

Modeling diffusion-control in the cure kinetics of epoxy-amine thermoset resins: An approach based on configurational entropy

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ABSTRACT

In this study we propose a new equation to describe the effect of diffusional limitations on the cure kinetics of epoxy-amine resins, based on (i) modeling the average diffusion coefficient D via a power-law relationship with the structural relaxation time τ (i.e. $D\tau^\xi = \text{const}$, with ξ a fractional exponent) and (ii) describing the increase of τ with the advancement of reaction in terms of configurational entropy reduction driven by covalent bond formation. The approach proposed reconciles the description of the diffusion-controlled kinetics with the configurational entropy-based description of the structural dynamics near vitrification, already applied successfully to epoxy-amine polymerization. The model equation is built on a modified version of the Kamal equation where the initial ratio of amino hydrogens to epoxy groups appears explicitly, in addition to the exponents m and n giving the effective order of reaction. Replacing each chemical rate constant with an overall diffusion-corrected one, allows us to describe the full polymerization process. A comparison with experimental data indicates that, contrary to what assumed in the literature, the effect of diffusional limitations cannot be properly described by assuming the diffusion coefficient to be inversely proportional to the relaxation time ($\xi = 1$). Rather, we find that for many systems the fractional exponent ξ takes values very close to the parameter β that measures the stretching of the relaxation function. Concerning the chemically intrinsic parameters, it is found that the rate constants k_{c1} and k_{c2} for all the systems scale onto a master-curve corresponding to thermally activated behavior with, surprisingly, the same activation energy for the non-catalytic and autocatalytic process. Moreover, m and n assume approximately constant values, independent of the temperature and molar ratio of the mixture, with $m \approx 1$ and n in the range between 1 and 2. Although these results contradict other reported findings and the widespread belief that the autocatalytic process has a lower activation energy, they are consistent with the expectation that a similar mechanism underlies the general reaction between epoxy group and amino hydrogen, and that m and n are related to the intrinsic reaction mechanism. The new modeling also removes some evident discrepancies among results from different studies.

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1. Introduction

In order that a chemical reaction may occur, two molecules have to diffuse distances comparable to the intermolecular distances before the reactive sites on them can collide and eventually bond. Therefore, the kinetics of reaction is sensitive both to the intrinsic rate of the chemical reaction process between molecules being at contact and to transport limitations of the molecules bearing the reactive sites. If the reactants may considerably diffuse within the time required for bonding, the rate of reaction depends only on

the concentrations and intrinsic reactivities of the reactive sites, with rate constants which are independent of the extent of reaction (*chemically-controlled* limit). If the transport of reactants is limited by a low diffusion coefficient, the rate of reaction is controlled mostly by the probability of encounter between the reacting pairs (*diffusion-controlled* limit). It often happens that a transition from chemically-controlled to diffusion-controlled limit occurs gradually as the reaction product decreases the diffusivities in the system. Many thermoset materials of widespread use such as epoxy-amine resins are the result of reactions where such crossover takes place [1–3].

The epoxy-amine cure progressively transforms an initially fluid small-molecule mixture into an insoluble network, which is typically solid. In the early stages of cure, when the system consists

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mainly of monomers and oligomers, the reactions are chemically controlled. As the reacting entities become bigger in size, diffusional effects begin to play a role in the kinetics. At high extents of reaction, the rate of polymerization is primarily determined by the mass transfer of the reactants. Therefore, modeling the cure kinetics of epoxy thermosets requires not only an accurate description of the reaction kinetics in absence of diffusional limitations but also a proper description of how diffusional limitations intervene at a later stage. With a good model, valid over the entire range of cure, it is possible to predict how the system will behave during cure and what its final condition will be, and consequently to optimize the processing conditions and control the performance of the final product. Indeed, the most striking effect of the attainment of the diffusion-control is that the reaction stops before full conversion of the reactants and dangling ends in the polymer network survive to the curing process, which can provide the poor mechanical properties of the product of reaction [4] and the ageing of the resin during its service life.

Despite several attempts made, there is still much scope for modeling diffusion-control in the cure kinetics of epoxy-amine thermosets. In this work, we propose a new modeling based on the configurational entropy approach employed to study chemical vitrification in epoxy-amine systems [5–7], which markedly improves the agreement with experimental data and provides new significant information. The paper is organized as follows. Sec. 2 recalls the main equations used to describe the chemically-controlled regime of epoxy-amine cure, and the main approaches to modify these equations in the diffusion-controlled regime of the reaction. Sec. 3 describes the new kinetic model. In Sec. 4–6 we test the model equation against a large number of epoxy-amine systems and discuss the implications of the results obtained. A summary and final remarks are presented in Sec. 7.

2. Background

2.1. Chemically-controlled regime

The chemistry involved in the epoxy-amine curing process is rather complex [8–11], with several reactions participating in the network formation: addition of the primary and secondary amino groups to the epoxy ring, reaction between an epoxy ring and a hydroxyl group of the forming products (etherification), and homopolymerization of epoxide. The mechanism of the mentioned individual partial reactions, whose relative importance depends on the curing conditions and the type of the epoxy-amine system, may be rather complicated, with the formation of various reactive or unreactive intermediary complexes [9,12–15]. Cyclization (i.e. formation of rings by intramolecular reactions) and substitution effects (i.e. dependent reactivity of a functional group on the reaction state of a neighboring functionality) may also be operative to a different extent depending on the character of the reagents. Moreover, for the addition of an amine to the epoxide (the strongly predominating reaction) two different reaction pathways, autocatalyzed by hydroxyl groups formed in the reaction and catalyzed by impurities initially present in the system, have to be considered. As a result of this complexity, it is almost impossible to describe rigorously the overall reaction mechanism of the system epoxide-amine, and existing kinetic models based on mechanistic considerations always involve certain assumptions and approximations which adjust the models to fit certain systems better than others.

Horie et al. translated a simplified reaction scheme into a simple kinetic equation [16]

$$d\alpha/dt = (k_1 + k_2\alpha)(1 - \alpha)(r - \alpha) \quad (1)$$

where α is the conversion of epoxy groups, k_1 and k_2 are respectively the non-catalytic and the autocatalytic rate constants, and $r \equiv [H_0]/[E_0]$ is the ratio of amino hydrogens to epoxy groups in the initial mixture. This equation takes into account the autocatalytic nature of the two-step epoxy-amine reaction and the possibility of stoichiometric unbalance of the mixture, but disregards the possibility of other reactions as well as of unequal reactivities of primary and secondary amino hydrogens. Cole et al. [17,18] extended the model to explicitly take into account the etherification reaction, but they had to retain the assumption of equal reactivities in order to obtain an exact solution. Attempts to include in the kinetic description less simplified reaction schemes complicate the mathematics considerably [19].

Semiempirical approaches, based on the modification of kinetic expressions that had been derived under simplifying assumptions, provide an alternative in favor of obtaining a good fit to the data in a large number of systems and in a wide range of curing conditions, at the expenses of the possibility of giving all the fit parameters a direct interpretation. The best-known equation to model cases where Eq. (1) is inadequate was proposed by Kamal and coworkers [20,21]

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (2)$$

Here m and n are empirical factors, with $m + n$ known as the overall reaction order. Letting the exponents m and n be temperature-dependent and assume fractional values, makes this equation more flexible than Eq. (1) and other more sophisticated equations [22–28].

2.2. Diffusion-controlled regime

While the adjustment of several parameters of the previous kinetic models allows one to obtain a good fit to experimental data in the first stages of reaction, systematic deviations are observed at high levels of conversion. In this region, the mobility of unreacted groups is more and more hindered due to molecular-size effects and the decreasing rate at which they diffuse within the bulk in turn decreases the rate at which they react. The resulting negative feedback between the physical process of diffusion and the chemical process of bonding brings both processes to vanishing levels, even if reaction has not reached its full extent.

The diffusion-control in the kinetics of cure is intimately connected with the slowing down of molecular motions leading to a frozen structure, and hence to the system vitrification [29]. Indeed, most of the approaches that have been used to describe the cure in the diffusion-controlled regime are inspired by glass transition theories, although a general consensus on the most appropriate way to do it is lacking.

A first approach considers the rate of polymerization to vanish at vitrification and introduces in Eq. (2) the maximum achievable conversion α_{\max} as a phenomenological parameter [30]. Other approaches account for the reduced but still not negligible diffusion in the glassy state by introducing a rate constant for diffusion k_d , whose combination with the chemical rate of reaction produces a continuous cure-dependent reduction of the overall reaction rate also beyond the vitrification point. The models proposed in the literature differ in the way in which they combine k_d with the chemical reaction rate, and for the expression used to describe the dependence of k_d on α .

Concerning the first issue, many authors have assumed that in the later stages of curing the rate of reaction $d\alpha/dt$ becomes multiplied by an α -dependent factor, $f(\alpha) = 1/[1 + \exp(\mathcal{D}(\alpha - \alpha_c))]$, where α_c is a critical conversion and \mathcal{D} is a constant that depends on the structure, system and curing temperature. The expression for

$f(\alpha)$ was originally derived by assuming that (i) $d\alpha/dt$ can be factorized into an α -dependent term and an Arrhenius term $k_c(T)$, the latter representing the chemically-controlled rate constant; (ii) the diffusion rate constant can be written as $k_d = k_c \exp[-\mathcal{D}(\alpha - \alpha_c)]$, as proposed by Chern and Poehlein [31]; (iii) k_c and k_d combine into an overall rate constant given by $k(\alpha)^{-1} = k_c^{-1} + k_d^{-1}$, according to the Rabinowitch model for small-molecule reactions [32]. Under these conditions, the normalized quantity $k(\alpha)/k_c = f(\alpha)$ provides an α -dependent correction to $d\alpha/dt$ that makes it equally applicable to the chemically and diffusion-controlled regime. However, because the chemical kinetic equations used for modeling the epoxy-amine reaction cannot be factorized according to the point (i), and the expression of Chern and Poehlein [31] is based on the approximation that the reciprocal free volume, or alternatively the glass transition temperature T_g varies linearly with α — which is clearly incorrect over a wide range of α — the use of the mentioned procedure should be only considered as an empirical practice. Other empirical expressions for $f(\alpha)$ have also been employed [33].

