Photo-DSC Investigation of Acetonaphthone Type Photoinitiators at Different Light Intensities

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The gelation of a 75% epoxy diacrylate (EA) and 25% tripropyleneglycol diacrylate (TPGDA) mixture (P-3038) was performed using 2-(*N*-methyl-*N*-phenyl)acetonaphthone (MPA) and morpholino acetonaphthone (MPM) as Type I photoinitiators at different light intensities by using a photo-differential scanning calorimetric (Photo-DSC) technique. Identical temperature values and initiator concentrations were used for the photopolymerization reactions. The results show that maximum rate of polymerization ($R_{p_{max}}$) and final conversion values present good correlation at different light intensities.

Keywords: Photopolymerization, Photoinitiator, Acetonaphthone, Photo-DSC, Light intensity

1. Introduction

Polymerization reactions of photoinitiated free radicals are extensively applied in many commercial areas. The processes of photoinitiated polymerization of acrylates and methacrylates provide a rapid production of polymeric materials. These materials are widely used as coatings, imaging materials, photoresists and polymeric materials in many applications for their well-defined properties [1-7].

Photoinitiators are capable of generating reactive species, e.g. free radicals or ions that are used in UV-curing systems and initiating polymerization of multifunctional monomers and oligomers. Their properties of in addition, the curing performance of a photoinitiator can be improved by a proper selection of polymerization rate (R_p), double bond conversion, and final adhesive properties [8,9]. Two types of photoinitiators are used in free radical polymerization: an α -cleavable initiator (Type I) and a hydrogen abstraction type photoinitiator (Type II). Type II initiators are responsible for yielding the initiating radicals by reacting with the H-donor compounds like tertiary amines, thiols, alcohols and ethers at the triplet state. Studies on this field have mostly focused on Type I photoinitiators, which produce two radical species by undergoing an α -cleavage process upon

irradiation [1,10,11]. Type I photoinitiators are highly reactive and they have very short triplet state lifetimes [12]. Therefore, the introduction of substituted α -aminoketone photoinitiators constituted a great development in this field. Since their molar absorptivities in the range of 300–400 nm are higher than the usual acetophenone type photoinitiators, these compounds can be used in the curing of pigmented systems [3,12]. Upon irradiation these ketones undergo type I cleavage to produce radical pairs with high rate constant and good efficiency. The addition of radicals to alkenes is one of the most important reactions in free radical polymerization. These photoinitiators yield α -aminoalkyl radicals as well as substituted benzoyl radicals. According to time-resolved IR spectroscopic studies, α -aminoalkyl radicals are more efficient compare to benzoyl radicals in initiation of free radical polymerization [13].

Photo-DSC (Photo-Differential Scanning Calorimetry) technique is widely used to investigate different parameters of curing reactions such as the extent of crosslinking and conversion, the order of reactions and the rate of polymerization. With this technique, the change in the heat flow of the investigated system is observed and interpreted [14]. Photoinitiated polymerization of multifunctional

monomers yields crosslinked polymers which induce particular behaviors with regard to kinetic reactions. Light intensity, thickness of sample, absorption properties and concentration of initiator constitute the main determinant factors of the rate of initiation, as well as the number of initiating species that are produced for each photon of light. The effect of light intensity and exposure time on photopolymerization has been also explored by different scholars. Accordingly, UV light intensity was identified among the most important factors which affect the reaction kinetics of resin systems and properties of formed gels [15,16].

In this study, 2-(*N*-methyl-*N*-phenyl) acetophenone (MPA) and morpholino acetophenone (MPM) (Fig. 1) were synthesized and used as Type I photoinitiators for the polymerization of 75% epoxy diacrylate (EA) and 25% tripropyleneglycol diacrylate (TPGDA) mixture (P-3038). Photo-DSC technique is used to investigate photopolymerization kinetics at different light intensities in the presence of MPA and MPM under nitrogen atmosphere. A strong correlation was found between the applied UV light intensity and maximum conversion rate ($C_{R_{pmax}}$), maximum rate of polymerization (R_{pmax}), and final conversion values.

Fig. 1. Structures of MPA and MPM.

2. Experimental

2.1. Materials

The synthesis of 2-(*N*-methyl-*N*-phenyl) acetophenone (MPA) and morpholino acetophenone (MPM) were made based on the previously described procedure [17,18]. A mixture (P-3038) of 75% epoxy diacrylate (EA) and 25% tripropyleneglycol diacrylate (TPGDA) (P-3038) was provided from Cognis France. Irgacure 369, Irgacure 651 and Irgacure 907 were provided from Ciba Specialty Chemicals and used as received. Acetonitrile (99% Merck) was used as received.

