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Cure kinetics of epoxy composite applied on stator bars insulation

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Abstract Cure kinetics study of epoxy resin composite, employed as stator bars insulation system, was evaluated through differential scanning calorimetry using the dynamic methodology, different heating rates. These experiments provided some important information about the system as activation energy ($E_a = 65.4$ kJ mol^{-1}), glass transition (T_g) values on different curing stages including the final cured material information and, besides that, it enables the comparison of these data with new materials under development. The activation energy value allows the determination of different energy needs of the system under evaluation, specially temperature for the material cure, improving the possibility of comparison between different insulation systems in use in the high voltage insulation business. The composite conversion degree based on the cure enthalpy (ΔH_{cure}) at different time of cure was also subject of analysis and from that it was possible to comprehend the cure pattern which allows the cure state prediction of further samples of this type of material and the more accurate evaluation of similar samples acquired directly from stator bars.

Keywords Epoxy resin · Cure kinetics · Activation energy · DSC · Insulation

Abbreviations

DSC	Differential scanning calorimetry
T_g	Glass transition
ΔH_{cure}	Cure enthalpy
ΔH	Enthalpy variation
DGEBA	Diglycidyl ether of bisphenol-A
MHHPA	Methylexahydrophthalic anhydride
E_a	Activation energy
ΔH	Enthalpy variation
q	Heating rate
T_p	Temperatures where maximum conversion rate occurs
α_x	Slope
β_y	y Intersection
A	Pre-exponential factor
k	Rate constant
α	Conversion degree

Introduction

The cure of a thermoset system is a very complex process, there are many controversies over literature [1, 3]. It is mainly influenced by the properties of the specific resin/hardener formulation and by the reaction temperature among other process parameters. The most important macroscopic phenomena are gelation and vitrification that occur along the thermoset curing [3]. The cure kinetics occurs along the alteration of the material rheological pattern. Initially the system viscosity decreases due to an exothermic event and, as the molecular weight of the chains rise, the crosslink begins, and the viscosity increases. This is fully correlated to the importance of the kinetic behavior, as the material processing and curing can be

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improved without compromising the mechanical properties of the final product [4].

The uncatalyzed reactions of epoxy resins and cyclic anhydrides are well described in literature [5], the reaction occurs by consecutive addition esterification involving carboxylic acid group intermediates and addition etherification as side reaction [6, 7]. In practice, however, the epoxy-anhydride systems cure is performed with accelerating or initiating agents. Tertiary amines have been widely used as accelerating agents leading to a more complex mechanism than the uncatalyzed curing. Tertiary amines participate in the carboxylate and alkoxide ions formation originating an anionic alternating copolymerization [8], and practically eliminating the epoxide homopolymerization [9], mechanism that also occurs with carboxylate salts accelerators as initiators, as zinc naphthenate.

The interest in epoxy resins cure behavior with different hardeners comes from the use of these materials as matrices in reinforced composites. In particular, diglycidyl ether of bisphenol-A (DGEBA) reacted with cyclic anhydrides, yielding thermosets which are widely used as insulating materials in the electrical industry.

To develop a proper curing process, it is important to understand the reactivity between curing agents toward the aimed epoxy structure. Relative reaction rates are often expressed in terms of the activation energy (E_a). E_a allows comparisons of reaction rates at different temperatures and it is influenced by the type of chemical reactions involved in the cure. Curing of epoxy resins with aromatic and aliphatic amines proceeds with a fairly low activation energy of 50–58.5 kJ mol^{-1}. Activation energies are higher when epoxy compounds having low hydroxyl content are cured alone in the presence of catalysts (92 kJ mol^{-1}) [10].

Epoxy-based thermoset polymers are widely used in the electrical insulation devices field. Insulating materials composed by mica tape (mica over glass fabric) impregnated with epoxy resin are usually applied as insulation of high voltage windings from rotating machines due to its special characteristics as excellent electrical performance and the robustness to mechanical and thermal stresses [1, 2].

