

Influence of temperature and UV intensity on photo-polymerization reaction studied by photo-DSC

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Abstract Photo-DSC was used to investigate the cure kinetics of a photo-initiated resin. The exothermal photo-polymerization reactions were performed in isothermal mode. The irradiation of photo-initiated resin was studied under different conditions of temperature, UV lamp intensity, and reaction atmosphere (nitrogen and air). The results obtained by photo-DSC allowed us to determine kinetic data of the photo-polymerized reactions: the global activation energy and reaction enthalpy, and the conversion as a function of time and temperature. Modulated temperature DSC measurements were carried out to verify whether vitrification occurs during polymerization. The conversion at the top and bottom of irradiated samples was obtained by FT-IR spectroscopy before and after photo-polymerization. A non-homogenous photo-polymerization into the material was observed, probably because of the light absorptions effects within the uppermost layers.

Keywords Photo-DSC · Photo-polymerization · Cure kinetics · MTDSC · FT-IR

Introduction

During the past few years, photo-initiated polymerized materials have received important attention because of their industrial applications, such as adhesives, coatings,

electronics, inks, and dental materials. The development of this technique is mainly promoted by its advantages: solvent-free systems, rapid curing rate, low costs to implement the process, and high-quality products [1–5].

Photo-polymerization is a frequently used process to convert the multifunctional macro-monomers into insoluble networks. In general, in this type of polymerization, a free radical mechanism is involved [6]. The initiation step consists in the absorption of UV light by a photo-initiator that decomposes and produces a reactive species, the radicals. The number of radicals formed is directly proportional with the number of absorbed photons. The reactive initiator radicals can react with the C=C bonds in the macro-monomer, initiating the growing polymer chains. The growth of this polymer chain continues simultaneously with the formation of new radicals and could be terminated by chain transfer and/or termination reactions [7].

To determine the kinetics for photo-initiated polymerizations, two techniques are widely used: real-time infrared spectroscopy (RT-FTIR) and photo-differential scanning calorimetry (Photo-DSC) [8, 9]. The photo-DSC measures the reaction heat liberated during photo-polymerization. By this technique, it is possible to obtain more information about the evolution of the average rate of polymerization in the sample.

In this article, we report the results of a photo-DSC study concerning the cure kinetics of a proprietary photo-initiated resin. The resin is a mixture of a multifunctional acrylic macro-monomer, a small amount of a UV-photo-initiator, and additives. Isothermal photo-polymerizations were performed using different cure temperatures and UV light intensities. The effect of oxygen on the reaction was studied by making a comparison between experiments using nitrogen or air as purge gas. The thermal properties of photo-polymerized samples were studied by modulated

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temperature DSC (MTDSC). Complementary FT-IR measurements were carried out to evaluate the conversion of the reacting groups, at the top and bottom of UV-irradiated samples.

Experimental

Photo-differential scanning calorimetry (photo-DSC)

Photo-DSC measurements were conducted using a differential scanning calorimeter (Q2000, TA Instruments) equipped with a photo-calorimetric accessory (PCA Novacure 2100, EXFO). UV light was delivered by a 100-W high-pressure mercury lamp. The PCA accessory provides a standard filter with wavelength range of 320–500 nm. In addition, we used a 405-nm band-pass filter (ThorLabs) and 1 % attenuation filter, for the transmittance of the light to the DSC cell-adjustable quartz light guides (work temperature range between -50 and 250 °C). Samples with a thickness of about $1,800$ μm and weighing 4 – 8 mg were placed in uncovered aluminum T_{zero} pans (TA Instruments). An empty uncovered aluminum T_{zero} pan was used as reference.

Modulated temperature differential scanning calorimetry (MTDSC)

The MTDSC measurements were performed on a T-zero DSC previously calibrated (Q2000, TA Instruments) and equipped with a refrigerated cooling system (RCS-90). Non-isothermal experiments were carried out using a heating rate of 10 K min^{-1} and standard temperature modulation conditions (amplitude A_T of 0.50 K and a period p of 60 s). Approximately 4 – 6 mg of sample placed in T_{zero} hermetic aluminum pans were examined between -150 and 50 °C. Nitrogen was used as purge gas at a flow rate of 25 mL min^{-1} during the MTDSC investigations.

Fourier transform infrared spectroscopy (FT-IR)

For the FT-IR measurements, a Nicolet 6700 infrared spectrometer (Thermo Fischer Scientific Inc.) was used, equipped with a rapid sampling *Smart iTR* diamond attenuated total reflectance (ATR) accessory. Spectra of non-irradiated and irradiated samples were recorded in a range of $4,000$ – 550 cm^{-1} with a resolution of 4 cm^{-1} . The absorbance spectra were evaluated after automatic baseline, ATR corrections, and normalization using Omnic Software (version 8.2, Thermo Fischer Scientific Inc.). The UV-curing behavior was followed by observing the changes in the absorbance of the C=C bond at 810 cm^{-1} . The

double bond conversion (α) after a given irradiation time (t) was calculated using following equation:

$$\alpha(t) = \frac{(A_{810})_0 - (A_{810})_t}{(A_{810})_0} \quad (1)$$

where $(A_{810})_0$ is the initial absorbance of the 810 cm^{-1} peak (time $t = 0$), and $(A_{810})_t$ is the absorbance of the 810 cm^{-1} peak at time t . The absorbances were calculated by integrating the 810 cm^{-1} peak.

