The Rheological Properties of Isothermal Curing of DGEBA/ TETA Epoxy System

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ABSTRACT
   In this study viscosity (η) of diglycidyl ether of bisphenol A / triethylenetetramine (DGEBA/TETA) system were measured through curing using a Brookfield viscometer at four different temperatures (30, 45, 60 and 80) °C. The measurements were carried out for two hardener/resin ratios (13 and 20) phr. The gel time was calculated for each hardener/resin ratio formulation; from the viscosity experimental data. The results showed that the gel time decrease with increasing curing temperature for each hardener/resin ratio formulation. Viscosity profiles were described by a model based on the Boltzmann function. The fitted results agreed well with the experimental values.
 Keywords: Epoxy Resin, Curing, Rheology, Hardener

دراسة الخواص الريولوجية بثبوت درجة الحرارة لعملية تقسية راتنج الايبوكسي بأستخدم مادة تراي اثلين تترا امين

الخلاصة
في هذا البحث تم قياس اللزوجة لنظام مكون من (DGEBA/TETA)   خلال عملية الانضاج بأستخدام مقياس اللزوجة من نوع   Brookfield في اربع درجات مختلفة (30,45,60,80) م^0 . تم أخذ القياسات باستخدام نسبتين للراتنج / المصلد وهما (13) و(20) جزء من المائة .
تم حساب زمن التصلب (gel time) لكل نسبة من الراتنج/ المصلد من قياسات اللزوجة . أظهرت النتائج بان زمن التصلد يزداد مع زيادة درجة الانضاج لكل نسبة من نسب الراتنج/ المصلد . تم وصف منحنى اللزوجة بموديل يعتمد على موديل (Boltzman) وتم مطابقة النتائج المستخلصة من الموديل مع النتائج المختبرية وظهر تطابق كبير بينهما .
الكلمات المرشدة : راتنج الايبوكسي , انضاج , رايولوجي , مصلد

INTRODUCTION

R HEOLOGY CAN BE DEFINED AS 'THE SCIENCE OF THE DEFORMATION AND FLOW OF MATTER', WHICH MEANS THAT IT IS CONCERNED WITH RELATIONSHIP BETWEEN VISCOSITY, STRESS, STRAIN, RATE OF STRAIN, AND TIME [1].
In practice, rheology is concerned with materials whose flow properties are more complicated than those of a simple fluid (liquid or gas) or an ideal elastic solid, although it may be remarked that a material whose behavior under same restricted range of circumstances is simple, may exhibit much more complex behavior under other circumstances. Many materials of industrial interest behave in a way such as to bring their study within the scope of rheology, and included in these epoxy resins [2].

Epoxy resins exhibit both viscous and elastic properties. During the curing process, their viscosity increases quickly in the gel region. The viscosity can be related to degree of cure. Rheological equipment can be used to measure effectively the epoxy resin properties, such as Brookfield viscometer, which provides a lot of information on the Epoxy resins in the way that helps in understanding the rheological behavior of this material [3].

Rheology Model

Viscosity Model

The viscosity of a curing resin system is determined by two factors: the degree of cure and the temperature. As the cure proceeds, the molecular size increases and so does the cross-linking density, which decrease the mobility and hence increase the viscosity of the resin system. On the other hand, the temperature exerts a direct effect on the dynamics of molecules and so the viscosity.

Much work has been done to develop appropriate mathematical models for the descriptions of the viscosity advancements for various thermosetting resins during cure. The variation of viscosity is the result of the combination of physical and chemical processes and can be empirically expressed as [4]:

$$\eta = \psi(T)\zeta(\alpha) \qquad \qquad \dots(1)$$

Where
$\psi(T)$ is a function of curing temperature only; $\zeta(\alpha)$ is a function of degree of cure. Terms $\psi(T)$ and $\zeta(\alpha)$ can be empirically expressed with the simple form respectively:

$$\psi(T) = \eta_o \text{ and } \zeta(\alpha) = \frac{1}{1-\alpha} \qquad \qquad \dots(2)$$

Where
η_o is the initial viscosity which is a constant at isothermal cure conditions; α is the degree of cure.
Substituting eq. (2), into eq. (1), to get the relationship of viscosity vs. the degree of cure:
The initial viscosity η_o depends on cure temperature and can be further expressed in Arrhenius equation:

$$\eta_o = A\eta e^{-\frac{E\eta}{RT}}$$

... (4)

Where

Aη and Eη are the initial viscosity at T = ∞ and the viscous flow activation energy, respectively. The degree of cure α in eq. (3), is a function of cure time.

Depending on the cure kinetics, the relationship of α vs. time t may have different forms. For the first order reaction, it can be expressed as:

$$\frac{d\alpha}{dt} = k(1-\alpha)$$

...(5)

For the first order reaction with the isothermal cure process, temperature T and rate constant k are constant:

$$\eta = \eta_o e^{kt}$$

... (6)

$$\ln \eta = \ln A_\eta + \frac{E_\eta}{RT} + tA_K e^{-\frac{EK}{RT}}$$

... (7)

where

A$_k$ and E$_k$ are the apparent rate constant at T = ∞ and the kinetic activation energy, respectively.

