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Modification of soybean oil for intermediates by epoxidation, alcoholysis and amidation

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Abstract−Vegetable oils are a major source of many base chemicals. Unfortunately, most vegetable oils exhibit lower thermal and oxidation stability because of double bonds and even worse low-temperature behaviors. These physical and chemical properties can be improved by various chemical modifications. The catalytic hydrogenation of soybean oil (SBO) over 25% Ni/SiO_2 and 5% Pt/C is one of them, and the epoxidation of soybean oil and reduced soybean oil (RSBO) was carried out by using 30% of hydrogen peroxide and acetic acid in the presence of conc. sulfuric acid, and/or acidic Amberlyst 15 resin catalyst. Various alcohols and amines were added to the epoxidized soybean oil (ESBO) in the hope of improving lubricant properties. The reaction products were carefully analyzed by means of ^{1}H-NMR, FT-IR spectroscopies and GC-MS spectrometry. This paper covers the epoxidation of virgin and RSBOs, alcoholysis and amidation of ESBO and SBO. Finally, the structures of cross linked products synthesized from ESBO and SBO with 1,6-hexamethylendiamine were proposed.

Key words: Epoxidation, Soybean Oil, Alcoholysis, Amidation, Cross Linking

INTRODUCTION

Petroleum oil has been an important source of a wide range of fine and industrial chemicals. However, these petroleum products have side branches on a main carbon chain, are not easily biodegradable and thus can cause serious problems of environmental pollution.

It is well recognized that the reserves of petroleum crude oil are decreasing while the risk of exhausting the existing reserves and the oil price are increasing. Therefore, it is good to substitute fossil fuel with other bio-sources if possible.

From an environmental point of view, the use of renewable and sustainable resources is of great interest. Vegetable oils are a particularly good candidate for lubricant due to their specific structure, providing a wear-protection property with a stable viscosity-temperature behavior [1,2] and a very low evaporation due to the high molecular weight of triacylglyceride. In addition, they are easily biodegradable.

The production of soybean oil in 2006, which was 6.65 million tons and 2.2 million tons imported in China, covers about 10% of the world production [3]. Currently, SBO is mainly used as edible oil. Since the recovered used frying oil (UFO) can be used in producing chemicals and fuels [4], the value of SBO needs to be further investigated in terms of environmental protection as well as energy conservation.

For these reasons, SBO was selected and used as the starting material. Since the viscosity of oil is too low to be directly used as lubricant, chemical modifications were needed to increase the viscosity of SBO. Additionally, the SBO consists of triglycerides with three long chain fatty acids, which are mainly unsaturated 18-carbon atom chains with one, two or three double bonds resulting in the poor oxidative stability because of the presence of α-CH_2 to the carbonyl group and allylic and bisallylic protons to the double bonds [5]. They are easily attacked by chemical oxidants to a depletion of double bonds [6] and by free radical; they subsequently undergo oxidative degradation to form various polar oxy compounds [7].

Fatty acids and/or their corresponding esters with only one double bond show somewhat higher resistance to oxidation and hydrolysis, and have a more favorable pour point than the polyenic ones [1]. Furthermore, one can improve the tribological properties by modifying the parent molecule through an addition reaction to the double bonds.

The double bonds present in vegetable oils offer an opportunity to chemically alter their structure to improve some of these properties. In one way, experiments were carried out to increase the viscosity, the oxidation stability, and other lubricant properties by epoxidation of oils followed by addition of alcohols and/or amines to ESBO through the ring opening reactions or amines to the virgin SBO.

Epoxidation has a long history and is one of the most important reactions among addition reactions of alkene. Epoxidation has been carried out either homogeneously [8-10] or by using a heterogeneous catalyst [11]. In the homogeneous catalysis, peracids are mainly used. For instance, peracetic acid generated in situ by mixing hydrogen peroxide with acetic acid was used to epoxidize vegetable oils. These ESBO are expected to show improved lubricity when used as a lubricant base fluid, because of their good lubricity and high oxidation stability in comparison to pure vegetable oils. Therefore, ESBOs have been synthesized and chemically modified SBOs were used as starting materials for the preparation of bio-lubricants.

Secondly, methanol, isobutanol and neopentanol were added to the ESBO over heterogeneous catalysts [12]. Also, some thiols such as 1-butanethiol, 1-decanethiol, 1-octadecanethiol, and cyclohexylmercaptane were added to ESBO [13].

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This paper contains the process of the epoxidation of the SBO using a mixture of acetic acid and 30% hydrogen peroxide in the presence of concentrated sulfuric acid. Heterogeneous epoxidation was also carried out by using Amberlyst 15 as the catalyst, which such alcohols as methanol, ethanol and isopropanol to 70% and 100% ESBO were added and the products confirmed by means of spectroscopies. Additionally, *n*-hexylamine and 1,6-hexamethylenediamine were added to the pure SBO and ESBO to provide further information for wider applications of SBO and its derivatives. Furthermore, new findings relating on aminolysis/amidation with a cross-linking should add an interesting information by themselves.

The potential of the new compounds as lubricants is under investigation and will be determined separately.

EXPERIMENTAL

1. Reduction of SBO [1,21,22]

Into a 500 mL Parr autoclave, 100 g of purified oil and 1.0 g catalyst (mainly 25% Ni/ SiO_2, [Johnson Matthey; BET surface area: 204.23 m^2/g; average pore size: 32.76 Å] and/or 5% Pt/C, [BET surface area: 922 m^2/g; average pore size: 18.59 Å]) were placed and heated to 180 °C with stirring. When the temperature reached at 180 °C, water vapor of oil and air were replaced by hydrogen gas three times, and the reaction conditions were set. Afterward, reactions were carried out at different temperatures as well as reaction times while keeping the hydrogen pressure at 5 atm. The reaction stopped and hydrogen ejected while the apparatus was cooled in a water bath. After cooling to the moderate temperature, the reaction mixture was filtered with a Büchner funnel while still warm. The products were analyzed by means of ^{1}H-NMR- and FT-IR-spectroscopies. The melting points of 30% and 50% reduced products were 32-34 °C and 41-43 °C, respectively.

2. Epoxidation of SBO and RSBO [8-12]

2-1. SBO

Into a one-necked 500 mL round bottom flask fitted with a condenser and a magnetic stirrer were placed 88 g (0.10 mol) of refined SBO, 12 g (0.20 mol) of glacial acetic acid, 30 g of 30% hydrogen peroxide (0.5 mol), and 0.5 g (5.0 mmol) of concentrated sulfuric acid. The mixture was stirred at 58-60 °C in a water bath for 30 h.

