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Research article

The Preparation and Characterisation of a Bioplastic Film from Acrylated Epoxidized Soybean Oil (AESBO)

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Abstract: This study successfully demonstrates the synthesis of epoxidized soybean oil (ESBO) via reaction with formic acid and hydrogen peroxide, followed by acrylation with varying ratios of acrylic acid. The characterization techniques, including FT-IR and ^{1}H-NMR, confirmed the formation of key functional groups such as oxirane and hydroxyl, as well as the reduction of carbon–carbon double bonds, indicating successful epoxidation and acrylation. The appearance of new peaks in the 1H-NMR spectra further supports the formation of the epoxide and acrylate functionalities. FT-IR analysis revealed clear spectral changes correlating with these transformations. The kinetics study using 5 wt% photoinitiator demonstrated that the acrylated epoxidized soybean oil (AESBO) film could be rapidly stabilized within 60 seconds under UV curing. These findings highlight the potential of AESBO as a sustainable precursor for bioplastic films, offering promising chemical stability. Further optimization may enhance its suitability for various biodegradable polymer applications.

Keywords: soybean oil; epoxidation; acrylation; UV cured; biopolymer

1. Introduction

Currently, vegetable oils are attracting increasing attention in various areas of research due to their biodegradability, environmental friendliness, and favorable performance characteristics [1]. There is a growing interest in replacing petroleum-based oils with vegetable oils, prompting the development of various chemical modification methods to produce fully biodegradable alternatives [2]. In terms of global production, soybean oil ranks among the highest, second only to palm oil. Between 2012 and 2016, soybean oil was widely utilized in numerous applications, both for consumption and industrial purposes. These include its use in lubricants, coatings, and printing inks, such as oil-based paints and ink formulations [3]. Soybean oil is a triglyceride rich in unsaturated fatty acids. It contains both saturated and unsaturated fatty acids, including stearic acid (a saturated fatty acid), oleic acid (with one double bond), linoleic acid (with two double bonds), and linolenic acid (with three double bonds), all of which are located along the fatty acid chains. A key characteristic of soybean oil is the presence of reactive double bonds within its chemical structure [4]. These double bonds enable the oil to undergo crosslinking reactions through processes such as polymerization, epoxidation, and UV curing. In particular, the modification of soybean oil via acrylation using acrylic acid, followed by UV curing, has gained increasing interest. This approach not only enhances the commercial value of soybean oil but also offers insights into the potential for similar modifications in other vegetable oils, supporting the development of sustainable, bio-based materials [5].

UV curing is an emerging technology that has gained significant attention in recent years for its precision, high processing speed, and alignment with sustainability objectives. It is regarded as an environmentally friendly method that aligns with the demands of modern industrial applications. Numerous studies have demonstrated the successful utilization of various vegetable oils, including sunflower oil, soybean oil, sesame oil, olive oil, and canola oil, in UV-curable systems. These oils are typically modified via acrylation reactions, in which acrylic acid serves as the primary reactant, producing materials that can be efficiently cured under UV irradiation [6]. In addition, other research has investigated the epoxidation of vegetable oils to facilitate UV curing [7, 8]. Because vegetable oils do not naturally contain epoxide groups, epoxidation is a necessary preliminary step. This process introduces epoxide groups onto the double bonds of fatty acid chains, typically using reagents such as hydrogen peroxide and formic acid. The resulting epoxidized oils can then undergo acrylation, forming acrylate groups capable of polymerizing under UV light.

One key factor enabling the UV-curable polymerization of vegetable oils is the acrylation process. Acrylation involves the introduction of acrylate (–CH=CH–COOR) or methacrylate groups into oil molecules, thereby incorporating vinyl functionalities (C=C) that can undergo radical polymerization. During UV curing, the addition of a photoinitiator generates free radicals that initiate polymerization of the vinyl groups, resulting in crosslinking and the formation of a polymer network. This modification renders the oils UV-curable and suitable for advanced material applications. Numerous studies have demonstrated the feasibility and efficiency of acrylating various vegetable oils. Acrylation increases the crosslinking density of cured films, thereby enhancing their mechanical properties, such as tensile strength and Young's modulus, due to the greater structural functionality of the prepolymers [9]. Additionally, the use of photoinitiators and suitable comonomers can optimize the UV curing process by reducing irradiation time and increasing double bond conversion efficiency [10]. For example, acrylated rapeseed oil (ARO) has shown improved UV-curing properties, especially when modified with a furan-based ester reactive diluent (UES), which significantly reduces viscosity. and enhances crosslinking density, leading to improved tensile strength and storage modulus [11]. The development of bioplastic films from the UV-curable polymerization of vegetable oils following acrylation offers several significant advantages. Primarily, by using sustainable and biodegradable alternatives to petroleum-based precursors, the technology addresses environmental concerns and resource depletion [1, 3]. Secondarily, UV curing is a high-speed, energy-efficient, and solvent-free processing method that enables film stabilization within seconds and is highly compatible with modern industrial sustainability objectives [6, 11]. This research, therefore, aims to investigate and analyze the structural and property changes in soybean oil after epoxidation with formic acid, followed by acrylation at varying ratios. Furthermore, it examines the film-forming ability of the acrylated product in the presence of a photoinitiator, focusing on the kinetics and optimal curing time for stable film formation.

