

# Crosslinking of Epoxidized Natural Oils with Diepoxy Reactive Diluents

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**ABSTRACT:** The different natural oils epoxidized with 3-chloroperbenzoic acid were crosslinked with diepoxy reactive diluents, bisphenol A propoxylate diglycidyl ether, and 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate, using cationic initiator at 60°C and photoinitiators at the room temperature. The insoluble fraction of the polymeric products was 59–90%. The Young modulus of the crosslinked polymer films ranged from 2 to 861 MPa. The 10% weight loss temperatures of the crosslinked polymers estimated by thermogravimetric analysis were in the

range from 250 to 420°C. The water vapor transmission rate of the crosslinked biopolymer films ranged from 6 to 49 g/m<sup>2</sup>/24 h. Biochemical oxygen demand and biodegradation in soil of the crosslinked polymers were studied. The crosslinked polymers showed higher biodegradation rate than cellulose, starch, and polyvinylalcohol. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2028–2038, 2010

**Key words:** biopolymers; crosslinking; photopolymerization; mechanical properties; thermal properties

## INTRODUCTION

Biodegradable polymers are niche market materials finding focused applications, including agricultural applications such as mulch films, flowerpots, controlled-release fertilizers, and packaging items such as carrier bags and food wrapping and containers. They have the potential to provide a solution to a range of environmental concerns: decreasing availability of landfill space, declining petrochemical sources, and also offer an alternative option to recycling.<sup>1</sup>

Natural oils are considered to be the most important class of renewable sources. Worldwide, three-quarters of natural oil production is for edible oil, but the large remainder is used in industrial applications such as surfactants, coatings, lubricants, adhesives, drying agents, cosmetics, printing inks, emulsifiers, and plasticizers. The polymerization and crosslinking of natural oils has recently received renewed attention in the context of producing new bioplastic materials.<sup>2–8</sup>

Crosslinked polymers from natural oils can be obtained using cationic initiators. Two ways of cur-

ing have been studied, that is, photocrosslinking<sup>9,10</sup> and curing in the dark at elevated temperatures.<sup>11–15</sup>

In both cases, the homopolymerization of the natural oils generally led to the viscous biopolymers, consequently the researches were concentrated on the development of biopolymers from chemically transformed natural oils and crosslinked copolymers mostly with alkenes, for example, with divinylbenzene.<sup>8,11,12</sup>

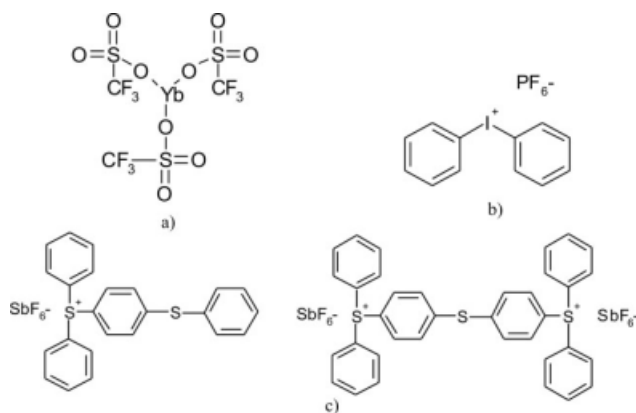
In this study, linseed oil, rapeseed oil, and fish oil based polymers were obtained using both of the aforementioned methods of curing. First, the natural oils were epoxidized and, then, crosslinked in the presence of diepoxy reactive diluents. The effect of the method of curing and of the addition of the reactive diluent on the thermal, mechanical properties, and biodegradability of the crosslinked polymers was studied.

## EXPERIMENTAL

### Materials

The natural oils used in this study were fish oil (Peter Moller, Norway), linseed oil (Aletovis, Lithuania), and rapeseed oil (Kolumbo, Germany). All these oils were purchased in the local supermarket and used without further purification. Ytterbium (III) trifluoromethane sulfonate [Fig. 1(a)], diphenyliodonium hexafluorophosphate [Fig. 1(b)], 50%

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**Figure 1** Structures of the initiators: ytterbium (III) trifluoromethane sulfonate (a), diphenyliodonium hexafluorophosphate (b), and triarylsulfonium hexafluoroantimonates (c).

mixture of triarylsulfonium hexafluoroantimonates in propylene carbonate [Fig. 1(c)], bisphenol A diglycidyl ether (**1** in Fig. 2), bisphenol A propoxylate diglycidyl ether (**2** in Fig. 2), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (**3** in Fig. 2), and 3-chloroperbenzoic acid were purchased from Sigma-Aldrich and used as received. Dichloromethane, dichloroethane, and acetone were purchased from Poch S.A. (Gliwice, Poland). The solvents were purified and dried by the standard methods.<sup>16</sup>

### Epoxidation of natural oils

The epoxidation of linseed oil, rapeseed oil, and fish oil was performed according to the procedure described in literature.<sup>17</sup> 3-Chloroperbenzoic acid (2.45 g) was added to the solution of natural oil (5 g in 20 mL of dichloromethane). The reaction mixture was stirred at 50°C during 48 h. Then, the reaction mixture was left overnight. The precipitate was filtered off. The clear filtrate was treated with 5 wt % sodium thiosulfate solution and further with a saturated solution of sodium bicarbonate in a separatory funnel to eliminate the acid and peroxy acid. The organic fraction was dried with anhydrous magnesium sulfate and filtered. The solvent was evaporated. The epoxidized oil obtained was dried in vacuum. The yield of epoxidized linseed oil was 67%, that of epoxidized rapeseed oil was 79%, and that of epoxidized fish oil was 58%.

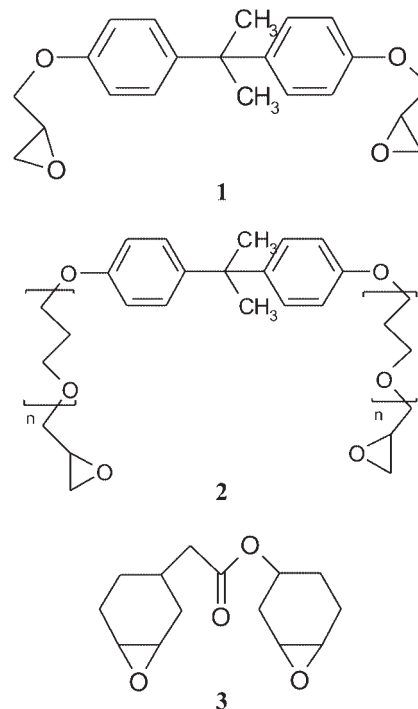
Epoxidized linseed oil IR ( $\text{cm}^{-1}$ ): 3467 ( $\nu$ , O—H), 3010 ( $\nu$ , =C—H), 2924 ( $\nu$ ,  $\text{CH}_3$ ), 2855 ( $\nu$ ,  $\text{CH}_2$ ), 2344 ( $\nu$ , C=O  $\text{CO}_2$ ), 2283, 1744 ( $\nu$ , C=O ester), 1652 ( $\nu$ , C=C), 1463 ( $\delta$ ,  $\text{CH}_2$ ), 1378 ( $\nu$ , C—C), 1240 ( $\nu$ , C—O), 1163 ( $\nu$ , C—O), 1100 ( $\nu$ , C—O), 823 ( $\nu$ , C—O epoxy), 751, 724 ( $\delta$ ,  $\text{CH}_2$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.85–1.07 ( $\text{H}_{17}$ ), 1.30 ( $\text{H}_{3-6}$ ), 1.60 ( $\text{H}_2$ ), 2.10 ( $\text{H}_7$  and  $\text{H}_{16}$ ), 2.32 ( $\text{H}_1$ ), 2.80 ( $\text{H}_{10}$  and  $\text{H}_{13}$ ), 2.92 ( $\text{H}_{8'}$  and  $\text{H}_9$ ),

