Development of New Photoinitiating Systems for Depth Curing of Thick Materials

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The production of thick materials by photopolymerization, such as those required for fiber-reinforced polymer is still rather scarce today. This fact is mainly attributed to the low penetration depth of the light into the composites. In this paper, it will be first shown that glass fiber composites can be formed easily by using a suitable photoinitiating system. Secondly, attention will be paid on carbon fiber composite where a dual-cure initiating system based on both a photoinitiator and a thermal initiating system is able to produce polymer part of few millimeters in a relatively short time scale.

Keywords: photopolymerization – dual-cure initiating system – photocyclic initiating system - fiber-reinforced polymer

1. Introduction

Nowadays photopolymerization represents a widely used technology leading to a large variety of applications ranging from the coating industry to microelectronics, graphic arts or optics [1-4]. Most of the applications concern thin films used either as coatings or as photoresists. Up to now, photopolymerization of thick samples was considered only in a limited number of applications such as dental materials. Although that the potential of development represents one exciting field, photocuring of fiber-reinforced composites, is still quite limited [5]. For such purpose, frontal polymerization has been proposed, in which i) a photobleachable photoinitiator is used to cure thick samples layer by layer [6] or ii) a thermal reaction is initiated by photopolymerization at the surface and propagates through the sample [7].

In this paper, two methods are employed to obtain photocomposites. Firstly, a selected photoinitiating system is used to cure on-demand a 3mm thick glass-fiber composite under LED at 395nm using methylmethacrylate as a resin. The effect of the photoinitiating system is discussed from the point of view of the photochemistry involved. It is shown that the reactivity of the photoinitiating system affects the molecular weight of the polymer, thereby influencing the mechanical properties. Secondly, a dual-cure system is presented in which a phosphine oxide is used to create an exotherm at the surface of the sample. This exotherm is high enough to prompt the decomposition of a cobalt/peroxide initiating system which allows the curing of thick carbon-reinforced composites.

2. Experimental

All the compounds used in this study are shown in Scheme 1. Isopropylthioxanthone (ITX) and ethyl 4-(dimethylamino)benzoate (EDB), tert-butylhydroperoxide (TBH), cobalt(II)-2-ethylhexanoate (CoII) were purchased from Sigma-Aldrich. 2-(4-Methoxy phenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine (TA) was obtained from PCAS (France). Cobalt(II) 2-ethylhexanoate, 6% in solvent mixture (NL51P) was obtained from AkzoNobel. Diphenyl(2,4,6-trimethylbenzoyl)
-phosphine oxide (TPO) was a gift from BASF. Peroxan ME 60-L (dimethyl phthalate, 2-Butanone peroxide, hydrogen peroxide in butanone) was a gift from Pergan. Methylmethacrylate (MMA, Sigma-Aldrich), Ebecryl 270 (Eb270, Cytec), tripropylene glycol diacrylate (TPGDA, Sartomer), Crestapol 1250 (Scott-Bader) were used as resin. All the compounds were used as received.

The composites are photopolymerized using a LED array emitting at 395 nm with a total light power of 12W (Firejet FJ200 150x20, Phoseon).

Real-time Fourier transform infrared spectroscopy (RT-FTIR) studies were conducted using a Vertex 70 FTIR spectrometer (Bruker Optik) [8-9]. The formulation was irradiated with a polychromatic light from a Hg-Xe lamp (Hamamatsu) with a reflector and a filter that specifically select the 365 nm. The conversion kinetics were observed using the acrylate band at 1636 cm⁻¹. The degree of conversion C is directly related to the decrease of the peak area A corresponding to the reactive functions according to:

\[ C(\%) = \frac{A_0 - A_t}{A_0} \times 100 \]  

where \( A_0 \) and \( A_t \) were the area of the IR absorption peak of the sample before exposure and at a given exposure time \( t \), respectively.

Confocal Raman microscopy (CRM) was performed on an inVia Reflex Raman microscope from Renishaw which is a combination of a Raman spectrometer and a Leica DM2500 microscope. The probe wavelength was provided by a helium–neon laser from Renishaw emitting 17 mW.cm⁻² at 633 nm. Depth conversion profiles (nominal displacement of the optical plate holding the sample) were plotted at different time using a method similar to eq. 1 [10-11].

3. Photoinitiating systems for fiber-reinforced thermoplastic.

From an industrial point of view, development of fiber-reinforced composites is considered as a major challenge. Environmental concerns would favor the use of thermoplastic resins which are quite interesting in terms of recyclability [12]. Remelting is one of the basic methods for recycling thermoplastics [13]. A more elegant method would be to create composite which would be easily reworkable. From that point of view, methacrylates appear to be among the best candidates as its corresponding polymer can be depolymerized back to the original monomer [14].

Photopolymerized fiber-reinforced composites represent an exciting topic in the literature [15]. Most of the papers deal with the use of type I photoinitiators which eventually lead to photobleaching during irradiation. In this case, a frontal photopolymerization propagates in depth, and curing thick samples appears to be possible [6,16-18]. In this paper, polymethylmethacrylate (PMMA) was chosen as typical example of photocurable thermoplastic. It is worth noting that the photopolymerization of neat methylmethacrylate (MMA) was not extensively described for the formation of thermoplastic [19].

