Curing Studies on the Epoxides of Carbono- and Thiocarbonohydrazones

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SYNOPSIS

The curing behavior of a new class of N — N bonded epoxy resins has been analyzed using the simultaneous DTA-TG, dynamic mechanical analysis (DMA), and thermomechanical analysis (TMA) techniques. The resin systems, viz, diglycidyl ether of furfuraldehydecarbonohydrazone (DGFCH), diglycidyl ether of furfuraldehydethiocarbonohydrazone (DGFTCH), and tetraglycidyl ether of vanillinthiocarbonohydrazone (TGVTCH) with the curative, diaminodiphenylmethane (DDM), taken in stoichiometric amounts have been examined. The curing exotherm could be resolved from the decomposition exotherm qualitatively using DTA-TG analysis. The DMA has been carried out in both the dynamic and isothermal mode to follow the curing process of the systems DGFCH/DDM and TGVTCH/ DDM. The storage modulus (G'), loss modulus (G"), complex viscosity (η) and creep factor (tan δ) were measured simultaneously. The crossover point of G' and G", taken as the gelation point in isothermal runs, was determined to obtain time to gelation at that temperature. The isothermal runs at different temperatures have been used to calculate activation energy of the curing process up to gelation. For the difunctional resin DGFTCH, the activation energy value was found to be 18.7 kcal/mol. The thermomechanical analysis (TMA) has been used to find the glass transition (T_{g0}), and melt transition (T_m) temperatures. The cured tetrafunctional TGVTCH/DDM system as expected, has higher T_g than those of the two difunctional resin systems. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In an attempt to prepare new energetic binders, a series of epoxy resins based on N — N bonded back bones were synthesized recently in our laboratory.[1,2] These resins were found to have several properties in their favor for consideration of their use in solid propellant compositions. Besides the presence of N — N bond contributing positively to the energetics of the propellant systems in terms of the high calorimetric values, the resins have convenient viscosities for processing high solid loadings. When used as solid propellant binders, they increase the burning rate of solid propellants based on ammonium perchlorate, significantly.[3] A serious consideration of their usage as binders necessitated a detailed study of their curing characteristics. This article reports the thermoanalytical and thermomechanical aspects of the crosslinking behavior of some typical resins.
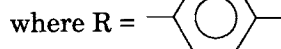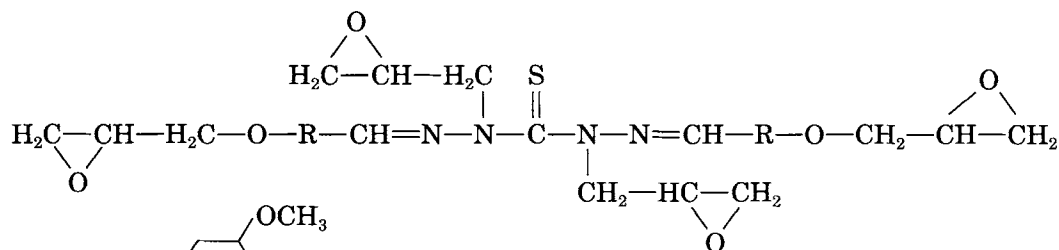
EXPERIMENTAL

Of the several epoxides of bis-carbonohydrazones and bis-thiocarbonohydrazones synthesized earlier,[1,2] the following three typical resins were chosen for the present study: (1) diglycidyl ether of furfuraldehydecarbonohydrazone (DGFCH); (2) diglycidyl ether of furfuraldehydethiocarbonohydrazone (DGFTCH); and (3) tetraglycidyl ether of vanillinthiocarbonohydrazone (TGVTCH).

The general structure of the furfuraldehyde resins could be represented as

H₂C—HC—H₂C   X
R—CH=N—N—C—N—N=CH—R
            CH₂—CH—CH₂
                  \O/

where X = O or S and R =
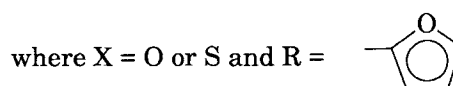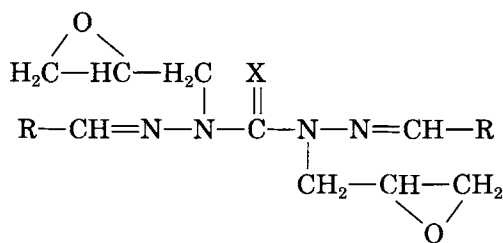
The structure of the tetrafunctional vanillin resin could be written as,

H₂C—CH—H₂C   S
H₂C—CH—H₂C—O—R—CH=N—N—C—N—N=CH—R—O—CH₂—CH—CH₂
  \O/   CH₂—HC—CH₂   \O/
                                \O/

where R =   —⟨O⟩— with OCH₃

The resins were cured with stoichiometric amounts of diphenyldiaminomethane (DDM), whenever required.

Thermal Analysis

Simultaneous DTA-TG thermal analyses on the cured resins and resin/curative mixtures were performed in flowing nitrogen using platinum cups at various different heating rates using a Shimadzu TA-40 thermal analyzer. About 10 mg samples were used. For isothermal curing studies the samples were heated rapidly at 50°C/min, and held at specified temperatures. For curing studies, the stoichiometric resin/curative mixtures were prepared and used soon after mixing.

Dynamic Mechanical Analysis

Torsion impregnated cloth analysis (TICA) was used for studying the rheological behavior of polymers. This method for studying the dynamic mechanical behavior uses a forced torsion technique,[4] whereby the sample is sinusoidally strained in a fixed frequency mode, and the in-phase and out-of-phase responses of the specimen are obtained through the analyses of time functions of the stress and strain signals. The forced torsion mode in TICA has the advantage of being able to obtain fixed frequency data mode, as well as multifrequency data in a single experiment.

