

Relationship between Viscoelastic Properties and Gelation in the Epoxy/Phenol-novolac Blend System with N-Benzylpyrazinium Salt as a Latent Thermal Catalyst

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ABSTRACT: A study of viscoelastic properties and gelation in epoxy/phenol-novolac blend system initiated with 1 wt % of N-benzylpyrazinium hexafluoroantimonate (BPH) as a latent cationic thermal initiator was performed by analysis of rheological properties using a rheometer. Latent behavior was investigated by measuring the conversion as a function of curing temperature using traditional curing agents, such as ethylene diamine (EDA) and nadic methyl anhydride (NMA) in comparison to BPH. In the relationship between viscoelastic properties and gelation of epoxy/phenol-novolac blend system, the time of modulus crossover was dependent on high frequency and cure temperature. The activation energy (E_c) for crosslinking from rheometric analysis increased within the composition range of 20–40 wt % phenol-novolac resin. The 40 wt % phenol-novolac (N40) to epoxy resin showed the highest value in the blend system, due to the three-dimensional crosslinking that can take place between hydroxyl groups within the phenol resin or epoxides within the epoxy resin involving polyaddition of the initiator with BPH. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2299–2308, 2001

Key words: epoxy; phenol-novolac; cationic latent thermal initiator; viscoelastic properties; gelation

INTRODUCTION

Epoxy–phenol resin systems are some of the most utilized thermoset–thermoset blends for encapsulation. Thermosetting resins have a variety of useful properties, including excellent insulating characteristics, good adhesive properties, outstanding chemical resistance, retention of properties under severe operating conditions, low moisture adsorption, and no formation of reaction by-products that can cause void formation or act as plasticizers.^{1–3} However, there are some limitations to the use because of

difficulties in control of the cure reaction. Thus, only very limited information is presented in the literature concerning the relationship between viscoelastic properties and gelation during the cure process.^{4,5}

Usually, amines or anhydrides serve as epoxy hardeners, reacting to form networks of alternating copolymers. Anhydride-cured epoxides are used for many advanced materials, and generally good high-temperature stability, and good physical and electrical properties, compared to amine-carried systems.^{6,7} However, tertiary amines have been widely used as hardeners for glycidyl ether resins, ring-saturated epoxy resins, and resins with internal epoxy groups.⁸ However, it is known that in the absence of catalyst, the anhydrides do not react directly with the epoxy group

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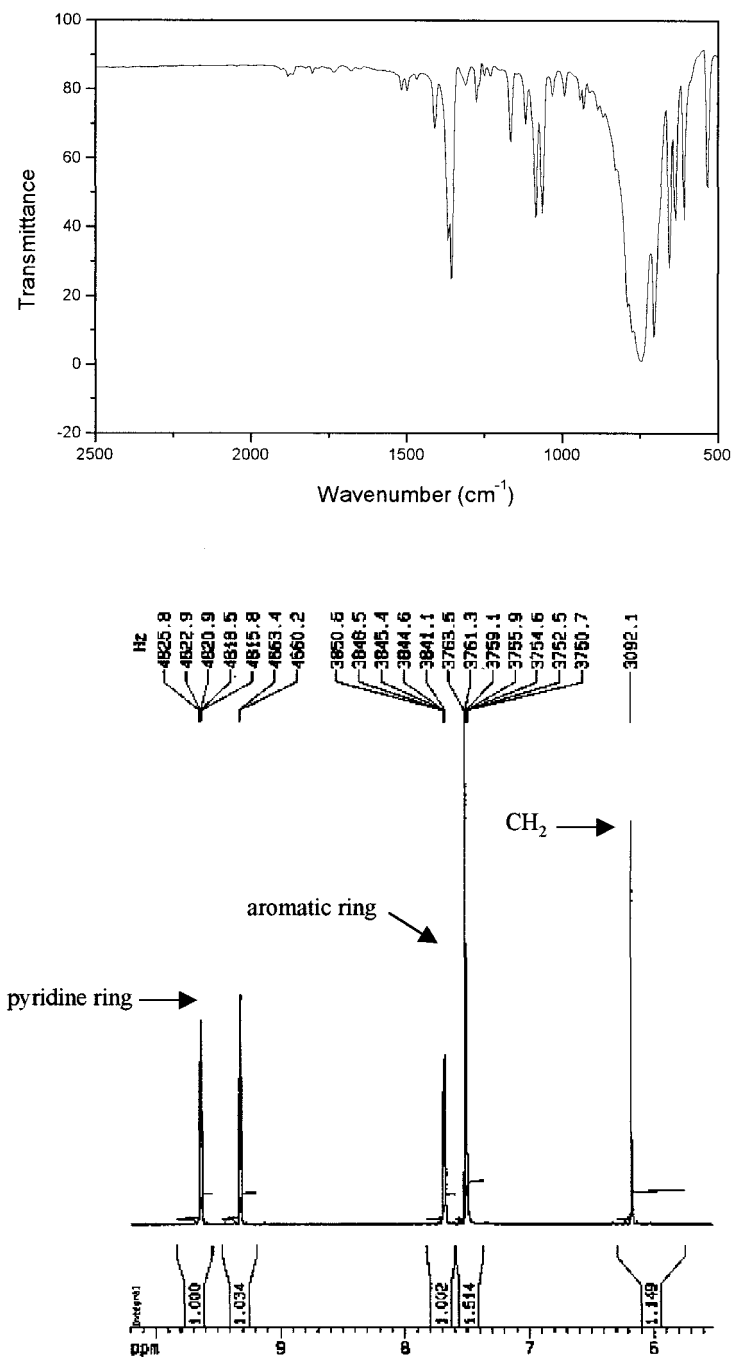


