BIODEGRADABLE POLYMERS FROM SESAME OIL WITH METHYL ACRYLATE AND METHYL METHACRYLATE CO-MONOMERS

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ABSTRACT
In this study biodegradable polymers were synthesised by the polymerization of alkyd resin of sesame oil with co-monomers like methyl acrylate(MA) and methyl methacrylate(MMA). Monoglyceride of sesame oil(SOMG) was first prepared by the glycerolysis of sesame oil at 220 - 230°C. Then the resin was prepared by the reaction of the monoglyceride with cyclohexane dicarboxylic anhydride at 80°C for 2 hours. The cross linked biopolymers were prepared by the free radical polymerization of the resin with various concentration of different monomers in presence of benzoyl peroxide as initiator. The newly prepared polymers were analysed for thermal and mechanical properties. Biodegradation of the polymers were also tested by soil burial test and SEM micrographs assess surface damage and to look for the presence and nature of microbial growth. The reactions were followed by H1 NMR and FT-IR spectroscopy.

KEYWORDS: Biodegradation, Thermal studies, Alkyd resin.

INTRODUCTION
Recently, the use of renewable sources in the preparation of various industrial materials has been revitalized because of the environmental concerns. More attention is being paid to studying and developing environment biodegradable plastics in order to retard or eradicate plastic pollution. Current interest in cheap biodegradable polymeric materials has recently encouraged the development of such materials from readily available, renewable, inexpensive natural sources such as starch, polysaccharides and vegetable oils.
Nowadays, there is a growing interest to produce vegetable oil-based biopolymers. These polymers have many advantages compared with polymers prepared from petroleum-based monomers. They are biodegradable and in many cases cheaper than petroleum-based polymers. Plant oils are now being considered as the most important renewable raw materials for the production of bio-based polymer materials. Plant oils are triglycerides (triesters of glycerol with long-chain fatty acids) with varying composition of fatty acid depending on the plant, the crop, the season, and the growing conditions.

Plant oils are predominantly made up of triglyceride molecules. The triglyceride contains many active sites such as the double bond, the allylic carbons, the ester group, and the carbon alpha to the ester group. These active sites can be used to introduce polymerizable groups on the triglyceride, similar to the synthesis of petroleum-based polymers. Vegetable oils have been used in paints and coatings for centuries, because the unsaturated oils can oligomerize or polymerize when exposed to the oxygen in air. In recent years, biorenewable fuels, mainly biodiesel, which can be used as an alternative engine fuel, have been prepared from vegetable oils by pyrolysis, catalytic cracking, and transesterification.

Recent reviews have focused on the development of crosslinked plant oils and their derivatives for thermosetting applications such as coating and resins. Thermal or cationic (co)polymerization of these plant oils with styrene or divinylbenzene is usually carried out to obtain thermosetting (bio)materials, ranging from elastomers to rigid and tough plastics, depending on the stoichiometry, the type of plant oils, and the co-monomers. Recently, new value-added applications have been obtained for nano composites derived from these plant oil-based thermosetting polymers.

Sesame oil is acquired from the seeds of Sesamum indicum plant. It naturally has yellow color, nutty flavor, and contains plenty of nutrients. Sesame oil is mainly composed of triglycerides of the singly saturated oleic acid (43%), doubly saturated linoleic acid (35%), palmitic acid (11%) and stearic acid (7%). Sesame oil is considered as semi drying oil and used for cooking. Besides for cooking, the oil is possibly applied topically for cosmetic purpose, especially skin health. Recently, a range of thermosets have been prepared by the cationic copolymerization of olive, peanut, sesame, canola, corn, soybean, grape seed, sunflower, low-saturation soy, safflower, walnut, and linseed oils with ST and DVB.
The present work comprises the study of cross linked ecofriendly biodegradable polymers prepared by the polymerization of alkyd resin of sesame oil with the co-monomers such as methyl acrylate and methyl methacrylate.

2. MATERIALS AND METHODS

2.1 Materials

Sesame oil was purchased from local market at Trivandrum. The chemicals Cyclohexane dicarboxylic anhydride (Sigma–Aldrich), Triethylene glycol dimethyl acrylate (TEGMA) (Sigma–Aldrich), Glycerol, Methyl acrylate, Methyl methacrylate, Benzoyl peroxide, N,N – dimethyl aniline were used without purification.