In the present study, a Rheometrics system[4] rheometer fitted with a parallel-plate test cell was

used.[5] The test sample was confined in the gap between two parallel 25 mm width plates. The top plate was oscillated at a given frequency and amplitude, while the bottom plate was mounted on a torque transducer for force measurements. A typical gap between the plates was 1.2 mm. The plates and test samples were enclosed in a heat chamber purged with nitrogen gas. The test chamber was preheated to the test temperature before loading each sample to insure precise gap settings. The amplitude of oscillation of the top plate was selected to assure that the strains imposed on the sample during measurements were within its linear viscoelastic response range while maintaining adequate torque values. Typical measurements on this particular system usually started at 2% strain level and varied up to 6%. Plate oscillatory motion was set at a frequency of $\omega = 10$ rad/s. The recorded cyclic torque values were decomposed into in-phase and out-of-phase components with respect to the oscillatory deformation imposed on the sample. The corresponding storage (G') and loss (G") moduli were obtained from these components. The variation in complex viscosity (η), and creep factor (tan δ), were also measured as a function of temperature, while heating the sample at 10°C/min, in the dynamic mode, and as a function of time in the isothermal mode.

Test samples for these studies were prepared by supporting the resin on an inert substrate, a heat-cleaned, unsized glass cloth. The fiber glass cloth of width 25 mm was melt impregnated with a stoichiometric resin/curative mixture. Three layers of the resin-impregnated clothes were piled up uni-

formly one above the other. This sample arrangement was found to be satisfactory for studying the resin behavior in the present case.

Thermomechanical Analysis (TMA)

In TMA, the deformation of a substance is measured under nonoscillatory load as a function of temperature as the substance is subjected to heat at a controlled rate. A Shimadzu TMC-40 model instrument equipped with a furnace capable of operating from −150 to 600°C was used in the present study. The TMC-40 unit employs a balance system. The balance is first equilibrated with the standard weights or by adjusting the position of the balance weight on the beam, and then a desired load is applied to the sample by putting weights on the weight pan, so that dimensional changes can be measured under a known load. The sample supporting base is connected to a micrometer via the sample support tube, so that adjustments can be done for each of the samples which differ in length from each other. Because the output voltage of the linear differential transformer is proportional to the movement of the core, the dimensional change of the sample can be exactly

measured by adjusting the amplifier to make the output voltage linearly proportional to the micrometer.

Thermomechanical analysis of the neat resins were carried out by applying the neat resin sample on the sample supporting base after noting down the micrometer scale value. The sample was then cooled down to −160°C and the thickness of the coating measured. Subsequently, the sample was subjected to heat at a constant rate. The TMA of the cured samples were analyzed in a similar manner after measuring the thickness at room temperature.

RESULTS AND DISCUSSION

The DTA-TG thermograms of the stoichiometric compositions of resins DGFTCH, DGFCH, TGVTCH, and DDM, obtained at 10°C/min heating rate are shown in Figure 1. In general, the thermograms of all the three resins are qualitatively similar. They all show broad exotherms in the 120–300°C range. These exotherms could easily be understood in terms of the curing process, but the TG curves of these resins show weight losses in this re-
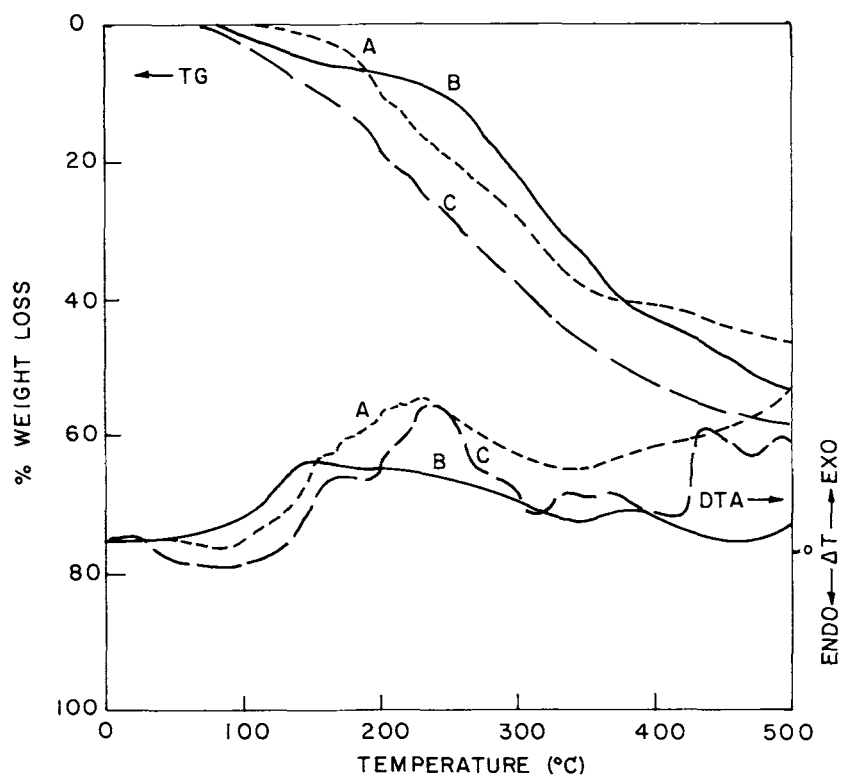