Equation (7) is the empirical four-parameter model of viscosity introduced by Roller [5]. For the nth order reaction, it can be expressed as:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n$$

... (8)

So for the isothermal nth order (n$\neq$ 1) reaction:

$$\ln\eta = \ln A_\eta + \frac{E_\eta}{RT} + \frac{1}{n-1}\ln(1 + (n-1)$$

... (9)

Equation (9) is the empirical five-parameter model of viscosity for the nth (n$\neq$1) order reaction introduced by Dusi [6].

The first and nth order viscosity models express viscosity as an exponential function of the cure time. The first and nth viscosity models have been frequently used in the rheological analysis of the cure process (Dusi et al. [6]; Theriault et al. [7]; Wang et al. [8]). These models do not incorporate the effect of gelation on the viscosity and the predication accuracy is not good. The modified Williams-Landel-Ferry (WFL) models for viscosity (Tajima and Crozier [9]; Mijovic and Lee, [10]) describe viscosity as the function of both cure temperature and glass transition temperature:

$$\frac{\eta(T,\alpha)}{\eta(T_o)} = (g\,\frac{M_w(\alpha)}{M_{wo}})^{3.4}$$

$$\frac{\exp\{c_1(T_r - T_{go})/(c_2 + T_r - T_{go})\}}{\exp\{c_1(T_r - T_g(\alpha))/(c_2 + T_r - T_g(\alpha))\}}$$

… (10)

Where

η is the viscosity, MW is the weight average molecular weight of the Epoxy resin, g is the ratio for the radii of gyration of a branched chain to the linear chain of the same molecular weight, T_r is a reference temperature, T_g is the glass transition temperature of the reacting system, and c_1 and c_2 are constants. These models have been extensively used and they were reported to achieve good accuracy (Karkanas and Partrige [11]). When applying the WFL models, one needs to know the relationship between the glass transition temperature and the cure time, which can be determined by thermal analysis.

Bidstrup and Sheppard [12] showed that the temperature-dependence of the ionic conductivity of a series of cured epoxy resin by varying molecular weight can be modeled by the WLF equation if the constant c_2 and the conductivity σ_g at the glass transition are taken as a function of T_g. They assumed that c_2 and log (σ_g) vary linearly with T_g; their model for conductivity then gives a five-parameter equation, which can be written as

$$\log \sigma = c_5 + c_6 T_g + \frac{c_1(T - T_g)}{c_3 + c_4 T_g + (T - T_g)}$$

… (11)

Where:

$$c_5 + c_6 T_g = \log(\sigma)$$

… (12)

$$c_3 + c_4 T_g = c_2$$

…. (13)

Sanford and McCllough [13] proposed a chemorheological model for predicting the viscosity variation of epoxy resin during isothermal cure, using the free volume concept. The underlying concept for this model is that the ability of molecules or chain segments to rearrange themselves is dependent on the existence of enough unoccupied space to accommodate motion. Where there is relatively a large amount of free volume the chain may move unhindered, however, as the free volume decreases, the chain becomes crowded by their neighbors. They found the following empirical expression for EPON828/PACM-20 resin system:

$$\eta = 2.1 \times 10^{-12} M_w w \exp[-0.62(1 - \frac{1}{f})]$$

…(14)

Where

M_w is the number of average molecular weight, f fraction of free volume which may be expressed as a linear function of the difference between the resin temperature and the glass transition temperature as:

$$f = f_g + \alpha_f (T - T_g)$$

... (15)

here f_g is the fractional free volume at T_g and α_f is the thermal expansion coefficient of free volume.

A percolation model for viscosity expresses the variation of viscosity with degree of cure by a power law. By introducing the degree of critical reaction into the model, the gel effect on the cure process was taken into account. It was reported that the percolation model fit the experimental data quite well [14]. For the application of the percolation model, a kinetics model is necessary in order to determine the relationship between the degree of cure and time. The characteristics of other viscosity models for cure applications were discussed by Halley and Mackay [15].

Sun et al. [16] predicted a model to describe the viscosity of the epoxy prepreg, the model proposed based on a Boltzmann function to produce a sigmoidal curve, which the viscosity profile for the isothermal cure process seems to follow, especially in the gel region.

$$\eta = \frac{\eta_o - \eta_\infty}{1 + e^{k(t - t_c)}} + \eta_\infty$$

... (16)

where η_o is the initial viscosity, η_∞ is the final viscosity; k is the rate constant of cure reaction and t_c is the critical time which follows Arrhenius behavior, i.e.

$$t_c = A_t e^{\frac{E_t}{RT}}$$

.... (17)

where

A_t is the pre-exponential factor and E_t is the activation energy.

Equation (16) is just a fitting function which is based on the mathematical knowledge instead of the rheological theory. It has a similar form as a Boltzmann function, but each parameter in eq. (16), has its own physical meaning. The parameters in eq. (16) are determined by the multiple non-linear regression method.

