Synthesis and characterization of polyacids from palm acid oil and sunflower oil via addition reaction

Ehsan Zeimaran\textsuperscript{a,b,*}, Mohammed Rafiq Abdul Kadir\textsuperscript{c}, Hussin Mohd Nor\textsuperscript{a}, Tunku Kamarul\textsuperscript{d}, Ivan Djordjevic\textsuperscript{b}

\textsuperscript{a} Department of Polymer Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81300 Johor, Malaysia
\textsuperscript{b} Department of Biomedical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
\textsuperscript{c} Department of Clinical Science, Faculty of Biosciences and Medical Engineering, Universiti Teknologi Malaysia, 81300 Johor, Malaysia
\textsuperscript{d} Department of Orthopedic Surgery, Tissue Engineering Group, NOCERAL, Faculty of Medicine, University of Malaya, 50603 Kuala Lumpur, Malaysia

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\textbf{A B S T R A C T}

In this study aliphatic polyacids were synthesized using palm acid oil (PAO) and sunflower oil (SFO) via addition reaction technique. The synthesized materials were characterized using Fourier-transform infra-red (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF-MS) and thermo-gravimetric analysis (TGA). Mixing formic acid and hydrogen peroxide with PAO or SFO at the ratio 3:10:1 produced the lowest iodine value of 10.57 and 9.24 respectively, indicating the increase in epoxidization of both oils. Adding adipic acid to the epoxidized oils at a ratio of 1:10 increases the acid values of SFO and PAO to 11.22 and 6.73 respectively. The existence of multi-acid groups present in synthesized polyacid was confirmed by MALD-ToF-MS. This feature indicates a possible value to the biomaterials development.

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The applications of polyacids (PA) have been described in many studies such as additive and drug intermediates as well as the formation of glass ionomer cements.\textsuperscript{1,2} Extracting PA through the use of polymerization in vegetable oil-based materials has received many interests due to their environmentally benign nature and cost-effectiveness.\textsuperscript{3–5} Vegetable oils are composed of long chain fatty acids in which the middle double bonds have lower activity as opposed to the end double bonds. To increase reactivity, epoxidation of these oils have been suggested, which have been shown to cause the formation of active oxirane ring at the carbon–carbon double bond.\textsuperscript{6} Oxirane ring has ability to easily open with chemicals such as alcohols, acids and water thereby increasing the oil's reactivity to its surrounding components.\textsuperscript{7} Formation of PAs is possible through addition reaction and the expected products would mostly present an advantage in development of novel biomaterials. In particular, PAs from eatable oils such as palm acid oil (PAO) and sunflower oil (SFO) could possibly be cross-linked with multi-functional alcohols (diols or triols) yielding biodegradable polyesters for tissue engineering applications.\textsuperscript{8} In order to explore such possibilities a detailed study of PA synthesis from PAO and SAO is needed. To our knowledge, the product from epoxidation and subsequent acidolysis of PAO and SFO has not been described previously. The present study was thus conducted in order to investigate the chemical structure and thermal stability of both oils following addition polymerization. Such PAs present a new potential in developing biocompatible materials used in clinical applications.

In this letter we describe the synthesis and structural analysis of PAO produced in two steps: (1) epoxidation of unsaturated acid (oleic acid) in PAO and SFO; and (2) addition reaction of epoxidized oleic acid with adipic acid in elevated temperature. The reactant ratio of 3:10:1 of formic acid: hydrogen peroxide: oil, was found to be optimal as demonstrated by the lowest Iodine value of 10.57 and 9.24 for PAO and SFO respectively. Acid value\textsuperscript{9} of poly-palm acid oil (PPAO) and poly-sunflower oil (PSFO) were 6.73 and 11.22 respectively (both measured for 3:10:1 ratios). We made an attempt to measure the acid value for PPAO produced in reactant ratio of 3:5:1. Due to the high degree of gelation of the PA, the results could not be obtained with acceptable accuracy.

Fourier-transform infra-red (FTIR) spectra (Fig. 1) were measured for the following: (a) pure reactants (SFA and PAO); (b) epoxidized reactants (ESFO and EPFO); and (c) PAs (PSFA and PPAO) and their comparison is shown in Figure 1. The exact IR frequencies (cm\textsuperscript{-1}) are presented in Table 1. The results indicate that both oils contain components with similar chemical structures (Fig. 1a).
Note that PAO has two additional peaks (1712 cm\(^{-1}\) and 942 cm\(^{-1}\)) when compared to SFO, which possibly represents the carboxyl groups and CH in plane deformation (CH\(_2\)CH) respectively. Both spectra (Fig. 1a) show the presence of peaks at 3005 and 1632 cm\(^{-1}\) which are assigned to double bonds (Table 1). These peaks disappeared after epoxidation and a new peak appeared in the spectra of the reaction products (Fig. 1b) at 824 and 838 cm\(^{-1}\) indicating a presence of epoxy groups.

FTIR spectra of PAs (PPAO and PSFO, Fig. 1c) show an increase in broad bands centered at 3459 cm\(^{-1}\) assigned to ester stretching (Table 1).\(^5\),\(^6\),\(^10\)–\(^15\) Note that addition esterification causes broadening of peaks which is generally observed in all macromolecular systems.

