

Time–temperature and time-irradiation intensity superposition for photopolymerization of an epoxy based resin

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Abstract

In this paper the photoinitiated polymerization of a commercially available epoxy based resin for stereolithography (SL5170) was studied by means of photo differential scanning calorimetry (pDSC) at different temperature and irradiation intensities. Experimental results showed that temperature and light intensity have the same qualitative effects on the reaction kinetics. Time–temperature and time–intensity superposition principle was applied to the experimental curves. In both cases, it was shown that curves shifting on the time axis determines a single master curve. Individual curves significantly diverge from the master curve for high conversions, indicating that different regimes are encountered during photocuring of commercial stereolithography cationic resin. For low conversions, the reaction is kinetically controlled, whereas it becomes mainly diffusion controlled when the glass transition temperature approaches the isothermal cure temperature. At high conversion, master curves were also built in the diffusion-controlled regime, using different shift factors. The applicability of master curves to photopolymerization of epoxy based resin for stereolithography indicates that the mechanisms involved in network formation in the kinetic controlled regime are the same regardless of temperature and irradiation intensity. Consequently, time temperature transformation (TTT) and time intensity transformation (TIT) curves were built, as the time needed to reach polymer vitrification at each temperature and irradiation intensity.

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1. Introduction

In recent years the growing interest in cationic photopolymerization is related to the development of very efficient photoinitiators and to the distinct advantages of this method of radiation curing. As a result, UV-initiated cationic photopolymerization is finding application in a wide variety of areas, including coatings, inks, adhesives, and electronics. In addition to these processes, stereolithography (STL) makes use of laser induced cationic polymerization in order to build three-dimensional (3D) parts. In this process a laser beam photopolymerize the cross sections of the model onto the surface of photo-curable liquid resin, leading to the 3D object adding a section to another [1]. Commercial STL equipments nowadays make

use of cationic photoactivated monomers, whose curing reaction is not affected by the presence of oxygen, and involves limited shrinkages when compared with radical curing of acrylate-based systems [1]. In a previous paper [2], the photocuring reaction of an epoxy based resin for stereolithography was studied by means of photo differential scanning calorimetry (pDSC), showing that increasing the irradiation intensity or the cure temperature, not only the rate of reaction, but also the maximum degree of reaction increases. This behavior was attributed to the dependence of reaction kinetics on diffusion-controlled phenomena in the last part of the polymerization [3–8]. During the isothermal photopolymerization of a thermosetting polymer, the crosslinking density and the glass transition temperature of the network increase [9]. When the glass transition temperature of the network of the polymer network is lower than the isothermal cure temperature, the reaction is kinetic controlled. When the glass transition temperature of the network equals the isothermal cure temperature, vitrification occurs and the diffusion of reactive species becomes the limiting stage in the crosslinking reaction [10,11].

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Moreover, non-equilibrium conditions can occur at very high rates of reaction, as those typically involved in photopolymerization. In this case, at sufficiently high rates of reaction, the rate of volume shrinkage cannot follow the rate of chemical conversion, thus leading to an excess of free volume, which is finally responsible for a delayed transition to the glassy state of the resin (i.e. delayed vitrification). This effect was reported for radical chain photopolymerization comparing the results of DSC with those obtained by shrinkage measurements [5,8]. Although the irradiation intensity has been shown to play a significant role on the rate of reaction and on the final degree of reaction of cationic formulations [2,12], the influence of light intensity on such non-equilibrium phenomena was not still reported.

The time temperature superposition principle is very well known in the analysis of polymer flow and mechanical properties [13,14]. The essential idea at the basis of the principle is that, in the framework of linear viscoelasticity, some property of the polymer remains substantially unchanged when temperature is modified with respect to a reference value, if the time scale at which the property is measured is properly modified. The time–temperature superposition principle has also been used to study the curing reaction of thermosetting resins, showing that the free-volume changes are essential in determining the rate of the reaction [11].

In this work, the combined effect of temperature and irradiation intensity on the reaction kinetics of an epoxy based resin for stereolithography has been studied by means of photo-differential scanning calorimetry (pDSC). Time–temperature superposition principle has been successfully applied to degree of reaction curves obtained from isothermal pDSC experiments. The same principle has been applied to the superposition of time and irradiation intensity at constant temperature.

2. Experimental

The resin studied was Cibatool SL5170 by Ciba Specialty Chemicals, Pontecchio Marconi, Bologna, Italy. As reported in the material safety data sheet, the resin is actually composed of a mixture of butandiol glycidylether and bis-(epoxycyclohexyl)-methyl carboxylate at 24 and 60% wt, respectively. The remaining weight fraction is a mixture of a photoinitiator, a photosensitizer and a divinyl ether monomer. The cure of the SL5170 resin was carried out in a differential scanning calorimeter Perkin–Elmer DSC-7, modified for irradiation of the sample using transparent quartz windows. The light source, produced by a 300 W xenon lamp Cermax LX 300, was limited to a wavelength interval of 325 + 4 nm using a monochromator, in order to simulate the narrow irradiation band of the He–Cd laser beam used in the STL apparatus. The beam was focused on the sample using a system of lenses and a mirror and neutral filters were used to adjust the irradiation

intensity. The light intensity was measured by means of a LaserPoint 3000 power meter. In order to maintain uniform sample thickness the meniscus arising from the surface tension between the aluminum pan and the liquid resin was minimized modifying the standard aluminum pans according to the geometry proposed by Tryson and Shultz [15]. Small size samples (0.9–1.1 mg) were tested, in order to achieve isothermal conditions and a uniform degree of reaction through sample thickness [16].

