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Camelina Oil- and Linseed Oil-Based Polymers with Bisphosphonate Crosslinks

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ABSTRACT: Natural oils are the attractive biobased alternatives for petroleum derived chemicals in the production of polymers. A series of new biodegradable polymers based on epoxidized camelina oil was synthesized and investigated. The thermal, mechanical, swelling properties, hydrolysis, biodegradation, and bioresistance of the camelina oil-based polymers with bisphosphonate crosslinks were studied and compared with those of the analogous polymers based on epoxidized linseed oil. The dependence of the polymer properties on the density of crosslinks was observed. The obtained results showed that the properties of the camelina oil-based polymers are comparable with those of the linseed oil-based polymers and that camelina oil is a promising starting material for the synthesis of polymers. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40683.

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INTRODUCTION

Recently, the search of the new renewable raw materials for the production of polymers exhibiting properties similar to those of conventional petroleum-derived polymers and able to decompose into harmless substances after use and release into the environment is of increased interest of both research and industry. In recent years, natural oils have become the center of attraction for the potential use as starting materials for the preparation of polymers due to ready availability, inherent biodegradability, limited toxicity, and existence of modifiable functional groups.[1,2] A variety of vegetable oil-based polymers was prepared by free radical, cationic, olefin metathesis polymerization, and by polycondensation. The polymers obtained display a wide range of thermophysical and mechanical properties from soft and flexible rubbers to hard and rigid plastics, which show promise as alternatives to petroleum-based plastics.[3–5] Recently, new value-added applications were reported for (nano)composites derived from the plant oil-based thermosetting polymers.[6–8]

Natural oil-based thermosetting materials are cured or set using heat, or heat and pressure, and/or irradiation. This leads to advanced materials for industrial applications due to their high modulus, strength, durability and resistance toward thermal stress, and chemical attacks as provided by high crosslinking density.[5] Vegetable oil-based thermosets bearing covalently bonded phosphorus demonstrating flame retardant properties were recently reported.[9–12] Polyphosphates possess unique characteristics of biodegradation, biocompatibility, and structure versatility which make it possible to develop a variety of novel polymeric materials for biomedical engineering.[13,14] Recently, a series of phosphoester crosslinked vegetable oil elastomers was prepared from two kinds of modified vegetable oil prepolymers, i.e. phosphorylated castor oil and epoxidized vegetable oils and investigated as potential implantable materials.[15]

In this work, we report on the synthesis and properties of the camelina oil-based polymers with bisphosphonate crosslinks. *Camelina sativa* (L.) Crantz, named camelina, false flax, German sesame, gold-of-pleasure, linseed dodder, Siberian oilseed or wild flax, is a rediscovered crop which belongs to the Family Cruciferae (Brassicaceae), genus *Camelina*.[16] *C. sativa* (L.) Crantz originated in Germany in approximately 600 B.C. and later spread to Central Europe. From the beginning of 20th century up to the 1930s, *C. sativa* was grown sporadically in France, Belgium, Holland, the Balkans, and Russia.[17] *C. sativa* was nicely adapted to the more northerly regions of North America, Europe, and Asia.[18] Recently, *C. sativa* is recognized as a mature oilseed crop for a large-scale cultivation and commercialization with the following advantages: very fast growing, short crop cycle, early spring growth, winter types, available

good rusticity, drought resistant, wide adaptability, and low input requirement.[19]

To our knowledge, this is the first study on camelina oil-based polymers. The comparison of the properties of the newly synthesized polymers with those of the linseed oil-based polymers is also presented. Linseed oil with a high content of double bonds, traditionally used as a drying oil for surface-coating applications, was recognized as one of the best representatives of the natural oils commonly used for the production of polymers.[1–5,20,21] In contrast, camelina oil was investigated mostly as a feedstock for biodiesel production[22–24] or for human nutrition.[25] Camelina oil was not an object of the polymer synthesis up to now, although it contains about 90% of unsaturated fatty acids of the following content: C 18 : 1 (12.6%–18.7%), C 18 : 2 (14.3%–19.6%), C 18 : 3 (28.6%–39.0%), and C 20 : 1 (11.6%–16.8%).[24,25] There was only one attempt to develop thermoplastics by grafting various vinyl monomers to camelina meal.[26]

It was found that the yield of insoluble fraction, the glass transition temperature, the thermal decomposition temperature, swelling in different solvents, and the values of the tensile strength of the camelina oil-based polymers with bisphosphonate crosslinks are lower in comparison with those of the linseed oil-based polymers. The values of hardness and elastic modulus of camelina- and linseed oil-based polymers are rather similar. Moreover, the values of elongation to failure and biodegradability are higher for camelina oil-based polymers.

