Rigid thermosetting liquid moulding resin from sunflower oil

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Sunflower oil monoglyceride (SFOM) has been prepared by transesterification of sunflower oil with glycerine in the temperature range 200-230°C using sol-gel prepared nanocrystalline MgO as catalyst. The catalyst has been characterized by powder XRD, BET surface area measurement and atomic force microscopy. The resulting SFOM has been reacted with maleic anhydride to produce SFOM maleate half esters, using 2-methyl imidazole as the catalyst. The effect of the catalyst concentration is optimized. Finally, the polyfunctional SFOM maleate half ester monomer is free radically copolymerized with reactive diluents such as styrene to produce hard, thermosetting liquid moulding resin. The polymer is characterized by differential scanning calorimetry and IR spectroscopic techniques.

Keywords: Nanocrystalline MgO, Sunflower oil monoglyceride, Sunflower oil maleate half ester, Free radical polymerization, Thermoset resin from sunflower oil

Vegetable oils find application as raw materials for many industries such as food, pharmaceutical, cosmetics, surface coatings and detergents\textsuperscript{1,2}. Environment friendly properties of plant oil products and renewability of the raw material are of growing interest for industries. Recently, fatty acid methyl esters derived from vegetable oils have assumed importance as a potential diesel fuel extender known as biodiesel with worldwide consumption approaching a billion gallons per year\textsuperscript{3}. Plant oil derived alkyd resins are extensively used as base in coating industries and share about 15% of the total surface coating market. Drying of alkyds require large amount of oxygen and alkyd based paints dry in presence of drying agents via air mediated peroxidative crosslinking at fatty acid unsaturations\textsuperscript{4}. Requirement of intimate contact with air necessitates alkyds to be used only as a thin film having low mechanical strength\textsuperscript{5}. Fatty acid double bonds are incapable of homopolymerization due to the facile chain transfer to many allylic positions\textsuperscript{6}. However, if monoglyceride derived from vegetable oils are esterified with maleic anhydride and the resulting polyfunctional monomer is copolymerized with reactive diluents such as styrene; highly cross linked polymer with good mechanical strength is expected to appear\textsuperscript{6,7}. Besides, unlike most of the thermosetting resins such as polyesters and vinyl esters synthesized from petroleum-based chemicals which are not biodegradable and pose disposable problem, plant oil derived polymers are expected to be biodegradable and environmental friendly. Recently, such an attempt has been made with soya oil\textsuperscript{6,7}.

Acids, bases and organic amines are the traditional solution catalysts used in transesterification and synthesis of monoglycerides\textsuperscript{8}. Use of homogeneous catalysts leads to the formation of high amount of salts and favour side-reactions leading to the degradation of oils. Use of heterogeneous basic catalysts can avoid these problems. An excellent review on the use of solid catalysts for synthesis of fatty esters of polyol from renewable sources has been written by Márquez-Alvarez et al\textsuperscript{9}. Hydrogenized unsubstantiated guanidine over organic polymers\textsuperscript{10} and solid basic oxides such as MgO, CeO, La\textsubscript{2}O\textsubscript{3} and ZnO are few examples of heterogeneous catalyst for transesterification reported recently\textsuperscript{11}. Nanocrystalline alkali earth metal oxides possessing very high surface to bulk mass ratio, large surface area and large number of unsaturated acid/base sites are expected to be a better catalyst for transesterification. To the best of our knowledge, there is no report on the nanocrystalline MgO catalyzed synthesis of sunflower
oil monoglyceride, its transformation to sunflower oil monoglyceride maleate and its polymerization with styrene. The present study was therefore undertaken (i) to evaluate the performance of nanocrystalline MgO catalyst in the transesterification of sunflower oil with glycerol to sunflower oil monoglyceride (SFOM), (ii) to characterise the catalyst, (iii) to optimize reaction conditions for conversion of SFOM to sunflower oil monoglyceride bismaleate, (iv) to copolymerize SFOM bis maleate with styrene and (v) to characterize the SFOM bis maleate-styrene copolymer.

