

A Thermal and Rheological Investigation During the Complex Cure of a Two-Component Thermoset Polyurethane

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ABSTRACT: The complex cure kinetics of the reaction between oligomeric diphenylmethane diisocyanate (PMDI) and glycerol was characterized through thermal and rheological techniques. Isoconversional analysis of Differential scanning calorimetry (DSC) data resulted in the activation energy varying with conversion. Isothermal analysis gave activation energies ranging from 5 kJ/mol to 33.7 kJ/mol, whereas nonisothermal data gave values for the activation energy ranging from 49.5 to 55 kJ/mol. Incomplete cure was evident in isothermal DSC, becoming diffusion controlled in the final stages of cure. DMA analysis on the cured material gave a glass transition temperature of $104 \pm 3^\circ\text{C}$, which was evidence for vitrification of the curing system. The primary and secondary hydroxyl group reac-

tivity was dependant on the isothermal cure temperature. Rheological studies of viscosity increase and $\tan \delta$ changes with time revealed a complex cure process, with primary and secondary hydroxyl reactivity also showing dependence on isothermal cure temperatures, reflecting similar results obtained from isothermal DSC studies. The independence of $\tan \delta$ on frequency was used to determine the point where the polymer formed an infinite network and was no longer able to flow, providing an overall activation energy attained at the gel point of 77.4 ± 4.4 kJ/mol. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3802–3810, 2009

Key words: activation energy; DSC; gelation; isoconversional analysis; polyurethanes; viscosity buildup

INTRODUCTION

The urethane network formed through the crosslinking reaction of oligomeric diphenylmethane diisocyanate (PMDI) and glycerol provides a continuous matrix which adds to the structural integrity of an industrial coating. A complete understanding of the curing process is required to determine the optimal curing conditions and ultimately, the final material properties. The kinetics of cure is therefore a key aspect in understanding and controlling the thermoset coating performance. Thermoset cure has been investigated extensively for idealized monomer units containing diisocyanate functional groups,^{1–9} however, very little work has been performed on the use of oligomeric isocyanates with trifunctional polyols.^{10–12}

Several different reactions can result during polyurethane polymerization due to: (a) varying reactivity of functional groups and (b) secondary reactions taking place at higher temperatures and during extended periods of curing.^{13,14} Mechanistically, the reaction system is therefore extremely complex. De-

spite this reaction complexity, many researchers assume only one reaction model that describes the entire curing process, to obtain a general idea of the kinetic parameters.^{1,5,15–17} Another approach, which yields more information about the mechanism of cure, without having to assume reaction variables, is the isoconversional method of Vyazovkin and Sbirrazzuoli¹⁸ and Vyazovkin.¹⁹ The advanced integral isoconversional method developed by Vyazovkin²⁰ states that at constant conversion the rate of reaction is only a function of temperature and allows the activation energy to be determined without choosing a reaction model. Isoconversional analysis has previously been used to describe the crosslinking reaction for a limited number of complex polyurethane systems.^{2,21,22} Differential scanning calorimetry (DSC) has been widely used to study thermoset reactions in both isothermal and nonisothermal modes.^{4,23–27} In this research, isoconversional analysis was used for isothermal and nonisothermal DSC data, to determine the kinetics of cure for this complex polyurethane system and to obtain information about the mechanism of curing by detecting changes in the activation energy as a function of conversion.

In addition, comprehensive rheological investigations were performed to further understand the cure profile of the stoichiometric ratio. The reacting polyurethane undergoes chain extension and subsequent

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branching due to the higher functional moieties present in the reacting components.²⁵ Following the viscosity buildup of the system, which is a consequence of the increase in molecular weight provides information on the reaction rate and cure profile.^{28,29} Two important transitions that are measurable through rheological investigations are gelation and vitrification. When the material is cured above its glass transition temperature, it will undergo gelation at a critical conversion, which is determined as the time where the polymer can no longer flow. Gelation is a critical component in thermosetting systems as it describes the formation of an infinite molecular network due to the crosslinking reaction.^{25,30} If the material is cured below its glass transition temperature, two transitions are noticed in rheological measurements: gelation and vitrification. Vitrification is a gradual process in which the curing kinetics changes from a chemically controlled to diffusion controlled system.³¹