Photo-polymerization kinetics

Photo-DSC can provide kinetics data, taking into account that the measured heat flow rate is proportional with the polymerization rate [10–15]. In general, this assumption is valid only if no other enthalpic events than polymerization occur. To obtain the photo-polymerization heat (H_t) as a function of time, the heat flow rate (q) curves recorded by photo-DSC were integrated (after subtraction of the baseline) (Eq. 2). This was transformed into the conversion (α) through division by the total heat of reaction (ΔH_{total}) chosen as the value obtained in the measurement at the highest (isothermal) temperature (Eq. 3).

$$H_t = \int_0^t q(t) dt \quad (2)$$

$$\alpha(t_1) = \frac{1}{\Delta H_{\text{total}}} \cdot \int_{t_0}^{t_1} q(t) dt \quad (3)$$

Photo-DSC experiments measure the overall heat released from photo-polymerization reactions which include initiation, propagation, and termination. Assuming a classical radical mechanism, the rate of photo-polymerization can be defined by the Eq. 4:

$$\frac{d[M]}{dt} = -k_p \cdot [M] \cdot [R^*] \leftrightarrow \frac{d[M]}{dt} = -k_p \cdot [M] \cdot \sqrt{\frac{I_a}{k_t}} \quad (4)$$

where $[M]$ is the monomer concentration; $[R^*]$ is the radical concentration; k_p and k_t are the propagation and termination rate constants, respectively; and I_a is absorbed radiation intensity. The constant rates are generally dependent on temperature and are described by Arrhenius' law (Eq. 5):

$$k = A \cdot e^{-\frac{E_a}{RT}} \quad (5)$$

where E_a is the activation energy, A is the frequency factor, R is the ideal gas constant, and T is the absolute temperature in Kelvin. Even at low conversions, k_t is controlled by segmental and translational diffusion and so decreases rapidly with conversion. Assuming that at low conversion the activation energy for termination is nearly

zero, the overall activation energy for a photo-polymerization reaction would be given by:

$$E_{a_{\text{overall}}} = E_{a_p} - \frac{1}{2} \cdot E_{a_t} \leftrightarrow E_{a_{\text{overall}}} = E_{a_p} \quad (6)$$

where $E_{a_{\text{overall}}}$ is the overall activation energy, E_{a_p} is the activation energy of the propagation step, and E_{a_t} is the activation energy of the termination step.

Results and discussions

Photo-DSC measurements were carried out in isothermal mode, using a 10-min stabilization step before and after 90-min irradiation time. A subsequent experiment (measured in the same conditions of temperature and light intensity) on the reacted sample was used as baseline (Fig. 1). Thereby, the exothermic effect of the reaction was obtained by subtracting the baseline curve from the first registered curve corresponding to the photo-cure of the sample.

To make sure that the baseline is recorded for a fully cured sample, between the first and the second runs at a certain temperature, a post-cure was performed at 50 °C for 180 min (irradiated), as is shown in the Fig. 2.

For all reaction exotherms shown in subsequent figures, the baseline was subtracted.

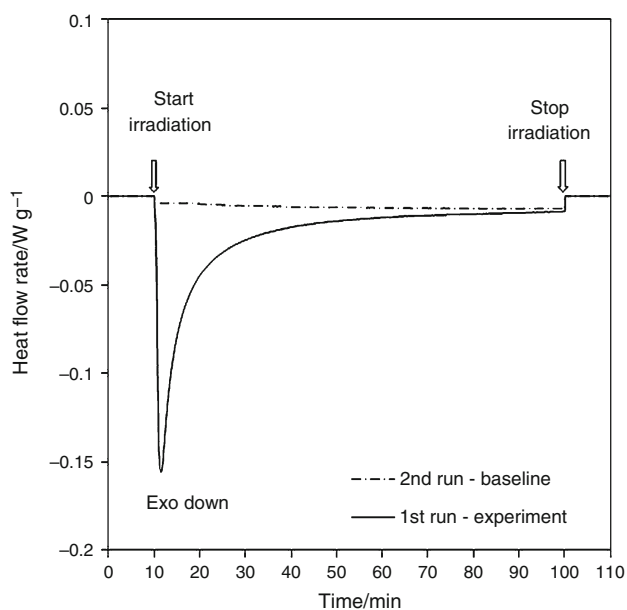


Fig. 1 Isothermal photo-DSC curves: a reaction experiment with an exothermic peak together with the subsequent baseline experiment on the reacted sample