EXPERIMENTAL

Instrumentation

FTIR spectra were recorded on a Perkin–Elmer Spectrum BX II FTIR spectrometer. The spectra were recorded using KBr pellets. The range of wavenumber was (400–4000) cm^{-1}. The number of scans was 10.

Differential scanning calorimetry (DSC) measurements were performed on a Perkin–Elmer DSC 8500 apparatus at a 10°C min^{-1} heating rate under nitrogen atmosphere (nitrogen flow rate 50 mL min^{-1}). The aluminum pans were used. Indium standard was used for calibration. The temperature ranged from −40°C to 130°C. The scan cycle was heating–cooling–heating. The data from the second heating scan were taken. The middle point of the transition was used to obtain the T_g from the DSC curves.

Thermogravimetrical analysis (TGA) was performed on a Perkin–Elmer TGA 4000 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 aluminum oxide pans were used. Iron and zinc standards were used for calibration.

The swelling values of crosslinked films were estimated by measuring the volume of samples swollen in distilled water, chloroform, and toluene at 18°C. The arithmetic average of the swelling value of the three film samples (20.00 (± 0.00) mm × 20.00 (± 0.00) mm × 0.05 (± 0.01) mm) of each polymer was calculated. The variation of experimental results did not exceed 5% within the group. The technique was described earlier.[27]

The stress–strain curves of the films were obtained with a material testing machine BDO-FB0.5TH (Zwick/Roell) at (22 ± 2) °C and (20–30) % relative humidity. The strain rate for tensile test for all the samples was 1 mm min^{-1}. The width of the films was 5.00 (± 0.00) mm, the thickness of the films was 0.05 (± 0.01) mm. The arithmetic average of the results of the 3–6 film samples of each film was calculated. The results whose variation did not exceed 15% within the group were taken for the calculation of the arithmetic average.

The density of crosslinks (N) of the synthesized polymers was calculated according to the theory of rubber elasticity. The following equation was used:

$$\sigma = NRT(\lambda - \lambda^{-2}) \quad (1)$$

where σ is stress (MPa), N is density of crosslinks (mol m^{-3}), R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is temperature (K), λ is strain (the same $\lambda = 1.2\%$ was taken for the calculation of the density of crosslinks for all synthesized polymers).[28]

The hardness of the films was estimated 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 the three film samples (thickness 0.05 (± 0.01) mm) was taken. The variation of experimental results did not exceed 5% within the group. The hardness of the films was calculated using eq. (2):

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

where H_H is the hardness of the specimen (MPa), F is the force acting on the specimen (N), S is the surface area of the circular patch of the specimen that interacts with the cone, Δh is the depth of penetration of the cone into the specimen, measured as a difference between the microindicator readings when the specimen is unloaded and loaded with 1500 g for 60 s (mm).

Materials

1-Hydroxyethane-1,1-diphosphonic acid ((HEDP) or Etidronic acid) (60% aqueous solution) was purchased from Sigma-Aldrich and used as received. Chloroform (Poch S.A., Poland) and toluene (Delta–Chem) were purified and dried by the standard methods.[29]

The epoxidation of camelina oil and linseed oil (both from LLC Vetagra, Lithuania) was performed according to the procedure described earlier.[30] The number of epoxy groups per triglyceride calculated from the data of ^{1}H-NMR spectra was 5.5 for epoxidized camelina oil and 6 for epoxidized linseed oil.

Crosslinking of Epoxidized Oils

The crosslinking of the epoxidized natural oils was performed according to the procedure described in literature.[15] The direct mixture of epoxidized linseed oil (for polymers **1–3**) (or epoxidized camelina oil (for polymers **4–6**)) and HEDP (ratio of P—OH group to epoxy group was 2 : 1, 1.5 : 1, and 1 : 1) without any additive was poured on a plastic film and cured at 40°C until the hard film was obtained (1–3 days).

Polymers **1–6** IR (KBr): ν = 3426–3431 (O—H), 2931–2856 (C—H), 2320–2316 (rest of P(O)—OH), 1746–1741 (C=O), 1638–

1632 (rest of C—OH), 1467–1462 (C—H), 1240–1238 (C—O—C), 1174–1169 (P═O), 1071–1067 (P—O—C), 724–720 (C—H) cm^{-1}.

Soxhlet Extraction

The Soxhlet extraction was performed in order to determine the amount of the crosslinked fraction in the synthesized products. The crosslinked polymer samples (0.2 g) were extracted with chloroform for 72 h using a Soxhlet extractor. After the extraction, the insoluble fractions were dried under vacuum until no changes in weight were observed. The amount of the insoluble fraction was determined as a difference of the weight of the sample taken for the extraction and the weight of the insoluble fraction obtained after extraction and drying.