EXPERIMENTAL

Materials

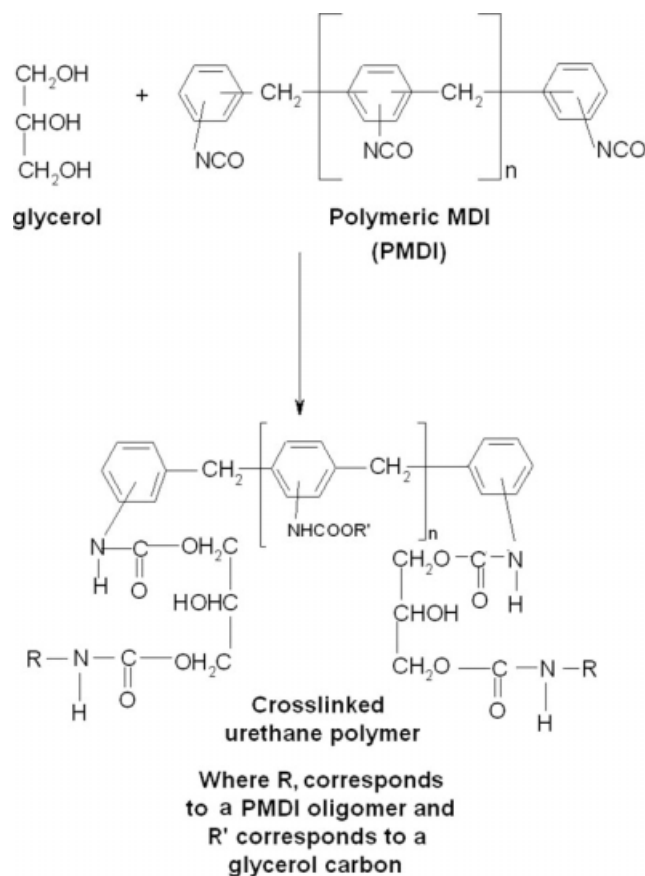
Oligomeric diphenylmethane diisocyanate (PMDI) with a functionality of 2.7 and viscosity of 200–250 mPa s was used as received from Dow Plastics (PAPI 20). Glycerol 99.9% pure was obtained from Sigma Aldrich and was used as received.

The stoichiometric ratio of isocyanate to hydroxyl groups was used to describe a model system. The materials were mixed at standard conditions using an overhead drill mixer with a 5 cm diameter fan blade. The general reaction for isocyanate and polyol is shown in Scheme 1.

DSC measurement

Kinetic studies were performed using a DSC 2920 (TA instruments). Samples were sealed in hermetic aluminum pans with an average sample weight of 5 ± 0.5 mg. Cell constant calibration was performed using an indium (99.99% pure) standard. Nitrogen at a flow rate of 50 mL/min was used as the purge gas.

The isothermal method used required the DSC cell to be preheated to the appropriate isothermal temperature before quickly placing the sample in the cell at one of the following isothermal temperatures of: 70°C, 80°C, 90°C, and 100°C. Thermal equilibrium was achieved within 1 min of sample insertion. The isothermal curing reaction was considered complete when the signal leveled off to the baseline with the total area under the exotherm giving the isothermal heat of reaction, Q_T . The samples were quickly cooled to room temperature using a water bath and



Scheme 1 Representation of the polyurethane reaction between glycerol and PMDI.

were ramped at 10°C/min to determine the residual heat of reaction (Q_{res}). A second nonisothermal run was then performed at 10°C/min from -10°C to 180°C to ensure no further exothermic event was evident. The ultimate extents of cure were determined by choosing the maximum heat of reaction (Q_{rxn}) of the sample, as the sum of the isothermal heat (Q_T) and the residual heat of reaction (Q_{res}) determined at 70°C .² This temperature was chosen due to the greatest extent of cure being achieved out of the temperature range. Difficulty existed in obtaining the isothermal exotherm at temperatures below 70°C , as lengthy cure times were required for the exotherm to return to baseline. The maximum heat of reaction achieved using this method, was $Q_{rxn} = 350 \pm 20$ J/g or 54 ± 2 kJ/mol equivalent isocyanate. Generally, polyurethane reactions have a reaction enthalpy between -80 and -90 kJ/mol equivalent isocyanate,^{10,32,33} with Chappel and Argust¹⁰ reporting a lower value of -69 kJ/mol equivalent isocyanate. It is important to note that the relative extents of cure were used for isoconversional DSC analysis, determined through integration of the DSC peaks of the isothermal curves up to a time of 30 min at each temperature.

Nonisothermal cure was determined as fractional areas of DSC peaks with the total heat release in each nonisothermal experiment assigned to $\alpha = 1$ for heating ramps of 5, 10, and 20°C/min. Samples were ramped between -10°C to 250°C, depending on the heating rate used. A second nonisothermal run was performed under the same conditions and showed no further exothermic event.³⁴

Rheological measurement

An AR-2000 controlled stress and direct strain control rheometer from TA Instruments (US) was used to study the cure profile of the coating system through gelation and viscosity build up. A 2 cm 2° cone and plate configuration was used to achieve a thin gap allowing a large surface to volume ratio for isothermal curing. Dynamic measurements in oscillatory mode were performed at a frequency of 1 Hz or using a multifrequency technique ranging from 1 Hz to 10 Hz with a strain of 0.1%, 10%, or 100% (initial tests were performed to ensure the response was in the viscoelastic region). A limitation of the equipment was the inability to change strains during the evolution of the network structure.³⁵ To detect the initial network formation, a higher strain (10%) was required and performed in multifrequency mode. To obtain information on the network formation as it evolved, without breaking the network structure, a small strain was needed and therefore repeated at 0.1% strain at 1 Hz. A strain of 100% strain was also used in multifrequency mode to detect the gel time when $\tan \delta$ becomes frequency independent.³⁰ A conditioning step with pre-shearing was used to provide the same deformation history for all samples. Isothermal measurements were performed at 70°C, 80°C, 90°C, and 100 °C.

