A new method to characterize the cure state of epoxy prepreg by dynamic mechanical analysis

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ABSTRACT

Dynamic mechanical analysis (DMA) is an alternative method to chemical techniques in investigating cure processes. However, methods to evaluate mechanical cure state and kinetic analysis for incomplete isothermal curing have not been properly developed. The objective is to find a suitable method to characterize cure state of epoxy prepreg by DMA, and to better understand mechanical incomplete cure processes. Single cantilever mode was applied to the prepreg. A new method was proposed using the dynamic storage modulus data to estimate the cure state, and to calculate ultimate mechanical conversions. Based on this method, the incomplete cure phenomenon was investigated. A linear relationship of the ultimate mechanical conversions with isothermal temperatures was observed. Two types of conversion curves were seen at high and low temperatures respectively. The Kamal model with the diffusion effect was fitted to the incomplete isothermal mechanical conversion curves, and can well predict the mechanical conversions at high temperatures.

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1. Introduction

Thermosetting resins are widely used as adhesives or matrices in fiber-reinforced composites, with applications in a variety of industries, e.g., automotive, aerospace, oil and gas, and marine industries [1]. Curing of the matrix resin is a determining step in manufacturing thermoset composites, for the quality of thermoset composite parts is to a great extent controlled by the cure cycle. Therefore, a clear understanding of the curing mechanisms and the ability to develop suitable kinetic models to simulate cure processes are essential to predict and control the performances of resin composites [2–5]. Many advanced composites are constructed from thin laminating sheets known as prepregs [6]. A more accurate cure analysis, believed by some researchers, would be obtained by directly measuring prepregs rather than neat resins due to the influence of fiber reinforcements on cure [7].

Chemical analysis techniques such as differential scanning calorimetry (DSC) and Fourier transformed infrared spectroscopy that detect conversions of reactive groups are generally used to study cure processes of thermoset resins and prepregs. However these techniques are insensitive to the changes occurring at the last curing stage due to increased consumption of reactive groups. Moreover, because of apparent insensitivity to the changes in the mechanical properties of a developing polymer network, what

these methods provide are difficult to directly correlate cure state with structural properties. The cure kinetic models by these techniques are focused on predicting chemical state of resin rather than the resulting mechanical properties. Since mechanical properties of thermosets depend on the thermal history of cure, it is of practical interest to develop kinetic methods which can predict the mechanical properties during cure [8–12].

An alternative technique to the traditional chemical analysis is the widespread and powerful technique, dynamic mechanical analysis (DMA). In its most common sense, DMA comprises all the techniques that apply a certain mechanical strain to the sample and measure the resulting mechanical stress by sensors [13]. It is also usually distinguished from rheologic techniques [14–16], by which the viscosity of the initial stage of curing (till gelation) are generally studied. As to DMA, it is the viscoelastic properties and the latter stage of curing (after gelation) that are generally investigated. Based on the changes in the mechanical properties, DMA can detect cure development and important transitions in the cure process such as gelation and vitrification [11,17,18]. It is also utilized to study the cure-induced residual stresses in thermoset resins [19]. In contrast to chemical analysis, DMA provide information on the mechanical behavior during the cure cycle, where thermosetting resin converts from a viscous liquid to a cross-linked solid; it is more sensitive to the transitions in the cure processes, and more suitable for practical property study. Moreover, it remains a high sensitivity to the last cure stage. Several dynamic mechanical analysis methods have been developed in the literature to study the cure processes, such as TBA [20,21], DTVM [8], DMTA [17,22] and photo-DMA [23], which

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differ in sample preparation, the accuracy in cure analysis and the mechanical parameters due to different loading modes. Samples are often applied to a support [10,18,20,21] or cured beyond the gel point before testing [11]. In the former circumstances accurate analysis requires the support not to significantly influence the values of dynamic mechanical data (e.g. E', E'' and $\tan \delta$) [17].

Although DMA technique has been widely used to explore the cure process in many aspects, generally the majority of the application of DMA to the curing is to obtain the glass transition, gelation, and vitrification points[6,18,20], which is complementary to chemical analysis methods. There are limited reports for mechanical cure state characterization and mechanical cure kinetic modeling by DMA, i.e. the estimation of the mechanical state of curing and the kinetic analysis based on dynamic mechanical measurements. Some authors used the difference in the storage modulus ($\Delta E'$) before and after cure, or the $\Delta E'$ normalized by the minimum E', or the maximum E' divided by the minimum E' to provide a qualitative view of the cure extent of the thermosets [11]. The most common mechanical cure state definition in the literature [8,16,17,22,24–27] is on the basis of the measured mechanical property as follows:

$$\alpha = \frac{M_t - M_0}{M_\infty - M_0} \qquad (1)$$

where α is the mechanical conversion of the cure state; M_t, M_0 and M_∞ are the measured mechanical property at the moment of time t, the onset (uncured) and the completion (fully cured) of reaction process respectively. As a universal definition, it can be used in a variety of testing circumstances. M can be any kind of mechanical parameters which represents the mechanical state of cure, such as storage modulus, complex modulus or torque, and it can be shear modulus G, flexural modulus E or any form of mechanical properties depending on the mode of the loadings. The meaning and value of the mechanical conversion α vary according to the specific mechanical property M, of which the selection should be in accordance with the demand property in application. The basic idea of this universal definition of conversion is simple and rational. However, due to the poor repeatability and high dispersibility of the measurements of M between samples, the parameters in Eq. (1) can hardly be obtained in different experiments. Usually, only one single experiment was conducted to assess the evolution of mechanical conversions based on the relative increment of M in the experiment. The minimum and maximum value of M during the test is assumed as the uncured and fully cured state respectively. Therefore, its accuracy would be strongly influenced by the actual initial and the ultimate cure state of the samples, which would departure from the assumed state due to a precure during the storage period or an incomplete cure at the end of the testing. This definition has so far only been applied to isothermal cure process to calculate relative degree of mechanical cure, or to characterize the curing above the limit glass transitional temperature $T_{g\infty}$ (the glass temperature of the fully cured resin) that full cure can be obtained. There were two other definitions of mechanical cure state in the literature by using the glass temperature T_g [10,21,28], or $\Delta \tan \delta$ the area under the $\tan \delta$ curve [17,29] as the indicator of the cure state. The definitions were as follows:

$$\alpha = \frac{T_g - T_{g,0}}{T_{g,\infty} - T_{g,0}} \qquad (2)$$

$$\alpha = \frac{\Delta \tan \delta - \Delta \tan \delta_0}{\Delta \tan \delta_\infty - \Delta \tan \delta_0} \qquad (3)$$

where the subscripts ∞, 0 refer to the fully cured state and the uncured state respectively. These definitions can be conveniently used to estimate the cure state of a partly cured sample, and can be applied to the curing under a variety of temperature conditions. However, they provide only indirect measurements of the mechanical property during the cure process. Moreover, a large number of samples would be needed for analyzing one cure process, because

just one single point of conversion was obtained per sample and sample deviations may not be ignored. The non-equilibrium thermodynamic fluctuation theory, the Avrami equation, the Flory's gelation theory [8], the autocatalytic kinetic model [16,22,27], and the recent isoconversional method [17] were applied to mechanical cure kinetic analysis in the literature. These methods were mostly used on the basis of the definition in Eq. (1), and were applied to describe the evolution of the relative degree of mechanical cure or the isothermal cure process beyond $T_{g\infty}$ that the resin can be fully cured.

