liquid. However, this effect is not major and the rest of the degradation is similar in both. In addition to cardanol, the raw cashew liquid

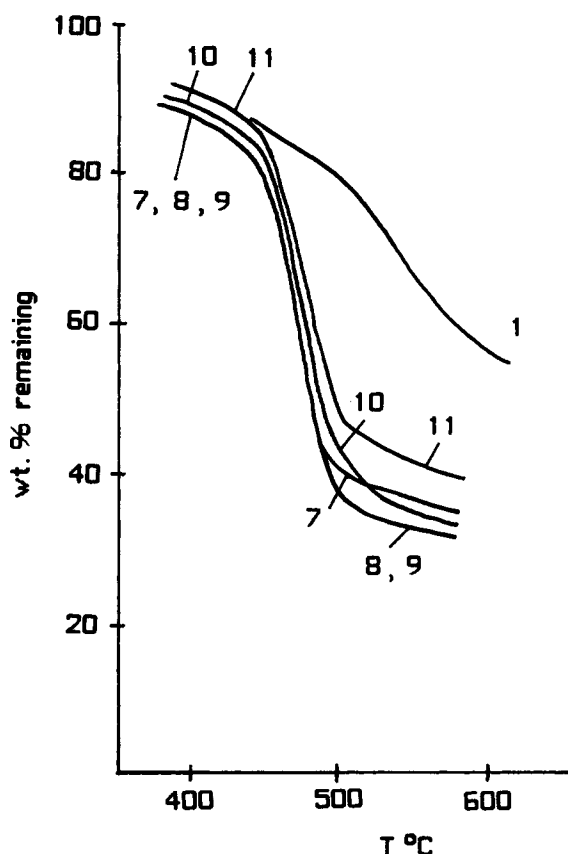


Fig. 2. TGA traces for cured resins produced from distilled cashew liquid and phenol. The TGA curves were recorded while the polymers were under air with no flow. The numbers on the diagram correspond to the resin numbers from Table I.

is believed to contain oligomeric phenolic compounds which are of lower thermal stability than the cardanol-formaldehyde resins. A ^{13}C NMR spectrum revealed that the distilled cashew liquid consisted of relatively pure cardanol monoene.

The thermal stability of a series of substituted phenol-formaldehyde resins was also investigated where the length of the alkyl side chain of the substituted phenol compound was varied. The TGA traces obtained for formaldehyde condensates with phenol, *o*- and *p*-cresol, *p*-nonylphenol, and *m*-penta-decylphenol, are shown in Figure 4. The trend observed in this series is that increased alkyl chain length results in lower thermal stability of the resin. Little difference between *ortho* and *para* substitution on the thermal stability of cresol resins is observed.

The amount of hexamethylene tetramine used to cure the resin also influences the thermal stability. A pre-resin containing a 2:1 ratio of formaldehyde to cashew and a 1.0:0.7 ratio of substituted phenol to formaldehyde was cured with varying amounts of hexamethylenetetramine. Figure 5 shows the TGA curves for resins cured with 5, 10, 15, 20, and 40 wt% curing agent. It appears that as the percent of curing agent rises from 5 to 10–15%, the

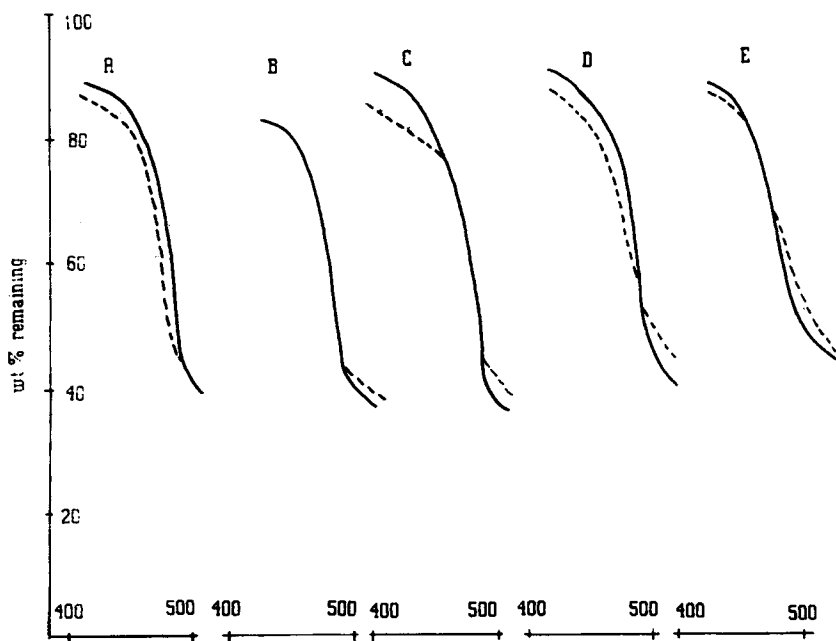


Fig. 3. Comparison of TGA traces for resins from raw and distilled cashew liquids. Raw cashew resins (---), distilled cashew resins (—). A = 100% cashew in resins, B = 80%, C = 60%, D = 40%, E = 20%.

