

Synthesis and Properties of Photocross-Linked Polymers of Epoxidized Linseed Oil with Different Reactive Diluents

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ABSTRACT: Cross-linked polymers were obtained by photopolymerization of epoxidized linseed oil with different reactive diluents (3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 1,4-cyclohexane dimethanol diglycidyl ether, bisphenol A diglycidyl ether, trimethylolpropane triglycidyl ether, and bis[4-(glycidyl)oxy]phenylmethane) using the mixture of triarylsulfonium hexafluoroantimonates as photoinitiator. The kinetic of photocross-linking reactions of compositions with different concentrations of reactive diluents was investigated. The 69%–91% conversion of epoxy groups of the compositions containing reactive diluents was reached. The mechanical properties, thermal stability, and swelling in polar and nonpolar solvents of the photocross-linked polymers were studied. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1290–1298, 2013

KEYWORDS: biomaterials; photopolymerization; crosslinking; kinetics; mechanical properties

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INTRODUCTION

The field of polymers derived from nonpetrochemical feedstocks is gaining a great deal of momentum from both a commercial and academic sense. Using annually renewable feedstocks for the production of new plastics can have both economic and environmental benefits. Fundamental research in the production, modification, property enhancement, and new applications of these materials is an important undertaking. The new materials, concepts, and usages that result from these efforts will shape the future of polymers from renewable resources.¹

In recent years, natural oils have become the center of attraction for their potential use as starting materials for the preparation of polymers. Vegetable oils are one of the cheapest and most abundant, annually renewable natural resources available in large quantities from various oilseeds. The unsaturation present in these oils makes them ideal for the preparation of bio-based polymers.^{2–7} A variety of biorenewable materials, including thermosetting resins, thermoplastics, and biocomposites have been prepared from vegetable oils and their derivatives.⁸

Linseed oil is traditionally used as a drying oil for surface-coating applications. To make it a superior drying oil in terms of film properties, linseed oil was polymerized directly or after chemical modification by cationic, free radical polymerization, and oxidative polymerization.³ The homopolymerization of

vegetable oils typically results in viscous fluids of limited use. To produce viable hard plastics, vegetable oils have to be copolymerized with more rigid and reactive aromatic comonomers.^{3,9,10} Some vegetable oil-based polymeric materials display conventional, industrially useful characteristics, as well as unique properties, such as good damping and shape-memory properties. The development of vegetable oil-based polymeric materials is a challenging research field with unlimited future prospects, which are far from being fully exploited.⁵

Several investigations of linseed oil-based copolymers with promising properties were reported in the last years. For example, it was found that the linseed oil-based copolymers with styrene and divinylbenzene exhibit comparable properties with those of petroleum-based polymers and can find numerous uses in complex structures, such as tubes, panels, and automotive parts.¹¹

The use of photoinitiated polymerization is continuously growing in industry as reflected by the large number of applications in not only conventional areas such as coatings, inks, and adhesives but also in high-tech domains, such as optoelectronics, laser imaging, stereolithography, and nanotechnology.¹² Until now, only few investigations were reported on photopolymerization or photocross-linking of epoxidized linseed oil and on the properties of resulting polymers. Bio-based rubbers prepared from a norbornenyl-modified linseed oil were reported by Jeong

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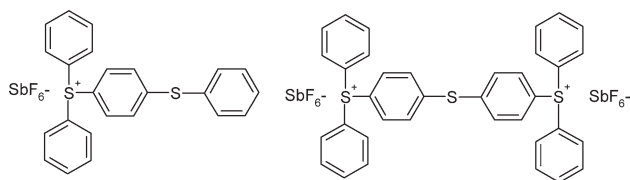


Figure 1. Structure of the photoinitiator, mixture of triarylsulfonium hexafluoroantimonates.

et al.¹³ Photopolymerization of the epoxycyclohexene derivatized linseed oil polymers was reported by Zou and Soucek.¹⁴ Zong et al.¹⁵ have found that the addition of reactive or non-reactive diluents reduced the viscosity of the formulations and had significant effect on epoxy conversion and the rate of polymerization of epoxynorbornane derivatized linseed oil. Soucek and coworkers¹⁶ have studied the properties of ultraviolet (UV)-curable hybrid films derived from epoxynorbornane-functionalized linseed oil and tetraethylorthosilane (TEOS) and observed that the incorporation of TEOS improved the performance of the films and enhanced tensile strength, fracture toughness, thermal stability, and general coating properties of epoxynorbornane-modified linseed oil.

This study is focused on the investigation of the influence of different reactive diluents to the cationic photocross-linking of epoxidized linseed oil and the properties of the resulting photocross-linked polymers.

The carbon double bonds present in the natural oil structures are not very active; therefore, usually they are chemically modified before the polymerization. The epoxidation of carbon double bonds was chosen in this study due to the high reactivity of epoxy groups in photopolymerization. In the last decade, many methods were used for the epoxidation of unsaturated fatty acid derivatives and vegetable oils both in laboratories and industry.¹⁷ One of the newest methods of epoxidation which uses methyltrioxorhenium as catalyst and hydrogen peroxide as the source of oxygen^{18–20} has seemed to be very successful in epoxidation of natural oils.^{21,22} This method was chosen in this study for the epoxidation of linseed oil.

