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Archives of Applied Science Research, 2017, 9 (1):7-12
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Modified Alkyd Resins as the Versatile Coating Materials derived from Vegetable Oils

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ABSTRACT

Over the years efforts have been made to design eco-friendly specialty chemicals from natural renewable resources. Among different renewable resources vegetable oils obtained from various seeds spotted largely due to their unique properties, functionalities and worldwide abundant availability. In the present review article efforts have been made to highlight the inside of the alkyd resins; oldest polymeric resin derived from vegetable oils, with respect to time to time technological modifications to improve the practical utilities. In view to reduce the use of organic solvents, synthesis and application of different types of water-born alkyds were enlightened in detailed. Furthermore, utilization of nontraditional and nonconventional seed oils in the development of versatile resin also accounted which ultimately provides profitable utilization to them as well as reduces the cost of final products.

Keywords: Vegetable oil, Renewable resource, Alkyd resin, Coating materials

INTRODUCTION

The consumer and industrial both interests in the progress of eco-friendly materials have catapulted the environmentally benign agricultural resources as feedstock for the production of valuable polymers. Over the years efforts have been made to design eco-friendly specialty chemicals from the spectrum of natural renewable resources [1-3]. Nature is blessed with numerous herbs and plants, abundantly yielding variety of bio-based feed stocks that can be tailor-made to various valuable materials [4,5].

Numerous polymeric materials have been synthesized using renewable resources such as starch, lignin, protein, wool fiber, vegetable oils and many others [6,7]. They find innumerable useful applications such as plasticizer, adhesive, biodegradable packaging materials, biological appliances, biomedical engineering, coatings and binder for paints [6,8,9]. Among different renewable resources vegetable oils obtained from the different seeds may prove to be ideal alternative for chemical industries [1, 2, 10]. Seed oils are cost effective, eco-friendly, les toxic towards human beings and moreover biodegradable in nature. Chemically vegetable oils are triglyceride of unsaturated and saturated fatty acids [2,6]. Numerous polymeric materials have been developed from the vegetable oils of enormous potential of utility [11,12].

One of the oldest polymers prepared from triglyceride oils is polyester resin and traditionally known as alkyd resin. Alkyd resins have acquired a prominent position in paints and coating industries because of their economy, ease of applications and good protection of materials from environmental attacks [4,8,10]. Moreover, they are known for biologically degradable polymers as they have repeating ester moieties [10]. The compositions and functionalities of fatty acids play the pivotal role in the properties of alkyd resins, whereas natures of dibasic acids, polyols also significantly affect the properties of the resins [8,13].

Drying and semi-drying oils, such as sunflower, coconut, castor, soybean and linseed oils are traditionally used in the preparation of oil-modified polyesters [4,8,10,13]. In addition to these numerous non-traditional vegetable oils such as rubber seed, orange seed, *Jatropha curcas*, Albiziabenth and tomato seed oils were also reported for the syntheses of polyester resins to provide a profitable utilization to these cheaply available raw materials [4,10,13-16]. In present communication efforts have been made to provide the insight of alkyd resin with respect to the modifications to inculcate viable applications as well as utilization of nonconventional and nontraditional vegetable oils in the development of versatile resin to maintain the equilibrium between demand and feed stocks.

