



# Article Cure Kinetics of Commercial Epoxy-Amine Products with Iso-Conversional Methods

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Abstract: The dependence of the apparent activation energy for the epoxy-amine reaction on the degree of conversion can be obtained by applying iso-conversional methods to the non-isothermal cure data obtained by using differential scanning calorimetry (DSC). The application of three iso-conversional methods has been utilized for the analysis of non-isothermal DSC cure data for three commercial high solids epoxy-amine coatings. The average apparent activation energy for cure of the fully formulated commercial product(s) is very similar to that previously reported for the epoxy-amine clear coats, indicating that the presence of additives does not influence the epoxy-amine apparent activation energy. Among the methods tested, Friedman's method performed the best in fitting the experimental DSC data. In addition, all three methods underpredict the experimental isothermal cure data for three commercial products at two different cure conditions (i.e., 23 °C/50% RH and 40 °C/70% RH), showing that the non-isothermal DSC experiments cannot capture the catalytic effect of water on the curing reaction of epoxy-amine coatings. Furthermore, for high-solids epoxy-amine products, at least 60% conversion is required to achieve the time when the applied coating will not show any tackiness (i.e., the T2 time measured using the Beck Koller method).

Keywords: model-free kinetics; epoxy-amine coatings; drying time; isothermal cure



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# 1. Introduction

Two-component (2K) epoxy-amine organic coatings, used for anticorrosion applications on structures such as automobiles, bridges, oil and gas pipelines, windmills, oil rigs, etc., cure by the reaction of epoxy groups with the amine groups following the step-growth polymerization process. This curing process is complicated and involves the ring-opening reaction of the epoxy ring, which produces secondary amines that further react with the epoxy groups to produce tertiary amines, causing branching or crosslinking (see Figure 1a). The hydroxyl group produced during the polymerization can form hydrogen bonds with the unreacted epoxy groups, thereby promoting the nucleophilic attack of the amino groups on the epoxy groups. Such a reaction is termed an autocatalytic reaction and is shown schematically in Figure 1b. The electrophilicity of the epoxy group and the nucleophilicity of the amino group determine the reaction kinetics for 2K epoxy-amine coatings [1]. In addition, temperature and catalysts also influence the curing kinetics for epoxy-amine coatings. Water and other compounds containing hydroxyl groups, in general, act as catalysts for epoxy-amine cure [2,3].

The curing process for epoxy-amine coatings involves different stages, such as gelation and vitrification, depending upon the type of epoxy resin, the curing agent, and the curing temperature used. Gelation happens when the three-dimensional polymeric network has formed throughout the network with significant chain branching. At this point, the average molecular weight can be considered to be infinity [4], and the coating seems to be a 'gel' with significant tackiness. Vitrification occurs if the cure temperature is sufficiently lower than the glass transition temperature ( $T_g$ ) of the formed polymer network, causing the transition from a gel-like structure to a glass-like structure. Vitrified epoxy-amine coatings can appear to be fully cured. Cure kinetics for epoxy-amine polymerization are influenced by both the gelation and vitrification processes since molecular mobility is reduced by both of these processes, causing diffusion limitations. Therefore, the initial stages of epoxy-amine polymerization are chemically controlled, whereas the later stages are considered diffusion-controlled [5,6].



**Figure 1.** (a) Schematic representation of the step-growth reactions between primary amines and epoxy rings and secondary amines and epoxy rings without autocatalytic effect. (b) Schematic representation of step-growth reaction between primary amine and epoxy ring with autocatalytic effect.

During the application of such coatings to steel structures, e.g., on different parts of a ship in a yard, cure kinetics play a significant role in determining the cost of application. For example, at low application temperatures during winter, a fast-curing epoxy-amine coating can reduce the overcoating interval, thereby increasing the application speed and reducing the overall cost of the application process. After application, curing kinetics govern how quickly the coating (or the coating system) can develop its required chemical, mechanical, and barrier properties since all these properties are strongly dependent on the final epoxy-amine polymer (along with other non-reactive additives such as extenders, hydrocarbon resins, etc.) present in the commercial coatings. Nevertheless, an optimum curing speed is always required, since too fast curing can generate significant internal stresses that cause cracking. Delamination of epoxy-amine coatings from the metallic substrate or from other coating layers is also sometimes attributed to high curing speeds, which do not allow entanglements of polymer chains.

For investigating the cure kinetics of epoxy resins with amine curing agents, the differential scanning calorimeter (DSC) is considered as one of the most important instruments since the ring-opening reactions of epoxy with molecules such as amines are exothermic. The rate of the epoxy-amine reaction is proportional to the heat released, which can be detected with DSC as exothermic heat flow. Consequently, the degree of cure, or conversion  $(\alpha)$  can be monitored as a function of curing time and temperature using DSC. Isothermal and non-isothermal cure experiments can be conducted using DSC. There are numerous studies dealing with the estimation of cure kinetic parameters for epoxy-amine polymerization with different types of epoxy resins [4–18], curing agents [19–28], catalysts [3,29–31], etc., where the DSC has been employed in both the isothermal and non-isothermal modes. In addition to DSC, other analytical techniques such as Fourier-Transform Infrared (FTIR with near-IR or mid-IR) [8,15,32,33], Nuclear Magnetic Resonance (NMR) [9,34–36], and Gel Permeation Chromatography (GPC) [20] have also been used to study the reaction between epoxy resins and different curing agents. NMR and GPC are considered suitable for the study of the initial stages of epoxy-amine polymerization. As the polymerization continues, the epoxy-amine thermoset becomes insoluble in the solvents used for NMR and GPC. Therefore, these techniques are not suitable for studying the later stages of epoxy-amine polymerization [1]. Cure kinetics for epoxy-amine clear coats have also been studied by coupling the DSC with a Fourier transform near-infrared spectrometer. The

