



Hyperbranched alkyd/magnetite-silica nanocomposite as a coating material



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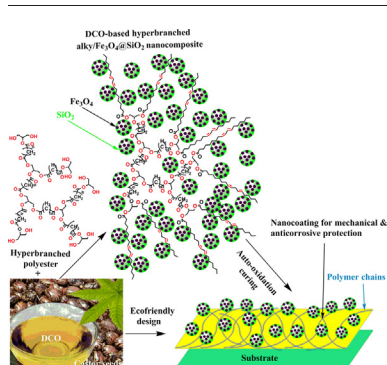
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HIGHLIGHTS

- A conformal series of castor oil based hyperbranched Alkyd/Fe₃O₄@SiO₂ nanocomposites was developed as a coating material.
- Structure-property relationship was studied by incorporating different nanofiller concentrations in the alkyd matrix.
- Shape and size control of nano-Fe₃O₄@SiO₂ is crucial to achieve well-dispersed nanospheres with good filler properties.
- Well-dispersed nanoparticles (especially 0.5%) in alkyd matrix exerted improved mechanical and anticorrosive properties.

GRAPHICAL ABSTRACT



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ABSTRACT

Engineering innovative nanomaterials with low volatile organic content (VOC) has awarded great interest to control air pollutant emissions. We designed a highly branched alkyd matrix suitable for surface coating from castor oil via polyesterification. A simple A₂ + B₃ (di- and tri-functional monomers) methodology was used to prepare the hyperbranched polyester from natural multifunctional monomers. Magnetite-coated silica (Fe₃O₄@SiO₂) particles with 60–70 nm average diameter were prepared by in situ method that binds magnetite nanoparticles to silica nanospheres. The magnetite size and attaching efficiency were controlled by the concentration of chemicals and reflux duration. The nanocomposite coating was prepared by solution casting. The structure-property relationship was studied for different concentrations of nanofiller in the alkyd matrix. The surface and anticorrosive properties were studied via contact angle and salt spray tests. Mechanical performance and thermal stability were assessed by various methods. The highest improvement was achieved with nanofiller insertion up to 0.5% Fe₃O₄@SiO₂ nanospheres.

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1. Introduction

Worldwide concern about environmental pollution and climate change has directed modern research toward green chemistry [1]. Polymeric alkyds are widely used for metal coating for their low cost, high performance, ease of application, bio-degradability and superior adhesion [2,3]. They are also better in color retention, durability, and anticorrosive performance [4]. One advantage of hyperbranched alkyd over

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other dendritic polymers is the possibility of single-step preparation from commercially available monomers [5,6]. The $A_2 + B_3$ approach, i.e. ester linkage formation between a dibasic acid and trifunctional alcohol, is a simple technique for preparing hyperbranched polyesters [7].

Alkyd resin paint is a polyester-based material derived from vegetable oil containing polyunsaturated fatty-acids [8,9]. Recently, vegetable oils have received great interests because of their renewability and sustainability [10]. Castor oil is a cheap raw material for the production of eco-friendly resins and one of the few naturally occurring glycerides as the fatty acid portion is 90% [11]. It is a non-drying oil but can be converted into a drying oil by dehydration [12]. Dehydration of castor oil is usually performed by catalytic processes at 250 °C under inert gas [11]. Coatings based on dehydrated castor oil (DCO) fatty acid can reach full cure via oxidative crosslinking [11–13]. Alkyd paints based on DCO fatty acid have advantages of non-yellowing, high durability, anticorrosion, and weather resistance [14]. Incorporation of inorganic nanofiller in alkyd resin can enhance its performances [15–17]. A great interest was given to bifunctional nanomaterials that possess dual structure and exhibit extra-ordinary characteristics [18]. Magnetite nanospheres with large surface area afford active sites suitable for different applications [19]. Using Stöber silica as a support for assembling magnetite nanoparticles (NPs) onto its surface can protect these nanomaterials from degradation and improves their biocompatibility [20].

$Fe_3O_4@SiO_2$ nanofiller structure combines the properties of two phases with varied chemical composition and crystal structure [21]. High anticorrosive properties were achieved by insertion of $Fe_3O_4@SiO_2$ in epoxy composite coatings [22]. The environmental impact of painting industry is mostly associated with the volatile organic content (VOC) level [23]. Highly branched alkyd nanocomposites provide newly developed materials with double merits: (i) get rid of VOC problems; (ii) property enhancement [24].