Gel Time Model

Gel time, which was detected by the rheological measurement, varies with the isothermal cure rate of reaction. Gonis et al. [17] expressed the curing process as:

$$\frac{d\alpha}{dt} = k(T) g(\alpha)$$

...(18)

Where
k(T) is the rate constant (which depends on the temperature T), and g(α) is a function of α only. It may have different forms, depending on the cure mechanism. The rate constant k (T) has the following definition as in eq. (19).

$$k = A \exp \frac{-\Delta E_a}{Rt} \qquad \text{....(19)}$$

By integrating eq. (18), from zero time to gel time t_{gel}, the relationship between t_{gel} and cure rate is obtained:

$$t_{gel} = \frac{1}{k(T)} \int_0^{\alpha_{gel}} \frac{1}{\alpha_{gel}} d\alpha \qquad (20)$$

Where
α_{gel} is the degree of cure at gel time.
Substitute eq. (19), into eq. (20), and take logarithm on both sides to get the relationship between the gel time and isothermal cure temperature:

$$\ln(t_{gel}) = \ln\left[\frac{1}{A_o} \langle \int_0^{\alpha_{gel}} \frac{1}{\alpha_{gel}} d\alpha \rangle + \frac{E_a}{RT} \right] \qquad \text{.... (21)}$$

According to Flory's expression [18], the degree of cure α_{gel} at gel time depends on the functionalities of the epoxy systems only. So it can be considered a constant for a given epoxy systems regardless the cure temperature.

By considering the first term on the left side of eq. (21), as a constant C, a linear relationship of $\ln(t_{gel})$ vs. $1/T$ is obtained and eq. (21), can be rewritten as:

$$\ln t_{gel} = C + \frac{E_a}{RT} \qquad (22)$$

From "(22)," the apparent activation energy can be calculated from the slope of the curve of ln(tgel) vs. 1/T.
Velazquez et. al. [19] studied the changes in rheological properties (gelation and vitrification) during non-isothermal curing of an epoxy resin (DGEBA) with different aliphatic amines using different resin/hardener ratio. A dynamic rheometer was used. It was found that the viscous modulus (G") represents two peaks. The first peak appears

when the system reaches the vitrification curve for the stoichiometric and amine rich systems, but the epoxy rich systems don't show peaks.

Grimsley et. al. [20] studied the cure kinetics and viscosity of two resins, an amine-cured epoxy system, Applied Poleramic, Inc. VR-56-4, and an anhydride-cured epoxy system, have been characterized for application in the vacuum assisted resin transfer molding (VARTM) of aerospace components. Simulations were carried out using the process model, COMPRO, to examine heat transfer, curing kinetics and viscosity for different panel thicknesses and cure cycles. Results of these simulations indicate that the two resins have significantly different curing behaviors and flow characteristics.

Ivancovic et. al. [21] investigated the chemorhelogy of a low-viscosity laminating system, based on a bisphenol A epoxy resin, an anhydride curing agent, and a heterocyclic amine accelerator. The steady shear and dynamic viscosity are measured throughout the epoxy/ anhydride cure. It was found that at the beginning of the cure, the viscosity slowly increases with time. Then, at a certain point a very rapid increase of the viscosity is observed. Gelation was assumed to occur when the rate of viscosity increase reached a maximum. A chomorheological model that describes the system viscosity as a function of temperature and conversion is proposed.

Costa et. al. [22] investigated the rheological, structural properties and cure kinetics of epoxy resin, prepared with diglycidyl ether of bisphenol-A (DGEBA) and triethylenetetramine (TETA), for different ratios of hardener (TETA) and epoxy (DGEBA), using a DSC and a rheometer. From the experimental results, it was found that the higher the ratio, the higher the onset temperature and the total heat of reaction and the lower the peak temperature. The cure reaction follows an autocatalytic model. The dynamic experiments showed that the complex viscosity and the elastic and loss moduli increased with the curing times.

The purpose of the work described in a series of papers [23] is to relate the rheological properties such as the viscosity to the gel time and cure process and test the existing models. A number of models have been reported recently. The first and nth order reaction models may be used with limited accuracy. To achieve high accuracy the model based on Bolzmann function and gel time model will be used and compared with experimental data.

EXPERIMENT WORK

The material used was DGEBA- Epoxy resin cured using aliphatic amines hardeners, which was Triethelenetetramine(TETA). Brookfield viscometer was used to measure the viscosity of the prepared samples of the DGEBA/TETA.

MATERIALS

Epikote 828 from Shell Co. was used as epoxy resin. Epikote 828 is an unmodified liquid bisphenol A –epoxide resin of medium viscosity.

The hardeners (curing agent) used in the experimental work was: Araldite HY 951 (Triethelentetramine TETA) from Ciba Company, which is a liquid of law viscosity of an aliphatic amine basis. Two hardener/resin ratios (13 and 20) phr were used in this work.

The prepared samples were mixed in a disposable container using a disposable stirrer then they were poured into the chamber of the Brookfield viscometer.