4.10–4.38 ( $\text{H}_a$  and  $\text{H}_c$ ), 5.25–5.55 ( $\text{H}_{11}$ ,  $\text{H}_{12}$ ,  $\text{H}_{13}$ ,  $\text{H}_{14}$ , and  $\text{H}_b$ ) (scheme in Fig. 4).

Epoxidized rapeseed oil IR ( $\text{cm}^{-1}$ ): 3467 ( $\nu$ , O—H), 2927 ( $\nu$ ,  $\text{CH}_3$ ), 2856 ( $\nu$ ,  $\text{CH}_2$ ), 1745 ( $\nu$ , C=O ester), 1466 ( $\delta$ ,  $\text{CH}_2$ ), 1378 ( $\nu$ , C—C), 1241 ( $\nu$ , C—O), 1163 ( $\nu$ , C—O), 1114 ( $\nu$ , C—O), 824 ( $\nu$ , C—O epoxy), 738 ( $\delta$ ,  $\text{CH}_2$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.88–1 ( $\text{H}_{17}$ ), 1.30 ( $\text{H}_{3-6}$ ), 1.60 ( $\text{H}_2$ ), 2.10 ( $\text{H}_7$  and  $\text{H}_{16}$ ), 2.32 ( $\text{H}_1$ ), 2.80 ( $\text{H}_{10}$  and  $\text{H}_{13}$ ), 2.92 ( $\text{H}_{8'}$ ), 4.13–4.34 ( $\text{H}_a$  and  $\text{H}_c$ ), 5.28–5.43 ( $\text{H}_{11}$ ,  $\text{H}_{12}$ ,  $\text{H}_{13}$ ,  $\text{H}_{14}$ , and  $\text{H}_b$ ) (scheme in Fig. 4).

Epoxidized fish oil IR ( $\text{cm}^{-1}$ ): 3468 ( $\nu$ , O—H), 3011 ( $\nu$ , =C—H), 2926 ( $\nu$ ,  $\text{CH}_3$ ), 2855 ( $\nu$ ,  $\text{CH}_2$ ), 2281, 1745 ( $\nu$ , C=O ester), 1465 ( $\delta$ ,  $\text{CH}_2$ ), 1378 ( $\nu$ , C—C), 1241 ( $\nu$ , C—O), 1161 ( $\nu$ , C—O), 1115 ( $\nu$ , C—O), 831 ( $\nu$ , C—O epoxy), 736, 723 ( $\delta$ ,  $\text{CH}_2$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.88–1 ( $\text{H}_{17}$ ), 1.30 ( $\text{H}_{3-6}$ ), 1.60 ( $\text{H}_2$ ), 2.10 ( $\text{H}_7$  and  $\text{H}_{16}$ ), 2.32 ( $\text{H}_1$ ), 2.79–2.98 ( $\text{H}_{10}$ ,  $\text{H}_{13}$ ,  $\text{H}_{8'}$ , and  $\text{H}_9$ ), 4.13–4.34 ( $\text{H}_a$  and  $\text{H}_c$ ), 5.28–5.43 ( $\text{H}_{11}$ ,  $\text{H}_{12}$ ,  $\text{H}_{13}$ ,  $\text{H}_{14}$ , and  $\text{H}_b$ ) (scheme in Fig. 4).

The epoxidation of natural oils was also performed in dichloroethane solution. In this case, the procedure was the same as described earlier but the reactions were performed at 70°C, and after the filtration of the precipitates, the solvent was evaporated and dichloromethane was added instead of dichloroethane. The yield of epoxidized linseed oil was 71%, that of epoxidized rapeseed oil was 60%, and that of epoxidized fish oil was 55%.



**Figure 2** Structures of the reactive diluents: bisphenol A diglycidyl ether (**1**), bisphenol A propoxylate diglycidyl ether (**2**), and 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (**3**).

Epoxidized linseed oil IR ( $\text{cm}^{-1}$ ): 3467 ( $\nu$ , O—H), 3010 ( $\nu$ , =C—H), 2927 ( $\nu$ ,  $\text{CH}_3$ ), 2855 ( $\nu$ ,  $\text{CH}_2$ ), 1744 ( $\nu$ , C=O ester), 1658 ( $\nu$ , C=C), 1465 ( $\delta$ ,  $\text{CH}_2$ ), 1378 ( $\nu$ , C—C), 1254 ( $\nu$ , C—O), 1164 ( $\nu$ , C—O), 1101 ( $\nu$ , C—O), 821 ( $\nu$ , C—O epoxy), 750, 724 ( $\delta$ ,  $\text{CH}_2$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.85–1.08 ( $\text{H}_{17}$ ), 1.30 ( $\text{H}_{3-6}$ ), 1.60 ( $\text{H}_2$ ), 2.10 ( $\text{H}_7$  and  $\text{H}_{16}$ ), 2.32 ( $\text{H}_1$ ), 2.80 ( $\text{H}_{10}$  and  $\text{H}_{13}$ ), 2.92 ( $\text{H}_{K'}$ ), 4.10–4.38 ( $\text{H}_a$  and  $\text{H}_c$ ), 5.25–5.55 ( $\text{H}_{11}$ ,  $\text{H}_{12}$ ,  $\text{H}_{13}$ ,  $\text{H}_{14}$ , and  $\text{H}_b$ ) (scheme in Fig. 4).

Epoxidized rapeseed oil IR ( $\text{cm}^{-1}$ ): 3468 ( $\nu$ , O—H), 2927 ( $\nu$ ,  $\text{CH}_3$ ), 2856 ( $\nu$ ,  $\text{CH}_2$ ), 2282, 1745 ( $\nu$ , C=O ester), 1575, 1466 ( $\delta$ ,  $\text{CH}_2$ ), 1378 ( $\nu$ , C—C), 1280 ( $\nu$ , C—O), 1257 ( $\nu$ , C—O), 1163 ( $\nu$ , C—O), 824, 750, 737 ( $\delta$ ,  $\text{CH}_2$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.88–1 ( $\text{H}_{17}$ ), 1.30 ( $\text{H}_{3-6}$ ), 1.60 ( $\text{H}_2$ ), 2.10 ( $\text{H}_7$  and  $\text{H}_{16}$ ), 2.32 ( $\text{H}_1$ ), 2.80–2.95 ( $\text{H}_{10}$ ,  $\text{H}_{13}$ ,  $\text{H}_8$ , and  $\text{H}_9$ ), 4.13–4.34 ( $\text{H}_a$  and  $\text{H}_c$ ), 5.28–5.43 ( $\text{H}_{11}$ ,  $\text{H}_{12}$ ,  $\text{H}_{13}$ ,  $\text{H}_{14}$ , and  $\text{H}_b$ ) (scheme in Fig. 4).