After the reaction was completed, the mixture was cooled to room temperature. The upper organic phase was separated and washed three times with water to remove any traces of acid remaining in the reaction mixture, and finally dried over anhydrous $MgSO_4$ overnight. The epoxidation degree was measured by ^{1}H-NMR-spectroscopy and confirmed by IR-spectrum by monitoring epoxide peaks at 8 μ, 11 μ and 12 μ. Yield was 88.9% and the degree of epoxidation was ~100%.

2-2. RSBO

2-2-1. With Conc. Sulfuric Acid

The authors used the same reduced products for this reaction as previously reported in our paper [1].

The procedure was the same for the epoxidation of pure SBO, except the recipe of molar ratio that was changed by the reduction degree of the oils.

Into a 250 mL one necked round bottom flask fitted with a condenser and magnetic stirrer were placed 44 g of 20% reduced soybean oil (0.04 mole based on double bond), 7.6 g of acetic acid, 13.6 g of 30% hydrogen peroxide (0.226 mol), 0.5 g conc. sulfuric acid, and the mixture was remained at 60 °C for 20 h with constant stirring. The yield was 92% and the degree of epoxidation was 92%.

2-2-2. With Amberyst 15 Resin Catalyst

In the case of 40% RSBO, one batch was additionally carried out under the same condition in the presence of acidic Amberlyst 15 ion exchange resin catalyst (Aldrich) for 30 h to compare the results obtained by using sulfuric acid as catalyst.

Amberlyst 15 has following physical data:
Trade name: Amberlyst 15 hydrogen form
Physical data: 16-50 mesh
Matrix: styrene-divinylbenzene
Wet bed volume: 1.8 meq/mL
Dry weight: 4.7 meq/g

3. Addition of Alcohols to the ESBO; Ethanol Addition

Into a one-necked 250 mL round bottom flask equipped with a magnetic stirrer and a condenser were placed 7 g (0.15 mol) of ethanol, 10 g of 100% ESBO oil (10 mmol) and 0.5 g of Amberlyst 15 ion exchanged resin (abbr. Amberlyst 15) as catalyst. The mixture was stirred at 60 °C in a water bath for 30 h [12].

After the reaction was completed, the mixture was cooled to room temperature. The organic phase was separated and the product in the flask was rinsed with anhydrous ether and with the same alcohols and finally combined with the mother liquor.

The combined ether solution was dried over anhydrous magnesium sulfate after sitting one overnight and filtered. The excess ether, and/or alcohol were evaporated with a vacuum evaporator. The other alcoholysis of epoxides was carried out under the similar conditions using the same procedure and is summarized in Table 1.

4. Addition of *n*-Hexylamine to ESBO [13,14]

Into a 1 L three necked round bottom flask equipped with N_2 gas inlet tube, a condenser, and a magnetic stirrer were placed 400 mL of methylene chloride, 25 g 100% ESBO (26 mmol) and 11.3 g of

Table 1. Epoxidation recipe and results

Substrate	Amount (g)	HAc (g)	30% H_2O_2 (g)	Time (h)	Yield (%) & epox. degree	
SBO	88 (0.1 mol)	12 (0.2 mol)	30 (0.5 mol)	30	89	100
20% RSBO	44 (0.04 mol)	7.6	13.6 (0.23 mol)	20	93	92
40% RSBO	44 (0.03 mol)	5.6	11.6 (0.18 mol)	20	92	100
40% RSBO[a]	44 (0.03 mol)	5.6	11.6 (0.18 mol)	30	95	77

Catalyst is conc. sulfuric acid, 0.5 g (5 mmol)
Reaction temperature: 58-60 °C
[a]Amberlyst 15 catalyst, 0.5 g

n-hexylamine (104 mmol). Under nitrogen atmosphere, 2.61 g of perchloric acid as catalyst was added dropwise into the reaction mixture for one hour with constant stirring. After addition of the catalyst, the mixture was refluxed for 16 h. Upon completion, the reaction mixture was cooled to room temperature. The organic phase was then separated and washed with 200 mL of 5% aqueous sodium bicarbonate solution followed by distilled water twice to remove any traces of acid catalyst in the system, and dried over anhydrous magnesium sulfate overnight and filtered. The solvent was removed under reduced pressure to give 35 g of residue (yield, 96%). The product was pale yellow soft solid.

5. Addition of 1,6-Hexamethylenediamine to ESBO and SBO

5-1. Addition of 1,6-Hexamethylenediamine to ESBO

The previous recipe and procedure were repeated to produce 1,6-hexamethlylene diamine adduct.

Into a 1 L three necked round bottom flask equipped with a N_2 gas inlet tube, a condenser and a magnetic stirrer were placed 400 mL of methylene chloride, 25 g 100% ESBO (26 mmol), and 15 g of 1,6-hexamethylenediamine (130 mmol). Under nitrogen atmosphere, 2.60 g of perchloric acid as catalyst was added dropwise into the reaction mixture for 1 hour with constant stirring. By addition of the catalyst, there occurred some turbidity only to disappear quickly. After addition of the catalyst, the mixture was refluxed for 15 h. After completion of reaction, the reaction mixture was cooled to room temperature, the organic phase was separated, washed with 200 mL of 5% aqueous sodium bicarbonate solution and distilled water each twice to remove any traces of acid catalyst in the system, then dried over anhydrous magnesium sulfate overnight and filtered. The solvent was removed under reduced pressure. The residue weighed 35 g (yield: 97.1%), which melted at 70-76 °C and its molecular weight was 1043. The product of 10 h reaction was pale yellow soft solid.

5-2. Addition of 1,6-Hexamethylenediamine to SBO

Using the same apparatus and recipe, the addition reaction was performed for the pure SBO. The reaction time was shortened to 10 h. Pale yellow solid resulted with the yield of 95%, melted at 80 °C, and its molecular weight was 958.

6. Transesterification of Products of SBO [4,15]

Into a 250 mL Erlenmeyer flask equipped with a magnetic stirrer and an air cooled condenser, 0.03 mole of each substrate, and 0.6 mole of methanol were placed, and a catalytic amount of potassium hydroxide (300 mg) was added. The mixture was allowed to react at 50 °C for 30 min with vigorous stirring (ca 500 rpm). After completion, the reaction mixture was neutralized with dilute hydrochloric acid and the excess methanol was evaporated through rotatory evaporator under reduced pressure. Then the glycerol in the lower phase was separated from the mixture. Injection volume was 1 μL for a gas chromatograph analysis.

