Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Nair, C. P. Reghunadhan , Bindu, R. L. and Ninan, K. N.(2003) 'Thermal Characteristics of Propargyl Ether Phenolic Resins', Journal of Macromolecular Science, Part A, 40: 4, 357 — 369

To link to this Article: DOI: 10.1081/MA-120019064

URL: http://dx.doi.org/10.1081/MA-120019064

JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. A40, No. 4, pp. 357–369, 2003

Thermal Characteristics of Propargyl Ether Phenolic Resins

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ABSTRACT

Addition curable propargyl ether phenolic resin of varying degrees of propargylation showed noticeably improved thermal stability in the lower temperature regime vis-à-vis cured resole. The crosslinking generated by the cycloalipahtic and linear polynene groups caused rapid decomposition at higher temperatures leading to a reduced char-content. The kinetics of non-isothermal decomposition showed the degradation occurring in two defined kinetic steps. The kinetic parameters computed from the mass-loss data showed an inconsistent variation in activation energy with composition. However, the computed rate constants confirmed that the first stage decomposition is facilitated by an enhanced propargyl content. The second step, associated with the carbonization process was systematically facilitated by enhanced crosslinking. Moderate propargyl functionalization was conducive for better thermal stability and anaerobic char residue. Analyses of char obtained by pyrolysis at 900°C showed it to be incompletely carbonized and amorphous in nature.

Key Words: Propargyl ether resins; Addition-Cure phenolics; Thermal decomposition kinetics; Pyrolysis.

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DOI: 10.1081/MA-120019064 1060-1325 (Print); 1520-5738 (Online)
www.dekker.com

INTRODUCTION

Phenol-formaldehyde resins are known as high temperature resistant polymeric materials that yield high amounts of char during pyrolysis. These characteristics render them useful as ablative and high temperature resistant molding materials in different fields.[1,2] Although conventional phenolics are thermally stable and are currently used for many high temperature applications, some of the properties of phenolics need further improvement for meeting the ever-increasing performance requirements. Some of the adverse properties which require research attention includes the moderate thermo-oxidative stability, inherent brittleness, condensation-cure nature, etc. Addition-cure phenolic resins possessing thermally stable groups could address some of these problems. Such polymers are useful in ablative compositions and as matrices in carbon/carbon composites.[3,4]

We have reported the synthesis of a few classes of such addition type phenolic resins bearing groups like phenyl maleimide,[5] phenyl maleimide-phenyl allyl,[6] acetylene[7] and phenyl ethynyl,[8] etc. These resins possessed enhanced thermal characteristics. Addition curable propargyl ether phenolics are also characterized by enhanced thermal stability, high Tg and long term high temperature durability.[9] The high Tg and low moisture absorption with good mechanical properties render them excellent substitutes for epoxies.[10] Propargyl ether modifications have been attempted for performance improvements in cases of adhesives based on phenol-formaldehyde resin.[11] Thermo-setting resins with good dimensional stability and heat resistance were obtained on mixing propargyl-etherified resin with resole.[12] Propargyl-ether phenolic resin based formulations are claimed to have good workability and curability for laminates, good heat- and moisture resistance and low dielectric constant.[13] Propargyl ether modification has resulted in improved thermal capabilities for ester-imide prepolymers,[14] polybenzoxazines,[15] etc. Available literature on propargyl phenolics is limited, but a decent number of reports on bispropargyl ether resins are available.[16–18] In a previous paper, we described the synthesis, characterization, and mechanical properties of composites of propargyl ether functional phenolic resin (PN resin).[19] To understand their utility as thermally stable materials for related applications, it is imperative to assess the thermal stability and degradation behavior of PN resins. The mechanism of the thermo-chemical degradation of phenolics has been investigated.[20] The thermo-oxidative process is the major path for degradation and takes place regardless of whether the pyrolysis reaction occurs in oxidative or inert atmosphere. The degradation process is accelerated by the presence of phenolic groups adjacent to the methylene bridges and hence, is dependent on the number of dihydroxy phenyl methane units. Since reducing the hydroxyl group concentration by way of etherification can reduce the thermo-oxidative susceptibility, the propargyl ether systems are expected to be thermally stable. This paper focuses on the thermal behavior, kinetics of thermal degradation and on the pyrolysis of the propargyl ether phenolic polymers, under limited temperature conditions.