ALKYD RESINS

Alkyd resins are the main product of poly (condensation) reaction between polyalcohols, polycarboxylic acids or their anhydrides in presence of fatty acids or vegetable oils. The systematic scheme for formulation of alkyd resin is illustrated by the general formula (Figure 1). Properties of the alkyd resins are governed by constituting materials and their proportions. The two most common methods are used for the synthesis of alkyds; i.e. monoglyceride process and fatty acid process. In the monoglyceride process; alcoholysis of vegetable oil with polyol followed by esterification with polyacids, whereas in fatty acid process polyacids, polyalcohol and fatty acids are added collectively in the reaction vessel and allow to the heat, no intermediate step involve in latter process. Alkyd resin classified on the basis percentage of oil in alkyds referred as oil length. The alkyd resins with oil content less than 40% refers to short oil alkyds, oil contents in between 40-60% medium oil alkyds, whereas, oil contents above than 60% are called long oil alkyds. Oil length is an important factor which governs the properties of final products. Short chain alkyds are useful for baking finishes on washing machine, refrigerator, automobiles, architectural equipments and many others [4,17]. Medium oil alkyds are normally synthesized from drying and semi drying oils. These resins are used in both airs drying and baking metallic primers and topcoats formulations. Such formulations are extensively used in industrial finishes, house hold articles, wooden and metallic furniture's, electric fans, railways cars, engineering equipments [18,19]. Long oil alkyds are mainly used in brushing enamels for both external and internal finishes [8].

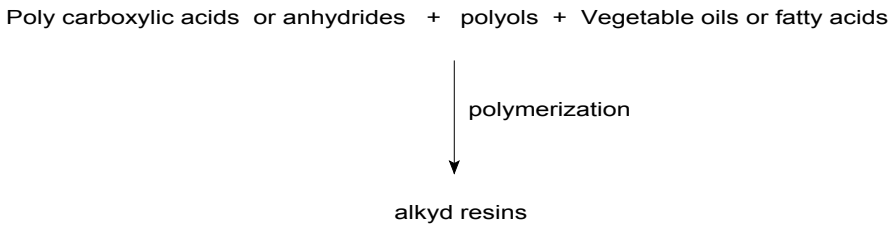

Figure 1: A systematic scheme for synthesis of alkyd resin.

Numerous aliphatic and aromatic polyacids or their anhydrides are used in alkyd resin preparations, like succinic anhydride, maleic anhydride, glutaric anhydride, phthalic anhydride etc. Alkyds of aromatic anhydrides known for better heat and moisture resistance performances as compare to alkyds of aliphatic anhydrides due to presence of benzene rings. The film forming time of the alkyds reduces on increasing the anhydride contents [20]. Furthermore, alkyd resin of maleic anhydride shows comparatively shorter time than the alkyds of other anhydride in same proportions [20]. Careful selection of the type of polyacids or anhydrides and polyalcohols may help in hampering the gelation of alkyd resin of choice and offers easy control of the process of polymerization for the alkyd resins.

MODIFIED ALKYDS

Alkyd resins of different vegetable oil extensively used as coatings and binder for making paints. However, these coatings and paints show inferior performance when expose to UV radiation, thermal fluctuation, high humid and salty conditions. Under these conditions paints show considerable chalking, color fading and loss of gloss within few months of exposures [15]. In view to provide more practical and viable utility to the alkyds, several chemical modifications were performed [4]. Modifications of alkyd resins with acrylic monomers offer the possibility of hybrid desirable application and film forming properties of the alkyd with the weathering resistance properties of acrylic systems [19].

The modifications by acrylization have been extensively investigated for different vegetable oil based alkyds [21,22]. Acrylation performed either by post-acrylation or by monoglyceride methods. C.O. Akintayo and co-workers reported the synthesis and characterization of acrylated Albiziabenth medium oil alkyds [15]. General route of chemical reaction is illustrated in (Figure 2). The developed acrylated alkyd resin with copolymer of n-butylmethacrylate and maleic anhydride (n-BMA-CO-MA) reported for improve performances in terms drying time, resistance to scratch, adhesion and chemical resistance ability in many corrosive environments [15].

