

Radical Induced Cationic Frontal Polymerization as a Versatile Tool for Epoxy Curing and Composite Production

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ABSTRACT: Radical induced cationic frontal polymerization (RICFP) is an extremely powerful and elegant alternative curing technique that allows cationic bulk curing of epoxy resins with very little energy consumption, as well as curing in compartments that are not readily accessible. We recently introduced a bisphenol-A diglycidylether (BADGE) based system that allows the bubble-free photocuring of this widely used epoxy resin. In this article, we describe the high storage stability and possibilities to influence the curing speed via the initiator concentrations of different formulations. These properties allow the adjustment of the frontal polymerization to ones need. We also

show that the (thermo)mechanical and electrical properties of frontal cured epoxy polymers compares favorably with those of state of the art material. Finally, different strategies to overcome the challenges on producing epoxy resin based mica composites via RICFP are presented. © 2016 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, 00, 000–000

KEYWORDS: BADGE; benzopinacol; bisphenol-A diglycidylether; cationic frontal polymerization; CFP; iodonium; radical induced cationic frontal polymerization; RICFP; TPED

INTRODUCTION Epoxy resins are used since several decades for numerous applications like coatings, casting formulations, adhesives, and composites with glass fibers, carbon fibers, or lacquers. Epoxy resins can either be polymerized thermally by polyaddition of amines or anhydrides, or by (light induced) cationic ring opening of the epoxy group.¹

Although thermal curing is cheap and very easy to use, it is either energy intensive or bears the disadvantage that the curing in place cannot be realized. The rather short potlife of highly reactive formulations needs the operator to mix the formulation right before usage. Manipulation is therefore very limited. On the other extreme, alternative strategies are very low reactive formulations that need either curing in ovens with high energy uptake (typical in vacuum-pressure-impregnation processes), or need hours to days for complete curing.

Classical cationic photopolymerization allows the curing of monomers with a large variety of functional groups like oxetanes, vinyl ethers, alkenes, or lactones. Unfortunately, this technique is limited to thin layers because of the low penetration depth of the UV light. To enable cationic photocuring, the use of cationic photoinitiators (e.g. diaryl iodonium salts)

which are also called photo acid generators (PAGs) is required. Upon excitation with (UV) light they cleave and form carbocations.² The polymerization process itself is either initiated by the formed carbocations or by protons that have been abstracted by the carbocations (Fig. 1).

The decomposition of the photoacid generator can be induced either by irradiation with (UV) light or alternatively also by a redox reaction with suitable radicals, leading to the process of radical induced cationic polymerization (RICP). Several basic research articles on this topic have been published, e.g. by Abdul-Rasoul et al.,⁴ Yagci and Reetz,⁵ Crivello and Liu,⁶ and Crivello et al.⁷ Those reactive radicals are formed by the thermal cleavage of classical radical, thermal initiators (RTIs) such as dibenzoylperoxide (BPO), azobis(isobutyronitrile) (AIBN), or C-C labile compounds like benzopinacol (TPED, see also Fig. 2). The disadvantage of this method is that the whole formulation has to be heated for polymerization.

To circumvent this drawback, an alternative curing method called frontal polymerization (FP) can be used. FP is a reaction in which, after a proper stimulus, a local reaction zone is formed which will start further reaction in its adjacent

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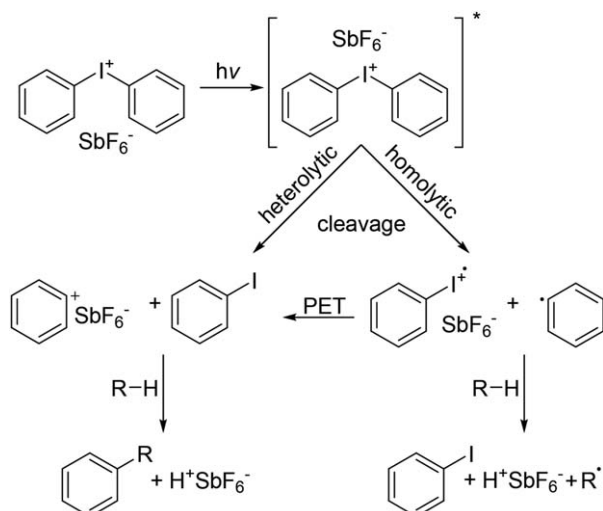


FIGURE 1 Example of light induced decomposition of a diphenyliodoniumsalt and subsequently photoacid generation. Also depicted is the possible photoinduced electron transfer (PET) from the radicalcation, adapted from Dadashi-Silab et al.³

regions leading to a so-called moving reaction front (Fig. 3). It was firstly described by Chechilo and Enikolopyan⁸ in 1974 and investigated in detail, among others, by Pojman et al.^{9–11} In this work, the term “frontal polymerization” always refers to a thermal frontal polymerization according to Pojman’s classification. The propagation of this reaction is mostly due to the thermal decomposition of suitable initiators. The required heat for the cleavage is delivered from the polymerization heat.

Radical induced cationic frontal polymerization (RICFP), the combination of FP and RICP, is the solution that overcomes both of the disadvantages of thermal and classical photocuring of epoxy resins: it allows bulk curing with evanescent energy consumption and fast curing in place in combination with long potlives.

