

Epoxy Resin Modified with Soybean Oil Containing Cyclic Carbonate Groups

Pawel G. Parzuchowski,¹ Magdalena Jurczyk-Kowalska,² Joanna Ryszkowska,² Gabriel Rokicki¹

¹Faculty of Chemistry, Warsaw University of Technology, 00-664 Warsaw, Poland

²Faculty of Materials Science and Engineering, Warsaw University of Technology, 00-664 Warsaw, Poland

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ABSTRACT: Carbonated soybean oil (CSO) containing five-membered cyclic carbonate groups has been obtained in the reaction of epoxidized soybean oil with carbon dioxide in the presence of KI activated by 18-crown-6 under 6 MPa CO₂ pressure at 130°C. The CSO was used for modification of bisphenol-A based epoxy resin. The composition epoxide-cyclic carbonate was cured using polyamine hardeners by one-step and two-step procedures. All cured compositions were characterized for their thermal and mechanical proper-

ties and compared with the parent epoxy network. The optimal properties were obtained for compositions containing CSO and cured by one-step method when phase separation takes place. The mechanical properties were discussed in terms of morphology observed by SEM. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2904–2914, 2006

Key words: carbonated soybean oil; epoxy resin; modified epoxy resin; phase separation; thermoset morphology

INTRODUCTION

Epoxy resins are used world-wide in large amounts. They combine attractive properties such as high strength and stiffness and excellent dimensional, thermal, and environmental stabilities. They exhibit good thermomechanical properties and excellent processability.¹ The main drawback associated with the application of highly crosslinked thermosetting polymers is related to their inherent brittleness that increases with crosslink density.¹

The use of epoxy thermosetting materials is limited by their toughness properties, which affect the durability (impact resistance, fatigue behavior, damage tolerance). To eliminate this, tougheners are usually added. Two types of modifiers are established: epoxy flexibilizers and epoxy toughening agents. Both are miscible with the uncured epoxy resin and should not deteriorate the low resin viscosity required to afford easy processing. In contrast to a flexibilizer, toughening agents improve toughness without sacrificing stiffness and glass transition temperature. Toughness can be achieved through different ways: (1) reduction of the crosslinking density, (2) use of plasticizers that lead to increased plastic deformation, and (3) addition of a second phase in the form of particles (depends on

their size, interparticle distance, and particle–matrix interaction).

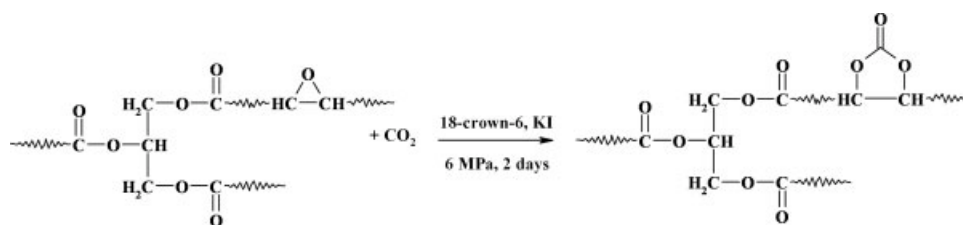
Since the pioneering advances at B.F. Goodrich Company, low molecular weight butadiene acrylonitrile copolymers bearing carboxyl, amine, or epoxy reactive end groups have been used extensively.^{2,3} Other important liquid rubbers are based upon poly(propylene oxide)^{4,5} and poly(tetrahydrofuran).^{6,7} During recent years, new types of impact modifiers based upon hyperbranched nanometer-scaled polymers, especially polyesters, have been introduced. Hyperbranched hydroxy-, carboxy-, and epoxy-terminated polyesters give low density blends. A few percent of such polyesters are sufficient to significantly improve toughness without sacrificing stiffness and glass transition temperature.^{8,9}

In this article, we concentrate on small particles formation during the curing process. In this area of interest, Russell and Chartoff reported recently the application of dispersed rubber particles in the primary phase in the epoxy system. The authors investigated the influence of the particle size and volume on the degree to which the epoxy resin is toughened.¹⁰ Day et al. used surface functionalized particles (with epoxy terminal groups) to ensure a good interface between the toughening particles and the epoxy matrix.¹¹ Acrylic core/shell particles, capable to swell under exposure to heat and gel before the epoxy resin is completely cured, were reported by Ashida et al.¹² Hyperbranched polymers functionalized with epoxy groups were also used as toughening agents for epoxy systems.^{9,13}

Vegetable oils have traditionally been used in organic coatings both as resins by themselves and as

Correspondence to: G. Rokicki (gabro@ch.pw.edu.pl).

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Scheme 1 Preparation of CSO.

raw material components for coating resins.¹⁴ Coatings based on vegetable oils and derivatives thereof have mostly been air-drying polyester resin or linseed oil coatings, consisting primarily of glycerides of unsaturated fatty acids (oleic, linoleic, and linolenic acid), and these coatings are characterized by good wetting and good mechanical properties.

