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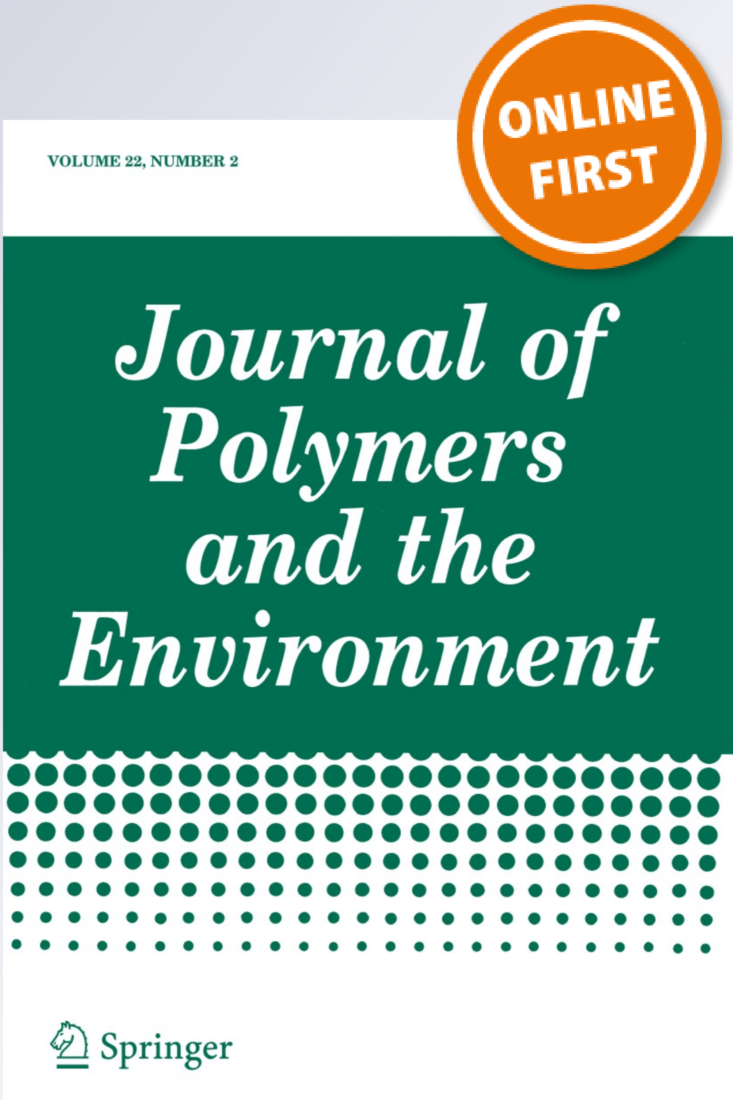

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ORIGINAL PAPER

Preparation and Characterization of Alkyd Resins of Jordan Valley Tomato Oil

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Abstract Tomato seeds represent a large waste by-product from the processing of tomatoes into products such as tomato juice, sauce and paste. One potential use for these seeds is as a source of vegetable oil. In this study, the seed oil of tomato obtained from Jordan Valley was extracted and analyzed to determine its physicochemical properties. The characteristics (iodine value, acid value, refractive index and saponification value) of the oils were determined. Tomato oil has an iodine value of 123, a refractive index of 1.467, a saponification value of 192, and an acid value of 2.3. Our alkyd resins results showed that the extracted tomato seed oil can be qualified to be used in the synthesize of alkyd resin. Three grades of tomato-based alkyd resins modified by varying the percentage of tomato seed oil contents were prepared according to the alcoholysis-polyesterification process. Fourier transform infrared, proton nuclear magnetic resonance spectroscopy and differential scanning calorimetry were employed to identify the structure of the resulting resins.

Keywords Alkyd resin synthesis · Tomato seed oil · Unsaturated vegetable oil · Physicochemical properties · Glass transition temperature

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Introduction

Alkyd resins are not only the major important binders but also they are the largest volume base of coatings and paints especially for decorative applications [1]. Studies are available on preparation and application of alkyd resins using fatty acids or oils [2–5]. Alkyd resins are used more than other binders because of their low processing cost, inexpensive raw material, easy manufacturing. Besides they can be dissolved in less expensive solvents. In addition, alkyd resins are used in other applications such as air drying, matt and semi matt varnishes of wood furniture [6].

