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Fully Bio-based Polymers Derived from Acrylated Epoxidized Soybean Oil by Thiol-ene Reaction

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Abstract: It has been estimated that more than 8.3 billion tonnes of plastics have been produced over the past decades and about 60 % of plastics have ended up either in landfills or in the natural environment. With the rapid growth of consumerism, research on innovative starting materials for preparation of polymers may help to reduce the negative impact of petroleum-based plastic materials on the global ecosystem and on animal and human health. Therefore, photochemical thiol-ene coupling reaction of squalene was performed to obtain thiol functional groups. Then, hexathiolated squalene was used as a cross-linker in UV curing reactions with acrylated epoxidized soybean oil. Two photoinitiators, 2-hydroxy-2-methylpropiophenone and ethylphenyl (2,4,6-trimethylbenzoyl) phosphinate, were tested in different quantities. Rheological properties of compositions were monitored by real time photorheometry. The obtained polymers were characterized by differential scanning calorimetry and thermogravimetry. Polymers possessed higher storage modulus and thermal characteristics due to the higher yield of insoluble fraction when ethylphenyl (2,4,6-trimethylbenzoyl) phosphinate was used as photoinitiator.

Keywords: thiol-ene; soybean oil; hexathiolated squalene; UV curing; biobased polymer

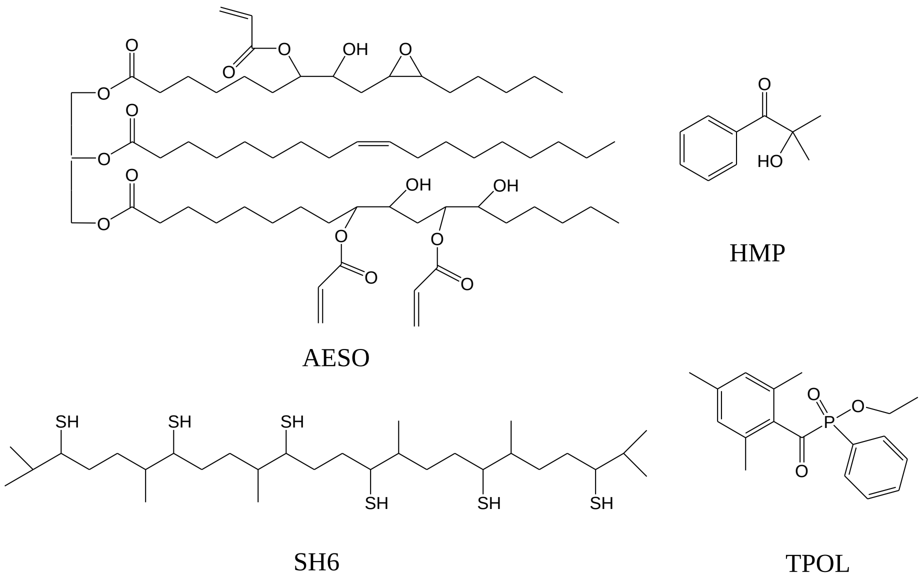
1. Introduction

The availability of petroleum-based resources has decreased significantly with the increase of worldwide demand for energy. Indeed, the depletion of fossil reserves associated with serious ecological problems related to greenhouse gas emissions forced researchers to develop new polymeric materials based on renewable and sustainable sources.

Acrylated epoxidized soybean oil (AESO) is already used in industry due to the various functional groups such as acrylic, epoxy, and hydroxy groups, and has Ebecryl 860 trademark [1]. AESO was already polymerized with various petroleum-derived compounds, such as styrene, divinylbenzene [2,3], as well as plant-derived compounds such as vanillin acrylates [4].

Biobased thiols synthesized from squalene and eugenol have been reported as suitable for thiol-ene reaction with the occurrence of side reactions that led to incomplete thiol-ene reaction [5]. Incomplete curing in case of using hexathiolated squalene (SH6) as thiol has been reported previously [6]. SH6 has a compact structure with a short distance among thiol groups and a quite hindered position of these groups in the whole molecular structure. These characteristics can lead to serious topological restrictions leading to an incomplete reaction and therefore to an undesired imbalance between thiol and acryloyl groups.

Commercially available petroleum-derived thiols have been already tested in photochemical thiol-ene rection with AESO [7,8]. Bio-based SH6 has been tested in thermal polymerization of AESO using 1-methylimidazole as a catalyst previuosly [9]. Photopolymerization is quite advantageous in front of thermal polymerization due to high reaction rates and performance at ambient conditions. Therefore, hexathiol synthesized from squalene (SH6) was selected for stoichiometric UV curing thiol–ene reaction with AESO (Scheme 1). Two photoinitiators, 2-hydroxy-2-methylpropiophenone (HMP) and ethylphenyl (2,4,6-trimethylbenzoyl) phosphinate (TPOL), were examined in thiol-ene reaction in different quantities to find out the highest yield of insoluble fraction (Scheme 1).



