

Curing Kinetics of *o*-Cresol-formaldehyde Epoxy Resin/3-Methyl-tetrahydrophthalic Anhydride/Organic-Montmorillonite Nanocomposite by Isoconversional Methods

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ABSTRACT

The cure reaction for a system of *o*-cresol-formaldehyde epoxy resin (*o*-CFER), with 3-methyl-tetrahydrophthalic anhydride (MeTHPA), *N,N*-dimethyl-benzylamine, and organic montmorillonite (org-MMT), as a curing reagent, an accelerator and an additive, respectively, was investigated by means of X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The XRD result indicates that an exfoliated nanocomposite was obtained. The curing kinetic data of *o*-CFER/MeTHPA and *o*-CFER/MeTHPA/org-MMT nanocomposites were obtained by non-isothermal differential scanning calorimetry. The nanocomposite has a slightly higher average value of activation energy than that of pure *o*-CFER due to the epoxy resins chains are inserted into the galleries of montmorillonite and the movement and diffusion of reactive groups are hindered. The curing kinetics analysis was performed by the isoconversional methods of Ozawa, Friedman, and Kissinger-Akahira-Sunose. The results showed that the Ozawa method is the best of the three models studied.

Key Words:

o-cresol-formaldehyde epoxy resin;
montmorillonite;
curing kinetics;
thermal analysis.

INTRODUCTION

Composite materials, in which inorganic or organic filler is dispersed within the polymer matrix on a nanometer scale, are called polymer nanocomposites. Because of the inorganic particles in the polymer matrix, these materials

generally exhibit significant improvements in mechanical properties, thermal stability, flame retardancy and dielectric properties etc, compared with the base polymer at very low loading levels. Epoxy resin-layered silicate nanocompo-

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sites are new hybrid materials of polymers with nanometer-sized inorganic particles that have recently been widely studied, principally due to the far-ranging application potential of epoxy resin in many fields [1-7].

Lan [8] demonstrated that the exfoliation of the clay is not only dependent on the reactivity of the epoxy system but also on the rate of intercalation of epoxy and curing reagent. The monolithic epoxy exfoliated-clay nanocomposites have been prepared from the reaction of alkylammonium-exchanged smectite clays with the diglycidyl ether of bisphenol-A and diamine as the curing agent by Pinnavaia et al. [2,3]. They found that the monolithic exfoliated clay nanocomposites have a tremendous improvement in tensile strength, modulus and glass transition temperature (T_g).

All of these publications [1-5,8] about epoxy-clay nanocomposites have focused on their formation mechanism, structure and applied properties.

The methods used to study the cure kinetics can be classified as mechanistic and phenomenological models. Mechanistic models are made from the balance of chemical species involved in the chemical reaction. In most cases, it is difficult to derive a mechanistic model because the epoxy resin cure reaction is very complex. Thus, phenomenological or empirical models are preferred to study the cure kinetics of these polymers [9]. Among them, there are several different methodologies for the determination of the curing kinetics of thermosetting materials which can be described as follows:

There are direct methods such as Borchardt-Daniels model [10], which employ a single dynamic scan by differential scanning calorimetry (DSC) to determine the kinetic parameters. There are approximation methods as Ozawa and Kissinger models [10,11], which relate the heating rates (β) employed with the peak exothermic temperatures (T_p) of the different thermograms to obtain the activation energy of overall cure process. Kamal model [6], arising from an autocatalytic reaction mechanism, was applied to isothermal DSC data.

The main disadvantage of these methods is the great variation in activation energy. Its value depends on the employed model. Besides, the system is so complex that their activation energies also change

with conversion degree during the curing process. Thus, the isoconversional methods reveal changes in process of curing kinetic and it is a big advantage.

Isoconversional models in epoxy-amine and unsaturated resins have been used successfully by DSC [12,13]. However, these models have not been used in *o*-CFER system. The aim of this paper is to show that the system has an isoconversional behaviour and study the effect of MMT on the curing process. In this work, the kinetics data of DSC were treated by Ozawa, Friedman, and Kissinger-Akahira-Sunose models [10,11].

EXPERIMENTAL

Materials

Analytically pure epichlorohydrin, *o*-cresol, formaldehyde, NaOH, KOH, acetone, ethyl alcohol, 3-methyl-tetrahydrophthalic anhydride and *N,N*-dimethyl-benzylamine hydrochloric acid were supplied by Beijing Chemical Reagent Co. (China).