Another strategy has been to consider that each rate constant k_i ($i = 1, 2$) that appears in the chemical kinetic equation, for example in Eq. (1) or Eq. (2), is itself the result of a chemical and a diffusional contribution combined together according to the Rabinowitch model [32]

$$k_i^{-1} = k_{ci}^{-1} + k_d^{-1} \quad (3)$$

Here, k_{ci} ($i = 1, 2$) is the intrinsic rate constant which is given by the chemistry of the system, and k_d is the rate coefficient for a system with no chemical barriers where reactions occur upon collision of functional groups. This last coefficient depends on the diffusion time scale of the system, that is an average parameter to which all the monomeric units contribute independently of the chemical process in which they are eventually involved. Eq. (3) simply states that the time required to form a new bond (through the autocatalytic or the non-catalytic pathway of reaction) is the sum of the amount of time required for two molecules of any size to approach each other plus the time required in order that repeated collisions between nearby molecules (assisted or not by hydroxyl groups) become fruitful to bond a reactive pair. Due to the parallel sum of k_{ci} and k_d , Eq. (3) represents control by chemical reaction in the early stages of reaction, when the system consists mainly of monomers and oligomers and the particle mobility is high ($k_d \gg k_{ci}$, hence $k_i \approx k_{ci}$), and represents control by diffusion at high extents of reaction, when the molecular-size dependence of the diffusion coefficient limits the reactivity of unreacted groups ($k_d \ll k_{ci}$, hence $k_i \approx k_d$). It should be noted that according to Eq. (3) the time scale of diffusion effects, k_d^{-1} , is the same for the autocatalytic and the non-catalytic process, and hence the onset of diffusion-control occurs earlier for the major (autocatalytic) reaction. Indeed, within such approach, the effects of diffusion on the rate constant of the minor (non-catalytic) reaction have sometimes been completely neglected [34].

Concerning the α dependence of k_d , it is generally assumed to vary with α in the same manner as the average diffusion coefficient D of the reacting entities, $k_d(\alpha) \sim D(\alpha)$, consistently with the fact that the time scale k_d^{-1} should be associated with the average diffusion time. As the relation between D and α is not known, it is assumed to be the same as τ^{-1} , with τ the structural relaxation time, i.e. $D(\alpha) \sim \tau^{-1}(\alpha)$. Several expressions for $\tau(\alpha)$ have been considered. Johari and coworkers [35] have used an empirical equation, $\tau \sim \exp(S\alpha^p)$, where S and p are temperature and system dependent parameters. Other authors have derived an expression by incorporating the α dependence of the glass transition temperature into an expression relating τ and T_g . Either empirical [34] or semiempirical $T_g(\alpha)$ expressions [36–40] have been inserted in phenomenological

$\tau(T_g)$ relations [41–43] (e.g. the Williams–Landel–Ferry relation) or in equations inspired by glass transition theories (e.g. the free volume theory [31,44–46], and the configurational entropy theory [47]).

It has to be pointed out that the assumption $D \sim \tau^{-1}$ — which we refer to as Debye–Stokes–Einstein (DSE) relation — follows from combining together the Stokes–Einstein (SE) and Debye–Stokes (DS) equations, the former predicting that the translational diffusion coefficient of a particle in a medium of viscosity η and temperature T is $D \sim T/\eta$, and the latter predicting that the rotational correlation time of the particle is $\tau \sim \eta/T$. As such, there are certain limitations to this assumption that might have an effect on the description of the diffusion-controlled kinetics. One limitation is due to the fact that the DS relationship between τ and η does not apply to network-forming thermosets [48,49]. Another limitation arises because the DSE relationship between translational diffusion and rotational relaxation is derived within the theory of macroscopic hydrodynamics, and consequently D and τ should refer to a macroscopic particle diffusing in a continuous medium. Although the SE and DS equations have been found to be well verified in ordinary liquids and in many simple glass-forming fluids, irrespective of the fact that they should be strictly valid for particles larger than the surrounding molecules, the existence of appreciable deviations from the expected behavior in high viscosity fluids close to the glass transition has been documented by a number of experimental works [50–58]. When these equations fail, their modification by the introduction of a fractional exponent has been found to correlate successfully the experimental data in many cases. Similar considerations are implicitly accounted for in the work by Deng and Martin [59], where the relationship between the overall diffusion coefficient D and the (dipole) rotational relaxation time τ during polymerization is written as a power-law

$$D\tau^\xi = \text{const} \quad (4)$$

with ξ a constant independent of conversion and reaction temperature. The central point in the diffusion model of Deng and Martin [59] is that the fractional exponent ξ is the same relating τ and σx_n^{-1} , with σ the ionic conductivity and x_n the number-average degree of polymerization, and hence ξ may be determined by means of dielectric measurements of ion conductivity and dipole relaxation time performed during the reaction.

Since a re-examination of this point plays an important role in the model presented in the next section, it is worth having a closer look at the reasoning of Deng and Martin [59], which consists of two fundamental steps. In the first step they correlate the monomer diffusion to the overall diffusion. Assuming that the diffusion coefficient of any molecule in a system polymerizing by a stepwise mechanism is inversely proportional to its size — the so-called Stokesian limit of diffusion — the overall diffusion coefficient, or the average diffusion coefficient of monomer unit, is formally written as $D = D_m x_n^{-1}$, where D_m is the diffusion coefficient of monomer. In the second step they correlate the monomer diffusion to the diffusion of ionic species present in the cure system. Assuming the validity of the SE equation, the ratio of the monomer diffusion coefficient to the diffusion coefficient of ions, D_m/D_i , is taken to be the ratio of the sizes of ions to that of monomer, and treated as a constant during an isothermal cure. Since $D_i \sim \sigma$ according to the Einstein relationship, the diffusion coefficient of monomer would be proportional to the ionic conductivity, $D_m \sim \sigma$. Combining gives $\sigma x_n^{-1} \tau^\xi = \text{const}$, which in principle allows to determine the exponent ξ from the plot of $\log(\sigma x_n^{-1})$ against τ . A critical evaluation of such procedure requires an analysis of the validity of the assumptions made in each step of the above reasoning. Concerning the first step, recent simulation data of step-

growth polymerization show that the expression $D = D_m x_n^{-1}$ provides an excellent modeling to D over the entire reaction, despite the assumption of Stokesian diffusion proves incorrect [60]. In the second step, instead, the result $D_m \sim \sigma$ is obtained within a hydrodynamic model and could be replaced by a fractional analogue, on the lines of what is done in the case of other mobility-related properties [50–58]. Consequently, the fractional exponent ξ relating τ and D in Eq. (4) would differ from that relating τ and σ .

Indeed, the kinetic model constructed by inserting into the Rabinowitch model (Eq. (3)) the diffusion coefficient determined from Eq. (4) — with ξ fixed to the value obtained from the experimental data of τ and σ — is able to capture the essentials of the diffusion-controlled kinetics during the cure of a thermosetting polymer, but still describes a change too fast of the conversion rate when approaching the glass transition, producing a non-negligible deviation from the experimental data [34]. This indicates that a better modeling of molecular diffusion is required, which may be the key ingredient to properly describe the diffusion-controlled kinetics in reacting systems.

3. Kinetic model

The classical Kamal equation (Eq. (2)) represents the model most often used to describe the chemical kinetics of thermoset resins on a semiempirical basis, since the presence of the variable exponents m and n ensures a good level of adaptability of the equation and usually makes it able to compensate for the effect of various reactions which are not taken explicitly into account in the derivation of the model case with $m = 1$ and $n = 2$ (Horie equation, Eq. (1)). The effect of a stoichiometric unbalance of epoxy and amino groups ($r \neq 1$) has generally been incorporated into the values of m and n , and Eq. (2) has been applied both to stoichiometric and non-stoichiometric cases without distinction. In the present work, we retain a semiempirical approach, but we adopt the following modification to the Horie equation

$$d\alpha/dt = (k_1 + k_2 \alpha^m)(1 - \alpha)^{n/2}(r - \alpha)^{n/2} \quad (5)$$

where the exponent n is equally distributed between the last two factors in the right-hand side. This equation contains explicitly the stoichiometric ratio r without introducing extra parameters with respect to the Kamal equation, to which it reduces in the stoichiometric case, $r = 1$. The advantages of using Eq. (5) in place of Eq. (2) will be discussed in Sec. 6.

Like Eq. (2), Eq. (5) with k_1 and k_2 taken as constant values throughout the reaction is typically able to reproduce the evolution of $\alpha(t)$ up to 60–70% of its final value, and even more for high temperatures of cure. However, beyond a certain point it generally overestimates the experimental data, as the reaction becomes diffusion-controlled. To describe the effects of a reduced molecular diffusion on the rate of reaction we use diffusion-corrected rate constants, as given by Eq. (3). The resulting kinetic model would account for chemically and diffusion-controlled reactions and also the crossover between the two, provided that an appropriate expression for $k_d(\alpha) \sim D(\alpha)$ is given.

As mentioned in the previous section, equations taken as such from the theory of macroscopic hydrodynamics are often inadequate to model diffusion in high viscosity fluids when approaching molecular length scales. Therefore, we agree with Deng and Martin [59] that the relationship between the overall diffusion coefficient of the molecules participating in the reaction and the structural relaxation time may be better written as a power-law, $D\tau^\xi = \text{const}$, where ξ is a fractional exponent which is constant during cure, rather than as an inverse proportionality, $D\tau = \text{const}$. However, on the basis of the considerations presented in the previous section

the exponent ξ is expected to differ from that obtained from the experimentally observed relationship between τ and σx_n^{-1} , and consequently we release any constraint on the value of ξ .