Triarylsulfonium hexafluoroantimonate was chosen as photoinitiator for photocross-linking of epoxidized linseed oil as it is stable at the room temperature and soluble in most of the epoxy resins. It does not lead to the solidification of epoxides without UV light and is very effective in the photocross-linking of epoxidized natural oils as it was established in the earlier study.²³

Reactive diluents increase the homogeneity of the reaction mixture and decrease its viscosity. With the decrease of the viscosity of the reaction mixture, the mobility of the molecules of monomer and of the growing chains increase which results in the increase in the reaction rate. When the reactive diluent reacts with the monomer the layers of the resulting cross-linked systems become more homogeneous and possess better mechanical properties. In this study, five different reactive diluents were chosen for the investigation of their effect on the kinetics of photocross-linking of epoxidized linseed oil and on the properties of the resulting polymers.

EXPERIMENTAL

Materials

The linseed oil (Aletovis, Lithuania) was purchased in the local supermarket and used without further purification. Methyltrioxorhenium (VII), 50% mixture of triarylsulfonium hexafluoroantimonates in propylene carbonate (Figure 1), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (1, Figure 2), the mixture of *cis*- and *trans*-isomers of 1,4-cyclohexanedimethanol diglycidyl ether (2, Figure 2), bisphenol A diglycidyl ether (3, Figure 2), trimethylolpropane triglycidyl ether (4, Figure 2), and bis[4-(glycidylloxy)phenyl]methane (5, Figure 2) were purchased from Sigma-Aldrich and used as received. Hydrogen peroxide (Standart, Poland), pyridine (Riedel de Haen), anhydrous sodium sulfate (Fluka), sodium sulfite (Reachim, Russia), and sodium chloride (Aldrich) were used as received. Dichloromethane, chloroform, acetone (all from Poch S.A., Poland), and toluene (Delta – Chem) were purified and dried by the standard methods.²⁴

Instrumentation

¹H-NMR spectra were recorded with Varian Unity Inova spectrometer at 300 MHz using CDCl₃ as a solvent. All the data are given as chemical shifts δ (ppm) downfield from (CH₃)₄Si. Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer Spectrum GX spectrometer. The spectra of the solid materials were recorded using KBr pellets.

The conversion of epoxy groups during photocross-linking was estimated from FTIR spectra of the thin layers of the compositions casted on Si plates at the fixed periods ranging from 0.02 min to 50 min. The signal of epoxy groups at 775 cm⁻¹ (intensity by ca. 10% of transmission) was used for the estimation of epoxy group conversion. The signal of C=O group at 1745 cm⁻¹ was used as an internal standard. The intensity of the internal standard signal was evaluated every time when the conversion of epoxy groups was measured to eliminate the affect of the spectrum background changes. The results of epoxy group conversion were assumed as average values of the three measurements. The variation of experimental results did not exceed 5% within the group.

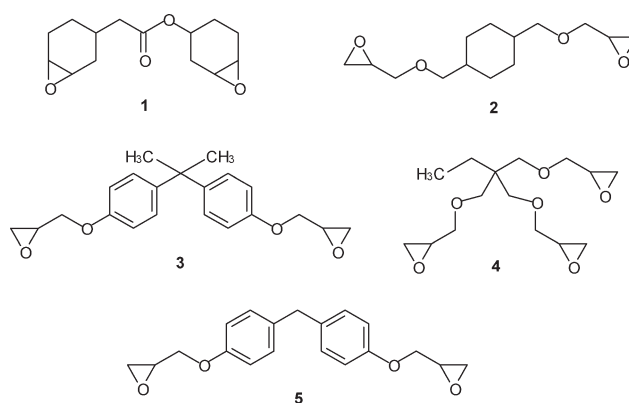


Figure 2. Structures of the reactive diluents: 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (1), 1,4-cyclohexanedimethanol diglycidyl ether (2), bisphenol A diglycidyl ether (3), trimethylolpropane triglycidyl ether (4), bis[4-(glycidylloxy)phenyl]methane (5).

Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 PC Luxx apparatus in the temperature range from the room temperature to 650°C at a heating rate of 10°C min⁻¹ under nitrogen atmosphere (nitrogen flow rate 100 mL min⁻¹).

The swelling value of films was obtained by measuring the volume of samples swollen in chloroform and toluene. The arithmetic average of the swelling value of three film samples (20.00 (±0.00) mm × 20.00 (±0.00) mm × 0.40 (±0.01) mm) of each composition was calculated. The variation of experimental results did not exceed 5% within the group.

The stress–strain investigation of the films was performed with a material testing machine BDO-FB0.5TH (Zwick/Roell). The strain rate for tensile test of all the samples was 300 mm min⁻¹. The width of films was 10.00 (±0.00), mm and the thickness of films was 0.40 (±0.01) mm. The arithmetic average of the results of the three-nine film samples of each composition was calculated. Only the results the variation of which did not exceed 15% within the group were taken for the calculation of the arithmetic average.