Epoxidized fish oil IR ( $\text{cm}^{-1}$ ): 3468 ( $\nu$ , O—H), 2926 ( $\nu$ ,  $\text{CH}_3$ ), 2855 ( $\nu$ ,  $\text{CH}_2$ ), 1744 ( $\nu$ , C=O ester), 1575, 1465 ( $\delta$ ,  $\text{CH}_2$ ), 1378 ( $\nu$ , C—C), 1256 ( $\nu$ , C—O), 1163 ( $\nu$ , C—O), 1115 ( $\nu$ , C—O), 832 ( $\nu$ , C—O epoxy), 751, 723 ( $\delta$ ,  $\text{CH}_2$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.88–1 ( $\text{H}_{17}$ ), 1.30 ( $\text{H}_{3-6}$ ), 1.60 ( $\text{H}_2$ ), 2.10 ( $\text{H}_7$  and  $\text{H}_{16}$ ), 2.32 ( $\text{H}_1$ ), 2.79–2.98 ( $\text{H}_{10}$ ,  $\text{H}_{13}$ ,  $\text{H}_8$ , and  $\text{H}_9$ ), 4.13–4.34 ( $\text{H}_a$  and  $\text{H}_c$ ), 5.28–5.43 ( $\text{H}_{11}$ ,  $\text{H}_{12}$ ,  $\text{H}_{13}$ ,  $\text{H}_{14}$ , and  $\text{H}_b$ ) (scheme in Fig. 4).

### Photocrosslinking

A typical formulation was prepared by mixing epoxidized natural oil with the different amount (from 20 to 50 wt %) of reactive diluent, bisphenol A diglycidyl ether (**1**), bisphenol A propoxylate diglycidyl ether (**2**), or 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (**3**) and 5 wt % of photoinitiator, diphenyliodonium hexafluorophosphate, or triarylsulfonium hexafluoroantimonate was added. The reaction mixture was stirred during 1 minute, poured on a Teflon plate, and kept at the room temperature under the middle pressure ( $10^5$  to  $3 \times 10^5$  Pa) lamp DRT-240 at the distance of 6 cm until the hard film was obtained (ca. 15 min).

### Crosslinking in the dark

A typical formulation was prepared by mixing epoxidized natural oil with the different amount (from 20 to 50 wt %) of reactive diluent, bisphenol A diglycidyl ether **1**, bisphenol A propoxylate diglycidyl ether (**2**), or 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (**3**), and 10 wt % of ytterbium trifluoromethane sulfonate solution in acetone was added. The reaction mixture was stirred during 1 min, poured on a Teflon plate, and then kept in an oven at  $60^\circ\text{C}$  until the hard film was obtained (from 24 to 48 h).

### Soxhlet extraction

The samples of the bulk polymers were extracted with acetone for 24 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. The soluble fractions were characterized by  $^1\text{H-NMR}$  and IR spectroscopy. The insoluble fractions were characterized by IR spectroscopy.

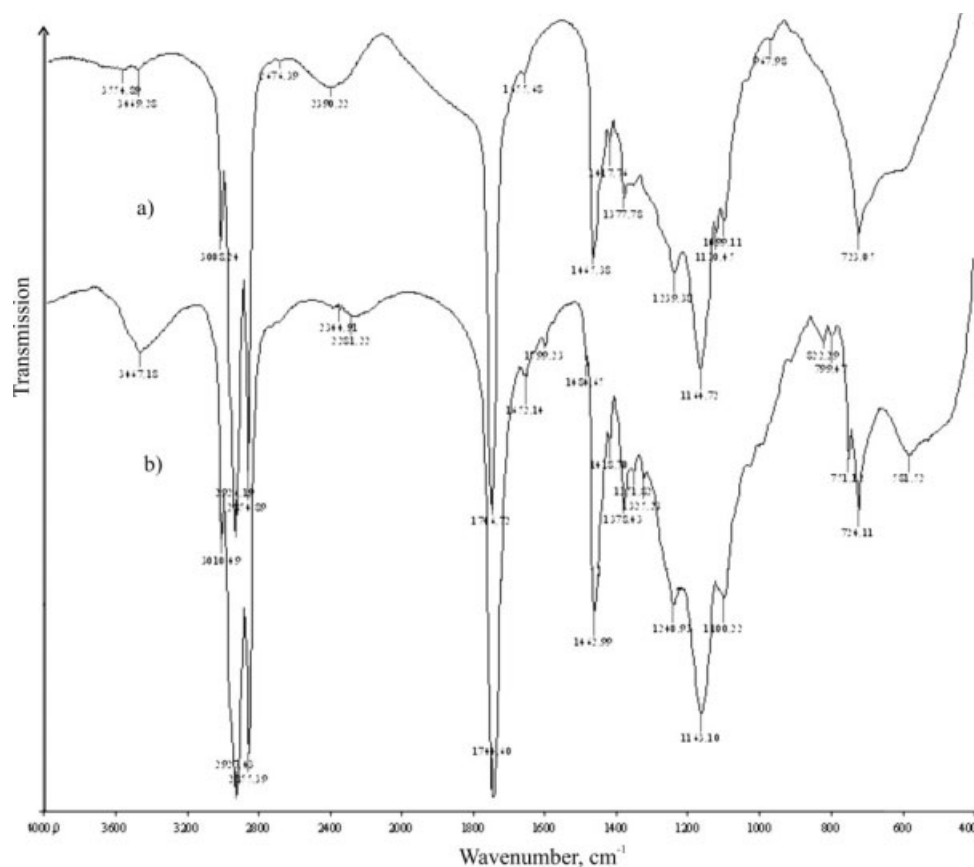
### Instrumentation

$^1\text{H-NMR}$  spectra were recorded with Varian Unity Inova spectrometer at 300 MHz using  $\text{CDCl}_3$  as a solvent. All the data are given as chemical shifts  $\delta$  (ppm) downfield from  $(\text{CH}_3)_4\text{Si}$ . FTIR spectra were recorded on a Perkin Elmer Spectrum GX spectrometer. The spectra of the liquid materials were measured placing the samples between KBr plates and the spectra of the solid materials were recorded using KBr pellets. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 PC Luxx apparatus in the temperature range from the room temperature to  $600^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}/\text{min}$  under nitrogen atmosphere (nitrogen flow rate 100 mL/min). The estimation of the water vapor transmission rate (WVTR) was performed according to the international standard 7783-1 : 1996.<sup>18</sup> The temperature during the experiment varied from 18 to  $21^\circ\text{C}$  and the relative humidity was changed from 29.9 to 41.1%. The Young modulus of the films was determined with a piezo-actuated microtensile-testing device.<sup>19</sup> The average value of the Young modulus of each of the three film samples was calculated as the origin slope of the strain–stress curves. The biochemical oxygen demand (BOD) was determined according to the international standard ISO 14851 : 1999.<sup>20</sup> Biodegradability in soil was determined after 40 days and 5 months. The films of the crosslinked polymers were fixed in frames, wrapped into the agrofilm, and buried in soil at 10 cm depth. The soil was watered regularly.