Isothermal reaction hypothesis was tested by writing the heat balance for the sample in the DSC furnace during photopolymerization:

$$\rho c_p \frac{dT}{dt} = k \frac{\partial^2 T}{\partial x^2} + \rho H_{\max} \frac{d\alpha}{dt}$$

where ρ , c_p , k are the polymer density, thermal capacity and conductivity, respectively, t is the time, T is the temperature, and x is the direction parallel to sample thickness (assuming that thermal gradients in the orthogonal directions can be neglected). The term $\rho H_{\max}(d\alpha/dt)$ represents the rate of heat generated by chemical reaction, which is given as the product of polymer density, maximum heat released during polymerisation, H_{\max} , and rate of reaction, $d\alpha/dt$. The following dimensionless variables can be introduced into the energy balance:

$$T^* = \frac{T - T_0}{T_{\text{ref}} - T_0}$$

$$x^* = \frac{x}{h}$$

$$t^* = \frac{t}{t_p}$$

where T_0 is the initial temperature of the polymer (equal to the DSC furnace temperature), h is the sample thickness, t_p is the time of polymerization, $\Delta T = T_{\text{ref}} - T_0$ is a reference temperature difference, in this case the maximum allowable temperature increase in the DSC sample pan. Using the dimensionless variables, the energy balance can be written as:

$$\frac{dT^*}{dt^*} = \text{De} \frac{\partial^2 T^*}{\partial x^{*2}} + \text{St} \frac{d\alpha}{dt^*} \quad (1)$$

In Eq. (1) the diffusion Deborah number De is defined as:

$$\text{De} = \frac{kt_p}{\rho c_p h^2} \quad (2)$$

representing the ratio between a time scale of the reaction t_p and a time scale of the heat transferred by conduction $\rho c_p h^2/k$. In Eq. (1), the Stefan number St was used:

$$\text{St} = \frac{H_{\max}}{c_p(T_{\text{ref}} - T_0)} \quad (3)$$

representing the relative weight of the latent heat associated with the chemical reaction with respect to the thermal

capacity of the material. In terms of these dimensionless groups, if $De \gg 1$ (i.e. 10 or more) negligible temperature gradients within the sample are attained [7,17,18]. For the system under investigation, with $c_p = 1000 \text{ J/(kgK)}$, $\rho = 1200 \text{ kg/m}^3$, $k = 0.2 \text{ W/(mK)}$, $h = 10^{-4} \text{ m}$, $t_p = 500 \text{ s}$ and $H_{\max} = 410 \times 10^3 \text{ J/kg}$, $(T_{\text{ref}} - T_0) = 1 \text{ }^\circ\text{C}$, from Eqs. (2) and (3) $De = 8330$ and $St = 410$. The very high value of De implies that temperature gradients can be neglected. Being the thermal resistance between DSC furnace and sample very low the temperature of the sample surface can be considered equal to the DSC furnace temperature [19]. The high De number, and the low thermal resistance between sample surface and DSC furnace, indicate that the temperature can be considered uniform in the sample, and constant during the photopolymerization of the system under investigation.

Isothermal scans were run at $30 \text{ }^\circ\text{C}$ at different irradiation intensities (1.44, 1.92, 2.48, 3.20, 3.44, 6.33 W/m^2). Isothermal scans were also run at different temperatures, 30, 40, 50, 60 and $70 \text{ }^\circ\text{C}$, at irradiation intensities of 2.48 and 6.33 W/m^2 . At each temperature and irradiation intensity, the reaction was considered completed until the pDSC signal becomes constants and levels on the baseline. The pDSC measurements were used for determination of the advancement of polymerization by assuming that the heat evolved at each time is proportional to the overall degree of reaction, given by the fraction of reactive groups consumed. Following this approach the degree of reaction, α , was defined as [5]:

$$\alpha = \frac{H(t)}{H_{\max}} \quad (4)$$

where $H(t)$ is the partial heat of reaction developed during a DSC experiment. As also described below, H_{\max} is measured combining an isothermal photocalorimetry experiment with a second DSC scan obtained heating the same sample in dark conditions [11,20]. The rate of reaction, $d\alpha/dt$, was obtained from the heat flow dH/dt as:

$$\frac{d\alpha}{dt} = \frac{1}{H_{\max}} \frac{dH(t)}{dt} \quad (5)$$

The maximum degree of reaction, α_{\max} , was obtained as the ratio between the total heat developed in an isothermal pDSC experiment, H_{iso} , and H_{\max} :

$$\alpha_{\max} = \frac{H_{\text{iso}}}{H_{\max}} \quad (6)$$

Photo-thermomechanical analysis was also performed at $30 \text{ }^\circ\text{C}$ with an irradiation intensity of 3.44 W/m^2 to test the effect of photopolymerization on the reduction of specific volume of SL5170. The same optical system as that described for photo DSC experiments was used. SL5170 films about 0.1 mm thick were placed between a quartz plate, transparent to UV radiation, and a standard DSC aluminum pan cap. A force of 1 mN was applied to the aluminum cap and the sample through the probe. Being the

sample about 3 mm in radius, this force corresponds to a pressure of about 35 Pa. The film was irradiated under UV light and its thickness was recorded during the test using a Perkin–Elmer TMA7 instrument.