The hardness of films was measured with a Hepler consistometer by pressing a steel cone with an angle of 53°08' into the specimen under a load of 1500 g for 60 s. The arithmetic average of the hardness of three film samples (thickness 1.21 (±0.01) mm) of each composition was taken. The variation of experimental results did not exceed 10% within the group. The hardness of films was calculated by following equations:

$$H_H = \frac{S}{F} = \frac{4 \cdot G}{\pi \cdot \Delta h^2} \quad (1)$$

where H_H is the hardness of specimen (N mm⁻²) and G is the real force acting on a specimen (N).

$$S = \frac{\pi \cdot \Delta h^2}{4} \quad (2)$$

where S is the contact surface of the specimen (mm²), Δh^2 is the square value of the difference between readings of the microindicator when sample is unloaded and under load (mm²).

Epoxidation of Linseed Oil

The epoxidation of linseed oil was performed according to the procedure described in literature.¹³ Methyltrioxorhenium (MTO) (0.0037 g, 0.015 mmol), linseed oil (1 g), dichloromethane (1 mL), and pyridine (0.003 mL, 0.36 mmol) were added to the reaction flask placed in the water–ice bath. Hydrogen peroxide (30% solution, 0.57 mL, 4.5 mmol) was added to the intensively stirred reaction mixture very slowly. The reaction mixture was stirred further for 10–20 h and diluted with 10 mL of dichloromethane. The resulted solution was extracted with 10 mL of brine and then with 10 mL of 10% solution of sodium sulfite. The extract was dried with anhydrous sodium sulfate, filtered, and evaporated with rotary evaporator. The epoxidized linseed oil obtained was dried in vacuum. The yield was 78%–82%. IR (cm⁻¹): 3435 (ν, O–H), 3010 (ν, =C–H), 2930 (ν, CH₃), 2855 (ν, CH₂), 2344 (ν, C=O, CO₂), 2284, 1731 (ν, C=O ester), 1654 (ν, C=C), 1458 (δ, CH₂), 1371 (ν, C–C),

Table I. Batches for Photocross-Linking and the Contents of Insoluble Fractions of Photocross-Linked Polymers

Batch	Reactive diluent	Concentration of reactive diluent (mol %)	Insoluble fraction (%)
C0	–	–	98
C1	1	10	93
C2		20	99
C3		30	98
C4	2	10	91
C5		20	98
C6		30	96
C7	3	10	92
C8		20	97
C9		30	94
C10	4	10	98
C11		20	96
C12		30	98
C13	5	10	98
C14		20	97
C15		30	97

1183 (ν, C–O), 1075 (ν, C–O), 775 (ν, C–O epoxy), 724 (δ, CH₂). ¹H-NMR (CDCl₃) δ (m.d): 0.8–1.2 (H₁₇), 1.2–1.7 (H_{3–6}), 2–2.10 (H₇ and H₁₆), 2.32 (H₁), 2.80–3 (H₁₀ and H₁₃), 2.9 (H₈ and H₉), 4.10–4.4 (H_a and H_c), 5.2–5.7 (H₁₁, H₁₂, H₁₃, H₁₄, and H_b) (see Figure S1 in the Supporting Information).

Photocross-Linking

A typical composition was prepared by mixing of 0.2 g (0.032 mmol) of epoxidized linseed oil with the different amount (10, 20, or 30 mol %) of reactive diluent, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (**1**), 1,4-cyclohexanedi-methanol diglycidyl ether (**2**), bisphenol A diglycidyl ether (**3**), trimethylolpropane triglycidyl ether (**4**), or bis[4-(glycidioxy)-phenyl]methane (**5**) and 3 mol % of photoinitiator triarylsulfonium hexafluoroantimonate was added (Table I). The reaction mixture was stirred rigorously with a magnetic stirrer, poured on a plastic film, and kept at the room temperature under the Helios Italquartz UV lamp (model G.R.E 500 W) with UV light intensity of 310 mW cm⁻² at the distance of 6 cm until the hard film was obtained (after (2–5) min).

Soxhlet Extraction

The samples of the bulk polymers (0.2 g) were extracted with chloroform for 72 h using a Soxhlet extractor. After the extraction, the solvent was evaporated to obtain the soluble part of the bulk polymer. The soluble and insoluble fractions were dried under vacuum until no changes of the weight were observed.

RESULTS AND DISCUSSION

The conversion of C=C double bonds up to 81% and the number of epoxy groups per triglyceride up to 5.3 (calculated from

$^1\text{H-NMR}$ spectra) were reached in epoxidation of linseed oil performed with methyltrioxorhenium as a catalyst and hydrogen peroxide as an oxidizer. The structure of epoxidized linseed oil was confirmed by IR and $^1\text{H-NMR}$ spectroscopy (see Experimental details and Supporting Information). It was confirmed by the spectral analysis that there are three types of reactive groups in the product of the linseed oil epoxidation, i.e., epoxy groups, hydroxy groups, and the rest of carbon double bonds. All these groups can participate in the photocross-linking reaction, but the most active groups are epoxy groups.

The photocross-linking of various batches with the different amount of reactive diluents and 3 mol % of photoinitiator was performed. The concentrations of reactive diluents and the contents of the insoluble fractions are given in Table I. The concentration of photoinitiator was chosen on the bases of the results of the preliminary tests. When such concentration of the photoinitiator was used, the resulting films were transparent, smooth, and the rate of curing was high.