2. Materials and Methods

2.1 Materials

Soybean oil (SBO) was sourced from Thai Vegetable Oil Public Company Limited, Thailand. Formic acid (90%) was obtained from Elago Enterprises Pty Ltd., Australia. Hydrogen peroxide (H_2O_2, 35%) was purchased from Chem-Supply Pty Ltd., Australia. Acrylic acid (AA, 99%) was supplied by Sigma-Aldrich Chemie GmbH, Germany. Ethyl acetate was purchased from Modern Chemical Co., Ltd., Thailand. The photoinitiator 2-hydroxy-2-methylpropiophenone (Darocur 1173; PI-1173) was purchased from Sigma-Aldrich, Germany. Sodium bicarbonate ($NaHCO_3$) and sodium chloride (NaCl) were obtained from Elago Enterprises Pty Ltd., Australia. Magnesium sulfate ($MgSO_4$) was sourced from Panreac Química S.L.U., Spain.

2.2 Preparation of ESBO

For the preparation of ESBO, a molar ratio of 1:4:4 (SBO: formic acid: hydrogen peroxide) was used.

Specifically, SBO (100 g), formic acid (23 g), and hydrogen peroxide (44 g) were mixed in a four-neck glass reaction vessel and maintained at 60°C for 2 hours. Laboratory installation of the epoxidation reaction apparatus used for soybean oil modification as shown in Figure 1. After completion of the reaction, the resulting oil was removed and cooled to room temperature. The product was then transferred to a separating funnel and washed with ethyl acetate, followed by repeated washes with distilled water, sodium bicarbonate ($NaHCO_3$), and sodium chloride (NaCl) until the aqueous phase reached pH 7. The cleaned oil layer was then separated, dried using magnesium sulfate ($MgSO_4$), and filtered through filter paper. The remaining solvent was removed by vacuum evaporation to obtain the purified ESBO—Schematic of ESBO reaction as shown in Figure 2.

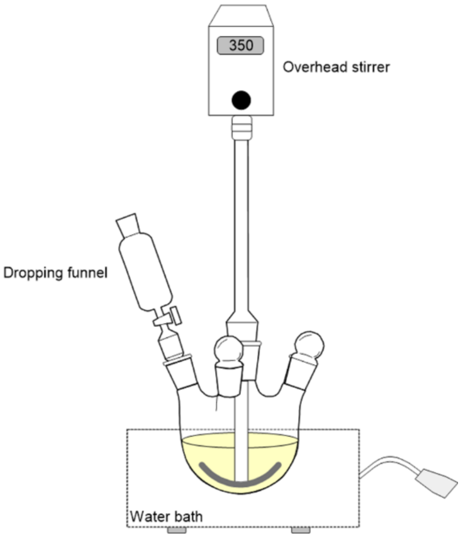

Figure 1. Example of installation of reaction equipment

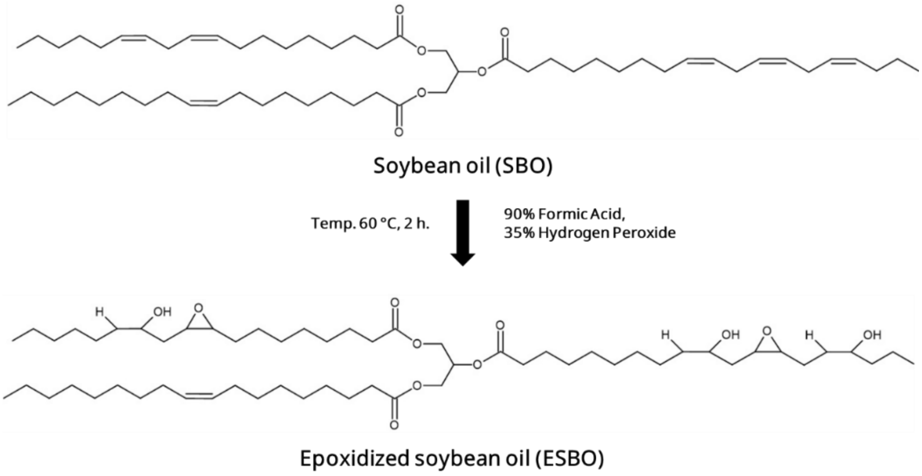

Figure 2. Schematic of ESBO reaction.

2.3 Preparation of AESBO

AESBO was prepared using ESBO-2–acrylic acid ratios of 1:1, 1:1.5, and 1:2 at 110°C for 8 h. Installation of acrylation reaction equipment is shown in Figure 3. After completion of the reaction, the AESBO was removed and allowed to cool to room temperature. It was then transferred to a separating funnel and washed with ethyl acetate, followed by repeated washings with distilled water, sodium bicarbonate ($NaHCO_3$), and sodium chloride (NaCl) until the aqueous layer reached neutral pH (7). The cleaned oil layer was then separated and dried using magnesium sulfate ($MgSO_4$), followed by filtration through filter paper. The solvent was subsequently removed by vacuum evaporation to obtain the purified AESBO—Schematic of

AESBO reaction as shown in Figure 4.

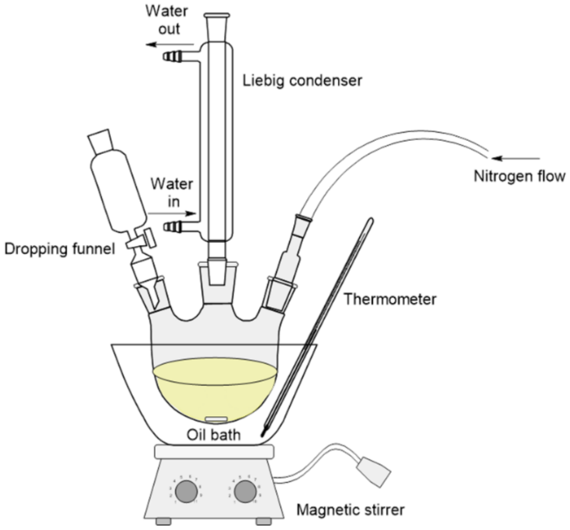

Figure 3. Installation of acrylic reaction equipment.