The study of the insulation system behavior is essential for improving its properties and performance, as well as its manufacture. The curing method study allows the detection of eventual residual uncured material in the final stator component that can possibly implicate on electrical failures due to state transformation during thermal cycles in machine operation or tests. With the kinetics analysis, the detailed mechanism of curing can be detected and if these materials thus this article addresses the thermal characterization by differential scanning calorimetry (DSC) of a particular insulation system (Micalastic©—epoxy resin, anhydride, zinc naphthenate, and mica tape).

Methods and materials

The epoxy resin, DGEBA, was acquired from Huntsman, having commercial name HY 790, was used as received. This resin is liquid at room temperature; it is bifuncional and presents an epoxy equivalent weight of 167–171 g eq^{-1}.

The hardener, methylexahydrophthalic anhydride (MHHPA), was acquired from Huntsman, having commercial name HY1102, was used as received. This material is a clear liquid at room temperature and it has an acid number >660 mg KOH g^{-1} and a maximum acid value of 1%.

The mica tape that is impregnated through the VPI (vacuum pressure impregnation) process, described later, contains fine mica paper with basic weight per area unit, zinc naphthenate accelerator, epoxy-based binder on a 23 g m^{-2} density fiberglass fabric support material.

The test objects were prepared by the impregnation of mica tape layers. This process starts with the drying step in the VPI tank under vacuum for at least 10 h. Then the resin is transferred from the storage tank to the impregnation vessel, and the pressure phase begins under nitrogen for a specified period of time. The chosen temperature, from 80 to 160 °C, to prepare the partially cured samples was 140 °C.

The DSC measurements were made using a NETZSCH DSC 200 F3 equipment previously calibrated, the scan was made in each heating rate from 30 to 280 °C. The measurements were carried on using about 15 mg sample mass in aluminum pans, under a 50 mL min^{-1} nitrogen dynamic atmosphere.

Results and discussion

The impregnated samples were used for two sets of experiments. First the dynamic kinetics study was carried out with two layers of freshly impregnated uncured mica tape. Dynamic curing studies were performed at different heating rates of 5.0, 7.5, 10.0, 12.5, 20.0, and 25.0 K min^{-1}.

The non-isothermal kinetics experiments of this system cure results are presented on Fig. 1. It is possible to observe a broad exothermic peak between 150 and 280 °C with the maximum value shifting from 197.5 °C (5.0 K min^{-1}) to 237.9 °C (25.0 K min^{-1}). This peak represents the main cure event with an enthalpy variation (ΔH) from 99.6 to 130.3 J g^{-1} (Fig. 1).

The kinetics of the epoxy–anhydride system was studied through phenomenological models of the nth-order reaction with auto-catalyzed system, characterized by the formation of some intermediate species that markedly accelerates the cross-linking reaction [11]. Considering preliminary observations, the peak maxima is the most reliable and reproducible data we can use to determine kinetic data. The

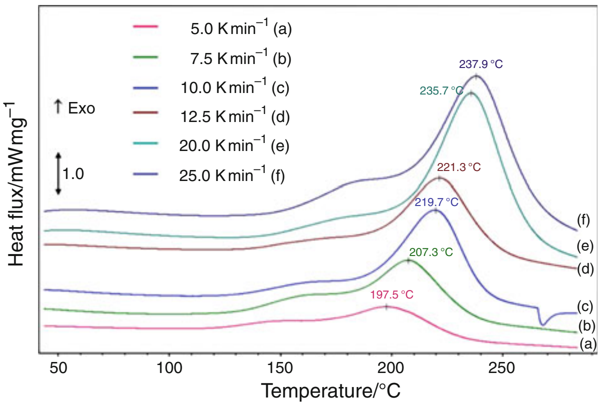

Fig. 1 DSC curves of composite cure in different heating rates (q) from 5 to 25 K min^{-1}, under dynamic nitrogen atmosphere

expressions derived from Kissinger method [12, 13] were used to investigate the cure kinetics, as this is a special type of the isoconversional method where the kinetic parameters are determined at the conversion corresponding to the peak maximum, allowing the calculation of the kinetic parameters through the relationship between q and temperatures where maximum conversion rate occurs (T_p).

