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Degradable epoxy coatings by photoinitiated cationic copolymerization of bisepoxide with ε-caprolactone

M. Sangermano [a,*], M. Tonin [a], Y. Yagci [b,*]

[a] Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, C.so Duca degli Abruzzi, 24, I-10129 Torino, Italy
[b] Istanbul Technical University, Department of Chemistry, Maslak, TR-34469 Istanbul, Turkey

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ABSTRACT

Thermal and hydrolytical degradable epoxy coatings based on bis-phenol-A-diglycidyl ether (DGEBA) and ε-caprolactone (CL) were prepared by photoinitiated cationic polymerization using triphenylsulfonium hexafluoroantimonate ($Ph_3S^+SbF_6^-$) as photoinitiator. The photopolymerization kinetics were followed by real-time FT-IR analysis. The effect CL concentration on the rate of polymerization was demonstrated. Mechanical properties of the resulting networks were studied by dynamic mechanical thermal analysis (DMTA). Thermal and hydrolytical degradation investigations were also performed. Higher degradability of the cured films with the increasing content of CL in the formulation suggests that UV cured coatings obtained this way can potentially be used as reworkable thermosets.

1. Introduction

Epoxy resins have long been used in a variety of industrial applications, such as coatings, reactive diluents, impregnation composites, encapsulation of electronic circuits' elements and printed circuit board coatings [1]. The epoxy resins are widely used since the uncured epoxy resins flow easily into complex shapes, and once fully cured the highly crosslinked three-dimensional networks have superior adhesive and thermo-mechanical properties. After curing, epoxy based materials, endows thermosetting networks with excellent mechanical properties, thermal and chemical stability [2].

In recent years degradability or *reworkability* of thermosetting materials are obtaining increasing interest in scientific research. The increase in research interest in degradable or biodegradable polymers, has led to the availability of a large variety of novel polymers with claims of degradability or bio-degradability [3]. A large number of biodegradable polymers have been used in biomedical applications.

Degradability is generally achieved by incorporating labile moieties susceptible to thermal or hydrolytical cleavage into the polymer backbone. The most common method of introducing these degradable linkages has been to utilize polycaprolactone-segments into the polymeric structure [4,5]. Polycaprolactone (PCL) is hydrophobic and insoluble in water but degradable through the hydrolytic attack of the ester bonds. The presence of ester groups in the three-dimensional network also increases the thermal degradability of the cured network. In fact ester groups are hydrolytical and thermal cleavable [6]. Each time when an ester group is cleaved, the local crosslink density decreased and therefore, the higher the proportion of esters the more is the degradable character of the modified epoxy resin.

The introduction of ester groups in the crosslinked epoxy resins was previously proposed by Ober and coworkers [7] and Wang et al. [8] to increase the reworkability of the cured epoxy resins, which can be employed in electronics. Buchwalter et al. synthesized epoxy monomers incorporating chemically cleavable acetal and ketal into their chemical structures [9]. The resulting thermoset

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* Corresponding authors.
E-mail addresses: marco.sangermano@polito.it (M. Sangermano), yusuf@itu.edu.tr (Y. Yagci).

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networks could be degraded by applying acidic-containing solvent mixtures. Yang et al. synthesized a series of epoxy monomers containing thermal and hydrolytical labile secondary and tertiary ester groups [10].

A possible alternative to the design of specific polymers or monomers containing labile groups, could be the copolymerization of epoxy monomer with ε-caprolactone, via cationic ring-opening polymerization, which will yield poly(ether–ester) chains. Many papers are reported in literature in which different mono and bislactones were copolymerized with epoxy monomer by cationic copolymerization initiated by rare earth triflates catalysts [11–13]. The interest in such copolymerizations lies in the introduction of ester linkages into the network structures, leading to thermosetting materials with improved degradability. However, only a few attempts have been made on the use of photoinduced process for the copolymerization of epoxy monomers with lactones. Ramis et al. reported cationic photocuring of a bisepoxide and spirobislactone and compared with the thermal counterpart using ytterbium triflate as an initiator [14,15].

The UV curing technique is getting an increasing importance in the field of coatings due to its peculiar characteristics [16]: it induces the polymer formation with a fast transformation of the liquid monomer into a solid film with tailored physical–chemical and mechanical properties. It can be considered as an environmental friendly technique, as it is a solvent free process, and it is usually carried out at room temperature, therefore guarantees the saving of energy. Furthermore, the cationic photopolymerization process of epoxy systems present some advantages compared to the radical one [17]: such as lack of inhibition by oxygen, low shrinkage, good adhesion and mechanical properties of cured films.