The montmorillonite was purchased from Qingshan Chemistry Agent Factory in Lin'an (China). The cation exchange capacity (CEC) value of Na⁺-montmorillonite was about 100 mmol/100g. The surfactant of clay, CH₃(CH₂)₁₅(CH₃)₃NBr, was supplied by the Research Institute of Xinhua Active Material in Changzhou (China).

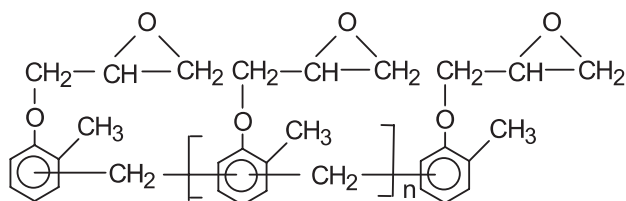
Preparation of Organically Modified Montmorillonite

An amount of 20 g of Na⁺-montmorillonite was dispersed into 500 mL of distilled water at 80°C. 9 g of CH₃(CH₂)₁₅(CH₃)₃NBr, a surfactant for the clay was dispersed in 100 mL of distilled water. Then the water solution of surfactant was poured in the hot MMT/water solution and stirred vigorously for 1 h at 80°C.

A white precipitate was formed and was separated by centrifugation. The precipitate was washed several times in hot distilled water until no bromide was detected in the filtrate by one drop of 0.1 N AgNO₃ solution, and then it was dried in vacuum. The dried organic MMT was grounded with a freezer/mill. The sieved organic clay powder less than 36 μm size was applied to make nanocomposites.

Synthesis of *o*-CFER and *o*-CFER/MeTHPA/org-MMT Nanocomposites

Epoxy resin based on *o*-cresol-formaldehyde (*o*-CFER) used in this work was synthesized from *o*-cresol-formaldehyde resin and epichlorohydrin [14]. The molecular structure of this epoxy resin has the following approximate form:



where $n=1\sim 3$. The epoxy value was determined according to HCl-acetone method [15] to be 0.357 mol/100g.

We had proved that the *o*-CFER/MeTHPA/org-MMT composite had good mechanical properties and thermal distortion temperature [16]. So that, the filled loadings of org-MMT in this study are applied in 0, 3 or 7 phr (parts per hundred resins mixture). The *o*-cresol-formaldehyde epoxy resin (*o*-CFER) was mixed with org-MMT under higher stirring rate. The org-MMT was dispersed uniformly in *o*-CFER at 80°C for 2 h. Then, the curing agent MeTHPA was added into the hybrid and mixed thoroughly by stirring in the presence of *N,N*-dimethyl-benzylamine as an accelerator. The molar ratio of carboxyl group to epoxy group is 1:1. The samples were cured for 2 h at 130°C and 4 h at 180°C.

X-Ray Diffraction (XRD)

A wide angle X-ray diffraction patterns were recorded by monitoring the diffraction angle 2θ from 1.5-10 on a RigakuD-max- γ A-ray diffractometer. The copper tube was used as target in diffractometer, CuK α ($\lambda=0.1542$ nm) radiation source operated at 40 kV and 100 mA. The scanning speed and the step size used were 2°/min and 0.02°, respectively.

DSC Method

Curing studies were carried out on a DSC (DT-41, Shimadzu Co. Ltd., Japan). DSC was calibrated with high-purity indium, and α -Al₂O₃ was used as the reference material. Approximately 10 mg of mixture was used for DSC sample preparation. The sample was put

into an aluminium DSC pan and sealed with an aluminium lid. The entire operation was carried out in a dry chamber. Later, the baseline "spline" was subtracted from the original thermogram.

Isoconversional methods were carried out with four heating rates (5, 10, 15 and 20°C/min) in a scanning temperature range from 30~280°C. The data obtained by DSC were fitted to the Ozawa, Kissinger-Akahira-Sunose [10], and Friedman methods.

RESULTS and DISCUSSION

X-Ray Diffraction Analysis

The wide angle X-ray diffraction patterns for *o*-CFER/MeTHPA/org-MMT composites containing different contents of org-MMT cured under the temperature of 180°C are shown in Figure 1. As reported [17], when polymer chains are inserted into the galleries of montmorillonite, the lattice spacing is enlarged. These XRD patterns reveal the change in org-MMT basal spacing that occurs in the epoxy curing process. For the *o*-CFER/org-MMT/MeTHPA system, it is noteworthy that the (001) diffraction peak shifted to a lower angle comparable to that of org-MMT. The intensity of diffraction peak increased with increased loading of org-MMT. The X-ray diffraction peak occurs at $2\theta=4.02^\circ$ for org-MMT, and at $2\theta=2.42^\circ \sim 2.46^\circ$ for *o*-CFER/org-MMT/MeTHPA composite.