thermal stability of the resin increases. However, if more than 15% curing agent is used the thermal stability of the resin will be lowered. This amount of hexamethylenetetramine is more than enough to react all of the available ring positions.

The thermogravimetric behavior of formaldehyde condensation products with phenol, *p*-cresol and bisphenol-A was reported by Learmonth and Searle.¹⁸ The TGA traces under nitrogen atmosphere at a heating rate of 50°C per min for two cured phenol-formaldehyde resoles with formaldehyde:phenol ratios of 1.25 and 2.0 to 1.0 were very close to each other. A residue of 68% remained after heating the polymers to 600°C which is consistent with the present studies. A resin containing formaldehyde and bisphenol-A (1.5 to 1.0 mole ratio) was thermally less stable than the straight phenol-formaldehyde polymer. For the bisphenol-A resin a residue of 40% remained after heating to 600°C. The isopropylidene linkage of the bisphenol-A resin is thermally less stable than the methylene linkage of the phenol-formaldehyde polymer. A resin containing bisphenol-A and *p*-cresol with formaldehyde (1.0:2.0:8.0 mole ratio) was intermediate in thermal stability; 50% weight residue remained after heating to 600°C. The high thermal stability of a phenol-formaldehyde resin is the result of the inherent rigidity of the dihydroxydiphenylmethane unit as a whole.

Based on our results, the thermally induced processes for substituted phenol-formaldehyde polymers in air are summarized as follows. First, a gradual weight loss occurs in the range of 200 to 400°C. This initial weight loss is believed to arise from further cross-linking reactions of the polymer.

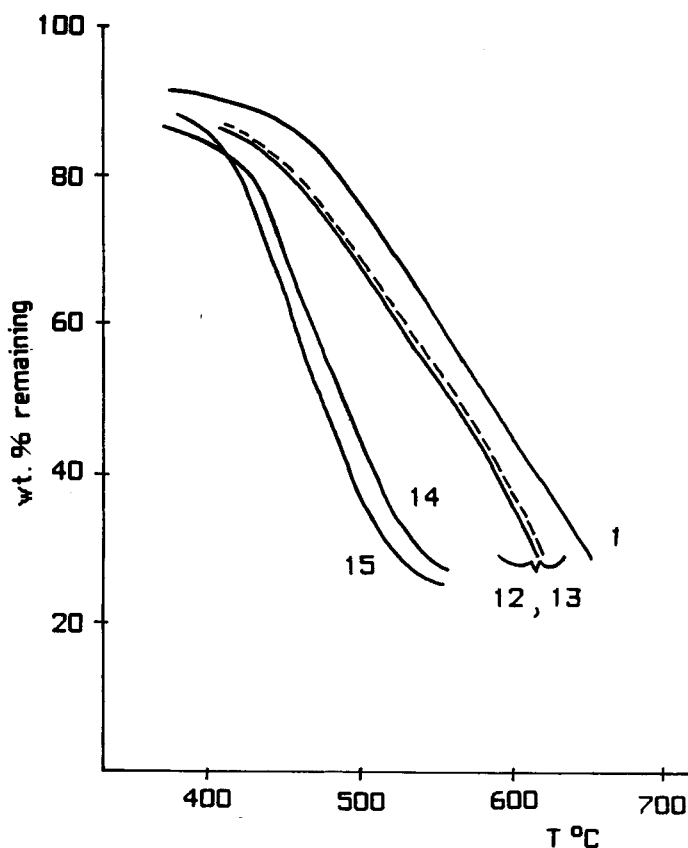


Fig. 4. TGA traces for cured resins containing formaldehyde with phenol, *o*- and *p*-cresols, *p*-nonylphenol, and *m*-pentadecylphenol. The numbers on the figure correspond to the resin numbers from Table II. Resins 12 and 13 are superimposed on each other.

