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Photocurable polythiol based (meth)acrylate resins stabilization: New powerful stabilizers and stabilization systems

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ABSTRACT

Photocurable thiol-ene formulations have tendency to undergo premature dark polymerization leading to a reduced pot-life and therefore only limited applications can be envisaged with these systems. New stabilizers and stabilization systems were experimented through thermal stability and photoreactivity studies. The experimental results highlighted their superior stabilization efficiency regarding photocurable thiol-(meth)acrylate resins. A stabilization system composed of lauryl gallate and triphenylphosphite showed excellent stabilization efficiency with enhanced photoreactivity of the thiol-(meth)acrylate resin and preserved thermo-mechanical properties of the photocured resin. Beyond the scope of stabilization of the target thiol-ene systems, lauryl gallate and triphenylphosphite can be envisaged as efficient stabilizers for other polymers against light ageing thanks to their friendly chemical nature. Origins and existing solutions in the art as regard to this stability issue are also discussed.

1. Introduction

Radical photopolymerized (meth)acrylate systems provide on demand rapid cure which is a particular advantage of processing of thermosets. However (meth)acrylates are generally known to shrink when cured by UV light and present other disadvantages related to yellowing and surface tackiness (due to oxygen inhibition) [1–7]. Photopolymerized thiol-enes provide an excellent solution to the above mentioned problems. In fact, reported results have shown that thiol-ene photopolymerization suffers much less from the oxygen inhibition and showed an enhanced photoreactivity. Those effects are attributed to the generation of thiyl radicals which have a poor sensitivity toward the oxygen inhibition [8–11]. This particularity of thiols brought a lot of interest in the coating community. Actually, the use of polyfunctional thiols with (meth)acrylates enables the formation of highly cross-linked polymer networks which could be formed with high functional group conversion, high polymerization rate and with lower shrinkage (due to the delayed gel point) than conventional (meth)acrylate polymerization systems [12–18]. Indeed, when the average functionality of thiol and “ene” components is higher than two, a three dimensional polymer network is created. New advanced materials with high mechanical properties could be designed using thiol-ene systems opening the door to many different applications such as dental resins, photo-curable coatings, adhesives, photoresists, implantable biomedical devices (shape memory materials), ceramic materials for MEMS and microfluidic device, liquid-crystalline materials, adhesives and pressure sensitive adhesives, optical components, high performance thermosets and stereolithography [8,19–26].

Thiol-olefine reactions were first described in 1905 [8,19,20,27]. The general thiol-ene polymerization mechanism depicted in Scheme 1, is described as a free radical step-growth mechanism involving two steps: an initial hydrogen abstraction of a thiol by a carbon centered radical to give a thiyl radical (step 1), and a subsequent addition of the thiyl radical to the carbon of another “ene” functional group (step 2). This two-step radical-chain process results in the addition of a thiol group onto an “ene” double bond [8,12,28].

It was shown that when specific monomer(s) which have tendency to homo-polymerize easily are used with thiol-enes (in binary, ternary or more thiol-ene mixtures), a more complex mechanism takes place. In the case of polymerization of (meth)acrylates and thiol mixtures, the strong homopolymerization tendency of the (meth)acrylate functional group results in a pseudo two-stage polymerization. The first stage is dominated by (meth)

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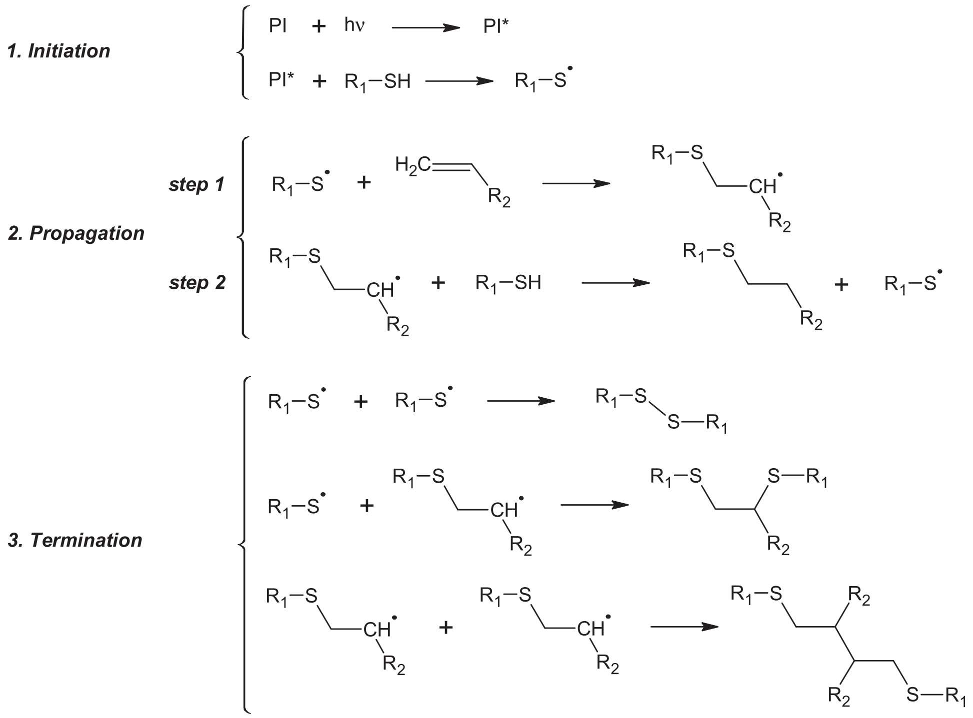


Scheme 1. General thiol-ene photopolymerization mechanism.

acrylate homopolymerization and chain transfer, and the second stage is dominated by thiol-ene polymerization [9,12,13,29–31].

Despite of all these advantages, one important drawback is limiting the use of thiol-ene chemistry. Indeed, the dark premature polymerization giving rise to reduced pot-life of the thiol-ene resins is the main issue. Several solutions were proposed to overcome this difficulty but they are still not satisfactory because of their insufficient stabilization performance [32].

In the present paper, it is attempted to investigate other systems from which efficient stabilization of thiol-enes and more particularly of thiol-(meth)acrylate based resins at the level of industry requirement is likely to stem. At first it is intended to understand the origin of the premature thiol-ene polymerization. Then, some stabilizers are selected according to a specific analysis of the state of the art results on the thiol-ene resins stabilization in particular and oxidation stabilizers in general. All the investigated stabilizers have different molecular functions and do not act according to the same mechanism. Therefore, synergies between different types of stabilizers are of course in the scope of the present work. The selected stabilizers and stabilization systems are then tested over a polythiol-(meth)acrylate based resin (TMBR) and the stabilization results are discussed. Finally, the impact of the most efficient selected stabilizers on the photoreactivity of the photocurable TMBR and on the thermo-mechanical properties of the photocured TMBR will be discussed.