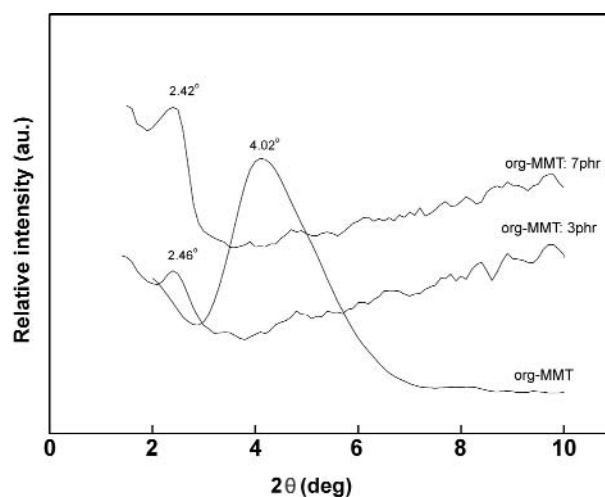


Figure 1. XRD Patterns of *o*-CFER/MeTHPA/org-MMT nanocomposites.

Obviously, the intercalated nanocomposite with the lattice spacing of 3.59~3.65 nm (according to $2d\sin\theta = n\lambda$) was obtained. The lattice spacing of the intercalated nanocomposite increases, but Bragg diffractions still exist in the diffractogram, which shifted to lower angle. If the lattice spacing continues to increase, exfoliated nanocomposite is formed, leading to the disappearance of Bragg diffraction.

Curing Kinetics Methods

The isoconversional methods are based on dynamic analysis by DSC. The equation of reaction rate, employed to study the kinetic curing of resin, can be expressed, in general, as:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \quad (1)$$

Considering that the rate eqn (1) is valid for dynamic curing, and $d\alpha/dt = \beta d\alpha/dT$, where β is the heating rate (K/min), the eqn (1) can be written as:

$$\beta \frac{d\alpha}{dT} = A \cdot e^{(-E/RT)} \cdot f(\alpha) \quad (2)$$

where T is the temperature (K), A is the pre-exponential factor, E is the activation energy, R is the gas constant (8.31 J/mol/K) and α is the degree of curing. In this way, the integral form of the rate equation can be expressed as:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{(-E/RT)} dT \quad (3)$$

The integral term of the right side of eqn (3) can be written by the following polynomial function:

$$\frac{E}{R} \cdot P\left(\frac{E}{RT}\right) = \int_0^T e^{(-E/RT)} dT \quad (4)$$

The function $P(E/RT)$ is the Doyle's approximation, which can be employed for $20 < E/RT < 60$, and is expressed as:

$$\log\left(P \cdot \frac{E}{RT}\right) = -2.315 - 0.4567 \cdot \frac{E}{RT} \quad (5)$$

In order to determine the kinetic parameters, the eqns

(3) and (5) can be combined and rearranged as:

$$\ln \beta = A' - 0.4567 \cdot \frac{E}{RT} \quad (6)$$

where $A' = \log AE/g(\alpha)R - 3.315$. The expression (6) is known as Ozawa method, which can be applied to different degrees of conversion [18]. Thus, for a given conversion degree, the activation energy, E , and the constant, A' , can be obtained from linear regression according to eqn (6), another expression similar to a proposal by Ozawa was the Kissinger-Akahira-Sunose model, which is described by eqn (7). In this case, the conversion-dependence functions ($f(\alpha)$ or $g(\alpha)$) are not required. It is required that for a given conversion degree the reactive process has the same mechanism of reaction, regardless of the curing temperature.