Viscosity Measurement

A Brookfield RV-II+ programmable rotational-type viscometer is used to perform isothermal viscosity measurements at the temperatures of 30, 45°C, 60°C & 80°C. For a given viscosity, the viscous resistance is related to the spindle rotational speed and the spindle geometry. In this study, the spindle used is disposable SC4-27, and the chamber used is disposable HT-2DB, both of them are specially designed for measuring sticky fluids. The clearance between the spindle periphery and the chamber inner wall is 3.15 mm. A temperature control unit maintains the sample at a fixed temperature. It is a fully computer controlled device with a well-defined menu system. The output data are viewed on a monitor in graphical and table form during the measuring time. For isothermal measurements, the sample chamber was preheated to the desired temperature and stabilized at that temperature for half hour. A water bath system was used to control the temperature. The sample was put into the chamber and measurement was started. The viscosity histories at different temperatures for each resin formulation are recorded with time.

**RESULTS AND DISCUSSION**
Viscosity Modeling

The viscosity profile of the DGEBA/TETA epoxy resin system with different hardener/resin ratio, as a function of time at different temperatures, is shown in Figs. (1) and (2).

The viscosity increased slowly at the beginning of each curing process, and then rose faster because of cross-linking reaction. At higher temperatures, the viscosity of the epoxy resin was initially lower, but then increased earlier due to the faster curing.

Based on the extent of the viscosity measurements, a model of viscosity for isothermal cure process of epoxy resin system is proposed and used to fit the experimental viscosity. As seen in eq. (16), the proposed viscosity model introduces two new parameters, the critical time t_c and final viscosity η_∞. All the parameters η_o, η_∞, t_c and k in eq. (16), are determined at the same time by fitting experimental viscosity with respect to time by nonlinear least square approach. The fitted curves are shown in Figs. (1) and (2). The predicted viscosities have very good agreement with the experimental data, even in the gel region. It seems clear that the viscosity profile at each temperature for a specific hardener/resin ratio can be well described by the proposed viscosity model. The regressed values of critical time t_c and rate constant k in eq. (16), for every hardener/resin ratio at each temperature are listed in Tables (1) and (2). The variation in critical time with respect to temperature is the same as one observed in gel time and can also be described by an Arrhenius law as eq. (17):
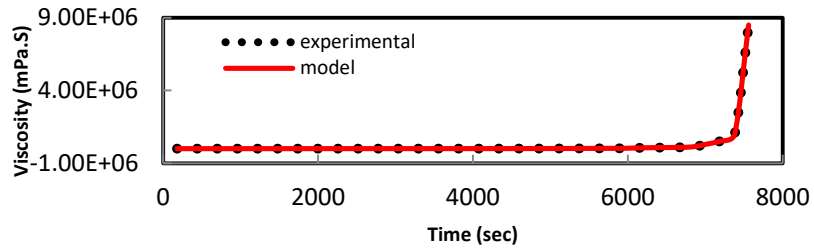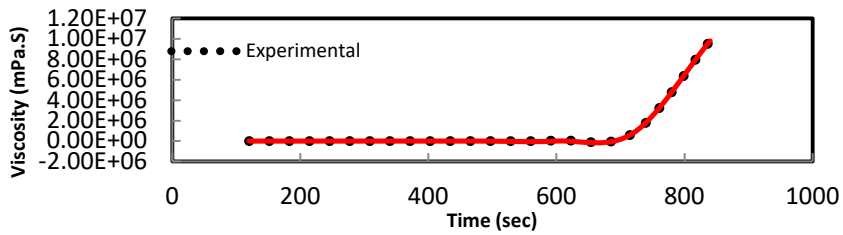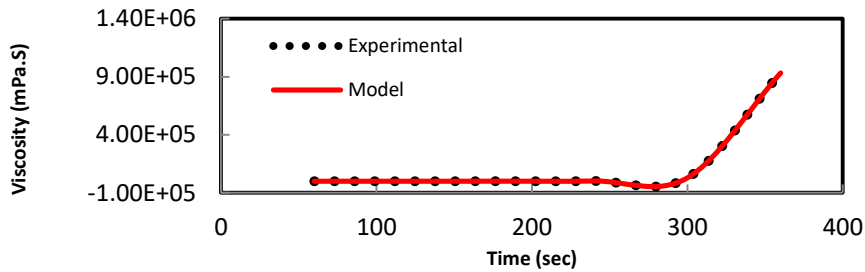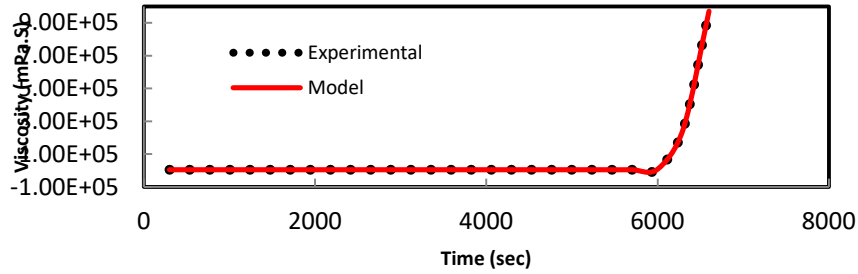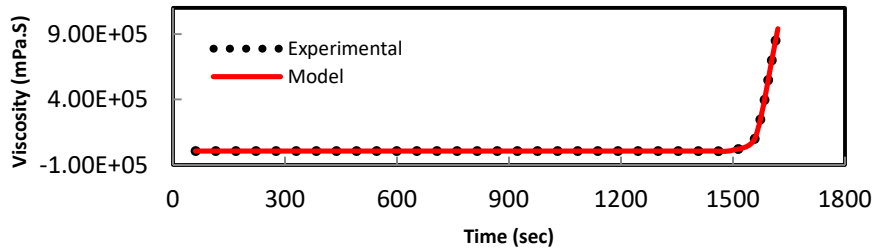
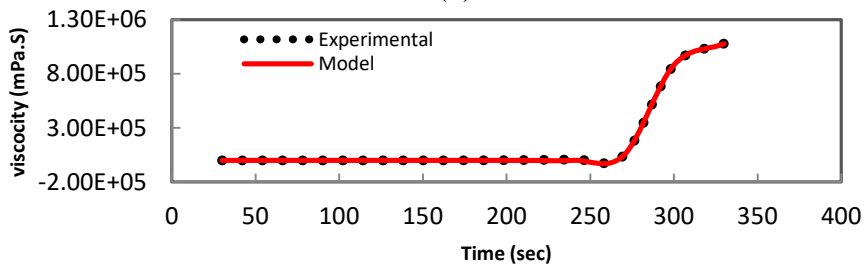**(a)**
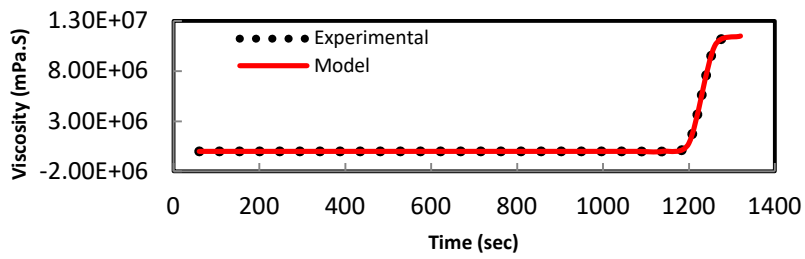
(b)

