

دراسة حركية راتنج م 6 / ثاني أكسيد التيتانيوم عن طريق التحليل بالقياس الوزني الحراري / المسح التفاضلي الحراري لتحسين صلابة راتنج

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الملخص:

الهدف من هذا البحث هو الحصول على إيبوكسي راتنج بأفضل الخصائص باستخدام (التحليل بالقياس الوزني الحراري / المسح التفاضلي الحراري). الاستقرار الحراري والخصائص الحركية للإيبوكسي راتنج بالاستخدام غير المتساوي للحرارة thermogravimetry/derivative thermogravimetry وذلك من أجل سلسلة من النسب المئوية المختلفة Tio₂-PC500 وهي كالتالي: 1%، 2%، 5% و 10%. تم تقدير مقدار متغير القيمة الحركية بطرق التكامل و التقريب.

أشارت النتائج إلى أن هذه الخصائص تعتمد على النسب المختلفة لثاني أكسيد التيتانيوم TiO₂ وفقا لمنحنيات قياس (الوزني الحراري) التي تظهر أن طاقة التنشيط (طاقة الحفز) تتزايد مع تزايد النسب المئوية لجسيمات ثاني أكسيد التيتانيوم (TiO₂)، و راتنج الالبوكسي التحليل بمجهر المسح الالكتروني أوفي بأن توزيع جسيمات ثاني أكسيد التيتانيوم TiO₂ كان بشكل منتظم ومتجانس ضمن المادة (إيبوكسي راتنج) هذا من جهة ومن جهة أخرى فالخاصية الميكانيكية التي هي الصلابة تحسنت مع زيادة النسب لجسيمات TiO₂.



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ORIGINAL ARTICLE

Kinetic study of the RTM6/TiO₂ by DSC/TGA for improved hardness of resin

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KEYWORDS

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TG/DTG;
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TiO₂;
Kinetic parameter;
Mechanical property

Abstract The aim of this paper is to obtain an epoxy resin with best properties such as good cure of polymer (by using DSC and TGA). The thermal stability and kinetic parameters of epoxy resin RTM6 using non-isothermal thermogravimetry/derivative thermogravimetry (TG/DTG) analysis with a series of different ratios of TiO₂-PC500 1%, 2%, 5% and 10% with epoxy resin were evaluated. The kinetic parameter was evaluated by integral and approximation methods. Results obtained indicated that these parameters were dependent on different ratios of TiO₂. According to the thermogravimetric curves it is shown that the activation energy at high of higher conversion increases with increasing the percentage of TiO₂ particles and epoxy resin. The SEM analysis suggests that TiO₂ particles are uniformly distributed within the material, besides the mechanical property of materials are found to the addition of TiO₂.

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1. Introduction

Epoxy/TiO₂ was prepared by a solution mixture method, in which epoxy resin and nano-TiO₂ powder were mixed (Hung et al., 2006). Epoxy resins are widely used in most industrial applications, such as preparation of composites. The kinetics of epoxy resin cure has been widely investigated in the literature under conventional thermal processing conditions (Navabpour et al., 2006).

Resin transfer moulding (RTM) is rapidly gaining acceptance as one of the most promising manufacturing routes for composite structures such as the aerospace and automotive industries. However, relatively limited information is available

on the chemistry and cure characteristics of the types of thermosetting resins used in such applications (Karkanis et al., 1996).

The aim of this study is to describe the kinetic investigation of a curing thermoset resin system. A lot of experimental techniques are suitable for following the rates and extents of cure reactions in thermosets. Among them thermal gravimetric analysis may be considered as one of the most interesting techniques for macrokinetic analysis of cure reactions and a detailed investigation of thermal decomposition of epoxy resins containing a commercial TiO₂ PC500 from Millennium at different percentages of 1%, 2%, 5% and 10%, for evaluating the thermal stability and to determine the thermal decomposition kinetic parameter (activation energy) and to measure the mechanical property (hardness).

2. Experimental

2.1. Reagents

The materials used in this work were of a commercially available grade of the diglycidyl ether of bisphenol A ((4-(2,3-epoxypropoxy)phenyl)propane) abbreviated as DGEBA. It was used under its commercial presentation (Dow Chemical Company; DER 332). The cure agent was 4,4'-DiaminoDiphenylSulfone (DDS).