In this work, we have investigated the preparation and characterization of degradable UV cured epoxy coatings achieved by bis-phenol-A-diglycidyl ether/ε-caprolactone copolymerization initiated by cationic UV induced process. The photopolymerization reaction was followed by real-time FT-IR analysis and the obtained cured materials characterized by DMTA and TGA analysis. Finally hydrolytical degradation study was investigated in order to evaluate both the hydrolytical and thermal degradability of the epoxy coatings containing ester groups. In this connection, it is worth to mention that structurally same polyester groups can also be incorporated to the epoxy networks by using PCL polyols in the photocurable formulations containing epoxy monomer and photoinitiator [1,2]. In this case, polymerization proceeds via activated monomer mechanism [18,19].

2. Experimental

2.1. Materials

Bis-phenol-A-diglycidyl ether (DGEBA, CY125 from Huntsman) was employed as epoxy monomer. ε-caprolactone was purchased from Aldrich and employed here without further purification. Triphenylsulfonium hexafluoroantimonate (Cyracure UVI6974, as 50% solution in propylene carbonate, PI), from Union Carbide ($Ph_3S^+SbF_6^-$) was added as an actual content of 2 wt.% to the epoxy formulations. The structures of the monomers employed are reported in Chart 1.

2.2. Samples preparation and characterization

The photocurable formulations were prepared by adding increasing amount of CL monomer to DGEBA: 0, 2, 5 and 10 wt.% of CL was added to the epoxy monomer. An actual amount of 2 wt.% of cationic photoinitiator was added to each formulation. The photocurable products were coated on different substrates and irradiated by means of UV light (Fusion lamp, medium pressure mercury lamp, light intensity on the surface of the sample of about 450 mW/cm^2 and a belt speed of 6 m/min) achieving transparent films of about 100 μm thickness.

The kinetic of photopolymerization was studied by Real-Time FT-IR spectroscopy, employing a Thermo-Nicolet 5700 instrument. The formulations were coated onto a silicon wafer. The sample was exposed simultaneously to the UV beam, which induces the polymerization, and to the IR beam, which analyzes *in situ* the extent of the reaction. Because the IR absorbance is proportional to the monomer concentration, conversion versus irradiation time profiles can be obtained. Epoxy group conversion was followed by monitoring the decrease in absorbance of the epoxy groups in the region of 750–780 cm^{-1}. A medium pressure mercury lamp (Hamamatsu LC-8) equipped with an optical waveguide was used to induce the photopolymerization (light intensity on the surface of the sample of about 30 mW/cm^2, measured with EIT instrument). Variation in the experimental conditions (light intensity, humidity, temperature) caused slight differences in the kinetic curves. For this reason, all the conversion (curves summarized and compared in one figure) were performed on the same day and under the same conditions, thus good reproducibility was obtained.

Dynamic mechanical thermal analyses (DMTA) were performed with a Rheometric Scientific MKIII (UK) instrument, at a frequency of 1 Hz in the tensile configuration.

The gel content was determined on the cured films by measuring the weight loss after 24 h extraction with chloroform at room temperature, according to the standard test method ASTM D2765-84.

Thermogravimetrical analysis (TGA) were performed using a LECO TGA-601 instrument in the range between 30 and 700 °C, with a heating temperature of 10 °C/min in air.

Hydrolytical degradation was performed using a buffer solution at pH7.4. The polymeric coatings were cut into 10 × 10 × 1 mm specimens, dried into an oven at 37 °C

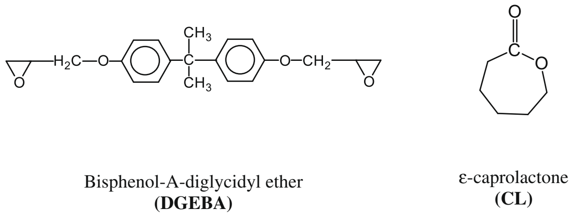


Chart 1. Chemical structures of the monomers employed.

for one week and weighted to an accuracy of 0.1 mg. Each sample was placed into an individual vial containing 15 ml of buffer solution and incubated at 37 °C. The samples were removed after different times, dried at room temperature for 4 days and reweighed. The degradation media was refreshed every one week.