3. Time–temperature–intensity superposition principle

According to the time–temperature superposition principle, a relationship between time and temperature can be established such that the behavior of the material for given time–temperature conditions is the same which could be achieved by different appropriate combinations of values of the same variables. The time–temperature superposition principle has been already applied to thermal activated polymerization reactions. A general form for the reaction kinetic can be given by:

$$\frac{d\alpha}{g(\alpha)} = K(T)dt \quad (7)$$

where t and T are time and temperature, respectively. The left hand side of Eq. (7) is only dependent on the reaction mechanism and thus it is explicitly independent on both time and temperature. As a consequence, when temperature is changed the time scale can be adjusted in order to respect the identity of Eq. (7). Consequently, when applied to the curing of thermosetting resin, the time–temperature superposition principle can be expressed as in Eq. (8):

$$\alpha(t_1, T_1) = \alpha(t_0, T_0) \Leftrightarrow t_1 = \frac{t_0}{a_{T}} \quad (8)$$

This equation states that the extent of reaction α at an arbitrary temperature T_1 and at a time scale t_1 is the same as the extent of reaction at a reference temperature T_0 and a reference time scale t_0 if the two time scales are related through Eq. (8). The parameter a_{T} is the temperature shift factor, which usually shows an Arrhenius or WLF dependence on temperature [21,22]. According to Eq. (8) the time–temperature superposition principle can be applied if the mechanism of reaction can be expressed, at any time, by Eq. (7).

From the original mathematical model derived in a previous work [2], it was shown that for cationic initiated photopolymerization the rate constants of initiation, propagation and termination are not only temperature dependent, but also dependent on irradiation intensity. Thus the general form of cationic photopolymerization kinetics can be written as in Eq. (9):

$$\frac{d\alpha}{g(\alpha)} = K(T, I)dt \quad (9)$$

where I is the irradiation intensity. In Eq. (9), the left hand side is a function of the polymerization mechanism, and is independent on time, temperature and irradiation intensity. As a consequence, when I is changed on the right hand side

of Eq. (9), time can be changed accordingly, in order to preserve the identity reported in Eq. (9). If the kinetic behavior is well represented by Eq. (9), the time-irradiation intensity principle is expressed according to Eq. (10), introducing an irradiation intensity shift factor a_{II} :

$$\alpha(t_1, I_1, T_0) = \alpha(t_0, I_0, T_0) \Leftrightarrow t_1 = \frac{t_0}{a_{II}} \quad (10)$$

A more general expression is obtained if the change of both process variables is performed. Time-temperature and time-irradiation intensity principles can simultaneously be applied according to Eq. (11), if Eq. (9) is a valid representation of the reaction kinetics.

$$\alpha(t_0, I_1, T_1) = \alpha(t_0, I_0, T_0) \Leftrightarrow t_1 = \frac{t_0}{a_{II}a_{IT}} \quad (11)$$

4. Experimental results

In order to obtain the value of H_{\max} three resin samples were photopolymerized at 70 °C using an irradiation intensity of 6.33 W/m² and then heated in dark conditions up to 250 °C at 10 °C/min. The average isothermal heat of photopolymerization was calculated to be 367 J/g. Then the samples, heated in dark condition, showed an average residual reactivity of 43 J/g. This residual reactivity can be attributed either to the presence of acid catalyst produced by the former exposition to UV light or to active centers developed during isothermal curing and entrapped in the polymer. In both cases, the reaction can continue once the glass transition temperature is exceeded [5]. This is confirmed observing that the onset of residual reactivity is at 75 °C, just 5 °C above the isothermal test temperature. The heat of photopolymerization measured at 80 °C, for the same irradiation intensity of 6.33 W/m², is about 412 J/g, which is roughly the same quantity which can be obtained as the sum of the heat released during isothermal photocuring at 70 °C, and the heat released during dynamic scan. These results indicate that the glass transition temperature of the fully cured system is in the range between 70 and 80 °C. The same value of the maximum heat of photopolymerization can be obtained either as the heat released during photocuring at 80 °C or higher, or as the sum of the heat released during photocuring at a temperature lower than 80 °C and the heat released during dynamic heating in dark conditions. The average maximum heat of reaction was taken as $H_{\max} = 410$ J/g.

After determination of H_{\max} , at each temperature and irradiation intensity, the degree of reaction was obtained as a function of time, according to Eq. (4).

A plot of the degree of reaction obtained at different temperatures during photopolymerization of the studied resin, using a light intensity of 2.48 W/m², is shown in Fig. 1.

An increase of the temperature is associated with a shift

of the curves at lower times and an increase of the slope in the initial part of the curve. The maximum value of the degree of reaction (α_{\max}), reported in Table 1, also increases, as a consequence of the delayed vitrification [2, 5,9].

A similar behavior can be observed for the degree of reaction obtained at different irradiation intensities at a temperature of 30 °C, as reported in Fig. 3, and for the maximum value of the degree of reaction, reported in Table 2.

In Fig. 1 and Table 1, a maximum degree of reaction (α_{\max}) lower than 1 is attributed to transition of the polymer to the glassy state in the latest stages of reaction, when the lower mobility of the reactants leads to a dramatic decrease in the rate of propagation. This reduced mobility of the growing network corresponds to the vitrification of the polymer, occurring when the glass transition temperature of the forming network reaches the isothermal cure temperature. In correspondence with vitrification, the free volume of the polymer reduces to a critical value, which limits the rotational mobility of the linear segments of the network, causing a decrease in the propagation rate [5–7,9,11]. A temperature increase determines a shift of vitrification at higher values of the degree of reaction, and consequently the final degree of reaction increases.

At constant temperature and changing irradiation intensity, a different behaviour would be expected. In this case, higher irradiation intensity would lead to a higher initiation rate, and a higher concentration of ionic centres. In such instance, an increase of irradiation intensity would act in the same way as an increase of the initiator or photosensitizer concentration. On the other hand, if photopolymerization takes place under equilibrium conditions, a one to one relation exists between degree of reaction, free volume and glass transition temperature [23,24]. Accordingly, under equilibrium conditions, vitrification is supposed to be related only to the cure temperature and hence it should occur at the same value of degree of reaction for all the curves reported in Fig. 2. This would lead to a value of α_{\max} which is independent on the irradiation intensity.