apparent activation energy (E) and the kinetics for epoxy-amine reaction estimated by either coupling these instruments together or using them separately were very similar [14]. A cure kinetics study employing both the DSC and FTIR provided similar apparent activation energies for the epoxy-amine reaction [32]. In the case of FTIR, it is important to mention that a straightforward correlation of the cure kinetics for the top few micrometers of the applied film with the cure kinetics in the bulk of the film may not be possible due to the limited penetration depth of, especially, the mid-IR. Near Infrared (NIR) is preferred over mid-IR because of its higher penetration depth and better peak resolution in comparison to mid-IR. More importantly, the effect of vitrification on the cure kinetics throughout the bulk of the applied film may not be easily studied using IR spectroscopy. In contrast, DSC provides information about the bulk of the applied film, and it can also measure (and separate from other transitions) the glass transition temperature ( $T_g$ ) of the polymerizing epoxy-amine network as a function of time and temperature, especially when operated in the temperature-modulated mode [37]. Therefore, DSC has been used to study the cure kinetics of commercial epoxy-amine coatings.

## 2. Theory of Kinetics Analysis

Cure kinetics deals with the measurement and parameterization of the curing process of, e.g., epoxy-amine thermosets. The epoxy-amine cure reaction can be stimulated with temperature changes; therefore, thermal analysis such as DSC can be used to study such processes [38,39]. In thermal analysis, the rate of epoxy-amine cure reaction  $(d\alpha/dt)$  is considered to be a function of temperature (T) and conversion ( $\alpha$ ), as shown by Equation (1).

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \mathbf{k}(\mathbf{T})\mathbf{f}(\alpha) \tag{1}$$

where, k(T) is the temperature-dependent rate constant and  $f(\alpha)$  is the conversion-dependent reaction model. The curing reaction of epoxy-amine releases heat, which is detected by DSC, and the conversion is measured as a fraction of the total heat released. The temperature-dependence of epoxy-amine curing is parameterized by using the Arrhenius Equation, so that Equation (1) becomes Equation (3).

$$k(T) = A \, \exp\left(\frac{-E}{RT}\right) \tag{2}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \mathrm{A} \, \exp\left(\frac{-\mathrm{E}}{\mathrm{RT}}\right) \mathbf{f}(\alpha) \tag{3}$$

where, A is the pre-exponential factor, E is the apparent activation energy for the reaction, and R is the universal gas constant. Regarding the  $f(\alpha)$  term, several reaction models have been proposed in the open literature [38,39] for the epoxy-amine curing process, but the most appropriate one seems to be the Kamal model, as shown in Equation (4) [38–40].

$$\frac{d\alpha}{dt} = [k_1(T) + k_2(T)\alpha^m](1-\alpha)^n$$
(4)

where  $k_1(T)$  and  $k_2(T)$  are the temperature-dependent rate constants for the regular epoxyamine addition reactions and the autocatalyzed reactions, and n and m are the orders of the regular epoxy-amine addition reaction and autocatalysis, respectively.

Two major approaches are used to study the kinetics of epoxy-amine cure. The first one, typically named the model-based approach, is based upon fitting the experimental cure data to the assumed reaction models. In this approach, it is common to use a single-step reaction model to fit the experimental data, which yields a single average E value for the whole curing process. Since multiple reactions are involved in the epoxy-amine curing process, this single averaged E value does not reflect the changes in the reaction mechanism and cure kinetics with varying cure temperature and conversion. Kamal's model is a good alternative to using single-step models, but the complexity of such curing reactions does not seem to be adequately captured by the standard model fitting techniques [23]. The second approach, commonly known as the iso-conversional methods or the model-free kinetics (MFK), does not consider a specific reaction model. The MFK approach assumes that the rate of reaction at a constant conversion is only a function of the applied temperature, which is shown by taking the logarithmic derivative of Equation (1).

$$\left[\frac{\partial \ln\left(\frac{d\alpha}{dt}\right)}{\partial T^{-1}}\right]_{\alpha} = \left[\frac{\partial \ln k(T)}{\partial T^{-1}}\right]_{\alpha} + \left[\frac{\partial \ln f(\alpha)}{\partial T^{-1}}\right]_{\alpha}$$
(5)

where the subscript  $\alpha$  represents iso-conversional values, i.e., the values related to a given conversion. Since at  $\alpha$  is constant,  $f(\alpha)$  is also constant, making the second term on the right-hand side of Equation (5) zero. Therefore, we can write:

$$\frac{\partial \ln\left(\frac{d\alpha}{dt}\right)}{\partial T^{-1}} \bigg|_{\alpha} = \frac{-E_{\alpha}}{R}$$
(6)

Equation (6) shows that, without using a reaction model, the temperature-dependence of the iso-conversional rate can be used to evaluate the iso-conversional apparent activation energy ( $E_{\alpha}$ ), and that's why this approach is termed MFK. Several MFK methods have been proposed that allow the evaluation of apparent activation energy as a function of conversion, and due to their simplicity, they are generally preferred over model-based approaches. Among the available MFK methods, some are classified as differential methods, while others are integral methods. The International Confederation for Thermal Analysis and Calorimetry (ICTAC) recommends using the Friedman (FM) method from the differential methods and the Kissinger-Akahira-Sunose (KAS) method and the Vyazovkin's (Vy) method from the integral methods for kinetic analysis due to their relatively better accuracies. For details regarding the model-based and MFK methodologies, interested readers are suggested to read the publications from the International Confederation for Thermal Analysis and Calorimetry (ICTAC) [38,39]. It is important to mention that non-isothermal DSC experiments with a constant heating rate ( $\beta$ ) are conducted when the aim is to study the cure kinetics of epoxy-amine thermosets with the MFK methods. For such experiments, Equation (3) is rearranged into Equation (7).