Experimental Procedure

Preparation of MgO catalyst

Aerogel MgO (AP-MgO) was prepared by hydrolysis of magnesium ethoxide as reported elsewhere. Cleaned Mg ribbons were refluxed with dehydrated methanol to give Mg(OCH₃)₂, which was dissolved in excess of toluene and hydrolysed with stoichiometric amount of double distilled water to precipitate Mg(OH)₂ as a milky white suspension. The solution was autoclaved for 4 h at 250°C. Thereafter, the solvent was removed and solid mass recovered by centrifugation. Mg(OH)₂ thus obtained was dried at 265°C and then dehydrated under vacuum in a tubular furnace by slowly raising the temperature to 400°C to give MgO. Conventional prepared MgO (CP-MgO) was prepared by precipitating Mg(OH)₂ from Mg(NO₃)₂ and calcining the resulting Mg(OH)₂ by procedure similar to that of AP-MgO. Commercially available MgO (CM-MgO), purchased from S. D. Fine-chem Limited, Mumbai, was used as such.

Glycerolysis of sunflower oil

50 g of glycerine, 220 g of sunflower oil and 20 g of commercial sunflower oil monoglyceride (SFOM) was taken in a 1 L four necked glass reactor equipped with a mechanical stirrer, thermometer pocket, condenser and nitrogen inlet, and heated to 220-230°C under nitrogen and kept under this temperature for 2 h to remove water. Sunflower oil monoglyceride is expected to function as emulsifier, help mixing of glycerine and oil and reduce time and temperature of glycerolysis. At the end of the reaction the emulsifier will become part of the product. MgO catalyst (0.1% of the total feed) was then added and reaction mixture further heated for few hours. After 2 h, 1 mL of reaction mixture was withdrawn from time to time, cooled to room temperature, and tested for its methanol tolerance which indicates the completion of reaction. Methanol tolerance is achieved when one volume of reaction mixture becomes fully soluble in three volumes of methanol at room temperature. The reaction mixture was then suddenly cooled to room temperature to avoid high concentration of diglyceride and separation of major portion of unreacted glycerol.

Synthesis of SFOM bis-maleate

Synthesis of SFOM bis-maleate was performed by reacting SFOM with maleic anhydride in presence of 2-methyl imidazole (2MI) as catalyst. SFOM, maleic anhydride and catalyst (typical wt ratio1:1.5:0.02) was taken in a 100 mL round bottom flask and heated to 80°C in a water bath under constant stirring for about 5 h to give SFOM maleate. The progress of reaction was monitored by withdrawing a small amount of the reaction mixture and recording its infrared spectrum on a Shimadzu 460-IR spectrometer. The SFOM maleate was obtained as a red-orange coloured viscous liquid which crystallizes at room temperature during storage.

Polymerization of SFOM bis-maleate with styrene and its characterization

A 250 mL three-necked round bottom flask fitted with a thermometer pocket, stirrer and condenser was charged with 45 g of SFOM bis-maleate mixture, 15 g of styrene and 0.5 g benzoyl peroxide. The flask was purged with nitrogen for half an hour and heated at 90°C till a viscous mass was obtained. The viscous material was poured in cubical mould of size (2.5 cm × 4 cm × 2.5 cm) and cured in a oven at 130°C for 24 h to get a hard rigid polymeric material.

DSC of the polymer was performed at 2910 modulated DSC. Swelling tests were performed by putting known weight of the polymers in a solvent and reweighing the sample at different time interval until polymer solvent uptake became constant.

Result and Discussions

Characterization of MgO

XRD diffractogram of AP-MgO was recorded on a Rigaku diffractometer using Cu-Kα radiation in the 20 angles range from 20° to 80° at a speed of 2°/min. The XRD diffractogram of AP-MgO is reproduced in Fig. 1 along with that of CP-MgO and CM-MgO. All peaks in the pattern match well with the characteristic reflections of AP-MgO reported and confirm the phase purity of the samples. Atomic force microscopy
(AFM) images were obtained on Nanoscope III from Digital Instruments Inc in the contact mode using a 100 µm long cantilever with a spring constant of 0.0625 N/m and a Si₃N₄ tip. All images were recorded in air at room temperature. Surface area was determined with the help of BET method at -196°C. Total pore volume and pore size distribution studies were conducted in a Quantachrome autosorb (1.24) instrument. Prior to the measurements the samples were ex-situ heat treated under vacuum at 500°C and sealed under argon.