EXPERIMENTAL

Materials

The PN polymers were synthesized by a procedure reported in an earlier publication.[19] Resole was obtained from Propellant Fuel Complex, VSSC prepared with a phenol/formaldehyde ratio of 1:0.8.

Thermal Curing

Curing of propargylated novolac was effected by gradual heating in a vacuum oven from ambient temperature to 250°C and maintaining that temperature for 2 h. The completion of cure was monitored by FTIR. Resole was cured by heating it in vacuum slowly from room temperature to 150°C and maintaining at this temperature for 2 h.

Instrumental Analyses

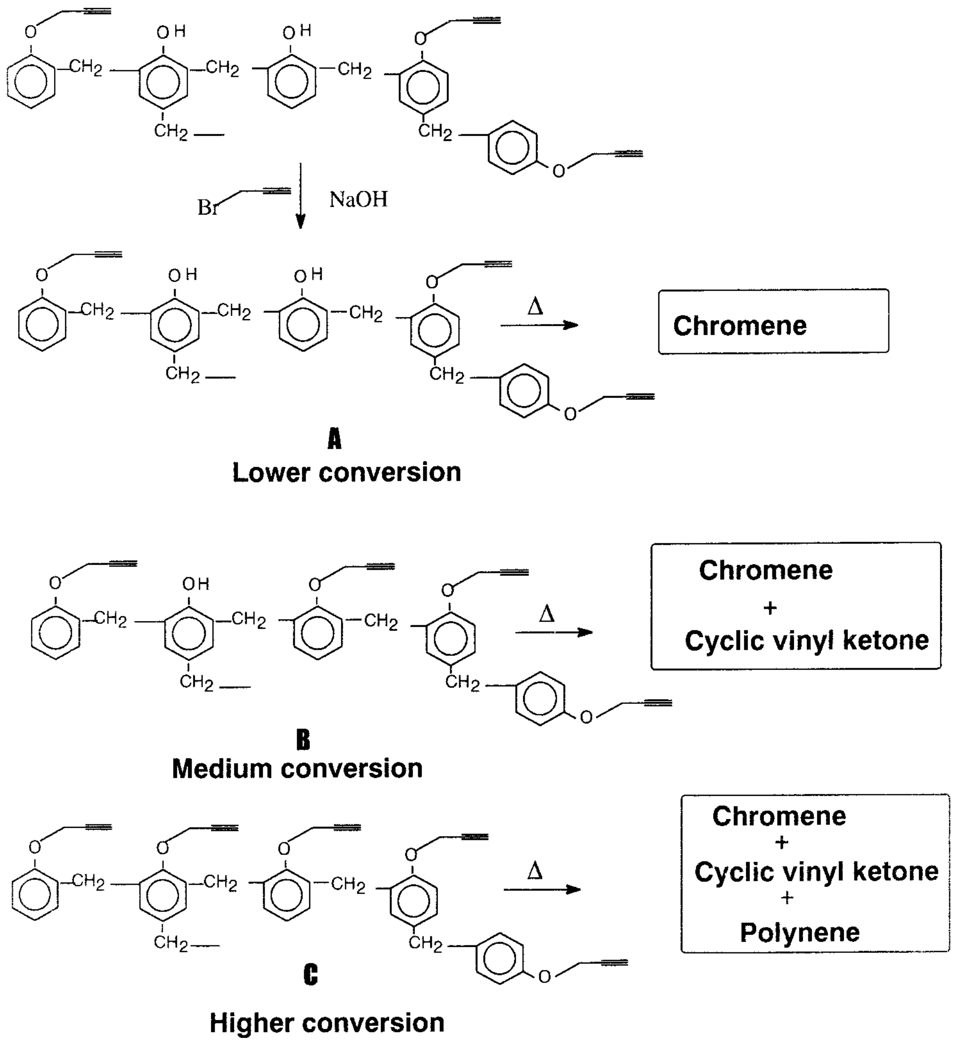
Thermogravimetric analysis (TGA) was performed on a Du Pont 2000 thermal analyzer in conjunction with 951-thermogravimetric analyzer in nitrogen atmosphere at a heating rate of 10°C min^{-1} over a temperature range from room temperature to 650°C. FTIR spectra were recorded with a Nicolet 510P instrument. Elemental analyses were performed on a Perkin Elmer model 2400 elemental analyzer. X-ray diffraction (XRD) analysis was carried out on a Philips XRD unit with PW 1729 X-ray generator having vertical goniometer with PW 1710 computer unit. Cu Kα radiation was used with accelerating voltage of 30 kV and tube current of 20 mA.

