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Abstract

Alkyd nanocomposites have attracted great attention in the field of heavy duty coating materials. This is due to the synergistic action of both alkyds (flexibility, biodegradability, compatibility, good gloss retention, durability, weathering resistance) and nanofillers (large surface area to volume ratio). Alkyd nanocomposites show good physico-mechanical, physico-chemical, anticorrosive, and antimicrobial performances and thermal stability, with application as anticorrosive, anti-fog, self-cleaning, self-healing, and antimicrobial coatings. In view of present drives and legislations towards environment-friendly coatings, alkyds have undergone modifications as waterborne, high solids, hyperbranched “greener” nanocomposites. The present chapter deals with a brief overview of alkyds, recent advances in environment-friendly alkyd nanocomposite coatings, and the effects of nanofillers on the performance (physico-mechanical, chemical/corrosion resistance, thermal stability, and others) of “greener” alkyd nanocomposite coatings.

Keywords: alkyds, nanocomposites, coatings, physico-mechanical, chemical resistance, thermal stability

1. Introduction

Alkyd resins are the most versatile vegetable seed oil (VSO)-based polymeric binders find applications in the paints and coatings industry. They are polyester-based materials modified with oil or oil derived fatty acids. Alkyd resins owe their wide applications to their versatility and capability to engineer a wide variety of acceptable properties in terms of usage by the Coat-
ings industry. Alkyds now account for approximately half of all the resins consumed in the field of protective coatings [1–6]. Chemically, alkyd resins have been defined as reaction product of condensation polymerization of polyhydric alcohol, polybasic acid, and monobasic fatty acid (saturated or unsaturated; Figure 1). They are best classified according to the amount of fatty acid and phthalic anhydride present (Table 1) [1].

<table>
<thead>
<tr>
<th>Content</th>
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<tr>
<td></td>
<td>Short alkyd</td>
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<td>Fatty acid content</td>
<td>30–42</td>
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<tr>
<td>Phthalic anhydride</td>
<td>37</td>
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Table 1 Alkyd classification.

Figure 1. Alkyd synthesis, where R=fatty acid chain (saturated or unsaturated). Where PA:Phthalic anhydride, Gly:Glycerol and TMPTMA: Trimethylolpropane Trimethacrylate.

The reaction of alkyd (Figure 1) is based on three basic fundamental building blocks:
i. VSO or corresponding fatty acids (in percentage): linseed (linolenic/linoleic 40/35), soybean (linoleic/oleic 55/28), tall (fatty acid/rosin 50/40), castor (ricinoleic/linoleic 90/4), dehydrated castor (conjugated fatty acid/ricinoleic 80/10), safflower (linoleic/oleic 59/37), tung (elaeostearic/oleic 79/11), coconut (saturated/monounsaturated fatty acid 91/6), as well as other nontraditional seeds oils;

ii. Polyhydric alcohols (polyols): glycerol, pentaerythritol, sorbitol, ethylene glycol, neopentyl glycol, trimethylol propane, and others; and

iii. Polybasic acids (or corresponding anhydride): phthalic, isophthalic, adipic, maleic, fumaric acids, and trimellitic anhydride [1].

Alkyd resins have good color retention, durability in exterior finishes, good weathering resistance, and moderate resistance to corrosive fumes but show poor resistance to chemical splash and spillage, especially in alkaline medium. The thermal stability of these resins goes up to 105°C [3]. The properties of alkyd coatings are derived mainly from the properties of drying oils used in the manufacture of the resins. The extent and kind of unsaturation in drying oil fatty acids have a profound effect on the properties of finished alkyd. The drying time, hardness, color, and moisture resistivity of the resin depends on the degree of unsaturation of the oil used [1,4]. These unsaturation sites are responsible for the curing of alkyd resins through auto-oxidation process (Figure 2). The process creates the active free radicals leading to the formation of a three-dimensional cross-linked network. [1,7].