$$\beta \frac{d\alpha}{dT} = Aexp\left(\frac{-E}{RT}\right)f(\alpha)$$
 (7)

Integration of Equation (7) yields Equation (8).

$$g(\alpha) \equiv \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = A \int_0^t \exp\left(\frac{-E}{RT}\right) dt$$
(8)

where  $g(\alpha)$  is the integral form of the reaction model term. Equation (8) is the foundation of the different integral methods. When used for the constant-heating rate experiments, the time integral in Equation (8) is replaced with the temperature integral, as shown in Equation (9). This rearrangement allows the introduction of an explicit value of heating rate into Equation (9), which means that its use is limited to processes in which the sample temperature does not deviate significantly from the reference temperature, such as in DSC.

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E}{RT}\right) dT$$
(9)

No analytical solution of the integral in Equation (9) is available. Only approximate solutions have been offered due to the fact that several integral methods are available. The integral method of KAS has the form shown in Equation (10), whereas Equations (11) and (12) show the integral method [41]. The details about the derivation, how to use different methods, and advantages and disadvantages of these methods can be found elsewhere [38,39]. Commercial software packages such as Kinetics Neo from NETZSCH have these methods built-in and allow the user to easily switch between different methods.

$$\ln\left(\frac{\beta_{i}}{T_{\alpha,i}^{2}}\right) = \text{Constant} - \frac{E_{\alpha}}{RT_{\alpha}}$$
(10)

$$\varphi(\mathbf{E}_{\alpha}) = \sum_{i=1}^{n} \sum_{j \neq 1}^{n} \frac{J(\mathbf{E}_{\alpha}, \mathbf{T}_{i}(\mathbf{t}_{\alpha}))}{J(\mathbf{E}_{\alpha}, \mathbf{T}_{j}(\mathbf{t}_{\alpha}))}$$
(11)

where the time integral is given by:

$$J(E_{\alpha}, T_{i}(t_{\alpha})) = \int_{0}^{t_{\alpha}} \exp\left(\frac{-E_{\alpha}}{RT(t)}\right) dt$$
(12)

The differential method proposed by Friedman [42] is based upon Equation (13), which is derived by applying the iso-conversional principle to Equation (3).

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[f(\alpha)A_{\alpha}] - \frac{E_{\alpha}}{RT_{\alpha,i}}$$
(13)

Equation (13) can be used for any temperature program, and at each given value of  $\alpha$ , the value of  $E_{\alpha}$  is estimated by the slope of the plot of  $\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i}$  versus  $\frac{1}{T_{\alpha,i}}$ , where different temperature programs are denoted by the index i. The temperature at which the conversion ( $\alpha$ ) is reached under the i<sup>th</sup> temperature program is denoted by  $T_{\alpha,i}$ . In the case of an isothermal program, i denotes the individual temperature used, whereas for the cases where a linear heating rate is applied (i.e., the non-isothermal experiments), i denotes the individual heating rate. To account for the heating rate ( $\beta$ ) employed in the non-isothermal experiments, Equation (13) is transformed into Equation (14), which assumes that the  $T_{\alpha,i}$  varies linearly with time in accordance with the applied heating rate  $\beta_i$  [39].

$$\ln\left[\beta_{i}\left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = \ln[f(\alpha)A_{\alpha}] - \frac{E_{\alpha}}{RT_{\alpha,i}}$$
(14)

The Friedman's method (FM) is typically more accurate than the integral methods (such as the KAS and Vy methods discussed above) because the differential methods do not use any approximations. Nevertheless, inaccuracies and imprecisions may occur by employing the differential methods, such as difficulties in determining the baseline of differential data obtained by employing DSC or differential thermal analysis (DTA), which can cause inaccuracies in the rate values. Similarly, if the reaction heat shows significant dependence on the applied heating rate, the inaccuracies in differential methods can be considerable [39].

By applying the MFK methods to the non-isothermal DSC curing experiments, the apparent activation energy for the epoxy-amine cure as a function of conversion ( $E_{\alpha}$ ) is obtained. The plot of  $E_{\alpha}$  vs.  $\alpha$  provides information about the start of the reaction, autocatalysis, and the presence of diffusion limitations during cure [6]. Several researchers have shown that, for the epoxy-amine clear coats,  $E_{\alpha}$  remains fairly constant up to 80% conversion, followed by a sharp increase [6,12,26,29] or decrease [6,16,43] in  $E_{\alpha}$  during the last 20% of conversion. Autocatalysis due to the formation of hydroxyl groups during the course of epoxy-amine polymerization is considered the reason for constant  $E_{\alpha}$  with increasing conversion. For the observed increase and decrease in the  $E_{\alpha}$  during the last 20% of conversion, both attributed to the presence of diffusion limitation due to gelation and vitrification of the crosslinking polymer, two different explanations exist in the available literature. According to some studies [16,43], gelation and vitrification of the polymerized

network reduce the molecular mobility, and these molecules can polymerize only after a series of diffusion jumps. As a result, the relatively low  $E_{\alpha}$  at very high conversions is attributed to high diffusion limitations. For such cases, the  $E_{\alpha}$  can be reduced to unusual values of less than 40 kJ·mole<sup>-1</sup> [38]. High diffusion limitations are also proposed as a possible reason when  $E_{\alpha}$  values in the final stages of epoxy-amine polymerization can be greater than 100 kJ·mole<sup>-1</sup> [26,38]. The time, temperature,  $\alpha$ , and  $E_{\alpha}$  data obtained from the application of MFK methods to the non-isothermal DSC experiments at constant heating rates can also be used to predict the isothermal conversions at different temperatures [6,38,39].

