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European Polymer Journal 44 (2008) 1046–1052

EUROPEAN POLYMER JOURNAL

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Synthesis of an epoxy functionalized spiroorthocarbonate used as low shrinkage additive in cationic UV curing of an epoxy resin

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Received 4 January 2008; received in revised form 25 January 2008; accepted 31 January 2008
Available online 9 February 2008

Abstract

The synthesis of an epoxy functionalized spiroorthocarbonate (SOC) is reported. The obtained monomer has been used a slow shrinkable additive in cationic UV curing of a commercially available dicycloepoxy resin. A polymer network flexibilization was evidenced by increasing the SOC content in the photocurable formulation. It has been demonstrated that SOC acts as shrinkage reduction additive reaching expansion on volume after polymerization in the presence of 10 wt% of the functionalized spiroorthocarbonate.

Keywords: Cationic UV curing; Spiroorthocarbonate; Shrinkage; Epoxy resin; DSC; DMTA

1. Introduction

Most epoxy thermoset resins shrink about 2–6% in volume during polymerization [1]. Volume shrinkage often causes a large build up of internal stress in the resin as well as the volumetric and dimensional changes [2]. The suppression or control of the volume shrinkage during polymerization is of great importance in the design of materials requiring precise dimensions or for the preparation of composites.

One way to make low shrinkage/low stress materials has been to incorporate spiroorthocarbonates, spiroortho esters and other strained bicyclic monomers in the polymer network [3,4].

During a polycyclic monomer ring-opening polymerization, it happens that for every bond that goes from a Van der Waals distance to a covalent distance, at least two bonds go from a covalent distance to a near Van der Waals distance. This is the reason why the polycyclic monomer ring-opening polymerization occurs essentially with zero shrinkage or expansion upon polymerization [6].

One of the most efficient monomer for such polymerization are the spiroorthocarbonates whose polymerization occurs with volume expansion [7].

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doi:10.1016/j.eurpolymj.2008.01.039

The high volume expansion may be based on the release of the very compact structure of the starting monomer by the successive double ring-opening polymerization mode. The flexibility introduced in the polymer network by spiroorthocarbonate copolymerization also reduced the internal stress in the resin [8].

Spiroorthocarbonates are two ring compounds with the central carbon atom connected with four oxygen atom. These double cyclic acetals are stable under basic conditions but easily undergo ring-opening polymerization catalyzed by cationic catalysts [5].

The literature on spiroorthocarbonates and other expanding monomers in oxirane resin systems has been deeply reviewed [9], but there is not reported any examples on the use of epoxy functionalized spiroorthocarbonates as low shrinkable additive in cationic UV curing.

More recently the cationic photopolymerization of a spiroorthocarbonate with an aromatic dioxirane was demonstrating to give rise to a copolymerization reaction [10]. The efficiency of a bicycloorthoester as low shrinkage additive in cationic UV curing of an epoxy resin was also shown: it has been demonstrated that the bicycloorthoester acts as shrinkage reduction additive or even as an expanding monomer in the epoxy UV-induced polymerization [11].

It is of great challenge the possibility to obtain UV-cured coatings that are produced with near zero shrinkage or expansion during polymerization. These materials could be useful for production of strain-free composites, high strength adhesives and precision castings.

Pursuing these investigations, in the current study, an epoxy functionalized spiro compound was synthesized and its behavior as low shrinkage additive was investigated in cationic UV curing of a typical dicycloaliphatic epoxy resin.

2. Experimental

2.1. Materials

1,2,3,6-tetrahydrobenzaldehyde, 37% formaldehyde aqueous solution, potassium hydroxide, tetraethyl orthocarbonate, oxone® ($K_2SO_5 \cdot KHSO_4 \cdot K_2SO_4$), and 18-crown-ether were purchased from Aldrich. 3,4-Epoxycyclohexylmethyl-3′,4′-epoxycyclohexanecarboxylate by Cytec (UVACURE1500, CE) was used as epoxy resin. An epoxy functionalized bicyclo-spiroorthocarbonate (SOC) was synthesized as following reported and used in the range between 5 and 10 wt% in the photocurable formulation. A commercially available mixture of hexafluorophosphate sulfonium salts (Omnicat 432) was supplied from IGM Resins: it is supplied as solution in propylene carbonate (50 w/w %) and it was added to the curable mixtures at a concentration equal to 2% wt/wt. The structure of the monomer employed is reported in Table 1.