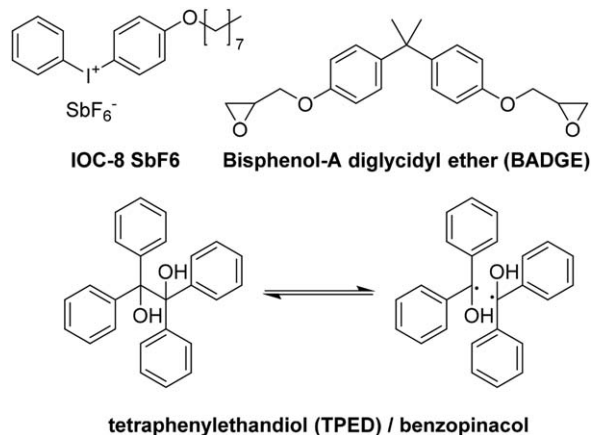


FIGURE 2 Structure of the photoacid generator IOC-8 SbF₆, the epoxy resin bisphenol-A diglycidyl ether (BADGE) and the scheme of the radical formation of the C-C labile compound benzopinacol (TPED) which is used as radical, thermal initiator (RTI).

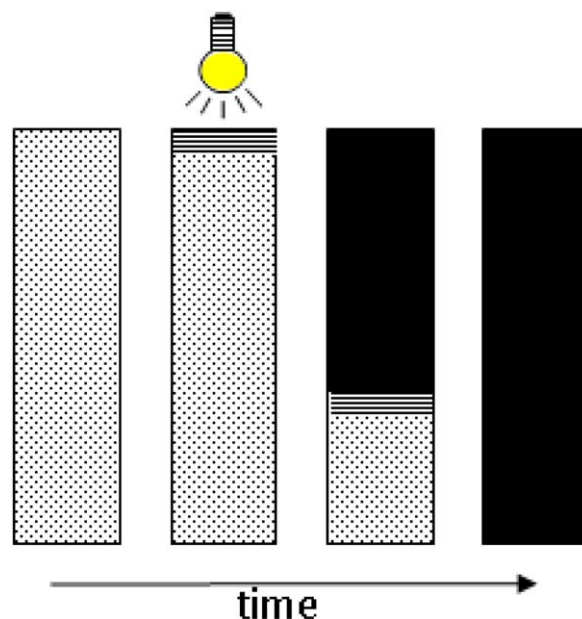


FIGURE 3 Scheme of an irradiation induced thermal frontal polymerization (dotted = uncured formulation, striated = reaction zone, black = cured polymer). [Color figure can be viewed at wileyonlinelibrary.com.]

The reaction mechanism of RICFP on epoxy resins was already described by Mariani et al.¹² RICFP can either be initiated by a thermal stimulus or by irradiation, like Mariani’s system. Scognamillo et al. used latent BF₃-amine initiators for the thermal initiated RICFP of trimethylolpropane triglycidylethers.¹³

In a previous article¹⁴ we described the newly developed system and compared it to state of the art cationic frontal polymerization. The combination of the widely used epoxy resin bisphenol-A-diglycidylether (BADGE) with the thermal, radical initiator benzopinacol (TPED), and a hexafluoroantimonate based iodoniumsalt (IOC-8 SbF₆) as photoacid generator (PAG) leads to nonporous polymers. The C-C labile compounds TPED showed very good reactivity towards the cleavage of iodonium based PAGs whereas all other tested RTIs were not able to sustain any stable front in combination with BADGE as curable resin. Sulfonium-based PAGs will not work for RICFP because of their inadequate redox potential which does not allow for proper cation formation.

In this article we present a detailed view on this system with respect to storage stability, influences of initiator concentration on the front parameters, mechanical and electrical properties of the resulting polymer, and sensitizer effects on the initiation in unfilled and filled systems.

EXPERIMENTAL

Materials

BADGE (Araldite MY 790-1, Huntsman), methylhexahydrophthalic anhydride (MHHPA, Aradur HY 1102, Huntsman), mica powder (calcinated, grain size 0–200 μm, Isovolt), and

bis-4-(methoxybenzoyl)diethylgermanium (Ivocerin, Ivoclar Vivadent) were kindly provided as gifts. 1,1,2,2-Tetraphenyl-1,2-ethandiol (TPED, Fluka) *p*(octyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-8 SbF₆, ABCR), 2-isopropylthioxanthone (ITX, Quantacure), and perylene (Sigma-Aldrich) were purchased and used as received. Methylene chloride (DCM, Donauchem) was distilled prior to usage.

As a benchmark system for the (thermo)mechanical and electrical properties, the commercially available Araldite MY 790-1 (BADGE) together with the hardener Aradur HY 1102 (MHHPA) was used in formulations with a 1:1 ratio by weight and the addition of 3 wt % (based on the whole formulation) of a Zn salt of an organic acid as accelerator. Typically curing conditions for this systems are in forced-air ovens at temperatures of 150 to 160 °C for 16 to 26 h.¹⁵ Usually the samples were cured for 1 day in the oven at 160 °C.

