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Effect of oxygen on the photopolymerization of a mixture of two dimethacrylates

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Abstract

In this work we study the influence of the presence of oxygen in the photocuring of a system obtained by mixing two dimethacrylates. Using an isoconversional method we have found the kinetic parameters with different atmospheres: nitrogen, air and oxygen. The inhibition effect of oxygen has been compensated by adding a greater proportion of initiator and increasing the intensity of the ultraviolet radiation. We have seen that the latter had more influence.

Keywords: Dimethacrylate monomers; Isothermal kinetics; Photocuring

1. Introduction

The photopolymerization is a process of great interest due to its advantages: fast curing speeds at room temperature, energy efficiency, low concentration of volatile organic compounds and low health risks. The most relevant applications of photocuring technology include: dental composites, films and coatings, adhesives, inks, fiber optics and electronics [1–7].

The application of photocuring technology requires the use of photoinitiators. There are mainly two types of them: free-radical and cationics [5]. One of the main drawbacks of free-radical polymerization is the negative influence caused by the presence of oxygen. This influence has been a subject of much interest because a lot of photocuring processes are carried out in air. Oxygen increases the induction period and decreases the reaction rate, the final conversion and the polymer chain length [1,5,8–11].

At the beginning of the photocuring process, the oxygen can be found dissolved in the system. This oxygen reacts with the initiator when the photoinitiation process is triggered and photopolymerization starts. Moreover, oxygen from the surrounding atmosphere can penetrate in the system by diffusion from the atmospheric air and then the conversion at the surface decreases [5,11]. The effect of oxygen is greater at the beginning of the process, because the increase in viscosity during the photocuring suppresses the diffusion rate of oxygen from the atmosphere [11]. To compensate the inhibition effect of oxygen it is possible to use a greater proportion of initiator, taking into account that the use of high proportions reduces light penetration in the regions separated from the surface and the conversion in these zones can decrease and be less homogeneous [12], thus decreasing the adhesion properties in coatings [5]. Acrylates and methacrylates are the most common monomers in free-radical photopolymerization, being methacrylates much less sensitive to oxygen than acrylates [11].

In this work we have studied the isothermal curing of a mixture of two dimethacrylates by photopolymerization in the presence of different atmospheres: nitrogen, air and oxygen. Using an isoconversional method [13,14] we have determined the activation energy and the pre-exponential factor at different degrees of conversion. We have also studied the effect of the increase of initiator concentration in oxygen atmosphere and the possibility of counteracting its inhibition effect with an increase of the intensity of the ultraviolet radiation.

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2. Experimental

2.1. Materials

Monomers 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane (bis-GMA) (512 g/mol, Aldrich) and triethyleneglycol dimethacrylate (TEGDMA) (286 g/mol, Aldrich) were used as received. The structure of these monomers can be found in the references [15,16]. 2,2-Dimethoxy-2-phenylacetophenone (Dmpa) (Aldrich) was used as photoinitiator.

Samples were prepared by dissolving the initiator in the TEGDMA monomer by means of magnetic stirring for 2 h at 30 °C. bis-GMA was subsequently added to obtain a formulation with a bis-GMA concentration of 50 wt.%. It was stirred for 2 h at 30 °C and kept at −20 °C before use to prevent polymerization.

The different mixtures used in this work will be identified as the following example: 50:50/3% Dmpa (mixture of 50% weight of the two monomers with 3% of initiator).

2.2. Photo-DSC

The isothermal photopolymerization study by means of photo-DSC was performed at different temperatures (30, 40, 50, 60, 80 and 100 °C) using a Mettler-DSC-821e calorimeter. It was modified to make irradiation possible using a Hamamatsu Lightningcure LC5 (Hg–Xe lamp) with two beams, one for the sample side and the other for the reference side. Two scans were performed on each sample in order to substract the thermal effect of the UV irradiation on the sample from the photocuring experiment. Each scan consisted of 4 min of temperature conditioning, 20 min of irradiation and finally four more minutes without UV light. We made experiences changing light intensity between 12.8 and 172.8 mW cm^{-2} (incident light intensity at the sample pan position measured by the carbon black method. In this method, the sample pan is filled with carbon black powder and the UV irradiation is blocked on the reference side. Exposing the sample at room temperature will lead to a constant heat flow due to the light. The measured step, in mW, normalized to the pan's cross-sectional area, delivers the irradiation, in mW cm^{-2}). The mass of the samples used was approximately 5 mg.

