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Alkyds from red silk-cotton (*Bombax ceiba*) seed oil and investigation on their microbial degradation

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ABSTRACT

The vegetable oils are being increasingly used for the synthesis of several types of polymers. In the present study red silk-cotton (*Bombax ceiba*) seed oil was used to synthesize alkyds which were characterized by Fourier transform infrared (FT-IR) and ^{1}H nuclear magnetic resonance (NMR) spectroscopic studies. The physico-chemical properties such as colour, acid value, free fatty acid content and iodine value of the alkyds were evaluated. The coating performance of the cured films was tested by measuring chemical resistance, thermal stability, pencil hardness, gloss and adhesion. Subsequently microbial degradation studies of the alkyds were done using *Pseudomonas aeruginosa* (MTCC1934) and *Bacillus subtilis* (MTCC1305) strains and the results indicated substantial degradation in each case.

1. Introduction

Synthetic polymers exhibit unique physical and chemical characteristics and can offer a cost effective and durable alternative to conventional materials such as wood, metals etc. However some characteristics of polymers like low biodegradability and high degree of persistence have fuelled environmental concerns. As a result there is increasing focus on materials which are biodegradable with low adverse environmental impact. This resulted in exponential growth in recent past in the use of bio based precursors in place of petroleum based, for the synthesis of polymers. Vegetable oil because of its universal availability is considered as one of the most important classes of bio resources. Though vegetable oils have been in use for a long time for manufacture of lubricants, paints and varnishes, there is a renewed interest in vegetable oils as precursors for variety of chemicals and polymers. The vegetable oils are triglycerides of long chain fatty acids and the composition of fatty acids varies with the oil. The fatty acid components of oil possess several functionalities like double bond, hydroxyl group and ester groups which can be modified to generate other types of functionalities. This provided a pathway for synthesizing new materials with a wide range of properties from structural to functional. Several classes of polymers like alkyds, polyesteramides, polyetheramides, polyurethanes, epoxies and polyols are synthesized from vegetable oils [1–5].

Among the various vegetable oils based polymers, alkyds have gained attention, both in academia and industry because of their several advantages viz. versatility in structure and properties, overall low cost, and ease of application [6]. In addition, alkyds are advantageous over acrylic resins in high solids coatings. Moreover, alkyds are synthesized from several non-edible oils like yellow oleander [7], karanja [8], Spanish broom [9], African locustbean [10], *Hura crepitans* [11], tobacco [12], *Jatropha curcas* [13], nahar [14], *Ricinodendron heudelotti* [15] etc. Many vegetable oil based polymers are already commercialized or are in the process of commercialization. So at this juncture it would be desirable to understand the biodegradability profiles of such materials. Such knowledge would be useful in deciding the end use of the material i.e. whether the polymer is intended to degrade safely in the environment or intended to be durable with long time resistance to biodegradation.

The red silk-cotton (*Bombax ceiba)* tree belonging to the Malvaceae family [16], locally known as shimul or simolu tree [Fig. 1], produces seasonal fruits containing about 25–28% (w/w) of seeds [17]. The seeds, usually discarded as agro-waste, contain an appreciable amount of oil ranging between 20–25% by weight and are quite comparable to cotton seed oil [18–20]. The oil is reported to be rich in unsaturated fatty acids and contains a variable proportion of cyclopropenoid fatty

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Fig. 1. Red silk-cotton tree grows in Gauhati University campus.

acids, mainly malvalic acid and sterculic acid [19]. Red silk-cotton oil is used as a substitute of cotton-seed oil in soap industry.

In the present work we describe the synthesis of alkyds from red silk-cotton seed oil, their characterization using FTIR, ^{1}H NMR, and evaluation of their physico-chemical properties. The alkyds were subsequently subjected to microbial exposure in order to investigate their biodegradability.

2. Materials and methods

2.1. Materials

Red silk-cotton *(Bombax ceiba)* seeds [Fig. 2] were collected in spring season from Guwahati, Assam, India. Mature seeds were dried in sunlight and then crushed in a grinder.