Titanium dioxide TiO₂-PC500 from Millenium Inorganic Chemicals (anatase > 99%, Surface area 250 m²), crystallite mean size = (5–10 nm) was used as received.

2.2. Apparatus

2.2.1. DSC

Dynamic scans were performed using a heat-flux DSC (Mettler Toledo TC11) under nitrogen purge. The instrument was calibrated with indium.

2.2.2. SEM

The scanning electron microscopic (SEM) studies were performed on a Hitachi S800-FE operated at 30 kV.

2.2.3. TGA

The thermogravimetry analysis (TGA) was carried out on a SETARAM 92-12 apparatus under an N₂ atmosphere.

2.3. Methods

2.3.1. DSC

Samples of the mixture of epoxy resin and curing agent were introduced in a furnace maintained at the temperature chosen for the experiment (100, 135 and 150 °C). They were successively removed and after different times they were elapsed (typically between 1 and 6 h with a step of 1 h) and submitted to a DSC analysis with a heating rate of 10 °C min⁻¹ from 30 to 350 °C. These scans allowed determining the heat of reaction $\Delta H_{\text{residual}}$ generated by the curing of the remaining epoxy resin not polymerized in the furnace.

A scan performed directly on a sample of the mixture epoxy resin/curing agent without heat treatment was allowed to determine the heat of reaction ΔH_{total} generated by the complete polymerization process.

2.3.2. TGA

2.3.2.1. *Sample preparation.* The epoxy samples were prepared by the following three steps:

1. Heating the epoxy resin in an oven at 40 °C.
2. Adding the TiO₂ at different percentage 1%, 2%, 5% and 10%.
3. Heating samples at 135 °C for 6 h.

The thermal property of Epoxy resin/TiO₂ sample was investigated by TG/DTG under N₂ environment. The analyses were carried out using heating rates of 5.0, 10.0, 20.0 and 30.0 °C min⁻¹ for each experiment with approximately 20.0 mg up to 850 °C.

3. Kinetic methods

3.1. Thermal analysis

The DSC plots were also fitted using the equation described by Karkanis et al. (1996). The reaction rates for this work are calculated from the DSC using the following equations:

$$\alpha = \frac{\Delta H_t}{\Delta H_{\text{Tot}}} \quad (1)$$

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_{\text{Tot}}} \frac{d\Delta H_t}{dt} \quad (2)$$

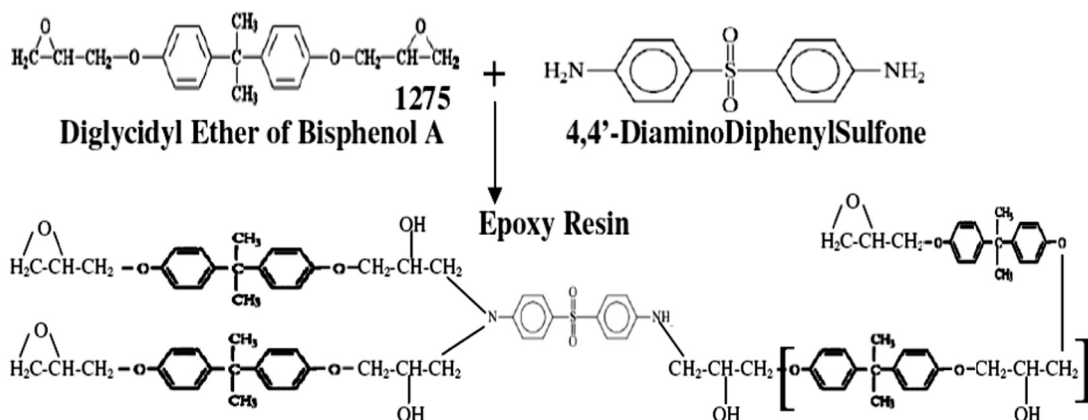


Figure 1 Chemical structures and cure reaction of DGEBA by DDS (Farquharson et al., 2007).

Table 1 Total heat of reaction of RTM6 resin at different heating rates.

Heating rate (°C min ⁻¹)	1	2	5	10	20	30
ΔH_{total} (J g ⁻¹)	439.29	435.32	437.00	434.05	432.89	439.57

where ΔH_t is the partial area under DSC trace up to time t and ΔH_{tot} is the total enthalpy of reaction measured as the area under the heat flow against time for DSC.