2.2. Synthetic procedure for the epoxy functionalized spiroorthocarbonate

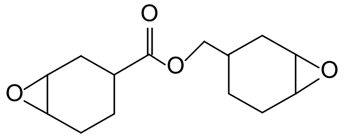
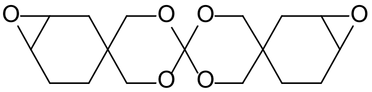
2.2.1. Preparation 3-cyclohexene-1,1-dimethanol (I)

In a three necked 250 ml round bottom flask provided with magnetic stirrer, condenser and thermometer were placed 13.6 g (0.123 mol) of tetrahydrobenzaldehyde and 30.8 g of 37% formaldehyde solution. Then 12.13 g (0.21 mol) of potassium hydroxide were dissolved in 72 ml of ethanol and added dropwise to the reaction mixture. Once that the addition is finished the temperature was raised to 55 °C and kept at this temperature for 1 h. Then the reaction mixture was heated to boiling point. After 3 h the mixture was allowed to cool to room temperature and the solvent was rotoevaporated. The resulting solid (I) was recrystallized in benzene (m.p. 55 °C). The yield of the reaction was 83%.^{1}H NMR ($CDCl_3$, 300 MHz) δ ppm: 1.8 (2H, m, $=CH-CH_2-CH_2-$); 2.0 (2H, m, $=CH-CH_2-CH_2-$); 2.2 (2H, m, $-C-CH_2-CH=CH-CH_2-CH_2$); 3.6 (4H, d, $-C-CH_2-OH$); 5.65 (2H, m, $-CH=CH-$).

2.2.2. Preparation of the orthospirocarbonate (II)

In a three necked 250 mL round bottom flask provided with magnetic stirrer, condenser, nitrogen

Table 1
Chemical structures of the epoxy monomer and of the bicycle-spiroorthocarbonate

	**CE**
	**SOC**

inlet and thermometer, were placed 5 g (0.035 mol) of cyclohexene dimethanol (I) and 3.38 g (0.017 mol) of tetraethyl orthocarbonate. Then 100 mL of dried toluene were added, followed by 0.125 g of *p*-toluenesulfonic, 2 g of molecular sieves and then the system was flushed with nitrogen to set anhydrous conditions. The mixture was refluxed reaching 95 °C. The reaction was discontinued after 4 h. The reaction mixture was filtered and the solvent was evaporated. The residue was purified by column chromatography using silica gel as the stationary phase and hexane:ethyl acetate 95:5 as eluent. A solid (II) with a melting point of 74 °C was obtained in 65% yield.

^{1}H NMR ($CDCl_3$, 300 MHz) δ ppm: 1.6 (4H, t, ${=}CH{-}CH_2{-}CH_2$); 1.95 (4H, s, $=CH{-}CH_2{-}CH_2$), 2.1 (4H, s, $-CH_2{-}CH{=}CH{-}$) 3.75 (8H, s, $-C{-}CH_2{-}O{-}$); 6.65 (4H, m, $-CH{=}CH{-}$).

