

New UV-LED technologies for carbon-fiber reinforced polymers

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Abstract :

Dual-cure initiating systems have emerged as promising alternatives to perform fast and on-demand curing of thick polymers. In this paper, a system based on pyrylium salt as photoinitiator and a hydroperoxide or a vinyl ether as coinitiator is reported to be efficient in the polymerization of epoxide resins. The chemical mechanisms involved are studied by spectroscopic methods. It is found that the interaction between pyrylium salts and coinitiator releases a proton that could initiate the polymerization reaction at room temperature as well as under UV or LED light. The combination of both methods allows the polymerization of a thick sample by photoinduced thermal polymerization. With this new dual initiating system, the photocuring of carbon-fiber reinforced polymers was demonstrated to be possible using a robotized LED at 395 nm. This work opens new opportunities to speed up the formation of fiber-reinforced polymer by light.

Introduction:

Epoxy resins are an important family of monomers and oligomers widely used in industry. They are particularly interesting for materials exhibiting good mechanical and thermal properties. Fiber-reinforced polymers represent today one of the most important developments today which use epoxy resin for the manufacturing of carbon composites. However, conventional systems based on epoxy resins in this field require long processing time (up to 16 hours) and quite often high temperature of curing (up to 160°C). This represents a severe drawback for productivity, leading to important lead time, high investment costs and high energy waste. From that point of view, photocuring of epoxy resins is quite fast and requires little amount of energy. However, photocuring is highly efficient as far as the light is able to

penetrate the medium. Obviously, in the case of carbon-fiber composite, the light does not penetrate in the substrate, and only a surface curing is expected to occur under light. Although it is quite easy to find a cationic photoinitiator that would be able to cure the epoxy resin under UV-blue light,¹ the situation becomes more tricky in the depth of an opaque sample.

In order to overcome this limit, we tried to development a new initiating system which can be effective both photochemically and thermally. The surface photopolymerization would release an exotherm which could thermally decompose the initiator in depth.²⁻⁴ This so-called photoinduced thermal frontal polymerization¹ would ultimately be able to cure the carbon-composite at room temperature and within a couple of minutes. For this purpose, the photochemical and thermal initiating ability of pyrylium salts was investigated. 2,4,6-triphenylpyrylium tetrafluoroborate (TPP⁺) was irradiated in a dicycloaliphatic epoxy resin and the conversion curve was monitored by Real-Time FTIR. The thermal reactivity at room temperature was also studied in the resin and in the presence of hydroperoxides or vinyl ethers as coinitiators. Finally, the dual-cure behavior is demonstrated allowing the fabrication of a 5mm thick carbon-fiber composite by irradiation with a robotized LED at 395 nm.

Results and Discussion:

a) Photopolymerization ability of TPP⁺

Triphenylpyrylium tetrafluoroborate (TPP⁺, see structure on Figure 1) is known to be a good photosensitizer.