Mid and near infrared spectroscopic analysis

A Nicolet FTIR Nexus 8700 spectrophotometer, fitted with a diamond ATR (attenuated total reflectance), was used to determine residual isocyanate and hydroxyl groups in the cured sample. The maximum penetration of infrared radiation into the sample was 1 μm and the average number of scans used, to obtain an infrared spectrum, was 32 at a resolution of 4 cm^{-1} . A background spectrum of air was collected before the IR spectrum for each sample. Figure 1(A) shows a typical IR spectrum of cured polyurethane, after three DSC runs (isothermal followed by two nonisothermal), with the isocyanate peak shown at a wavelength of 2270 cm^{-1} . Residual hydroxyl groups were also detected at approximately 7000 cm^{-1} using near infrared-ATR of a sample. The sample was cured isothermally at 70°C for 24 h followed by postcuring for 3 h at 180°C [Fig. 1(B)].³⁶⁻³⁸

Dynamic mechanical analysis

DMA measurements were performed using a TA Instruments DMA Q800 in single cantilever bending deformation mode. The samples were cured isothermally at 70°C for 24 h followed by postcuring at 180°C for 3 h. DMA tests were carried out at a frequency of 1 Hz, amplitude of 20 μm , in the temperature range of -100 °C to 180 °C with heating ramp of 2°C/min.

The glass transition temperature T_g was taken as the temperature at which the loss factor $\tan \delta$ reached a maximum. Liquid nitrogen was used to achieve the subambient temperatures. The ultimate glass transition temperature (T_g) of the cured material, determined by DMA, from an average of three samples.

RESULTS AND DISCUSSION

Investigation of reaction kinetics through DSC

Figure 2 displays the heat flow profiles for the system cured isothermally at four different temperatures. The isothermal heat of reaction (Q_T) after 30 min of curing increased with an increase in isothermal cure temperature with the exception of 100°C (Table I). In contrast, a reduction in the heat of reaction was observed with an increase in isothermal cure temperature when the isothermal signal was allowed to level off to baseline [Table I: 70°C (120 min) 80°C (60 min), 90°C (40 min), 100°C (16 min)]. This indicates the complexity of the curing reaction and the change in reaction conditions. The polyurethane system was isothermally cured at temperatures below its ultimate glass transition temperature, which was determined by DMA to be $T_g = 104 \pm 3^\circ\text{C}$. As mentioned above, curing below the T_g allows gelation and vitrification to occur during the course of reaction, resulting in incomplete cure. Unreacted isocyanate and hydroxyl groups [Fig. 1(A,B), respectively] were also detected after the DSC samples underwent isothermal curing followed by two nonisothermal scans, confirming vitrification of the system. This phenomenon is caused by diffusion limitation of the reactive groups embedded in the polymer matrix on crosslinking. Thus, the polyurethane system undergoes incomplete cure, reaching what is known as the ultimate extent of cure.^{34,39} The ultimate extent of cure, at time t , was calculated from eq. (1) and shown in Table I for 30-min and 120-min time intervals.

$$\alpha = \frac{\int_0^t \frac{dQ}{dt} dt}{Q_{\text{rxn}}} \quad (1)$$

where α is the conversion at time t .

