

Research Article

Self-Healing Photocurable Epoxy/thiol-ene Systems Using an Aromatic Epoxy Resin

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A rapid and efficient method to obtain self-healing epoxy resins is discussed. This method is based on the use of a thiol-disulfide oligomer obtained by partial oxidation of a multifunctional thiol using a hypervalent iodine (III) compound as oxidant. The oligomer was characterized by Fourier transform infrared spectroscopy (FTIR), Raman and nuclear magnetic resonance spectroscopies, and gel permeation chromatography (GPC). The oligomer was a joint component of the thiol-ene system along with a tetra-allyl-functionalized curing agent. The kinetics of the photopolymerization of diglycidylether of bisphenol A (DGEBA) revealed that conversions of the epoxy groups as high as 80% were achieved in only 15 minutes by increasing the concentration of the thiol-ene system in the formulation. The disulfide bonds introduced in the copolymer using the thiol-disulfide oligomer allowed the repairing of the test specimens in as little as 10 minutes when the specimens were heated at 80°C or for 500 minutes at room temperature. The analysis of the mechanical properties using dynamic mechanical analysis (DMA) showed that the specimens displayed a healing efficiency up to 111% compared with the unhealed specimens, depending on the amount of polythioethers present in the copolymer.

1. Introduction

In the last two decades there has been a plethora of investigations relating to the obtention of self-healing polymeric materials. These materials have attracted a lot of attention from both scientific and technological points of view. The potential application of this phenomenon in areas such as aerospace, automotive, electronics, biomedics, adhesives, and coatings could be of significance, considering that defective materials that fail due to mechanical stress or aging can almost recover entirely their original mechanical properties after the self-healing process.

Self-healing polymers can be defined as materials that have the ability to repair damage automatically and autonomously without any external intervention [1]. These self-healing polymers can be classified as extrinsic self-healing and intrinsic self-healing [2]. For extrinsic self-healing materials it is necessary to add an encapsulated healing agent, to the bulk of the polymer. The healing agent will be liberated

at the point of failure with the time of healing depending on the type of encapsulated monomer and catalyst used [3–6]. Intrinsic polymers can be healed by introducing functional groups in the polymer that can undergo dynamic exchange reactions between reversible covalent bonds. A variety of chemical reactions have been utilized to achieve the self-healing process such as those that promote the formation of covalent bonds like the Diels-Alder reactions between furan and maleimide groups [7, 8], cycloaddition reactions [2 + 2] with cinnamoyl derivatives [9], and photochemical cycloaddition reactions [4 + 4] with anthracene derivatives [10]. Another approach for intrinsic self-healing is by means of the formation of covalent bonds that allow chain exchange reactions such as the dynamic reversible formation of acylhydrazones [11], trithiocarbonates reshuffling [12], the reaction exchange of siloxane segments [13, 14], and the metathesis reaction of disulfide bonds [15–17].

The industrial importance of the epoxy resins has encouraged several research groups to develop self-healing

epoxy resins. The most commonly used healing methods are of the extrinsic self-healing type. For instance, encapsulated dicyclopentadiene has been utilized in the presence of ruthenium-based Grubbs catalyst for the autorepair process of epoxy resins [18]. Guadagno et al. [19] used encapsulated 5-ethylidene 2-norbornene (ENB) as the healing agent for the epoxy resins in conjunction with the first-generation Hoveyda-Grubbs catalyst (HG1). The healing process occurred via ring opening metathesis polymerization (ROMP). Other types of Grubbs type catalysts have also been investigated [20]. The advantage of these extrinsic methods is that they can be used for epoxy composites without significant loss of mechanical properties. However, the main drawback is that the Grubbs catalyst used are not thermally stable at the curing temperatures of the epoxy resin (120–150°C). Therefore, several studies have been conducted to determine the stability of the different types of Grubbs catalyst under processing conditions [21, 22].

There are few reports concerning intrinsic self-healing epoxy resins; for instance, Lei and collaborators reported the use of a polysulfide aliphatic diglycidylether in the preparation of self-healing remoldable epoxy resins [23]. The flexibility of the prepared polyether-polydisulfide allowed the autorepair process even at room temperature. The result was repeated restoration of the mechanical properties. Pepels et al. [24] reported a similar approach as they also used polysulfide aliphatic diglycidyl ethers. They found that the self-healing ability was due to the disulfide-thiol exchange rather than disulfide-disulfide and that the process was pH-dependent. Interesting research undertaken by Lafont and collaborators [25] showed that the healing efficiency of a thermoset aliphatic epoxy resins with disulfide bonds in its structure depended on the level of crosslinking achieved using trifunctional or tetrafunctional thiols as crosslinking agents. The level of crosslinking influenced the density and mobility of disulfide bonds, which resulted in the tetrafunctional thiol displaying greater healing efficiency.

One challenge relating to self-healing epoxy resin is introducing this process in commercial aromatic epoxy resins, such as DGEBA. The rigidity and high glass transition (T_g) characteristics of these epoxy polymers reduce or impede the mobility of the crosslinked network making the metathesis of the disulfide bonds difficult.