The DSC plots were also fitted using the equation described by Karkanis et al. (1996) and Puglia et al. (2003).

$$\frac{\partial \alpha}{\partial t} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n \quad (3)$$

$$\frac{\partial \alpha}{\partial t} = k_1(1 - \alpha)^{n_1} + k_2 \alpha^m(1 - \alpha)^{n_2} \quad (4)$$

where k_1 and k_2 are the rate constants, m and n are the reaction orders.

In the non-isothermal experiments carried out with a thermobalance, the sample mass is measured as function of temperature (see Fig. 1).

The calculation of kinetic data is based on the kinetic Eq. (5):

$$\frac{\partial \alpha}{\partial t} = k \alpha^n$$

where a is the amount of sample undergoing reaction, n is the reaction order, and k is the specific rate constant. The temperature dependence of k is expressed by Arrhenius Eq. (6):

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

where A is the Arrhenius constant, E_a is the activation energy, and R is the gas constant.

The activation energy can be determined by Kissinger's method without a precise knowledge of the reaction mechanism, using the following Eq. (7).

$$\ln\left(\frac{\beta}{T_{\text{max}}^2}\right) = \left\{ \ln \frac{AR}{E} + \ln \left[n(1 - \alpha)^{n-1} \right] \right\} - \frac{E}{RT_{\text{max}}} \quad (7)$$

where T_{max} is the temperature corresponding to the inflection point of the thermodegradation curves which correspond to the maximum reaction rate, α_{max} is the conversion at T_{max} and n is the reaction order. Taking into account the Kissinger's approximation which states that:

$$f'(\alpha_{\text{max}}) = n(1 - \alpha_{\text{max}})^{n-1} \cong \text{const} \quad (8)$$

The activation energy can be determined from a plot of $\ln(\beta/T_{\text{max}}^2)$ against $1/T_{\text{max}}$.

4. Results and discussion

Table 1 shows the enthalpy of cure for DSC curing for isothermal temperature after curing using DSC.

Fig. 2 shows the plots of conversion and reaction rate for the isothermal curing of RTM6 cured using DSC. The conversions and reaction rates were obtained using the DSC curves and Eqs. (2) and (3).

The curves of reaction rate on time were fitted to the kinetics Eq. (4). The equation was modified to account for the diffusion effect, which occurs when the resin is transformed from the rubbery to glassy state (Navabpour et al., 2006).

The time interval to reach that maximum value is different for each cure temperature and shifts to longer times for lower cure temperatures.

All the above observations lead to the conclusion that the cure of the specific epoxy-amine system follows a complex reaction mechanism, with autocatalytic phenomena occurring during the early stages of the cure.

The reaction schemes for epoxies are relatively well established and mainly involve primary and secondary amino group addition to the epoxy group, for normal curing conditions. Under extreme conditions of high cure temperatures, etherification may also occur. These reactions may be catalysed by any impurities present in the resin, or by the hydroxyl and tertiary amine products formed, resulting in autocatalysis (Shoichiro et al., 2005).

Table 2 summarizes the parameters obtained from fitting the experimental data to the Eqs. (4) and (5). Values of pre-exponential factor and activation energy were calculated from