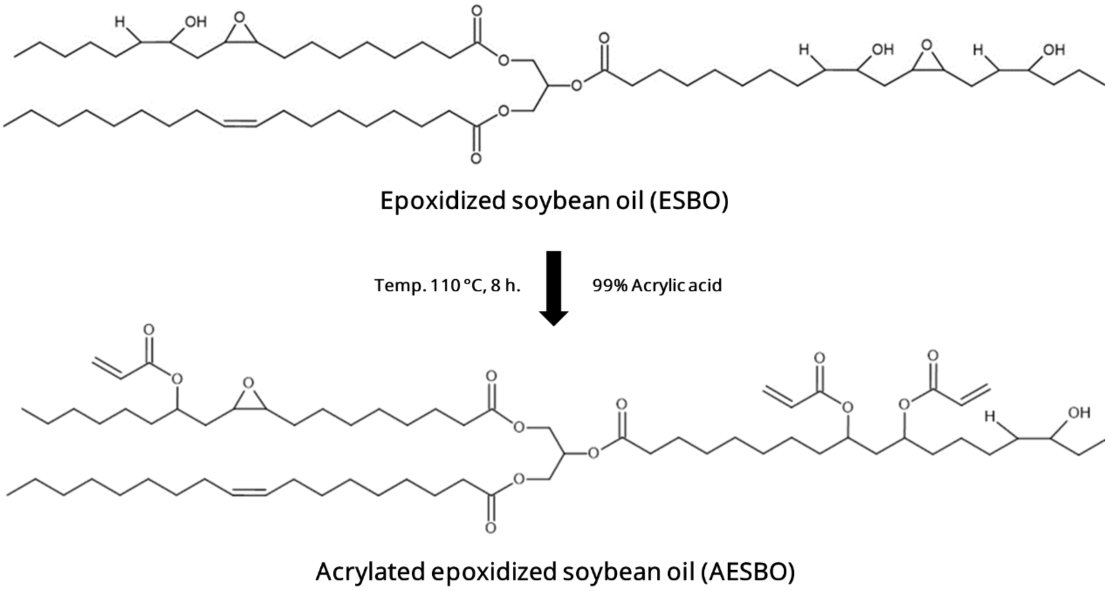

Figure 4. Schematic of AESBO reaction.

2.4 Preparation of the UV-curable bioplastic films

Photoinitiator (Darocur 1173) was incorporated at concentrations of 5 wt%. Darocur 1173 was added to AESBO-1, AESBO-1.5, and AESBO-2 formulations. Following this, the AESBO film samples were formed by casting into silicone molds with a cavity size of 4 cm x 10 cm x 0.3 cm and cured using a UV source with a power output of 400 W. The distance between the film samples and the center of the UV lamp was maintained at 15 cm. The UV curing kinetics were studied over 0-420 seconds. The preparation process for the UV-cured AESBO film is shown in Figure 5.

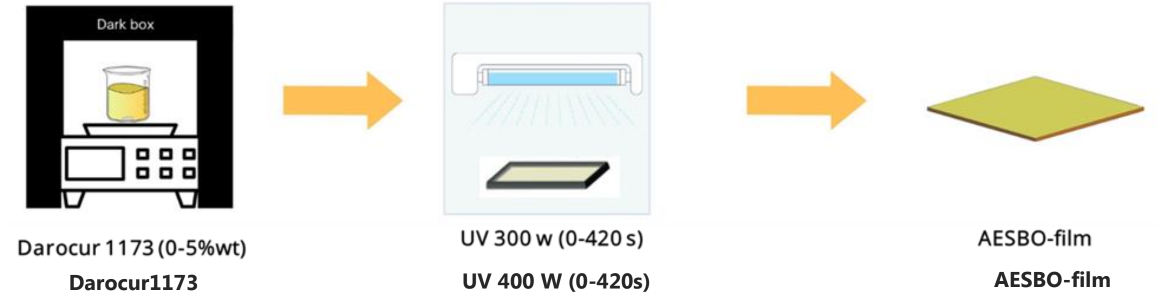

Figure 5. Preparation process of UV-cured AESBO film.

2.5 Chemical analysis of SBO

The chemical properties of the modified SBO were analyzed. The acid value was determined by titration to assess the free fatty acid content of the oil, following ISO 660:2009. The hydroxyl (OH) value was measured by titration to determine the number of hydroxyl groups in the oil structure, in accordance with ISO 14900:2001. The iodine value, used to evaluate the degree of unsaturation (double bonds), was determined via titration according to ISO 3961:2009.