Rheometry for Storage Stability

For the evaluation of the storage stability, formulations with 1 and 2 mol % each of the PAG and RTI were prepared. These formulations were compared to the uncured benchmark formulation. All formulations have been stored protected from light at 50 °C in a forced air oven.

The viscosity measurements were done on an Anton Paar MCR 300 Rheometer with Peltier oven and CP-50 measurement system. Measurement was conducted in rotation with a shear rate of 100 s⁻¹ for the duration of 100 s at a constant temperature of 50 °C (to prevent shear induced crystallization at temperatures around the melting point). For the analysis the last viscosity value of this 100 s period was taken. All measurements have been conducted in triplicate and the results have been averaged.

Frontal Polymerization

The frontal polymerization setup and method is described in detail in our recent article.¹⁴ The setup for the evaluation of RICFP consists of a mold for the polymerization made from poly(tetrafluoroethylene) (PTFE), a lightguide (8 mm diameter), and UV source (Exfo, Omnicure S 2000 series) for the initiation of the polymerization, thermocouples, and a camera for the analysis of the front properties (Supporting Information Fig. S1). The front is able to propagate horizontally along a length of 70 mm with a constant width of 10 mm. The mold is 5 mm deep. The initiation is done on one end of the mold, on an area of about 1 cm² with UV/Vis-light of 320 to 500 nm, with a light intensity of 3 W/cm² at the tip of the light guide and a light intensity of ~500 mW/cm² at the surface of the formulation. After the initiation the reaction will propagate without further irradiation being necessary. Preliminary experiments showed that the light intensity varies along with the radius with its highest intensity in the center. However, this does not influence the onset of the front, since the frontal polymerization starts from all points equally.

Frontal Polymerization Sample Preparation

Preparation of the samples is described in our last article.¹⁴ A typical formulation for three frontal polymerizations

consists of 15 g BADGE resin (44 mmol), 0.163 g TPED (1 mol %) as RTI, and 0.287 g IOC-8 SbF₆ as PAG (Fig. 2). To ease the dissolution of the initiators, they are dissolved in methylene chloride (typically 3 mL) prior to mixing with the resin. Afterwards the methylene chloride has to be removed completely in vacuum (typically 0.02 mbar for 3 h) to prevent bubble formulation during the polymerization step.

(Thermo)Mechanical Investigations

DSC Measurements

For the *T_g* measurements, the samples were taken from the center part of the RICFP polymer sticks and milled with a Retsch Cryomill to yield a fine polymer powder. For the *T_g* determination of the benchmark system the broken specimens from tensile testing were taken and milled like the other samples. Also pure photocured BADGE was analyzed towards its *T_g*. For this purpose, unused samples of the conductivity measurements were taken and milled like the RICFP samples.

These powders were accurately weighed into aluminum pans and the DSC signal was measured on a Netsch STA 449 F1 in two cycles from 25 to 250 °C with 30 K/min, held 5 min at 250 °C and subsequently cooled to 25 °C with 20 K/min. The *T_g* was determined from the second run. Each measurement was done in triplicate.

Tensile Testing

For tensile testing, specimens (75 × 4 × 3 mm) according to ISO 527-2, type 5A, were manufactured using a PTFE mold (dimensional sketch is depicted in Supporting Information Fig. S4). The formulation used to prepare the specimens of the cationic cured BADGE consisted of 1 mol % IOC-8 SbF₆ in BADGE resin. The formulation was cured in an Uvitron IntelliRay 600 broadband UV chamber at ambient temperature at 50% intensity for 120 s. Cut out of the specimens of a RICFP polymerized plate was not possible, due to the brittleness of the resulting polymer. For the specimens of the benchmark system a formulation like described in the Materials section was prepared in the same molds.

After polymerization of the materials the specimens were polished to remove any artefacts from the surfaces. Tensile testing was done using a Zwick Z050 tensile testing machine equipped with a 1 kN load sensor. Crosshead speed was 2 mm/min, strain was measured with a mechanical extensometer. From every material at least three specimens were tested.

(Charpy) Impact Resistance

The polymer samples were polymerized using a poly(dimethylsiloxane)-mold with cavities of 80×10×4 mm. A formulation with 1 mol % of PAG in BADGE was prepared and cured with an Uvitron IntelliRay 600 UV-chamber at ambient temperature with 50% intensity for 120 s. The mold was placed exactly horizontal to achieve flat and uniform samples. Also here it was not possible to cut the specimens out of a RICFP polymerized plate due to the high brittleness of the resulting polymer. Even notching of the samples for a notched impact

resistance was not possible, which was the reason for testing all specimens unnotched.

The samples of the benchmark system were prepared in the same mold with a formulation and curing process like described in the Materials section.

Five polymer samples of each formulation were polished and measured according to DIN EN ISO 179-1eU at ambient temperature on a CEAST 9050 impact pendulum equipped with a 4 J hammer. The final impact resistance value was normalized to the width and thickness of the tested specimen. The ratio of work necessary to break a specimen to the cross-section of the sample at the fracture site yielded the desired impact resistance.