The aim of this work is to study the cure kinetics of fully formulated commercial epoxyamine coatings with selected MFK methods since the majority of the open literature on this topic deals with the clear coats of different epoxy resins and curing agents. Commercial epoxy-amine coatings contain several ingredients (e.g., solvent(s), filler(s), hydrocarbon resin(s), etc.) that may influence their cure kinetics. Therefore, we have tested three MFK methods with respect to their ability to model the non-isothermal DSC data of three commercial high-solids epoxy-amine coatings at three different heating rates. By employing the Kinetics NEO software, it has been shown that Friedman and Vyazovkin's methods perform the best for this purpose with only minute differences.  $E_{\alpha}$  values of the three commercial coatings are found to be very similar to those reported in the open literature for epoxy-amine clear coats, confirming that in the presence of different additives, the apparent activation energy for the epoxy-amine cure reaction does not change. In addition, by comparing the isothermal cure predictions with the actual experimental isothermal cure data of three commercial coatings at two different conditions, it has been shown that the non-isothermal DSC experiments do not capture the effect of humidity on the epoxy-amine cure kinetics. Moreover, this work shows that the cure kinetics of epoxy-amine coatings measured by DSC can be used to develop methods of commercial relevance. This has been performed by showing that at least 60% conversion is required to achieve the time by which the applied coating shows no tackiness (i.e., the T2 time, which is typically measured according to ISO 9117-4:2012 or the ASTM D5895 standards).

#### 3. Experimental Part

Three commercial epoxy-amine coatings developed by Jotun AS, Norway, for the protection of marine structures such as ships against corrosion were used. Table 1 provides information related to the resin type, curing agent type, and mixing ratio of each product. All products used are high-solids products. Component A of each product contained the epoxy resin along with other additives of the formulation, while the amine curing agent was present in component B of each product.

	Epoxy Resin Type in Component A	Curing Agent in Component B	Mixing Ratio (A:B) by Weight
Product 1	Bis-phenol F	Polyamine	100:21.7
Product 2	Bis-phenol A	Polyamine	100:20.4
Product 3	Bis-phenol A	Polyamine	100:16.0

Table 1. Information about the products and corresponding mixing ratios used.

Differential Scanning Calorimetry (DSC) analysis of the samples was performed on a Q200 DSC instrument from TA Instruments. To measure the total heat of reaction or enthalpy of each epoxy-amine product, DSC was used in non-isothermal conventional mode at three different heating rates of  $2 \,^{\circ}\text{C}\cdot\min^{-1}$ ,  $5 \,^{\circ}\text{C}\cdot\min^{-1}$ , and  $10 \,^{\circ}\text{C}\cdot\min^{-1}$ . For each non-isothermal sample, 50 g of component A were added to a metallic can, followed by the addition of the required amount of component B. This mixture was then thoroughly stirred with a spatula before adding 10 to 16 mg of the liquid sample into a hermetic aluminum DSC cell. A hole was made in the lid of the DSC cell prior to running DSC analysis. The DSC temperature program was made in such a way that all samples were first cooled down to at least -25 °C, followed by the first heating scan up to 200 °C to 250 °C (to confirm that all the reaction heat has been obtained as shown in Figure 2) at one of the heating rates mentioned above. Afterwards, the sample was cooled down at the ramping rate to zero or -50 °C, followed by the second heating scan at the same ramping rate. Replicate runs were mostly conducted at 5 °C·min<sup>-1</sup> and 10 °C·min<sup>-1</sup>, as these experiments need less time. The total heat of reaction (or the enthalpy of reaction or the reaction exotherm) (H<sub>T</sub>) was obtained by integrating the area under the curve obtained in the first heating scan (see Figure 2 as an example). TA Universal Analysis software from TA Instruments was used for analyzing the results.



**Figure 2.** Representative exotherm in a non-isothermal DSC experiment conducted at  $5 \, {}^{\circ}\text{C} \cdot \text{min}^{-1}$  for 3 products. Area under the curve shows the total heat of reaction (H<sub>T</sub>) for each product.

For the isothermal cure experiments, 250 µm films of each product were applied with an applicator on a Mylar plastic film fixed on a glass panel. Each sample was cured in climate chambers with controlled conditions of 23  $^\circ$ C/50% relative humidity (RH) and 40 °C/70% RH for different time intervals. At the end of each time interval, DSC samples in aluminum hermetic cells were prepared by removing 10–15 mg from the desired panel. The lid of each hermetic cell was closed, and a hole was made prior to DSC analysis. These samples were analyzed in temperature-modulated DSC (MDSC) in one heating cycle unless mentioned otherwise. An average heating rate of 5 °C·min<sup>-1</sup> with  $\pm 0.80$  °C modulation every 60 s was used as the heating program. For all DSC experiments, the samples were kept under continuous nitrogen flow during analysis. MDSC can separate the overlapping transitions in polymers and provide information about (for example) the glass transition temperature (Tg), exothermic reactions due to residual reactive groups after a certain cure time, melting, etc., simultaneously. More details about the MDSC can be found elsewhere [37]. Figure 3 shows an example of MDSC heat scans obtained from isothermally cured samples of product 2 at different times. T<sub>g</sub> development with curing time and residual heat after curing times of 2.5 h and 4.5 h are shown. This remaining fractional heat of reaction ( $H_t$ ) and the total heat of reaction ( $H_T$ ) can be used to calculate the degree of cure or conversion ( $\alpha$ ) after a given curing time using the following equation. Multiplication with 100 provides the  $\alpha$  as a percentage. The value of  $\alpha$  was estimated as a fraction of one.

