

Photoinitiated Frontal Polymerization for Rapid Repair and for Studying Spherically Propagating Thermal Fronts

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Abstract

Frontal polymerization is a localized reaction zone that propagates from the coupling of thermal transport with the Arrhenius dependence of the reaction rate of an exothermic polymerization. In the photoinitiated process, light is used to initiate a thermal front that converts monomer into a crosslinked network. The advantage of the process is that rapid curing of virtually unlimited depth can be achieved. We use a photoinitiated frontal polymerization process, which is an extension of the frontal polymerization process for curing filled and unfilled monomer resins. We also can study spherically propagating polymerization fronts.

Introduction

Composites are materials that are comprised of a matrix binder and filler. The choice of the filler and matrix materials will dictate the physical and mechanical properties of the cured composite. Composites are generally applied in a monomer form and cure slowly via chemical reactions that produce a network that serves as a binder for the filler. Frontal polymerization is a self-propagating localized reaction that allows rapid curing without any intrinsic limits to the size of the sample. The front propagates from the coupling of the heat release of the reaction, thermal diffusion and the strong dependence of the reaction rate on temperature. It is basically a ‘flame’ that propagates through the liquid resin and instead of leaving ash in its wake, the front leaves a solid polymer.

Frontal polymerization is a process in which the reaction propagates directionally through the reaction vessel. The three types of frontal polymerizations are thermal frontal polymerization (TFP), which uses an external energy source to initiate the front,¹⁻⁴ photofrontal polymerization in which the localized reaction is driven by an external UV source,⁵⁻⁹ and isothermal frontal polymerization (IFP), which relies on the Norrish-Trommsdorff, or gel effect,^{10, 11} that occurs when monomer and initiator diffuse into a polymer seed (small piece of polymer).¹²

Thermal frontal polymerization begins when a heat source contacts a solution of monomer and thermal initiator. Alternatively, a UV source can be applied if a photoinitiator is also present.¹³ The area of contact (or UV exposure) has a faster polymerization rate, and the energy from the exothermic polymerization diffuses into the adjacent region, raising the temperature and increasing the reaction rate in that location. The result is a localized reaction zone that propagates down the reaction vessel as a thermal wave.¹⁻⁴ The simplest example is a front propagating down a glass tube (Figure 1).

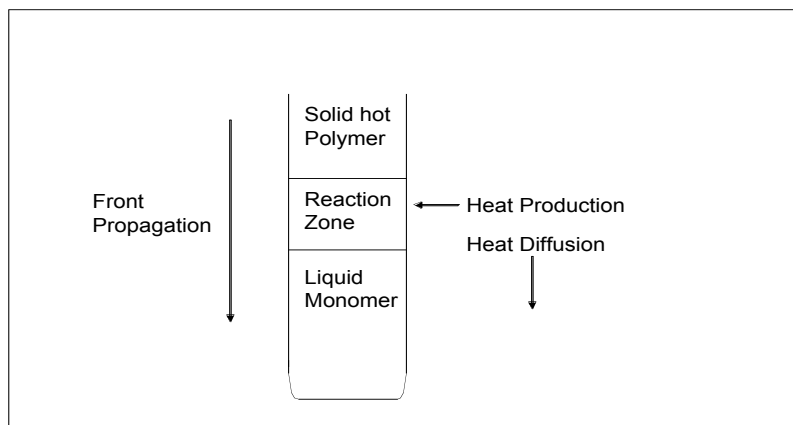


Figure 1. Schematic of Frontal Polymerization

An overwhelming majority of work with TFP has been on free-radical systems but other chemistries can be used. Begishev et al. studied frontal anionic polymerization of ϵ -caprolactam,^{14, 15} and epoxy chemistry has been used as well.¹⁶⁻²⁰ Mariani et al. demonstrated Frontal Ring-Opening Metathesis Polymerization.²¹ Fiori et al. produced polyacrylate-poly(dicyclopentadiene) networks frontally,²² and Pojman et al. studied epoxy-acrylate binary systems.²³ Polyurethanes have been prepared frontally^{24, 25} as well as polyurethane-nanosilica hybrid nanocomposites.²⁶ Frontal atom transfer radical polymerization has been achieved²⁷ as well as frontal polymerization with thiol-ene systems.²⁸ Crivello has developed photoactivated cationic frontal polymerization, which can be performed in thin layers.^{29, 30}