Naturally occurring epoxidized vegetable oils can be found in plants such as *Euphorbia lagascae* or *Vernonia galamensis*^{14,15} and much work has been done to characterize, purify, and study^{16–20} their potential use in material applications.²¹ A cheap alternative to the natural epoxy functional oil is to epoxidize unsaturated vegetable oils such as soybean oil, and to use them in similar coating systems, utilizing the same reactions to obtain a crosslinked product.^{22,23} Since almost any type of vegetable oil can be modified via this route, it affords larger quantities available at a reasonable cost, although it involves a chemical modification step. Epoxidized soybean oil (ESO) is mainly used as a plasticizer and stabilizer for PVC. ESO shows excellent promise as a inexpensive, renewable material for other industrial application.^{24,25}

Carbon dioxide is an abundant, inexpensive resource of carbonate linkages. Much attention has been paid for the fixation of CO₂ in organic compounds. Among them the reaction of oxiranes with

CO₂ leading in a high yield to five-membered cyclic carbonate is the most attractive one from economical and environmental point of view.²⁶ This reaction is usually carried out under pressure and in the presence of different catalysts.²⁷ Five-membered carbonates react with primary aliphatic amines under mild conditions yielding β -hydroxyurethane linkages.²⁸ There are also reports on the incorporation of carbon dioxide into soybean oil and preparation of nonisocyanate polyurethane networks.^{29,30}

The objective of this work was the synthesis of carbonated soybean oil (CSO) for the modification of diglycidyl ether of bisphenol-A (DGEBA) epoxy resins. The effect of CSO content on the curing behaviors, thermal, and mechanical interfacial properties of the epoxy resin/CSO composition has been studied and discussed. The toughening system described in this article involved the formation of small oil particles during the curing process of the epoxy resin in the presence of various amine hardeners. Commercially available ESO could not be used in this work since symmetrically substituted epoxy groups are not reactive with aliphatic amines under ambient temperature. A one-step reaction of ESO with carbon dioxide eliminates those problems. The soybean oil containing cyclic carbonate groups is easily soluble in epoxy resin and can readily react with aliphatic amine hardeners.

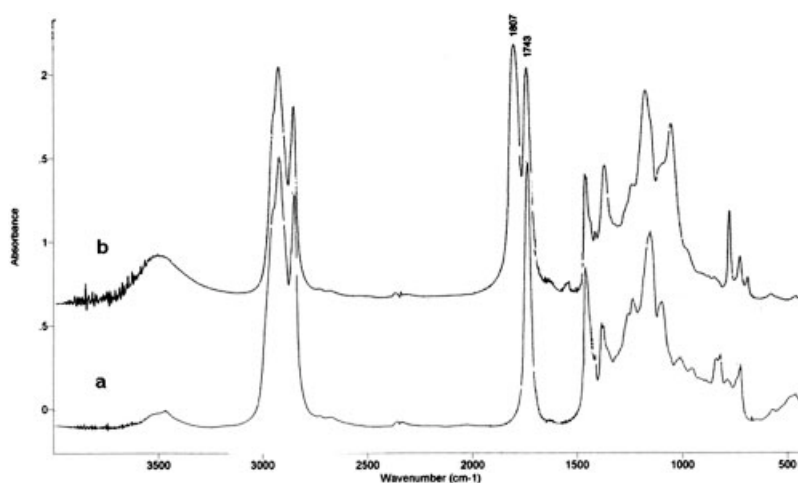


Figure 1 FTIR spectrum of the ESO (a) and the product of CO₂ addition to epoxidized oil (CSO) (b).

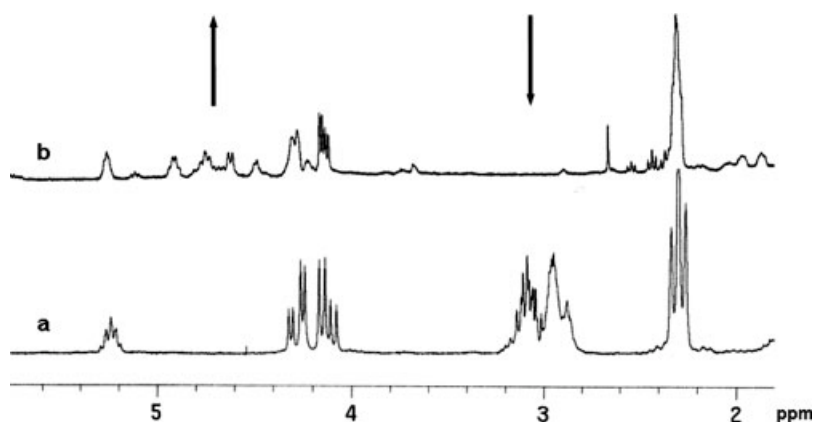


Figure 2 ^1H NMR (CDCl_3 , 400 MHz) spectrum of the ESO (a) and the product after the CO_2 addition (b).

EXPERIMENTAL

Materials

ESO (Ergoplast ES) (epoxide number EN, 0.40 val/100 g) was commercially available from Boryszew S.A. (Poland). Epoxy resin was a diglycidyl ether of bisphenol-A (DGEBA) (Epidian 5 of EN = 0.49 val/100 g was purchased from Organika Sarzyna S.A. (Poland)). 1,6-Hexanediamine (HMDA), triethylenetetraamine (TETA), diethylenetriamine (DETA), isophoronediamine (IPDA), 18-crown-6, potassium iodide, and ion-exchange resin Amberlyst A-26 were purchased from Aldrich. The CO_2 gas was obtained from Multax, Poland. All the chemicals were used as received.

Instrumentation

^1H NMR spectra were recorded on a Varian VXR 400 MHz spectrometer using tetramethylsilane as an internal standard. FTIR spectra were recorded on a Biorad FTIR Spectrometer FTS165. Mechanical properties were determined on Instron 5566. Viscosity was measured with Mettler RM180 Rheomat at 25°C . DSC studies were performed in the temperature range from -120°C to $+60^\circ\text{C}$ using a PerkinElmer Pyris 1 calorimeter at a heating rate of $20^\circ\text{C}/\text{min}$ for samples of 10–25 mg mass. Glass transition temperature (T_g) was calculated from the inflection point in the break in the heat

flow curves. Gel points and exotherm profiles were measured using 10 g samples in a thermostated bath at 25 and 50°C . Scanning electron microscopy (SEM) was done using a LEO 1530 apparatus (at 20 kV). SEM specimens were carbon coated.