If cure is performed at a temperature below $T_{g\infty}$ the thermosetting system cannot reach full cure due to vitrification and diffusion effect, which is a common phenomenon in thermosets. In actual processing of thermoset materials, the curing temperature is often lower than $T_{g\infty}$. Therefore an accurate characterization of incomplete cure is very important to give a more realistic description of the cure evolution after vitrification [5]. However, for mechanical cure analysis, no research has so far been reported in the literature to characterize and model this phenomenon in isothermal cure processes by DMA. The purpose of this paper is to seek an appropriate technique to evaluate the mechanical cure state of the incomplete isothermal cure process by DMA, based on which a better understanding of the mechanical isothermal cure processes can be obtained. A glass fiber/epoxy prepreg was investigated in order to reveal the evolution of the mechanical property of the composite during cure process. The dynamic mechanical properties of the prepreg during isothermal cure processes were directly measured (without any supports) by the single cantilever mode of a DMTA instrument. A new method to properly characterize the cure state of the prepreg by DMA was provided on the basis of the dynamic storage modulus data, so that the mechanical cure state of the partly cured samples and the maximum mechanical conversion of the incomplete isothermal curing can be easily estimated. The autocatalytic model and the diffusion effect were applied to the mechanical conversion data for analyzing the mechanical cure kinetics of the prepreg.

2. Experimental

2.1. Materials

The resin used in the study was a phenol novolac epoxy resin (EPN, F-46) from Shanghai Resin Factory Corporation. Boron tri-fluoride monoethylamine complex (BF$_3$-MEA) obtained from Beijing Changyang Zhenxing Chemical Co. was selected as the curing agent of the epoxy resin. The glass fiber SC8-12 × 20 FE-5 from Nanjing Fiberglass Research & Design Institute was an untwisted roving and used as the reinforcement. All the raw materials were used without further treatment.

2.2. Sample preparation

The resin system was prepared by dissolving the EPN and the required amount of BF$_3$-MEA (3 phr by weight of EPN) in acetone to mix them together. The curing reaction scheme of epoxy resin initiated with BF$_3$-MEA was shown in Fig. 1. It follows a single cationic polymerization mechanism. The resin system is a high temperature curing system with the cure reaction temperature ranging from 100 °C to 220 °C (dynamic DSC test by a heat flux DSC-SP instrument from Rheometrics Inc., 5 °C/min). The solution impregnation method was used to manufacture the unidirectional prepreg, of which the resin content was controlled to be 30% by weight and the volatile content is below 1.0 wt%. The prepreg was put into the refrigerator for storage. For DMA testing, first let the prepreg defreeze to the room temperature, then cut it into a rectangular

(a)

(b)
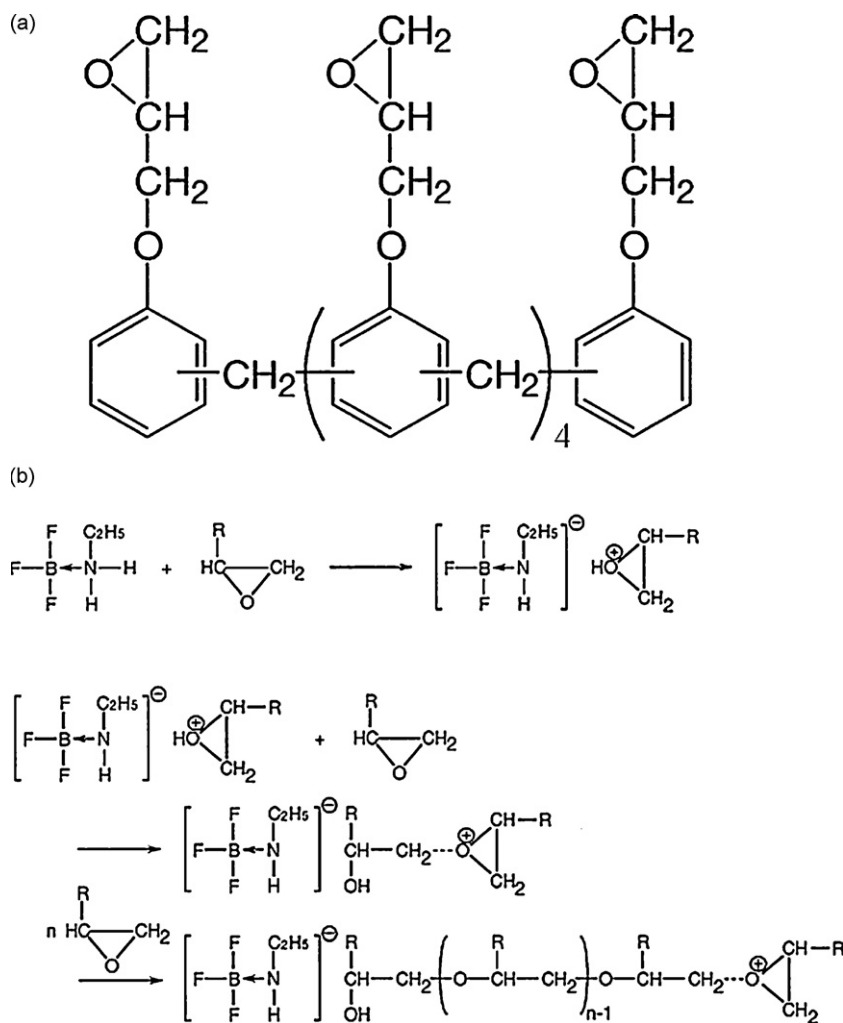
Fig. 1. The chemical structure and the reaction scheme of the matrix resin system. (a) Molecular structure of the EPN and (b) curing reaction scheme of epoxy resin initiated with BF3-MEA [30].

specimen by 20.0 mm × 6.0 mm × 0.20 mm (5.0 mm free length in DMTA measurement). All the testing samples were made of one layer of the prepreg. And the longitudinal direction of the fiber in the prepreg was parallel to the length of the samples.

2.3. Dynamic mechanical analysis experiment

The DMA measurements were carried out by constant strain control mode in a single cantilever clamp of DMTA-IV equipment from Rheometrics Inc. which continuously measures force (F), displacement (D) of the drive shaft and phase angle (δ) between stress and strain vectors during tests. The storage modulus E', loss modulus E'' can be obtained automatically by the following equation:

$$E' = \frac{l^3}{wt^3} \frac{F}{D} g \sin \delta$$
$$E'' = \frac{l^3}{wt^3} \frac{F}{D} g \cos \delta$$

(4)

where l is the sample length dependent on the size of the frame chosen, w, t are the width, thickness of the sample respectively, g is the gravitational constant. According to the above formula the accuracy of the DMA measurements was highly dependent on the accuracy of sample geometries.

