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ORIGINAL PAPER

Biodegradable Photo-Crosslinked Thin Polymer Networks Based on Vegetable Oil Hydroxy Fatty Acids

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Abstract Novel crosslinked thin polymer networks based on vegetable oil hydroxy fatty acids (HFAs) were prepared by UV photopolymerization and their mechanical properties were evaluated. Two raw materials, castor oil and 7,10-dihydroxy-8(*E*)-octadecenoic acid (DOD) were used as sources of mono- and di-HFAs, respectively. Poly (ethylene glycol) (PEG) diacrylate and poly(ε-caprolactone) diacrylate were synthesized and used as crosslinking agents to form crosslinked polymer networks by UV-initiated free-radical polymerization with acrylated castor oil or acrylated DOD. The synthesis of acrylate derivatives was confirmed using FT-IR and ^{1}H-NMR spectroscopic techniques. The composition of the reaction mixture and the type/length of crosslinking agent were changed to obtain crosslinked polymer networks with various mechanical properties. For polymers prepared from high molecular weight (20,000) PEG, a 58–60% of the initial weights decreased in 35 days in phosphate buffer solution (pH 7.2) containing lipase enzyme. These potentially biodegradable polymers based on vegetable oil HFAs can be used as eco-friendly materials for various applications to replace the existing petroleum-based polymers currently used.

Keywords Castor oil · 7,10-Dihydroxy-8(*E*)-octadecenoic acid · Photo-crosslinked polymer network · Eco friendly · Biodegradable

Abbreviations

ACO	Acrylated castor oil
ADOD	Acrylated 7,10-dihydroxy-8(*E*)-octadecenoic acid
AESO	Acrylated epoxidized soybean oil
CO	Castor oil
DMPA	2,2-Dimethoxy-2-phenylacetophenone
DOD	7,10-Dihydroxy-8(*E*)-octadecenoic acid
HFA	Hydroxyfatty acid
PCLDA	Poly(ε-caprolactone) diacrylate
PEGDA	Poly(ethylene glycol) diacrylate
UV	Ultraviolet

Introduction

Hydroxy fatty acids (HFAs), originally found mainly in plant systems [1], are known to have special properties such as higher viscosity and reactivity compared with other normal fatty acids [2, 3]. These special properties confer HFAs a high potential for a wide range of industrial applications including resins, waxes, nylons, plastics, lubricants, cosmetics and additives in coatings and paintings. HFAs can be used not only as specialty chemicals, but also as bioactive agents such as antifungal agents [4–6]. Castor oil (CO) is a triglyceride in which approximately 90% of the fatty acid chains are ricinoleic acid. Oleic and linoleic acids are the other significant components. Ricinoleic acid, a monounsaturated, 18-carbon fatty acid, is unusual in that it has a hydroxyl functional group on the twelfth carbon. CO was the

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first vegetable oil to be used as a source of polyol monomers and is still currently used as a polyol source for polyurethane production [7]. Microorganisms oxidize fatty acids either at the terminal carbon or inside of the acyl chain to produce hydroxyl or keto fatty acids [8]. One of the new products discovered by Hou et al. [9], 7,10-dihydroxy-8(*E*)-octadecenoic acid (DOD) which was produced from *Pseudomonas aeruginosa* PR3, has anti-microbial activity. DOD was also tested as raw material for the synthesis of industrial products such as rigid polyurethane foams [10].

The widespread use of nonbiodegradable, petroleum-based polymers has raised many concerns in terms of both economical and environmental aspects. There is a growing interest in biomaterials derived from renewable resources such as vegetable oils [11, 12]. These biopolymers offer the advantages of low cost, ready availability of starting materials, and possible biodegradability. Wool et al. [13–15] extensively synthesized various different types of thermoset polymers from different vegetable oil-based monomers, including acrylated epoxidized soybean oil (AESO) and modified fatty acids. Various different polymeric materials ranging from soft rubbers to tough and rigid plastics have been prepared by the copolymerization of vegetable oils with styrene and divinylbenzene [16]. Even though these thermosets can be considered biobased, their applications as biodegradable and biocompatible materials would be limited because the comonomers used (styrene and divinylbenzene) are toxic and the biodegradability of the resulting polymers is unknown.

Recently, we prepared novel soybean oil-based polymer networks which have different chemical structures from those previously reported by others and can be potentially used as biodegradable and biocompatible materials for various biomedical and other applications [17]. Poly(ethylene glycol) diacrylate (PEGDA) and poly(ε-caprolactone) diacrylate (PCLDA) were synthesized and used as crosslinking agents to prepare polymer networks by UV-initiated free-radical polymerization with AESO. In this study, this preparation method was extended to vegetable oil HFAs to broaden the spectrum of raw materials and to obtain various polymer structures and properties. CO and DOD were used as sources of mono- and di-HFAs, respectively. Photopolymerization reaction conditions were changed to obtain crosslinked polymer networks with various mechanical properties. Lipase degradability was studied by measuring weight loss in a phosphate buffer solution (pH 7.2).

