

Visible light polymerization of epoxy resins: design for in-orbit curing of spatial structures

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ABSTRACT

The curing reaction developed to meet the needs of in-orbit curing of ultralight composite structures for spatial applications involves the visible light induced photopolymerization of epoxy resins initiated by cyclopentadienyl iron arene salt photolabile Lewis acids. The reactivity of photosensitive formulations including various types of epoxy resins and initiators was studied by monitoring the rate of initiator photolysis under different visible light sources. The resulting polymerization of epoxy functions was also monitored by FTIR analysis to examine the kinetic profile of the reactions as a function of composition and treatment (light source, temperature, thermal post-curing).

INTRODUCTION

The development of original architectural concepts such as inflatable and rigidizable structures for satellite equipments and spatial habitats is driving the need for new in-orbit rigidization methods.

Various original technologies have been considered and evaluated in the recent years.¹ They can be classified on the basis of the phenomenon inducing rigidization. Mechanical rigidization is obtained by stretching a polymer/aluminum laminate above its yield strain. Physical rigidization is obtained by inducing a phase transition in a polymer based material (cooled below its glass transition temperature), using shape memory components or by evaporation of a plasticizer or of a solvent. Chemical rigidization is obtained either by thermally or UV-induced polymerization. In orbit thermal curing can be triggered or accelerated by gaseous catalysts carried by the inflation gas. In this study, we are particularly interested in visible light induced photopolymerization of epoxy resins.

IN-ORBIT RIGIDIZATION METHODS

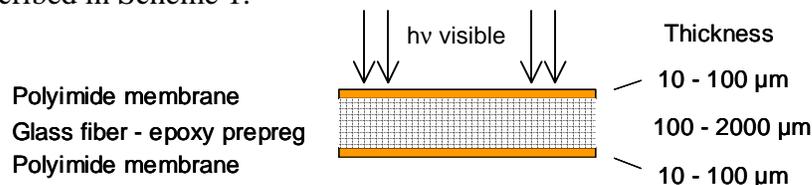
Fiber-reinforced composite materials with organic matrices are widely used in space applications and a variety of on-ground cured composites are qualified for in-orbit use. In a step further towards new uses of polymer composites in space applications, thermal processing methods developed and tested on ground in view of flight experiments.²

Light-initiated curing of composites in free space environment appears as a promising alternative process to turn a foldable, inflatable package into a rigid, load-bearing structure.³ However, many design and processing requirements are associated with the curing in free space environment of composites with complex constitution. The main aspects are listed for the different phases of the structure life.

For the manufacturing and during the non rigid phase, requirements relating to structural and fabrication complexity, compaction ability, foldability, shelf life, storage constraints, etc., must be taken into account. At the rigidization stage, the desired features are essentially associating on-command curing, fast treatment, energetic efficiency, for the reactivity aspects, together with low outgassing in space conditions. In the rigidized state, material properties must comply with the thermo-mechanical performances and exhibit sufficient dimensional stability, resistance to aging factors (vacuum, UV, atomic oxygen, electrons, protons...), as well as some specific properties regarding the particular functionality of the structure.

One major advantage of radiation-initiated polymerization is the temporal control by triggering the formation of a three-dimensional network resulting in the hardening of the starting resin material. Typical photocurable resin formulation includes network precursors, generally oligomers and monomers fitted with appropriate polymerizable groups (acrylates in the case of a free radical mechanism, epoxy or vinyl ethers for a cationic process) and an initiator (in small quantity typically about a few percents) whose function is to release the active centers when activated by deliberate exposure to UV or visible radiation. Various types of chemistries exist with a number of formulation options. The chemical nature of the propagation mechanism (i.e. free radical or cationic) is a choice deserving particular attention because of the possible incidence on major features of the design and processing of the rigidizable structure.

Unlike free radical systems, in cationic systems, the curing process does continue after the light source is turned off, but polymerization sometimes proceeds to a minimal extent, thus requiring a thermal bump, or prolonged heating, to be effective. The term “pseudo-living” polymerization is sometimes used to name this specific behavior. The many advantages of this option prompted us to develop an efficient curing procedure for a multi-laminate having the typical structure described in Scheme 1.



Scheme 1 – Typical structure and constitution of the foldable multi-laminate to be rigidized on-command by cationic curing under visible light.

To obtain by this curing method rigid networks exhibiting a glass transition temperature T_g significantly above the operating temperature, commercial epoxy resins derived from an aromatic were selected and adequately formulated. The model formulations studied for the present report are based on the prepolymers shown in Chart 1.