![](_page_7_Figure_2.jpeg)

**Figure 3.** MDSC heat scans for the product 2 after isothermal curing for 2.5 h and 4.5 h at 40 °C/70% RH. Glass transition temperature ( $T_g$ ) development, remaining fractional heat of reaction ( $H_t$ ), and increasing curing time are also indicated.

The drying times of the three products were measured according to ASTM D5895 using a Beck Koller drying time recorder inside the climate chambers with controlled curing conditions of 23  $^{\circ}C/50\%$  RH and 40  $^{\circ}C/70\%$  RH.

Kinetics NEO software [44] from NETZSCH was used for fitting the selected MFK methods to the non-isothermal DSC experimental data at different heating rates and to obtain the isothermal cure predictions at different temperatures.

#### 3.1. Cure Kinetics of Product 1

Figure 4 shows the fitting results of three different iso-conversional methods to the exotherms obtained in DSC at three different heating rates and the corresponding conversion of the product 1 at each heating rate. Good reproducibility of the DSC experiments is evident from the replicate runs. The DSC exotherms of this product obtained at different heating rates show a single peak temperature. Therefore, it is reasonable to assume that the curing process of this product can be considered a single-step process for which the iso-conversional methods are recommended [38,39]. Among the three methods used, Friedman's method is a differential method, whereas the KAS and Vy methods are integral iso-conversional methods. It is evident from Figure 4 that the Friedman and Vy methods provide a nearly similar level of fit to experimental data, with R<sup>2</sup> values of 0.9996 and 0.9989, respectively. The KAS method did not fit the experimental DSC data of this product very well, as shown in Figure 4c,d, with a relatively low R<sup>2</sup> value of 0.9600. Figure 4d clearly shows that the KAS method underpredicts the conversion at low temperatures, while at high temperatures, the conversion is overpredicted by this method.

The apparent activation energy of the product 1 was estimated by using these three methods in Kinetics NEO software, and Figure 5 shows the dependence of the apparent activation energy of this product on conversion. The average of the E values over the whole conversion range and the average error estimated for the product 1 by using three different methods are shown in Table 2. In general, all the used methods show that during the initial stages of polymerization (i.e., at  $\alpha \leq 5\%$ ), E for this product tends to increase, followed by a fairly constant E value up to 85% conversion (see Figure 5). The initial rise in the E value at very low conversion can be attributed to the presence of negligible amounts of water or the hydroxy groups in the additives, which catalyze the initial stages of polymerization [2,3]. After 5% conversion of this product, due to epoxy-amine addition,

there are enough hydroxyl groups present in the curing mixture that the mechanism of cure shifts towards the autocatalytic process, which helps to keep a fairly constant E value up to ~85% conversion. At conversions higher than 85%, E starts to increase, which has been observed by various researchers [12,19,26] and is attributed to the diffusion limitations caused by the gelation during curing of epoxies with amine curing agents.

![](_page_8_Figure_2.jpeg)

**Figure 4.** (**a**,**b**) Fitting of DSC exotherm and conversion of product 1 with Friedmann's method. (**c**,**d**) Fitting results of DSC exotherm and conversion of product 1 with KAS method. (**e**,**f**) Fitting results of DSC exotherm and conversion of product 1 with Vy method.

In general, Figure 5 and Table 2 show that all three methods provide nearly the same average E values for this product, which are in very good agreement with available literature values (dealing with similar epoxy and amine curing agents) of around 50–60 kJ/mole when using clearcoats/model coatings [7,11,12,14,21,26,43]. Since the values reported here are obtained from a fully formulated high-solids commercial epoxy-amine product, it is important to highlight that the good agreement between the experimental E values obtained here and those previously published for the model coatings clearly shows that the presence of additives may not influence the average activation energy for epoxy-amine reactions. It is interesting to note that while the Friedman and Vy methods both provide very similar E values of approximately 57 kJ·mole<sup>-1</sup> at the start of the curing process (i.e., at  $\alpha < 5\%$ ), the

KAS method provides an E value of 53 kJ·mole<sup>-1</sup>, which is lower than that provided by the two other processes (see Figure 5). Similarly, the E value estimated by using the KAS method at each  $\alpha$  value in the latter stage (i.e.,  $10 \le \alpha \le 90\%$ ) and deep conversion stage (i.e.,  $\alpha > 90\%$ ) is also lower than those calculated by the Friedman and Vy method. Overall, these differences in the E values estimated by the Friedman, Vy, and KAS methods can be attributed to the relatively poor fitting of the experimental DSC exotherms at different heating rates with the KAS method as compared to the Friedman and Vy methods (see Figure 4c,d). These results show that for such commercial products, E values estimated with the KAS method might lead to an overpredicted degree of cure at a given temperature.

![](_page_9_Figure_2.jpeg)

Figure 5. Comparison of E vs. α using Friedmann, KAS, and Vy method for product 1.