7. Analysis

1) GC Analysis [1,4,15]:

The hydrolyzed products were analyzed by means of GC with a capillary column. The operation conditions were as follows:

Instrument: Younglin D 5000

Column: DB-Wax; 30 m×0.25 mm×0.25 μm

Detector: FID detector with injector temperature at 250 °C.

Oven temperature program: Beginning at 150 °C for 5 min, increased by 10 °C/min up to 250 °C, and then maintained at 250 °C for next 10 min.

Split ratio: 50-100 : 1,

Carrier gas: N_2 with a flow rate of 0.5-1.0 mL/min

2) ^{1}H-NMR Analysis:

The products were analyzed by means of ^{1}H-NMR spectroscopy to quantify the degree of reduction and epoxidation. The amounts of double bonds in triglyceride oil and biodiesel were quantified by ^{1}H-NMR. The solvent was $CDCl_3$.

Instrument: DRX-300 FT (German Brucker)

3) FT-IR Analysis: To monitor the formation of new bonds and disappearance of the characteristic peaks of epoxide, amide, amine, carbonyl etc, FT-IR-spectrometer was used.

Instrument: Bio-Rad Digilab Division, FTS-165 FT-IR Spectrophotometer.

RESULTS AND DISCUSSION

1. Reduction of SBO

Hydrogenation of the double bond of the unsaturated fatty compounds is used on large scale in industry. This process improves the stability by increasing the melting points of partially and/or completely hydrogenated compounds. Selective hydrogenation is of great interest not only in the area of lubricant but also in all fields of chemistry in general.

The authors monitored the reduction rate of each double bond, which exist in oleic, linoleic, and linolenic fatty acid esters. By aforementioned SBO reduction, the double bonds in linolenic and linoleic esters should be reduced to the oleic acid resulting in a similar composition to olive oil. Also, it is considerable to recognize or identify the configuration of *cis-/trans* isomerization [1,16,17]. In our work, the FT-IR spectrum of the reduced product obtained at 200 °C for 80 min showed no peaks originating from *trans*-isomer.

Fig. 1(a) shows the ^{1}H-NMR spectrum of SBO. The assignment of each signal is given as follows in ppm: -CH_3, 0.830-0.885, consequent methylene protons, 1.228-1.323, β-CH_2 to carbonyl group,

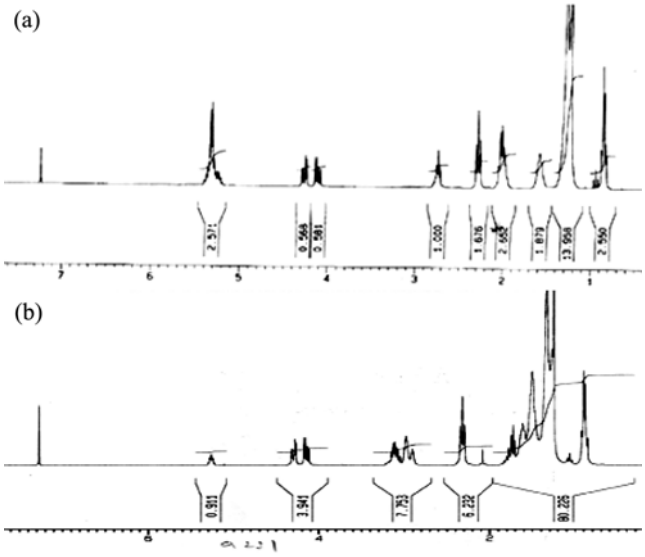

Fig. 1. Proton-NMR spectra of soybean oil (a) and of 100% epoxidized soybean oil (b).

1.582, allylic protons, 1.989-2.030, α-protons to carbonyl group, 2.257-2.313, bisallylic protons, 2.723-2.761, four methylene protons of backbone, 4.06-4.145 and 4.242-4.296, one methine proton of backbone, 5.252-5.276 and olefinic protons appear at 5.288-5.368 as a multiplet [18]. The RSBO was analyzed by means of ^{1}H -NMR to measure the reduction degree. The signals at 5.35 (multiplet) and at 4.12 and 4.26 (double doublet) were chosen as standard signals for analysis. The former originated from the olefinic protons, and the latter from the two CH_2 glyceryl protons of backbone. Intensity of the signal at 5.35 only decreased as the reductive reaction proceeded [1]. By the proceeding of the hydrogenation, the product is solidified. The melting point of 30% reduced was 32-34 ºC and that of 50% reduced was 41-43 ºC, respectively. It is clear that the more reduced the compound is, the higher the melting point is.

2. Epoxidation of SBO

As mentioned in the introduction, epoxide can be a promising starting material. The industrial epoxidation of SBOs and their derivatives is carried out with in situ-generated peracids, mixing performic acid with peracetic acids [9,12]. These peracids are produced from the oxidation of organic acids with hydrogen peroxide using strong mineral acids, e.g., sulfuric acid as catalyst. For environmentally benign production, it is desirable to replace such strong mineral acids by heterogeneous catalysts, for example Amberlyst 15, in order to avoid problems such as corrosion or the production of large amounts of salt from their neutralization [16,20]. However, the use of in situ-generated peracids in the presence of sulfuric acid apparently gave better results than Amberlyst 15 in the epoxidation of SBO. The results of epoxidation are summarized in Table 1.