The degradability was evaluated using the following formula:

$$D\% = (M_0 - M_h/M_0) * 100 \quad (1)$$

Where M_0 is the mass of the polymer before hydrolysis and M_h is the mass of the polymer after different time of hydrolysis.

3. Results and discussion

In this work, we focused on the preparation and characterization of UV cured epoxy/ε-caprolactone thermosets and evaluated degradation properties. Copolymerization reaction is performed in the presence of cationic photoinitiators which, under UV light is able to generate strong Brönsted acid and initiate cationic ring-opening polymerization of both monomers. As a result, formation of a polyether–polyester cured copolymer network is achieved.

The ε-Caprolactone monomer was added to a bis-phenol-A-diglycidyl ether epoxy resin in the range between 5 and 10 wt.%. The limit of 10 wt.% was defined by kinetic investigations of the photocurable formulations. In fact, kinetic characterization of the reactive system is not only important for the better understanding of structure–properties relationships but also for fundamental in optimizing process conditions and product quality.

In Fig. 1, the conversion curves as a function of irradiation time are reported for the pristine epoxy resin and for photocurable formulations containing increasing amount of CL monomer. While the slope of the curve gives an indication of the rate of polymerization, the plateau value gives the final epoxy group conversion. It is evident that, by increasing the CL content in the photocurable formulation there is a slight increase on the rate of photopoylmerization together with an increase of the epoxy group conversion. The pristine resin achieved a final epoxy group conversion of about 59% after 2 min of irradiation. The formulation containing 10 wt.% of CL reached a final epoxy group conversion of about 76% after 2 min of irradiation.

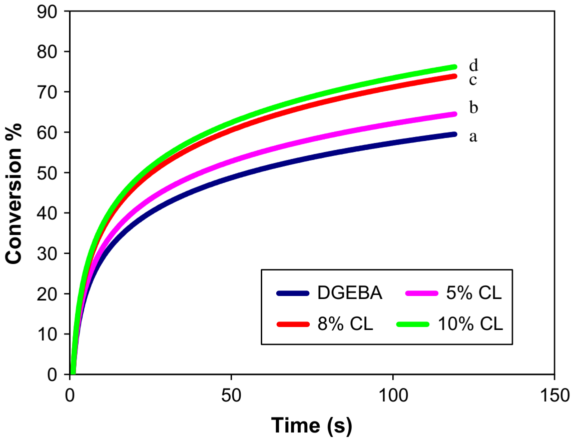


Fig. 1. FT-IR conversion curves as a function of irradiation time for the pristine epoxy resin (curve a) and in the presence of 5 (curve b), 8 (curve c) and 10 (curve d) wt.% of CL monomer.