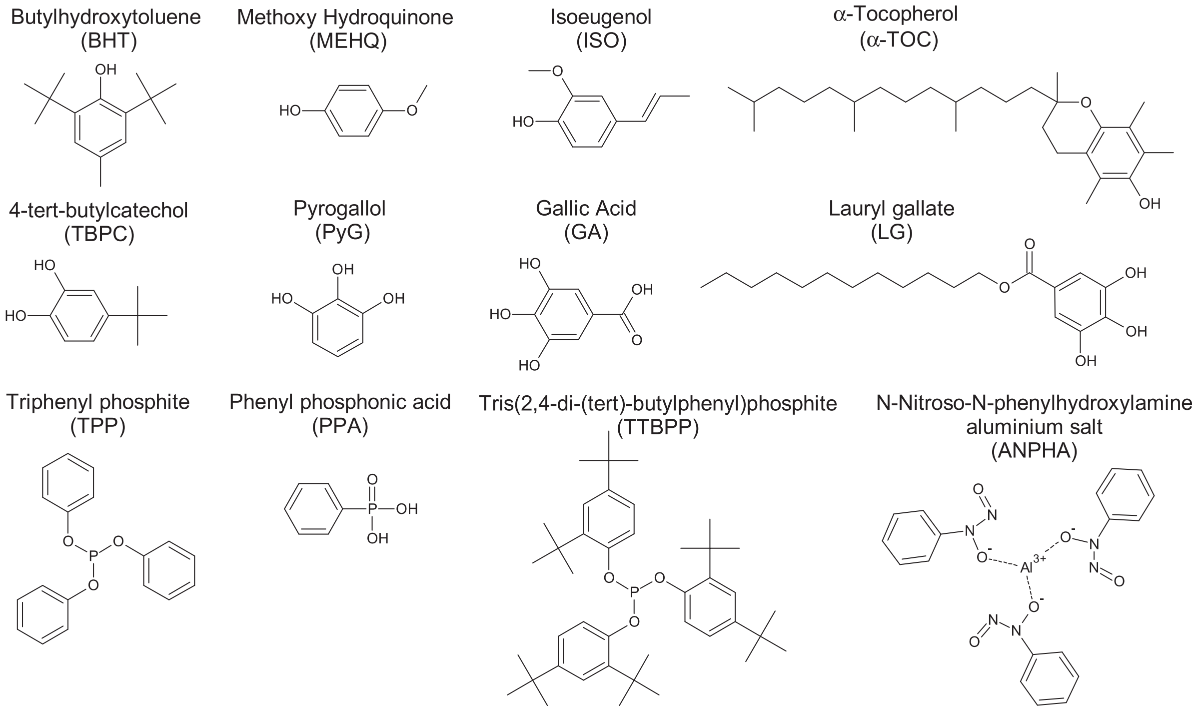
2. Materials and methods

The multifunctional (meth)acrylate based resin is composed of ethoxylated bisphenol-A di(meth)acrylate, an urethane diacrylate, trimethylolpropane triacrylate purchased from Sartomer and of Type I radical photoinitiators as 2,2-dimethoxy-1,2-diphenylethan-1-one (Irgacure 651) and 2,4,6-trimethylbenzoyldiphenylphosphine oxide (Lucirin TPO) purchased from BASF. The (meth)acrylate based resin was then modified by adding 5 wt% of pentaerythritol tetrakismercaptopropionate (PETMP) purchased from Bruno Bock. This final resin constitutes the thiol-(meth)acrylate based resin called TMBR.

The different stabilizers used are shown in Scheme 2. The thermal stability of the thiol-methacrylate based resin (TMBR) with different stabilizers and stabilization systems was performed in dark.

The different samples were stored at room temperature during 60 days and an acceleration test was carried out by storing the samples at 60 °C during 31 days. In order to compare their relative stabilization efficiency, the same molar concentration of stabilizers was used for all the samples. Therefore, a total concentration of 23.5 mM for one component stabilizer was used for each sample. In the case of bi-component stabilizer systems, a concentration of 11.75 mM for each component was used and in the case of tri-component stabilizer systems, a concentration of 7.83 mM was used for each component. The viscosity of the different samples was monitored through the time using a Haake RS 80 rotational viscometer at 30 °C. The initial viscosity of the formulation was about 1130 mPa s. The error on the viscosity values was estimated to be ±1%.

Photoreactivity investigations were performed using the real time FT-IR technique using a Bruker Vertex 70 spectrophotometer equipped with a MCT detector (spectral resolution of 4 cm^{-1}). The spectrophotometer was associated with a Xenon–Mercury UV source (Lighting Cure LC5 from Hamamatsu) equipped with an anti-calorific filter and an interferential filter at 366 nm. The lamp was calibrated to deliver an intensity of 30 $mW/cm^2 \pm 5\%$ using an Ocean Optics USB4000 spectrophotometer. The photocurable viscous liquid formulation was applied onto a BaF_2 disk using a bar coater of 12 μm to obtain a 10–12 μm thickness. The initial absorbance of the IR band at 1410 cm^{-1} was controlled before each measurement to be 0.7 ± 0.03. The decay of the (meth)acrylate double bond stretching vibration band at 1636 cm^{-1} was monitored as a function of photo-curing time. The stable band at



Scheme 2. Stabilizers used in this work.

1580 cm^{-1} was used as internal reference. Each sample was analyzed two times. Rates of polymerization and final conversion were determined as described elsewhere [33,34]. The error was about 10% on the rates of photopolymerization and about 2% on the final conversions.

Thermo-mechanical investigation was performed on fully photo-cured standardized test specimens. The standard test specimens were fabricated by pouring the photocurable liquid formulation in a specially designed silicone mold which was then UV irradiated in a curing station which delivers a power density of 1.9 mW/cm^2 during 60 min (6.84 J/cm^2). The tensile, flexural and bend notch tests were carried out using a Zwick 1454 universal testing machine (Zwick Roell, Ulm, Germany) at 23 °C. For the tensile tests, dog bones shaped test specimens having a dimension of 79 × 13.5 × 4 mm with a gauge length of 20 mm were extended with a crosshead speed of 2 mm/min (ISO 527-2). The experiment was repeated three to four times and the mean values for the tensile modulus and the elongation were reported with a deviation error of ±5% and ±10% respectively. For the three-point bending tests or flexural tests, the bars shaped test specimens having a dimension of 80 × 10 × 4 mm were subjected to a force at a crosshead speed of 2 mm/min (ISO 178). The experiment was repeated three to four times and the mean value was reported. The calculated error was ±5%. For the bend notch test, bars shaped specimens having a dimension of 60 × 12.5 × 4 mm (ISO 13586) were used. Before the testing, a notch (depth 2.47 mm) was placed in the center of the specimen using a diamond cutting disc and a sharp pre-crack was added using a razor blade. The crosshead speed was set at 10 mm/min and the fracture sites were inspected using a Wild M3C stereomicroscope (Heerbrugg, Switzerland) equipped with an Intralux 5000-1 cold light source Illuminator (Volpi) and a Kappa messtechnik MFK measurement unit. The heat deflection temperature test was performed using a Vicat Zwick Roell machine. Thin bars shaped test specimens having a dimension of 80 × 10 × 4 mm were immerged in an oil bath and subjected to a constant load of 1.80 MPa. Toughness of the cured samples was evaluated from the strain energy release rate G_{IC} and critical stress intensity factor K_{IC} as described in Refs. [35,36].

3. Results and discussion

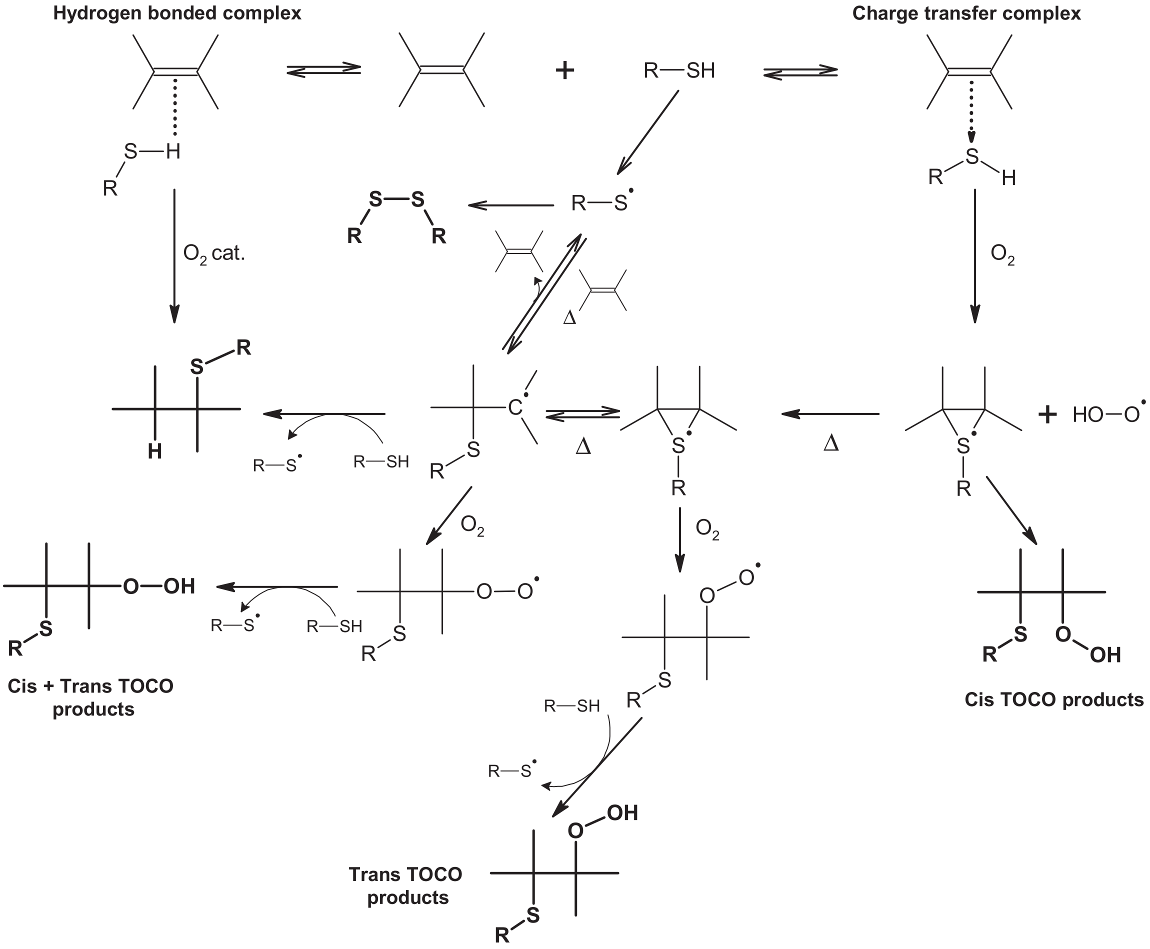
3.1. Origin of the premature polymerization in thiol-ene systems

