Thermochimica Acta 509 (2010) 56–61

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Kinetics characterization of a novel photopolymerizable siloxane-modified acrylic resin

C. Esposito Corcione*, A. Previderio, M. Frigione

Dipartimento di Ingegneria dell'Innovazione, Università del Salento, via per Monteroni, 73100 Lecce, Italy

ARTICLE INFO

Article history:
Received 8 February 2010
Received in revised form 1 June 2010
Accepted 1 June 2010
Available online 11 June 2010

Keywords:
Photopolymerizable acrylic resins
Kinetics
Thermal analysis
UV radiation

ABSTRACT

An experimental study was carried out for the development and characterization of innovative photopolymerizable siloxane-modified acrylic formulations for possible use as protective coatings. The kinetics of the radical photopolymerization mechanism induced by UV and visible radiations in presence of suitable photoinitiators was studied by a calorimetric analysis by varying the testing conditions (temperature, light power emission, atmosphere).

The reactivity, expressed in terms of both heat developed and rate of reaction, was generally found to decrease when the photopolymerization was carried out in air, due the inhibiting action of the oxygen towards the free-radical polymerization. The addition of both a silane coupling agent or a high molecular weight polysiloxane monomer to the acrylic resin was found to reduce the heat of reaction.

Experimental data were fitted to a kinetic model to quantify the effects of light intensity and temperature on reaction rates and extent of reaction. A good agreement between the experimental data and the theoretical model was generally found.

1. Introduction

Polymers based on acrylic and methacrylic monomers are widely used for the protection and conservation of stone buildings, due to their ability to form water repellent and optically clear coatings [1–17]. There are, however, durability issues on the use of acrylic systems for the long term protection of historical buildings and are preferably used for indoor applications [18–20].

In addition to the insufficient intrinsic chemical stability the deficiency of acrylic coatings can be also be attributed to two main factors, respectively poor adhesion to porous substrates and insufficient water repellence to allow the drainage of the water from the surface.

In recent years water-borne silane modified acrylic resins and partially fluorinated acrylic copolymers have been evaluated as protective coatings for porous stone surfaces [3–17].

In these specific applications the free radicals for the initiation of the polymerization are generally produced by the decomposition of a peroxide initiator by the heat generated with the use of IR lamps. This is a serious limitation for the coating of large areas, particularly for outdoor applications. High energy radiation curing, on the other hand, has been widely used industrially for the curing of coatings, inks and even adhesives. These include ultraviolet (UV) sources but little use has been made to-date of such systems as UV-curable products for the protection of stones [21,22].

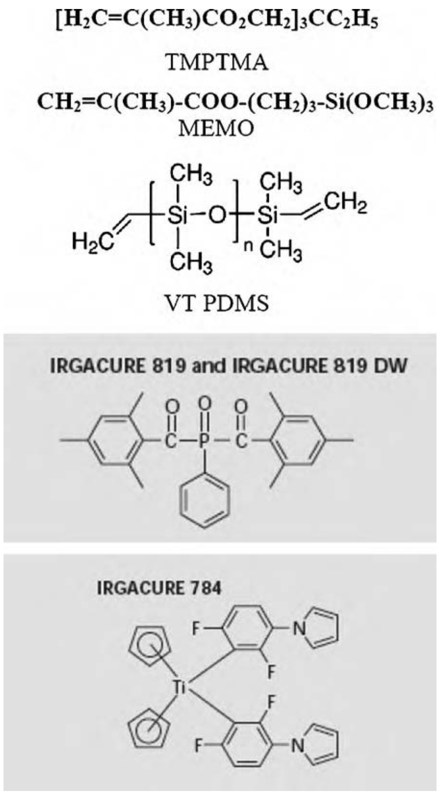
The present work represents the initial stage of a programme intended to overcome both the deficiencies associated with the chemical composition of acrylic coatings as well as the curing method through the use of UV and visible radiations expressly for protection of stone historical buildings and artworks. To achieve these objectives a methacrylate resin system was used as a basis identifying the main structural parameters to improve water repellence, increase adhesion to stone substrate and allow the use of UV and visible light curing methods.

In this initial study the kinetics of the radical photopolymerization induced by UV/visible radiations, and in the presence of suitable photoinitiators for a particular siloxane-modified acrylic resin system, were studied by calorimetric analysis using various light power emissions and temperatures. A trifunctional acrylic resin, selected for its high reactivity, was mixed with a silane coupling agent, containing two types of reactive functionality – inorganic and organic – in the same molecule. A silane coupling agent places at the interface between an inorganic substance (such as glass, metal or mineral) and an organic material (such as organic polymer, coating or adhesive) to bond or couple the two dissimilar materials [3]. The silane coupling agent can also be an effective adhesion promoter when used as an additive to coatings or adhesives. The silane must migrate to the interface between the adhered product and the substrate to be effective. In order to increase the hydrophobicity and the viscosity of the acrylic-silane mixture, a high molecular weight polysiloxane monomer was also selected

---

* Corresponding author.
E-mail address: carola.corcione@unile.it (C.E. Corcione).