**Table 2.** Average E values and average error estimated for each iso-conversional method for the product 1.

Iso-Conversional Method	Product	Average E (kJ/mol)	Average Error	
Friedman	1	61.2	±2.98	
KAS	1	59.2	±1.94	
Vy	1	61.2	±2.98	
Friedman	2	53.77	±0.72	
KAS	2	53.33	$\pm 0.56$	
Vy	2	53.76	±0.72	
Friedman	3	59.93	±2.09	
KAS	3	56.80	±1.19	
Vy	Vy 3		±2.09	

#### 3.2. Cure Kinetics of Product 2

The product 2 is a high-solids bisphenol-A epoxy product cured with a polyamine curing agent. Using the above-mentioned non-isothermal DSC experiments, the reaction exotherms of this product at 3 different heating rates were also fitted with the three iso-conversional methods used, and the obtained results are shown in Figure 6. The good reproducibility of the experiments is evident from the overlapping exotherms at 5 and  $10 \,^{\circ}\text{C}\cdot\text{min}^{-1}$  heating rates. All exotherms showed a single peak temperature without any shoulders, confirming that the curing process of this epoxy-amine product can also be considered a single-step process. As seen for the previously discussed coating, Figure 6 also

shows that the KAS method does not fit the experimentally measured exotherms very well, whereas the Friedman's and Vy methods provided a satisfactory fit to the experimental data. While comparing the two latter methods at low conversion levels (i.e., at  $\alpha < 20\%$ ), the Vy method slightly overestimates the degree of conversion (see Figure 6f), which was not observed by using the Friedman's method. The R<sup>2</sup> values obtained by using the Friedman, KAS, and Vy methods for fitting the DSC exotherms at different heating rates were 0.9998, 0.9515, and 0.9990, respectively.

![](_page_10_Figure_2.jpeg)

**Figure 6.** (**a**,**b**) Fitting of DSC exotherm and conversion of product 2 with Friedmann's method. (**c**,**d**) Fitting results of DSC exotherm and conversion of product 2 with KAS method. (**e**,**f**) Fitting results of DSC exotherm and conversion of product 2 with Vy method.

The comparison of the apparent activation energy calculated by the three different methods used and its dependence on the degree of conversion of this product is shown in Figure 7. The average E values of this product over the whole conversion range estimated by the three methods are very similar (i.e., around 53.5 kJ·mole<sup>-1</sup>), as shown in Table 2. These E values are in very good agreement with the literature E values for typical epoxyamine model coatings [7,11,12,21,26]. Nevertheless, the average E value of product 2 is slightly lower than the average E value of product 1, which can probably be attributed to the differences in the epoxy resins and curing agents used in these two products. The dependence of  $E_{\alpha}$  on  $\alpha$  obtained using Friedman and Vy methods is nearly the same, i.e., both methods show that the E value of this product can be considered fairly constant from 0 to ~90% conversion, followed by a slight rise during the final 10% conversion (i.e., the deep conversion state), typically attributed to the diffusion limitations caused by the gelation of the curing network. In contrast, the KAS method shows that this product needs a relatively low E value (of 50 kJ mole<sup>-1</sup>) at the start of polymerization, followed by a sharp rise in  $E_{\alpha}$ value up to 5% conversion, after which the  $E_{\alpha}$  value remains fairly constant with increasing conversion up to ~90%, after which the diffusion limitations cause a slight rise in the  $E_{\alpha}$ value. In general, it can be concluded that the dependence of  $E_{\alpha}$  on the product 2 over its conversion estimated by the Friedman and Vy methods is more reliable in comparison to that estimated by employing the KAS method due to the better fitting of the reaction exotherms with the former two methods.

![](_page_11_Figure_3.jpeg)

Figure 7. Comparison of E vs. α using Friedmann, KAS, and Vy methods for the product 2.

### 3.3. Cure Kinetics of Product 3

Figure 8 shows results obtained by fitting the reaction exotherms of the product 3 obtained by the non-isothermal DSC experiments with the three different iso-conversional methods. At the applied heating rates, all exotherms showed a single peak temperature with good reproducibility. The presence of no shoulders in the reaction exotherm obtained by the non-isothermal DSC experiments confirms that the curing of this product can also be treated as a single-step process. It is evident from Figure 8c-f that the KAS method cannot provide a satisfactory fit of the experimental data at all heating rates, whereas the integral Vy method provides a reasonably good fit of the experimental data. The best-fitting results have been obtained by using the differential method of Friedman, as shown in Figure 8a,b. The R<sup>2</sup> values of the Friedman, KAS, and Vy methods obtained were 0.9997, 0.9241, and 0.9983, respectively. These results are in good agreement with those obtained for the previous two products, confirming that among the iso-conversional methods, the differential method of Friedman's performs the best in fitting the experimental curing exotherms of epoxy-amine products, followed by the integral method of Vyazovkin. The KAS method, also an integral iso-conversional method, may not be the best choice for studying the cure process of commercial epoxy-amine products using non-isothermal DSC

![](_page_12_Figure_1.jpeg)

experiments. Furthermore, one can also observe by comparing Figures 4f, 6f and 8f that the Vy method overestimates the experimental conversion at low conversions.

**Figure 8.** (**a**,**b**) Fitting of DSC exotherm and conversion of product 3 with Friedmann's method. (**c**,**d**) Fitting results of DSC exotherm and conversion of product 3 with KAS method. (**e**,**f**) Fitting results of DSC exotherm and conversion of product 3 with Vy method.

The dependence of the activation energy of product 3 on its conversion, obtained by the different methods, is plotted in Figure 9, whereas the average E values are presented in Table 2, which are in good agreement with the values available in the open literature. Slight differences in the activation energies of the three commercial epoxy-amine products shown in Table 2 can be attributed to the differences in the used epoxy resins and curing agents, but in general, it would be appropriate to consider that the epoxy-amine activation energies of these products are approximately the same. In agreement with the previously discussed results for the two other products, both the Friedman's and Vy methods provide similar dependence of E on  $\alpha$  over the whole conversion range. Qualitatively, the KAS method also provided the same trend between E and  $\alpha$  of the product 3, but due to the unsatisfactory fitting results obtained with this method (see Figure 8c,d), the E values may

not be reliable. Figure 9 shows that, when Friedman and Vy methods are used, the E value of this product remains fairly constant up to approximately 45% conversion, followed by a slow increase in the activation energy up to 80% conversion, after which the activation energy increases exponentially over the last 20% conversion, attributed to the diffusion limitations reducing the mobility of the unreacted epoxy and amine molecules.