A significant issue for applying frontal polymerization to real-world applications is the issue of pot life, i.e., how long can the initiator-monomer solution remain at room temperature before reacting homogeneously. McFarland et al. sought to address this issue by microencapsulating a free-radical initiator, cumene hydroperoxide, and dispersing the capsules throughout a mixture of 1,6 hexanedioldiacrylate (HDDA) and silica gel.^{31, 32} Because the initiator was sequestered from the monomer, it could not initiate polymerization until the capsule burst open upon heating.

A current comprehensive bibliography of frontal polymerization can be obtained at <http://pojman.com/FP.html> along with movies and explanations of the FP process.

The first example of UV-initiated frontal polymerization was in a patent in 2001 on “Ultraviolet curable resin compositions having enhanced shadow cure properties.”³³ UV-ignited frontal epoxy curing was studied by Mariani et al.³⁴ In 2005, Nason et al. reported a detailed study of UV-Induced frontal polymerization of multifunctional (meth)acrylates.¹³ Recently Pojman et al. reported UV-ignited spherical fronts.³⁵



Figure 2. A hole was drilled in block of polyethylene. The resin, initiator and filler (calcium carbonate) were placed into the hole. The front was ignited with a lamp, and seconds a rock-hard material was formed.



Figure 3. A front propagating in a free-standing resin

Advantages over traditional Methods

Composites are traditionally cured by using a two-part formulation that reacts upon mixing or by using an autoclave to cure the formulation at a high temperature. BONDO and fiberglass are cured by mixing two components, one of which uses a redox reaction to slowly initiate the polymerization at room temperature. Five-minute epoxy is also a two part formulation that starts reacting upon mixing. The disadvantage is that once the components are mixed, the systems is reacting and so the time for setting up the materials is limited. Large composites such as for aerospace applications are usually cured in a large oven, or autoclave.

Frontal polymerization avoids the problem of a system curing at room temperature and of the necessity of mixing two components. All the components required for reaction are present in the formulation. All that is required is the initial input of energy to start the front. Also, because the reaction uses its own heat release to drive the process, no autoclave is necessary.

Experimental

Monomers were obtained from UCB Chemicals and Aldrich Chemical Company. Luperox 231 (1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane) was obtained from Atofina. Darocur 4265 and 1173 were obtained from Ciba. All chemicals were used as received.

Materials

Trimethylolpropane triacrylate (TMPTA-N) was obtained from CYTEC, Surface Specialties. Trimethylolpropane tris(3-mercaptopropionate) (TT1), and Triethyl amine were purchased from Aldrich. 1-hydroxy-cyclohexyl-phenylketone (SARCURE SR1122) was purchased from Sartomer. 1,1-Bis(ter-butylperoxy)-3.3.5-trimethylcyclohexane (Luperox® 231P75) was obtained from Arkemagroup. All of the chemicals were used without purification.

1, 6 hexanediol diacrylate (90% technical grade), ammonium persulfate, and dimethyl sulfoxide (DMSO) were used as received from Aldrich.

Experiments with 1, 6 hexanediol diacrylate in DMSO

An 8.0 mM solution of ammonium persulfate was prepared fresh daily by adding 0.072 g of ammonium persulfate to 40 mL of DMSO. An aliquot of 30. mL of this solution was transferred to a 150 mL beaker and stirred with 20. mL of HDDA. Then 2.7 grams of CAB-O-SIL was slowly stirred until all the powder was dispersed. The photoinitiator solution consisted of 0.33 g of Irgacure 184 dissolved in 10 mL of HDDA to which 0.67 g of CAB-O-SIL was dispersed. The HDDA-DMSO solution with silica gel was added to half of the reactor. A small amount of the photoinitiator solution was injected into the HDDA-DMSO solution. The reactor was then completely filled with the HDDA solution.