RESULTS AND DISCUSSION

Phenolic resins bearing varying proportions of propargyl functions (PN) were synthesized by reacting novolac with propargyl bromide as per Scheme 1. By regulating

Table 1. Composition and molar mass characteristics of PN resins.

Polymer reference	Extent of propargylation (NMR)	Molecular weight (GPC)		
		M_n	M_w	M_w/M_n
Novolac	0	2600	17200	6.60
PN-18	18	4200	34100	8.10
PN-45	45	5230	48100	9.00
PN-54	54	6350	57200	9.00
PN-82	82	6780	43700	6.45



Scheme 1.

the concentration of propargyl bromide, the degree of etherification was controlled. The maximum etherification achieved was 82%, as estimated by NMR analysis. The polymers were characterized by spectral, chemical analyses and by GPC as described earlier.[19] The characteristics of the novolac and the propargyl polymers used for thermal analyses are given in Table 1. The increase in molecular weight of the derivative vis-à-vis the precursor novolac is disproportionate to the extent of substitution. This implied that there is the possibility for partial chain extension through a minor addition reaction of propargyl groups during synthesis. The partial reaction accounted for the broad dispersity of the polymers.

Thermogravimetry

Phenyl propargyl ether resin is known to cure through a Claisen rearrangement to chromene followed by addition polymerization.[16] In the present case, the cure completion was ascertained from the complete disappearance of the $\equiv$C–H group absorption at 3272 cm^{-1} in FTIR. The FTIR of the precursor and the cured polymer are shown in Fig. 1.

The thermal stability of the cured PN resins was studied by thermogravimetry in N_2 atmosphere. The thermograms of the resins with a different degree of propargylation along with that of cured resole are shown in Fig. 2. TGA showed apparently single step decomposition starting above 380°C and ending at around 640°C for the cured PN resins. The decomposition parameters obtained from TGA thermograms are compiled in Table 2. The thermal stability of the PN resins with respect to initial decomposition temperature (T_i) and char residue at high temperature is significantly higher than that of conventional resoles systems. Whereas resole starts to decompose significantly at 300°C, the decomposition is triggered only at 380° for the PN resins. This advantage in thermal stability must be a consequence of the protection of the OH groups by etherification that