The sample loading of the single cantilever mode was shown in Fig. 2. Due to a semisolid mechanical behavior of the prepreg and a

broad modulus measurement range of the single cantilever mode, the dynamic mechanical properties of the prepreg during isothermal cure processes can be directly measured without any extra supports for samples. So the measuring results would avoid the influence of the support and would be closer to the actual mechanical properties of the composite parts during cure processes.
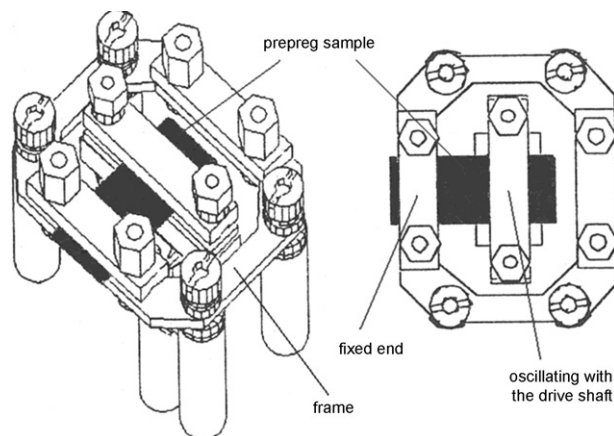
Fig. 2. Scheme of the measuring system in DMA.

Aluminum foils were used to wrap the ends of the unidirectional prepreg to prevent it from undesirable deformation during test meanwhile not to interfere with the testing of the sample. Then the ends of the specimen were clamped to the rigid frame. During test one end of the sample is oscillating up and down with the drive shaft while the other end is fixed to the frame. A strain sweep experiment was conducted first to confirm the linear viscoelastic region based on which the amplitude of the dynamic strain was determined. Then the dynamic time sweep tests (isothermal curing tests) were performed in the following conditions: frequency = 1 Hz, strain amplitude = 0.01% in a set temperature ranging from 110 °C to 240 °C. Considering an incompletion of isothermal cure below 220 °C due to a diffusion effect, after the isothermal runs, the partly cured samples were rapidly cooled down and post-cure test was conducted later at a temperature of 240 °C which was high enough for the sample to be fully cured. The limit glass temperature ($T_{g\infty}$) was measured by temperature ramping experiment on the fully cured samples and was set as the endpoint of the glass transition region [31].

3. Results and discussion

A typical isothermal curing plot of the prepreg measured by DMTA at 1 Hz was shown in Fig. 3, including the storage modulus E', the loss modulus E'' and the loss factor $\tan\delta$. The whole process including three stages can be properly displayed by the above-described method (see Section 2). In the first curing stage E' is decreasing continuously while $\tan\delta$ and E'' are rising upward to a maximum point then falling down. The decreasing of E' is slow at first then accelerated and at last slows down again to an approximate plateau and reaches a minimum value. Note that the major part of this stage is under a rapid temperature rise condition (the heating rate is about 30 °C/min) before the instrument and sample achieve the set temperature, this stage can be roughly considered a physical softening process caused only by the temperature. The peak of $\tan\delta$ in this stage indicates the glass transition point of the softening process. The second stage is a rapid increasing period for E', where $\tan\delta$ continues to decrease and E'' increases to a peak then decreases. The peak of E'' in this stage is corresponding to the gelation transition. And the point that the storage modulus began to increase is taken as the start of cure process in this research. The third stage is a slow evolution of all three dynamic mechanical parameters. The small peak in E'' or the shoulder in $\tan\delta$ indicates the vitrification transition.
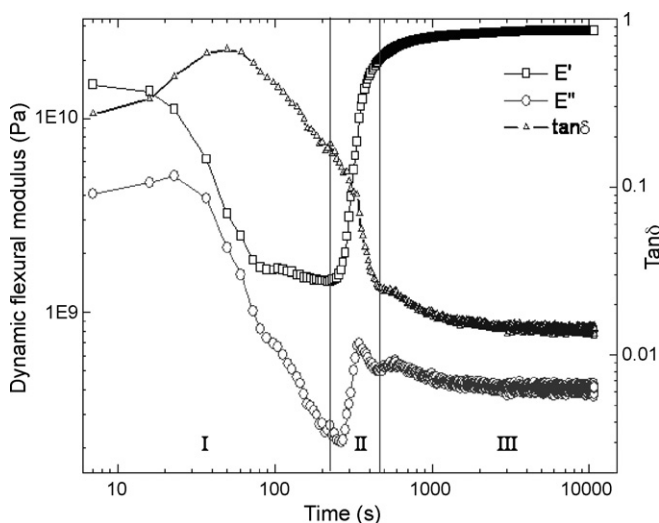

Fig. 3. Typical isothermal measurement of prepreg by means of DMA.
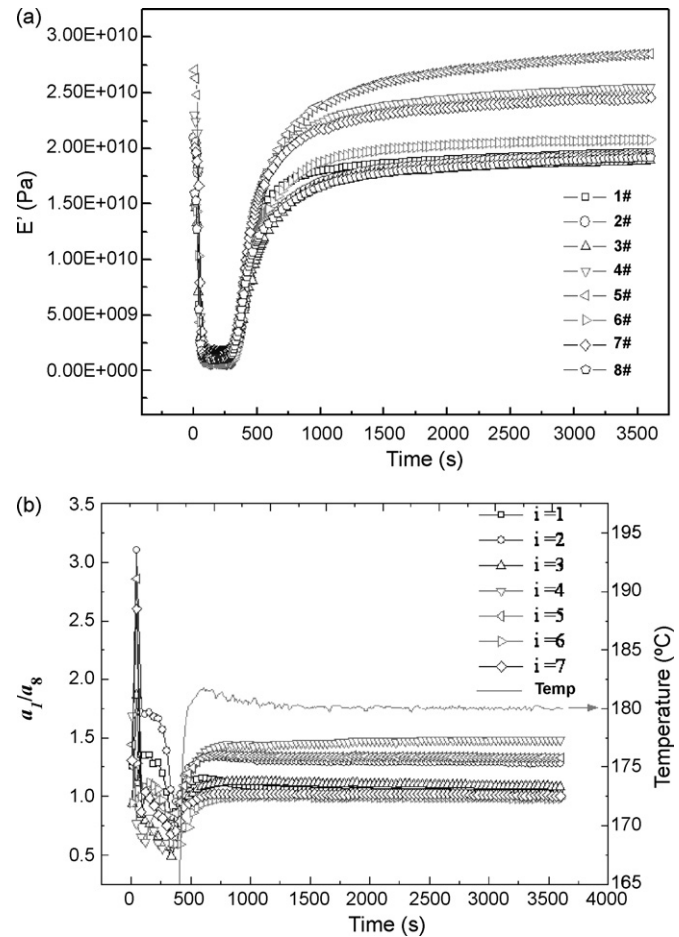

Fig. 4. Typical repeatability experiments of isothermal curing by means of DMA. (a) Plots of storage modulus vs. time during isothermal cure for eight identical samples. (b) Ratio of the modifying factors a_i/a_8 using the No. 8 sample as reference where subscript i refer to the mark number of the sample.

