

Condensation–Addition-Type Resole Resins with Phenyl Ethynyl Functions: Synthesis, Characterization, and Thermal Properties

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ABSTRACT: Novel phenolic resins bearing methylol and phenyl ethynyl functions and curing by both condensation and addition mechanisms were synthesized by the reaction of 3-(phenyl ethynyl) phenol (PEP) with formaldehyde under alkaline conditions. Resins with varying relative concentration of the two functional groups were synthesized and characterized. The resins underwent a two-stage cure, confirmed by both DSC and DMA analyses. The low-temperature cure due to methylol condensation led to early gelation of the system. The ultimate curing through addition reaction of phenylethynyl group required heating at 275°C. The cured resins exhibited better thermal stability and anaerobic char yield in comparison to a conventional resole. The thermal stability and char-yielding property showed a diminishing trend with enhanced methylol substitution. Resin with F/P ratio less than unity offered excellent thermal stability and anaerobic char yield. The thermal degradation of the cured resins occurred in two kinetic steps. Methylene groups favored the initial degradation, whereas the higher temperature carbonization process was independent of the network structure. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3371–3377, 2001

Key words: phenolic resole resin; addition-cure resins; acetylene containing polymer; phenyl ethynyl functional polymer; high-char polymer

INTRODUCTION

Despite the emergence of a variety of high-temperature resistant, high-performance resins, phenolic resole resins are still the matrix of choice for composites for thermostructural applications. In combination with silica and carbon reinforcements they are extensively used in thermostructural applications in the aerospace industry.^{1,2} In carbon composites, the resin characteristics have a dominant role to play in deciding the ablative characteristics.³ Phenolics also enjoy an undisputed place among the matrices for the conven-

tional method of making C/C composites.^{4,5} The ease of synthesis, attractive cost factor, excellent tack and drape of the prepreg, good thermal stability and char-yielding property, and ablative characteristics are some of the features responsible for their dominance in the field.

Although phenolic resins are gifted with good thermal stability and char-yielding property, further improvement in these properties is desirable for their effective application in thermostructural applications and as matrices in C/C composites.^{6,7} This is achievable to a certain extent by rendering the resin thermally more stable and avoiding the condensation cure. In this perspective, addition cure phenolic resins that cure through thermal polymerization of groups such as phenyl maleimide,⁸ propargyl ether,⁹ acetylene,¹⁰ phenyl ethynyl,¹¹ etc., were synthesized. These polymers ex-

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hibited enhanced thermal and char-yielding characteristics. However, they required comparatively high-cure temperature, where the associated melt flow of the resin poses some processing difficulties. In such cases, it is imperative to induce partial curing at lower temperature to arrest the melt flow of the resin at the ultimate cure temperature. One way to confer such a property to phenolic resin is to let the resin cure to a minor extent by the conventional condensation method, the major curing being achieved through the addition mechanism. Thus, this article describes the attempt to realize a condensation–addition-type phenolic resole resin that cures partly by addition polymerization of phenyl ethynyl groups. Phenyl ethynyl functional polymers have attracted a great deal of attention in thermally stable thermoset resins. Several oligomeric resins containing phenyl ethynyl groups and possessing interesting thermal and mechanical properties are reported.^{12–17} A recent report concerns curing of a phenyl ethynyl terminated amic acid oligomer that shows the dual cure nature by condensation and addition mechanism.¹⁸ In another article, we have reported thermally stable novolac-type resins bearing phenyl ethynyl groups.¹¹

The present article focuses on the synthesis and characterization of resole resins based on 3-phenyl ethynyl phenol. The cure characteristics and thermal property of the cured resins have been described.

