



Role of acid hydrocarbon chain length on the cure kinetics and thermal degradation of epoxy- dicarboxylic acid vitrimers

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ABSTRACT

This study investigates the cure kinetics and thermal degradation of epoxy-dicarboxylic acid vitrimers, focusing on the effect of methylene chain length. A diffusion-controlled, modified autocatalytic kinetics model was applied, based on Differential Scanning Calorimetry (DSC) data, whilst Thermogravimetric Analysis (TGA) was used to assess degradation. Increasing the methylene chain length enhanced thermal stability, with decomposition temperatures ranging from 430 °C for the hexanedioic acid formulation to 500 °C for the tetradecanedioic acid formulation. The curing process transitioned through three distinct kinetics regimes: an initial non-catalysed phase, followed by an autocatalytic stage, and finally, a diffusion-limited phase at high crosslink density. This shift leads to a 30 %-70 % reduction in apparent activation energy during the early stages. The activation energy displays a complex behaviour, initially decreasing with longer methylene sequences before rising due to competing effects of chain flexibility and reduced reactivity. Kissinger and isoconversional analyses confirmed reliable activation energy values. Despite some discrepancies in the dodecanedioic acid formulation due to secondary reactions, the model exhibits a good approximation, with an average goodness-of-fit of 84.4 %. This analysis improves understanding of vitrimer cure kinetics and thermal behaviour, providing insights for optimising industrial applications.

1. Introduction

Vitrimers, introduced in 2011, are a class of materials that blend the advantages of thermosetting and thermoplastic polymers, combining the superior structural properties of crosslinked polymers with the reprocessability of thermoplastics [1]. This unique combination of properties has led to extensive research into various aspects of vitrimer chemistry and applications to gain a comprehensive understanding and expand the potential uses of these materials.

Among the realm of vitrimers, transesterification-based vitrimers are the most studied variety. This is because the initial concept of vitrimers was based on the transesterification exchange mechanism, and subsequent studies have continued to build on this foundational idea. For example, epoxy-based vitrimers incorporating dynamic ester bonds have demonstrated excellent reprocessability and mechanical performance, making them ideal for applications such as self-healing materials and recyclable composites [2]. Other examples include polyimine vitrimers, which utilise imine exchange reactions and have shown promise in areas like 3D printing and shape memory materials [3,4]. The extensive

investigation of transesterification-based vitrimers in terms of nature of the exchanging bonds relating to their ability to relax, the thermo-mechanical and mechanical properties of these materials and their application in high performance composite materials with reinforcement such as carbon fibre [5,6], glass fibre [7], graphene [8,9] and other nano particles [10] has led to innovations in their design as well as to broadening their scope from basic scientific research to industrial applications in fields such as aerospace, automotive, and electronics [11–13].

Diglycidyl ether of bisphenol-A (DGEBA) as a main precursor for epoxy resins, has historically been used in curing with carboxylic acids, especially their organic derivatives. The curing process of such systems has been investigated with the aim of optimising industrial manufacturing cycles [14]. Understanding and application of curing kinetics can enhance final product quality and streamline process development [15]. Furthermore, kinetics models can be instrumental in shortening the curing cycle and, when integrated with heat transfer and chemo-rheological models, can be used to optimise the processing of thermosetting polymers and their composites [16–19].

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Over the years, substantial progress has been made in understanding the kinetics of epoxy-dicarboxylic acid curing, with studies shedding light on the molecular mechanisms and factors governing the curing reaction rate [7,8]. The study of cure kinetics has not been extended to the investigation of their vitrimeric systems. The existing literature only covers a very small scope of limited vitrimers with most of the work reported comparing the influence of different types of catalysts and their concentration. Furthermore, there is a significant lack of deeper understanding of how the introduced dynamic bond exchange interacts with cure reactions and of its influence on the cure kinetics [20].

The esterification of epoxy resins with carboxylic acids is a complex process, associated with potential side reactions. At its core, the reaction involves the epoxy\de ring of the epoxy resin undergoing a ring-opening reaction, mediated by ring-opening catalysts. The interaction between the epoxide groups and carboxylic acids results in the formation of slower-reacting ester linkages, often necessitating catalysts for efficiency. Base-catalysed conditions are typically favoured over acid catalysis to mitigate competing epoxy homopolymerisation [21]. Notable base catalysts include imidazoles [22–26], tertiary amines [25,26], phosphonium bromide [27], and certain metal salts [1,28,29].

The general path of the epoxy-carboxylic acid reaction is illustrated in Fig. 1. In the presence of a base catalyst, such as imidazole or tertiary amine, the carboxylic acid undergoes deprotonation to produce a carboxylate anion [30]. This anion then initiates a nucleophilic attack on the epoxy group electrophilic carbon, leading to epoxide ring-opening. The intermediate alkoxide ion undergoes rearrangement to yield a β -hydroxy ester linkages, signifying the esterification completion. Concurrently, the protonated base transfers a proton to the negatively charged oxygen of the epoxide ring, converting it into a hydroxyl group. This series of reactions results in a three-dimensional network, imparting the cured epoxy with its high performance characteristics [31]. The formation of β -hydroxy esters under stoichiometric conditions is pivotal for transesterification [28,29]. The dicarboxylic acid choice and its concentration intricately influence the curing rate, the cured epoxy properties, and the material suitability for specific applications [32]. The reaction efficiency and selectivity hinge on several factors, including the catalyst type, the reactants stoichiometric ratio, and the reaction temperature [30]. In a system with a 1:1 stoichiometric ratio of epoxy and dicarboxylic acid functional groups, typically only addition esterification proceeds in the initial stage, as the $-\text{COOH}$ group, being a much stronger acid than the corresponding alcohols and phenolic groups due to the presence of a resonance-stabilized carboxylate ion, has higher reactivity groups [33]. However, deviations in the stoichiometry of the epoxy and acid groups can alter product distributions with further reactions such as etherification (in the case of excess epoxy), condensation esterification (with excess carboxylic acid), and hydrolysis of the epoxy [34,35] operative only after the dicarboxylic acid or epoxide have been consumed [36]. These secondary reactions, which occur only after the complete consumption of either the dicarboxylic acid or epoxide, have higher activation energies and proceed more slowly than esterification [37]. Such reactions are more likely to occur in chemically

imbalanced systems, resulting in more complex structures, increased crosslink density, and potential phase separation.

Unlike traditional thermosetting systems, vitrimers exhibit dynamic bond exchange reactions that influence cure kinetics, particularly in the late stages of curing when ester bonds are established, and the reaction becomes diffusion-limited [38]. While transesterification is considered an equilibrium reaction [39] and thus difficult to detect through thermal analysis, the increased mobility introduced during the process leads to a rise in crosslinking density [40].

Elevated temperatures accelerate the reaction, but degradation risks must be managed. Side reactions, such as etherification or epoxy homopolymerisation, may be manifested under specific conditions, emphasising the need to fine-tune reaction conditions and catalyst selection in this intricate esterification process.

As with traditional thermosetting polymers, understanding the kinetics of vitrimers is crucial for optimising their properties and processing conditions. However, contrary to the extensively researched cure kinetics of traditional thermosetting epoxies, the kinetics mechanisms of vitrimers emphasises bond-exchange-induced relaxation. This relaxation is explored more comprehensively and in greater depth than the cure reaction kinetics associated with reactant curing. Typically, the former is assessed using mechanical techniques such as stress relaxation or creep [41], implemented through rheological [42] or thermo-mechanical means. In contrast, the study of curing and crosslinking formation predominantly relies on detecting heat energy changes using Differential Scanning Calorimetry (DSC).

The curing reaction of an epoxy resin is an exothermic reaction, and the power generated during the process is proportional to the rate of consumption of reactive groups [43]. The exothermic heat emanating during the curing phase of thermosetting resins [44] can be investigated under variable time–temperature conditions. The data obtained and associated analysis allow determining the degree of cure, reaction enthalpy, and an array of kinetics parameters, including activation energies and reaction orders.

One of the common techniques for kinetic analysis is non-isothermal DSC, where the thermal effects are recorded throughout the curing reaction. Models are established based on the curing reactions, and the experimental data is compared with the predicted models. Additionally, a combination of non-isothermal and isothermal DSC tests has been employed in kinetics analysis, not only for obtaining a broad overview, but also for pinpointing specific reactions and analysing slower reactions relevant to real-world scenarios, such as isothermal resin curing in manufacturing [45]. Other instrumental techniques used in the analysis of time dependent behaviour of polymers include Thermogravimetric Analysis (TGA) for thermal stability and degradation [46,47], Dynamic Mechanical Analysis (DMA) for mechanical properties [48], Fourier Transform Infrared Spectroscopy (FTIR) for reaction monitoring [49], Dielectric Analysis (DEA) for the evolution electrical properties during curing [50], rheometry for viscosity changes [51], and Nuclear Magnetic Resonance (NMR) for molecular dynamics, mobility, and chemical transformations [52]. Each method provides different insights, often used together for a comprehensive understanding of the curing process.