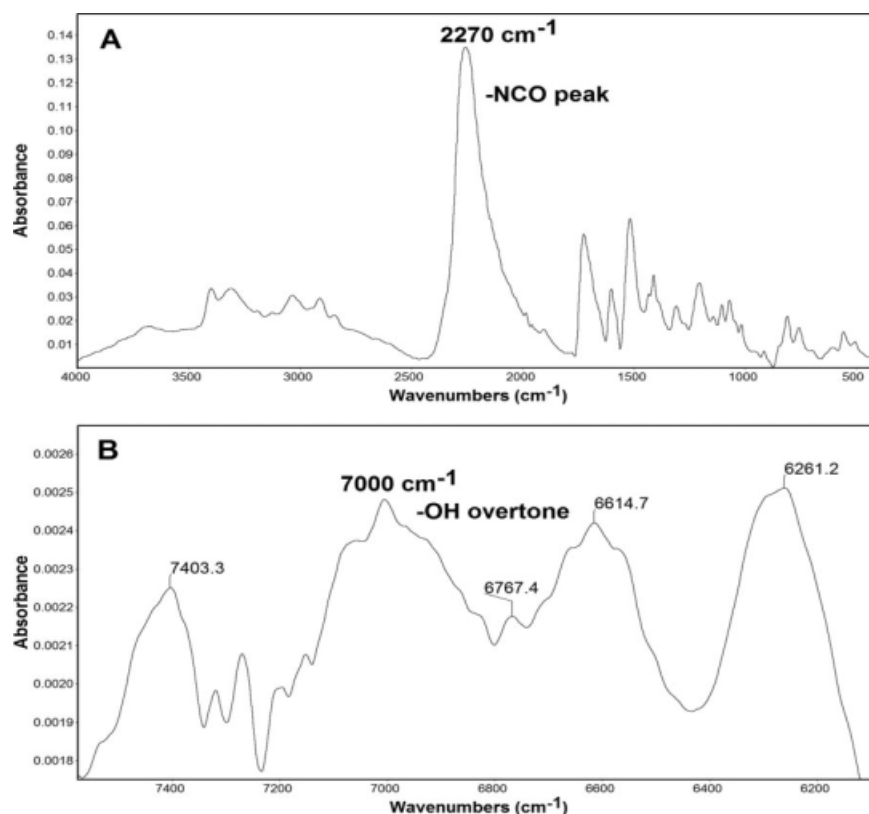


Figure 1 A) FTIR showing unreacted isocyanate groups after DSC cure (isothermal scan followed by two nonisothermal scans) and (B) FTNIR of isothermally cured polyurethane at 70°C, showing residual hydroxyl groups present.

Referring to Table I, it is evident that the conversion trend changes, depending on the isothermal cure time. An increase in conversion with temperature (except 100°C) is indicative of the chemically driven reaction kinetics, obtained at 30 min of curing. At 100°C, the isothermal temperature approaches the glass transition temperature, which retards the chemical reaction. More importantly, greater conversions are achieved at longer cure times (120 min) for the isothermal temperatures of 70°C and 80°C, which could indicate the presence of functional groups with inconsistent reactivity. The cure process of this system is dependent on the reactions between the isocyanate groups from the PMDI and hydroxyl groups form the glycerol monomer, which includes both fast primary hydroxyl reactions, as well as the slower reactions of the secondary hydroxyl group.¹⁰ The presence of a secondary hydroxyl group in glycerol, if provided sufficient time to react is likely to increase the conversion at lower temperatures. The difference in the apparent activation energies of primary and secondary hydroxyls has been investigated elsewhere.⁴⁰ Using curve fitting software (Origin 7.5) and fitting two peaks to the isothermal heat flow versus time curves for 70°C (120 min), 80°C (60 min), 90°C (40 min), and 100°C (16 min), the conversion due to the primary and secondary hydroxyls can be differentiated.

An example is shown for an isothermal run performed at 70°C [Fig. 3(A)]. The experimental data fitted well to a Gaussian model, with a reduced chi-squared of 7.74×10^{-6} , COD of 98 and correlation of 0.99 (iterations performed = 200 with a 0.95 confidence interval and a tolerance of 0.05, DOF = 52 and number of points = 58). The conversion of the primary hydroxyl group was calculated as the area under the first peak fitted to the heat flow curves, whereas the conversion of the secondary hydroxyl group was calculated as the area of the second peak fitted to the heat flow curves. The secondary hydroxyl group conversion for the isothermal

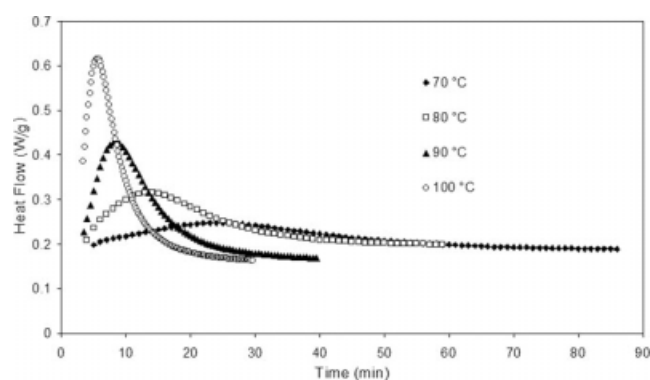


Figure 2 Heat flow profiles for the polyurethane system cured at varying isothermal temperatures.

TABLE I
Isothermal heat flow and ultimate extents of cure for two time intervals at varying isothermal cure temperatures

Isothermal temperature (°C)	Q_T (J/g) 30 min	Q_T (J/g) 120 min	%Conversion at 30 min	%Conversion at 120 min
70	48.4 ± 3.4	252.6 ± 12.62	13.8 ± 1.1	72.2 ± 4.3
80	104.7 ± 4.1	155.5 ± 7.3	29.9 ± 1.5	44.5 ± 2.6
90	128.9 ± 1.1	133.2 ± 2.7	36.8 ± 1.3	38.1 ± 1.5
100	73.4 ± 1.6	73.4 ± 1.6	21.0 ± 0.8	21.0 ± 0.8

temperature of 100°C was omitted from the data-set presented, because the reaction ceased too early for reliable determination of the second peak area. Plotting the conversion versus time at each temperature for both peaks and taking the slope of the line, the relative reaction rates of the primary and secondary hydroxyls can be elucidated and is shown in Figure 3(B). The primary hydroxyl was found to react three times faster than the secondary hydroxyl in glycerol, which has also been reported by Chappel and Argust,¹⁰ using an alternative method.