2.5.1 Determination of Acid Value

The acid value is determined to assess the acidity of SBO before and after chemical modification. A 5 g sample of oil is accurately weighed and transferred into a clean Erlenmeyer flask. Then, 50 mL of the titration solvent, prepared by mixing benzene and ethanol in a 1:1 volume ratio, is added. The mixture is shaken thoroughly to ensure uniform dissolution. Titration is then performed with 0.1 N potassium hydroxide (KOH) solution, using phenolphthalein as the indicator. The endpoint of the titration is indicated by a color change from colorless to pale pink, which persists for at least 30 seconds. The volume of KOH used is recorded and used to calculate the acid value using the following formula:

$$\text{Acid no.} = 56.1\times\frac{\mathrm{A-B}}{\mathrm{W}}\times \mathrm{N} \tag{1}$$

Where A is the volume of KOH used to titrate the sample, (mL)
B is the volume of KOH used to titrate the blank (mL)
W is the weight of the sample (g)
N is the KOH concentration, (N)

2.5.2 Determination of Hydroxyl (OH) Value

The hydroxyl value is determined to quantify the number of hydroxyl groups in SBO before and after modification. A 3 g sample of the oil is accurately weighed and placed in a round-bottom flask. To this, 20 mL of the phthalic mixture (prepared by mixing 1 part phthalic anhydride with 6 parts pyridine by volume) is added. The mixture is then refluxed at 100 ± 5°C for 1 hour. After refluxing, the mixture is cooled to room temperature, and 50 mL of distilled water is carefully added through the mouth of the condenser. The mixture is then titrated with 1 N potassium hydroxide (KOH) using phenolphthalein as the indicator. The endpoint is reached when the color changes from colorless to pink. The volume of KOH used is recorded, and the hydroxyl value is calculated using the following formula:

$$\text{OH-Value} = 56.1\times\left[\frac{(v_2-v_1)}{W}\right]+Acid\ no. \tag{2}$$

Where V_1 is the volume of KOH used to titrate the sample, (mL)
V_2 is the volume of KOH used to titrate the blank (mL)
W is the weight of the sample (g)

2.5.3 Determination of Iodine Value

The iodine value is used to assess the degree of unsaturation, i.e., the number of double bonds in the SBO structure before and after modification. A 0.05 g sample of oil is accurately weighed and transferred into a clean Erlenmeyer flask. Then, 20 mL of Wijs solution (iodine dissolved in glacial acetic acid with iodine monochloride as the active reagent) is added to the flask. The mixture is kept in the dark at room temperature for 30 minutes to allow the reaction to proceed. After the reaction period, the mixture is titrated with 0.1 N sodium thiosulfate solution, using starch solution as an indicator. The endpoint of the titration is identified by a color change from brown to colorless. The volume of sodium thiosulfate used is then recorded and used to calculate the iodine value using the following formula:

$$\text{Iodine no.} = \frac{[(V_1 - V_2) \times N \times 126.9 \times 100]}{W \times 1000} \tag{3}$$

Where V_1 is the volume of Sodium thiosulfate used to titrate the blank (mL)
V_2 is the volume of Sodium thiosulfate used to titrate the sample, (mL)
W is the weight of the sample (g)
N is Sodium thiosulfate concentration, (N)

2.6 Characterizations

The ^{1}H-NMR spectra were recorded using a Bruker 400 Fourier Transform spectrometer operating at 400 MHz to investigate the chemical structure of the modified SBO. Samples were dissolved in $CDCl_3$, with tetramethylsilane (TMS) used as the internal standard. The FTIR-ATR technique was employed to examine the chemical bonds and interactions among SBO, ESBO, and AESBO. The kinetics of AESBO photo-crosslinking reactions were monitored by real-time infrared spectroscopy in ATR transmission mode using a Tensor 27 Fourier Transform Infrared Spectrometer (Bruker, Germany) over a wavenumber range of 4000 cm^{-1} to 500 cm^{-1}.

3. Results and Discussion

3.1 Modification of SBO

In Table 1, SBO initially exhibited an iodine value within the standard range of 127–138 I_2/100 g. The oil was then structurally modified via epoxidation with formic acid and hydrogen peroxide at a molar ratio of 1:4:4. Following the reaction, the iodine value decreased to 12.06 I_2/100 g, indicating that epoxide rings had replaced the double bonds in the main structure. This is because the iodine value reflects the number of double bonds present in the structure. At the same time, the acid number and hydroxyl (OH) value increased to 10.90 mg KOH/g and 242.22 mg KOH/g, respectively. Subsequently, ESBO-2 was acrylated with acrylic acid at ratios of 1:1, 1:1.5, and 1:2. The acid number increased, indicating an excess of unreacted acrylic acid, which corresponded to the increasing ratio. A similar trend was seen with the OH value. However, at a 1:2 ratio, the oil became denatured, forming a gel rather than remaining a liquid, and therefore could not be tested, as shown in Figure 6.

Following 2 hours of epoxidation, the resulting ESBO-2 exhibited a cloudy white appearance, in contrast to the clear yellow color of the unmodified SBO, as shown in Figure 6. Upon acrylation, the AESBO-1 sample showed increased viscosity and a darker yellow hue than ESBO-2. When compared further with AESBO-1.5, it was observed that AESBO-1.5 had even higher viscosity and a slightly deeper color than AESBO-1. However, in the case of AESBO-2, the material underwent a phase transformation from a viscous liquid to a non-flowing gel, indicating over-crosslinking or excessive reaction extent. This transformation is attributed to two simultaneous reaction mechanisms. Firstly, the high molar ratio of acrylic acid facilitated extensive ring-opening of the epoxide groups, leading to a high density of acrylate functionalities on each triglyceride molecule, which promoted premature intermolecular crosslinking. Secondly, under the reaction conditions of 110 °C for 8 h, the excess acrylic acid likely underwent self-polymerization, leading to the formation of an interconnected poly(acrylic acid) network entangled with the modified oil matrix, resulting in a rigid three-dimensional structure and gelation even before UV curing was initiated [21]. Based on these observations, AESBO-1.5 was selected as the optimal formulation for studying UV curing kinetics due to its suitable viscosity and stability.

Table 1. Chemical characteristics of SBO before and after modification.