0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.06.001



Scheme 1. Chemical structure of: trimethylolpropane trimethacrylate (TMPTMA); alkoxysilane methacrylate functionalized, MEMO; vinyl terminated polydimethylsiloxane (VT PDMS); and two differed types of photoinitiator, Irgacure 819 and Irgacure 784.

among silane products. It is expected to provide water repellency and enhance the protection, either if it is used as a post-treatment or is added in the mix [3].

2. Experimental

2.1. Materials

Trimethylolpropane trimethacrylate (TMPTMA) was chosen for its high reactivity and low viscosity (45 mPa s at 25 °C). The product used was supplied by Cray Valley.

A trimethoxypropyl silane methacrylate monomer, produced by Dow Corning as Z6030, known as MEMO, was used as a coupling agent to enhance the adhesion of the coatings to the stone substrates.

A vinyl terminated polydimethylsiloxane (VT PDMS), supplied by Aldrich, was added to the acrylic mixture to enhance the water repellence of the coatings. The VT PDMS used has a number average molecular weight in the region of 25,000.

Two differed types of photoinitiator, Irgacure 819 and Irgacure 784 were supplied by Ciba. These were chosen for their broad absorption characteristics and being capable to operate under both UV and visible radiations, respectively. A poor initial solubility of the photoinitiator Irgacure 819 in the siloxane VT PDMS was observed and, as a consequence of this, the content of the initiator in all the mixtures was limited to 1.5 wt. part per hundred (pph). Conversely, no solubility peculiarities were noticed when the visible-photoinitiator, Irgacure 784, was added to the mixture containing VT PDMS. In any case, the content of this photoinitiator in all mixtures was again limited to 1.5 wt. pph for consistency purposes. All the formulations obtained in presence of both the photoinitiators were accurately stocked in dark conditions.

The structure and chemical nomenclature of all the components are shown in Scheme 1.

2.2. Curing kinetics

The composition of all the mixtures is outlined in Table 1.

Curing of the mixture was carried out in a Differential Scanning Calorimeter Perkin Elmer DSC-7, modified to allow the irradiation of the sample by means of a UV/visible lamp. This technique is known as p-DSC. The light source, produced by a 300 W Xenon lamp Cermax LX 300, is limited to a wavelength of 370 nm (UV radiation) or 470 nm (visible radiation) using a monochromatic. Small size samples (0.9–1.1 mg) were used in order to achieve isothermal conditions and a uniform degree of cure through the sample thickness [23–25]. The photocalorimetric experiments were repeated at least three times to check the accuracy of results. Isothermal scans were run at different temperatures, respectively 10, 25 and 40 °C, and with light radiations intensity ranging from 0.16 to 9.60 $\mu W/mm^2$. At each temperature and light radiation intensity curing of the mixture was carried out until no residual exothermal signal could be detected. The calorimetric experiments were performed in both air and nitrogen atmosphere, as a way to evaluate the possible inhibition effect of oxygen on the reactivity of the mixtures. In all the DSC experiments each sample was maintained in dark condition and irradiated only after 30 s from the beginning of the test. During the first 30 s, in fact, the sample was maintained under dark conditions. The tangent to the heat flow curve during the test under dark conditions was used as baseline for the peak integration. This means that the isothermal temperature steady state has been reached before starting irradiation. The latter procedure reduced the possibilities that the slow recovering of the base line used for the kinetic analysis is inside of the experimental errors.

p-DSC measurements were used to monitor the advancement of polymerization, by considering that the heat evolved at any times is proportional to the overall extent of reaction for the fraction of reactive groups consumed. The extent of reaction, α, can be defined as [26]:

$$\alpha = \frac{H(t)}{H_{\max}} \tag{1}$$

Table 1
Composition of all the formulations produced.

Sample	Weight composition
T_{819}	TMPTMA + 1.5 pph IRGACURE 819
$MEMO_{819}$	MEMO + 1.5 pph IRGACURE 819
VT $PDMS_{819}$	VT PDMS + 1.5 pph IRGACURE 819
90T-$10M_{819}$	90% TMPTMA + 10% MEMO + 1.5 pph IRGACURE 819
97T-$3PDMS_{819}$	97% TMPTMA + 3% VT PDMS + 1.5 pph IRGACURE 819
87T-10M-$3PDMS_{819}$	87% TMPTMA + 10% MEMO + 3% VT PDMS + 1.5 pph IRGACURE 819
T_{784}	TMPTMA + 1.5 pph IRGACURE 784
90T-$10M_{784}$	90% TMPTMA + 10% MEMO + 1.5 pph IRGACURE 784
97T-$3PDMS_{784}$	97% TMPTMA + 3% VT PDMS + 1.5 pph IRGACURE 784
87T-10M-$3PDMS_{784}$	87% TMPTMA + 10% MEMO + 3% VT PDMS + 1.5 pph IRGACURE 784