![Figure 2. Autoxidation of alkyd.](image-url)

The standard alkyds are usually soybean and linseed oil alkyds, which show moderate and faster drying rates, respectively. The former has good color retention, whereas the latter reduces the color retention requirement. Dehydrated castor and soybean oil-based alkyds are used for baked finishes. These alkyds in combination with urea formaldehyde and melamine formaldehyde resin exhibit shorter baking time and produce harder film. For light color and maximum color retention, nondrying oils, such as coconut, castor, and cottonseeds, may be used. The alkyd of this type does not dry because of the nonoxidizing character of the parent VSO. They must be blended with some cross-linkers and baked with amine resin, such as urea or melamine formaldehyde, at high temperature (Figure 3).
Figure 3. Curing reactions of alkyd resins with amino resins.

Nondrying VSO-based alkyds are also used as resinous plasticizers and other lacquer-type polymers. Tung and oiticica in combination with other VSO-based alkyds show faster drying and achieve earlier hardness. Safflower oil-based alkyd has excellent drying properties and color retention [1,8]. Besides these, some nontraditional VSO-based alkyds, such as nahar (Mesua ferrea Linn), kamala (Mallotus phillipinensis), mahua (Madhuca longifolia), barbados nut (Jatropha curcas), burra gokharu (Tribulus terrestris), undi (Calophyllum inophyllum), karanja (Pongamia glabra), karinotta (Samera indica), nigerseed (Guizotia abyssinica), babul (Acacia arabica), and neem (Azardirachta indica), have been reported and used as coating materials [4,9–11]. Tobacco seed oil has been reportedly used in alkyd preparation for wrinkled finish paints [10]. The use of pentaerythritol as a polyhydric alcohol produces faster drying, greater hardness, better gloss, and better water resistance than alkyds based on glycerol of equal fatty acid content [12].

Modifications of alkyd resins are continuously carried out to achieve improved mechanical and chemical resistance properties and these systems find a wide scope of application as corrosion protective coatings. The modification with acrylic monomer, such as styrene, methyl methacrylate, vinyl toluene, and others, has been extensively done by researchers through unsaturation to improve the performance of resins up to the desired level [13]. Butylmethacrylate-co-maleic anhydride copolymer modified linseed and rubber seed oil alkyds through functional groups are used as co-curing resins with melamine formaldehyde resin to prepare baking-type coating compositions, whereas Albizia benth medium oil-based alkyd gives room temperature cured resin, with superior film properties [3,14,15]. The modification of alkyd with chlorinated rubber resulted in improved adhesion as well as improved acid, alkali, and water resistance. The chlorination of soybean and A. benth oil-based alkyd transforms into an air-drying, nonconvertible film former with improved mechanical properties [3,16,17]. Chain-stop alkyds from solvent fractionated Argeone and rubber seed oil are used for specialty alkyd [18]. Heated rubber seed oil-based films show excellent resistance to acid and salt solution. Its combination with cashew nut shell liquid formaldehyde resin has improved the drying ability and chemical resistance [19]. The phenol-modified alkyd resin improves gloss retention as well.
as water and alkali resistance. Waterborne-baked and air-drying alkyds have also been developed from different VSO having properties similar to their solvent-borne counterparts and found application in paint and coatings [20,21]. In addition, alkyd resins can be modified with epoxies and polyurethanes or other thermoplastic resins to give coatings of improved performance. For example, urethane oils are prepared by reacting diglycerides with toluene diisocynate. The resulting oils are used in alkyd resin preparation or as additive for coatings. Besides these, other alkyds are also prepared, such as imide-modified alkyd, amide-modified alkyd, tetrachlorophthalic anhydride-based alkyd resin with fire-retardant properties, ketene and acetic anhydride modification with terminal hydroxyl groups of alkyd, zinc chromate containing alkyd resin, triphenyl phosphate containing alkyd resin with improved color and drying properties, oil-less alkyds, ultraviolet (UV) light hardenable pigmented alkyd resin laquer preparation, and maleic anhydride-cyclopentadiene adduct in alkyd preparations [22–24].