![](_page_13_Figure_2.jpeg)

Figure 9. Comparison of E vs. α using Friedmann, KAS, and Vy methods for the Product 3.

It is noteworthy that during the initial stages of polymerization, the activation energies of the products 2 and 3 show a constant activation energy value, whereas the activation energy of the product 1 shows a slight increase (compare Figures 5, 7 and 9 up to 5% conversion). Initial stages of epoxy-amine polymerization are of particular interest with respect to the standard and winter grades of the products. It is easy to visualize that a winter-grade epoxy-amine coating should have a low activation energy so that the curing process can be started at low application temperatures. Moreover, the influence of catalyst(s) on the early stages of epoxy-amine polymerization can be better understood by analyzing the first part of the E vs.  $\alpha$  correlation (though there is a lack of such work in the open literature). Significantly high activation energies (i.e., 121 kJ·mole<sup>-1</sup>) in the initial phases of epoxy-amine polymerization can be attributed to the addition of primary amines to the epoxy groups, and as the polymerization proceeds (i.e., the conversion increases), the activation energy reduces due to the (auto)catalytic effect of the formed hydroxyl groups during the epoxy-amine addition reaction [6]. During the autocatalysis, activation energy remains nearly constant with increasing conversion. The current results show that none of the commercial products used here have considerably high activation energies in the initial stages of polymerization, and autocatalysis can be considered as the main polymerization reaction since the activation energies of all three products are fairly independent of conversion up to approximately 80%-85% conversion. In the deep conversion state, the correlation between E and  $\alpha$  of the products 1 and 3 shows a similar exponential rise, whereas the rise in E value of the product 2 in the final stages of cure is much less in magnitude as compared to the products 1 and 3 (compare Figures 5, 7 and 9) between 85 and 100% conversion). The lowest activation energy of product 2 in the final stages of cure will certainly help it to achieve 100% conversion earlier than the other two products, and the reasons for this difference in the correlation between the E and  $\alpha$  of these products are certainly attributable to the differences in the used epoxy resins and the curing agents. Very often, different catalysts/accelerators are blended into the epoxy resins and/or amine curing agents by the manufacturers, which helps keep the activation energy

low at all stages of cure. Consequently, the correlation between E and  $\alpha$  of epoxy-amine commercial coatings, determined by using MFK/iso-conversional methods, can be used as a tool to understand the curing process of different grades (e.g., standard vs. winter grades, etc.), the influence of catalysts/accelerators on the whole curing process, and to predict the degree of cure of products under different application conditions.

### 3.4. Experimental vs. Predicted Conversion of Coatings

The apparent activation energy for each epoxy-amine product, estimated by using three different iso-conversional methods, was used to predict the degree of cure of each product under isothermal conditions of 23 °C and 40 °C using the Kinetics NEO software. The details regarding the equations used to predict the isothermal conversion using the apparent activation energy are published elsewhere [6,38,39]. These predictions are compared with the experimentally measured isothermal conversion of the corresponding product at 23 °C/50% RH and 40 °C/70% RH in Figure 10. It is evident that all the used iso-conversional methods underestimated the isothermal degree of cure of each product. The highest underpredictions were observed for product 1 for which the differences between the experimental and predicted values were found to be as high as 69% for some data points. The average error between the experimental and predicted values at 23 °C and 40 °C for product 1 was 52% and 29%, respectively. It is important to mention that the difference between the experimental and predicted values is high at low conversions, as can be seen in Figure 10. The most probable reason for this mismatch between the experimental and predicted isothermal conversion of these products is the fact that the non-isothermal DSC experiments did not consider the effect of humidity on the curing process of the used products since DSC experiments were performed under continuous nitrogen flow. On the other hand, isothermal curing of the samples of each product was performed under fixed humidity levels of 50% and 70% for a given time. It is well known that water acts as a catalyst for epoxy-amine crosslinking reactions [2,3], and consequently, the experimentally measured conversion of each product was higher than that predicted by the three different iso-conversional methods. Figure 10 also shows that the isothermal conversion predicted for each product at two temperatures by employing the KAS method is initially lower and finally higher than those predicted by the Friedman and Vy methods. This can be attributed to the activation energy values estimated by the KAS method, which are lower than those calculated by the Friedman and Vy methods, as discussed in the previous section. Note that the isothermal predictions obtained by employing the KAS method are less reliable due to the poor fitting of the non-isothermal DSC exotherms (see, e.g., Figure 8c). These results clearly show that the non-isothermal DSC experiments may not capture the effect of humidity on the activation energy for commercial epoxy-amine products.

#### 3.5. Conversion at Different Drying Times

The drying or curing speed of commercial coatings is typically measured by following the ISO 9117-4:2012 standard or the ASTM D5895 standard. It is generally accepted that the faster the drying time of a coating, the faster the coated structure can be handled for the next phase of construction or put back into service. The drying times of commercial organic coatings are measured at different curing conditions, which allows one to compare the drying or curing speeds of coatings under the conditions of interest. The details related to the required equipment and the procedure for these tests can be found elsewhere [45,46]. The outcome of this test is typically related to five different times: the start of drying/curing (T0), set-to-touch time or end of flow back (T1), surface dry or tack-free time (T2 or T2.5), surface hardening commenced or hard dry time (T3), and surface hard or through-dry time (T4). A schematic representation of these times is shown in Figure 11.