Hölderich and coworkers [12] investigated intensively the epoxidation of vegetable oils over heterogeneous catalysts, such as immobilized lipase, Ti-MCM-41 and Amberlyst 15 to develop an environmentally friendly process. They concluded that the Amberlyst 15 is the most recommended catalyst, in many respects. We epoxidized the SBO with different degrees of completion, 100% as well as certain degrees of epoxidation by varying reaction conditions such as

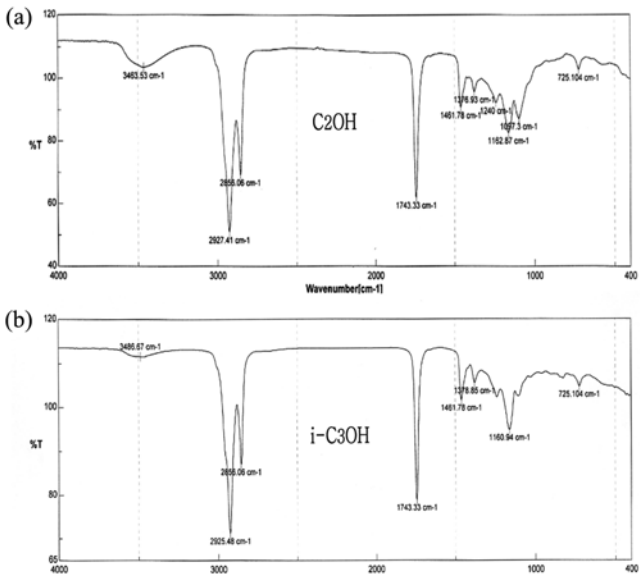

Fig. 2. IR spectra of ethanol adduct (a) and isopropanol adduct (b) of 100% ESBO.

reaction time, temperature, and amounts of reagent (see Table 1). The concentration of peracetic acid was quantified by iodometry in the range of 40-54.5%. The epoxidation degree was also analyzed by same means of ^{1}H-NMR spectroscopy as that of reduction degree. As shown in Fig. 1(b), the ^{1}H-NMR spectrum of 100% epoxidized product was assigned as follows in ppm: -CH_3, 0.810-0.878, α-C**H$_2$**- to carbonyl, 2.242-2.202, epoxide ring -C**H**-C**H**-, 3.016-3.096, four protons of backbone, -C**H$_2$**-CH-C**H$_2$**-, 4.066-4.278, one methine proton of back bone, 5.213, respectively. Compared to that of SBO, the epoxide ring protons shifted to 3.016-3.096 from 4.106- and 4.262 of the olefinic protons as the allylic protons disappeared. Biswas wrongly assigned the bisallylic protons at 1.67 as a multiplet as shown in the Fig. 2 of his paper [14], but correctly assigned this peak at 2.8-3.0 in the discussion. By the diamagnetic shielding effect of two oxygen atoms, it should be shifted a little bit to the down field [19].

In FT-IR spectrum, the stretching vibration of carbonyl group, $\upsilon_{C=O}$, at 1,744 cm^{-1}, and the characteristic epoxide bands υ1,240 cm^{-1}, δ_{as} 843, δ_{sym} 824 cm^{-1} clearly appeared. However, the peaks of ca 50% epoxidized product did not appear clearly, because of the low concentration of epoxide, except 11 μ peak. This phenomenon appeared also in the case of epoxidation of RSBO.

Afterwards, these epoxides were put into the alcoholysis and amidation. These kinds of chemical modifications should bring different properties and can be applied for the development of bio-induced lubricants.

3. Epoxidation of RSBO

As shown in Table 1, 40% RSBO was epoxidized by 92% with sulfuric acid and only by 77% with Amberlyst 15. Therefore, it is carefully concluded that the epoxidation with in situ-generated peracids with sulfuric acid is a better method than using an Amberlyst 15 as catalyst to obtain higher yield.

When 20% RSBO was epoxidized, the degree of epoxidation was 91-100%, and gave similar results for the case of 40% RSBO leading to the conclusion that the epoxidation of the RSBO with in situ-generated peracids was suitable for obtaining a higher yield. In both cases of epoxidation with sulfuric acid and with Amberlyst 15, the conversion/yield of the latter case was lower than that in sulfuric acid. The reasons may be attributable to the blocking of active sites by adsorption of compounds in the reaction system, smaller contact area and smaller surface area of Amberlyst 15 [12,21,22].

4. Addition of Alcohols to ESBO

Alcohols were added to the ESBO, which was produced by using the standard procedure of an in situ-generated peracetic acid. The addition reactions of simple alcohols such as methanol, ethanol, *i*-propanol and *n*-butanol were studied.

Addition of alcohols to the ESBO was successfully achieved over catalysts such as sulfuric acid or Amberlyst 15. Addition of methanol, for example, to an epoxide ring of 40% RSBO was nearly completed. Also, the same reaction with 20% RSBO showed the same result.

IR spectra (Fig. 2) of the adducts of ethanol and of *i*-propanol showed the stretching vibration ν_{OH} at 3,463 cm^{-1} (ethanol) and 3,486 cm^{-1} (*i*-propanol), respectively, which originated from the hydroxyl group resulting from an epoxide ring opening, and which did not appear in the IR spectrum of epoxides. Also in ^{1}H-NMR spectra of 100% ESBO, a quartet centered at 3.71 ppm appeared which ori-

ginated from the methylene protons of ethoxide group (which is not represented in a figure), while the septet caused by splitting of spin-spin coupling of methine proton of isopropyl group was not found. The reason may be attributable to the very low concentration of the isopropyl group as shown also in Fig. 2(b).

The analysis of mass spectra of the alcohol adduct of SBO was relatively uncertain and difficult, because the molecular weight of SBO is so large with different compositions. Generally, the parent peak cannot be found in the spectrum because of high molecular weight.

5. Transesterification of Alcohol Adducts of ESBO

In order to ensure the alcohol addition to the ESBO, we first transesterified 70% and 100% ESBO in ethanol and in isopropanol, respectively, and investigated the products by means of GC-Mass. For example, as seen in the ethanol adduct to 70% ESBO (Fig. 3(a)) as well as isopropanol adduct to 100% ESBO (Fig. 3(b)), the gas chromatogram of Fig. 3(a) shows the unepoxidized oleic (14.45 min) and linoleic acids (15.24 min) as well as saturated fatty acids such as palmitic (10.70 min), stearic (14.09 min), arachidic (C_{20}, 22.14 min) methylesters and *n*-hexadecanoic acid (21.73 min).

In a GC-MS spectrum of 70% epoxidized ethanol adduct (Fig. 3(a)), two additional products appeared at 25.50 min and 26.16 min, respectively. A very small peak that appeared between them was ignored. The first peak at 25.50 min counted the molecular weight as 358; 9-ethoxy-10-hydroxy methylstearate. GC-MS spectrum (Fig. 4(a)) showed a few more m/e at 327 [M^+ - (CH_3O-), trace], m/e 281 [327 - (C_2H_5OH), trace], m/e 215 [M^+ - CH_3-$(CH_2)_7$-CHOH), 100%]. They are equivalent to the rest part of the molecule, m/e 155 [O=C<$(CH_2)_7$-CHO- or $CH_3(CH_2)_7$-CHOH-CH-, 53%], m/e 171 [155+1/2 O_2; -O-C(=O)- $(CH_2)_7$-CHO; or $CH_3(CH_2)_7$-CH<OC_2H_5- 45%], m/e 201 [171+>CHOH, trace] and m/e 187 [OH-CH<$(CH_2)_7COOCH_3$, 36%].

