

# Polyesters from Renewable Resources: Preparation and Characterization

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**ABSTRACT:** Polyesters were synthesized with monoglycerides prepared from rubber seed oil, a renewable resource. Monoglycerides were obtained by an alcoholysis method from the oil, which was neat or modified by treatments with different amounts of maleic anhydride at 230°C. The polyester resins were subsequently prepared by the condensation polymerization of the monoglycerides with phthalic anhydride. The monoglycerides and resins were character-

ized by spectroscopic analysis and measurements of the physicochemical properties. The chemical resistance of the polyesters was also studied. The results revealed that the polyesters prepared from the modified monoglycerides possessed better properties. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3748–3755, 2006

**Key words:** polyesters; renewable resources; rubber

## INTRODUCTION

Polyesters constitute a variety of materials with different chemical structures and mechanical properties that are widely used in laminates, industrial construction and installation, molding compounds, coatings, and adhesives. They are usually synthesized by the polycondensation reaction of a dibasic acid or anhydride and a polyol (usually glycols) or hydroxyl acid.<sup>1</sup> These monomers are obtained from petroleum products. The use of petroleum-based monomers in the manufacture of consumer products is expected to decline in coming years because of the continuous rise in the price of oil and the high rate of depletion of known oil reserves.<sup>2</sup> This, coupled with strict government legislation all over the world on environmental protection against degradation, has inspired the investigation of renewable natural resources as a viable alternative.<sup>3</sup>

Fats and oils (animal or vegetable in origin) have long been identified as possible substitutes for petrochemical derivatives in the production of polymers for many applications.<sup>3–7</sup> Fats and oils make up the greatest proportion of the current consumption of renewable raw materials in the chemical industries as they

offer to chemistry a large number of possible applications.<sup>5,6</sup>

To meet the increasing demand for these renewable raw materials, the use of modern biotechniques and genetic engineering approaches have proved successful for oil plants such as soybean and rapeseed. This modern universal approach for changing the amount and composition of the stored oil has enabled the optimization of the resources for different specific applications.<sup>3,7</sup> Also, underused and new seeds such as rubber seed, African locust bean seed, and jathropa seed have continuously been sourced for nonedible applications.<sup>8–12</sup>

Rubber seed oil (RSO), an agricultural byproduct abundantly available in Nigeria and rich in unsaturated hydrocarbons, is an excellent starting material for many products. An estimation of potential production, based on a world planted area of 9.37 million hectares<sup>13</sup> and an average production rate of rubber seeds of 287 kg/ha/year,<sup>14,15</sup> is over 1.08 million tons of RSO per annum. This figure is expected to increase substantially with the expansion of natural rubber production, although RSO has no commercial value to our knowledge.

Previous research studies have shown that RSO is a potential raw material for the production of alkyd resins,<sup>16,17</sup> the processing of polymers,<sup>18,19</sup> and the production of biodiesel.<sup>20,21</sup> Despite the potential of RSO in the production of alkyd resins, the produced resins are usually dark, and this limits its application in nonpigmented coatings.<sup>21</sup> In this article, a different approach for synthesizing RSO-based polyester resins is described. It involves the treatment of RSO with

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TABLE I  
Recipes for the Formulation of Polyesters

| Component (g)      | I      | II     | III    |
|--------------------|--------|--------|--------|
| RSO                | 30.183 | 30.183 | 30.183 |
| Glycerol           | 25.024 | 25.022 | 25.024 |
| MA                 | —      | 0.805  | 2.415  |
| Phthalic anhydride | 16.101 | 16.100 | 16.100 |

maleic anhydride (MA) followed by alcoholysis with glycerol. The resulting modified monoglyceride is subsequently used to produce a polyester resin.

### EXPERIMENTAL

RSO was obtained from Murugesan and Sons (Tamil Nadu, India). Phthalic anhydride, MA, glycerol, and calcium oxide were obtained from S.D. Fine Chemicals, Ltd. (Mumbai, India).

#### Fatty acid composition

The fatty acid composition of RSO was determined by GLC with its methyl ester derivatives according to American Oil Chemists Society (AOCS) method Ce-2-66.<sup>22</sup> Fatty acid compositions were analyzed with a Hewlett-Packard (Avondale, PA, USA) 5890 series II gas chromatograph with a flame-ionization detector. The injection and detection temperatures were maintained at 250 and 300°C, respectively. The flow rate of the carrier gas, nitrogen, was 20 mL/min. The oven temperature was programmed at 100–180°C at a rate of 5°C/min. Methyl esters of RSO were identified and quantified by a comparison of the retention times and the areas under the peaks of the unknown with those of standard methyl ester.