The best quality films were obtained when 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (1), bisphenol A diglycidyl ether (3), and bis[4-(glycidyl)oxy]phenylmethane (5) were used as reactive diluents. These films were transparent, flexible, and wrinkle-free.

The fastest curing which lasted ca. 2 min was observed for batches containing 10 mol % of reactive Diluents 1 and 5. The curing of batches with reactive Diluents 2, 3, and 4 lasted up to 5 min.

Various types of reactive groups can participate in the photocross-linking of the studied systems. For example, epoxy groups part of which is converted to hydroxy groups, rest of carbon double bonds, and the epoxy groups of reactive diluents. The photocross-linking of the epoxidized linseed oil was performed in the presence of the cationic photoinitiator. However, several mechanisms of the reaction were possible: free radical polymerization with opening of carbon double bonds, cationic polymerization by the activated monomer mechanism with the participation of hydroxy groups,²⁵ and cationic ring-opening polymerization of epoxy groups by active chain end mechanism.²⁶ The homopolymerization of reactive diluents was possible, especially when the reactive Diluent 1 was used. In molecules of the reactive Diluent 1, epoxy groups are linked to the cyclohexane ring and are of particular activity. However, the spectral analysis of the products of photocross-linking showed that the homopolymerization of the reactive diluents was not prevailing and that the greater part of the reactive diluents participated in the photocross-linking of the epoxidized linseed oil.

The yield of the insoluble fraction of the photocross-linked films after the extraction with chloroform was (91–99)% (Table I) and did not depend on the concentration of reactive diluent. The high amount of insoluble fraction shows that both epoxidized linseed oil and reactive diluent participated in the photocross-linking. The IR spectral analysis confirmed that photocross-linked polymers were constructed from the fragments of epoxidized linseed oil and reactive diluents. The absorption bands attributed to both components were present in the IR spectrum of the insoluble fraction of cross-linked polymers (see Figure S2 in the Supporting Information).

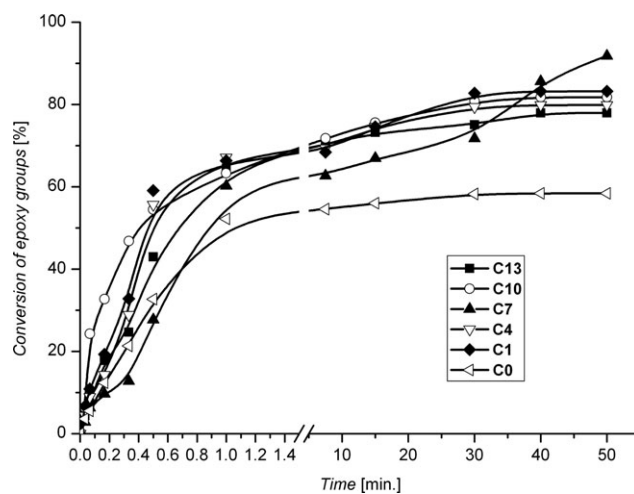


Figure 3. Conversion of epoxy groups versus the photocross-linking time for the epoxidized linseed oil compositions with the reactive diluents 1 (C1), 2 (C4), 3 (C7), 4 (C10), 5 (C13), and without reactive diluent (C0) (3 mol % of photoinitiator and 10 mol % of the reactive diluents).

The dependence of the epoxy group conversion on the photocross-linking time of the epoxidized linseed oil containing no reactive diluent and with 10 mol % of different reactive diluents is presented in the Figure 3. The estimated *P*-value calculated by Anova program was below 0.05 within the groups. The chemical structure of the reactive diluents and the concentration of the reactive diluents in the initial composition significantly affected the conversion of epoxy groups.

In the initial stage of the photocross-linking process the highest reaction rate was showed by Batch C10 in which the reactive Diluent 4 was used. The conversion of epoxy groups of 62% was reached after 1 min in this case. The photocross-linking of the most of the batches (C1, C4, C10, and C13) proceeded in the similar way and the reaction rate was higher than that observed for the Composition C0 containing no reactive diluent. The conversion of epoxy groups of (63–74)% was reached after 1 min, (73–74)% after 15 min, and (78–83)% after 50 min for the Compositions C1, C4, C10, and C13. The photocross-linking of the Composition C0 containing no reactive diluent proceeded very slowly and the final conversion of only 58% was observed. The kinetics of photocross-linking of Batch C7 containing reactive Diluent 3 was different than that of the other compositions. The conversion of 60% was reached after 1 min, and further the reaction proceeded with more or less constant rate. The conversion of 67% was reached after 15 min, and the final conversion of 91% was reached after 50 min. This is the highest final conversion of epoxy groups observed in this study.