Based on Kissinger equation for cure kinetics $1/T_p$ versus ln (q/T_p^2) graphic was plotted (Fig. 2). Trough this slope (α_x) it is possible to calculate the E_a, which is 65.4 kJ mol^{-1}, and the pre-exponential factor (A) obtained from the y intersection (β_y).

$$\alpha_x = E_a/R \Leftrightarrow E_a = 65.4\,\mathrm{kJ\,mol^{-1}}$$

$$\beta_y = -\ln(AR/E_a) \Leftrightarrow A = 3.29 \times 10^6\,\mathrm{min^{-1}}$$
$$= 1.98 \times 10^8\,\mathrm{h^{-1}}$$

These kinetic parameters allow the expression of the overall rate constant (k) in different temperatures as shown in Table 1, where k values were calculated for all temperatures that this material can be cured at.

$$k(\mathrm{h^{-1}}) = A \exp\,(E_a/RT) = 1.98 \times 10^8 \exp\,(65400/RT)$$

It is feasible to compare this value with other epoxy systems and observe that it is very similar to many already studied systems [14, 15]. Although the comparison with epoxy system amine [8] catalyzed systems brings up the important information that the zinc naphthenate accelerated system needs more energy to cure and this is relevant due to the allowance to make a better tune of the final material cure degree in comparison to the amine catalyzed insulation system, as it is more stable to small temperature fluctuation in the manufacturing process, even though it needs more energy to reach the same curing state. This value is also very important for comparison of E_a on further studies about the system advances as the improvement of accelerator concentration, curing temperature verification, among other factors.

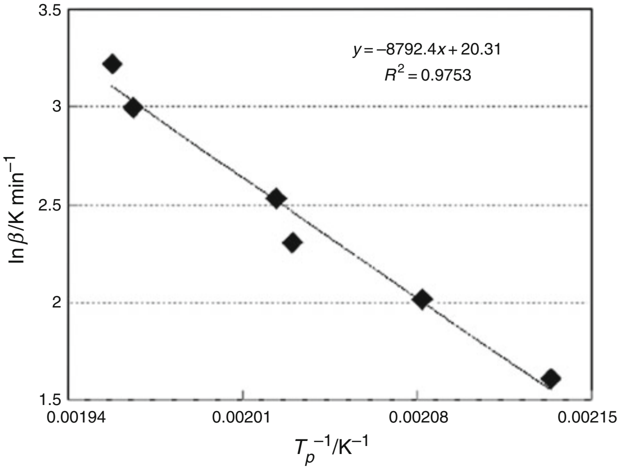

Fig. 2 $1/T_p$ versus ln (q/T_p^2)

Table 1 k values for all cure temperatures

	Temp./°C	k/h^{-1}
k_{80}	80	0.04
k_{90}	90	0.08
k_{100}	100	0.14
k_{110}	110	0.24
k_{120}	120	0.41
k_{130}	130	0.67
k_{140}	140	1.07
k_{150}	150	1.68
k_{160}	160	2.58

The second set of DSC experiments were carried out at heating rate of 10 K min^{-1} with samples after times of cure of 0, 1, 2, 4, 6, 8, 10, 12, and 48 h. This experiment had the focus on observing the conversion degree of the monomers into the polymer. In this experiment (Fig. 3), the peak observed is related to the polymerization event and some of the DSC parameters are shown in Table 2. The total enthalpy variation for the cure exothermic event (ΔH_{cure}) of the fully uncured material was determined to be about 104.5 J g^{-1} and with this data it was possible to estimate the conversion degree during the during process.