Figure 1 FTIR and ¹H NMR analyses of BPH.

and the tertiary amines are of the toxicity combined with low heat resistance.

Recently, N-benzylpyrazinium salts have been shown to be excellent latent thermal initiators for curing of epoxy resins.^{9–12} These initiators are not hygroscopic, dissolve readily in epoxy resins, exhibit a longer pot-life than the more commonly

used BF₃–4-methoxyaniline complex, and overcome the disadvantages of current hardeners that cause excessively rapid gelation, high hygroscopicity, and light instability.¹³ Also, the initiator activity of N-benzylpyrazinium salts can be enhanced by decreasing the nucleophilicity of the counterion, SbF₆⁻, and by introducing an electron-

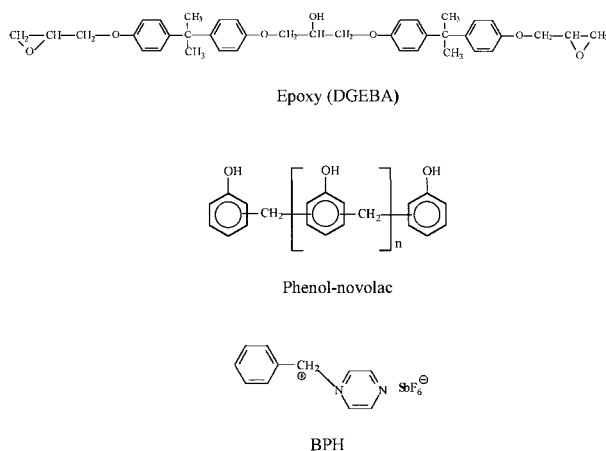


Figure 2 Chemical structures of epoxy, phenol-novolac, and BPH.

donating substituent on the phenyl ring of the benzyl group.¹⁴

Rheological properties such as the viscosity and the dynamic modulus can be directly correlated to the evolving physical and mechanical properties of blend system during the cure process.^{15,16} Because one of the most important factors influencing the processing of thermosetting resins is gelation, viscoelastic studies of the crosslinking process are essential for optimization of the processing cycle.¹⁷⁻¹⁹

The objectives of this study were to understand the effect of different amounts of phenolic resin on the relationship between dynamic viscoelastic properties and gelation, and to determine the applicability and limitations of the simple criterion of measuring time to gelation for the epoxy/phenol-novolac resin blend system initiated by N-benzylpyrazinium salt as a latent cationic thermal catalyst.

EXPERIMENTAL

Materials and Sample Preparation

The epoxy resin used in this study was the diglycidyl ether of bisphenol A (DGEBA, YD-128 supplied from Kukdo Chem. Co. of Korea). The epoxide equivalent weight of the DGEBA was 185–190 g · eq⁻¹, and the density was 1.16 g · cm⁻³ at 25°C. The phenol-novolac resin was supplied from Kukdo Chem. Co., and BPH as a cationic initiator was synthesized in our lab scale.⁹ The purity and the chemical structures of product were con-

firmed by FTIR and ¹H NMR, as shown in Figure 1. For elemental analysis of BPH, calculated for C₁₁H₁₁N₂SbF₆ is C: 32.45 %, H: 2.70%, and N: 6.88%, and found for C₁₁H₁₁N₂SbF₆ is C: 32.90%, H: 2.74%, and N: 6.91%, respectively.

The DGEBA, phenol-novolac, and BPH structures are shown in Figure 2.

In this study, all resin compositions consisted of different weight ratios of epoxy to phenol-novolac resin prepared with 1 wt % of BPH. The concentration of phenol-novolac resin added was 0, 5, 10, 20, and 40 wt %. Epoxy and phenol-novolac resins were mixed in oil bath at 65°C for about 1 h, and then the catalyst dissolved in acetone was added to the mixture. The mixture was fully stirred for about 3 min and degassed in a vacuum oven for 2 h to eliminate residual solvent and air before measuring. Each sample was immediately tested and stored in a refrigerator after testing.

Measurements

DSC Thermograms and Evaluation of Latent Initiator Properties

DSC thermograms of epoxy/phenol-novolac/BPH blend systems were measured using dynamic DSC analysis (Perkin-Elmer DSC-6 supported by a Perkin-Elmer thermal analyzer). Dynamic heating experiments were conducted under a nitrogen flow of 30 mL/min, with a heating rate of 10°C/min and calibration range of 30–350°C. The amount of sample was limited to 12–15 mg to minimize experimental error. The latent thermal properties of the initiator used were also evaluated as a function of curing temperature using dynamic DSC method.