Oil type	Ingredients (mol)		Acid no. (mg KOH/g)	OH-Value (mg KOH/g)	Iodine no. (I_2/100g)
	ESBO-2	Acrylic acid			
SBO [6]	-	-	0.3-3.0	4-8	127-138
ESBO-2	-	-	10.90	242.22	12.06
AESBO-1	1	1	9.87	265.21	-
AESBO-1.5	1	1.5	13.52	223.67	-
AESBO-2	1	2	-	-	-

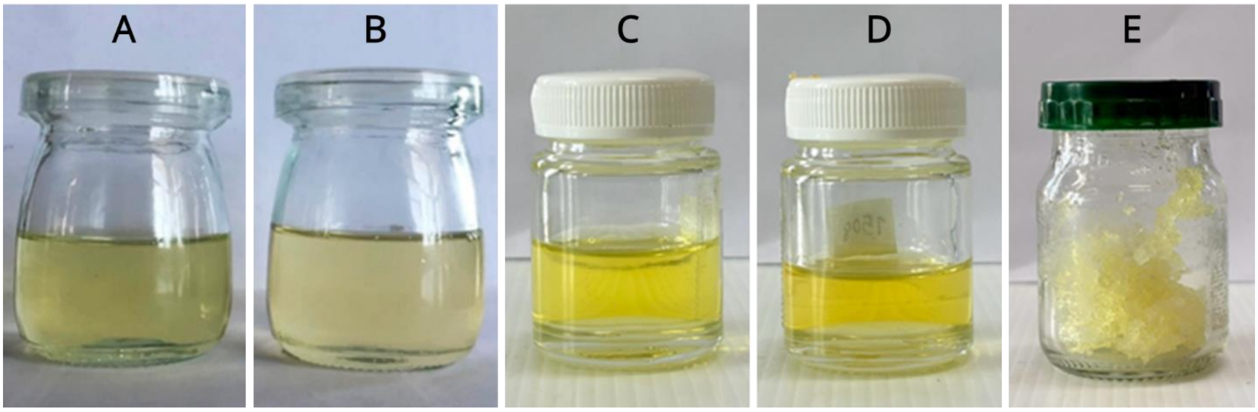

Figure 6. Visual appearance of (a) SBO, (b) ESBO-2, (c) AESBO-1, (d) AESBO-1.5, and (e) AESBO-2.

The ^{1}H-NMR spectra of SBO and modified SBO are shown in Figure 7. After 2 hours of reaction, significant structural changes were revealed. In the unmodified SBO, a prominent signal was observed at 5.3–5.6 ppm, corresponding to the carbon–carbon double bonds (C=C) present in the fatty acid chains. Following epoxidation with formic acid and hydrogen peroxide, the signal intensity decreased markedly, indicating successful conversion of the double bonds. Concurrently, a new signal emerged at 3.0–3.15 ppm, which is characteristic of the methine protons in the oxirane (epoxide) ring, confirming the formation of ESBO-2 [12].

The structure of AESBO was confirmed by ^{1}H-NMR spectroscopy. Signals observed at 4.0–4.4 ppm correspond to the glyceride backbone, while those in the range of 2.8–3.3 ppm are attributed to the methine protons of the epoxide ring. Following the acrylation reaction, a noticeable reduction in the intensity of the epoxide-associated peaks was observed, indicating ring-opening. Simultaneously, new peaks emerged in the range of 5.6–6.4 ppm, which are characteristic of the vinyl protons of the acrylate ester. These signals confirm the successful introduction of acrylate groups, as they represent the three distinct protons attached to the carbon–carbon double bond (C=C) of the acrylate moiety [13–16].

The FT-IR spectra of SBO and modified SBO are shown in Figure 8. After 2 hours of reaction with formic acid and hydrogen peroxide, significant structural changes were revealed. The absorption band at 3010 cm^{-1}, attributed to the =C–H stretching vibrations in SBO, decreased in intensity during the reaction, indicating consumption of double bonds. In contrast, the broad peak at 3400 cm^{-1}, corresponding to hydroxyl (–OH) groups, was observed to increase in the spectrum of ESBO-2, suggesting the formation of hydroxyl groups via side reactions or ring-opening. Additionally, a distinct absorption at 820 cm^{-1} appeared, confirming the presence of oxirane (epoxide) rings in the modified oil.