2.2.3. Synthesis of SOC

The orthospirocarbonate (II) obtained was oxidized with oxone. The method was as follows: 8 g (0.027 mol) of orthospirocarbonate dissolved in 75 ml of dichloromethane were charged in a 1 l reactor provided with overhead mechanical stirring and two addition funnels. Then 100 ml of acetone and 2 g of 18-crown ether were added to the reaction system. The pH of the reaction was controlled by the addition of 500 ml of a buffer solution (pH 7.4). The flask was placed in an ice bath and maintained at 0–5 °C. Oxone (33.68 mol) was dissolved in 150 ml of water and added dropwise to the reaction mixture. To maintain a neutral pH, a 1 N NaOH solution was simultaneously added dropwise. After stirring for 12 h the organic and aqueous phases were separated. The organic layer was washed three times with 100 ml of water and dried with sodium sulphate. The resulting mixture was rotoevaporated and the residue was purified by column chromatography using silica gel as the stationary phase and a mixture of hexane:ethyl acetate 90:10. The desired product (M1) was obtained in 53% yield (m.p. 135 °C).

^{1}H NMR ($CDCl_3$, 300 MHz) δ ppm: 1.1–2.2 (12H, m, cyclohexyl H); 3.1–3.2 (4H, m, $-CH{-}O{-}CH{-}$); 3.5–3.8 (8H, m, $-CH_2{-}O{-}C{-}O{-}CH_2$).

2.3. Samples preparation and characterization

Photocurable formulations were prepared by dissolving SOC into chloroform and adding its solution into the epoxy monomer, in the range between 0 and 10 wt% of SOC into CE. In all the mixtures 2 wt% of cationic photoinitiator was added. The chloroform was evaporated and the formulations were coated on glass substrate by means of a wirewound applicator and photocured with a Fusion lamp with a light intensity on the surface of the sample of about 350 mW cm^{-2}. Transparent film of about 100 μm thick were obtained and characterized.

^{1}H NMR spectra were obtained with a 300 MHz JEOL NMR spectrometer (Peabody, MA) at room temperature. Routine infrared spectra were performed on a Magna Nicolet 550 Infrared spectrometer (Middleton, WI).

The kinetics of the photopolymerization were determined 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 the absorbance of the epoxy groups in the region 760–780 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}). Variation in the experimental conditions (light intensity, humidity, and temperature) caused slight differences in the kinetic curves. For this reasons 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.

Shrinkage measurements were obtained by measuring the density of the system before and after curing. The solution density was measured by weight a precise amount of liquid formulation. The density of cured film was measured by means of a Sartorius balance YDK01 with density determination kit. The Archimedes principle is applied for determining the specific gravity of a solid with this measuring device:

a solid immersed in a liquid is exposed to the force of buoyancy. The values of this force are the same as that of the weight of the liquid displaced by the volume of the solid. The density measurements have been performed with the Sartorius hydrostatic balance which enables to weigh the solid in air as well as in a liquid; the specific gravity of the solid is determined when the density of the liquid causing buoyancy is known, through the following formula:

$$\rho = W(\mathrm{a})\rho(\mathrm{l})/W(\mathrm{a}) - W(\mathrm{l}) \tag{1}$$

ρ = specific gravity of the solid
$W(\mathrm{l})$ = density of the liquid
$W(\mathrm{a})$ = weight of the solid in air
$W(\mathrm{l})$ = weight of the solid in liquid

The chosen liquid was ethanol with a density values at 25 °C of $d^{25} = 0.78506$. The specific volume of the system before and after curing was defined as the inverse of the density and the shrinkage calculated with the following formula:

$$\Delta = [V_\mathrm{p} - V_\mathrm{s}/V_\mathrm{s}] * 100 \tag{2}$$

Δ = volume change
V_p = specific volume of the solid
V_s = specific volume of the starting liquid formulation