Established kinetics analysis techniques, originally devised for traditional thermosetting systems, have been adapted for vitrimers. In cure kinetics of epoxies the reaction rate is often approximated by an expression such as:

$$\frac{d\alpha}{dt} = \sum_i k_i(T) f_i(\alpha) \quad (1)$$

where α is the degree of cure or fractional conversion, T the temperature, $f_i(\alpha)$ functions of the degree of cure specifying the type of kinetics followed and $k_i(T)$ rate constants, which follow an Arrhenius dependence on temperature:

$$k_i(T) = A_i e^{-\frac{E_{ai}}{RT}} \quad (2)$$

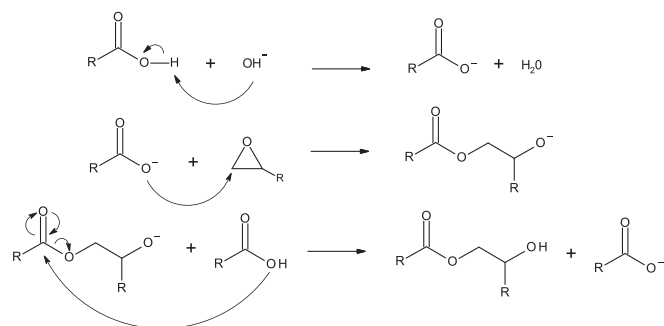


Fig. 1. Curing mechanism of epoxy and carboxylic acids with base catalyst.

Here E_{ai} are activation energies, A_i pre-exponential factors and R is the universal gas constant. Accurate estimation of the kinetics parameters is important for optimising and controlling reaction conditions in various industrial and laboratory settings [53]. For vitrimer cure kinetics, phenomenological models have been predominantly employed. Their primary appeal lies in their foundation on empirical observations, circumventing the need to delve deeply into the intrinsic chemical mechanisms governing the reactions. These models are primarily based on the observed relationship between variables. The most common phenomenological models are listed in Table 1. In the context of epoxy-dicarboxylic acid curing kinetics, the reaction mechanism is predominantly autocatalytic, a characteristic attributed to the formation of hydroxyl groups during the reaction [54–56].

Various methods have been suggested to calculate E_a , based on the temperature integral approximation. The traditional Kissinger method, which employs non-isothermal experiments, posits that the reaction rate reaches its zenith at the peak temperature [57]. A notable challenge in model-fitting approaches is the kinetics compensation effect [15], becoming especially pronounced in dynamic settings. Isoconversional methods have been put forward to address the oversimplification of reaction mechanisms. These allow the estimation of activation energy based on conversion, acknowledging its fluctuation, a feature particularly useful for materials like polymers [58]. The Flynn-Wall-Ozawa (FWO) method [59] has been built upon the Kissinger-Akahira-Sunose (KAS) [60] model, which is better suited for non-isothermal scenarios. Starink's model [61] offers a holistic view, encompassing both the reaction model and the conversion rate.

Given the multiple reactions involved in epoxy dicarboxylic acid curing, isoconversional methods have become essential in analysing the cure kinetics across various stages of the reaction. Generally, there is an initial decline in the activation energy from the start of the cure, suggesting a shift in the reaction mechanism from non-catalytic to autocatalytic, influenced by the rising concentration of hydroxyl groups. The average apparent activation energy decreases from initial values of 94–100 kJ·mol⁻¹ to 71–76 kJ·mol⁻¹ when sebacic acid and DGEBA react with 10 % and 20 % epoxidised soybean oil (ESO) respectively, up until the reaction achieves 25 % completion [62]. As the degree of reaction increases further, the activation energy of the reaction increases due to the counterbalance of autocatalysis and increasing molecular weight when $\alpha < 0.7$. However, as mobility limitations continue to increase as molecular chains grow and crosslinking density increases, the reaction starts to shift from chemical to diffusion control resulting in the activation energy of the reaction rising sharply for $\alpha > 0.7$ [63].

Kinetics studies suggest that the structure of monomers plays a pivotal role in determining the parameters of epoxy-carboxylic acid curing reactions. Numerous studies have identified a single exothermic peak associated with epoxy-carboxylic acid curing reaction, with the reaction peak temperature ranging from 115 to 200 °C, contingent upon the reactivity of the involved components [64]. For instance, the incorporation of sulphur in the β position of the carboxylic group increases the acidity of the carboxylic acid, thereby enhancing the reactivity of the acid proton towards the epoxy group [65]. A comprehensive study examining the impact of elongating the chain length of linear α,ω -dicarboxylic acids revealed a rise in peak reaction temperature and a decline in total enthalpy for dicarboxylic acids with greater chain lengths [66]. This phenomenon can be attributed to the increased likelihood of polymeric or oligomeric chain entanglement, which amplifies

steric hindrance during the curing reaction, consequently diminishing curing reactivity [66]. In the curing of epoxidised linseed oil (ELO) with succinic acid, which has a relatively shorter chain, there is a heightened pre-exponential factor, resulting from enhanced transport and collision efficacy with the epoxy group [67]. A study of the curing of DGEBA-amidodicarboxylic acids systems underscored the multifaceted nature of curing, which often occur in sequential stages [68]. Notably, the DGEBA/CPPA (4-carboxyphenyl phthalamic acid) system has an elevated apparent activation energy, stemming from the CPPA inherently rigid structure.

This study addresses the cure kinetics and thermal degradation behaviour of epoxy-linear dicarboxylic acid and their dependence on the acid length. The curing of DGEBA with five linear dicarboxylic acids, assisted by Zn(acac)₂ as an epoxy ring-opening and transesterification catalyst is investigated through both isothermal and non-isothermal calorimetry. The thermal stability of the cured product is evaluated using TGA. The evolution of the reaction mechanism throughout the cure is also studied using isoconversional methods. Cure kinetics models are developed and a link between the acid structure and the relevant parameters is established.

2. Experiment and theoretical models

2.1. Materials and formulation of vitrimers

Diepoxy (DGEBA), five linear dicarboxylic acids with different chain length, and Zn(acac)₂ as a transesterification catalyst were used in the synthesis of vitrimer systems. The properties of the chemicals are summarised in Table 2. All chemicals were sourced from Merck Life Science UK Limited.

Acid crystals were ground to a fine powder to ensure uniform acid dispersion in the epoxy. Stoichiometric proportions of acid and epoxy were weighed, and 1 mol% Zn(acac)₂ catalyst was incorporated, yielding 5 distinct vitrimer formulations. The epoxy, acid, and catalyst were combined and stirred to obtain homogeneous mixtures. The mixtures were degassed at 90 °C for an hour to remove air entrapped during mixing, then cast in rubber-sealed glass moulds. The samples were subsequently cured at 160 °C for 2 h. Cured samples were used for TGA

Table 2
Chemical structure and information of the ingredients for vitrimer.

Chemical structure	Compound	Formula	Molecular weight (g/mol)
	Bisphenol A diglycidyl ether (D.E.R.™ 332)	C ₂₁ H ₂₄ O ₄	340.4
	Tetradecanedioic acid (1,14-Tetradecanedioic acid)	C ₁₄ H ₂₆ O ₄	258.35
	Dodecanedioic acid (1,12-Dodecanedioic acid)	C ₁₂ H ₂₂ O ₄	230.30
	Sebacic acid (1,10-Decanedioic acid)	C ₁₀ H ₁₈ O ₄	202.25
	Suberic acid (1,8-Octanedioic acid)	C ₈ H ₁₄ O ₄	174.19
	Adipic acid (1,6-hexanedioic acid)	C ₆ H ₁₀ O ₄	146.14
	Zinc acetylacetonate hydrate	C ₁₀ H ₁₄ O ₄ Zn·xH ₂ O	263.61

Table 1

Common kinetics models used for modelling thermoset cure; m and n denote reaction orders.

Model	Equation
nth order	$f(\alpha) = k(T)(1 - \alpha)^n$
Autocatalytic	$f(\alpha) = k(T)\alpha^m(1 - \alpha)^n$
Kamal-Sourour	$f(\alpha) = [k_1(T) + k_2(T)\alpha^m](1 - \alpha)^n$

analysis, whilst DSC tests were carried out using the degassed uncured resin. Formulation names were based on the acid carbon chain length, e. g., formulation C6 denotes the vitrimer made of DGEBA and adipic acid with 1 mol% Zn(acac)₂.

2.2. Thermogravimetric analysis (TGA)

TGA tests were performed on a TA Q500. Approximately 5 to 10 mg of sample was excised from the cured vitrimer plates before and placed onto a platinum sample pan. The samples were subjected to heating from 25 °C to 600 °C at 10 °C/min under nitrogen flow of 60 ml/min. For each material the test was repeated three times to minimise experimental error. The 5 and 10 % weight loss points were also recorded for evaluation of the material thermal stability.

