Acrylated Vegetable Oils as Photocrosslinkable Materials

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ABSTRACT: Acrylated soybean oil was irradiated in the near UV in the presence of free radical photoinitiators. Given the high substitution density of acrylic moieties, these oils responded very rapidly to the photopolymerization giving high yields of crosslinked materials within a few seconds. The activity of three photoinitiators was compared and the ensuing networks were characterized in terms of crosslink density through swelling measurements. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3218–3221, 2006

Key words: renewable resources; epoxidized acrylated soybean oil; photopolymerization; radical polymerization; network formation

INTRODUCTION

UV-initiated photopolymerizations have received considerable attention in the last few decades, because of their application in the rapid and solvent-free curing of films, including adhesives, coatings, inks, varnishes, printing plates, and electronic resists.[1–4] Among these phtoreactive systems, free-radical polymerizations play a very important role, particularly with acrylates and methacrylates, which are among the most reactive monomers in this context. It is worth noting that triglyceride-based thermosets were the object of different investigations aiming at the study of their polymerization and the mechanical properties of the ensuing materials.[5,6]

We had recently begun a thorough investigation on the possible use of chemically modified vegetable oils as photocurable materials, and submitted a study on the preparation of castor and soybean oils bearing pendant acrylic and styrenic moieties[7] in view of their use in photocrosslinking reactions involving free radical and cationic initiation, respectively. The present report deals with the UV-induced free radical polymerization of acrylated soybean oil and the properties of the ensuing crosslinked material.

EXPERIMENTAL

Materials

The acrylated soybean oil used in this study (AESO), whose synthesis and characterization is reported else-

where,[7] contained an average of five acrylic moieties per triglyceride molecule (Scheme 1) and had a viscosity of 17 Pa s, measured at 500 s^{-1}. The photoinitiators selected to promote the crosslinking reaction of AESO were 2-hydroxy-2-methyl-1-phenyl-propan-1-one, 1-hydroxy-cyclohexyl-phenyl-ketone, and 2,2-dimethoxy-1,2-diphenylethan-1-one (respectively, Darocure 1173, Irgacure 184, and Irgacure 651 from Ciba-Geigy; Scheme 1). The other reagents and solvents were commercial products of high purity.

Acrylation of epoxidized soybean oil with acrylic acid

About 10 g (10.9 mmol) of epoxidized soybean oil having 4.9 epoxy groups by one molecule of soybean oil was dissolved in 10 g of chloroform and placed into a 250-mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser. The reaction mixture was brought to reflux under nitrogen and then 100 g (1.38 mol) of acrylic acid and 1 g (9 mmol) of hydroquinone were slowly added. The reflux was maintained for the reaction time, and at the end, the reaction mixture was poured into an excess of distilled water. The organic phase was dried over sodium sulfate and the solvent was evaporated under reduced pressure to isolate the acrylated oil (AESO).

Photopolymerization

Kinetic experiments called upon FTIR spectroscopy and were performed in a 0.1-mm-thick cell made up of a teflon spacer held between NaCl plates. Samples of the acrylated oil (AESO), diluted in methylene chloride (50% w/w), were introduced in the cell and exposed to the UV radiation (λ > 280 nm) of a medium-

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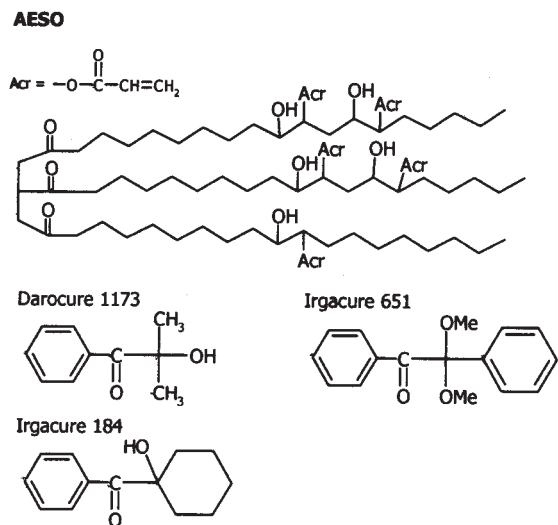
Scheme 1 Structure of the acrylated soybean oil and the photoinitiators used in this study.

pressure mercury lamp, similar to those used in the coating industry for the UV-curing of varnishes and printing inks. Its power output was 80 W cm^{-1}. Samples were passed several times under the lamp (with a gap of 10 cm), at a constant speed of 30 m min^{-1}. The kinetic set up was followed *in situ* between the NaCl pellets, which avoid the use of internal standard peak, since the thickness of the films remained constant during the kinetic studies. The intensity of the peak at 1619 cm^{-1}, attributed to C=C of acrylic moieties, was followed as a function of time.