One method to solve the problem of brittleness of the epoxy resins caused by the high level of crosslinking characteristic of the thermoset polymers is by concurrently curing the epoxy resins with a “soft” polymer such as an elastomer, a thermoplastic or a diglycidyl monomer with a flexible spacer like an ethylene oxide chain [26]. The toughness is enhanced by reducing the crosslink density or by promoting a phase separation. [27]. Several research groups including ours have worked on improving the toughness of the epoxy resin by concurrently polymerizing them with a thiol-ene system [28–30]. It has been demonstrated that the flexible and low T_g polythioethers produced during thiol-ene photopolymerization can effectively improve the toughness of the obtained polyether-polythioether copolymers. When the epoxy resins were cationically polymerized in conjunction with a thiol-ene system that included either acrylates or allylic

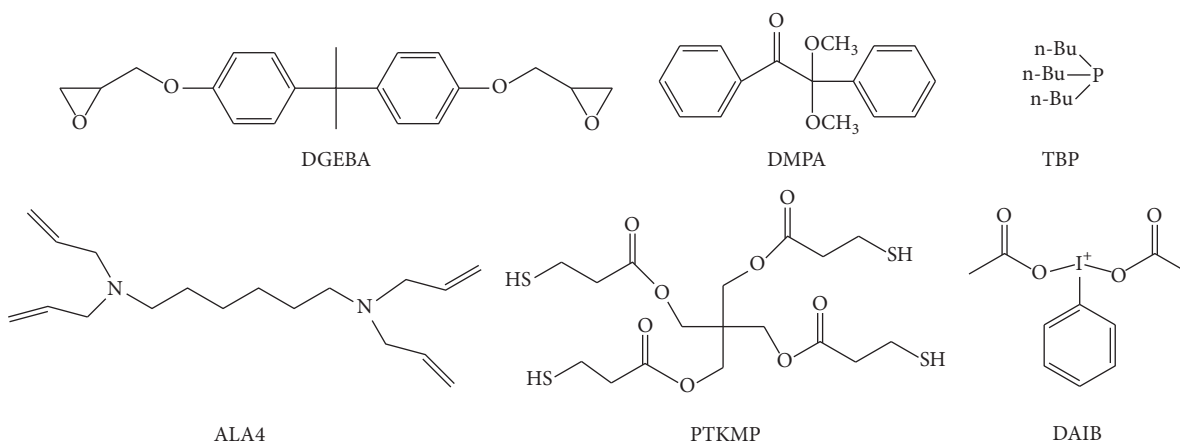
compounds with a multifunctional thiol, it was found that due to the basic nature of the formed polythioethers, these species interrupted the cationic polymerization of the epoxy resin [28]. Therefore, most of the epoxy monomer remained uncured in the polymer. However, when the polythioethers reacted with the growing oxonium terminated polyether chains, trialkyl sulfonium salt-terminated polyethers formed. These salts are known as efficient catalysts for the thermal polymerization of the epoxy resins. Therefore, a dual photo-post-thermal treatment was used to obtain the polyether-polythioether copolymers with improved toughness [31]. The main drawback of this method was the long times required to achieve full conversion of the epoxy resins (3–5 hours at 120°C after irradiation).

Further investigations by our research group revealed that a better approach to obtain epoxy/thiol-ene systems was to anionically polymerize the epoxy resin with allyl-functionalized tertiary amines as curing agents in conjunction with a multifunctional thiol and a radical photoinitiator [32, 33]. These anionic epoxy/thiol-ene systems displayed high reactivity, achieving quantitative conversions of the epoxy groups in less than 10 min when polymerized with 40 mW/cm² of UV light intensity at a temperature of 85°C [34]. The involvement of several basic initiating species, capable of ring opening polymerization reactions, such as tertiary amines, thiolates, alkoxides, and the formed polythioethers, resulted in high polymerization rates [35]. In addition, the presence of the flexible polythioethers in the prepared copolymers markedly enhanced the mechanical properties of the obtained materials.

Therefore, in continuing with this research, this paper presents a study in which self-healing photocurable epoxy resins were obtained by using a thiol-disulfide oligomer as comonomer in an epoxy/thiol-ene system. The oligomer was prepared by partial oxidation of a multifunctional thiol. The kinetics of photopolymerization of the epoxy system were analyzed using Real-Time FTIR spectroscopy (RT-FTIR). Additionally, the mechanical properties of the unhealed and healed polymers were compared using dynamic mechanical analysis (DMA). Evidence of the self-healing process (photographs and a video) is provided.

2. Experimental

2.1. Materials and Equipment. DGEBA, pentaerythritol tetrakis mercaptopropionate (PTKMP), iodobenzene diacetate (IBDA), tributylphosphine (TBP), and dimethoxyphenyl acetophenone (DMPA) were purchased from Aldrich Mexico. The curing agent N¹, N¹, N⁶, N⁶-tetrallylhexane-1,6-diamine (ALA4) was prepared according to a previously reported method [32]. The chemical structures of all these compounds are depicted in Scheme 1. Characterization of the products and kinetics of photopolymerization were determined in a Thermofisher, Nicolet 6700. Proton NMR spectra were obtained with a 500 MHz Bruker (Billerica, MA) spectrometer at room temperature. The molecular weight of the oligomer was determined using a Waters Alliance 2695 gel permeation chromatograph (Milford, MA) and high performance liquid chromatography (HPLC) grade chloroform.



SCHEME 1: Chemical structure of the compounds used in this study.

A Horiba Scientific Raman Xplora One was also used (Clifton Park, NY). Viscoelastic properties were determined using a TA Instruments Dynamic Mechanical Analyzer Q800 (New Castle, DE). The photographs of the healing process were taken using an Olympus BX60 optical microscope equipped with *Image Pro 7.0* software.

2.2. Oxidation of PTKMP. To a 250 mL Erlen-Meyer flask with a stopper and a magnetic stirrer we added 60 mL of chloroform followed by 9.90 g (0.030 moles) of IBDA. The mixture was stirred until the solid dissolved. We then added 15 g (0.030 moles) of PTKMP, after which the flask was immersed in a controlled temperature bath at 25°C for 15 minutes. The mixture was filtered off and rotoevaporated to eliminate the solvent and by-products. A colorless liquid denser than PTKMP was obtained in quantitative yield.