The photopolymerization of MMA was first evaluated using a type I photoinitiator (TPO) and a type II photoinitiating system (ITX/EDB). As can be seen in Figure 1, TPO does not lead to a good conversion of MMA. By contrast 80% of conversion was reached when using ITX/EDB. However, in such a case, the conversion rate is rather slow with less than 60% of conversion obtained after 800 s of irradiation. This effect may be attributed partly to the formation of ITX ketyl radicals (ITXH•) which are known to act as terminating agents [19-20]. Addition of a triazine derivative (TA), which acts as oxidizing agent towards the ketyl radical, permits to turn ITXH• into the starting ITX and an additional initiating radical (Scheme 2). Therefore, the detrimental effect of ITXH• is suppressed and further irradiation of the recovered ITX can leads to an increase in the concentration of initiating radicals.

![Scheme 1. Compounds used in the different initiating systems.](image-url)
Scheme 2. Reaction mechanism involved in the ITX/EDB/TA photocyclic initiating system.

Consequently, ITX/EDB/TA leads to a fast photopolymerization of MMA as can be seen on Figure 1.

Fig. 1. Conversion profiles of MMA using ITX/EDB, ITX/EDB/TA and TPO as photoinitiating systems (UV irradiation at 366 nm, 147 mW/cm$^2$).

The use of triazine derivative allows to increase the molecular weight of PMMA by decreasing the concentration of ITXH$^\cdot$ terminating agents. Indeed, ITX/EDB system leads to PMMA with $\text{Mn} = 6760$ g.mol$^{-1}$ and PDI = 5.6. In the presence of 1wt% of TA, Mn reaches 12240 g.mol$^{-1}$ and PDI = 3.2 (Hg/Xe lamp, 520 mW/cm$^2$). This is expected to affect the mechanical properties that are increased when Mn increases.

Photopolymerization of unidirectional glass fiber-reinforced composites was performed under LED at 395 nm. A six glass-fiber plies composite was successfully polymerized as shown in Figure 2.

Fig. 2. Photopolymerized unidirectional glass fiber-reinforced PMMA using ITX/EDB/TA as photoinitiating system and MMA as resin.

### 4. Dual-cure photochemical / thermal initiating system

Although that glass fiber reinforced composites can be relatively easily cured under LED, as shown previously, carbon-fiber composites are still quite difficult to photoactivate. This is merely due to the absorption of the light by the carbon fibers. In such a case, a photopolymerization process should be prompted at the surface, and the heat produced during this reaction should be able to decompose the thermal initiating system.

Such a system was developed using Peroxane ME 60-L as peroxide (0.5 wt%), NL51P as catalyst (0.2 wt%), TPO as photoinitiator (3 wt%) and crestapol 1250 as multifunctional acrylate resin.

Fig. 3. Temperature profiles measured by optical pyrometry for the photochemical / thermal curing of 50 g pure crestapol 1250 (20 mm thick).

Figure 3 shows that in the absence of light, the polymerization process starts after a reaction time of 156 min (as determined from the maximum temperature $T_{\text{max}}$ at the surface of the sample). In that case, the initiation mechanism is caused by the reaction of peroxide with cobalt, as described by the Haber-Weiss cycle (Scheme 3).
Scheme 3. Haber-Weiss cycle involved in the initiation of the polymerization using a peroxide/cobalt system.

In the presence of light, TPO leads to a photopolymerization of the composite surface, which increases its temperature to a value high enough that the decomposition of the peroxide (> 60°C) is accelerated. Figure 3 shows that 3 min of irradiation operated 5 min after mixing decreases the time needed to reach the maximum temperature T\text{max} at the surface of the sample. Indeed, at 50 mW/cm², T\text{max} is obtained after 99 min, whereas at 420 mW/cm², only 33 min are required to reach T\text{max}. Frontal polymerization occurs in the sample and the thick resin sample is cured within a time scale much faster than in the absence of light (Figure 3).

This effect can be explained in terms of photoinduced pre-gelation of the resin. Figure 4 shows the confocal Raman microscopy profiles of the conversion of an acrylate resin (Ebecryl 270 : tripropylene glycol diacrylate, 50:50 wt ratio) containing TBH (1 wt%) / Co\text{II} (0.2 wt%) / TPO (0.1 wt%). Low light intensity was used to illustrate the change in conversion profile with time. Under irradiation of the sample (mercury lamp, 2 mW.cm⁻²), it is clear that the photopolymerization induced the gelation of a 80µm thick layer 220 µm above the surface. This prevents further oxygen inhibition of the deepest layer, a fact that promotes the thermal polymerization. Consequently, the polymerization of the resin is accelerated under UV light [21].

This resin was used to produce a composite formed of four carbon fiber plies (400g/m² each), leading to a total thickness of 3.4 mm. Barcol hardness of the sample were found to be similar for the irradiated and non-irradiated sample after 240 min of delay, showing that the photochemical/thermal process leads to similar surface properties than the thermal system.

Fig. 4. Time evolution of the conversion profile in depth using photochemical/thermal initiating system (see text).

5. Conclusion

In this paper, the photocuring of glass-fiber and carbon-fiber reinforced polymers was demonstrated using different methods. Glass-fiber thermoplastics based on PMMA can be obtained by choosing a photocyclic initiating system that allows a one-step irradiation under LED at 395 nm. By contrast, due to the absorption of light, carbon-fiber reinforced polymers can be obtained only using a dual photochemical/thermal initiating system in which the photopolymerization at the surface prompts the decomposition of the thermal system. This work opens new opportunities to speed up the formation of fiber-reinforced polymer by light.

References