Mechanical properties tests

Tensile strength was measured on dumb-bell shaped type IV samples according to standard ASTM D-638. The samples were obtained by the die-casting method. Measurements were carried out at ambient temperature using a constant crosshead speed of 2 mm/min and the gauge length of 45 mm. Minimum five specimens were tested in each case to obtain an average value.

Flexural strength was measured with samples of $120 \times 5 \times 2.5 \text{ mm}^3$ according to the standard ASTM D-790, using the same machine at a crosshead speed of 2 mm/min. The flexural strength was performed using a 3-point bending method. In this work, the flexural strength was reported as the load at yield measured at 5% deformation of the outer surface for the samples that did not break or at break. In each case the flexural modulus was also calculated.

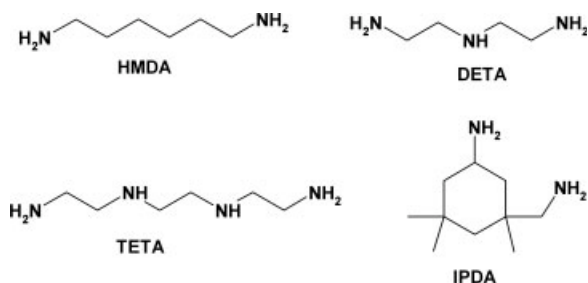
Impact resistance of the samples was performed by a Charpy impact strength method (ASTM D-256, Method B). Results are presented as the energy to break per fractured area.

TABLE I
Characteristics of the Carbonated Soybean Oil (CSO)

Epoxy group conversion (%)	Reaction time (h)	Viscosity (Pa s) ^a		Epoxy number (mol/100 g)	Carbonate content (mol/100 g)
		99 L/s ^b	23.3 L/s		
0	0	0.51	0.45	0.403 ± 0.012	0
20.5	12	0.91	0.87	0.320 ± 0.005	0.080 ± 0.005
68.7	48	12.9	12.4	0.126 ± 0.003	0.246 ± 0.003
98.3	120	30.2	30.0	0.007 ± 0.001	0.337 ± 0.001

^a At 20°C .

^b Shear rate.



Scheme 2 Polyamines used as curing agents.

Epoxy number and carbonate groups content determination

The epoxy number (EN) was determined by standard titration with hydrogen chloride in dioxane.³¹ The results were calculated and corrected accordingly to the results of titration of phenyl glycidyl ether as a standard sample. The molar content of carbonate groups in CSO was calculated as a difference of the EN before and after CO₂ addition.

Reaction of epoxidized soybean oil with carbon dioxide

To a pressure reactor equipped with a magnetic stirrer and manometer 200 g of ESO (Ergoplast ES) was introduced and then 0.4 g of 18-crown-6 with 0.6 g of potassium iodide were added. The reactor was closed and pressurized with carbon dioxide up to 6 MPa at -15°C. The reactor was placed in an oil bath and heated to 130°C for a required time. After cooling and depressurizing, the product was analyzed. The reaction progress was monitored by FTIR spectroscopy (the intensity of the absorption band at 1807 cm⁻¹ characteristic of the carbonyl group of five-membered cyclic carbonate was measured).

Curing of epoxy resin-carbonated oil compositions

In each experiment a sample consisted of commercial epoxy resin, CSO, and polyamine curing agent. All for-

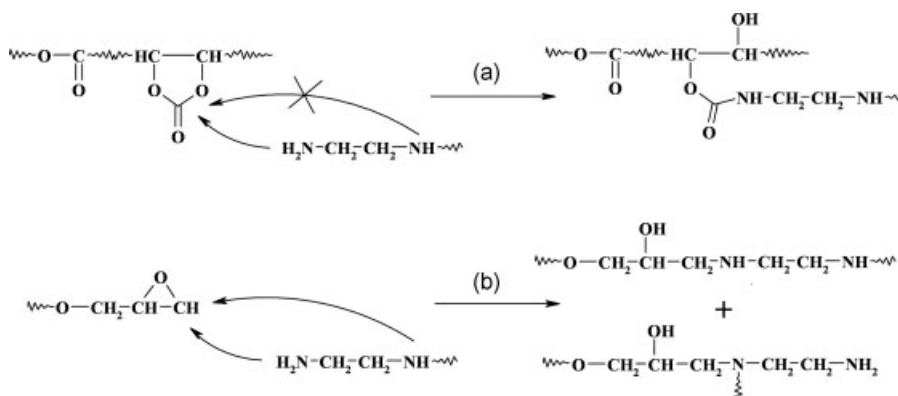
mulations were mixed with a stoichiometric amount of amine hardener. The curing process was performed by two different methods. In the one-step procedure, the epoxy resin was mixed with CSO and then the amine was added. After mixing, the resulting composition was degassed and poured into a steel mold, degassed again and cured at room temperature for 12 h. In the two-step method, carbonated oil was firstly reacted with the amine hardener at 70°C for 3 h and then the resulting viscous adduct was mixed with the epoxy resin and introduced into the steel molds and cured under the same conditions.