EXPERIMENTAL

Materials

3-Phenyl ethynyl phenol (PEP) was synthesized as described earlier.¹¹

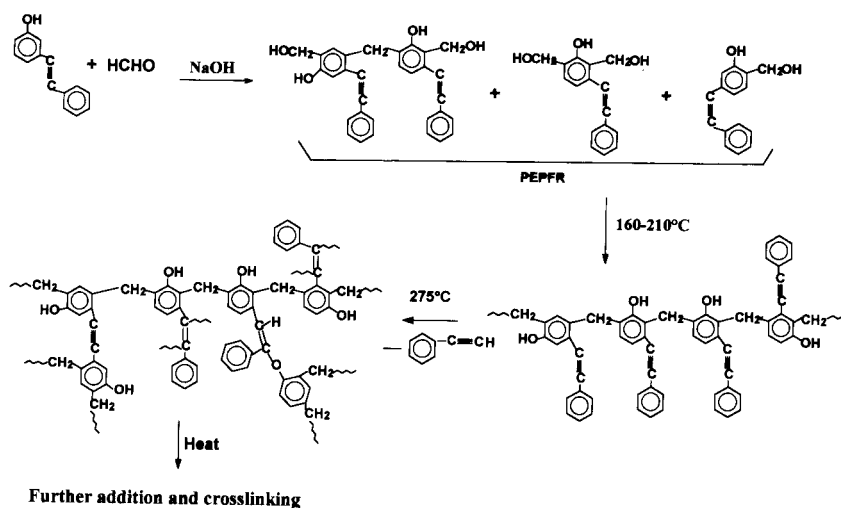
Formalin (34 wt % aqueous solution, Sisco Research, Mumbai, India) and sodium hydroxide (SD Fine Chemicals, India) were used as received.

Instruments

The cure characteristics of the resins were studied by DSC using a Mettler DSC-20 analyzer at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was performed on a DuPont 2000 thermal analyzer in conjunction with 951-thermogravimetric analyzer in nitrogen atmosphere at a heating rate of 10°C/min over the temperature range from room temperature to 700°C. NMR spectra were recorded with a Bruker 400AMX spectrometer. Gel Permeation Chromatography (GPC) analysis was performed on a Waters GPC model Delt prep. 3000 using THF as eluent and with DRI-R 401 refractive index and UV (at 254 nm) detectors. Polystyrene standards were used for calibration. Dynamic Mechanical Analyzes (DMA) were carried out on a DuPont DMA 983 with a DuPont 9900 thermal analyzer in nitrogen atmosphere. Nonisothermal measurements were done at a heating rate of 5°C/min.

Synthesis of Phenyl Ethynyl Phenol–Formaldehyde Resole Resin (PEPFR)

Phenyl ethynyl functional resole resins were synthesized from PEP and formalin using sodium hydroxide as a catalyst. The phenol to formaldehyde ratio was varied as 1 : 1, 1 : 1.5, and 1 : 2. Thus, 3-(phenyl ethynyl) phenol (1 g, 5.15 mmol) and formaldehyde (0.42 mL of 34% formalin, 1 mol/mol phenol) were heated in the presence of sodium hydroxide (0.2 mol %, 41.24 mg) for 4 h at



Scheme 1 Synthesis of PEPFR resin and probable mechanism of crosslinking.

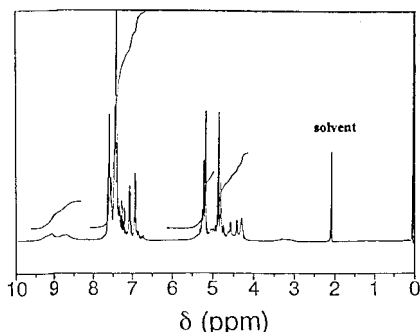


Figure 1 Proton NMR of PEPFR-1 in d_6 acetone.

75°C. After the reaction, the mixture was cooled to ambient and acidified with dil. sulfuric acid to neutral pH. The resin was purified by repeated washing with water. The purified polymer was dissolved in chloroform and dried over anhydrous sodium sulfate and filtered. The solvent was removed in vacuum at 40°C for 12 h. The product was characterized by spectral, thermal, and GPC analyses.

Curing

The PEPFR resins were cured by heating them progressively from ambient to 275°C, and maintaining at this temperature for 2 h in a vacuum.