The second peak at 26.16 min suggested that the 9-ethoxy-10-hydroxymethyl-12-octadecenoate, namely one of the two double bonds, was epoxidized leaving one double bond at 12^{th} carbon position. Fortunately, the mass spectrum (Fig. 4(b)) indicated the parent peak at m/e 356 although its intensity is very small with additional m/e at 215 [M^+ - $CH_3(CH_2)_4CH$=CH-CH_2-CHOH-, 100%], m/e 155 [M^+ - O=C<$(CH_2)_7$-CHO-, 55%], m/e 187 [O-C<$(CH_2)_7COOCH_3$, 20%], m/e 338 [M^+ - H_2O, trace].

In 100% epoxidized isopropyl adduct (Fig. 3(b)), the molecular weight was counted to be 372. However, the alcoholysis in isopropanol did not complete as the case of ethanol. Much of the epoxide peak was still found in the reaction mixture at 21.10 min. The reason may be attributable to the steric hindrance of bulky secondary

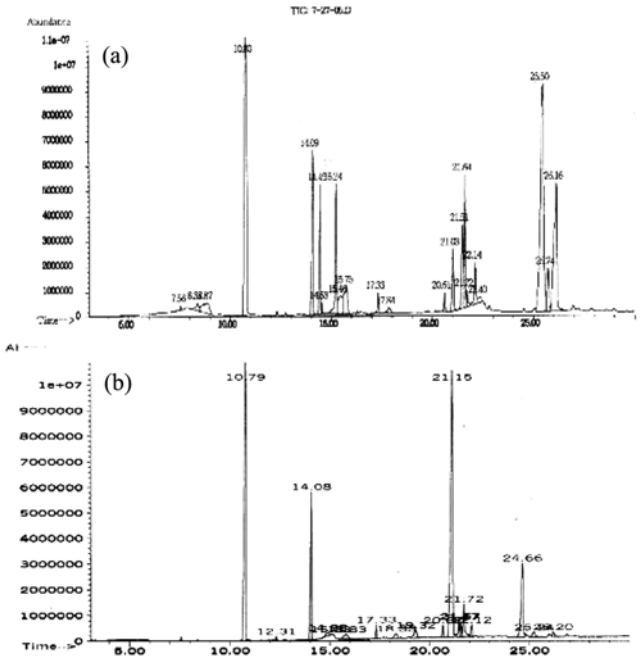

Fig. 3. The gas chromatograms of ethanol adduct of 70% ESBO (a) and isopropanol adduct of 100% ESBO (b) after transesterification.

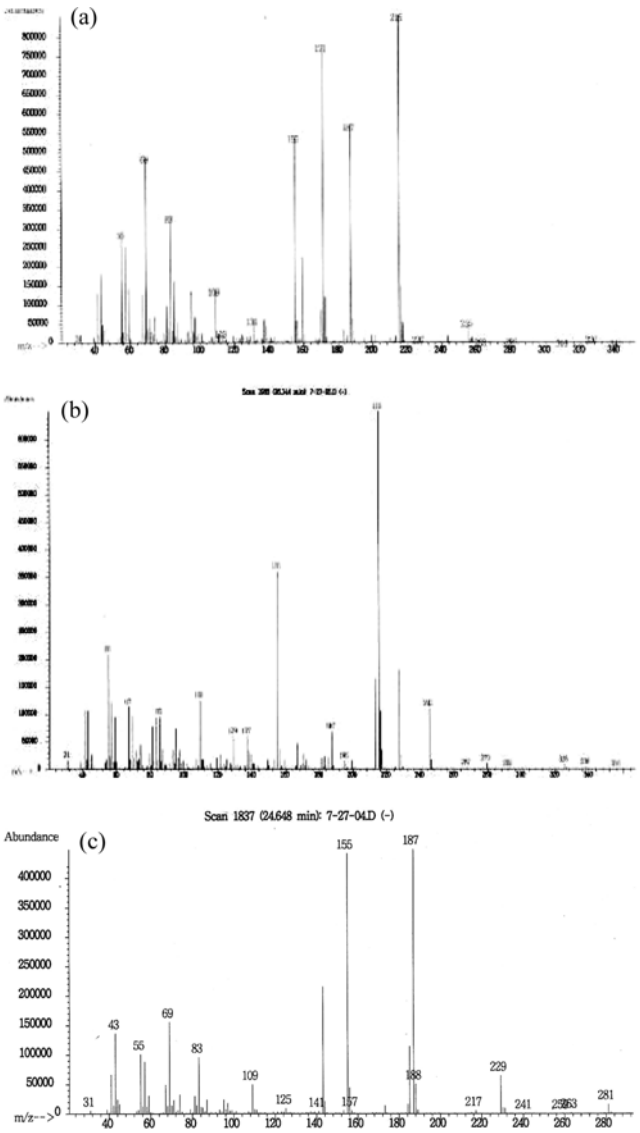

Fig. 4. (a) GC-MS spectrum of the peak at 25.10 min in Fig. 3(a) [9-Ethoxy-10-hydroxymethylstearate]. (b) GC-MS spectrum of the peak at 26.14 min in Fig. 3(a) [9-Ethoxy-10-hydroxymethyl-12-octadecenoate]. (c) GC-MS spectrum of the peak at 24.66 min in Fig. 3(b) [9-Isopropyloxy-10-hydroxymethylstearate].

isopropyl group compared to the linear primary ethyl group. In the GC-Mass spectrum (Fig. 4(c)), the peak at 24.66 min showed m/e 229 [M^+ - CH_3-$(CH_2)_7$-CHOH] 20%], m/e 187 [229 - $(CH_3)_2$C-, 100%], m/e 155 [$CH_3(CH_2)_7$-CHOH-CHO-, or O=C<$(CH_2)_7$-CHO 100%], m/e 143 [CH_3-$(CH_2)_7$-CHOH, 43%], respectively. Especially, m/e 187 supports clearly the presence of isopropyl group. From these analyses, isopropanol adduct of ESBO was verified as 9-isopropyloxy-10-hydroxymethylstearate.