## RESULTS AND DISCUSSION

### Epoxidation of natural oils

In the last decade, many methods were used for the epoxidation of unsaturated fatty acid derivatives and vegetable oils both in laboratories and in industry.<sup>21</sup> Nevertheless, the epoxidation of natural oils is still an area of research. The most widely used method was the epoxidation of natural oils with peracids, that is, *m*-chloroperbenzoic acid, performic acid, and peracetic acid. In this study, we have



**Figure 3** FTIR spectra of linseed oil (a) and epoxidized linseed oil prepared at 50°C (b).

chosen the epoxidation with *m*-chloroperbenzoic acid as one of the cheapest methods.

The epoxidation of natural oils with 3-chloroperbenzoic acid as epoxidation agent was performed at two different temperatures to estimate the effect of the temperature on the epoxidation rate and the conversion of the carbon double bonds. The products were characterized by FTIR and  $^1\text{H-NMR}$  spectroscopies.

Analysis of the FTIR spectra confirmed formation of epoxy groups. The new small absorption bands at  $821\text{--}824\text{ cm}^{-1}$  attributed to the C—O stretching of the epoxy groups appeared in the FTIR spectra of all epoxidized natural oils obtained at the different temperatures. The wide absorption bands at  $3467\text{--}3473\text{ cm}^{-1}$  attributed to the O—H stretching of hydroxyl groups appeared in the spectra of the epoxidized oils. This observation confirmed that part of epoxy groups was converted to hydroxyl groups. In addition, the bands at  $3008\text{--}3010\text{ cm}^{-1}$  attributed to C—H stretching of =CH groups had lower intensities in the spectra of the epoxidized linseed oils synthesized at different temperatures and the epoxidized fish oil prepared at 50°C as compared with the spectra of the corresponding natural oils. These bands disappeared completely in the spectra of the epoxidized rapeseed oils prepared at different temperatures and

the epoxidized fish oil prepared at 70°C. The absorption band at  $1654\text{ cm}^{-1}$  attributed to CH=CH stretching had lower intensities in the spectra of the epoxidized linseed oils prepared at different temperatures as compared with the spectrum of the natural linseed oil. These absorption bands disappeared completely in the spectra of the epoxidized rapeseed oils and epoxidized fish oils prepared at different temperatures. As an example, the FTIR spectra of linseed oil and epoxidized linseed oil synthesized at 50°C are presented in Figure 3.

Figure 4 shows the  $^1\text{H-NMR}$  spectra of linseed oil and epoxidized linseed oil prepared at 50°C. The signal at 5.25–5.55 ppm corresponding to the protons of the glycerol center ( $\text{H}_b$ ) and to the protons of the vinyl groups ( $\text{H}_8$ ,  $\text{H}_9$ ,  $\text{H}_{11}$ ,  $\text{H}_{12}$ ,  $\text{H}_{14}$ ,  $\text{H}_{15}$ ) of linseed oil [Fig. 4(a)] decreased after the epoxidation of all natural oils. The signal at 2.92 ppm corresponding to the protons of the epoxy group ( $\text{H}_8'$  and  $\text{H}_9'$ ) of epoxidized linseed oil [Fig. 4(b)] appeared in the  $^1\text{H-NMR}$  spectra of all epoxidized oils.

The values of degree of unsaturation, expressed as a number of C=C bonds per triglyceride, calculated from the data of  $^1\text{H-NMR}$  spectra according to the equation presented in literature,<sup>13</sup> the percentages of conversion of the carbon double bonds, and the number of epoxide groups per triglyceride,



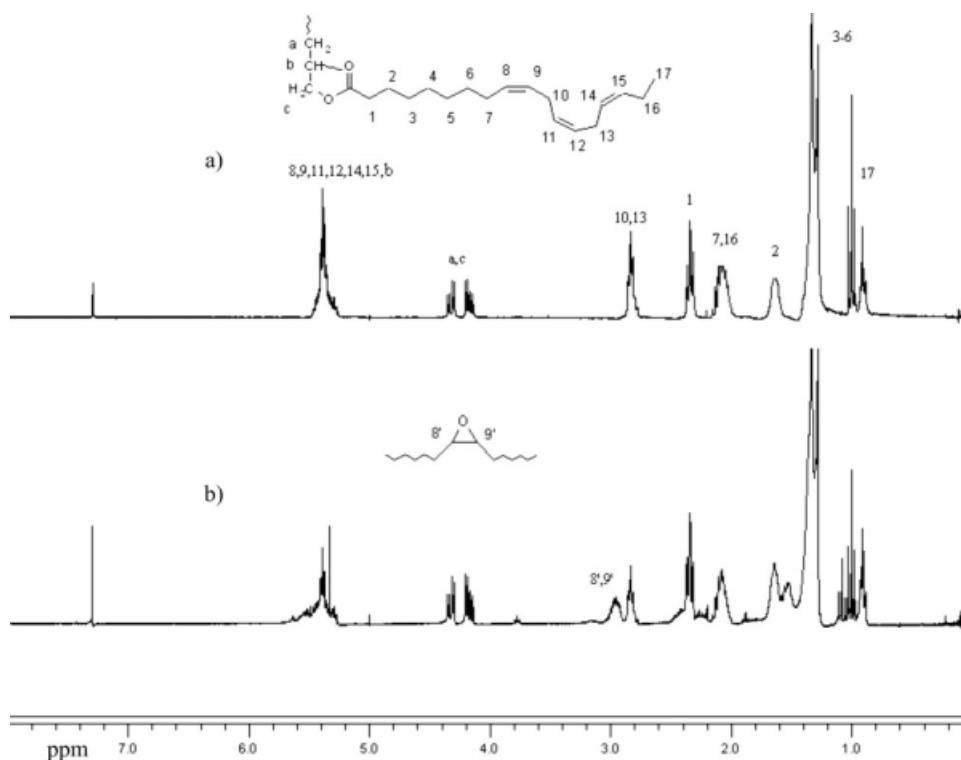


Figure 4  $^1\text{H-NMR}$  spectra of linseed oil (a) and epoxidized linseed oil (b).

calculated from the data of  $^1\text{H-NMR}$  spectra are summarized in Table I.

The increase of the temperature increased the conversion of the carbon double bonds. Some epoxy groups were converted into hydroxyl groups as it was confirmed by IR spectrometry. Hydroxyl groups can also participate in the crosslinking reactions.