Alaminov and co-workers¹⁹ reported a DTA thermogram for a phenol-formaldehyde polymer which had been cured with 15% hexamethylenetetramine. An exotherm in the DTA trace for this polymer was observed in the range of 150 to 275°C which is related to higher crosslinking of the polymer. Ammonia is driven off as a byproduct from the decomposition of hexamethylenetetramine and is responsible for the weight loss. Second, a steep decline in weight is observed for resins made from alkyl-substituted phenols in the range of 450 to 500°C. The resulting weight loss in this step is believed to be due to the breakdown of the methylene linkages in the alkyl chains. The longer the length of the alkyl chain or the higher the content of alkyl-substituted phenol in the polymer, the steeper will be the decline in weight during this step, although the position of the substituent of the ring has only a minor effect. Vogel and Marvel²⁰ found that totally aromatic polybenzimidazoles remained stable up to 600°C in nitrogen. However, a similar polymer containing a tetramethylene chain instead of an aromatic ring in the main chain underwent rapid degradation in the range of 450 to 500°C. Anderson and Freeman²¹ found that polyethylene underwent a steep degradation from 425 to 450°C when heated under vacuum. This is consistent with the temperature at which the methylene linkages in the substituted phenolics degrade.

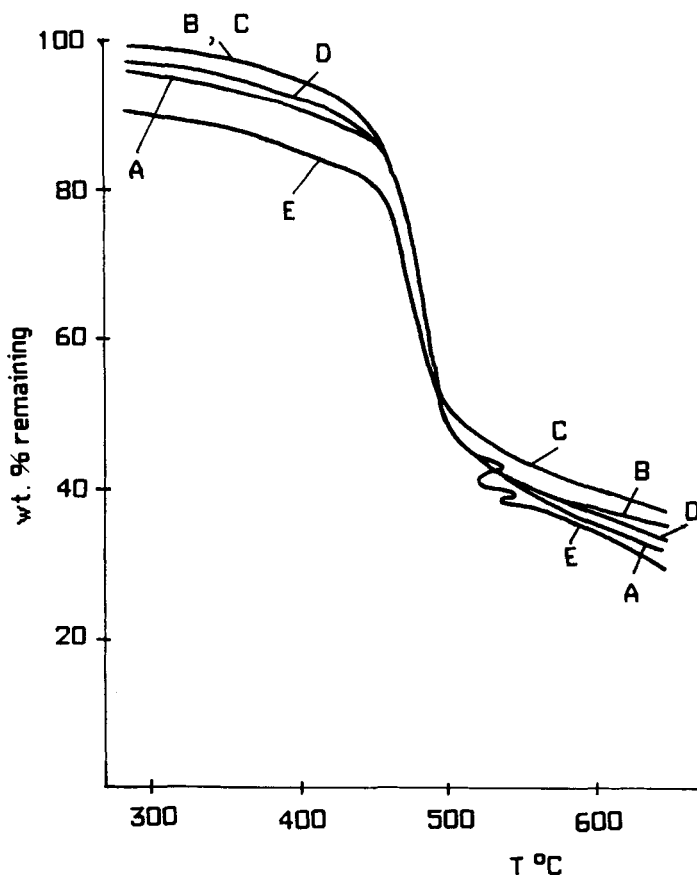


Fig. 5. TGA traces for resins cured with varying amounts of hexamethylenetetramine. A = 5%, B = 10%, C = 15%, D = 20%, E = 40%.

The mechanism of thermal and oxidative degradation of phenol-formaldehyde condensation products has been previously investigated by solid-state ^{13}C NMR.²²⁻²³ The ^{13}C NMR spectra of thermally oxidized substituted phenol resins showed evidence for ketone and carboxylic acid carbonyl groups which originate from the methylene groups. Pyrolysis yielding polycyclic fragments such as naphthyl and biphenyl may also occur during degradation. This is consistent with the current work as the alkyl substituents degrade well before the aromatic rings.

CONCLUSIONS

The thermal stability of a phenol-cashew-formaldehyde resin depends on the relative proportions of phenol and cashew phenolic compound in the polymer. The higher the amount of phenol the greater the thermal stability of the resin. The series of resins containing the raw cashew liquid were slightly less thermally stable than the resins containing distilled cashew liquid in that the raw cashew resins start degrading at lower temperatures. The shorter the

length of the alkyl side chain of a phenolic compound the more thermally stable will be the formaldehyde resin which is derived from it. The order of thermal stability of resins increases in the order: pentadecylphenol < nonylphenol < cresols < phenol, with the position of the substituent playing only a minor role. The level of hexamethylenetetramine used to cure the polymer influences the stability of the resin. A level of 10–15% curing agent maximizes the thermal stability of the polymer.

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