#### Modification of RSO

RSO was treated with different proportions of MA at 210°C under a nitrogen atmosphere for about 1.5 h.

#### Preparation of the polyesters

Three samples of polyesters (I–III) were prepared with RSO glycerol, phthalic anhydride, and MA according to the recipe shown in Table I. The reactions were carried out in a 100-mL, three-necked flask fitted with a thermometer, reflux condenser, and nitrogen gas inlet tube to create an inert atmosphere in the reaction flask.

In a typical reaction, RSO, glycerol, and 0.1% CaO (catalyst) were poured into the reaction flask. Heating was effected with a thermostated oil bath. The reaction temperature was raised and maintained at 230°C for about 3.5 h under nitrogen. This alcoholysis process

was stopped when the mixture became soluble in anhydrous methanol (1:3 oil/methanol). After cooling, the unreacted glycerol was removed from the resulting glyceride mixture (this glyceride mixture was subsequently used for polycondensation reaction in stage 2). A sample from the glycerides was collected and dissolved in an equal mixture of *n*-hexane and diethyl ether. The resulting mixture was washed with water and dried over sodium sulfate, and the solvent was removed *in vacuo*. The acid value and monoglyceride content were determined with standard methods (AOCS).<sup>22</sup>

The glyceride mixtures, phthalic anhydride, and dry xylene were poured into a three-necked reaction flask. The reactor was then fitted with a motorized stirrer and a Dean–Stark apparatus carrying a water-cooled condenser. The reaction was carried out in an inert atmosphere created by the bubbling of nitrogen gas into the reactor at 230°C. The efflux was drained into the Dean–Stark apparatus, in which xylene was separated from water released during the condensation reaction and returned to the reactor through the overflow point. The progress of the reaction was monitored by the determination of the acid value of aliquots of the reaction mixture until an acid value of less than 10 mg of KOH/g was reached. A sample of the polyester resin was collected and characterized. Similar reactions were carried out with MA-modified RSO.

#### Characterization

<sup>1</sup>H-NMR spectra of polyesters were recorded with a Bruker 300-MHz NMR spectrophotometer in CDCl<sub>3</sub> containing a small amount of tetramethylsilane as an internal standard. About 25–30 mg of a sample was dissolved in 1 mL of CDCl<sub>3</sub>.

TABLE II  
Physicochemical Properties of RSO

| Property                                  | Value                |
|---|----------------------|
| Color (Lovinbond 1" cell)                 | 22R, 23.2Y           |
| Specific gravity (at 30°C)                | 0.916                |
| Free fatty acid (as oleic acid; %)        | 21.40                |
| Acid value (mg of KOH/g)                  | 43.62                |
| Saponification value (mg of KOH/g)        | 202.91               |
| Iodine value (g of I <sub>2</sub> /100 g) | 136.21               |
| Fatty acid composition of RSO (%)         |                      |
| Saturated                                 |                      |
| C <sub>16:0</sub>                         | Palmitic acid 17.51  |
| C <sub>18:0</sub>                         | Stearic acid 4.82    |
|   | Total 22.33          |
| Unsaturated                               |                      |
| C <sub>18:1</sub>                         | Oleic acid 25.33     |
| C <sub>18:2</sub>                         | Linoleic acid 37.50  |
| C <sub>18:3</sub>                         | Linolenic acid 14.21 |
|   | Total 77.04          |
| Others                                    | 0.63                 |

**TABLE III**  
Assignments of FTIR Peaks for RSO

| Absorption<br>( $\text{cm}^{-1}$ ) | Assignment                               |
|------------------------------------|--|
| 3009                               | C—H stretching frequency of unsaturation |
| 2853                               | C—H stretching frequency of alkane       |
| 1740                               | C=O frequency of carbonyl group          |
| 1164                               | C—O stretch frequency of ester           |
| 1653                               | C=C stretch frequency of alkene          |
| 881                                | C—H stretching frequency of alkane       |

IR spectra were recorded with an Impact 400 D Nicolet Fourier transform infrared (FTIR) spectrophotometer. The samples were spread over NaCl cells, and their spectra were recorded. IR spectra were recorded in the range of  $4000\text{--}400\text{ cm}^{-1}$ .

The properties of the polyesters were determined by ASTM methods.