Because of the complexity of this reaction, modeling the cure kinetics using conventional models^{17,41–43} is futile, thus, the advanced integral isoconversional method of Vyazovkin^{20,44} was used to better understand the cure process. In general, absolute extents of

cure are used when evaluating the cure profile; however, for reactions undergoing incomplete cure, this yields an error in the activation energy at higher conversions.³⁴ Therefore, the relative extent of cure was used to determine the activation energy as a function of conversion and is presented in Figure 4 (100°C data was unreliable, as it approached the T_g and was thus omitted from the calculations). It is noticed that the activation energy (E_a) increases up to a critical conversion (approximately 60%) after which a decrease occurs. This suggests a diffusion controlled process is apparent in the later stages of the reaction.⁴⁵ A similar convex-shaped activation energy profile was obtained for a polyurethane process using model free kinetics and was attributed to autocatalytic cure in the initial stages, followed by diffusion control.²¹ The activation energy ranges from 5 kJ/mol to 33.7 kJ/mol, which is ~30% lower than reported values in the literature for polyurethane systems.^{32,41,46} This is apparent due to only the first 30 min of the reaction being used to calculate the activation energy profile, resulting in mainly the cure of the faster primary hydroxyl groups.

As a comparative study, nonisothermal DSC kinetics was analyzed using isoconversional methods. The profile is shown in Figure 5 and a steady decrease in activation energy with conversion was observed with a small increase in the later stages of conversion. This small increase, toward the later stages of cure is the formation and reaction of allophanate, which is known

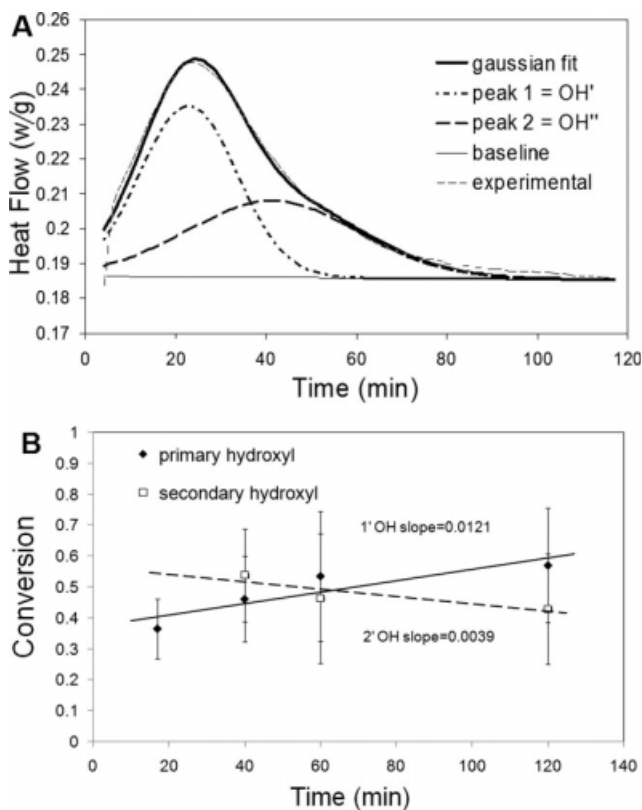


Figure 3 (A) Gaussian fit of heat flow curve during isothermal cure at 70°C: two peaks fitted pertaining to primary and secondary hydroxyls and (B) Rate of cure pertaining to primary and secondary hydroxyls in glycerol.

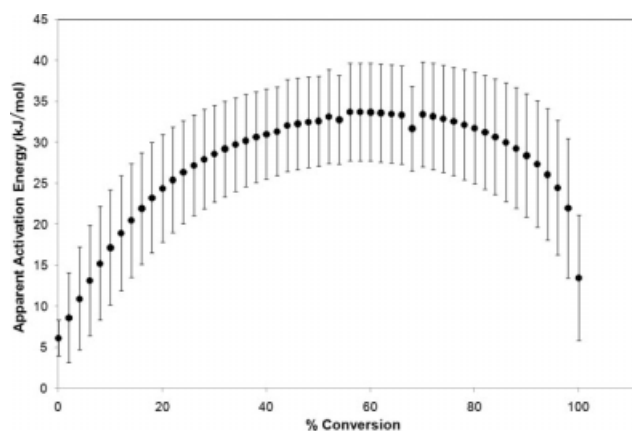


Figure 4 Variation of the apparent activation energy with conversion for isothermal DSC scans of the polyurethane system.

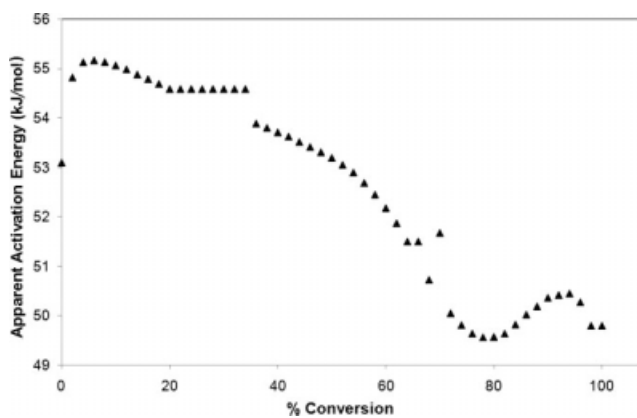


Figure 5 Activation energy dependence on conversion for nonisothermal DSC scans of the polyurethane system.

to occur in polyurethane systems at temperatures above 140°C.^{2,14} Although the activation energy does change as a function of conversion, this is quite minimal, displaying a range from 49.5 kJ/mol to 55 kJ/mol, which are similar to the values reported in the literature.^{32,41} The nonisothermal method is a more reliable representation of the activation energy for the overall reaction, which includes the reactions of both primary and secondary hydroxyl groups.