Materials and Methods

Materials

Castor oil (CO) was obtained from Aldrich (Milwaukee, WI, USA). The hydroxyl content of this oil was 2.7 groups per triacylglycerol molecule. DOD was produced from oleic acid by *P. aeruginosa* PR3 [9]. PEGDA (molecular weight 258) and PEG (molecular weight 20,000) were obtained from Fluka (Buchs, Switzerland). PCL diol (molecular weight 2,000) was obtained from Aldrich. Acryloyl chloride, triethylamine, the UV initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA), were all obtained from Aldrich. Lipase from *Candida rugosa* was obtained from Sigma (St. Louis, MO, USA). All other chemicals used were of reagent grade and were used without further purification.

Synthesis and Characterization of Acrylated Derivatives

The hydroxyl groups in CO, DOD, PEG (molecular weight 20,000) and PCL diol (molecular weight 2,000) were end-capped with acrylate groups to form a polymerizable macromer [18, 19]. Acrylated derivatives were prepared by the acylation of hydroxyl functional groups and acryloyl chloride. Triethylamine was used as a base. Typically, 4.0 g of these hydroxyl compounds was dissolved in 40 mL of benzene in a 100-mL of round-bottomed flask. Triethylamine and acryloyl chloride were added to the flask at a ratio of 3 mol/mol hydroxyl groups. The reaction mixture was stirred for 3 h at 75 °C. After the reaction, the mixture was filtered to remove triethylamine hydrochloride. The acrylated macromer was obtained by pouring the filtrate into a large excess of hexane. Solvent from the filtrate was removed by rotary evaporation. The resulting syrup containing the viscous macromer was dried under vacuum for 1 day.

FT-IR spectra were measured using a Bomem MB100 spectrophotometer. The ^{1}H-NMR spectra were measured with a Bruker Avance-500 MHz spectrometer in $CDCl_3$.

Preparation of CO- and DOD-Based Crosslinked Polymer Networks

Poly(ethylene glycol) diacrylate (PEGDA) (molecular weights 258 and 20,000) or PCLDA (molecular weight 2,000) were dissolved in chloroform at 50% (w/v) concentration and mixed with acrylated CO (ACO) or acrylated DOD (ADOD) at various weight ratios. Crosslinked polymer networks were formed by free radical-initiated UV photopolymerization of the mixture solution. The initiator solution (0.1 g of DMPA dissolved in 1 mL of 1-vinylpyrrolidinone) was added to the reaction mixture at 2% (DMPA w/w macromer). Polymer samples were prepared as thin films with a thickness of ca. 100 μm by simple solution casting. Then, 0.7 mL of solution containing the reaction mixture was placed between two glass plates (150 mm × 150 mm) and then polymerized for 20–70 min using a low-intensity UV lamp (20 W) at 366 nm under air at room temperature.

Characterization of Crosslinked Polymer Networks

Gel contents, the extents of conversion of acrylated derivatives with crosslinking agent to the crosslinked networks, were measured using chloroform extraction. After polymerization, samples were dried under vacuum for 24 h. The films were weighed (W_1), and were then extracted with chloroform for 24 h. The films were dried again and weighed (W_2). The gel content was calculated as W_2/W_1.

To measure the tensile properties of the crosslinked polymer networks, the tensile tests specimens with a dimension of 45 mm × 5 mm were prepared by cutting the sheets. Tensile tests were performed using a universal testing machine (LR-30 K, Lloyd Instruments, Hampshire, UK) at room temperature according to ASTM D638 [17].

Lipase Degradation

Crosslinked polymer network films (initial weight: 0.14 g, film dimensions: 30 mm × 30 mm, and thickness: 0.10 mm) was immersed in 100 mL of 0.1 M phosphate buffer solution (pH 7.2) which contains lipase enzyme (7,000 units, 0.01 g)