#### Evaluation of the film properties

Samples of the polyester were mixed with 0.5 and 0.03% calcium and cobalt naphthalate drier, respectively. These mixtures were thinned with xylene. The prepared solutions were spread on clean glass plates. The drying schedules of the polyester samples were evaluated. The test panels were assessed for their re-

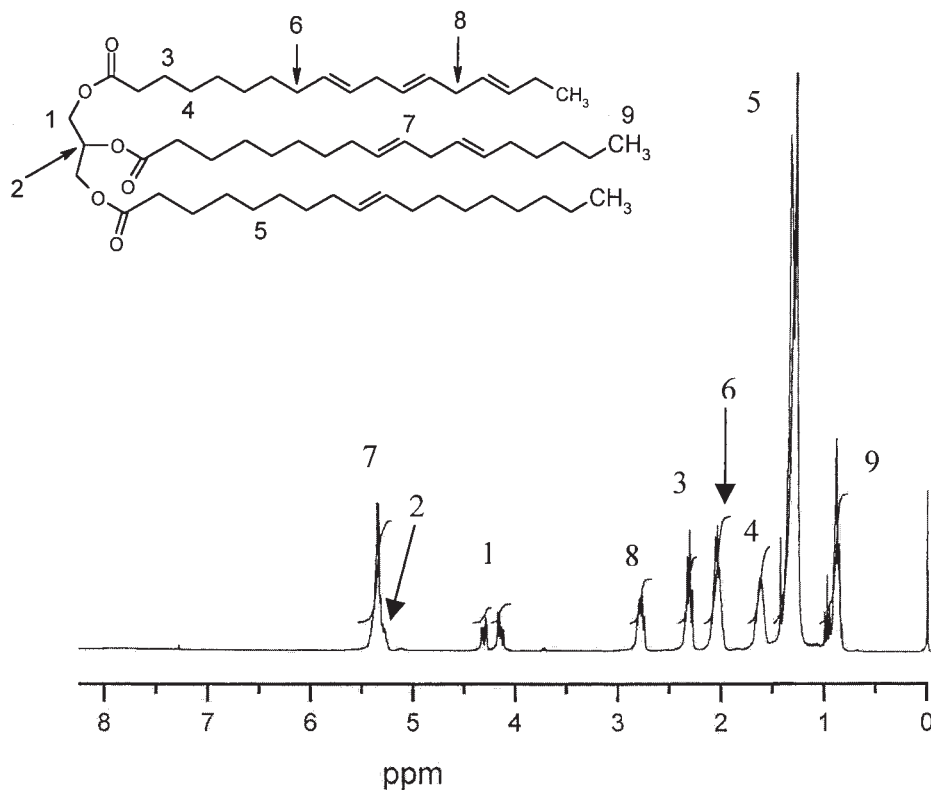
sistance to different service media by an immersion method for 24 h. The service media used were distilled water, a 5% (w/v) sodium chloride solution, and 0.1M KOH and  $\text{H}_2\text{SO}_4$  solutions (ASTM D 1308-57).

#### RESULTS AND DISCUSSION

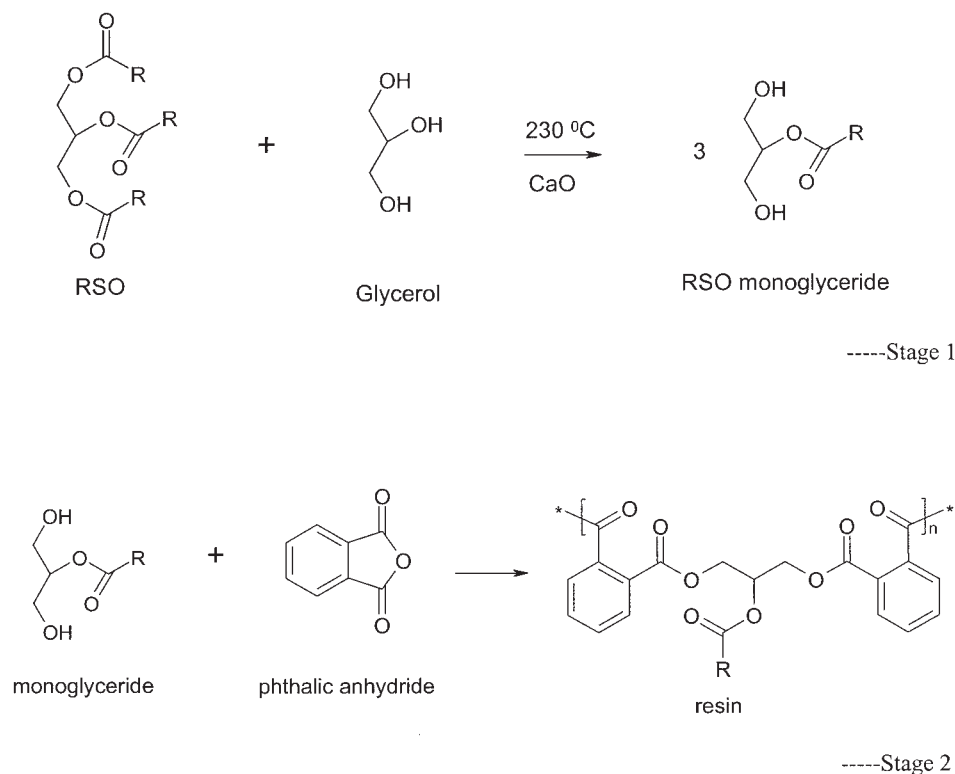
The properties of RSO are presented in Table II. The fatty acid composition of RSO showed that it consisted of 22.3% saturation comprising palmitic and stearic acids and 77.0% unsaturation comprising mainly oleic, linoleic, and linolenic acids. The high content of unsaturated fatty acid in RSO gave rise to the high iodine value of 136.21 g of  $\text{I}_2/100\text{ g}$  of oil. This iodine value is lower than that of linseed oil but similar to that of soybean oil, which are commonly employed in surface coatings.<sup>8</sup> Thus, RSO may be regarded as a semidrying oil because of the lower content of linolenic acid (14.2%) in comparison with linseed (ca. 44–45%). These properties were further confirmed by IR results presented in Table III, with a stretching vibration of C=C at  $1653\text{ cm}^{-1}$  and C—H unsaturation at  $3009\text{ cm}^{-1}$ .  $^1\text{H-NMR}$  with peak assignments in Figure 1 also reveals the presence of CH=CH unsaturation at  $\delta = 5.3\text{ ppm}$ .