The samples of epoxidized natural oils with the highest conversion of double bonds were used for the crosslinking studies. The possible structure of epoxidized triglycerides is presented in Figure 5.

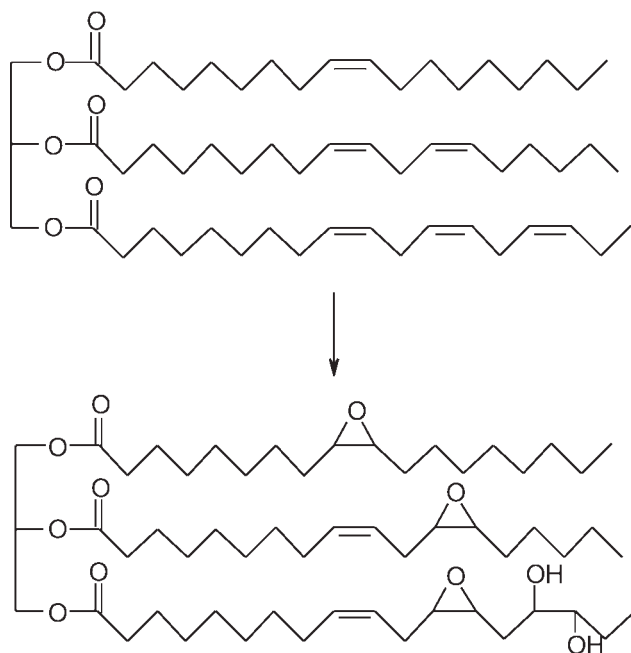
### Crosslinking

Three kinds of the reactive functional groups of the epoxidized oils can in principle participate in the crosslinking reactions, that is, epoxy groups,

hydroxyl groups, and the residual of double bonds. In addition, epoxy groups of the reactive diluents can take part in crosslinking. Although the crosslinking of epoxidized natural oils was performed using cationic initiators and photoinitiators crosslinking by the radical mechanism with participation of the double bonds can not be fully excluded, especially in the case of dark polymerization at elevated temperatures. Because of the presence of hydroxy groups cationic (photo)crosslinking can occur both by active chain and mechanism and by activated monomer mechanism. The later mechanism was discussed in detail previously.<sup>22,23</sup> For the photocrosslinking, the cationic mechanisms are definitely prevailing since expose to the UV light of the systems containing no photoinitiators did not lead to the appreciable hardening.

TABLE I  
Characteristics of Epoxidized Natural Oils

Natural oils	Degree of unsaturation of natural oils	Epoxidation temperature ( $^{\circ}\text{C}$ )	Degree of unsaturation of epoxidized natural oils	Conversion of $\text{C}=\text{C}$ (%)	Number of epoxy groups per triglyceride
Linseed oil	5.19	50	3.23	38	1.88
		70	0.72	86	4.44
Rapeseed oil	3.05	50	2.05	33	0.8
		70	1.31	57	1.70
Fish oil	4.41	50	2.33	47	2.03
		70	2.18	50	2.21



**Figure 5** The simplified scheme of the epoxidation of triglycerides.

In principle the homopolymerization of the reactive diluents is also possible, especially using 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate **3**, which contains very reactive epoxy groups. However, the data presented in the next chapter showed that the homopolymerization was not dominant and the major part of the reactive diluent participated in the crosslinking reaction of the natural oils.

We have tested two different photoinitiators for the photocrosslinking of epoxidized natural. Diphenyliodonium hexafluorophosphate was poorly soluble in the epoxidized natural oils and the resulting crosslinked films were heterogeneous and opaque. All the crosslinked polymer films prepared by photocrosslinking of the epoxidized natural oils with triarylsulfonium hexafluoroantimonate were homogeneous and transparent. Therefore, we have chosen the later photoinitiator for the further photocrosslinking studies.

The photocrosslinking of the epoxidized natural oils without reactive diluents resulted in the viscous products, however, the addition of the reactive diluents increased the hardness of the films significantly. The films obtained were lightly brown and homogeneous. The crosslinking in the dark of the epoxidized natural oils at 60°C without reactive diluents resulted to the homogeneous, transparent, lightly yellow, solid but sticky films.

The films produced with the reactive diluent **1** were brittle. It was very difficult to remove them from the surface of the Teflon plate. Therefore, the

diepoxy compound **1** was not used for the further investigations.

The crosslinking of the epoxidized natural oils with the reactive diluent **2** resulted in the smooth transparent solid films, lightly yellow but rather supple. These films were not friable. The crosslinking of the epoxidized natural oils with the reactive diluent **3** resulted in the rigid solid films, which were transparent and smooth. The crosslinked polymer films prepared with the reactive diluents **2** and **3** were used for the investigations of their structure and properties.

### Structure of the crosslinked polymers

Characteristics of the crosslinked polymers obtained by the different methods from the different epoxidized oils are given in Table II. The yield of the insoluble fraction of the polymers ranged from 59 to 90%. The increase of the amount of the reactive diluent in the initial reaction mixture increased the yield of the crosslinked polymer. The yield of the crosslinked polymers obtained from the epoxidized linseed oil was higher than that of the crosslinked polymers obtained from the epoxidized rapeseed and fish oil. The crosslinked polymers prepared in the dark at 60°C had higher content of the insoluble fraction than those prepared by photocrosslinking at the room temperature. The contents of the insoluble fractions observed in this work were slightly higher than those earlier reported for the crosslinked polymers prepared with alkenes.<sup>12–14</sup>

The FTIR spectral analysis showed that the network of the crosslinked polymers consisted of the fragments of the natural oil and of the reactive diluent. As an example, the FTIR spectra of the epoxidized fish oil, the reactive diluent **2** and the insoluble fraction of the crosslinked polymer **FP2-50** are shown in Figure 6. The specific absorption bands attributed to the both components (at 1741  $\text{cm}^{-1}$  corresponding to the C=O groups of the epoxidized fish oil and at 1607 and 1508  $\text{cm}^{-1}$  corresponding to the aromatic carbon double bonds of the reactive diluent **2**) are present in the FTIR spectrum of the insoluble fraction of the crosslinked polymer **FP2-50**.