Alkyd resins are unsaturated hydroxylated polyesters resins modified with vegetables/marine oils or their fatty acid. Therefore alkyd resins are main product of poly condensation reactions between poly carboxylic acids and poly alcohol in presence of fatty acids or vegetable oils. This kind of reaction can be represented by the following formula:

$$\text{Poly carboxylic acid} + \text{Poly alcohols} + \text{Fatty acids/Vegetable oils} \rightarrow \text{Alkyd Resin} + \text{water}$$

Poly alcohols which are mainly used for condensational polymerization reactions of alkyd resins comprise ethylene glycol, propylene glycol, diethylene glycol and pentaerythritol. In addition poly carboxylic acids are divided into two different branches: aromatic-based poly acids and aliphatic-based poly acids. For the synthesis of alkyd binders, aromatic poly carboxylic acids derived from phthalic anhydride and isophthalic acid, are usually employed. Cycloaliphatic anhydrides such as hexahydrophthalic anhydride, and malic anhydride have also been used for alkyd resins esterification reactions [7].

Careful selection of of the type of poly basic acids and poly alcohols may help in preventing gelation of alkyd resin of choice, and offers easy control of the process of polymerization of alkyd resins. Benzoic acid and other mono basic carboxylic acid are used for alkyd resins formulation including high functionality system to act as chain stopper [8, 9].

Millions of tons of tomato are processed results in large amounts of waste [10, 11]. 33–40 % of the raw tomatoes end up as processing waste [12, 13]. Seeds and skins constitute the main by-product of the tomato processing industry [14, 15]. To maximize profits, tomato processors need to find other applications for these waste materials. Tomato seeds have been shown to contain 24–25 % of oil, but 15–17 % oil can be recovered by crushing in expellers [16]. The aim of this paper is to extract tomato oil from the seeds of tomato obtained from Jordan Valley, then to synthesize and evaluate tomato seed oil-based alkyd resins.

Materials and Methods

Materials

Tomato seeds were dried, crushed and the tomato seed oil was extracted using petroleum ether (60–80 °C) in a Soxhlet extractor. Technical grade phthalic anhydride, glycerol, benzoic acid and calcium carbonate used in chemical characterization of tomato seed oil were all of analytical grade (BDH).

Preparation of Alkyds

The resins were prepared according to published procedure [5] with minor modifications (Quantities are given in Table 1).

Tomato seed oil was first heated to 240 °C, then glycerol and calcium carbonate were added at the same temperature and the mixture kept at 240 °C for 1 h and a half. At the end of the alcoholysis step, both phthalic anhydride and benzoic acid were added to the mixture. The reaction temperature was maintained at 240 °C for 4.5 h. After cooling to room temperature, the solid was first washed three times with cold ethanol then three times with diethyl ether. Further purification was performed by stirring the solid with tetrahydrofuran (THF) for several hours. Finally, the solid was dried under vacuum.

In general, the reaction takes place in two steps: The alcoholysis step, and the condensation step. The yields and some physical properties of the produced solid resins are given in Table 3.

Table 1 Amounts of chemicals used in the synthesis of the resins

Resin	Tomato oil (g)	Glycerol (g)	$CaCO_3$ (g)	Phthalic anhydride (g)	Benzoic acid (g)
1	5.0	2.35	0.040	5.0	0.96
2	3.5	1.175	0.020	2.501	0.483
3	2.248	0.587	0.010	1.257	0.245

Characterization Techniques

The IR spectra of the samples were recorded on a Perkin Elmer Spectrum. Infrared spectra were measured with a DIGILAB DIVISION BIO-RAD 3240-SPC FTS-40 spectrometer over the frequency range 4,000–400 cm^{-1}. The spectra were obtained on KBr pellets (0.5 mg substance per 100 mg KBr) at a resolution of 4 cm^{-1}.

The ^{1}H-NMR spectra of the synthesized alkyd resins were recorded on a Varian Gemini 2000, 300 MHz spectrometer. The samples were dissolved in deuterated DMSO.

Glass transition temperatures (Tg) were determined with a Perkin-Elmer. DSC 7 differential scanning calorimeter was used with samples (11–16 mg) prepared from powders and sealed in aluminum pans. The heating rate was 10 °C/min.

The refractive index of the oils was measured at room temperature using the Abbey refractometer (Prince Optical Works, Malka Ganj Delhi). The chemical parameters (iodine value, saponification value and acid value) were determined using standard methods [17].