According to Decker, the higher final degree of conversion observed at higher irradiation intensities can be attributed either to an increase in the sample temperature at high irradiation intensities, which provides more molecular mobility and leads to higher ultimate conversion, or to a longer time lag between conversion and shrinkage, which generates a greater excess of free volume and thus increases the molecular mobility [25].

The first hypothesis assumes that non isothermal polymerisation takes place during UV irradiation, due to the exothermal nature of the polymerisation reaction. Nevertheless, according to the observations previously reported, for the very thin samples used in this work, the temperature rise during photocuring is expected to be much lower than 1 °C. This low temperature variation cannot

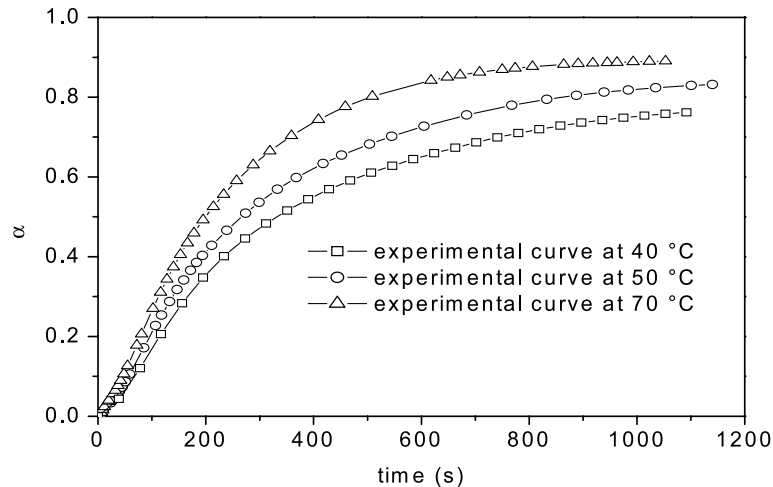


Fig. 1. Experimental degree of reaction at 2.48 W/m² and 40 °C (□) 50 °C (○), and 70 °C (△).

explain the observed differences in the final degree of conversion.

Therefore, non-equilibrium conditions, in which the one to one relation between degree of cure and free volume is no longer valid, are likely to occur. In fact, as reported by Kloosterboer [26], the chemical reaction is responsible of the free volume reduction, which is responsible for the diffusion of reacting species. For very fast polymerisation reaction, the rate of volume shrinkage cannot follow the rate of chemical conversion. As a consequence, at each time, an excess free volume exists, which is responsible of a rate of reaction higher than the rate of reaction which would be observed under equilibrium conditions, particularly in the diffusion controlled regime [5]. This effect is dependent on the rate of chemical conversion, determining at each time the equilibrium free volume, and the rate of increase of the bulk modulus, determining the free volume relaxation time [27].

In order to test that a delayed free volume relaxation with respect to chemical conversion occurs, DSC results were compared with TMA results obtained at the same temperature under the same irradiation intensity. The DSC signal is representative of the rate of chemical conversion, whereas the TMA signal is an indication of the free volume reduction. As reported in Fig. 3 the TMA conversion, calculated as the difference between the initial sample thickness and the sample thickness at time t , follows the DSC conversion only in the initial stages of reaction. Because of the very low bulk modulus of the material at this

stage of reaction, the relaxation time of the free volume is low enough to ensure that at each time the free volume is at the equilibrium condition, determined from the chemical conversion. As the cure time increases, and the polymer goes through gelation, the increase of the bulk modulus involves an increase of the relaxation time of the free volume, which is no longer capable to follow the chemical conversion. For very long times, when the chemical conversion is virtually completed, the volume of the material is continuously decreasing towards the equilibrium value corresponding to the degree of conversion attained during photocuring.

The results reported in Fig. 3 show that for the fast reacting SL5170 resin, which is actually composed of a mixture of diglycidyl ether, cyclo-epoxy and vinyl ether, the free volume relaxation time scale is higher than the time scale of reaction, thus leading to an excess free volume which is responsible of an increased conversion as irradiation intensity increases.

Accordingly, temperature and irradiation intensity have the same effect on the polymerization reaction, both leading to higher rate of reaction and final degree of conversion.

5. Time–temperature and time-irradiation intensity shifting

Experimental curves obtained at different temperatures

Table 1

Maximum degree of reaction, shift factors in the kinetic and diffusion controlled regime and degree of reaction determining vitrification at different photopolymerization temperatures and 2.48 W/m²

Temperature (K)	α_{\max}	a_{iT}	α_{vitk}	a_{iTd}	α_{vitd}
303	0.72	1.61	0.47	1	–
313	0.77	1.56	0.49	0.97	0.50
323	0.83	1.32	0.53	0.95	0.54
333	0.85	1.12	0.65	0.77	0.65
343	0.89	1	–	0.76	0.69

Table 2
maximum degree of reaction, shift factors in the kinetic and diffusion controlled regime and degree of reaction determining vitrification at different irradiation intensities and 30 °C