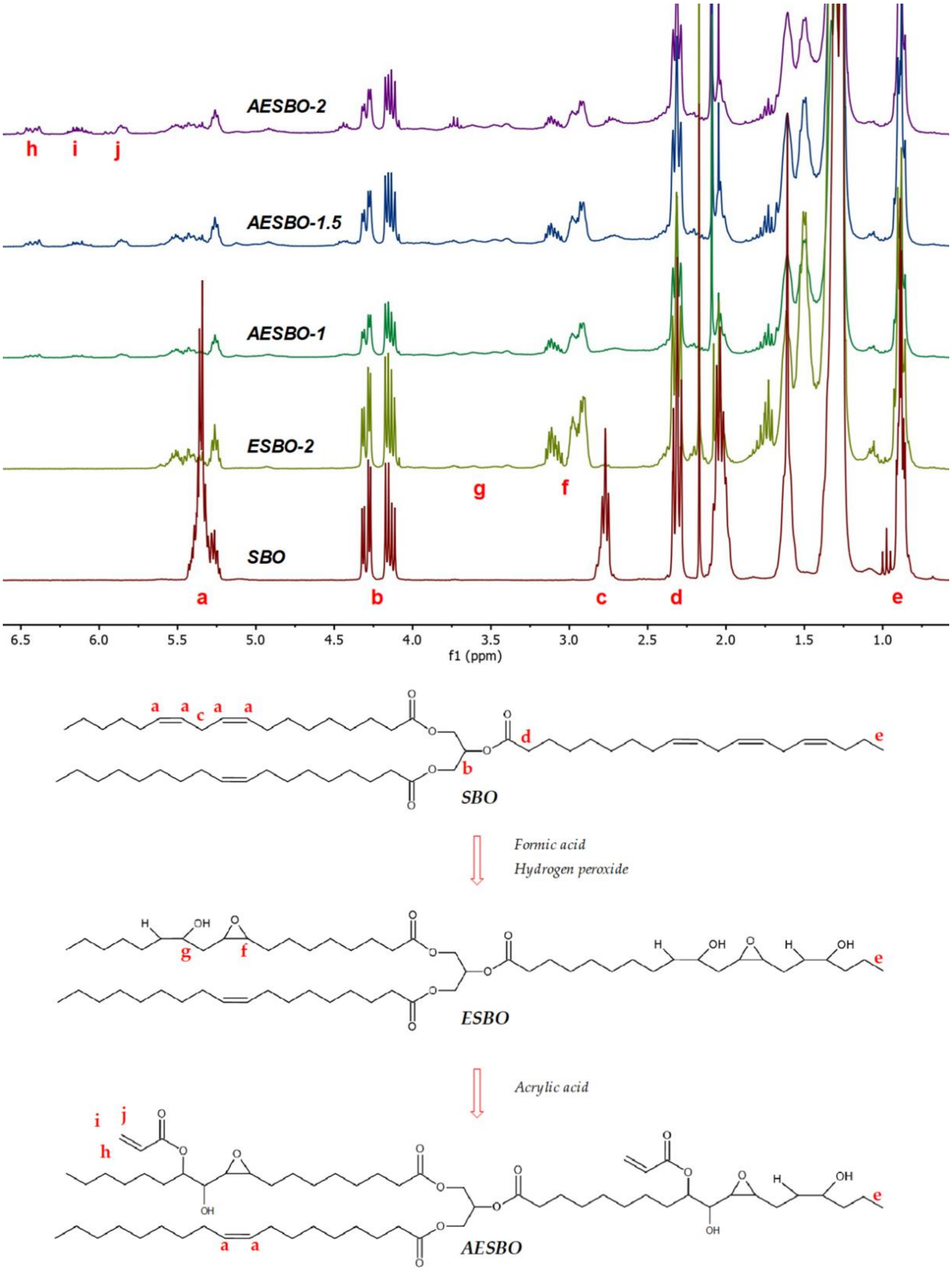

Figure 7. ^{1}H-NMR spectra of a series of SBO, ESBO-2, and AESBO with a difference ratio of acrylic acid.

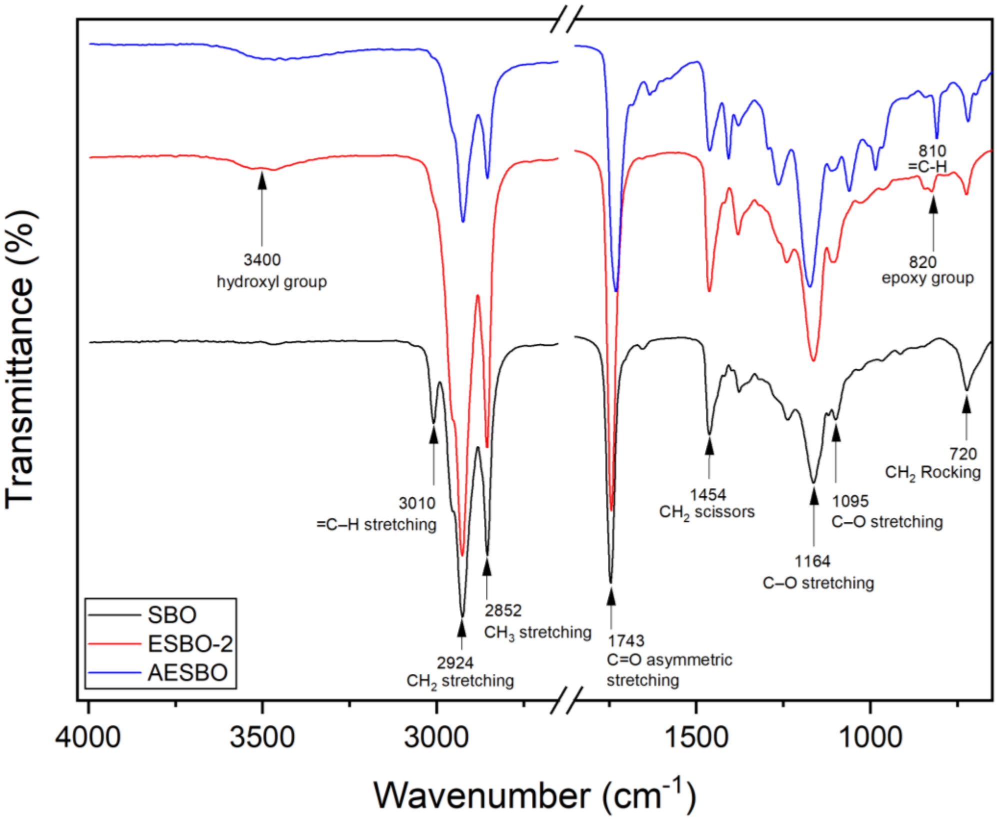

Figure 8. The FT-IR spectra of SBO, ESBO-2, and AESBO.