![](_page_15_Figure_1.jpeg)

**Figure 10.** (**a**,**b**) Comparison of isothermal degree of conversion at two conditions with the predictions obtained by three different methods for the product 1. (**c**,**d**) Comparison of isothermal degree of conversion at two conditions with the predictions obtained by three different methods for the Product 2. (**e**,**f**) Comparison of isothermal degree of conversion at two conditions with the predictions obtained by three different methods for the product 3.

![](_page_16_Picture_2.jpeg)

**Figure 11.** Representation of different drying times measured according to ISO 9117-4:2012 or the ASTM D5895 standards.

As can be seen, the results from this test do not quantify the degree of cure at different times under conditions of interest, so the test results can be subjective. For commercial epoxy-amine coatings, T2 and T3 are of particular interest as they provide information about the remaining tackiness and the possibility to walk on the applied coating without damaging it. Therefore, an attempt has been made to correlate the T2 and T3 drying times of the three products with their isothermal conversions measured by DSC at 23 °C/50% RH and 40 °C/70% RH, respectively. For this purpose, following the international standards mentioned above, the Beck Koller recorder was used to measure the drying time of each product used. The isothermal conversion data of each coating at both conditions (i.e., 23 °C/50% RH and 40 °C/70% RH) was first fitted with the logarithmic function available in MS Excel to account for the missing data points, as shown in Figure 12 for the product 1. Afterwards, the developed logarithmic equation was used to estimate the actual conversion at the experimentally measured T2 and T3 of each product. Table 3 shows the experimentally measured drying times and the fitted logarithmic equation at two conditions for each product, along with the calculated conversions at the corresponding T2 and T3 drying times. It is interesting to note that for all the commercial products used, the lower limit of conversion at T2 (i.e., the time by which the applied coating shows no tackiness) is higher than 60%. This means that for the considered epoxy-amine coatings, the applied coating will not show tackiness when the conversion is higher than 60%. Since T2 and T3 for these products are very similar for both curing conditions, it can be proposed that T3 (i.e., the time by which one can walk on the applied coating without damaging it) corresponds to at least 65% conversion of the epoxy-amine groups under the given application conditions. These results clearly show that the isothermal conversion of high-solid epoxy-amine products obtained by using DSC can be correlated with the drying times measured by Beck Koller recorders according to ISO 9117-4:2012 or the ASTM D5895 standards. Therefore, the use of isothermal conversion data of commercial epoxy-amine products obtained (e.g.,) by DSC can provide a more reliable alternative method for the accurate and less subjective estimation of drying times that are of commercial interest during the application of such coatings.

![](_page_17_Figure_3.jpeg)

**Figure 12.** Fitting of the isothermal cure data of product 1 at two different curing conditions with the logarithmic function in MS Excel. Conversion at T2 and T3 drying times calculated by using the fitted equation is plotted with different colors.

**Table 3.** Experimentally measured T2 and T3 drying times for each product, a logarithmic function fitted to the isothermal conversion data, and the calculated conversion of each product at the corresponding T2 and T3 drying times.  $\alpha$  = conversion, and t = time in hours.

Product	<b>Curing Condition</b>	BK T2 (h)	BK T3 (h)	Fitted Equation	$\alpha$ at T2	$\alpha$ at T3
1	23 °C/50% RH	7.75	8.5	$\alpha = 0.2012 \times LN(t) + 0.2711$	0.68	0.70
1	40 °C/80% RH	1.75	2.0	$\alpha = 0.1228 \times LN(t) + 0.6307$	0.70	0.72
2	23 °C/50% RH	9.0	9.0	$\alpha = 0.2199 \times LN(t) + 0.2842$	0.77	0.77
2	40 °C/80% RH	3.0	3.0	$\alpha = 0.1646 \times LN(t) + 0.6745$	0.86	0.86
3	23 °C/50% RH	6.5	8.0	$\alpha = 0.2037 \times LN(t) + 0.2301$	0.61	0.65
3	40 °C/80% RH	1.5	1.7	$\alpha = 0.1343 \times \text{LN}(t) + 0.6099$	0.66	0.68

# 4. Conclusions

Model-free kinetics are a useful tool to study the kinetics of the epoxy-amine curing reaction. Three iso-conversional methods were applied to the non-isothermal DSC cure data of three high-solids commercial epoxy-amine coatings for the estimation of their apparent activation energy as a function of their conversion. The apparent activation energies of the three products were found to be very similar within the range of 53 to 61 kJ·mole<sup>-1</sup>, which are not different from the values reported in the literature and mostly estimated from the clear coats of epoxy resins and amine curing agents. Among the iso-conversional methods used, Friedman's method performed the best, followed by Vyazovkin's method, in fitting the non-isothermal DSC cure data of the three products. The method of Kissinger–Akahira–Sunose did not provide a satisfactory fit to the experimental data. Therefore, the apparent activation energies estimated from the former two methods are more reliable. All the iso-conversional methods underpredicted the isothermal degree of conversion of all the used products at two different conditions. The disagreement between the experimental and predicted isothermal conversions was most probably due to the fact that the non-isothermal DSC experiments were performed under a nitrogen atmosphere, whereas the isothermal curing of the samples was conducted in a controlled humid environment. Consequently, the catalytic effect of water on the epoxy-amine cure was not accounted for in the predictions obtained by using the non-isothermal DSC cure data. Using the experimentally measured isothermal degree of cure of the three commercial products, it has also been shown that the T2 drying time of the epoxy-amine coatings measured by the Beck Koller method according to ISO 9117-4:2012 or the ASTM D5895 standards corresponds to at least 60% conversion at two curing conditions. This means that for the high-solids epoxy-amine coatings, no tackiness should be expected after 60% conversion.

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