Based on literature report, the dark polymerization mechanism of thiol-ene systems seems to be not yet totally understood. One explanation based on the “thiol-olefin addition-cooxidation reaction” model (TOCO) under non radical-inducing conditions which describes the reaction of a thiol with an olefin in absence of oxygen (addition) or presence of an excess of oxygen (cooxidation), as shown in Scheme 3 [8,10,37–39].

It was observed that when the reaction is performed in the absence or in the presence of low concentration of oxygen, a predominant addition of the thiol on the olefin compound takes place. Finally, it was found that a very slow oxidation reaction of charge transfer complexes with oxygen in dark and at room temperature occurs in thiol-ene systems [39]. This oxidation reaction could be an explanation for the premature dark polymerization of thiol-ene systems.

Thiol–ene can also polymerize through the decomposition of peroxide impurities [20]. Additionally, in the case of (meth)acrylate, the premature dark polymerization could be initiated through a base or acid catalyzed thia-Michael addition reaction [40–45].

In the system used in the present work, the pentaerythritol tetrakismercaptopropionate (PETMP) has a relatively low pH (pH ≈ 4–5). The latter is mixed with a polyfunctional methacrylate mixture which also has a low pH (pH ≈ 4–5). Moreover, no catalyst was added to the mixture. In these conditions, the thia-Michael addition reaction should not occur at room temperature. Nonetheless, it was seen in practice that this resin undergoes a premature dark polymerization, meaning that a thiol-ene radical addition mechanism takes place rather than a thia-Michael addition reaction. In order to understand how the radicals could be generated, an



Scheme 3. Overview of the various pathways by which a thiol-ene can interact with each other and with oxygen.

experiment was performed to examine the role of oxygen in the generation of radicals via the TOCO mechanism. The PETMP and the polyfunctional dimethacrylate mixture were first dried separately using activated molecular sieves. Then, they were mixed together (in a ratio of 1/1 by weight) in an inerted glovebox at room temperature and in dark conditions (UV protected lab). After one day storage, the mixture has completely polymerized. The same experiment was carried out in ambient air at room temperature and in dark conditions. After three days storage at room temperature the mixture jellified. The experiment showed that the dark polymerization occurred even faster than when the mixture is not under inert atmosphere. This result can let us think that oxygen has no determining role in the reaction and that the dark polymerization is essentially generated by radicals produced in another way. This experiment is in agreement with ESR and UV spectroscopic investigation that have demonstrated the formation of radicals just after mixing together thiol and enes, in the absence of oxygen [46,47].

It should be considered that radicals could be also generated through different other sources as contaminants coming from the storage conditions such as metals from metallic drums [48,49] and by-products coming from raw materials (monomer synthesis protocols) or compounds that easily oxidize at room temperature to produce peroxides, chloride ions and base–amine catalysts [20].

3.2. Thiol-ene stabilization: state of the art

Attempts to stabilize thiol-ene resins have been described in several papers and patents [20,26,32,47,50–66]. It seems that the addition of radical scavenger additives was the best method which could more or less stabilize thiol-ene resins. That, indirectly, means that radicals were present in the media. An art search was performed in order to have a broad view about the different used radical scavengers and to identify the most promising ones for the studied thiol-(meth)acrylate based resin.

In 1971, free radical scavengers were proposed as vinyl stabilizers to improve shelf life of photo-curable polythiols and burn resistance of cured resins [52]. A lot of stabilizers were proposed such as vinyl amines, vinyl sulfurs, arsenites and stannites, vinyl phosphores, vinyl phenols, vinyl nitrates, vinyl phosphines, vinyl stilbene, vinyl arsine and vinyl bismuthine compounds, the preferred one being triallyl phosphite. Later was reported the use of phosphorous acid, conventional hindered phenolic antioxidant stabilizers and aromatic amines [53,54]. In 1991, chloranil (tetrachloro-p-benzoquinone) and 1,4-diazabicyclo[2,2,2] octane (DABCO) have been tested as stabilizers [55]. The same year, a patent also described several stabilizers examined in norbornene-thiol compositions: phenol based stabilizers, pH modifiers, sacrificial mercaptans, amine based stabilizers, sacrificial ene monomers, metal chelators, some phosphorous or boron based stabilizers. It was found that these compounds have little or no effect on the stability of norbornene-thiol compositions. By contrast, non-acidic nitroso compounds were found successful as stabilizers, the preferred nitroso compounds being the aluminum and ammonium salts of N-nitroso phenylhydroxylamine [56]. In 1992, the useful effect of the addition of sulfur and potassium iodide-iodine mixtures in norbornene-thiol formulations was reported [26,57]. Many works reported some beneficial effects of nitrosohydroxylamine derivatives [50,58,61–63]. In 1993, some radical stabilizers as pyrogallol, hydroquinone and catechol in dithiol-diene mixtures were experienced [59]. In 1996, was reported the stabilization effect of pyrogallol with molar equivalent mixture of 1,4-butanediol dimercaptopropionate with diallyl succinate in dark cure conditions [47]. In 2007 the inhibition effect of butylhydroxytoluene (BHT) and a nitroxide inhibitor was studied in a mixture of pentaerythritoltetrakis(3-Mercaptopropionate (PETMP) and tri(ethylene glycol) divinyl ether (TEGDVE). A good stabilization effect of BHT at room temperature was found but not at high temperature whereas the nitroxide inhibitor showed a good stabilization effect even at high temperature [64]. Very recently, a blend of stabilizers was proposed which was based on a phenolic radical scavenger used to scavenge free radicals and an acidic compound used to prevent the thia-Michael addition reaction (acting as a buffer). A synergistic effect between these two components was claimed to confer good stability efficiency at RT and at elevated temperature (65 °C) [32,66].

3.3. *Selection of the different stabilizers and stabilization systems*

Different types of stabilizers are classified: the hydrogen donors, the hydroperoxide decomposers, the alkyl radical scavengers and the metal deactivators [67]. Hydrogen donors are known to scavenge radicals by hydrogen abstraction process. Hydroperoxide decomposers such as phosphites and phosphonites are stabilizers which react with hydroperoxides to form the corresponding alcohol. Alkyl radical scavengers are stabilizers which react with alkyl radicals and form unreactive radicals. Metal deactivators form stable complexes with metal ions preventing the formation of reactive radicals [67,68].

The strategy of this work is first to test individually the efficiency of some stabilizers from each class in the TMBR. Then, combinations of the most efficient stabilizers of each class will be made in order to maximize the trapping of the different radicals which can be involved in the premature dark polymerization of the TMBR.

3.3.1. *Phenolic stabilizers*

Phenolic stabilizers such as butylhydroxytoluene (BHT), methoxy hydroquinone (MEHQ), 4-terbutylcatechol (TBPC), α-tocopherol (α-TOC) and pyrogallol (PyG) were selected. Other phenolic stabilizers were identify from the literature such as isoeugenol (ISO), gallic acid (GA) and lauryl gallate (LG). Isoeugenol is described in literature as a good antioxidant and is easily available. Gallic acid has a very high antioxidant activity demonstrated by its high Trolox equivalent antioxidant activity (TEAC) [69,70]: it was shown that the TEAC value of gallic acid was equal to 3.01 ± 0.05 mM compared to 1.91 ± 0.02 mM for pyrogallol and 1 mM for α-tocopherol. These reported results justify the motivation to test the activity of gallic acid. Lauryl gallate plays the role of metal chelating agent and has an antimicrobial effect. It is used as antioxidant food additive (E-312), meaning that it is a safe chemical [71–73]. For those considerations, lauryl gallate was the preferred selected radical scavenging stabilizer.