3. Results and discussion

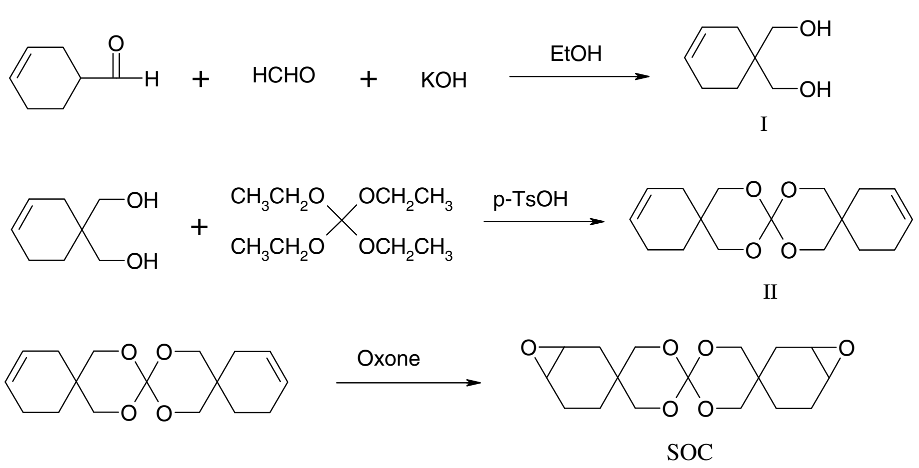
The aim of the research was the synthesis of an epoxy functionalized spiroorthocabronate to be used as low shrinkage additive in cationic UV curing of an epoxy resin.

The synthesis of the functionalized spiroorthocabronate (SOC) occurred in three stages: The formation of the cyclohexene dimethanol (I), the transesterification of the diol with tetraethyl ortho carbonate (II) and finally the epoxidation of the double bond of intermediate II to obtain the desired monomer SOC (see Scheme 1).

The first reaction proceeds by the well known Cannizaro reaction in the presence of tetrahydrobenzaldehyde with formaldehyde and potassium hydroxide. The obtained diol was transesterificated with the tetraethylorthocarbonate according to the method developed by Bailey and collaborators [12]. The epoxidation of the compound II was carried out with oxone® under phase transfer catalyst conditions.

In Fig. 1 the FT-IR spectra of compounds I, II and of the final product SOC are reported. When compound I is esterificated with the tetraethyl orthocarbonate to form compound II, the disappearance of the broad peak corresponding to the OH groups is well evident. When oxidation with oxone is taking place a clear disappearance of the peak centered at 3013 cm^{-1}, corresponding to the double bond of compound II, is evident as well as the appearance of the peaks of the epoxy group of SOC around 810, 795 and 779 cm^{-1}.

Once that the SOC monomer was prepared, different CE/SOC formulations containing SOC in the range between 0 and 10 wt% were investigated. The monomer CE was chosen because of it's widely spread use in the radiation curing industry.



Scheme 1. Synthetic pathway for the preparation of SOC.

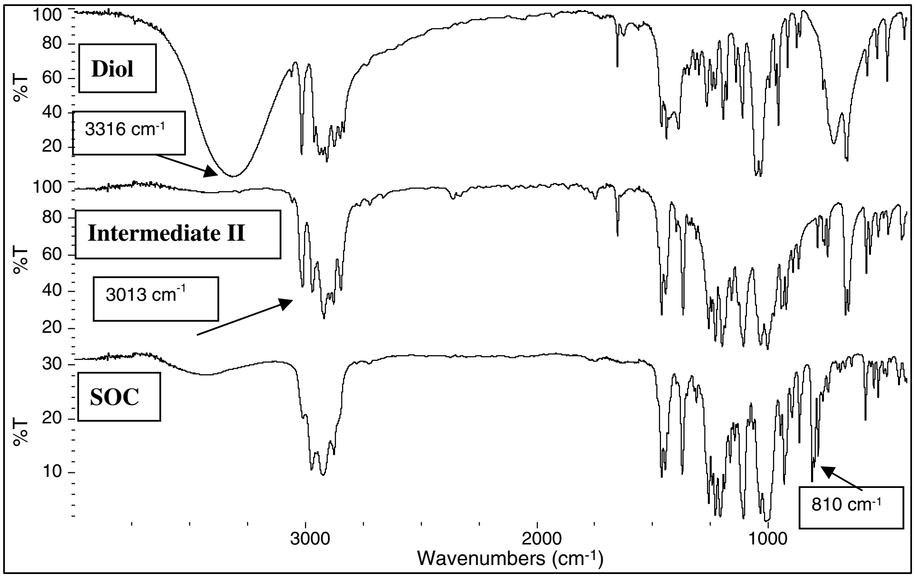


Fig. 1. FT-IR spectra of diol (I), Intermediate compound (II) and SOC.