(c)

(d)

Figure (1): Experimental and calculated viscosity for DGEBA/TETA of 13 phr hardener/resin ratio at isothermal temperatures: (a) 30°C, (b) 45°C, (c) 60°C and (d) 80°C
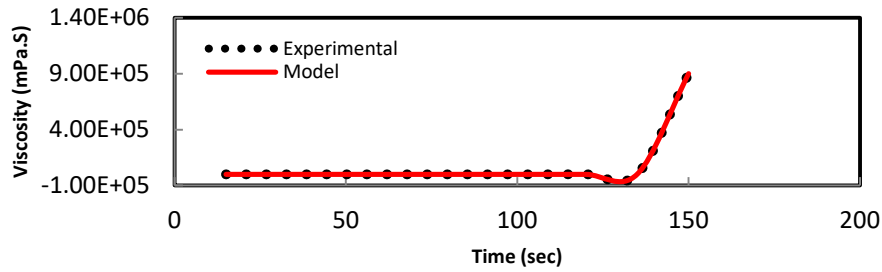

(a)

(b)

(c)

(d)

Figure(2): Experimental and calculated viscosity of the DGEBA/TETA system for 20 phr hardener/resin ratio at isothermal temperatures: (a) 30°C, (b) 45°C, (c) 60 °C and (d) 80°C

As seen in Figs. (3) and (4), there is a very linear relationship between the logarithmic critical time and the reciprocal of absolute temperature. The rate constant in eq. (16), also obeys an Arrhenius equation as a function of temperature. The relationship of ln k vs. 1/T and the linear fit are given in Figs. (5) and (6). The fitted values of pre-exponential factor and activation energies are listed in Tables (1) and (2).
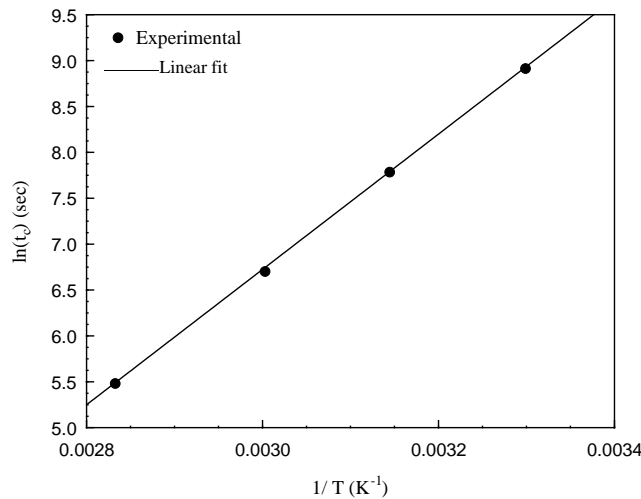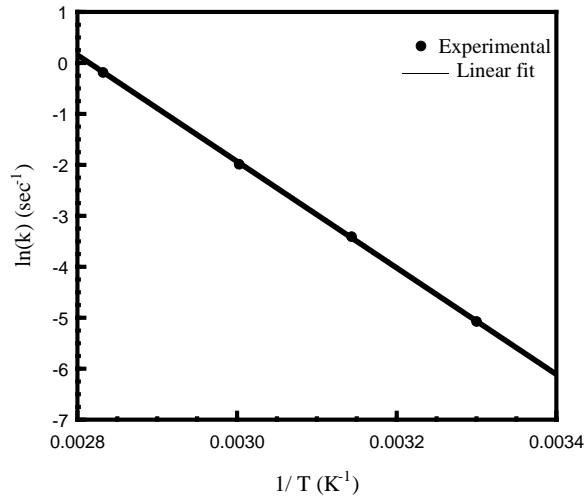