Now, in order to define $k_d(\alpha)$ it remains to give an expression for $\tau(\alpha)$. In recent studies of epoxy-amine systems we have shown that the increase of the structural relaxation time during step-growth polymerization can be successfully rationalized in terms of configurational entropy reduction, controlled by the increasing number of covalent bonds between the reacting molecules [5–7]. The model provides the α dependence of τ as

$$\tau = \tau_0 \exp\left(\frac{B\alpha}{\alpha_0 - \alpha}\right) \quad (6)$$

where τ_0 and B are system dependent parameters, the former approximately independent of both T and α and the latter only dependent on T , while α_0 is a parameter that, in the appropriate α and T range [61], is only determined by the molar ratio and functionality of the reagents in the mixture, according to $\alpha_0 = 1/\bar{f}$, where \bar{f} is the average epoxy functionality. According to Eq. (6), the progressive slowdown of the dynamics during cure strongly resembles the classical vitrification process of supercooling, with a rapidly increasing and apparently diverging relaxation time at high conversions.

Substitution of Eq. (6) in Eq. (4) yields for $k_d(\alpha) \sim D(\alpha)$ the following expression

$$k_d = k_0 \exp\left(-\frac{\xi B \alpha}{\alpha_0 - \alpha}\right) \quad (7)$$

where k_0 , ξ , B and α_0 are constants. The parameters B and α_0 are the same describing the behavior of the structural relaxation time.

The concept underlying this equation is that reducing the number of configurations available to the system not only increases the time needed by the molecules to relax, but also decreases their ability to move through the sample. However, the movements required to perform a structural rearrangement may differ from the movements required to diffuse, and then the configurations available to the system may not be equally effective to the two processes. In the terms of the Adam-Gibbs theory [62], the critical configurational entropy s_c^* of the smallest cooperative subsystem that can perform a transition into another configuration ‘effective’ to the process, as well as the potential energy barrier hindering the rearrangement, will be different for the relaxation and the diffusion processes. As the average transition probability is given by $\bar{W} \sim \exp(-\Delta\mu s_c^*/k_B T S_c)$ — where S_c is the molar configurational entropy of the macroscopic sample, and $\Delta\mu$ is largely the potential energy hindering the cooperative transition per mole of rearranging units — the value of the fractional exponent ξ is given by the ratio of $\Delta\mu s_c^*$ for the diffusion and the relaxation processes.

Eq. (5) with k_1 and k_2 determined by Eq. (3) and k_d given by Eq. (7) represents the full version of the diffusion-controlled kinetic model used in the present work. For further use we write it explicitly as

$$\frac{d\alpha}{dt} = \left[\frac{k_{c1}}{1 + \frac{k_{c1}}{k_0} \exp\left(\frac{\xi B \alpha}{\alpha_0 - \alpha}\right)} + \frac{k_{c2}}{1 + \frac{k_{c2}}{k_0} \exp\left(\frac{\xi B \alpha}{\alpha_0 - \alpha}\right)} \alpha^m \right] (1 - \alpha)^{n/2} (r - \alpha)^{n/2} \quad (8)$$

4. Experimental section

We test the model Eq. (8) by analyzing the kinetic data of many different epoxy-amine systems. Most of them are taken from the literature. Table 1 lists the chemicals involved in the studied

Table 1

List of the reagents in the epoxy-amine systems investigated. In parentheses is the abbreviation used in this paper. f is the functionality.

Epoxy	f
Diglycidyl ether of bisphenol-A (DGEBA) ^a	2
Triglycidyl ether of triphenylolmethane (TACTIX) ^b	3
Amine	
Aniline (AN)	2
3-Chloroaniline (3CA)	2
4-Chloroaniline (4CA)	2
<i>n</i> -Hexylamine (HA)	2
Cyclohexylamine (CHA)	2
<i>n</i> -Butylamine (BA)	2
Ethylenediamine (EDA)	4
4,4'-diaminodiphenylmethane (DDM)	4
<i>p</i> -Aminodicyclohexylmethane (PACM)	4
4,4'-diamino-3,3'-dimethyldicyclohexylmethane (3DCM)	4
4,4'-Methylenebis(2,6-diethylaniline) (MDEA)	4
4,4'-(1,3-Phenylene-diisopropylidene) bisaniline (BSA)	4
Diethylenetriamine (DETA)	5

^a DGEBA samples with seven slightly different values of the epoxy equivalent weight, $\text{eew} = 170, 172, 174, 185, 187, 188, 190$ g/mol, have been used in different studies.

^b TACTIX-742 is a trademark of Dow Chemical Co.

polymerizations, with their abbreviation and functionality f . Data used refer to two epoxy prepolymers, with $f = 2$ (DGEBA) and $f = 3$ (TACTIX), cured both with bifunctional amines (AN, 3CA, 4CA, HA, CHA and BA) and with multifunctional amines (EDA, DDM, PACM, 3DCM, MDEA and BSA with $f = 4$, and DETA with $f = 5$). All reagents are commercial products; their source and specifications are described in the original papers. Data analyzed refer both to reactions yielding linear chain polymers, and to reactions with the presence of a multifunctional reagent, yielding network polymers. Both stoichiometric and non-stoichiometric mixtures are present. Table 2 lists the only reactions for which both the epoxy conversion and the evolution of the structural relaxation time during cure are available; however, more reactions are analyzed to further test the model introduced. The epoxy conversion is measured by differential scanning calorimetry (DSC) [6], except for the DGEBA/DDM system where it is obtained by Fourier-transform infrared spectroscopy (FTIR) [34]. Relaxation times are obtained from three different spectroscopic techniques sensitive to structural dynamics — dielectric spectroscopy (DS), depolarized photon-correlation spectroscopy (PCS) and heat-capacity spectroscopy (HCS) — as $\tau = 1/2\pi\nu_{\text{max}}$, where ν_{max} is the frequency at which the imaginary part of the measured susceptibility has a maximum. For each reaction, carried out isothermally,

Table 2

Isothermal polymerization reactions and source of the data for epoxy conversion, α , and structural relaxation time, τ . B and α_0 are the best-fit parameters obtained by using Eq. (6) to fit the structural relaxation time data. \bar{f} is the average epoxy functionality of the mixture. The column *Err* reports the percentage of deviation between the measured α_0 and $1/\bar{f}$.

Mixture	T (°C)	Refs. ^a [α]	Refs. ^a [τ]	B	α_0	$1/\bar{f}$	Err (%)
DGEBA/DETA ^b 5:2	28	PW	[48]	3.3 ± 0.4	0.69 ± 0.02	0.70	1
	32	PW	[48]	3.3 ± 0.3	0.68 ± 0.02	0.70	3
DGEBA/DETA ^b 4:3	25	[6]	[6], [48]	4.9 ± 0.3	0.89 ± 0.02	0.88	1
	30	[6]	[6], [48]	4.2 ± 0.4	0.89 ± 0.02	0.88	1
DGEBA/DETA ^c 5:2.6	25	[63]	[63]	8.3 ± 0.3	0.75 ± 0.02	0.76	1
DGEBA/DETA ^b 5:2.8	26	PW	[48]	5.0 ± 0.5	0.78 ± 0.02	0.78	0
DGEBA/DETA ^b 10:3	32	PW	[48]	4.3 ± 0.5	0.64 ± 0.02	0.65	2
DGEBA/DETA ^b 10:9	22	PW	[48]	4.8 ± 0.5	0.95 ± 0.02	0.95	0
DGEBA/EDA ^c 2:1	23	[64]	[6]	5.3 ± 0.9	0.76 ± 0.03	0.75	1
	25	[65]	[6]	4.3 ± 0.4	0.80 ± 0.03	0.75	7
	29.8	[63]	[63]	3.5 ± 0.3	0.78 ± 0.02	0.75	4
	32.1	[64] ^f	[6]	5.5 ± 0.2	0.75 ± 0.01	0.75	0
DGEBA/EDA ^c 1:1	25	[66]	[5], [67]	2.9 ± 0.1	1.00 ± 0.03	1.00	0
DGEBA/BA ^c 1:1	25	[68]	[5], [69]	2.3 ± 0.1	1.01 ± 0.02	1.00	1
DGEBA/CHA ^c 1:1	27	[70]	[70]	7.9 ± 0.6	1.01 ± 0.02	1.00	1
	41	[71]	[71], [72]	5.5 ± 0.1	1.00 ± 0.01	1.00	0
	50	[72]	[72]	4.3 ± 0.1	1.03 ± 0.03	1.00	3
	70	[72]	[72]	2.7 ± 0.1	1.07 ± 0.03	1.00	7
DGEBA/DDM ^d 2:1	55	[73]	[73]	2.5 ± 0.2	0.75 ± 0.02	0.75	0
	60	[73]	[73]	2.6 ± 0.4	0.77 ± 0.03	0.75	3
	68	[73]	[73]	2.2 ± 0.4	0.79 ± 0.03	0.75	5
	75	[73]	[73]	1.3 ± 0.3	0.77 ± 0.03	0.75	3
	82	[73]	[73]	2.0 ± 0.4	0.78 ± 0.03	0.75	4
	90	[73]	[73]	1.5 ± 0.4	0.80 ± 0.03	0.75	7
	98	[73]	[73]	1.0 ± 0.4	0.80 ± 0.03	0.75	7
	115	[73]	[73]	1.5 ± 0.2	0.83 ± 0.03	0.75	11
DGEBA/3DCM ^e 2:1	60	[74]	[74]	6.0 ± 0.6	0.94 ± 0.02	0.75	25
	70	[74]	[74]	5.1 ± 1.6	0.95 ± 0.05	0.75	27
	80	[74]	[74]	5.0 ± 0.8	0.98 ± 0.03	0.75	31
	90	[74]	[74]	5.2 ± 0.4	1.02 ± 0.02	0.75	36
	100	[74]	[74]	5.3 ± 0.3	1.05 ± 0.02	0.75	40
DGEBA/PACM ^c 2:1	35	[75] ^g	[75]	10.2 ± 0.6	0.95 ± 0.03	0.75	27
TACTIX/AN 2:3	58.8	[76]	[76]	9.5 ± 0.8	0.88 ± 0.02	0.83	6
TACTIX/3CA 2:3	87.4	[76]	[76]	14 ± 3	1.19 ± 0.08	0.83	43
TACTIX/4CA 2:3	76.3	[77]	[77]	10.3 ± 0.8	1.05 ± 0.02	0.83	27

^a PW, present work. Data from the literature are also included.