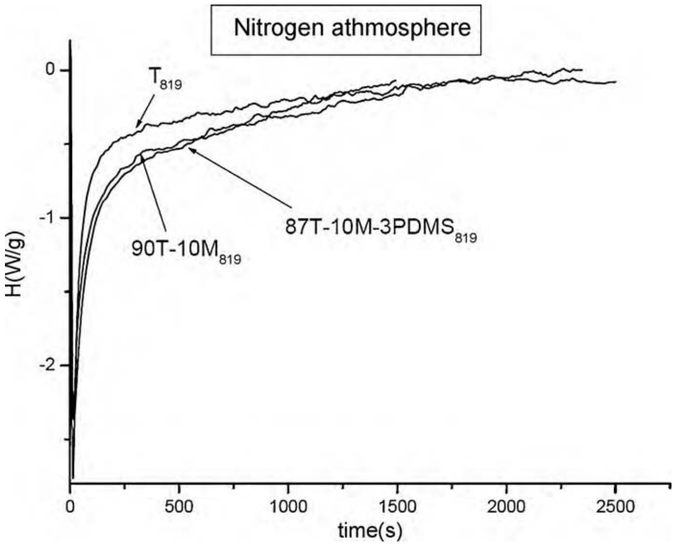


Fig. 1. p-DSC thermograms relative to the calorimetric isothermal scans on the acrylic formulations activated by radiation light with intensity of 1.6 μW/mm^2 with the photoinitiator IRGACURE 819 in nitrogen.

where $H(t)$ is the heat of reaction developed at time t during a DSC experiment and H_{max} represents the maximum heat of reaction measured at each power light irradiation and temperature. The rate of reaction ($d\alpha/dt$) is therefore obtained from the heat flow dH/dt as [26]:

$$\frac{d\alpha}{dt} = \frac{1}{H_{max}}\frac{dH}{dt} \tag{2}$$

After each isothermal p-DSC test, a second dynamic scan was always performed on the same specimen using the same Differential Scanning Calorimeter Perkin Elmer DSC-7 without the UV light source equipment. The dynamic tests were always performed in nitrogen atmosphere, at a heating rate of 10 °C/min, from −10 to 250 °C.

3. Results and discussion

The p-DSC isothermal scans, performed in a nitrogen atmosphere at room temperature and activated by radiation with intensity of 1.6 μW/mm^2, are shown in Figs. 1 and 2. The results obtained in air atmosphere are shown in Fig. 3. The maximum heat of reaction H_{max} and the time to reach the exothermic peak for both nitrogen and air atmosphere are reported in Table 2.

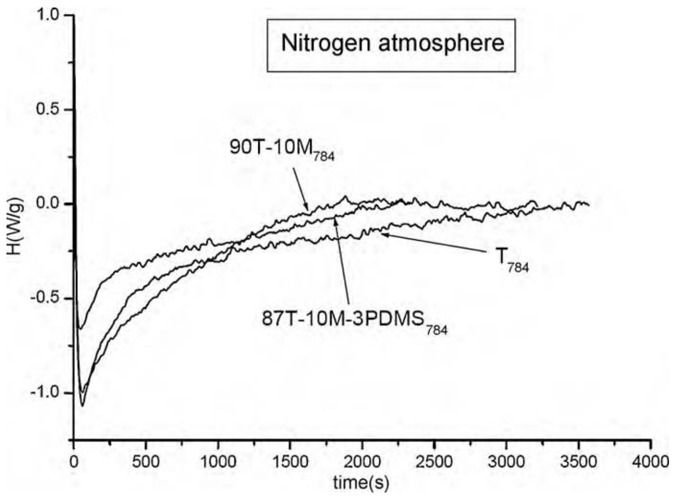


Fig. 2. p-DSC thermograms relative to the calorimetric isothermal scans on the acrylic formulations activated by radiation light with intensity of 1.6 μW/mm^2 with the photoinitiator IRGACURE 784 in nitrogen.

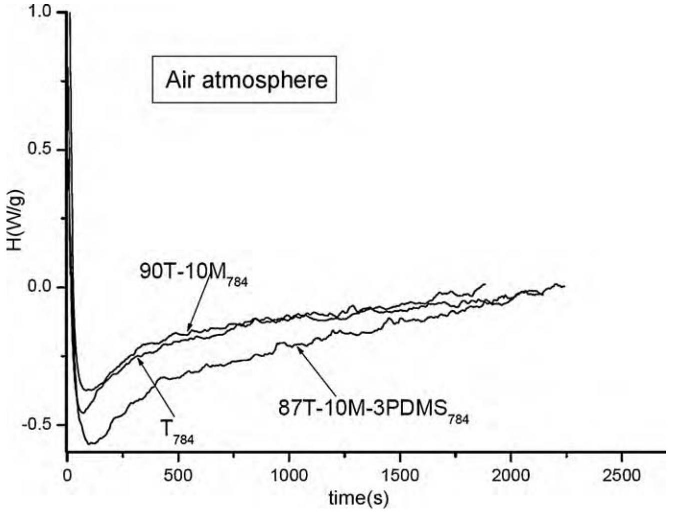


Fig. 3. p-DSC thermograms relative to the calorimetric isothermal scans on the acrylic formulations activated by radiation light with intensity of 1.6 μW/mm^2 with the photoinitiator IRGACURE 784 in air.