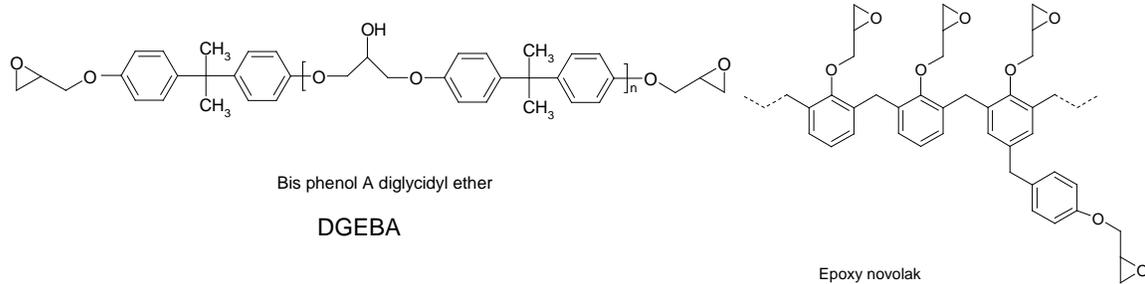


Chart 1- Examples of epoxy aromatic resins evaluated as matrix precursors in the prepregs

For an efficient exploitation of the incident UV-visible light, the absorption spectrum of the photoinitiator (or photoinitiating package) has to be adjusted to the spectral characteristics of both the multi-laminate and the light source. In the case of a representative structure where the radiation curable material is sandwiched between protecting thermoplastic films, the light filtering effect of the latter shall be overcome by minimizing the screen thickness, or alleviated by selecting an initiator exhibiting a long wavelength absorption dependent on the spectral features of the enveloping film.

The transmission spectra of Figure 1 clearly show the cut-off line at 320 nm by a 10 μm thick poly(ethylene terephthalate) [PET] film, whereas polyimide [PI] films do not allow the penetration of light for wavelengths shorter than 400 nm. Additionally, the dramatic reduction of transmitted light can be calculated at various operating wavelengths as a function of film thickness. Obviously, if PET absorption spectrum makes it possible to use a photoinitiator to cure the inner composite material with UV-A light, initiators sensitive to visible light are requested when using polyimide films.

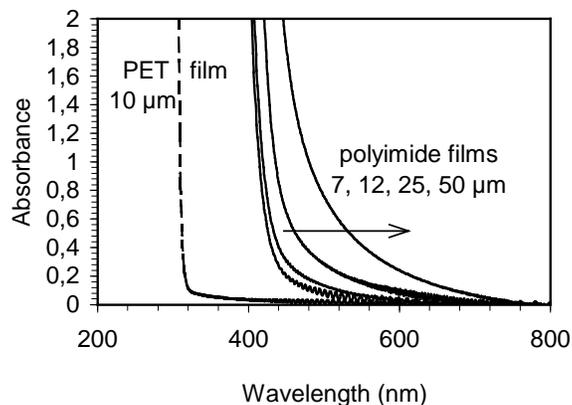


Figure 1 – UV-visible absorption spectra of protective thermoplastic films.

Various types of cationic initiators responding to visible light activation have been evaluated, including by means of spectral sensitization, electron transfer and free radical reduction of onium salts.⁵ On the basis of screening tests involving a preselection of cationic photoinitiators reported in the literature, the higher relative efficiency of arene cyclopentadiene iron salts prompted us to further investigate their ability to cure the multi-laminates in the desired irradiation conditions.⁴ The spectra reproduced in Figure 2 clearly show the extended absorption range of the 1-methylnaphthalene complex, offering a larger response domain beyond the cut-off line of a standard polyimide film.⁶

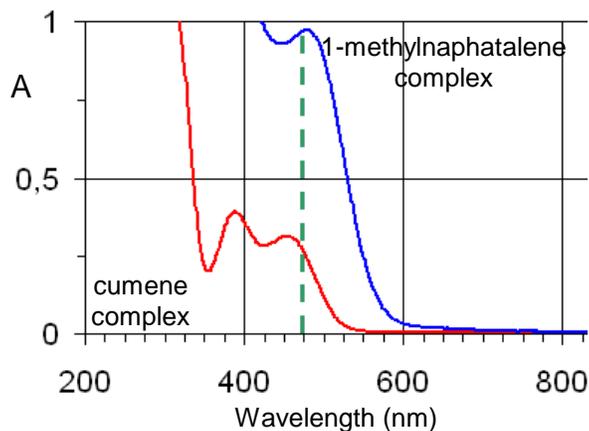
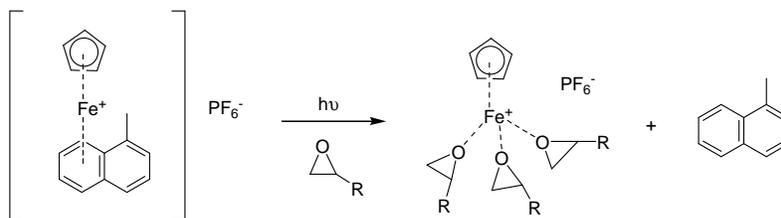