3. Theroretical analysis

The absolute degree of conversion at a time t was calculated as the quotient between the heat release up to t and the total reaction heat associated with complete conversion of all reactive groups. The reaction rate, $d\alpha/dt$ was expressed as the ratio between the instant heat released (dh/dt, calorimetric signal) and the total heat of reaction, 300 J g^{-1}, which was calculated as the average value of reaction heat obtained non-isothermally at different heating rates (2, 5, 10 and 15 °C min^{-1}) using 3% of benzoil peroxide as initiator.

If we accept the Arrhenius equation, the kinetics of the reaction is usually described by the rate equation:

$$\frac{d\alpha}{dt} = kf(\alpha) = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \quad (1)$$

where t is the time, A the pre-exponential factor, E the activation energy, T the absolute temperature, R the gas constant and $f(\alpha)$ is the differential conversion function.

In this work we use the isoconversional method to find the activation energy and the pre-exponential factor at different stages of the process. The basic assumption of this method is that the reaction rate at constant conversion is only a function of the temperature [12]. By integrating Eq. (1) in isothermal conditions, we obtain:

$$\ln t = \ln\left[\frac{g(\alpha)}{A}\right] + \frac{E}{RT} \quad (2)$$

where $g(\alpha)$ is the integral conversion function. According to Eq. (2), the activation energy and the constant $\ln[g(\alpha)/A]$ can be obtained for a constant value of α from the slope and the intercept of the linear relationship $\ln t$ against T^{-1}, respectively. If the reaction model, $g(\alpha)$, is known, the corresponding pre-exponential factor can be calculated for each absolute conversion.

To determine the kinetic model we use the reduced master curves [17,18], where $\alpha = 0.5$ is the reference point. Then the following differential master equation is easily derived from Eq. (1), assuming that kinetic parameters are relatively constants during the curing.

$$\frac{f(\alpha)}{f(0.5)} = \frac{d\alpha/dt}{(d\alpha/dt)_{0.5}} \quad (3)$$

where $(d\alpha/dt)_{0.5}$ and $f(0.5)$ are the reaction rate and the differential conversion function at $\alpha = 0.5$, respectively. In this case we used the relative degree of conversion [19]. Different conversion functions were studied: diffusion (D_1, D_2, D_3 and D_4), Avrami-Erofeev ($A_{3/2}$, A_2, A_3 and A_4), power law (P_2), phase-boundary-controlled reaction (R_2 and R_3), reaction-order n ($n = 3$, 2, 1.5 and 1) and autocatalytic ($n + m = 1$, 2 and 3 with different values of n and m) [17,18]. Once kinetic model is determined, we can calculate A for each absolute conversion, using $g(\alpha)$ and $\ln[g(\alpha)/A]$ isoconversionally calculated.

4. Results and discussion

Fig. 1 plots the degree of conversion versus time of the photopolymerization process of the system 50:50/3% Dmpa, at a temperature of 50 °C, with a light intensity of 12.8 mW cm^{-2} and with different atmospheres: nitrogen, air and oxygen. It can be seen that when the atmosphere is air or oxygen the reaction is delayed, due to the interaction between initiator and oxygen. This influence is greater with pure oxygen, because the proportion of oxygen in air is only 21% in volume. Furthermore, the behaviour in air is more similar to the behaviour in pure nitrogen (0% oxygen), because the proportions of oxygen in these atmospheres are less different than the proportions of the same substance in air and pure oxygen.

After the first stage of the process, the presence of oxygen decreases the reaction rate, but the behaviour in air is still more similar to the behaviour in pure nitrogen. The final conversion of the process decreases if the oxygen proportion of the atmosphere increases, but the behaviour of the system with air is not so similar to the behaviour in pure nitrogen.