RESULTS AND DISCUSSION

Synthesis of carbonated soybean oil

The CSO was obtained in the reaction of the commercial ESO with CO₂ carried out in the presence of various catalysts (Scheme 1). It was found that in contrast to monosubstituted oxiranes, the reaction rate of 1,2-disubstituted oxiranes is slower and longer time is needed to achieve complete conversion of epoxy groups into 1,3-dioxolan-2-one ones.²⁷ In the presence of catalysts such as tetraalkylammonium salts (benzyltriethylammonium chloride, tetrabutylammonium bromide, Amberlyst A-26) the conversion of epoxy groups at 130°C under 6 MPa pressure of CO₂ was lower than 10% after 5 days. However, when KI activated with 18-crown-6 was used as catalyst, almost complete conversion was achieved after the same time. The reaction progress was monitored by means of FTIR and ¹H NMR spectroscopies as well as by EN determination.

Figure 1 shows (a) FTIR spectra of ESO and (b) the product of CO₂ addition to epoxidized oil. As it can be seen in the figure, as a result of the reaction, a new absorption band of carbonyl group of five-membered cyclic carbonates appeared at 1807 cm⁻¹ in the FTIR spectrum. In the product the intensity of the absorption band of the carbonate carbonyl groups was greater than that of the ester groups (1743 cm⁻¹).



Scheme 3 Possible reaction pathways during the curing process.

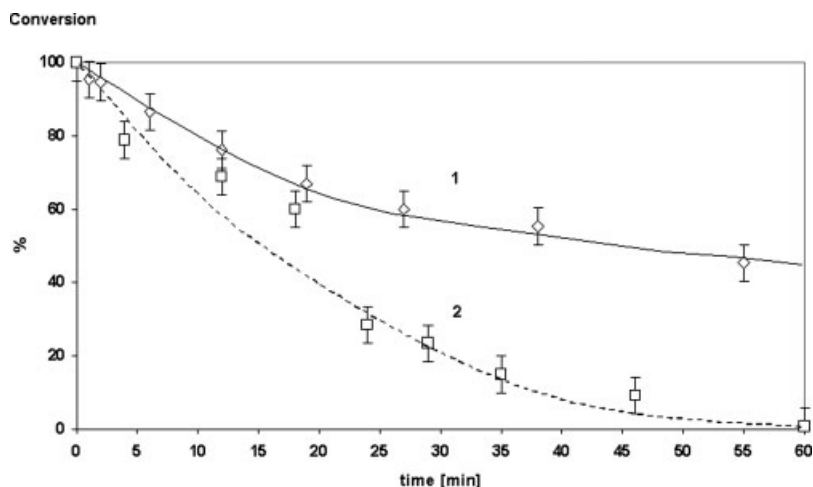


Figure 3 Relative reactivity of the cyclic carbonate groups in CSO (1) and epoxy group in the epoxy resin (2) in the reaction with equimolar amount of *n*-butylamine at 50°C.

The reaction progress was also monitored by means of ^1H NMR spectroscopy. The signals corresponding to the protons of the epoxy groups present at 2.85–3.20 ppm disappeared after the reaction with carbon dioxide [Fig. 2(b)]. The new signals at 4.45–4.95 ppm can be assigned to the protons of disubstituted 1,3-dioxolan-2-one rings. The pattern of these signals corresponds to both *cis*- and *trans*-isomers of cyclic carbonates. It is worth mentioning that in soybean oil only unsaturated bonds of *cis*-configuration are present.

The viscosity of the product strongly depends on the conversion of epoxy groups into five-membered cyclic carbonate ones. The complete conversion of epoxy groups leads to the viscosity of 20 Pa s at 20°C. This viscosity growth can be explained by the appearance of polar carbonyl groups and hydrogen bonds formation. The high viscosity can also be explained by the molecular weight growth due to possible Diels–Alder reac-

tion. Table I shows the characteristics of the CSO as a function of the epoxy group conversion.

Curing of epoxy resin–CSO compositions with amines

The CSO is miscible without limits with the bisphenol-A based epoxy resin and moreover, five-membered carbonate groups present in the carbonated oil readily react with primary aliphatic amines (Schemes 2 and 3).

It was found that the reaction of 2,3-disubstituted oxiranes with amines proceeds with much lower rate than that with monosubstituted oxirane, such as in DGEBA.

Scheme 3 shows the possible reaction pathways which take place during the curing process. The cyclic carbonate groups react with primary amine groups of the amine hardener leading to urethane derivatives, but do not react with secondary amines [Scheme 3(a)].

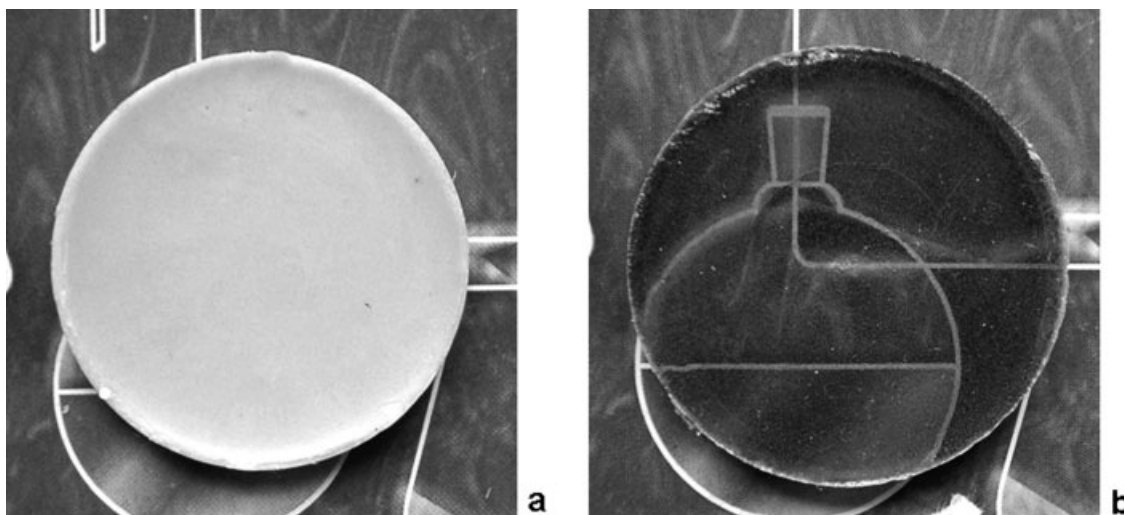


Figure 4 CSO-modified epoxy resin cured with TETA hardener in a one-step procedure (a) and two-step procedure (b).