Measurement of the Electrical Conductivity

For the preparation of all electrical characterization samples a formulation with 1 mol % PAG in BADGE was used. Since the preparation method for this kind of samples is not suitable for curing resins thermally, the relevant data for comparison with the benchmark system were taken from the technical datasheet of the manufacturer.¹⁵

Sample Preparation

For the conductivity measurements photopolymerized disks with 50 mm diameter and 0.5 mm height were used. They were prepared with the aid of a photorheometer with a plate to plate measuring (PP50 stainless steel, disposable) system. The uniform UV irradiation was produced by an Omnicure S2000 series with a 320 to 500 nm filter and a 5 mm liquid filled lightguide. The duration of irradiation was 480 s and during the irradiation there was no oscillation/spinning of the measuring system to prevent shear-induced crystallization.

Conductivity Measurement

The conduction current measurements were performed in a three-terminal cell by means of a Keithley 617 electrometer. The test setup is illustrated in Supporting Information Figure S4. In order to protect the electrometer from over-currents, the instrument was connected to the measuring electrode via a series resistor. The poling DC voltage was supplied to the sample via a Rogowski-profiled electrode made of aluminum.

The calculation of the volume resistivity is explained in detail in the supplementary document (section 5).

AC Breakdown Measurement

For the AC breakdown measurements samples of 50 mm diameter but 2 mm height were used. They were prepared with the same setup, formulation and method as the samples for the conductivity measurements but with a higher gap size (2 mm).

The AC breakdown test setup uses cylindrical electrodes. The test samples and electrodes are immersed in mineral oil to avoid potential flashovers. The rate of voltage rise is 2 kV/s. The experimental setup is depicted in Figure S5 in the Supporting Information.

Photo-DSC

For photoreactivity studies a photo-DSC 204 F1 from Netzsch was used. The resins were accurately weighed into an aluminum pan (25 ± 1 mg) and irradiated with filtered light for 15 min (Exfo OmniCure series 2000, 320–500 nm, 3 W/cm² measured at the tip of the light guide). An empty pan was used as reference and irradiation was conducted at 50 °C under inert atmosphere (N₂ flow of 20 mL min⁻¹). The heat flow of the photopolymerization was recorded as a function of time. After the first irradiation period the sample was irradiated for another 15 min to correct the polymerization heat flow by the heat generated from light absorption of the sample. The curve from the second run was always subtracted from the curve of the first. All measurements were conducted in triplicate.

For the analysis of the results two parameters have been used: The time until the maximum heat flux is reached (t_{Max}) and the conversion of the monomer based on the heat released by the exothermic polymerization reaction. To calculate the conversion the area under the DSC curve was set in relation to the theoretical polymerization heat of BADGE, which was determined to be 487.6 J/g (see Supporting Information section 7).

RICFP of Composite Materials

The formulations for the RICFP of composite materials were prepared with the same method as for the basic RICFP studies. The initiators were dissolved in the smallest possible amount of dichloromethane, and the weighed amount of mica powder was mixed with this solution prior to the addition of the BADGE resin. Subsequent removal of the solvent was conducted in vacuum identical to the aforementioned method.

The polymerization process, irradiation parameters, and the mold were the same for the composite studies as for the basic studies.

For the unsensitized formulations where the photoinitiation was not possible, initiation was done by holding the tip of a common soldering iron (set to temperatures of about 250 °C) in the formulation at one end of the mold. If initiation did not happen within 2 min or only local polymerization without formation of a front occurred, the experiment was noted as negative.

RESULTS AND DISCUSSION

Basic RICFP Studies

Storage Stability

Storage stability of prepared formulations is crucial for their widespread acceptance not only in industrial applications but also in basic research. Not only economic considerations but also reproducibility of the polymerization process are the driving forces for this interest.

To analyze the storage stability mixtures of the bisphenol-A diglycidyl ether resin (BADGE) together with the radical,

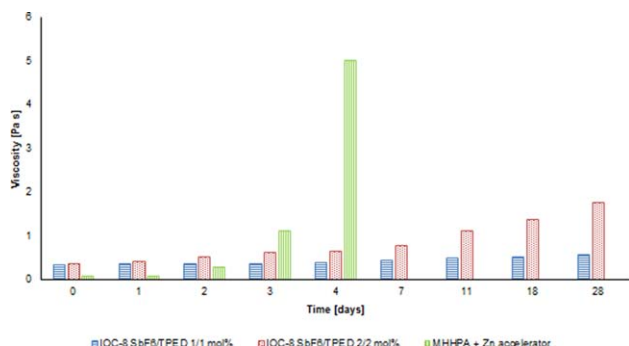


FIGURE 4 Viscosity of three different BADGE formulations depending on the date of measurement. [Color figure can be viewed at wileyonlinelibrary.com.]

thermal initiator (RTI) and the photoacid generator (PAG) were prepared in two different concentrations. Based on previous experiments concentrations of 1 and 2 mol % of each thermal initiator and photoacid generator were selected.¹⁴ Also a commercially available system containing BADGE and an anhydride based hardener (MHHPA) together with an organic Zn salt as accelerator was tested as a benchmark system. Since the BADGE formulations tend to crystallize if stored at temperature below 50 °C all formulations were stored at 50 °C and protected from light to prevent unwanted activation of the photoinitiator.

To get a general idea of the storage stability regarding pregelation of the formulations their viscosities were measured by rheometry directly after mixing and after certain time intervals.