2.2 Methods

Preparation of polymers

Glycerolysis of sesame oil was carried out by heating 2:1 mixture of sesame oil and glycerol at 220-230°C for 5 hours. The monoglyceride formed and cyclohexane dicarboxylic anhydride in the ratio 2:1 is heated to 80°C for 2 hours. The resin thus prepared was polymerized with different concentration of methyl acrylate (MA) using benzoyl peroxide as initiator and N,N- dimethyl aniline as accelerator. 1 ml of triethylene glycol dimethyl acrylate (TEGMA) was added as cross linking agent. The mixture was then casted on a clean silicone oil spreaded glass plate and was placed in an oven at 50°C for 2 hours and the temperature was increased upto 100°C and curing takes place at this temperature for 2 hours.

Same procedure was followed for the preparation of various polymers by mixing the resin with different concentration of Methyl methacrylate (MMA) co-monomer.

3. CHARACTERIZATION

3.1 Spectral studies

The progress of the reaction was studied by analyzing the FT-IR and H1 NMR spectra of the oil, monoglyceride and the resin.

3.2 Thermal and mechanical studies

The thermal analysis of the biopolymers was determined by TG–DTA analysis. Thermo gravimetric analysis (TGA) was performed by Perkin’s Elmer thermo gravimetric analyzer over the temperature ranging from 30 to 700 °C at a heating rate of 10 °C/min under nitrogen gas atmosphere.
The tensile strength of the biopolymers prepared were determined using Instron UTM; 10 ton static Universal Testing Machine. The values represented are an average mean of about 4-5 samples. The crosslink densities, \( \nu_c \), were determined from the rubbery modulus plateau based on the theory of rubber elasticity \( E' = 3\nu_cRT \),\(^{[21, 22]} \) where \( E' \) is the storage modulus (Young’s) of crosslinked polymer in the plateau region, \( R \) is the universal gas constant (8.314 J·mole\(^{-1}\)·K\(^{-1}\)) and \( T \) is the absolute temperature (K).

### 3.3 Biodegradation - Soil burial test

Biodegradation of the polymers were studied by soil burial test. For the soil burial test the replicate pieces of the sample (5 x 3 cm) were buried in the garden soil at the depth of 30 cm from the ground surface for 3 months, inoculated with the sewage sludge having the ability to adhere and degrade the polymer film.\(^{[23]} \) The test specimen was periodically removed from the soil and then the specimen was gently washed to remove the attached soil and dust after being dried in vacuum oven. The extent of degradation was examined by measuring the weight loss after 30 and 60 days which was calculated using the relation,\(^{[24]} \)

Degree of biodegradation, \( D = \frac{(M_0 - M_t)}{M_0} \times 100 \)

Where; \( M_0 \) – weight of original film

\( M_t \) – weight of residual film after degradation for different time.

### 3.4 Swelling analysis

The swelling analyses of the polymeric samples were carried out in different solvents viz., saline (20% NaCl), alkaline (2% NaOH), acidic (2%H\(_2\)SO\(_4\)) and toluene. The polymeric samples were allowed to remain in the solution for 72 hours at room temperature and then weighed as soon as they were removed from the solvent. The samples were weighed after 2, 4, 6, 8, 12, 24, 48 and 72 hours. The swelling ratio, \( q_v \) of various polymers at equilibrium \(^{[25]} \) was determined using the Equation;

\( q_v = \frac{\text{volume of swollen polymer}}{\text{volume of dry polymer}} \)

### 3.5 Chemical resistance

Chemical resistance of the newly prepared polymer samples were studied by immersing the polymer samples in various solvents such as CCl\(_4\), CHCl\(_3\), acetone, benzene, toluene, H\(_2\)O\(_2\), HCl, ethanol, H\(_2\)O and NaCl and measuring the dimensional changes after 1 week and 4 weeks.\(^{[26]} \) The weight loss was also measured after 30 days.
4. RESULTS AND DISCUSSIONS

4.1 Spectral analysis

The progress of the chemical reaction was studied by analyzing FT-IR, and H\textsuperscript{1} NMR spectra of the oil, monoglyceride and the resin. Figure 1a, 1b and 1c shows the FT-IR spectra of sesame oil, sesame oil monoglyceride and sesame oil monoglyceride cyclohexane dicarboxylate resin.