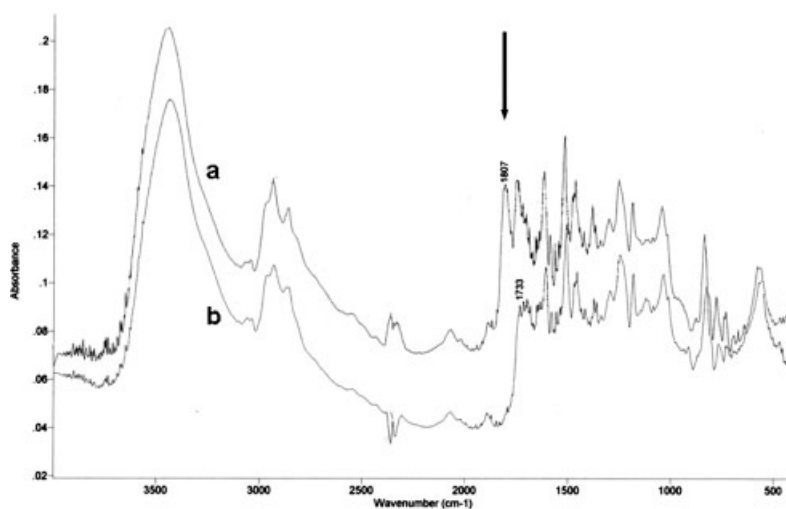


Figure 5 FTIR spectra of epoxy resin–CSO compositions cured with TETA: (a) in a one-step procedure and (b) in a two-step procedure.

In contrast, epoxy groups of DGEBA readily react with both primary and secondary amines [Scheme 3(b)].

The reactivity differences between epoxy and cyclic carbonate groups in the reaction with primary amine were observed. Figure 3 shows the conversion of cyclic carbonate and epoxy groups versus time in the reaction with equimolar amounts of *n*-butylamine. It can be seen that the concentration of the epoxy groups decreases rapidly and after 60 min the reaction carried out at 50°C is almost completed. In the case of cyclic carbonate there is a relatively slow decrease of cyclic carbonate groups concentration under similar conditions. After 60 min 45% of unreacted carbonate groups were present in the reaction mixture.

The curing of epoxy compositions was performed by two different ways: one-step method (when all the reagents were mixed together) and two-step method (when first CSO was reacted with the amine hardener

used in an amount calculated for both epoxy and cyclic carbonate groups, then the resulting adduct was added to the epoxy resin and the curing process was continued). In Figure 4, the samples cured using (a) one-step and (b) two-step procedures are presented.

Figure 5 shows the FTIR spectra of samples containing 40% of CSO cured according to two different methods. In the spectrum of the sample prepared according to the one-step method the absorption band at 1807 cm^{-1} is still present, which indicates that cyclic carbonate groups are not completely consumed. In the FTIR spectrum of the sample cured in the two-step method there is no absorption band characteristic of cyclic carbonate.

As was presented above, epoxy groups are more reactive than cyclic carbonate ones. In the homogeneous mixture of the epoxy resin with CSO, epoxy groups react with polyamine first forming networks. The

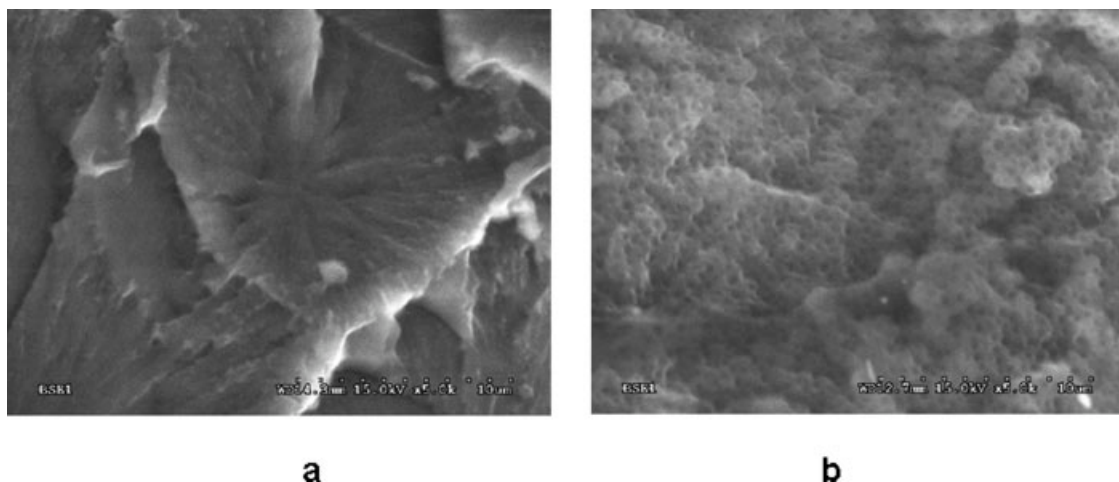


Figure 6 SEM images of the surfaces of the epoxy resin cured with TETA (a) and epoxy resin modified with 40% of CSO cured with TETA in a one-step procedure (b); magnification $\times 5000$.