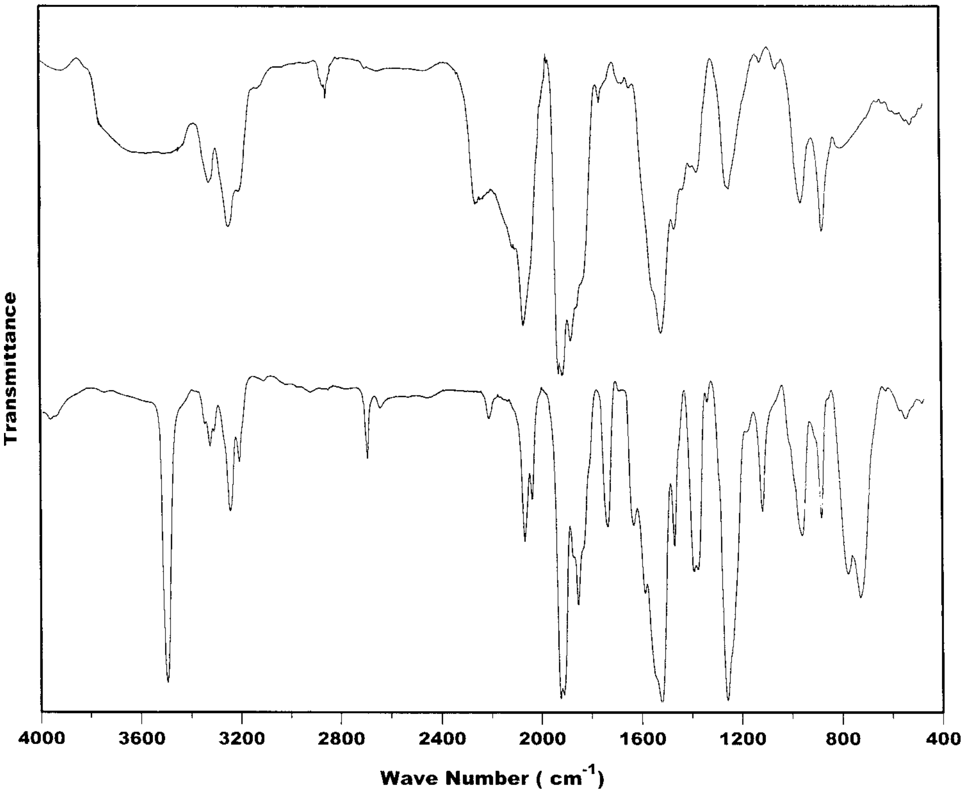


Figure 1. FTIR spectra of precursor (bottom) and cured resin (top), KBr pellet.

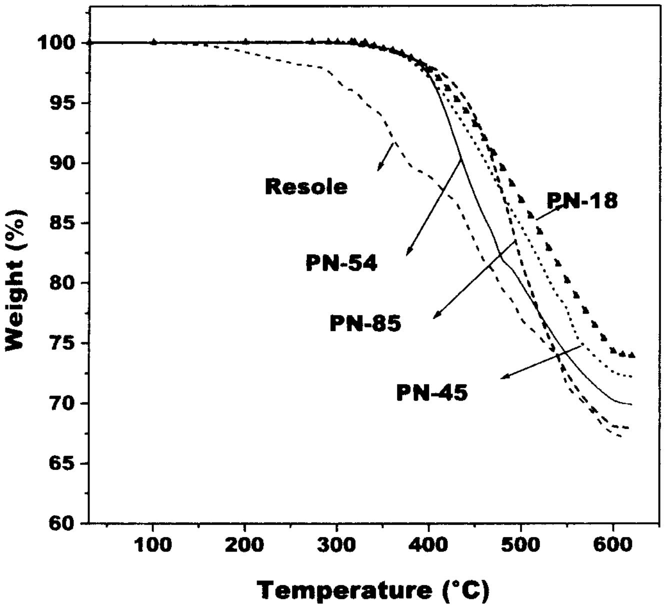


Figure 2. Thermograms of various PN resins and resole in N_2. Heating rate 10°C/min.

reduces the susceptibility of the methylene protons for degradation as already reported.[20] It is found that even a minor degree of propargylation and curing is conducive for boosting the Ti values by about 70°C. Although decomposition is initiated only at higher temperature, the degradation is found to be quite rapid for all the systems. Despite the increased crosslink density with enhanced extent of propargylation, TGA manifested nearly identical T_I values. Contrary to expectation, the degradation becomes more rapid and the char-yield decreases with an increase in the propargyl-content and crosslink density. The rapidity is clearly manifested in the systematic drift of the T_{max} to lower temperature as the degree of propargylation increases. This unexpected behavior can be ascribed to two reasons. As the propargyl-content increases, the cured polymer possesses