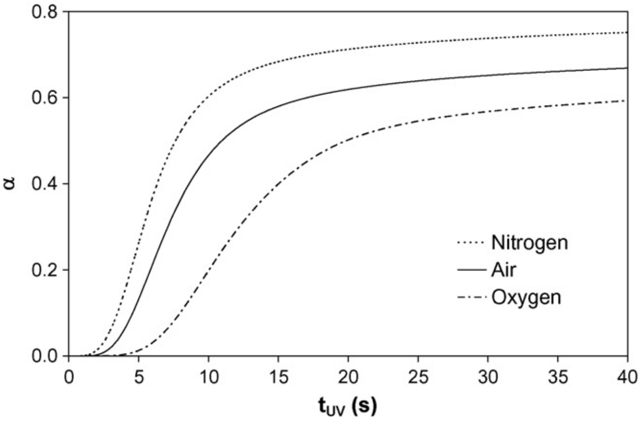

Fig. 1. Degree of conversion vs. the curing time for the photocuring at 50 °C of the system 50:50/3% Dmpa with a light intensity of 12.8 mW cm^{-2} in different atmospheres.

Fig. 2 shows the conversion rate versus the time for the same system of Fig. 1 and with the same atmospheres. Oxygen increases the time at which the reaction rate reaches its maximum, due to the delay in the beginning of the reactive process. In addition, the height of the peak is smaller because the reaction rate decreases as well.

In Fig. 3 we have represented the conversion degree versus the curing time for the system 50:50/3% Dmpa cured using a light intensity of 12.8 mW cm^{-2} in oxygen atmosphere at different temperatures. An increase in curing temperature leads to an earlier reaction start and a quicker process. Furthermore, at the end of the process the conversion is higher, because vitrification occurs when the system reaches a greater conversion. After vitrification, the reaction proceeds very slowly and the conversion hardly changes with time. Accordingly, Fig. 4 shows that the time of maximum reaction rate decreases, but its value increases.

The results obtained applying the isoconversional method in the same system and atmosphere are shown in Fig. 5. We have represented the logarithm of time versus the inverse of the temperature at different conversions, and we can see the linear dependence between these magnitudes, as it is indicated in Eq. (2). Then, we can obtain the values of the activation energy and $\ln[g(\alpha)/A]$ for every degree of conversion. The values of the regression coefficients have been higher than 0.99 for all the conversions and atmospheres.

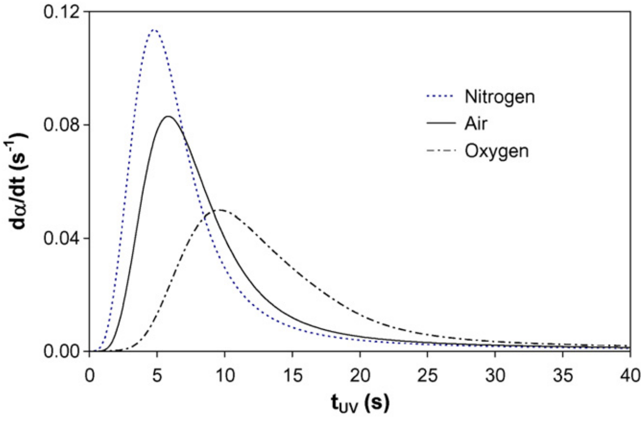

Fig. 2. Conversion rate vs. the curing time for the photocuring at 50 °C of the system 50:50/3% Dmpa with a light intensity of 12.8 mW cm^{-2} in different atmospheres.

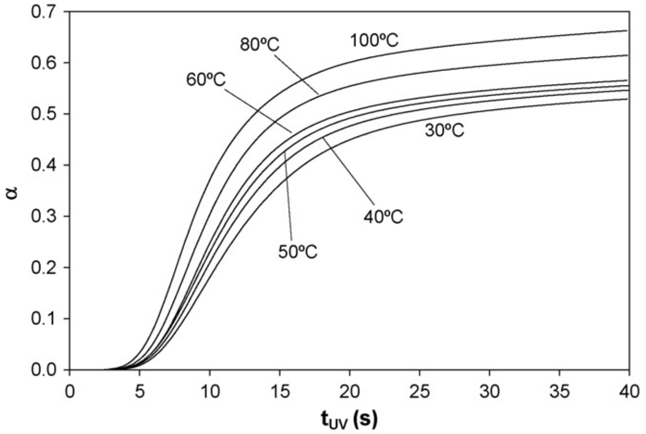

Fig. 3. Degree of conversion vs. the curing time for the photocuring at different temperatures of the system 50:50/3% Dmpa with a light intensity of 12.8 mW cm^{-2} in oxygen atmosphere.