3.3.2. *Hydroperoxides decomposers*

The efficiency of triphenylphosphite (TPP) compared to triphenylphosphine, tri-p-tolyl-phosphine, tri-m-tolyl-phosphine and diphenyl (p-tolyl)phosphine to stabilize thiol/allyl ethers systems has been already reported [63]. Also, it was shown that phenylphosphonic acid (PPA) improves the stabilization of thiol-methacrylate resins when it is mixed with pyrogallol but not when it is used alone [32]. Therefore, phenylphosphonic acid was tested in different stabilization systems. It was found also interesting to examine tris(2,4-di-(tert)butylphenyl)phosphite (TTBPP). Indeed, its chemical structure let think that the phosphite compound would be quite stable at high temperature regarding a possible Michael addition reaction between the phosphite and the methacrylate. Methyl groups in the phenyls linked to the phosphorus atom should increase the steric hindrance of the molecule and reduce the possible nucleophilic attack of the phosphorus on the ene.

3.3.3. *Alkyl radical scavengers*

Several nitroso compounds were examined. It seems that the aluminum salt of N-nitroso-N-phenylhydroxylamine (ANPHA) is the most popular stabilizer used to stabilize thiol-ene systems and was therefore selected to be examined in the TMBR.

3.4. *Thermal stability results and discussion*

3.4.1. *Stability tests using single stabilizers*

Table 1 reports the viscosity increase of the stabilized TMBRs with single selected stabilizers after 60 days storage at room temperature and after 31 days storage at 60 °C. It can be seen from the table that for many systems the viscosity of the resin increase with time even in the presence of stabilizer. The stabilization efficiency (SE) was defined as:

$$SE = \frac{\eta_i}{\eta_t}$$

where η_i is the initial viscosity (1130 mPa s) and η_f is the viscosity after storage. By looking at Fig. 1, which depicts the stabilization efficiency of the single stabilizers, the first observation highlighted by this study is that the monohydroxy phenolic stabilizers are the less efficient. Indeed, noticeable viscosity increase was observed for BHT, MEHQ, and α-tocopherol. Isoeugenol appears to have a destabilizing effect, as the increase in viscosity is higher in that case than in its absence. This effect may be attributed to the presence of the alkene group in isoeugenol structure. Isoeugenol showed an acceleration effect of the premature dark polymerization of the TMBR.

Dihydroxy phenolic stabilizer, TBPC, leads to a much lower viscosity increase than the monohydroxy phenolics and trihydroxy phenolics showed improved performances. Then, it clearly appears that more there are hydroxyls on the stabilizer more the radical scavenging capacity of the phenolic stabilizer is high. This could be attributed to the better stabilization of the phenoxy radical formed after hydrogen abstraction. Indeed, antioxidant properties of phenols were already compared with respect to photopolymerization

Table 1
Viscosity increase after 60 days storage at RT and after 31 days storage at 60 °C of the different stabilized TMBR with different single stabilizers.

Stabilizers in TMBR	Viscosity increase (%) 60 days at RT	Viscosity increase (%) 31 days at 60 °C
No stabilizer	26.8	Gelified
α−TOC	17.1	Gelified
MEHQ	17.0	Gelified
BHT	18.5	Gelified
ISO	88.5	Gelified
TBPC	10.3	Gelified
PyG	3.60	72.0
GA	7.69	26.64
LG	5.24	19.2
TPP	−0.45	Gelified
TTBPP	5.70	Gelified
PPA	2.63	Gelified
ANPHA	4.82	50.5

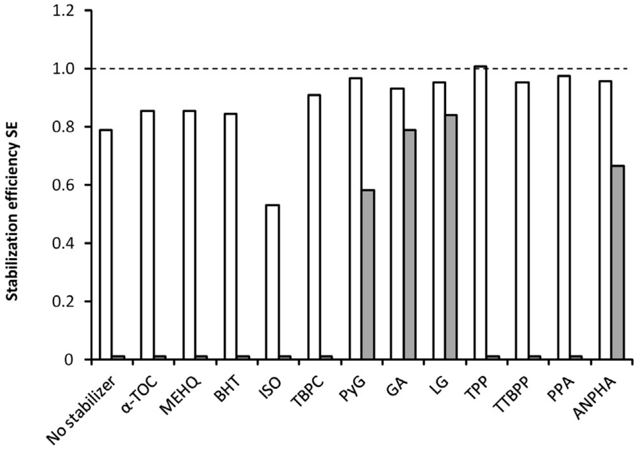


Fig. 1. Stabilization efficiency of the thiol-(meth)acrylate based resin with single stabilizers at RT for 60 days (white) and 60 °C for 31 days (grey).

reaction. It was found that the efficiency rather depends on physico-chemical properties rather than the number of hydroxyl groups present on the structure [74,75]. The tested trihydroxy phenolics stabilizers have a similar viscosity increase, but pyrogallol seems to be more efficient than lauryl gallate which is, in turn, more efficient than gallic acid. It is possible that their stabilization efficiency difference is linked to their mobility or their ability to diffuse through the resin.

Hydroperoxide decomposers showed also interesting results and among all the tested stabilizers, triphenylphosphite is the most efficient. It shows no viscosity increase during 2 months at RT. The fact that TPP not only acts as radical scavenger but also acts as viscosity reducer even at low concentration could be one of the explanation for this result. Also, a very slight viscosity increase of about 2.6% was measured for phenylphosphonic acid. However, TTBPP showed a slightly higher viscosity increase probably due to its restricted mobility in the viscous resin media and to its steric hindrance.

Finally, the alkyl radical scavenger ANPHA, showed interesting results at room temperature with a moderate increase in viscosity.

According to these results, it seems that the stabilizers which are performing the best at room temperature are the hydroperoxide decomposers. Then, the di- and trihydroxy phenolic stabilizers and ANPHA showed also interesting stabilization effect of the TMBR. That means that different types of radicals should be involved in the premature dark polymerization.

The same formulations from the same batches than those used before were stored 31 days at 60 °C and their viscosities were continuously measured (Fig. 1).

It could be seen from Fig. 1 that PyG, GA, LG and ANPHA are the best stabilizers. All the other samples have gelified or solidified more or less rapidly. TMBR itself gelified after 5 days. The samples containing the conventional phenolic stabilizers showed a relatively improved thermal stability at 60 °C. The most stable monohydroxy phenolic stabilizers which seem to be BHT and TBPC gelified respectively after 13 days and 12 days. The samples containing the hydroperoxide decomposer stabilizers as triphenylphosphite and phenylphosphonic acid have gelified after 3 days storage, i.e. exhibiting a shorter pot-life than the formulation without stabilizer. A catalytic effect of the phosphorous compounds on the Michael addition reaction of PETMP on methacrylate monomers is probably taking place. However, the sample containing TTBPP showed a better thermal stability than the latters. The sample gelified after 7 days storage.

This can be explained by the steric hindrance of tertiobutyl groups on phenyls of TTBPP which makes tougher the nucleophilic attack from phosphorus to the electro-deficient carbon of the (meth)acrylate groups making difficult the Michael addition reaction. However, trihydroxy phenolic stabilizers as well as the alkyl radical scavenger showed better results. Lauryl gallate seems to be the most efficient stabilizer. Then, gallic acid, aluminum N-nitroso-N-phenylhydroxylamine and pyrogallol showed a viscosity increase of 26.6%, 50.5%, and 72%, respectively.