Figure 1 DTA-TG thermograms of resin/DDM (A) DGFCH; (B) DGFTCH; (C) TGVTCH.
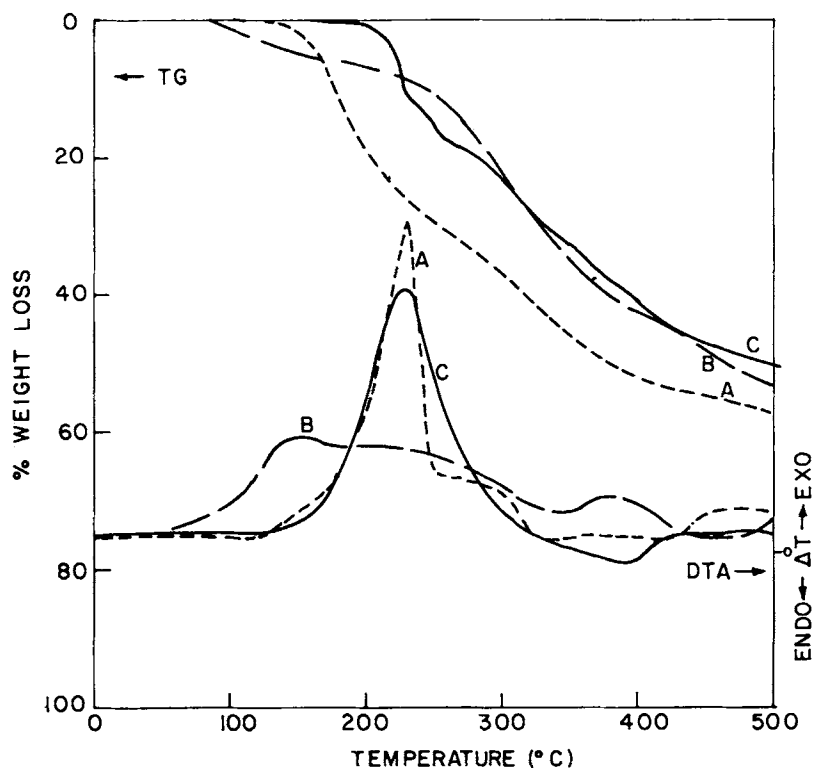
Figure 2 DTA-TG thermograms of DGFTCH. (A) Neat resin; (B) Resin/DDM (uncured); (C) Resin/DDM (cured).

gion. It is seen that after undergoing a small weight loss (< 5%) there is a plateau region around 170°C. This region is followed by rapid weight loss around 230°C. From the DTA curve of TGVTCH, one can identify the presence of two peaks clearly in this broad region, one around 170°C and the other at 230°C, which could be associated with the curing and decomposition processes, respectively. However, the DTA curve of DGFTCH and DGFCH do not show any distinct peak in this region. The combined DTA-TG data, however, point out that the broad exotherm may be a result of the overlap of both the curing[6,7] and decomposition processes.

Above 230°C the weight loss continues to 40–58% at 500°C, with the DTA curves showing another exotherm in the 400°C region. The DGFCH shows a comparatively larger exotherm in this region than the other two with the corresponding weight loss. This could be due to the presence of oxygen in the C — O of DGFCH, which could favor partial oxidatory decomposition. Overall, the TG data show comparable thermal stability of the two di-epoxy resins. The TCH-based resin appears to be more stable below 400°C; however, it degrades faster above this temperature. The tetra epoxide,

TGVTCH, shows considerably less overall thermal stability than the difunctional resins.

The presence of curing exotherms in these resins was ascertained by comparing the thermograms of the neat, cured, and uncured (resin + curative) DGFTCH samples, obtained at a constant heating rate, 10°C/min (Fig. 2). The mixture (resin + curative) shows curing exotherm peaking around 150°C, and no exotherm is seen around this temperature in the case of the neat resin and the cured sample. Apparently, the neat resin decomposes exothermally at the same temperature, viz. 230°C as the cured sample. From these observations, it is concluded that curing exotherm peak occurs around 150–170°C in the uncured samples, whereas the decomposition exotherm peaks around 230°C, in all the cured, neat, and uncured samples. The exothermic nature of decomposition of N — N bonded compounds, especially the hydrazones and thiocarbonohydrazones, has also been observed in our earlier studies.[8–10] These DTA-TG data, thus, clearly differentiate between the curing and the decomposition exotherms. In air, the decomposition (weight loss) starts at even lower temperatures, and the exotherm observed at 270°C in the case of TGVTCH
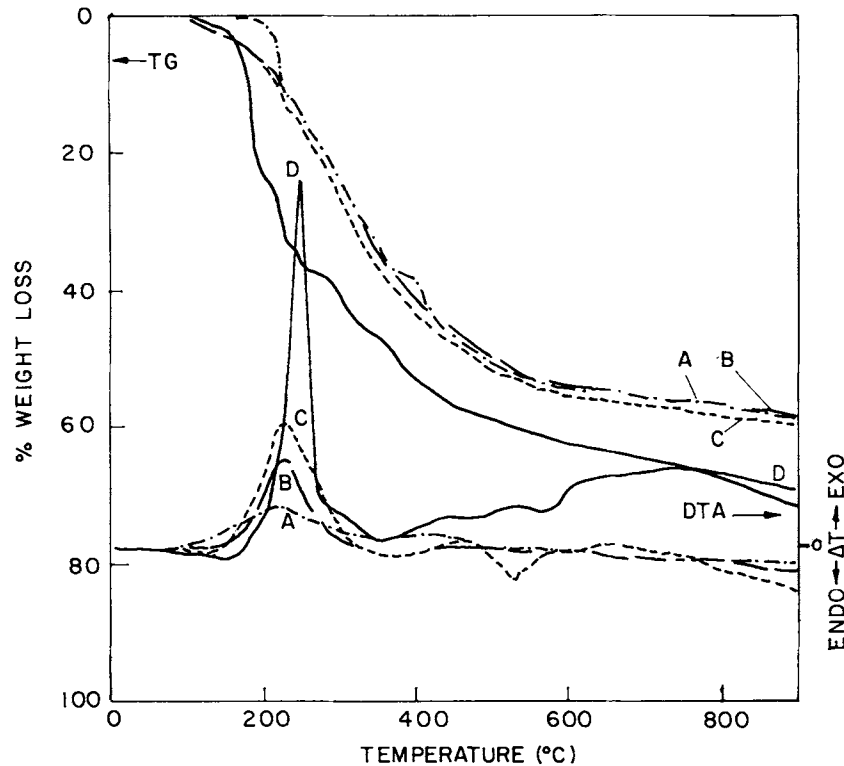
Figure 3   DTA-TG thermograms of cured DGFTCH/DDM at different heating rates.
(A) 5°C/min; (B) 10°C/min; (C) 20°C/min; and (D) 50°C/min.

in an earlier study[1] may not be due to isomerization of the resin, as reported therein.