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{R \cdot A}{E \cdot g(\alpha)}\right) - \frac{E}{RT} \quad (7)$$

Friedman Method relates the logarithm of reaction rate with the inverse temperature for a given cure degree. In this way, the expression can be written as:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln f(\alpha) \cdot A - \frac{E}{RT} \quad (8)$$

When a dynamic method is applied, the typical basic parameters $d\alpha/dt$ and α are required and can be obtained from the DSC exothermal curves. The reaction rate is obtained by dividing the peak height dH/dt at time t by the total heat of curing reaction, ΔH_0 .

$$\frac{d\alpha}{dt} = \frac{dH}{dt} / \Delta H_0 \quad (9)$$

The α is determined as the ratio between the heat released up to a time ($t(\Delta H_p)_t$) and the total heat of the reaction.

$$\alpha = (\Delta H_p)_t / \Delta H_0 \quad (10)$$

The samples were cured dynamically at different heating rates. The DSC curves of non-isothermal curing for *o*-CFER/MeTHPA and *o*-CFER/MeTHPA/org-

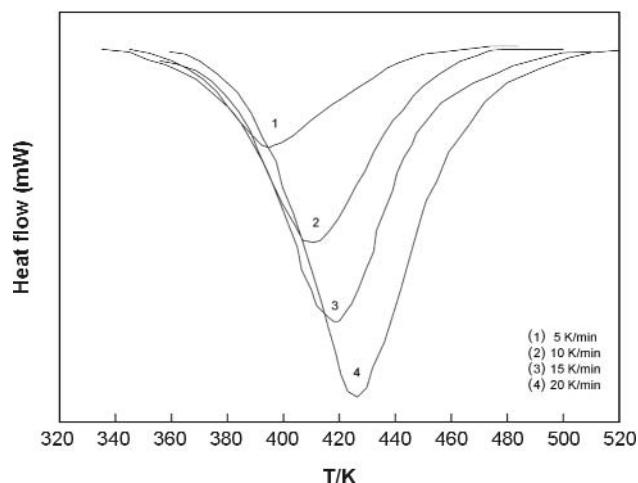


Figure 2. DSC Curves of non-isothermal curing for *o*-CFER/MeTHPA.

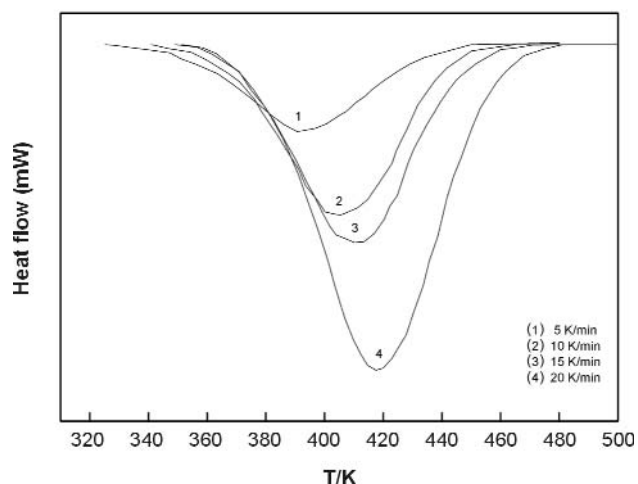


Figure 3. DSC Curves of non-isothermal curing for *o*-CFER/MeTHPA/org-MMT (7phr).

MMT nanocomposites are shown in Figures 2 and 3. As seen from Figures 2 and 3, the trends of curves are similar, and the exothermic peaks are all observed. The results indicate that the curing reaction of these systems is an exothermic reaction. The heating rate shows a great influence on the curing process. At low heating rates, the exothermic peaks appear first. While at higher heating rate, the areas of the peak are greater and the exothermic peaks and conversion curves shift to high temperature. Figures 4 and 5 show the curves of curing conversion vs temperature for *o*-CFER/MeTHPA and its org-MMT nanocomposite, respectively. The data obtained were applied to iso-conversional method of Ozawa, Kissinger-Akahira-Sunose, and Friedman to determine the kinetic param-

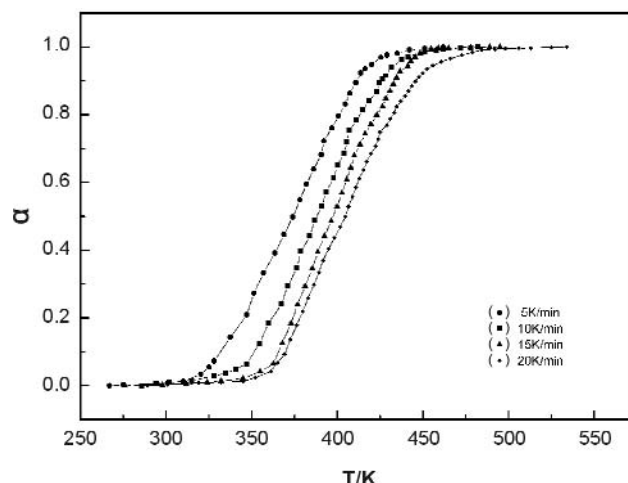


Figure 4. Curing degrees of *o*-CFER/MeTHPA vs temperature.