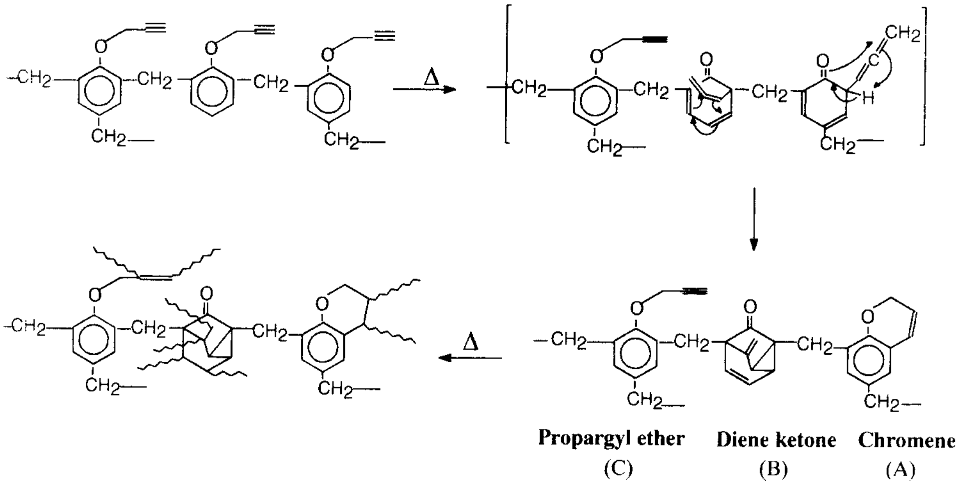
Table 2. Thermal decomposition characteristics of PN resins (TGA).

Polymer reference	T_i (°C)	T_{max} (°C)	T_e (°C)	Char at 600°C (%)
Resole	320	380	650	68
PN-18	390	510	640	74.3
PN-45	385	450	640	72.6
PN-54	380	360	650	70.3
PN-82	405	350	650	68.1

Ti = Onset of decomposition, T_{max} = temperature for maximum decomposition rate, T_e = end decomposition temperature.

more aliphatic groups. The enhanced crosslinking achieved through the aliphatic groups may not be conducive for enhancing the thermal stability, as these links are thermally fragile. Moreover, the PN polymers synthesized at different extent of propargyl etherification is likely to possess varying substitution patterns. Despite using a higher concentration of propargyl bromide and prolonging the reaction time, the etherification reaction could not be carried out beyond 82%, whereas in simple diphenols, quantitative etherification could be achieved. This shows that steric hindrance could play a significant role in controlling the etherification of phenol groups. This being the case, it can, in all probability be presumed that the propargyl etherification should preferably be occurring at the least steric hindered terminal phenol groups and the ortho-para substituted ones (Struct. A). Then the priority of substitution is in the ortho-ortho methylene substituted phenols (Struct. B) and the least preference should be for the 2,4,6-tris methylene substituted phenyl molecules (Struct. C, which acts as branching position on the novolac backbone), as shown in Scheme 1.

The thermal reactions of phenyl propargyl ether groups of different substitution pattern have been studied.[21] The same mechanism can be extended to propargyl novolac polymers. The type (A) propargyl ether can rearrange to the chromene prior to polymerisation[16] giving rise to comparatively thermally stable cyclic structure as indicated in Scheme 2. Type B giving the cyclic ketone and type C giving the polyene are thermally fragile entities. It has been established that the propargyl group can undergo polymerization through cyclotrimerization of the acetylene function in the presence of certain specific catalysts.[22] In the uncatalyzed state, as in this work, such a possibility can be ruled out. As propargylation increases, the crosslinking density increases and should result in enhanced thermal stability. However, the crosslinks generated by thermally fragile groups (by structures resulting from B and C type substitutions) undergo easy thermal degradation. This could account for the rapid thermal degradation and lower char-yield for the high-propargylated PN systems. For these reasons, thermal stability is found



Scheme 2.

to be good at medium crosslinking only. Evidence for the formation of the ketone structure (from Type B structure) was obtained from the FTIR spectrum with the broad absorption around 1740 cm^{-1} as seen in Fig. 1.