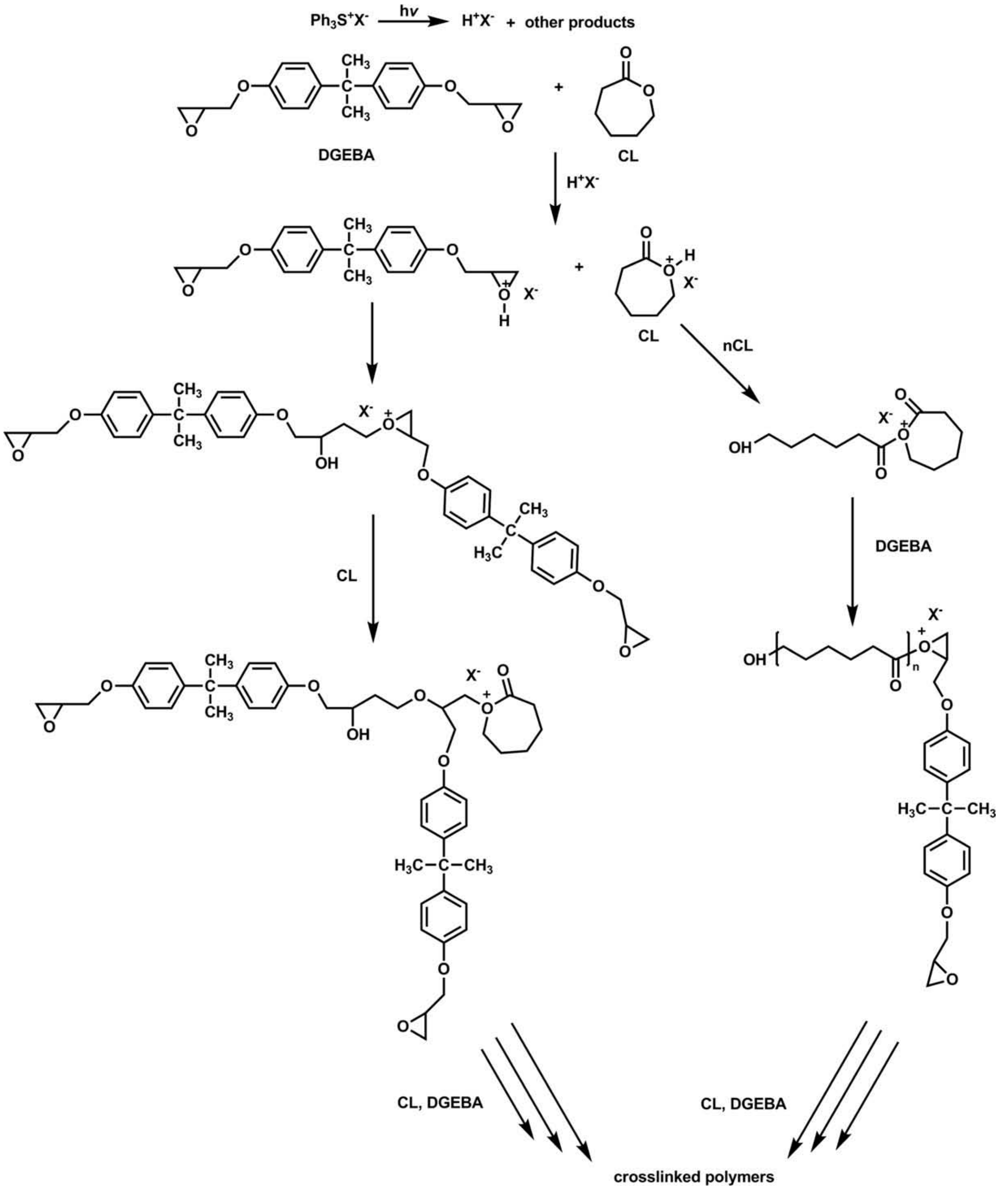
Both the increase on photopolymerization rate and epoxy group conversion can be attributed to the introduction in the cured networks of PCL segments: the flexibilization effect is due both to the reduction of crosslinking density due to the copolymerization of a monofunctional monomer (the CL monomer) and to the insertion into the epoxy network of a long aliphatic chain of the polycaprolactone structure. The flexibilization has also been confirmed by DMTA analysis (vide infra). As a result of the flexibilization effect a delay on vitrification can be expected, therefore a higher mobility of the reactive species is allowed with a consequent increase on photopolymerization rate and a higher epoxy group conversion.

By further increasing CL content above 10 wt.%, a strong decrease on epoxy group conversion was induced: formulations containing CL content of 20 wt.% did not polymerized at all, and the formulation remained almost liquid. It is possible to explain these results probably taking into consideration the well known inhibiting effect on cationic UV curing polymerization process induced by the presence of ester groups [20]. It was shown by Crivello that the presence of ester groups greatly retard the epoxy rate of photopolymerization. Molecular modeling studies indicated that the ester carbonyl group can interact with the initially formed protonated oxiranium cation to give bicyclic dialkoxycarbenium ions. These species are both more sterically hindered and less reactive than the oxiranium cation precursor and can importantly decrease the propagation rate or even strongly inhibit the polymer network formation.

Therefore, UV cured epoxy based films containing CL monomer up to 10 wt.% were obtained by photopolymerization and the cured materials were characterized. The schematic representation of copolymerization reaction between the epoxy monomer and CL monomer is reported below in Scheme 1.

The gel content determination on UV cured films containing up to 10 wt.% of CL monomer clearly indicated the almost absence of extractable monomers or oligomers: gel content values, after 24 h extraction with chloroform, were always close to 100% (see Table 1). This is an indirect but clear evidence of the occurrence of a copolymerization reaction and chemical incorporation of CL units into the network structure. The formation of linear PCL chain can be discarded. If formed linear polymer dispersed within the epoxy network would have been extracted with a consequent drastic reduction of the gel content values.