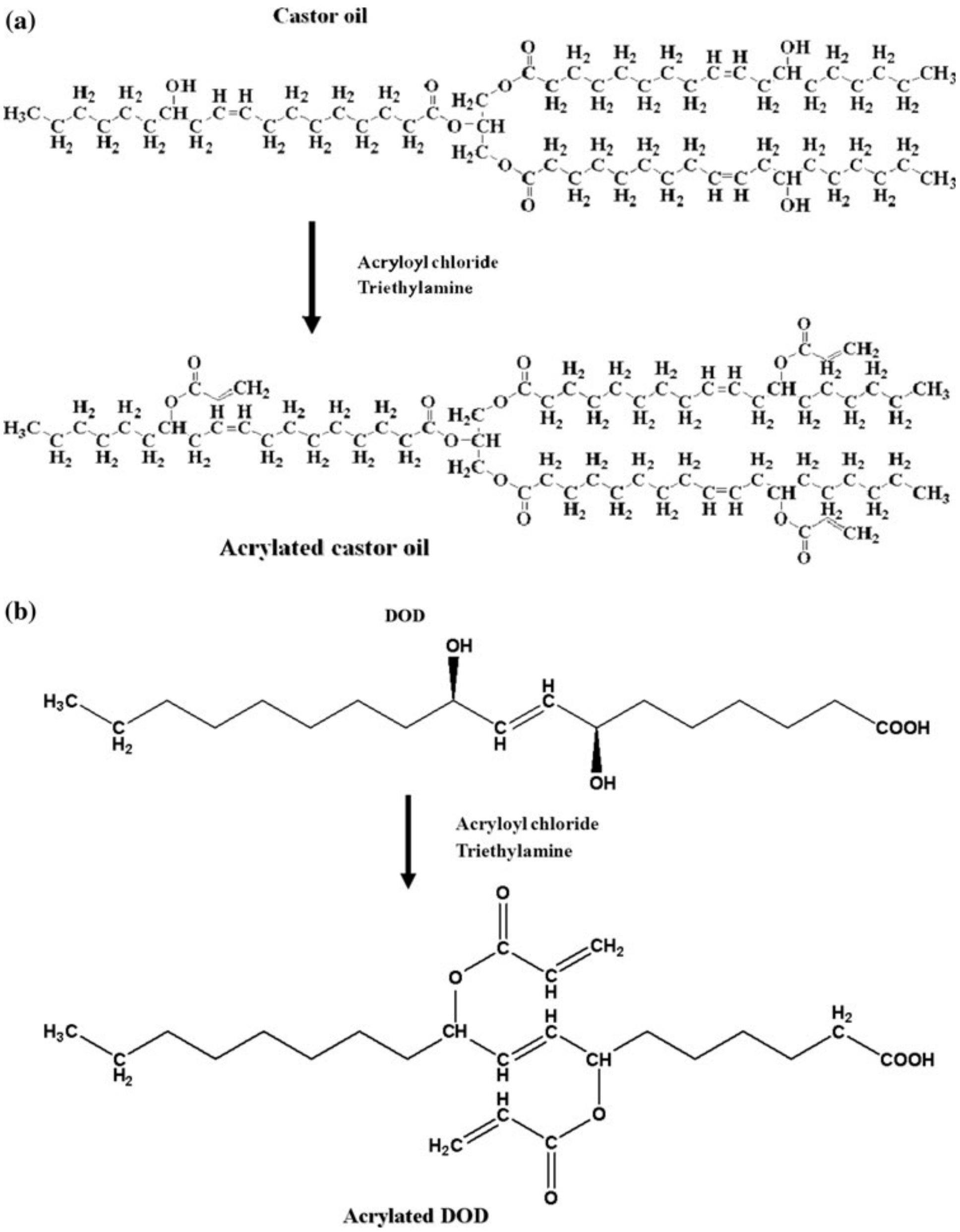

Fig. 1 Chemical structures of **a** CO and **b** DOD before and after acrylation

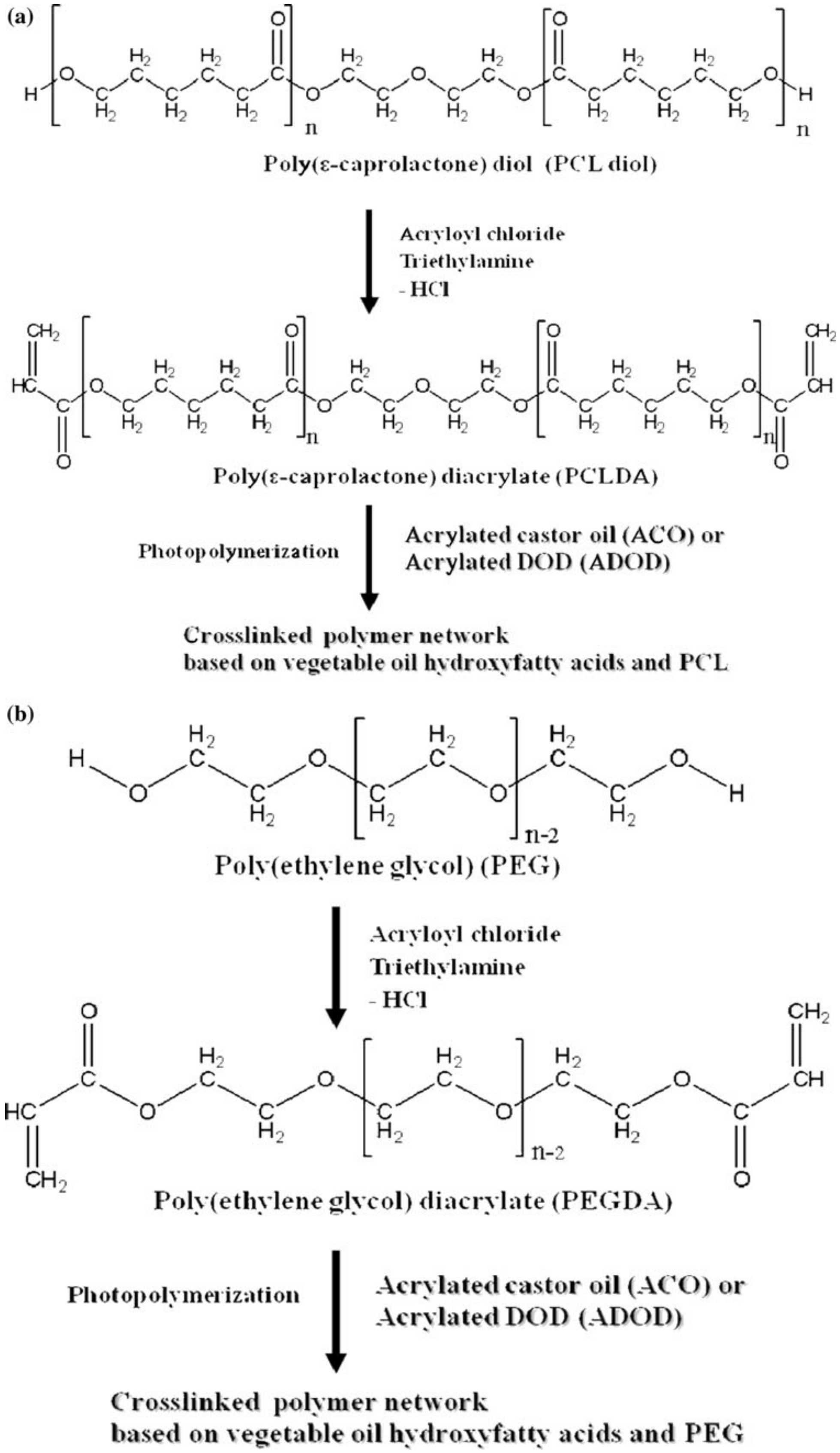

Fig. 2 Reaction schemes for the synthesis of polymerizable diacrylate and crosslinked polymer network. **a** HFAs/PCL polymer and **b** HFAs/PEG polymer