The  $^1\text{H-NMR}$  and FTIR spectra showed that the soluble fractions of the polymers consisted of several compounds. The  $^1\text{H-NMR}$  spectra of the epoxidized fish oil, the reactive diluent **2**, and the soluble fraction of the crosslinked polymer **FP2-50** are shown in Figure 7. The signals at 7.5–8 ppm confirmed the presence of the residual photoinitiator, the signals at 4.1–4.4 ppm and 5.3–5.5 ppm were attributed to glycerol and the protons of vinyl groups of the epoxidized fish oil respectively, while the signals at 6.8–7.2 ppm were attributed to the reactive diluent **2**. The analysis of  $^1\text{H-NMR}$  and FTIR spectra of the

TABLE II  
Characteristics of the Crosslinked Polymers

Polymer <sup>a</sup>	Insoluble fraction (wt %)	$T_{\text{dec.-10\%}}$ (°C)	Young modulus (MPa) (thickness of the film (μm))	Biochemical oxygen demand (mg/g)	
				7 days	14 days
LD	78	270	–	46.6	85.3
LP	–	270	–	–	–
LD3-50	90	–	864.1 (60)	–	–
LD3-40	–	–	329.7 (200)	–	–
LD3-30	88	277	160.7 (60)	–	–
LP3-50	82	–	41.1 (160)	–	–
LP3-40	81	419	38.2 (200)	–	–
LP3-30	76	–	18.1 (210)	63.0	83.2
LP3-20	–	320	–	–	–
LD2-50	89	–	5.9 (190)	–	–
LD2-40	–	–	4.9 (190)	–	–
LD2-30	85	306	3.2 (150)	–	–
LP2-50	85	–	12.9 (100)	–	–
LP2-30	81	380	–	–	–
RD	75	308	–	0	12.2
RP	–	308	–	–	–
RD3-50	–	–	59.0 (100)	–	–
RD3-30	–	267	–	–	–
RP3-50	77	–	37.2 (135)	–	–
RP3-40	74	360	7.1 (115)	–	–
RP3-30	73	–	2.3 (140)	45.0	85.0
RP3-20	71	360	1.9 (150)	–	–
RD2-50	83	–	–	–	–
RD2-30	80	343	1.9 (170)	–	–
RP2-50	83	–	2.6 (170)	22.8	86.5
RP2-40	–	–	2.2 (130)	–	–
RP2-30	80	389	–	36.8	80.3
FD	61	250	–	57.0	87.3
FP	–	250	–	–	–
FH3-50	87	–	242.0 (150)	–	–
FH3-30	85	366	70.9 (200)	–	–
FP3-50	71	–	320.1 (60)	–	–
FP3-40	67	420	292.3 (90)	–	–
FP3-30	59	–	105.1 (70)	58.1	86.8
FP3-20	64	255	94.0 (70)	–	–
FD2-50	85	–	3.3 (150)	–	–
FD2-40	–	–	3.3 (225)	–	–
FD2-30	85	302	1.6 (180)	–	–
FP2-50	84	–	2.9 (150)	43.3	89.3
FP2-40	–	–	2.3 (180)	–	–
FP2-30	80	369	1.6 (140)	49.4	84.1

<sup>a</sup> The abbreviations in the polymer sample designations are as follows: L, linseed oil; R, rapeseed oil; F, fish oil; P, photocrosslinking; D, crosslinking in the dark; 1, 2, and 3, numbers of the reactive diluents; 20, 30, 40, and 50, concentration of the reactive diluent in the reaction mixture. For example, a polymer sample prepared by crosslinking of epoxidized linseed oil without any reactive diluent in the dark is named as LD; a polymer sample prepared by photocrosslinking of epoxidized linseed oil with 30 wt % of the reactive diluent 3 is named as LP3-30.

soluble and insoluble fractions of the other polymers gave the similar results.

### Thermal stability

TGA showed that the thermal degradation of the bulk crosslinked polymers in nitrogen atmosphere started above 200°C. All the crosslinked materials exhibited one-stage thermal degradation. As an

example, the TGA curve of the crosslinked polymer RP3-40 is presented in Figure 8. The 10% weight loss temperatures ( $T_{\text{dec.-10\%}}$ ) of the crosslinked polymers ranged from 250 to 420°C (Table II). The  $T_{\text{dec.-10\%}}$  of the crosslinked polymers prepared without reactive diluents were lower than those of the polymers prepared with reactive diluents. This observation was not surprising. The addition of the reactive diluent increased the number of reactive

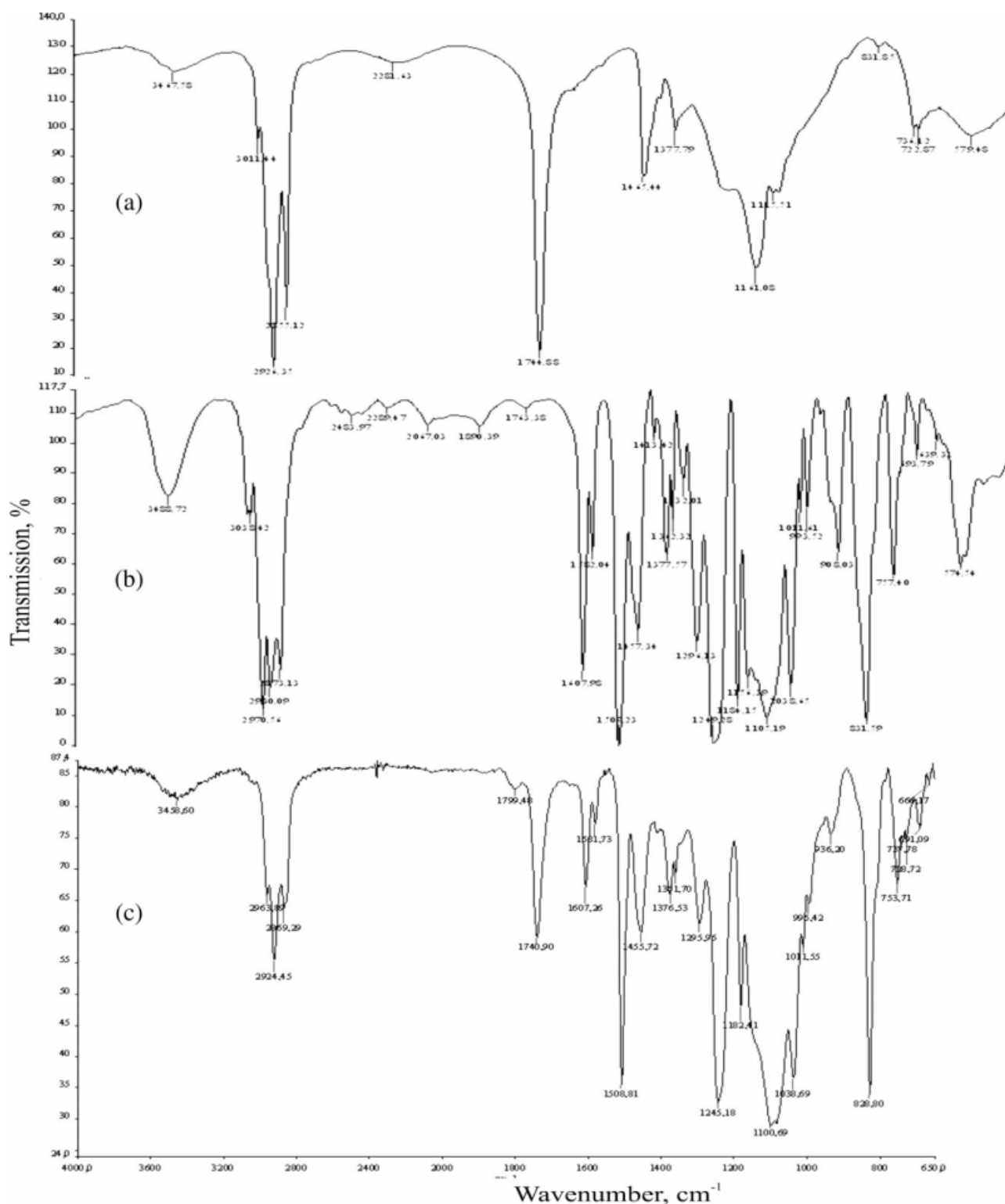
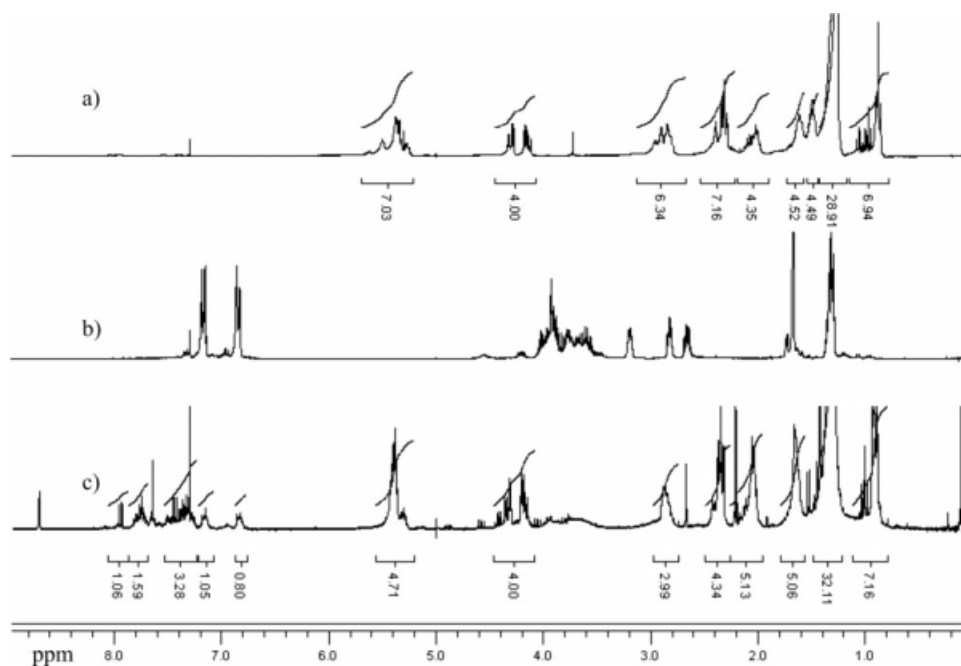