In recent years, due to concerns related to energy consumption and environmental contamination, regulations, and legislations directing us toward “sustainable development” and innovations, efforts are being focused towards the development of (i) “greener” environmentally benign materials (ii) with improved performance characteristics to meet the present-day demands. Environment-friendly technologies such as high solids, hyperbranched, waterborne, and UV curable, are being used to eliminate the use and/or generation of hazardous chemicals and emissions harmful to environment. For improvement in performance, the inclusion of nanosized fillers as nanoreinforcements is being accomplished. In this context, the world of alkyds has also witnessed greater modifications such as switching to high solids, hyperbranched, waterborne and UV curable alkyds (Figure 1)[22,23,25–29]. In our recent review articles, we have described alkyds and their modifications in terms of both in property enhancements and environment-friendly approaches, occurring in the last decade [22,23]. This manuscript provides a brief overview of environment-friendly recent advances that have taken place in the field of alkyds and also focuses on the properties and performance characteristics of high solids, hyperbranched, and waterborne alkyd nanocomposites along with the unexplored areas in the field and possible future research directions.

2. Environment-friendly recent advances in alkyds towards “greener” coatings

Considering the future predictions, energy concerns, associated hazards, and legislations, research progresses in the quest for improved and updated performance characteristics in every field. Alkyds have undergone several modifications recently in consideration of the aforementioned, such as the use of reactive diluents, resorting to solvent free approaches, and others. In alkyd-based coatings, towards the step to eliminate the use of organic solvents, which are often added to achieve the desired viscosity for application over the substrate, tung oil (TO)-based reactive diluents were added to soy alkyd formulations. TO-reactive diluents were modified with alkoxysilane, tetraallyl ether, and fluororinated side chain. These diluents participated in the film formation process and significantly reduced the viscosity of alkyds,
thereby serving as effective diluents. Alkoxysilane-modified diluents showed somewhat enhanced performance due to *in situ* polycondensation of silicon alkoxide within the organic polymer matrix, which provided an additional functionality for cross-linking [30]. To reduce the content of solvents and to achieve desirable viscosity, carboxymethyl cellulose nitrate ester/coconut alkyl blends were prepared, which resulted in hydrophilic transparent films [31,32].

In a recent “greener” approach, *Jatropha* oil (JO)-based alkyd was blended with citric acid cured JO-derived epoxy. The final product showed enhanced tensile strength, elongation at break, hardness, increment in gloss due to uniform and smooth surface morphology, good scratch hardness and adhesion conferred by highly cross-linked networks, flexibility of oil chains, and the presence of polar functionalities in the backbone, which also contributed to excellent resistance to solvents (water and ethanol), salt solution, and good acid and alkali resistance [33]. An interesting research includes the synthesis of alkyds from postconsumer polyethylene terephthalate (PET) bottles. Herein, waste PET was glycolyzed using glycerol, trimethylol-ethane, trimethylolpropane, and pentaerythritol, giving tetra- and hexafunctional glycoly-zates. PET glycolyzed were then used as hydroxyl components in the synthesis of alkyd resins. The approach has multiple advantages: (i) value addition to a waste material (i.e., PET), (ii) reduction in the amount of waste PET in dumps and landfills, (iii) reduction in amount of phthalic anhydride, and (iv) improved performance of alkyd. The best performance was achieved by the inclusion of trimethylethane and trimethylolpropane, as they had four sterically unhindered primary hydroxyl groups that produced alkyds with higher degree of branching, consequently higher molar mass, which led to improved mechanical, drying, and chemical resistance properties [34].

