Green Energy, Environment and Sustainable Development
C. Wang et al. (Eds.)

doi:10.3233/ATDE230384

Effect of Curing Agent Type on Curing Reaction Kinetics of Epoxy Resin

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Abstract. Curing agent types have a great influence on the reaction kinetics and post-curing properties of epoxy resins. The dynamic process of epoxy resin curing reaction will affect the structure, morphology and mechanical properties of cured products. In this paper, low molecular weight polyamides, aromatic amines and anhydrides were selected as three kinds of curing agents and their isothermal viscosity-time properties were studied to investigate the operational time and curing speed of the resin system. The non-isothermal Differential Scanning Calorimetry (DSC) method was conducted to study the curing reaction kinetics of three kinds of curing agent/epoxy resin systems so as to deduce the curing reaction kinetics model and calculate the corresponding kinetic parameters. Results showed that a low molecular weight polyamide curing agent blend resin system can occur at a lower temperature of curing reaction and the cure rate is fast. The curing process of the aromatic amine curing agent blend resin system is divided into two steps, while the anhydride curing agent blend system should be able to cure at high temperatures and have a long operating time. The theoretical curing temperatures of the three curing agents of low molecular polyamide, aromatic amine, primary curing and secondary curing and acid anhydride are respectively 74.13℃, 86.31℃, 165.24℃ and 152.90℃, which are also the recommended curing temperatures of the corresponding curing agents.

Keywords. Curing agent type, curing reaction kinetics, non-isothermal dSC

1. Introduction

The new technology of polymer matrix composite with self-sensing function has shown good advantages in engineering structure monitoring, especially providing a new idea to solve technical difficulties such as poor deformation coordination and long-term working performance of sensors [1-5].

Commonly used polymer matrices in polymer matrix composites can be roughly divided into thermosetting materials (such as resins [6]), thermoplastic materials and elastic materials (such as rubber [7], PDMS [8]), etc. Due to the advantages of high

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reactivity and adjustable and controllable strength of epoxy resin and the special volume effect, tunnel effect and quantum size effect of conductive fillers such as CNTs, epoxy resin-based conductive composites exhibit excellent mechanical [9], electrical [10], thermodynamic [11], optical and other properties. In addition to the different types of epoxy resins, the curing agent types have a great influence on the reaction kinetics and post-curing properties of epoxy resins [12, 13]. In recent years, much research has been carried out on the curing agent of epoxy resin [14-18]. Choi et al. [19] studied the curing behavior by dynamic DSC for epoxy nanocomposites with amine functionalized multiwall carbon nanotubes. However, the current research related to curing agents mainly focuses on the comparative analysis of the properties after curing reaction [20, 21]. Furthermore, when selecting the polymer matrix, mechanical indexes will be used to screen the polymer matrix, and the stiffness coordination between the matrix and road materials will be tested by adjusting and optimizing indexes such as the modulus and toughness of the polymer matrix, so as to avoid the difference of strain variation amplitude between the two due to the stiffness difference between materials, which will lead to large measurement errors in the detection process [9, 22].

In this paper, low molecular weight polyamides, aromatic amines and anhydrides were selected as three kinds of curing agents, and the isothermal viscose-time properties were studied to investigate the operational time and curing speed of the resin system. The change of heat flow under different heating rates was studied based on DSC so as to study the curing process temperature and curing reaction kinetic parameters of the resin system.

2. Experimental Section

2.1. Materials

The thermosetting epoxy resin was purchased by commercially. The polyamide curing agent is widely used for its low toxicity, good construction performance, strong adhesion and well elasticity. The low molecular weight polyamides curing agent was prepared by condensation of dimer vegetable oil fatty acids and polyvinyl polyamines. The amine value of the low molecular weight polyamides is 200±20 mg KOH/g. Aromatic amine hardeners are liquid admixtures formed by the reaction of aromatic polyamines and glycidyl ether. The curing agent is provided by Kunshan Jiulimei Electronic Materials Co., LTD. The anhydride curing agent is synthesized from the biological lactic acid monomer as the basic raw material. The structural formulas of the selected low molecular weight polyamide, aromatic amine and anhydride have been listed along with the epoxy resin monomer (Figure 1).

2.2. Sample Preparation

Firstly, the bisphenol-A epoxy resin was be conducted with pre-vacuumized and defoamed. The blending percentages were shown in Table 1. The blending ratios were chosen according to the instruction manuals of commercial curing agent products, which contain the recommended mix ratios. After the physical blending of 600 rpm for 10 min, the mixture blends were shaped and cured for various measurements.