In the FT-IR spectrum of sesame oil the peaks at 3007.44 cm\textsuperscript{-1}, 2952.48 cm\textsuperscript{-1} and 2855.1 cm\textsuperscript{-1} correspond to the C-H stretching frequencies for olefinic, methylene and methyl groups. The peak at 1745.26 cm\textsuperscript{-1} corresponds to the C=O stretching frequency of ester group. The peaks at 1460.81 cm\textsuperscript{-1}, 1374.03 cm\textsuperscript{-1} and 722.21 cm\textsuperscript{-1} correspond to the C-H bending vibration of CH\textsubscript{2} and CH\textsubscript{3} groups. The peaks at 1238.08 cm\textsuperscript{-1} and 1163.83 cm\textsuperscript{-1} correspond to the C-C and C-O stretching vibrations. The presence of additional peak at 3473.17 cm\textsuperscript{-1} in the FT-IR spectrum of linseed oil monoglyceride corresponds to the presence of OH groups (i.e. confirms the formation of partial glycerides). The disappearance of intense peak at 3473.17 cm\textsuperscript{-1} in the FT-IR spectrum of the resin indicates the formation of alkyd resin.

![Figure 1a: FT-IR spectrum of sesame oil](image1)

![Figure 1b: FT-IR spectrum of sesame oil monoglyceride](image2)
Figure 1c. FT-IR spectrum of sesame oil monoglyceride cyclohexane dicarboxylate resin

Figure 2a, 2b and 2c shows the H¹ NMR spectrum of sesame oil, sesame oil monoglyceride and sesame oil monoglyceride cyclohexane dicarboxylate resin.

Figure 2a: H¹NMR spectrum of sesame oil

Figure 2b: H¹NMR spectrum of sesame oil monoglyceride
Figure 2c: H\text{1}NMR spectrum of sesame oil monoglyceride cyclohexane dicarboxylate resin

In the H\text{1}NMR spectrum of sesame oil, the peak at 0.834 corresponds to the terminal methyl protons, the peaks at 1.252 and 1.562 correspond to CH\text{2} and CH protons, the peaks at 1.990 and 2.257 for protons in allylic and bis allylic carbons, the peak at 2.715 for protons in CH\text{2} - O carbon, the peaks at 4.102 and 4.262 for the methylene protons in the ester group and the peak at 5.285 corresponds to the olefinic protons (protons of glycerol backbone). In the H\text{1}NMR spectrum of sesame oil monoglyceride, the additional peak at 5.1 for the OH protons which confirms the formation of monoglyceride and the multiplet peak at 3.2-3.8 corresponds to the CH\text{2} protons attached to the OH group. In the H\text{1}NMR spectrum of resin, the multiplet at 4 – 4.3 corresponds to the protons in the cyclohexane ring.

4.2 Thermal analysis

Thermo gravimetric analysis (TGA) is used to investigate the thermal stability of the polymers. Figure 3a & 3b show the TG-DTA and TG-DTG curves of SESMGMA and figure 3c & 3d show the TG-DTA and TG-DTG curves of SESMGMMMA under nitrogen atmosphere which shows the decomposition behavior of the polymer samples.
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Figure 3a: TG-DTA curve of sesame oil monoglyceride cyclohexane dicarboxylate – methyl acrylate (SESMGMA) copolymer

Figure 3b: TG-DTG curve of sesame oil monoglyceride cyclohexane dicarboxylate – methyl acrylate (SESMGMA) copolymer

Figure 3c: TG-DTA curve of sesame oil monoglyceride cyclohexane dicarboxylate – methyl methacrylate (SESMGMMA) copolymer