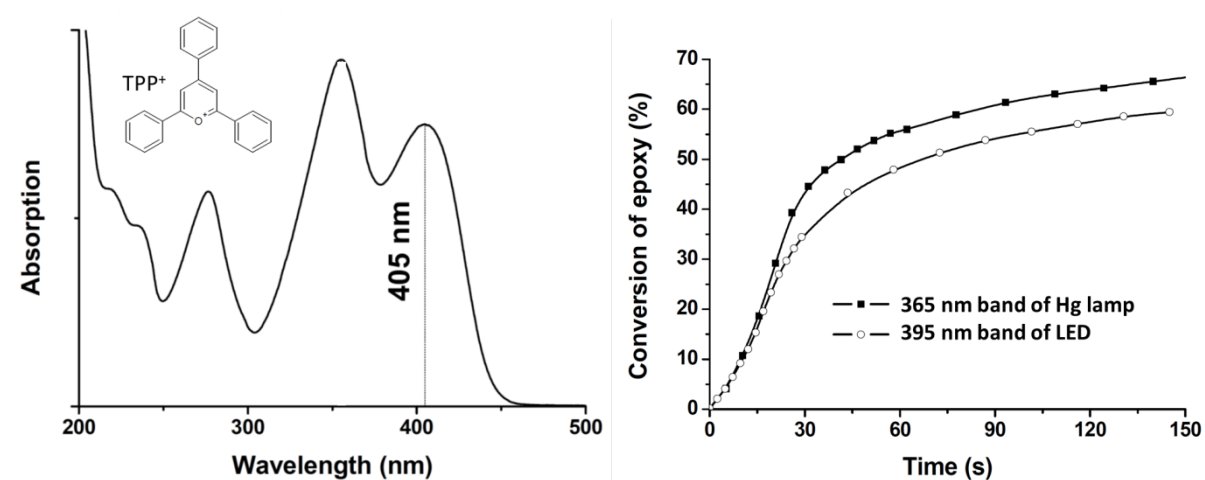


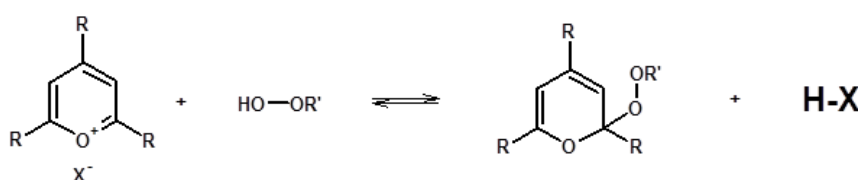
Figure 1. Absorption spectrum of TPP⁺ (left) and photopolymerization under LED at 395 nm and 365 nm band of a mercury lamp (right).

It exhibits an absorption band (lowest transition located at 405 nm in acetonitrile) that matches quite well both the 365 nm emission of a mercury lamp and the 395nm emission band of a LED (Figure 1).⁵ When using 3wt% of TPP⁺ as photoinitiator, the photopolymerization of (3,4-epoxycyclohexane)-methyl-3,4-epoxycyclohexylcarboxylate (EPOX) was found to be quite effective under both LED at 395 nm and filtered Hg lamp at 365 nm (70 mW/cm², Figure 1). This demonstrates that TPP⁺ can act as cationic photoinitiator, leading to about 60% of conversion under these experimental conditions.

b) Thermal initiation at room temperature

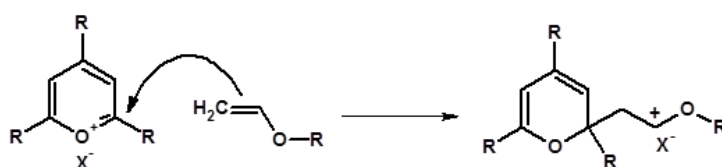
3 wt% of TPP⁺ in EPOX leads to the formation of a gel in the dark within 3-4 hours and a glassy polymer in about one day. In order to speed up the thermal curing, two different cointiators were employed, namely hydrogen peroxide (HP) and isobutylvinylether (IBVE).⁶

HP is able to react with TPP⁺ according to Scheme 1, leading to the release of a proton. As expected, the proton acts as a reactive species towards EPOX speeding up the curing process. Indeed, a gel time of 15 min is observed.⁷



Scheme 1

In the case of IBVE, a nucleophilic attack of the 2- and 4- positions of TPP⁺ occurs, leading to an addition reaction. A reactive carbocation is formed which could initiate the polymerization of EPOX (Scheme 2). A gel time of 20 min is observed in that case (Scheme 2).⁸



Scheme 2

Therefore, when using HP or IBVE, a reactive initiating system is formed allowing the curing of EPOX within 15-20 min.

As can be seen, TPP⁺ is a quite effective thermal initiator provided that a coinitiator is added to speed up the reaction.

c) Dual-cure process

As both photopolymerization and thermal polymerization can take place using TPP⁺, this system is potentially usable to cure fiber-reinforced polymer through a photoinduced thermal frontal polymerization.⁹ A mixture of 3wt% of TPP⁺ and EPOX was placed in a silicone mould of 12 mm of diameter, 20 mm of depth and irradiated with UV light (700 mW cm⁻²) during 1 min. The temperature jump due to polymerization reaction was measured simultaneously by thermocouples at the surface and in the bulk at different depths.