Irradiation intensity (W/m ²)	α_{\max}	a_{II}	α_{vitk}	$a_{II d}$	α_{vitd}
1.44	0.61	5.88	0.42	1	–
1.92	0.66	4.18	0.45	0.83	0.45
2.48	0.72	2.88	0.47	0.68	0.47
3.20	0.74	2.29	0.58	0.56	0.57
3.44	0.83	1.59	0.69	0.51	0.68
6.33	0.89	1	–	0.36	0.73

with an irradiation intensity of 2.48 W/m² were shifted according to the procedure described in Eq. (8). Determination of the values of the shift factor required the minimization of the objective function OF:

$$\text{OF} = \sum_i \frac{\left[\alpha_i \left(\frac{t_0}{a_{II}}, T_1 \right) - \alpha_i(t_0, T_0) \right]^2}{[\alpha_i(t_0, T_0)]^2}$$

where the summation is limited to the points having $\alpha < 0.3$. Curves were shifted using the curve at 70 °C as reference. Accordingly, the shift factor for the curve at 70 °C is unity. The shift factors determined for the curves obtained at different temperatures are reported in Table 1. The results reported in Fig. 4 show that curve shifting according to the time–temperature superposition principle is very efficient in the initial stages of the curing reaction, which is kinetically controlled. Therefore, a single master curve can be obtained in the initial stages of the photocuring reaction. Whereas chemical kinetics usually requires the assumption of kinetically controlled reactions, very often during curing of thermoset polymers diffusion controlled reactions take place in correspondence of the last part of the reaction [10, 11,28]. The change in reaction mechanism from kinetic to diffusion controlled involves the divergence of the individual curves reported in Fig. 4 from the reference curve. Accordingly the value of the degree of reaction, α_{vitk} ,

at which each individual curve in Fig. 4 diverges from the reference curve at 70 °C can be considered as the point, where vitrification sets up, and the reaction becomes diffusion controlled [29].

The threshold value of α determining the onset of vitrification was calculated as the point, where the quantity

$$\frac{\left| \alpha_i \left(\frac{t_0}{a_{II}}, T_1 \right) - \alpha_i(t_0, T_0) \right|}{\alpha_i(t_0, T_0)}$$

becomes higher than 0.01.

As expected, the values of α_{vitk} , reported in Table 1 and marked in Fig. 4, increase with curing temperature.

For the reference curve obtained at the higher temperature it was not possible to determine the value of α_{vitk} , since this is defined as the value, where each curve diverges from the reference curve.

Besides this known shifted procedure, the new one proposed in this study is obtained keeping constant the temperature (30 °C) and shifting the experimental kinetic data measured at different irradiation intensities using the curve at 6.33 W/m² as reference. The results of this time–intensity superposition, shown in Fig. 5, were obtained using the shift factors reported in Table 2.

Also in this case, the curves shifted according to the time–intensity superposition principle significantly diverge in the latest stages of reaction. The degree of reaction, α_{vitk} ,

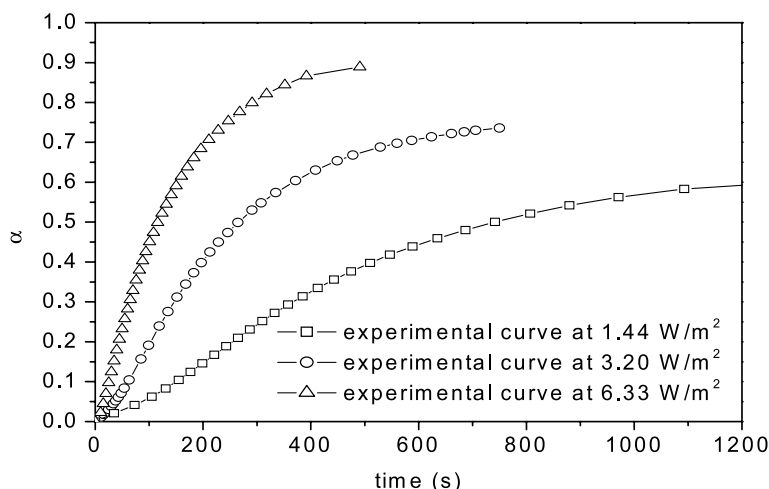


Fig. 2. Experimental degree of reaction at 30 °C and 1.44 W/m² (□) 3.20 W/m² (○), and 6.33 W/m² (△).

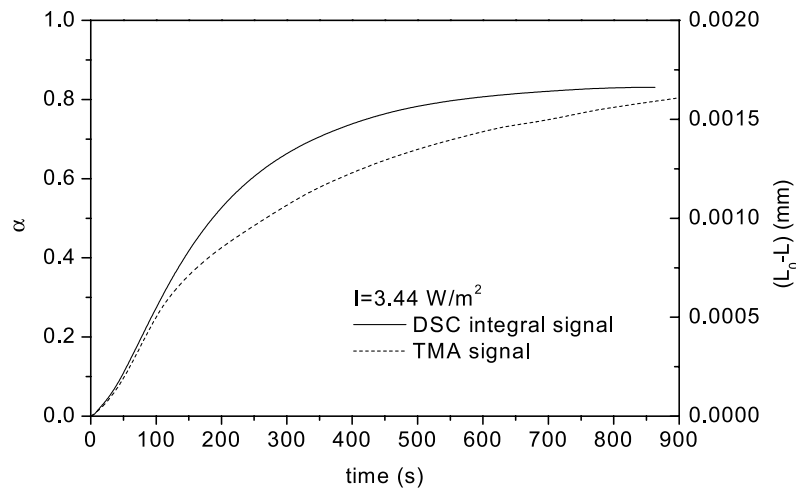


Fig. 3. Degree of chemical conversion at 30 °C and 3.44 W/m² determined from DSC analysis (—) and volume reduction determined from TMA (- - -).

at which the shifted curves in Fig. 5 diverge from the reference one (6.33 W/m²) is reported in Table 2 and marked in Fig. 5. As for the time–temperature shift, it was not possible to determine the value of α_{vitr} for the curve obtained at the higher irradiation intensity, used as reference. Comparing the results reported in Figs. 4 and 5 it can be observed that, even in this case, the curve shifting provides good results in the initial stages of reaction. The value of α_{vitr} (Table 2) at which each curve diverges from the master curve increases with irradiation intensity.