2.3. Differential scanning calorimetry (DSC)

DSC experiments were conducted with a TA Discovery DSC 250 to investigate the curing behaviour of the vitrimers. Approximately 5 mg of sample was extracted from the mixed sample mixture before curing and subsequently placed in individual hermetic aluminium pans. The pans were sealed using hermetic aluminium lids applied with a Tzero press. Similarly, an empty reference sample was prepared using an hermetic aluminium pan and sealed with a corresponding precision lid. The heat flow measurements were conducted under both under dynamic and isothermal conditions. All tests were performed under a constant flow of nitrogen at a rate of 50 ml/min. The cure characterisation was carried for five formulations containing 1 % catalyst namely C6, C8, C10, C12 and C14. Prior to undergoing the dynamic heating programme, the samples were initially stabilised at a temperature of 40 °C before being heated to the start temperature at a heating rate of 50 °C/min aiming to minimise both the effect of the shadowing of the reaction peak due to carboxylic acid melting and any crosslinking occurring during the ramp. The start temperature for dynamic experiments was 160 °C and the final temperature 320 °C. The rates used were of 2.5 °C/min, 5 °C/min, and 10 °C/min. Isothermal DSC experiments were carried out at 160 °C, 170 °C, 180 °C. The heat flow curves were subsequently analysed using the TA instrument Trios software. Integrations were carried out using a linear baseline for dynamic experiments and a horizontal baseline for isothermal tests. The reaction rate was computed based on the assumption of proportionality between reaction rate and heat flow:

$$\frac{d\alpha}{dt} = \frac{dH}{dt} \frac{1}{\Delta H_{total}} \quad (3)$$

where $\frac{d\alpha}{dt}$ represents the reaction rate, $\frac{dH}{dt}$ is the heat flow and ΔH_{total} is the peak area of the reaction, i.e., the total enthalpy.

Experimental data underlying this study can be accessed through the Figshare repository at <https://doi.org/10.6084/m9.figshare.27060847> [69].

2.4. Cure kinetics modelling

2.4.1. Estimation of activation energy using Kissinger's method

Assuming a single mechanism represented by a single term in Eq. (1) and combining with the Arrhenius dependence of rate constant on temperature as expressed in Eq. (2) yields:

$$\frac{d\alpha}{dt} = A e^{-\frac{E_a}{RT}} f(\alpha) \quad (4)$$

The Kissinger method [70] allows the estimation of the apparent activation energy based on peak temperature (T_p) measurements at the maximum curing rate. Eq. (3) under the condition of maximum reaction rate becomes:

$$\left[\frac{E_a \beta}{RT_p} + A f'(\alpha_p) e^{-\frac{E_a}{RT_p}} \right] \left(\frac{d\alpha}{dt} \right)_p = 0 \quad (5)$$

where $f'(\alpha)$ is the derivative of the degree of cure functional form in Eq. (3) and subscript P denotes the values related to peak rate, T_p corresponds to the temperature at which the maximum reaction rate occurs, and β is the instantaneous heating rate:

$$\beta = \frac{dT}{dt} \quad (6)$$

After rearrangement:

$$\frac{E_a \beta}{RT_p} = -A f'(\alpha_p) e^{-\frac{E_a}{RT_p}} \quad (7)$$

By rearranging and taking the natural logarithm on both sides, Eq. (7) is transformed into the Kissinger equation:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a} f'(\alpha_p)\right) - \frac{E_a}{RT_p} \quad (8)$$

By plotting $\ln(\beta/T_p^2)$ against $\frac{1}{T_p}$, the apparent activation energy can be determined from the slope of the fitting. The Kissinger method is valid for one-step processes only where $f'(\alpha_p)$ is independent of β .

2.4.2. Isoconversional method

To address the limitation of oversimplifying the reaction, isoconversional methods involve analysis of the entire curing process. The activation energy dependence can be evaluated without making any assumptions about the reaction mechanism, using:

$$\left[\frac{d \ln(d\alpha/dt)}{dT^{-1}} \right]_{\alpha} = \left[\frac{d \ln k(T)}{dT^{-1}} \right]_{\alpha} + \left[\frac{d \ln f(\alpha)}{dT^{-1}} \right]_{\alpha} \quad (9)$$

The $f(\alpha)$ term is constant at a fixed degree of cure leading to

$$\left[\frac{d \ln f(\alpha)}{dT^{-1}} \right]_{\alpha} = 0 [43]. \text{ As a result:} \quad (10)$$

$$\left[\frac{d \ln(d\alpha/dt)}{dT^{-1}} \right]_{\alpha} = -\frac{E_a}{R}$$

The accuracy of this method depends on the numerical approximation obtained from solving the temperature-dependent integral, known as the Arrhenius temperature integral $p(y)$ described as follows:

$$p(y) \cong \frac{e^{-Ay+B}}{y^K} \quad (11)$$

where $y = E_a/RT$ while A , B and K are constants with values determined to minimise the deviation between the approximation function and the exact integral. Then $p(y)$ is used to derive isoconversional models for activation energy determination in the general form of:

$$\ln \frac{\beta}{T_a^K} = -A \frac{E_a}{RT_a} + C \quad (12)$$

where T_a is the temperature corresponding to a fixed degree of cure.

In this study, three isoconversional integral methods were utilised: the Flynn-Wall-Ozawa (FWO) method [71], the Kissinger-Akahira-Sunose (KAS) method [57], and the Starink method [72]. These three methods use different values of A and K aiming to achieve high accurate approximation. The values of the constants are listed in Table 3. Among

Table 3
Values of the parameters for three integral isoconversional methods.

Model	K	A
Flynn-Wall-Ozawa (FWO)	0	1.052
Kissinger-Akahira-Sunose (KAS)	2	1.000
Starink	1.92	1.0008

these methods, the Starink method demonstrates lower deviations and higher accuracy, particularly when $y < 10$. For the analysis of polymer cure kinetics, the recommendation of Vyazovkin et al. [58] was followed, where a range of α values from 0.05 to 0.95 was examined with increments of 0.05.

2.4.3. Phenomenological model

For the selection of the cure kinetics model, the conversion degree for the maximum of two functions: $y(\alpha)$ and $z(\alpha)$ are denoted as α_M and α_p^∞ , where $y(\alpha)$ and $z(\alpha)$ are defined as:

$$y(\alpha) = \frac{d\alpha}{dt} e^x \quad (13)$$

$$z(\alpha) = \pi(x) \frac{d\alpha}{dt} \frac{T}{\beta} \quad (14)$$

Here $x = E_a/RT$, $\pi(x) = \int \frac{E_a}{RT} dT$ which can be approximated by [73]:

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (15)$$

The value of isoconversional E_a used is obtained using the Starink method. According to the Malek method, when $\alpha_p^\infty \neq 0.632$ and $0 < \alpha_M < \alpha_p^\infty$, the empirical Sestak-Berggren model [74] Eq. (2–16) proves to be the most suitable kinetics model.

$$f(\alpha) = \alpha^m (1 - \alpha)^n \quad (16)$$

A transition from chemical kinetics to diffusion control was also incorporated in by adopting an expression formulated by Cole et al. [75] and Hubert et al. [76] The final model is:

$$\frac{d\alpha}{dt} = \frac{Ae^{\frac{E_a}{RT}} \alpha^m (1 - \alpha)^n}{1 + e^{[C(a - (\alpha_{C0} + \alpha_{CT}T))]} \quad (17)$$

Here, C represents the diffusion constant, α_{C0} represents the critical degree of cure at absolute zero, and α_{CT} represents a constant that accounts for the increase in the critical resin degree of cure with temperature. This modified kinetics model incorporates the influence of diffusion due to proximity to vitrification. As the reaction progresses and approaches the critical degree of cure, the cure undergoes a notable deceleration, representing diffusion control.

This study utilises the mapping of the reaction rate on temperature and degree of cure. The activation energy of the reaction is first obtained using Kissinger's model. Experimental analysis and cure modelling were carried out assuming an initial degree of cure of 1 % which is commonly done in epoxy systems to allow the utilisation of autocatalytic kinetics [77,78]. The minimisation of error for fitting was carried out using the Generalised Reduced Gradient Nonlinear Optimisation method implemented in Solver of Microsoft Excel [79].