The photopolymerization kinetics were monitored by real-time FT-IR following the decrease of the epoxy group peak centered at $750\,\mathrm{cm}^{-1}$. The conversion curves as a function of irradiation time are reported in Fig. 2. both for the pure epoxy monomer and for the CE/SOC formulations.

While the plateau value gives the final epoxy group conversion, the slope of the curve gives an indication of polymerization rate. From the curves reported in Fig. 2. It is possible to observe that, by increasing the SOC content in the photocurable formulation an increase of epoxy group conversion is achieved. It is possible to explain this result on the basis of a flexibilization effect induced by the insertion into the polymeric network of SOC flexible structure.

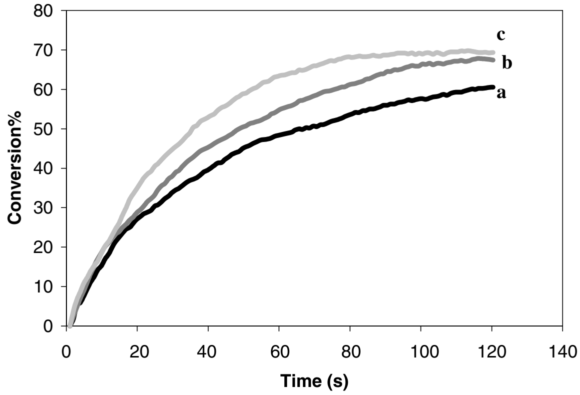


Fig. 2. Real-Time FT-IR conversion curves as a function of irradiation time for the pure CE monomer (curve a) and in the presence of 5 wt% (curve b) and 10 wt% (curve c) of SOC monomer.

The epoxy functionalized spiroorthocarbonates can react both via a spiro-ring opening copolymerization with the CE epoxy groups or via epoxy-ring opening copolymerization. In both cases it is possible to foresee a copolymerization mechanism between the two monomers, as previously demonstrated in the literature [10].

Further investigations are under progress to better elucidate the copolymerization mechanism between the functionalized spiroorthocarbonate and the epoxy monomer.

Since SOC acts as a flexibilizing reactive diluent, higher mobility of reactive species can be obtained; as a result an increase on photopolymerization rate and epoxy group conversion is achieved, as demonstrated by Real-time FT-IR investigations.

The flexibilization effect was evaluated by DMTA analysis. In Figs. 3A and 3B the $\tan\delta$ curves and storage modulus obtained by DMTA thermograms for the cured films are reported: $\tan\delta$ curve shows a maximum which is assumed as the T_g of the cured films.

It is possible to observe a shift of maximum of $\tan\delta$ curves towards lower values by increasing the amount of SOC in the photocurable formulation (see Fig. 3 and values reported in Table 1). The presence of a single $\tan\delta$ peak is also an evidence of a copolymerization mechanism between CE and SOC additive.

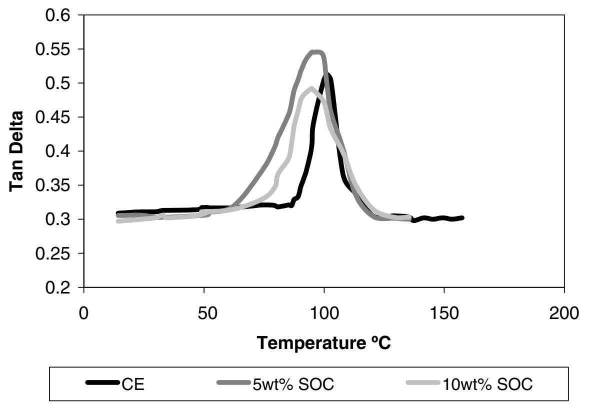


Fig. 3A. Tan δ curves obtained by DMTA analysis of the pure CE cured film and the films obtained in the presence of increasing amount of SOC monomer.