#### Properties of the RSO monoglyceride and polyester

The reaction scheme for the preparation of the RSO polyester resin is outlined in Scheme 1, where R rep-



**Figure 1**  $^1\text{H-NMR}$  spectrum of RSO.



**Scheme 1** Synthetic route of RSO based polyester.

resents the fatty acid or MA-modified fatty acid group of the starting oil. Stage 1 is the simplified chemical equation for glycerolysis because monoglyceride is the predominate product. The extent of alcoholysis (stage 1) is usually measured by the determination of the solubility of the reaction mixture in methanol. The reaction is considered completed when one part of the reaction mixture is soluble in two parts of methanol.<sup>11,16,17</sup> This solubility test is not an accurate measure of the extent of monoglyceride formation, although it provides a quick and convenient assessment test. The results of the alcoholysis products monitored by thin-layer chromatography and solubility testing are presented in Table IV. The IR spectra of the alcoholysis products (sample I) that were further separated by a column chromatograph (AOCS Cd 11C-93)<sup>22</sup> are presented in Figure 2. Some notable features of the IR spectra include 3370–3470 ( $\nu$ O—H), 3009 ( $\nu$

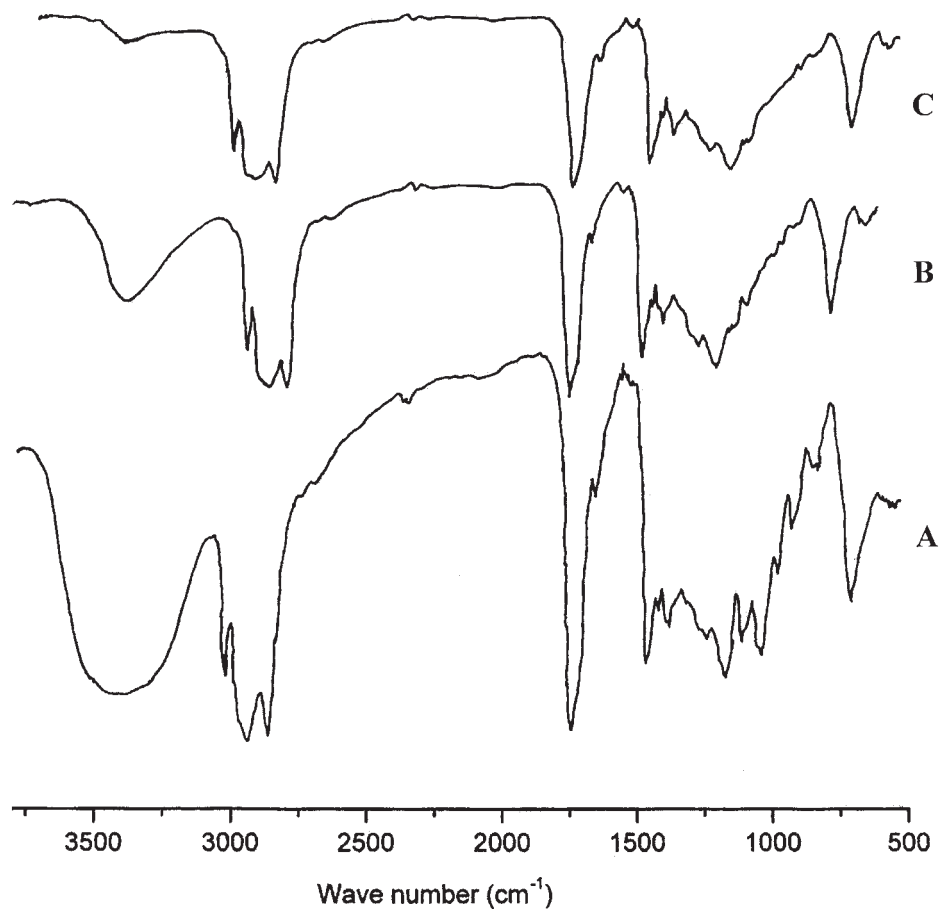
C—H unsaturation), 2924 ( $\nu$  C—H Saturation), 1747 ( $\nu$  C=O), 1249 and 1165 ( $\nu$  C—O—C), and 1655  $\text{cm}^{-1}$  ( $\nu$  CH=CH). The O—H vibration frequency between 3370 and 3470  $\text{cm}^{-1}$  present in Figure 2(A,B) is completely absent in Figure 2(C). This shows that spectrum C represents triglyceride present in the alcoholysis product. Spectrum A has a broad absorption peak and a higher absorbance ratio between OH (3450  $\text{cm}^{-1}$ ) and CH<sub>2</sub> (2960  $\text{cm}^{-1}$ ) in comparison with spectrum B. Spectrum A, with a high proportion of hydroxyl, indicates monoglyceride, whereas spectrum B represents diglyceride.