3. Result and discussion

3.1. TGA

Fig. 2 illustrates the thermal degradation behaviour of materials as a function of temperature, from room temperature to 600 °C. Upon heating, the materials generally begin to decompose at around 300 °C, marked by a sharp decline in weight, which eventually stabilises at a final plateau. The temperature at which this weight loss reaches a plateau varies: C6 shows the lowest onset of stabilisation at approximately 430–440 °C, while C8 and C10 reach a plateau at around 490 °C, and C12 and C14 exhibit the highest onset of stabilisation temperatures at around 500 °C. The decomposition rate for all the formulations displayed in Fig. 2(b) shows that while the decomposition of C6 predominantly occurs at temperatures below 410 °C, C10, C12, and C14 involve reactions at greater temperatures over 450 °C and C8 follows an intermediate behaviour with a broad yet more symmetric single-peak shape,

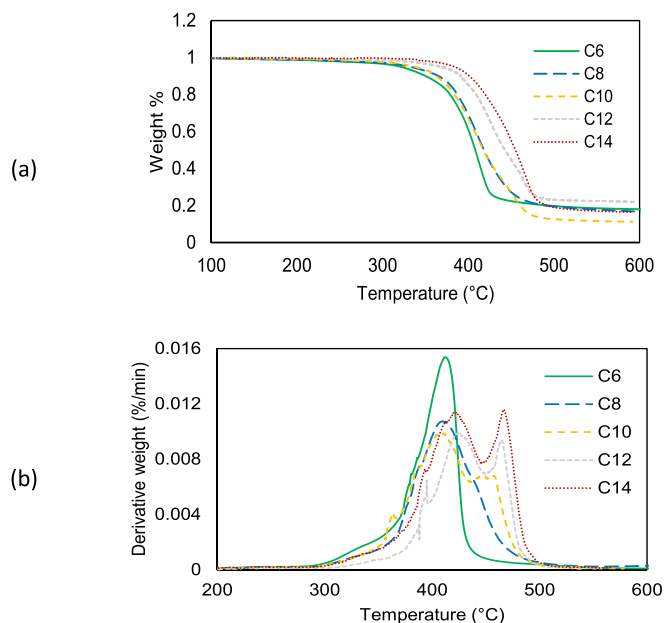


Fig. 2. (a): Thermal degradation of vitrimers containing 1% catalyst in terms of weight loss (b) Rate of the thermal degradation vs. temperature curves of vitrimers containing 1% catalyst.

with a maximum at around 410 °C. The temperatures at which 5 % and 10 % weight losses occur for each material are reported in Table 4. Increasing the dicarboxylic acid chain length is associated with increased thermal stability. The temperatures corresponding to 5 % ($T_{d5\%}$) and 10 % ($T_{d10\%}$) weight losses increase by 43.5 °C and 34.1 °C, respectively, when transitioning from C6 to C14. As polymer scission predominantly occurs at the propyl group situated between the aromatic rings and the carbon–oxygen bond opposite these rings [80,81], a plausible explanation for the observed trends is that an extended dicarboxylic acid chain length reduces the proportion of bonds susceptible to decomposition, leading to an elevated overall degradation temperature. This is consistent with findings on diesters derived from linear dicarboxylic acids, in which thermal stability was found to increase with the carbon number [82].

Studies on the thermal degradation mechanism of polyesters indicate that the presence of hydrogen in the beta position to the ester group facilitates the scission of aliphatic fragments predominantly through β -hydrogen scission. This occurs via a six-membered cyclic transition state, involving the transfer of a hydrogen atom from the alkyl group in beta position to the ester group to the ester carbonyl group [83]. The initial pyrolysis predominantly yields vinyl and carboxyl-terminated compounds, which subsequently undergo decarboxylation [84,85]. These carboxyl-terminated compounds may further degrade into diacid, diolefin, and other short-chain products. In the vitrimers investigated here, the variable factor in monomer structure is the number of methylene units in the aliphatic chain. As degradation progresses, dicarboxylic acids are formed. A study of the thermal decomposition of a series of linear dicarboxylic acids showed an increase in decomposition temperature from 200 °C for succinic acid (C4H6O4) to 250–300 °C for glutaric

Table 4

5% and 10% weight loss temperature for all vitrimeric materials.

Material	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)	$\sigma T_{d5\%}$ (°C)	$\sigma T_{d10\%}$ (°C)
C6	320.6	350.3	1.3	0.7
C8	337.4	367.6	8.5	5.8
C10	337.2	362.4	0.9	0.7
C12	357.7	383.5	10.0	7.4
C14	364.1	384.4	23.5	16.8

acid (C₅H₈O₄), and then to 350–400 °C for adipic acid (C₆H₁₀O₄) [86]. However, the degradation pathway of dicarboxylic acids containing more than seven carbons has not been extensively analysed. Analysis of the decomposition reactions reveals differences between adipic and sebacic acid derivatives. The latter undergoes a minor yet significant decomposition process at temperatures exceeding 425 °C, whereas the former degrades in a single step [87]. A similar mechanism could play role in the high temperature peaks observed here. The increased degradation temperature not only enables vitrimers to withstand better high-temperature environments for high-temperature applications, but also broadens the temperature window for remoulding, improving the overall performance and versatility of the vitrimers. Additionally, conducting TGA with various heating rates could provide valuable insights into the differences in activation energy for these formulations throughout thermal degradation, offering a deeper understanding of their thermal stability and decomposition mechanisms [88].

3.2. DSC

Fig. 3 presents the measured heat flow data for all the formulations under dynamic conditions. All the materials primarily exhibit broad peak curves, occurring at temperatures ranging from 180 to 230 °C. The heat flow peaks for C6 (vitriimer made of adipic acid-C₆H₁₀O₄) appear at a lower temperature range of 165–245 °C, than those observed for C8, C12, and C14, for which the peaks end at around 265 °C. For C10, the peaks end at even higher temperatures, specifically at 265 °C, 285 °C, and 305 °C for heating rates of 2.5 °C/min, 5 °C/min, and 10 °C/min respectively. The peak temperature (T_p), total enthalpy, and final temperature (T_f) for all rates and formulations are reported in Table 5. The results show a strong dependence of peak temperature and final temperature on heating rate. When subjected to a higher heating rate, the heat flow peak tends to shift to a higher temperature, exhibit a higher magnitude, and appear broader. This behaviour can be attributed to the fact that a higher heating rate means the material stays at a particular temperature for a shorter period of time, with reaction proceeding at greater temperatures for higher rates.

In addition to the main reaction peaks in Fig. 3, two distinct types of secondary peaks are observed at higher temperatures. The first type is represented by minor peaks occurring at relatively high temperatures,

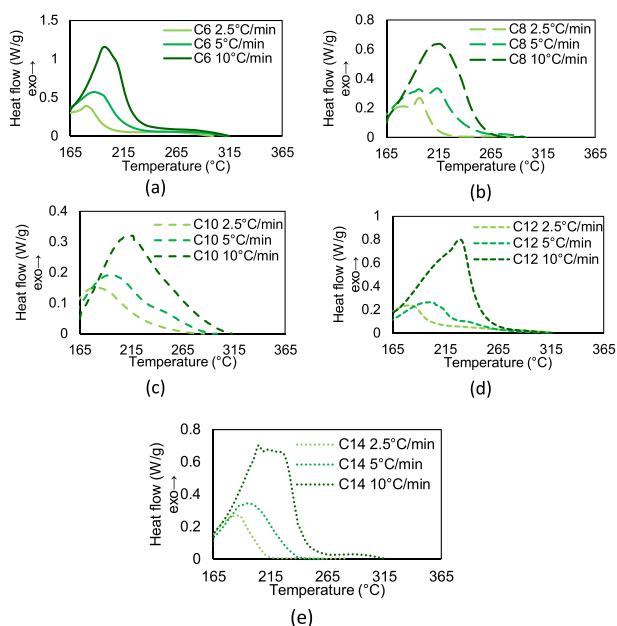


Fig. 3. Dynamic DSC curves of heat flow as a function of temperature for (a) C6; (b) C8; (c) C10; (d) C12; (e) C14; at different heating rates.

Table 5

Curing data obtained from the dynamic DSC thermograms recorded at 2.5, 5, 10 °C/min heating rate for all formulations.