Results and Discussion

Tomato-Seed Oil

Table 2 reports the physiochemical characteristics of some seed oils. The refractive index value for tomato oil was found to be of about 1.467 in close agreement with values reported for conventional oils from soybean (1.471),

Table 2 Physiochemical properties of some seed oils

Seed oils	Refractive index @ 25 °C	Saponification value (mg KOH/g)	Relative density @ 25 °C	Iodine value (g I_2/100 g)	Acid value (mg KOH/g)
Tomato	1.467	192	0.918	123	2.3
Soyabean [18]	1.471	189.2	0.923	128.4	0.341
Orange [19]	1.475	198.1	0.933	105.2	2.3
Pumpkin [19]	1.473	191.4	0.917	121.5	1

Table 3 Properties of the resins

Resin	Tomato oil %	Yield (g)	Solubility in toluene	Color
1	37.45	8.961	Insoluble	Pale brown
2	45.58	6.271	Sparingly soluble	Brown
3	51.7	1.323	Soluble	Dark brown

orange (1.475) and pumpkin (1.473). The refractive index of our oil confirms the presence of high number of carbon atoms in its fatty acids [20]. Refractive index also increases as the number of double bonds increases [21]. Our oil has specific gravity of 0.918, this is closer to the 0.917 specific gravity reported for both pumpkin oil and soyabean oil but less than the 0.933 reported for orange seed oil [19].

The iodine value is a measure of the degree of unsaturation in the oil and could be used to quantify the amount of double bonds present in the oil which reflects the susceptibility of the oil to oxidation. The iodine value, reported herein, suggests the presence of high percentage of unsaturated fatty acids in our tomato seed oil. The iodine value is, slightly, greater than 100 and so it could be classified as semi drying oil. The acid value of our oil is within the acceptable range (0–3 mg KOH/g Oil [22]) for our oil to find application in cooking.

The physiochemical properties of our oils (Table 2) also show that the saponification value range from 189.2 to 198.1. This means that our oils have low unsaponifiable matter content.

Physical Properties of Tomato Oil-Based Alkyd Resin

Table 3 highlights the yields, the solubility and the color of the resulting three tomato oil-based alkyd resins. In order to test for solubility, 0.5 g of each resin was dissolved in

Table 4 IR data for the alkyd resins

Assignment	Major peaks (cm^{-1})			
	Resin 1	Resin 2	Resin 3	Tomato oil
O–H str	3,448 (vs, br)	3,448, 3,422 (vs)	3,557, 3,479, 3452, 3,414 (vs)	3,420 (s)
C–H str	3,060 (w), 2,928 (s), 2,856 (s)	2,950, 2,924, 2854 (s)	2,960 (s), 2,923 (vs), 2,853 (s)	2,926, 2,855 (vs)
C=O str	1,730 (vs)	1,730 (s)	1,739 (m)	1,740 (vs)
C=C str	1,601, 1,580 (w)	1,635 (s)	1,639, 1,616 (m)	–