With regard to the UV activated reactions carried out in nitrogen, the presence of MEMO in the mixture brings about a small reduction in the heat of reaction (about 6%). This effect could be attributed the low reactivity of the silane MEMO, which was confirmed by the observation that, as seen in Table 2, the calculated heat of reaction of MEMO in presence of 1.5 wt. pph Irgacure 819 is much lower than that of the acrylic resin TMPTMA, using the same experimental conditions.

The addition of 3 wt.% of VT PDMS was found to cause an even greater reduction (around 25%) in the heat of reaction with respect to the acrylic resin, when the reaction was carried out in an inert atmosphere. The possible cause of the reduced reactivity can be, again, related to the low heat of reaction measured for VT PDMS in presence of 1.5 wt. pph of Irgacure 819, as reported in Table 2. Similar results were found in a previous study conducted on a acrylate functional polydimethylsiloxane (AF-PDMS) added as a reactive additive in UV-curable coating formulations based on mixtures of TMPTA (trimethylol propane triacrylate) and polyester acrylate, although in that case the photopolymerization was carried out only in air [27]. Moreover, one cannot exclude the possibility of a small effect arising from the poor solubility of the UV-photoinitiator in the liquid mixture with VT PDMS, as already pointed out.

Referring to the time to reach the peak value (t_{peak}), the effect of MEMO is to slow down the reaction. On the other hand, a t_{peak} similar to the value for the TMPTMA resin is obtained when VT PDMS is also present in the mixture.

The reactivity, expressed in terms of both heat developed and rate of reaction, was generally found to decrease when the UV-photopolymerization was carried out in air, always at room temperature and with a radiation intensity of 1.6 μW/mm^2, due the inhibiting action of the oxygen towards the free-radical polymerization [23].

It is known that oxygen inhibition of free-radical photopolymerization causes numerous deleterious effects on free radically cured products, including slow polymerization rates, long induction periods, low conversion, short polymeric chain length and tacky surface properties [28–31]. The reaction mechanism of free-radical photopolymerization can be represented with three subsequent steps: initiation, propagation and termination. In absence of oxygen, the initiation reactions can be schematically described by the follow-

Table 2
Maximum heat of reaction (H_{max}) and time to reach the exothermal peak (t_{peak}) for nitrogen and air atmosphere (operative conditions: room temperature; intensity of radiation: 1.6 μW/mm^2).

Sample	H_{max} (W/g) Nitrogen	t_{peak} (s)	H_{max} (W/g) Air	t_{peak} (s)
T_{819}	768.52 ± 43.4	14.01 ± 1.4	321.76 ± 32.1	16.02 ± 1.6
$MEMO_{819}$	496.12 ± 13.1	23.08 ± 0.7	-	-
VT $PDMS_{819}$	328.52 ± 21.1	37.69 ± 2.4	-	-
90T-$10M_{819}$	722.98 ± 78.8	18.48 ± 2.1	289.47 ± 28.9	30.00 ± 3.0
87 T-10 M-3 $PDMS_{819}$	576.16 ± 43.9	13.5 ± 2.1	306.02 ± 3.5	21.00 ± 1.2
T_{784}	779.38 ± 44.6	60.0 ± 10.6	411.42 ± 0.8	61.09 ± 19.96
90 T-$10M_{784}$	596.05 ± 66.4	61.0 ± 8.4	388.96 ± 5.0	105.09 ± 47.1
87 T-10 M-3 $PDMS_{784}$	593.57 ± 11.8	46.98 ± 3.8	407.18 ± 7.8	97.02 ± 18.0

ing:

$$I + h\nu \xrightarrow{k_d} R^* \tag{3}$$

$$R^* + M \xrightarrow{k_i} M_1^* \tag{4}$$

In the first step, Eq. (3) represents the photolysis of initiator, I, to give two primary radicals, R^*, while Eq. (4) is the chain initiation process. In this latter reaction, a primary radical reacts with monomer, M, to form the first repeat unit of the growing polymer chain, M_1^*. The rate of both reactions is controlled by the kinetic constants for photolysis of the initiator, k_d, and the chain initiation, k_i, respectively.

The pathways of curing under nitrogen are modified by the presence of oxygen present in air [28–31]. In particular, in addition to reactions schematized with Eqs. (3) and (4), the chain initiation process comprises another reaction:

$$R^* + O_2 \xrightarrow{k_0} RO_2^* \tag{5}$$

where k_0 is the kinetic constant of the radical scavenging by O_2 molecules. When the reaction is conducted in air, then, a part of radicals, R^*, are subtracted by reacting with the monomer since they can also react with oxygen molecules present in air. As a consequence, the reaction is slowed and proceeds with a lower conversion.