The dependence of the epoxy group conversion on the photocross-linking time for the epoxidized linseed oil compositions containing 30 mol % of different reactive diluents is presented in the Figure 4. For the comparison conversion versus time curve for the batch containing no reactive diluent is shown. When the higher concentration (30 mol %) of the reactive diluents was used in the compositions (C3, C6, C9, C12, and C15), the lower by 10% final conversion of epoxy groups was

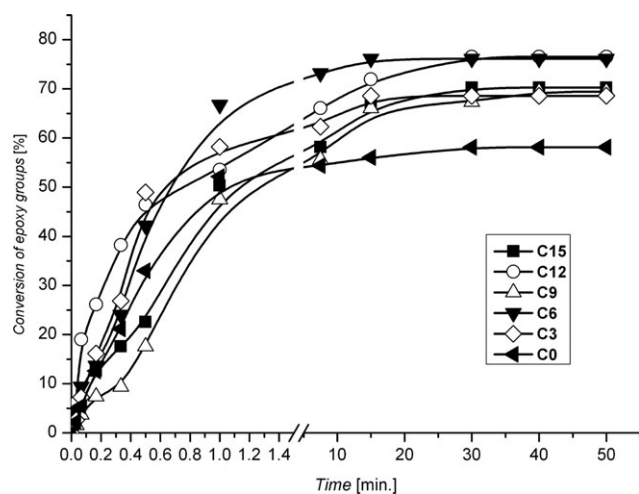


Figure 4. The dependences of the epoxy group conversion on the photocross-linking time for the epoxidized linseed oil mixtures with the reactive Diluents 1 (C3), 2 (C6), 3 (C9), 4 (C12), 5 (C15), and without reactive diluent (C0) (3 mol % of photoinitiator and 30 mol % of the reactive diluents).

reached at the same time. In the early stage of the photocross-linking process (up to 0.5 min), the highest rate was observed for the Batch C12 containing reactive Diluent 4. The conversion of 52% was reached after 1 min. A considerably higher conversion of 67% after 1 min was observed for Batch C6 containing reactive Diluent 2. The conversion of (47–54)% was observed for the other Compositions C3, C9, and C15 after 1 min. Again, the photocross-linking of Batch C9 containing reactive Diluent 3 proceeded differently than those of the other batches. The process occurred with the constant rate and the conversion of 72% was reached after 50 min. The conversion of epoxy groups observed after 50 min for the Compositions C3, C6, C12, and C15 was comparable and reached (69–77)%.

The highest rate of conversion of epoxy groups was observed for the compositions containing reactive Diluent 4 with three epoxy groups. The epoxy group conversion of 25% was reached after 6 s and 50% conversion was reached after 22 s by Composition C10 containing 10 mol % of reactive Diluent 4. The epoxy group conversion of 25% was reached after 8 s and 50% conversion was reached after 40 s by Composition C12 with 30 mol % of reactive Diluent 4. The reaction rate was higher when the aliphatic reactive Diluents 1, 2, and 4 were used (C1, C3, C4, C6, C10, and C12). The reaction was slower when the aromatic reactive Diluents 3 and 5 were used (C7, C9, C13, and C15) and in the case of the composition without any reactive Diluents (C0).

It was reported in the literature^{15,27} that photopolymerization of epoxidized linseed oil with 4 mol % of photoinitiator (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate and without any reactive diluent after 1 min yielded 28% conversion of epoxy groups. In our study, when 3 mol % of photoinitiator, mixture of triarylsulfonium hexafluoroantimonates, was used for the initiation of photopolymerization of epoxidized linseed oil without any reactive diluent, 50% conversion of epoxy groups was

reached after 1 min. This is almost twice higher conversion observed at the lower concentration of photoinitiator. However, photopolymerization of epoxynorbornenyl-functionalized linseed oil with 4 mol % of photoinitiator (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate lead to 57% conversion of epoxy groups was after 1 min.⁶ Addition of 20 mol % of reactive diluent di(ethyleneglycol) diethylether to epoxynorbornenyl-functionalized linseed oil in the presence of 4 mol % of photoinitiator (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate, lead to 45% conversion of epoxy groups after 1 min.⁶ The similar conversion of epoxy groups (47%) was observed in this work for photopolymerization of Batch C15 which contained 30 mol % of reactive Diluent 3 and 3 mol % of photoinitiator, mixture of triarylsulfonium hexafluoroantimonates.

The swelling of cross-linked polymers is important in numerous applications including biomedical, bioengineering, pharmaceutical, veterinary, food industry, agricultural, and related fields. The swelling of cross-linked polymers can be exploited in the design of controlled-release devices for drugs, cosmetic ingredients, in the production of storable foods/feeds, in the removal of some undesirable agents such as waste water in sanitary, industrial and in environmental applications, in which the swelling polymers can be used as carriers of agrochemicals and soil conditioners, etc.^{28–31} The swelling of polymer films in polar and nonpolar solvents is important in terms of the potential application of polymers, as well as gives some information on the structure and properties of polymers.

The kinetic curves of swelling in chloroform and in toluene of the insoluble fraction of the photocross-linked film of the epoxidized linseed oil using no any reactive diluent (C0) are presented in Figure 5. The swelling in nonpolar solvent toluene proceeds with low rate and the swelling value of only 167% is reached. The swelling in polar solvent chloroform proceeds faster and the swelling value of 333% is reached.