Material	Heating rate (°C/min)	T_p (°C)	T_f (°C)	ΔHT (J/g)	ΔHT (J/mol)
C6	10	198	315	317	77.5
	5	187	312	344	84.1
	2.5	179	300	382	93.4
C8	10	223	280	243	62.8
	5	208	298	245	63.4
	2.5	195	240	319	82.5
C10	10	212	313	140	38.2
	5	197	298	155	42.3
	2.5	185	287	178	48.5
C12	10	222	316	263	75.4
	5	204	315	189	54.2
	2.5	190	317	288	82.6
C14	10	215	317	237	71.3
	5	198	238	194	58.4
	2.5	186	221	225	67.7

such as the temperature range of 255–285 °C for C6 in Fig. 3(a) and around 295 °C during the 10 °C/min run of C14 in Fig. 3(e). These peaks exhibit insignificant enthalpy release and may be associated with degradation or minor secondary reactions. The second type is characterised by noticeable shoulders adjacent to the main reaction peak. This phenomenon is evident in C8 at heating rates of 2.5 °C/min and 5 °C/min. The splitting of the primary reaction peak, as seen in C8 and C14, may be caused by the inhomogeneous monomer mixture. However, in the experiments C6 and 5 °C/min for C10 and C12, the secondary peaks are located around 260 °C. This could be linked to the incomplete portion of the reaction resulting from the crosslinking process. During the curing process, when crosslinks are being established, the movement of the reactants can potentially be hindered due to steric hindrance. However, the increase in temperature affects vitrimeric materials in a way that facilitates molecular mobility due to increased bond exchange, giving them a second opportunity to react. There is also a negative relationship between the total enthalpy of the reaction and the heating rate. At lower heating rates, the materials undergo a prolonged cure, resulting in an average increase of about 13 % in enthalpy as indicated by the results provided in Table 5. The majority of the molar reaction enthalpy falls within the range of 60–80 kJ/mol, with an 8.0 % difference between the highest enthalpy range for C6 and the lowest for C14 with the exception of C10, which shows a substantially lower value compared to the other materials.

The reaction rate under dynamic conditions is illustrated in Fig. 4. In contrast to the single-peak shape observed in C8, C10, and C14, in the case of C6 and C12 shown in Fig. 4(a), prominent secondary reaction

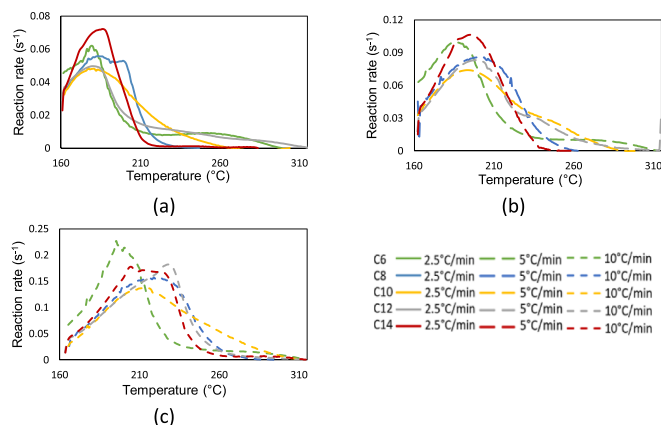


Fig. 4. Reaction rate as a function of temperature curves for vitrimers with heating rate of (a) 2.5 °C/min (b) 5 °C/min and (c) 10 °C/min.

peaks are observed within the temperature range of 220–240 °C for C6 and 280–300 °C for C12. It is also noticed that similar peak exists in the temperature range of 265 °C to 315 °C for C14 at the heating rate of 2.5 °C/min. As reported by Palmieri et al. [89], a second peak in the curing profile is also observed in epoxy-anhydride vitrimer systems, while it is absent in their thermosetting counterparts lacking bond exchange catalysts. The data presented here confirms this trend, but also demonstrates that the prominence of the second peak is closely related to the heating rate. At slower heating rates, these reactions become more pronounced at higher temperatures, due to the extended time spent at each stage, which amplifies the effects of the slower bond exchange processes.

The curing of dicarboxylic acid and epoxy involves two primary reactions: (i) addition esterification of epoxy and acid groups (Fig. 5(a)); and (ii) transesterification reaction, leading to the formation of a diester and a diol (Fig. 5(b)). The first reaction accounts for the abundant energy release whilst the second reaction creates a crosslinked structure and results in the adaptability for vitrimers. The process of transesterification happens at a much slower rate compared to the addition esterification reaction. The first reaction for the materials occurs within 60 min at temperatures greater than 160 °C. As in Fig. 4(a), all the first peaks for all the materials are completed before 220 °C except the C10 vitrimer for which the reaction ends up at around 260 °C. In contrast, the second process can take tens of hours to complete [38]. In the case excess reactive groups are present after esterification, usually possible in non-stoichiometric systems, two secondary reactions may occur as illustrated in Fig. 5(c) and Fig. 5(d): (i) the etherification of hydroxyl and epoxy groups [90]; and (ii) the condensation polyesterification involving hydroxyl and carboxyl groups. However, the rates of these secondary reactions are significantly lower compared to the addition esterification reaction, particularly when transesterification takes precedence, and the availability of epoxy or carboxyl groups becomes limited. At the same time, these two reactions take place at higher temperatures compared to addition esterification of epoxy and acid due to the greater activation energy.

Materials C6 and C12 exhibit a more pronounced second reaction peak during the curing process (Fig. 4), which occurs at higher temperatures and at a slower rate. This is likely due to transesterification, given the stoichiometric ratio of epoxy and carboxylic groups and the thermal stability of the material. Although transesterification is an

equilibrium process that does not directly produce any thermal signal, the increase in temperature significantly accelerates the rate of bond exchange. This acceleration allows functional groups, previously constrained by the crosslinked network, to react and continue curing. As demonstrated in our recent article of the stress relaxation of the systems investigated here [91], the relaxation time of these vitrimers follows Arrhenius law:

$$\ln \tau = \ln \frac{1}{K_0} + \frac{E_{ar}}{RT} \quad (16)$$

where τ is the relaxation time, pre-exponential factor K_0 represents the frequency of collisions and E_{ar} is the activation energy for bond exchange. The fitting parameters are shown in Table 6. The relaxation time of these materials (depicted in Fig. 6) decreases dramatically with increasing temperature, from 6500–85000 s at 180 °C to 110–500 s at 280 °C. This sharp reduction in relaxation time facilitates macromolecular diffusion, enabling reactive groups attached to crosslinked chains to overcome diffusion barriers and engage in further curing reactions, resulting in the observed second peak. This behaviour is more pronounced for C6 and C12 may be due to the substantial inhibited crosslinking at early stage and the temperature dependant bond exchange as well as the chain mobility as a result of their molecular structure. In other formulations, such phenomena may not be observed as a result of the overlapping temperature range of the main reaction peak and the bond exchange induced reaction which appear as the broadened primary reaction peak.

Considering that transesterification is inherently slow and occurs over an extended period, the observed disparity in enthalpy values documented in Table 5 can be attributed to the supplementary energy released through transesterification during the prolonged reaction time for tests conducted at different heating rates. Variations in the extent of the second stage of reaction among the formulations underscore differences in their curing and bond-exchange capabilities.

Fig. 7 presents the isothermal DSC results for the five systems. For all materials, the reaction is fast at the beginning and the rate of reaction is strongly dependent on temperature. After the initial fast reaction phase, the enthalpy curves start to plateau. As the reaction is accelerated by increased temperature, curing at higher temperatures results in earlier completion. The cure of C6, C8, C10 and C14 at 180 °C is completed within 40 min. For C12, the enthalpy levels off around 70 min into the reaction.

The total enthalpy of the isothermal tests does not reach the same value as for the dynamic tests. In the case of C8, C10 and C14, the degree of cure reaches more than 85 %. In contrast, for C6 and C12, the final degree of cure only reaches 55–65 % and 70–85 %. As observed in 2.5 °C/min dynamic DSC tests (Fig. 4 (a)), for these two formulations, the secondary reactions start at a temperature around 230–240 °C which is significantly greater than the temperature at which the isothermal experiments were conducted. Therefore, the partial cure under isothermal conditions can be attributed to the limited occurrence of secondary reactions.

Fig. 8 shows the reaction rate as function of degree of cure for the isothermal curing of the all the formulations. The reaction rate exhibits an initial increase, culminating in a maximum value, followed by a subsequent deceleration. This behaviour strongly suggests an autocatalytic mechanism [92,37] for the reaction, rather than nth order. In the context of the autocatalytic mechanism, the hydroxyl group generated during the initial phase of the reaction functions as a catalyst, inducing

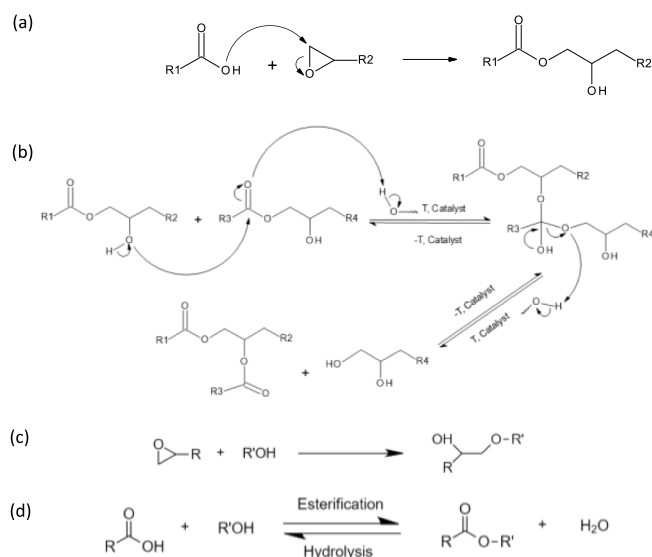


Fig. 5. Reaction Mechanisms: (a) carboxylic acid-epoxy addition, (b) diester formation through transesterification, (c) etherification and (d) polyester condensation.