A comparison of the DTA-TG data of the cured samples of DGFTCH/DDM system at various heating rates is shown in Figure 3. The decomposition exotherm that occurs around 230°C shows a strong dependence on heating rate. As the heating rate increases from 5 to 50°C/min the intensity of the exotherm increases with the shifting of the peak of the exotherm to higher temperatures. Irrgang et al.[11] also observed a similar effect in some conventional epoxy systems. The sample experiences around 25 to 45% weight loss, depending upon the heating rate employed.

Isothermal DTA thermograms at 100 and 120°C of DGFCH with DDM in stoichiometric ratios are shown in Figure 4. In these studies, the baseline is usually taken as this final steady-state signal, and horizontal negative extrapolation to intersect with the initial exotherm is taken as zero time for the reaction.[12] The initial strong endotherm in the present case could be due to the melting of the curative which is in stoichiometric composition with the resin. This is immediately followed by an exotherm, which apparently is due to curing. This exotherm is

larger at the higher temperature. The pattern of the exotherm shows the curing maximum occurs after about third and fourth minute, respectively. Soon
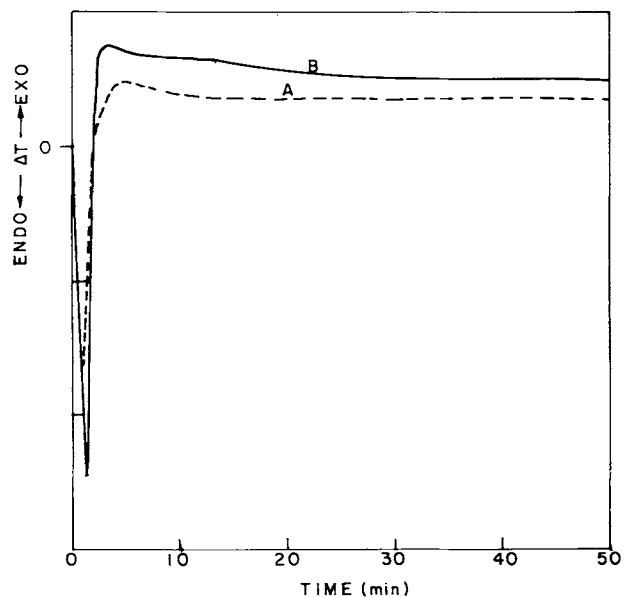

Figure 4   Isothermal DTA of DGFTCH/DDM (A) at 100°C; and (B) at 120°C.

after the exotherm, the temperature profile shows a steady state. The curing process in this region proceeds very slowly. As the reaction proceeds, the larger species are formed because it follows the condensation or step-reaction kinetics. As the curing reaction becomes diffusion controlled, the rate of reaction attains a near constant value and curing exotherm levels off, by keeping the curing mixture below gel glass transition temperature, $_{gel}T_g$.[13] It is apparent, however, that the curing of these resins could be accomplished by keeping the resin curative mixture $< 100°C$ for a sufficiently long time and then postcuring at higher temperature.

The dynamic mode of analysis on TGVTCH/DDM, shown as the change in storage modulus (G'), loss modulus (G''), complex viscosity (η), and the creep factor $(\tan \delta)$, as a function of temperature, is given in Figure 5. The spectrum shows an increase in modulus and viscosity starting at around 170°C. It is understood that an increase in temperature lowers the chemoviscosity at a given extent of reaction, but it also increases the curing reaction rate, which eventually leads to an increase in the resin viscosity.[5] As a typical example of epoxy curing, the spectrum also shows a significant increase in modulus values. Although to begin with, the magnitude

of the loss modulus (G'') is higher, the rate of increase in storage modulus (G') is more. Consequently, the G' curve crosses over the G'' plot at a certain temperature, corresponding to the gelation point of the system. Even though there are many methods to determine the gel point,[14] the cross over point of G' and G'' identified as gelation point (GP) is more precise and free of operator error than the conventional methods.[15] Also, Winter[16] has shown that the stress relaxation at GP, of the stoichiometrically balanced end linking networks and those having excess of crosslinker, obeys the following relationship,

$$G(t) = St^{-1/2}$$

where S is the strength and t, the time. It is further established that a relaxation modulus having relaxation exponent equal to $-\frac{1}{2}$ gives congruent moduli:

$$G'(T, \omega) = G''(T, \omega) = \sqrt{\pi/2}\, S(T)\omega^{1/2},$$

(at critical conversion)
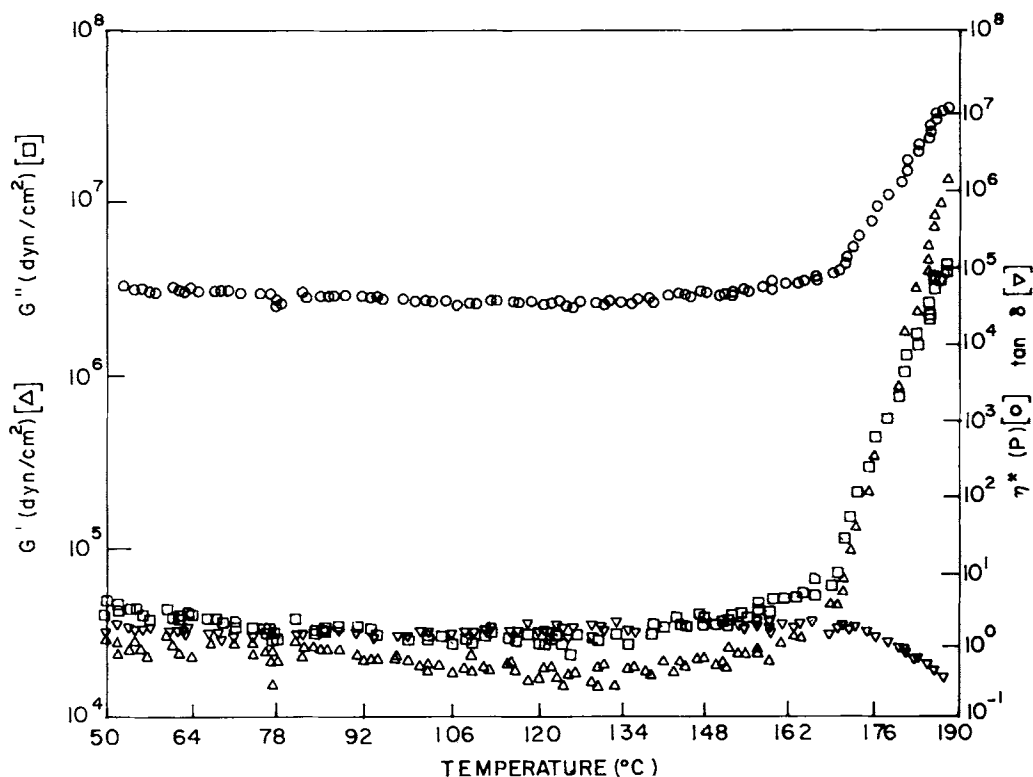and a loss tangent;