3.4.2. *Stability tests using blends of stabilizers*

In the purpose to improve the thiol-ene resins dark stability, different blends of stabilizers were elaborated. Two combination types are possible. Combinations inducing a homosynergistic effect and combinations inducing a heterosynergistic effect [67]. The first type deals with blends of stabilizers from the same family or having the same stabilization mechanism. The second type deals with blends of stabilizers from different families or having different stabilization mechanisms. The first type of combinations was tested using phenolic stabilizers: MEHQ/α-TOC, MEHQ/BHT, BHT/α-TOC, and MEHQ/ISO. Several stabilizing systems were investigated in order to find out some heterosynergistic combinations: phenolic hydrogen donors and hydroperoxide decomposers (PyG/TPP, GA/TPP, LG/TPP, PyG/PPA, GA/PPA, PyG/TTBPP, and LG/TTBPP), alkyl radical scavenger and hydrogen donors (ANPHA/GA), alkyl radical scavenger and hydroperoxide decomposers (ANPHA/TBPC, ANPHA/TPP) were tested. Actually, combinations of alkyl radical scavengers, hydrogen donors and hydroperoxide decomposers were investigated by selecting the best single stabilizers of each class (ANPHA/TPP/PyG, ANPHA/TPP/GA and ANPHA/TPP/LG).

Table 2 reports the viscosity increase of the stabilized TMBRs with stabilization systems after 60 days storage at room temperature and after 31 days storage at 60 °C.

As it can be seen in Fig. 2, regarding the monohydroxy phenolic stabilizers combinations, no surprising homosynergistic effect was observed. MEHQ/BHT, MEHQ/α-TOC, BHT/α-TOC and MEHQ/ISO stabilization systems are performing at similar level than their respective single monohydroxy phenolic stabilizers.

The stabilization systems involving a trihydroxy phenolics and hydroperoxide decomposers showed interesting results in general. The stabilization systems constituted of PyG/PPA, GA/PPA and LG/PPA showed good stabilization efficiency with low viscosity

Table 2
Viscosity increase after 60 days storage at RT and after 31 days storage at 60 °C of the different stabilized TMBRs with different stabilization systems.

	Viscosity increase (%) Storage 60 days at RT	Viscosity increase (%) Storage 31 days at 60 °C
No stabilizer	26.8	Gelified
MEHQ/BHT	17.2	355.0
MEHQ/α–TOC	16.9	Gelified
BHT/α–TOC	16.9	350.5
MEHQ/ISO	22.9	Gelified
PyG/PPA	5.1	22.8
GA/PPA	5.3	14.3
LG/PPA	2.88	Gelified
PyG/TPP	0.00	3.84
GA/TPP	2.57	7.54
LG/TPP	−0.27	12.5
PyG/TTBPP	5.70	106.6
LG/TTBPP	18.9	25.4
ANPHA/TBPC	1.93	47.5
ANPHA/TPP	2.83	77.5
ANPHA/GA	8.82	29.3
ANPHA/TPP/PyG	5.61	54.6
ANPHA/TPP/GA	1.75	32.5
ANPHA/TPP/LG	3.14	45.3

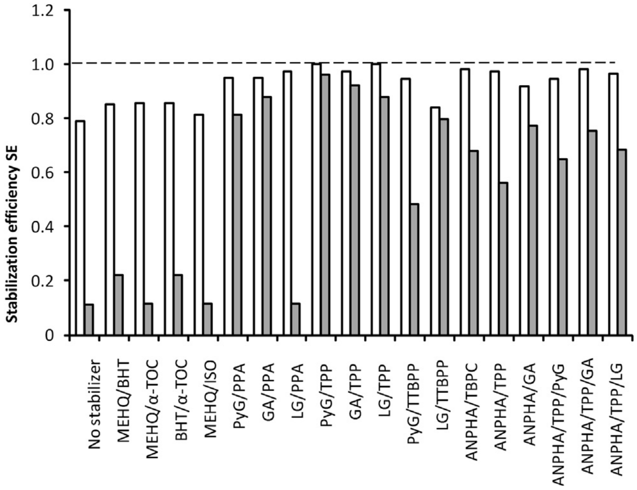


Fig. 2. Stabilization efficiency of the thiol-(meth)acrylate based resin using blends of stabilizers at RT for 60 days (white) and 60 °C for 31 days (grey).

increase. However, no real additional stabilization effect was observed with respect to the single stabilizers. Trihydroxy phenols and triphenylphosphite systems exhibited slightly better results. Almost no viscosity increase was observed for PyG/TPP and LG/TPP systems. When using TTBPP, lower stabilization efficiencies were obtained. ANPHA in combination with di or trihydroxy phenolic look to be similar or even less efficient than trihydroxy phenolics/hydroperoxide decomposers. Indeed, ANPHA/TBPC and ANPHA/TPP exhibited low viscosity increase. By contrast, ANPHA/GA has lower stability efficiency.

Among the three-stabilizer systems, the best results were obtained for ANPHA/TPP/GA which exhibits almost no increase of the viscosity. By contrast, although exhibiting moderate increase in viscosity, ANPHA/TPP/PyG and ANPHA/TPP/LG are less efficient than Pyg/TPP or LG/TPP.

To summarize these best results obtained after 60 days storage at RT, apart the mono hydroxyl phenolics, most of the combinations lead to viscosity increase lower than 10%. Some combinations performed very well with viscosity increase lower than 2%: the best stabilization efficiencies were obtained for mixtures of trihydroxy phenolics with hydroperoxide decomposers (PyG/TPP and LG/TPP). Similarly, ANPHA/TBPC showed a synergistic effect, and among the three-component systems, ANPHA/TPP/GA showed good stabilization efficiency.

The same study was therefore repeated by storing the freshly made formulations at 60 °C during 31 days. The results reported in Table 2 are collected in Fig. 2. The graph shows clearly that the monohydroxy phenolics based stabilization systems do not permit an efficient stabilization. The best stabilization systems are those based on trihydroxy phenolics and the hydroperoxide decomposers. The other stabilization systems are much less stable than they were at room temperature. It appears more precisely that the stabilization systems PyG/TPP, GA/TPP, LG/TPP and GA/PPA give the best results with viscosity increase lower than 15%.

These thermal stability studies at RT and at 60 °C permitted us to evaluate some single stabilizers and stabilization systems. Regarding single stabilizers experiments, it appeared that the hydroperoxide decomposers and more precisely triphenylphosphite and phenylphosphonic acid have a high stabilization effect on the TMBR at room temperature but not at 60 °C. Also, it was seen that the trihydroxy phenolic stabilizers lauryl gallate, gallic acid and pyrogallol have a very good stabilization effect on the TMBR at room temperature and at 60 °C. The alkyl radical scavenger, aluminum N-nitroso-N-phenylhydroxylamine, showed also a good stabilization effect at room temperature and at 60 °C. Regarding the stabilization systems, it was seen that the combinations of the trihydroxy phenolic stabilizers with hydroperoxide decomposers have a very good stabilization effect on the TMBR at room temperature and at 60 °C. The most efficient systems seemed to be the combinations PyG/TPP, GA/TPP, LG/TPP, GA/PPA, PyG/PPA and LG/TTBPP. However, the addition of such stabilizers could affect the photoreactivity of the TMBR and the final mechanical properties of the cured thiol-(meth)acrylate based resin. Further investigations were undertaken to assess the influence of the best stabilizers and stabilization systems on the photoreactivity and on the mechanical properties of the TMBR.

3.5. *Photoreactivity experiments results*

RT-FTIR experiments were performed in order to evaluate the photoreactivity of stabilized TMBR. In order to investigate the effect of the single stabilizers on the photopolymerization behavior of the thiol-(meth)acrylate based resin, a first set of experiments were done with samples containing pyrogallol, gallic acid, lauryl gallate, triphenylphosphite and aluminum N-nitroso-N-phenylhydroxylamine at the same concentrations than those used previously. Then, a second set of experiments was done with the most interesting stabilization systems, i.e. PyG/TPP, GA/TPP, LG/TPP, GA/PPA and LG/TTBPP. Fig. 3 shows the conversion profiles of the TMBR without stabilization additives and with different selected single stabilizers. The average conversions and polymerization rates were reported in Table 3.