The data in Table 2 confirmed that the heat of reaction of TMPTMA resin decreased when the reaction was carried out in air instead of in nitrogen (by about 58%). Under air atmosphere, the values of heat of reaction calculated for all the mixtures are similar, and can be attributed primarily to the reaction of the acrylic resin. In fact, when the reaction is conducted in air, it was not possible to register any heat for the reaction of MEMO or VT PDMS in presence of the UV-photoinitiator, when using a low power UV lamp, such as that operating in the p-DSC. In Table 2, in fact, null values are reported for the latter compounds tested in p-DSC in air. The trend observed for the time to reach the enthalpy peak of all the mixtures is similar to that observed when the reaction is carried out in an inert atmosphere.

When the photopolymerization was activated by visible light, the effect of presence of MEMO and VT PDMS on heat of reaction and time to reach the peak is similar to what observed in the UV-activated photopolymerization process, irrespective to the atmosphere used.

From this observation it can be inferred that, irrespective to the wave length of the light intensity, the presence of oxygen always inhibits the radical photopolymerization of these systems. The reactivity of the additional components present in the acrylic mixture, i.e. MEMO and VT PDMS, is very low under air atmosphere using a visible light source, similarly to what observed when the photopolymerization was conducted in air using an UV source. The heat of reaction of the mixtures, in fact, almost corresponds to that of the acrylic resin in isolation, which is, in turn, reduced with respect to the value measured in nitrogen. As already stated, under an inert atmosphere the presence of VT PDMS generally reduces the heat of reaction of TMPTMA resin. This fact was mainly attributed to the poor reactivity of the siloxane and only in a minor extent to the poor solubility of both photoinitiators in VT PDMS. On the other hand, the time to reach the peak is mainly influenced by the presence of MEMO, which generally reduces the reaction rate, particularly in air.

In Table 3 the values of residual heat of reaction ($H_{residual}$) and of the glass transition temperature (T_g), obtained through a second dynamic scan performed after the isothermal photopolymerization carried out in nitrogen and air atmosphere, are reported for all the formulations realized. All the sample photopolymerized in inert atmosphere does not exhibit any residual heat of reaction, irrespectively from the temperature of photopolymerization. This was taken as a confirmation that the reactions carried out in nitrogen reached completion during the photopolymerization stage. The same samples showed a T_g ranging from 85.3 to 91.2 °C, again reported in Table 3, depending on the temperature of the isothermal photopolymerization process.

On the other hand, when the photopolymerization was conducted in presence of oxygen, in the subsequent dynamic DSC scan the samples showed a residual reactivity, which was found to decrease with increasing the isothermal photopolymerization temperature, as shown in Table 3. The observed residual reactivity was attributed to the effect of inhibition of the free-radical photopolymerization due to the presence of oxygen in the air atmosphere, as already explained. Also in this case, the samples analyzed showed a T_g depending on the temperature of the previous isothermal photopolymerization process, reported in Table 3. It can be observed that the values of the T_g of the samples photopolymerized in air (ranging from 28.0 to 32.0 °C) are much lower than those measured on the same samples photopolymerized in nitrogen, as a further confirmation of the adverse action of oxygen towards the free-radical photopolymerization.

The effect of the UV power input on the kinetic of radical photopolymerization was then examined by varying the power light intensity from 0.16 to 9.60 μW/mm^2, performing p-DSC isothermal scans on formulation 87T-10M-$3PDMS_{819}$ at 10, 25 and 40 °C both in nitrogen and in air atmosphere. At each temperature both

Table 3
87 T-10 M-3 $PDMS_{819}$, I = 9.60 μW/mm^2.

Temperature of first isothermal test (photopolymerization process) (°C)	Second dynamic scan performed after the isothermal photopolymerization, carried out in			
	Nitrogen		Air	
	$H_{residual}$ (W/g)	T_g (°C)	$H_{residual}$ (W/g)	T_g (°C)
10	0	85.3 ± 1.4	84.0 ± 0.4	28.0 ± 0.6
25	0	89.1 ± 1.2	72.2 ± 1.1	31.2 ± 1.0
40	0	91.2 ± 0.8	58.1 ± 1.3	32.0 ± 0.9

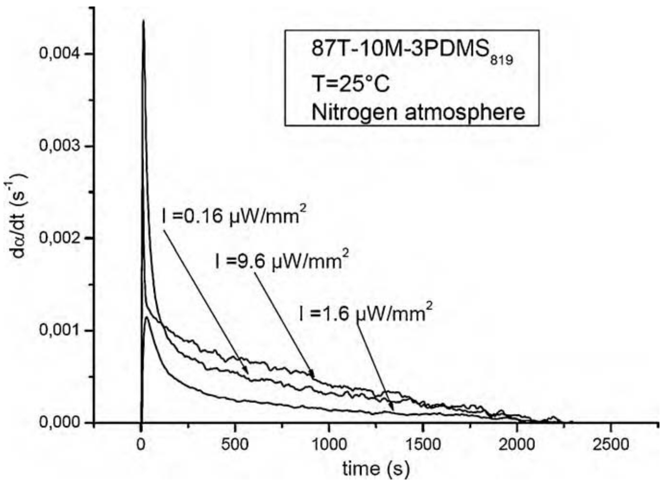


Fig. 4. Reaction rate ($d\alpha/dt$) versus time as function of UV light intensity at a constant temperature of 25 °C for the formulation 87T-10M-3PDMS$_{819}$.