3.1. Incomplete isothermal curing analysis

In calorimetric cure analysis the ultimate extent of incomplete cure can be estimated by dividing the isothermal heat output by the total enthalpy obtained from the dynamic runs. However in mechanical cure, no investigation has so far considered the incomplete ultimate state in defining mechanical conversions and in calculating mechanical cure kinetics for incomplete isothermal cure. The reason may due to high data dispersibility of repetitive experiments of dynamic mechanical properties and the corresponding difficulty in direct comparing absolute values of dynamic mechanical properties in different experiments, which were also observed in our measurements. This phenomenon was a consequence of multiple random measuring errors but mainly of the indeterminate dimension errors caused by the actual difficulty in getting accurate size of the deformable semisolid state prepreg. In other circumstances of samples with extra supports the poor repeatability could come from the incontrollable sample thickness such as coatings and the influence of the support materials.

3.1.1. Measurement error treatment

In order to eliminate the impact of the above-mentioned repeatability problem, repeatability experiments were conducted on the same batch of samples and indicated the 20–40% relative error in dynamic mechanical modulus as shown in Fig. 4(a) were to a large extent due to the inaccuracy of the sample dimensions. One way to diminish the dimensional errors is to enlarge the sample

sizes however it will cause other measurement troubles and errors such as temperature gradient in the testing sample, the shear component error in measuring flexural modulus. Another method to tackle this problem is to directly eliminate the difference between measured values of different experiments on the same batch of samples. As stated by Eq. (4), sample dimensions are multiplication factors in the modulus formulas, therefore by multiplying a modifying factor a the measured $E'_{measured}$ can approach the truth value of E'_{truth} as depicted in following equation:

$$E'_{truth} = E'_{measured} \frac{w_{measured} t^3_{measured}}{w_{truth} t^3_{truth}} = E'_{measured} a \qquad (5)$$

where the subscripts "measured" and "truth" denote the measured value and truth value respectively. When two prepreg samples of the same batch (of the same matrix resin system and of the same structure with fiber and resin) are at an identical mechanical cure state, the following expressions can be obtained:

$$E'_{1truth} = E'_{2truth}$$
$$E'_{1measured} a_1 = E'_{2measured} a_2 \qquad (6)$$
$$E'_{1measured} = E'_{2measured} \frac{a_2}{a_1}$$

where the subscripts 1, 2 refer to the mark numbers of the two samples. If the dimensions of the sample are changing, then the modifying factor a is not a constant during the cure. However if the dimensional changes are dimension proportional, the ratio of modifying factors of the two samples at the same mechanical cure states will be constant. Therefore two individual dynamic modulus curves of the curing under the same measuring conditions can be correlated to each other by multiplying one curve by the ratio of the modifying factors of one to the other at the identical mechanical cure state (as depicted in Eq. (6)) which is equal to the ratio of measured values of the two samples. Fig. 4(b) depicted the modifying factor ratios of the samples to the reference sample respectively during isothermal testing from repeatability experiments. It can be observed from Fig. 4(b) that the modifying factor ratios of two identical samples were constant under stable isothermal conditions, which means that the pretreatment of modulus data would be effective under stable isothermal conditions. Note that this error treatment was conducted between samples of the same batch with the same chemical composition and the same physical structure; it was supposed that each sample bears the identical dynamic mechanical properties at the identical mechanical cure state. Moreover, this treatment aimed at eliminating the poor repeatability of dynamic mechanical property testing of the same batch of samples, so it cannot be executed for samples with different structures or chemical compositions or under different testing conditions such as temperatures and frequencies. Based on this treatment a more proper definition for incomplete cure state by DMA would be possible.

3.1.2. Mechanical cure state definition

The cure states here in the dynamic mechanical analysis referred to the mechanical conversions, i.e. the conversion of the mechanical properties of the samples from uncured state to the completely cured state. A new definition for incomplete cures based on dynamic mechanical analysis is provided in this article. It is a modification of the above definition in Eq. (1) considering the maximum extent of mechanical conversions for the isothermal cure based on both the isothermal measurements and the post-cure data. The post-cure testing was conducted at 240 °C to reach the completely cured state after the first isothermal measurement. And the original post-cure data were pretreated by the above methods in the previous section by choosing the whole modulus curve of uncured samples at 240 °C as the reference curve and assuming completely
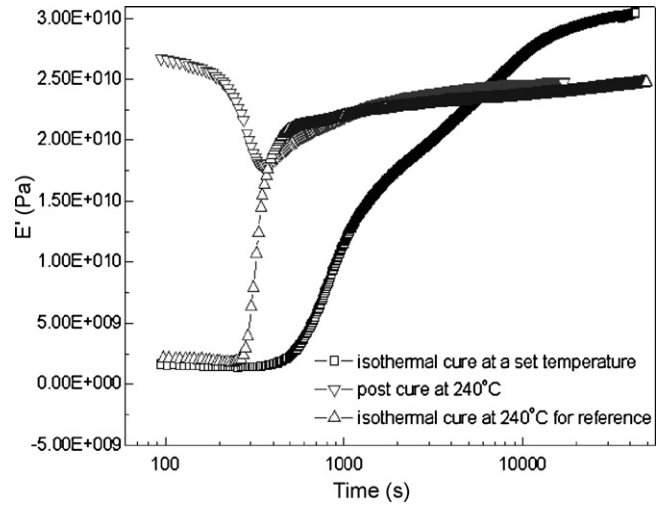

Fig. 5. Typical modulus curves for mechanical conversion definition.

cured state as the identical state. Thereafter the post-cure data in this paper would refer to the pretreated data. The typical plots for mechanical cure state evaluation were shown in Fig. 5 including the storage flexural modulus curves of the isothermal cure, the post-cure and the reference mechanical curve of uncured sample at 240 °C.

Prior to the definition some assumptions and simplifications have to be made. First it is assumed that no reaction occurred in the initial decreasing period of the storage modulus curve and the minimum point of the modulus is considered to be the uncured state and the start of isothermal curing. Note that due to the actual difficulty in putting samples in DMTA after the setting temperatures are attained, samples must go through a rapid heating-up period before achieving the set temperatures, so when it is set high (in this paper is above 200 °C) the onset of the isothermal curing would be in the temperature ramping period and it is impossible to obtain the truth minimum value of the reference curve of uncured sample at 240 °C. However as seen from Fig. 5, deviations between the initial values of E' plateaus of the normal isothermal cure curve and the reference curve could be negligible, which was also observed under other isothermal temperatures. So it is assumed the minimum value of the E' curve that is regarded as the start of cure is independent of the temperature, and the minimum value of the reference 240 °C E' curve is taken as the truth value of the uncured state at 240 °C. Second due to the increased difficulty to detect the change of the storage modulus at the very late stage of the isothermal cure, the end of the isothermal cure is taken as no more increase in the storage modulus for at least 1000 s and the maximum modulus is referred to the end state of the isothermal curing samples. Note that the accuracy of the calculated maximum mechanical conversion is affected by the accuracy in estimating the end point of the isothermal curing that is dependent on the criterion for assessing the change of modulus. More strictly the criterion is set more accurate the calculated conversion would be obtained.