TMBR itself exhibited a final conversion of 83% and a conversion rate of 0.37 s^{-1}. In the presence of trihydroxy phenolics, both the rate of polymerization and the final conversion decreased. However, there is a significant difference between pyrogallol which showed a conversion of 69% and a polymerization rate of 0.28 s^{-1} and the two others, lauryl gallate and gallic acid which showed higher final conversions and polymerization rates. The fact that trihydroxy phenolic stabilizers inhibit the photoreactivity could be understood by the consumption of a part of the initiating radicals coming from the photodissociation of the initiator molecule by the trihydroxy phenolic stabilizers which consequently diminishes the amount of the initiating radicals. The fact that pyrogallol inhibits more the photoreactivity could come from its easier mobility in the resin due to its smaller size and, as seen during the sample preparation, to its better solubility in the (meth)acrylate matrix than the others. These results are in line with known behavior of phenolic compounds towards radical photopolymerization [74–76]. Very

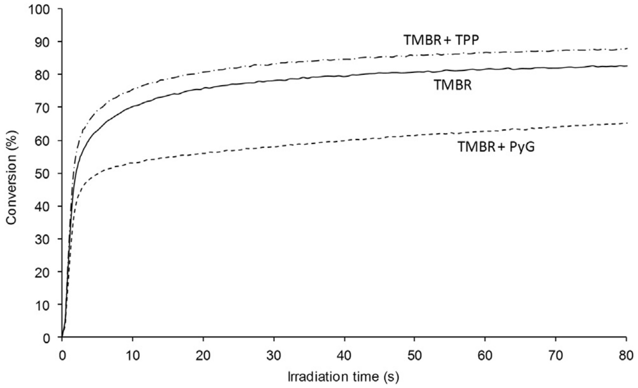


Fig. 3. Conversion profiles of the thiol-(meth)acrylate based resin without stabilizers and with the selected single stabilizers.

Table 3
Polymerization rates and conversion values obtained for the thiol (meth)acrylate based resin in the presence of stabilizers.

	Rp/[M$_0$] (s^{-1})	Conversion (%)
None	0.37	83
PyG	0.28	69
GA	0.34	76
LG	0.35	79
ANPHA	0.38	84
TPP	0.45	88
PyG/TPP	0.33	84
GA/TPP	0.37	86
LG/TPP	0.40	88
LG/TTBPP	0.37	87
GA/PPA	0.36	84

interestingly, it appears that ANPHA does not affect the photoreactivity. The photopolymerization behavior is quite similar than that of the non-stabilized TMBR, with a conversion of 84% and a polymerization rate of 0.38 s^{-1}. Finally, the triphenylphosphite stabilizer showed the best photopolymerization behavior. A conversion of 88% and a polymerization rate of 0.45 s^{-1} were reported. Here, it is clearly seen that triphenylphosphite enhances the photopolymerization behavior of the TMBR, an effect already reported for triphenylphosphine for the photopolymerization of acrylates under air [77]. The fact that the TPP stabilized TMBR has a lower viscosity could delay the gelation time of the resin and then could lead to higher conversion.

To summarize, the trihydroxy phenolic stabilizers showed an effect on the photoreactivity of the TMBR. They reduce the conversion and the polymerization rate. Lauryl gallate showed better photopolymerization properties than gallic acid and pyrogallol. Then, ANPHA seems to not interfere on the TMBR photoreactivity. It showed similar photopolymerization properties than the non-stabilized TMBR. Actually, triphenylphosphite showed the best photopolymerization behavior with the TMBR with higher conversion and photopolymerization rate than the non-stabilized TMBR.

The stabilization systems which showed the best stability efficiencies at room temperature and at 60 °C were then evaluated (Table 3). Fig. 4 shows the conversion profiles of the stabilized TMBR and shows the conversion values as well as the polymerization rates for the different stabilization systems.

It appears that all the stabilization systems do not affect negatively the photopolymerization behavior of the thiol-(meth)acrylate based resin. The samples have almost the same conversion than the TMBR except the stabilization systems LG/TPP, LG/TTBPP and GA/TPP which showed a little better conversion than the non-stabilized TMBR. However, it appears slight differences in term of polymerization rates. Indeed, the system PyG/TPP showed a polymerization rate of 0.33 ± 0.03 s^{-1} which is much lower than the one of the non-stabilized TMBR. GA/PPA, GA/TPP and LG/TTBPP showed similar photopolymerization rates as TMBR. Interestingly, LG/TPP system reached a rate of about 0.40 s^{-1} which is slightly higher than TMBR itself. It seems that the combination of a trihydroxy phenolic which has a tendency to decrease the polymerization rate with triphenylphosphite which have the opposite effect rises to an equilibrium which permits to keep the same photopolymerization behavior than that of TMBR resin. By the way, it was observed during the experiments that the trihydroxy phenolics/TPP stabilization systems and more notably LG/TPP seemed to attenuate the yellowing of the cured TMBR.

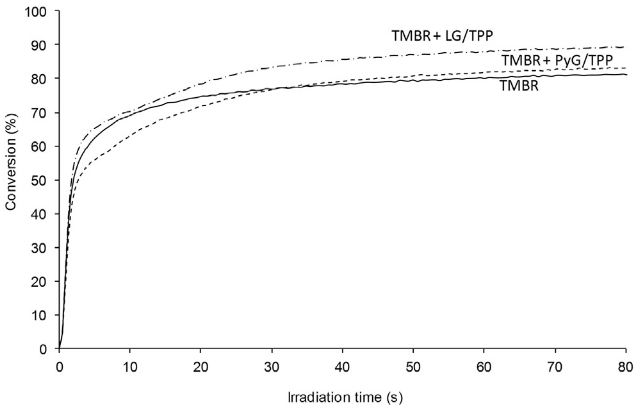


Fig. 4. Conversion profiles of the thiol-(meth)acrylate based resin without stabilizers and with the selected stabilization systems.

It should be noted that no optimization of stabilizer concentration was performed in this work. In the case of LG/TPP, a fine tuning of the concentrations might afford higher stabilization ability and lower influence on the resin reactivity. This optimization should also take into account the exact nature of the resin to be stabilized as well as the expected pot-life.

3.6. LG/TPP stabilization system influence on thermo-mechanical properties of the thiol-(meth)acrylate based resin

Following the photopolymerization results, it was decided to investigate the thermo-mechanical properties of the LG/TPP stabilized thiol-(meth)acrylate based resin. Indeed, LG/TPP stabilization system showed very interesting thermal stability results at room temperature and at 60 °C and showed enhanced photoreactivity as regard to other stabilization system. Flexural, tensile, bend notch and HDT testing were performed on the cured parts following ISO standards.

Table 4 reports the thermo-mechanical results of the cured TMBR and of the cured LG/TPP stabilized TMBR. It appears that the flexural modulus of the stabilized TMBR decreased of 18% compared to the non-stabilized TMBR and the flexural elongation increased of 37%. The material seems to be more flexible. However, tensile tests showed that there is almost no loss in tensile modulus (only 2.4% compared to the non-stabilized TMBR). The tensile tests confirm the flexibility improvement of the stabilized TMBR with a tensile elongation increase of about 130%. Actually, the stabilized TMBR showed a low decrease in the heat deflection temperature at 1.80 MPa. The temperature decreased from 41 °C to 38.5 °C, a fact which is due to the increased flexibility of the stabilized material.

Toughness is defined as the resistance of a material to rapid crack propagation It can be characterize by the minimal stress intensity factor K_{IC} and the strain energy release rate G_{IC} for that a fracture occurs [35,36]. For the samples tested here, a good toughness of the material was observed, a slight decrease of only 7% in K_{IC} and a noticeable increase of 35% in G_{IC} were found in the presence of LG/TPP stabilizing system.

Table 4
Thermo-mechanical results (with percent deviation) of the TMBR compared to the LG/TPP stabilized TMBR.

	TMBR	TMBR + LG/TPP
Flexural modulus (GPa)	1.46 (0.05)	1.19 (0.06)
Flexural elongation (%)	11 (0.64)	15.1 (0.14)
Tensile modulus (GPa)	1.41 (0.05)	1.38 (0.03)
Tensile elongation (%)	5.1 (0.14)	11.7 (2.4)
HDT (°C)	41 (2.91)	38.5 (0.55)
K_1C (MPa m$^{1/2}$)	1.09 (0.03)	1.01 (0.04)
G_1C (KJ m$^{1/2}$)	0.94 (0.06)	1.0 (0.09)

The thermo-mechanical results showed that the stabilization system lauryl gallate/triphenylphosphite does not affect negatively the thermo-mechanical properties of the TMBR. However, an increasing in flexibility of the TMBR material was observed. This material behavior could be attributed to the higher final conversion reached with the LG/TPP stabilization system as seen in the photoreactivity study.