Similar tendencies were observed when the photocross-linked films of compositions containing reactive diluents were soaked in toluene and chloroform. The photocross-linked films of the Compositions C1–C15 swell more in the polar solvent (chloroform) than in nonpolar solvent (toluene). As an example, the swelling kinetic curves of the insoluble fraction of the photocross-linked Compositions C1, C2, and C3 with different

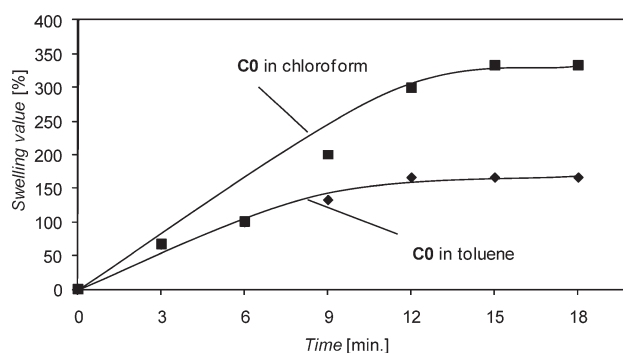


Figure 5. The kinetic curves of swelling of the insoluble fraction of the photocross-linked Batch C0 in chloroform and in toluene.

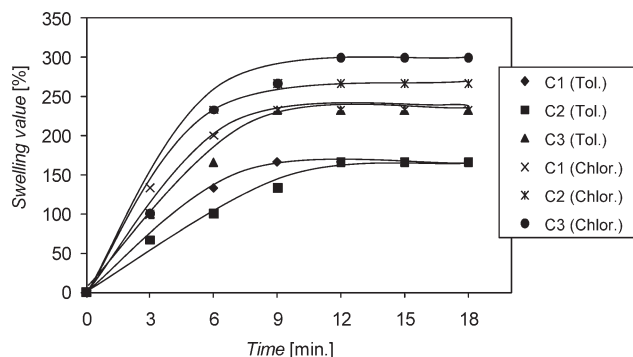


Figure 6. The swelling kinetic curves of the insoluble fraction of the photocross-linked Compositions C1, C2, and C3 containing 10, 20, and 30 mol % of reactive Diluent 1, respectively, in toluene (tol.) and in chloroform (chlor.).

amount of the reactive Diluent 1 in toluene and in chloroform are presented in Figure 6. In toluene, the highest swelling value of 233% was shown by the photocross-linked film of Batch C3. The swelling value of the same film in chloroform was higher (300%). The similar tendency was observed when the swelling in toluene and in chloroform of the photocross-linked Compositions C1 and C2 was investigated. Moreover, the swelling value was increased when the concentration of the reactive Diluent 1 was increased in the composition. However, such tendency is not characteristic of the swelling of the films of the photocross-linked Compositions C1 and C2 in toluene.

The swelling values of the photocross-linked films of all the Batches C0–C15 are summarized in Table II. The swelling values of the photocross-linked polymers of epoxidized linseed oil in chloroform range from 233% to 300%, while the swelling value in toluene ranges from 167% to 233%. The different swelling

Table II. Swelling Values of the Photocross-Linked Films

Film	Swelling value (%)	
	Toluene	Chloroform
C0	167	333
C1	167	233
C2	167	267
C3	233	300
C4	167	267
C5	200	233
C6	233	300
C7	133	233
C8	133	200
C9	167	233
C10	133	200
C11	200	267
C12	233	200
C13	167	267
C14	167	233
C15	233	233

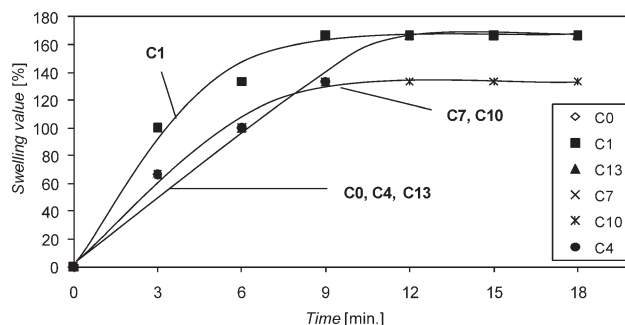


Figure 7. The swelling kinetic curves of the insoluble fraction of the photocross-linked Compositions C0, C1, C4, C7, C10, and C13 with 10 mol % of reactive Diluent 1, 2, 3, 4, and 5, respectively, in toluene.

value of the photocross-linked polymers of different compositions can apparently be explained by the different density of the cross-links and the formation of the longer molecular chains between crosslinking points in the polymer network when the concentration of the reactive diluent was increased in the initial compositions.

The kinetic curves of swelling in toluene of the insoluble fractions of the photocross-linked Compositions C0, C1, C4, C7, C10, and C13 with the same amount of the different reactive Diluents 1, 2, 3, 4, and 5, respectively, are presented in Figure 7. The highest swelling rate was observed for the film of Batch C1 with the reactive Diluent 1. However the final swelling value (167%) of this film was the same as for the photocross-linked Compositions C0, C4, and C13. The swelling rate of the films of the photocross-linked Compositions C7 and C10 in the initial stage was similar to that if the photocross-linked films of the Compositions C0, C4, and C13, however the final swelling value was lower (133%).

The different results were obtained when the same films were soaked in chloroform (Figure 8). The highest swelling value of 333% was reached by the film of the photocross-linked Composition C0 containing no any reactive diluent even though its swelling rate was the lowest one. Among the photocross-linked compositions containing reactive diluents, the highest swelling value of 267% was observed for C4 and C7. The swelling of the films of the photocross-linked Compositions C1, C10, and C13 was very similar in the initial stage of the process, but the different final swelling values were reached.