Analytical grade phthalic anhydride (Merck, India), maleic anhydride (SRL, India), litharge (PbO) (Qualigens, India) and glycerol (Fisher scientific, India), commercial grade epoxy resin, epoxy hardener and cobalt-octoate (Archana enterprise, Kharagpur, India) were used as received. Silica gel (60–120 mesh), petroleum ether (40–60 °C) and ethyl acetate (Merck, India) were also used as received.

KH_2PO_4, $MgSO4.7H_2O$, $(NH_4)_2SO_4$, Na_2HPO_4, $CaCl_2.2H_2O$, $FeSO_4$, $CuSO_4.7H_2O$, $MnSO_4$, $ZnSO_4.7H_2O$, $H_3BO_3.5H_2O$ and MoO_3 for preparation of bacterial broth culture were obtained from Merck, India. Two bacterial strains *Pseudomonas aeruginosa* (MTCC1934) and *Bacillus subtilis* (MTCC1305) were procured from Institute of Microbial Technology, Chandigarh, India.

2.2. Oil extraction and purification

The oil was extracted from the crushed red silk-cotton seeds in a soxhlet extractor with petroleum ether. The solvent was then removed at 45 ºC in a rotary vacuum evaporator to get the crude oil. Crude oil [Fig. 3] was purified by column chromatography over silica gel using a mixture of 98% petroleum ether (40–60 °C) and 2% ethyl acetate as eluent.

Fig. 2. Red silk-cotton seed.

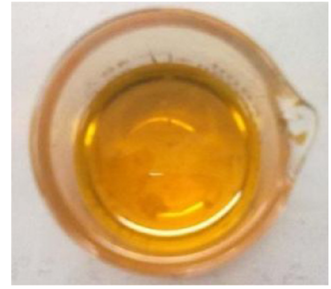

Fig. 3. Red silk-cotton seed oil.

2.3. Synthesis of alkyds

Six different alkyds viz. APM-100, APM-90, APM-80, APM-70, APM-60 and APM-50 were synthesized by following a two stage alcoholysis-polyesterification method [7], using varied amount of phthalic anhydride (PA) and maleic anhydride (MA). The amounts of various ingredients used are shown in Table 1.

In the two stage process, the oil was first converted to a monoglyceride precursor, by reaction with glycerol. The monoglyceride was then reacted with PA and MA to synthesize the alkyds [Fig. 4]. It was observed that when percentage of MA exceeds 50%, gelling always occurs. The alcoholysis-polyesterification reaction was carried out in a three necked round bottomed flask equipped with a mechanical stirrer (Heidolph, Germany), a thermometer and a nitrogen gas inlet. A mixture of 35.12 g (0.04 mol) of red silk-cotton oil, 7.36 g (0.08 mol) of glycerol and 0.05 wt percent (with respect to the oil) of PbO was heated at 230 °C (± 5 °C) with continuous stirring at a constant speed of 600 rpm under nitrogen atmosphere for 30 min until monoglyceride was formed. Monoglyceride formation was confirmed by methanol solubility test. One part of reaction mixture was mixed with three parts of methanol in a sample vial at room temperature. Complete dissolution in methanol giving a clear liquid indicated the formation of monoglyceride [21]. Once the formation of monoglyceride was confirmed from the solubilty test, the reaction mixture was cooled to 120 °C and 0.12 mol of acid anhydride in finely divided form was added along with 1.98 g glycerol (27%). The reaction temperature was then raised to 210 °C (± 5 °C) and the heating was continued until an acid value in the range of 30–40 mg KOH/g was obtained.

2.4. Instrumentation and measurements

2.4.1. Determination of specific gravity

Specific gravity of the purified oil was determined according to ASTM D5355-95 standards [22].

2.4.2. Determination of refractive index

Refractive index of the purified oil was determined according to

Table 1
Compositions of different alkyds.

Alkyd type	Composition	Oil (g)	PA (g)	MA (g)	Glycerol (g)
APM-100	100% PA + 0% MA	35.12	17.774	0	9.36
APM-90	90% PA + 10% MA	35.12	15.997	1.177	9.36
APM-80	80% PA + 20% MA	35.12	14.219	2.353	9.36
APM-70	70% PA + 30% MA	35.12	12.442	3.529	9.36
APM-60	60% PA + 40% MA	35.12	10.664	4.706	9.36
APM-50	50% PA + 50% MA	35.12	08.887	5.883	9.36