This experiment allowed the determination of the glass transition (T_g) variation during the cure. T_g was only observed and determined from 6 h of curing, the first verified value is 85.8 °C this material presents about 79.49% conversion degree ($\Delta H_{\mathrm{cure}} = 14.9$ J g^{-1}). The T_g value increases with the curing time, as expected. And in 48 h of cure the ΔH_{cure} is 0.50 J g^{-1}, that represents a conversion degree of 99.49% and for this material the registered curve shows a T_g of 133.70 °C. This value can be compared to the T_g of this material under the ASTM

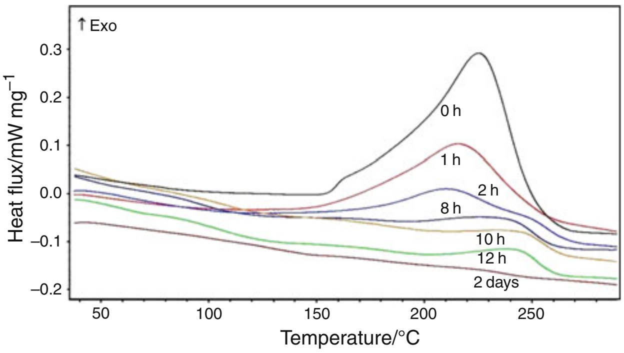

Fig. 3 DSC curves of composite samples with different times of cure from 0 h to 2 days, under dynamic nitrogen atmosphere, at heating rate of 10 K min^{-1}

Table 2 Data from ΔH_{cure}, conversion degree, and T_g for composites with different time of cure

	Time/h	ΔH_{cure}/J g^{-1}	Conversion degree/%	Glass transition/°C
t_0	0	104.5	0.00	–
t_1	1	52.7	46.50	–
t_2	2	31.0	68.53	58
t_4	4	20.2	79.49	67
t_6	6	14.9	84.87	86
t_8	8	10.7	89.14	93
t_{10}	10	7.5	92.39	983
t_{12}	12	6.4	93.50	108
t_{48}	48	0.5	99.49	134

D3418 (Standard Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by DSC) methodology that guarantees the complete cure of the material, that the value is 138 °C.

Treating the data from Table 2 (conversion degree (α) versus time (t)) it can be found that the cure perfectly obeys the nth-order kinetics, expression $d\alpha/dt = k\,(1 - \alpha)^n$. The reaction order ($n$) has been determined as 1.86 ± 0.08 and the empirical k for 140 ± 5 °C was observed to be 0.88 ± 0.06 h^{-1}. Considering the methods variation, it is possible to conclude that the k attained in this experiment and the calculated above for a similar temperature are similar, fact that shows the consistency of the experiments (Fig. 4).

From these results, we can understand from the chemical point of view the main characteristics of the cure of the insulation. Based on the conversion degree values, it is possible to assure an impressive curing state at t_{12} that is observed in the laboratory body-proof, as observed in the final product along its extension. Supported by these results, it is now possible to know the cure degree of any other specimen of the manufactured composite, independently of knowing the time and cure temperature, improving the quality assurance, allowing the better control of the final product homogeneity.

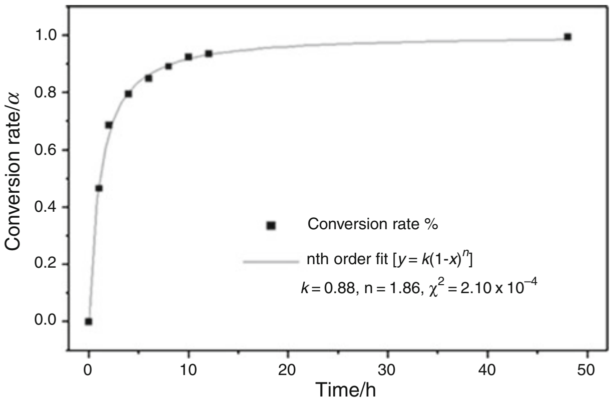

Fig. 4 Conversion degree versus time

Conclusions

The composite cure kinetics study resulted in the system activation energy ($E_a = 65.4$ kJ mol^{-1}), from the data k and A could also be calculated, being possible to determine the complete kinetic triplet so that the modeling of curing is feasible for any temperature regime. Besides that the systems comparison and cure criteria evaluation have now better kinetic basis. Observing the T_g variation, it is also allows further comparison with improved systems or similar ones. Conversion degree based on the ΔH_{cure} was also subject of analysis and resulted in a good method for curing state prediction of insulation in different stages of polymerization and under different polymerization temperatures.

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