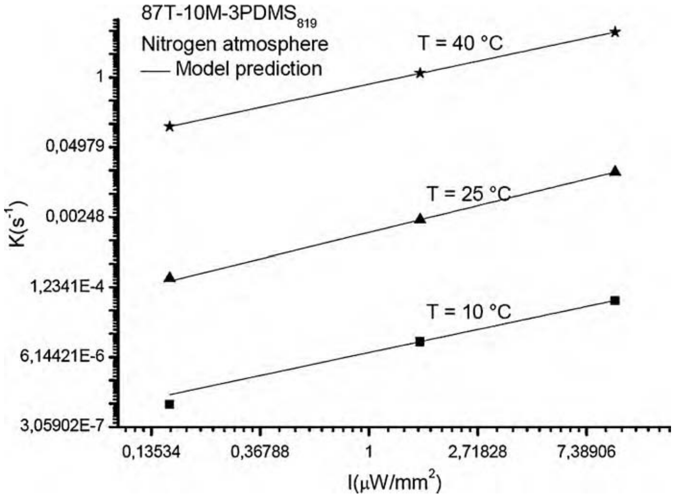


Fig. 5. Comparison between the experimental data and the prediction from Eq. (7) at 10, 25 and 40 °C for the formulation 87T-10M-3PDMS$_{819}$ in nitrogen atmosphere.

the heat ($H(t)$), the rate ($d\alpha/dt$) and the maximum extent of reaction ($\alpha_{\max}$) were found to increase with increasing UV light intensity, as shown in Fig. 4 for reactions carried out at 25 °C, in a inert atmosphere. Similar results were found when the reactions were conducted in air, as can be seen in Table 4.

It is possible to describe the kinetic behavior of the photopolymerization of the systems analyzed by a simple n order kinetic equation, proposed by Maffezzoli and Terzi [32] for the free-radical polymerization of unsaturated polyester and acrylic matrix composites for dental applications:

$$\frac{d\alpha}{dt} = K(1-\alpha)^n \tag{6}$$

where K is a kinetic constant and n is a positive setting parameter which does not depend on temperature. The latter gives an indication of the kinetic order of the reaction. The reaction rate, $d\alpha/dt$, was calculated following Eq. (2) where the maximum heat of reaction, $H_{\max}$, at each temperature, for the reaction performed in inert atmosphere, was calculated as the heat developed during the reaction carried out in nitrogen atmosphere at the same isothermal temperature, since the reaction was proved to be complete when the photopolymerization was carried out in a inert atmosphere.

All the curves of Fig. 4 were fitted to Eq. (6). The order of reaction calculated for the formulation 87T-10M-3PDMS$_{819}$ is 2 and it does not depend on the light intensity. The kinetic constants obtained at each temperature and light intensity are reported in Table 4.

The effect of the absorbed light intensity (I) on the kinetic constant (K) at each temperature can be described by a power-law expression [32]:

$$K = K_0(T) * I^b \tag{7}$$

where b is a dimensionless parameter and $K_0(T)$ is a temperature dependent kinetic constant [32]. As observed by Tryson and Schultz [23], a value between 0.5 and 1 for the exponent b may be observed if termination occurs trough both unimolecular and bimolecular pathways.

Table 4
Kinetic constants obtained at each temperature and light intensity from Eq. (6).

87T-10M-3PDMS$_{819}$			
I (μW/mm^2)	T = 10 °C K (s^{-1})	T = 25 °C K (s^{-1})	T = 40 °C K (s^{-1})
Nitrogen atmosphere			
0.16	8×10^{-6}	1.8×10^{-4}	1.2×10^{-1}
1.6	1.2×10^{-5}	2.2×10^{-4}	1.2
9.6	7×10^{-4}	1.7×10^{-3}	1.2×10^{1}
Air atmosphere			
0.16	4×10^{-8}	2.4×10^{-6}	1.24×10^{-3}
1.6	7×10^{-7}	6.2×10^{-5}	9×10^{-2}
9.6	9×10^{-5}	8.9×10^{-4}	1.4

The comparison between the experimental data and the prediction from Eq. (7) at each temperature is shown in Fig. 5. The values of K_0 and b obtained at each temperature and light intensity are reported in Table 5. For the exponent b, a value on the order of 1 is confirmed when the reactions take place in an inert atmosphere, irrespective of the temperature used in the isothermic scan.

The change in the maximum extent of reaction, $\alpha_{\max}$, with light intensity, I, calculated starting from Eq. (1), was fitted to a power-law relationship, similar to that of Eq. (7) [32]: i.e.

$$\alpha_{\max} = \alpha_0 * I^c \tag{8}$$

where c is a dimensionless parameter.

The data in Fig. 6 show that for the system 87T-10M-3PDMS$_{819}$ there is a good agreement between the experimental data and the predictions of Eq. (8) when the reaction is carried out in nitrogen at 25 °C.