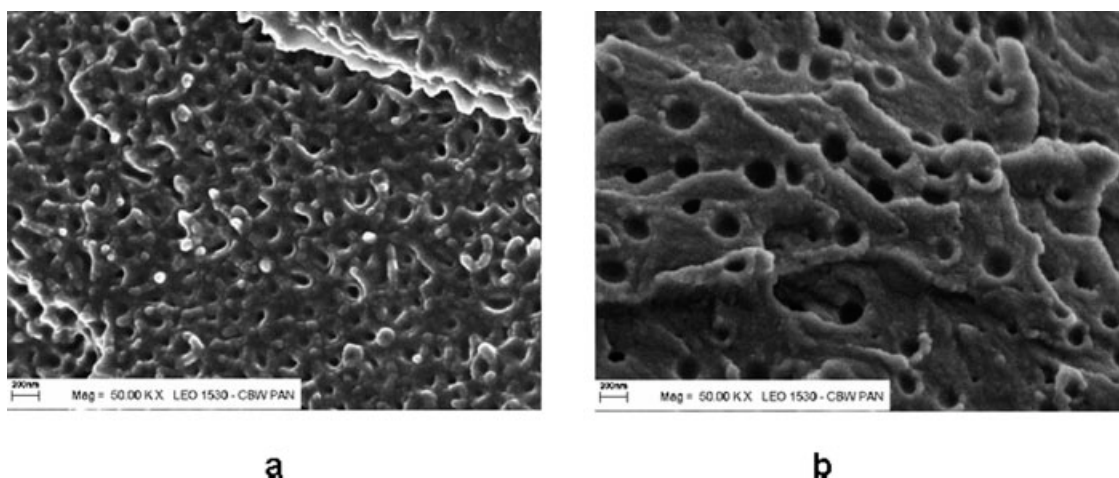


Figure 7 SEM images of the surfaces of epoxy resin containing 40% of CSO cured with IPDA in a one-step procedure (a), 20% of CSO cured with TETA in a one-step procedure (b); magnification $\times 50,000$.

unreacted CSO is not soluble in the hyperbranched and partially cured composition and the system becomes heterogeneous.

Indeed, it was found that the compositions of the epoxy resin with CSO cured with TETA or another amine hardener according to a one-step method led

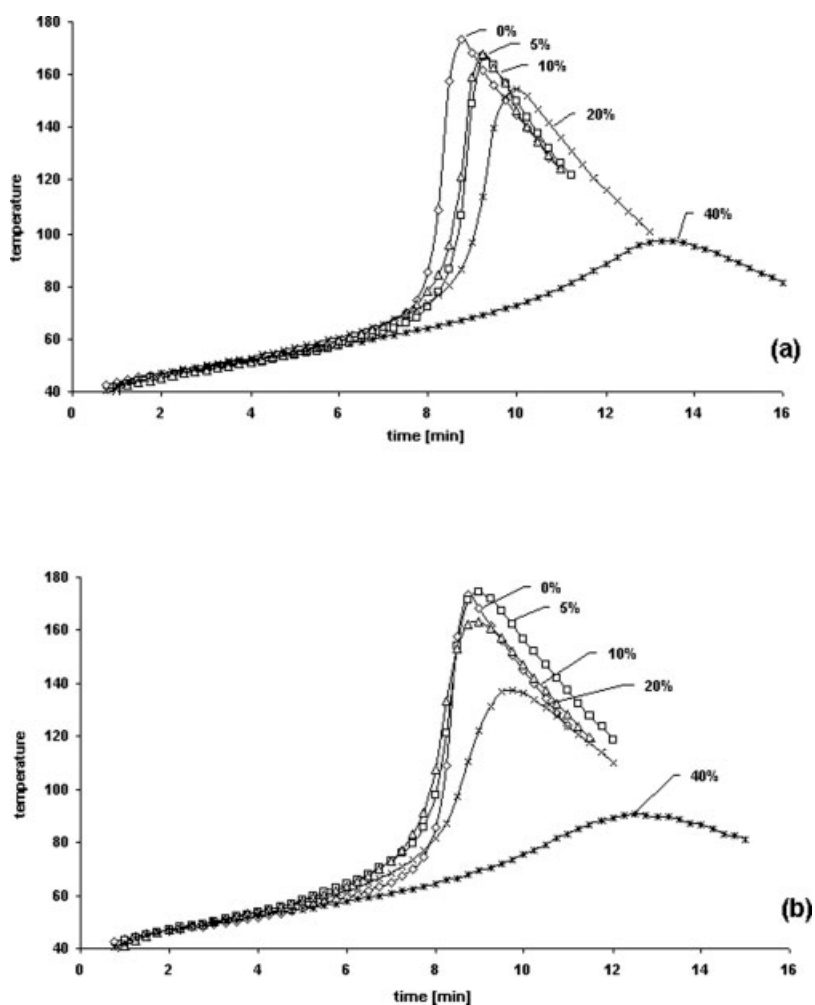


Figure 8 Exotherm profiles of the epoxy resin modified with different amounts of CSO cured with DETA hardener: (a) one-step procedure and (b) two-step procedure.

to ivory opaque products. The mixture of epoxy resin, CSO, and amine hardener at the beginning is homogeneous and during the curing process the second phase is formed as small domains of carbonated oil [Fig. 5(a)].