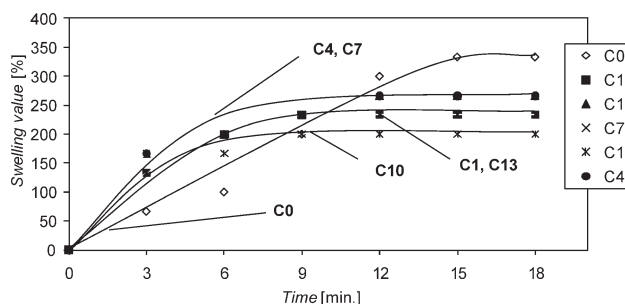


Figure 8. The kinetic curves of swelling in chloroform of the insoluble fractions of the photocross-linked Compositions C0, C1, C4, C7, C10, and C13 with 10 mol % of reactive Diluent 1, 2, 3, 4, and 5, respectively.

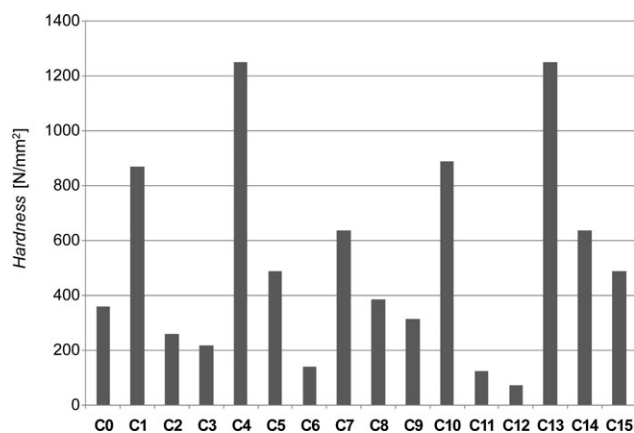


Figure 9. Hardness of the photocross-linked films of Compositions C1–C15.

The obtained results of the swelling of the photocross-linked polymers show, that the use of reactive diluents results in the reduction of the swelling capacity of the cross-linked polymers, especially in polar solvents. The cross-linked polymers with such swelling value could be applicable as soft films, coatings, or seals. On the other hand, the high swelling value accelerate the biodegradation of the cross-linked films what is desirable for the products of the short-term use. The further investigations would be necessary to find the more specific application of the newly synthesized polymers.

The hardness values of the photocross-linked films of the different compositions measured by Hepler consistometer are summarized in Figure 9. They vary from 71 to 1248 N mm⁻². The estimated *P*-value calculated by Anova program was below 0.05 within the groups. The chemical structure of the reactive diluents and the concentration of the reactive diluents in the initial composition significantly affected the hardness of the photocross-linked films. The highest hardness values were demonstrated by the films of the Compositions C4 and C13 containing 10 mol % of the reactive Diluents 2 and 5, respectively. The hardness of the films decreased when the concentration of the reactive diluent was increased in the initial compositions with all reactive diluents used in this work. This observation can apparently be explained by the formation of the longer molecular chains between crosslinking points in the polymer network. This assumption is confirmed by the swelling values of the photocross-linked films. In the most cases the swelling values of the films increased when the concentration of the reactive diluent was increased in the initial compositions. The hardness of the most of photocross-linked films of epoxidized linseed oil mixtures with different reactive diluents were found to be significantly higher than those observed for the commodity polymer films ((31–84) N mm⁻² for PE-LD, PP, PET, and PVC) established at the same experimental conditions. Only the hardness of the film of the photocross-linked Batch C12 was of the same order of magnitude as those observed for the commodity polymer films. Low hardness of this film can apparently be explained by the high amount of the aliphatic reactive Diluent 4.

The mechanical characteristics of the cross-linked films of different compositions determined by the stress–strain test are summarized in Figure 10. The estimated *P*-value calculated by

Anova program was below 0.05 within the groups. The chemical structure of the reactive diluents and their concentrations in the initial compositions significantly affected the tensile strength, elongation to failure, and Young modulus of the photocross-linked films.

The incorporation of the reactive diluents into the compositions resulted in the increase of the tensile strength of the photocross-linked films of epoxidized linseed oil. Nevertheless, the tensile strength of the photocross-linked films obtained using different reactive diluents which ranged from 0.67 to 6.21 MPa and was significantly lower than that of commercial polymer films established at the same experimental conditions ((26.37–68.31) MPa for PE-LD, PP, PVC, and 190.08 MPa for PET). The tensile strength of the films containing aromatic moieties was higher than that of polymeric films composed only from aliphatic moieties. The highest tensile strength of 5.72 and 6.21 MPa was demonstrated by films of the Compositions C7 and C13 obtained with 10 mol % of aromatic reactive Diluents 3 and 5, respectively.

The elongation at break of the photocross-linked films was in the range of (1.29–6.27)% and was lower by one order of magnitude than that of commercial polymer films established at the same experimental conditions ((12.63–56.39)% for PE-LD, PP, PVC, and PET). A tendency of the increase of the elongation at break of the cross-linked materials with the increase of the concentration of the reactive diluent was observed. However, no dependence of the elongation at break on the chemical structure of photocross-linked polymers was observed.