^b DGEBA with $\text{eew} = 174$ g/mol.

^c DGEBA with $\text{eew} = 190$ g/mol.

^d DGEBA with $\text{eew} = 172$ g/mol.

^e DGEBA with $\text{eew} = 170$ g/mol.

^f $\alpha(t)$ has been calculated using the isothermal calorimetric data from Ref. [64] and the value of total heat of reaction given in Ref. [65], $\Delta H_{\text{tot}} = 230.5$ kJ/(mol of DGEBA).

^g $\alpha(t)$ has been calculated using $\Delta H_{\text{tot}} = 207$ kJ/(mol of DGEBA). A value of $\Delta H_{\text{tot}} = 214$ kJ/(mol of DGEBA) is reported by the same authors in subsequent papers [78,79]; this last value would change α_0 in 0.98 ± 0.03 , without any other significant change in the kinetic parameters evaluated in this work.

experimental data of τ as function of conversion are fitted by Eq. (6), with τ_0 , B and α_0 as free parameters (see, for instance, Fig. 1(b)). The values of B and α_0 obtained from the fit are listed in Table 2 for the set of the 35 polymerizations studied.

5. Data analysis

As an example, Fig. 1(a) and (b) show the data of epoxy conversion and of relaxation time as function of conversion for the DGEBA/DETA system, studied both in stoichiometric (molar ratio 5:2) and non-stoichiometric composition (molar ratios 10:3, 5:2.8, 4:3, 10:9) at different temperatures. It can be seen in Fig. 1(a) that for all the mixtures the rate of polymerization increases during the first stage of reaction and then progressively decreases, revealing the autocatalytic nature of the reaction. The temperature, at the values indicated, has only an effect on the rate of polymerization of a given mixture, without significantly changing the plateau value of the conversion curve; instead, the epoxy-amine ratio has a systematic effect on the maximum value of conversion achieved by different mixtures, with the higher plateau value the lower the relative epoxy content. In no case the epoxy conversion attains the ideal maximum value corresponding to a total consumption of epoxy groups ($\alpha = 1$ for the stoichiometric and amine-excess DGEBA/DETA mixtures, and $\alpha = 0.75$ for the epoxide-excess mixture DGEBA/DETA 10:3),

thus revealing the presence of diffusion-control in the last stage of reaction. Indeed, Fig. 1(b) shows that the slowdown of the dynamics during cure already occurs rapidly over a relatively small range of conversion preceding the point where the conversion curve starts to level out. In the reaction DGEBA/DETA 4:3 at $T = 30^\circ\text{C}$, for instance, the structural relaxation time increases by ~ 5 orders of magnitude in the region $0.6 < \alpha < 0.75$ [the region within the dashed square in Fig. 1(a)]; the remaining part of the cure, up to $\alpha \sim 0.8$, then proceeds under conditions of even more reduced structural mobility, and eventually in the glassy state.

We illustrate in the case of a typical reaction, DGEBA/DETA 5:2 at $T = 28^\circ\text{C}$, the strategy of data analysis performed in this work. Fig. 2 (a) and (b) show the evolution of α vs. t and $d\alpha/dt$ vs. α , and the effect of different approximations for k_1 and k_2 on the description of the advancement of reaction using Eq. (5). In this case, $r = 1$ (stoichiometric mixture) and Eq. (5) reduces to the Kamal equation. When it is fitted to the experimental data by keeping k_1 and k_2 as α -independent parameters, the upper limit of the α range where a good agreement to the data is obtained is ~ 0.42 , i.e. about a 70% of the final α value. The best-fit parameters are $k_1 = (2.16 \pm 0.03) \cdot 10^{-5} \text{ s}^{-1}$, $k_2 = (1.80 \pm 0.06) \cdot 10^{-4} \text{ s}^{-1}$, $m = 0.83 \pm 0.02$, $n = 1.54 \pm 0.03$. At higher conversions, the kinetic model with α -independent rate constants departs from the experimental data, to reach $d\alpha/dt = 0$ at $\alpha = 1$ (dashed line in Fig. 2(a) and (b)). In this region, i.e. for α approximately between 0.42 and 0.61, the diffusion

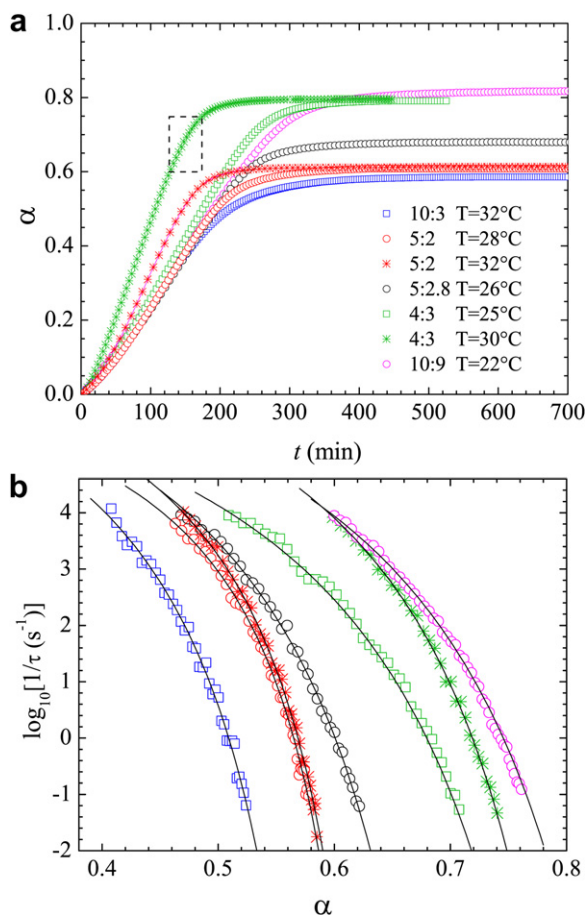


Fig. 1. (a) Epoxy conversion, α , as a function of the time of reaction, t , during cure of the DGEBA/DETA system at different values of the epoxy-amine molar ratio and different temperatures as indicated in the legend. (b) Dependence on α of the structural relaxation time, τ , measured by photon-correlation spectroscopy during cure of the DGEBA/DETA system; the symbols are the same as in panel (a). Solid lines are the best fit with Eq. (6). The dashed square in panel (a) locates the region corresponding to the increase of τ reported in panel (b) for the system DGEBA/DETA 4:3 at $T = 30^\circ\text{C}$.

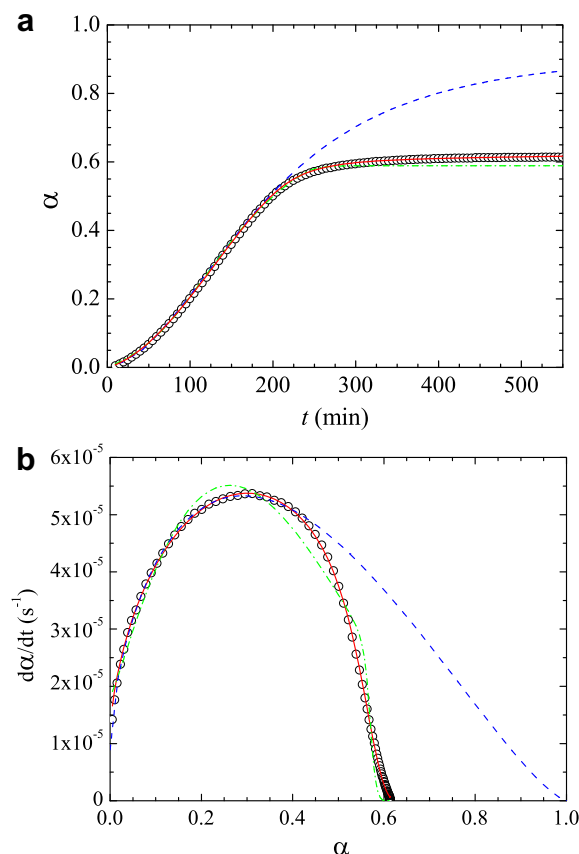


Fig. 2. (a) Epoxy conversion, α , as a function of the time of reaction, t , during cure of the system DGEBA/DETA 5:2 at $T = 28^\circ\text{C}$. Symbols are experimental data. The dashed line represents the fit of the Kamal equation (Eq. (5) with $r = 1$) to the first part of the reaction, up to $\alpha = 0.42$, using α -independent rate constants. The dash-dotted line is the best fit, to all the data, of Eq. (8) with $\xi = 1$, using $B = 3.3$ and $\alpha_0 = 0.69$ as obtained from the fit of $\tau(\alpha)$ with Eq. (6). The solid line is the best fit of Eq. (8) with $B = 3.3$ and $\alpha_0 = 0.69$, by releasing the constraint $\xi = 1$. (b) Conversion rate, $d\alpha/dt$, as function of α , from the experimental data and the fit curves shown in panel (a).

at molecular level is increasingly hindered by the reduction of configurational entropy associated to the growth of oligomers and polymer structures, as also reflected in the marked increase of the structural relaxation time measured by PCS and reported in Fig. 1 (b). The $\tau(\alpha)$ behavior is fitted by Eq. (6) with $B = 3.3 \pm 0.4$ and $\alpha_0 = 0.69 \pm 0.02$. On the other hand, the structural arrest is so rapid that an equally rapid evolution of the molecular diffusion coefficient would make the reaction come to an all too abrupt deceleration. To illustrate this important point, we show in Fig. 2(a) and (b) the results of fitting Eq. (5) to the experimental kinetic data using Eq. (3) for the definition of k_1 and k_2 and Eq. (7) for the expression of $k_d(\alpha)$, using $\xi = 1$, $B = 3.3$ and $\alpha_0 = 0.69$ as fixed parameters; or equivalently, of fitting Eq. (8) with $\xi = 1$, using the parameters B and α_0 which describe the $\tau(\alpha)$ behavior. This choice is equivalent to assuming a diffusion rate constant proportional to the rate of structural relaxation, $k_d \sim \tau^{-1}$. The dash-dotted line obtained from the fit procedure shows that this assumption tends to overestimate the reaction rate in the first part of the reaction, $0.15 < \alpha < 0.30$, and to compensate afterwards, giving a sudden change at $\alpha \sim 0.56$; finally, the fit curve closes at a lower value as compared to the experimental data. This result suggests that molecular diffusion diverges more slowly than the structural relaxation, a situation that can be modeled by a fractional power-law $k_d \sim \tau^{-\xi}$ with $0 < \xi < 1$, and hence by leaving ξ as a free parameter in Eq. (8). The solid line in Fig. 2(a) and (b) is obtained under these circumstances. It can be seen that, in this case, the fit function is able to reproduce very well the behavior of α vs. t and $d\alpha/dt$ vs. α over the whole reaction range, describing a smooth transition from the chemical to the diffusion-controlled regime.