Table 6
Relaxation fitting parameters.

Material	C6	C8	C10	C12	C14
$E_{ar}/R(K)$	8,833	12,945	11,808	12,009	10,459
$\ln(1/K_0)(s)$	-9.65	-17.8	-15.9	-16.6	-14.3

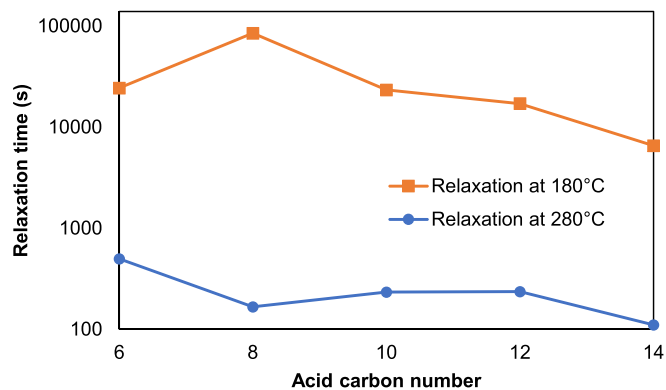


Fig. 6. Relaxation times of vitrimer at different temperatures.

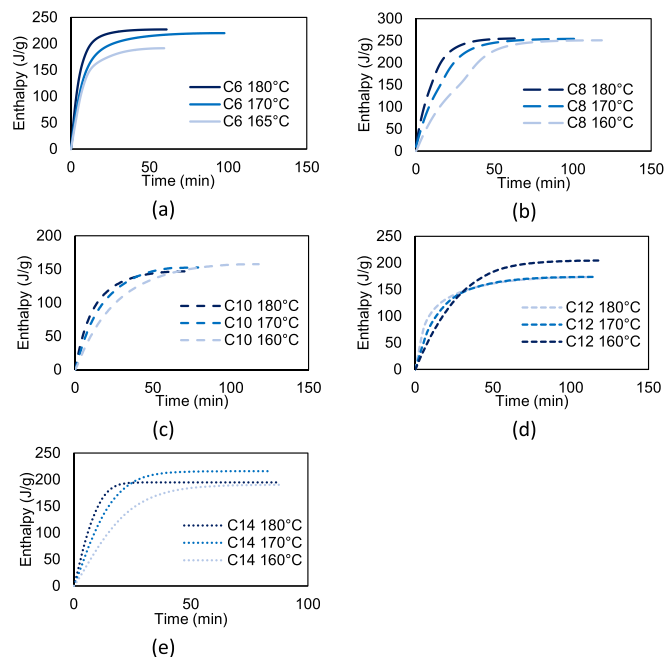


Fig. 7. Enthalpy as a function of time curves for vitrimers (a) C6; (b) C8; (c) C10; (d) C12; (e) C14 cured at different temperatures.

an acceleration of the reaction [3,92] before the reaction rate commences a decline attributed to diminishing reactant concentration.

The dynamic data at identical temperature and degree of cure were superimposed with the isothermal reaction rates to compare the curing kinetics under both dynamic and isothermal conditions and assess the consistency of the reaction mechanism. Aligning the reaction rate curves helps determine if the curing behaviour is governed mainly by temperature and degree of cure, rather than the thermal history. Overall, there is a small difference between the data points obtained from the dynamic and isothermal tests, resulting in an overall relative error of 9.2 % in terms of reaction accuracy. This confirms that the reaction mechanism remains consistent with a representation of the reaction rate as a unique function of temperature and degree of cure despite the variation in thermal history.

3.3. Cure kinetics modelling of epoxy-dicarboxylic acid vitrimer

Kissinger's method was employed to estimate the apparent activation energy of the curing reactions of reaction of the formulation using the dynamic DSC data stated in Table 5 by plotting $\ln(\beta/T_p^2)$ against $1/T_p$. The detailed linear fittings of the model and the corresponding

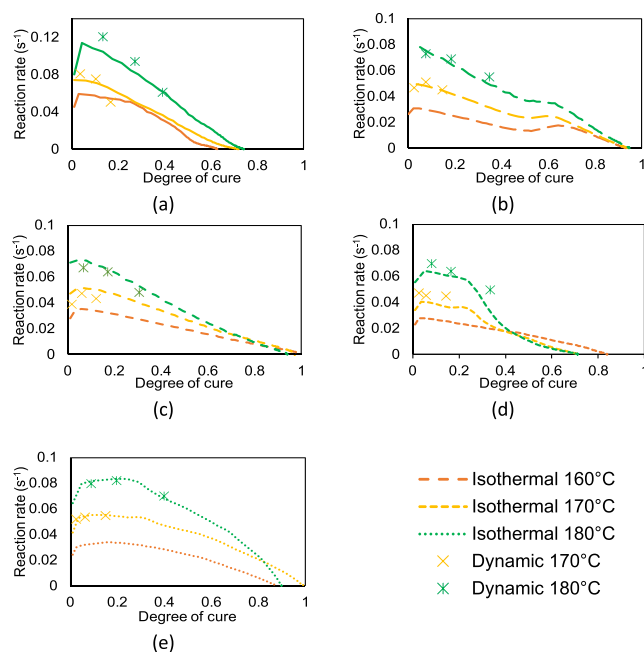


Fig. 8. Superposition of dynamic and isothermal DSC data for vitrimers (a) C6; (b) C8; (c) C10; (d) C12; (e) C14.

slopes representing E_a for all five vitrimers are illustrated in Fig. 9 (a) and the corresponding data are summarised in Table 7.

Fig. 9 (b) illustrates the relationship between carbon number and E_a . As the carbon number increases, the activation energy (E_a) initially decreases from C6 to C12 before rising again for C14. This trend can be explained by the increased flexibility of the monomer backbone, due to the addition of methylene units, which facilitates monomer rotation and reduces the energy required for the reaction [93,94]. However, the slight electron-donating effect of the methylene groups [95,96] diminishes the electron-withdrawing power of the carboxyl groups over longer distances, making them less reactive toward epoxy groups. Additionally, longer chains tend to reduce miscibility [97], which is associated with more energy to initiate the reaction, thereby potentially raising the activation energy for longer-chain acids.

To demonstrate the evolution of activation energy using Starink's method, $\ln(\beta/T_p^{1.92})$ for three different temperature ramp rates against

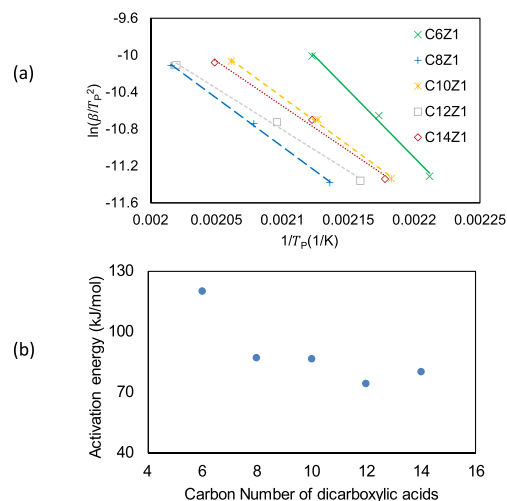


Fig. 9. (a) Fitting curve for the apparent activation energy for vitrimers; (b) relationship between apparent activation energy obtained using the Kissinger model and dicarboxylic acid chain length.

Table 7

Cure kinetics parameters, pre-exponential factor and the goodness of the fitting obtained from dynamic DSC runs of all five vitrimer formulations at different heating rate using Kissinger's method.