2.3. Determination of Kinetics of Photopolymerization of the Epoxy Resin by RT-FTNIR. The reactivity of the self-healing epoxy resins was analyzed by RT-FTNIR. The samples were subjected to a simultaneous photothermal treatment. The required temperature for curing of the epoxy resin was 85°C and the UV light intensity was 40 mW/cm². Unfiltered radiation was used in the range of 200 nm to 400 nm with maximum peaks at 254 nm and 365 nm. A Pike technologies heated solid transmission cell was used to increase the temperature of the sample. The thiol-ene system included the curing agent ALA4, the PTKMP thiol-disulfide oligomer at a ratio of 2:1, and the photoinitiator DMPA at 1 mol% with respect to ALA4. We also added TBP at 1% w/w in relation to the total mass of the formulation. The thiol-ene system was added at 20, 30, 40, and 50 mol%, to the epoxy resin DGEBA. In Table 1 the components of each formulation are listed. The epoxy resin was mixed, with the curing agent ALA4, the DMPA, and the TBP. At the end, we added the oxidized oligomer derived from PTKMP. The components of the formulation were mixed in a vial. A drop of the formulation was poured onto a round piece of corona-treated polypropylene film with a radius of 1 cm that was covered with an identical piece of film, to form a sandwich. This sandwich was placed in the heated solid transmission cell and was heated to 85°C. The

tip of the wand of a UVEX UV lamp was placed at 45°C with respect to the IR laser of the equipment. The light intensity was measured with a control cure radiometer (UV Process Supply Inc.). Once the temperature was set, the UV lamp was turned on at the same time as the IR scanning of the sample. The sample was scanned for 900 s. The peak at 4475 cm⁻¹ corresponding to the double bonds and the peak at 4527 cm⁻¹ corresponding to the epoxy groups were monitored. The decrease in the absorbance profiles was determined using the software *OMNIC Series*. Kinetic profiles of the samples were obtained by measuring the decrease in the absorbance of the bands of the functional groups at a determined time and were compared to the initial absorbance.

2.4. Preparation of Test Specimens and the Measurement of the Self-Healing Process. The test specimens were prepared by bulk photopolymerization. The formulations were prepared in the same way as those described for the kinetics analysis. The liquid formulation was poured onto a stainless steel mold with 10 mm × 40 mm × 2 mm cavity. The mold was then placed in the UV chamber for 15 minutes. The temperature inside the chamber was 85°C as a result of the heat liberated by the lamp, and the light intensity was 40 mW/cm². The obtained test specimen was allowed to cool and was cut in two equal pieces with a cutter. The two pieces were put together into the cavity of the mold, placed on a heating plate at a predefined temperature. The healing process was followed with an optical microscope that has the capability of taking photographs every 30 s. At specified periods the test specimen was withdrawn from the mold and tested to see if the two halves were completely fixed together.

2.5. Analysis of Viscoelastic Properties. The test specimens for DMA analysis were prepared in the same way as those for the healing process. The DMA measurements were performed using a frequency of 1 Hz and a heating rate of 5°C/min over a range of 30°C to 150°C in a nitrogen atmosphere. Two specimens were analyzed, one without cut that served as a control and the second one that was cut in two pieces and healed with a thermal treatment. Both specimens underwent the same thermal treatment.

TABLE 1: Composition of the photocurable epoxy/thiol-ene formulations in equivalents and grams.

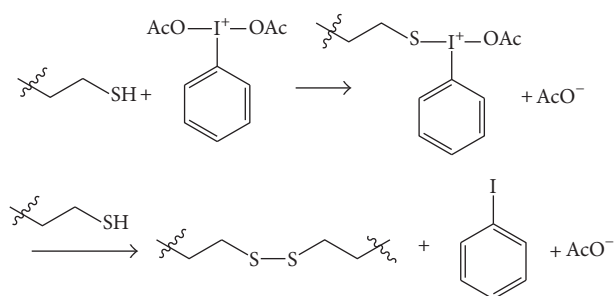
Formulation	DGEBA		ALA4		PTKMP OX		DMPA		TBP
	MW = 340		MW = 276		MW = 1837		MW = 256		MW = 204
	Eq	g	Eq	g	Eq	g	Eq	g	g
20% thiol-ene	1	2.0	0.2	0.324	0.1	1.080	0.001	0.0030	0.034
30% thiol-ene	1	2.0	0.3	0.487	0.15	1.62	0.001	0.0045	0.041
40% thiol-ene	1	2.0	0.4	0.649	0.2	2.16	0.001	0.0060	0.048
50% thiol-ene	1	2.0	0.5	0.811	0.25	2.70	0.001	0.0075	0.055

MW = molecular weight, PTKMP OX = oligomer thiol-disulfide, Eq = Equivalents, and g = grams.

3. Results and Discussion

3.1. Synthesis of the Thiol-Disulfide PTKMP Oligomer. Previous investigations of photocurable anionic epoxy/thiol-ene systems revealed that these kinds of systems were very reactive, achieving full conversion of epoxide groups in less than 10 min [34, 35]. A multifunctional thiol was used in conjunction with a tetra-allyl bifunctional tertiary amine to cure the epoxy resin DGEBA. Considering this fact, it was thought that it might be possible to obtain self-healing epoxy resins if we could partially oxidize the multifunctional thiol in order to introduce disulfide bonds in the cured polymer. Therefore, we tried different methods to partially oxidize the PTKMP, for instance, oxidation with air using basic catalyst or with hydrogen peroxide in the presence of quaternary ammonium salts or using iodine as oxidant. These methods were unsuccessful because it was not possible to control the oxidation obtaining in all cases an insoluble polydisulfide. We then tried iodonium salts like hydroxytropylium iodobenzene and IBDA and obtained better results with the last one due to a better solubility in chloroform. The efficiency of several hypervalent iodine (III) compounds as oxidants has already been reported by Rattanangkool et al. [36] who found that the IBDA promoted the rapid oxidation of 4-chlorothiophenol to form the disulfide at 87% yield in only 1 min. The authors proposed the mechanism shown in Scheme 2. First, a ligand exchange of IBDA with the thiol occurred, liberating an acetate group and forming a sulfenyl iodide intermediate. Next, a second thiol group attacked the sulfenyl intermediate generating the disulfide and iodobenzene. In our case the oxidation of PTKMP proceeded very rapidly and efficiently, without the exclusion of air or moisture. The equivalents of IBDA were varied from 0.25 to 1 equivalent. A further increase of the oxidant resulted in the formation of the insoluble polydisulfide.