Figure 2 – UV-visible absorption spectra of arene cyclopentadienyl iron hexafluorophosphate (arene = cumene or 1-Me naphthalene, dichloromethane solution).

In the presence of epoxy functions, the photolysis of 1-methyl naphthalene cyclopentadienyl iron hexafluorophosphate leads to an exchange of ligand between the arene and three epoxy molecules to give the active species which induces cationic polymerization (Scheme 2).



Scheme 2 - Photolysis of arene cyclopentadienyl iron hexafluorophosphate in the presence of epoxides.

Our research was thus focused on the specific constraints of free environment conditions on the polymerization of epoxy resins initiated with visible light, and optional amplification by limited thermal post-curing. The behavior of the model formulations including the arene cyclopentadienyl iron complex salts was investigated in some details.

MONITORING AND MODELING OF PHOTOLYSIS

Kinetic modeling of the photolytic activation of the latent initiator with visible light was achieved using the data collected by UV-visible monitoring in representative conditions the decrease of the characteristic band of the selected photo-initiator at 475nm. The photolysis is followed by exposing the sample directly to the lighting source, or with a PET film (90 μm) and PI film (25, 50, 75 or 100 μm).

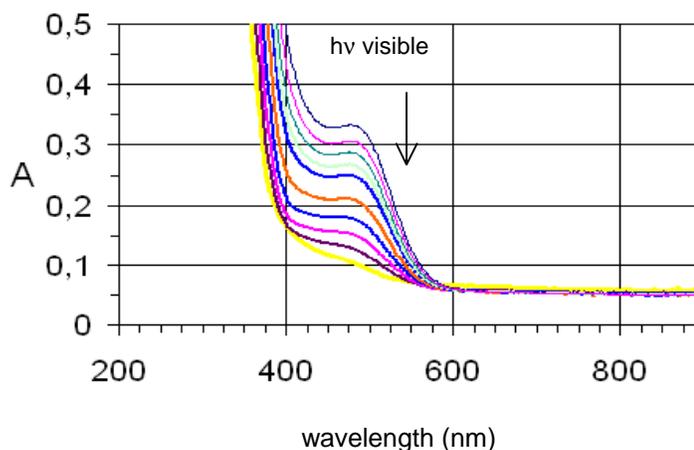


Figure 3 - Monitoring by UV-vis spectroscopy of 1-methyl naphthalene cyclopentadienyl iron hexafluorophosphate photolysis, 2 wt-% in DGEBA (irradiation under a cold visible light source with PET + PI film 25 μm).

The apparent reaction order has been determined by a graphical method. For the particular conditions of Figure 3, simple kinetic models based on integer orders were proposed. Without PI film a fractional apparent order n , $0 < n < 1$, is observed, whereas in the presence of polyimide films a neat 1st order is obeyed ($-\text{Ln}\alpha = k_{\text{app}} t$, with α the mol fraction of absorbing initiator at instant t), in agreement with the approximation derived from the Beer-Lambert law applied to low absorbance media ($I_{\text{abs}}(t) \propto [\text{initiator}]_t$).

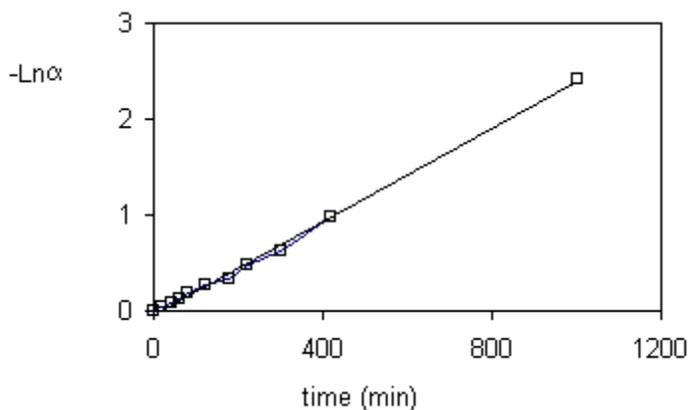


Figure 4 - Graphical determination of the 1st order kinetic constant for the photolysis of 1-methyl naphthalene cyclopentadienyl iron hexafluorophosphate photolysis, 2 wt-% in DGEBA ($-\text{Ln}\alpha = k_{\text{app}} t$, same conditions as for Figure 3).