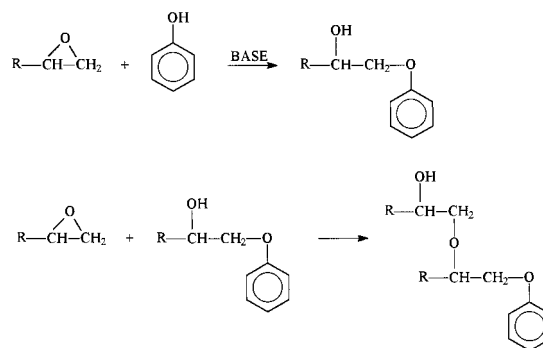


Figure 3 Epoxide-phenol and epoxide-secondary hydroxyl reaction.

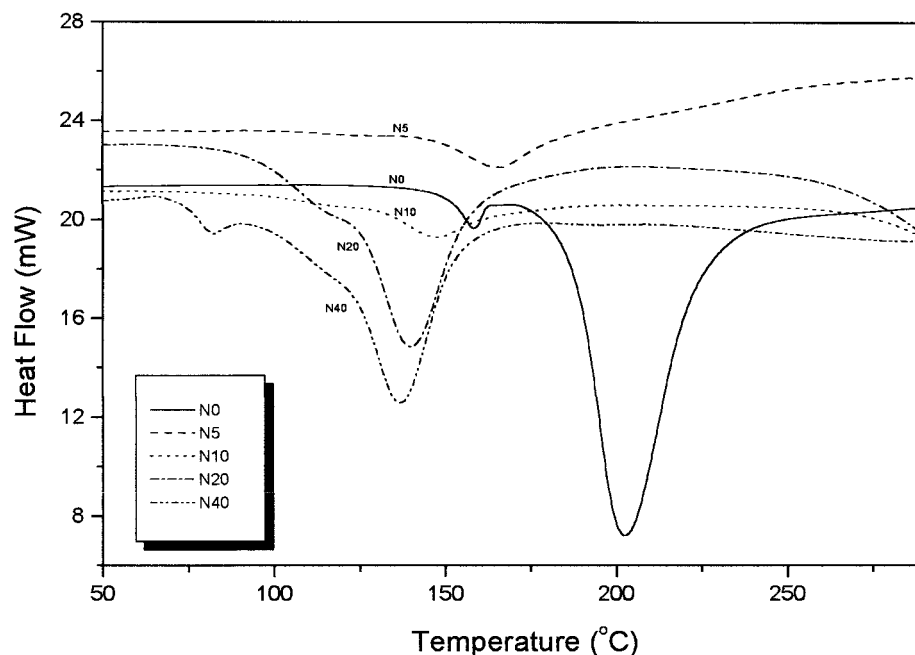


Figure 4 Dynamic DSC thermograms of uncured samples.

Rheological Properties

The rheological measurements at isothermal conditions were monitored using Physica (Rheo Lab. MC 100) with parallel plate geometry. The 50-mm disposable plates were preheated in the rheometer environmental chamber for approximately 10 min at setting temperature before tests. The gap between the plates was fixed to 0.5 mm. After loading the sample into plates, the temperature of the chamber was equilibrated to setting temperature in less than a minute. Experiments were performed at 110, 130, and 150°C, and the frequency were 3, 5, 7, and 10 ω , respectively.

RESULTS AND DISCUSSION

Generally, the cure reactions of epoxides with phenol-novolac resins take place almost exclusively through the addition of the phenolic hydroxyl to the epoxide,²⁰ although a second reaction consists of the secondary hydroxyl (produced by the main reaction) reacting with another epoxide, as reported before by Gagnebien et al and shown in Figure 3.²¹

Figure 4 shows a series of DSC thermograms obtained for dynamically cured epoxy/phenol-

volac/BPH systems as a function of curing temperature. The maximum of the exothermic peak is shifted to lower temperature with increasing phenol-novolac resin content. In addition to the main exothermic peaks, small peaks of lower temperature range were seen. This phenomenon founding in two exothermic peaks estimates that the above cure reactions are generated in sequential or simultaneous reaction.

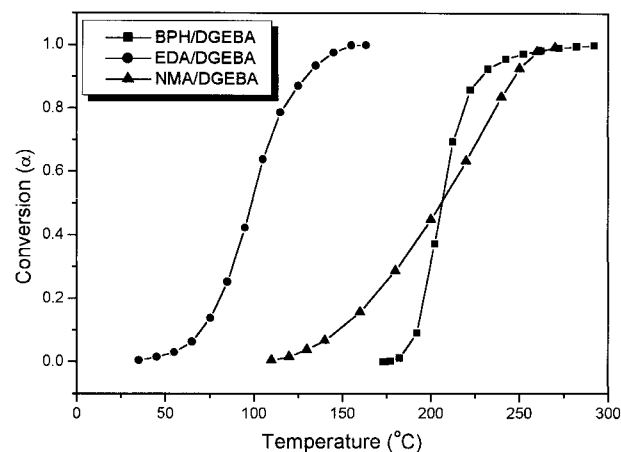


Figure 5 Conversion of epoxy system for different commercial types of curing agents as a function of curing temperature.