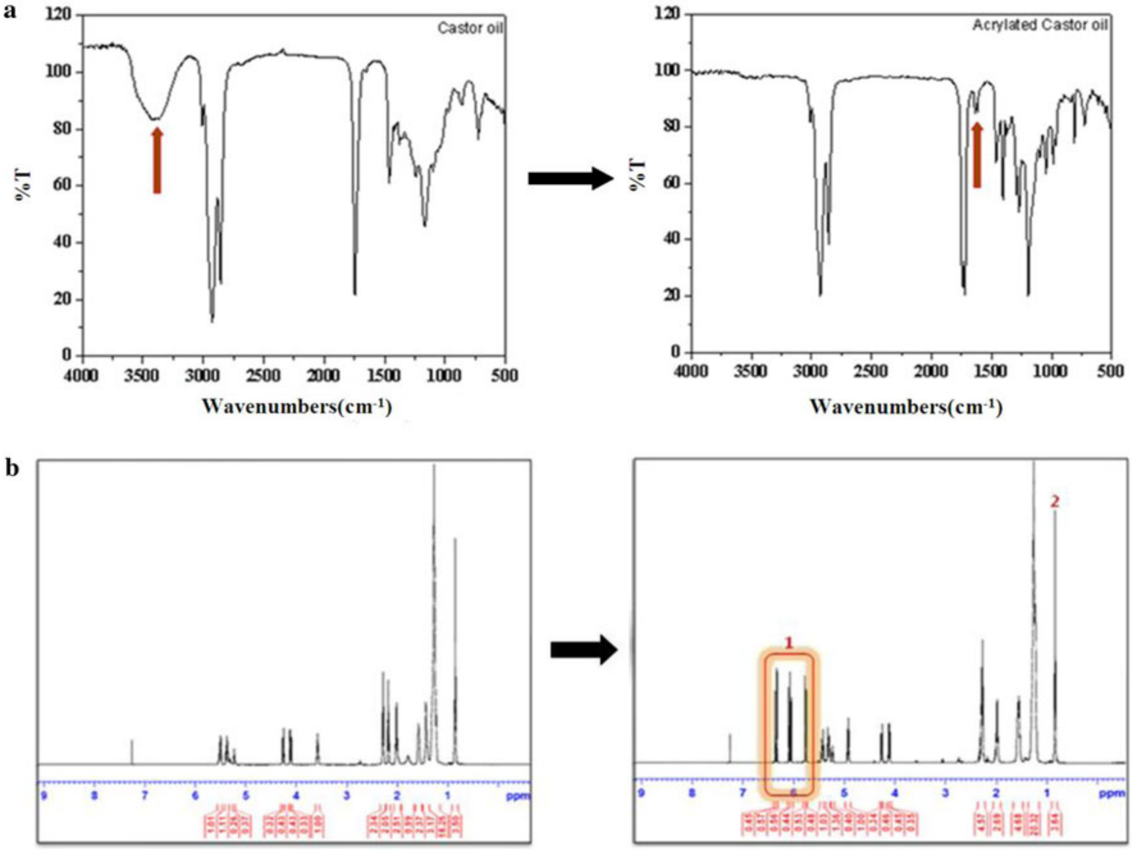

Fig. 3 **a** FT-IR spectra of CO (*left panel*) and ACO (*right panel*) and **b** ^{1}H-NMR spectra of CO (*left panel*) and ACO (*right panel*). Peaks 1 and 2 are acrylate protons and protons in the terminal methyl groups, respectively

in a sterilized conical flask. The reaction mixture was incubated at 37 °C with shaking at 200 rpm. The films were periodically removed, rinsed with water and dried to constant weight before analyses. Weight loss was monitored gravimetrically at various intervals of time.

Results and Discussion

Synthesis and Characterization of Polymerizable Acrylated Derivatives

Figure 1a, b show the chemical structures of CO and DOD before and after acrylation. The overall reaction schemes for the synthesis of polymerizable acrylated derivatives and the crosslinked polymer networks are shown in Fig. 2a, b. The FT-IR spectra of CO and ACO are shown in Fig. 3a. An absorption band at 3,414 cm^{-1} shown in CO is attributable to the hydroxyl group, which disappeared in ACO due to acrylation. The peaks at 1,642 cm^{-1} in ACO are ascribed to the double bond signals of acrylate functionalities. The formation of ACO was also confirmed through the ^{1}H-NMR spectrum as shown in Fig. 3b. The vinyl groups of ACO appeared within the range of 5.79–6.43 ppm. The conversion of CO to ACO was calculated as 93% using the integral intensities of peaks 1 (acrylate protons) and 2 (protons in the terminal methyl groups) from the ^{1}H-NMR spectrum. The acrylation reaction of hydroxyl groups in CO with acryloyl chloride has been previously reported [20]. Similarly, DOD was converted to ADOD with 99% conversion. The FT-IR and ^{1}H-NMR spectra of DOD and acrylated DOD are shown in Fig. 4a, b.

The chemical structures and reaction schemes for the synthesis of two crosslinking agents (PCLDA and PEGDA) are also shown in Fig. 2a, b. They were used as crosslinking agents due to their biodegradable and biocompatible properties. PEGDA was synthesized from PEG (molecular weight 20,000) with a conversion of 98%. PCLDA was also synthesized from PCL diol (molecular weight 2,000) with a conversion of 88%. The FT-IR and ^{1}H-NMR spectra of PEGDA and PCLDA were reported in our previous papers [17, 19].

Gel Contents and Tensile Properties of Crosslinked Polymer Networks

Various crosslinked polymer networks were synthesized by altering the weight ratio of acrylated derivatives (ACO and ADOD) to the crosslinking agent, the molecular weight of PEG (258 and 20,000), and the type of crosslinking agents