As can be seen in Figure 4, the formulation with 1 mol % of each PAG and RTI is perfectly stable if stored at 50 °C and light protection. If the concentrations of the initiators are raised to 2 mol % each the viscosity slightly increases after 1 week of storage but is still suitable for processing. The benchmark formulation with the anhydride shows strong increase of the viscosity already after 3 days. At day 5 the formulation got inhomogeneous and measurement of the viscosity was not possible anymore. The vast difference in storage stability is most probably due to the different hardening mechanisms of the formulations. The photopolymerizable formulations are stored at a temperature where the cleavage of the radical, thermal initiator rarely occurs. For the thermal curing system the addition reaction of the anhydride and the epoxide is already quite quick which leads to a very limited storage stability if the accelerator is already mixed within the formulation.

To see if the storage time has influence on the front properties, a formulation with 1 mol % of each RTI and PAG in BADGE was stored at 50 °C under light protection. With this formulation, FP was conducted during a week on every day, and the results show that storage time has no significant influence on the front parameters. Details can be found in

the Supporting Information chapter 2 (Influence of the storage time on frontal polymerization parameters).

Influence of Initiator Concentrations

According to Pojman et al.,¹⁰ the front velocity as well as the front temperature are dependent on the concentration of the cationic and radical initiators in formulations based on the cycloaliphatic resin 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexylcarboxylate. Hence it was one aim of this study to analyze if the same trends go with the formulations based on the frequently used, but low reactive, BADGE in combination with the RTI and the PAG.

In Figure 5 the front velocity is displayed in dependency of the RTI and PAG concentrations. It can be seen that with increasing concentrations of each initiator the front velocity increases too, with a steeper increase in case of the higher PAG concentration. Concentrations below 1 mol % of PAG could not be frontally polymerized with success.

Front temperature showed in general a decreasing trend with increasing RTI concentration and varied between 170 and 210 °C; details on this study can be found in the Supporting Information chapter 3 (Dependency of front temperature on initiator concentration).

Material Characterization

(Thermo)Mechanical Investigations

Beside the chemical behavior of the RICFP system also the (thermo)mechanical properties of the cured polymers were of interest in this study.

Based on the above studies a formulation containing each 1 mol % of the RTI as well as the PAG in BADGE has been selected due to the good performance in RICFP. To see if there was an influence on the T_g also a formulation with 2 mol % of each initiator has been analyzed.

Glass Transition Point

The glass transition temperature (T_g) was determined by DSC. This allowed an easy and fast determination of the T_g of the RICFP cured BADGE polymer.

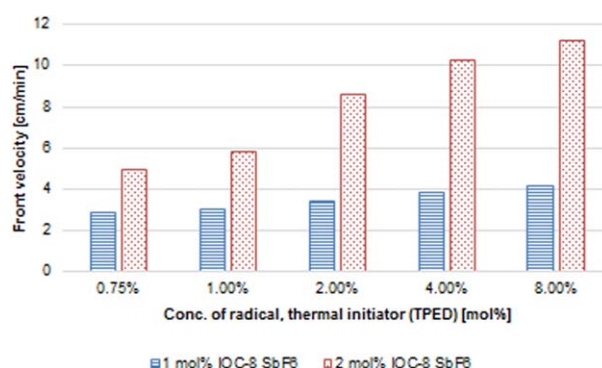


FIGURE 5 Comparison of the front velocity depending on different concentrations of RTI and PAG. [Color figure can be viewed at wileyonlinelibrary.com.]

TABLE 1 Glass Transition Temperature (T_g) Based on Different Concentrations of PAG and Radical, Thermal Initiator (RTI) Determined by DSC

c(PAG) [mol %]	c(RTI) [mol %]	T_g (°C)
1	1	168 ± 2
2	1	160 ± 3
2	2	156 ± 4

From Table 1 it can be seen that there is a weak trend towards lower T_g values with increasing initiator concentrations. The fact that the T_g decreases with increasing initiator concentration for both the cationic as well as the thermal initiator may be due to shorter kinetic chain lengths. With a higher initiator concentration more chains are started simultaneously and lead therefore to a lower overall chain length.

Additionally to the RICFP cured samples also the T_g value of the benchmark system and a formulation containing PAG in 1 mol % in BADGE, which was classically photocured, was determined (Table 2).

It can be seen that the T_g of the RICFP cured system is not significantly higher compared to the common photocured polymer (both 1 mol % of PAG). The thermally cured benchmark material shows a reduced T_g compared to the cationically cured BADGE polymers. Hence, a better stability at elevated temperatures is expected for the cationically cured polymers. In literature the T_g from the anhydride cured BADGE benchmark system is listed with 140 ± 5 °C in the datasheet.¹⁵ The fact that the T_g was determined here slightly higher (154 vs. 140 °C) is most probably due to the increased heating rate (30°/min vs. 20°/min) during the DSC determination, which allowed a better change of the c_p value and therefore a more reliable determination.

Tensile Testing and Impact Resistance

The mechanical properties of the cationically cured BADGE polymers have been tested and were compared to the anhydride cured reference material. For this purpose two types of specimens have been produced and afterwards tested according to ISO 527-2.