RESULTS AND DISCUSSION

PEPFR resins were prepared by reacting PEP with formaldehyde in the presence of aqueous NaOH as shown in Scheme 1. Three types of resole resins were prepared by varying the phenol to formaldehyde ratio as 1 : 1, 1 : 1.5, and 1 : 2. The reaction temperature was fixed as 75°C. and duration as 4 h, when the reaction mixture became sufficiently viscous. The purified resins were characterized by $^1\text{H-NMR}$, GPC, and DSC. $^1\text{H-NMR}$ showed multiple peaks due to various types of methylene bridges (4.2–4.7 ppm), me-

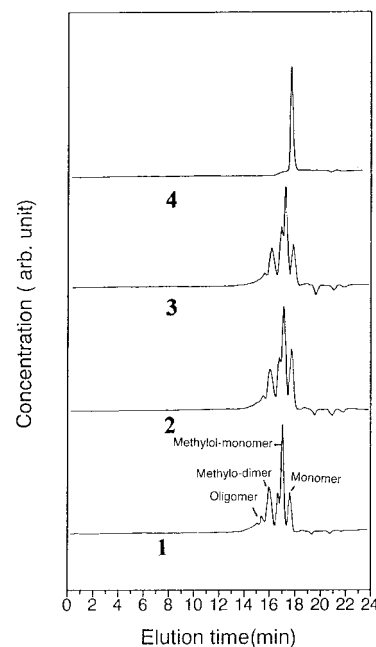


Figure 2 High-resolution GPC traces of the different resoles: (1) PEPFR-1; (2) PEPFR-1.5; (3) PEPFR-2; (4) PEP.

thoxy or methylol protons (4.8–5.2 ppm), and aromatic protons (6.9–7.5 ppm). The OH signals appeared at 8.3–9.0 ppm (broad). A $^1\text{H-NMR}$ s of resole resins is shown in Figure 1. The minor signals from 4.2 to 4.4 ppm are due to the different types of methylene bridges. The intense ones at 4.75 and 5.2 ppm are due to the methylol groups; the down field one is assignable to the one formed at the 6-position, which is more deshielded. All the methylene and methylol groups are found to be deshielded due to the presence of electron-withdrawing phenyl ethynyl group in conjugation with the phenolic ring, as already observed in the case of novolac of PEP.¹¹ As the formaldehyde to phenol ratio increased, the relative concentration of the methylene groups (in comparison to the methylol groups) decreased. The relative ratio of methylol to methylene is given in Table I for the three cases.

Table I Characteristics of PEPFR Resins

Polymer Ref.	Formaldehyde/ Phenol Ratio (F/P)	Relative Ratio —CH ₂ —O—/ —CH ₂ — from NMR	Different Components (%) in PEPFR Resin from GPC		
			Monomer	Mono- and Dimethylol Product	Dimer and Higher Oligomers
PEPFR-1	1	2.7	14.6	49	36.4
PEPFR-1.5	1.5	3.5	18.7	50.3	31.0
PEPFR-2	2.0	5.0	14.9	54.7	30.4

Table II Cure Characteristics of PEPFR Resins

Polymer Ref	Methylol Condensation				Ethyne Cure		
	ΔH (J/g)	T_i	T_m	T_e	T_i	T_m	T_e
PEPFR-1	91.3	170	196	230	260	300	320
PEPFR-1.5	100.9	170	198	230	270	320	340
PEPFR-2	142.3	160	202	220	255	280	325
PEP	—	—	—	—	300	320	350

T_i , T_m , and T_e are cure initiation, cure maximum, and cure end temperatures, respectively in °C.

GPC of all resole systems in the high-resolution column showed the presence of multicomponents. Because the concentration of formaldehyde is high and the medium is alkaline, the reaction stops after two or three steps of chain extension. Therefore, the reaction medium contains monomer, monomer with one or two methylol groups, dimer, and a small percentage of chain extended polymer. From the area of various peaks, the relative concentrations of all the likely components were determined. These are included in Table I. The peak assignments could be done from the relative retention times expected for a particular component. The monomer peak appeared separately. Increasing concentration of formaldehyde increases the proportion of methylol-substituted monomer with a consequent decrease in the concentrations of dimer and higher molar-mass components. The GPC profiles for all the three systems in comparison to the unreacted monomer are shown in Figure 2.