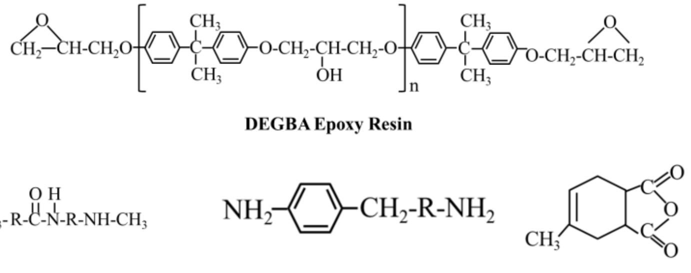


Figure 1. Structural formulas of epoxy resin and three types of curing agents.

Table 1. The blending ratios and the specimen codes of samples with different agents.

Sample number	Bisphenol-A epoxy resin/wt.%	Curing agent type	Curing agent/wt.%
CA-1#	100	Low molecular weight polyamides	65
CA-2#	100	Aromatic amines	30
CA-3#	100	Anhydrides	80

2.3. Characterization Measurements

The instrument used for DSC testing is DSC25 (TA Instruments) which belongs to the heat flow type. After sample preparation, about 5 mg of each epoxy blend sample was taken, weighed accurately and placed in the heater sample pot with the reference material covered with an aluminum lid. The non-isothermal DSC method can be used to study the curing reaction process of materials. Under the constant flow rate of nitrogen of 50 mL/min, non-isothermal scanning (0-250°C) was carried out on the samples of the three kinds of curing agent blend resin system at three different heating rates of 5 K/min, 10 K/min and 15 K/min respectively. Under the condition of the same input power of the sample and the reference substance, the temperature difference (ΔT) between the two ends of the sample to be tested and the reference substance was measured to characterize the heat change of the blend resin system. According to the heat flow equation, the temperature difference (ΔT) is converted into the heat flow difference as the signal output. After the test, the heat flow curve of the reaction peak and the DSC curve of the blended resin system can be obtained. The initial peak temperature (T_i), peak temperature (T_p) and peak end temperature (T_f) of the reaction exothermic peaks of each blend system can be obtained by DSC curves. The curing reaction kinetic parameters were further analyzed.

3. Results and Discussions

It is well known that the properties of epoxy resins are mainly determined by the network structure of the cured material. The structure of the curing network depends on the materials structure and curing technology [23, 24]. The study of curing reaction kinetics of epoxy resin plays important basis for the research of epoxy composite technology.

Studies [9, 22, 25] believe that the reaction mechanism of the epoxy resin curing process is related to temperature, and the reaction mechanism will change with different temperatures. Therefore, the authors adopt the non-isothermal DSC method to study the curing reaction kinetics of three kinds of curing agent/epoxy resin system, deduce the curing reaction kinetics model, determine the curing process of different kinds of curing agent for epoxy resin curing system and calculate the corresponding kinetic parameters.

3.1. Heat Flow Changes

By mixing the epoxy resin system with three kinds of curing agents, the DSC test was conducted at the heating rates of 5 K/min, 10 K/min and 15 K/min respectively and the results were shown in Figure 2. In the DSC curve, the upward peak represents exothermic heat, while the downward peak represents endothermic heat. It can be seen from the figure that the heating rate β has a great influence on both the peak and peak shape of the DSC curves. The higher the heating rate β, the higher the peak temperature, the sharper the peak shape and the larger the peak area of the three kinds of curing agent blended epoxy resin system. The area surrounded by the peak in the DSC curve is proportional to the change of enthalpy, indicating that the greater the heating rate β, the greater the heat absorption of the blending system reaction. For the same curing agent, the peak in the DSC curve shows a trend of moving to the right with the gradual increase of β, indicating that the higher the heating rate, the higher the temperature of the blend system needs to be solidified. The DSC curves displayed much difference for the three kinds of curing agents. There is only one endothermic peak in the polyamide curing agent and anhydride curing agent blends, indicating that the curing process is one-step curing. However, the DSC curve of the aromatic amine curing agent blend resin system showed two endothermic peaks, which indicated that the aromatic amine curing agent was carried out step by step when curing epoxy resin.