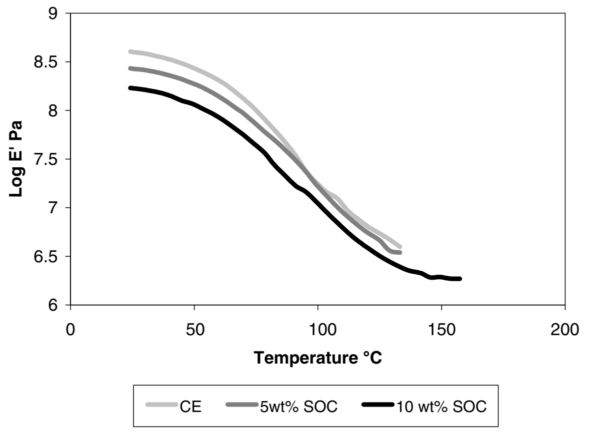


Fig. 3B. Storage modulus obtained by DMTA analysis of the pure CE cured film and the films obtained in the presence of increasing amount of SOC monomer.

Table 2
Properties of UV-cured films

Sample	T_g (°C) DMTA	Gel content (%)
CE	105	98
CE/SOC 95:5	98	97
CE/SOC 90:10	95	98

High gel content values are always obtained for the cured films (above 95%, see Table 2) indicating the formation of a tight crosslinked network.

The efficiency of SOC as low-shrinkable additive was determined by measuring the density of the starting formulations and of the corresponding cured films. The density values together with the calculated shrinkages are reported in Table 3.

Table 3
Density of liquid formulation and of solid polymers and calculated shrinkage values upon photopolymerization

Sample	d_{solution} (g ml^{-1})	d_{polymer} (g ml^{-1})	V_{solution}	V_{polymer}	Δ Shrinkage
CE	1.1637	1.2113	0.8593	0.8255	−3.93
CE/SOC 95:5	1.1627	1.2000	0.8600	0.8333	−3.10
CE/SOC 93:7	1.1748	1.1878	0.8512	0.8418	−1.10
CE/SOC 90:10	1.1876	1.1744	0.8420	0.8515	1.12

An important decrease on shrinkage extent upon photopolymerization was evidenced in the cured films obtained in the presence of SOC. An expansion of volume during polymerization was even reached by photocuring the CE/SOC 90:10 wt% formulation.

We can conclude that SOC acts as shrinkage reduction or expandable monomer additive for epoxy UV-curable formulations. The volume changes are proportional to the feed ratio of SOC monomer, with a shrinkage reduction by increasing SOC content and reaching expansion on volume in the presence of 10 wt% of the functionalized spiroorthocarbonate.

4. Conclusions

An epoxy functionalized spiroorthocarbonate (SOC) was synthesized with the aim to investigate the effect of an epoxy functionalized spiroorthocarbonate as a low shrinkable additive in cationic photopolymerization of an epoxy monomer. The SOC and the dicycloaliphatic epoxy resin (CE) are compatible in the range between 5 and 10 wt% of SOC. The formulations, under UV irradiation, give rise to transparent cured copolymeric networks. A flexibilization increase was evidenced by increasing the SOC content in the photocurable formulation. The copolymerization reaction has been confirmed by the presence of a single tan δ peak in DMTA thermogram and further investigations are under progress in order to better elucidate the copolymerization mechanism. Shrinkage during photopolymerization was calculated by measuring the density of the starting formulations and of the corresponding cured films; it has been demonstrated that SOC acts as shrinkage reduction additive or even as an expanding monomer in the epoxy UV-induced polymerization.

Acknowledgements

The Italian Foreign Ministry and CONACYT (Mexican National Council of Science and Technology) are gratefully acknowledged for covering the exchange expenses.

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