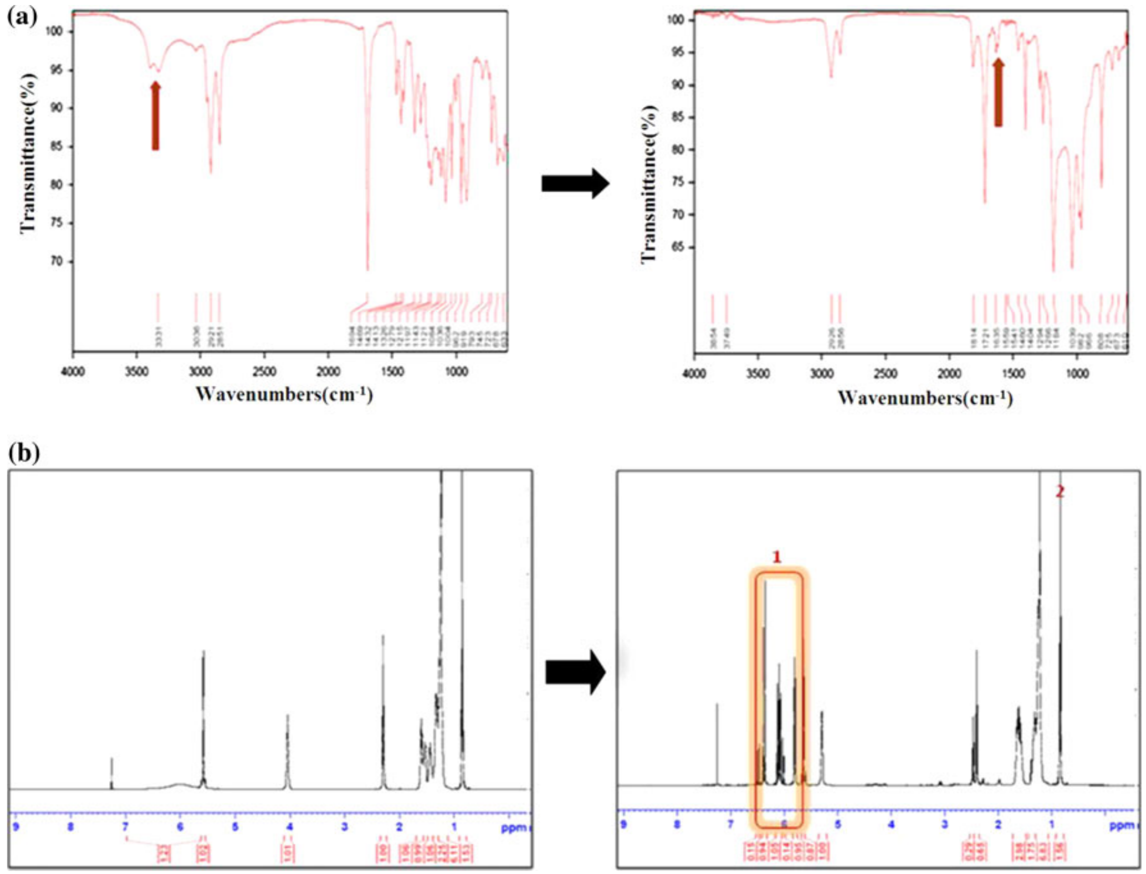

Fig. 4 **a** FT-IR spectra of DOD (*left panel*) and ADOD (*right panel*) and **b** ^{1}H-NMR spectra of DOD (*left panel*) and ADOD (*right panel*). Peaks 1 and 2 are acrylate protons and protons in the terminal methyl groups, respectively

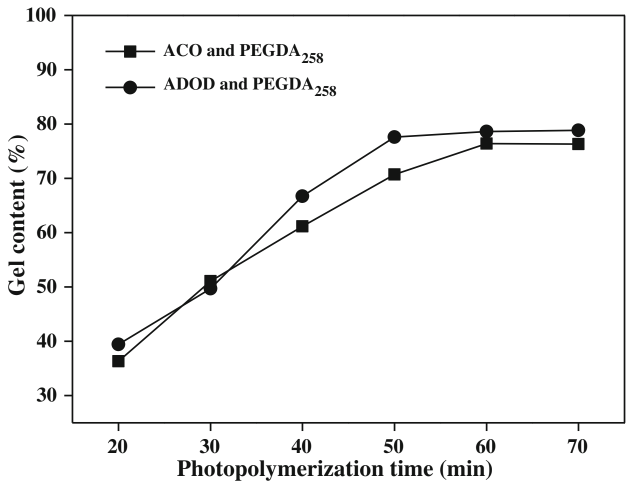

Fig. 5 Effect of photopolymerization time on gel contents of CO- and DOD-based polymer networks with 50% PEGDA (molecular weight 258) as the crosslinking agent

(PEGDA and PCLDA) to control the mechanical properties and degradation rates. The extents of conversion of acrylated derivatives (ACO or ADOD) with 50% PEGDA (molecular weight 258) to the crosslinked networks (gel content) with the exposure time to UV light are shown in Fig. 5. The gel contents of both CO- and DOD-based polymer networks increased to constant values with UV irradiation time and ranged from 39 to 78%. The highest gel contents were obtained when the photopolymerization time was over 60 min. The maximally cured films with 75–78% gel content were used in all tensile and degradation tests.

The tensile properties of various CO-based photopolymerized networks are shown in Fig. 6a–c. The tensile strengths of polymer networks prepared from low molecular weight (258) PEGDA as the crosslinking agent were less than 0.5 MPa, while higher values (1.2–2.3 MPa) were obtained with polymers from high molecular weight (20,000) PEGDA. Polymers from PCLDA (molecular weight 2,000) showed low tensile strengths (<1 MPa). Elongation at breaks of polymer networks prepared from ACO and PEGDA (molecular weight 258) decreased with an increasing PEG fraction, ranging from 6 to 9%, due to the low flexibility of low molecular weight PEG compared with ACO. Higher elongations of 17–20% were obtained from the networks prepared with ACO and high molecular weight PEG because PEG 20,000 is more flexible. With PCLDA as crosslinking agent, elongations of 12–21% were obtained.