The FTIR spectra of the oxidized PTKMP in the range of 400–1000 cm^{-1} are shown in Figure 1. Rising weak bands at 735 cm^{-1} and 450 cm^{-1} were observed when concentration of IBDA was increased. The same oxidation reactions were also analyzed by proton NMR spectroscopy (see Figure 2). The triplet corresponding to the methylene adjacent to the carbonyl group appears at 2.67 ppm while the quadruplet of the protons of the carbon next to the thiol group were at 2.76 ppm. The proton of the thiol groups was located at 1.65 ppm as a triplet. The concentration of IBDA was then



SCHEME 2: Mechanism of the oxidation of thiols using IBDA.

augmented and the intensity of a triplet at 2.92 ppm corresponding to the protons of the carbon neighboring the disulfide bond was increased. We also observed that the resolution of the peaks of the oligomer diminished with increasing oxidation of PTKMP. By measuring the integrals of these groups a ratio of thiol groups to disulfide groups of 2 : 1 was determined (see ^1H NMR spectrum of oxidized PTKMP with integrals in Supplementary Material available online at <http://dx.doi.org/10.1155/2016/8245972>).

The obtained oxidized PTKMP was also characterized by Raman spectroscopy. New bands at 248 cm^{-1} and at 493 cm^{-1} were observed, which is characteristic of the disulfide groups (see Figure 3). The oligomer was characterized by GPC using chloroform as solvent. A mixture of two species was found: a thiol-disulfide oligomer with M_n of 1837 g/mol with polydispersity of 1.43 that approximately corresponds to four unities of PTKMP ($MW = 488 \text{ um}$) and a small fraction (9%) of a polymer with M_n of 38096 g/mol that fits for 76 unities of the tetrafunctional thiol with a polydispersity of 2.61. This implies that one equivalent of IBDA is the concentration limit that can be used because further increase results in complete oxidation of the PTKMP. Theoretically, four equivalents of IBDA would be needed to oxidize the tetrafunctional thiol. The simplified chemical structure of the thiol-disulfide oligomer is depicted in Scheme 3. If we consider the molecular weight that fits for four units of PTKMP, then the proposed structure correlates well with all the data obtained as it has 8 thiol groups and 4 disulfide groups. The oxidation was performed under the same conditions several times to ensure a reproducible process.

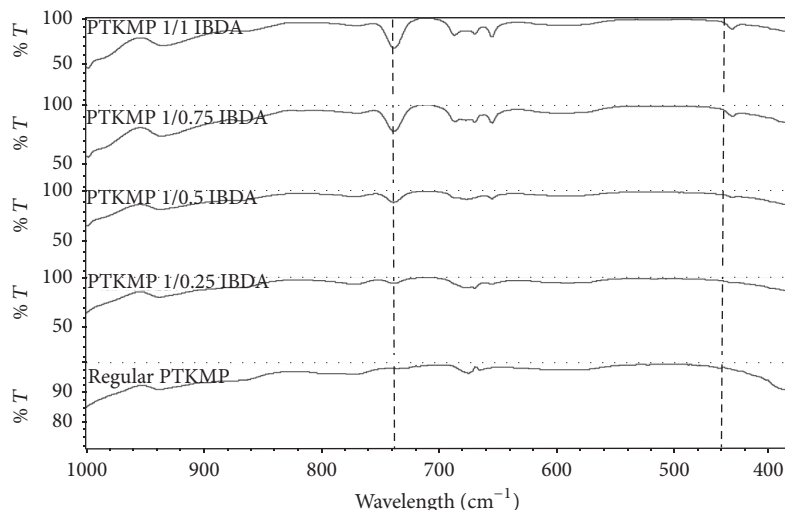


FIGURE 1: FTIR spectra of PTKMP with varying concentrations of IBDA.

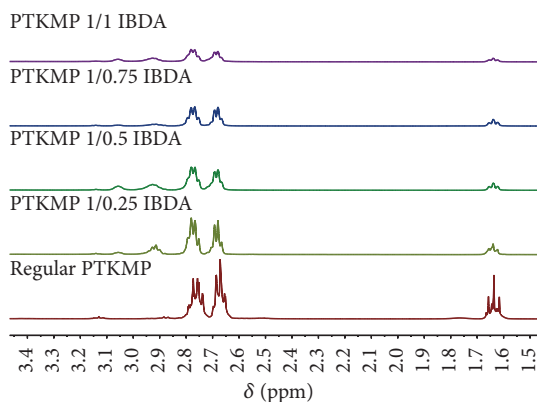


FIGURE 2: ^1H NMR spectra of the oxidation of PTKMP with varying concentration of IBDA.