For the gel content measurements, 2 g of AESO and the appropriate quantity of photoinitiator were placed in a 1-mm-thick teflon mold. Samples were irradiated with the lamp as described earlier for a cumulated time of 360 s. After completion of the reaction, the photopolymer was soxhlet extracted with methylene chloride for 24 h. The gel content was calculated as the mass of the polymer remaining after extraction relative to the mass of the initial sample.

Analytical techniques

Infrared spectroscopy was conducted with a Perkin–Elmer Paragon-1000 FTIR spectrophotometer. The electronic absorption spectra of the different photoinitiators or photosensitizers were obtained from samples diluted in spectrophotometric dichloromethane, using a Thermospectronic UNICAMUV 500 apparatus. The extent of swelling in methylene chloride after irradiation was assessed by measuring the differences in weight between the dried and the swollen film. The weight of the swollen film was measured immediately after blotting it between sheets of filter paper. The following equation was used to calculate the swelling ratio S:

$$S = \frac{W_s - W_d}{W_d}$$

where W_s and W_d are the weight of the swollen and dried films, respectively.

RESULTS AND DISCUSSION

Photopolymerization of AESO

When the acrylated soybean oils were exposed to the UV radiation in the presence of Darocure, its free radical polymerization took place rapidly and led to the product PPAESO. Figure 1 shows the FTIR spectra of AESO before and after 12 s irradiation in the presence of 2% of Darocure. The occurrence of the polymerization was clearly confirmed by the strong decrease in the intensity of the acrylate moiety peaks (i) at 1617–1636 cm^{-1} for the C=C stretching, (ii) at 1406 cm^{-1} for the in-plane CH$_2$ deformation, (iii) at 810 cm^{-1} for the out-of-plane deformation, and (iv) at 984 cm^{-1} for the out-of-plane deformation. Moreover, the double carbonyl peak, attributed to both the glyceride and acrylate ester moieties, became a single absorption after the transformation of the acrylic moiety into a saturated ester group, following its polymerization.

A brief kinetic study was also performed by following the decrease in the intensity of the peak at 1619 cm^{-1} with time, which monitored the rate of acrylate moiety consumption during the polymerization. The results are presented in Figure 2 and confirmed the very high rate of polymerization of AESO, and thus, its suitability as an additive in photocurable films. The spurious presence of variable amounts of residual atmospheric oxygen in the AESO films was the most probable cause of the very modest induction period observed in some cases.

An increase in the concentration of photoinitiator induced a modest increase in the rate of polymerization (Fig. 2), probably because 2% of Darocure already ab-
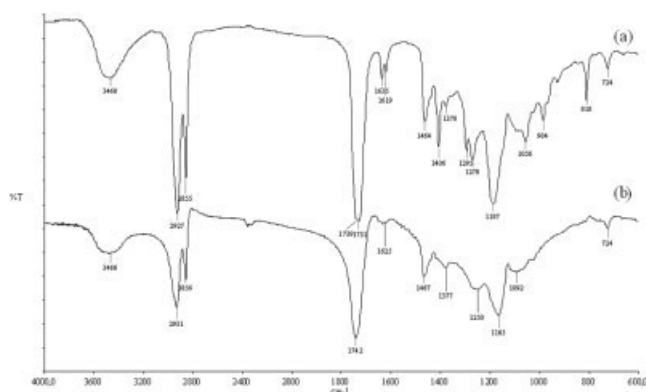
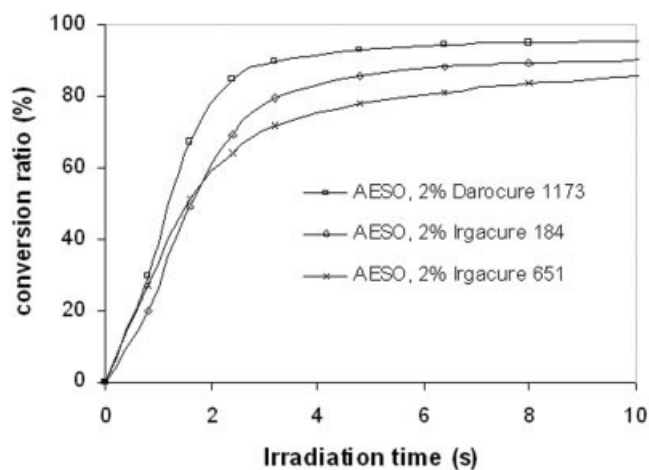**Figure 1** FTIR spectra of AESO before (a) and after (b) irradiation.
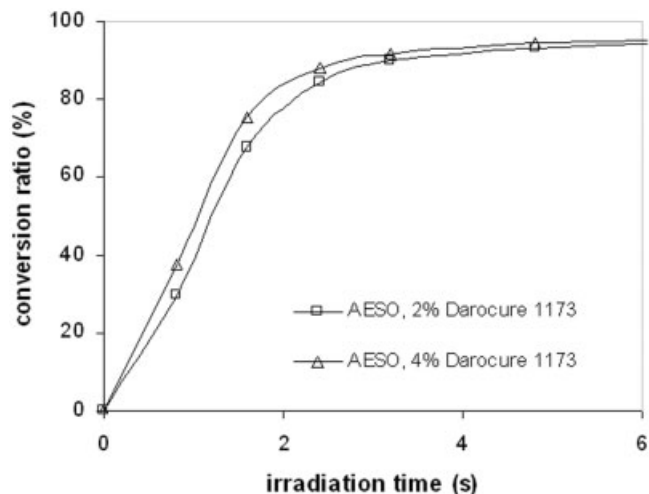
Figure 2 Kinetics of the AESO C=C consumption with two concentrations of Darocure 1173.
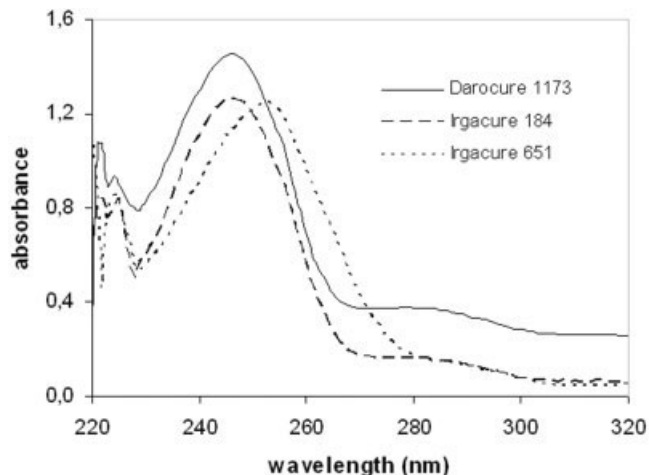
sorbed most of the relevant radiation. The fact that the acrylic moiety consumption did not reach 100% was related to the lack of mobility of the crosslinked product.