Rheological characterization

Rheological behavior of polyurethane network formation was monitored for the duration of cure. During isothermal cure, viscosity changes are detected due to increases in molecular weight. The viscosity was found to increase with time (Fig. 6) due to urethane bond formation; however, many stages are

noticed indicating a complex reaction system. The inset in Figure 6 represents the initial stages of viscosity build up (90°C data omitted for clarity). It is noticed from the Figure 6 inset, that the reaction mixture is initially homogeneous, with the more reactive functional groups combining until the point in time where a slight decrease is observed before further increases in viscosity. This reduction in viscosity is caused by heterogeneous curing, because the reaction product is insoluble in the reacting matrix.⁴⁷ It is suggested that formation of microgel particles and the start of gelation occur at this point, after which a rapid increase in the rate is observed, transitioning to two main stages of viscosity build up. The two stages seen in Figure 6 arise from the difference in reactivity of the primary and secondary hydroxyl groups in the glycerol as was established using DSC. Furthermore, at each of these two stages of viscosity build up, a change in the rate is noticed, which is apparent due to the difference in reactivity of the terminal isocyanate groups to the internal isocyanate groups of the varying weight oligomers in PMDI.²² Sekkar et al.⁴⁸ observed a similar rate change due to the difference in reactivity of isocyanate functional groups using toluene diisocyanate.

The evolution of the elastic modulus, G' , loss modulus, G'' , and $\tan \delta$ for each temperature is shown in Figure 7. The behavior of $\tan \delta$ depends on the cure temperature and can be related to the two main stages of viscosity build up and the sudden increases in G' and G'' .

With the cure temperature below the ultimate glass transition temperature, two $\tan \delta$ peaks are present and are in direct relation to the slope changes observed in the viscosity profiles. The $\tan \delta$

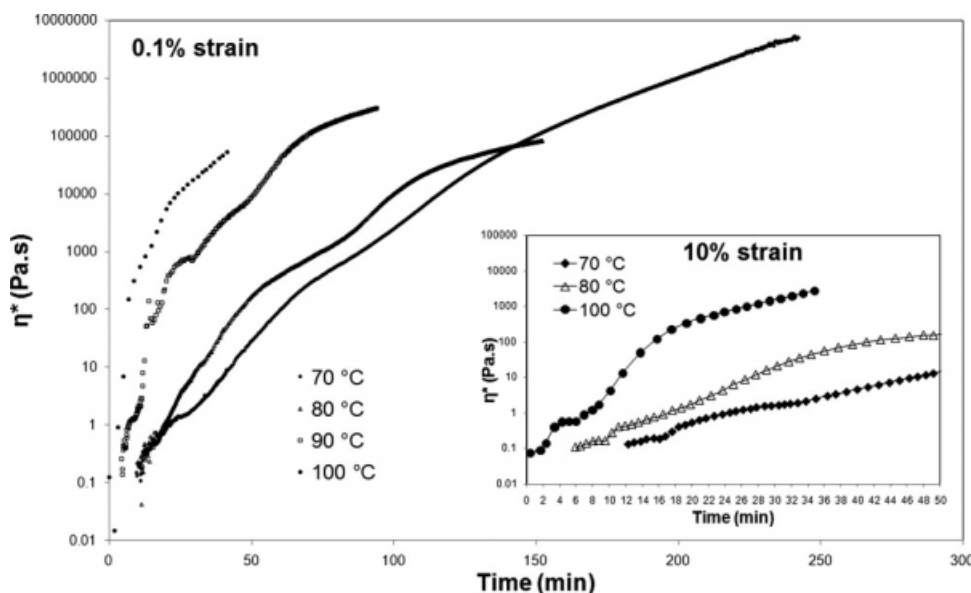


Figure 6 Viscosity build up of the polyurethane system at various isothermal temperatures at 0.1% strain and insert at 10% strain showing initial viscosity build up.