Figure 6 FTIR spectra of the epoxidized fish oil (a), reactive diluent 2 (b), and insoluble fraction of the polymer FP2-50 (c).

sites in the reaction mixture, and consequently allowed the formation of the denser network. The polymers prepared by photocrosslinking at the room temperature exhibited the higher  $T_{\text{dec.}-10\%}$  values as compared with the polymers prepared by crosslink-

ing in the dark at 60°C. The polymers prepared from the natural oils by crosslinking them with alkenes showed the similar temperatures of the onset of the thermal degradation, however their thermal degradation occurred in three stages.<sup>11-14</sup>





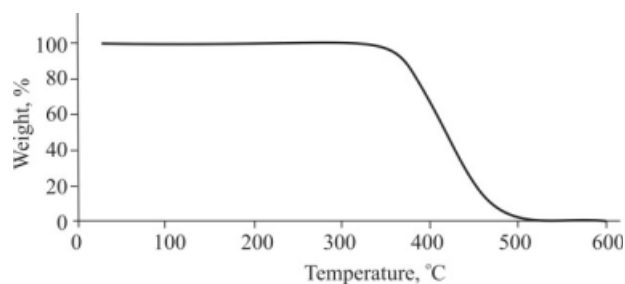
**Figure 7**  $^1\text{H-NMR}$  spectra of the epoxidized fish oil (a), reactive diluent 2 (b), and soluble fraction of the polymer FP2-50 (c).

### Mechanical properties

The Young modulus values of the crosslinked polymer films ranged from 2 to 864 MPa (Table II). The increase of the amount of the reactive diluent in the reaction mixture leads to the increase of the Young modulus of the crosslinked polymer film. The highest values of the Young modulus were observed for the films of linseed and fish oil crosslinked in the dark at 60°C with the reactive diluent 3. They were several times higher than those of the polymers prepared from natural oils crosslinked with alkenes (13.0–125.6 MPa, thickness 3 mm)<sup>13</sup> and comparable with that of the starch films (171–769 MPa, thickness 94–95  $\mu\text{m}$ ) established at the same experimental conditions.

### Water vapor permeability

The WVTR and permeability of the selected polymers prepared by crosslinking the epoxidized natural oils with diepoxy reactive diluents are given in