Cure Studies

DSC showed two cure exotherms confirming a two-stage curing, as expected. The first exotherm

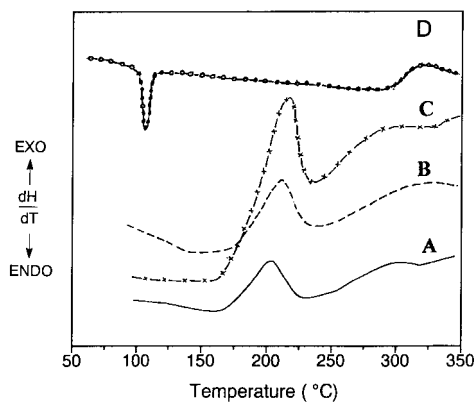


Figure 3 DSC thermograms of PEPFR resins: (A) PEPFR-1; (B) PEPFR-1.5; (C) PEPFR-2; (D) PEP, heating rate 10°C/min.

at 160–220°C is due to the condensation of methylol groups, and the second broad exotherm at 260–340°C is due to the polymerization of the phenyl ethynyl group. For the first step, the peak temperature is more or less the same, but the heat of reaction (ΔH) increases with increase in formaldehyde to phenol ratio (Table II). This is due to the increase in concentration of free methylol groups. The second cure steps are identical, and are initiated practically at the same temperature as the novolac-bearing phenyl ethynyl groups,¹¹ although the peaks are comparatively more pronounced. The cure temperatures are lower than that of the PEP monomer. The DSC thermograms of the resins are shown in Figure 3. Cure details are included in Table II.

The cure characterization done by nonisothermal DMA of the single-ply glass prepreg of the PEPFR-1 resole resin is shown in Figure 4. The $\tan \delta$ (E''/E') confirmed the two-stage curing, because the curve manifested two depressions in the temperature ranges of 150–220 and 225–325°C, almost in league with the DSC cure temperatures. The drive signal, proportional to the E' showed a continuous decrease from 75°C to the point of onset of cure at 150°C due to the viscosity reduction. The $\tan \delta$ curve showed the cure initiation due to the phenyl ethynyl group at around

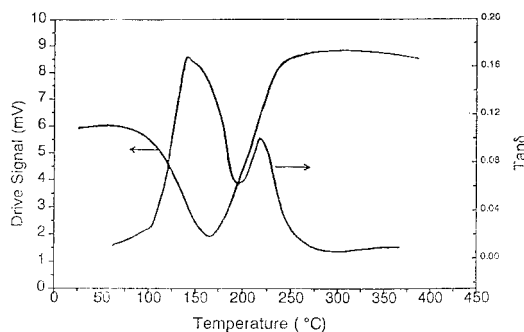


Figure 4 Nonisothermal DMA spectrum of PEPFR-1.5 in nitrogen, heating rate: 5°C/min, 1 Hz.

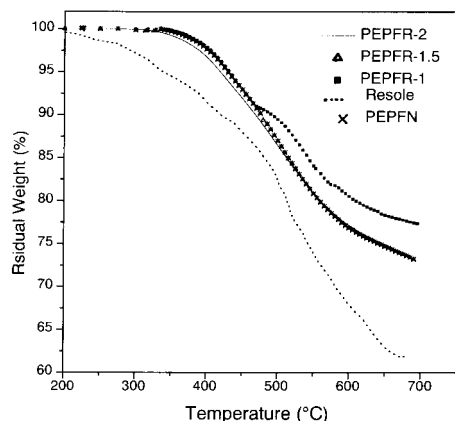


Figure 5 TGA traces of the cured resins in nitrogen. Heating rate 10°C/min.