As can be seen in Table 3 the Young's modulus (E_t) of the RICFP cured material is slightly higher compared to the benchmark system, cured with the anhydride MHHPA. This is also true for the tensile strength. The same trend can be seen for the elongation at break (ϵ_b). The impact resistance

TABLE 2 Glass Transition Temperature (T_g) of Cured BADGE Polymers Based on Different Curing Methods Determined by DSC

Curing method	Curing agent	T_g (°C)
Photocuring	PAG	163 ± 2
Frontal curing	PAG + RTI	168 ± 2
Thermal curing	MHHPA	154 ± 4

TABLE 3 Young's Modulus (E_t), Tensile Strength (σ_b), Elongation at Break (ϵ_b), and Impact Resistance (a) of Cationically Cured and Anhydride Cured BADGE Formulations

Sample	E_t (MPa)	σ_b (MPa)	ϵ_b (%)	a (kJ/m ²)
PAG	3804 ± 113	64 ± 8	3.33 ± 0.84	14.9 ± 2.8
MHHPA	3390 ± 147	44 ± 8	1.71 ± 0.39	3.7 ± 1.1

(a) from the Charpy test is much higher for our cationically cured BADGE, mostly because of the alternative polymer architecture due to the different hardening process.

The determined values of Young's modulus of the benchmark system are in good accordance with the literature value, whereas the values of tensile strength and elongation at break were slightly lower compared to the values reported in literature.¹⁵ However, no data concerning the impact resistance of the anhydride cured benchmark system has been published in the datasheet of Huntsman.

Conductivity of the Resulting Polymer

Since BADGE resins are also used in composites with mica-tapes as insulating materials in power generators or other big electrical machines an impaired resistivity would be a disadvantage. The conductivity of the produced polymer samples was of special interest because the protons that were liberated during the curing process could stay in the cured resin and can therefore influence the conductivity of the cationically cured material. To compare the conductivity of insulating polymers usually the volume resistivity is consulted. It is the reciprocal value of the conductivity.

Since the preparation method for the volume resistivity and breakdown samples is not suited for the preparation of thermally cured resins, here we only compare the literature data from the benchmark system to those of our photocured system. The results of the volume resistivity determination are listed in Table 4.

TABLE 4 Volume Resistivity (ρ) Values from Literature of Cast Epoxy Resin, the Commercial Anhydride Cured Benchmark BADGE Resin and the Measured Values of the Photocured BADGE Resin

Hardening Type	Temperature (°C)	ρ (Ω cm)
Cast epoxy resin ^a	–	1×10^{14} to 1×10^{15}
Anhydride cured ^b	30	1×10^{17} to 2×10^{17}
Anhydride cured ^b	50	3×10^{17} to 4×10^{17}
Anhydride cured ^b	70	6×10^{17} to 7×10^{17}
Photoacid cured	30	1.78×10^{18}
Photoacid cured	50	4.27×10^{15}
Photoacid cured	70	7.72×10^{14}

^a Literature values taken from Ref. 16.

^b Literature values taken from Ref. 15.

The general volume resistivity value for cast epoxy resin (without filler material) is 10^{14} to 10^{15} Ω cm.¹⁶ Similar to this, Huntsman lists volume resistivities between 1×10^{17} and 7×10^{17} Ω cm depending on the temperature for the anhydride cured benchmark system in their datasheet.

The comparison of the measured resistivity values shows that the resistivity of this material is higher than the general literature value¹⁶ of insulating epoxies at 30 °C and 50 °C and our samples still show higher values at 30 °C compared with the anhydride cured benchmark system. The reduced resistivity at higher temperatures may be because of an increased mobility of the residual ions.

Also the breakdown voltage, which is defined as the voltage that is required to make a part of an insulator electrical conductive, was a subject of our studies. The general AC breakdown value for basic epoxy resin is 19.7 kV/mm.¹⁷ The benchmark material (cured with MHPA) here used exhibits an AC breakdown strength of 24 to 28 kV/mm.

The AC breakdown voltage of the cationically cured BADGE is around 19 ± 2.9 kV/mm. So the AC breakdown strength of the produced BADGE polymer here is similar to the general value for electrical application. However, compared to the commercial benchmark material, the cationically cured BADGE showed lower breakdown strength.

RICFP of Composite Material

The UV-Vis induced frontal curing of epoxy resins containing filler material for the production of composite materials bears difficulties: the limited penetration depth of light due to scattering on the filler particles that might inhibit the starting of the a front and the heat uptake of the inert filler material during frontal polymerization, which reduces the energy that is available for the cleavage of the thermal initiator. Therefore, there is a natural limit of inert filler material that can be added to the formulation so that the formulation is still able to undergo frontal polymerization.

Selection of a Proper Sensitizer Based on Photo-DSC Experiments

The penetration depth of light is directly dependent of the wavelength. Therefore shortwave UV-irradiation as it is usually applied for cationic photoinitiation¹⁸ has its limitation, since typical PAGs like iodonium salts show absorption only below 350 nm.² Sensitizing is a very common technique in which a molecule (the sensitizer) is added to a formulation that contains a photoinitiator which does not absorb in the spectral region the irradiation source provides. The sensitizer in contrast usually absorbs at higher wavelengths and gets thereby excited by the light. Subsequently, the excitation energy is transferred to the photoinitiator, which reacts by cleavage and release of the reactive species.