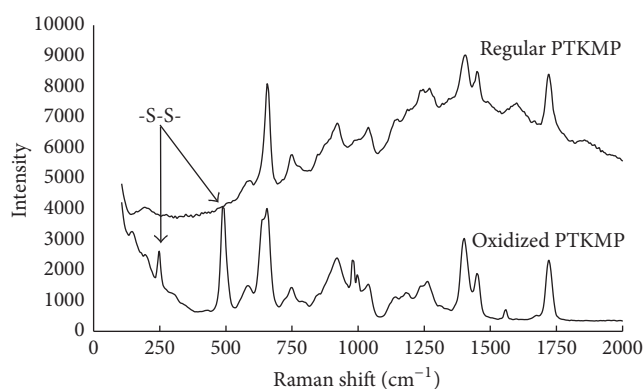
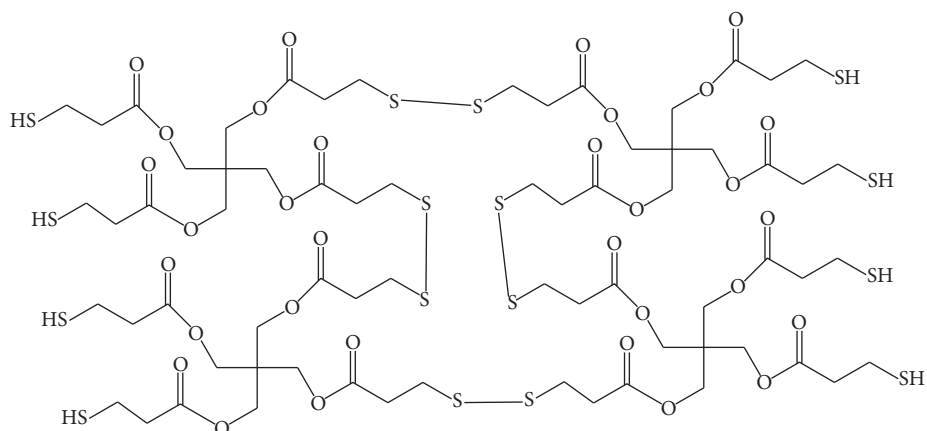


FIGURE 3: Raman spectra of the regular and oxidized PTKMP.

3.2. Study of the Kinetics of Photopolymerization. The comparison of the kinetic profiles of the photopolymerization of DGEBA with the increasing concentration of the thiol-ene system is depicted in Figure 4. We found that the photocurable anionic epoxy/thiol-ene formulations were quite

reactive, achieving a conversion of the epoxy groups as high as 80% when 50 mol% of the thiol-ene system was added to DGEBA. We observed that increasing the concentration of the thiol-ene system resulted in higher photopolymerization rates and conversions. On the whole, all systems displayed two stages during the photopolymerization: the first was characterized by a higher photopolymerization rate, and the second occurred after a plateau and had a decelerating effect. This behavior can be explained on the basis of the basic species formed during the photopolymerization. At the beginning of the polymerization reaction, the tertiary amine groups react with the epoxy groups, inducing their anionic ring opening polymerization. At the same time the double bonds of the hardener react with the thiol groups of the prepared oligomer, forming polythioethers by means of thiol-ene chemistry. An acid-based reaction is also possible between the tertiary amine groups and the thiol groups to form thiolate groups and a quaternary ammonium salt. Due to the presence of different basic species, the proton of the quaternary ammonium group is in equilibrium with all the basic species, at some point regenerating the thiol groups that will be available to react with the double bonds of ALA4. Indeed, during the RT-FTIR kinetics it was not possible to detect the band for the thiol groups at 5550 cm^{-1} , which supports our theory. Therefore, during the first stage there is a rich concentration of basic species able to initiate the anionic ring opening polymerization of the epoxy groups that results in higher photopolymerization rate. However, as the polymerization proceeds, some fraction of the epoxy groups gets trapped in the crosslinked network. Nonetheless, as the concentration of the thiol-ene system is augmented, the concentration of the polythioethers increases, thus improving the mobility of the polymeric network due to the flexibility of those species. The formed polythioethers are also basic enough to react with the remaining epoxy groups via anionic ring opening polymerization, thus forming a copolymer polyether-polythioether with disulfide bonds in its structure. Due to the restricted mobility of the trapped epoxy groups, the second stage is slower than the first.



SCHEME 3: Simplified structure of the prepared thiol-disulfide oligomer.

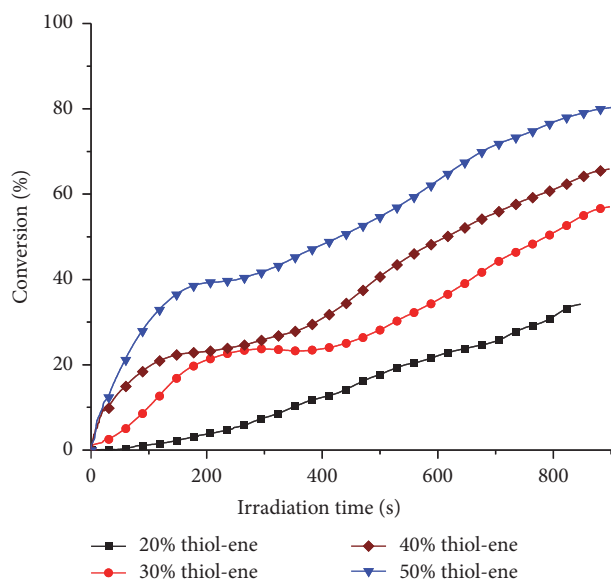


FIGURE 4: Comparison of the kinetic profiles of the epoxy groups during the photopolymerization of DGEBA with varying concentrations of the thiol-ene system. The photopolymerizations were performed at a temperature of 85°C and UV light intensity of 40 mW/cm^2 . The photoinitiator DMPA and the catalyst TBP were added at 1%.

The kinetic behavior of the double bonds of the curing agent ALA4 in the studied epoxy/thiol-ene systems is shown in Figure 5. A rapid increase in the conversion of these groups was observed in the first 50 s in all cases. A similar situation was observed for the epoxy groups. The conversion increased with increasing concentration of the thiol-ene system and the photopolymerization rate was decelerated after approximately the first 100 s. The reaction of the double bonds with the thiol groups is more favored at higher concentration of the thiol-ene system. Here, as mentioned in the above discussion, in the first stage of the kinetic profiles, the double bonds of the curing agent can react directly with the thiol groups or with the regenerated thiol groups during the equilibrium