The kinetics of the initiator photolysis have been studied with different light sources (Xe lamps, electro-luminescent diodes, cold visible light source). The influence on the kinetics of the quantity of photo-initiator in the resin and of the light filtering effect of the PI film was examined as well.

Photo-initiator half-life was shown to vary almost linearly as a function of PI film thickness (Figure 5). The collected data made it possible to obtain quantitative information on the kinetics of the initiator photolysis ($t_{1/2}$, k_{app} first order) and thus to determine the durations of exposition relating to a maximum photolysis (almost to completion). These results enabled us to study and model post-polymerization starting from well-defined chemical states.

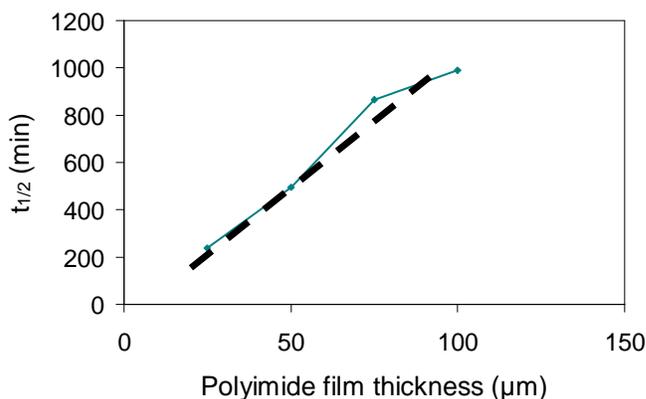


Figure 5 - Variation of photo-initiator half-life as a function of PI film thickness.

MONITORING AND MODELING OF POLYMERIZATION

In order to study the properties of the cured matrices, samples of the epoxy resins in the form of 2mm thick bars were prepared by controlling the curing parameters. The factors under investigation were the irradiation temperature, the post-curing temperature and post-curing duration. The conversion of epoxy functions of the resin is determined by infrared analysis. The results show that maximum conversion π is obtained from infrared measurements at 915 cm^{-1} (epoxy band), after irradiation and after 30-60 min of post-irradiation baking.

The various experiments conducted with epoxy resins of the DGEBA or novolak type exhibit common features. The epoxy conversion measured after complete initiator photolysis is low, not exceeding 15 to 20 mol-%. Post-curing allows the thermal activation of the polymerization process and to amplify the effect of photolysis. The significant increase of the limiting conversion by increasing the post-baking temperature was in all cases consistent with a typical control of the reaction by gradual vitrification. The values of the temperature of the primary thermo-mechanical relaxation ($T_{\alpha} \approx T_g$) measured by DMA confirms the possibility to achieve the formation of densely cross-linked networks (Figure 6). The somewhat anomalous behavior observed for post-baking temperatures exceeding 130°C will require further investigation on network microstructure.

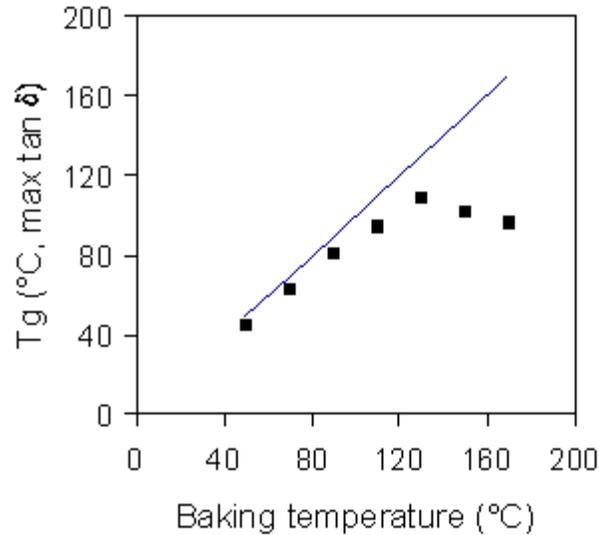


Figure 6 – Relation between thermo-mechanical relaxation (T_{α} or T_g) and baking temperature in DGEBA formulations containing 3 wt-% of initiator cured by exposure under visible light and post-curing.