It has to be noticed that, with the parameters B and α_0 known from $\tau(\alpha)$ the fit procedure adjusts six parameters. However, if the effect of diffusion on the cure kinetics is unimportant in the early stage of reaction, four of them are expected to be shared by the description of the first part of the cure. Indeed, without any constraint imposed, the intrinsic rate constants k_{c1} and k_{c2} , as well as the exponents m and n , determined by fitting all the data with Eq. (8), are coincident within the errors with the parameters obtained by fitting with the Kamal equation the first part of the reaction only, up to $\alpha \sim 0.42$ [The best-fit parameters are $k_{c1} = (2.25 \pm 0.09)10^{-5} \text{ s}^{-1}$, $k_{c2} = (1.80 \pm 0.2)10^{-4} \text{ s}^{-1}$, $m = 0.85 \pm 0.05$, $n = 1.43 \pm 0.11$]. The same does not happen if the constraint $\xi = 1$ is used. This result demonstrates that the developed approach is able to account for the α -dependent effect of diffusion without affecting the parameters describing the

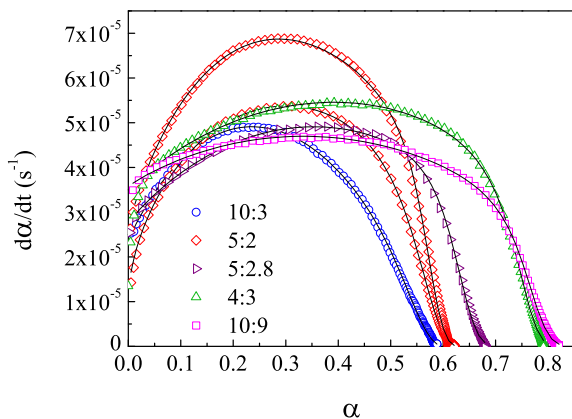


Fig. 3. Conversion rate, $d\alpha/dt$, as function of α , during cure of the DGEBA/DETA system at different values of the epoxy-amine molar ratio (and different cure temperatures) as indicated in the legend (data from the present work). Solid lines are the best fit of Eq. (8), with B and α_0 fixed from the behavior of $\tau(\alpha)$.

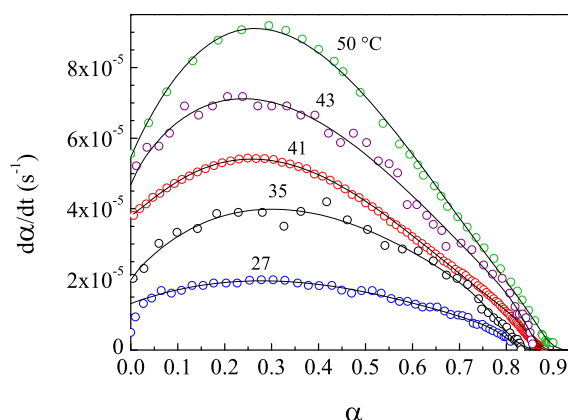


Fig. 4. Conversion rate, $d\alpha/dt$, as function of α , during cure of the DGEBA/CHA 1:1 system at different cure temperatures (data taken from Refs. [70–72]). Solid lines are the best fit of Eq. (8), with B and α_0 fixed from the behavior of $\tau(\alpha)$.

chemically-controlled regime. With the intrinsic parameters known from the early stage of cure, the diffusion-controlled kinetic model has only two extra adjustable constants, i.e. k_0 and the fractional exponent ξ . Nevertheless, instead of a two-step procedure we prefer to perform a single-step fit of the kinetic data, with six adjustable parameters all at once, in order not to leave out the possibility of a small but non-negligible effect of diffusion since the first stages of reaction.

6. Results and discussion

The fit procedure described above has been extended to the whole set of epoxy-amine reactions for which both the epoxy conversion and the structural relaxation time during cure are available (see Table 2). For each reaction, experimental data of $d\alpha/dt$ as function of α have been fitted by Eq. (8), with the parameters B and α_0 fixed to the values describing the behavior of $\tau(\alpha)$ according to Eq. (6). The results of the fit are shown in Figs. 3–9.

Data of other reactions have been analyzed without information on the structural relaxation time, by using α_0 as an additional free parameter. An example is shown in Fig. 10 for the reaction DGEBA/DETA 5:2 at $T = 60, 70, 80^\circ\text{C}$. In this case, the fit with Eq. (8) cannot determine ξ and B separately and their product defines a single fit parameter. The results, compared with those obtained

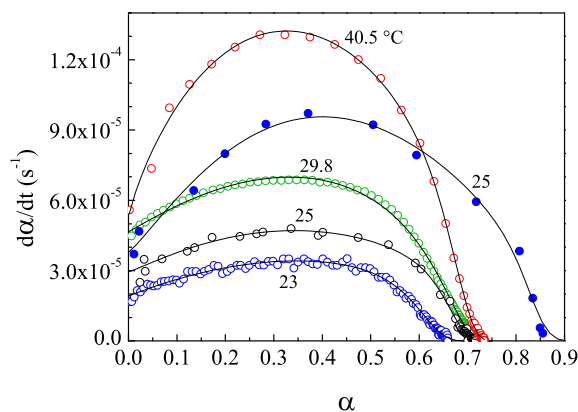


Fig. 5. Conversion rate, $d\alpha/dt$, as function of α , during cure of the DGEBA/EDA system at different cure temperatures. Open symbols are for DGEBA/EDA 2:1 (data from Refs. [63–65]), closed symbols for DGEBA/EDA 1:1 (data from Ref. [66]). Solid lines are the best fit of Eq. (8), with B and α_0 fixed from the behavior of $\tau(\alpha)$.

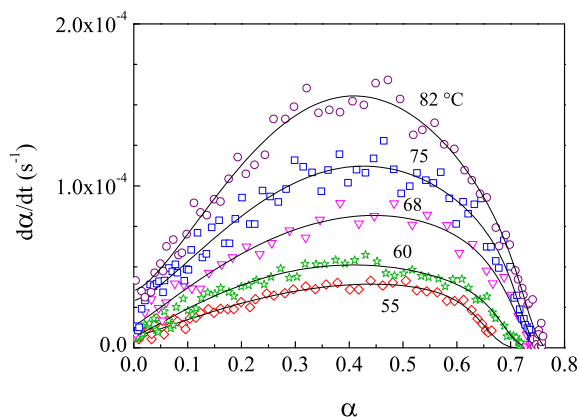


Fig. 6. Conversion rate, $d\alpha/dt$, as function of α , during cure of the system DGEBA/DDM 2:1 at different curing temperatures. Epoxy conversion data (from Ref. [73]) are measured by FTIR. Solid lines are the best fit of Eq. (8), with B and α_0 fixed from the behavior of $\tau(\alpha)$.

from the τ -constrained fit, are useful to assess the robustness of the kinetic model.

6.1. Comparison with the predicted value of α_0

In almost all the reactions reported in Table 2, the experimental value of α_0 obtained by fitting the relaxation time data is very close to that calculated from the stoichiometry of the mixture according to $\alpha_0 = 1/\bar{f}$, with \bar{f} the average epoxy functionality. For a generic epoxy/amine $N_e : N_a$ mixture one has $\bar{f} = f_e N_e / (N_e + N_a)$, where f_e is the number of epoxy groups on a monomer. This result indicates that in many systems a range of curing conditions does exist where the theoretical value of α_0 can be used with a good confidence. In these cases, the routine use of Eq. (8) for describing the kinetics of cure does not necessarily require the separate characterization of the structural relaxation by a spectroscopic technique.

As discussed at length in Ref. [61], the conditions under which the configurational entropy-based model has been derived limit the α and T range where it is expected to hold. In particular, increasing the temperature brings the system out of the range of validity of Eq. (6), and the reaction is expected to proceed to an extent greater than the value of α_0 predicted on a molecular basis. As a matter of fact, any polymerization can be brought to its full extent by progressively increasing the reaction temperature, and

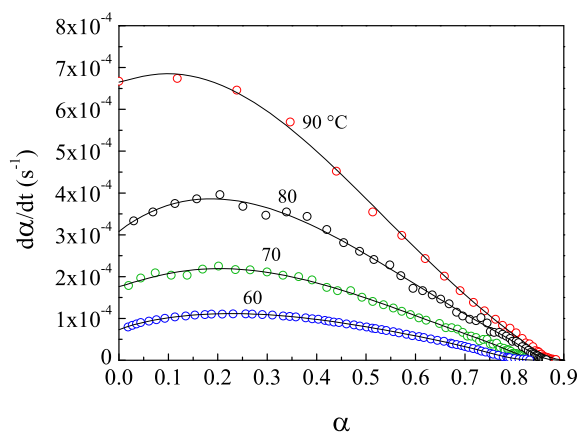


Fig. 7. Conversion rate, $d\alpha/dt$, as function of α , during cure of the DGEBA/3DCM 2:1 system at different cure temperatures (data from Ref. [74]). Solid lines are the best fit of Eq. (8), with B and α_0 fixed from the behavior of $\tau(\alpha)$.