Hydrolysis

The hydrolysis experiment of the synthesized crosslinked polymers was performed since polyphosphates can decompose not only under the action of microorganisms but also by hydrolysis. The samples of the polymers (10.00 (± 0.00) mm × 10.00 (± 0.00) mm × 0.05 (± 0.01) mm) were weighed and immersed in potassium sodium phosphate buffer solution with fungicide (pH = 7.4) at 37°C. The pH value of the solutions was inspected and refreshed if needed. The samples were slightly shaken during the experiment, taken out, and weighed after the surface water was removed with filter paper at regular time intervals. The arithmetic average of the change of the sample weight before and after immersing into buffer solution of the three samples of each polymer was calculated. The variation of experimental results did not exceed 2% within the group.

Biodegradability by Soil Burial Test

About 5 L volume desiccators filled with soil from organic farming (sandy loam Haplic Luvisol; pH_{KCl} 5.8; humus 1.284%; the moisture content (20–30)%) were used for the polymer biodegradability tests. The polymer specimens (10.00 (± 0.00) mm × 10.00 (± 0.00) mm) were put into 50.00 (± 0.00) mm × 60.00 (± 0.00) mm bags of poly(vinyl chloride) with 0.05 mm mesh diameter, buried into the soil, and incubated at (26 ± 2)°C. Monthly, the specimens were removed and analyzed regarding the fungal colonization and their weight loss. For isolation of degrading fungi, the specimens were removed from the soil, washed with sterile physiological water (0.9% NaCl in distilled water), and their replicas were made on Malt Extract Agar with chloramphenicol (50 mg L^{-1}) to stop bacterium growth. The isolated fungi were purified and identified according to the morphological features. The biodegradability of the polymers was estimated according to their relative weight loss: $(a - b)/a \times 100\%$, where: a is the initial weight of the specimen (g); b is the specimen weight after incubation. The polymer specimens were weighed by means of an analytical balance with high precision (± 0.001). For the estimation of soil microbial activity the cotton wool (1 g) was buried and its mass loss made up 25% after 3 months.

Estimation of Bioresistance by Environmental Chamber Method

The selected polymer specimens were rinsed with sterile distilled water, blotted dry, and inoculated with fungal suspension (10^6 spores mL^{-1}) 10 µL/1 cm^2. Two fungal strains *Aureobasidium pullulans* (de Bary) G. Arnaud 15-03 and *Aspergillus sp.* KP-13 used were taken from the collection of the Biodeterioration Research Laboratory of the Nature Research Centre (Lithuania). *A. pullulans* was selected for testing as fenoloxidase, lipase, amylase, pectinase, and endogluconase producers and *Aspergillus sp.* was isolated from synthetic polymer buried in soil. The inoculated specimens were placed into the chamber (> 90 % relative humidity) and incubated at (26 ± 2) °C for three months. The control specimens were not inoculated with the fungal suspension. Monthly visual assessment of the degree of specimen colonization was performed using four-grade scale[31]:

- grade 0—no growth apparent even under the microscope;
- grade 1—growth invisible or hardly visible to the naked eye but clearly visible under microscope;
- grade 2—slight growth covering less than 25% of the specimen surface;
- grade 3—growth covering more than 25% of the specimen surface.

The bioresistance of the polymers was estimated according to the percentage of their weight change after 3 months as described above.

RESULTS AND DISCUSSION

The camelina oil and linseed oil polymers with bisphosphonate crosslinks **1–6** were synthesized by the reactions of the epoxidized camelina oil or epoxidized linseed oil and HEDP using different molar ratios of the starting materials (Table I) without catalyst. The possible structure of the crosslinked polymers **1–6** is shown in Figure 1.

The chemical structure of the crosslinked polymers was confirmed by FTIR spectroscopy. The signal of epoxy group at 822 cm^{-1}, which is present in the IR spectra of epoxidized natural oils, disappeared in the IR spectra of all crosslinked polymers **1–6**. The signal of P(O)—OH group absorption at (2320–2316) cm^{-1} and C—OH group absorption at (1645–1638) cm^{-1}, which are present in the IR spectrum of HEDP, decreased considerably in the IR spectra of the crosslinked linseed oil polymers **1–3** and camelina oil polymers **4–6**. The characteristic P—O—C stretch at (1071–1067) cm^{-1} appeared in the IR spectra of all crosslinked linseed oil polymers **1–3** and camelina oil polymers **4–6**. The intense signal at (3426–3431) cm^{-1} confirms the presence of OH groups in the structure of the crosslinked linseed oil polymers **1–3** and camelina oil polymers **4–6**. One part of OH groups is formed after the opening of epoxy rings, another part of OH groups is unreacted OH groups of bisphosphonate fragments. The latter statement is confirmed by the presence of low-intensity signals at (2320–2316) cm^{-1} and (1645–1638) cm^{-1}, which can be assigned to the rest of P(O)—OH groups and C—OH groups, respectively. The IR spectra of the epoxidized camelina oil (a), HEDP (b), and crosslinked camelina oil polymer **4** (c) are presented in Figure 2, for the illustration of the above stated.