The crystallite size calculated by Debby Scherrer’s formula is found to be 5.21 nm, 8.38 nm, 9.71 nm for AP-MgO, CP-MgO and CM-MgO, respectively. Crystals of the size of 5-15 nm can be seen in the AFM images of the AP-MgO surfaces shown in Fig. 2.

Density of the sample was found to be 0.09 and is appreciably less compared to 0.78 of chemically prepared MgO. The pore size, pore volume and pore area for AP-MgO and CP-MgO are summarized in Table 1. The increase in surface area of AP-MgO compared to chemically prepared CP-MgO can be attributed to much smaller particle size of AP-MgO sample.

**Synthesis of SFOM and its maleinization**

Temperature and time taken for obtaining methanol tolerance for transesterification of sunflower oil to sunflower oil monoglyceride with few basic catalysts such as LiOH, CP-MgO and AP-MgO are shown in Table 2. In the technology of glycerolysis methanol tolerance can be taken as completion of reaction. It can be seen that reaction is completed at lower temperature and in lesser time when AP-MgO is used as catalyst. This implies lower activation energy and faster rate of glycerolysis using AP-MgO. Better performance of AP-MgO can be attributed to its higher surface area, large number of uncoordinated sites and high surface/bulk mass ratio.

<table>
<thead>
<tr>
<th>Property</th>
<th>AP-MgO</th>
<th>CP-MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro pore volume</td>
<td>1.99E-4</td>
<td>2.94E-3</td>
</tr>
<tr>
<td>Micro pore area</td>
<td>9.934 m²/g</td>
<td>1.035 m²/g</td>
</tr>
<tr>
<td>External surface area</td>
<td>3.69E+02 m²/g</td>
<td>5.897E+1 m²/g</td>
</tr>
<tr>
<td>Total pore volume</td>
<td>5.55E-1</td>
<td>8.40E-2</td>
</tr>
<tr>
<td>Average pore diameter</td>
<td>1.039E+2 Å</td>
<td>4.849E+1 Å</td>
</tr>
<tr>
<td>Total surface area</td>
<td>380 m²/g</td>
<td>69.3 m²/g</td>
</tr>
</tbody>
</table>

**Table 1**—The summary of the pore size, pore volume and pore area of AP-MgO and CP-MgO

**Fig. 1**—XRD diffractograms of (A) CM-MgO, (B) CP-MgO and (C) AP-MgO.

**Fig. 2**—Atomic force micrographs of AP-MgO (a) 3D (50x50x 10 nm) and (b) 3D(15x15x4 nm)
The effect of catalyst 2-methyl imidazole (2MI) concentration on the rate of SFOM maleate formation is shown in Table 3. The progress of reaction was monitored by recording the intensity of OH stretching mode of monoglyceride, maleic anhydride (MA) reaction mixture in the region 3000-4000 cm\(^{-1}\) at different time intervals. One such typical record is shown in Fig. 3. Reduction in the intensity of OH stretching mode indicated the progress of reaction. Heating was continued till there was no further reduction in the band intensity. It is worth mentioning that the intensity of OH stretching mode will not completely vanish, since only half maleate is expected to be formed and one OH group still remains free. Although the rate was almost proportional to the catalyst concentration, the polymer quality improved up to 2% of catalyst. Further increase in catalyst concentration led to increase in brittleness and decrease in mechanical strength of the polymer.

### Table 2—Transesterification of sunflower oil to sunflower oil monoglyceride with LiOH, CM-MgO, CP-MgO and AP – MgO catalysts

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Oil: Glycerine (Molar ratio)</th>
<th>Catalyst (0.1%)</th>
<th>SE</th>
<th>Temperature (°C)</th>
<th>Time of completion of the reaction (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1:2</td>
<td>LiOH</td>
<td>7%</td>
<td>255</td>
<td>5</td>
</tr>
<tr>
<td>2.</td>
<td>1:2</td>
<td>CM-MgO</td>
<td>7%</td>
<td>225</td>
<td>4.5</td>
</tr>
<tr>
<td>3.</td>
<td>1:2</td>
<td>CP-MgO</td>
<td>7%</td>
<td>225</td>
<td>4</td>
</tr>
<tr>
<td>4.</td>
<td>1:2</td>
<td>AP-MgO</td>
<td>7%</td>
<td>225</td>
<td>3</td>
</tr>
</tbody>
</table>