The Young modulus values of the photocross-linked films prepared using different reactive diluents were in the range of (6.97–26.02) N mm⁻². This observation shows that these films can be regarded as soft materials. The Young modulus of some photocross-linked films was of the same order of magnitude as those of polypropylene (20.94 MPa) and low density polyethylene (27.18 MPa) established at the same experimental conditions. A tendency of the decrease of the values elongation at break of the cross-linked materials with the increase of the concentration of the reactive diluents in the initials compositions

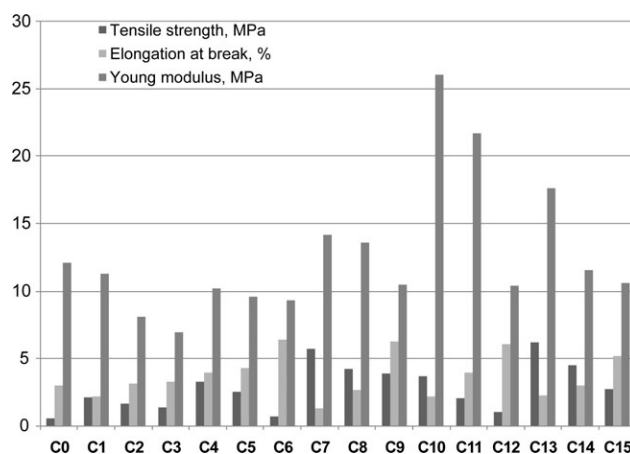


Figure 10. Tensile strength, elongation at break, and Young modulus of the photocross-linked films of Compositions C1–C15.

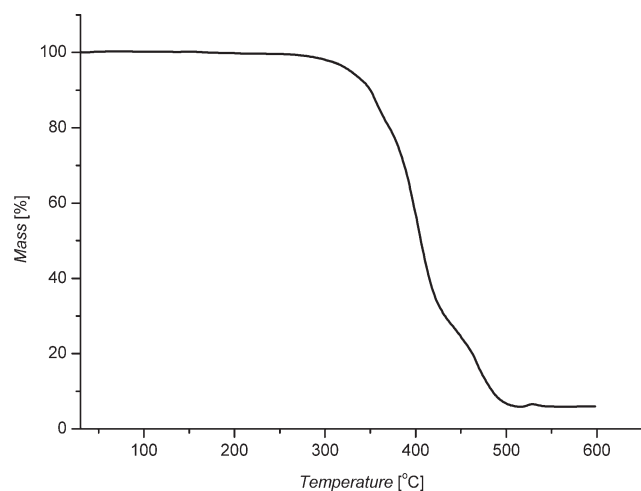


Figure 11. TGA curve of photo-crosslinked polymer of Composition C6.

was observed. The highest Young modulus was demonstrated by photocross-linked polymers of Compositions C7, C8, and C13 with aromatic reactive Diluents 3 and 5, and by photocross-linked polymers of Compositions C10, and C11 with the aliphatic reactive Diluent 4.

The concentration of reactive diluent does not have any significant effect on the thermal stability of the films prepared from the photocross-linked mixtures of the epoxidized linseed oil with the reactive diluents. The films demonstrated relatively high thermal stability sufficient for the industrial and consumer products. Their 10% weight loss temperatures determined by TGA in nitrogen atmosphere were found to be in the range of (300–325)°C. They were higher than those of the photocross-linked film of epoxidized linseed oil prepared using no any reactive diluent (260°C) and of fish oil copolymers ((244–292)°C),³² and lower than those of soybean oil copolymers with divinylbenzene ((360–420)°C),³³ and linseed oil–styrene–divinylbenzene copolymers (350°C).³⁴ The shapes of TGA curves of the films prepared from the photocross-linked mixtures of the epoxidized linseed oil with the reactive diluents are similar. As an example, the TGA curve of photocross-linked polymer of Composition C1 is presented in Figure 11.

CONCLUSIONS

Cross-linked polymers were obtained by photopolymerization of epoxidized linseed oil with different diepoxy reactive diluents using the mixture of triarylsulfonium hexafluoroantimonates as photoinitiator. The (69–91)% conversion of epoxy groups of compositions with reactive diluents was reached and it was higher by (20–40)%, when compared with that observed for photocross-linking of epoxidized linseed oil containing no reactive diluent. The swelling value of the films prepared from epoxidized linseed oil-based compositions ranged from 200% to 300% in chloroform and from 133% to 233% in toluene. The hardness values of the photocross-linked films of the different compositions measured by Hepler consistometer were found to be in the range of (71–1248) N mm⁻² and in most cases were significantly higher than those observed for the commodity

polymer films established at the same experimental conditions. The tensile strength of the photocross-linked films obtained using different reactive diluents ranged from 0.67 to 6.21 MPa and were significantly lower than that of commercial polymer films established at the same experimental conditions. The elongation at break of the films was found to be in the range of (1.29–6.27)% and was lower by one order of magnitude than that of commercial polymer films established at the same experimental conditions. The Young modulus values of the films were in the range of (6.97–26.02) N mm⁻². The Young modulus of some photocross-linked films was of the same order of magnitude as those of polypropylene and low density polyethylene established at the same experimental conditions. The 10% weight loss temperatures of the films were in the range of (300–325)°C.

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