230°C. Although the drive signal (proportional to E') indicated an apparent completion of modulus buildup at around 280°C, a close watch of the $\tan \delta$ depression showed that the cure extends to around 320°C, in league with the DSC observation. The nominal difference in cure profile can be due to the difference in heating rate for DSC and DMA. It can also be understood from DMA that the buildup in mechanical properties due to the methylol condensation is higher than that due to curing by ethynyl group. A previous study on the isothermal DMA of phenyl ethynyl novolac had confirmed that the cure of ethynyl groups is practically complete in about an hour at 275°C.¹¹ The ethynyl groups in the resole are also expected to cure identically, and no separate study was done to confirm this. Analogy with the corresponding novolac,¹¹ the resole resins were cured by heating them progressively from ambient to 275°C and maintaining at this temperature for 1 h. The cured resins were completely insoluble in common organic solvents. FTIR of the cured resin did not provide much information on the structure of the cured resin except for the disappearance of a very weak peak at around 2100 cm^{-1} present in the virgin resin. The cure mechanism of phenyl

ethynyl group has not been established unambiguously. Earlier proposals suggest polyaddition of ethynyl groups as the major cure path.^{14,17} A later study by Wood et al.¹⁹ using a model compound suggested addition of phenolic OH groups to the triple bond. Dimerization of two ethynyl groups accompanied by elimination of diphenyl ethylene was also suggested as a major cure mechanism. A cure mechanism for the present resin, extrapolated from Wood's hypothesis is depicted in Scheme 1.

Thermogravimetric Analyses

The TGA curves of the cured resins are shown in Figure 5. As the F/P ratio increases from 1 to 2, the thermal stability of the resulting polymer decreases. The char yield at 700°C also shows a diminishing trend. The initial decomposition temperatures (T_i) as well as the maximum temperature of decomposition (T_m) decrease with increase in F/P ratio. The thermal decomposition data are compiled in Table III. In comparison to the novolac resin of phenyl ethynyl phenol (PEPFN), its resole has enhanced thermal stability at a higher temperature regime, especially when the formaldehyde-content is less. The higher percentage of methylene groups in the resole resin (formed under higher F/P ratio) causes an easy triggering of thermal decomposition of the polymer at the methylene bridges, as is known.²⁰ Thus, although the PEPFR resole with higher F/P ratio is more crosslinked than the PEPFN, the benefits of higher crosslinking are not visible. Figure 5 contains also the thermograms of conventional resole synthesized at F/P ratio of 1, and that of phenyl ethynyl functional novolac (PEPFN) resin derived from PEP. Conventional resole was cured at 150°C for 2 h, and PEPFN was cured under the same conditions as for PEPFR. From the point of view of thermal stability, PEPFN, PEPFR-1.5, and PEPFR-2 exhibit identical thermal behavior. All phenyl ethynyl systems are superior to the

Table III Thermal Decomposition Characteristics of PEPFR Resins

Polymer Ref.	F/P Ratio (Molar)	T_i (°C)	T_m (°C)	T_e (°C)	Char at 700°C (%)
PEPFR-1	1	365	540	680	77.4
PEPFR-1.5	1.5	360	460	640	73.2
PEPFR-2	2	355	450	640	73.6
PEPFN	0.8	360	460	645	73.2
Resole	1	300	510	650	60

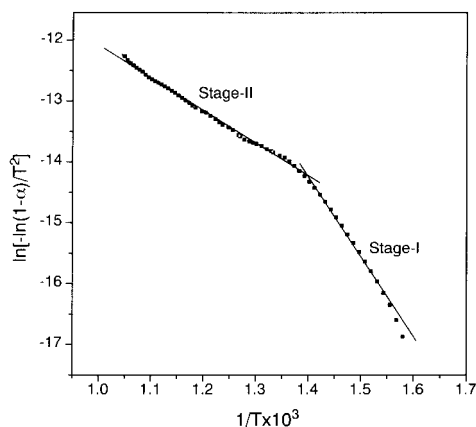


Figure 6 First-order kinetic plot of Coates-Redfern model for PEPFR-1.5.