Figure 3 shows the conversion profiles for the photopolymerization of AESO with different photoinitiators, which shows that Darocure 1173 was the most efficient one and Irgacure 651 the least efficient. To explain these results, we focused on the photochemical behavior of the different photoinitiators. Their absorption spectra are depicted in Figure 4 and the values of the absorption maxima and the corresponding extinction coefficients are summarized in Table I.

All absorption spectra had the same shape and their maxima were all located around 250 nm, with a shoulder near 285 nm. However, Darocure 1173 had the highest extinction coefficient, followed by Iracure 184, and finally Iracure 651, i.e., this parameter followed

Figure 4 UV absorption spectra of the different photoinitiators at 10^{-5} mol/L in dichloromethane.

the same trend as the efficiency of the photoinitiators, a feature which explains the latter behavior.

Characterization of the irradiated oils

The results of the extraction of the remaining soluble polymers are presented in Table II, together with the final consumption of acrylic moieties. First, the amount of crosslinked product never attained 100%, even for complete monomer unit consumption. This suggests that diffusion problems, associated with the very high viscosities attained at high gel conversions, strongly affected the macromolecular mobility, and therefore, a small but significant proportion of growing chains could not participate in the network formation and gave instead soluble oligomeric products. The differences observed between experiments carried out with different proportions (2% or 4% w/w) of initiator were not significant, confirming the interpretation given earlier in the context of the polymerization kinetics for these two experiments.

Second, values of maximal conversion ratios were systematically higher than the corresponding values of gel content. This can be readily rationalized by the fact that the conversion takes into account all acrylate double bonds that had reacted, including those that led to the formation of soluble oligomers quenched into the very viscous network.

Figure 3 Kinetics of the AESO C=C consumption with 2% of various photoinitiators.

TABLE I
Maximum Absorption Wavelengths and Molar
Extinction Coefficients of the Photoinitiators

	ε (mol L^{-1} cm^{-1})	λ_{max} (nm)
Darocure 1173	14,781	247
Irgacure 184	14,460	246
Irgacure 651	12,855	253

TABLE II
Gel Contents and Maximal Conversion Ratios of the Photopolymers

|	Gel content (%)	Maximum conversion (%)
2% Darocure 1173	76.1	97.06
2% Irgacure 184	80.2	92.6
2% Irgacure 651	80.7	90.6
4% Darocure 1173	81.6	97.1

Third, the gel content increased when a less-efficient photoinitiator was used. This was explained in terms of classical nonlinear polymerization behavior. When a more efficient photoinitiator was used, the polymerization rate increased, and consequently, the onset of gel formation occurred more rapidly, leaving a higher proportion of residual oligomers.