The composition percentages from column chromatography analysis were 48.30, 36.66, and 15.04% mono-, di-, and triglycerides, respectively (in the alcoholysis product of sample I). However, titrimetric determination of monoglyceride revealed that periodic acid oxidation only gave 29.41% in that sample (Table IV). The difference must have been due to the presence of  $\beta$ -monoglyceride. Periodic acid only oxidizes  $\alpha$ -monoglyceride,<sup>23</sup> and it is known that monoglycerides exist in two different structural modifications, namely,  $\alpha$ -monoglyceride and  $\beta$ -monoglyceride.<sup>23,24</sup> These results therefore show that solubility testing is an approximate measure of the extent of monoglyceride formation.

The IR and NMR spectra of the prepared alcoholysis products were similar, except in intensity. Therefore,

**TABLE IV**  
Monoglyceride Contents and Acid Values of the Alcoholysis Products (Samples I–III)

| Sample | Monoglyceride content (%) | Acid value (mg of KOH/g) |
|--------|---------------------------|--------------------------|
| I      | 29.41                     | 2.68                     |
| II     | 24.30                     | 3.02                     |
| III    | 23.29                     | 5.11                     |

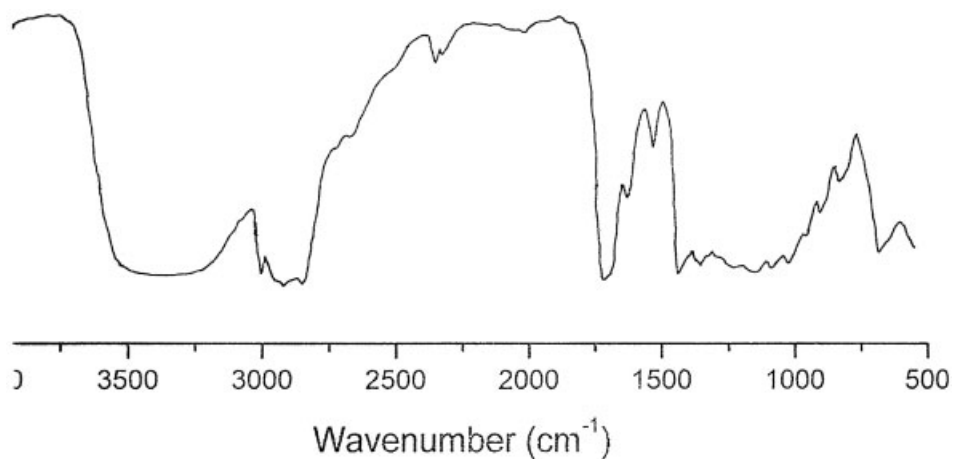


**Figure 2** FTIR spectra of partial glycerides: (A) monoglyceride, (B) diglyceride, and (C) triglyceride.

the IR and NMR spectra of a typical partial glyceride used for the preparation of the polyester are presented in Figures 3 and 4. The characteristic absorption at  $3393\text{ cm}^{-1}$  and  $\delta = 3.74\text{ ppm}$  is due to OH. This indicates the presence of the hydroxyl group in the product.