The yield of the insoluble fraction of the crosslinked polymers obtained after Soxhlet extraction in chloroform for 72 h was (69–81) % (Table I). The yield of insoluble fraction increased with the decrease of the amount of HEDP in the reaction mixture. This observation shows that the higher amount of the

Table I. Yields of the Insoluble Fractions and Thermal Characteristics of the Crosslinked Linseed Oil Polymers 1–3 and Camelina Oil Polymers 4–6

Polymer	Epoxydized oil	Molar ratio P—OH : epoxy group	Insoluble fraction (%)	Density of crosslinks (mol/m^3)	T_g[a] (°C)	$T_{dec\text{-}10\%}$[b] (°C)
1	Linseed oil	2 : 1	76	4.47×10^{-4}	2	275
2		1.5 : 1	80	2.92×10^{-4}	3	290
3		1 : 1	81	2.44×10^{-4}	1	313
4	Camelina oil	2 : 1	69	4.06×10^{-4}	−4	265
5		1.5 : 1	71	2.44×10^{-4}	−5	270
6		1 : 1	72	1.62×10^{-4}	−4	275

[a] Glass transition temperature.
[b] Decomposition temperature at the weight loss of 10%.

crosslinked fraction was formed in the synthesized product when the lower amount of HEDP was taken for the reaction. More linear or/and branched structures were formed when the higher amount of HEDP was used. The values of the density of crosslinks of the polymers **1–6** calculated according to the theory of rubber elasticity are presented in the Table I. The lower amount of HEDP was taken for the reaction the lower density of crosslinks was obtained. The yield of insoluble fraction and the density of crosslinks of the linseed oil-based polymers **1–3** were slightly higher as compared with that for camelina oil-based polymers **4–6.** This was presumably due to slightly higher crosslinking due to a slightly higher number of epoxy groups per triglyceride of the epoxidized linseed oil used in the reactions (5.5 for epoxidized camelina oil and 6 for epoxidized linseed oil as calculated from the data of ^{1}H-NMR spectra).

DSC confirmed that the synthesized crosslinked polymers **1–6** were amorphous materials. Only glass transitions were observed in the DSC curves of all the polymers prepared (Figure 3). The glass transition temperatures (T_g) of the crosslinked polymers prepared from both vegetable oils are similar: (1–3) °C for the linseed oil-based polymers **1–3** and (−5 to −4) °C for the camelina oil-based polymers **4–6** (Table I). The T_g of the linseed oil-based polymers **1–3** are slightly higher in comparison with camelina oil-based polymers **4–6**, apparently due to the slightly higher crosslinking.

The crosslinked polymers **1–6** exhibit high thermal stability as shown by TGA. Their thermal decomposition temperatures at

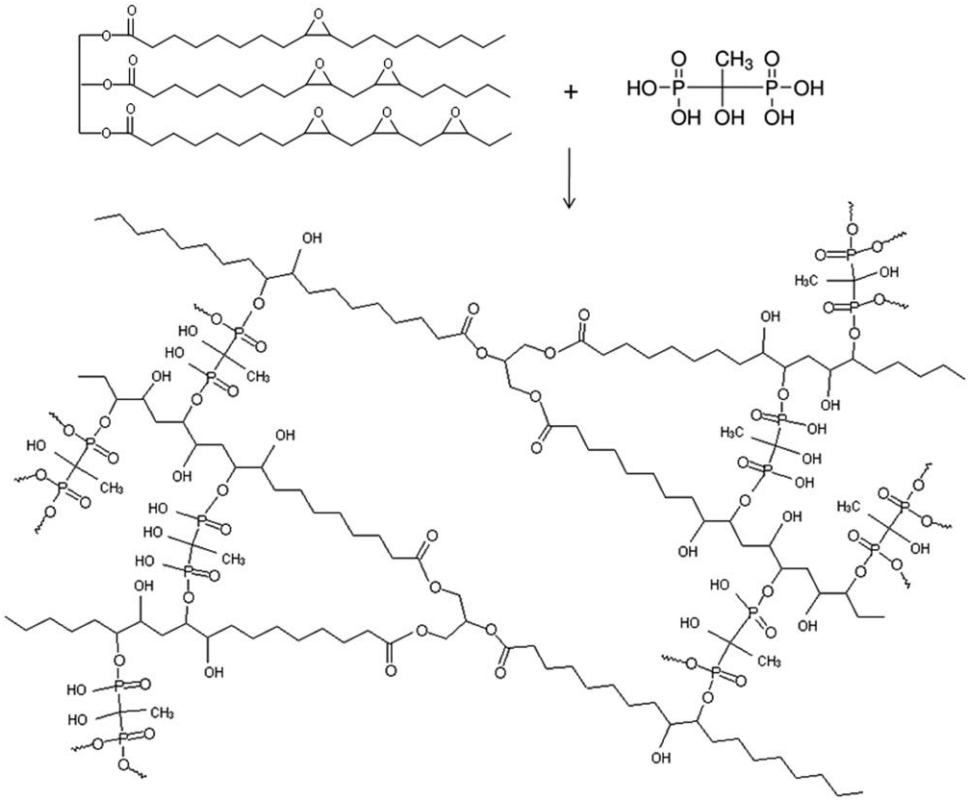

Figure 1. Crosslinking of epoxidized natural oil.