In order to more clearly and quantitatively characterize the curing process and curing reaction temperature of the three kinds of curing agent blended epoxy resin system, the initial peak temperature (T_i), peak temperature (T_p) and peak end temperature (T_f) of endothermic peaks at different heating rates were listed, as shown in Table 2. At the turning point of the curing process, T_i was obtained by making the intersection of two tangent lines and T_f was obtained by making the intersection of two tangent lines at the end of curing. T_p represents the max value of the exothermic peak of the curing reaction. It can be seen from the table that the T_i, T_p and T_f of three kinds of curing agent blended epoxy resin system all show an increasing trend with the increase of heating rate β and the increasing trend of T_p and T_f is more obvious. This is because the increase in heating rate makes the thermal inertia of the system stronger and the curing time shorter. The system does not have enough time to cure at a low temperature, resulting in the system's curing exothermic lag, which shows the trend of the exothermic peak moving to the high-temperature region on the DSC curve. Under the three heating rates selected in the experiment, the initial curing temperature of the low molecular polyamide curing agent blending system (CA-1#) is about 40°C-55°C. In this paper, the temperature selected for the determination of isothermal viscosity time properties was 50°C, indicating that the blending system immediately began the curing reaction during the determination of isothermal viscosity time properties. For the aromatic amine curing agent blend system (CA-2#), the temperature difference of the two-step curing reaction is large, so the corresponding multi-step curing step should be set rationally. For the aromatic amine curing agent blend system (CA-2#), two types of amino groups existed. One kind is the amino group which is attached to the benzene ring directly, and the other kind is the fatty amine which is attached to the benzene ring. During the reaction, due to steric hindrance, the fatty amine on the benzene ring is preferentially cured with the epoxy resin (the first step), while the amino group attached to the benzene ring is cured again (the second step). For the anhydride curing agent blend system (CA-3#), the initial curing temperature is more than 100°C, so the anhydride curing agent should be cured at a high temperature after the end of the blending.