To prevent cracking, diethyl phthalate was used. The optimal solution was 35% HDDA, 53% DMSO, 12% diethyl phthalate and 6.7% CAB-O-SIL.

To ignite the front, a 3 mW 365 nm UV light source was shone on the sample until polymerization began in the center.

Thiol-Ene System Gel Formation

303 mL of TMPTA-N and 123.48 mL of Trimethylolpropane tris(3-mercaptopropionate) were mixed inside a 1000 mL, 89 mm-400 screw cap, wide mouth glass jar with a stir motor equipped with a

3-bladed propeller at 430 rpm. The jar was kept inside a 0 °C ice-water bath during the mixing. The TMPTA-N and trimethylolpropane tris(3-mercaptopropionate) were mixed for 1 minute. After 1 minute, the stirrer was turned off, and 6.48 mL of 1,1-Bis (ter-butylperoxy)-3,3,5-trimethylcyclohexane and 2.16 mL of Triethyl amine were added to the mixture and mixed with the same stirrer and propeller at the same speed. After the mixing, vacuum was applied to the solution for 1 hr to remove dissolved gas. After applying the vacuum, the jar was kept inside the cooling bath for 3 and a half more hours, and then it was taken out of the cooling bath. 1 cm³ of initiator gel, which contained photo initiator and thermal initiator, was held in the center of the solution with a needle, and the solution was left to gel for 1 and a half hours. The solution gelled after 6 hours from the beginning of the application of vacuum. After those 6 hours, the gel was exposed to a 365 nm radiation from a Novacure lamp, which had an intensity of 16 mW cm² for 2 minutes to ignite the front in the center. The light guide was placed over the jar, 10 cm from the center of the gel.

Initiator Gel

25.25 mL of TMPTA-N, 10.29 mL of Trimethylolpropane tris(3-mercaptopropionate), 0.36 mL of 1-hydroxy-cyclohexyl-phenylketone, 0.74 mL of 1,1-Bis(ter-butylperoxy)-3,3,5-trimethylcyclohexane and 0.092 mL of Triethyl amine were mixed inside a 100 mL glass beaker with a magnetic stirrer for 5 minutes. The beaker was kept inside the ice-water bath for 5 hours, after which, it became a gel. After gelation, 1 cm³ of this gel was placed in the center of the gel that contained only the thermal initiator.

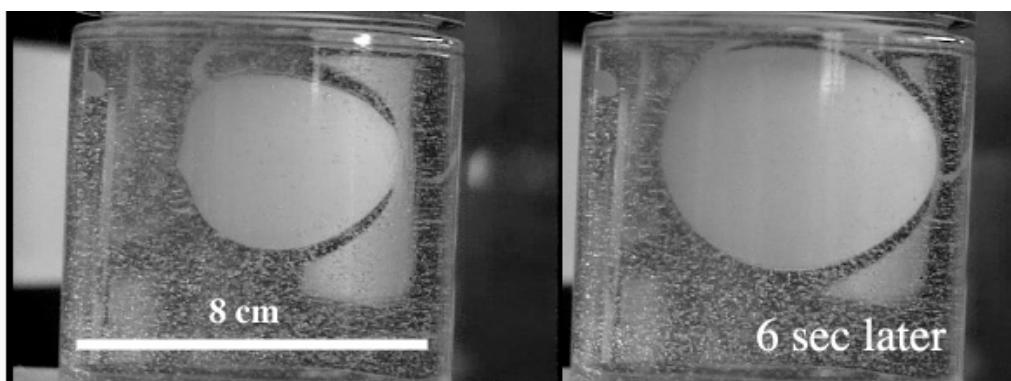


Figure 4. A front propagating in a solution of 1,6 hexanediol diacrylate (35%), DMSO (53%), diethyl phthalate (12%) and CAB-O-SIL (6.7%). Ammonium persulfate was the thermal initiator and Irgacure 184 the photoinitiator.