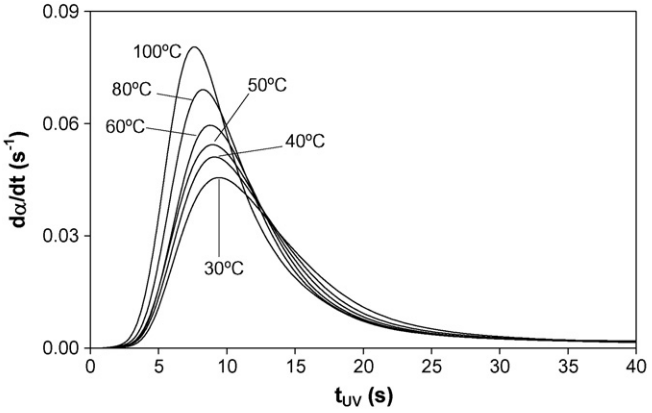

Fig. 4. Conversion rate vs. the curing time for the photocuring at different temperatures for the system 50:50/3% Dmpa with a light intensity of 12.8 mW cm^{-2} in oxygen atmosphere.

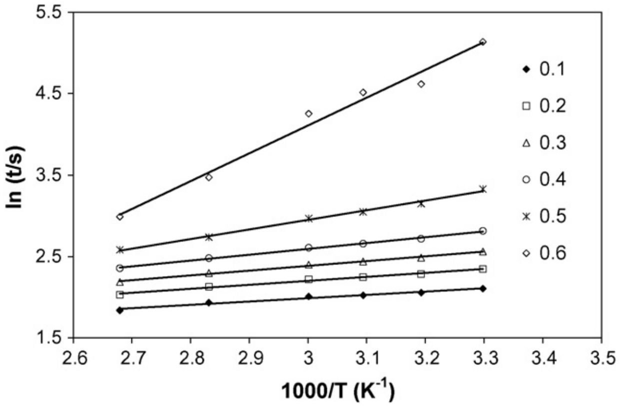

Fig. 5. Logarithm of curing time vs. the inverse of the temperature for different degrees of conversion for the system 50:50/3% Dmpa photocured with a light intensity of 12.8 mW cm^{-2} in oxygen atmosphere.

Table 1
Values of the activation energy, the pre-exponential factor and the rate constant at 50 °C for different degrees of conversion of the system 50:50/3% Dmpa photocured with a light intensity of 12.8 mW cm^{-2} in different atmospheres

α	E (kJ mol^{-1})			A (s^{-1})			$k_{50\,°C}$ (s^{-1})		
	Nitrogen	Air	Oxygen	Nitrogen	Air	Oxygen	Nitrogen	Air	Oxygen
0.1	2.4	2.9	3.4	5.7	5.2	3.8	2.32	1.77	1.07
0.2	3.2	3.5	4.1	6.5	5.7	4.3	1.98	1.52	0.94
0.3	4.0	4.0	4.9	7.8	6.1	5.1	1.76	1.36	0.83
0.4	5.0	5.0	6.0	10.1	7.4	6.6	1.58	1.18	0.71
0.5	6.7	6.4	9.8	16.4	10.5	19.8	1.37	0.98	0.51
0.6	8.0	11.3	28.4	23.1	43.7	5523	1.17	0.65	0.14

The rate constant at 50 °C has been found using the Arrhenius equation: $k = A\exp(-E/RT)$.