The ultimate mechanical conversion of an isothermal cure process can be evaluated by comparing the post-cure data to the reference cure curve of uncured sample, based on which the mechanical cure state definition of an isothermal cure process can be carried out as follows:

$$\alpha_{max} = \frac{E'_{post\,cure,min} - E'_{reference,min}}{E'_{reference,max} - E'_{reference,min}}$$
$$\alpha = \frac{E'_{T,t} - E'_{T,min}}{E'_{T,max} - E'_{T,min}} \alpha_{max} \qquad (7)$$

where α, α_{max} are the conversions at a given time t and the maximum conversion of the isothermal curing respectively; $E'_{post\,cure,min}$ is the minimum value of pretreated post-cure modulus curve; $E'_{reference,min}$, $E'_{reference,max}$, are the minimum and maximum E' value of the reference cure curve of uncured samples respectively; and $E'_{T,t}$, $E'_{T,min}$, $E'_{T,max}$, are the storage flexural modulus at time t, the minimum and maximum value of E' of the isothermal cure process respectively. Repeatability experiments have indicated a good precision in obtaining maximum conversions of isothermal cures with a 2% relative error (the ratio of the maximum deviation between conversion values to the mean value of the conversions) in this research. The first part of the definition in Eq. (7) can be used not only for maximum conversion of isothermal cure process but also for any other degree of mechanical conversion that attained at any time of the cure process under a variety of temperature conditions. Moreover, note that this new definition is established on the basis of the previous universal definition of mechanical cure state, so the basic idea and the method used would not be restricted by the structure forms of the curing samples (i.e. the prepreg in this article) or by the loading modes on the sample. Based on this new mechanical cure definition, the degree of mechanic property accretion during incomplete isothermal cure can be described and more hidden cure mechanisms such as the diffusion effect at the latter isothermal cure stage can be examined by dynamic mechanical analysis in a similar way to the traditional calorimetric cure analysis. In this work, the application of the definition for incomplete isothermal cures is to obtain the conversion curves during cure and analyze mechanical cure kinetics.

3.2. Isothermal mechanical cure curves

The mechanical cure curves (i.e. the mechanical conversion curves during cure) on the basis of the above cure definition at each temperature were shown in Fig. 6. It can be observed that the mechanical conversions quickly rise up after a short plateau period at the initial stage, then slower down during a major part of the cure process, and finally reach to a practically constant value indicating the stop of the cross-linking which is caused by the increasing of molecular mass and high hindering mobility. Two types of conversion curves can be observed in Fig. 6. One is the curves at the low temperature region of 110–140 °C which includes a distinct transitional region, while the other type of the curves at the higher temperature region do not have. This indicates that different mechanisms exist in the mechanical cures in different temperature regions. Similar observation of isothermal cure behavior by TBA was
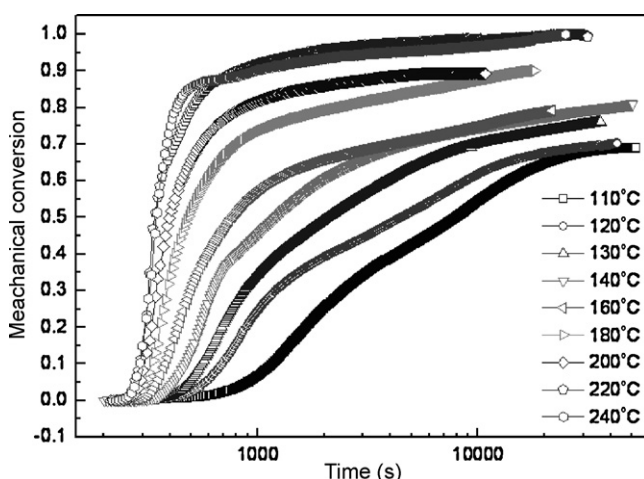

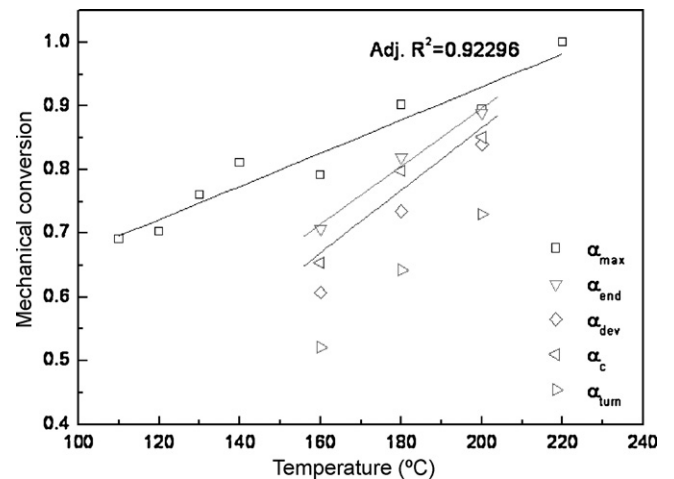**Fig. 6.** Mechanical conversion curves during isothermal cures.

Fig. 7. Critical conversions at different temperatures.

reported in Gillham's research [32]. The transitional regions at low temperatures have not been observed in DSC characterizations in the literature for curing systems with a single cure mechanism as studied here, which may be a specific feature of mechanical cure.

An approximately linear relationship between the maximum conversion α_{max} and the isothermal temperature T can be seen in Fig. 7 and described as $\alpha_{max} = 0.414 + 0.00258T$ ($T \geq 220\,°C$) where T is the temperature expressed in °C. This result was similar to the reported results of other thermoset systems by chemical analysis in the literature [33–35]. The deviation of experimental points from the linear fit in Fig. 7 may be caused by the above-mentioned measurement errors and the inaccuracy of the assumptions. Using this linear relationship, the percentage of the increase in storage modulus of the prepreg from uncured to the fully cured state under a certain temperature can be calculated.

3.3. Phenomenological kinetic models

The kinetic models based on the above mechanical cure state definition are to describe the evolution of the mechanical conversions during cure process. In general, kinetic models can be classified into two categories, phenomenological models and mechanistic models. The intrinsic kinetic mechanisms for the mechanical cure process are very complex involving the impacts of the cure reaction and the structure that relates to the cure state. Therefore it is very difficult to establish the mechanistic models, and the phenomenological or empirical models which relate to the main features of the process would be preferred in the paper. The phenomenological kinetic models for cure reaction process measured by the chemical analysis methods have already been successfully applied to several thermoset resins in the literature. For mechanical cure process, cure reaction is still the main cause for the evolution of the mechanical conversions. Therefore it would be possible to apply empirical cure kinetic models to the mechanical cure processes to investigate mechanisms of the evolution of the mechanical conversions. Furthermore, it may provide a possibility for future comparison between the mechanisms of evolution of the two conversions in cure processes. It should be noted that when applying cure models to mechanical cure process the meanings and the values of the parameters in the models would be different from those in chemical analysis. The autocatalytic model and the diffusion effect model were used for kinetic analysis in this research.