The different pattern of the shifted curves observed in Figs. 4 and 5 after α_{vitr} is due to the different regimes encountered during photocuring. In the initial stages under the kinetic control, Eq. (9) can well represent the reaction mechanism and the time–temperature and time–intensity superposition can be applied according to Eq. (11). At higher curing times α_{vitr} marks the limit afterwards the reaction becomes mainly diffusion controlled [11,20] as a consequence of the transition of the growing network to the

glassy state. The results reported in Figs. 4 and 5 show that in correspondence with vitrification the rate reaction of reaction decreases but it is not actually zero. This is consistent with reported observations on curing reactions of thermoset materials, showing that the actual propagation rate constant can be higher than zero even after vitrification [10,28–30]. The continuous polymerisation reaction taking place after vitrification can be better detected by looking at the TMA results reported in Fig. 3, showing that with an irradiation intensity of 3.44 W/m² the vitrification does not mark a sudden zeroing of the free volume reduction. According to the results reported in Table 2 vitrification is observed for $\alpha = 0.69$, corresponding to a photopolymerization reaction of 330 s. On the TMA curve it can be observed that at about 330 s the rate of volume reduction decreases but does not reach zero. This indicates that both chemical conversion and volume shrinkage continue even after the onset of vitrification.

For $\alpha > \alpha_{\text{vitr}}$, it can be assumed that the rate of reaction is

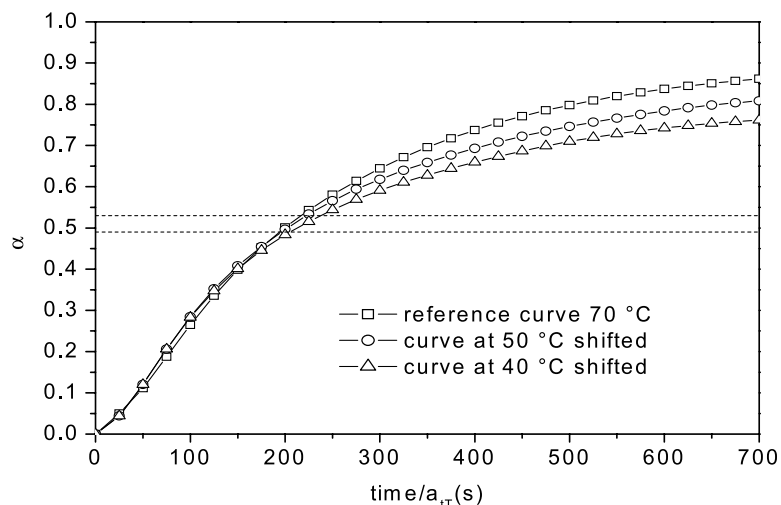


Fig. 4. Degree of reaction vs. reduced time at 2.48 W/m² and different temperatures, 70 °C (□) 50 °C (○) and 40 °C (△). The dashed lines represent the limit of the kinetic regime for the curves at 40 °C and 50 °C.

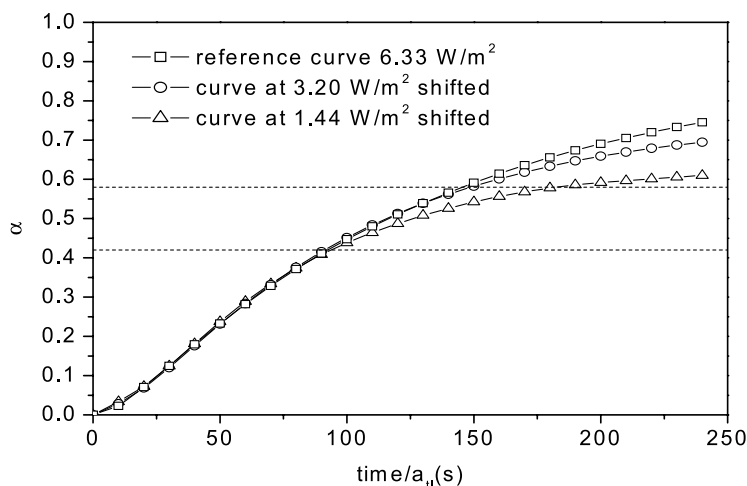


Fig. 5. Degree of reaction vs. reduced time at 30 °C and different irradiation intensities, 6.33 W/m² (□), 3.20 W/m² (○) and 1.44 W/m² (△). The dashed lines represent the limit of the kinetic regime for the curves at 3.20 and 1.44 W/m².

driven by the difference between the final degree of reaction, and the actual degree of reaction. Accordingly, Eq. (9) can be re-written as:

$$\frac{d\alpha}{g(\alpha_{\max}(T, I) - \alpha)} = K(T, I)dt \quad (12)$$

where α_{\max} is the maximum degree of reaction, depending, as observed in Figs. 1 and 2, on irradiation intensity and temperature. According to Eq. (12), in the diffusion controlled regime, a master curve can be built for $(\alpha_{\max} - \alpha)$. The results of the shifting are reported in Fig. 6 for the curves obtained at different temperatures, using the curve at 40 °C as reference. In this case, the curve at 40 °C was used as reference in order to determine the onset of the diffusion controlled regime for the data obtained at the highest temperature (70 °C). The shifting procedure, with the shift factors a_{ITd} reported in Table 1, provides a good agreement between experimental data in the diffusion controlled

regime, as shown in Fig. 6. In this case, the superposition holds after vitrification, when the reaction is not anymore under the kinetic control.