A broad variety of molecules were already tested for their ability to act as sensitizer in cationic polymerization by Green.¹⁹ We selected two typical sensitizers (ITX and perylene) for iodonium salts for our studies. A balanced

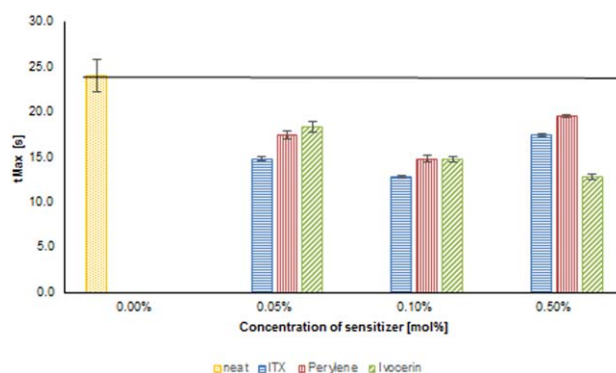


FIGURE 6 Comparison of the time to reach the maximum of the heat flow (t_{Max}) in the photo-DSC depending on type and concentration of different sensitizers and the radical PI Ivocerin. [Color figure can be viewed at wileyonlinelibrary.com.]

sensitizer concentration is important as too much sensitizer might reduce the performance due to light shielding effect. Therefore different concentrations should be tested.

Another approach to red shift is the absorption and therefore to increase the depth of penetration of the irradiation is to use radical photoinitiators that can react with the PAGs. Therefore an important requirement of this approach is that the formed radicals of the radical PI are able to react with the PAG (e.g. diaryliodonium salt) in a way to liberate the active species needed for the polymerization of the cationically curable monomer. For wavelengths over 400 nm, very common PIs are *bis*(acetylphosphinoxides) (BAPOs). Nevertheless, BAPO would be no choice for this particular application, because it was already shown by Allonas et al.¹⁸ that the formed 2,4,6-trimethylbenzoyl radicals cannot directly react with diaryl iodonium initiators. Further the shielding effect of the BAPO molecule in the relevant absorbing region of the PAG prevents the cleavage of the cationic photoinitiator.²⁰ Therefore the germanium based radical PI Ivocerin was selected to be tested as suitable enhancer of this reaction. It is known from recent studies by Ganster et al.²⁰ that germanium based photoinitiators like Ivocerin are also capable of cleaving onium salts by radical induced cationic decomposition.

Photo-DSC experiments were selected to evaluate the effect of the different sensitizer molecules.

All formulations for the photo-DSC study consisted of BADGE resin with 1 mol % PAG. Although the usage of sensitizers is mostly needed for filled systems, we have decided to skip this filler in this study as we wanted to evaluate the pure sensitizing effect independent of the filler. Therefore, for this basic photo-DSC study the BADGE formulations were conducted with 1 mol % PAG, and different concentrations of the sensitizers ITX, perylene, and Ivocerin.

The time to reach the maximum heat flow (t_{Max}) is a good indication for the reaction speed. Figure 6 shows that a concentration of 0.1 mol % of the sensitizers perylene and ITX

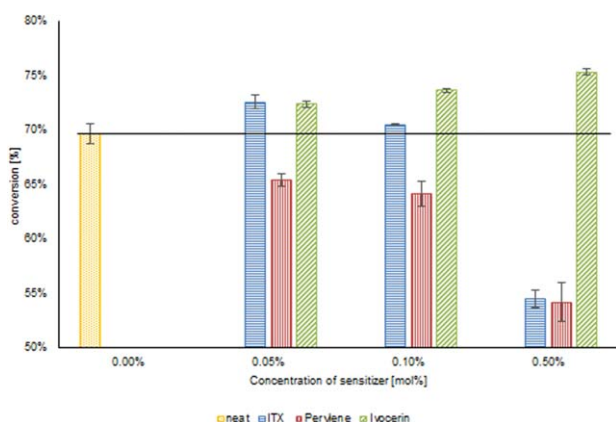


FIGURE 7 Comparison of the conversion calculated from the polymerization heat from photo-DSC measurements depending on type and concentration of different sensitizers and the radical PI Ivocerin. [Color figure can be viewed at wileyonlinelibrary.com.]

performs best. At higher concentrations a shielding effect seems to occur. This effect is not true for Ivocerin due to the excellent photobleaching behavior.²⁰ Comparison of each sensitizer shows that ITX outperforms any other tested sensitizer.

As a second parameter the conversion based on the polymerization heat was determined (Fig. 7).

The difference between the tested substances and the neat formulation is less prominent compared to the difference of the t_{Max} values. Again, perylene and ITX perform worse at high concentrations than the neat formulation. This now confirms the shielding effect of the sensitizers at higher concentrations. The good performance of Ivocerin even at higher concentration (0.5 mol %) can also be seen again and be assigned to its good photobleaching effect.²⁰ It has to be accepted that perylene reduces the conversion in every concentration compared to the neat formulation.