In the light of these findings the same measurements and model predictions were applied for photopolymerization experiments carried out in air atmosphere using 9.60 μW/mm^2 power at each temperature (10, 25 and 40 °C). In this case, since the reaction was not completed when the photopolymerization process was carried out in air atmosphere, the maximum heat of reaction, $H_{\max}$, used to calculate the heat of reaction, $d\alpha/dt$, from Eq. (2) was obtained by adding the heat developed during photopolymerization plus the residual heat of reaction evolved during the subsequent dynamic scan, reported in Table 3.

When the kinetic behavior of the reactions performed in air was fitted with Eq. (6) the order of reaction calculated for the formulation 87T-10M-3PDMS$_{819}$ in air atmosphere was again found to be approximately equal to 2 irrespective of the light intensity used.

Table 5
Values of K_0 and b obtained at each temperature and light intensity from Eq. (7).

87T-10M-3PDMS$_{819}$				
	Nitrogen atmosphere		Air atmosphere	
T (°C)	b	K_0 (s^{-1})	b	K_0 (s^{-1})
10	0.98	7.47×10^{-6}	1.42	3.58×10^{-7}
25	1.01	1.3×10^{-4}	1.44	3×10^{-5}
40	0.99	7.4×10^{-1}	1.53	4.4×10^{-3}

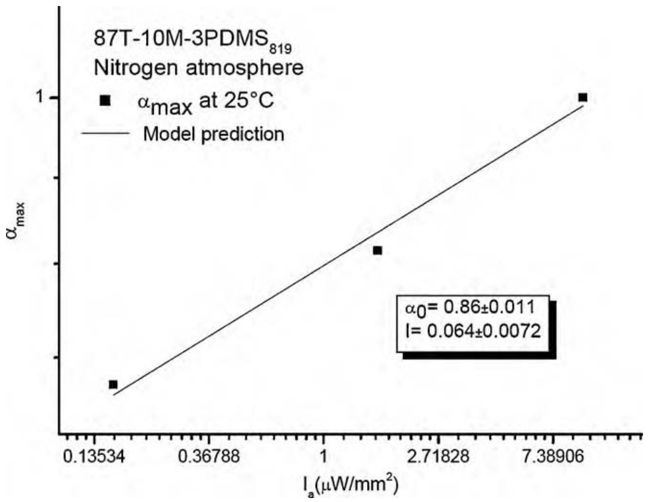


Fig. 6. Comparison between the experimental data and the predictions of Eq. (8) for the system 87T-10M-3PDMS819, in nitrogen atmosphere at 25 °C.

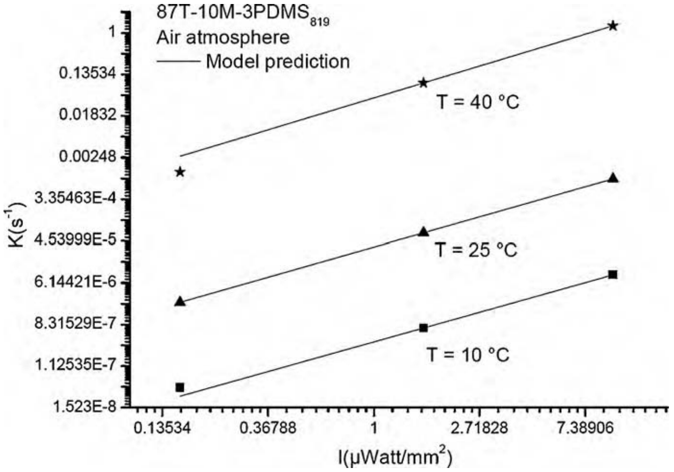


Fig. 7. Comparison between the experimental data and the prediction from Eq. (7) at 10, 25 and 40 °C for the formulation 87T-10M-3PDMS$_{819}$ in air atmosphere.

The kinetic constants obtained at each temperature and light intensity are also reported in Table 4.

The effect of the absorbed light intensity (I) on the kinetic constant at each temperature was also determined using the power-law expression in Eq. (7). Once more the experimental data were in good agreement with the model predictions of Eq. (7), as can demonstrated by the plots in Fig. 7. The values of K_0 and b obtained at each temperature and light intensity are reported in Table 5. These show also that, in this case, b increases to reach values in the region of 1.4–1.5 when the reactions are carried out in presence of oxygen.

4. Conclusions

The photopolymerization of a siloxane-modified methacrylate resin mixture, initiated by the addition of an appropriate photoinitiator for UV and visible activated free-radical reactions, was analyzed as potential coating systems for stone surfaces.

From kinetic studies carried out with calorimetric analysis in nitrogen atmosphere it was found that the presence of both methacrylate silane coupling agent and vinyl terminated polydimethyl siloxane reduces appreciably the heat of reaction, probably due to their low reactivity.

When the reaction is carried out in air, the reactivity generally decreases, due the inhibiting action of the oxygen towards the free-radical polymerization, irrespective to the composition of the mixtures. The reactivity of the mixture, in this case, is mainly determined by the reactivity of the acrylic resin.