3.3.1. Autocatalytic kinetics model

The most frequently used phenomenological cure kinetic model is an autocatalytic model proposed by Kamal et al. as shown
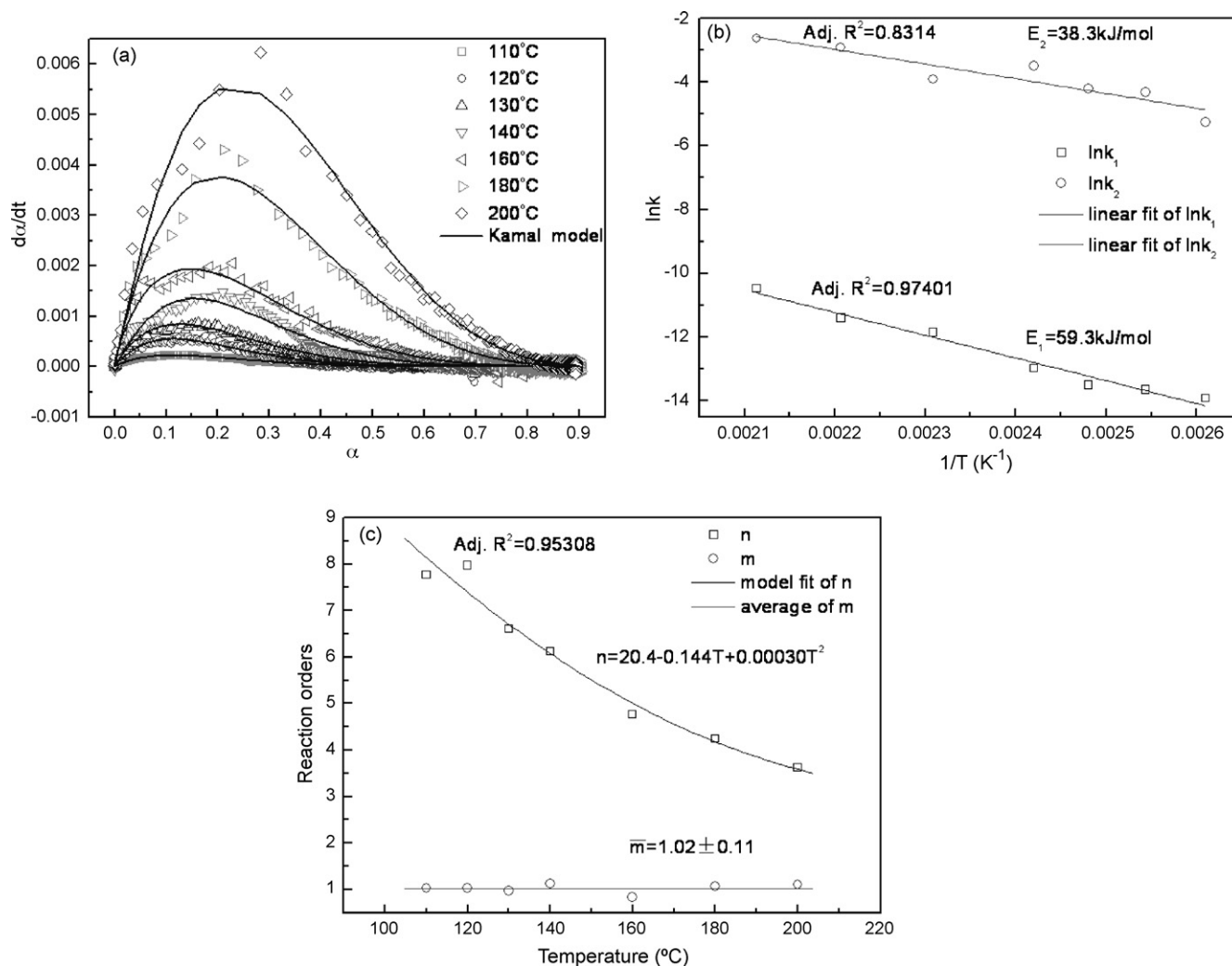
Fig. 8. The kinetic parameters at different isothermal temperatures. (a) Conversion rates vs. conversion, (b) Arrhenius plots of rate constants k_1 and k_2 and (c) plots of exponents in Eq. (8) vs. temperature.

in Eq. (8).

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n$$

$$k_1 = A_1 \ \exp\left(-\frac{E_1}{RT}\right), k_2 = A_2 \exp\left(-\frac{E_2}{RT}\right)$$

(8)

where α is the fractional conversion, $d\alpha/dt$ is the reaction rate, m and n are the reaction orders of the autocatalytic and n order paths respectively, k_1 and k_2 are the rate constants assumed to be constant at a given temperature and follow an Arrhenius temperature dependence. A_1, A_2 are the pre-exponential factors, E_1, E_2 are the apparent activation energy, R is the gas constant, and T is the absolute temperature. In the literature this model has made good predictions for early cure stages of many thermoset resin systems by DSC, but deviations were observed in the later stages particularly near vitrification when the reaction is primarily diffusion controlled [36]. The typical feature of this autocatalytic model is that reaction rate is not zero at the beginning and attains a maximum value at some intermediate conversion.

Fig. 8 depicted the main results of the fitting procedure of applying this model to mechanical conversion data of the isothermal cure processes. As can be seen in Fig. 8(a), the conversion rate increases with the temperature and the maximum conversion rate is at a conversion of 10–30%, similar to the results of epoxy systems with the maximum reaction rates at the generally reported

40–50% conversions by means of DSC. The difference in the conversion range may due to the different natures of the two conversions. For calorimetric cure, the cure conversions represents the chemical conversions, while for mechanical cure it represents the mechanical and structure conversions. And the values of conversions evaluated by these two characterization methods would be different as can be seen in some researches [17,24,29]. The constant rate k_1 can be simply obtained from the initial conversion rate when $\alpha = 0$. The other kinetic parameters k_2, m, and n of Eq. (8) were made to fit the experimental data in Fig. 8(a) by nonlinear curve fitting using Mathematica 5 software. The fitting curves were also shown in Fig. 8(a). A good agreement between experiment data and the fitting curves can be observed. A linear fit of $\ln k_i$ ($i = 1$, 2) vs. $1/T$ as seen in Fig. 8(b) were to calculate parameters in the Arrhenius expressions in Eq. (8). Fig. 8(c) showed the estimated exponents in Eq. (8) at different isothermal temperatures, of which m is 1.02 on the average and n can be estimated by a polynomial expression $n = 20.4 - 0.144T + 0.0030T^2$ (where T is expressed in °C). The values of the exponents and the constant rates were similar to the results reported in the literature of epoxy/BF$_3$-amine systems by DSC [37,38].

