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Utilization of sunflower acid oil for synthesis of alkyd resin

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ABSTRACT

Sunflower acid oil, a by-product of sunflower oil refining is an important source of free fatty acids with minor amounts of glycerides and sterols. Sunflower acid oil was utilized to synthesize alkyd resin by alcoholysis-polyesterification method due to its availability and low cost. Three different alkyd resins have been synthesized from sunflower acid oil by using different ratios of phthalic and maleic anhydride. The various physico-chemical properties of sunflower acid oil like acid value, saponification value, iodine value, volatile matter, etc. and fatty acid composition was determined. In this study, physico-chemical properties of alkyd resins like acid value, viscosity, saponification value, volatile matter, etc. were measured and compared with refined sunflower oil based alkyd resins as well as commercial alkyd resin. The structural characterization of the resins was carried out using Fourier transform infrared (FTIR) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopic techniques. The drying properties of the alkyd resins had been significantly improved with the increase of maleic anhydride content in the resin. The film coating performance of the alkyd resins was characterized by drying time, pencil hardness test, cross-cut adhesion test, gloss measurement and chemical resistance test. It can be concluded that the sunflower acid oil can find potential application as a raw material in surface coating purposes.

1. Introduction

The production system of the world is unsustainable due to the large increase in resources used and waste produced [1]. Many of these resources and wastes are inevitable byproducts of human activity. Nowadays, proper management of industrial wastes or byproducts is one of the environmental challenges faced by many universities and industries. The vegetable oil industry of India is gradually exploring the possibility of value addition to the byproducts of oil. This area has vast potential and promises for scientists, researchers, technologists and R&D personnel to focus their attention on. Utilization of byproducts of oil is expected to have the potential not only to enhance the efficiency and productivity but also to reduce wastes in terms of environmental concern. These products based on renewable resources must meet the technical and industrial standards of fastness to exposure, durability, chemical resistance, etc. and also meet all ecological standards.

Vegetable oils, fatty acids and other byproducts from vegetable oil refining have been used as sustainable alternatives to petroleum-based materials for industrial applications such as soaps, detergents, cosmetics, lubricants, coatings and paints [2]. Major seed oils like linseed, soybean, coconut and castor oil have been traditionally used for the synthesis of different kinds of polymeric resins like alkyd [3], epoxies [4] and polyester amide [5]. The other oils like cashew nut [6], karanja [7], annona squamosa [5], natural rubber oil [8], etc. are also under progress for synthesis of polyurethane [9], polyester amide and alkyd resins [3]. These resins have applications in different field such as paint, coating, adhesives and binder for composites. Vegetable oils and other green renewable raw materials are common sources in the organic coating industry, especially for alkyd resin synthesis in preference to petroleum products due to increased worldwide awareness of environmental concerns [10].

Alkyd resins have acquired great importance because of their economy, availability of raw materials, biodegradability, durability, flexibility, good adhesion and ease of application. Alkyd resins are a special family of polyesters synthesized by polycondensation reaction of fatty oils or fatty acids, dibasic acids or acid anhydrides and polyols with hydroxyl functionality greater than 2 [11]. The traditional oils such as soybean oil [12] castor oil [13], linseed oil [14], sunflower oil [15] and coconut oil [16] are used in the synthesis of alkyd resin. So far it has been reported that non-traditional

Abbreviations: SAO, sunflower acid oil; RSO, refined sunflower oil; CAR, commercial alkyd resin; PA, phthalic anhydride; MA, maleic anhydride; MTO, mineral turpentine oil; FTIR, Fourier transform infrared; ^{1}H NMR, proton nuclear magnetic resonance.

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oils such as tobacco seed oil [17], nahar seed oil [18], rubber seed oil [19], karanja oil [20], karawila seed oil [21], jatropha seed oil [22], African locust bean seed oil [23] are used as potential sources for alkyd resins synthesis. Sibban Singh has reported the synthesis and analysis of alkyd resin from deodorizer distillate based fatty acids as byproduct of vegetable oil refineries which can be used in architectural coating [24].

Sunflower acid oil (SAO) is a by-product of vegetable oil refineries consisting of a mixture of fatty acids obtained by the treatment of soap-stock with a mineral acid solution. SAO consists of free fatty acids along with small amounts of acylglycerols, moisture and sterols [25]. It possesses many advantages such as environment friendly nature, low cost and ease of availability in significant quantity as unutilized by-product [26].

Although, researchers tried to use different oils for the synthesis of resin, there is practically no information available for synthesis of alkyd resin using SAO. In this paper, an attempt has been made to utilize the SAO as a substitute of fatty acid in order to synthesize alkyd resin. The resins with varying amount of phthalic and maleic anhydride were synthesized by using SAO. They were studied for their physico-chemical and film performance properties which was compared with refined sunflower oil (RSO) based alkyd resin and commercial alkyd resin (CAR).