Laccases are enzymes first discovered in Japanese lacquer tree *Rhus vernicifera* by Yoshida in 1883, which are found in fungi, different bacteria, and plants. In an effort to completely replace the toxic heavy metals by nontoxic and environment-friendly catalysts, laccase-mediator systems have been considered as potential cross-linking and functionalizing agents for alkyds [35]. In the synthesis of alkyds, heterogeneous base catalysts are used such as hydroxides of calcium, potassium, sodium, lithium, oxides of calcium, zinc, and others. Recently, CuO nanocatalyst was introduced, which had dual effects: (i) it catalyzed the alcoholysis-polyesterification reaction, reducing the reaction time, and (ii) it conferred antimicrobial properties to the resin [36]. Thus, the addition of nanofillers leads to enhancement in several properties, often drastically, such as aesthetic appeal, UV resistance, corrosion resistance, scratch resistance, impact resistance, thermal stability, and others, thus reinforcing the matrix, without losing transparency and other properties. The enhancement in properties is a consequence of the much greater surface-to-volume ratio of the nanofiller. The incorporation of nanoparticles in the polymer matrix offers significant barrier properties for corrosion protection. It reduces blistering or delamination and also enhances the integrity and durability of coatings (the fine particles uniformly dispersed in coatings can fill cavities and can cause crack bridging, crack deflection, and crack bowing) [37,38]. After having a brief idea of the recent advances in the field towards environment-friendly “greener” coatings, in the proceeding sections, we will discuss about some of the recent developments in alkyd-based environment-friendly (waterborne, high solids, hyperbranched) nanocomposite coatings.
3. Waterborne alkyd nanocomposite coatings

In these types of coatings, the alkyd matrix selected is waterborne and is further modified with nanoreinforcements depending on the property that needs improvement (Figure 4). Thus, the choice of nanofillers for modification depends on the property that is needed to be augmented or enhanced. The inclusion of nanoalumina improved the scratch, corrosion, UV, and abrasion resistance of coatings. The increased content of nanoalumina reduced the pinhole formation tendency and defended the coatings against humidity [37]. The corrosion protection occurred by (a) nanoparticles occupying the vacant spaces in the coating matrix, (b) reducing porosity, (c) bridging and interconnecting the constituents of matrix, (d) increasing cross-linking, (e) providing longer diffusion paths to corrosive ions, and (f) improving barrier performance [39]. A similar enhancement in the performance of coatings was also observed when waterborne alkyd coatings were modified with nano-Fe$_2$O$_3$ by the described corrosion protection mechanism. Even at the lower loading of nano-Fe$_2$O$_3$ (0.05%, 0.1%, and 0.2%), the corrosion process was delayed, whereas, at 0.3% loading of nano-Fe$_2$O$_3$, adequate coating performance was achieved [40,41]. Nano-silica modification improved scratch resistance, abrasion resistance, adhesion properties, impact resistance, glass transition temperature, and thermal stability [42,43]. The introduction of ZnO nanoparticles improved film compactness and abrasion resistance and had a catalytic influence on curing reaction, thus facilitating the formation of hard and complex network. The stronger interactions between nanoparticles and alkyd matrix also conferred enhancement in mechanical properties. As nano-ZnO has UV blocking properties, the incorporation of nano-ZnO also improves the UV resistance of coatings [44–46].

Figure 4 Waterborne alkyd nanocomposites.
Poly(methacrylate-butylacrylate)/nanocalcium carbonate, prepared by emulsion polymerization, was blended with alkyd coating with 50 wt% water as solvent, in various ratios, with dual objectives: (i) using polymer nanocomposite as partial binder and (ii) As a filler to improve the properties. The coatings showed good gloss, mechanical and thermal properties; however, impact resistance was found to be lower. The highly crystalline calcium carbonate nanoparticles deteriorate the impact strength at locations in coatings where the aggregation of particles occurs, thus generating stress at these specific sites [47].

4. Hyperbranched alkyd nanocomposite coatings

The use of dendritic or hyperbranched polymers as binders in coatings is considered as one of the effective ways to reduce volatile organic compounds (VOCs; Figure 5).

![Figure 5 Hyperbranched alkyd](image)

Figure 5 Hyperbranched alkyd, where I=dimethylolpropionic acid, II–IV=hyperbranched polyesters (HBPs), and V–VII=their respective hyperbranched alkyls; a–c are dipentaerythritol, pentaerythritol, and 1,3,5-tris(2-hydroxyethyl)cyanuric acid, respectively; and R=fatty acid chain (unsaturated or saturated).