In contrast, in the two-step method complete conversion of cyclic carbonates takes place and as can be seen in Figure 4(b), there is no formation of a new phase and the sample remains transparent [Fig. 5(b)].

The process of phase separation depends not only on the method of curing, but can also be controlled by the degree of conversion of epoxy groups into cyclic carbonates of the soybean oil (Scheme 1). For the CSO with high content of cyclic carbonate groups (98.3% conversion), there was no formation of a second phase for both methods. This is due to covalent bounding of the CSO into the resin lattice. The CSO of lower epoxide conversion (20.5%) showed the formation of a second phase during the curing process, when its concentration was higher than 10%. However, all samples containing 5% of CSO were transparent after curing, no matter which procedure was used.

There were no significant differences observed for different hardeners, except IPDA. The IPDA hardener contains a less reactive amine group located at disubstituted carbon atom, which slowed down the curing process. Because of this behavior, there were more transparent samples in the series. Because of the differ-

ent reactivity of the amine groups, a gel fraction appears at higher conversion of functional groups than that with an amine hardener of equal reactivity groups. In this case, the composition remains homogeneous at higher reaction progress degree.³²

SEM analysis

The formation of a new phase can be observed in the SEM images. Figure 6 shows the images of the fracture surfaces of an unmodified epoxy resin cured with TETA (a) and a sample containing 40% of CSO cured with TETA in a one-step method (b). In the picture, particles containing CSO can be observed for modified resin (b). A smooth glassy fractured surface with cracks in different planes for unmodified epoxy resin, indicating brittle fracture, which accounts for the poor impact strength of the unmodified resin, can be observed. Figure 7 shows pictures of samples of cured modified epoxy resin at higher resolution. As can be seen in Figures 7(a and b), the modified resin with CSO formed spherical domains of the oil dispersed within the continuous epoxy phase. Uniform distribution of the oil particles throughout the matrix is very important for toughening. It allows the yielding process to operate throughout the matrix.³³ The average domain size depends on the amount of CSO added to the composition. The samples with 40% of CSO cured with

TABLE II
Maximum Temperatures and Corresponding Times Reached by Samples
During Curing Process of the Epoxy Resin Modified with CSO for
Different Amine Hardeners

Hardener CSO content (%)	One-step process		Two-step process	
	Time (min)	Temperature (°C)	Time (min)	Temperature (°C)
TETA				
0	8.7	167	8.7	167
5	9.5	160	9.5	147
10	9.2	162	11.0	128
20	10.2	140	13.0	105
40	14.2	88	14.7	61
DETA				
0	8.7	173	8.7	173
5	9.2	167	9.0	174
10	9.2	167	9.0	163
20	10.0	154	9.7	137
40	13.5	97	12.5	91
HMDA				
0	10.2	172	10.2	172
5	10.2	156	9.0	153
10	10.2	161	9.5	135
20	11.0	145	9.7	128
40	15.0	87	13.5	69
IPDA				
0	26.5	72	26.5	72
5	22.5	81	23.0	75
10	23.5	68	25.0	61
20	25.0	61	19.0	58
40	27.0	55	18.0	54

TABLE III
Glass Transition Temperature (T_g) of the Epoxy Resin Modified with CSO Cured According to the One-Step Method with TETA and IPDA

Hardener CSO content (%)	T_g (°C)
TETA	
0	98
10	92
20	57
40	53
IPDA	
0	87
40	64

TETA contained particles of 335 ± 50 nm diameter, while those with 20% of the carbonated oil promoted formation of smaller particles (184 ± 30 nm). The application of the hardener of lower reactivity (IPDA) as a curing agent led to the formation of smallest particles (70 ± 30 nm) even for 40% of the CSO addition. The oil domains did not undergo cavitation, suggesting good adhesion between CSO and the epoxy resin matrix. Some cyclic carbonate can react with epoxy resin via amine hardener and effectively lock the domains to the matrix. A similar phenomenon was reported by Boogh et al.³³

TABLE IV
Impact Resistance of the Modified Epoxy Resin with Different Amounts of CSO for Different Hardeners and Curing Procedures

Hardener CSO content (%)	Impact resistance	
	(One-step procedure) (kJ/m ²)	(Two-step procedure) (kJ/m ²)
TETA		
0	14.7 ± 2.3	14.7 ± 2.3
5	6.0 ± 1.2	8.0 ± 1.3
10	10.5 ± 2.1	6.1 ± 1.6
20	18.8 ± 2.5	5.6 ± 1.0
40	31.9 ± 2.6	2.8 ± 1.3
DETA		
0	14.0 ± 1.3	14.0 ± 2.5
5	10.8 ± 1.8	10.8 ± 1.2
10	9.4 ± 1.8	12.2 ± 2.3
20	16.1 ± 1.1	8.4 ± 1.7
40	21.4 ± 2.8	14.4 ± 2.5
HMDA		
0	27.0 ± 3.3	27.0 ± 2.0
5	17.0 ± 2.9	17.3 ± 2.4
10	24.2 ± 2.4	18.0 ± 1.3
20	27.1 ± 4.5	2.8 ± 1.0
40	32.7 ± 2.3	2.3 ± 1.3
IPDA		
0	8.5 ± 1.4	8.5 ± 0.9
5	5.5 ± 1.3	5.6 ± 1.1
10	12.1 ± 2.1	6.0 ± 1.8
20	21.1 ± 3.3	6.5 ± 1.3
40	18.1 ± 2.7	6.9 ± 1.4

Curing thermal analysis

The epoxy resin-CSO compositions were cured with four different amine hardeners. Two sets of experiments were performed: one-step and two-step curing procedures.