4. Conclusion

In this paper, the stabilizing effect of a set of candidates towards the dark polymerization of a thiol-(meth)acrylate mixture was studied. Several candidates were revealed to have superior stabilization performances than the existing thiol-ene stabilizers. The stability tests performed on the single stabilizers at RT showed that the hydroperoxide decomposers, the di- and trihydroxy phenolic stabilizers and the alkyl radical scavenger (ANPHA) have good stabilization efficiency. Triphenylphosphite and phenylphosphonic acid showed the best stabilization performance. The same tests performed at 60 °C showed that the trihydroxy phenolic stabilizers as well as the alkyl radical scavenger (ANPHA) did not jellify even after 31 days storage. Lauryl gallate showed the best stabilization efficiency at that temperature. The stability tests performed on the stabilization systems at room temperature showed different stabilization effects. The systems consisting on the combination of PyG/TPP and LG/TPP showed the best stabilization efficiency and several other systems were found to have a good heterosynergistic effect with good stabilization efficiency. Regarding the stability tests performed at 60 °C, a huge heterosynergistic effect was observed for the system PyG/TPP which presented the best stabilization performance. Then, the photoreactivity study of the TMBR stabilized with the most interesting stabilizers and stabilization systems showed that TPP increases the polymerization rate and the conversion of the TMBR, ANPHA does not interfere in the photoreactivity of the TMBR and trihydroxy phenolics decrease the polymerization rate and the conversion. However, it was shown that all the selected stabilization systems composed of trihydroxy phenolics and hydroperoxide decomposers are able to maintain or improve the photoreactivity of TMBR. Finally, a thermo-mechanical study was performed on the LG/TPP stabilized TMBR because of the high stabilization performance and the best photoreactivity observed for the LG/TPP system. The results showed that LG/TPP stabilization system enhance the flexibility of the TMBR and does not affect the toughness and the tensile modulus of the TMBR.

References

[1] Kilambi H, Reddy SK, Schneidewind L, Stansbury JW, Bowman CN. Copolymerization and dark polymerization studies for photopolymerization of novel acrylic monomers. Polymer 2007;48:2014–21.

[2] Decker C, Jenkins AD. Kinetic approach of oxygen inhibition in ultraviolet- and laser-induced polymerizations. Macromolecules 1985;18:1241–4.

[3] O'Brien AK, Bowman CN. Impact of oxygen on photopolymerization kinetics and polymer structure. Macromolecules 2006;39:2501–6.

[4] Bowen RL. Properties of a silica-reinforced polymer for dental restorations. J Am Dent Assoc 1963;66:57–64.

[5] Patel MP, Braden M, Davy KWM. Polymerization shrinkage of methacrylate esters. Biomaterials 1987;8:53–6.

[6] Ferracane JL. Developing a more complete understanding of stresses produced in dental composites during polymerization. Dent Mater 2005;21:36–42.

[7] Jian Y, He Y, Jiang T, Li C, Yang W, Nie J. Polymerization shrinkage of (meth) acrylate determined by reflective laser beam scanning. J Polym Sci Part B: Polym Phys 2012;50:923–8.

[8] Jacobine AF. Polymerisation mechanisms. In: Fouassier JD, Rabek JF, editors. Radiation curing in polymer science and technology, vol. III; 1993. p. 219. London.

[9] Cramer NB, Bowman CN. Kinetics of thiol–ene and thiol–acrylate photopolymerizations with real-time fourier transform infrared. J Polym Sci A Polym Chem 2001;39:3311–9.

[10] Kharasch MS, Nudenberg W, Mantell GJ. Reactions of atoms and free radicals in solution. XXV. The reactions of olefins with mercaptans in the presence of oxygen. J Org Chem 1951;16:524–32.

[11] O'Brien AK, Cramer NB, Bowman CN. Oxygen inhibition in thiol–acrylate photopolymerizations. J Polym Sci Part A: Polym Chem 2006;44:2007–14.

[12] Morgan CR, Magnotta F, Ketley AD. Thiol/ene photocurable polymers. J Polym Sci Polym Chem Ed 1977;15:627–45.

[13] Reddy SK, Okay O, Bowman CN. Network development in mixed step-chain growth thiol–vinyl photopolymerizations. Macromolecules 2006;39:8832–43.

[14] Gush DP, Ketley AD. Thiol/acrylate hybrid systems. Mod Paint Coatings 1978:58.

[15] Eisele G, Fouassier JP, Reeb R. Kinetics of photocrosslinking reactions of a DCPA/EA matrix in the presence of thiols and acrylates. J Polym Sci Part A: Polym Chem 1997;35:2333–45.

[16] Cramer NB, Couch CL, Schreck KM, Carioscia JA, Boulden JE, Stansbury JW, et al. Investigation of thiol-ene and thiol-ene–methacrylate based resins as dental restorative materials. Dent Mater 2010;26:21–8.

[17] Lee TY, Smith Z, Reddy SK, Cramer NB, Bowman CN. Thiol–allyl ether–methacrylate ternary systems. polymerization mechanism. Macromolecules 2007;40:1466–72.

[18] Lee TY, Carioscia J, Smith Z, Bowman CN. Thiol–allyl ether–methacrylate ternary systems. Evolution mechanism of polymerization-induced shrinkage stress and mechanical properties. Macromolecules 2007;40:1473–9.

[19] Woods JG. Radiation curable adhesives. In: Pappas SP, editor. Radiation curing science and technology, New York; 1992. p. 333.

[20] Hoyle CE, Lee TY, Roper T. Thiol–enes: chemistry of the past with promise for the future. J Polym Sci A Polym Chem 2004;42:5301–38.

[21] Lowe AB. Thiol-ene "click" reactions and recent applications in polymer and materials synthesis. Polym Chem 2010;1:17–36.

[22] Nair DP, Cramer NB, Scott TF, Bowman CN, Shandas R. Photopolymerized thiol-ene systems as shape memory polymers. Polymer 2010;51:4383–9.

[23] Reddy SK, Cramer NB, Cross T, Raj R, Bowman CN. Polymer-derived ceramic materials from thiol-ene photopolymerizations. Chem Mater 2003;15:4257–61.

[24] Senyurt AF, Wei H, Phillips B, Cole M, Nazarenko S, Hoyle CE, et al. Physical and mechanical properties of photopolymerized thiol–ene/acrylates. Macromolecules 2006;39:6315–7.

[25] Carioscia JA, Schneidewind L, O'Brien C, Ely R, Feeser C, Cramer N, et al. Thiol–norbornene materials: approaches to develop high Tg thiol–ene polymers. J Polym Sci Part A: Polym Chem 2007;45:5686–96.

[26] Jacobine AF, Rakas MA, Glaser DM. Stereolithography method. U.S. Patent 5167882; 1991.

[27] Posner T. Beiträge zur Kenntniss der ungesättigten Verbindungen. II. Ueber die Addition von Mercaptanen an ungesättigte Kohlenwasserstoffe. Ber Der Dtsch Chem Ges 1905;38:646–57.

[28] Kharasch MS, Read AT, Mayo FR. The peroxide effect in the addition of reagents to unsaturated compounds. XVI. The addition of thioglycolic acid to styrene and isobutylene. Chem Indus 1938:752.

[29] Reddy SK, Anseth KS, Bowman CN. Modeling of network degradation in mixed step-chain growth polymerizations. Polymer 2005;46:4212–22.

[30] Okay O, Bowman CN. Kinetic modeling of thiol-ene reactions with both step and chain growth aspects. Macromol Theory Simul 2005;14:267–77.

[31] Rydholm AE, Reddy SK, Anseth KS, Bowman CN. Controlling network structure in degradable thiol–acrylate biomaterials to tune mass loss behavior. Biomacromolecules 2006;7:2827–36.

[32] Esfandiari P, Ligon SC, Lagref JJ, Frantz R, Cherkaoui Z, Liska R. Efficient stabilization of thiol-ene formulations in radical photopolymerization. Polym Chem 2013;51:4261–6.

[33] Tarzi OI, Allonas X, Ley C, Fouassier JP. Pyrromethene derivatives in three-component photoinitiating systems for free radical photopolymerization. J Polym Sci Part A: Polym Chem 2010;48:2594–603.

[34] Ibrahim A, Maurin V, Ley C, Allonas X, Croutxe-Barghorn C, Jasinski F. Investigation of termination reactions in free radical photopolymerization of UV powder formulations. Eur Polym J 2012;48:1475–84.