Above results showed that the addition of light alcohols (C1-C3) to ESBO producing ethanol and isopropanol adducts was successfully performed and identified for the first time by means of IR- and GC-MS spectroscopies.

6. Addition of 1- Hexylamine to 100% ESBO

Aminolysis of 100% epoxidized SBO with *n*-hexylamine was performed in the presence of acidic catalysts such as conc. sulfuric acid and/or Amberyst 15 in benzene at 60 °C for 3-5 h. The reactions did not proceed well in either case. However, the thiolysis of ESBO with *n*-butanehtiol was completed in 4 h without cleaving an ester linkage. Therefore, the reaction conditions were changed according to Sharma's method [13] using perchloric acid as catalyst and methylene chloride as a solvent. The reaction proceeded very slowly in our case. This might be attributable to the lower nucleophilicity of the amino group. After 10 h reaction, the reaction mixture was treated and analyzed by means of IR- and proton NMR-spectroscopies. Surprisingly, as seen in Fig. 5(a), the NMR spectrum indicated the disruption of some ester bonds of triglyceride. The signal at 4.26-4.28 ppm was decreased while the new signals appeared at 2.68 ppm, which could be attributable to the methylene >CH-NH-**CH_2**- group and also at 5.29-5.30 ppm attributable to the OH group. The product was solidified after solvent evaporation. This result suggests strongly that the cross linking occurred by amine.

In the IR-Spectrum (Fig. 5(b)), a sharp new ν_{NH} at 3,324 cm^{-1} and δ_{asNH} scissor at 1,637 cm^{-1}, δ_{symNH} 1,544 cm^{-1} peaks and ν_{CN} at 1,163 cm^{-1} appeared, while $\nu_{C=O}$ 1,743 cm^{-1} was strongly reduced and the most of epoxide ring peaks disappeared. Instrumental analyses data suggested that the reaction progressed toward the amidation instead of aminolysis. The diethylamine aminolysis of ESBO with intact ester group was performed over $ZnCl_2$ without solvent at 80 °C in 4 h [14].

7. Addition of 1,6-Hexamethylenediamine to 100% ESBO and SBO

In the reactions of ESBO with *n*-hexylamine, the authors found that the reactions routed to the path of amidation with cross-linking instead of aminolysis. Therefore, we put into the investigation a diamine and the hexamethylenediamine in place of monoamine or *n*-hexylamine. The amidation of 100% ESBO and of pure SBO was carefully performed. The cross-linked ESBO products could open new ways of application especially in developing quality lubricants. In many cases, plant oil based chemistry is focused on the polymeric composites with different inorganic compounds [23,24] and on introducing functional group to polymers [18,25]. However, in this work we synthesized new products for the first time which could be applicable to the lubricants.

7-1. Addition of 1,6-Hexamethylenediamine to 100% ESBO

In the case of 100% ESBO, which was previously reacted for

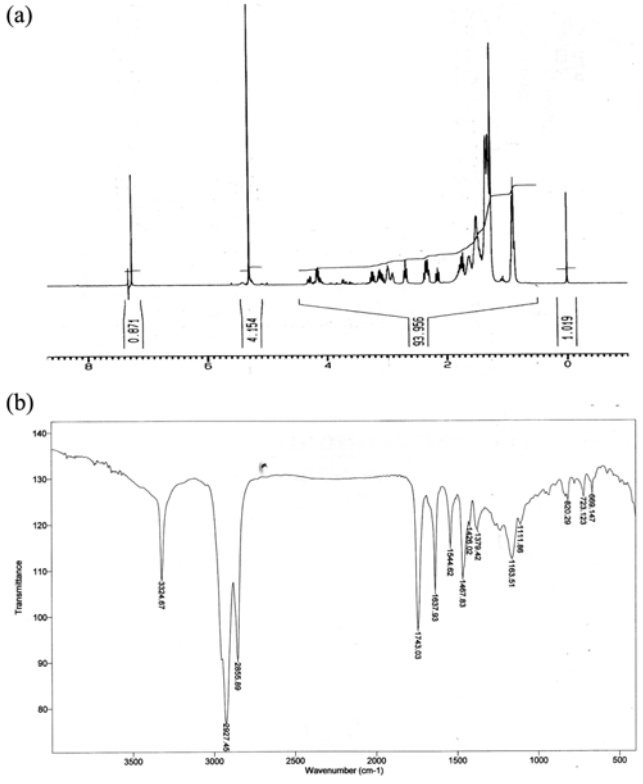

Fig. 5. ^{1}H-NMR-(a) and FT-IR spectra (b) of the product of ESBO with *n*-hexylamine.

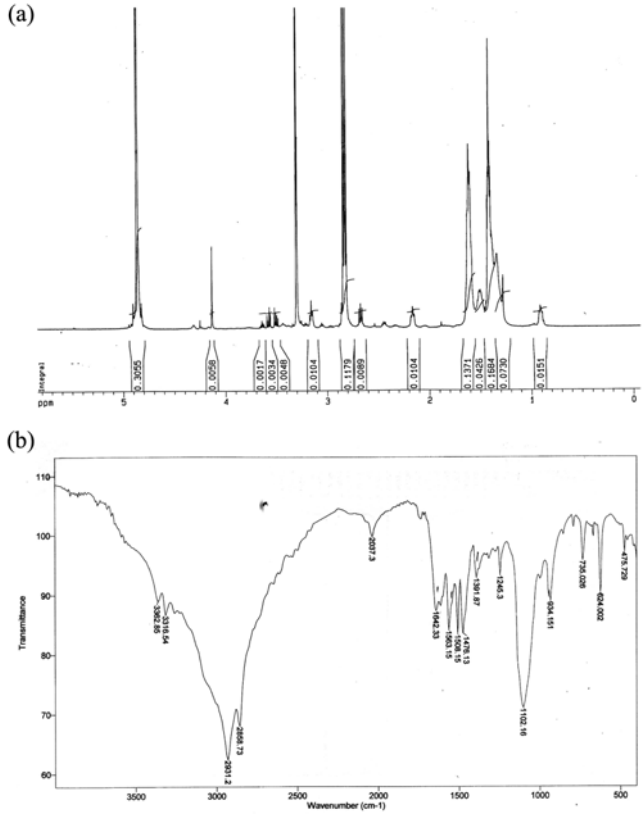

Fig. 6. ^{1}H-NMR-(a) and FT-IR-spectra (b) of ESBO-HMDA reaction product for 16 h.