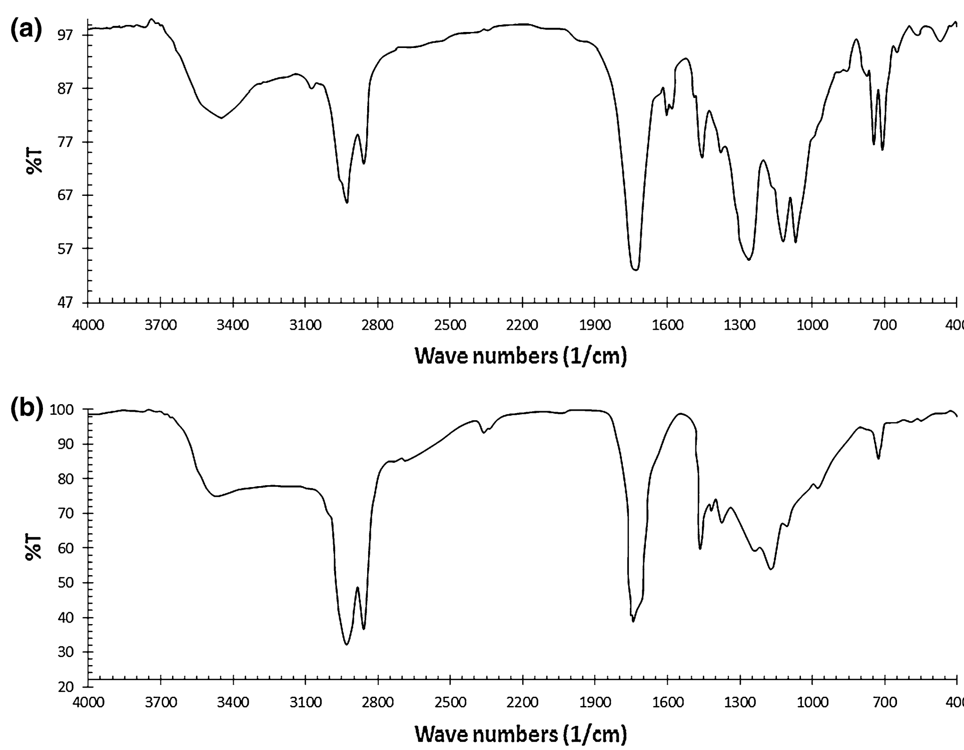

Fig. 1 FTIR Spectra of **a** alkyd resin1 and **b** tomato oil

Table 5 [1]H-NMR data (in ppm) for the alkyd resins in DMSO

Assignment	Major peaks			
	Resin 1	Resin 2	Resin 3	Tomato oil
CH_3	0.85	0.85	0.85	0.85
$COCH_2CH_2(C\underline{\mathbf{H}}_2)_n$	1.2	1.2	1.25	1.25
$COCH_2C\underline{\mathbf{H}}_2(CH_2)_n$	1.6	1.55	1.53	1.6
$COC\underline{\mathbf{H}}_2CH_2(CH_2)_n$	2.3	2.3	2.3	2.3
C–C**H**(O)–C	3.5	3.7	3.5	–
$ArCOOC\underline{\mathbf{H}}_2CH(O)C$	4.5	4.2	–	4.2
Ar (*m*-)	7.6	7.5	7.3	–
Ar (*o*-)	7.95	8.0	8.0	–

10 ml of each of ethanol, butanol, THF and toluene; all alkyds were completely insoluble in ethanol, butanol and THF. In toluene alkyd2 was brown and sparingly soluble, alkyd3 was dark brown and soluble. The only insoluble resin was alkyd1 with a pale brown color; this is probably due to a high extent of polymerization in the preparation of this resin.

Identification of Tomato Oil-Based Alkyd Resin

FTIR Spectra

Some of the characteristic peaks in the IR spectra of the resins, along with their assignments, are shown in Table 4. The formation of the ester bond is indicated by the presence of strong peaks at 1,730–1,740 cm^{-1} for the C=O stretching frequency as well as 1,250–1,270 and 1,120–1,170 cm^{-1} for the C–O stretching frequency. Aromatic C=C stretching frequencies in the range 1,600–1,640 cm^{-1} indicate the presence of the phthalate system in the resins. A representative spectrum is shown for alkyd resin 1 in Fig. 1 along with that of tomato oil. A characteristic peak at about 750 cm^{-1} for ortho-substituted benzene ring can be seen in the spectrum of alkyd resin 1.

^{1}H-NMR Spectra

The chemical shifts in the ^{1}H-NMR spectra of the resins are shown in Table 5. Again, the formation of the ester bond is indicated by the appearance of peaks at about 3.5 ppm in the alkyd resin spectra. The aromatic system is apparent by the newly formed peaks in the 7–8 ppm range. The spectra for alkyd resin 1 and tomato oil are shown in Fig. 2.

DSC Measurement

In order to obtain information regarding the formation of tomato seed oil-based alkyd resins, differential scanning calorimetry (DSC) was employed. As it comprises the highest percentage in our alkyd resin 1 (Table 3), phthalic anhydride was analyzed for its melting temperature (Fig. 3a). Phthalic anhydride is a toxic, white crystalline compound used in the manufacture of phthaleins and other