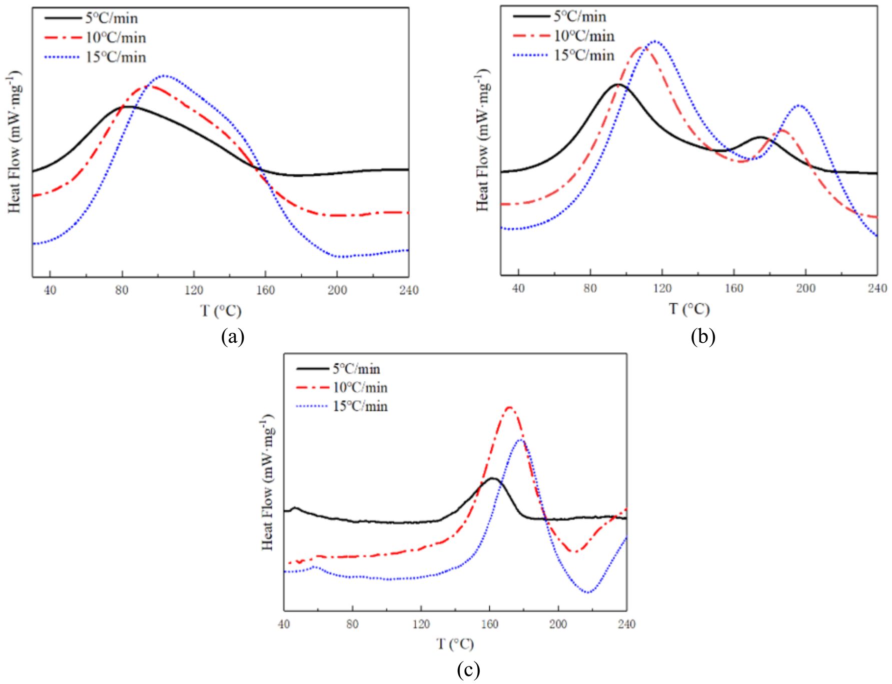


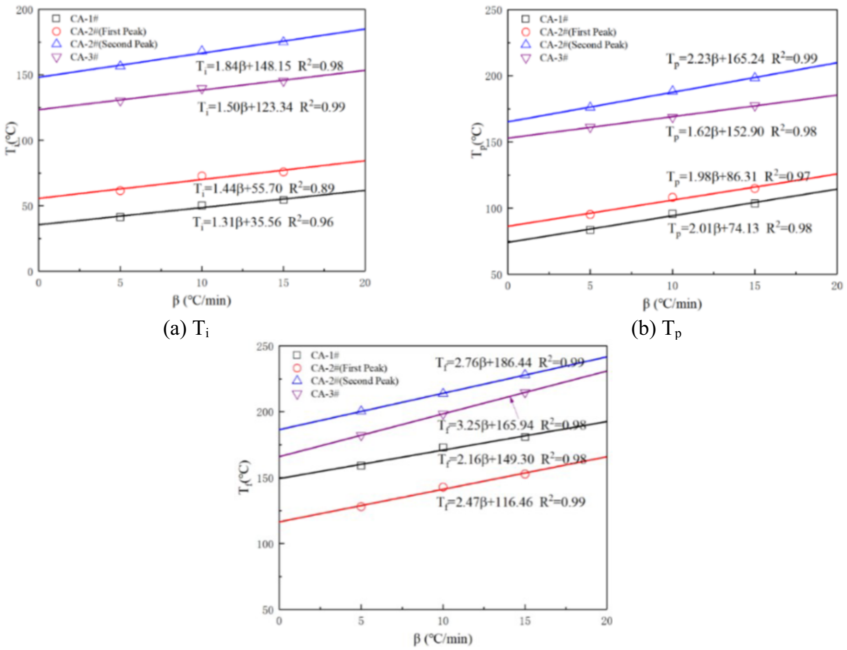
Figure 2. DSC curves of three kinds of curing agent blended epoxy resin system at different heating rates: (a): CA-1#; (b): CA-2#; (c): CA-3#.

Table 2. DSC data at different heating rates of blend systems with different cure agents.

Title 1	β/°C·min^{-1}	T_i/°C	T_p/°C	T_f/°C
	5	41.35	83.46	159.20
CA-1#	10	50.13	95.73	172.77
	15	54.43	103.59	180.83
	5	61.49	95.15	128.02
	10	72.81	108.13	142.77
CA-2#	15	75.84	114.90	152.73
	5	156.58	176.00	200.38
	10	168.08	188.35	213.75
	15	174.97	198.32	227.98
	5	130.25	161.22	175.21
CA-3#	10	139.57	168.73	200.35
	15	145.28	177.46	214.69

3.2. Curing Process Temperature Study

In order to further study and determine the curing temperatures of three kinds of curing agents during resin curing, the changes of T_i, T_p and T_f with the heating rate β were plotted and fitted respectively, as shown in Figure 3. As can be seen from the figure, the T_i, T_p and T_f have a good linear relationship with the heating rate β. In the actual production and application process, the curing temperature adopted in the same step curing process is constant (heating rate β=0), so this paper adopts the epitaxial method to the fitted line to the heating rate β=0. The intercepts obtained at β=0 by fitting the linear equation of T_i, T_p and T_f-β are consistent with the corresponding theoretical initial setting temperature (T_{gel}), curing temperature (T_{cure}) and post-treatment temperature (T_{treat}) of three kinds of curing agents during epoxy resin curing respectively.



(a) T_i (b) T_p (c) T_f

Figure 3. T_i, T_p and T_f change with β.

The corresponding T_{gel}, T_{cure} and T_{treat} data of the three kinds of curing agents during epoxy resin curing are shown in Table 3. The T_{gel}, T_{cure} and T_{treat} of the three kinds of curing agent mixed resin system show the same rule, which showed the rule of secondary curing of aromatic amine curing agent>anhydride curing agent>the primary curing of aromatic amine curing agent>low molecular polyamide curing agent. The curing temperatures obtained from extrapolation of three curing agents of low molecular polyamide, aromatic amine, primary curing and secondary curing and acid anhydride are 74.13℃, 86.31℃, 165.24℃ and 152.90℃, respectively, which are also the recommended curing temperatures of the corresponding curing agents. As can be seen from the curing temperature, the low molecular polyamide curing agent can be cured at a low temperature, the aromatic amine curing agent needs to be cured at a low temperature for one step and then at a high temperature for two steps, the acid anhydride curing agent needs to be cured directly at a high temperature belonging to the heating curing agent.

Table 3. T_i, T_p and T_f with different agents.

Sample number	T_{gel}/°C	T_{cure}/°C	T_{treat}/°C
CA-1#	35.56	74.13	149.30
CA-2#	55.70	86.31	116.46
CA-2#	148.15	165.24	186.44
CA-3#	123.34	152.90	165.94

3.3. Curing Reaction Kinetic Parameters Study

The kinetics of curing reaction can be obtained by Kissinger equation and Crane equation. The Kissinger equation can be expressed as follows:

$$\ln(\beta/T_P^2) = \frac{-E_a}{R} \cdot \frac{1}{T_p} + ln\frac{AR}{E_a} \tag{1}$$

where β is the heating rate, K/min; T_p stands for peak temperature, K; R is the ideal gas constant 8.3144 J/(mo1·K); E_a is the apparent activation energy (J/mol) and A is the pre-exponential factor.