[35] International Organization for Standardization. ISO 13586, plastics – determination of fracture toughness (GIC and KIC) – linear elastic fracture mechanics (LEFM) approach. 2000.

[36] Balkenhol M, Köhler H, Orbach K, Wöstmann B. Fracture toughness of cross-linked and non-cross-linked temporary crown and fixed partial denture materials. Dent Mater 2009;25:917–28.

[37] Oswald AA, Wallace TJ. The chemistry of organic sulphur compounds. In: Kharasch N, Meyers CY, editors. Symposium Publications Division. Pergamon Press; 1966.

[38] Fava A, Reichenbach G, Peron U. Kinetics of the thiol-disulfide exchange. II. Oxygen-promoted free-radical exchange between aromatic thiols and disulfides. J Am Chem Soc 1967;89:6696–700.

[39] D'Souza VT, Nanjundiah R, Baeza HJ, Szmant HH. Thiol-olefin cooxidation (TOCO) reaction. 9. A self-consistent mechanism under nonradical-inducing conditions. J Org Chem 1987;52:1729–40.

[40] Li G-Z, Randev RK, Soeriyadi AH, Rees G, Boyer C, Tong Z, et al. Investigation into thiol-(meth)acrylate Michael addition reactions using amine and phosphine catalysts. Polym Chem 2010;1:1196–204.

[41] Mather BD, Viswanathan K, Miller KM, Long TE. Michael addition reactions in macromolecular design for emerging technologies. Prog Polym Sci 2006;31:487–531.
[42] Chan JW, Wei H, Zhou H, Hoyle CE. The effects of primary amine catalyzed thio-acrylate Michael reaction on the kinetics, mechanical and physical properties of thio-acrylate networks. Eur Polym J 2009;45:2717–25.
[43] Azizi N, Khajeh-Amiri A, Ghafuri H, Bolourtchian M. A highly efficient, operationally simple and selective thia-Michael addition under solvent-free condition. Green Chem Lett Rev 2009;2:43–6.
[44] Wabnitz TC, Yu J-Q, Spencer JB. Evidence that protons can be the active catalysts in Lewis acid mediated hetero-Michael addition reactions. Chem A Eur J 2004;10:484–93.
[45] Movassagh B, Shaygan P. Michael addition of thiols to α,β-unsaturated carbonyl compounds under solvent-free conditions. ARKIVOC; 2006. p. 130.
[46] Sensfuß S, Friedrich M, Klemm E. Untersuchungen zur thiol/en-polymerisation: elektronenspinresonanzspektroskopischer Nachweis spontaner Radikalbildung. Die Makromol Chem 1991;192:2895–900.
[47] Kühne G, Diesen JS, Klemm E. New results of the self-initiation mechanism of SH/En addition polymerization. Die Angew Makromol Chem 1996;242:139–45.
[48] Wallace TJ. Reactions of thiols with metals. I. Low-temperature oxidation by metal oxides. J Org Chem 1966;31:1217–21.
[49] Mishra M, Reetz I, Yagci Y. Chemical initiation by metals or metal-containing compounds. In: Mishra M, Yagci Y, editors. Handbook of vinyl polymers, vol. 20081175. CRC Press; 2008. p. 49–76.
[50] Christmas BK, Ho H, Ngo T, Brenes D. RadTech 2002 UV/EB conference & exhibition: curing at the speed of light: technical conference proceedings. In: RadTech 2002 UV/EB conference & exhibition: curing at the speed of light: technical conference proceedings, vol. 1. Chevy Chase, MD: RadTech International North America; 2002. p. 712.
[51] Cramer NB, Bowman CN. Thiol-ene and thiol-yne chemistry in ideal network synthesis. In: Lowe Andrew B, Bowman Christopher N, editors. Thiol-x Chemistries in polymer and material science; 2013. p. 22.
[52] Stahly EE. Process for the preparation of shelf-stable, photocurable polythiols. U.S. Patent 3619393; 1971.
[53] Guthrie JL, Rendulic FJ. Radiation curable polyene-polythiol. U.S. Patent 3855093; 1974.
[54] Kehr CL, Wszolek WR. Photocurable liquid polyene-polythiol polymer compositions. U.S. 3661744; 1972.
[55] Klemm E, Sensfuß S. Untersuchungen zum selbstinitiierungs-mechanismus der thiol/en-polymerisation. Die Makromol Chem 1991;192:159–64.
[56] Dowling JP, Quigley K, Richardson SC. Stable thiol-ene compositions. U. S Pat 0428342 (B1); 1991.
[57] Woods JG, Jacobine AF. In: RadTech 2002 UV/EB conference & exhibition: curing at the speed of light: technical conference proceedings, vol. 1. Chevy Chase, MD: RadTech International North America; 1992. p. 173.
[58] Glaser DM. Stabilization of thiolene compositions. U.S. Patent 5208281; 1993.
[59] Klemm E, Sensfuß S, Holfter U, Flammersheim HJ. Free-radical stabilizers for the thiol/ene-systems. Die Angew Makromol Chem 1993;212:121–7.
[60] Glaser DM, Jacobine AF, Grabek PJ. High purity resins for thiol-ene polymerizations and method for producing same. U.S. Patent 5399624; 1993.
[61] Glaser DM, Jacobine AF, Grabek PJ. Stabilizer system for thiol-ene and thiol-nene compositions. U.S. Patent 5459173; 1993.
[62] Glaser DM, Jacobine AF, Grabek PJ. Thiol-ene compositions with improved cure speed retention. U.S. Patent 5371181, 1994.
[63] Davidson RS, Mead CJ, Holman RJ. Stabilisation of thiol-ene formulations. In: Proceedings of the RadTech Europe 2003 conference, Berlin, vol. 1; 2003. p. 579.
[64] Cook WD, Chen F, Pattison DW, Hopson P, Beaujon M. Thermal polymerization of thiol–ene network-forming systems. Polym Int 2007;56:1572–9.
[65] Maandi E, Perez E, Woods JG, Schall JD, Grant S. Liquid stable thiol-acrylate/vinyl ether compositions. U.S. Patent 0105795 (A1); 2010.
[66] Esfandiari P, Cherkaoui ZM, Liska R. Stable curable thiol-ene formulation. WO2012126695 A1. 2012.
[67] Zweifel H. Stabilization of polymeric materials. Springer-Verlag; 1998.
[68] Zweifel H. In: 3rd annual UNESCO school & IUPAC conference on macromolecules & materials science. South Africa: University of Stellenbosch; 2000.
[69] Rice-Evans CA, Miller NJ, Paganga G. Structure-antioxidant activity relationships of flavonoids and phenolic acids. Free Radic Biol Med 1996;20:933–56.
[70] Rice-Evans C, Miller N, Paganga G. Antioxidant properties of phenolic compounds. Trends Plant Sci 1997;2:152–9.
[71] Kubo I, Masuoka N, Ha TJ, Shimizu K, Nihei K. Multifunctional antioxidant activities of alkyl gallates. Open Bioact Compd J 2010;3:1–11.
[72] Kubo I, Fujita K, Nihei K, Masuoka N. Non-antibiotic antibacterial activity of dodecyl gallate. Bioorg Med Chem 2003;11:573–80.
[73] Kubo I, Masuoka N, Xiao P, Haraguchi H. Antioxidant activity of dodecyl gallate. J Agric Food Chem 2002;50:3533–9.
[74] Dossot M, Sylla M, Allonas X, Merlin A, Jacques P, Fouassier J-P. Role of phenolic derivatives in photopolymerization of an acrylate coating. J Appl Polym Sci 2000;78:2061–74.
[75] Dossot M, Obeid H, Allonas X, Jacques P, Fouassier JP, Merlin A. Photopolymerization of acrylates in the presence of phenolic derivatives: role of the photoinitiating system. J Appl Polym Sci 2004;92:1154–64.
[76] Mauguière-Guyonnet F, Burget D, Fouassier JP. On the inhibiting effect of phenolic compounds in the photopolymerization of acrylates under high-intensity and polychromatic UV/visible lights. J Appl Polym Sci 2007;103:3285–98.
[77] Belon C, Allonas X, Croutxé-barghorn C, Lalevée J. Overcoming the oxygen inhibition in the photopolymerization of acrylates: a study of the beneficial effect of triphenylphosphine. J Polym Sci Part A: Polym Chem 2010;48:2462–9.