**Figure 8** TGA curve of the crosslinked polymer RP3-40.

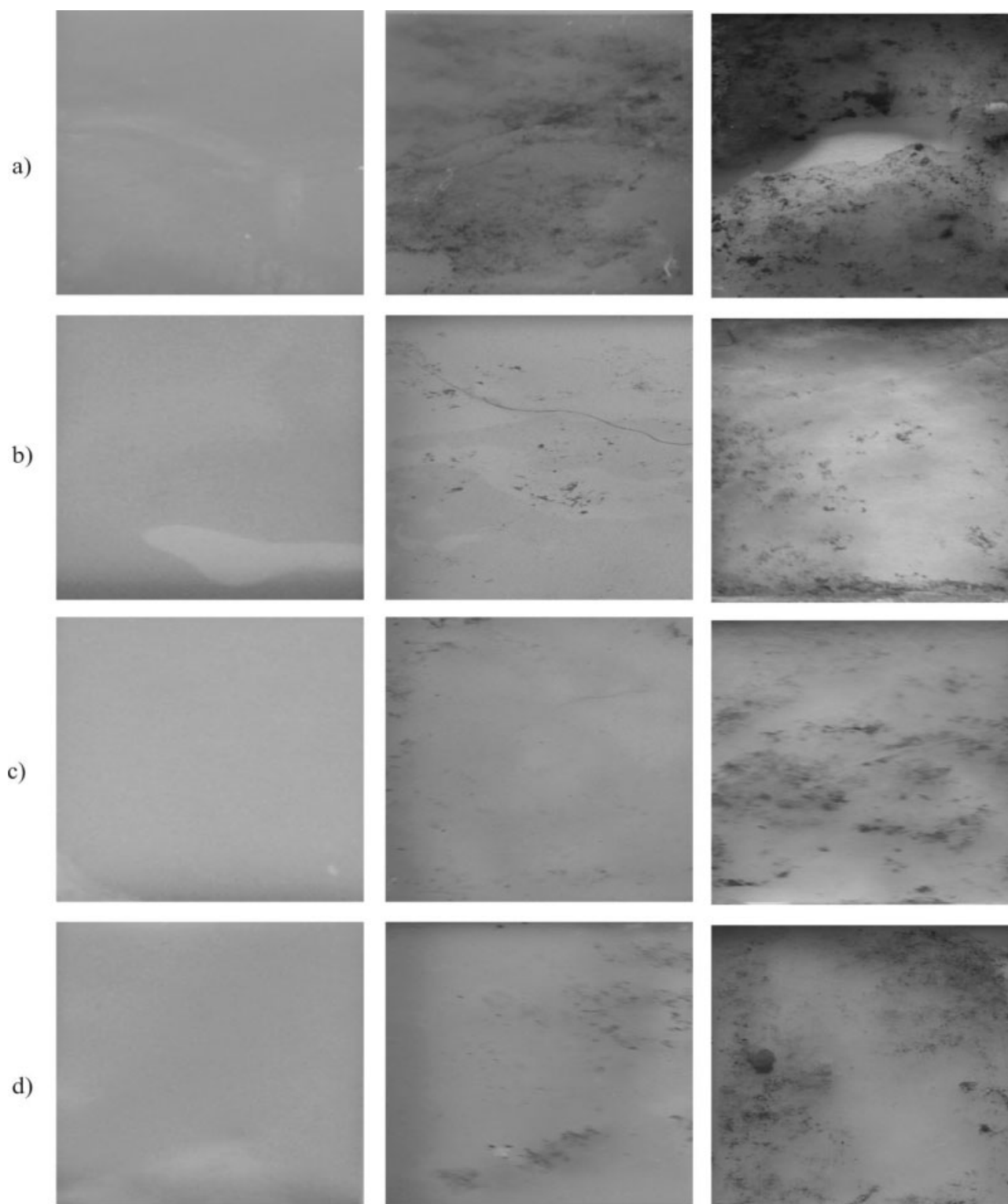
Table III. The increase of the amount of reactive diluent used for the crosslinking epoxidized linseed oil lead to the decrease of WVTR and water vapor permeability. This observation can be explained by the higher density of the crosslinks in the network of the polymers prepared using the higher amount of the reactive diluent. The crosslinked polymers prepared using the reactive diluent 3 showed higher WVTR values that those prepared using the same amount of the reactive diluent 2. The values of WVTR of all the tested crosslinked polymers prepared from natural oils with diepoxy reactive diluents are in the same range of magnitude as those of the conventional polymers. WVTR values for HDPE, LDPE, PET, PVC, and PS films ranges from 4.5 to 75  $\text{g}/\text{m}^2/24 \text{ h}$ .<sup>24</sup>

### Biochemical oxygen demand

The BOD values of the crosslinked polymers prepared from the epoxidized natural oils ranged from

**TABLE III**  
Water Vapor Transmission Rate and Water Vapor Permeability of the Crosslinked Polymers

Polymers	Thickness of the film ( $\mu\text{m}$ )	WVTR ( $\text{g}/\text{m}^2/24 \text{ h}$ )	Water vapor permeability ( $\text{mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ )
LP3-50	373	22.5	$3.7 \times 10^{-14}$
LP3-40	308	34.1	$4.5 \times 10^{-14}$
LP3-30	289	48.9	$6.4 \times 10^{-14}$
LP2-50	320	5.4	$8.0 \times 10^{-15}$
LP2-30	270	9.9	$1.2 \times 10^{-14}$



**Figure 9** Pictures of the fish oil crosslinked polymer films taken before composting (left picture), after 40 days of composting (middle picture), and after 5 months of composting (right picture): polymer crosslinked at 60°C without reactive diluent (a), polymer crosslinked at 60°C with 50 wt % of the reactive diluent 3 (b), polymer crosslinked at 60°C with 50 wt % of the reactive diluent 2 (c), and polymer photocrosslinked with 50 wt % of the reactive diluent 2 (d).

22.8 to 57 mg/g after 7 days and from 80.3 to 89.3 mg/g after 14 days (Table II). The use of the reactive diluent decreased the BOD. The crosslinked polymers prepared using the reactive diluent 3 showed

higher BOD values than the polymers prepared using the same amount of the reactive diluent 2. The BOD values of the crosslinked polymers from natural oils were higher than those of the conventional

polymers measured in the same conditions. The BOD of starch, cellulose, polyvinylalcohol JF-17, and JF-05 (both from Vam & Poval Co., Japan) after 7 days were 5, 4, 31.7, and 25.3 mg/g, and after 14 days: 5.9, 8.2, 47.7, and 33 mg/g respectively. Consequently, the biodegradation rate of the crosslinked polymers from natural oils was higher than that of the conventional polymers measured at the same conditions.

### Biodegradation in soil

The pictures of the different fish oil crosslinked polymer films before composting, after 40 days and 5 months of composting are presented in Figure 9. The biodegradation of the crosslinked polymers from natural oils just started after 40 days of composting. The degradation of the films of the crosslinked polymers of natural oils prepared without diepoxy reactive diluents both after 40 days and after 5 months of composting was more obvious than that of the films prepared with the diepoxy reactive diluents. No real difference was observed in the biodegradability of the crosslinked polymer made by photocrosslinking and crosslinking in the dark at 60°C, and in the biodegradability the polymers prepared with the reactive diluents 2 and 3.

### CONCLUSIONS

Linseed oil, rapeseed oil, and fish oil were epoxidized with 3-chloroperbenzoic acid. The double bond conversion increased with the increase of the temperature. At 70°C, it ranged from 36 to 86%. The epoxidized natural oils were crosslinked with diepoxy compounds, bisphenol A propoxylate diglycidyl ether, and 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate either in the dark using cationic initiator at 60°C or under UV irradiation with photoinitiators at the room temperature. The photocrosslinking was more efficient with the use of triarylsulfonium hexafluoroantimonate as photoinitiator. Crosslinking of epoxidized natural oils in the absence of diepoxy compounds resulted in viscous polymers. The addition of the diepoxy reactive diluents increased the hardness of the polymer films prepared by both, photocrosslinking and crosslinking in the dark. The yield of the insoluble fraction of the polymers was found to be 59–90%. It depended on the curing method and on the ratio of the epoxidized oil and the reactive diluent in the reaction mixture. The Young modulus of the crosslinked polymer films ranged from 2 to 861 MPa. The crosslinked polymer obtained with the reactive diluent 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate showed the highest Young moduli. The Young modulus increases with the increase of the

amount of the reactive diluent. The TGA indicated that the crosslinked polymers were thermally stable up to 200°C in nitrogen atmosphere. The 10% weight loss temperature of the polymers ranged from 250 to 420°C. The WVTR of the crosslinked polymer films was in the range of 6.2–48.9 g/m<sup>2</sup>/24 h. The increase of the amount of the reactive diluent used leads to the decrease of the water vapor transmission in the polymer films. The measurements of the BOD indicated that the crosslinked polymers showed higher biodegradation rate than cellulose, starch, and polyvinylalcohol. The composting of the polymer films indicated that the crosslinked polymers of natural oils prepared without diepoxy reactive diluents showed higher biodegradability than those prepared with the reactive diluents.

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