We tried to get some FT-IR evidences of the copolymerization process but because of superpositions of key absorption peaks it was not possible to put in evidence the polyether–polyester bonds formation. Nevertheless, we can affirm a copolymerization process between the two monomers on the basis of previous papers reporting the occurrence of epoxy-lactones copolymerization [11–13] and on the gel content values.



Scheme 1. Photoinitiated cationic copolymerization of DGEBA and CL.

Dynamic mechanical characterization of the cured films were performed by means of DMTA analysis, which allowed the evaluation for the elastic (E': storage modulus) and viscous (E'': loss modulus) components of the materials in a large temperature interval. In Fig. 2 (A and 2B), the DMTA thermograms for the cured systems containing an increasing amount of CL monomer are reported. In the T_g region a strong decrease of E' is evident (Fig. 2A), while the tan δ curve (tan $\delta = E''/E'$: loss modulus/storage modulus ratio) shows a maximum which is assumed as the T_g of the cured films [21] (Fig. 2B). The collected data are reported in Table 1 together with the gel content values for UV cured films.

These data clearly evidenced a decrease of the T_g of the cured network by increasing the CL monomer in the photo-

Table 1
Properties of UV cured films.

Samples	Gel content [%][a]	Tg [°C][b]
DGEBA	100	223
DGEBA/CL 95:5	99	186
DGEBA/CL 92:8	100	166
DGEBA/CL 90:10	100	142

[a] Determined gravimetrically ASTM D2765–84.
[b] Determined by DMTA analysis, tensile configuration, 1 Hz frequency.

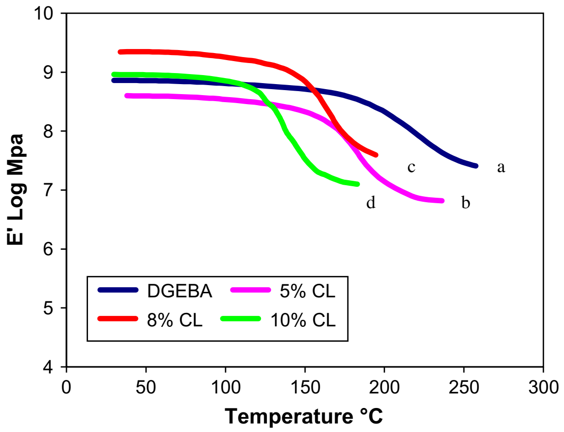


Fig. 2a. Storage modulus curves obtained by DMTA analyses for the pristine epoxy UV cured network (curve a) and for the cured network containing 5 (curve b), 8 (curve c) and 10 (curve d) wt.% of CL monomer.

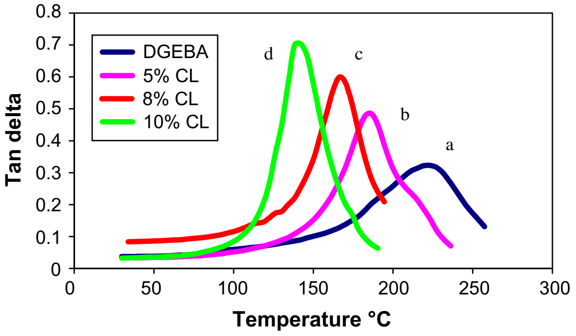


Fig. 2b. Tan δ curves obtained by DMTA analyses for the pristine epoxy UV cured network and for the cured network containing increasing amount of CL monomer.

curable formulation. A clear shift towards lower temperature of the maximum of tan δ values is evident from the curves of Fig. 2B. This flexibilization behavior is in accordance with the previously discussed kinetic results, and it has to be attributable to the introduction of flexible ester linkages into the epoxy network together with the crosslinking density decrease, as discussed above.

The polyether–polyester three-dimensional structures obtained by epoxy/ε-caprolactone copolymerization should be more easily thermal and hydrolytical degradable, than the thermosets obtained from pure epoxy resin, due to the presence of ester linkages. The introduction of ester groups in the thermosetting materials has been used as one of the most useful strategies to improve the reworkability of the thermosets. It is important to underline that the concept of reworkable thermosets indicate the possibility to break-down some network bonds more easily under controlled conditions, either by hydrolysis or thermal degradation. This means that the polymer cannot be re-used or recycled but only partially degraded and removed from the surface where it was applied. This rework strategy allows the reparation, replacement or recycling of electronic devices assembled with such materials [11–13,22–25].

