Progress in Organic Coatings 77 (2014) 949–956

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Preparation and characterization of water reducible alkyd resin/colloidal silica nanocomposite coatings

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ARTICLE INFO

Article history:
Received 14 June 2013
Received in revised form 13 January 2014
Accepted 15 January 2014
Available online 10 February 2014

Keywords:
Alkyd resin
Colloidal silica
Nanocomposite
Water reducible alkyd
Film properties
Surface coating material

ABSTRACT

In this study, water reducible alkyd resins containing different amounts of colloidal silica were synthesized for the first time. In order to achieve this, alkyd resin, which has an oil content of 35%, was prepared with tall oil fatty acid, isophthalic acid, trimellitic anhydride, and trimethylolpropane. The alkyd resin was neutralized with triethylamine, and was dissolved in an isobutyl alcohol-isopropyl alcohol-butyl glycol mixture to produce 75% (wt.) solution, which was called stock alkyd resin. The stock alkyd resin was diluted with water to 50% (wt.) concentration with water and colloidal silica mixture in order to prepare an alkyd solution containing 0%, 5%, 10%, 15% and 20% colloidal silica. Then the effect of the silica nanoparticle addition on the surface coating properties, thermal behaviors and surface morphologies of water reducible alkyd resins was investigated. As a result, the addition of colloidal silica has improved surface coating properties and thermal behaviors of nanocomposite water reducible alkyd resin.

1. Introduction

Alkyd resins are condensation polymers of dibasic acids, polyhydric alcohols and fatty acids. The name “alkyd” comes from its ingredients; alcohols and acids. These resins are polyesters modified with monobasic fatty acids [1]. Alkyds are fundamental binder materials for the manufacture of different types of surface coating [2]. Alkyds have been a part of the coating industry since 1926 [3]. Alkyd based coatings have good surface coating properties such as good corrosion protection, high gloss, fast dryness, and these resins have good interactions with polar substrates such as wood and steel [3–5]. The coatings of standard conventional alkyds are solvent based resins, and these resins are diluted with an organic solvent such as toluene, xylene, white spirit and a mixture of these solvents [5]. The emission of toxic volatile organic compounds (VOC) during the application and curing process from solvent based alkyd resins causes many environmental problems [5,6]. In order to overcome these disadvantages of alkyds, two different types of alkyd resins were developed. These resins are acrylic modified alkyd emulsions and water reducible alkyd resins [5,7,8]. Acrylic modified alkyd emulsions were synthesized with different techniques. For example, the blending of an alkyd with an acrylic dispersion is prepared by emulsification of an alkyd in the presence of an acrylic dispersion [7] or carboxy-functional acrylic copolymer is used for preparation of an alkyd resin such as a dicarboxylic acid component [8]. Alkyd resins with high acid values can be made water reducible by neutralization of their free carboxyl groups with amine compounds such as triethylamine, diethanolamine [9–12]. Compared to their solvent-based counterparts, these resins have many advantages such as lower VOC, reduced odor, and lower flammability [12].

In recent years, organic–inorganic nanocomposites have attracted attention in various fields such as material science, paints, high-quality paper coatings, electronics, cosmetics and biotechnology because of their excellent performances compared to conventional materials [13–15]. Nanotechnology is also extremely important for the paint industry [16]. The inorganic nanoparticles used for the polymeric coatings are SiO_2, TiO_2, Al_2O_3, $CaCO_3$, ZnO, Fe_2O_3 and organo clay [17–25]. Especially silica based nanocomposites are widely used in coatings for the improvement of water resistance, mechanical and thermal properties of resins [26,27]. For example, Ye et al. synthesized nano-silica/polyacrylate composite emulsions via in-situ emulsion polymerization technique [26]. Zhu et al. used the suspension-dispersion-polymerization method to prepared poly(styrene-buthylacrylate-acrylic acid)-grafted-silica nanocomposites. The Authors reported that nanocomposites containing 1.5 wt.% silica showed a significant improvement in adhesion properties, mechanical properties and UV and water resistance of films [27]. Wada et al. prepared composite materials from acrylic resin emulsions and colloidal silica by emulsion polymerization [15]. Işın et al. and Jacquelet et al. investigated the

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http://dx.doi.org/10.1016/j.porgcoat.2014.01.017

preparation and characterization of epoxy/silica and polyester/melamine-pyrogenic silica nanocomposite coatings, respectively [14,16].

As shown in this literature survey, there are many studies on nanocomposite coatings containing silica and there are several papers about modified alkyd resins with nano particles such as zinc oxide, iron oxide titanium dioxide, silica and organo clay [18–20,28–31]. In previous work, we also investigated preparation and film properties of alkyd-melamine formaldehyde resin containing colloidal silica [22]. A literature survey has not yielded any research on the water reducible alkyd resins containing colloidal silica.

In the present study, water reducible alkyd resins containing different amounts of colloidal silica were synthesized for the first time. Then the effect of a silica nanoparticle addition on the surface coating properties, thermal behaviors and surface morphologies of water reducible alkyd resins was investigated.