The fitted isothermal conversion curves were shown in Fig. 9(a) and (b), which were in a good agreement with the experimental data at the initial part of curing but deviated from the latter part of experimental curves at all temperatures. Two kinds of devia-
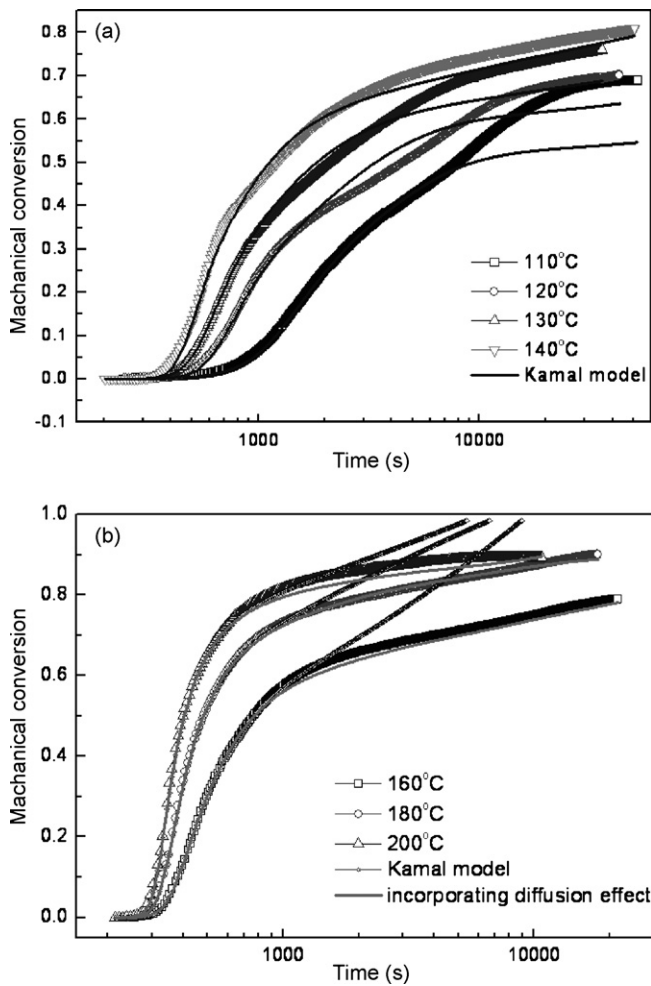
Fig. 9. The isothermal mechanical conversion curves fitted by different models. (a) Low temperature conversion curves and (b) high temperature conversion curves.

tions were observed. One occurred at the low temperature region where the theoretical curves deviated from the experiment curves since the beginning of the transitional regions and were much lower than experimental values at the final cure stage. The other was of the high temperature region with curves of no transitional regions where the simulation curves were deviated above the experimental data since a certain conversion α_{dev}. The latter kind of departure was similar to the reported results in the literature of fitting autocatalytic model to isothermal cure data measured by DSC, of which the reason was considered due to the vitrification of resin and a diffusion controlled cure mechanism [39]. The relationship of the α_{dev} with the isothermal temperature was shown in Fig. 7. And the diffusion effect would be added to the Kamal model to describe the latter part of conversion curves in high temperature range in the following section.

3.3.2. Incorporating diffusion effect

In the literature the typical approach to mathematically treat the diffusion controlled mechanism is using the overall effective rate constant K_e which is expressed in terms of the diffusion-controlled rate constant K_d and the rate constant for chemical kinetics K_c as follows [40]:

$$\frac{1}{K_e} = \frac{1}{K_d} + \frac{1}{K_c} \tag{9}$$

Then a diffusion factor $f(\alpha)$ is defined based on free volume considerations and a semi-empirical model by Cole et al. [41] and

Chern and Poehlein [42]:

$$f(\alpha) = \frac{K_e}{K_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \tag{10}$$

where C is a constant that depends on the structure, system and curing temperature, α_c is the critical conversion. For $\alpha \ll \alpha_c$ the diffusion factor $f(\alpha)$ approximates unity, the effect of diffusion is negligible and the reaction is kinetically controlled. As α approaches α_c, $f(\alpha)$ begins to decrease and approaches zero as the reaction effectively stops. The overall effective reaction rate is equal to the chemical reaction rate multiplied by this factor as depicted in Eq. (11); here the Kamal model is used to express the chemical controlled kinetics:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n f(\alpha) \tag{11}$$

Fig. 10 depicted the curves of $f(\alpha)$ vs. α at different temperatures. It can be clearly observed that the evolutions of $f(\alpha)$ were different between low and high temperature curves. The plot of $f(\alpha)$ with α at a high temperature follows a typical S-shaped curve as those obtained by DSC in the literature while at a low temperature a distinct rise of $f(\alpha)$ occurred at the mid conversions until it reached to a peak value and then decreased, which again indicated a different mechanism from high temperature cure process. The high temperature $f(\alpha)$ data were used to fit the Cole's diffusion
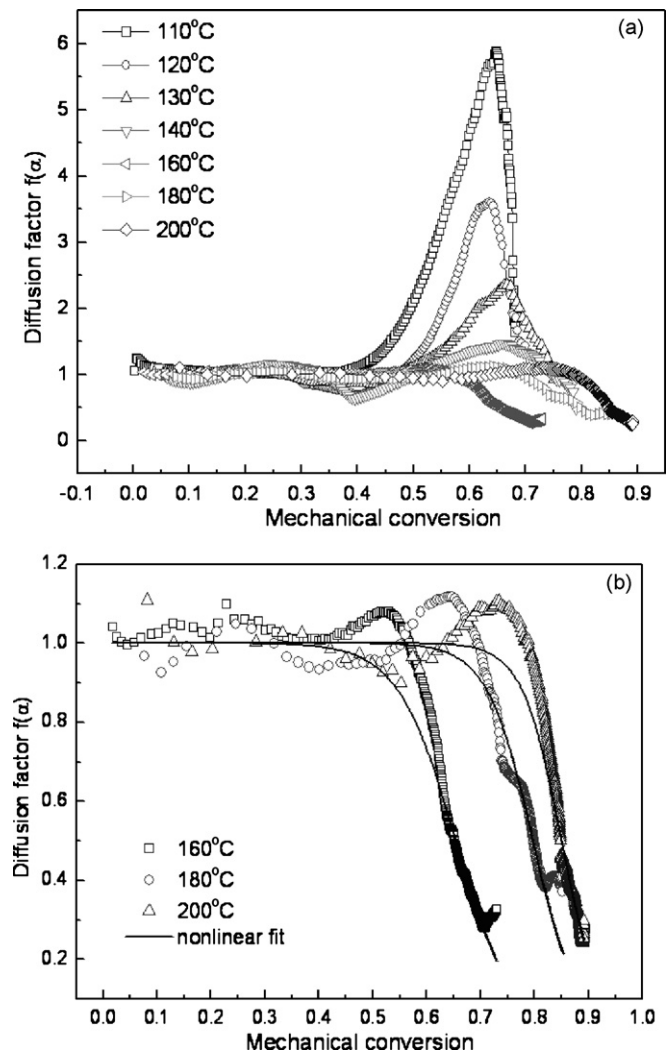