Results

We created fast curing putty with TMPTA, Luperox and calcium carbonate. A hole of any depth could be filled with the putty (Figure 2) and then cured in seconds by initiating the front with UV light. It was also possible to create freestanding putties (Figure 3).

We created spherically-propagating fronts using liquid-solid systems. By adding silica gel we can suppress convection but still have an initially transparent system. Figure 4 shows such a system in which a drop of photoinitiator was injected in the center of the HDDA-DMSO-persulfate solution that

contained enough silica gel to make it highly viscous. By exposing the system to 365 nm radiation, the front ignited in the center.

The thiol-acrylate system is a crosslinked gel. Using the thiol-acrylate system, we initiated a front from a gelled cube containing photoinitiator (Figure 5.)

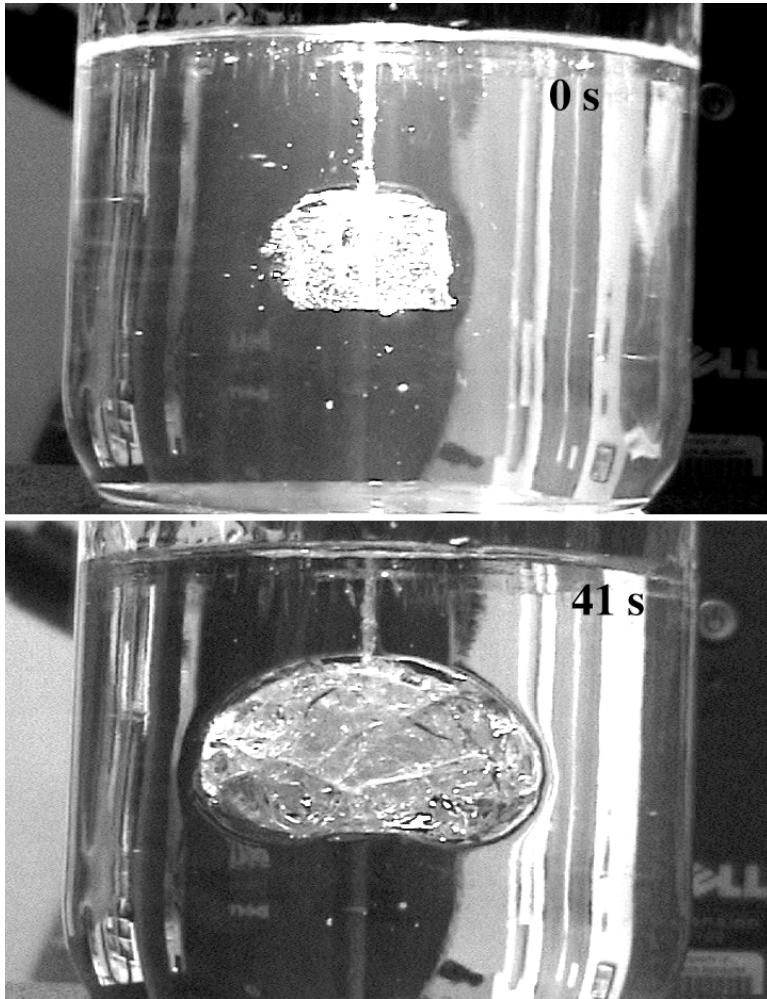


Figure 5. Using a cube of photoinitiating gel it is possible to initiate fronts with non-spherical initial conditions. Diameter of reactor is 8 cm.

Conclusions

Photoinitiated frontal polymerization can be used for rapid curing of putties for the repair of holes in many materials. A long pot life can be combined with rapid curing that can be initiated by UV light. There is no limit to the depth of the cure that can be obtained

Photo-initiation can be used to create spherically-propagating polymerization fronts. Gels created with thiol-acrylates are the most impressive since fronts can be initiated from any initial geometry.

Acknowledgements

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