16 h, the proton NMR spectrum (Fig. 6(a)) showed two new signals at 4.82-4.90 ppm and at 3.29-3.30 ppm, which were not present in the starting materials. The latter could be attributed to >CO-NH-**CH_2**-. The signal at 4.82-4.90 ppm (the former) cannot be assigned at this moment. The signal at 2.81-2.85 ppm which can be attributable to -NH-**CH_2**- of hexamethylenediamine and also appeared in the *n*-hexylamine product with 100% ESBO. In the NMR spectrum, the signal at around 5.30 ppm, which could be correspondent to -OH did not appear. The -OH signal appeared at 5.29-5.30 ppm in the reaction product of ESBO with *n*-hexylamine and in the 10 h reaction product of ESBO and HMDA. These results indicated that in the longer reaction the dehydration of hydroxyl group along with a hydrogen of amino group took place to form a new >C-NH-**CH_2** bond, which eventually induced to cross linking. The absence of -OH signal in the 16 h reaction well supported this explanation agreeing with above observations. The methyl signal at 0.98 ppm decreased strongly due to the hydrolysis of ester linkage and/or some of esters might be washed out during washing processes.

In the IR spectrum (Fig. 6(b)), there appeared no carbonyl peak around 1,744 cm^{-1} and at 1,642 cm^{-1} while showing a new amide peak of O=CNH and a very strong ν_{CN} at 1,102 cm^{-1}. Also, two weak ν_{NH} peaks at 3,362 and 3,316 cm^{-1} appeared. The last two peaks could be attributed to each different -NH- group in different environment.

In a 10 h reaction (Fig. 7(a)), backbone CH_2 disappeared while two protons from -NH-**CH_2**- appeared at 2.65 and 3.21 ppm, respectively, although the intensity is smaller than that of 16 h reaction product. In the 10 h reaction, the -OH signal appeared at 5.27 ppm

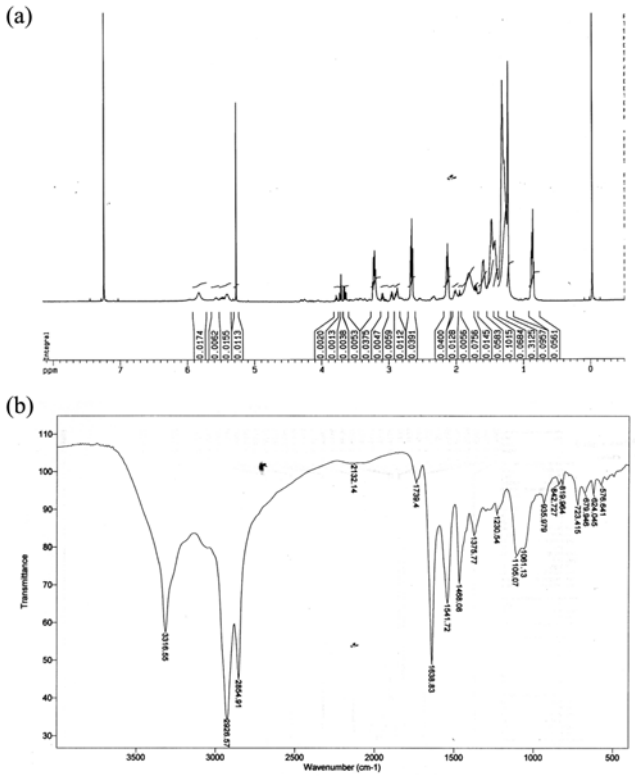

Fig. 7. ^{1}H-NMR-(a) and FT-IR-spectra (b) of ESBO-HMDA reaction product for 10 h.

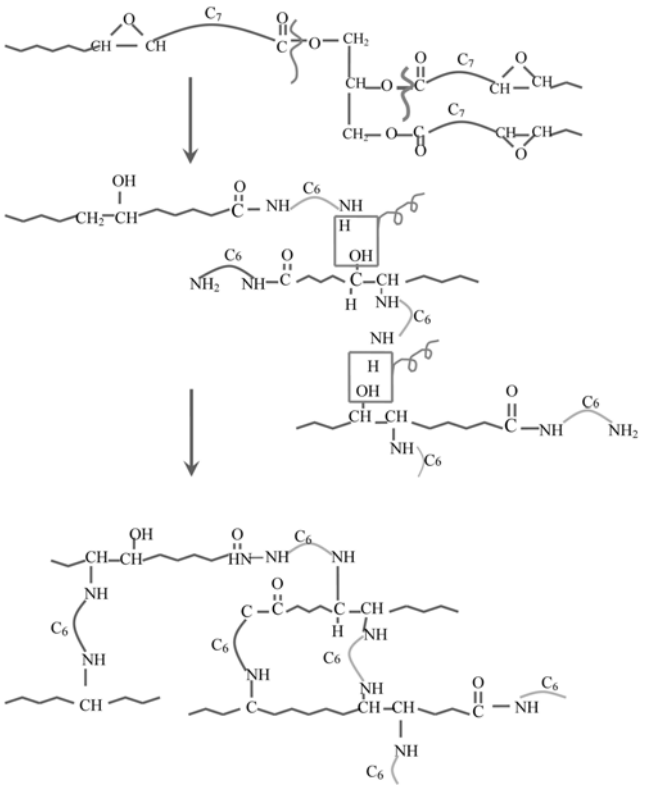

Fig. 8. Proposed product structure of reaction of [100% ESBO+ HMDA] (catalyst. $HClO_4$).

which did not appear in the product of 16 h reaction. Instead of that in IR spectrum, a stronger and sharper ν_{NH} peak at 3,316 cm^{-1}, and stronger O=CNH- at 1,638 cm^{-1} appeared, while a weaker ν_{CN} peak at 1,105 cm^{-1} appeared (Fig. 7(b)).

From these instrumental analyses, the structure of the product was tentatively proposed as shown in Fig. 8. In the presence of an acid catalyst, the strained epoxide ring opened easily to produce the carbocation to which the nucleophilic amino group added. On the other hand, the amine group at other side attacked the carbonyl carbon, accelerating the hydrolysis of ester linkage. Another possibility is that the dehydration of hydroxyl group from ring opening formed a new >C-NH- bond with one hydrogen of amino group, which induced a cross linking. Therefore, the IR spectrum of the product showed two amine peaks at 3,362 and 3,316 cm^{-1}.