As the etherification of hydroxyl group stabilizes the methylene bridges against degradation, the decomposition must be triggered at the propargyl ether-derived crosslinks, occurring at a comparatively higher temperature. This boosts the Ti values for PN systems. Due to enhanced degradation of the PN polymers at higher temperature, the char residue reduces to the level of resole, which undergoes a slow rate of degradation. In other words, the advantage of enhanced T_i is lost by its fast degradation through loss of the propargyl ether-derived crosslink moieties. However, it may be remarked that the addition curable PN resins lose only 2% mass on curing, whereas resole loses 22–26% mass at the initial stages of curing. In short, the overall char residue of PN resins is superior to that of resole when a comparison is done based on virgin resins.

Decomposition Kinetics

The kinetic parameters for the non-isothermal degradation can be derived from the TGA mass-loss data.

The rate expression for non-isothermal reaction is given as:

$$d\alpha/dt = A\cdot e^{-E/RT}\cdot(1-\alpha)^n\cdot\phi$$

α is the fractional conversion at temperature T, R the gas constant, and ϕ the heating rate and A and E being the pre-exponential factor and activation energy, respectively.

α is calculated for a particular degradation step using the relation:

$$\alpha_T = (W_0 - W_T)/(W_0 - W_e)$$

where W_0, W_T and W_e are the mass at the onset of degradation step, at any temperature T and at the end of the reaction, respectively. Usually, W_e is taken from the mass corresponding to the plateau region of the TGA thermogram. For multi-step degradation, W_0 and W_e are common for all steps.

Some of the integrated forms of the above equation are:

Coats-Redfern Equation (CR)[23]

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

MacCallum-Tanner equation (MT)[24]

$$\log g(\alpha) = \log(AE/\phi R) - 0.483E^{0.435} - (0.449 + 0.217E)\times 10^3/T$$

$$(E \text{ in } kcal/mol)$$

Madhusudhanan–Krishnan–Ninan equation (MKN)[25]

$$\ln\{g(\alpha)/T^{1.9215}\} = \ln(AE/\phi R) + 3.7721 - 1.9215\ln E - 0.12039\, E/T$$

Where, $g(\alpha) = \{1-(1-\alpha)^{1-n}\}/(1-n)$;

When $n = 1$, $g(\alpha) = -\ln(1-\alpha)$.

In the cases of crosslinked PN polymers, a first order kinetics was assigned since they are expected to undergo degradation by a random process.

The factor $g(\alpha) = \ln(1 - \alpha)$ was calculated and using the above integral equations, the kinetic plots were made. From the linear plot, the activation energy (E) and Pre-exponential factor (A) were calculated.

The first order plot for the entire range of decomposition by C-R equation showed the existence of two major sectors in all cases, evidenced from the difference in slope of the curves as seen in Fig. 3 for a typical plot. This implies a complex decomposition mechanism, although TGA showed an apparently single-step decomposition. The two steps, which occurred in more or less the same temperature regime for all compositions, were analyzed separately by the three kinetic equations and activation energy and pre-exponential factors were calculated. The three different methods give nearly consistent values for a given step. The results are compiled in Tables 3 and 4. Comparison with thermal degradation of bispropargyl ether resin[26] indicates that the first stage decomposition is caused by a chromene network. It is also likely that this stage is contributed partly by methylene bridge decomposition. Initially, the *E* and *A* values increase with crosslink density, but at higher crosslinking they tend to decrease. Since the activation energy computed from non-isothermal method could be apparent as it is associated with a proportionate change in A also, the rate constant (k) values calculated at an arbitrary temperature of 400°C were compared for the first step decomposition. The results included in Table 3 shows that although this step is initially facilitated with increased propargyl content, the higher crosslinking is helpful in retarding the overall rate of degradation.