Scheme 1. Chemical structures of acrylated epoxidized soybean oil (AESO), hexathiolated squalene (SH6), 2-hydroxy-2-methylpropiophenone (HMP), and ethylphenyl (2,4,6-trimethylbenzoyl) phosphinate (TPOL).

2. Experiments

2.1. Materials

Acrylated epoxidized soybean oil (AESO, having an average number of acryloyl groups per molecule calculated from ^{1}H NMR spectrum as 2.7 and 0.3 of epoxide groups), squalene, thioacetic acid, 2,2-dimethoxy-2-phenylacetophenone, 2-hydroxy-2-methylpropiophenone (HMP), and ethylphenyl (2,4,6-trimethylbenzoyl) phosphinate (TPOL) were purchased from Sigma-Aldrich (Darmstadt, Germany). Inorganic salts were recieved from Scharlab (Barcelona, Spain). Methanol and chloroform were purchased from Carlo Erba (Barcelona, Spain). All materials were used without further purification.

2.2. Synthesis of Hexathiolated Squalene (SH6)

The product was obtained following a two-step procedure as previously reported [10], which includes photochemical thiol–ene coupling reaction of squalene with thioacetic acid and saponification of the resulting thioacetates. The purification of SH6 was carried out by silica gel column chromatography using hexane/ethyl acetate 8/2 mixture as eluent. The yield of the pale yellow viscous liquid was 70%.

^{1}H NMR (CDCl3, δ in ppm), 2.60 broad (–CH–S–, 6H), 1.10–1.95 unresolved broad signals (–CH2–, –CH– and –SH, 32H), and 0.8–1.05 broad (CH3–, 24H).

IR (KBr): 2955 (ν CH2 aliph.), 2923, (ν C–H aliph.) 2570 (ν S–H) cm^{-1}.

2.3. Chemical Structure Analysis

A Varian Gemini 400 spectrometer (Palo Alto, CA, USA) was used to register the ^{1}H NMR spectra. $CDCl_3$ was used as a solvent. For internal calibration the solvent signal corresponding to $CDCl_3$ was used: $\delta(^1H) = 7.26$ ppm.

A Perkin-Elmer (Llantrisant, UK) Spectrum BX II FT-IR spectrometer was used to record IR spectra of cross-linked polymers. The spectra were performed in KBr pellets and acquired from 10 scans. The range of wavenumber was (400–4000) cm^{-1}.

2.4. Real-Time Photorheometry

UV/Vis curing tests were performed with stoichiometric AESO and SH6 compositions (ratio of acrylate/SH groups 1:1) using 1-5 mol.% of photoinitiator (HMP or TPOL) (Table 1) on a MCR302 rheometer (Anton Paar, Graz, Austria) equipped with the plate/plate measuring system. The Peltier-controlled temperature chamber with the glass plate (diameter 38 mm) and the top plate PP15 (diameter 15 mm) was used. The measuring gap was set to 0.1 mm. The samples were irradiated by UV/Vis light in a wavelength range of 250-450 nm through the glass plate of the temperature chamber using UV/Vis spot curing system OmniCure S2000 (Lumen Dynamics Group Inc., Mississauga, Ontario, Canada). Shear mode with the frequency of 1 Hz and shear strain of 1 % were used in all cases. Storage modulus G' was recorded as a function of irradiation time.

Table 1. Compositions of photopolymerization

Composition	**Photoinitiator (mol.%)**
1HMP	1
2HMP	2
3HMP	3
4HMP	4
5HMP	5
1TPOL	1
2TPOL	2
3TPOL	3
4TPOL	4
5TPOL	5

2.5. Soxhlet Extraction

A Soxhlet extractor was used to determine the amount of insoluble polymer fraction. The samples of the cross-linked polymers (0.2 g) were put into a filter package and placed in a Soxhlet apparatus. Extraction was performed with chloroform for 24 h. Insoluble fractions were dried under vacuum to a constant weight. The amount of insoluble fraction was calculated as the difference of the sample weight before and after extraction.

2.6. Differential Scanning Calorimetry

The glass transition temperature (T_g) of the photocross-linked polymers were estimated by differential scanning calorimetry (DSC). The measurements were performed on a DSC 8500 apparatus (Perkin Elmer, Llantrisant, UK) with a heating-cooling-heating rate of 10 °C·min^{-1} under a nitrogen atmosphere (nitrogen flow rate 50 mL·min^{-1}). The T_g value was taken as the middle point in the heat capacity step of the glass transition.

2.7. Thermogravimetric Analysis

Thermal stability of polymers prepared was determined by thermogravimetric analysis (TGA). The measurements were performed on a Perkin-Elmer TGA 4000 apparatus in the temperature range from room temperature to 800 °C at a heating rate of 20 °C·min^{-1} under nitrogen atmosphere (nitrogen flow rate 100 mL·min^{-1}).