The curve at 70 °C of Fig. 6 diverges from the reference curve in correspondence of $(\alpha_{\max} - \alpha) = 0.20$ indicating that, for the photopolymerization at 70 °C and 2.48 W/m², vitrification occurs at $\alpha_{\text{vitd}} = 0.69$ (Table 1).

A similar time-irradiation intensity shifting procedure can be applied to photopolymerization curves obtained at a constant temperature (30 °C). The results are reported in Fig. 7 using the shift factors a_{ITd} reported in Table 2. The value of α_{vitd} determining vitrification at 6.33 W/m² and 30 °C is 0.73, as reported in Table 2. As expected the values of α_{vitk} and of α_{vitd} in Tables 1 and 2 are very close, both representing the limit of the transition from kinetic to diffusion control.

An example of the application of Eq. (11) for simultaneous temperature and irradiation intensity shifting

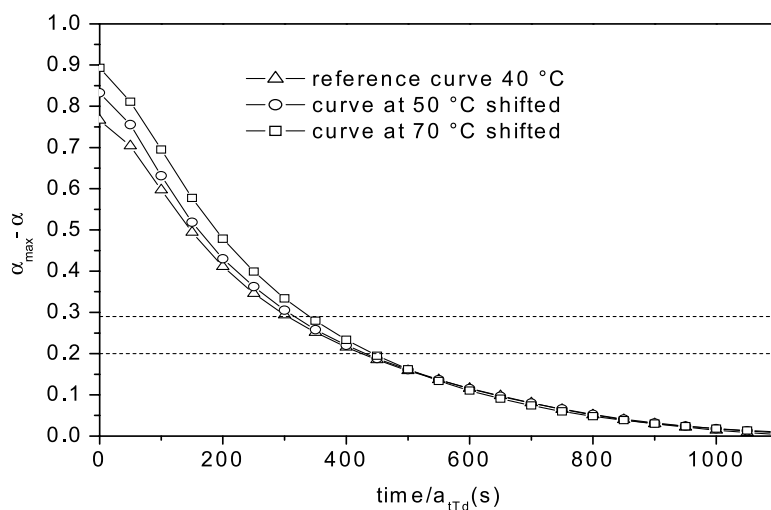


Fig. 6. Degree of reaction vs. reduced time at 2.48 W/m² and different temperatures, 70 °C (□), 50 °C (○) and 40 °C (△), in the diffusion controlled regime. The dashed lines represent the onset of the diffusion controlled regime for the curves at 50 and 70 °C.

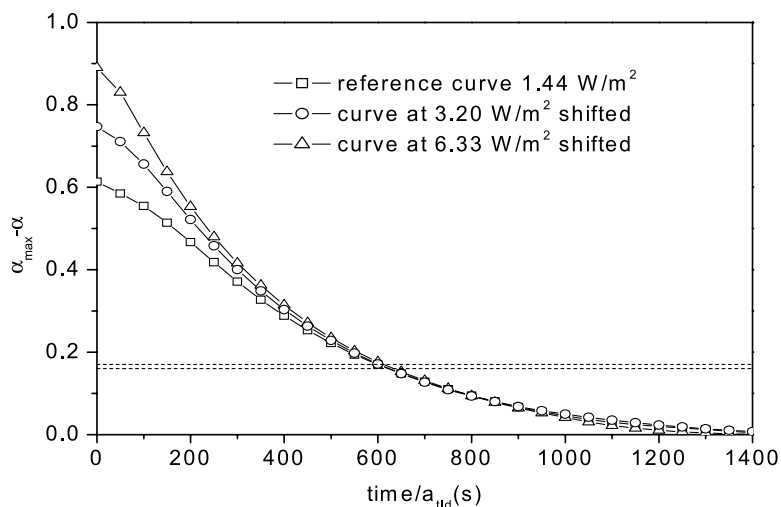


Fig. 7. Degree of reaction vs. reduced time at 30 °C and different irradiation intensities, 6.33 W/m² (□), 3.20 W/m² (○) and 1.44 W/m² (ρ), in the diffusion controlled regime. The dashed lines represent the onset of the diffusion controlled regime for the curves at 3.20 and 6.33 W/m².

is given in Fig. 8. Two representative curves were chosen, the first one, taken as reference curve, obtained at 70 °C with an irradiation intensity of 2.48 W/m², the second one at 30 °C with an irradiation intensity of 1.44 W/m². Shifting of the second curve with respect to the reference curve is equivalent to shifting it first with respect to irradiation intensity (a_{II}) and then with respect to temperature (a_{IT}). From the results reported in Table 2, $a_{II} = 5.88/2.88 = 2.04$, and from Table 1 $a_{IT} = 1.61$. According to Eq. (11), the shift factor can be determined as the product of the two shift factors, and the master curve can be built as reported in Fig. 8.

Combining the results of the two shifting procedures presented above, it may be concluded that an increase of the irradiation intensity acts in the similar way as an increase of temperature on the reaction rate and on the final degree of reaction. An increase of either temperature or irradiation intensity results in a delayed vitrification leading finally to a higher maximum degree of reaction. Furthermore, the

photopolymerization reaction can be regarded as a two-stage process, the first one being kinetic controlled, the second diffusion controlled. The two superposition procedures represents a powerful tool to separate the two regimes.