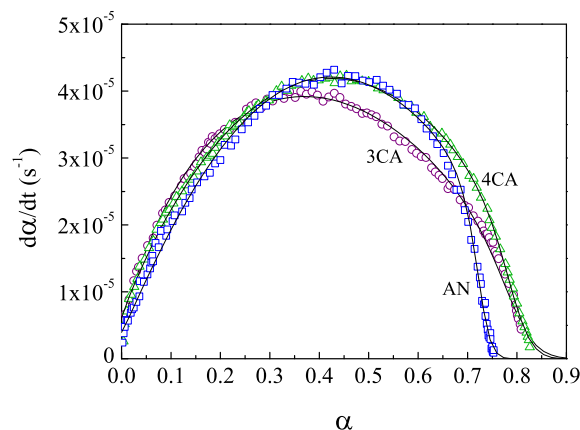


Fig. 8. Conversion rate, $d\alpha/dt$, as function of α , for the reaction of TACTIX with different curing agents in molar ratio 2:3 (data from Refs. [76,77]). Solid lines are the best fit of Eq. (8), with B and α_0 fixed from the behavior of $\tau(\alpha)$.

this is normally used to evaluate the total heat of reaction via calorimetry. Also the characteristics of the reagents (their structure and reactivity) may be responsible for a departure from the ideal Flory's conditions underlying Eq. (6). In this case, $1/\bar{f}$ is expected to represent only a lower limit to the α value at which τ tends to diverge. The high percentage of excess-deviation between the measured α_0 and $1/\bar{f}$ in the reactions involving 3DCM, 3CA and 4CA, for example, could be an indication that significant cyclization, substitution effects, or secondary reactions, occur in the reactive system.

It is important to note that, while the prediction $\alpha_0 = 1/\bar{f}$ does not apply when the reaction temperature is high or the system deviates significantly from the Flory's hypotheses, anyway the experimental observation indicates that the α dependence of τ remains well represented by Eq. (6). Therefore, the use of Eq. (8) for describing the kinetics of cure can be continued with the parameters α_0 and B provided by the analysis of spectroscopic data. Fig. 11 shows for the systems DGEBA/DDM 2:1 and DGEBA/DETA 5:2 that α_0 obtained from the fit of relaxation time data (solid symbols) has a tendency to move over the predicted value (horizontal lines) for temperatures exceeding, respectively, ~ 360 K and ~ 325 K. Open symbols, obtained from the fit of kinetic data without any constraint on the parameter α_0 , confirm that a tendency of τ to diverge (i.e. of D to vanish) occurs at increasingly high values of α . The match between

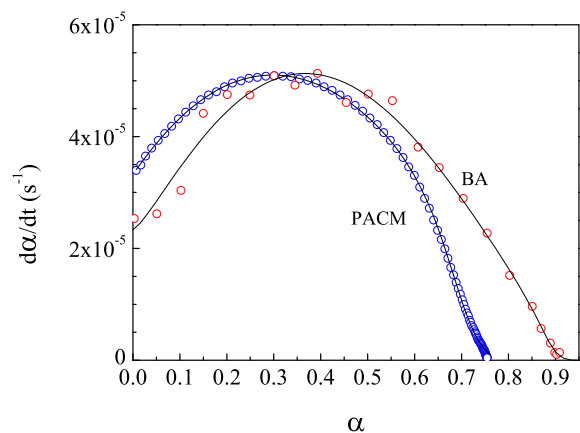


Fig. 9. Conversion rate, $d\alpha/dt$, as function of α , for the reaction DGEBA/BA 1:1 at 25 °C (data from Ref. [68]) and DGEBA/PACM 2:1 at 35 °C (data from Ref. [75]). Solid lines are the best fit of Eq. (8), with B and α_0 fixed from the behavior of $\tau(\alpha)$.

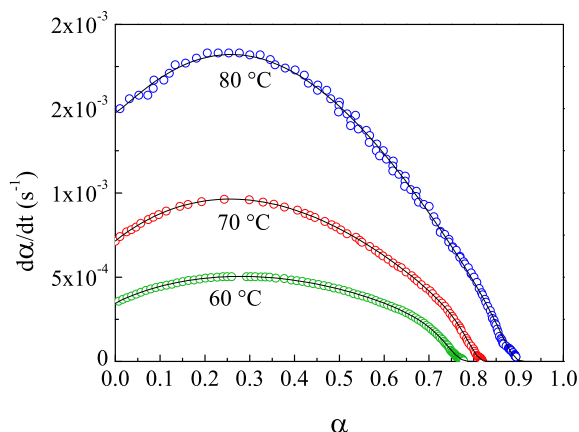


Fig. 10. Conversion rate, $d\alpha/dt$, as function of α , for the reaction DGEBA/DETA 5:2 (data from Ref. [80]). Solid lines are the best fit of Eq. (8), with B_2^* and α_0 as free parameters.

the trend of the closed and open symbols indicates that, even in the absence of information from the structural relaxation behavior, Eq. (8) is able to determine the parameter α_0 self-consistently.

6.2. Chemical rate constants

Fig. 12(a) shows the Arrhenius-plot representation of the chemical rate constants k_{c1} and k_{c2} for all the reactions that have been carried out isothermally at more than two different temperatures. In all systems a linear dependence of $\log k_{ci}$ vs. $1/T$ is found, fitted by the relationship

$$k_{ci} = k_{0i} \exp\left(-\frac{\varepsilon_i}{RT}\right) \quad i = 1, 2 \quad (9)$$

where ε_i is the activation energy, R the gas constant and T the absolute temperature. The activation energies ε_i are found to be in a range comparable to that reported by many other authors. One question that is not been resolved, however, is that of the relative value of ε_1 and ε_2 . While it is frequently reported as a reasonable finding that ε_2 is lower than ε_1 because ε_2 represents the catalytic

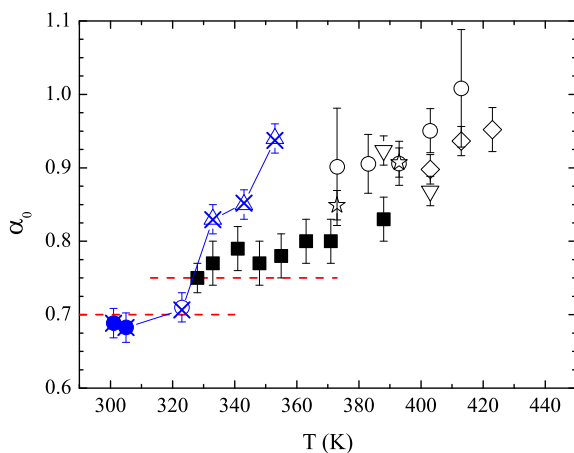


Fig. 11. Parameter α_0 vs. the reaction temperature for the system DGEBA/DDM 2:1 (disconnected symbols) and DGEBA/DETA 5:2 (connected symbols). Solid symbols represent values obtained from the fit of τ vs. α . Open symbols represent values obtained from the fit of $d\alpha/dt$ vs. α using Eq. (8) with all parameters free. For each system, different symbols correspond to a different source for the kinetic data [DGEBA/DETA: (cross circles) present work; (cross triangles) Ref. [80]. DGEBA/DDM: (■) Ref. [73]; (◇) Ref. [81]; (○) Ref. [82]; (open stars) Ref. [83]; (▽) Ref. [44]. Horizontal lines represent the theoretically predicted values of α_0 .

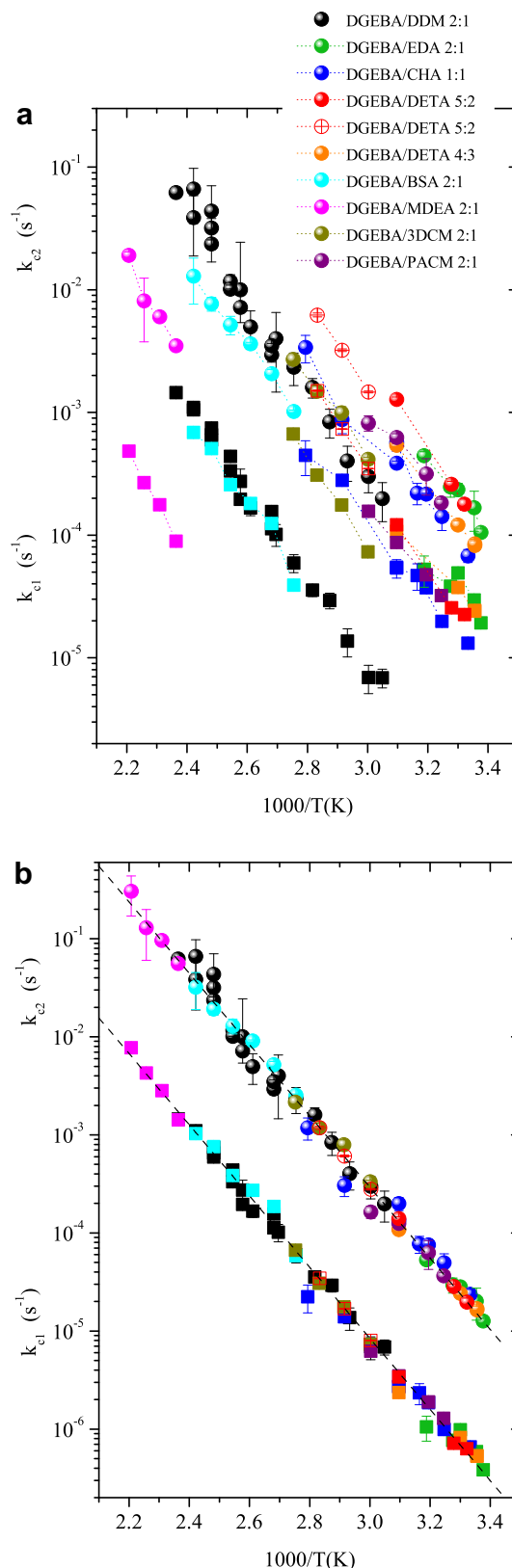


Fig. 12. (a) Dependence of k_{c1} (square symbols) and k_{c2} (circles) on the reciprocal temperature for different reactions. (b) Master curve obtained by multiplying by an appropriate factor each set of data in panel (a); same legend. The dashed lines are the Arrhenius fit to the data for the DGEBA/DDM reaction.