These polymers have three-dimensional compact structures. They show low viscosity even at higher molecular weight. Thus, the development of hyperbranched nanocomposites has double advantages: (i) overcomes the use of VOCs and (ii) leads to property enhancement.
In a recent research, nanosilver was embedded in hyperbranched urethane alkyd by an *in situ* approach that prevented agglomeration of nanoparticles (Figure 6). The nanocomposites showed good antibacterial activity against *Serratia marcescens*, as studied by using agar overlay and disk diffusion methods, and the coatings were gloss retentive and nonleaching. The resin required much lesser solvent for coating formulation and showed improved mechanical properties [48].

An interesting research work was performed on carbon nanofiller modification of hyperbranched alkyd. Here, three geometrically different carbon nanofillers, carbon black (CAB), multiwall carbon nanotubes (MWCNT), and graphene (GR), were treated with a surfactant Nonidet P-40 (Figure 7). This led to the uniform dispersion of carbon fillers as facilitated by the interactions of π-electron clouds of carbon nanofillers with the delocalized π-electrons of the surfactant and H-bonding interactions between surfactant and hyperbranched alkyd backbone. The former interactions reduce the van der Waals forces present between carbon nanofillers, and the latter interactions improve the interfacial adhesion between the matrix and...
nanofillers. Due to their stronger interactions with the alkyd backbone and the high aspect ratio and surface area, MWCNT and GR showed better dispersion in the matrix relative to CAB. Thus, modifications with MWCNT and GR provided relatively higher scratch resistance, adhesion, and tensile strength to alkyd coating as well as higher thermal stability. The water vapor transmission rate was found to be lower in nanocomposite alkyd, and least in GR alkyd (due to its plate-like structure), compared to the unmodified alkyd, as the nanofillers provided tortuous path to water and oxygen molecules hindering them to reach the substrate of the coating easily. However, compared to others, GR-alkyd showed the highest corrosion resistance performance due to good dispersion and adhesion of GR; moreover, its plate-like structure also proved advantageous in enhancing the corrosion resistance [49]. The modification with silicones reduces the drying times and improves the adhesion to the substrate, hardness, and gloss of coating (Figure 6) [50].

Figure 7 Hyperbranched alkyd urethane/GR or MWCNT nanocomposites.
5. Future suggestions and conclusion

Environment-friendly alkyd nanocomposites are an emerging field of research. They comprise a vast field for commercial coating applications. They find promising applications as corrosion-protective, antimicrobial, eco-friendly coatings. However, more efforts are required in the field to be established further as “greener” coatings in terms of performance, cost, and environment-friendly applications. A lot of modifications have been accomplished and much remains unexplored.

The synthesis of alkyds requires higher temperatures and longer reaction times. In view of this, alkyd synthesis can be performed via microwave-assisted methods that reduce reaction times and often temperatures. Another alternative is the synthesis by enzymatic approach. Hydroxylated oils (or polyols) can be used to prepare monoglycerides, which would introduce extra hydroxyl functionality in alkyd backbone increasing the adhesion of coatings produced due to polar hydroxyls. The alkyd with extra hydroxyls in its backbone will serve as alkyd polyol. Considering the present drives towards environment-friendly coatings, efforts should be laid on the development of low solvent or solvent-free alkyd nanocomposite coatings to reduce the use of harmful solvents during the synthesis, processing, formulation, and application of coatings. More emphasis should be laid on the development of waterborne, high solids, hyperbranched, and UV curable alkyd nanocomposites using different nanofillers. A completely water-soluble alkyd nanocomposite would be a significant achievement in the field. Greener isocyanates may be used as curing agents for alkyd polyurethane nanocomposites. The introduction of nanoparticles by in situ approach may reduce reaction steps and also the problems associated with the agglomeration of nanoparticles. Blending with cost-effective reinforcing components will also effectively reduce cost and improve performance characteristics. The greater utilization of nonedible and nonmedicinal oils in the preparation of alkyds must be encouraged to add value to underutilized oil as a bioresource. Efforts may also be focused on studying the biodegradation behavior of these materials to determine their eco-friendly disposal.

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