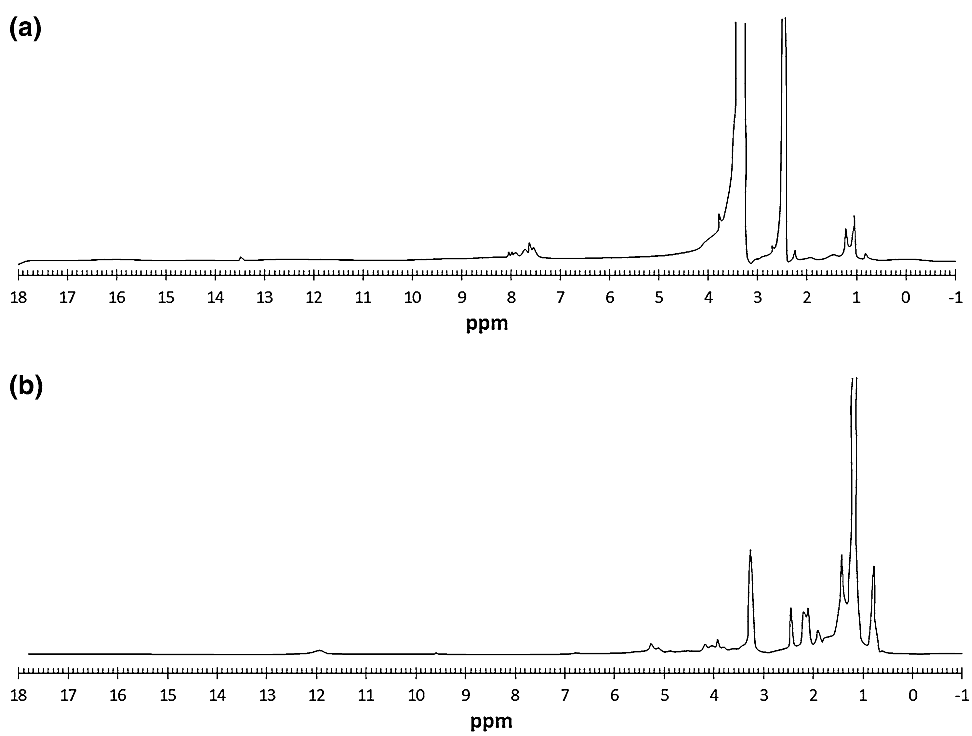

Fig. 2 ^{1}H-NMR spectra of alkyd resin 1 (**a**) and tomato oil (**b**)

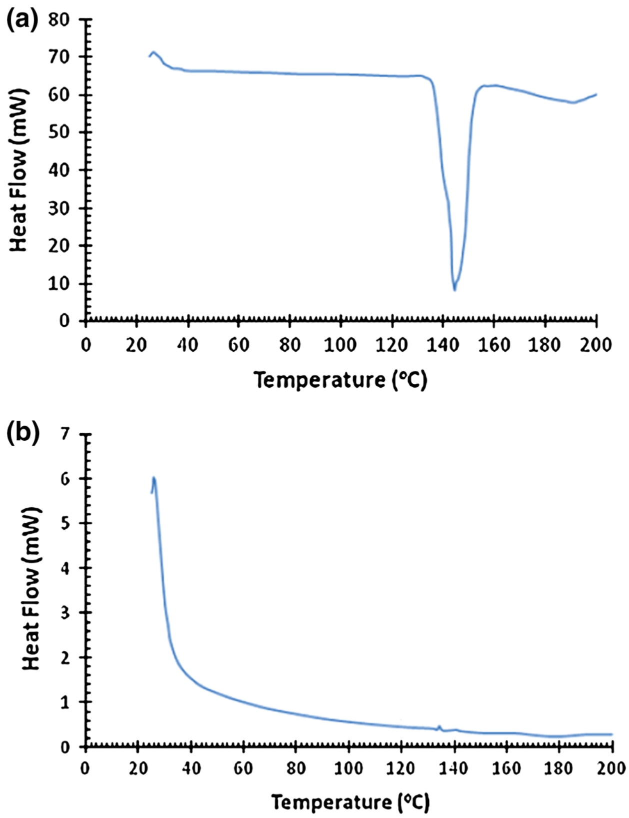

Fig. 3 DSC of phthalic anhydride (**a**) and alkyd resin 1 (**b**)

dyes, resins, plasticizers, and insecticides. It's colorless, aromatic chemical solid, which forms needle shaped crystals. It melts at a temperature of 131 °C and changes over to gas state at 256 °C [23].

Differential scanning calorimetry reveals a melting temperature of 140 °C for the crystalline phthalic anhydride (Fig. 3a) which disappears completely upon formation of the tomato oil-based alkyd resin. The resin, instead, exhibits a glass transition temperature (Tg) of about 135 °C. The disappearance of the melting temperature and the appearance of one glass temperature confirms no phase separation and proper formation of tomato oil-based alkyd resin.

Conclusions

The characteristics of tomato seed oils were found to comply with ASTM standard vegetable oils and was found to be suitable to carry out alkyd resin synthesis. The physiochemical properties of the oil were compared with some other oils' properties and it showed acceptable agreement. Extracted tomato seed oils were used in the preparation of alkyd resin of varying oil content. Tomato oil based- alkyd resins were prepared by the alcoholysis method from tomato oil, glycerol, benzoic acid and phthalic anhydride with the help of $CaCO_3$ catalyst. The solubility and the color of the synthetic alkyd resins was found to be strongly dependent on the percentage of tomato seed oil contents. The synthetic alkyd resins were characterized by FTIR, ^{1}H-NMR spectroscopy and DSC.

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