Figure (3): Critical time vs. Isothermal cure temperature of 13 phr hardener/resin ratio of DGEBA/TETA system
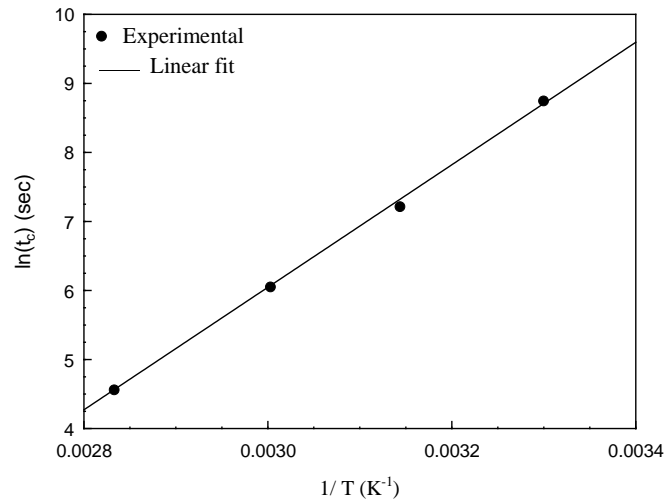
Figure(4): Critical time vs. Isothermal cure temperature of 20 phr hardener/resin ratio of DGEBA/TETA system
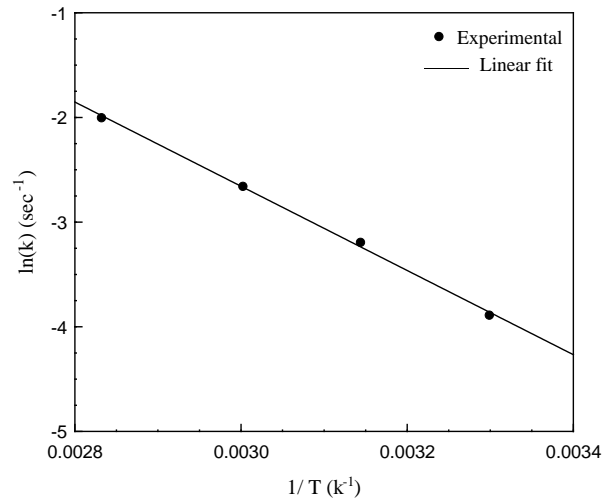
Figure (5): Rate Constant in eq. (16) vs. Isothermal Cure Temperature for the 13

phr hardener/resin ratio

Figure (6) Rate Constant in eq. (16) vs. Isothermal Cure Temperature for the 20 phr hardener/resin ratio

Table (1): Kinetic parameters in eq. (16) of the viscosity model for 13 phr hardener / resin ratio of DGEBA/TETA system

Temperature (°C)	tc (sec)	SE (sec)	K (sec^{-1}) ×10^{-2}	SE(sec^{-1})×10^{-3}
30	7510.99	2.18	1.80	0.60
45	2202.684	1.74	4.10	1.20
60	765.989	1.26	5.34	1.40
80	327.9047	0.31	12.93	1.30
Pre-exponential factor At (sec^{-1})	2.05052×10^{-7}			
SE (sec^{-1})	6.005×10^{-8}			
Activation energy Et (KJ/mol)	62.309			
SE (KJ/mol)	0.542			

Table (2): Kinetic parameters in eq. (16) of the viscosity model for 20 phr hardener / resin ratio of DGEBA/TETA system

Temperature (°C)	tc (sec)	SE (sec)	K(sec^{-1}) ×10^{-2}	SE(sec^{-1})×10^{-3}

30	6371.664	5.27	1.5	4.12
45	1586.236	2.18	8.2	3.26
60	290.225	0.20	15.32	2.84
80	155.282	0.10	43.81	1.42
Pre-exponential factor At (sec^{-1})	1.16563×10^{-9}			
SE (sec^{-1})	7.62×10^{-10}			
Activation energy Et (KJ/mol)	69.778			
SE (KJ/mol)	2.06			

Table (3): Gel time for the (13 and 20) phr hardener/ resin ratio at different temperature and activation energy

hardener/resin ratio	13 phr				20 phr			
Temperature (°C)	30	45	60	80	30	45	60	80
t$_{gel}$ (sec)	7560	2380	840	360	6600	1360	330	150
E$_a$ (KJ/mol)	63.64				67.19			
SE (KJ/mol)	0.95				0.41			