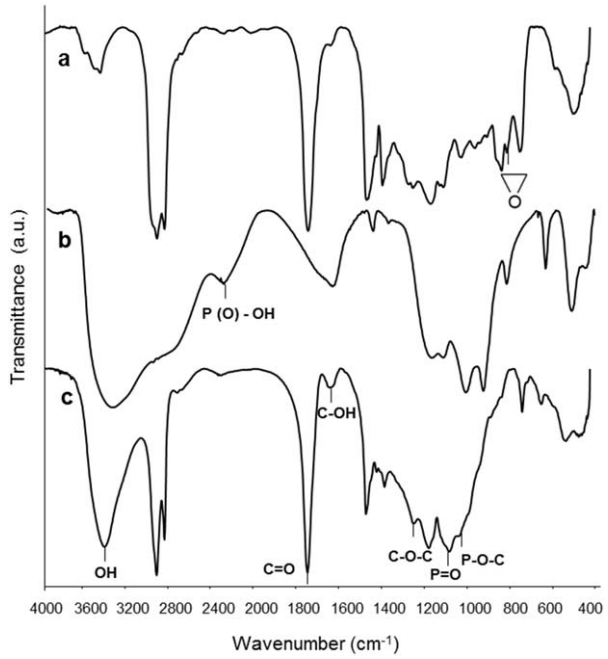

Figure 2. IR spectra of the epoxidized camelina oil (a), HEDP (b), and the crosslinked camelina oil polymer **4** (c).

the weight loss of 10% ($T_{dec\text{-}10\%}$) are in the range of (265–313) °C (Table I) and increase with the increase of the amount of the formed crosslinked fraction. The thermal stability of the linseed oil-based polymers is higher by about (10–38) °C in comparison with the camelina oil-based polymers due to the higher amount of the formed crosslinked fraction in the polymers. The thermal decomposition of the crosslinked polymers **1–6** proceeds in two steps (Figure 4). The mass of the fraction lost in the first step increases with the increase of the amount of triglyceride fragments in the polymer. The thermal decomposition temperatures at the weight loss of 50% ($T_{dec\text{-}50\%}$) are in the range of (350–413) °C. At this point the first step of the thermal decomposition is finished for the polymers **1**, **4**, and **5** and still proceeds for the polymers **2**, **3**, and **6**. This observation indirectly shows that triglyceride fragments decompose firstly. The temperature of the maximum thermal decomposition is the same for the all crosslinked polymers **1–6** and is 488°C. However, the char content ((11–17) %) depends on the amount of the formed crosslinked fraction in the polymers. The higher char content is observed when the higher amount of the crosslinked fraction is formed in the polymer.

The dependency of the swelling value on the swelling time of the crosslinked polymers **1–6** was estimated in distilled water [Figure 5(a)], non-polar organic solvent toluene [Figure 5(b)], and polar organic solvent chloroform [Figure 5(c)] at 18°C. The polymers with lower density of crosslinks exhibited the higher degree of swelling in all the solvents. However, the degree of swelling of the crosslinked polymers **1–6** was very low. The highest degree of swelling reached in toluene and chloroform was 48% after 1.5 h. The highest degree of swelling observed in distilled water was only 6.5% after 3.0 h. Such low degrees of swelling of the synthesized crosslinked polymers in the distilled water can be due to the poor polymer–solvent interaction. The hydrophobic triglyceride fragments of the crosslinked polymers tend to repel water.

The mechanical characteristics of the films of the crosslinked polymers **1–6** estimated by the stress–strain tests at (22 ± 2) °C and (20–30) % relative humidity are summarized in Figure 6. The tensile strength of the crosslinked polymer films ranged from 4.66 MPa to 18.42 MPa. The elongation to failure of the films was found to be in the range of (20.36–49.56) %. The Young modulus ranged from 6.37 MPa to 13.51 MPa. The hardness of the polymer films measured with a Hepler consistometer ranged from 40 MPa to 64 MPa. The mechanical characteristics of the polymers appeared to be dependent on the amount of the triglyceride fragments in the polymer chains and the density of crosslinks. The higher amount of the triglyceride fragments and the lower density of crosslinks (going from polymer **1** to polymer **3** and from polymer **4** to polymer **6**) the lower values of all the mechanical characteristics were observed. Also, the difference between the mechanical properties of the linseed oil-based polymers and those of the corresponding camelina oil-based polymers can be explained by the lower density of crosslinks of the camelina oil-based polymers. However, the values of