WATER SOLUBLE ALKYD RESINS

Water based organic coating materials are eco-friendly and more economical than solvents based coating materials. Furthermore, environmental legislation on volatile organic solvents utilization directed the attention of researchers to developed water based organic coating materials. Alkyd resins of high acid values were prepared for water soluble

applications and then neutralized with amines. A general reaction scheme for waterborne alkyd is depicted in (Figure 3). Aigbodion and co-worker used the rubber seed oil in the production of alkyd emulsion [23]. Triglyceride oil was treated with maleic anhydride in variable ratios for maleinization and then maleinized seed oil was used to prepare water soluble alkyds [23]. Nakayama described several oil based alkyd resin blends for water-born paints [24]. The resins were developed by the copolymerization of acrylic acid, glycidyl methacrylate, esterified with unsaturated fatty acid, styrene, methyl methacrylate and by copolymer of styrene-allyl alcohol esterified with linseed oil fatty acids followed by addition reaction of maleic anhydride was processed. Castor oil based water born alkyd resins modified by s-triazine ring were prepared and claimed for better performances in alkaline media too, where normal alkyds show poor performances due to their sensitivity towards alkaline hydrolysis [25]. Polymerization of stable acrylic emulsions in presence of an alkyd resin results in a hybrid resin, which consist of two different oil and water soluble polymers. The resulting polymer forms a nano size dispersion of hybrid resin in water medium [26,27]. The technique of mini emulsion was used to copolymerize methyl methacrylate, butyl acrylate and acrylic acid in presence of alkyd resin. It was reported that the resulting emulsion is stable. The ^{13}C-NMR spectroscopy studies reveals that 20-30% alkyds double bonds are reacted, which confirm that grafting of copolymer on alkyd resin [28]. A copolymer of n-butyl acrylate and maleic anhydride was grafted on modified palm oil, and a water reducible acrylic alkyd resin was developed; reported for excellent water, acid and alkaline resistant ability [29]. To minimize the amount of un-reacted residual monomers post polymerization techniques was employed by N. Hiskanen etal [21]. The process affected the structure and morphology of the resulting hybrid resin. This technique of emulsion polymerization was used to prepare 46% solid content with 97% conversion of acrylic monomers on unsaturated alkyd resin [30]. Effect of ZnO on the mechanical and heat resistance performances on silicon-modified alkyd-based water born coatings was investigated by Dhoke et al. [31]. They developed silicon-modified alkyd-based waterborne coating using hexamethylmethoxymelamine (HMMM) as cross-linking agent and paratoluenesulphonic acid (p-TSA) as catalyst. Nano-ZnO particles were added to the system in different ratios. The developed nano-composite coatings were applied on mild steel panel to investigate the performances. They claimed that coatings obtained had enhanced heat stability and mechanical properties than the conventional silicon modified alkyd resins [31].