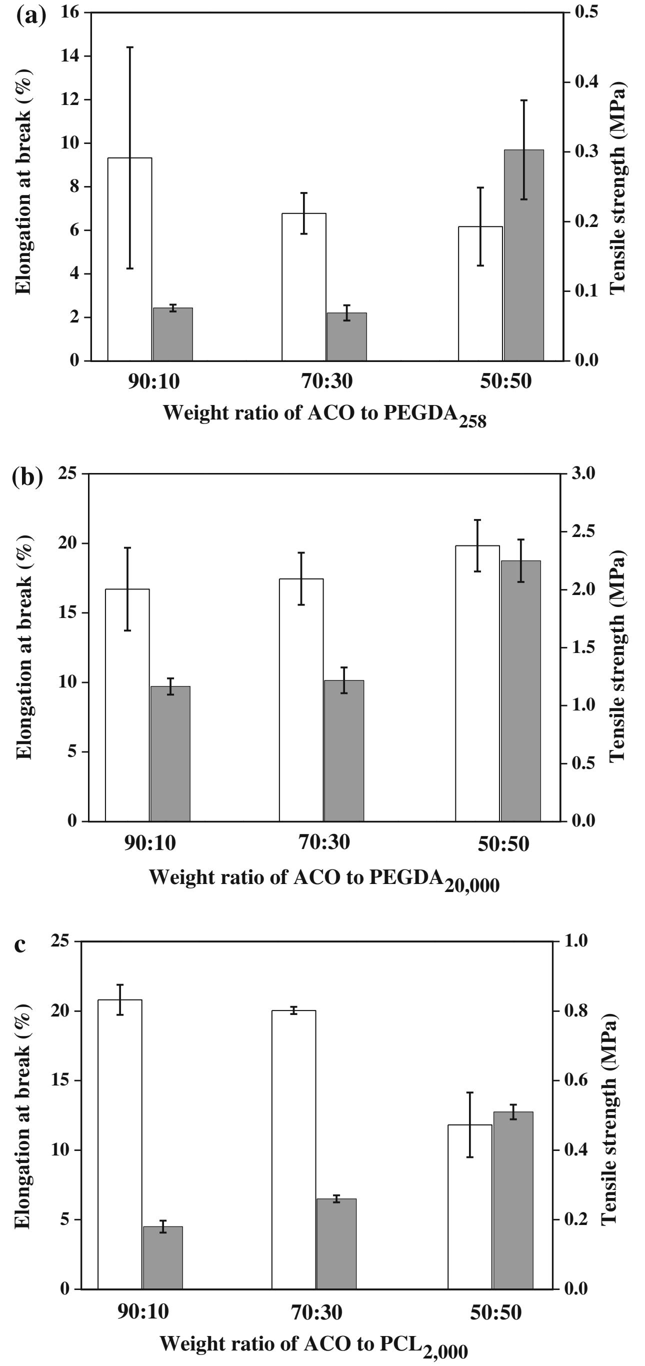

Fig. 6 Elongation at breaks (*white*) and tensile strengths (*grey*) of CO-based polymer networks with **a** PEGDA (molecular weight 258), **b** PEGDA (molecular weight 20,000), and **c** PCLDA (molecular weight 2,000) as the crosslinking agent

The mechanical properties of DOD-based polymer samples (50% crosslinking agents) are shown in Fig. 7. The tensile strengths and elongation at breaks of polymer networks prepared from low molecular weight (258) PEGDA were 0.5 MPa and 6%, respectively. Much higher tensile strength and elongation (4.0 MPa and 56%) were obtained with polymers from high molecular weight (20,000) PEGDA. Polymers from PCLDA (molecular weight 2,000) showed moderate tensile strength and elongation (2.7 MPa and 15%).

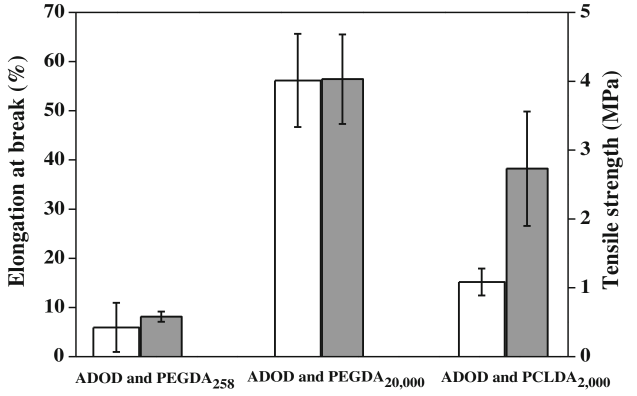

Fig. 7 Elongation at breaks (*white*) and tensile strengths (*grey*) of DOD-based polymer networks with 50% PEGDA (molecular weight 258), PEGDA (molecular weight 20,000), or PCLDA (molecular weight 2,000) as the crosslinking agent

In summary, the highest tensile strength and elongation at break were obtained with polymers from high molecular weight (20,000) PEGDA. DOD-based polymer networks showed higher tensile strengths and elongation at breaks than CO-based polymers at the same compositions. By changing the type and composition of HFAs/crosslinking agents, tensile strengths and elongation at breaks of the vegetable oil-based polymer networks could be controlled. The ranges of tensile strengths and elongation at breaks obtained were 0.07–4 MPa and 6–56%, respectively. These values were lower than those of soybean oil-based polymer networks previously reported by us (0.5–11 MPa and 7–200%) [17]. Compared with current petrochemical-based polymers, elongation at breaks of these vegetable oil-based polymers are comparable but tensile strengths are lower. More efforts should be devoted to improving their mechanical properties in order to ultimately replace petroleum-based polymers with more environmentally benign alternatives.