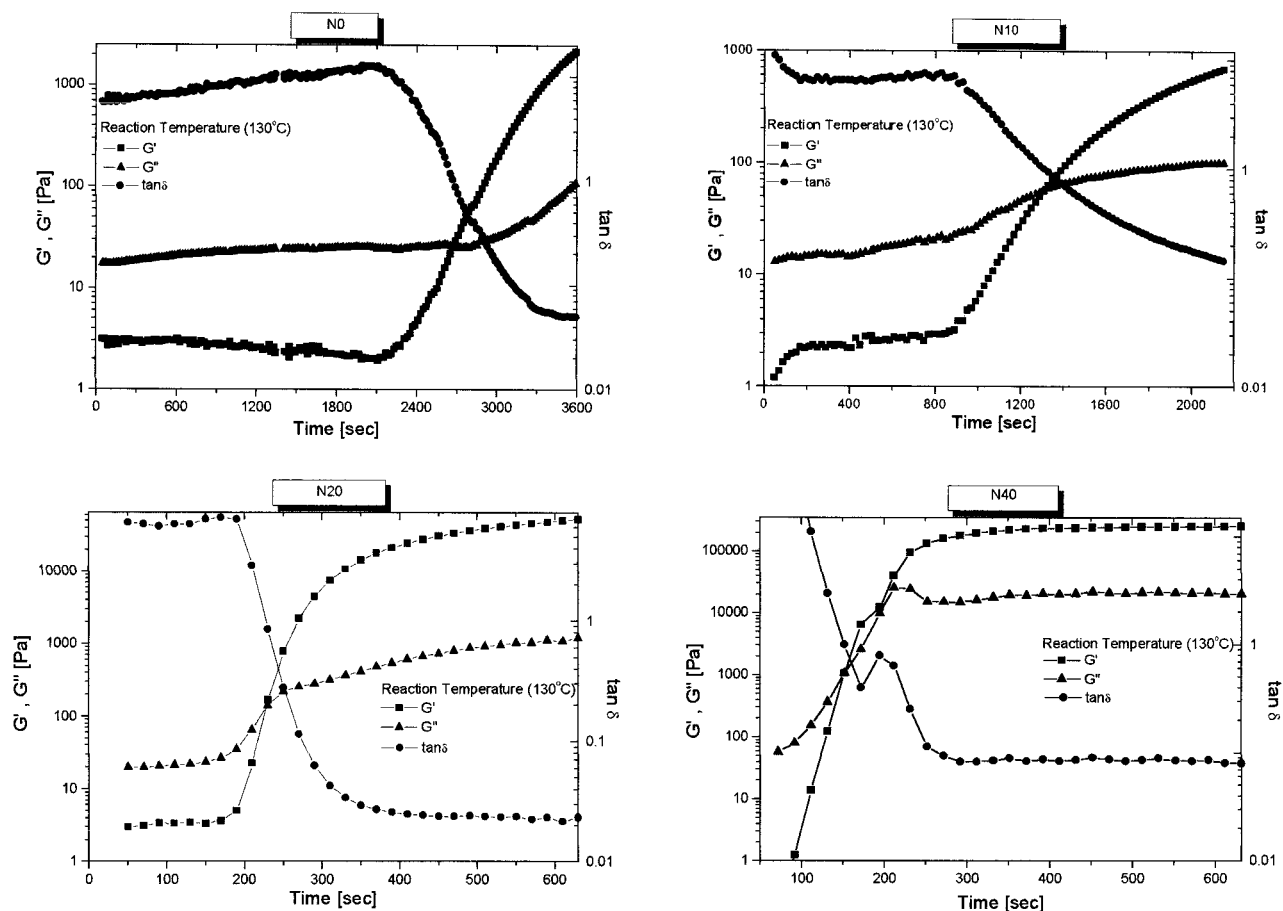


Figure 6 Storage (G'), loss modulus (G''), and damping factor ($\tan \delta$) of epoxy/phenol-novolac/BPH blend system, measured at 130°C.

Figure 5 shows the conversion of epoxy system for different commercial types of curing agents as a function of curing temperature using dynamic DSC. Conversions for all compositions are activated in a given specific temperature. However, for the ethylene diamine (EDA) curing agent, the conversion is activated at a lower temperature, resulting in short pot-life of room temperature. In the case of the nadic methyl anhydride (NMA), the conversion is activated at a higher temperature but never a much broader temperature range. On the other hand, the conversion using the BPH shows a sharp onset and rapid cure as the reaction temperature increases. BPH appears to be an excellent latent thermal initiator in this blend system, with a well-defined temperature of cure.