The obtained UV cured coatings containing increasing content of CL monomer were characterized in term of their thermal stability through TGA analysis. The degradation curve for the pristine epoxy network is reported in Fig. 3 and compared with the degradation curves of the networks containing increasing CL content. The TGA values for the 5 wt.% (T5) and 10 wt.% (T10) weight loss are reported in Table 2.

Those data clearly indicate that the crosslink degradation occurs at lower temperature when CL monomer was added to the photocurable formulations. By adding 5 wt.% of CL monomer to the epoxy resin the T5 decrease from 380 °C down to 333 °C and the T10 decreased from 417 °C down to 378 °C. When adding 8 wt.% or 10 wt.% of CL a further decrease of the T5 and of the T10 temperature is achieved. The enhanced degradation of the epoxy crosslinked networks is due to the presence of ester groups in the structure.

Hydrolytical degradation was also investigated by immersing the UV-cured samples into a buffer solution of pH 7.4 for several weeks. In these conditions degradation of the network can occur through the hydrolytic attack of

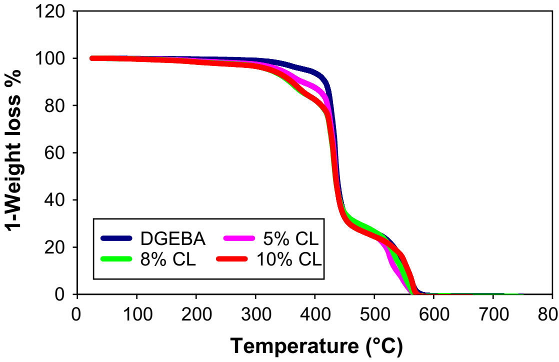


Fig. 3. TGA curves for the pristine epoxy UV cured network and for the cured network containing increasing amount of CL monomer.

Table 2
Thermal and hydrolytical degradation values.

Samples	T5 [°C][a]	T10 [°C][b]	Hydrolytical weight loss [%][c]
DGEBA	380	417	0.03
DGEBA/CL 95:5	333	378	2
DGEBA/CL 92:8	317	350	3
DGEBA/CL 90:10	317	350	5

[a] Determined as the temperature at which 5 wt.% loss is achieved.
[b] Determined as the temperature at which 10 wt.% loss is achieved.
[c] Weight loss after 2 months of extraction in buffer solution at pH 7.4 at 37 °C.

the ester bonds. The samples were weighted every 1 or 2 weeks until a plateau was reached after 2 months of water immersion. In Table 2 the hydrolytical weight loss is reported for the pristine UV cured epoxy resin and for the cured formulations containing increasing CL monomer content. While the pure epoxy network is practically not attacked by hydrolysis, since the weight loss is negligible after 2 months immersion in water, the cured films achieved in the presence of CL monomer showed an increase of weight loss by increasing the CL content. When 10 wt.% of CL was added to the photocurable formulation, the weight loss after 2 months in water extraction was around 5 wt.%. It is interesting to note that the mass loss on hydrolysis is not correlated by the amount of CL in the network but is about half of this. This observation may be interpreted in terms of the different sequences CL monomer in the network structure.

4. Conclusions

Bis-phenol-A-based epoxy resin was copolymerized with CL in the ratio between 95:5 and 90:10 wt.% by photoinitiated cationic polymerization. The introduction of CL moieties within the bis-phenol-A-epoxy network causes reduction in crosslinking density because of the presence of aliphatic chains. The flexibilization effect was confirmed by DMTA analysis, which showed a shift of the maximum of tan δ peak toward lower temperature by increasing the CL monomer content in the photocurable formulation. The flexibilization effect was also responsible of the increase of epoxy group conversion during UV curing because of the delay of vitrification.

The resulting networks were shown to be more readily thermal and hydrolytical degradable than those obtained from pure epoxy resin. For the network formed in the presence of CL monomer, lower temperature degradation and significant hydrolytic weight loss were noted.

In conclusion, labile ester groups susceptible to thermal or hydrolytical cleavage can be introduced to the epoxy based networks by taking the advantage of photoinitiated cationic copolymerization of epoxy and caprolactone monomers. The higher degradability character for this new epoxy cured materials make them good candidate as reworkable thermosets in electronic applications.

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