The results of the AESBO reaction, confirmed by FT-IR analysis, demonstrated the appearance of new absorption bands at 1630 cm^{-1} and 810 cm^{-1}, both corresponding to the stretching vibrations of carbon–carbon double bonds (C=C). These peaks provide clear evidence that acrylation occurred through ring-opening of the epoxide rings, leading to the formation of acrylate functional groups. The distinct peak at 810 cm^{-1}, in particular, is indicative of C=C stretching in the acrylate moiety. Similar absorption patterns have been reported in the FT-IR spectra of acrylated epoxidized flaxseed oil polymers [17, 18].

3.2 Photo-crosslinking of AESBO

The kinetics of the UV curing of AESBO-1.5 containing 5 wt% Darocur 1173 (AESBO-1.5-PI5%) were analyzed using FT-IR spectroscopy, as shown in Figure 9. Key absorption peaks associated with the acrylate (C=C) groups were observed at 810 cm^{-1} and 1640 cm^{-1}. These peaks decreased in intensity with increasing UV irradiation time, reflecting the consumption of C=C bonds through photopolymerization [19]. The decrease in the 810 cm^{-1} band, in particular, was used to monitor the crosslinking kinetics of the AESBO film, as it corresponds to the out-of-plane deformation of the C=C bond in acrylate groups [6]. Upon UV exposure from 0 to 420 seconds, the conversion of double bonds increased steadily. After 60 seconds of irradiation, the 810 cm^{-1} peak showed no further change, indicating that the UV-curing process had reached completion. This confirms that AESBO-1.5, when combined with 5 wt% Darocur 1173, can be fully cured within 60 seconds under 400 W UV light [20].

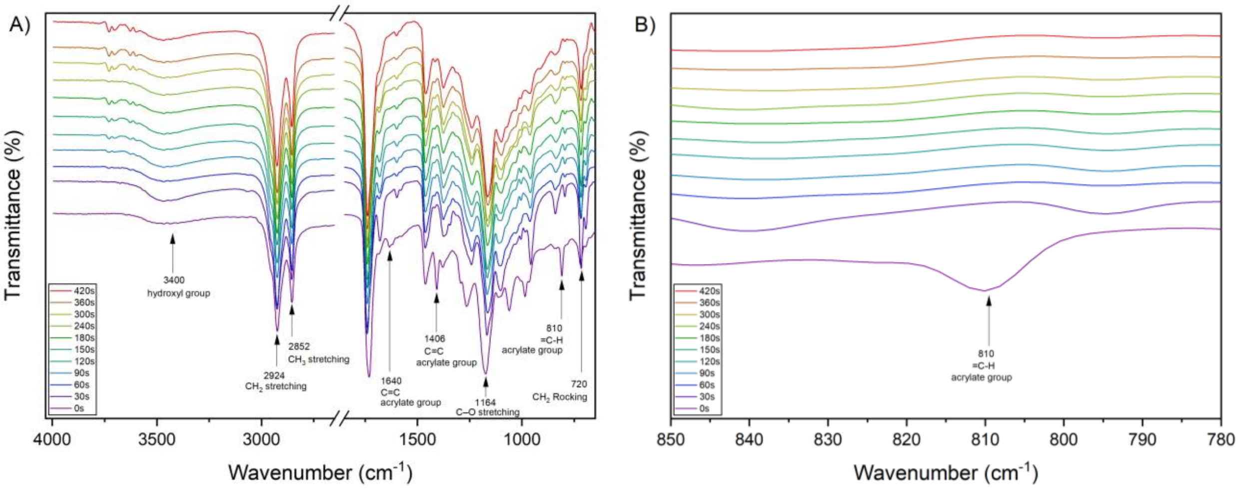

Figure 9. FT-IR spectra of UV-cured reaction kinetics of AESBO-1.5-PI5%.

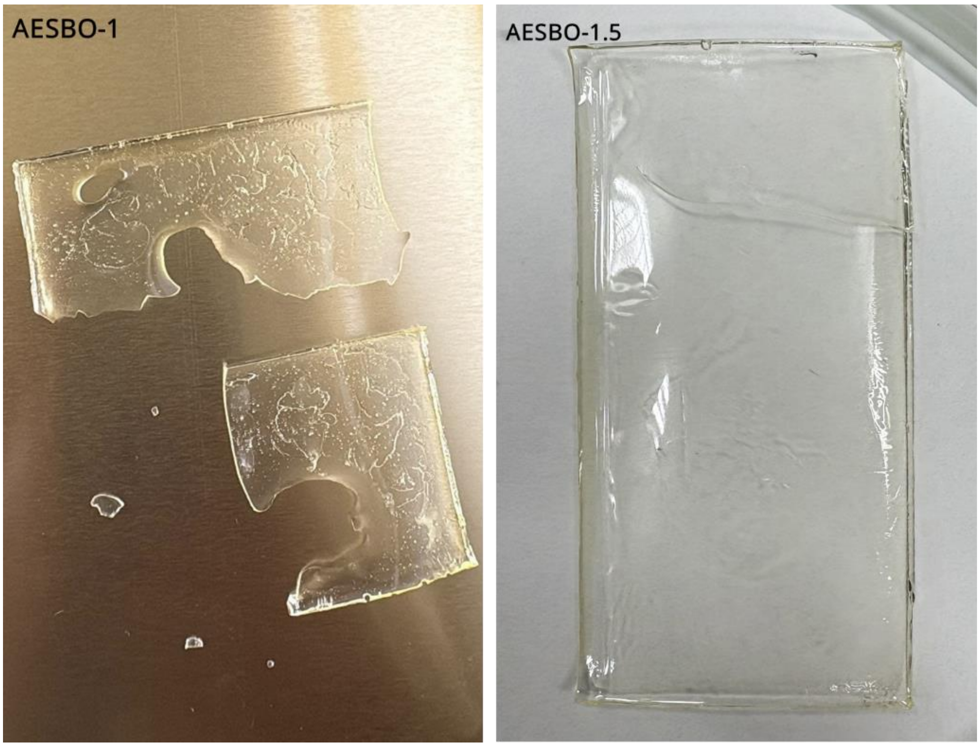

Figure 10. The AESBO-1 and AESBO-1.5 films.