Figure 6(a) and (b) gives the results of dynamic mechanical properties of epoxy/phenol-novolac/

BPH blend system taken at 130 and 150°C, and at angular frequency of 5 Hz varying different weight percents of phenol-novolac resin. The cure temperature is above the maximum glass transition temperature of the fully cured resin. For all compositions, it is seen that the storage modulus (G') sharply increases with cure time, and then gradually levels off as the cure approaches completion. The loss modulus (G'') becomes consistent after crossover of G' and G'' (i.e., $t_{\tan \delta=1}$). At higher temperatures, the crosslinking occurs faster, leading to a reduction in the gel time.

Tung and Dynes²² reported that the time at which the crossover point of G' and G'' ($\tan \delta=1$) occurs during the isothermal cure of epoxy resins coincide with the gel time independently measured by the standard gel time test (ASTM D2471-72). That is, loss tangent, being the ratio of energy lost to energy stored in a cyclic deforma-

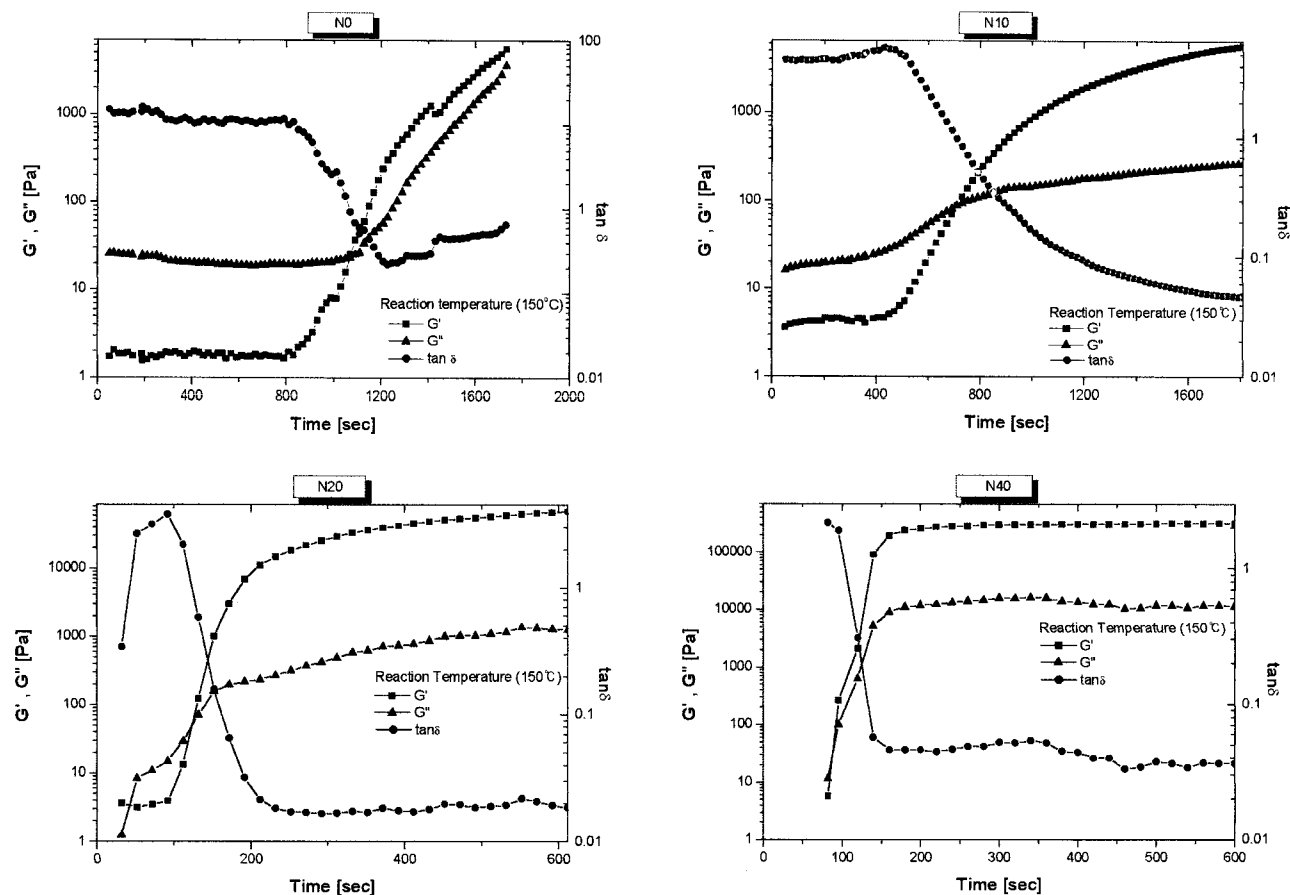


Figure 6 (Continued from the previous page)

tion ($\tan \delta = G''/G'$), measures the relative contribution of elasticity and viscosity of a resin system. The $\tan \delta$ of a viscous liquid should, therefore, be greater than 1, while that of an elastic solid should be less than 1. When the cure temperature is above the glass transition temperature (T_g), the system proceeds from a viscous liquid through gelation to an elastic solid (e.g., rubber or glass). Under these conditions, the $\tan \delta$ of gelation, and the transition between viscous liquid and elastic solid, would be expected to be equal to 1. Table I gives a summary of $t_{\tan \delta=1}$ (i.e., gel time) for the epoxy/phenol-novolac/BPH blend system at various cure temperatures. The increase of phenol-novolac resin content to epoxy resin with increasing cure temperatures leads to a decrease of gel time in all blending system studied. This is probably due to the formation of three-dimensional crosslinking network structure between epoxide ring and hydroxyl group of phenol resin.