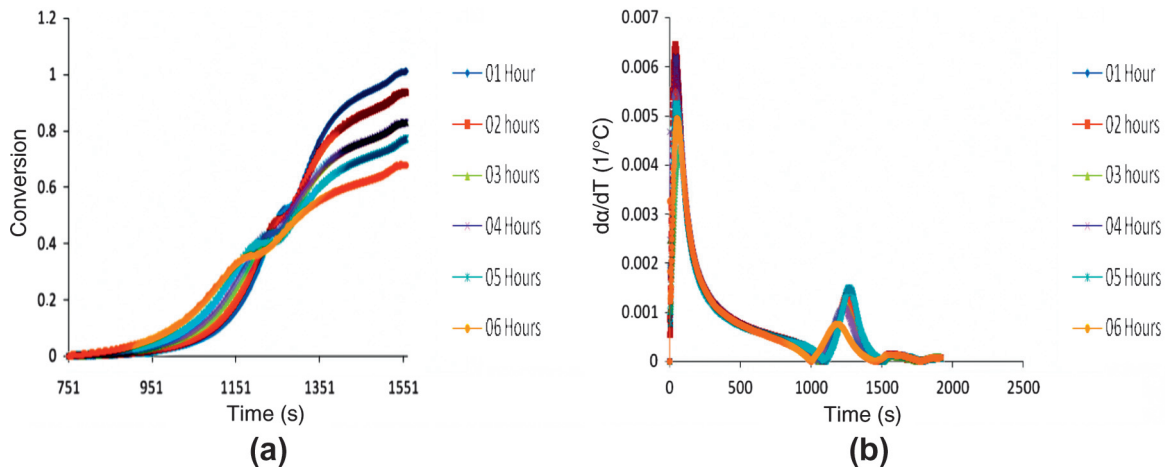


Figure 2 (a) Fractional conversion for isothermal Cure at 100 °C for different time of reticulation. (b) Reaction rates for dynamic cure at different times of cure for RTM6 at 100 °C.

Table 2 Parameters obtained from fitting the isothermal curing results using DSC.

Cure temperature (°C)	k_1 (10^{-5} s^{-1})	k_2 (10^{-3} s^{-1})	m	n	n_1	n_2
Eq. (4)	$\frac{\partial \alpha}{\partial t} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n$					
100	2.21	0.53	0.95	0.59	–	–
135	3.52	0.92	1.09	0.66	–	–
150	4.30	1.35	1.11	0.79	–	–
Eq. (5)	$\frac{\partial \alpha}{\partial t} = k_1(1 - \alpha)^{n_1} + k_2 \alpha^m(1 - \alpha)^{n_2}$					
100	2.15	0.51	0.95	–	0.52	0.66
135	3.43	0.89	1.07	–	0.58	0.73
150	4.11	1.28	1.05	–	0.71	0.86

the temperature dependence of k_1 and k_2 using the Arrhenius equation. Values of E_1 and E_2 for the conventionally cured samples are in agreement with those obtained by Karkanis and Partridge. The values of A_1 and A_2 were, however, much smaller than the values obtained by them. As in their analysis they did not correct the kinetics models for diffusion control, the fits to the experimental data were not as good as in this work, and this might explain the observed differences in pre-exponential factors (see Fig. 3).

$$\begin{aligned} A_1 &= 22420 \text{ s}^{-1}, E_1 = 71.1 \text{ kJ mol}^{-1} \\ A_2 &= 10256 \text{ s}^{-1}, E_2 = 55.65 \text{ kJ mol}^{-1} \end{aligned} \quad (4)$$

$$\begin{aligned} A_1 &= 25820 \text{ s}^{-1}, E_1 = 73.6 \text{ kJ mol}^{-1} \\ A_2 &= 25460 \text{ s}^{-1}, E_2 = 61.84 \text{ kJ mol}^{-1} \end{aligned} \quad (5)$$

4.1. SEM

For appreciation dispersion of Nanoparticles TiO_2 .

As shown in Figs. 4 and 5 of SEM, the epoxy resin has a smooth and flat surface in without TiO_2 , with addition of percentage of TiO_2 it is observed that a relatively little amount of TiO_2 particles are attached to the surface of resin with a good dispersion.

The SEM analysis suggests that TiO_2 particles are uniformly distributed within the materials.

The non-isothermal kinetic study of weight loss during a thermal decomposition process of epoxy resin containing

TiO_2 at 1%, 2%, 5% and 10%. Two different methods, all based on Arrhenius kinetic theory, were used for the kinetic analysis of the TG/DTG data: one based on differential method and other based on integral method. In all of these methods, calculations were performed to estimate the kinetic parameter activation energy.

For obtaining the kinetic information, such as the activation energy, the TGA study has been conducted with the variation of the heating rates.

Fig. 6(a) shows the TGA thermograms of epoxy resin containing different percentage of TiO_2 1%, 2%, 5% and 10% at a constant heating rate $10^\circ\text{C min}^{-1}$.

Fig. 6(b) shows the TGA thermograms of epoxy resin containing a 1% of TiO_2 , corresponding to dynamic experiments carried out at different heating rates (5, 10, 20, and $30^\circ\text{C min}^{-1}$).

The corresponding differential (DTG) curves of this sample are shown in Figs. 7 and 8. The thermal decomposition process in two steps degradation, probably corresponding to epoxy resin two step corresponding to the degradation of ether group structures in the polymer matrix (Santos et al., 2002; Shoichiro et al., 2005; Hansmann et al., 2003).