In Figure 10, the AESBO-1 and AESBO-1.5 film sheets can be clearly distinguished. The AESBO-1 film appeared brittle and lacked sufficient strength to maintain its shape fully. In contrast, the AESBO-1.5 film exhibited improved strength and better shape retention, although brittleness remained. This indicates that increasing the acrylic acid ratio in the reaction enhances the film's ability to maintain its form more completely. A schematic diagram of the crosslinking reaction of AESBO is shown in Figure 11. Several strategies can be employed to enhance the toughness of bioplastic films derived from acrylated epoxidized soybean oil (AESO). To avoid excessive brittleness, the crosslink density can be optimized by incorporating flexible bio-based plasticizers, such as citrate esters or oligomeric polyols, which improve chain mobility. A tougher polymer matrix can be produced by blending ductile biodegradable polymers. Energy absorption during deformation can be improved by adding bio-based elastomeric modifiers, rubber nanoparticles, or core–shell impact modifiers. Toughness may be increased by reinforcement with well-dispersed nanofillers, such as cellulose nanocrystals or graphene oxide, at low loadings, thereby improving crack deflection and stress transfer mechanisms. Additionally, tailoring the photoinitiator content, UV intensity, and UV curing time can help achieve a balanced network structure, and incorporating chain extenders or reactive diluents to increase molecular entanglement can significantly improve elongation at break and impact resistance without compromising mechanical strength.

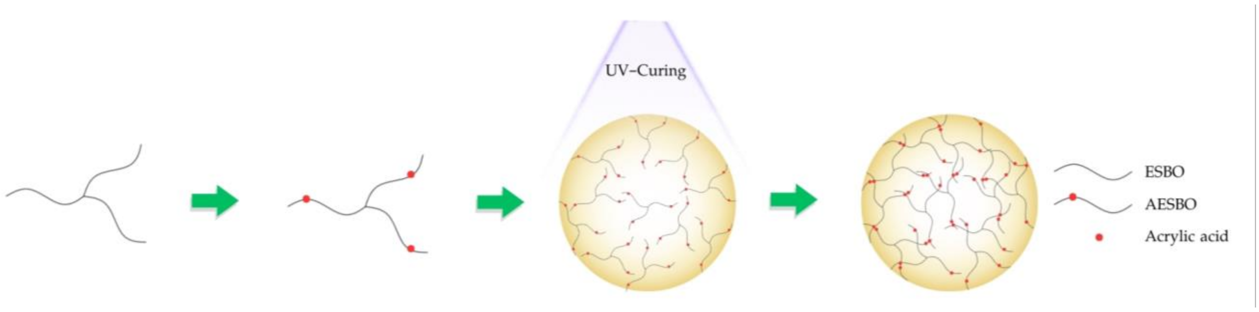

Figure 11. A schematic diagram of the crosslinking reaction of AESBO.

4. Conclusions

This study focuses on the development of a sustainable and environmentally friendly UV-cured material derived from AESBO. The process began with the epoxidation of SBO using formic acid and hydrogen peroxide at 60°C for 2 hours, followed by a ring-opening reaction. Acrylation was then performed using acrylic acid at molar ratios of 1:1, 1:1.5, and 1:2 for 8 hours. The structural modifications were confirmed through FT-IR and ^{1}H-NMR spectroscopy. The UV-curing behavior of the AESBO was investigated using 5 wt% Darocur 1173 as a photoinitiator under 400 W UV irradiation. Kinetic analysis revealed that film stability increased over time, reaching complete stability at 60 seconds, beyond which no significant changes were observed. These results highlight the potential of AESBO as a renewable and UV-curable material suitable for environmentally conscious applications. However, plastic films can be successfully fabricated from soybean oil–based materials; their physicochemical and functional properties must be fully evaluated before practical application. In particular, the systematic investigation of potential residual chemicals remaining from the synthesis and curing reactions is essential to ensure material safety, stability, and regulatory compliance. Detailed characterization of residual monomers, initiators, and other reactive species will provide critical insight into the suitability of the film for end-use applications, especially in contexts where human or environmental exposure may occur. The production of bioplastic film from soybean oil with UV curing offers several distinct advantages over the production of conventional petroleum-based plastics and thermally cured biopolymers. The use of renewable, plant-based resources reduces dependence on fossil fuels and lowers the carbon footprint, while UV curing enables rapid polymerization at ambient temperatures, minimizing energy consumption, processing time, and thermal degradation. Compared with traditional plastics such as polyethylene and polypropylene, soybean oil-based films can provide improved sustainability, inherent flexibility due to their long aliphatic chains, and tunable mechanical and barrier properties through formulation control. Compared with other bioplastics, such as polylactic acid, UV-cured soybean oil films often exhibit greater toughness and less brittleness, along with solvent-free and low-VOC processing. Overall, the combination of renewable feedstock and energy-efficient UV curing makes soybean oil-based bioplastic films an environmentally friendly, versatile, and industrially attractive alternative to conventional polymer films.

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Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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