2.2. Analysis

A Varian UV-visible Cary 50 spectrophotometer was used for the analysis of UV-visible spectra. Photo-DSC experiments were performed using a

TA DSC 100 instrument and a TA Q PCA photo unit that were equipped with a high pressure mercury lamp.

2.3. Photo-differential scanning calorimetry

The heat released during the polymerization corresponds to the amount of reacted acrylates in the system. Formula 1 helps to specify the conversion of the acrylate groups (C) or the extent of the reaction by integrating the area under exothermic peak:

$$C = \Delta Ht / \Delta H_0^{\text{theory}} \quad (1)$$

In this formula, ΔHt represents the reaction heat evolved at time t and $\Delta H_0^{\text{theory}}$ represents the theoretical heat for complete conversion. An acrylate double bond polymerization was carried out with a heat of $\Delta H_0^{\text{theory}} = 86 \text{ kJ/mol}$ [19]. A direct relationship was found between the rate of polymerization (R_p) and the heat flow (dH/dt), which is represented by the general formula 2:

$$R_p = (dC/dt) (dH/dt) / \Delta H_0^{\text{theory}} \quad (2)$$

Samples were accurately weighed into the aluminum pans and irradiated with the light source of the photo unit at different light intensities. The properties were measured in isothermal mode at 25 °C under an inert atmosphere of nitrogen (50 mL min⁻¹). The polymerization rates and conversion percentages were calculated.

3. Results and discussion

The structural analysis for the synthesis of cleavable photoinitiator of 2-(*N*-methyl-*N*-phenyl) acetophenone (MPM) and morpholino acetophenone (MPM) were performed by spectral and elemental analysis. Both MPA and MPM exhibit good absorption properties with high molar absorptivities compared to commercial Type I photoinitiators, as shown in Fig. 2.

Photo-DSC is capable of indicating the performance of a photoinitiator accurately and fastly. Photopolymerization of P-3038 containing photoinitiators MPA and MPM under nitrogen atmosphere was observed through photo-DSC technique and the effect of light intensity on the rate of polymerization and conversion percentage was tested using four different light intensities. Figures 3-9 show time dependencies of the polymerization heat flow, polymerization rate and their conversion percentages for P-3038 formulations obtained from

photo-DSC.

It was clearly seen that photopolymerization behaviour of MPM is different from that of MPA. In the sample containing MPM as photoinitiator UV light intensity increased from 10 to 60 mW·cm⁻², the extent of heat flow, rate of polymerization and conversion percentage values also increased in good order (Figs. 3-5). Most probably, increase of light intensity provides greater efficiency for initiation, leading to more formed primary radicals on the surface of the solution.

Fig. 2. Absorption spectra of 7.25×10^{-4} M MPA and MPM (λ_{max} : 329 and 332 nm, ϵ : 1840 and 1733 L·mol⁻¹·cm⁻¹), Irgacure 369, Irgacure 651 and Irgacure 907 in acetonitrile.

Final conversion values increased properly with the increasing light intensity and reached 41.5% when the light intensity was 60 mW·cm⁻² (Fig. 5, Table 1).

The conversion percentage of P-3038 to polymer reached 11.9% (Table 1) during 19.1 sec. of irradiation time with 60 mW·cm⁻² light intensity. The conversion was completed after nearly 300 sec of irradiation with 41.5% of conversion percentage (Fig. 5. and Fig. 9).

Further experiments were carried out for the P-3038 formulation with the same concentration of MPA at four different light intensities. For MPA,

Fig. 3. Photopolymerization heat flow curves of EA/TPGDA with various UV light intensities in the presence of MPM as photoinitiator.

Fig. 4. Photopolymerization rate curves of EA/TPGDA with various UV light intensities in the presence of MPM as photoinitiator.