Using the reduced master curves (Eq. (3)) we have seen that the kinetic model closest to the behaviour of our system in the different atmospheres used is the autocatalytic, with $m = 0.9$ and $n = 2.1$. This result is consistent with the autoacceleration shown in Figs. 2 and 4. For the kinetic model obtained:

$$f(\alpha) = \alpha^{0.9}(1-\alpha)^{2.1},$$

$$g(\alpha) = \frac{1}{0.1}\left(\frac{\alpha}{1-\alpha}\right)^{0.1} + \frac{1}{1.1}\left(\frac{\alpha}{1-\alpha}\right)^{1.1} \qquad (4)$$

From this expression of $g(\alpha)$ and the isoconversional parameters of $\ln[g(\alpha)/A]$ we have found the values of the pre-exponential factor, for every degree of conversion. The calculated results of the activation energy and the pre-exponential factor are indicated in Table 1. Furthermore, in this table we have also put the values of these magnitudes for the same system when the photocuring process is carried out in nitrogen and air.

The values of the activation energy and the pre-exponential factor depend on the conversion for the three atmospheres. The activation energy is higher with oxygen and lower when nitrogen is used. Air presents intermediate values with the exception of the conversions of 0.4 and 0.5. On the other hand, the pre-exponential factor is smaller with oxygen atmosphere at conversions lower than 0.5. This tendency changes at higher conversions. The values for air are usually intermediate between the other two. The same trends have been seen working with relative conversions instead of absolute conversions. Then, the increase in the values of the activation energy is real and not fictitious.

In the same table we have indicated the values of the rate constant at 50 °C calculated using the Arrhenius equation. The values of this magnitude always decrease when the oxygen proportion of the atmosphere increases. The values obtained for air are more similar to the calculated ones for nitrogen than for oxygen, except for the highest degree of conversion ($\alpha = 0.6$). All these comments are in agreement with the experimental results presented in Figs. 1 and 2. The increase of E and the decrease of $k_{50\,°C}$ with increasing conversion could be in agreement with a kinetic change when the viscosity of the system increases and the concentration of the reactives decrease.

The kinetic parameters obtained isoconversionally show the effect of the atmosphere over the cure kinetics. This method is simple and it is not necessary to make hypothesis related to: (a) the reactivity of the different types of radicals; (b) the type of termination; (c) *the steady-state concentration of free radicals*, etc., which are necessary when the cure kinetics are studied from a mechanistic point of view [20]. Therefore the kinetic parameters obtained isoconversionally are more consistent than that obtained using a mechanistic methodology.

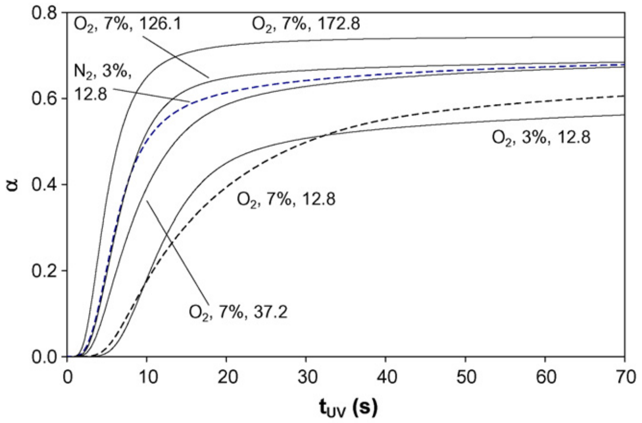

Fig. 6. Degree of conversion vs. the photocuring time at 30 °C. The atmosphere used, the percentage of initiator and the light intensity (in mW cm^{-2}) are indicated.

Figs. 6 and 7 show, respectively, the conversion and the conversion rate versus time at a photocuring temperature of 30 °C for the system 50:50/3% Dmpa in atmospheres of nitrogen and oxygen using a light intensity of 12.8 mW cm^{-2}, and for the

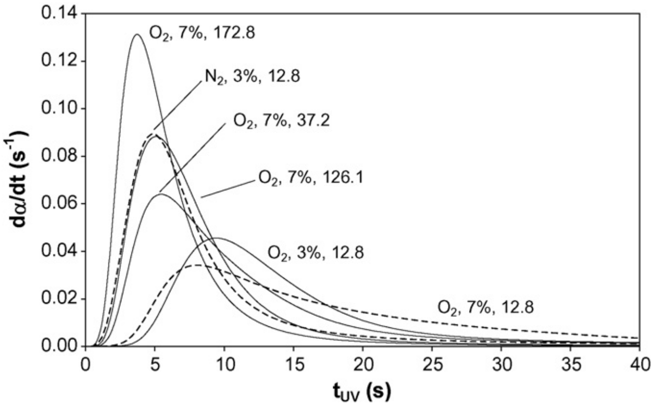

Fig. 7. Conversion rate vs. the photocuring time at 30 °C. The atmosphere used, the percentage of initiator and the light intensity (in mW cm^{-2}) are indicated.

system 50:50/7% Dmpa photocured at the same temperature in oxygen atmosphere and varying light intensity.