Figure 8 shows exotherm profiles for the compositions cured with DETA. They illustrate the influence of the CSO concentration on the maximum temperature reached during crosslinking. The temperature maxima and times needed to reach them are collected in Table II. Up to 10% of CSO the changes in profiles were very small. Samples containing 20 and 40% of the CSO show bigger reduction of the maximal temperature. The smaller internal stress in a five-membered 1,2-dioxolan-2-one ring compared to a three-membered ring, and a lower crosslinking density in comparison to that of the epoxy resin are additional factors generating the smaller thermal effect of epoxy-cyclic carbonate compositions curing.

Thus, samples prepared in a one-step mode showed higher maximum temperatures. In this case both epoxy and cyclic carbonate groups react simultaneously and an exothermic effect was registered. In case of two-step process, the thermal effect of the reaction between amino and carbonate groups was not recorded and samples showed lower maximum temperature.

Similar results were obtained for other hardeners. The shortest time to reach the maximum temperature was observed for TETA and DETA hardeners, slightly longer for HMDA and significantly longer for IPDA. The latter hardener contains the less reactive amine group at secondary carbon atom (Scheme 2).

It is known that the glass transition temperature of epoxy resin highly depends on the curing conditions. The higher curing temperature, the higher glass transition temperature of the hardened resin is observed. In our case epoxy-cyclic carbonate compositions were cured at room temperature. However, as was shown in the previous paragraph, the compositions temperature increased while they reacted. The exothermic effect was higher for the samples containing less CSO additive. The DSC data were in agreement with this behavior. Thus, up to 10% of CSO there was only small reduction of T_g of the cured resin. The lowest glass

TABLE V
Tensile Strength of the CSO Modified Epoxy Resin Cured with TETA in a One-Step Procedure

CSO content (%)	Tensile strength (MPa)	Elongation at break (%)
0	45 ± 4	6.2
5	65 ± 2	8.7
10	69 ± 3	9.2
20	43 ± 4	8.4
40	41 ± 5	9.7

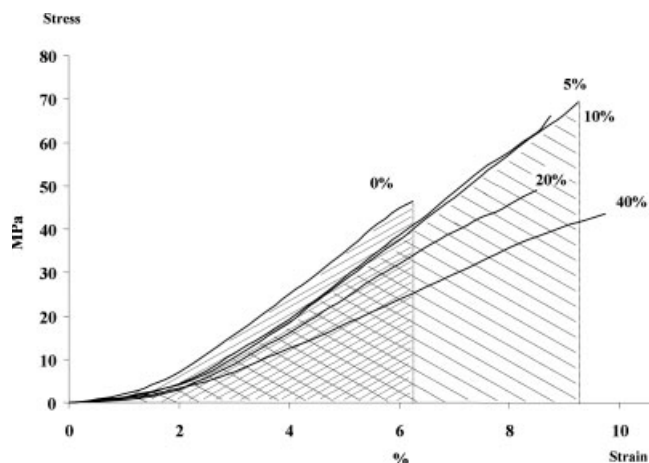


Figure 9 Stress–strain curves for the CSO-modified epoxy resin cured with TETA in a one-step procedure.

transition temperatures were observed for samples containing higher amounts (20 and 40%) of CSO.

For higher amounts of CSO there was no significant decrease in T_g because of phase separation. Thus, glass transition temperature was reduced from 57°C for 20% of CSO to 53°C for 40% of the carbonated oil (Table III). Significant depression of T_g observed for the composition with a lower amount of CSO in comparison to that of unmodified epoxy resin is due to the plasticization phenomenon that was also observed for other compositions of epoxy resin containing rubber modifiers.³⁴

Physical properties

The modification of epoxy resin with CSO strongly influences the physical properties of the resin. The mode of curing the samples also plays an important role in obtaining a material of desired properties.

Phase separation is an important factor affecting the impact strength. Samples where phase separation took place exhibited higher impact resistance. The impact tests were performed by the Charpy's method. The results are presented in Table IV.

The polyamine at the interphase is expected to react with both cyclic carbonate groups of the oil and epoxy groups of the resin to form chemical bonds between the rigid resin matrix and rubbery CSO particles leading to a toughening effect. A similar effect was observed by Achary et al. for typical rubber modifier.^{34,35} However, for lower amounts of CSO as well as using the two-step curing method, the impact strength of the cured composition was lower than that of the unmodified resin.

It was found that the epoxy resin containing up to 10% of CSO cured with TETA in a one-step procedure exhibited higher tensile strength than that of unmodified resin. For a higher amount of carbonated oil the tensile strength remained on the level of the unmodi-

fied epoxy resin, whereas, the elongation at break increased within the modifier amount present (Table V). The amount of work required to break a sample is visualized in Figure 9. It is represented by the surface area below the stress–strain curves. By simple comparison it can be seen that the samples containing 10% of CSO require twice as much work to break as those of unmodified resin.

The combination of tensile strength and elongation at break shows that the energy required to break the sample containing CSO was higher than that of unmodified resin, which means increased toughness.

CONCLUSIONS

An epoxy resin modified with CSO, biodegradable and renewable material,³⁶ when cured with a polyamine hardener at room temperature in a one-step method indicates phase separation. The phase separation was studied using SEM. The phase separated networks exhibit higher impact strength as well as tensile strength than those of unmodified epoxy resin and composition containing CSO but cured by a two-step method. Thus, the samples containing CSO exhibit increased toughness—the energy the sample of modified resin can absorb before it breaks is higher than that of unmodified resin.

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