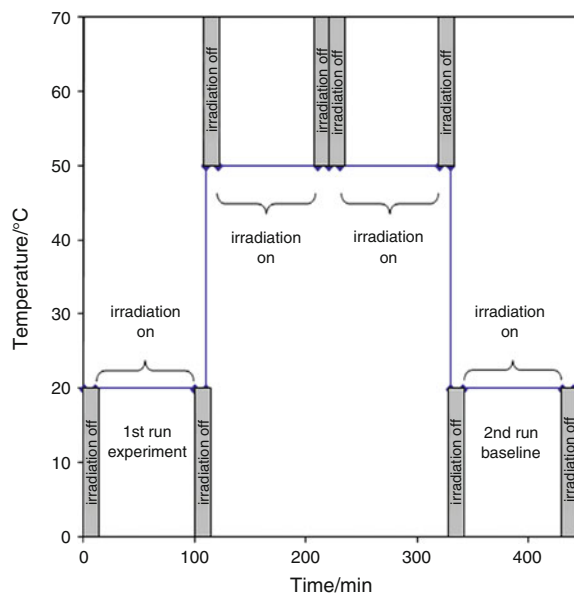


Fig. 2 Full temperature versus time experimental program used to photo-polymerized a sample at 20 °C

Influence of temperature

To study the effect of temperature, photo-DSC measurements were performed in isothermal mode at temperatures ranging between -10 and 50 °C and using a constant UV irradiation provided by setting the PCA accessory to a value of $8,000 \text{ mW cm}^{-2}$ for light intensity. Figure 3 shows a series of photo-polymerization traces at various temperatures. As can be seen, the exothermic effect becomes more significant by increasing the temperature. The maximum heat flow rate, corresponding to the maximum photo-polymerization rate, is registered at 50 °C, 1 min after the UV irradiation was started.

For all the studied reactions, the recorded heat flow rate behaviors are typical for a photo-induced radical polymerization reaction mechanism. The increase of photo-polymerization rate by rising the temperature is mainly due to the activation energy of the propagation rate constant, as clearly described by the overall activation energy (Eq. 6).

Figure 4, giving the conversion versus time profiles, also shows that the final conversion increases with raised temperature.

The numerical values of amount of the heat released during photo-polymerization, the maximum heat flow rate, the time for peak maximum, and the conversion after 90 min as derived from Fig. 3 and Fig. 4 are presented in Table 1.

For our experiments, the maximum heat released (115.1 J g^{-1}) resulted when the sample was photo-irradiated during 90 min at 50 °C.

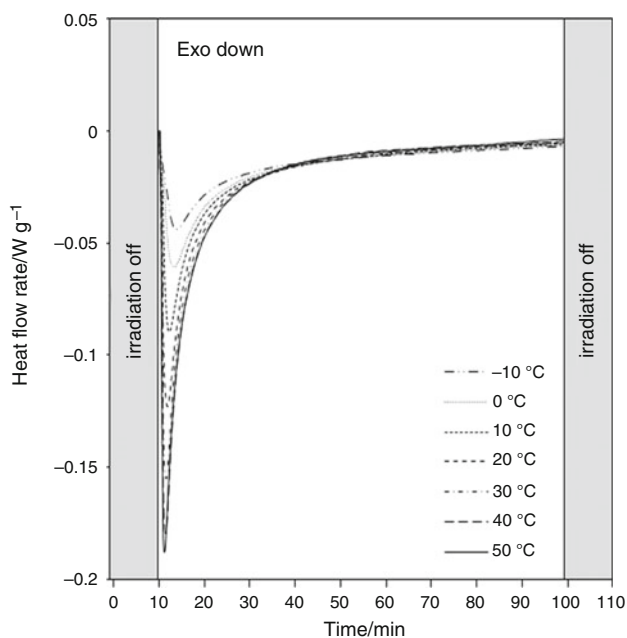


Fig. 3 Photo-DSC exotherms for the photo-polymerization reactions at various temperatures

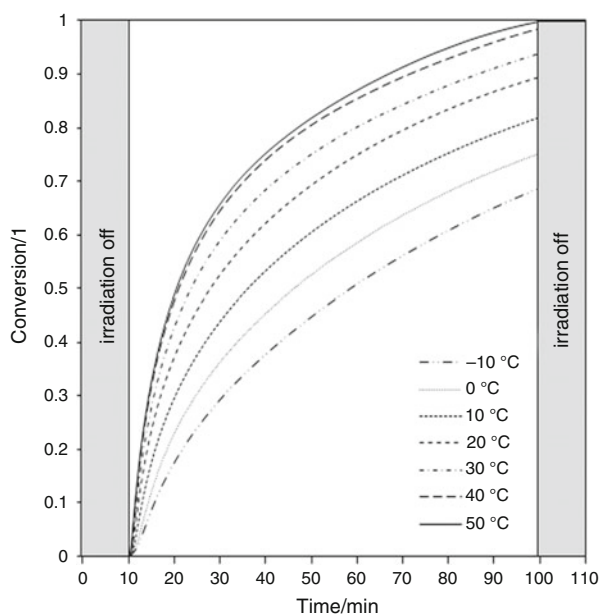


Fig. 4 Conversion profiles for the photo-polymerization reactions at various temperatures

According to Arrhenius' law, the $E_{a\text{overall}}$ can be calculated from photo-DSC data at various cure temperatures using the slope (equal with $-E_a R^{-1}$) of the best fitted line of $\ln v$ (rate of reaction) versus $1/T^{-1}$ (evaluated at a given conversion).