#### RSO polyester

The IR spectra of the RSO polyesters (Fig. 5) show a strong band at  $1731\text{ cm}^{-1}$  characteristic of the stretching frequency of the carbonyl group, and the bands (doublet) at  $1600$  and  $1575\text{ cm}^{-1}$  are indicative of the



**Figure 3** FTIR spectrum of a typical alcoholysis product.

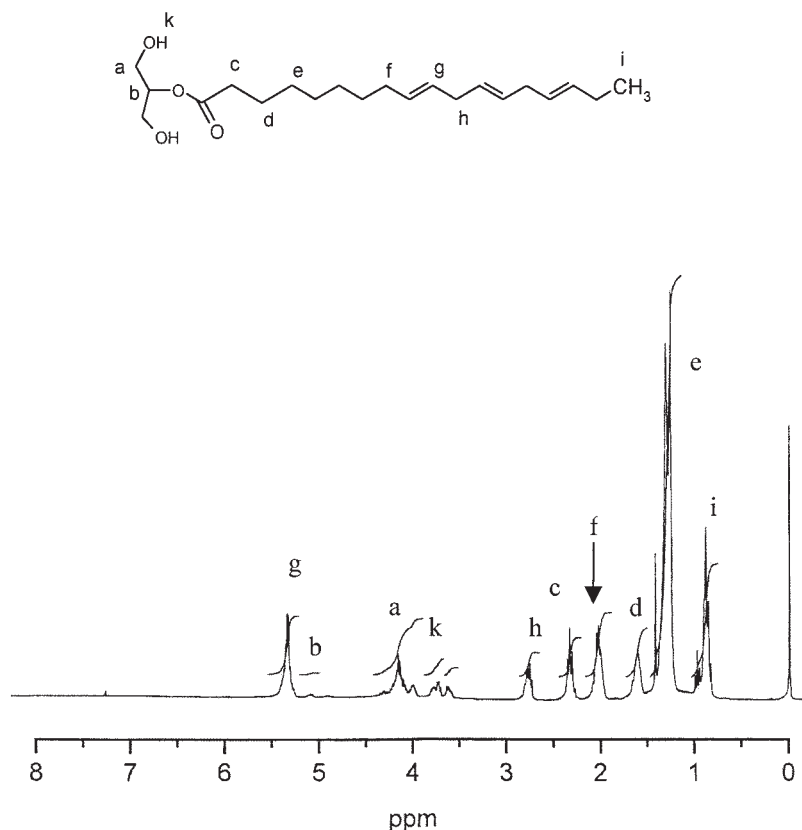


Figure 4  $^1\text{H-NMR}$  spectrum of a typical monoglyceride.

unsaturation of the aromatic group of the polyester. The band at  $1276\text{ cm}^{-1}$  indicates C—O—C linkages of the ester. Other aromatic nuclei bands are present at  $1163$ ,  $1071$ , and  $742\text{ cm}^{-1}$ . The NMR spectra of all three