$$\tan \delta = G''/G' = 1$$

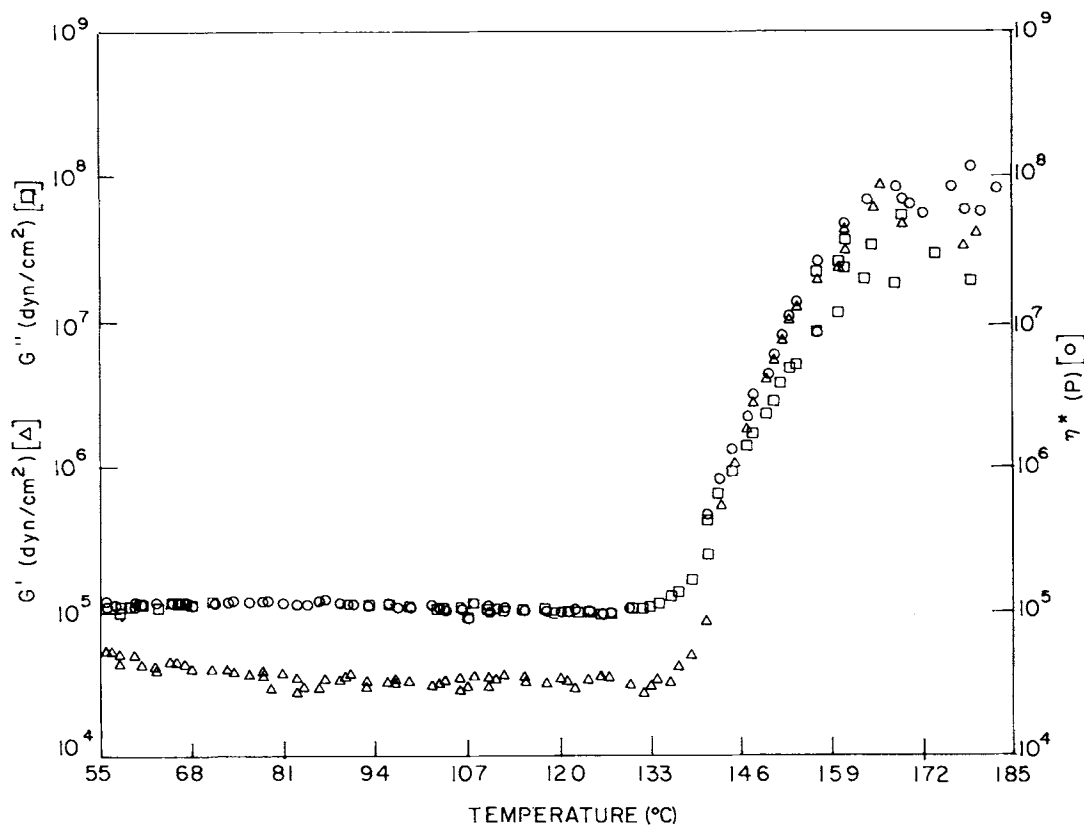**Figure 5**   DMA plots of TGVTCH/DDM in the dynamic mode.

Figure 6 DMA plots of DGFCH/DDM in the dynamic mode.

Thus, for any frequency or temperature, the storage modulus has the same value as the loss modulus. It is clear, therefore, that GP is reached when G' and G" cross each other. Because the systems involved in the present study are stoichiometrically balanced, the crossover point could be considered as the gelation point.[16]

The viscosity profile also show rapid increase near the crossover. Thus, it is apparent that, in a typical curing reaction, the viscosity behavior dominates the initial part of the experiment (G" > G') and elastic behavior dominates the end of the experiment (G' > G"). Both modulii increase as a result of the increase in crosslinking density, but the elastic component rises more sharply than the viscous component. Such an evaluation of the dynamic storage and loss modulii is characteristic for network formed by endlinking reactions with balanced stoichiometry.[16]

The crossover point of G' and G" occurs at 179°C (Fig. 5) in the TGVTCH/DDM system. The modulus and viscosity values at this point are of the order of 10^6 dynes/cm^2 and 10^6 Poise, respectively. Both these values are an order of magnitude higher than those for a commercial epoxy resin, Hercules

3501-6.[5] The rate of viscosity buildup appears to be maximum at the crossover. The viscosity continues to increase after the crossover point. However, the curing reaction gets stagnated after the gel point due to the limitated diffusion of smaller molecules from the three dimensional network of a larger polymer molecule, which results in a polymer with larger molecular weight dispersity and, therefore, poor mechanical properties. The system could provide the ultimate properties only by avoiding the gel point during the curing process,[17] until it reaches near maximum extent of curing. The DMA spectrum of TGVTCH/DDM, thus, points to the fact that the system should be cured below 179°C in order to render the ultimate mechanical properties. The curing behavior of a difunctional resin was also analyzed using DMA. An analysis of the DGFCH/DDM system in dynamic mode is given in Figure 6. The crossover of G' to G" in this case occurs at around 143°C. The modulus values at this point are of the order of 10^5 dynes/cm^2, the viscosity value being about 10^5 Poise.