Fig. 5. Conversion spectra of photopolymerization of EA/TPGDA with various UV light intensities in the presence of MPM as photoinitiator.

heat flow and polymerization rate was extended to $60 \text{ mW}\cdot\text{cm}^{-2}$ as the UV light intensity increased from 10 to $60 \text{ mW}\cdot\text{cm}^{-2}$ (Figs. 6 and 7). However, an irregularity was observed in conversion percentages with the increasing light intensity (Fig. 8). Accordingly, monomer was converted to polymer with 39.8% conversion percentage at $40 \text{ mW}\cdot\text{cm}^{-2}$. When light intensity reached $60 \text{ mW}\cdot\text{cm}^{-2}$, conversion percentage value of the formulation dropped to 38.8% (Figs. 8 and 9). It is of high possibility that high light intensity leads to a high cross-section for initiation, which results in production of more formed primary radicals on the surface of the solution. These excess radicals formed on the surface of the coating restricted the penetration of UV light into the samples by creating a filter effect, which resulted in a decrease of the final conversion values at high light intensities [1, 15,16].

Fig. 6. Photopolymerization heat flow curves of EA/TPGDA with various UV light intensities in the presence of MPA as photoinitiator.

Fig. 7. Photopolymerization rate curves of EA/TPGDA with various UV light intensities in the presence of MPA as photoinitiator.

Fig. 8. Conversion spectra of photopolymerization of EA/TPGDA with various UV light intensities in the presence of MPA as photoinitiator.

Fig. 9. Final conversion values of photopolymerization of EA/TPGDA with various UV light intensities in the presence of MPA and MPM as photoinitiators.

As can be seen in Figs. 3-8 and Table 1, because MPA polymerizes faster than MPM, the filter effect can be observed more clearly for MPA.

Table 1 shows $t_{\max}$ (time to reach polymerization rate), $R_{p\max}$ (maximum polymerization rate) and $C_{R_{p\max}}$ (maximum conversion rate) values versus four light intensities during EA/TPGDA photopolymerization.

According to the results of Table 1, for both initiators, when light intensity was increased, $t_{\max}$ values dropped and polymerization rates expectedly increased. When the light intensity reached the maximum value, maximum polymerization rate increased up to 11.9 s^{-1} and MPM reached 7.6 s^{-1} rate value during 19.1 seconds of irradiation. On the other hand, there was an adverse effect between final conversion values of MPA and MPM. Since polymerization of MPA occurred faster than MPM, final conversion values of MPM were less for the

Table 1. The values of various parameters measured using photo-DSC for different light intensities during diacrylate, EA/TPGDA photopolymerization.

PI	Light Int. (mW.cm ⁻²)	$t_{\max}$ (s)	$10^3 \cdot R_{p\max}$ (s ⁻¹)	$C_{Rp\max}$ (%)
MPA	10	15.7	4.2	5.0
MPM	10	58.5	1.6	8.2
MPA	30	11.9	7.1	5.8
MPM	30	26.7	3.8	6.4
MPA	50	8.1	8.9	5.2
MPM	50	28.3	5.4	11.4
MPA	60	4.9	11.9	4.5
MPM	60	19.1	7.6	11.9

light intensities 10, 30 and 50 mW.cm⁻². However, for 60 mW.cm⁻², because of the filter effect on MPA, final conversion of MPM is higher than MPA (Fig. 9).

The type of initiator is an important parameter, which reveals the effect of oxygen inhibition on the photopolymerization reaction. In this study, we have used MPA and MPM as type I initiators. The oxygen inhibition was not harmful and also photo-DSC experiments were carried out under nitrogen atmosphere.

4. Conclusion

In this study, photopolymerization of P-3038 monomer was investigated using two acetophenone type photoinitiators with different light intensities. The results show that rate of polymerization and final conversion values present good correlation at different light intensities. According to the results from our previous studies it was observed that photoinitiators MPA and MPM produce naphthoyl and α -aminoalkyl radicals under UV irradiation [17,18] and when the polymerization of MMA is performed using MPA as the initiator, the conversion values are higher compared to MPM [17].

For photo-DSC results, MPA polymerizes faster than MPM and this shows us different α -aminoalkyl radicals produce from the initiators have different initiation effects [20-22]. The increase of the rate of polymerization is dependent upon the structure of the α -aminoalkyl radical. In the case of MPM, the morpholino group is a bulky substituent and addition rate constant of the α -aminoalkyl radical to

acrylate double bond is less compare to MPA. This is most probably due to steric effects. Besides aromatic *N*-methyl aniline substituent in MPA is probably resonance stabilized and α -aminoalkyl radical is more stable and efficient on addition on acrylate double bond. However, previous studies have shown these radicals efficiency of fast curing of acrylates [22].

Polymerization mechanism and efficiencies of α -aminoalkyl radicals can be investigated in detail by ESR (electron spin resonance) and laser flash photolysis methods as advanced techniques [12,23,24].

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