Figure 5 plots the natural logarithm of the rate of reaction ($\ln v$) against $1,000/T^{-1}$, using the values of reaction rate registered when the photo-polymerization

attained 0.2 conversion. Photo-DSC measurements at five different temperatures and constant light intensity were taken into account.

The obtained values of overall E_a using the method described above are presented in Fig. 6. The overall E_a calculated taking into account the reaction rate at four values of conversion are very similar, finally obtaining an average about 26.9 kJ mol^{-1} .

Influence of the glass transition

Using low curing temperature could be inconvenient for the process, because vitrification might occur, depending on the increasing glass transition (T_g) of the polymerized monomer/polymer mixture. In general, if the T_g approaches the curing temperature, the molecular mobility of the matrix decreases, and the propagation reaction may become diffusion-controlled, and so the photo-polymerization rate slows. Raising the cure temperature increases the segmental mobility of the polymer chains and permits more residual unsaturated sites to continue the polymerization reaction. To evaluate whether vitrification might have played a role, the glass transition was measured using MTSDC.

MTSDC measurements were carried out on the UV-cured samples using the conditions described in the experimental part. The experiments were made 1 week after UV exposure, the samples being kept at room temperature in proper conditions, avoiding non-desirable light irradiation or thermal effects. Once removed from the open T_{zero} aluminum pans used in the photo-DSC experiments, the samples were placed in closed T_{zero} aluminum pans used for MTSDC experiments.

The resulting T_g values of a non-irradiated sample was compared with those obtained for the samples irradiated at various temperatures. Only the values of T_g registered in the second heating step were taken into account. As expected, small changes in the measured T_g of samples after photo-polymerization reaction were observed. The differences between the T_g of the uncured materials and the T_g of irradiated samples are less than 5° . For example, for a sample irradiated at 50°C the T_g increases from -91°C (non-irradiated material) to -87°C (irradiated sample). From this observation, one can conclude that during photo-polymerization only light cross-linkage occurs in the material.

Influence of UV light intensity

The influence of the UV light intensity on the photo-polymerization process was studied by setting the irradiance from PCA accessory at four values of intensity (2000, 4000, 8000, and $10,000 \text{ mW cm}^{-2}$). Figure 7 shows the exothermic effects registered by photo-DSC for photo-polymerizations conducted at 20°C using various UV light

Table 1 Cure parameters for the photo-polymerization reactions at various isothermal curing temperature (irradiation time = 90 min)

Cure temperature/°C	Heat flow rate maximum/W g ⁻¹	Peak maximum/min	ΔH/J g ⁻¹	Conversion/1
-10	-0.044	3.8	-79.1	0.68
0	-0.060	3.1	-86.3	0.75
10	-0.089	2.1	-94.1	0.81
20	-0.122	1.7	-102.9	0.89
30	-0.154	1.4	-107.8	0.93
40	-0.179	1.3	-113.4	0.98
50	-0.188	1.1	-115.1	1