The non-isothermal kinetic study of weight loss during a thermal decomposition process of RTM6/ TiO_2 samples is extremely complex because of the presence of two components and their consecutive reactions. Two different methods, all based on Arrhenius kinetic theory, were used for the analysis of TG/DTG data, one on integral method and the other based on approximation method. In all these methods, calculations

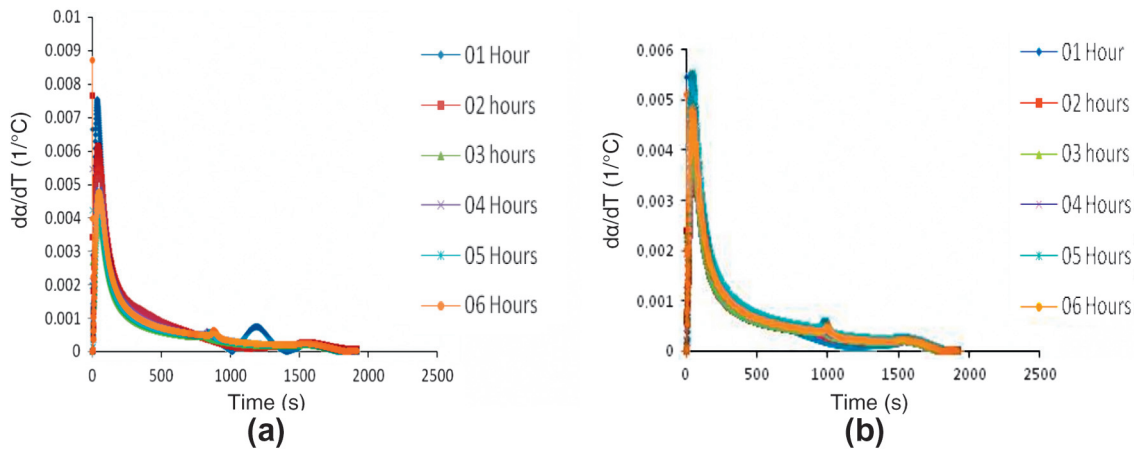


Figure 3 (a) Reaction rates for dynamic cure at different times of cure for RTM6 at 135°C . (b) Reaction rates for dynamic cure at different times of cure for RTM6 at 150°C .

SEM

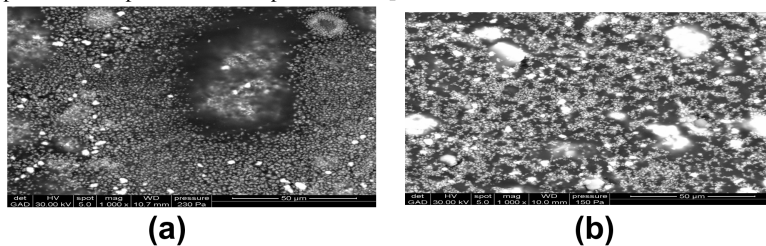
For appreciation dispersion of Nanoparticles TiO₂

Figure 4 (a) SEM image of RTM6 + 1% TiO₂, (b) SEM image of RTM6 + 2% TiO₂.

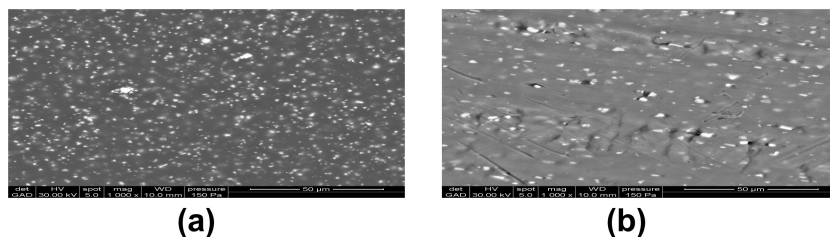


Figure 5 (a) SEM image of RTM6 + 5% TiO₂, (b) SEM image of RTM6 + 10% TiO₂.