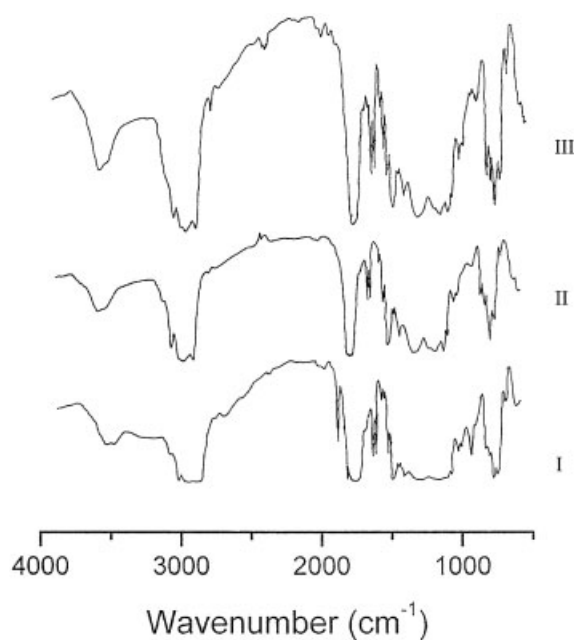
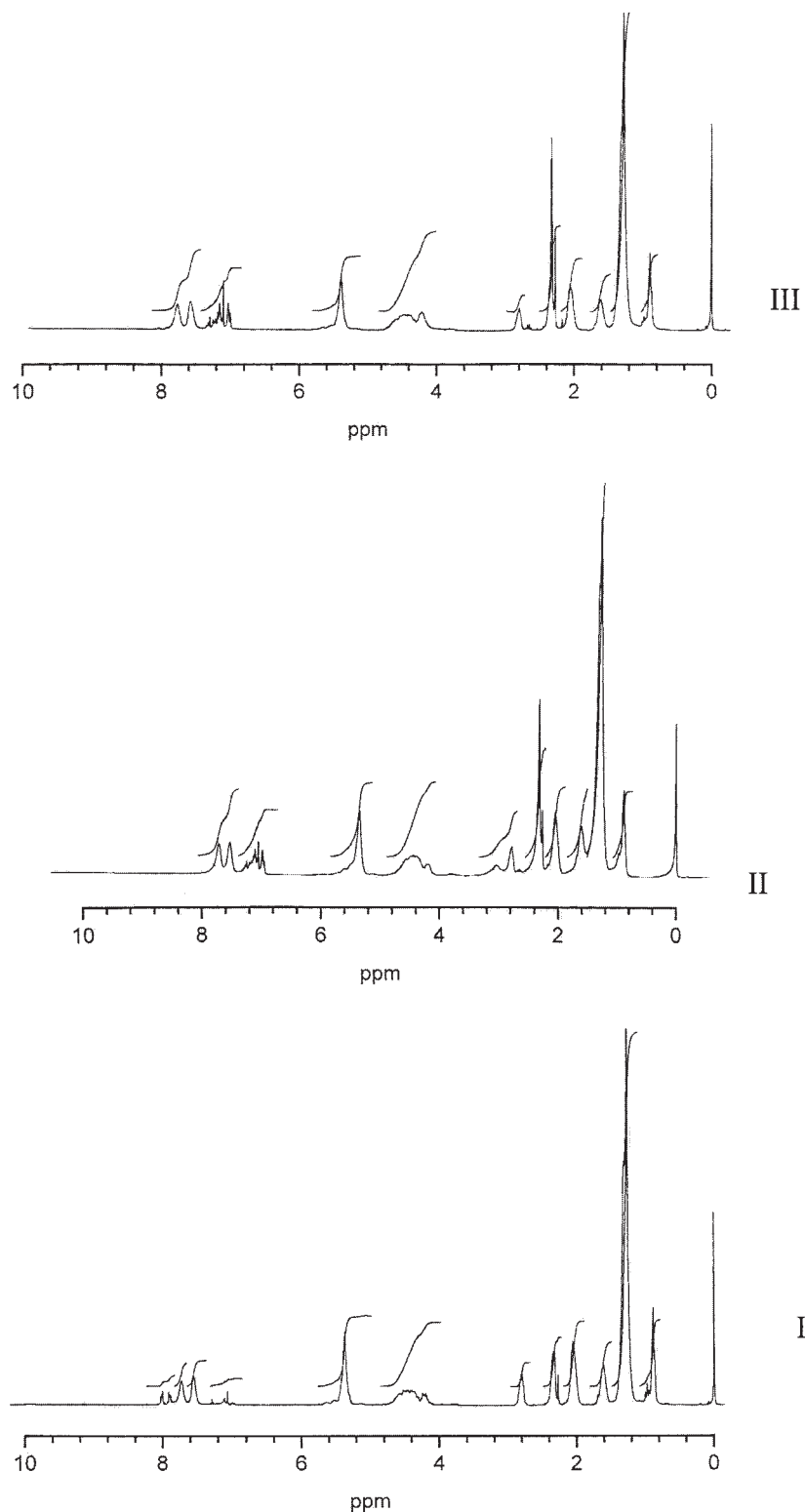


Figure 5 FTIR spectra of RSO polyesters.

polyesters presented in the figures are similar. The peak at  $\delta = 0.88\text{ ppm}$  represents the terminal methyl group of the fatty acid chain. The  $\text{CH}_2$  proton of the glyceryl can be found between  $4.11$  and  $4.43\text{ ppm}$ . However, the peak of the olefinic group at  $5.34$ – $5.59\text{ ppm}$  must have enveloped CH of the  $\beta$  glyceryl group. The broad peak at  $2.78\text{ ppm}$  represents the proton of  $\text{CH}_2$  attached to the carbonyl group of the fatty acid chain, whereas the multiplet peaks between  $1.25$  and  $2.31\text{ ppm}$  represent the internal  $\text{CH}_2$  group at different positions of the fatty acid chain. These observations further confirm the structure of the polyester represented in Scheme 1.