reaction of the epoxy compound with the amine [34,44,81,83], the evidence for this is not entirely convincing. In fact, the opposite has been reported [18] and also conflicting data for a given system. The case of DGEBA/DDM is illustrative of this last situation. Huguenin and Klein [44] and Deng and Martin [34] analyzed the first stages of cure of DGEBA/DDM by means of the Horie equation, obtaining $[\varepsilon_1 \text{ (kJ/mol)}, \varepsilon_2 \text{ (kJ/mol)}] = [71.2, 49.4]$ and $[63.2, 48.8]$, respectively. Ramirez and coworkers [81] and Kim and Char [82] analyzed the reaction in a similar temperature range with the Kamal equation, obtaining respectively $[94.3, 61.5]$ and $[67.9, 52.0]$. Liu and coworkers [83] obtained $[66 \pm 4, 51 \pm 9]$ by using a generalized Kamal equation derived from a mechanistic model. Interestingly, re-analyzing the data of the previous authors by means of Eq. (8), we find a close agreement of all the k_{c1} and k_{c2} data from different studies, with the same value of activation energy for the autocatalytic and non-catalytic processes ($\varepsilon_1 = 69.5 \pm 1.6$ kJ/mol, $\varepsilon_2 = 70 \pm 4$ kJ/mol). Moreover, a comparison of the data for different systems (Fig. 12) shows that while the autocatalytic process is the dominant one, with a rate constant k_{c2} at least one order of magnitude higher than k_{c1} , the activation energies are very similar for the two processes in all systems. The autocatalytic mechanism cannot therefore be easily dismissed as an effect associated with a lower energy barrier for the reaction of the epoxy–hydroxyl complex with the amine. Instead, it appears to have a significant effect on the chemical mechanisms which determine the pre-exponential factor in Eq. (9), by making k_{02} much higher than k_{01} .

Furthermore, we find that by using an appropriate scaling factor for each set of data, they all collapse on the activation lines of the DGEBA/DDM system (Fig. 12(b)). This scaling indicates that the activation energy is the same for all the reactions investigated, and suggests a similar mechanism underlying the reaction between epoxy group and amino hydrogen, independently of the details of the molecular structure to which they are attached and of the relative concentration of epoxy and amino groups.

6.3. Exponents m and n

There is no general agreement in the literature about the values of m and n and about their temperature dependence. Values of $m + n$ from 2 to 4 have been observed. Constant values of m and n have been reported, but also their variation (either increase or decrease) with the curing temperature. The comparison of results of different studies is made more difficult by the sensitivity of the two exponents m and n , especially n , to the kinetic model used to describe the experimental data, and by the fact that the sum $m + n$ has sometimes been additionally constrained to be 2 or 3.

Fig. 13 shows the values of the exponents m and n obtained for all the reactions analyzed in the present work, including those reactions carried out at a single temperature, by fitting the experimental data with Eq. (8) without any constraint on m and n . The value of m is always very close to 1. Within experimental error, the value of n is temperature-independent for a given mixture, but the values for different mixtures spread out over the range from 1 to 2, which yields an overall reaction order $m + n$ between 2 and 3, depending on the system investigated. Thus the constraint $m + n = 2$ or 3, as found in the literature, seems not to be a posteriori justified within our model.

A comparison between the fit parameters obtained by using Eq. (5) to describe the chemical kinetics and those obtained by describing the chemical kinetics with the Kamal equation may be useful to assess the merits of Eq. (5), where the stoichiometric ratio r appears explicitly. Fig. 14 shows this comparison for the exponents m and n in the DGEBA/DETA mixture at six different compositions including the stoichiometric balance 5:2, and shows that the

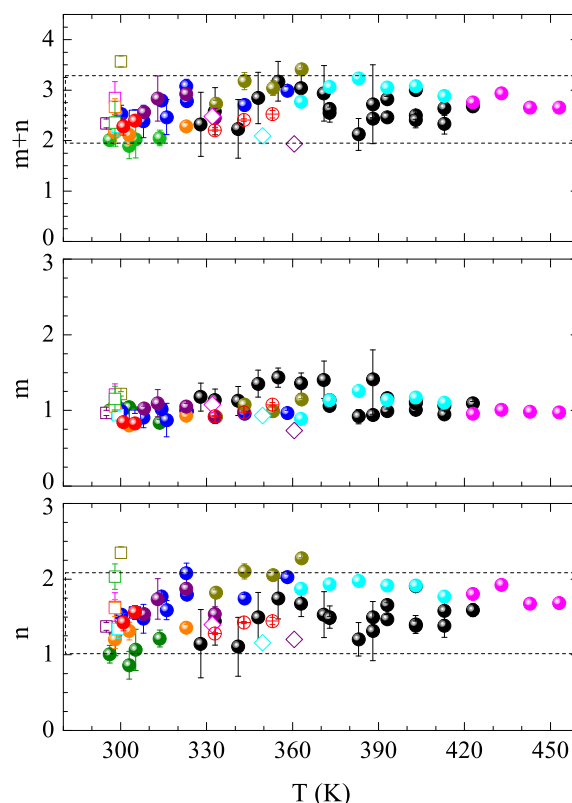


Fig. 13. Exponents m and n and overall reaction order $m + n$ for all the reactions analyzed. Solid symbols are the same as in Fig. 12. Open symbols correspond to single-temperature reactions, not shown in Fig. 12.

difference is very slight for the parameter m ($\approx 0.93 \pm 0.08$), while there is a systematic effect on the value of n . Using Eq. (5) increases n in mixtures with an excess of amino hydrogens ($r > 1$) and decreases n in mixtures with an excess of epoxy groups ($r < 1$), producing the overall effect that all mixtures have the same value of

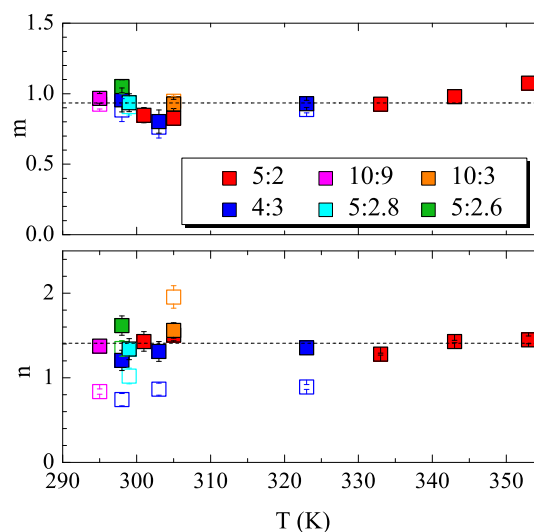


Fig. 14. Exponents m and n for the mixture DGEBA/DETA in six different compositions as indicated in the legend. The ratio 5:2 corresponds to the stoichiometric composition. Solid symbols are obtained by fitting the kinetic data with Eq. (8). Open symbols are obtained by replacing the chemical part of Eq. (8) with the Kamal equation, or equivalently using Eq. (8) with $r = 1$.

$n(\approx 1.4 \pm 0.1)$ independently of the stoichiometric ratio. This finding is quite consistent with the basic idea that m and n should be exponents related to the mechanism of reaction, which is expected not to change for a given system by changing the relative concentration of epoxy and amino groups.

6.4. Fractional exponent ξ and stretching parameter β

For each system, at all temperatures, a good agreement between Eq. (8) and experimental data is found with the value of the power-law index ξ , which relates the structural relaxation time to the overall diffusion coefficient (see Eq. (4)), in the range $0.2 \leq \xi \leq 0.45$, i.e. much smaller than that corresponding to inverse proportionality between τ and D , $\xi = 1$, and also smaller than the value $\xi = 0.81$ used in Ref. [34] for the DGEBA/DDM system. This result suggests that the use of $\xi = 0.81$ made in Ref. [34], based on the assumption that diffusion constants are proportional to particle sizes and that the SE equation still holds close to the glass transition, is too simplified and that the complex nature of a step-polymerizing system reflects in a large departure from the SE diffusion law.

Another parameter that is found to take values remarkably small in step-polymer systems, is the stretching parameter β , which describes the degree of nonexponentiality of the relaxation function $\Phi(t) \sim \exp[-(t/\tau)^\beta]$. (A stretched-exponential relaxation is also known as KWW relaxation.) It is observed that β decreases when a second component is added to a one-component system, and that the value of β can be varied by changing the relative amount of the two components [7]. In experiments using probe molecules dispersed in two-monomer thermoset matrixes, the β parameter of the probe rotation correlation function decreases with the increasing amount of the minor reagent [84]. The departure from exponential relaxation is attributed to heterogeneity in the dynamics of the material. Pronounced nonexponential relaxation (or broadening of the relaxation time distribution) is observed in other systems with complex structures like crosslinked polymers, polymer blends and block copolymers, where substantial spatially heterogeneous dynamics is expected.