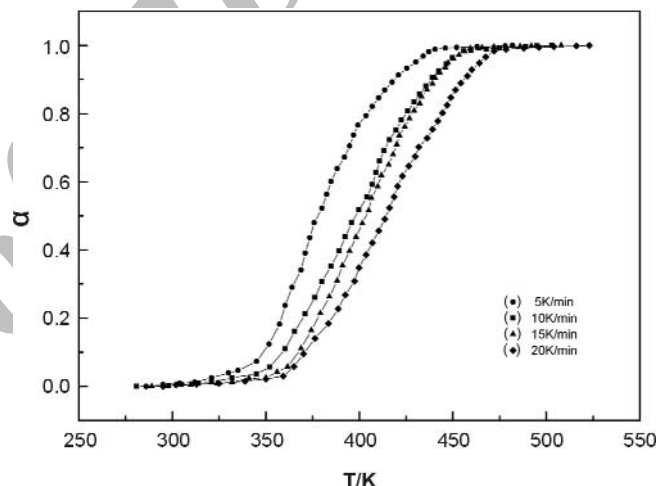


Figure 5. Curing degrees of *o*-CFER/MeTHPA/org-MMT (7phr) vs temperature.

eters in curing process of resins.

On the basis of Ozawa method, eqn (6) is applied to different conversion degrees of curing.

According to this equation, for each conversion degree the logarithm of the heating rate is correlated with the inverse temperature. For a given heating rate, the temperature at different curing degrees is obtained from the curves α - T , calculated by dynamic DSC runs (Figures 4 and 5). Table 1 shows the values obtained for the activation energy, E , and the constant, A' , of both *o*-CFER/MeTHPA and its org-MMT nanocomposites. In most cases, the linear correlation coefficient is included between 0.98 and 1. It can also be observed that activation energy changes with the curing degree. Thus, the activation energy, E , in both

Table 1. Kinetic parameters of samples curing at different conversion degrees determined by Ozawa method.

<i>o</i> -CFER			Nanocomposite			
α (%)	A'	E(mol/kJ)	R	A'	E(mol/kJ)	R
2	6.966	33.122	0.999	8.758	45.328	0.991
10	7.103	38.877	0.998	9.081	53.219	0.994
20	7.422	42.373	0.995	9.124	55.489	0.996
30	7.493	43.693	0.998	9.151	56.199	0.999
40	7.976	48.106	0.995	9.207	58.074	0.998
50	8.646	54.032	0.999	9.221	59.243	0.995
60	8.662	55.258	0.996	9.313	59.607	0.995
70	9.557	63.022	0.994	9.521	63.347	0.999
80	9.733	65.631	0.994	9.468	64.541	0.997
90	9.525	65.948	0.999	9.494	66.852	0.999
95	9.697	66.598	0.993	9.038	64.756	0.996
98	8.716	64.482	0.999	9.191	66.238	0.998
100	8.571	66.301	0.998	8.612	69.381	0.985

A'=log AE/g(α)R-3.315

R: linear correlation coefficient

resins, begins to increase slightly, then tends to maintain it constant ($\alpha=50\sim 60\%$) and finally rises again. In the last stage of curing process, the activation energies increase due to the reaction which was controlled by diffusion rather than by kinetic factor [19]. The average values of activation energy, E, of curing process are 54.42 and 60.17 kJ/mol for *o*-CFER/MeTHPA and nanocomposite of org-MMT, respectively. Although the activation energies are similar in both cases, but the nanocomposite has a slightly higher average value of activation energy than that of pure *o*-CFER. It may be due to that the epoxy resins chains are inserted into the spaces of montmorillonite and the movement and diffusion of reactive groups were hindered.

Table 2 shows the results obtained with both samples after fitting the data to Kissinger-Akahira-Sunose model (eqn (7)). The values of R are similar to those of the Ozawa method. The evolution of activation energy with the cure degree in both samples is similar to the above mentioned diffusion controls. It can be observed that the nanocomposite is slightly more reactive than *o*-CFER/MeTHPA, however, in the range of about 95% conversion degree this trend is reversed. This fact could be due to the vitrification phenomenon, which takes place later in the nanocomposite. The average values of the activation energy of *o*-CFER/MeTHPA and nanocomposite are 111.06 and

Table 2. Kinetic parameters of samples curing at different conversion degrees determined by Kissinger-Akahira-Sunose method.