Polymer Degradation

Figure 8a and b show lipase degradation characteristics of vegetable oil HFAs-based polymer networks (50% crosslinking agent) in a phosphate buffer solution at 37 °C. Biodegradation usually refers to mineralization to CO_2 and water. In this study, however, only weight losses in water-soluble fraction were measured to monitor polymer degradation. In fact, lipid hydrolysis could occur in the apparently non-degraded samples because they are less soluble in water. All polymer samples showed weight losses during the test despite some petroleum-based components (crosslinking agents) being introduced. The order of weight losses for both CO- and DOD-based polymers

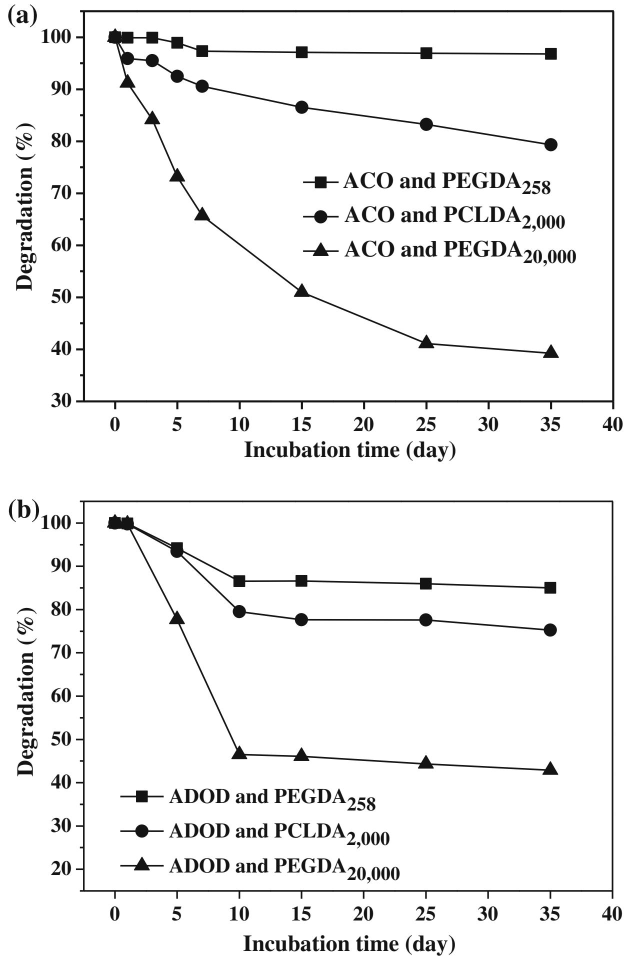

Fig. 8 Degradation curves of **a** CO-based polymers and **b** DOD-based polymers with 50% PEGDA (molecular weight 258), PEGDA (molecular weight 20,000), or PCLDA (molecular weight 2,000) as the crosslinking agent

was: polymer from PEGDA (molecular weight 20,000) >polymer from PCLDA (molecular weight 2,000) >polymer from PEGDA (molecular weight 258). The degradation rate of the polymer network is a function of the crosslinking density, as well as the hydrolytic and enzymatic susceptibility [18, 21]. Hydrophilic polymers prepared from PEGDA (molecular weight 20,000) degraded fast in lipase solution. A decrease of 57–60% of their initial weights were observed in 35 days, which were higher than 20–25% degradation of polymers prepared from biodegradable PCLDA during the same period. The weight losses of polymers prepared from PEGDA (molecular weight 258) was only 3–15%, indicating that high crosslinking density of the polymer network resulted from low molecular weight PEG might block the lipase attack sites, i.e., the ester bonds present in ACO or ADOD. Biodegradability of PEG and its derivatives by activated sludges has been reported [22]. Plastic foams based on soybean oil or castor oil were also proved to be biodegradable during soil burial [23–25].

Conclusion

We prepared novel biodegradable photo-crosslinked polymer networks from two vegetable oil HFAs, CO and microbially transformed DOD. PEGDA and PCLDA macromers were synthesized to use as crosslinking agents. Various crosslinked polymer networks were prepared by changing the composition of the reaction mixture, and the type and length of crosslinking agent. Tensile strengths and elongation at breaks ranged from 0.07 to 4 MPa and 6 to 56%, respectively, depending on the composition of reaction mixture. The order of degradation for the polymer networks was: polymer from PEGDA (molecular weight 20,000) >polymer from PCLDA (molecular weight 2,000) >polymer from PEGDA (molecular weight 258). Mechanical properties were superior with polymers prepared from DOD than from CO.

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