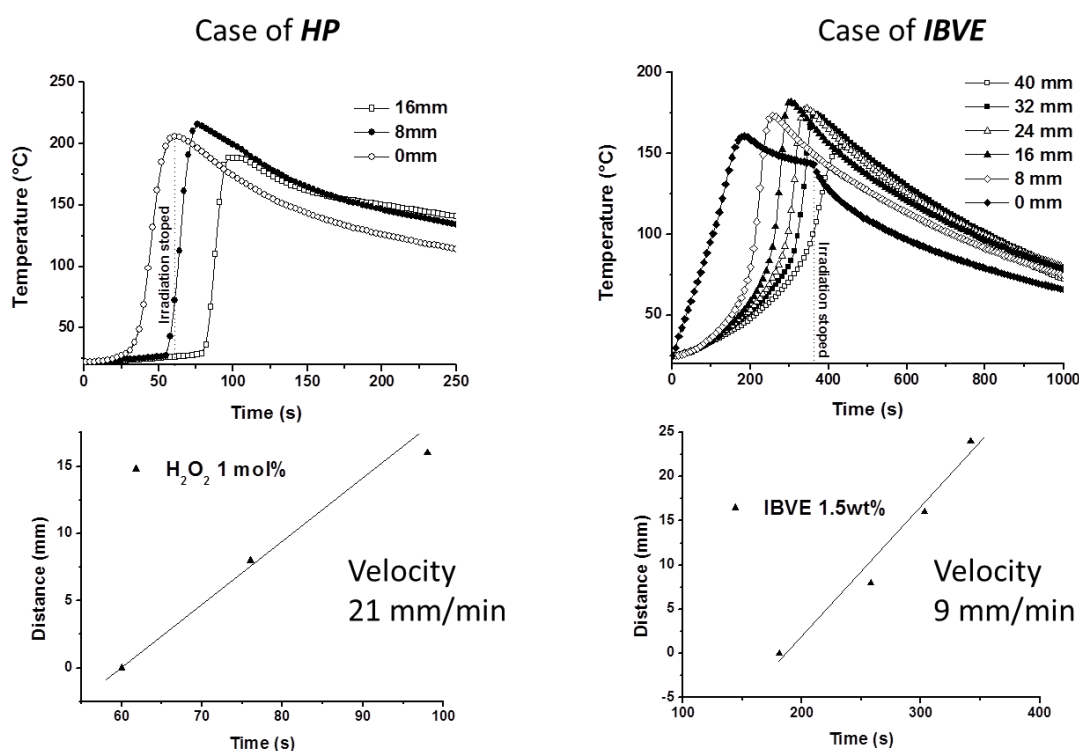


Figure 2. Up: photoinduced thermal frontal polymerization using TPP⁺ in EPOX in the presence of a reactive resin for HP as coinitiator (left) and IBVE (right). Down: corresponding velocities of the frontal polymerization.

Then the light is switched on for 60 sec and the temperature profiles are monitored. Figure 2 shows the change in temperature for both systems based on TPP⁺ (3wt%), EPOX and coinitiator (either HP at 1 mol% or IVBE at 1,5 wt%). First it can be seen that the surface

temperature raises rapidly by virtue of the exotherm of the photopolymerization. Secondly, this temperature increase induces a thermal decomposition in depth and a nice thermal front propagates within the medium. From these curves, a front velocity can be determined to be 21 mm/min for HP and 9 mm/min for IBVE, demonstrating the photoinduced thermal frontal polymerization of EPOX under light.

a) Dual-curing of carbon-fiber composite

In order to avoid a premature gelation of the resin through thermal polymerization during the preparation process of the composites and before irradiation, we have used some inhibitors. A pot-life of more than one hour can be ensured, leaving enough time for the process.