After identification of the gel point, the isothermal DMA data were carried at different tempera-

Table I   Properties Associated with the Crossover Point G'(t) and G"(t), during the Isothermal Curing of the Resins

Resin/ DDM	Temperature (°C)	Time (min)	G'(=G") (dyne/cm²) × 10⁵	Viscosity (P) × 10⁵
DGFCH	90	58.75	5.605	2.301
DGFCH	100	42.57	3.449	4.830
DGFCH	120	22.41	3.887	5.670
TGVTCH	150	43.00	169.8	245.1
TGVTCH	170	14.52	22.87	31.50

tures as a function of time. A summary of the data collected for various resins is given in Table I. The isothermal data for the TGVTCH/DDM system at 150°C, shows that the crossover of G' and G" occurs at forty-third minute. To check the upper critical temperature for gelation, isothermal run was carried out on the same system at 170°C (Fig. 7). In this case, the sensible curing reaction starts at around eighth minute and the crossover point occurs at fourteenth minute. The absence of very sharp change in viscosity or creep factor implies that this is a partially gelled system.

Typical isothermal runs for the system DGFCH/DDM carried out at 120°C and 100°C are shown in Figures 8 and 9, respectively. At 120°C, the curing reaction starts at around sixteenth minute and the gelation occurs around twenty-second minute, whereas at 100°C, the curing and gelation occurs at twenty-seventh minute and around forty-second minute, respectively, and at 90°C curing and gelation occurs at thirty-fifth and fifty-eighth minute (Table I). The rapidity of the curing process at and above 100°C emphasize the importance of conducting the cure reaction below this temperature. The postcur-
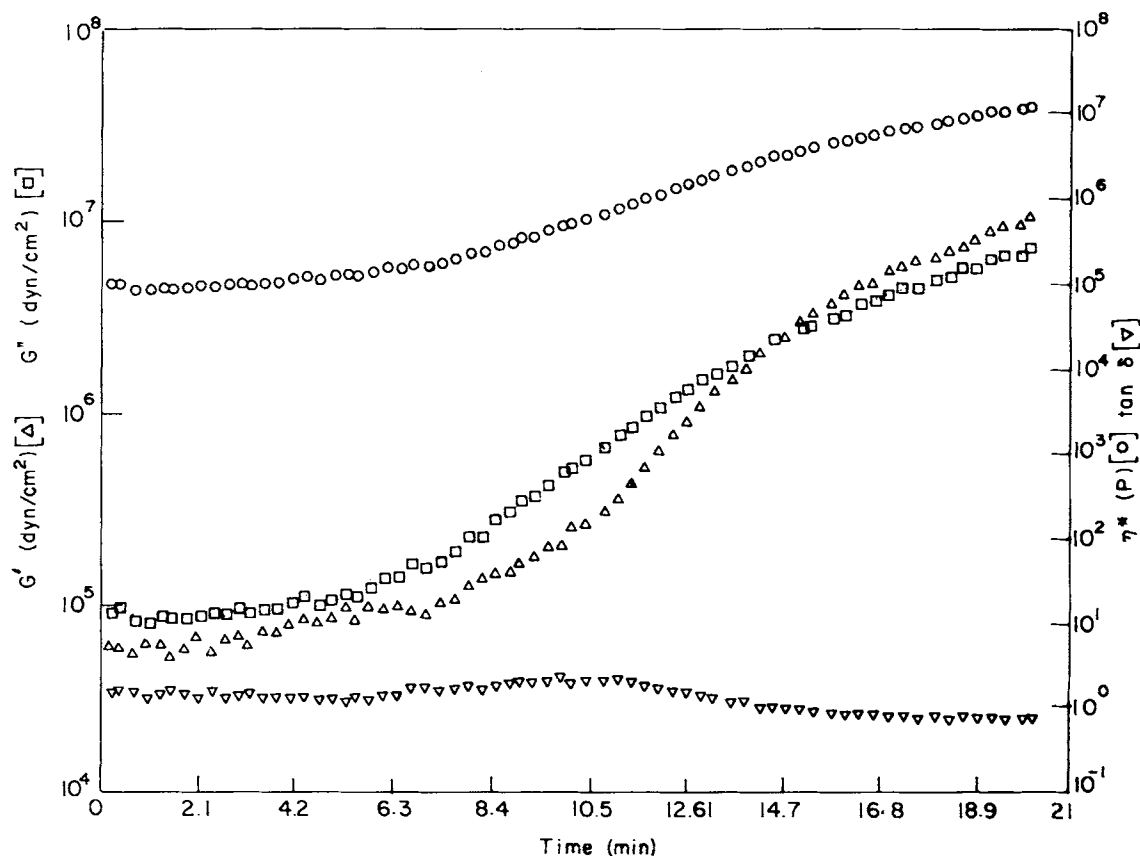
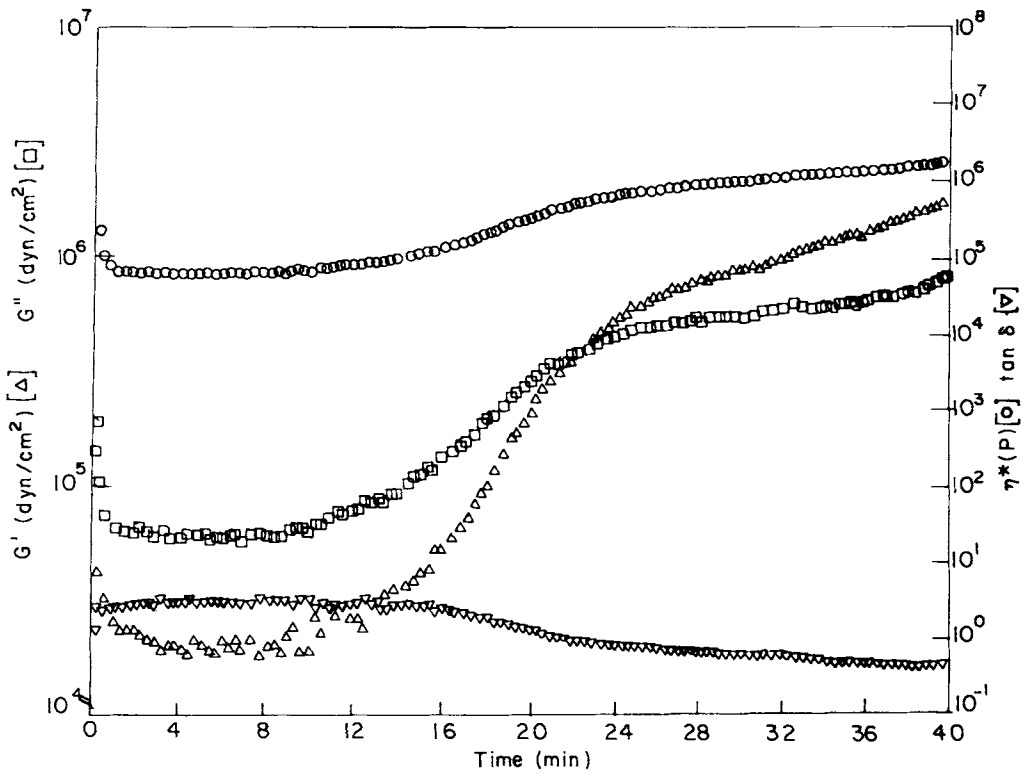**Figure 7**   Isothermal DMA of TGVTCH/DDM at 170°C.