6. Conclusions

In this paper a new time–intensity superposition principle have been proposed for the cationic photopolymerization of an epoxy based resin. The time–intensity superposition has been associated to a more traditional time–temperature superposition drawing a parallel between the effects of temperature and irradiation intensity. The master curves obtained from curve shifting of experimental data at different temperatures or irradiation intensities indicate that these two variables affects in a similar way the curing process. As photopolymerization temperature increases,

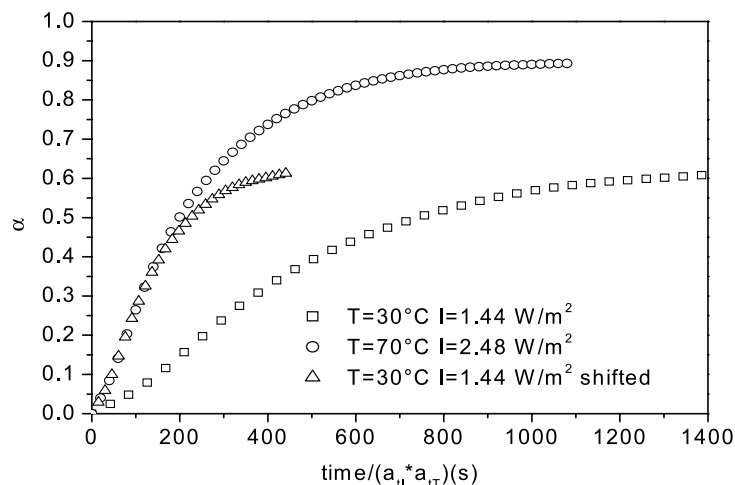


Fig. 8. Application of Eq. (11) for simultaneous temperature and irradiation intensity shifting.

delaying of vitrification at higher values of the degree of reaction is responsible of a higher final conversion. Similarly, increasing the irradiation intensity, a higher final conversion, associated to non equilibrium conditions, is attained.

The lack of an adequate superposition at high degree of reaction is an indication of a double stage mechanism, the first one being kinetic controlled, the second diffusion controlled. Reaction is essentially kinetic controlled when the degree of reaction is lower than the critical conversion determining the onset of vitrification. From the vitrification point up to the end of reaction the diffusion of reactive groups governs the reaction kinetics leading to a dramatic decrease of the rate of reaction. A time-irradiation superposition and a time-temperature superposition is still possible in the diffusion controlled regime using for ($\alpha_{\max} - \alpha$) as dependent variable.

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References

- [1] Jacobs PF. Stereolithography and other RPM technologies. Michigan: Society of Manufacturing Engineering; 1996.
- [2] Esposito Corcione C, Greco A, Maffezzoli A. *J Appl Polym Sci* 2004; 92:3484–91.
- [3] Pappas SP. Radiation curing: Science and technology. New York: Plenum Press; 1995.
- [4] Odian G. Principles of polymerization. 3rd ed. New York: Wiley; 1991.
- [5] Maffezzoli A, Terzi R. *Termochim Acta* 1998;321:111–21.
- [6] Mita I, Horie K. *J Macromol Sci Rev Macromol Chem Phys* 1987; C27(1):91–169.
- [7] Kenny JM, Maffezzoli A, Nicolais L. *Compos Sci Technol* 1990;339–358:38.
- [8] Kloosterboer JG, Van De Hei GMM, Gossink RG, Dortant GCM. *Polym Commun* 1984;25:322–5.
- [9] Nunez L, Fraga F, Castro A, Nunez MR, Villanueva M. *Polymer* 2001;42:3581–7.
- [10] Tai HJ. *J Polym Res* 2000;7:221–7.
- [11] Lin HL, Yu TL. *Polymer* 1996;37:581–6.
- [12] Nelson EW, Jacobs JL, Scranton AB, Anseth KS, Bowman CN. *Polymer* 1995;36:4651–6.
- [13] O’Connell PA, McKenna GB. *Mech Time-Depend Mater* 2002;6: 207–29.
- [14] Miranda Guedes R, Torres Marques A, Cardon A. *Mech Time-Depend Mater* 1998;2:113–28.
- [15] Tryson GR, Schultz AR. *J Polym Sci Polym Phys* 1979;17:2059–75.
- [16] Flammershein HJ, Kunze W. *J Therm Anal* 1998;52:125–30.
- [17] Maffezzoli A, Terzi R. *Termochim Acta* 1995;269/270:319–35.
- [18] Torre L, Maffezzoli A, Nicolais L. *Revue de l’Institut Francais du Petrole* 1995;50:135–9.
- [19] Simon SL. *Macromolecules* 1997;30:4056–63.
- [20] Harismendy I, Gomez CM, Del Rio M, Mondragon I. *Polym Int* 2000; 49:735–42.
- [21] Dusek C. *Adv Polym Sci* 1986;78:1–59.
- [22] Chan JH, Balke ST. *Polym Degrad Stab* 1997;57:127–34.
- [23] Ferry JD. *Viscoelastic properties of polymer*. 3rd ed. New York: Wiley; 1980.
- [24] Lunak S, Vladyka J, Dusek K. *Polymer* 1978;19:931–3.
- [25] Decker C. *Polym Int* 1998;45:133–41.
- [26] Kloosterboer JG. *Adv Polym Sci* 1987;84:1–61.
- [27] Verstegen EJK, Faasen JHP, Stapert HR, Duineveld PC, Kloosterboer JG. *J Appl Polym Sci* 2003;90:2364–76.
- [28] Barral L, Cano J, Lopez AJ, Lopez J, Nogueira P, Ramirez C. *J Appl Polym Sci* 1996;61:1553–9.
- [29] Stefani PM, Moschiar SM, Aranguren MI. *J Appl Polym Sci* 2001;79: 1771–9.
- [30] Tai HJ, Chou HL. *Eur Polym J* 2000;36:2213–9.