We have analyzed the available experimental data from DS and PCS during epoxy-amine polymerization, including our recent results [6,7,48], as well as earlier data [63,69,70,72,73,75–77,79,85–88]. In the PCS experiments β was determined by fitting the time dependent signal using the KWW form for the normalized autocorrelation function of the scattered electric field; in the DS experiments β was obtained by fitting the normalized dielectric spectra in the frequency domain to the Fourier transform of the KWW function. Looking for a possible correlation between ξ and β , we have plotted the first as a function of the second quantity. In Fig. 15, this dependence is shown for 16 different polymerizing systems. Fig. 15 immediately points out that ξ approximately corresponds to β in the studied systems.

Note that for many mixtures β has not a constant value during the reaction, and tends to decrease as the polymerization progresses. However, it is almost constant over the late stage of reaction, which is also the stage determining the value of ξ . Moreover, within experimental error, the values of ξ and β are temperature-independent for a given mixture. Consequently, each point in Fig. 15 represents the quantities ξ and β over the diffusion-controlled part of the reaction, averaged over all the reaction temperatures.

There is no a priori reason why the fractional exponent ξ relating the structural relaxation time to the diffusion coefficient should be correlated with the extent β of nonexponentiality of the structural relaxation, in the sense that no theory of the glass transition predicts an explicit relationship between them. Hence, the observed relation between ξ and β in many step-polymerizing mixtures, in the form of Fig. 15 is striking. Its existence strongly

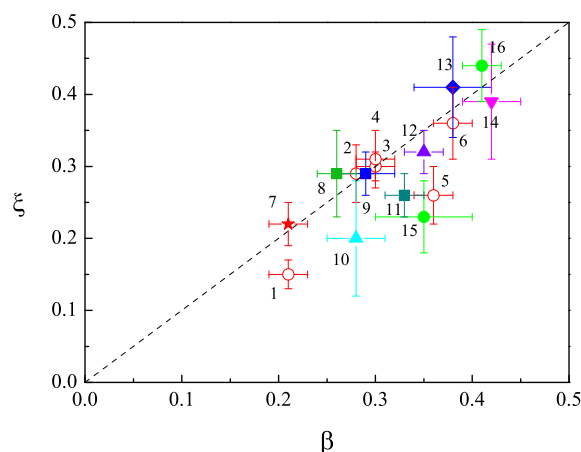


Fig. 15. Correlation of the power-law index ξ with the stretching β parameter. The dashed line represents $\xi = \beta$. Different systems are labeled on the plot as: 1, DGEBA/DETA 10:3; 2, DGEBA/DETA 5:2; 3, DGEBA/DETA 5:2.6; 4, DGEBA/DETA 5:2.8; 5, DGEBA/DETA 4:3; 6, DGEBA/DETA 10:9; 7, TACTIX/AN 2:3; 8, TACTIX/3CA 2:3; 9, DGEBA/PACM 2:1; 10, DGEBA/DDM 2:1; 11, TACTIX/4CA 2:3; 12, DGEBA/HA 1:1; 13, DGEBA/BAM 1:1; 14, DGEBA/CHA 1:1; 15, DGEBA/EDA 2:1; 16, DGEBA/EDA 1:1.

suggests that the two parameters share a common origin, or equivalently that they are associated to the same mechanism. Our finding highlights that the parameter ξ quantifies the effect of dynamic heterogeneity in terms of enhancement of translation in the same way as the parameter β does in terms of departure from exponentiality of relaxation.

It is interesting to note that the change in scaling law from $D \sim \tau^{-1}$ to $D \sim \tau^{-\xi}$ can be qualitatively described as enhancement of translational diffusion over rotational diffusion, and therefore the correlation between ξ and β observed here recalls the correlation between enhanced translation and nonexponential relaxation observed by Ediger and coworkers [52,53,57]. These authors used the ratio $D\tau/(D\tau)_{\text{DSE}}$, i.e. the product $D\tau$ normalized to the value of this product predicted by the DSE equation (a measure of the deviation from the hydrodynamic results) to quantify the enhancement of translation at the glass transition for different probe molecules in glass-forming host matrixes. In the following we show how their correlation between this ratio and the parameter β can be read in terms of our findings.

If the DSE equation is replaced near vitrification by $D\tau^\xi = \text{const}$, this ratio can be written as $D\tau/(D\tau)_{\text{DSE}} \sim \tau^{(1-\xi)}$. When it is evaluated at the glass transition point — where the relaxation time has a reference value of $\tau \approx 10^2$ s — one has $[D\tau/(D\tau)_{\text{DSE}}]_{\text{glass}} \sim 10^{2(1-\xi)}$. By applying the result in Fig. 15, i.e. $\xi \approx \beta$, it becomes $[D\tau/(D\tau)_{\text{DSE}}]_{\text{glass}} \sim 10^{2(1-\beta)}$, i.e. a straight line with slope -2 in a logarithmic plot vs. β . While a linear correlation between enhanced translation and KWW β parameter at the glass transition is qualitatively observed in Fig. 9 of Ref. [53], apparently there is no agreement with the slope.

To explain this disagreement and compare further, it should be taken into account that the quantities correlated in Fig. 15 refer to neat samples, while those correlated in Fig. 9 of Ref. [53] characterize the rotational and translational motion of probes of different size dissolved in the samples. The effect of probe size on breakdown of the SE equation in glass-forming liquids has been studied by Heuberger and Sillescu [54], showing that breakdown is suppressed for probe sizes exceeding the size of the solvent molecules. Recently, Rajian et al. [58] have collected data from the literature and pointed out that these clearly delineate a dependence of the extent of enhanced translation $[D\tau/(D\tau)_{\text{DSE}}]_{\text{glass}}$ on the relative size of probe-to-host, with a sharp increase when the size ratio is near unity and an enhancement of translational diffusion of about 3

decades for probes smaller than the host. Moreover, Wang and Richert [89] have shown that the rotation correlation function of probe molecules matches the collective nonexponentiality of the host liquid when the probe-to-host size ratio is lower than unity, but a relatively sharp transition to exponentiality occurs as the ratio begins to exceed 1. On the basis of these findings, we conclude that only the data in Fig. 9 of Ref. [53] that correspond to probes smaller than the host should match the expectation that $\log([D\tau]/(D\tau)_{\text{DSE}}]_{\text{glass}})$ is approximately linear vs. β with a slope of about -2 . Indeed, if we restrict to these data, we find that the dependence of enhanced translation on the stretching parameter is in good agreement with the expectation based on the results of the present work.

7. Conclusions

In this study we have introduced a new equation to describe the kinetics of epoxy–amine polymerization over the entire range of cure, built on a modification of the Horie equation to account for the chemically intrinsic rate of reaction, and the Rabinowitch model to account for the effect of diffusional limitations through a α -dependent diffusion rate constant. This rate constant and its dependence on the extent of reaction can be properly associated with the average diffusion coefficient and hence with the structural relaxation time, assuming a power–law relation between D and τ . In contrast to one of the commonly found approximations in the literature, the results of this study clearly indicate that the effect of diffusional limitations cannot be properly described by assuming that τ^{-1} , the relaxation rate directly gives the diffusional rate. Neither does the quantity $\tau^{-\xi}$ with $\xi \approx 0.8$. We have found that a fractional exponent $\xi \approx \beta$, with β the KWW stretching parameter ranging between 0.2 and 0.4 in the systems investigated, is required to reproduce the experimental results well, suggesting that β in these systems provides a measure of the decoupling between the translational diffusion of the chemically reacting sites and the reorientational motion of molecular entities that appears as relaxation measured by PCS and DS.

Another key ingredient of the equation proposed has been modeling the increase of structural relaxation time, and associated decrease of diffusion coefficient on polymerization in terms of configurational entropy reduction driven by covalent bond formation. Thus, the approach proposed reconciles the description of the diffusion-controlled kinetics of reaction, where diffusion has a leading role when approaching the glass transition, with the configurational entropy-based description of the structural dynamics near vitrification that has been applied successfully to epoxy–amine polymerization in previous studies.

We have obtained a very good agreement of the model equation with the experimental data of a large number of systems in a wide range of temperature, both in the chemically-controlled and diffusion-controlled regime of the reaction as well as in the cross-over region between the two. The equation is able to determine the parameter α_0 (the α value at which the configurational entropy of the system tends to vanish) consistently with the theory's expectation and with its limit of validity, while the parameters that characterize the intrinsic rate of reaction reveal a homogeneous behavior among different systems. In particular, two remarkable results have been found. The first concerns the behavior of the m and n exponents: for each epoxy–amine system investigated m and n assume approximately constant values, independent of the temperature and molar ratio of the mixture, which is in agreement with our expectation that these exponents are related to the intrinsic reaction mechanism, not changing by changing the reaction temperature or the relative concentration of epoxy and amino groups. The value $m \approx 1$ found in all systems suggests that the

overall order of the epoxy–amine reaction is suitably described by the introduction of only one parameter, n . It remains, however, an open question how to give an interpretation of such exponents in mechanistic terms. The second result concerns the intrinsic rate constants: for each constant (k_{c1} or k_{c2}) we can collapse the data for all the systems onto a master-curve corresponding to thermally activated behavior with, surprisingly, the same activation energy for the two constants k_{c1} and k_{c2} . Although such result, obtained by analyzing the data with Eq. (8), contradicts the widespread belief that the autocatalytic process has a lower activation energy, interestingly it removes some evident discrepancies existing in the literature among results reported for a given system in different studies.

The analysis of the diffusion-controlled regime is not weakened by the use of a phenomenological equation to describe the chemically-controlled limit of the epoxy–amine reaction. Indeed, the soundness of the approach adopted to model diffusion-control in the case of epoxy–amine systems — which is based on replacing each chemical rate constant with an overall one, built on the Rabinowitch model and the assumption of proportionality between k_d and the overall diffusion coefficient — also emerges from the recent simulation of irreversible polymerization in a model system, which does not suffer from ambiguity in the intrinsic chemical kinetics and permits a precise determination of the diffusion coefficient [60].

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