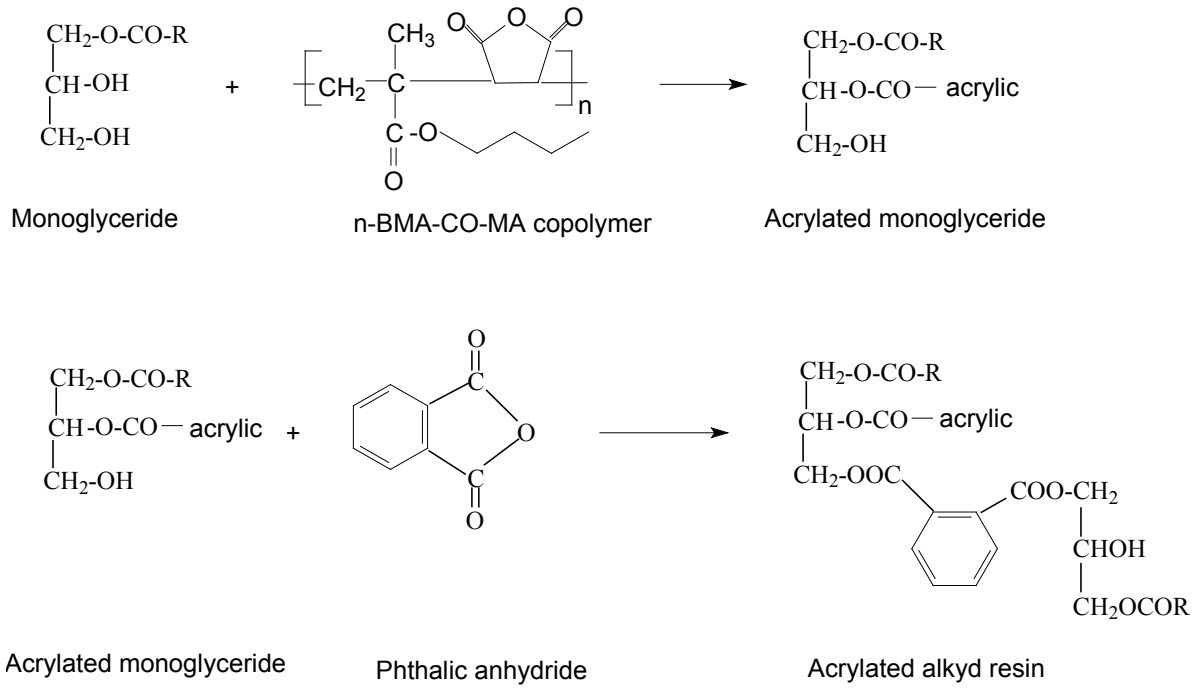

Figure 2: Scheme for synthesis of acrylated alkyd resin.

ALKYD RESINS DERIVED FROM NON-CONVENTIONAL VEGETABLE OILS

In order to reduce the pressure of demands on traditional vegetable oils, furthermore, most of them are edible and some are having medicinal values too; numerous nontraditional vegetable oils are successfully utilized in tailoring the viable alkyd resins. Such developments reduce the cost of final products and also provide practical utility to the

waste materials a precursor of nature. Jojoba seedoil is a natural product extracted from the seeds of slow–growing perennial shrub. It is mainly composed of monoester of C_{20} and C_{22} acids and alcohols [32]. Alkyd resins having different oil contents 35%, 47%, 60%, and 78% (w/w) were prepared thorough alcoholosis-polyestrification process. The developed resins were characterized by physico-chemical analyses. The physic-mechanical analyses as well as chemical resistance performances of polymeric films in acids, alkaline, water and organic solvents were also investigated. The alkyd with the least oil content had the highest viscosity and lowest color value and also reported for quick drying characteristic. Alkyd resins derived from Jojoba seed oil reported to show comparable properties to the commercial alkyds [32].