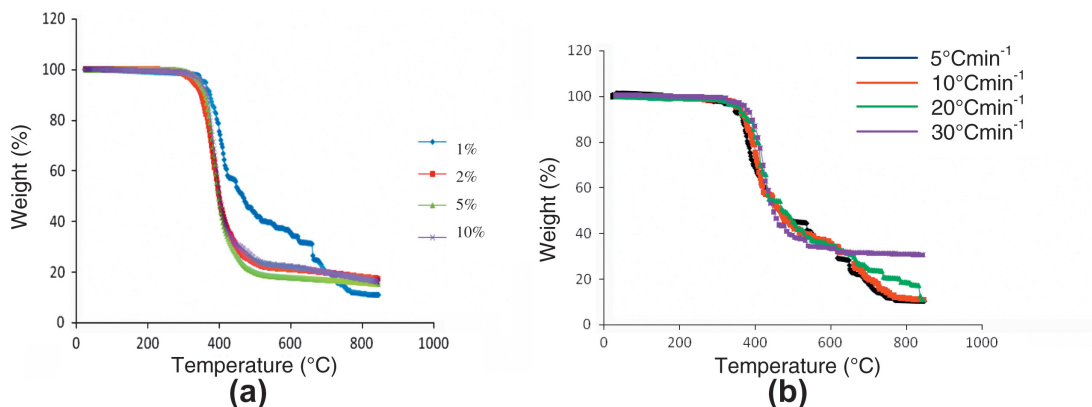


Figure 6 (a) TGA thermograms of RTM6 with TiO₂ constant heating rate of 10 °C min⁻¹, (b) TGA thermograms of RTM6 with 1% of TiO₂ at different heating rates.

were performed to estimate the kinetic parameter as activation energy (Ng et al., 1999).

Using the Kissinger Eq. (11), lines of $\ln(\beta/T_{\max}^2)$ versus $1/T_{\max}$ for each stage of the thermal degradation were plotted for all samples. Fig. 9(a) shows the representative plots for each stage of the thermal degradation of epoxy resin at 1% of TiO₂. The calculated decomposition activation energies for epoxy step of all samples are listed in Table 2. The activation energies for epoxy resins contain a different percentage of TiO₂ as compared to them.

The all steps mainly involve the degradation of carbonyl groups in the resin matrix. However, the activation energies at higher conversions increase with increasing the percentage of TiO₂.

Another procedure for calculating the activation energy is taking the Flynn–Wall–Ozawa equation. At given value of the conversion, the activation energy can be obtained from a

logarithmic plot of heating rates as a function of the reciprocal of temperature, since the slope of such a line is given by $0.4567 E/R$. For the present work, the conversion values of 50% and 98% were used. The fitting lines of different samples at the selected conversion values are shown in Fig. 9. All of the calculated activation energies are listed in Table 3. The activation energy at different conversions increases with increasing the percentage of TiO₂ (Lu et al., 2004).

The experiment realized with different heating rates indicates the same mechanisms with variation kinetic parameter values. The kinetic parameter obtained by integral and approximation methods presented good correlation. In general, the values obtained by the Kissinger method were high for the first step than the values obtained by the Flynn–Wall–Ozawa method and for the second step the values obtained by Kissinger were small than the values obtained by the Flynn–Wall–Ozawa method. In the present study, the two

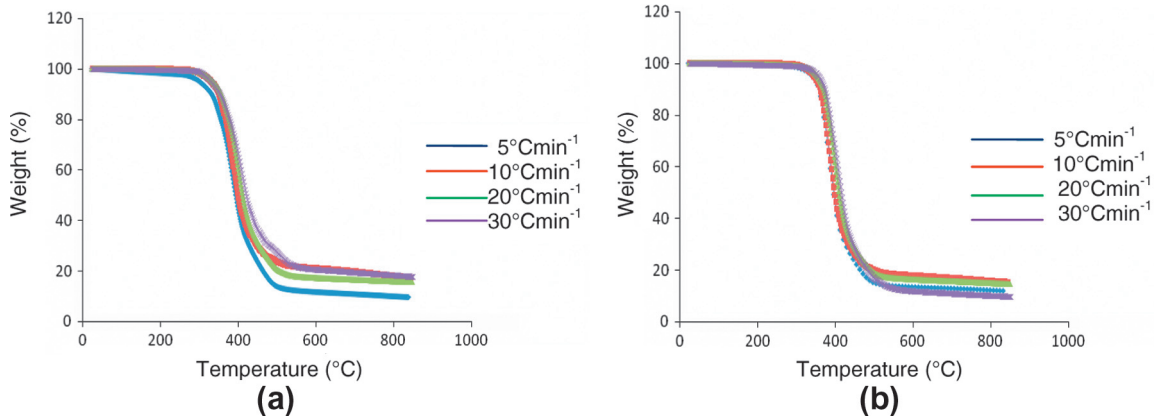


Figure 7 (a) TGA thermograms of RTM6 with 2% of TiO₂ at different heating rates, (b) TGA thermograms of RTM6 with 5% of TiO₂ at different heating rates.

