Synthesis and Characterization of Acrylated Rubber Seed Oil

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Abstract

Acrylated rubber seed oil was prepared by reacting polyhydroxylated rubber seed oil with acrylic acid at various polyol: acrylic acid ratios, at 60°C for 1h. The acrylated oil was recovered and dried at 90°C for 12h. Spectroscopic (FTIR and 1H NMR) analysis of the acrylated oil samples revealed a decrease in the absorption band characteristics of the OH group and an increase in the absorption band corresponding to the carboxylates group in the FTIR spectra; and the disappearance of the hydroxyl protons and appearance of acrylic protons in the 1H NMR spectra of the samples. The mechanical properties of the acrylated rubber seed oil depended on the polyol: acrylic acid ratio and were tensile strength 1.60 - 6.2 MPa, elongation at break 6.24 - 45.10 %, modulus 0.015 - 0.240 GPa, ultimate tensile strength 2.30 - 9.92 MPa and hardness 1.23 - 1.38 MPa. The thermal stability of the acrylate oil samples showed little dependence on the polyol; acrylic acid ratio and gave values of temperature of incipient degradation of about 200°C and of second stage degradation well above 300°C. These results together with the low degree of swelling in organic solvent should make the acrylated rubber seed oil suitable for use in the formulation of ink and water-dispersible paint.

Keywords: absorption, acrylic, characteristics, degradation, rubber seed oil, tensile strength

Introduction

The utilization of renewable resources in energy and materials application has received considerable attention in the past several years due to concern about environmental sustainability. The continuous depletion of fossil resources, unstable price of problem have given added impetus for the development of polymeric materials from renewable resources1. The most widely used renewable raw materials include polysaccharides (mainly cellulose and starch), wood, proteins and vegetable oils2. Vegetable oils represent promising route to renewable chemicals and polymers. Unmodified vegetable oils have been used to prepare biorenewable polymers by thermal, radical or ionic polymerization methods, having advantage of the carbon-carbon double bonds in fatty acid chains2-4. Chemical modification of vegetable oils provides added routes, to obtain industrial products. One useful reaction for the modification of vegetable oils has been epoxidation. The epoxidation method of vegetable oil and oleochemicals has been known for many years5 and has been used to produce epoxidized soy bean oil6 which are commercially available and epoxidized rubber seed oil7, which are useful as plasticizers for poly(viny chloride). Facile controlled cleavage of the oxirane in the epoxidized oil and leads to formation of polyol.

In this work we report on the acid catalyzed reaction of polyhydroxylated rubber seed oil with acrylic acid and the spectroscopic examination and mechanical properties as
well and thermal stability determination of
the acrylated rubber seed oil produced.

Materials and methods

The polyhydroxylated rubber seed oil used
in this study was prepared in our laboratory.

Table 1: Physico-chemical properties of RSO, ERSO and RSOP

<table>
<thead>
<tr>
<th></th>
<th>RSO</th>
<th>ERSO</th>
<th>RSOP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>Dark brown</td>
<td>golden yellow</td>
<td>orange-yellow</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.9231</td>
<td>9.4820</td>
<td>1.019</td>
</tr>
<tr>
<td>AV (mg KOH/g)</td>
<td>53.259</td>
<td>18.006</td>
<td>14.733</td>
</tr>
<tr>
<td>SV (mg KOH/g)</td>
<td>201.245</td>
<td>210.11</td>
<td>239.17</td>
</tr>
<tr>
<td>IV (gI2/100g)</td>
<td>136.800</td>
<td>14.604</td>
<td>9.240</td>
</tr>
<tr>
<td>HV (mg KOH/g)</td>
<td>-</td>
<td>14.772.</td>
<td>203.47</td>
</tr>
<tr>
<td>Oxirane content (%)</td>
<td>-</td>
<td>5.491</td>
<td>0.402</td>
</tr>
</tbody>
</table>

Gandini. In a typical experiment, the rubber
seed oil polyol (6.25g; 0.006 mol) was
charged into a three-necked flask and
maintained at 40°C. Acrylic acid (4.65g;
0.06 mol) was added to the flask drop wise
with stirring and the temperature was raised
to 120°C and then the reaction was allowed
to proceed for 60 min. The reaction scheme
for the preparation of acrylated rubber seed
oil is given in scheme 1. The reaction
mixture was allowed to cool down, diluted
(2-fold) with diethyl ether and washed with
1% sodium phosphate to neutral pH. The
acrylated oil was then dried at 70°C for 2h.
Acrylated rubber seed oil was prepared at
1:10; 1:9; and 1:8 polyol: acrylic acid ratios.

Characterization of acrylated rubber seed
oil

FT-IR spectroscopic analysis of the
acrylated rubber seed oil was carried out using Agilent Technologies cary 660 FTIR
to which an ATR was attached. 1H NMR
analysis of the acrylated rubber seed oil was
carried out using a 500 MHz JNM-ECX Jeol Nuclear Magnetic Spectrophotometer on a 5
mg sample in CDCl3 and trimethyl silane
internal standard. The hardness and elastic
modulus of the acrylated rubber seed oil
samples were measured using the
nanoindentation technique on a Hystron TI
950 Triboindenter with standard diamond
indenter probe, using the ASTM E2546-07
method. Tensile mechanical properties was
measured on a Tinius Olsen H50KS
Universal Testing Machine, using ASTM D
3930, method, 50KN force at a speed of
50mm min⁻¹ and gauge length of 12.04 mm.
Thermal stability of the acrylated rubber
seed oil was determined on s Netzsch STA
449 FI Jupiter Thermal analyser at a heating
rate of 10°C min⁻¹ up to a temperature of
600°C under nitrogen atmosphere. The
degree of swelling of the acrylated rubber
seed oil in toluene was determined at
ambient temperature using the method
described by Ferrer et al.
**Result and Discussion**