Comparisons of a typical partial glyceride spectrum with that of polyester reveal the presence of the hydroxyl group in RSO monoglyceride with a broad absorbance at  $3393\text{ cm}^{-1}$  (IR) and a peak at  $3.74\text{ ppm}$  (NMR). However, the intensity of this absorbance band in IR was drastically reduced in the polyester resin, with the complete absence of the peak in  $^1\text{H-NMR}$ . This reveals that the free hydroxyl in monoglyceride was used up for ester linkage. Also, the  $^1\text{H-NMR}$  and IR spectra of the polyester resins reveal the aromatic protons from the phthalic anhydride of the polyesters at a chemical shift between  $7.5$  and  $8.0\text{ ppm}$  and the aromatic doublet absorbance at  $1600$  and  $1575\text{ cm}^{-1}$ .

The properties of the RSO polyesters are given in Table V. The acid value ranged from  $10.49\text{ mg}$  of



**Figure 6**  $^1\text{H-NMR}$  spectra of RSO polyesters: (I) neat, (II) 2.5%, and (III) 7.4% MA modified.

KOH/g for sample II to 17.46 mg of KOH/g for sample III. The saponification value, iodine value, and curing time decreased as the percentage of MA increased. The moderate acid and iodine values of the polyesters could enable proper crosslinking with a

reasonable time of gelation with or without reactive diluents such as styrene, depending on the application. This indicates that the resin can be used as a matrix for reinforced composites, coatings, and paint applications.<sup>25</sup>

The iodine value decreased with an increase in the MA content, but the time required for the thin layer of the polyester resin to dry to a hard film decreased with an increase in the MA content (Table V). During the modification of unconjugated oils with MA, a hydrogen atom could be abstracted from the methylene group in the  $\alpha$  position to a double bond in a fatty acid chain at temperatures greater than or equal to 200°C.<sup>24</sup> The resultant methylene radical may resonate with existing unsaturation to introduce conjugation followed by the Diels–Alder reaction. It is therefore apparent that male-nization is a means of introducing more active group into the fatty acid chain, thereby increasing its reactivity, and this consequently improves the rate of polymeriza-tion. This must have been responsible for the observed improved drying rate, regardless of the decrease in the iodine value, as shown in Table V.

The performance characteristics of the resins im-proved with an increased level of malenization (Table VI). The results also showed that the polyesters were not affected by salt solutions. Samples I and II were slightly affected by acid and water. However, all the polyesters had poor resistance to alkali. This must have been due to the alkali hydrolyzable ester group present in the poly-ester. The results also revealed that modified polyester III was highly resistance to dilute acid, aqueous sodium chloride, and water. Therefore, sample III exhibited bet-ter and improved characteristics in comparison with the other samples. This study, therefore, opens a new hori-zon in industrial applications of RSO.

### CONCLUSIONS

Polyesters were synthesized from RSO, a renewable resource. The results revealed that the properties of the MA-modified resin were superior to those of polyester from neat RSO. The polyester resin could be used as a binder in surface coatings and composites.

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**TABLE V**  
Physicochemical Properties of the RSO Polyesters

| Property                                 | I         | II     | III    |
|--|-----------|--------|--------|
| Color                                    | Brown     | Brown  | Brown  |
| Acid value (mg of KOH/g)                 | 12.73     | 10.49  | 17.46  |
| Saponification value (mg of KOH/g)       | 317.07    | 295.78 | 290.08 |
| Iodine value (g of I <sub>2</sub> /100g) | 85.86     | 72.65  | 61.52  |
| Drying through (min)                     | Nondrying | 65     | <30    |
| Volatile content (%)                     | 13.57     | 8.35   | 18.84  |

**TABLE VI**  
Chemical Resistance of the RSO Polyesters

|                                     | Polyester |    |     |
|-------------------------------------|-----------|----|-----|
|                                     | I         | II | III |
| Water                               | 2         | 2  | 1   |
| NaCl (5%)                           | 1         | 1  | 1   |
| 0.1M KOH                            | 4         | 4  | 4   |
| 0.1M H <sub>2</sub> SO <sub>4</sub> | 3         | 3  | 1   |

1 = no visible change; 2 = slight whitening that disap-peared on drying; 3 = wrinkled; 4 = film removed.

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