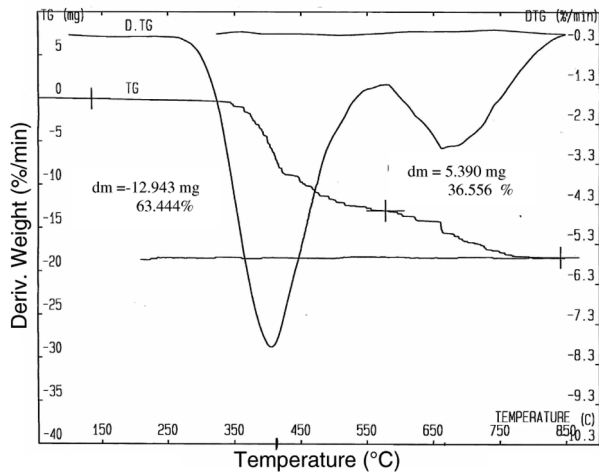


Figure 8 DTG curve of a sample at a constant heating rate of 10 °C min⁻¹.

methods show good agreement when used to determine the decomposition activation energies at certain conversion values.

The activation energy for the first step of the decomposition is very low (about 25 kJ/mol or 6 kcal/mol). It is too low for the overwhelming majority of high-temperature reactions. It seems that such energy could be attributed to activation energy

of a viscous flow. The blends undergo melting and non-cross-linked reagents leave the samples. Maybe the rate of their escape inversely depends on the viscosity. Of course, catalytic reactions with a diffusion control are possible as well. The diffusion coefficient is inversely proportional to the viscosity. When nano-TiO₂ particles are dispersed in epoxy resin, the interaction between larger surface areas of particles and substrate will help reduce the activity of substrate bond. This interaction improves the hardness of materials such as the mechanical property of the epoxy resin/TiO₂. It can be seen from Fig. 10 that when the concentration of nanosized TiO₂ powder increases, the hardness of materials will be improved (see Tables 4 and 5).

5. Conclusions

A combination of *n*th order and autocatalytic reaction kinetics was applied to fit data from dynamic and isothermal DSC scans of a commercial RTM resin. A unique set of kinetic parameters was obtained for the dynamic case, suggesting a constant reaction mechanism throughout the range of the heating rates used. In the isothermal case, the kinetic parameters required to achieve a good fit were different from those found in the dynamic runs; in particular, the reaction orders had to be allowed to vary with cure temperature. The thermal

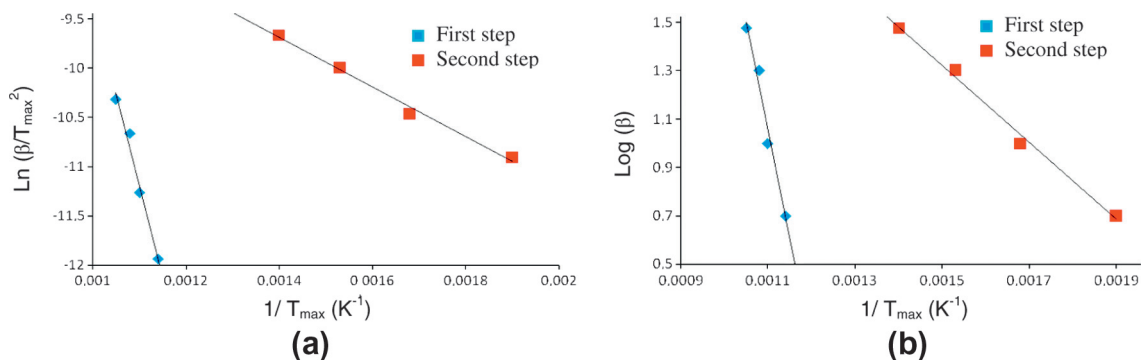
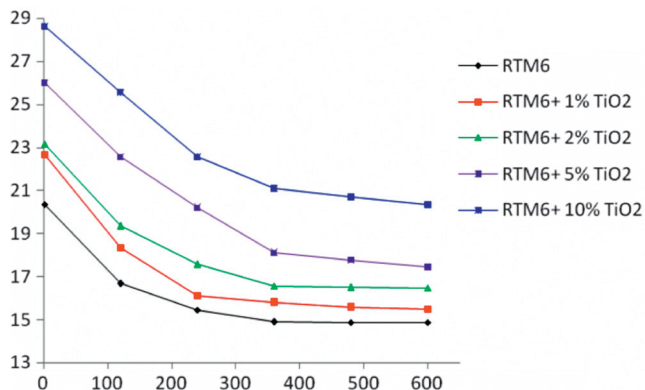