Figure 3d: TG-DTG curve of sesame oil monoglyceride cyclohexane dicarboxylate – methyl methacrylate (SESMGMMA) copolymer
Two distinct temperature regions are observed in the TGA curves of the polymer samples where the samples experienced significant weight loss (150-250°C and 300-450°C). It is clear from the TGA curve that, most of the unreacted free oil disappears at the temperature range 150 - 250°C (stage 1), ie. this region corresponds to the evaporation of the unreacted free oil. On the other hand, the insoluble substances were found to be highly cross linked thermosets that decompose at temperatures greater than 300°C (stage 2). This decomposition stage corresponds to the carbonization of the cross linked polymer network. Stage-I in the TGA curves involves two major steps, i.e. diffusion of the free oil to the surface of the bulk polymer and subsequent evaporation. The diffusion of the free oil is retarded by highly cross linked materials, but the evaporation of free oil from the polymer surface occurs rather rapidly at high temperature. From the preceding results, it is clear that the thermal stability of the polymers is limited by the first decomposition stage in the TGA thermograms, which is directly related to the amount of unreacted free oil in the bulk polymer.

In this study, the temperature at 10% weight loss was selected as a reference for evaluating the thermal stability of each polymer material. At high oil concentration in the original composition, the temperatures at 10% weight loss of the resulting polymers appear to be relatively independent of the oil concentration. The temperature at 10% weight loss are therefore predominantly determined by the diffusion process, rather than the subsequent evaporation. However, when the amount of unreacted free oil present in the bulk polymer is very high, diffusion of the free oil to the polymer surface occurs rapidly, minimizing the difference in the temperature of 10% weight loss at these relatively high oil concentrations. From the TGA curve it is known that 10% weight loss occur in the first stage of decomposition and 50% weight loss occur in the II stage of decomposition. Table 1 shows the temperature at which the polymer samples shows 10% and 50% weight loss during the thermo gravimetric analysis.

Table 1: TGA data of polymer samples from sesame oil

<table>
<thead>
<tr>
<th>Polymer sample</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10% weight loss</td>
</tr>
<tr>
<td>SESMGMA</td>
<td>220°C</td>
</tr>
<tr>
<td>SESMGMMMA</td>
<td>225°C</td>
</tr>
</tbody>
</table>

The presence of endothermic peak at 100-150 °C in the DTA curve of both the polymer samples correspond to the melting point and exothermic peak at 400-450 °C correspond to the decomposition temperature of the polymer samples.
The study of TGA is supplemented by the study of its first derivative (DTG) curves. The DTG curves show the rate of thermal decomposition (mg/min) with respect to temperature. The DTG curve in Figure 3b shows that the polymer SESMGMA has two significant peaks at 227.46°C and 401.82°C with corresponding 0.225 mg/min and 0.579 mg/min rate of decomposition and the DTG curve in Figure 3d shows that the polymer SESMGMA has similar peaks at 241.68°C with 0.453 mg/min and at 393.12°C with 0.862 mg/min rate of decomposition.

4.3 Mechanical Studies
The mechanical properties of the polymer samples are determined from the tensile studies which are shown in the table 2. From the data, it is clear that the polymer samples prepared are having high tensile strength and modulus relative to other thermosetting plastics. The new polymeric materials exhibit tensile stress–strain behavior relatively to plastics. All the cured materials showed high toughness, elastomeric and good transparency. Comparing the two samples analyzed, methyl methacrylate containing polymer is having high tensile strength and modulus.

<table>
<thead>
<tr>
<th>Polymer sample</th>
<th>Cross link density (x10^-3)</th>
<th>Tensile strength x 10^5 Pa</th>
<th>% of elongation</th>
<th>Young’s Modulus x 10^5 Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>SESMGMA</td>
<td>0.715</td>
<td>5.94</td>
<td>111.35</td>
<td>54</td>
</tr>
<tr>
<td>SESMGMA</td>
<td>2.726</td>
<td>17.65</td>
<td>111.75</td>
<td>206.05</td>
</tr>
</tbody>
</table>

4.4 Bio degradation - Soil Burial test
Biodegradation (i.e. biotic degradation) is a chemical degradation of materials (i.e. polymers) provoked by the action of microorganisms such as bacteria, fungi and algae. This process refers to the degradation and assimilation of polymers by living microorganisms to produce degradation products. Growth of microbial species on a polymeric material requires the presence of environmental moisture.