In the case of the second step spreading from 480–630°C also, the apparent activation energy increases with an increase in propargyl content. This should imply an enhanced thermal stability. For reasons of kinetic compensation, the rate constants at a temperature

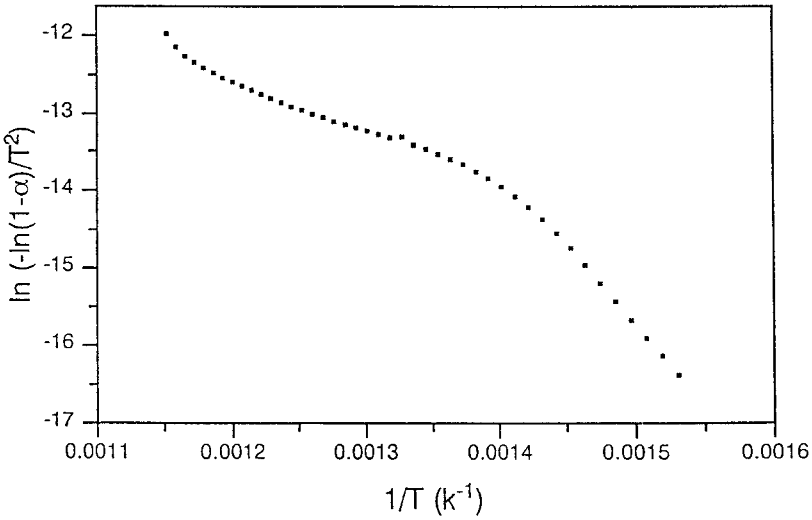


Figure 3. C-R plot for PN polymer showing the two-stage degradation.

Table 3. Thermal decomposition kinetics of cured PN resins (First Stage: 390–470°C, E in kJ/mol).

		Kinetic parameters					
		C-R		M-T		M-K-N	
Polymer	$k_{400} \times 10^4 (s^{-1})$	E	$A(s^{-1})$	E	$A(s^{-1})$	E	$A(s^{-1})$
PN 18	2.53	97.5	7.86×10^2	99.1	1.56×10^4	97.90	9.16×10^3
PN 45	3.18	121.4	8.41×10^5	122.9	1.66×10^6	121.71	9.64×10^5
PN 54	6.14	158.8	1.30×10^9	159.7	2.59×10^6	159.10	1.46×10^9
PN82	2.30	106.3	4.08×10^4	108.5	8.92×10^4	106.64	4.75×10^4

k_{400} = rate constant at 400°C.

of 525°C were compared. The rate constants were found to increase with an increase in propargyl-content, showing decreased thermal stability for the PN resins at a higher percentage of propargylation, in association with the actual pattern of the thermogram in the higher temperature regime. The second step can be attributed to the carbonization process involving phenyl rings, residual methylene bridge and propargyl ether-derived moieties. The associated carbonization process is characterized by a low pre-exponential factor implying the significance of volatilization process in controlling the kinetics.

The kinetic parameters of both steps of degradation are not considered absolute as they are calculated based on a single heating rate method, and are useful for kinetics comparison in the series and for predicting the decomposition profile at any given temperature.

Isothermal Pyrolysis

Although TGA helps in deriving an overall assessment of the thermal stability and anaerobic char residue under dynamic heating mode, a true understanding of

Table 4. Thermal decomposition kinetics of cured PN resins (Second Stage: 480–630°C), E in kJ/mol.

		Kinetic parameters					
		C-R		M-T		M-K-N	
System	$k_{525} \times 10^3 (s^{-1})$	E	$A(s^{-1})$	E	$A(s^{-1})$	E	$A(s^{-1})$
PN 18	1.6	86	1.47×10^3	89.9	4.29×10^3	86.5	1.76×10^3
PN 45	2.05	63.6	3.01×10^1	67.9	9.86×10^1	64.1	3.70×10^1
PN 54	2.61	53.4	1.01×10^1	57.4	2.76×10^1	53.9	1.03×10^1
PN82	3.18	76.3	3.16×10^2	80.6	9.95×10^2	76.8	3.82×10^2

k_{525} = rate constant at 525°C.