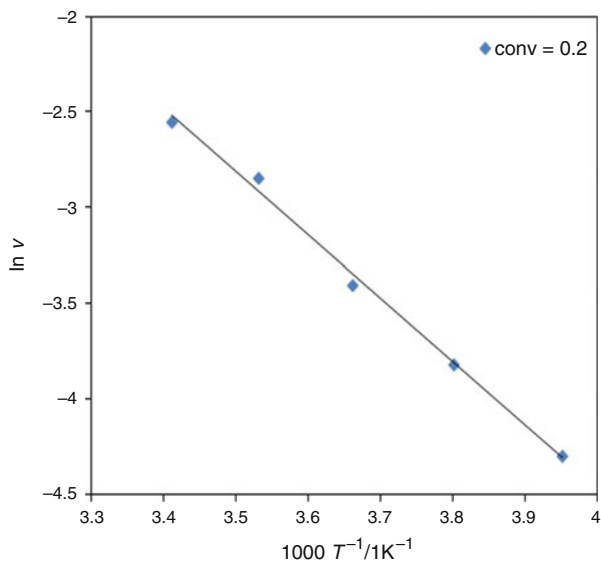


Fig. 5 Plot of $\ln v$ versus $1000 T^{-1}$ evaluated at conversion = 0.2

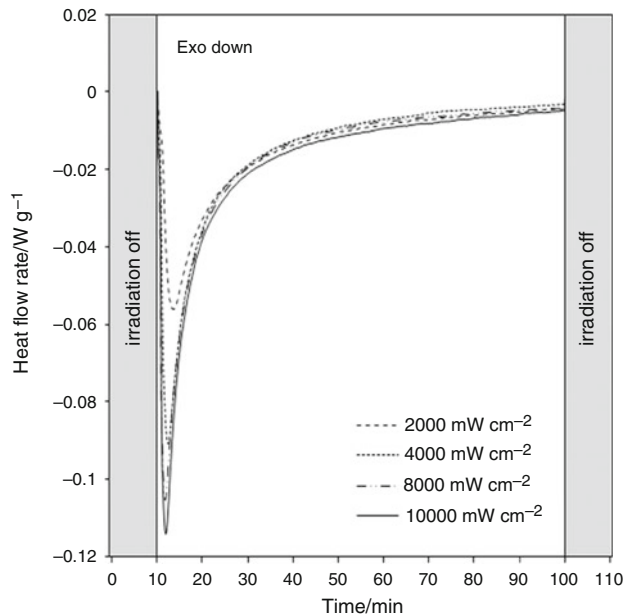


Fig. 7 Photo-DSC exotherms obtained for photo-polymerizations at various UV light intensities

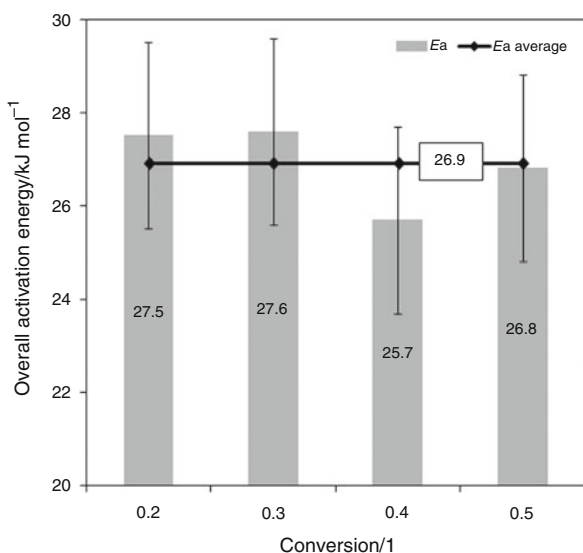


Fig. 6 Overall E_a calculated taking into account data at different attained conversions

intensities. It is observed that the rate of photo-polymerization decreases with lower UV light intensity, while the time necessary to reach the maximum rate (minimum in heat flow rate) increases.

The rate of formation of initiator radicals is proportional to the quantity of absorbed light. Therefore, raising the UV light intensity causes an increase in the rates of initiator decomposition, radical formation, and chain propagation, and increases the double bond conversion reached at a certain time. The rate at which the monomer is converted in a photo-polymerization reaction also depends on the efficiency to exploit the absorbed energy for radical formation, the reactivity of the radicals with the monomer molecules, and the presence of inhibiting or retarding species.

In Table 2 the kinetics analysis results for the photo-polymerizations at 20 °C and various PCA UV light intensities are summarized. It is clearly revealed that the UV intensity has an important influence on the overall rate of polymerization as it controls the initiation step.

Table 2 Cure parameters for the photo-polymerization reactions in isothermal mode (20 °C) at various UV light intensities (irradiation time = 90 min)

Cure UV light intensity/mW cm ⁻²	Heat flow rate maximum/W g ⁻¹	Peak maximum/min	ΔH/J g ⁻¹	E _a average/kJ mol ⁻¹
2,000	-0.056	3.4	-76.3	26 ± 2
4,000	-0.090	2.3	-80.7	27 ± 2
8,000	-0.103	1.8	-87.7	26 ± 2
10,000	-0.114	1.5	-97.9	27 ± 2

The values of the overall activation energy (E_a) obtained for the samples irradiated at different UV light intensities are very similar, which demonstrates the temperature dependence is controlled by the propagation reaction, respecting the Arrhenius law.

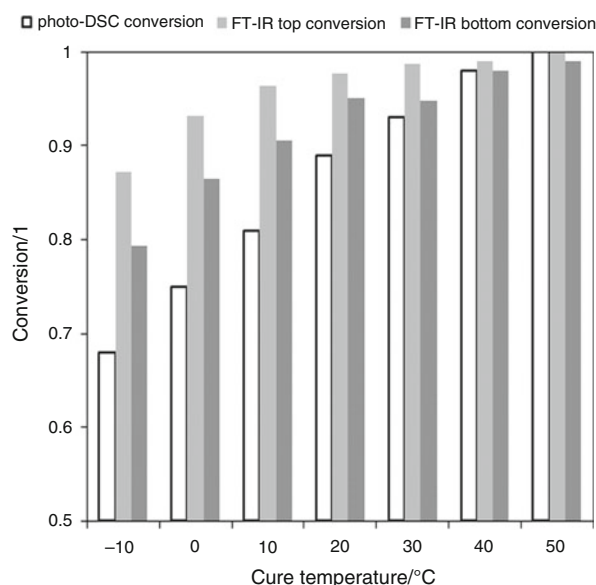
Non-uniform photo-polymerization

In photo-DSC measurements, the sample was placed in open T_{zero} aluminum pans and was irradiated at the top. At the start of the irradiation, the light intensity reaching a certain depth in the sample can be estimated by Lambert-Beer's law:

$$I_x = I_0 - I_{abs} = I_0 \cdot (1 - \exp(-\varepsilon \cdot [PI] \cdot x)) \quad (7)$$

where I_x is the light intensity reaching the depth x into the sample, I_{abs} is the light intensity absorbed by the sample between the surface and depth x , I_0 is the incident light intensity, ε is the molar absorption coefficient, and $[PI]$ is the photo-initiator concentration. Thus, as the light goes deeper into the sample, the light intensity will decrease, since an increasing amount of light is absorbed by the photo-initiator present in the layer above. As a result, the photo-initiation is initially faster at the irradiated top surface, and the photo-polymerization rate (or the conversion reached after a certain irradiation time) might be higher at the top than at the bottom of the sample, leading to a non-uniform photo-polymerization.

To investigate whether there is a significantly different polymerization rate at the top and bottom surface, the conversion of double bonds was followed by ATR-FT-IR spectroscopy, using the decrease of the absorption band at 810 cm⁻¹ (stretching vibration of the -C=C- bond). For an ATR FT-IT experiment using the diamond *iTR* accessory, the penetration depth is estimated to be about 2 μm (as compared to a sample thickness of 1,800 μm). Using the Fig. 8, the FT-IR conversions obtained by measurements carried out at the top and at the bottom of samples previously irradiated for 90 min in photo-DSC experiments are presented. These results are compared with the conversion values obtained by photo-DSC measurements at different cure temperatures. It can be observed that the conversion at the top of the samples is always somewhat bigger than the

**Fig. 8** FT-IR conversion (top and bottom of exposed sample) after 90 min of irradiation (8,000 mW cm⁻²) for the photo-polymerization reactions at various temperatures in the photo-DSC

conversion at bottom, which can be explained by a non-homogenous reaction resulting from a higher absorption and photo-initiation rate at the top surface. As the photo-initiator is being consumed faster closer to the top surface, over time, an increasing amount of light will reach the lower layers, accelerating the initiation and photo-polymerization there.

Figure 5 also shows that the FT-IR conversion is in nearly all cases slightly bigger than the photo-DSC conversion. It is quite common to find differences in the conversions determined using FT-IR and photo-DSC [16, 17]. This was attributed to a certain delay in the measurement of the heat released during the curing reactions in the photo-DSC module, in comparison with the monitoring by FT-IR spectroscopy of the decrease in the absorbance peak, corresponding to the consumption of monomer's -C=C- bond [18]. Using the photo-DSC technique an average conversion for the entire photo-polymerized sample is obtained, while ATR FT-IR spectroscopy gives the conversion at the surface, because of the limited penetration of infrared light beam (ca. 2 μm).

Table 3 Cure parameters for the photo-polymerization reactions at various isothermal cure temperatures for 90 min using air as purge gas

Cure temperature/°C	Heat flow rate maximum/W g ⁻¹	Peak maximum/min	$\Delta H/J$ g ⁻¹	Conversion/l
-10	-0.039	4.2	-66.4	0.58
0	-0.059	3.1	-75.1	0.66
10	-0.090	2.2	-82.7	0.73
20	-0.109	1.7	-88.8	0.78
30	-0.141	1.2	-95.8	0.84
40	-0.163	1.1	-103.2	0.91
50	-0.180	1	-109.6	0.96

Effect of oxygen

It is well known that one of the major disadvantages of free-radical photo-polymerization is its susceptibility to oxygen inhibition. The presence of oxygen leads to an induction period before polymerization takes place or to a retardation of the photo-polymerization, because the oxygen biradical reacts very rapidly with photo-generated free radicals, forming a peroxy radical that is much less reactive. Thus, oxygen acts as a chain terminator and reduces the rate of polymerization until all oxygen in the system has been consumed [19, 20]. This is known to lead to incomplete cure of surfaces exposed to oxygen.

To see how oxygen influences the photo-polymerization reaction of the resin used in our studies, photo-DSC measurements using air as purge gas were carried out. The same conditions (sample mass, cure temperature, and UV light intensity) were chosen as in the photo-DSC measurements carried out using nitrogen as purge gas. The cure parameters obtained from the photo-DSC data are presented in Table 3.

Figure 9 compares the traces of heat flow rate (a) and conversion (b) measured during the photo-polymerization at 50 and -10 °C, using nitrogen or air as a purge gas. At high temperature, only a small difference was observed. For lower temperatures, the oxygen effect seems to be more significant.