Material	Heating rate (°C/min)	$\ln(\beta/T_p^2)$	$1/T_p(1/K)$	$E_a(\text{kJ/mol})$	α_p	R^2
C6	10	198	315	120.7	47.0 %	0.993
	5	187	312		44.4 %	
	2.5	179	300		45.6 %	
C8	10	223	280	87.5	62.6 %	0.999
	5	208	298		64.2 %	
	2.5	195	240		67.4 %	
C10	10	212	313	86.8	42.2 %	0.997
	5	197	298		41.9 %	
	2.5	185	287		40.8 %	
C12	10	222	316	74.4	59.5 %	0.996
	5	204	315		54.0 %	
	2.5	190	317		52.7 %	
C14	10	215	317	80.6	57.8 %	0.992
	5	198	238		55.9 %	
	2.5	186	221		57.5 %	

inverse temperature for five materials is plotted in Fig. 10 (a). The dotted lines correspond to the best fit for each degree of conversion. There is a noticeable deviation between the data points and the linear fit at the extremes of the spectrum, as observed when the degree of cure exceeds 0.8. This suggests that under these conditions, the model does

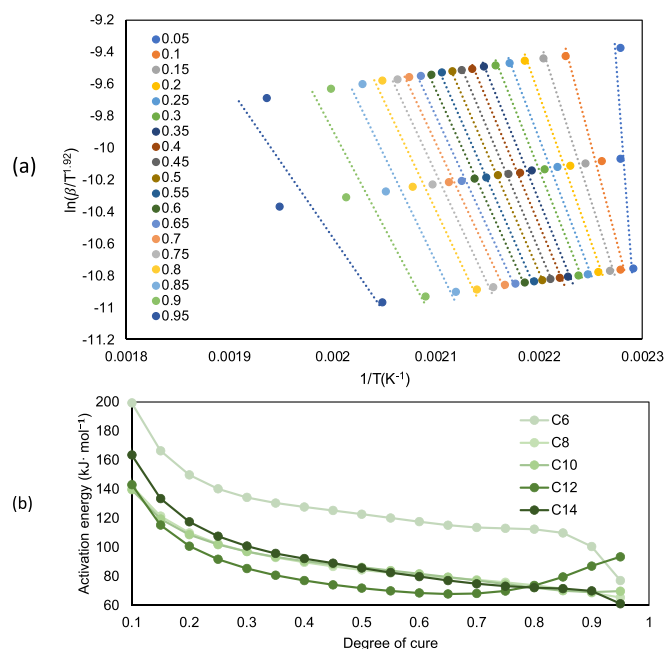


Fig. 10. (a) Plot corresponding to Starink method for vitrimer C6 in the degree cure range of 0.05–0.95 (b) Estimation of the activation energy of all vitrimers throughout the reaction using Starink method.

not predict accurately the curing behaviour. This can be attributed to hindered mobility resulting from diffusion limitations towards the latter stages of the reaction.

The activation energy values estimated using the three isoconversional models are presented in Table 8. These results show a high level of consistency in the activation energy across all three models. The greatest difference, observed between the Kissinger method and Starink method, is 8.2 % for the E_a of C14 when the reaction reaches 0.95 of total cure. Meanwhile, the disparities between the FWO method and KAS method are consistently below 1 % across all cases. Although Kissinger's method may simplify the reaction and yield a single activation energy in agreement with the assumption of single-step kinetics [98] when comparing the results of these isoconversional models to Kissinger's method, where the activation energy is measured at the stage of the highest reaction rate ($\alpha = 41.6\% - 64.7\%$), the variation remains within an acceptable margin of error, ranging from 5.2 % to 9.7 % across all five formulations. This underscores the robustness of Kissinger's method, instilling a high degree of confidence in the derived activation energy values.

While the consistency of activation energy estimates reinforces the reliability of these methods, isoconversional analysis reveals a more complex picture when examined in relation to the degree of cure. Substantial variation in activation energy across different stages of the reaction indicates that the curing process cannot be fully captured by a single activation energy value. The reaction can be divided into three stages based on activation energy changes: (i) Early reaction stage: At the onset of the reaction, when the autocatalytic effect is prominent, there is a significant drop in activation energy. This drop is particularly pronounced when degree of cure increases from 0.05 to 0.1, with C6 exhibiting a decrease of approximately 70 %. Even after excluding data of $\alpha = 0.05$, a substantial drop of about 30 %–40 % in activation energy is still observed for the early stage of the reaction ($0.1 \leq \alpha \leq 0.3$). This rapid reduction in activation energy suggests a significant change in the reaction mechanism, transitioning from a non-catalysed reaction to an autocatalytic reaction due to the increase in hydroxyl groups [37,62]. (ii) Stabilised reaction stage: Throughout most of the reaction, the activation energy remains relatively stable for all formulations. However, towards the end of the reaction, a decrease of 10 %–20 % in E_a occurs when α reaches 0.8 compared with the value at 0.3. (iii) Diffusion-controlled stage: Other researchers have also observed a continuous reduction in activation energy during the final stage of curing, particularly when the system reaches high conversion ($\alpha > 0.8$) [15,99]. As the polymer chains grow and the system approaches vitrification, the mobility of reactants is hindered, requiring moieties to undergo diffusion jumps before participating in chemical reactions [100]. However, isoconversional models may oversimplify this transition by assuming a constant activation energy at each degree of cure, failing to account for the varying mechanisms at play, particularly in systems like vitrimers.

A varied behaviour is observed in the change of activation energy with respect to the reaction progress, specifically for C12. Starting from a degree of cure of 0.65, the activation energy undergoes an increase of approximately 42 % as illustrated in Fig. 10(b). This phenomenon indicates that the reaction mechanism undergoes a more significant shift in the case of C12 compared to the other systems. This is also observed in Fig. 4. The increase in activation energy might reflect the heightened diffusion limitations as the crosslinked network establishes toward the end of the cure. The restriction of chain segments within the crosslinked structure creates larger energy barriers for chain movement, increasing the overall activation energy [63]. On the other hand, this behaviour could also be influenced by the bond exchange rate in the system. Accelerated bond exchange can facilitate diffusion and reduce energy barriers by allowing segments to rearrange, easing the diffusion limitations. The variation in activation energy seen across systems possibly reflects the interplay of these two mechanisms—diffusion constraints and bond exchange. In the case in which bond exchange dominates, a

Table 8
Activation energy obtained from three isoconversional methods with degree of cure (α) from 0.05 to 0.95 using KAS, FWO and Starink (S) method.

Formulation α	C6			C8			C10			C12			C14		
	KAS	FWO	S	KAS	FWO	S	KAS	FWO	S	KAS	FWO	S	KAS	FWO	S
0.05	672	699	694	193	195	194	192	195	193	219	223	222	243	248	246
0.10	198	201	199	143	143	142	141	140	140	144	144	143	163	165	164
0.15	166	167	166	123	122	121	121	120	119	117	116	115	135	134	134
0.20	150	151	150	112	110	110	111	109	109	103	101	101	120	118	118
0.25	141	141	140	105	103	102	105	102	102	95	92	92	110	108	108
0.30	136	135	134	100	98	97	100	98	97	89	86	85	104	101	101
0.35	132	131	130	96	93	93	97	94	93	84	81	81	99	96	96
0.40	129	128	128	93	90	90	94	91	91	81	77	77	95	93	92
0.45	127	126	125	90	87	87	92	89	88	78	74	74	92	90	89
0.50	125	123	123	88	85	84	90	87	86	76	72	72	89	86	86
0.55	122	121	120	86	83	82	88	84	84	74	70	70	86	83	83
0.60	120	118	118	84	83	81	86	82	82	73	69	69	84	80	80
0.65	118	116	115	83	83	79	84	80	80	72	68	68	81	77	77
0.70	116	114	114	82	83	78	81	77	77	73	68	68	79	75	75
0.75	115	114	113	80	83	76	79	75	75	74	70	70	77	73	73
0.80	115	113	112	78	83	74	77	72	72	78	74	74	77	73	72
0.85	113	110	110	76	83	71	75	70	70	84	80	80	76	72	72
0.90	104	101	101	73	83	69	74	69	69	91	87	87	75	70	70
0.95	82	77	77	70	83	65	75	70	70	97	94	93	66	61	61

decrease in activation energy is observed, highlighting the limitations of isoconversional models in capturing this dynamic behaviour. The final evidence as shown by the change in activation energy is therefore a result of both diffusion limitations and bond exchange effects.

3.3.1. Cure kinetics model fitting and prediction

A diffusion control modified autocatalytic kinetics model is employed for this study following Eq. (7). The model parameters obtained by fitting for each of the materials are listed in Table 9. The value of the obtained pre-exponential factor (A) follows a similar trend to that of activation energy reported in Fig. 9(b) showing a general reduction as the dicarboxylic acid chain length increases with the exception of C12, for which the value is abnormally low compared to the expected trend. Since the value of pre-exponential factor represents the frequency of collisions for the reaction to take place, this result is in agreement with the fact that increasing the chain length results in a reduction in functional group density and thus with lower probability of reaction. The autocatalytic reaction order (m) ranges from 0.02 to 0.23 whilst the value of n is 1.14–2.08. The value of m represents the influence of the autocatalytic process of the reaction and plays a primary role in the initial stages of the reaction. In the cases of C8 and C10, the model predict a much weaker influence of the autocatalytic effect caused by the generated hydroxyl.

The values of α_{C0} and α_{CT} are of importance in terms of when the diffusion starts to play a role in the reaction. The systems are not expected to experience such behaviour at the early stage of the cure when the mobility is high. The value of $(\alpha_{C0} + \alpha_{CT}T)$ at the temperatures of isothermal experiments should be close to the final degree of cure at the correspondent temperature. Table 10 lists the values of these terms for isothermal experiments and compares them to the final degree of cure

Table 9
Cure kinetics parameters for the autocatalytic model of vitrimers.