2. Experimental

2.1. Materials

Tall oil fatty acid (TOFA) was used in the preparation of alkyd resins. TOFA [Sylfat 2S, iodine value (IV) 155, acid value (AV) 197] was obtained from Arizona Chemicals (USA). Trimethylolpropane (TMP) and isophthalic acid (IPA) were obtained from Perstorp (Sweden). Trimellitic anhydride (TMA) was obtained from KP Chemical (Korea). Colloidal silica suspension (50% wt., LUDOX TM-50) was obtained from Sigma–Aldrich (USA). The rest of the materials were obtained from Merck (Germany). Drier for water based coatings (ready-to-use cobalt/zirconium/lithium water miscible drier combination; Nuodex Combi Web Aq) was obtained from Aktif Kimya (Turkey). All solutions were prepared to use deionized water.

2.2. Preparation of water reducible alkyd resins containing colloidal silica

Alkyd formulated to have oil content 35% was prepared with TOFA, IPA, TMA, TMP. "*K* alkyd constant system" was used for the formulation calculations of the alkyd resins [32]. The *K* constant was 1, and the ratio of basic equivalents to acid equivalents (*R*) was 1.32. The reaction was carried out in a round bottom flask equipped with a Dean–Stark piece, gas bubbler, contact thermometer and mechanical stirrer system. TOFA, IPA, TMP were charged to the flask and the system heated to 200 °C. Azeotropic solvent xylene was added to the reaction mixture, and the reaction mixture was heated to 250 °C. Then, the temperature of the reaction was kept constant at 240–250 °C. The reactions were followed with acid value (AV). Condensation reaction was allowed to continue until the acid value of the resin was approximately 10 mgKOH/g. The acid values were determined by titration of samples dissolved in ethanol–toluene with 0.1 N KOH solution. Then, the temperature was reduced to 150 °C, and TMA was added to the reaction mixture and the temperature was raised to 185 °C. Reaction was allowed to continue until the acid value of the resin was 50 mgKOH/g. Then, the alkyd resins were neutralized with triethylamine (TEA) at 120 °C. The alkyd resin was dissolved in isobutyl alcohol-isopropyl alcohol-butyl glycol mixture to produce 75% (wt.) solution which is called stock alkyd resin (SA). The pH was adjusted to slightly alkaline (pH 8.3) with 25% ammonia solution. The stock alkyd resin was diluted with water to 50% (wt.) concentration [11,33]. Then, water and a colloidal silica mixture were added, and the solution was agitated vigorously. Thus, alkyd solutions which are solid content of 50% (wt.) containing 0%, 5%, 10%, 15% and 20% colloidal silica were prepared with colloidal silica and a distilled water mixture. The symbols and properties of water reducible alkyd resin (WRAR) containing colloidal silica were given in Table 1.

Table 1
Symbols and properties of alkyd resins.

Symbols of alkyd resins	Solid content (wt.%)	Colloidal silica ratio (wt.%)
Stock alkyd resin (SA)	75	–
WRAR (reference resin)	50	0
WRAR-5	50	5
WRAR-10	50	10
WRAR-15	50	15
WRAR-20	50	20

Table 2
Properties of stock alkyd resin.

Properties of stock alkyd resin	
Solid content	75 wt.%
Acid value	50 mg KOH/g
Viscosity (determined by Gardner Bubble Tube)	92 s

In addition, properties of SA such as solid content, acid value and viscosity were given in Table 2. The viscosity of SA was determined by a Gardner Bubble Tube according to the Gardner-Holdt method, which had been given in ASTM D-1545.

2.3. Scanning electron microscope (SEM) analysis

The scanning electron micrographs of the resins were taken at different magnification of with a *FEI Quanta FEG 450* SEM with an EDAX energy dispersive X-ray analytical system.

2.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out by Linsesis STA PT 1750 model under air at a rate of 10 °C/min with about 20 mg of resins.

2.5. Film properties of water reducible alkyd resins

WRAR films, which contain 2% drier, were prepared for physical and chemical surface coating tests. The films cast by 50 μm applicators from the solutions were dried at 25 ± 1 °C for 72 h (air dried). In addition, some of the films were oven cured at 150 °C for 1 h (oven cured).

2.5.1. Physical film properties of water reducible alkyd resins

Drying time was determined by an Erichsen 415/E apparatus, which gave results according to DIN 53150. Determination of drying time of the resins is estimated by adherence or non-adherence of paper or glass beads. There are seven drying stages of this method, and the maximum drying degree is 7. Stage 1 is determined with glass beads, and the remaining stages are determined with disks of typewriter paper (loads range from 5 to 5000 g/cm^2). The glass beads are allowed to remain on film for 10 s, and the loads on the disks remain for 60 s [30,34].

Hardness was determined by König Pendulum, which gave results according to the DIN 53 157 standard. The procedure of hardness determination with König Pendulum is based on the measurement of the damping of a pendulum oscillating on the paint film. The oscillations of a standardized König pendulum placed on the test surface are damped in proportion to the "softness" of the coating [30,34].

Adhesion strength of the films was determined by the cross-cut method according to ASTM D 3359-76.