2. Materials and methods

2.1. Materials

Sunflower acid oil (SAO) and refined sunflower oil (RSO) were obtained from M/s Godrej Industries Ltd, Mumbai, India. Glycerol (≥99%), litharge (lead mono-oxide) (≥98%), phthalic anhydride (PA) (≥98%), maleic anhydride (MA) (≥99%), benzoic acid (≥99%) used to synthesize the alkyd resins were procured from M/s Thomas Baker Ltd., Mumbai. Other solvents such as methanol (≥99.8%), ethanol (≥99.8%), toluene (≥99.5%), xylene (≥99%) were used as received. Mineral turpentine oil (MTO a mixture of saturated aliphatic and alicyclic C7–C12 hydrocarbons with a maximum content of 25% of C7–C12 alkyl aromatic hydrocarbons) (≥99%) used as solvent was supplied by M/s Deep Enterprises, Mumbai. Driers (6% cobalt octoate, 6% zirconium octoate and 10% calcium octoate) and methyl ethyl ketoxime (≥99%) used in the present study were procured from M/s Maldeep Catalyst Pvt. Ltd., Surat, India. Gift sample of commercial alkyd resin (CAR) was used as reference sample, obtained from Perstorp India Pvt. Ltd., Mumbai. It is a medium oil alkyd resin and it was produced by using soybean oil, glycerol, phthalic anhydride and benzoic acid.

2.2. Synthesis of alkyd resin from SAO and RSO

Alkyd resin from SAO and RSO was synthesized by using two stage alcoholysis-polyesterification methods. A four-necked 1000 ml round-bottom flask was equipped with a mechanical stirrer, thermometer, nitrogen gas inlet and condenser with dean stark apparatus to remove the water of reaction azeotropically. The reactor was flushed with nitrogen. Stoichiometric amount of SAO or RSO (0.04 mol), glycerol (0.08 mol), 0.05 wt.% (with respect to the oil) lead mono-oxide were charged into the reactor with continuous stirring. Then the mixture was heated first at 160 °C and raised to 225–230 °C for 45–60 min until it formed monoglyceride. The first stage alcoholysis reaction was confirmed by solubility in methanol (resin: methanol = 1:3 v/v) [27]. The heating was stopped and the mixture was allowed to cool to 125 °C while stirring. Then the polyesterification reaction was carried out at 240 °C after introducing stoichiometric amount of acid anhydrides (0.12 mol) such as PA and MA in different proportion along with known amount of benzoic acid (0.03 mol) as a chain stopper in the form of fine powder, excess glycerol (27%, w/w) and xylene (5%, v/w on raw materials) as azeotropic solvent [14,20,28]. The compositions of the three different resins for both the fatty raw materials are shown in Table 1. Three different alkyd resins for each oil such as SAO-AR 1, SAO-AR 2, SAO-AR 3, RSO-AR 1, RSO-AR 2 and RSO-AR 3 were synthesized by alcoholysis-polyesterification procedure. The reactions were monitored by determination of acid value of an aliquot of the reaction mixture at regular time intervals and it was continued until the acid value decreased in the range of 10–22 mg KOH/g.

2.3. Preparation of dry films

The resins were cooled to 160–170 °C and diluted with MTO to 60% of solid content. Film properties were evaluated by using 100 g of diluted alkyd resin in MTO with driers (0.02 g of 6% cobalt octoate, 0.25 g of 6% zirconium octoate and 0.6 g of 10% calcium octoate) and 0.2% of methyl ethyl ketoxime was added as anti-skinning agent. After 10 min of continuous mixing the resins were uniformly coated in the form of thin film on metal panel and cured at ambient condition. After seven days of drying, film performance properties were examined.

2.4. Characterization of SAO, RSO and alkyd resins

Physical properties such as the acid value, saponification value, iodine value, moisture content, flash point, pour point etc. of SAO and RSO were determined by ASTM standard methods [29]. Fatty acid composition of SAO and RSO was determined by gas chromatography equipped with capillary column and a flame ionization detector (FID), where nitrogen was used as a carrier gas. Physicochemical properties such as specific gravity (ASTM D 1475-08), volatile matter and acid value (ASTM D1639-96) of the alkyd resins were also determined. The viscosity of the resin solutions was measured using Brookfield viscometer. FTIR spectra of SAO, RSO and alkyd resins were recorded on Shimadzu IR affinity 1S FTIR spectrometer using ATR sampling accessory. ^{1}H NMR spectra of both the oils and alkyd resins were recorded in $CDCl_3$ at 300 MHz using Bruker Advance II 400 NMR spectrometer.

The performance film properties of alkyd resins were examined using following test methods: set-to-touch drying time and dry-to-touch drying time was studied at 60% humidity and ambient temperature as per ASTM D1640. After maturing the film for 7 days at ambient temperature, film hardness was measured using a pencil hardness tester. The pencil hardness was determined by standard sets of lead pencils graded from 6B to 6H as per ASTM D3363-05. Adhesion was tested by using a cross-hatch cutter, according to ASTM3359-09. Specular gloss measurements were performed at an angle of incidence of 60° with a Rhopoint glossmeter as per ASTM D

Table 1
Compositions of different synthesized alkyd resins.

Resins	Composition of anhydride (0.12 mol)	SAO or RSO (mol)	Glycerol (mol) + 27% excess	PA (mol)	MA (mol)	Benzoic acid (mol)
AR 1	90% PA + 10% MA	0.04	0.08	0.108	0.012	0.03
AR 2	70% PA + 30% MA	0.04	0.08	0.084	0.036	0.03
AR 3	50% PA + 50% MA	0.04	0.08	0.06	0.06	0.03