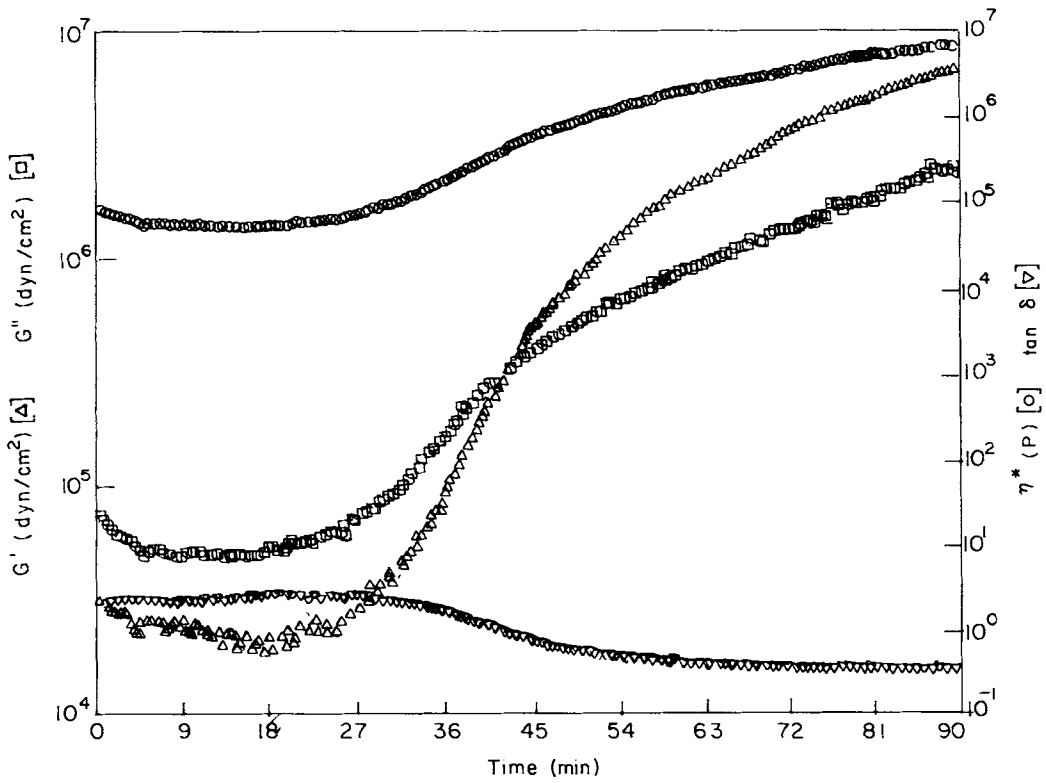**Figure 8**   Isothermal DMA of DGFCH/DDM at 120°C.
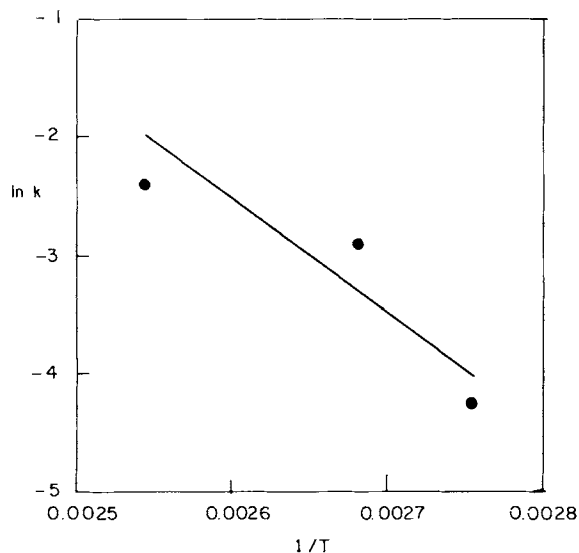

Figure 9   Isothermal DMA of DGFCH/DDM at 100°C.

Figure 10 Arrhenius plot of the curing reaction in DGFCH/DDM.

Table II Transition Temperature of the Neat Resins and the Cured Samples

	Transition Temperatures (°C)		
Resin	(T_{go}) (Neat)	(T_m) (Neat)	(T_g) (Cured with DDM)
DGFCH	−76	−14	75
DGFTCH	−48	−10	70
TGVTCH	−40	−8	116

ing can be carried out at slightly higher temperatures to make the relaxation process faster.

The isotherml runs of both the difunctional and the tetrafunctional systems follow the same pattern

of decrease in curing and crossover time with increase in isothermal temperature as reported by Hou et al.[5] Also, the modulus and the viscosity values of the tetrafunctional TGVTCH/DDM system follow the same pattern, i.e., decreasing modulus and viscosity values at crossover with increase in isothermal temperature, as reported, whereas the DGFTCH does not follow this pattern. In this case, the values at the crossover point are almost the same, regardless of increase in isothermal temperature.