Bio degradation of the newly prepared polymer samples are carried out by soil burial test and are reported in table 3. From the data obtained by soil burial test (table 3) it is clear that, the extent of biodegradation increases with decrease in the concentration of monomers. Comparing the two polymers, the rate of biodegradation is high for methyl methacrylate polymer. The outcome of these studies revealed that the newly prepared cross linked bio-polymers are potential biodegradable material for various consumer application like package materials and agricultural applications.
Scanning electron microscope (SEM) is used to study the morphological behavior of polymers. Surface damage and microbial growth on the polymers were studied from SEM analysis. SEM micrographs of the polymers before and after soil burial were analyzed which shows the degradation of the polymers by microbial action. Figure 5 and 6 shows the SEM micrographs of the polymers SESMGMA and SESMGMMA before and after degradation.

<table>
<thead>
<tr>
<th>Polymer sample</th>
<th>Degree of Biodegradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 DAYS</td>
</tr>
<tr>
<td>SESMG60MA</td>
<td>13</td>
</tr>
<tr>
<td>SESMG40MA</td>
<td>18</td>
</tr>
<tr>
<td>SESMG20MA</td>
<td>21</td>
</tr>
<tr>
<td>SESMG60MMA</td>
<td>13</td>
</tr>
<tr>
<td>SESMG40MMA</td>
<td>29</td>
</tr>
<tr>
<td>SESMG20MMA</td>
<td>38</td>
</tr>
</tbody>
</table>

Table 3: Percentage of biodegradation of polymer samples from sesame oil

Figure 4: Percentage of biodegradation of various polymer samples

Figure 5. SEM image of SESMGMA before and after degradation
4.5 Swelling analysis

The samples have been tested for swelling in alkaline, acidic, and brine solutions, as well as in toluene. All the polymeric samples show minimum swelling in alkaline solution and maximum swelling in toluene, acidic and brine (NaCl) solution. Figure 7 and 8 show the swelling ratios at different time intervals for the polymer samples in different solutions which represent the time dependence of the swelling ratios. A sharp rise in $q_V$ values is observed at the early stages of swelling. After particular period, the $q_V$ values show little change (almost remain constant). This may be explained in terms of the catastrophic rupture of the polymer network due to the internal stress caused by diffusion of the liquid into the polymer network.

![Figure 6. SEM image of SESMGMMA before and after degradation](image)

**Figure 7:** Swelling of SESMGMA in various solvents

**Figure 8:** Swelling of SESMGMA in various solvents

4.6 Chemical resistance

Table 4 shows the percentage of weight loss of polymer samples after 30 days. All the polymeric samples prepared are highly stable but undergoes slight degradation in ethanol, NaCl and $H_2O_2$. (table 4) Both the samples are highly stable except in ethanol and NaCl. The
dimension of the polymer samples immersed in HCl, H2O and NaCl did not change after 4 weeks, but the dimension of the polymers immersed in organic solvents (CCl4 and CHCl3) changed after 1 week. The dimension could not be measured after 4 weeks due to their fragility.

**Table 4: Weight loss the polymers in various solvents**

<table>
<thead>
<tr>
<th>Solvents</th>
<th>SESMGMMA</th>
<th>SESMGMA</th>
<th>Weight loss in 30 days (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>20</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>H2O2</td>
<td>9</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>10</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>CCl4</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>CHCl3</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

5. CONCLUSION
1. A variety of novel bio degradable polymers have been synthesized by the free radical copolymerization of sesame oil monoglyceride cyclohexane dicarboxylate with MA and MMA, as co-monomers.
2. The polymers are found to be typical thermosetting materials. They exhibited good tensile stress–strain behavior relatively to plastics.
3. Two distinct decomposition stages are found upon thermo gravimetric analysis, which correspond to evaporation of the unreacted free oil present in the bulk polymer and carbonization of the cross linked polymer. The thermal stability of the polymers is mainly determined by the amount of the unreacted free oil present in the bulk polymer.
4. From the soil burial test it is known that the newly prepared polymers are biodegradable and can play very important role in biological applications.
5. The polymer samples prepared are also stable towards the chemicals except ethanol.

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