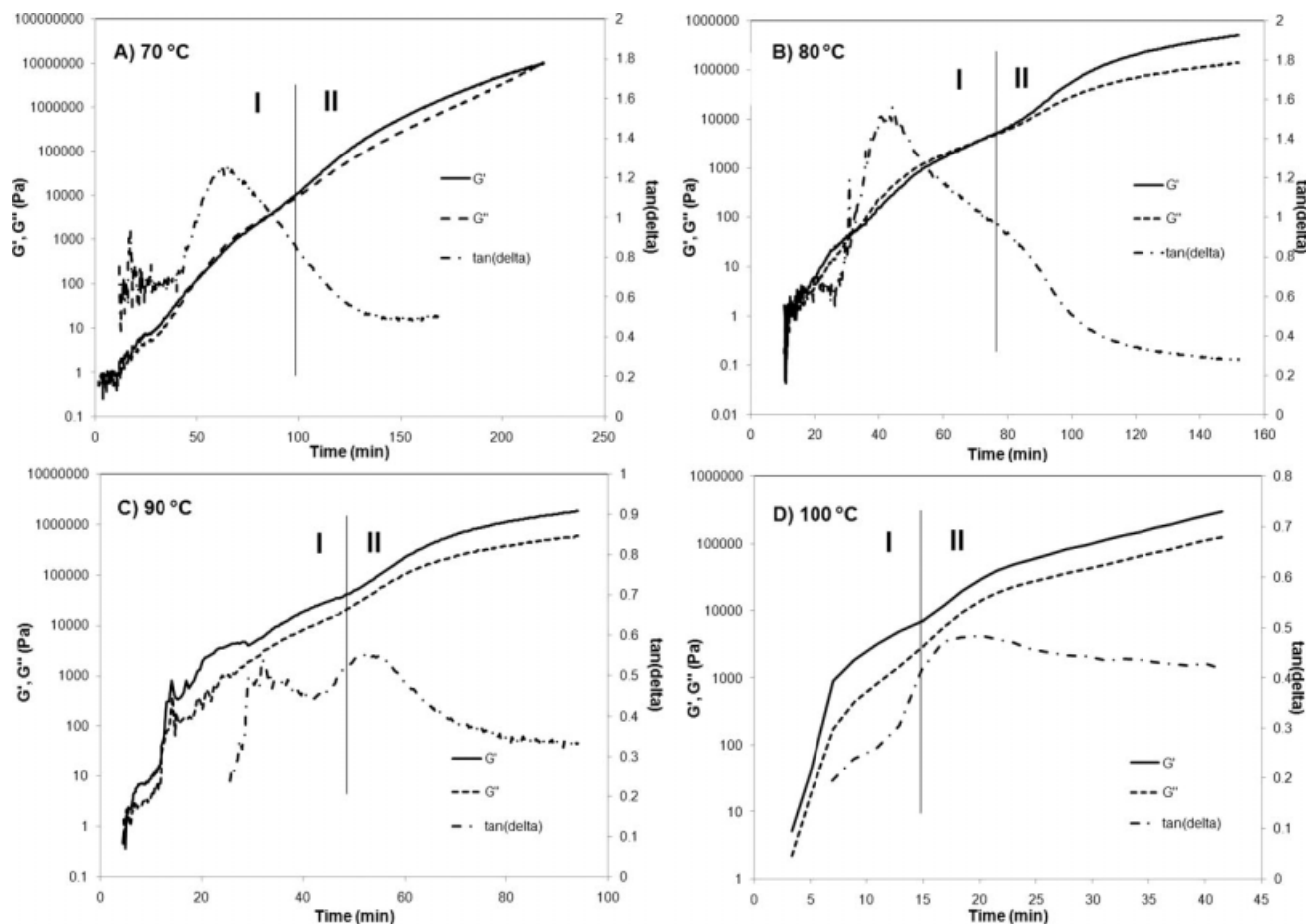


Figure 7 Evolution of G' , G'' , and $\tan \delta$ at various isothermal cure temperatures at 0.1% strain, 1 Hz.

peak is broad and spans over a longer period of time at 70°C; forming a shoulder at 80°C, while at 90°C, two distinct peaks are observed. This variation in $\tan \delta$ with increasing temperature, where a more distinct second peak is observed at higher isothermal curing temperatures, confirms that primary and secondary hydroxyls respond differently to temperature. This same influence of temperature was also seen in isothermal DSC scans.

At 100°C, the isothermal temperature matches the glass transition temperature resulting in a lower viscosity build up in the later stage of cure. In contrast, at temperatures below the glass transition temperature, there is an onset of diffusion control resulting in an increase of the magnitude of viscosity build up, G' and G'' .

The initial cure behavior was monitored at 10% strain because the evolution of G' , G'' , and $\tan \delta$ at 0.1% strain was highly scattered. Initially, the loss modulus starts growing while the storage modulus is below the sensitivity of the equipment. After the crossover of G' and G'' determined at 10% strain and shown in Table II, the behavior is followed using 0.1% strain, as shown in Figure 7. The variation of G' and G'' depends on the isothermal temperature used. At 70°C and 80°C the same profile is observed for G' and

G'' , whereby the storage modulus rises above the loss modulus until a point where the loss modulus grows faster than the storage modulus and coincides with the peak in $\tan \delta$. Once past the maximum $\tan \delta$, the storage modulus continues to grow and increases at a rate which is faster than the loss modulus pertaining to a more elastic system. This growth of the storage modulus occurs from the reactions between the primary hydroxyl and less reactive isocyanate groups as discussed earlier. The storage modulus undergoes a second rate rise which, as discussed above, occurs through reactions of the secondary hydroxyl groups. It can be seen in Figure 7(A) at 70°C, the storage and loss modulus start to come together toward the end of