For the system with a 3% of initiator, when the atmosphere changes from nitrogen to oxygen, as seen in Figs. 1 and 2, a delay in the reactive process occurs, the reaction rate decreases and the degree of conversion at the end of the process is lower. When the photocuring of this system and the other with the higher photoinitiator concentration (50:50/7% Dmpa) are compared, both in oxygen atmosphere, it can be seen that increasing the amount of initiator makes the reaction begin earlier. At the beginning of the process, the reaction rate is greater, but afterwards it is smaller and more time is needed to attain the end of the process, though the final conversion is greater.

When the light intensity is increased for the system 50:50/7% Dmpa photocured in oxygen atmosphere, the reactive process begins earlier, the reaction rate increases, the system reaches the end of the process earlier and achieves a greater degree of conversion. At a light intensity of 126.1 mW cm^{-2}, prior to the maximum conversion rate the shape of the curve is almost identical to the one of the system 50:50/3% Dmpa in nitrogen atmosphere and at a light intensity of 12.8 mW cm^{-2}. Therefore, if the atmosphere is switched from nitrogen to oxygen, it is more convenient to increase the intensity of the radiation rather than just increasing the photoinitiator concentration in order to compensate the inhibition effect of oxygen on the photocuring process. A lower light intensity would not be enough to activate a sufficient number of photoinitiator molecules due to light blocking on the superior layers.

Using the isoconversional method we have analyzed the photocuring of the system 50:50/7% Dmpa in oxygen atmosphere with a light intensity of 126.1 mW cm^{-2}. In Table 2 the activation energy, the pre-exponential factor (found with the same $f(\alpha)$ used before) and the rate constant at 50 °C are indicated. The value of this constant is very similar to the value found for the system 50:50/3% Dmpa photocured in nitrogen atmosphere with an intensity of 12.8 mW cm^{-2}; this fact is in agreement with the results shown in Figs. 6 and 7. Though the atmosphere is different, if the number of activated photoinitiator molecules is the same, the curing can proceed at a similar rate. This shows that oxygen acts only as a radical inhibitor but does not modify the curing mechanism.

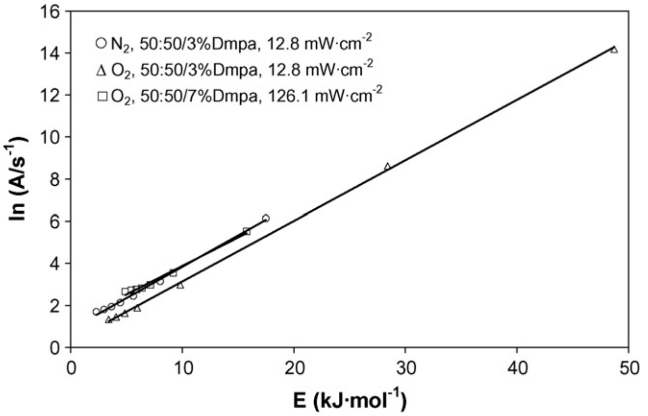

Fig. 8. Logarithm of the pre-exponential factor vs. the activation energy for the indicated systems.

Complex processes are characterized by the dependence of the activation energy and the pre-exponential factor on the degree of conversion. This generally reflects the existence of a compensation effect through the equation:

$$\ln A_\alpha = aE_\alpha + b = \frac{E_\alpha}{RT_{\text{iso}}} + \ln k_{\text{iso}} \qquad (5)$$

where a and b are constants, and the subscript α represents the degree of conversion that produces a change in Arrhenius parameters. The slope a is related to the isokinetic temperature (T_{iso}), and the intercept $b = \ln k_{\text{iso}}$ is related to the isokinetic rate constant. Eq. (5) represents an isokinetic relationship (IKR), and can be deduced by re-ordering Eq. (1). The appearance of the IKR shows that only one mechanism is present, whilst the existence of more than one IKR or parameters that do not meet the IKR implies that there are different reaction mechanisms [21,22].