Table 5. Pyrolysis results of PN resin and resole.

Polymer reference	Mass loss on curing, (%)	%Char at 700°C (TGA)	% Char at 700°C 1 h	%Char 2 h at 900°C		Elemental composition (%)		
				1 h	2 h	C	H	O[a]
PN 45 (virgin)	—	—	—	—	—	81.16	5.56	13.28
PN 45	2.0	68	62	62	61	78.3	1.50	20.20
Resole	22.3	62	60	59	59	—	—	—

[a] Indirectly estimated.

the carbonization process warrants isothermal pyrolysis and char analysis, which has been done for a selected polymer, PN-45 in a limited temperature range. The pyrolysis data are important from the point of view of its application as ablative materials and as matrices for the preparation of C/C composites. The pyrolysis has been done at 700°C and 900°C, and the char yield and nature of char were analyzed. The isothermal pyrolysis was affected in an inert atmosphere of argon for different time intervals. The char residue does not change significantly with a rise in temperature in this regime. The char obtained was analyzed for elemental composition and also by FTIR spectroscopy and XRD. The elemental composition of the residue obtained after pyrolysis at 900°C is given in Table 5.

Elemental analysis shows an increase in carbon content in the char in comparison to the virgin polymer. However, there is a significant decrease in hydrogen concentration of the char. The oxygen content is considerably enhanced. The char possesses a significant amount of oxygen. This implies the possibility of loss of hydrogen and carbon as hydrocarbon as the major decomposition reaction during pyrolysis. The increase in oxygen is due to a decrease in carbon content and practically no oxygen is lost. Complete pyrolysis for elimination of oxygen needs still higher temperature, which remains to be investigated.

FTIR spectra of the pyrolyzed samples showed weak broad absorption at 1000–1200 cm^{-1}. This may be assigned to the residual C–O linkages present in the char. Very minor absorption corresponding to C–H groups and C–OH groups were observed at 2900–2980 cm^{-1} and 3300–3600 cm^{-1}, respectively. Since the OH absorptions are very weak, it can be presumed that the oxygen exists as ether groups, as supported by the strong IR absorption in the 1000–1200 cm^{-1} range. The FTIR spectra are nearly the same for pyrolyzed resole and PN polymer. Despite higher thermal stability, the PN resins do not give much of an advantage in terms of anaerobic char residue in comparison to resole. However, comparison based on virgin resin shows that the PN resins provide an overall increase of 20% in char yield in comparison to resole (at 900°C).

XRD analysis showed the char to be amorphous in nature as is generally observed for low temperature pyrolyzed phenolic resin.[27,28]

CONCLUSION

Thermosetting propargyl ether phenolic resin of varying degrees of functionalization showed an enhanced initial decomposition temperature vis-à-vis resole. However, the decomposition was found to be faster for the more crosslinked system, since the crosslinks were constituted by aliphatic groups. The enhanced proportion of thermally fragile crosslinks led to relatively poor thermal performance at a higher extent of propargyl functionalization. The PN resins provided an overall increase of 20% char in comparison to resole. The kinetics of non-isothermal degradation showed the degradation to be occurring in two defined kinetic steps. The activation energy for thermal decomposition activation varied inconsistently with composition. However, the computed rate constants confirmed that the first stage decomposition is initially facilitated by enhanced propargyl content, although higher crosslinking tends to retard the decomposition. The second step, associated with the carbonization process was systematically facilitated by enhanced crosslinking. The study showed that moderate crosslinking is conducive for better thermal stability and anaerobic char residue. Analyses of char showed it to be incompletely pyrolyzed and amorphous in nature.

ACKNOWLEDGMENTS

The authors are grateful to their colleagues in the Analytical and Spectroscopy Division for support in various analyses. The Director, VSSC is thanked for permission to publish the results. R. L. Bindu acknowledges CSIR, New Delhi for a fellowship.

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Received August 2002
Revised October 2002