Fig. (7) represents the transient profile of the viscosity for a 13 phr of hardener/resin ratio at 45, 60 and 80 °C. When curing at 45 °C, the viscosity starts to increase after 16 minutes of cure. It can be noticed that after 10 minutes of cure at 60 °C, the viscosity starts to increase, and after some minutes, there is a sharp increase in the viscosity. While at 80 °C, the viscosity increased rapidly after several minutes of the cure. At this time, it was observed during the experiment that the resin became a gel-like material. The sharp increase in the viscosity, noticed at all temperatures, is due to the crosslink reaction. Therefore, this behavior occurs earlier at higher temperatures [24].
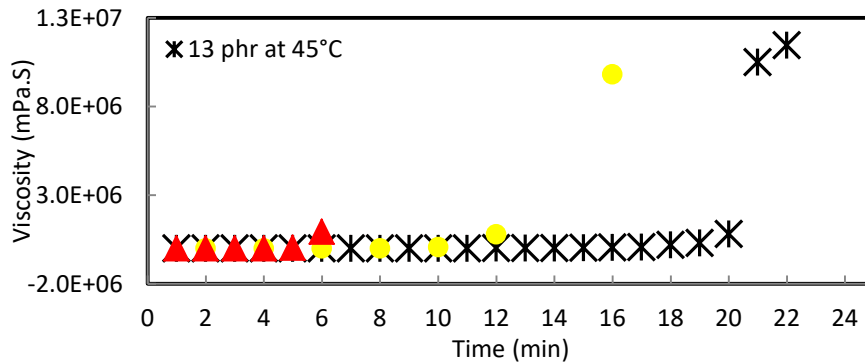
Figure (7): Viscosity versus cure time for 13phr of DGEBA/TETA system at 45, 60 and 80° C

The transient profile of the viscosity for the 20 phr hardener/resin ratio at 45, 60 and 80 °C is shown in Fig. (8). At 45 °C, the viscosity increased after 20 minutes of cure, several minutes a sharp increase in the viscosity is noticed. At 60 °C, the viscosity increases much faster than that for 13 phr hardener/resin ratio; within several minutes of cure it increases rapidly, in seconds of cure there's a sharp increase in the viscosity of the 20 phr hardener/resin ratio at this temperature; this is due to the higher amount of amino groups in this formulation where the crosslinking takes place in a short time depending also on the temperature which accelerate the curing process [22]. At 80°C, the viscosity increases in just 2 minutes of the cure, that's faster than at 60 °C and 45 °C which indicates that as the temperature was increased the epoxy resin reached the gel point faster and that means that the curing happens faster.
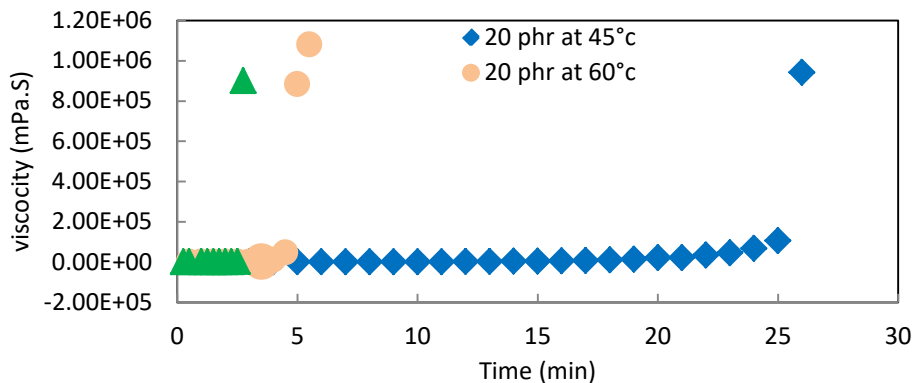

Figure (8) : Viscosity versus cure time for 20 phr DGEBA/TETA at 45, 60 and 80°C

Gel Time and Apparent Activation Energy (Ea)
During the isothermal reaction, a phenomenon of critical importance can occur, which is gelation. Gelation is characterized by the incipient formation of a material of an infinite molecular weight and indicates the conditions of the processability of the material. Prior to gelation, the system is soluble, but after gelation, both soluble and insoluble materials are present. As gelation is approached, viscosity is increased dramatically and the molecular weight goes to infinite; gelation doesn't inhibit the curing process [24].
The gel point of the cure process is closely related to rheological properties. It indicates the beginning of cross-linking for the cure reaction, where the resin system changes from a liquid to a rubber state. The gel time can be determined according to different criteria [25],[26]. The commonly used criteria for gel time are as follows:
• Criterion 1, the gel time is determined from the crossing point between the base line and the tangent drawn from the turning point of storage modulus G' curve [4],[27].
 • Criterion 2, the gel time is thought as time where the tangent of phase angle (tan δ) equals 1, or the storage modulus G' and the loss modulus G" curves crossover [26], [28].
• Criterion 3, the gel time is taken as the point where tan δ is independent of frequency [29], [30].

• Criterion 4, the gel time is the time required for viscosity to reach a very large value or tends to infinity [31].