<i>o</i> -CFER			Nanocomposite	
α (%)	E(mol/kJ)	R	E(mol/kJ)	R
2	65.196	0.999	92.656	0.987
10	76.831	0.998	109.347	0.992
20	84.393	0.993	114.267	0.994
30	87.198	0.998	115.649	0.999
40	97.009	0.994	119.724	0.998
50	110.298	0.999	122.241	0.993
60	112.796	0.994	122.775	0.994
70	130.374	0.993	131.039	0.999
80	136.087	0.994	133.437	0.996
90	138.424	0.999	138.238	0.999
95	140.259	0.993	133.063	0.996
98	129.706	0.999	129.092	0.987
100	135.215	0.998	141.531	0.981

123.31 kJ/mol, respectively. The deviation of these data is lower than 2%, which is also according to the results obtained by the application of Ozawa model.

In Friedman method, eqn (8) is employed to different degrees of conversion. For each conversion degree, the logarithm of the heating rate is correlated with the inverse temperature. But this model is different from other models because in this case, for a given temperature, the reaction rates (r) at different curing degrees are obtained from the thermograms curve which are obtained by dynamic DSC runs.

Table 3 shows the results of the activation energy, E, logarithm of pre-exponential factor, lnA, and the linear correlation coefficient, R, for both resins. In this model, the values of lnA are determined as a result of function $f(\alpha)$, which is substituted by an expression of first order ($n=1$). The values of R obtained for *o*-CFER/MeTHPA and its org-MMT nanocomposite indicate a suitable fit of their respective kinetic parameters. Even, the fits are not so satisfactory as in the case of the Ozawa and Kissinger-Akahira-Sunose models. This fact is due to the error associated with the calculus of reaction rate. The average values of activation energy are 56.68 and 60.15 kJ/mol for *o*-CFER and its nanocomposite, respectively. The polymer decomposition at 90-98% of conversion will take place where the activation energy decreases.

Table 3. Kinetic parameters of samples curing at different conversion degrees determined by Friedman method.

α (%)	o-CFER			Nanocomposite		
	E(mol/kJ)	$\ln A$	R	E(mol/kJ)	$\ln A$	R
2	34.481	9.673	0.995	51.388	12.651	0.995
10	38.841	9.341	0.992	53.153	12.008	0.997
20	42.98	10.741	0.989	55.641	12.248	0.998
30	44.341	11.211	0.993	55.874	11.822	0.997
40	49.715	12.743	0.994	57.839	12.016	0.992
50	56.799	14.673	0.995	59.011	12.074	0.985
60	57.777	14.715	0.993	59.219	11.681	0.988
70	67.057	17.186	0.987	63.567	12.465	0.997
80	69.843	17.659	0.993	64.555	12.196	0.991
90	69.583	17.026	0.999	66.986	12.172	0.998
95	65.35	17.689	0.991	64.148	10.895	0.992
98	64.388	14.683	0.999	62.243	9.982	0.986
100	67.681	13.998	0.998	68.34	9.528	0.979

The results obtained with Friedman model are different from the Ozawa and Kissinger-Akahira-Sunose models. Three models under studies show that R value is fitted in them and although the results are good, Friedman model, however, is not as good as the other methods under investigations. Ozawa and Kissinger-Akahira-Sunose models describe similar evolution of the activation energy with the curing degree. The main advantage of Ozawa method is the chance to determine the kinetic constants of curing process without knowing the function $f(\alpha)$. Ozawa Method is the best of the three models studied, but it does not allow calculating the reaction order of the resin curing process.

CONCLUSION

- The XRD indicates that the epoxy resins chains are inserted into the spaces of montmorillonite and an *o*-CFER/MeTHPA/org-MMT nanocomposite was obtained.
- The isoconversional kinetics methods can be applied to study the curing process of this resin and its nanocomposite. In the three kinetic methods under investigation, the variation of the activation energy at different curing degrees is similar in both samples.
- The nanocomposite has a slightly higher average

value of activation energy than that of pure *o*-CFER due to the presence of organic montmorillonite. It may be due to the epoxy resins chains which are inserted into the spaces of montmorillonite and the movement and diffusion of reactive groups are hindered.

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