The simplified Crane equation is expressed as follows:

$$\frac{\ln(\beta)}{\ln(1/T_{p)}} = -\frac{E_a}{nR} \tag{2}$$

where n is the reaction order.

$\ln(\beta/T_p)^2$, $\ln(\beta)$ and $1/T_p$ were calculated respectively and the scatter plots of $\ln(\beta/T_p)^2$-1/Tp and $\ln(\beta)$ -$1/T_p$ under the three curing agent/resin systems were plotted respectively. Corresponding lines were obtained after linear regression fitting, as shown in Figure 4. E_a/R can be calculated according to the Kissinger equation and the slope k of the line in Figure 5, AR/E_a can be calculated from the intercept of the line and then the apparent activation energy E_a and the pre-exponential factor A of the reaction system can be obtained. The slope and intercept of the line fitted by the Kissinger equation and Crane equation are shown in Table 4.

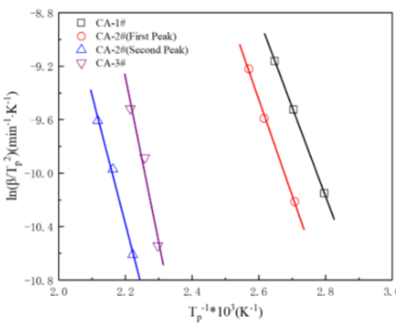


Figure 4. Fitted line of experimental data with Kissinger equation.

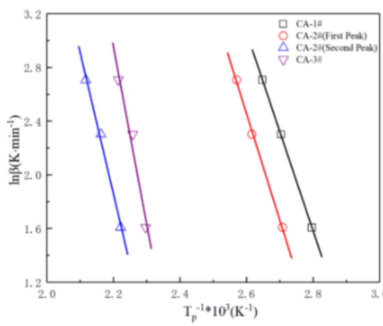


Figure 5. Fitted line of experimental data with Crane equation.

Table 4. Fitted line of experimental data with Kissinger equation and Crane equation.

Sample number	Kissinger equation		Crane equation
	Slope k	Intercept	Slope k
CA-1#	-6.648	8.443	-7.383
CA-2#	-7.169	9.191	-7.926
CA-2#	-9.606	10.751	-10.528
CA-3#	-12.333	17.848	-13.221

4. Conclusion

In this work, the effects of three cure agents with the pure bisphenol-A epoxy resin and the properties of the blends were systematically studied. The main conclusions are summarized as follows:

- Heat flow cures show that the heating rate β has a great influence on both the peak and peak shape of the DSC curve. The higher the heating rate β, the higher the peak temperature, the sharper the peak shape and the larger the peak area of the three kinds of curing agent blended epoxy resin system. For the same curing agent, the peak in the DSC curve shows a trend of moving to the right with the gradual increase of β, indicating that the higher the heating rate, the higher the temperature of the blend system needs to be solidified.
- There is only one endothermic peak in the polyamide curing agent and anhydride curing agent blends, indicating that the curing process is one-step curing. However, the DSC curve of the aromatic amine curing agent blend resin system showed two endothermic peaks, which indicated that the aromatic amine curing agent was carried out step by step when curing epoxy resin.
- T_{gel}, T_{cure} and T_{treat} of the three kinds of curing agent mixed resin system show the same rule, which is the secondary curing of aromatic amine curing agent>anhydride curing agent>the primary curing of aromatic amine curing agent>low molecular polyamide curing agent, respectively. The theoretical curing temperatures of the three curing agents of low molecular polyamide, aromatic amine, primary curing and secondary curing and acid anhydride are respectively 74.13℃, 86.31℃, 165.24℃ and 152.90℃, which are also the recommended curing temperatures of the corresponding curing agents.

References

[1] Xin X, Qiu Z. Novel conductive polymer composites for asphalt pavement structure in Situ Strain Monitoring: Influence of CB/CNT and GNP/CNT Nano/Micro hybrid fillers on strain sensing behavior. IEEE Sensors Journal. 2020;22(5):3945-3956.