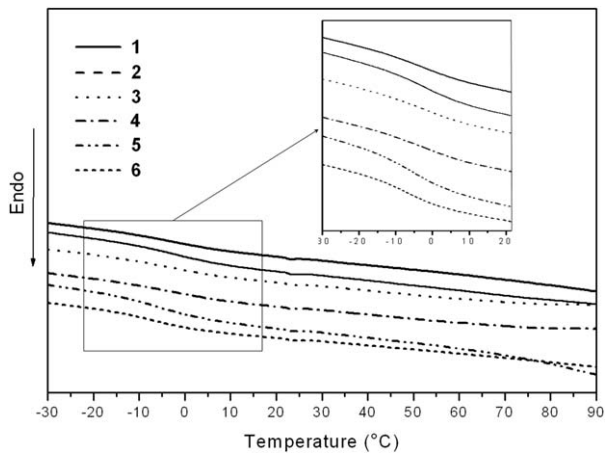

Figure 3. DSC curves of crosslinked linseed oil polymers **1–3** and camelina oil polymers **4–6.**

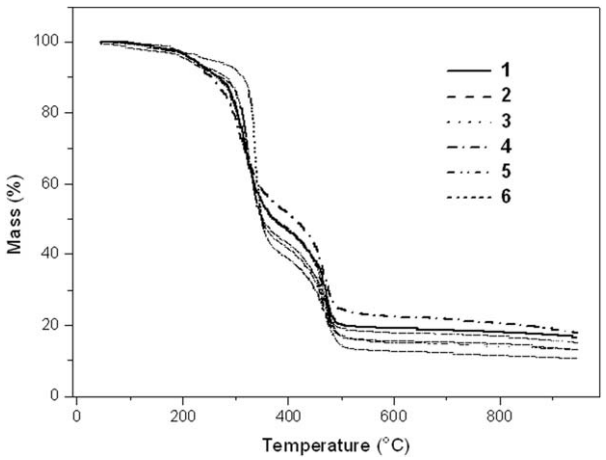

Figure 4. TGA curves of crosslinked linseed oil polymers **1–3** and camelina oil polymers **4–6.**