The more pronounced influence of oxygen at lower temperatures might be explained by a higher solubility of oxygen at low temperatures. The solubility of gas molecules in polymers can be described as a thermally activated process that obeys Arrhenius behavior, as is shown in Eq. 8 [21]:

$$S = S_0 \cdot e^{\frac{-\Delta H_s}{RT}} \quad (8)$$

where S is the solubility, S_0 is the pre-exponential factor, ΔH_s is the heat of solution, R is the ideal gas constant, and T is the absolute temperature in Kelvin.

However, the literature does not support this, if we take into consideration the small endothermic value (+1.2 kJ mol⁻¹) for materials with similar composition as our proprietary material [22, 23].

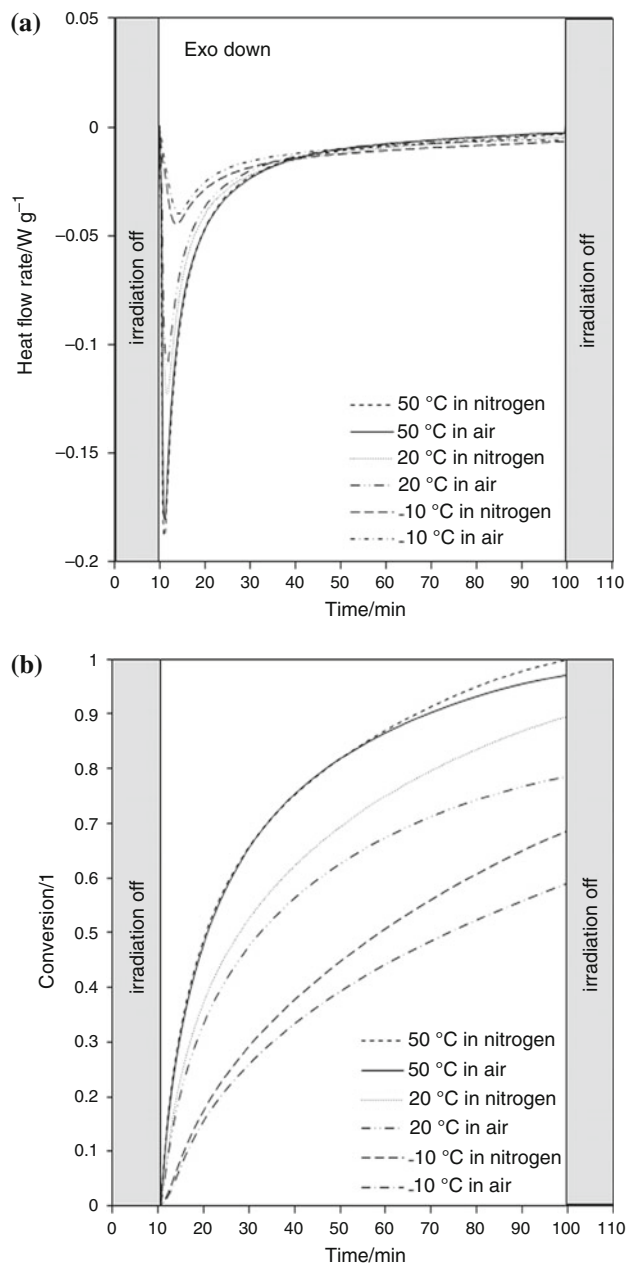


Fig. 9 Photo-DSC exotherms (a) and conversion curves (b) for the photo-polymerization reactions at 50 and -10 °C using different purge gases (N₂ and air)

On the other hand, the more pronounced influence of oxygen at lower temperatures might be caused by a lower activation energy of the oxygen inhibition reaction as compared to the propagation reaction. Indeed, the ratio of the rate constants of the reaction of a growing radical with oxygen (inhibition) over the reaction with monomer (propagation) will increase with decreasing temperature if the inhibition reaction has a lower activation energy (slowing down less as temperature decreases). As a result, the retarding effect of oxygen would be more pronounced at lower temperatures.

Conclusions

Photo-DSC was used to investigate the photo-polymerization process of a photo-initiated resin under different conditions of temperature, light intensity, and reaction atmosphere. Kinetic parameters as overall activation energy, total heat of reaction, and conversion were determined. After the irradiation, samples were investigated using MTDSC and FT-IR to find out the changes in glass transition during the photo-polymerization and the uniformity of the conversion of the reacting groups, respectively.

As expected, higher temperatures and higher UV light intensities lead to a higher reaction rate and to a shorter time necessary to attain complete polymerization. The MTDSC measurements showed a very small increase of the glass transition, which is attributed to a lightly cross-linked structure of the material after photo-polymerization. From the ATR FT-IR investigations, it was noticed that there is a higher conversion at the top versus the bottom of irradiated samples, which can be explained by a non-homogenous reaction inside the material resulting from a higher light absorption in the top layer where the radiation is incident. Oxygen inhibition or retardation seems to be not so important for this photo-initiated resin, its effect being only observed at low temperatures.