Nuclear magnetic resonance (NMR) spectra (Fig. 2) were recorded for epoxidized oils and polyacids in both \(^1\)H and \(^{13}\)C modes. Inserts show magnified peaks assigned to the protons and carbon atoms bonded to the oxirane ring (Fig. 1a).\(^4\),\(^13\),\(^14\) The peaks related to the double bonds (125–130 ppm in \(^{13}\)C and 5.4–6 ppm in \(^1\)H NMR) disappeared almost completely after epoxidation. Furthermore, a new peak appears after addition reaction at 3.4–3.3 ppm in \(^1\)H spectrum (Fig. 2a) which is assigned to esterified –O– groups present in PA.\(^9\) The intensity of the peaks related to oxirane groups (3–3.2 ppm in \(^1\)H NMR and 53–58 ppm in \(^{13}\)C NMR), dropped dramatically after addition esterification with adipic acid. This indicates the ring opening polymerization in which adipic acid is added to oleic acid chain forming a branched macromolecular structure.

In order to confirm findings in NMR experiment we performed a matrix assisted laser desorption time-of-flight mass spectrometry (MALDI-ToF-MS) analysis (Fig. 3). The MALDI-ToF-MS spectra (top) show two mass ranges which both confirmed formation of macromolecules between oleic acid and adipic acid through epoxidation and subsequent addition reaction. The theoretical value for \([\text{M+Na}^+\]) was calculated for the top peak in the low mass range of the MS. The proposed structure is presented in Figure 3 (bottom). The formation of sodiated complex (PA–COONa) can occur in ionization chamber thus causing the increase (+22) in m/z from the theoretical value.\(^8\),\(^16\),\(^17\) Sodiated complexes are common for macromolecules with terminal hydroxyl and carboxyl groups.\(^17\) The small shift towards higher m/z values in experimental data can be attributed to the detector saturation with small molecular ions.

### Table 1

<table>
<thead>
<tr>
<th>cm(^{-1})</th>
<th>Assignment</th>
<th>cm(^{-1})</th>
<th>Assignment</th>
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<td>SFO</td>
<td>Epoxidized oils</td>
<td>Polyacid</td>
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<tr>
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<td>3471</td>
<td>3471</td>
<td>C=O ester and OH stretching</td>
</tr>
<tr>
<td>3005</td>
<td>3005</td>
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<td>C=C stretching</td>
</tr>
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<td>2926</td>
<td>2926</td>
<td>2926</td>
<td>CH(_3) asymmetric stretching</td>
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<tr>
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<td>CH(_3) asymmetric stretching</td>
</tr>
<tr>
<td>1632</td>
<td>1656</td>
<td>—</td>
<td>CH=CH</td>
</tr>
<tr>
<td>1712</td>
<td>—</td>
<td>—</td>
<td>C=O carbonyl or carboxyl</td>
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<td>CH(_2) bending vibration</td>
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<td>CH(_2) chain rocking vibration</td>
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</table>

Figure 1. FTIR spectra for: (a) pure oil; (b) epoxidized oil; and (c) polyacids from PAO and SFO.
fragments. This phenomenon is common in MALDI-ToF-MS experiments. The unimodal peak distribution with the interval of $D_m/z = 28$ could possibly be attributed to the addition reaction with trace unsaturated acids present in both PAO and SFO. The high molecular weight range in MALDI-ToF-MS can be explained as further reaction of PA with epoxidized oleic acid thus forming larger branched structures.

Figure 4a shows that epoxidized vegetable oils are stable at temperatures below 392°C. Thermal gravimetric analysis (TGA) result demonstrates a 2% of gradual weight loss in ESFO at temperatures below 300°C. This may be attributed to the opening of the epoxide ring. Weight loss of 81% appears to occur between 392–500°C for EPAO. The dropping in weight at 220°C for the EPAO is a result of the moisture evaporation process. TGA thermogram (Fig. 4b) suggests good thermal stability of the PAs at 373°C as indicated by the lowest amount of weight loss. This is most likely a result of the minimum amount of unreacted components present. However, PAs are less stable than epoxidized oils in which the abrupt weight loss of 88% and 72% can be seen at 373 and 500°C for PSFO and PPAO respectively. On the other hand, PSFO appears to be more stable than PPAO. Differential thermal analysis (DTA) diagram obtained for PAs (Fig. 4c) shows the maximum weight loss at the peak temperature of 400°C. The peak observed at 280–300°C is attributed to hemicelluloses and cellulose decomposition, similar to that observed by Yang et al.

PAs were successfully synthesized from PAO and SFO using addition polymerization. FTIR, NMR and MALDI-ToF-MS analysis demonstrate that PAs were formed with branched structures, consisted mostly of triacids. Further investigation is needed to determine if these macromolecules could be further cross-linked in order to form elastomers or hydrogels for biomedical applications.

Figure 2. (a) $^1$H NMR and (b) $^{13}$C NMR spectra of the epoxidized oil (top) and polyacid (bottom); insert describe disappearance of double bond and formation of oxirane ring upon epoxidation of PAO and SFO.

Figure 3. MALDI-ToF-MS spectrum of polyacid (top) and proposed structure for the peak detected at $m/z = 642$ (bottom).
Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.bmcl.2013.10.053.

References and notes