In order to ascertain if the studied systems are kinetically equivalent, Fig. 8 shows the logarithm of the pre-exponential factor versus the activation energy for the system 50:50/3% Dmpa photocured in nitrogen and oxygen atmospheres with a light intensity of 12.8 mW cm^{-2} and for the photocured in oxygen atmosphere with an intensity of 126.1 mW cm^{-2}. It can be observed an excellent correspondence between the linear dependence corresponding to the system 50:50/7% Dmpa under oxygen at 126.1 mW cm^{-2} and that of the system 50:50/3% Dmpa photocured in nitrogen atmosphere with an intensity of 12.8 mW cm^{-2}, in agreement with the results commented previously. The system 50:50/3% Dmpa photocured in oxygen

Table 2
Values of the activation energy, the pre-exponential factor and the rate constant at 50 °C for different degrees of conversion of the system 50:50/7% Dmpa photocured with a light intensity of 126.1 mW cm^{-2} in oxygen atmosphere

α	50:50/7% Dmpa, oxygen, 126.1 mW cm^{-2}			50:50/3% Dmpa, nitrogen, 12.8 mW cm^{-2}
	E (kJ mol^{-1})	A (s^{-1})	$k_{50\,^\circ\mathrm{C}}$ (s^{-1})	$k_{50\,^\circ\mathrm{C}}$ (s^{-1})
0.1	4.9	14.3	2.32	2.32
0.2	5.4	15.1	1.99	1.98
0.3	5.9	15.8	1.76	1.76
0.4	6.4	16.8	1.56	1.58
0.5	7.1	19.6	1.37	1.37
0.6	9.2	34.6	1.13	1.17

The rate constant at 50 °C has been found using the Arrhenius equation: $k = A\exp(-E/RT)$. The values of the rate constant at 50 °C of the system 50:50/3% Dmpa photocured with a light intensity of 12.8 mW cm^{-2} in nitrogen atmosphere are indicated for comparison.

Table 3
Parameters a and b of Eq. (5) for the systems indicated in Fig. 8

System	a (mol kJ^{-1})	b (s^{-1})
50:50/3% Dmpa, nitrogen, 12.8 mW cm^{-2}	0.298	0.860
50:50/3% Dmpa, oxygen, 12.8 mW cm^{-2}	0.288	0.257
50:50/7% Dmpa, oxygen, 126.1 mW cm^{-2}	0.271	1.166

atmosphere with an intensity of 12.8 mW cm^{-2} presents a different linear dependence, but parallel to the others. This shows that the systems 50:50/3% Dmpa (nitrogen, 12.8 mW cm^{-2}) and 50:50/7% Dmpa (oxygen, 126.1 mW cm^{-2}) are kinetically equivalents, but the system 50:50/3% Dmpa (oxygen, 12.8 mW cm^{-2}) presents slightly different kinetics due to the lower amount of active radicals. The linear dependences of Fig. 8 show a compensation effect between the activation energy and the pre-exponential factor: this suggests, for all the studied systems, that though the kinetics parameters slightly change during the curing process, these parameters are compensated, and therefore the kinetics of the cure hardly depend on the degree of conversion.

In Table 3 the values of the parameters a and b of Eq. (5) are indicated for the three systems in Fig. 8.

5. Conclusions

The presence of oxygen decreases the rate of the photocuring process of the studied systems. The results obtained with the application of the isoconversional method to the different atmospheres are in agreement with the observed tendencies in the experimental results. To compensate the inhibition effect of oxygen over the curing process it is more convenient to increase the intensity of the ultraviolet light used. The isoconversional methodology shows the effect of the atmosphere, the initiator proportion and the intensity of the radiation over the cure kinetics without needing to make hypotheses regarding the reaction mechanism, and can be used to study the photocuring in a general form, as an alternative to mechanistic methodologies.

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