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References

- Palanisamy W, Rao BS. Photo-DSC and dynamic studies on UV curable compositions containing diacrylate of ricinoleic acid amine derived from castor oil. *Prog Org Coat.* 2007;60:161–9.
- Cook WD, Nghiem QD, Chen Q, Chen F, Sangermano M. Simultaneous photoinduced silver nanoparticles formation and cationic polymerization of divinyl ethers. *Macromolecules.* 2011;44:4065–71.
- Cho JD, Hong JW. Photo-curing kinetics for the UV-initiated cationic polymerization of a cycloaliphatic diepoxide system photosensitized by thioxanthone. *Eur Polym J.* 2005;41:367–74.
- Voytekunas VY, Ng FL, Abadie MJM. Kinetics study of the UV-initiated cationic polymerization of cycloaliphatic diepoxide resins. *Eur Polym J.* 2008;44:3640–9.
- Uygun M, Cook WD, Moorhoff C, Chen F, Vallo C, Yagci Y, Sangermano M. Photopolymerization kinetics and dynamic mechanical properties of silanes hydrolyzed without evolution of byproducts. Tetrakis[(metacryloyloxy)ethoxy]silane-diethylene glycol dimethacrylate. *Macromolecules.* 2011;44:1792–800.
- Jakubiak J, Sionkowska A, Lined LA, Rabek JF. Isothermal photo differential scanning calorimetry. Crosslinking polymerization of multifunctional monomer in presence of visible light photoinitiators. *J Therm Anal Calorim.* 2001;65:435–43.
- Nowers JR, Narasimhan B. The effect of interpenetrating polymer network formation on polymerization kinetics in an epoxy-acrylate system. *Polymer.* 2006;47:1108–18.
- Esen DS, Karasu F, Arsu N. The investigation of photoinitiated polymerization of multifunctional acrylate with TX-BT by Photo-DSC and RT-FTIR. *Prog Org Coat.* 2011;70:102–7.
- Corcione CE, Malucelli G, Frigione M, Maffezzoli A. UV-curable epoxy systems containing hyperbranched polymers: kinetics investigation by photo-DSC and real-time FT-IR experiments. *Polym Test.* 2009;28:157–64.
- Phinyocheep P, Duangthong S. Ultraviolet-curable liquid natural rubber. *J Appl Polym Sci.* 2000;78:1478–85.
- Duran H, Meng S, Kim N, Hu J, Kyu T, Natarajan LV, Tondiglia VP, Bunning TJ. Kinetics of photopolymerization-induced phase separation and morphology development in mixtures of a nematic liquid crystal and multifunctional acrylate. *Polymer.* 2008;49:534–45.
- Scott TF, Cook WD, Forsythe JS. Photo-DSC cure kinetics of vinyl ester resins. I. Influence of temperature. *Polymer.* 2002;43:5839–45.
- Chen S, Cook WD, Chen F. Photopolymerization of vinyl ether networks using an iodonium initiator: effect of radiation intensity and iodonium concentration. *Macromolecules.* 2009;42:5965–75.
- Kahveci MU, Uygun M, Tasdelen MA, Schnabel W, Cook WD, Yagci Y. Photoinitiated cationic polymerization of vinyl ethers using substituted vinyl halides. *Macromolecules.* 2009;42:4443–8.
- Adom OK, Guymon CA. Photopolymerization kinetics of poly(acrylate)-clay composites using polymerizable surfactants. *Polymer.* 2008;49:2636–43.
- Corcione CE, Malucelli G, Frigione M, Maffezzoli A. UV-curable epoxy systems containing hyperbranched polymers: Kinetics investigation by photo-DSC and real-time FT-IR experiments. *Polym Test.* 2009;28:157–64.
- Kerbouc'h P, Lebaudy P, Lecamp L, Bunel C. Numerical simulation to correlate photopolymerization kinetics monitoring by RT-NIR spectroscopy and photocalorimetry. *Thermochim Acta.* 2004;410:73–8.
- Corcione CE, Frigione M, Maffezzoli A, Malucelli G. Photo-DSC and real time FT-IR kinetic study of a UV curable epoxy resin containing o-Boehmites. *Eur Polym J.* 2008;44:2010–23.
- O'Brien AK, Bowman CN. Impact of oxygen on photopolymerization kinetics and polymer structure. *Macromolecules.* 2006;39:2501–6.
- Bentivoglio Ruiz CS, Machado LDB, Volponi JE, Pino ES. Oxygen inhibition and coating thickness effects on UV radiation curing of weatherfast clearcoats studied by photo-DSC. *J Therm Anal Calorim.* 2004;75:507–12.
- Zhang H, Cloud A. The permeability characteristics of silicone rubber. 38th ISTC, Dallas 2006.
- Andrzejewska E. Sulfur-containing polyacrylates: V. Temperature effects on the photoinitiated polymerization of diacrylates. *Polymer.* 1996;37:1039–45.
- Brandrup J, Immergut EH, Grulke EA. *Polymer handbook*, 4th edition, Wiley, New York 1999.