conventional resole. Among the PEPFR resins, the char yield decreased with enhanced methylol content and the PEPFR-1 showed remarkably high char yielding property. It is concluded that PEPFR resins with very low concentration of methylol groups may be a compromise system from the viewpoint of processability and thermal stability. A lower F/P ratio is conducive for reducing the condensation cure character and enhancing the thermal characteristics of the resin. All systems are superior to conventional resole. While resole (F/P = 1) loses about 15% mass during cure, PEPFR-1 gives off only approximately 8% volatiles. As against a char-yield of 60% for the former, the new resin furnishes 77% char. Effectively, based on the virgin material, the new resin provides 71% char as against 51% for resole at 700°C. This indicates the advantage of PEPFR over the resole for applications demanding superior char yielding property, such as in C/C composites. Although, the polymers have to be treated at least up to 1000°C for understanding the true char yielding property, our previous studies on pyrolysis of various phenolic resins have shown that the relative trend in TGA behav-

our observed at lower temperature (700°C) is nearly *in toto* maintained under isothermal pyrolysis conditions at 900°C.²¹

Decomposition Kinetics

The kinetics of thermal degradation was evaluated using the mass-loss data from TGA. The data for the entire range were analyzed by the Coats-Redfern method based on the following equation for a first-order reaction:²²

$$\ln\{(-\ln(1-\alpha))/T^2\} = \ln\{(AR/\phi E) \times (1 - 2RT/E)\} - E/RT \quad (1)$$

where α is the fractional conversion at temperature T ; R is the gas constant; and ϕ is the heating rate. A and E are the preexponential factor and activation energy, respectively. The reaction was assigned a first-order kinetics because crosslinked polymers undergo degradation by random scission. The kinetic plots according to eq. (1) for a first-order reaction showed a two-step degradation mechanism for all the polymers. A typical plot is shown in Figure 6. A similar behavior had been observed for the novolac resins based on copolymer of PEP and phenol.²³ The two steps were analyzed separately, and the kinetic parameters are compiled in Table IV. The first stage is found to have higher activation energy than the second stage. Among the three polymers, the variation in E is random, but with an associated proportional variation in A , a phenomenon common in nonisothermal kinetic treatment. Hence, for comparison, the rate constant at an arbitrary temperature was calculated for each stage using the Arrhenius relation. The rate constants at 400°C for the first stage showed that the PEPFR-2 has the highest rate of decomposition than PEPFR 1 and PEPFR1.5. The latter two polymers have nearly same rate constants, con-

Table IV Kinetic Parameters for Thermal Degradation (E in kJ/mol; A and k in s^{-1})

Polymer Ref.	Temp Range (°C)	Stage I				Stage II				
		α Range	E	$A \times 10^{-5}$	$k_{400} \times 10^4$	Temp Range (°C)	α Range	E	$A \times 10^{-5}$	$k_{500} \times 10^3$
PEPFR-1	365–450	0.025–0.310	109.3	1.38	4.55	485–680	0.43–0.98	48.94	2.13	1.048
PEPFR-1.5	350–435	0.012–0.208	114.1	3.14	4.40	460–680	0.30–0.98	46.68	1.50	1.047
PEPFR-2	335–415	0.158–0.173	94.7	1.16	5.50	430–675	0.23–0.98	44.42	1.04	1.033

forming to their TGA pattern. This shows that increase in methylene crosslinks beyond a certain extent renders the system thermally fragile. The second step of decomposition is more or less same for the three systems. In all probability, this step corresponds to the carbonization process,²⁴ where the mechanism can be expected to be same for all the three polymers, and where the structural variation after the initial volatilization will have a minimum effect. The low *A* values for both cases further confirm the significance of volatilization in the kinetics of the decomposition process. Interestingly, the activation energies for both these steps are in the same range as for the two steps observed for the degradation of phenyl ethynyl functional novolac.²³

CONCLUSIONS

Novel condensation–addition phenolic resins bearing methylol and phenyl ethynyl functions were synthesized by the reaction of PEP with formaldehyde under alkaline conditions. The relative concentration of the two functional groups was varied by regulating the phenol/formaldehyde ratio. The resins underwent a two-stage cure confirmed by both DSC and DMA analyses. The cured resins exhibited better thermal stability and anerobic char yield than conventional resole. The thermal stability and char-yielding property showed a diminishing trend with enhanced methylol substitution. It is concluded that phenyl ethynyl functional resole with a F/P ratio less than unity could provide excellent thermal stability and char yield, superior to the corresponding novolac.

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