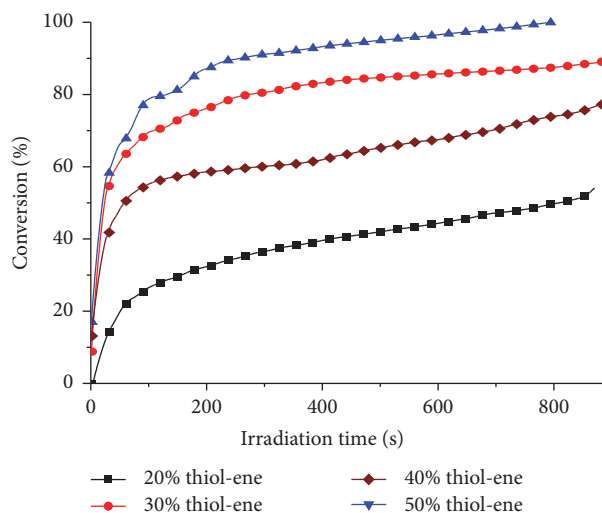


FIGURE 5: Comparison of the kinetic profiles of the double bonds during the photopolymerization of DGEBA with varying concentrations of the thiol-ene system. The photopolymerizations were performed at a temperature of 85°C with UV light intensity of 40 mW/cm^2 . The photoinitiator DMPA and the catalyst TBP were added at 1%.

of the proton of the formed quaternary ammonium salt, with the other basic species. In the second stage when the photopolymerization rate decelerates, this can be attributed to the reduced mobility of the unreacted thiol groups and the double bonds as a result of the increasing level of crosslinking in the network.

3.3. Determination of the Healing Time. The process of self-healing by metathesis of the disulfide bonds has been demonstrated by Lei et al. [23] using mixtures of several model compounds. Their experiment yielded a mixture of several disulfide compounds with alkyl chains different than those of the original compounds, when the mixture was stirred at room temperature for 3 h. This process can be radical or anionic in nature. In our case due to the basic character of our photocurable system, we decided to use TBP as a catalyst

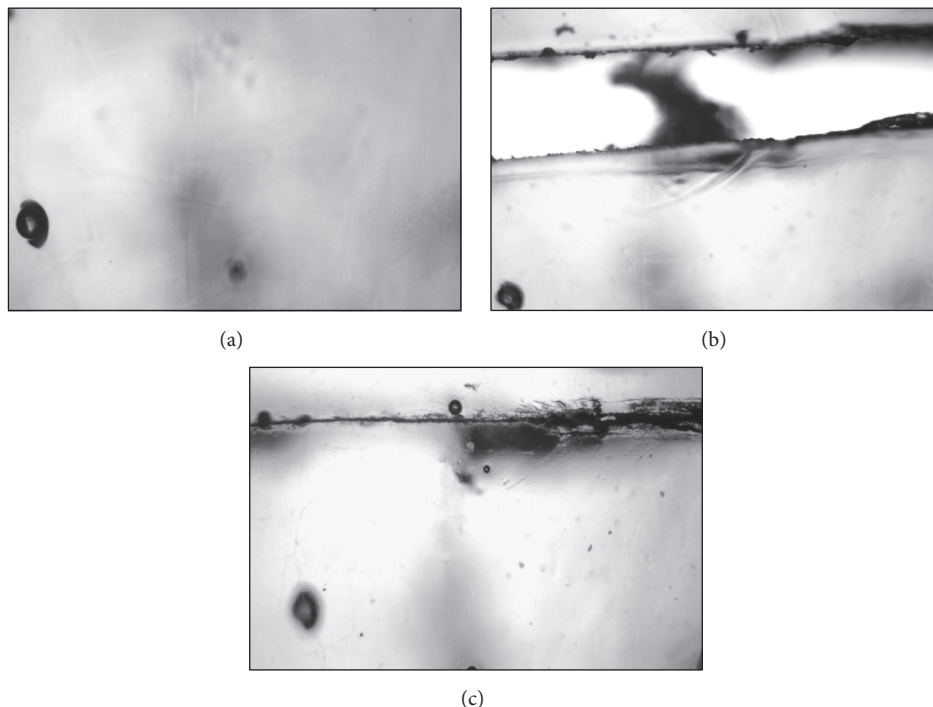


FIGURE 6: Photographs of the epoxy test specimen with 40 mol% of thiol-ene system: (a) before the cut, (b) after the cut, and (c) after healing. The healing was carried out at 70°C.

to accelerate the healing of the specimens. This catalyst accelerates the metathesis reaction of the disulfide bonds [37], according to the mechanism proposed in Scheme 4. The TBP can nucleophilically attack one of the sulfur atoms of the disulfide bond to form transient species with phosphonium and thioxides groups. Thereafter, the thiolates can attack the sulfur atoms adjacent to the phosphonium groups generating new disulfide bonds. This is a dynamic process, in which the number of disulfide groups do not change; they are always available whether they are in the bulk of the polymer or on the cut surface.