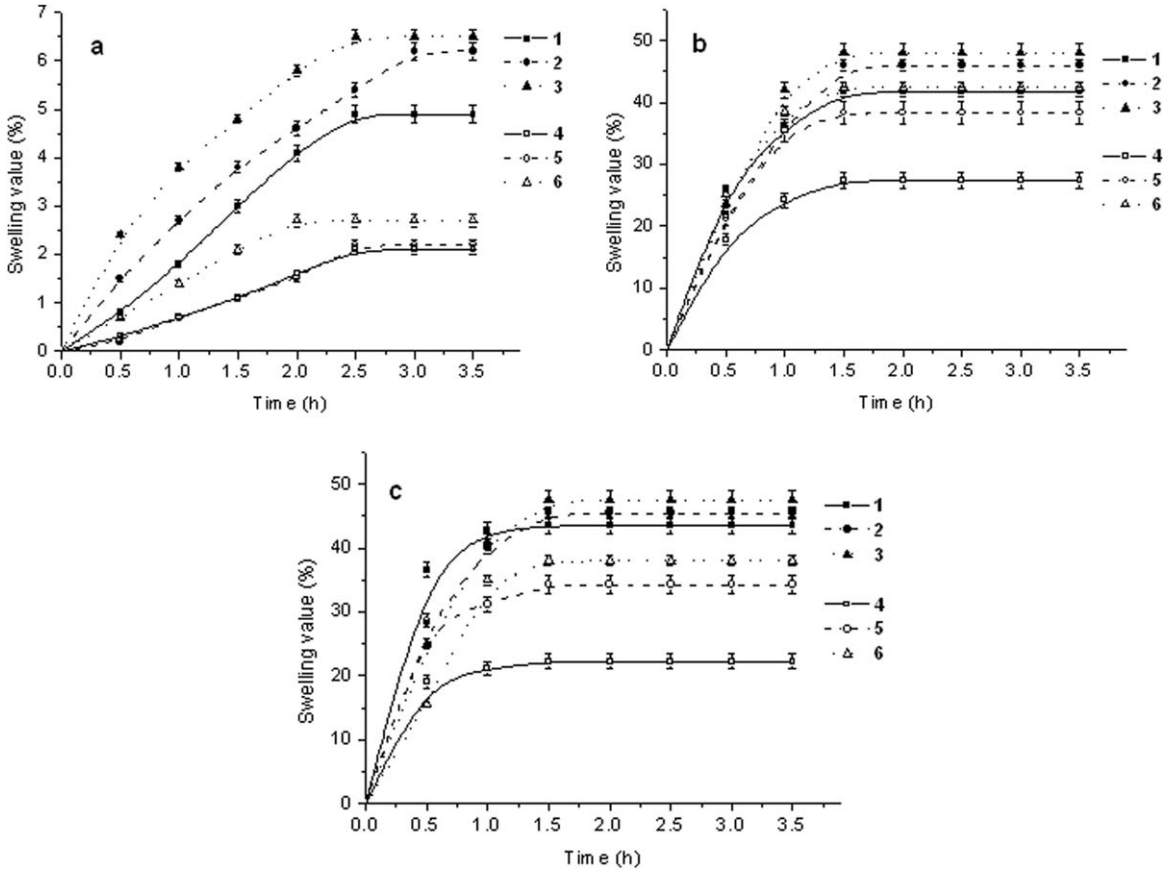

Figure 5. Swelling value versus time curves for the crosslinked linseed oil polymers **1–3** and camelina oil polymers **4–6**: in distilled water (a), in toluene (b), and in chloroform (c) at 18°C.

the hardness and the elastic modulus of the linseed oil-based polymers and the camelina oil-based polymers are rather similar. The values of the tensile strength are higher for the linseed oil-based polymers, and the values of elongation to failure are higher for camelina oil-based polymers.

The hydrolysis of the crosslinked polymers **1–6** was investigated in the conditions simulating human body as most of the synthesized polyphosphoesters were designed for biomedical applications.[13,14] Another purpose was the comparison of the obtained characteristics with those of the phosphoester crosslinked elastomers earlier synthesized from modified natural oils.[15] The whole hydrolysis process of the crosslinked polymers **1–6** contained three stages (Figure 7). In the first stage, the weight of the samples increased rapidly due to the swelling of water solution until the equilibrium of the sample weight was reached after one day. The equilibrium was maintained about ten days. Then the weight of samples started to decrease due to their decomposition in the third stage. The dependence of the mass change on the amount of the crosslinks in the structure of polymers **1–6** was observed. The camelina oil-based polymer **6** with the lowest amount of the crosslinks demonstrated the highest rate of hydrolysis. The rate of hydrolysis of the all camelina oil and the linseed oil polymers with bisphosphonate crosslinks **1–6** was considerably slower than that of the phosphoester crosslinked elastomers obtained from phosphorylated castor oil and epoxidized soybean oil or epoxidized linseed oil which hydrolyzed completely within 27 days[15] probably due to the considerably higher amount of crosslinks. The mass loss of the camelina oil-based polymers with bisphosphonate crosslinks **4–6** was only (2–7) % and that of the linseed oil-based polymers with bisphosphonate crosslinks **1–3** was (3–5) % after 27 days.

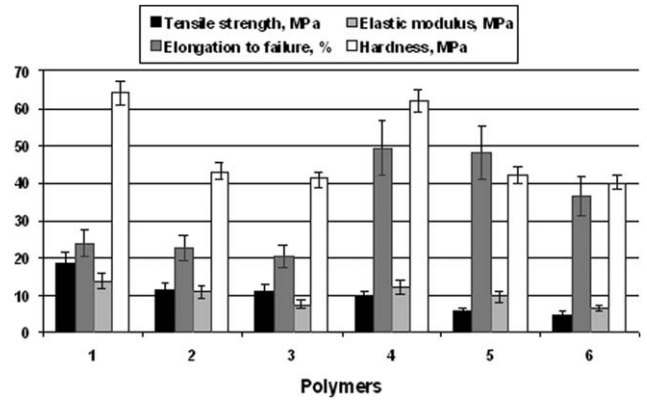

Figure 6. Mechanical characteristics of the crosslinked linseed oil polymers **1–3** and camelina oil polymers **4–6** films.

The biodegradability of the crosslinked polymers was tested using a soil burial experiment in the laboratory under the

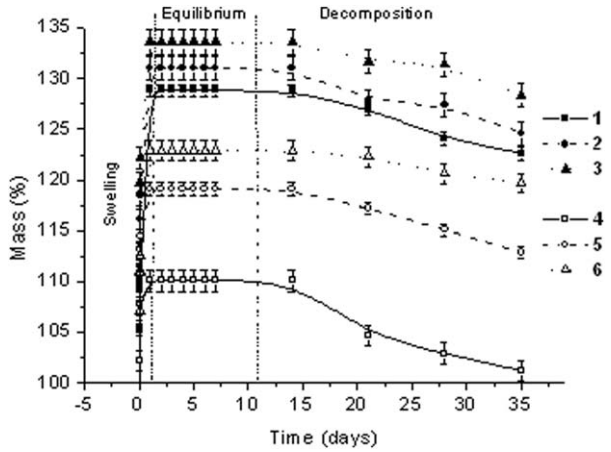

Figure 7. Hydrolysis of linseed oil polymers **1–3** and camelina oil polymers **4–6** (37°C, pH = 7.4).