Fig. 10. The plot of diffusion factor $f(\alpha)$ vs. conversion at different temperatures. (a) $f(\alpha)$ vs. α at low and high temperatures and (b) model fitting at high temperatures.
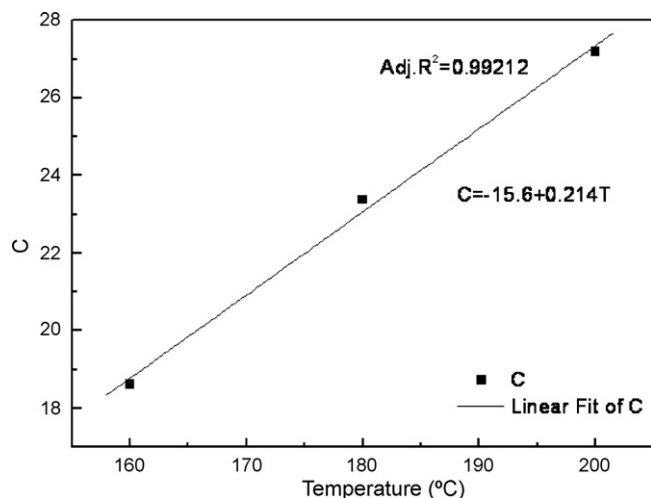
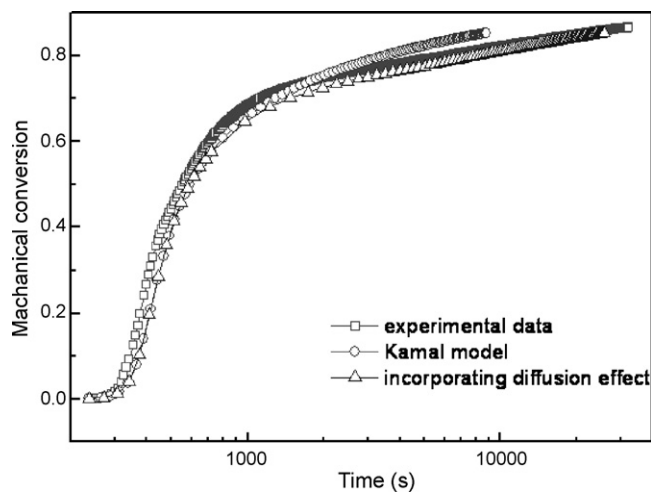**Fig. 11.** Linear fit of parameter *C* vs. temperature.

Fig. 12. Prediction of isothermal cure at $T = 170\,°C$.

effect model and the results were shown in Fig. 10(b). A generally good agreement was obtained between the model and the actual curve of $f(a)$ except for the turning section where $f(a)$ began to decrease notably and the end section where $f(a)$ stopped decreasing. And the corresponding fitting conversion curves were much lower than the experimental conversion curves due to the inaccurate fitting in the end section. So the Cole's model was no longer used to predict the diffusion factors in the end section since the deviation conversion α_{end} at which the Cole's theory curve deviated from the actual curve of $f(\alpha)$ as seen in Fig. 10(b). Instead, the value of $f(\alpha = \alpha_{end})$ calculated by Cole's model at the beginning of the end section was set as the value of the diffusion factors for the whole end section, as it is approximately equal to the average value of $f(\alpha)$ at the end section. The fitted parameters α_c and C in Eq. (10) and the critical conversion α_{end} of the end section were related to the isothermal temperatures and the linear fitting results were shown in Figs. 7 and 11 and Table 1 respectively. Table 1 listed the definitions, meanings and the expressions of the critical conversions related to the diffusion effect in this paper. It can be seen from Fig. 7 that critical conversions take place in the isothermal cure processes in the order of $\alpha_{turn} < \alpha_{dev} < \alpha_c < \alpha_{end} < \alpha_{max}$, which provides a rough picture of how the diffusion effect acts during the cure processes at different temperatures. By fitting with the diffusion effects, much better results were obtained for high temperature cures as seen from Fig. 9(b). However for low isothermal temperature curves none of the reported diffusion effect models can successfully correct the deviation of the model curves at the latter part of the isothermal cure, which needs further investigation to illuminate the particular evolution mechanism of the mechanical conversions at low temperatures.

Table 1
The critical conversions in characterizing the diffusion effect.

	Definition	Expression and meaning
α_{dev}	The point at which the theory curve were deviated from the experimental curve	
α_c	The point when the diffusion factor $f(a) = 0.5$	$\alpha_c = -0.12 + 0.0049T$ (where T is expressed in $°C$)
α_{turn}	The point where $f(a)$ begins to decrease notably	The tunning point of $f(a)$ meaning the diffusion effect starts to operate
α_{end}	The point at the beginning of the end section where the $f(a)$ model curve deviated from the experimental curve	$\alpha_{end} = -0.014 + 0.0046T$ (where T is expressed in $°C$)

The validation work of the above methods for maximum conversion calculation and kinetic analysis including the above-obtained expressions of the kinetic parameters was conducted on predicting an isothermal mechanical conversion curve at $170\,°C$, i.e. in the high temperature region. The results were shown in Fig. 12 and confirmed the validation of the above models. It can be clearly observed that there was a good agreement between the experimental data and the predicted curves using the Kamal model and the diffusion effect.

From the above phenomenological kinetic analysis on mechanical cure processes, a generally good applicability of the most common cure kinetic models to the mechanical conversion data can be observed in the early part of the cure processes and for the whole cure processes in high temperature region, which indicates the domination of the contribution of cure reaction to the kinetic mechanisms of the mechanical conversion processes in these circumstances. The inapplicability of the cure kinetic models to the latter stage of the low temperature mechanical cure may due to the less impact of the cure reactions and more impact of other structural or mechanical aspects.

4. Conclusions

The isothermal mechanical cure process of a glass fiber/epoxy prepreg can be directly measured by the single cantilever mode of DMTA without any support. A new method to define the cure state and to estimate mechanical conversions for incomplete isothermal cure processes was proposed based on the dynamic storage modulus data, by which the ultimate mechanical conversion that the prepreg reaches at the end of the isothermal cure, and the degree of mechanical cure state during the incomplete cure process can be calculated. The new definition for mechanical cure provides a more proper way to characterize the mechanical state of the prepreg during cure as compared to the most commonly used relative mechanical conversion definition, and indicates an estimation of the proportion of the increase in mechanical property during cure to the full extent of increase in mechanical property from the uncured to the fully cured state. Two types of mechanical conversion curves occur at high and low temperatures respectively, indicating different mechanisms in the two temperature regions. The maximum mechanical conversions under a certain temperature can be estimated by a linear empirical equation. The Kamal model can successfully predict the evolution of the mechanical conversion curves at the initial stage of incomplete isothermal cures. Incorporating the diffusion effect, the model can also predict the

latter cure stage of the isothermal curing at high temperatures. This paper provides a new approach to better utilize the dynamic mechanical methods in mechanical cure characterization and cure analysis, and to estimate conversions in the mechanical properties of the thermosets by the cure cycle. Further investigation would focus on revealing the increment mechanisms in mechanical conversion and applying the dynamic mechanical methods to cure processing optimization.

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