7-2. Addition of 1,6-Hexamethylenediamine to SBO

Amidation of pure SBO was performed with the same recipe as that of 100% epoxide. In this case the reaction time was 10 h. Comparing the NMR spectrum of the amidation product to that of SBO, (Fig. 9(a)), some new signals appeared at 1.46 ppm which attributable to -**NH**-CH_2-, at 3.19-3.21 ppm attributable to -NH-C**H_2**- [19] and small signals between 3.50-3.80 ppm. As in the ESBO-hexylamine case, the signals centered at 4.28 ppm originating from one of -CH_2 backbone disappeared. Also, the signals of olefinic protons centered at 5.3 ppm and a methine proton located at a little downfield appeared. The new signal at 2.11-2.16 (t) could not be assigned but suggested to be an amine group related one. Disappearance of -OH signal around 5.2 ppm in the NMR spectrum explained our observation and well agreed with our logical expectation.

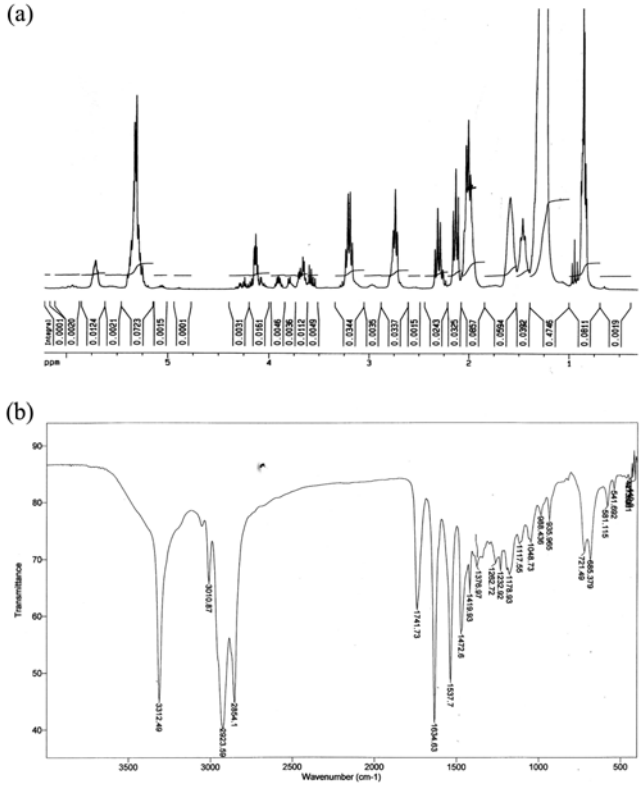

Fig. 9. ^{1}H-NMR-(a) and FT-IR-spectra (b) of SBO-HMDA reaction product.

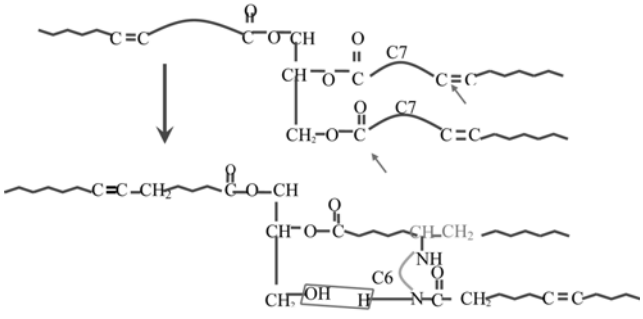

Fig. 10. Proposed product structure of (SBO+HMDA) reaction.

In the IR spectrum (Fig. 9(b)), sharp and strong new ν_{NH} peaks at 3,312 cm^{-1}, $\nu_{C=CH}$ 3,010 cm^{-1}, and strong δ_{asNH} scissor at 1,634 cm^{-1}, and δ_{symNH} 1,537 cm^{-1} appeared while $\nu_{C=O}$ 1,741 cm^{-1} was markedly reduced.

The cross-linked products were tentatively proposed for the first time as shown in Fig. 10 based on the instrumental analyses of the amidation products. The amidation to carbonyl group could readily occur. Also, the addition of amino group to some double bonds in the presence of acid catalyst could be suggested. The integration intensities of methyl and olefinic protons in SBO are 2.55 to 2.57, while those of the product are 0.081 to 0.0723, respectively, indicating that about 12.8% of double bonds took part in the cross linking reaction.

From the spectroscopic results in the reactions of SBO and ESBO with *n*-hexylamine and hexamethylenediamine, the ester linkage of substrates was partially hydrolyzed or completely forming cross-linked products.

CONCLUSIONS

1. To obtain different types of base oils for lubricants, the SBOs were reduced at high pressure and high temperature with catalysts (25% Ni/SiO_2, 5% Pt/C), epoxidized, then alcoholysis and amidation to epoxides was performed, and finally transesterification to analyze the final products.

2. Processes of the epoxidation of SBOs and RSBOs as well as the addition of alcohols to ESBOs were established.

(1) Addition of alcohols such as methanol, ethanol, and isopropanol to the ESBO was successfully achieved by the use of catalyst sulfuric acid and/or Amberlyst 15.

(2) Addition of methanol and ethanol to the epoxides of different degrees of RSBOs proceeded completely, that of isopropanol was incomplete. The reason was attributed to the bulkiness of the isopropyl group compared to a linear ethyl group.

(3) In IR spectra of ethanol and isopropanol adducts, there appeared ν_{OH} around 3,500 cm^{-1} proving the addition of alcohols as side chains. In ^{1}H-NMR spectrum of ethanol adduct, the quartet from -CH_2 of ethoxide was confirmed.

(4) Transesterification of alcohol adducts of ESBO was analyzed by GC-Mass spectrometry and identified for the first time as the 9-ethoxy-10-hydroxy-methylstearate, 9-ethoxy-10-hydroxymethyl-l 2-octadecenoate, and 9-isopropyl-oxy-10-hydroxy-methylstearate.

3. Aminolysis of *n*-hexlyamine and 1,6-hexamethylenediamine to ESBO and SBO did not proceed well, while the amidation products readily formed cross-linking products.

4. Structures of cross-linked products of ESBO and of SBO with HMDA were tentatively proposed for the first time based on the instrumental analyses.

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