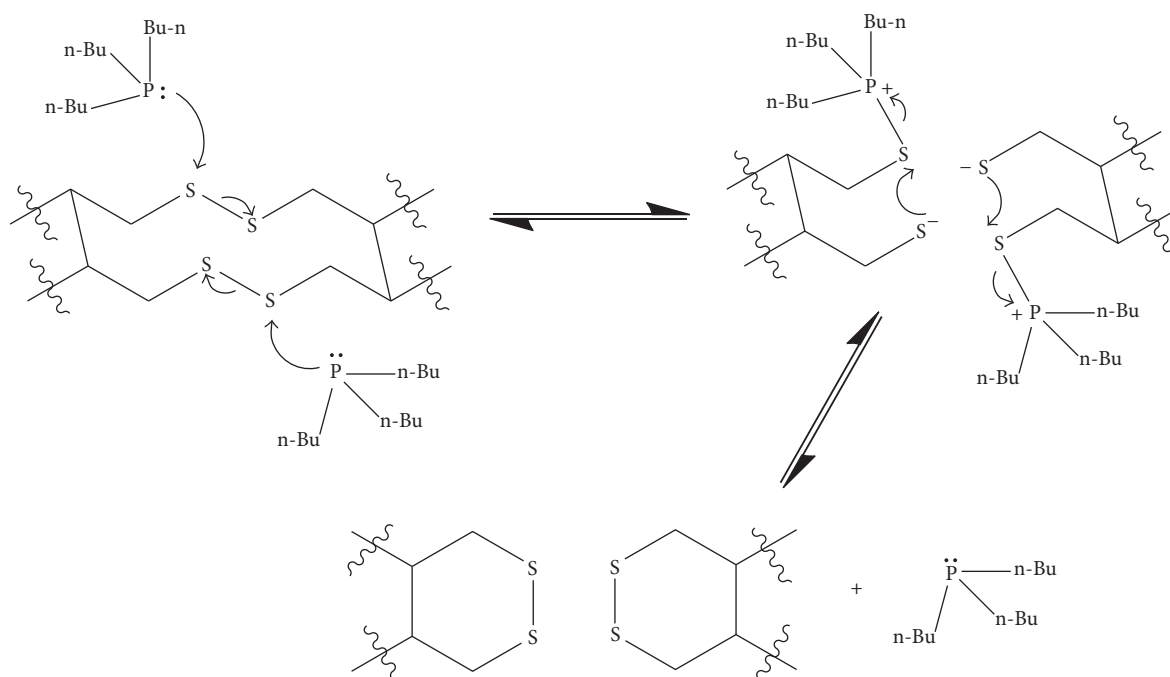
The thickness of the prepared test specimens was 2 mm. After curing, the test specimens were cut in half and put back in the mold to ensure that the sample did not move during the healing process. We found that the test specimens with 20% and 30% of the thiol-ene system did not repair themselves. The stiffness of the specimens did not allow close contact between the polymer chains of the two cut pieces, thus preventing the metathesis of the disulfide bonds. On the contrary, the test specimens with 40 mol% and 50 mol% of the thiol-ene system did have enough mobility in their polymeric matrixes to be repaired. Table 2 shows the healing times at different temperatures for the specimens with 40 mol% of the thiol-ene system. Although the samples that were heated above the T_g were more rapidly repaired, the healing process of the specimens occurred even at room temperature. For instance, at 80°C the healing time is of 10 min for the specimens with 40 mol%, while at room temperature it was required 500 min to achieve complete healing. These are very rapid times for the samples to become healed considering their thickness. Other studies have reported the healing of

TABLE 2: Healing times for the test specimens with 40% mol and 50 mol% of the thiol-ene system.

Temperature of the healing process (°C)	Time required to achieve full healing of the test specimen with 40 mol% of thiol-ene (min)	Time required to achieve full healing of the test specimen with 50 mol% of thiol-ene (min)
30	500	430
40	440	350
50	240	195
60	180	144
70	40	32
80	10	7

scratches in the surface of the polymer [38]. In the case of the samples with 50 mol% of the thiol-ene system, the process is slightly faster as a result of the higher concentration of disulfide bonds in the copolymer. Here, the presence of both hard and soft segments in the copolymer imparts mobility to the polymer network thus allowing the rebonding of the disulfide bonds. When the polymers are heated above the T_g the segmental mobility of the network is higher, resulting in a faster self-healing process. A video of the healing of the sample with 40 mol% of the thiol-ene system when heated at 80°C is included in the supplementary material.

Figure 6 depicts the photographs of the healing process at 70°C, of the test specimen when 40 mol% of the thiol-ene



SCHEME 4: Mechanism of the TBP catalyzed reaction of metathesis of disulfides.

system was added to the epoxy resin. Photographs were taken of parts of the specimen where there were some small defects in order to use them as a point of reference during the process. It can be seen that after healing the sample was completely repaired. The scar from the healing is visible and even where the pieces were not completely assembled and a hole was produced, it could be seen using the microscope that the holes were almost filled due to the healing process. Figure 7 shows the photographs of the specimen with 50 mol% of the thiol-ene system, before and after the repairing process also at 70°C. The sample was again completely healed as can be seen in the photographs. It is important to note that the process of self-healing in both cases occurs even when the polymer is quite rigid.

3.4. Analysis of Viscoelastic Properties by DMA. An easy method to determine if the material is completely or partially repaired is to measure the degree of loss of mechanical properties of the material before and after the self-repairing. A fast and efficient method is by determining the viscoelastic properties of the materials using DMA. As mentioned in the experimental part, two specimens for each concentration were analyzed, one control specimen that was not cut and one specimen that was cut and healed. The control sample underwent the same thermal treatment as the healed sample. Figure 8 shows both the storage modulus and the tan delta parameters for the specimens with 40 and 50 mol%. It can be seen in Figure 8(a) that the storage modulus curves for the control and the healed samples are very similar for the samples with 40 mol% of thiol-ene. In the case of 50 mol% the curves are nearly identical: this implies that the healed samples surpassed or retained almost intact their mechanical

properties compared with the control sample. For instance, the moduli for the control and healed samples with 40 mol% of thiol-ene were 980 MPa and 1096 MPa, respectively. In the case of the samples with 50 mol% of thiol-ene the modulus was 404 MPa for the control specimen and 398 MPa for the healed sample. The decrease in the modulus by changing from 40 mol% of thiol-ene to 50 mol% is due to the increased mobility of the crosslinked network as a result of the augmented concentration of polythioethers in the copolymer. We considered the healing efficiency as the ratio of the modulus of the healed sample to the modulus of the control sample. Therefore, the healing efficiencies were 111% and 98% for the samples with 40 mol% and 50 mol% of thiol-ene, respectively. Although unusual, values above 100% of healing efficiency have been reported by other research groups [39]. In our case, we can hypothesize that during the healing of the sample, the macromolecules were arranged in a more convenient configuration that allowed us to obtain higher viscoelastic properties. We have to bear in mind that the disulfide bonds undergo a dynamic exchange reaction that induces realignment of the crosslinked network. The width of the test specimens was 2 mm, which means that the self-healing process occurred in this whole area; as the sample was heated above the T_g , it resulted in higher mobility of the crosslinked network. At some point, therefore, the healed sample can present slightly higher viscoelastic properties.