A kinetic model, accounting for the effect of light intensity, temperature and atmosphere on the reaction kinetics, was applied to the experimental data obtaining a good agreement. The numerical values found for the model parameters proved that the termination reactions occurring in an inert atmosphere take place through unimolecular and bimolecular pathways. Moreover, the order of the photopolymerization reactions was found to equal to 2, irrespective the operative conditions used, thereby confirming the reliability of experimentally obtained calorimetric data.

Acknowledgement

The support of a fellowship by Apuliam Regional Founds to the second author is gratefully acknowledged.

References

[1] M. Lazzarini, M. LaurenziTabasso, Il Restauro della Pietra, CEDAM, Padova, 1986.
[2] A. Torrisi, J. Cult. Herit. 9 (2) (2008) 135–145.
[3] C.V. Horie, Materials for Conservation, Butterworth-Heinemann, Oxford, 1987.
[4] L. Toniolo, T. Poli, V. Castelvetro, A. Manariti, O. Chiantore, M. Lazzari, J. Cult. Herit. 3 (4) (2002) 309–316.
[5] G. Amoroso, Trattato della scienza e conservazione dei monumenti, Alinea Editrice, Firenze, 2002.
[6] C. Miliani, M. Ombelli, A. Morresi, A. Romani, Surf. Coat. Technol. 19 (2002) 151–152.
[7] E. Hansen, R. Lowinger, F. Sadoff, J. Am. Inst. Conservat. 32 (1993) 1–14.
[8] P. Cardiano, S. Sergi, M. Lazzari, P. Piraino, Polymer 43 (2002) 6635–6640.
[9] G. Alessandrini, M. Aglietto, V. Castelvetro, F. Ciardelli, R. Peruz, L. Toniolo, J. Appl. Polym. Sci. 76 (2000) 962–977.
[10] O. Chiantore, M. Lazzari, Polymer 42 (2001) 17–27.
[11] C.M. Hansen, Prog. Org. Coat. 42 (2001) 167–178.
[12] C. Della Volpe, A. Penati, R. Peruzzi, S. Siboni, L. Toniolo, C. Colombo, J. Adhes. Sci. Technol. 14 (2000) 273–299.
[13] A. Torrisi, Appl. Surf. Sci. 254 (9) (2008) 2650–2658.
[14] A. Torrisi, N. Tuccitto, G. Maccarrone, A. Licciardello, Appl. Surf. Sci. 255 (4) (2008) 1527–1530.
[15] M. Aglietto, V. Castelvetro, F. Ciardelli, V. Fassina, C. Botteghi, U. Matteoli, 5th International Symposium on The Conservation of Monuments in the Mediterranean Basin, Seville (Spain), 2000.
[16] P. Kotlik, J. Ignas, J. Zelinger, Stud. Conservat. 25 (1980) 1–13.
[17] C. Priest, N. Stevens, R. Sedev, W. Skinner, J. Ralston, J. Colloid Interface Sci. 320 (2) (2008) 563–568.
[18] M. Lettieri, A. Calia, A.M. Mecchi, G. Quarta, Proceedings of 6th Int. Symp. on the Conservation of Monuments in the Mediterranean, 2004, pp. 442–447.
[19] S.A. Kulinich, M. Farzaneh, Surf. Sci. 573 (3) (2004) 379–390.
[20] R. Fort Gonzalez, M.C. Lopéz de Azcona, F. Mingarro Martin, M. Alvarez de Buergo, J. Rodriguez Blanco, Proceedings of 9th Int. Congress on Deterioration and Conservation of Stone, 2000, pp. 235–243.
[21] E.W. Nelson, T.P. Carter, A.B. Scranton, Macromolecules 27 (1994) 1013–1019.
[22] C. Decker, Prog. Polym. Sci. 21 (1996) 560–593.
[23] G.R. Tryson, A.R. Schultz, J. Polym. Sci. B Polym. Phys. 17 (1979) 2059–2075.
[24] H.J. Flammersheim, W. Kunza, J. Therm. Anal. Cal. 52 (1998) 125–130.
[25] J. Jakubiak, A. Sionkowska, L. Lindén, J.F. Rabek, J. Therm. Anal. Cal. 65 (2001) 435–443.
[26] C. EspositoCorcione, A. Greco, A. Maffezzoli, J. Therm. Anal. Cal. 72 (2003) 687–693.
[27] H.K. Kim, H.T. Ju, J.W. Hong, Eur. Polym. J. 39 (2003) 2235–2241.
[28] T.Y. Lee, C.A. Guymon, E. SonnyJönsson, C.E. Hoyle, Polymer 45 (2004) 6155–6162.
[29] M.D. Goodnera, C.N. Bowman, Chem. Eng. Sci. 57 (2002) 887–900.
[30] C. Decker, A.D. Jenkins, Macromolecules 18 (1985) 1241–1244.
[31] K. Studer, C. Decker, E. Beck, R. Schwalm, Prog. Org. Coat. 48 (2003) 92–100.
[32] A. Maffezzoli, R. Terzi, Thermochim. Acta 321 (1998) 111–121.