[2] Xin X, Liang M. Self-sensing behavior and mechanical properties of carbon nanotubes/epoxy resin composite for asphalt pavement strain monitoring. Construction and Building Materials. 2020;257:119404.

[3] Su L, Luan X. Sensing performance and optimizing encapsulation materials of a coordinated epoxy-encapsulated sensor for strain monitoring of asphalt pavement layered structures. IEEE Sensors Journal. 2022;22(10):9811-9823.

[4] Xin X, Yu R. Dynamic mechanical and chemorheology analysis for the blended epoxy system with polyurethane modified resin. Journal of Renewable Materials. 2022;10(4):1081.

[5] Ding S, Ruan Y. Self-monitoring of smart concrete column incorporating CNT/NCB composite fillers modified cementitious sensors. Construction and Building Materials. 2019;201:127-37.

[6] Paluvai N, Mohanty S. Synthesis and modifications of epoxy resins and their composites: A review. Journal of Macromolecular Science: Part D-Reviews in Polymer Processing. 2014;53(16):1723-1758.

[7] El Eraki, El Lawindy. The physical properties of pressure sensitive rubber composites. Polymer Degradation and Stability. 2006;91(7):1417-1423.

[8] Wolf M, Salieb G. PDMS with designer functionalities—Properties, modifications strategies, and applications. Progress in Polymer Science. 2018;83:97-134.

[9] Li G, Sun J, Hou W, et al. Three-dimensional porous carbon composites containing high sulfur nanoparticle content for high-performance lithium–sulfur batteries. Nature communications. 2016;7(1):10601.

[10] Nurazzi N, Asyraf M. A review on mechanical performance of hybrid natural fiber polymer composites for structural applications. Polymers. 2021;13(13):2170.

[11] Forintos N, Czigany T. Multifunctional application of carbon fiber reinforced polymer composites: Electrical properties of the reinforcing carbon fibers–A short review. Composites Part B: Engineering. 2019;162:331-343.

[12] Li Y, Pan D, Chen S, et al. In situ polymerization and mechanical, thermal properties of polyurethane/graphene oxide/epoxy nanocomposites. Materials & Design. 2013;47:850-856.

[13] Moghadam AD. Mechanical and tribological properties of self-lubricating metal matrix nanocomposites reinforced by carbon nanotubes (CNTs) and graphene-a review. Composites Part B: Engineering. 2015;77:402-420.

[14] Hutchinson J M, Moradi S. Thermal conductivity and cure kinetics of epoxy-boron nitride composites—A review. Materials. 2020;13(16):3634.

[15] Cruz-Cruz I, Ramírez-Herrera C A, Martínez-Romero O, et al. Influence of epoxy resin curing kinetics on the mechanical properties of carbon fiber composites. Polymers. 2022;14(6):1100.

[16] Zhao H, Xu S, Guo A, et al. The curing kinetics analysis of four epoxy resins using a diamine terminated polyether as curing agent. Thermochimica Acta. 2021;702:178987.

[17] George J S, Thomas S. The effect of polymeric inclusions and nanofillers on cure kinetics of epoxy resin: A review. Polymer Science, Series A. 2021;63:637-651.

[18] Lu M, Liu Y, Du X, et al. Cure kinetics and properties of high performance cycloaliphatic epoxy resins cured with anhydride. Industrial & Engineering Chemistry Research. 2019;58(16):6907-6918.

[19] Choi W J, Powell R L, Kim D S. Curing behavior and properties of epoxy nanocomposites with amine functionalized multiwall carbon nanotubes. Polymer composites. 2009;30(4):415-421.

[20] Ding J, Peng W, Luo T, et al. Study on the curing reaction kinetics of a novel epoxy system. Rsc Advances. 2017;7(12):6981-6987.

[21] Mather P, White S. Viscoelastic properties of an epoxy resin during cure. Journal of Composite Materials. 2015;35(10):121-123.

[22] Pathak AK. Improved mechanical properties of carbon fiber/graphene oxide-epoxy hybrid composites. Composites Science and Technology. 2016;135:28-38.

[23] Ma H, Zhang X. A study on curing kinetics of nano-phase modified epoxy resin. Scientific Reports. 2018; 8(1):1-15.

[24] Apostolidis P, Liu X. Chemo-rheological study of hardening of epoxy modified bituminous binders with the finite element method. Transportation Research Record. 2018;2672(28):190-199.

[25] Baeza F, Galao O. Effect of aspect ratio on strain sensing capacity of carbon fiber reinforced cement composites. Materials & Design. 2013;51:1085-94.