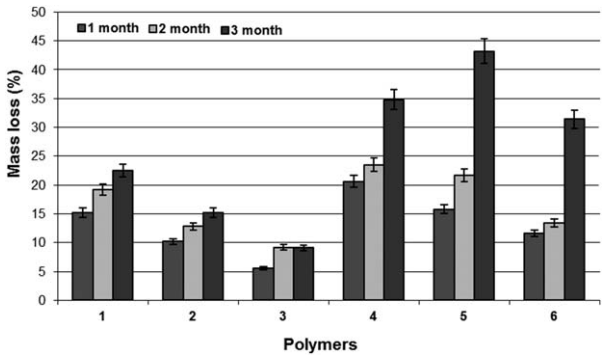

Figure 8. Biodegradation of linseed oil polymers **1–3** and camelina oil polymers **4–6** in soil (26°C, pH = 5.8).

temperature (26 ± 2) °C and humidity (20–30) % optimal for fungi development. The mass loss was observed even after the first month (Figure 8). After this period of time, the highest value of the mass loss of 20.6% was recorded for the sample of the crosslinked polymer **4**. The lowest mass loss of 5.5% was observed for the sample of the crosslinked polymer **3**. An evident dependency of the mass loss on the amount of the crosslinks was observed. The polymers with the lower density of crosslinks decomposed faster. The camelina oil-based polymers decomposed faster than the linseed oil-based polymers.

Soil is rich in various microorganisms with different enzymatic activity. They can use materials of different chemical composition as nutrient substrate and consequently decompose them. After three months, fungi of five different genera were isolated from the buried specimens of the crosslinked polymer **1–6** (Table II). Fungi of *Trichoderma* and *Verticillium* genera were detected on all the tested specimens. The present soil burial test showed that there were some fungal species able to develop on the polymer specimens tested and that they could be degraded to some degree by soil inhabiting fungi.

The specimens of the crosslinked polymers **1–6** were inoculated with *A. pullulans* 0015-03 and *Aspergillus sp.* KP-13 pure culture suspensions in the increased humidity conditions (> 90 % relative air humidity and the temperature of (26 ± 2) °C). Their growth was not observed after the three months of exposure and the specimen colonization was estimated as 0 grades according to the four-grade scale. The weight of specimens did not change either. The additional fungi genus developed on the polymer specimens during burying into the soil (Table II). It can be assumed that only certain species of fungi, having certain physiological characteristics may violate these polymers.

The results showed that the polymers tested **1–6** were not resistant to fungal attack and contained available nutritive substance for them though the resistance of polymers depended on the fungus species attacking them.

CONCLUSIONS

The soft, transparent films of the camelina oil- and linseed oil-based polymers with bisphosphonate crosslinks were obtained in the mild conditions without any catalyst. The yield of the insoluble fraction of the crosslinked polymers was (69–81) %. The glass transition temperatures of the crosslinked polymers were in the range of (−5 to 3) °C. The thermal decomposition temperatures at the weight loss of 10% were in the range of (265–313) °C. The degree of swelling reached 48% in toluene and chloroform, and 6.5% in distilled water. The tensile strength of the crosslinked polymer films ranged from 4.66 MPa to 18.42 MPa. The elongation to failure of the films was found to be in the range of (20.36–49.56) %. The Young modulus ranged from 6.37 MPa to 13.51 MPa. The hardness of the polymer films ranged from 40 MPa to 64 MPa. The mass loss of the crosslinked polymers was (3–9) % after 35 days of hydrolysis and (5.5–20.6) % after one month of exposure in soil. The crosslinked polymers were not resistant to fungal attack and their bioresistance depended on the fungus species attacking

Table II. Fungi Isolated from the Samples of the Crosslinked Linseed Oil Polymers **1–3** and Camelina Oil Polymers **4–6** After Exposition in Soil

	Fungal genera				
Polymer	Gongronella	Peniciliium	Talaromyces	Trichoderma	Verticillium
1	+			+	+
2	+	+		+	+
3			+	+	+
4	+			+	+
5		+		+	+
6	+			+	+

them. The dependence of the polymer properties on the density of crosslinks was observed. The yield of insoluble fraction, thermal decomposition temperature, swelling value in different swelling agents increased, and the hardness, tensile strength, elongation at break, Young modulus, the extent of hydrolysis, and biodegradation in soil of the polymer films decreased with the increase of the density of the crosslinks in the polymers. The obtained results showed that the properties of the camelina oil-based polymers are comparable to those of the linseed oil-based polymers and that camelina oil is a promising starting material for the synthesis of polymers.

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