SE = Self emulsifier

### Table 3—Effect of catalyst (2-methyl imidazole) concentration on the maleinization of SFOM with maleic anhydride (MA)

<table>
<thead>
<tr>
<th>S.N</th>
<th>SFOM/MA (weight ratio)</th>
<th>2MI/SFOM (weight ratio)</th>
<th>Time of completion of reaction (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1.5:1</td>
<td>0.01</td>
<td>5.5</td>
</tr>
<tr>
<td>2.</td>
<td>1.5:1</td>
<td>0.02</td>
<td>4.0</td>
</tr>
<tr>
<td>3.</td>
<td>1.5:1</td>
<td>0.03</td>
<td>3.0</td>
</tr>
<tr>
<td>4.</td>
<td>1.5:1</td>
<td>0.04</td>
<td>2.5</td>
</tr>
</tbody>
</table>

The effect of catalyst 2-methyl imidazole (2MI) concentration on the rate of SFOM maleate formation is shown in Table 3. The progress of reaction was monitored by recording the intensity of OH stretching mode of monoglyceride, maleic anhydride (MA) reaction mixture in the region 3000-4000 cm\(^{-1}\) at different time intervals. One such typical record is shown in Fig. 3. Reduction in the intensity of OH stretching mode indicated the progress of reaction. Heating was continued till there was no further reduction in the band intensity. It is worth mentioning that the intensity of OH stretching mode will not completely vanish, since only half maleate is expected to be formed and one OH group still remains free. Although the rate was almost proportional to the catalyst concentration, the polymer quality improved up to 2% of catalyst. Further increase in catalyst concentration led to increase in brittleness and decrease in mechanical strength of the polymer.

### Radical polymerization of SFOM maleate with styrene and its characterization

The possible reaction scheme is shown in Fig. 4. DSC record of the final rigid polymer is shown in Fig. 5. The material resembled with dry wood in strength and appearance. It was as hard like Bakelite and was suitable for fabrication on machine. The material seems to possess different heat capacity at different temperatures. The endothermic peak around 139°C can be attributed to solvent removal and further crosslinking of the polymer. Since polymer was already cured at 130°C for 24 h the peak seems to be due to further crosslinking.

On further heating the polymer seems to crystallise. The endothermic peak at 235°C can be attributed to the degradation of polymer or melting of some impurity. CCl\(_4\) uptake of the polymer is depicted in Fig. 6. The curve is linear initially which approach a limiting nature with elapse of time. The water absorption data (1.05% at 25°C in 24 h and 4.7% at 100°C in ½ h) compared well with the commercial polyesters and vinyl ester resins.

An FTIR spectrum of the polymer recorded on JASCO, FTIR 660 Plus spectrophotometer is shown in Fig. 7. Appearance of the bands in the region 3000-3200 cm\(^{-1}\) can be assigned to C-H stretching modes of benzene ring and band appearing at 3500 cm\(^{-1}\) can be assigned to OH stretching modes of free carboxylic acid group. The bands appearing in the region 1844-1734 cm\(^{-1}\) to C=O stretching modes due to carboxylic group of fatty acid moiety. This mode seems to have merged with C=C stretching modes of benzene ring.
It is worth mentioning that during heating, some part of maleate may isomerize to fumarate. However, because of higher reactivity of fumarates for free radical polymerization with styrene than that of maleate, partial polymerization to fumarate will not be detrimental to quality of the polymer.

Conclusions
Nanocrystalline AP-MgO catalyst has been prepared by sol-gel method and characterised by surface area measurement, XRD and atomic force microscopy (AFM). The catalyst has shown best performance for transesterification of sunflower oil to...
sunflower oil monoglyceride (SFOM) compare to CP- and CM-MgO and traditional catalyst LiOH. The catalyst is better than water soluble bases and organic amines since it can be recovered, purified and reused and hence posses no disposal problem. The resulting SFOM has been reacted with maleic anhydride to produce SFOM maleate half esters, using 2-methyl imidazole as the catalyst. Finally, the polyfunctional SFOM maleate half ester monomer was copolymerised with styrene using benzyl peroxide as initiator to produce hard, thermosetting liquid moulding resin. The polymer was characterized by differential scanning calorimetry and IR spectroscopic techniques.

References