The isothermal DMA data obtained were used to obtain the activation of the curing process. Figure 10 shows the Arrhenius plot for the glass cloth com-
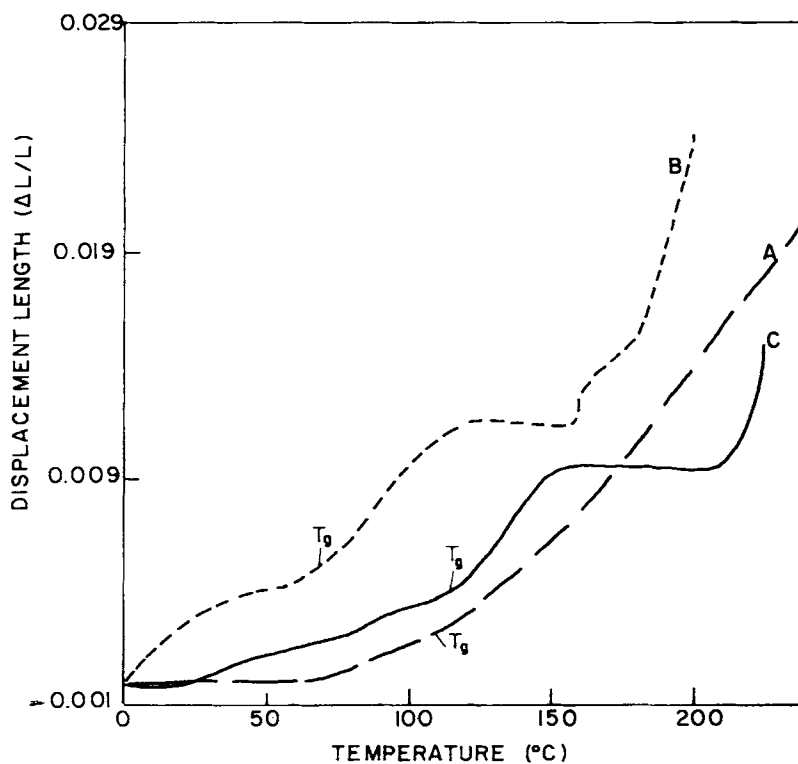

Figure 11   Thermomechanical analysis of cured samples of (A) DGFCH; (B) DGFTCH; (C) TGVTCH.

posite at the stoichiometric ratio of DGFCH/DDM system. The rate constants, k at various temperatures were calculated from the slopes of the viscosity–time curves. The viscosity–time curves were considered up to the gelation or crossover point. The plot of ln k vs. $1/T$ shows an approximate linear relationship over the temperature range of 90–120°C. The activation energy, E_a, of the system was, thus, found to be 18.7 kcal/mol. As Wingard et al.,[18] in their recent study, have shown that the glass cloth has very little effect on the activation energy of the resin, this value appears reasonable for the curing process.

An analysis of the DTA-TG and the dynamic mechanical analysis data, thus, provide valuable information about the curing temperature and time, although the results obtained in isothermal DTA runs are somewhat different. The TG-DTA data could provide the useful temperature range of curing without decomposition or weight loss, whereas the DMA provides valuable information regarding the temperature and time to avoid the gel point.

The glass transition temperatures of the neat resins and the cured samples were obtained from their thermomechanical analysis data. The TMA curves showing variation of the dimensionless expansion ($\Delta L/L$) with temperature of the neat resins DGFTCH, DGFCH, and TGVTCH were obtained. From the change in slope in the expansion plot, the glass transitions of various resins were derived. These data are listed in Table II. The glass transitions of DGFCH and DGFTCH occur at $-76°$C, and $-48°$C, respectively, whereas for TGVTCH it occurs at $-40°$C. The melting transitions occur at $-14, -10$ and at $-8°$C, respectively, for DGFCH, DGFTCH, and TGVTCH systems.

Figure 11 shows the dimensionless expansion ($\Delta L/L$) of the samples TGVTCH, DGFTCH, and DGFCH cured with DDM, as a function of temperature in nitrogen atmosphere while being heated at 10°C/min. The T_g onset is seen at 116°C for the cured TGVTCH/DDM, at 70°C for DGFTCH/DDM and at 75°C for DGFCH/DDM systems (Table II). Above the glass transition the expansion rate is higher and the large expansion is obviously the manifestation of large molecular relaxation, normally exhibited by the elastic materials, whereas the expansion below T_g is as exhibited by glassy materials. After the linear expansion, TGVTCH- and DGFTCH-based systems show a plateau or no expansion which may correspond to vitrification. The plateau regime occurs between 120–160°C and 155–210°C, respectively, for DGFTCH/DDM and

TGVTCH/DDM systems. Beyond this regime, the increase in dimensionless expansion is linear with respect to temperature up to 225°C. This may be attributed to devitrification or char formation. The DGFCH-based system does not show any plateau regime.

The higher T_g of cured TGVTCH, as compared to those of DGFTCH and DGFCH systems, could be due to the higher crosslink density of the tetrafunctional resin.[19-21] A relationship between T_g and concentration of crosslinks or crosslinking density has been proposed,[19,20] which obeys the following Fox and Loshaek relationship,[19]

$$T_g = T_{gu} + aX/(1 - bX)$$

where T_{gu} is the glass transition temperature of uncrosslinked system, "a" and "b" are constants, and X is the crosslinking density. The above equation has been overlooked for many years in the literature, but apparently is more suitable for highly crosslinked systems.[20] The two bifunctional cured resins, on the other hand, have comparable T_g, meaning thereby, that replacement of the central carbonyl grouping by the thiocarbonyl, do not affect the T_g significantly. However, other transitions of DGFTCH are more akin to the TGVTCH system.

CONCLUSION

The N—N bonded resins, studied in the present investigation, start decomposing soon after the curing process is complete, if heated further. An analysis of the curing behavior carried out by the DTA-TG and DMA provides valuable information about the maximum cure temperature without decomposition, and also the time to gelation. The magnitude of the activation energy of the curing process compares favorably well with the conventional epoxy systems. The glass and melt transition temperatures of the neat and cured resins identify them to be useful materials as binders.

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