Table I Gel Times of Epoxy/Phenol-Novolac/BPH Blend System Studied in Given Cure Temperatures

Sample	Reaction Temperature [°C]	Gel Time [s]
N0	110	3720
	130	2673
	150	1071
N5	110	2530
	130	1850
	150	960
N10	110	1635
	130	1313
	150	840
N20	110	457
	130	225
	150	123
N40	110	344
	130	150
	150	84

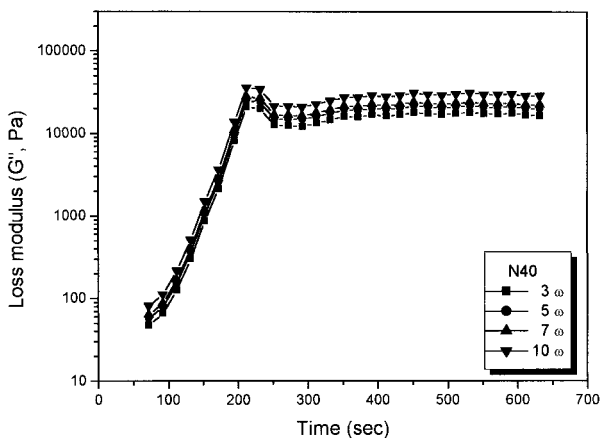


Figure 7 Loss modulus (G'') vs. cure time measured at various angular frequencies ($T = 130^\circ\text{C}$).

Figure 7 describes the dependence of loss modulus (G'') on frequency (ω), and Figure 8 also ascribes the function of dynamic viscosity (η') on ω , for the epoxy/phenol-novolac/BPH blend system measured at 130°C . Note that η' is the quantity derived from G'' using the relationship $\eta' = G''/\omega$. It is seen that not only the magnitude of G'' (or η'), but also the shape of the G'' curve (or η' curve) are strongly dependent upon the frequency (ω) imposed on the solution. More specifically stated at a given cure time, G'' increases with increasing ω , whereas η' decreases as ω increases.

From a molecular theory, Han and Jhon²³ related G' to G'' by eq. (1):

$$\log G' = 2 \log G'' + \log(6/5G_N^0) \quad (1)$$

where $G_N^0 = \rho RT/M_e$, ρ is the density, R the gas constant, T the cure temperature, and M_e the entanglement molecular weight.

This eq. (1) is proposed to be well adapted in the terminal region, and the theoretical prediction indicates that the polymer solution gives a slope of 2, if it is isotropic and homogeneous.²³

Figure 9 shows a plot of G' against G'' for the epoxy/phenol-novolac/BPH blend system in the time interval of 1 min at 130°C . As a result, G' is linearly related with G'' for the N0 composition, and its slope is 1.92, which is slightly lower than the theoretically predicted value 2 for the isotropic homogeneous solution. The slight deviation of slope from 2 may be partly ascribed to a little heterogeneity of the solution system. However, as seen in Table II, indicated in all slopes studied with in-

creasing the phenol-novolac resin content, the slope is decreased from 1.92 to 1.78. The reduction in slope suggests that a morphological change take place with curing time or with phenol-novolac content. These results indicate that the time of cure or the content of phenol-novolac resin has a significant effect on the rheological properties of epoxy/phenol-novolac blend system using BPH as a catalyst.

Figure 10 shows the frequency dependence of the time to gelation for the isothermal cure of an epoxy/phenol-novolac/BPH blend system. The increase in frequency shown for each step increases in gel time, and the tendency is investigated in all compositions studied. This result is analogous to the increase in glass transition temperature with higher frequency observed for most polymers.²⁴ In an isothermal cure, increasing the frequency produces a higher T_g , which results in a longer time to gel.²⁵

It is well known that the temperature, at which the measurement is performed, is one of the important factors for gelation. In torsion braid studies of thermoset curing, Babayevsky and Gillham²⁴ showed that a test temperature of $T > T_g$ is necessary if the gelation is to be observed without influencing the vitrification, which occurs at $T \cong T_g$. The gelation represents a specific extent of reaction, and the temperature dependence of the time on gel should be described by the Arrhenius equation.²⁶

The gel time as determined from the time at which $G'' = G'$ is plotted vs. experimental cure temperatures, as seen in Figure 11. The important feature of these curves is that with increasing the phenol-novolac resin content, the gel time gets