Model parameters	C6	C8	C10	C12	C14
$A(s^{-1})$	2.10×10^{13}	1.53×10^9	8.52×10^8	4.42×10^7	3.26×10^8
$E_a(kJ/mol)$	120.7	87.5	86.8	74.0	80.6
n	2.08	1.14	1.84	1.85	1.45
m	0.139	0.026	0.002	0.177	0.227
c	61.16	0.98	4.50	4.99	13.33
α_{C0}	4.75	−0.85	2.96	2.15	−0.14
$\alpha_{CT}(K^{-1})$	0.0120	0.0002	0.0086	0.0065	0.0019
Total error	4.51	3.83	4.95	9.48	5.49

Table 10
Comparison between the degree of cure for the isothermal tests compared to their dynamic test and the degree of cure when diffusion limitation was effective for all vitrimeric materials.

Material	T (K)	$(\alpha_{C0} + \alpha_{CT}T)$	α	Difference	Average difference
C6	438.15	0.63	0.62	1.0 %	5.0 %
	443.15	0.72	0.72	0.0 %	
	453.15	0.88	0.74	14.0 %	
C8	433.15	0.92	1.00	8.0 %	4.0 %
	443.15	0.92	0.94	2.0 %	
	453.15	0.93	0.95	2.0 %	
C10	433.15	0.75	1.00	25.0 %	11.0 %
	438.15	0.79	0.77	2.0 %	
	443.15	0.83	0.98	15.0 %	
C12	453.15	0.92	0.94	2.0 %	9.3 %
	433.15	0.67	0.84	17.0 %	
	443.15	0.73	0.71	2.0 %	
C14	453.15	0.80	0.71	9.0 %	6.3 %
	433.15	0.95	0.88	7.0 %	
	443.15	0.97	1.00	3.0 %	
	453.15	0.99	0.90	9.0 %	

obtained in the DSC experiment. Overall, there is a 4 % to 11 % difference between the value of the degree of the cure and $(\alpha_{C0} + \alpha_{CT}T)$ at the isothermal temperature, showing an appropriate choice of the parameters.

For the diffusion-limitation modified autocatalytic model, the predicted values as shown in Fig. 11, are in good agreement with the experimental data from the dynamic DSCs. The accuracy of the estimation of the models is quantified as the mean square error (MSE), root mean square error (RMSE) and R^2 values listed in Table 11. Based on the results presented in Table 11, the MSE values for all formulations indicate small error, demonstrating a high level of goodness of fit. The overall closeness between the observed and fitted values is quantified at 84.4 %, with the majority of the fitting exceeding 90 %. However, there are exceptions, notably the fitting for C12. Although its dynamic run at a heating rate of 5 °C/min, along with the isothermal test conducted at 160 °C and 170 °C, exhibit high R^2 values of 94.2 %, 86.1 %, and 83.7 % respectively, the remaining experimental data do not align well with the established model. The R^2 values for the dynamic test with a heating rate of 2.5 °C/min and 10 °C/min, and the isothermal tests conducted at 180 °C, are lower, at 8.1 %, 36.2 %, and 40.3 % respectively. One possible explanation for this discrepancy could be the occurrence of significant secondary reactions at temperatures higher than those utilised in the isothermal tests, as well as the variation in the reaction mechanism

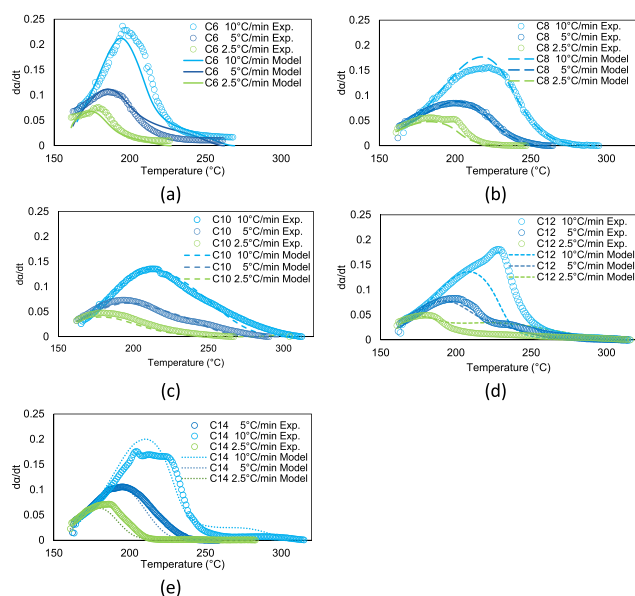


Fig. 11. Comparison of autocatalytic cure kinetics model and experimental data for vitrimers (a) C6; (b) C8; (c) C10; (d) C12; (e) C14; under dynamic heating conditions.

Table 11

MSR, RMSR and R2 values of the autocatalytic model for all the vitrimer formulations.

Formulation	DSC Method	Heating rate (°C/min) / Temperature (°C)	MSE (s ⁻²)	RMSE (s ⁻¹)	R-square
C6	Dynamic	2.5	0.0088	0.089	0.945
		5	0.0079	0.099	0.959
		10	0.0151	0.214	0.951
	Isothermal	165	0.0029	0.049	0.940
		170	0.0018	0.031	0.972
		180	0.0056	0.136	0.794
C8	Dynamic	2.5	0.0063	0.079	0.855
		5	0.0031	0.045	0.982
		10	0.0057	0.101	0.975
	Isothermal	160	0.0028	0.047	0.708
		170	0.0024	0.043	0.922
		180	0.0027	0.048	0.962
C10	Dynamic	2.5	0.0053	0.073	0.889
		5	0.0047	0.063	0.954
		10	0.0062	0.093	0.967
	Isothermal	165	0.0022	0.040	0.886
		170	0.0070	0.110	0.780
		180	0.0049	0.081	0.862
C12	Dynamic	2.5	0.057	0.155	0.081
		5	0.009	0.063	0.942
		10	0.044	0.454	0.362
	Isothermal	160	0.002	0.037	0.861
		170	0.002	0.049	0.837
		180	0.006	0.121	0.403
C14	Dynamic	2.5	0.0048	0.099	0.904
		5	0.0072	0.130	0.917
		10	0.0137	0.207	0.927
	Isothermal	160	0.0022	0.031	0.951
		170	0.0038	0.072	0.885
		180	0.0047	0.062	0.947
Average			0.0084	0.0973	0.8439

observed in dynamic tests under different heating rates. The fitting of the data best describes the behaviour observed in the dynamic test at a heating rate of 5 °C/min. However, in the case of the dynamic tests at a heating rate of 10 °C/min, the corresponding fit appears to be shifted to a lower temperature range, indicating a limited ability to account for the

contribution of the secondary reaction. Conversely, for the dynamic test at a heating rate of 2.5 °C/min, the fit seems to overestimate the influence of the secondary reaction. Considering the characteristic behaviour of vitrimeric materials, one plausible explanation for this phenomenon is that the rapid initiation of the reaction results in a swift increase in crosslinking density, thereby impeding the movement of reactive molecules with higher temperature ramp rates. Consequently, a higher proportion of the secondary reaction is likely to occur, leading to the observed discrepancies in the fitting results.

4. Conclusion

This study provides a comprehensive analysis of the cure kinetics of epoxy and dicarboxylic acid-based vitrimers. The primary exothermic reaction in these systems is the esterification between epoxy and carboxyl groups, which is complemented by a transesterification reaction facilitating crosslinking and macromolecular mobility. Thermal analysis demonstrated that all five vitrimer formulations exhibit high thermal stability, with no decomposition observed below 300 °C. Increasing the dicarboxylic acid chain length enhances the thermal stability of these vitrimers. Dynamic DSC experiments revealed a distinct additional peak at around 260 °C for C6 and C12, suggesting restrained esterification due to established crosslinked chains. Using Kissinger's method, the activation energy displayed a complex behaviour, initially decreasing with longer methylene sequences before rising due to competing effects of chain flexibility and reduced reactivity. A three-stage reaction mechanism—transitioning from non-catalysed to autocatalytic and diffusion-limited phases—was revealed by iso-conversional models. A diffusion-limited autocatalytic model was introduced, achieving a goodness-of-fit of 84.4 %, though discrepancies were noted in systems with secondary reactions at higher temperatures. Future studies should explore the bond exchange mechanism through isothermal DSC at elevated temperatures, and the development of a refined model is recommended for better prediction of vitrimer cure behaviour.

CRedit authorship contribution statement

Shouqi Shen: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Alexandros A Skordos:** Writing – review & editing, Visualization, Validation, Supervision, Software, Methodology, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data is uploaded to Figshare and the link is stated in the article. Experimental data underlying this study can be accessed through the Figshare repository at <https://doi.org/10.6084/m9.figshare.27060847>.

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Role of acid hydrocarbon chain length on the cure kinetics and thermal degradation of epoxy- dicarboxylic acid vitrimers

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