Figure 5 shows the swelling behavior of PPAESOs obtained with 2% and 4% of Darocure 1173. The equilibrium swelling ratios were used to calculate the average mass between two crosslink points and the crosslink density of the network using the classical Flory–Rehner equations:

$$\overline{M}_c = \frac{V_{s,\,mol} d_p \left(\dfrac{\Phi_p}{2} - \Phi_p^{1/3} \right)}{\ln(1 - \Phi_p) + \Phi_p + \Phi_p + \chi \Phi_p^2}$$

$$n = \frac{-\left(\ln(1 - \Phi_2) + \Phi_2 + \chi \Phi_2^2 \right)}{v_{s,mol} \left(\Phi_2^{1/3} - \dfrac{\Phi_2}{2} \right)}$$

where $\overline{M}_c$ is the average molecular mass between two crosslink points, $V_{s,mol}$ is the solvent molar volume (here 64.34 mL mol^{-1} for methylene chloride at room temperature), d_p is the polymer density (here we took a value close to unity, as calculated from the weight and the volume of the polymer samples under inves-
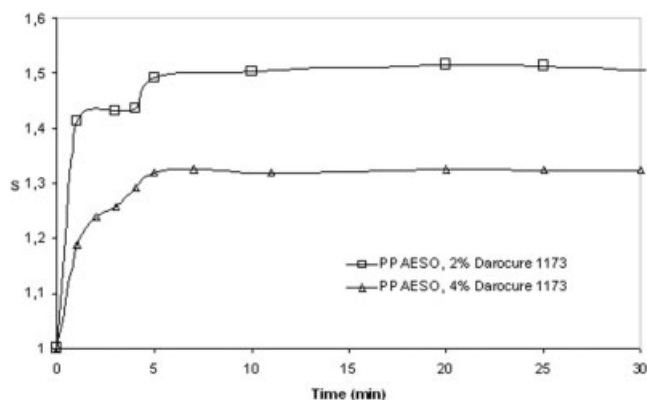
TABLE III
Crosslink Densities (n) and Average Molecular Mass between Two Crosslink Points ($\overline{M}_c$)

	$\overline{M}_c$ (g/mol)	n (mol/cm^3)
2% Darocure	683	0.0015
4% Darocure	191	0.0048

tigation), ϕ_p is the volume fraction of the crosslinked polymer network, n is the crosslink density, and χ is the Flory polymer–solvent interaction parameter (here we took the value of 0.856 for polymethylmethacrylate at room temperature[8]).

Table III shows the values of n, and $\overline{M}_c$ for the two samples. The networks formed were quite dense, as expected for starting triglyceride bearing five polymerizable acrylic moieties. This high crosslink tightness is promising in terms of the envisaged application of these photoreactive oils in thin film coatings.

Some preliminary experiments were carried out using dynamic mechanical analyses and showed that the modulus of oil-based films was about 10^9 and 10^7 Pa, for the glassy and rubbery states, respectively. These performances are encouraging, but more work is needed. Work is in progress to confirm these relatively good properties.

CONCLUSIONS

This investigation showed that the acrylation of epoxydized soybean oils leads to a dramatic improvement of their photoactivity, since they can react under UV radiation and form crosslinked photopolymers within a few seconds. The photopolymerization of AESO with a small amount of photoinitiator gave very satisfactory results, characterized by high gel content and conversions, even in the presence of atmospheric oxygen. This is very promising for the possible use of these modified commercial oils as vehicles in UV inks and other film coatings.

The mechanical properties of these materials as thin films are being assessed.

Figure 5 Room temperature swelling kinetics of two PPAESO samples in CH$_2$Cl$_2$.

References

1. Decker, C. Prog Polym Sci 1996, 21, 593.
2. Reiser, A. Photoreactive Polymers: The Science and Technology of Resists; Wiley: New york, 1989.
3. Roffey, C. Photogeneration of Reactive Species for UV Curing; Wiley: New York, 1997.
4. Fouassier, J.-P. Photoinitiation Photopolymerization and Photocuring: Fundamentals and Applications; Hanser Publishers: Munich, 1995.
5. La Scala, J.; Wool, R. P. Polymer 2005, 46, 61.
6. Khot, S. N.; La Scala, J. J.; Can, E.; Morye, S. S.; Williams, G. I.; Palmese, G. R.; Kusefoglu, S. H.; Wool, R. P. J Appl Polym Sci 2001, 82, 703.
7. Pelletier, H.; Gandini, A. Eur J Lipid Sci Technol, to appear. Pelletier, H. Ph.D. Dissertation, Institut National Polytechnique de Grenoble, 2005.
8. Hang, Q.; Hill, D. A.; Bernstein, G. H. J Vac Sci Technol B 2003, 21, 91.