6 plies of carbon fiber (200g/m²) were used for the fabrication of a composite. Infusion of the formulation (3wt% TPP⁺, 1,5wt% IBVE, 1wt% inhibitor, 94,5 wt% of a modified epoxy resin) was operated under vacuum. The total amount of resin was 34wt%. After infusion, the preparation was irradiated by a LED emitting at 395 nm (FireJet FJ200, 12 W from Phoseon) having a maximum irradiance peak at 395 nm (FWHM = 15 nm) and mounted on the arm of a robot (Kuka, see Figure 3). Irradiation time was 2 min at full intensity. During the irradiation, the surface temperature increased up to 105°C as a consequence of the curing process. After 20 min of cooling at room temperature, the composite was removed from the mould and analyzed.

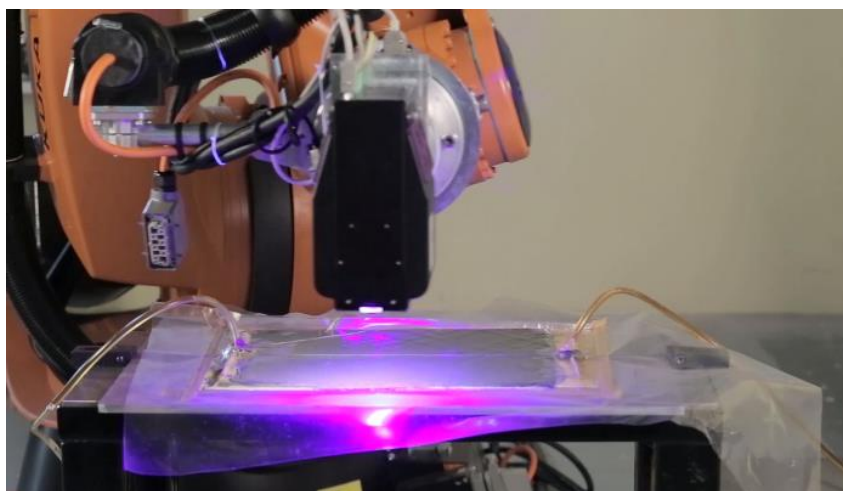


Figure 3. Experimental robotized setup for the irradiation of the composite with a LED.

Flexural modulus was measured using three-point bending test (ISO 14125). A mean value of 52.4 GPa was found for the carbon-fiber composite, demonstrating the validity of the process. Obviously, this new initiating system can be used either for opaque fibers as well as for transparent ones. Figure 4 shows the carbon-fiber composite discussed above and a glass-fiber sample made of 20 plies. The maximum thickness obtained using this process for carbon-fiber was 20 mm in our lab.

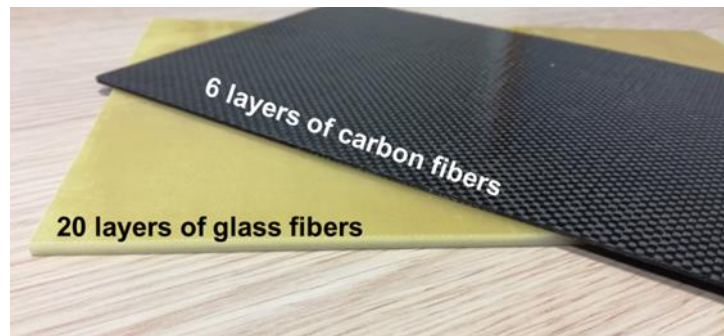


Figure 4. Example of carbon-fiber and glass-fiber samples obtained using the dual-cure technology.

Conclusion:

As shown in this paper, the dual-cure concept could be considered today as a smart technology for the curing of thick epoxy media. This “cure-on-demand” process opens up new opportunities to improve the manufacturing of carbon-fiber composites within a few minutes. Such systems appear to be promising alternatives to conventional high temperature processes.

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