Regarding the Tan delta curves for both control and healed specimens we found that they were also very similar within each concentration (see Figure 8(b)). The maximum of these curves was considered as the T_g . The T_g of the control and healed samples with 40 mol% and 50 mol% of thiol-ene was 73°C and 65°C, respectively. These T_g 's are quiet high in comparison with the T_g of -36°C reported for self-healing

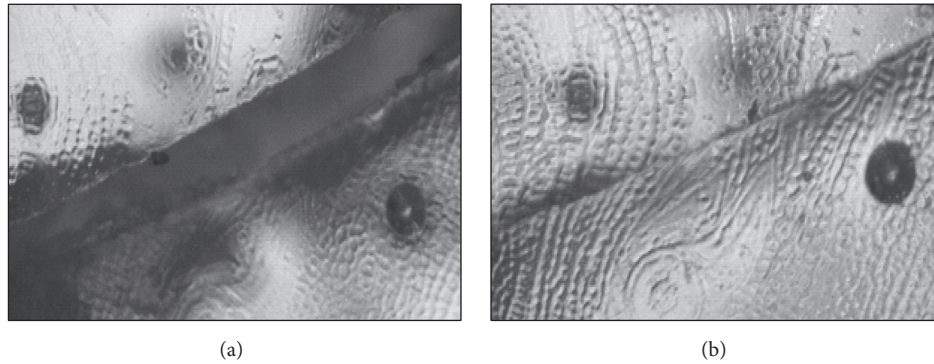


FIGURE 7: Photographs of the epoxy test specimens with 50 mol% of the thiol-ene system: (a) after the cut in halves and (b) after the healing at 70°C.

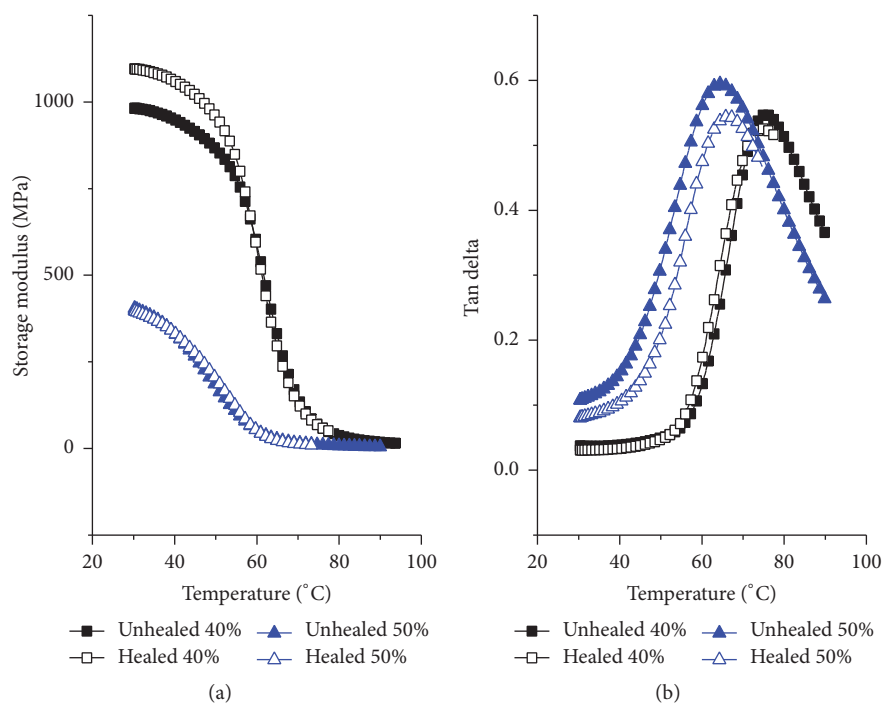


FIGURE 8: Results of the DMA analysis of the unhealed and healed specimens (a) storage modulus versus temperature and (b) tan delta versus temperature.

aliphatic epoxy resins [40] and the T_g of -3.6°C for aromatic epoxy resins [25].

Therefore, the optimum concentration of the thiol-ene system was 40 mol% because the healing efficiency with mechanical properties was greater than that of the specimens with 50 mol% of the thiol-ene system.

4. Conclusions

This paper reports an easy method for obtaining a thiol-disulfide oligomer that can be used as a comonomer in the anionic ring opening photopolymerization of a self-healing epoxy/thiol-ene system. The epoxy resin DGEBA was anionically photopolymerized by the action of a thiol-ene system

that included the prepared thiol-disulfide oligomer and the curing agent ALA4. Kinetic analysis of photopolymerization revealed that the photopolymerization proceeded in only 15 m at working conditions, resulting in copolymers with increasing concentration of polythioethers. Only the samples with 40 mol% and 50 mol% of the thiol-ene displayed the self-healing ability due to the increased mobility provided for the polythioethers in the copolymer, thus allowing the healing process. The mechanical properties of the healed samples were retained compared to the control samples. In comparison with other reports dealing with self-healing epoxy resins, we obtained hard and rigid materials with T_g 's around 65–75°C. This process could have potential utility in applications such as aerospace engineering.

Competing Interests

The authors confirm that this article content has no conflict of interests.

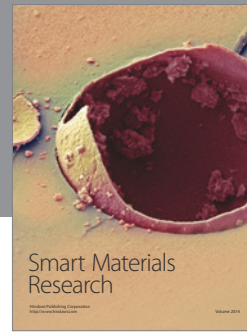
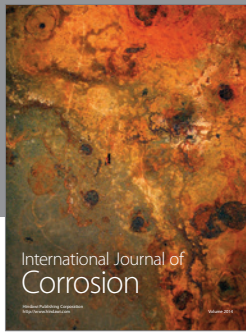
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