The profile plotted in Figure 7 represents the temporal dependence of conversion in a BADGE formulation containing 3 wt-% of initiator cured by exposure under visible light and post-curing at 80°C. The steep initial slope weakens only when conversion approaches its maximum because of monomer depletion and of mobility restrictions. The continuous description by means of a phenomenological model⁷ was performed using the formalism of equation (1) with adjustable parameters c_{1-3} :

$$Conversion = \pi = (c_1 \times t) + c_2 - \frac{1}{(c_3 \times t) + c_2^{-1}} \quad (1)$$

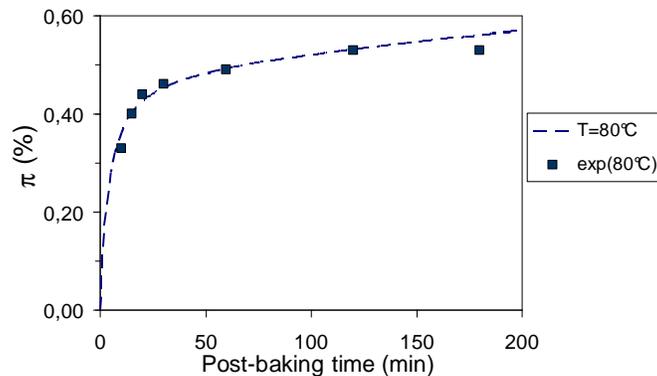


Figure 7 - Evolution of epoxy conversion versus time in a DGEBA sample (3 phr of initiator) during post curing at 80°C after irradiation: exp.points (■) and modelled profile (dotted lines).

Additional experiments conducted at temperatures ranging from 60 to 140° with a 20°C step allowed to determine and to quantify the influence of thermal activation on the different numerical parameters c_{1-3} .

It was thus possible, starting from the T_g vs conversion curve of a given epoxy resin, to predict the glass transition temperature of the final material on the basis of the treatment parameters (post baking duration and temperature). The curing of various prepregs designed for exhibiting a glass transition at a desired temperature (from -20°C to $+140^\circ\text{C}$) was achieved by using the developed model.

CONCLUSION

A novel photocurable material triggered by visible light has been designed for in-orbit curing of composite laminates. The structure and the constitution of the multilayered-system sandwiched between protective PI layers induces stringent requirements on the spectral characteristics of the initiating system. Monitoring by UV-visible spectroscopy of the photoinitiator photolysis (dissolved in a representative epoxy resin) allows to obtain quantitative information on the kinetics ($t_{1/2}$, k_{app} first order).

For simple models formulation based on DGEBA or related epoxy resins, photolysis and polymerization can be precisely monitored (conversion rate, thermo-mechanical properties...) by using suitable analytic techniques. The profiles representing the progress of conversion as a function of curing time can be easily modeled by means a phenomenological equation. The glass transition of the corresponding material can be predicted on the basis of applied processing conditions. Further work is under way to propose novel prepolymers curable by this procedure and fully compliant with the processing and low-outgassing criteria required for in-orbit curing.

ACKNOWLEDGEMENTS

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REFERENCES

- 1- "Rigidization Mechanisms and Materials", Dave Cadogan, ILC Dover, in Gossamer spacecraft : Membrane and inflatable structures technology for space applications, Edited by H. M. Jenkins, Progress in Astronautics and Aeronautics, Vol 191, Chapter 7, pp257-279.
- 2 - D. Savini, P. Besso, P. Tatalias, K. van't Klooster and W. Ritz, "Electrical Performance of a 10-m Inflatable Reflector for Land Mobile Communications." *ICAP 91 - 7th International Conference on Antennas and Propagation, York (UK), April 15-18, Proceedings 2, pp853-856, (1991).*
- 3 - B. Defoort, V. Peypoudat, M. C. Bernasconi, K. Chuda, X. Coqueret, in "Computational methods in applied sciences", Vol 3, Textile composites and inflatable structures, Eds. E. Oñate and B. Kröplin, pp 259-283, Springer Dordrecht 2005.
- 4 - B. Defoort, X. Coqueret, D. Lacour, Rigidization of structures to be deployed by inflation, particularly for use in space - PCT Patent WO 2006 043009.
- 5 - J.P.Fouassier, "Photoinitiation, Photopolymerization and Photocuring Fundamentals and Applications", Hanser, 1995.
- 6 - K. Meier, H. Zweifel, SME Technical Paper, Radcure Europe 1085, 417 (1985).
- 7 - B. Defoort, D. Defoort, X. Coqueret, EB initiated polymerization of acrylate compositions, 2 Simulation of thermal effects in thin films. *Macromol Theory Simul.* 2000, 9, (9), 725-734.