3. Results

3.1. Kinetics of Photocross-linking

The kinetics of photocross-linking was monitored by real-time photorheometry. As an example, the typical curves of storage modulus G′ are presented in Figure 1. G′ increased very fast when irradiation of the reaction mixture started. This shows the quick chain size growth and the network formation in the initial part of photocross-linking. With the increase of concentration of photoinitiator, storage modulus changed unevenly. The highest storage modulus was obtained when 5 mol.% of HMP and 3 mol.% of TPOL were used (2.89 MPa and 2.67 MPa, respectively). These values were similar to those of AESO polymers with aromatic dithiols tested with the same real-time photorheometry method (2-9 MPa) [8]. G′ of compositions with TPOL increased very fast during the first 10 s and continued to increase slowly with time due to the gel aging and settled down into a steady-state (plateau) indicating the end of the gelation process. While G′ of compositions with HMP increased evenly until plateau was reached. Thus, the rate of photopolymerization and the value of G′ of the composition was the highest when 3 mol.% of TPOL was used.

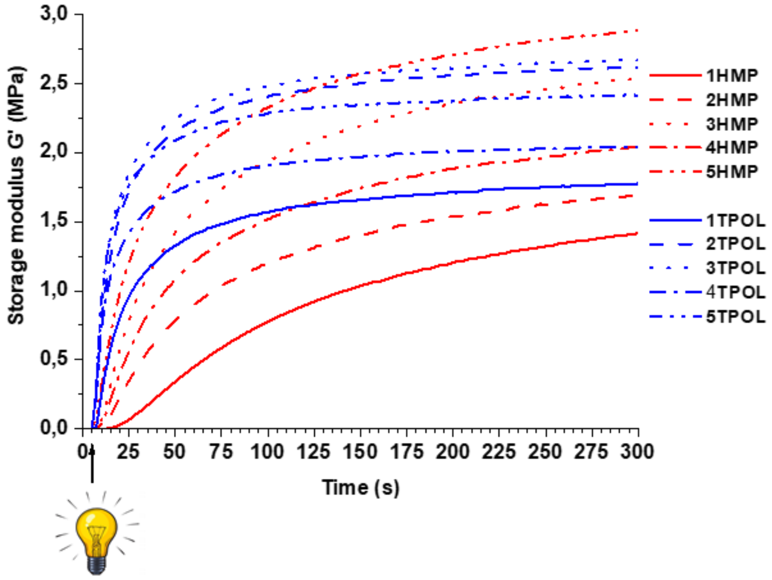


Figure 1. Curves of storage modulus G' versus irradiation time of the compositions with different photoinitiators.

3.2. Thermal Properties

Thermal characteristics of polymers investigated by DSC and TGA are summarized in Table 2. Glass transition temperatures (T_g) of polymers prepared using TPOL as photoinitiator (from -2 °C to 0 °C) were higher than those of polymers prepared with photoinitiator HMP (from -20 °C to -6 °C). The same behavior was noticed with the temperature at the weight loss of 10 % ($T_{dec.-10\%}$). This could be explaned by the higher yield of insoluble fraction of the crosslinked polymers (Table 2). Polymer **3TPOL** with the highest yield of insoluble fraction (98 %) exhibited the highest T_g and $T_{dec.-10\%}$ values

(0 °C and 344 °C, respectively). These values were similar to those of AESO polymer with aromatic dithiol (1 °C and 342 °C respectively) [8].

Table 2. Yield of the insoluble fraction and thermal characteristics of the cross-linked polymers.

Polymer	Yield of Insoluble Fraction [1] (%)	T_g [2] (°C)	$T_{dec.-10\%}$ [3] (°C)
1HMP	68	-20	333
2HMP	85	-6	333
3HMP	90	-7	330
4HMP	88	-9	331
5HMP	88	-11	331
1TPOL	96	-1	340
2TPOL	97	-1	342
3TPOL	98	0	344
4TPOL	97	-2	340
5TPOL	96	-2	334

[1] After Soxhlet extraction with chloroform for 24 h; [2] Glass transition temperature estimated by DSC; [3] Temperature at the weight loss of 10 % obtained from TGA curves.

4. Conclusions

Hexathiol was prepared from squalene as a starting biobased material. Hexathiolated squalene was used as monomer in the thiol-ene reaction with acrylated epoxidized soybean oil using two different photoinitiators, 2-hydroxy-2-methylpropiophenone and ethylphenyl (2,4,6-trimethylbenzoyl) phosphinate, in different quantities. Polymers had the higher storage modulus and thermal characteristics due to the higher yield of insoluble fraction when ethylphenyl (2,4,6-trimethylbenzoyl) phosphinate was used in the compositions. The obtained polymers of the present study can be considered as fully bio-based.

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Conflicts of Interest: The authors declare no conflict of interest.

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