TABLE II
Critical rheological times obtained using the frequency independence of $\tan \delta$

Isothermal temperature (°C)	$\tan \delta$ frequency independence (min)
70	218
80	119
90	54
100	25

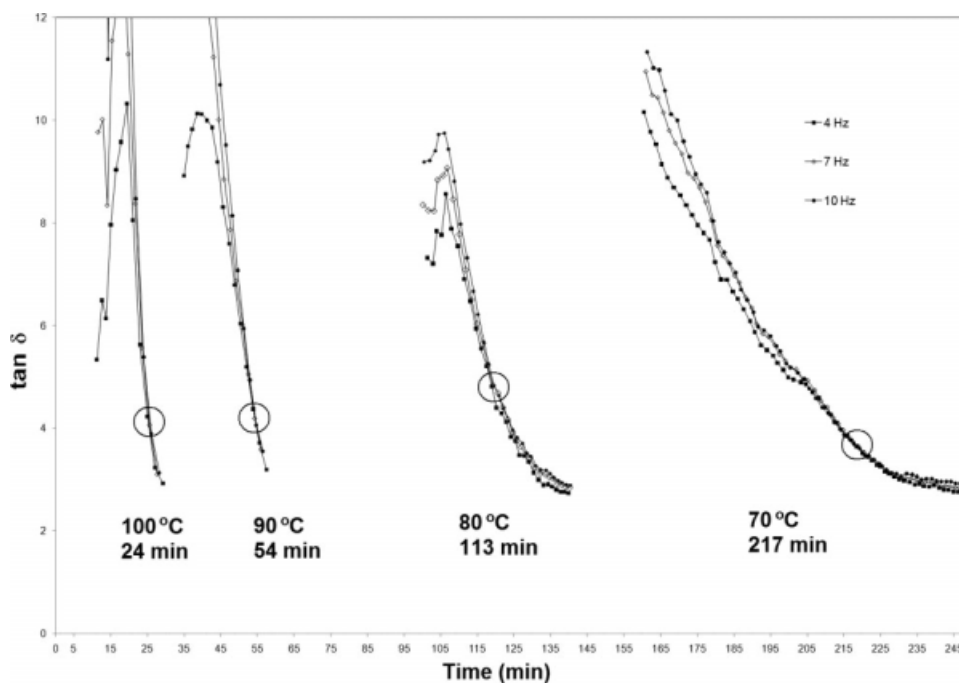


Figure 8 Dependence of the gel point on the isothermal curing temperature for the polyurethane system.

the profile. At this point, the system no longer flows and represents the end of gelation. Gel times were established using the multifrequency technique where $\tan \delta$ becomes independent of frequency and are given in Table II. The dependence of gel time on isothermal cure temperature is depicted in Figure 8. The point where $\tan \delta$ intersects for all frequencies is highlighted by a circle. As the cure temperature gets closer to the glass transition temperature of the system, the gel time is harder to detect by the crossover of the $\tan \delta$ curves, as the onset of diffusion control and gelation occur at the same time, giving rise to very complex rheological behavior.⁴⁹

The degree of conversion at the gel point can be considered as a constant for thermosetting systems^{27,30,50} allowing for a direct relationship between the gel time (t_{gel}) and the apparent curing constant K_c .^{30,51}

$$t_{\text{gel}} = A' \times \left(\frac{1}{K_c} \right) \quad (2)$$

The curing process can be described by an overall activation energy E_a where the temperature dependence of the gel time follows the Arrhenius law ($K_c(T) = A'' \exp(-E_a/RT)$), and can be obtained by plotting:

$$\ln(t_{\text{gel}}) = A''' + \frac{E_a}{RT} \quad (3)$$

The overall activation energy attained at the gel point is 77.4 ± 4.4 kJ/mol. This value is much higher than the variable activation energy range obtained

using DSC analysis. It is suggested that during isothermal cure in DSC, the material does not reach the gel point and the majority of the heat flow measured represents the reaction of the faster primary hydroxyl groups, especially at higher isothermal cure temperatures.

CONCLUSIONS

The polymerization of oligomeric diisocyanate monomers using glycerol, containing two fast reacting primary hydroxyl groups and one slower reacting secondary hydroxyl group, were investigated using thermal and rheological techniques. This work highlighted the complexity of cure for this system. The reactivities of the primary and secondary hydroxyl groups were found to vary with isothermal temperature or during extended periods of curing. The primary hydroxyls were found to react three times faster than the secondary hydroxyl groups as corroborated by similar systems investigated in the literature using different characterization techniques.

Isoconversional kinetic DSC analysis resulted in the activation energy varying with conversion for the stoichiometric system. Incomplete cure was evident in isothermal DSC, becoming diffusion controlled in the final stages of cure. DMA analysis on the cured material showed evidence of vitrification of the curing system. Rheological studies of viscosity increase and $\tan \delta$ changes, also revealed primary and secondary hydroxyl reactivity having a

dependence on isothermal cure temperatures, reflecting similar results obtained from isothermal DSC studies.

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