Figure 9 (a) Plot of $\ln(\beta/T_{max}^2)$ versus $1/T_{max}$ of RTM6 with 1% of TiO₂ for calculating the activation (b) Plots of $\log \beta$ versus $1/T$ of RTM6 with 1% of TiO₂ for calculating the activation energies by Kissinger method Flynn–Wall–Ozawa.

Table 3 Calculated decomposition activation energies for every stage of all samples by Kissinger method.

Samples	First step			Second step		
	Temperature range (°C)	D_m (%)	T (°C)	Temperature range (°C)	D_m (%)	T (°C)
RTM6 + 1%TiO ₂	280–500	63.44	410.10	500–834.12	26.42	650.11
RTM6 + 2%TiO ₂	280–500	65.43	415.78	500–834.12	28.67	654.67
RTM6 + 5%TiO ₂	280–500	68.45	425.76	500–834.12	30.45	699.98
RTM6 + 10%TiO ₂	280–500	74.76	435.56	500–834.12	33.56	673.45

**Figure 10** Hardness of epoxy/TiO₂ on different concentration of TiO₂.

stability of epoxy resin containing nanocharges TiO₂ was evaluated by thermogravimetric curves and activation energy obtained from thermogravimetric data. The results obtained indicated that the activation energies at higher conversions increase with increasing the percentage of TiO₂. The degradation activation energies, decomposition temperatures and weight

loss rates were altered by the TiO₂ nanocharges. The kinetic parameters obtained by approximation and integral methods were satisfactory and present good correlation.

This experiment attempts to process materials, using epoxy resin and nanosized TiO₂ powder, the hardness will increase with the increase of concentration of TiO₂.

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Table 4 Calculated decomposition activation energies for every stage of all samples by Kissinger method.

Samples	Region	Conversion α	T_{max} (K) ($\beta = 10$ °C.min ⁻¹)	Activation Energy E_a (kJ/mol)	Correlation coefficient r
1% TiO ₂	1 Step 0.00–0.50	0.00–0.50	673	21	0.995
	Step 0.50–0.98	0.50–0.98	953	155	0.998
2% TiO ₂	1 Step 0.00–0.50	0.00–0.50	675.67	23	0.998
	2 Step 0.50–0.98	0.50–0.98	960.34	157	0.997
5% TiO ₂	1 Step 0.00–0.50	0.00–0.50	678.56	25	0.993
	2 Step 0.50–0.98	0.50–0.98	967.78	161	0.995
10% TiO ₂	1 Step 0.00–0.50	0.00–0.50	683.56	29	0.996
	2 Step 0.50–0.98	0.50–0.98	971.56	168	0.998

Table 5 Calculated decomposition activation energies for every stage of all samples by Flynn–Wall–Ozawa method.

Samples	Region	Conversion	Activation Energy E_a (kJ/mol)	Correlation coefficient r
1% TiO ₂	1 Step 0.00–0.50	0.00–0.50	29	0.995
	2 Step 0.50–0.98	0.50–0.98	146	0.998
2% TiO ₂	1 Step 0.00–0.50	0.00–0.50	25	0.998
	2 Step 0.50–0.98	0.50–0.98	153	0.997
5% TiO ₂	1 Step 0.00–0.50	0.00–0.50	28	0.993
	2 Step 0.50–0.98	0.50–0.98	159	0.995
10% TiO ₂	1 Step 0.00–0.50	0.00–0.50	31	0.996
	2 Step 0.50–0.98	0.50–0.98	170	0.998

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