Effect of Nickel Doping on the Cure Kinetics of Epoxy/Fe₃O₄ Nanocomposites

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S1. Isoconversional kinetic methods

Friedman model

Friedman model is defined based on the following equation:

$$ln\left[\beta_{i}\left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = ln\left[f(\alpha)A_{\alpha}\right] - \frac{E_{\alpha}}{RT_{\alpha,i}},$$
(S1)

By plotting $ln[\beta_i(d\alpha/dT)_{\alpha,i}]$ vs. $1/T_{\alpha}$ the value of activation energy ($E\alpha$) in each α can be obtained from the slope of Figure B1.



Figure S1. Plots of $ln(d\alpha/dt)$ vs. 1/*T* the prepared samples based on *Friedman* model at β = 5 °C/min.

KAS method

KAS method was defined by the following equation:

$$ln\left(\frac{\beta_i}{T_{\alpha,i}^{1.92}}\right) = Const - 1.0008 \left(\frac{E_\alpha}{RT_\alpha}\right),\tag{S2}$$

Plotting $ln(\beta_i/T_{\alpha,i}^{1.92})$ vs. $1/T_{\alpha}$ gives a straight line; its slop gives the activation energy (Figure S2).



Figure S2. Plots of $ln(\beta/T^{1.92})$ vs. 1/T for prepared samples based on *KAS* model.

S2. Selection of curing reaction model

Friedman model

Based on the *Friedman* method, the model of epoxy curing reaction can be determined using Eq. (S3). The shape of plot of $ln[Af(\alpha)]$ vs. $ln(1-\alpha)$ denotes the deviation from nth order reaction (Figure S3).

$$ln[Af(\alpha)] = ln\left(\frac{d\alpha}{dt}\right) + \frac{E}{RT} = lnA + nln(1 - \alpha),$$
(S3)

For *n*th-order cure mechanism a straight line was obtained by plotting $ln[Af(\alpha)]$ v.s. $ln(1-\alpha)$ which slope gives the reaction degree (*n*).



Figure S3. Plots of $ln [Af(\alpha)]$ vs. $ln(1-\alpha)$ for the samples under heating rate of 5 °C/min used in calculation of activation energy via Friedman method.

Malek Method

The kinetic model based on the Malek method is determined using the following equations:

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right)_{\alpha} exp\left(\frac{E_0}{RT_{\alpha}}\right) = Af(\alpha), \qquad (S4)$$

$$z(\alpha) = \left(\frac{d\alpha}{dt}\right)_{\alpha} T_{\alpha}^{2} \left[\frac{\pi(x)}{\beta T_{\alpha}}\right],$$
(S5)

The term in the brackets of equation (S5) has not significant effect on the shape of the $z(\alpha)$ function and can be omitted [S1, S2]. In the equation (S4) the amount of E_0 is determined by *FWO* method, where the change in the activation energy with variation of α remains constant, from the following equation:

$$ln(\beta_i) = Const - 1.052 \left(\frac{E_{\alpha}}{RT_{\alpha}}\right),$$
(S6)

In the *FWO* method activation energy is determined from the slope of $ln(\beta i)$ vs. 1/T as shown in Figure S4.



Figure S4. Plots of $ln(\beta)$ vs. 1/T for epoxy resin and prepared nanocomposites derived from *FWO* model.

This method gives the activation energy in depended of conversion. By *FWO* method the values of activation energy is obtained 64.9, 55.3 and 52.6 for neat epoxy, EP/Ni-Fe₃O₄ and EP/Fe₃O₄, respectively. The experimental values of $y(\alpha)$ and $z(\alpha)$ for EP, EP/Fe₃O₄ and EP/Ni-Fe₃O₄ nanocomposite as a function of conversion are shown in Figure S5 and compared with theoretical master plots.



Figure S5. Variation of $y(\alpha)$ and $Z(\alpha)$ versus conversion for prepared samples based on *Malek* model.

 $y(\alpha)$ and $z(\alpha)$ was normalized as follows to vary between 0 and 1:

$$y_n(\alpha) = \frac{y(\alpha)}{\max[y(\alpha)]},$$
(S7)

$$z_n(\alpha) = \frac{z(\alpha)}{\max[z(\alpha)]},$$
(S8)

The maximum values, $max[y(\alpha)] = \alpha m$ and $max[z(\alpha)] = \alpha_p$, can be found from the following expressions:

$$f'(\alpha_m) = 0, \tag{S9}$$

$$f'(\alpha_p)g(\alpha_p) = -1, \tag{S10}$$

S3. Determination of degree of reaction

The degrees of autocatalytic reaction (n and m) and the pre-exponential factor (A) can be determined through the following equations:

$$ValueI = ln\left(\frac{d\alpha}{dt}\right) + \frac{E_{\alpha}}{RT} - ln\left[\frac{d(1-\alpha)}{dt}\right] - \frac{E_{\alpha}}{RT'} = (n-m)ln\left(\frac{1-\alpha}{\alpha}\right),$$
(S11)

$$ValueII = ln\left(\frac{d\alpha}{dt}\right) + \frac{E_{\alpha}}{RT} + ln\left[\frac{d(1-\alpha)}{dt}\right] + \frac{E_{\alpha}}{RT'} = (n+m)ln(\alpha - \alpha^2) + 2lnA,$$
(S12)

The slope of the plot of *ValueI* vs. $ln [(1-\alpha)/\alpha]$ (Figure S6) gives the value of (n-m) and the slope and intercept of the plot of *ValueII* vs. $ln(\alpha-\alpha^2)$ (Figure S7) give the value of (n+m) and 2lnA.



Figure S6. Plots of *Value I* calculated using DSC data for prepared epoxy system under heating rate of 5 $^{\circ}$ C/min.



Figure S7. Plots of Value II calculated for prepared samples under heating rate of 5 °C/min.

S4. Model validation

In order to validate the kinetics parameters, curing rate $(d\alpha/dt)$ was calculated by determining $f(\alpha)$ and compared with the experimental value. For this purpose the averaged values of m, n and lnA at different heating rates and apparent activation energies that obtained from differential Friedman and integral KAS models were introduced into Eq. (2) and the theoretical $d\alpha/dt$ values were obtained. The simulated curves calculated by Friedman and KAS methods using Eq. (2) and the experimental curves for EP, EP/Fe₃O₄ and EP/Ni-Fe₃O₄ are shown in Figure S8. As can be observed, $d\alpha/dt$ values calculated from differential Friedman and integral KAS approaches are in well agreement with the experimental data at early stage of cure when the chemical reaction between curing moieties prevails. The simulated $d\alpha/dt$ curves begin to diverge from the experimental data by progress in curing reaction at the elevate temperature (high conversion stage) when the diffusion effect became stronger due to occurrence of vitrification event. Vitrification gradually occurs and leads to increment of diffusion effect so it can be inferred the mobility of curing moieties was decreased due to the viscosity upturn. Therefore, in the late stage of cure, cross-linking reaction is under the control of diffusion leading to the occurrence of some deviation between the models and experiments. Nevertheless, deviations between the simulated curves and the experimental curves are not so obvious which indicate that autocatalytic model (Eq. 2) is adequate to describe the curing reaction of EP, EP/Fe₃O₄ and EP/Ni-Fe₃O₄.



Figure S8. Comparison of experimental data with the kinetic models for prepared samples at heating rate of 5 °C/min based on *Friedman* and *KAS* model.

References

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[S2] Montserrat, S., Málek, J. and Colomer, P., 1998. Thermal degradation kinetics of epoxyanhydride resins: I.: influence of a silica filler. Thermochimica acta, 313(1), pp.83-95.