As ITX performs as the best sensitizer for this system (it reduces the t_{Max} value significantly while slightly increasing the conversion) it should be used in all subsequent studies.

By additional studies (see chapter 9 of the Supporting Information) it could be shown that the use of ITX has no influence on the frontal polymerization parameters.

RICFP Cured Composites

Photopolymerization of composite materials can be challenging due to the limited penetration depth of UV-light based on scattering and absorption of the irradiation. In case of RICFP, two challenges were faced: the disperse phase (mica powder) (a) will take up some polymerization heat that is required for the cleavage of the thermal initiator and (b) absorb the UV-light required for the direct excitation and cleavage of the cationic PI.

To analyze those challenges, formulations were prepared with concentrations from 5 to 20% phr of mica powder and their eligibility for RICFP was tested. Also 25% phr was tried but this formulation could no longer be processed due to the paste like consistency. For all formulations 1 mol % of PAG was used. Based on the preceding photo-DSC study a sensitizer concentration of 0.2 mol % has been chosen because of the following reasons: (a) the 0.1 mol % sensitizer concentration performed the best in unfilled systems, but mica is expected to scatter light and (b) a significant decrease of the conversion is expected only at concentrations of 0.4 mol %. The frontal polymerization parameters were determined equally to the basic RICFP studies. To determine whether a light shielding effect or the polymerization heat consumption (thinning effect) is responsible for a failure in frontal polymerization, thermal initiation experiments were additionally performed. In this case the concentration of the thermal, radical initiator has been chosen with 8 mol % because this concentration was still easily soluble in the resin but showed a significant higher reactivity, as has been shown in the basic RICFP studies.

TABLE 5 Comparison of Composite Formulations with Different Concentrations of Radical, Thermal Initiator (RTI) Filler Material (mica) and Different Sensitizers

Front Stab.	c(RTI) (mol %)	c(Mica) (% phr)	Sensitizer	c(Sens.) (mol %)	V_F (cm/min)	t_s (s)
+ ^a	8	5	–	0	4.0	– ^c
+ ^a	8	10	–	0	3.8	– ^c
+ ^a	8	15	–	0	3.7	– ^c
– ^a	8	20	–	0	–	– ^c
+	1	5	ITX	0.2	3.1	25
+	1	10	ITX	0.2	2.9	27
+	1	15	ITX	0.2	2.8	33
– ^b	1	20	ITX	0.2	–	36
+	8	5	Ivocerin	2.0	3.1	–

a) Only thermal initiation possible.

b) Front starts and moves but is not stable.

c) Cannot be applied to thermally initiated fronts.

As can be seen in Table 5, the formulations without any sensitizer could not be initiated by irradiation, even at low (5% phr) concentrations of mica. However, the initiation was possible with local application of heat with a soldering iron and the front was stable up to mica concentrations of 15% phr. Above this a front formation could be observed but the front ceased at least once in three cases prematurely. With this experiment the top most concentration of mica could be determined under these conditions.

From the preceding photo-DSC studies, ITX was selected as the most suitable sensitizer concerning the initiation part. From Table 5 it can clearly be seen that the addition of only 0.2 mol % of ITX allows the photoinitiation of the tested formulations even up to 20% phr. In case of 20% phr the front was not stable and ceased prematurely like in the not sensitized formulation, so it can be concluded that the sensitization does not influence the stability of the front. The decreased front velocity (V_F) of the irradiation initiated formulations compared to those thermally initialized can be assigned to the lower concentration of the thermal initiator in the systems with ITX which have shown to be sufficient if the initiation is conducted with UV irradiation.

As already described before, an alternative sensitization method is the addition of radical photoinitiators, which absorb light in the desired wavelength range, to cleave the PAGs by radical induced decomposition.

The preceding photo-DSC study already showed that not only the conversion could be increased by the addition of Ivocerin but also the initiation time could be decreased. Therefore Ivocerin was also investigated for its capability to enhance the photoinitiation properties of epoxy based mica composite formulations. It turned out that by addition of Ivocerin, photoinitiation of the RICFP was possible in formulations containing 5% phr mica powder. Since this was only a proof of concept and ITX allows a more versatile sensitization strategy, no further detailed studies have been conducted with higher mica concentrations.

CONCLUSIONS

In a previous article¹¹ we described the discovery of a versatile system based on a radical, thermal initiator (RTI) TPED, and the photoacid generator (PAG) IOC-8 SbF₆ together with several cationically curable resins to undergo radical induced cationic frontal polymerization (RICFP). This article presents a more detailed look on the best performing system, which shows a high storage stability also compared to a commercial benchmark system (based on anhydride cured BADGE). We showed that with simple variation of the initiator concentration the front velocity of the here presented system can be adjusted to ones need and still yield a reliable polymerizing formulation. The polymer produced via RICFP compares favorably with state of the art material (cured by anhydride addition) regarding mechanical properties. It could also be shown that, despite the usage of ionic initiators, the electrical resistivity of the system presented here is

very similar to that of the selected state of the art system, which is used for electrical applications. Finally the challenges of curing filled systems could be mastered by a proper sensitizing strategy despite the hindered light penetration. Therefore RICFP is a very powerful tool for quick and energy efficient curing of epoxies for numerous applications including the manufacturing of composite materials.

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