Spectroscopic Characterization of acrylated rubber seed oil:

FT-IR spectra of the acrylated rubber seed oil samples are shown in Fig. 1 in comparison with the spectra of polyhydroxylated rubber seed oil. The characteristic absorption bands given in Table 2 indicate marked reduction in the absorption band at 3400 cm\(^{-1}\) of the –OH groups of the polyol. The appearance of the carbonyl stretching vibration band at 1710 cm\(^{-1}\) and of the –CH\(_2\) out-of-plane deformation band of the acrylic acid at 800 cm\(^{-1}\) are indication of the formation of acrylated rubber seed oil.
Fig. 1: FTIR spectra of acrylated rubber seed oil and polyhydroxylated rubber seed oil

Table 2: FTIR of functional absorption bands of acrylated rubber seed oil

<table>
<thead>
<tr>
<th>Peaks (cm⁻¹)</th>
<th>assignment</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400</td>
<td>-OH</td>
<td>hydroxyl</td>
</tr>
<tr>
<td>2800, 2920</td>
<td>-CH assym str vib</td>
<td>aliphatic</td>
</tr>
<tr>
<td>1710</td>
<td>-C=O str. Vib</td>
<td>carbonyl</td>
</tr>
<tr>
<td>1448, 1415</td>
<td>-CH bending scissoring</td>
<td>aliphatic</td>
</tr>
<tr>
<td>1160, 1100, 1010</td>
<td>-C-Ostr vib</td>
<td>ester</td>
</tr>
<tr>
<td>800</td>
<td>-CH₂ OOP deform</td>
<td>acrylate</td>
</tr>
<tr>
<td>720</td>
<td>-CH₂ bending</td>
<td></td>
</tr>
</tbody>
</table>

The ¹H NMR spectra of acrylated rubber seed oil (polyol: acrylic acid; 1:10) is given in Fig.2 in comparison with the spectrum for polyhydroxylated rubber seed oil. It can be seen that the
hydroxyl protons at 3.4 – 3.7 ppm in the NMR spectrum of the hydroxylated rubber seed oil are absent in the acrylated oil and the characteristic acrylic protons at 5.8 – 6.7 ppm are present in NMR spectrum of the acrylated oil. The spectroscopic evidence clearly shows the formation of acrylated rubber seed oil under the reported experimental conditions.

**Physico-mechanical properties of acrylated rubber seed oil:**

**Hardness:** the hardness of acrylated rubber seed oil samples was measured by the anoindentation technique. The method provides data from which the hardness and elastic modulus of a material can be obtained from load-displacement data during a cycle of load and unloading events. Typical loading and unloading curves of acrylated rubber seed oil samples are shown in Fig. 3, from which the elastic modulus and hardness were calculated (Table 3). The result indicate the hardness of the acrylated rubber seed oil samples was about the same order of magnitude, differing only marginally with variation in the polyol: acrylic acid ratio. The elastic modulus of the acrylated rubber seed oil sample prepared at 1:9 polyol: acrylic acid ratio was found to be more than 15-fold higher than the corresponding value of the acrylated oil sample from a 1:10 polyol: acrylic acid ratio.

![Fig. 2: $^1$H-NMR of acrylated rubber seed oil oligomer (ARSO I) and RSOP.](image)
Table 3: Mechanical properties of polyurethanes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average* Modulus (GPa)</th>
<th>Average* Hardness (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Ultimate True Stress (MPa)</th>
<th>Yield Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARSO I</td>
<td>0.0145± 004</td>
<td>1.230± 001</td>
<td>2.03</td>
<td>41.8</td>
<td>3.18</td>
<td>1.26</td>
</tr>
<tr>
<td>ARSO II</td>
<td>0.240± 002</td>
<td>1.382± 002</td>
<td>6.21</td>
<td>6.27</td>
<td>9.92</td>
<td>6.21</td>
</tr>
<tr>
<td>ARSO III</td>
<td>NA</td>
<td>NA</td>
<td>1.60</td>
<td>45.1</td>
<td>2.30</td>
<td>1.5</td>
</tr>
</tbody>
</table>

*Determined by nanoindentation method

Tensile mechanical properties: Typical values of the properties tensile strength, elongation at break, stress-strain curves for the acrylated rubber seed oil samples are shown in Fig. 4 and the
ultimate tensile strength and yield stress derived therefrom are given in Table 3. It would appear that polyol:acrylic acid ratio 1:9 yielded acrylated rubber seed oil with optimum tensile strength (6.27 MPa), elongation at break (6.27%), ultimate tensile strength (9.92 MPa) and yield stress (6.21 MPa).

Thermal stability of acrylated rubber seed oil: Thermograms of acrylated rubber seed oil samples are shown in Fig 5. The results show that within the range of polyol: acrylic acid used in this study, the resulting acrylated oils show similar thermal stability pattern: similar temperature of incipient degradation (205°C) about the same temperature of second stage degradation (332-340°C) and the same temperature of decomposition (460°C). The three-stage pattern of decomposition is similar to those reported for polyurethane samples prepared from rubber seed oil monoglycerides.

Degree of swelling: the degree of swelling of the acrylated rubber seed oils in toluene at ambient temperature was found to be rather low (1.52- 1.72 %) and suggest that the materials may be water-dispersible.

Conclusion: We have in this study demonstrated the synthesis of a potentially useful vegetable oil-based polymer material.
The range of properties shown by the acrylated rubber seed oil should make it useful in the formulation of water-dispersible surface coating applications.

References