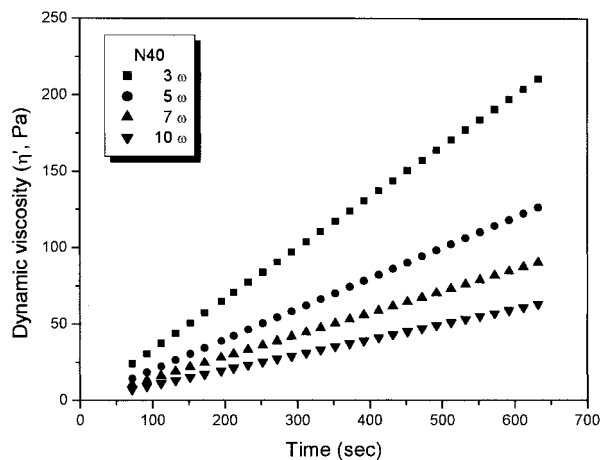


Figure 8 Dynamic viscosity (η') vs. cure time measured at various angular frequencies ($T = 130^\circ\text{C}$).

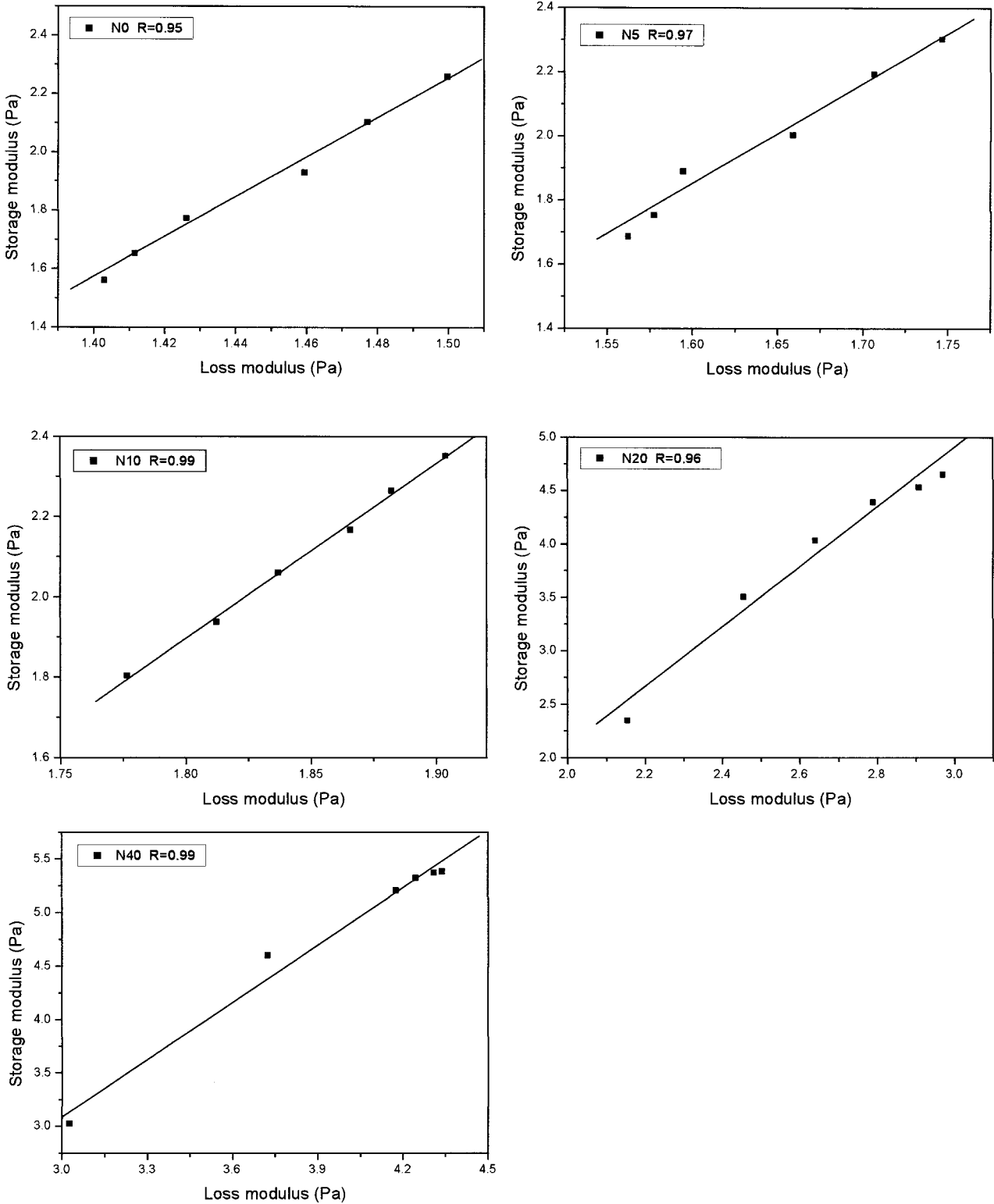


Figure 9 Plots of G' against G'' for epoxy/phenol-novolac/BPH blend system, measured at 130°C, (R is the coefficient of regression).