In this study, the determination of gel time was based on the forth criterion. The values for gel time, determined from Fig. (1) and Fig. (2) by criterion 4, are listed in Tables (3) . As the isothermal temperature increases, the gel time decreases, where the temperature increases the crosslinking [27].

The relationship between gel time and temperature is analyzed by cure kinetics. The kinetic model as eq. (18) is used for the gelation analysis. Equation (22) shows the relationship between the gel time and isothermal cure temperature.

According to eq. (22), the semi-logarithmic plot of gel time vs. the reciprocal of the absolute temperature for the 13 phr hardener/resin ratio is drawn in Fig. (9). A linear fit of the experimental data gives a value for the apparent activation energy of 63.636 KJ/mol. The semi-logarithmic plot of gel time vs. the reciprocal of the absolute temperature for the 20 phr of hardener/resin ratio is shown in Fig. (10). A linear fit of the experimental data gives a value for the apparent activation energy of 67.192 KJ/mol.

It is interesting to note that the activation energies obtained from gel time in eq. (22) and the critical time in eq. (16), for the 13 phr hardener/resin ratio are close to each other, with the values of 63.64 and 62.309 KJ/mol, respectively. Also, for the 20 phr hardener/resin ratio 67.19 and 69.778 KJ/mol. The gel time for the above stoichiometric ratio 20 phr at all the temperatures is higher than that for the stoichiometric ratio 13 phr, that's due to the higher amount of amine groups which will speed the cross-linking, resulting in reaching the gelation in a shorter time.
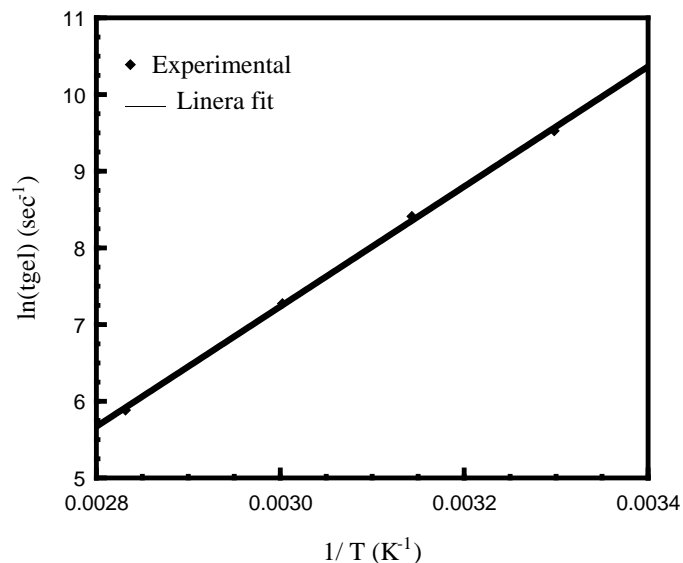
Figure (9) Gel time as a function of isothermal cure temperature for 13 phr hardener/resin ratio
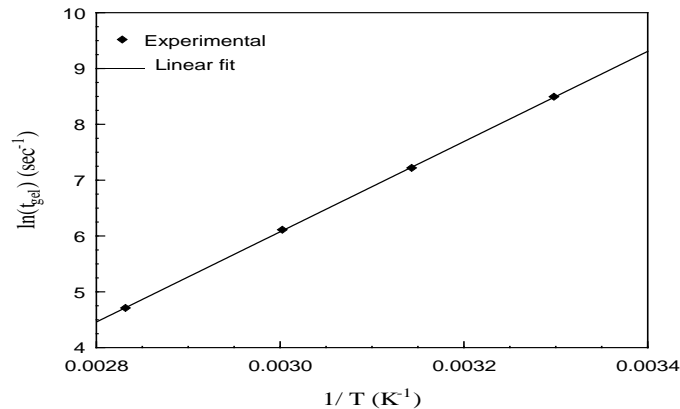
Figure(10) Gel time as a function of isothermal cure temperature for 20 phr hardener/resin ratio

CONCLUSION

1. The isothermal rheological measurements show that the gel time decrease with increasing temperatures for both stoichiomeric and above stoichiometric ratio (13 and 20 phr) of DGEBA/TETA system. The isothermal rheological measurements show that the gel time for the above stoichiometric ratio (20 phr) is lower than the stoichiometric ratio (13 phr) of DGEBA/TETA system at the four temperatures (30,45,60and 80) °C, that's due to the higher amount of amine groups. The relationship of gel time vs. temperature follows the Arrhenius law and thus the apparent activation energy can be obtained. The isothermal rheological measurements show that the viscosity increased slowly at the beginning of each curing process, and then rose faster because of crosslinking reaction. At higher temperatures, the viscosity of the epoxy resin was initially lower, but then increased earlier due to the faster curing.

2. During the curing process, the variation of viscosity vs. time is predictable by a model based on the Boltzmann function and it agrees very well with the experimental data, for both the stoichiometric and above stoichiometric ratios (13 and 20 phr). The critical time in the viscosity model decreases with the increment of the isothermal temperature and the relationship can be described by an Arrhenius equation, for both the 13 and 20 phr hardener/resin ratios. The activation energies determined by the gel time and critical time are close to each other.

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