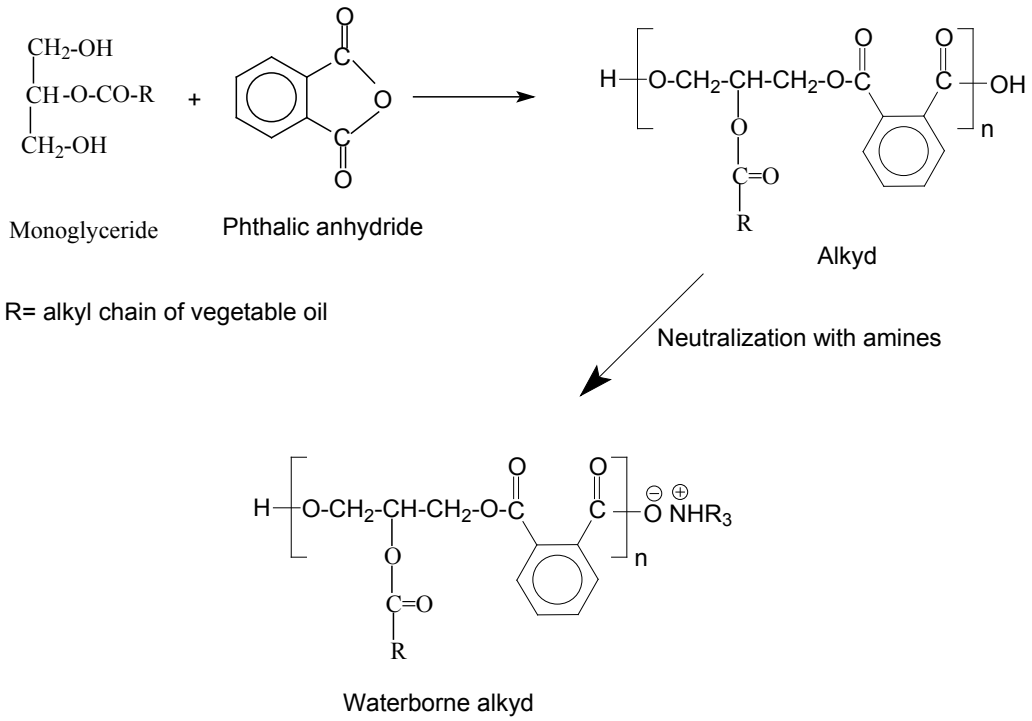

Figure 3: Reaction scheme for vegetable oil based waterborne alkyd.

Synthesis and characterization of rubber seed oil modified alkyd resins of different oil lengths using phthalic acid as polyacid and glycerol as polyol through two-stage alcoholysis method was reported by Aigbodion et al. [33]. Changes in the characteristics of the reaction medium were monitored by measuring the acid values at regular intervals. Molecular weight average and molecular weight distribution (MWD) of the resulting alkyds were investigated by GPC, cryoscopy and end group analyses. MWD vary with changes in the formulation and was reported to a significant criterion that determines their performance as binders. Rubber seed oil alkyd with 50% oil content was reported optimum composition [33].

Mesuaferrea L. (Nahar) seed oil based short oil polyester (alkyd) was synthesized in view to provide practicable utility to a renewable resource. The prepared short oil alkyd of Nahar seed oil blended partially with butylated melamine formaldehyde (BMF) resin was used for formulation of stowing paints. Developed systems were reported to show comparable characteristic to the industrially used castor oil based alkyd paints having same recipe and processing conditions. However, cost of starting material Nahar seed oil is significantly lower than castor oil [34].

Vegetable oils extracted from tomato seeds, obtained from the waste by products while processing the tomatoes into different commercial products, such as tomato juice, tomato paste and sauce [35]. Seed oil characterized as per standard methods and utilized for the syntheses of alkyd resins. Three different grades of alkyd resins were developed by varying the triglyceride oil contents using alcoholysis- poly(esterification) process [16]. The developed resins were characterized by physico-chemical analyses, FTIR, ^{1}H-NMR spectroscopy and differential scanning calorimetry (DSC). The result of DSC indicates that single gloss-transition temperature (Tg) about 135ºC, support no phase separation and proper formation of alkyd resins of the tomato seed oil [16].

CONCLUSION AND PROSPECTS

Alkyd resins, derived from different seed oils, extensively used as protective coatings and paints are discussed. The performances of the final resins mainly govern with constituting poly acids and fatty acid compositions of the vegetable oils used as well as their compositions. Careful selections of these materials are required for the syntheses of alkyds of different usages and also to complete the process without any technical difficulties such gelation and charring. Numerous modifications on vegetable oil based alkyds were performed in view to make the polymeric resin more fruitful. In view to reduce the usage of organic solvents, syntheses and applications of different types of water-born alkyds were enlightened in detailed. Furthermore, utilization of nontraditional and nonconventional seed oils in the development of versatile resin also accounted which ultimately provides profitable utilization to them, as well as reduces the cost of final products. The reported properties of different modified alkyd resins have already shown their novelty, however, further innovation is required to provide more versatile applications especially in the area of water based alkyds, which ultimately cut down the organic volatile components. In this review article efforts have been made to provide some state-of-the art-modifications of vegetable oil based environment friendly alkyd resins on a single platform. These approaches are also required to employ on the non-edible, non-medicinal and are left unutilized or meagerly utilized vegetable oils to heaping up the feed stocks, to meet the requirement of continuously increasing populations.

ACKNOWLEDGMENTS

The authors would like to thank the authorities of G. F. College, Shahjahanpur, UP, India for providing necessary facilities to carry out this study and Dr. A. Moheman for valuable suggestions.

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