Table II Slopes of Epoxy/Phenol-Novolac/BPH Blend System Obtained from G' against G'' at 130°C

Sample	Slope Value
N0	1.92
N5	1.88
N10	1.83
N20	1.80
N40	1.78

shorter at each of cure temperatures. It is then noted that this result is contrary to the increase in gel time expected as the cure temperature approaches T_g .²⁷ In this work, an explanation of this behavior is that as the cure temperature approaches T_g , the storage modulus rises in a specific region. So, it is then resulted that this is not a result of gelation, but rather is due to onset of vitrification.

Figure 12 shows experimental values of $\ln t_{gel}$ plotted as a function of reciprocal cure temperature ($1/T$) in the epoxy/phenol-novolac/BPH blend system. From the slope of the straight lines, the activation energies (E_c) are obtained, as listed in Table III. As an experimental result, above 20 wt % of phenol-novolac resin contents, the activation energies for crosslinking are larger than neat epoxy resin. This implies that the three-dimensional crosslinking reaction may take place due to the complex formation between hydroxyl group within phenol resin or epoxide ring within epoxy resin and BPH.

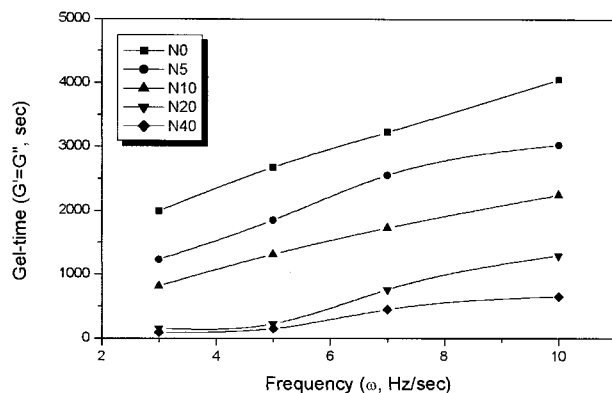


Figure 10 Frequency dependence of time of modulus crossover of epoxy/phenol-novolac/BPH blend system, measured at 130°C.

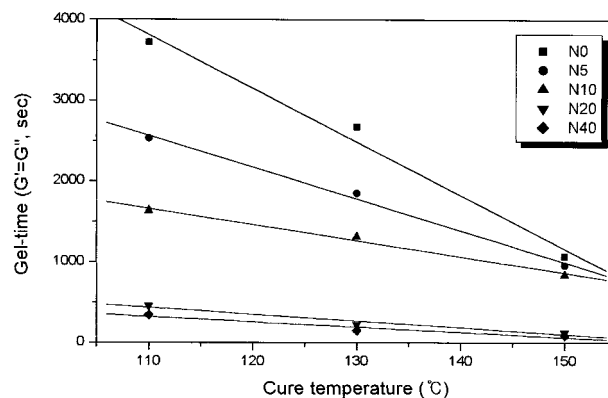


Figure 11 Correlation of cure temperature and time of modulus crossover of epoxy/phenol-novolac/BPH blend system measured at 130°C.

CONCLUSION

In this work, the effect of different weight percents of phenolic resin to neat epoxy resin on relationship between dynamic viscoelastic properties and gelation was investigated, from which a relationship between viscoelastic properties and gelation of epoxy/phenol-novolac blend system was established in this system, resulting in the gel time being frequency and cure temperature dependent. Based on the Han and Jhon theory, it was clearly found that a morphological change of the blend system occurred according to the curing time or phenol-novolac resin content for the cure process initiated by BPH as a catalyst.

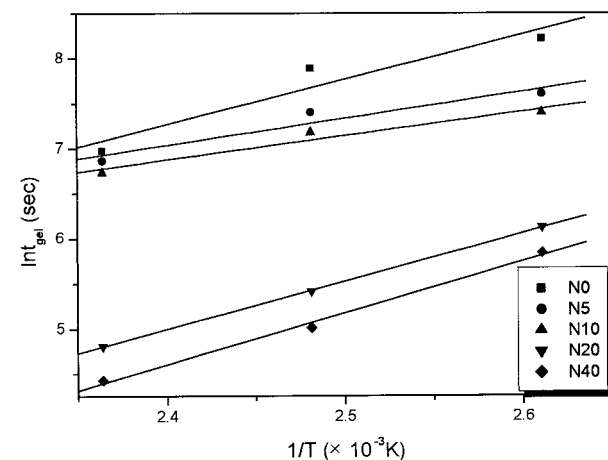


Figure 12 Arrhenius plots of $\ln t_{gel}$ vs. $1/T$ for the epoxy/phenol-novolac/BPH blend system.

Table III Crosslinking Activation Energies (E_c) of Epoxy/Phenol-Novolac/BPH Blend System

Sample	E_c [kJ/mol]
N0	42
N5	23
N10	22
N20	46
N40	48

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