This study introduces castor oil-based hyperbranched alkyd/ $Fe_3O_4@SiO_2$ nanocomposites as a cost effective and green material with enhanced coating characteristics. An in-situ large scale synthesis method that efficiently attaches magnetite NPs to silica nanospheres is reported in this work. To the best of our knowledge, this is the first study to prepare and evaluate the tailored alkyd/ $Fe_3O_4@SiO_2$ nanocomposites. This research highlights the significance of the extent of dispersion of $Fe_3O_4@SiO_2$ nanofillers in determining the improvement in the mechanical, thermal and anticorrosive properties of the nanocomposites.

2. Experimental

2.1. Chemicals

Adipic acid ($(CH_2)_4(COOH)_2$), glycerol ($HOCH_2CHCH_2OH$) and dibutyltin oxide ($(C_4H_9)_2SnO$), Iron(III) acetylacetonate ($Fe(acac)_3$, 99.9%), tetraethoxysilane (TEOS, 99.9%), tetraethylene glycol (TEG, 99%), cetrimonium bromide (CTAB, $\geq 98\%$) and Brij-56 (polyoxyethylene (10) cetyl ether, non-ionic detergent, 98%) were supplied from Sigma–Aldrich and used as received. DCO fatty acid was obtained from John L. Seaton & Co. (UK) and all driers including cobalt octoate, calcium octoate, and zirconium octoate were supplied by Merck, India. Sodium hydrogen sulfate ($NaHSO_4$), anhydrous ethanol (AR), sodium hydroxide, hydrochloric acid, (HCl, 37%); acetone was delivered from Acros (Belgium). All solvents are analytical reagent grade and were used as received.

2.2. Preparation of hyperbranched alkyd resin

2.2.1. Synthesis of hyperbranched polyesters

Polycondensation was carried out with adipic acid and glycerol in the presence of dibutyltin oxide catalyst according to previous literature [7]. Briefly, in a 250 mL three neck flask flushed with nitrogen, 35.7 g of adipic acid was mixed with 30 g of glycerol ($[-OH]/[-COOH] = 2.0$) and 0.3285 g of dibutyltin oxide (0.5 wt%), heated to $140^\circ \pm 5^\circ C$ and stirred

for 11 h. The heating was stopped and stirring was continued for cooling down to R.T. The product was colorless viscous liquid. 1H NMR spectrum (300 MHz, DMSO): 3.42 (CH_2-OH), 4.1 (CH_2-OR), 4.64 (OH -terminal).

2.2.2. Synthesis of hyperbranched alkyd resins

The hyperbranched polyester was reacted with DCO fatty acid to give hyperbranched alkyds (Scheme 1). Polycondensation was carried out by using 0.1476 mol of polyester containing hydroxyl groups with DCO fatty acid (0.03 mol) and 0.5% P-TSA catalyst. A three neck flask, thermometer, condenser and nitrogen gas were used for the reaction which was performed at 220 °C until the acid value is below 10 mg KOH/g [25].

The acid value is the mass (mg) of potassium hydroxide (KOH) required to neutralize 1 g of alkyd and was determined for the small amount of samples collected during the reaction.

The percent yield, which is calculated by dividing the amount of the obtained alkyd by the theoretical yield, was shown to be 85%; 1H NMR (300 MHz, $CDCl_3$): 1–1.25 (DCO-fatty acids), 1.5–2.8 (CH_2 and CH -fatty acid), 4.64 (CH_2-OR), 5.40 ($-CH=CH-$) (ESI, Fig. S1).

2.3. Preparation of $Fe_3O_4@SiO_2$ hybrid

Spherical non-mesoporous silica with an average diameter size of 60–70 nm was prepared via a simple and cost effective technique [26, 27]. Surfactant CTAB (0.51 g) and Brij-56 (0.025 g) were dissolved in 150 mL of pH 7, 10 mM phosphate buffer. After heating the solution to $95 \pm 2^\circ C$, TEOS (2.337 g) was added slowly, and the reaction continued for 8 h. The product was collected by centrifugation, washed with water and ethyl alcohol and dried in vacuum at 80 °C.

$Fe_3O_4@SiO_2$ nanoparticle was prepared in-situ via modified Stöber method [26,28]. Briefly, 200 mg of the silica NPs were dispersed in 2 mL water and sonicated for 1 h. Then 20 g of tetraethylene glycol and 0.35 g of $Fe(acac)_3$ were added to the mixture with continuous stirring at R.T. The temperature was raised to $110 \pm 2^\circ C$ under nitrogen for 2 h, then to $210 \pm 2^\circ C$ for 2 h. The mixture was then refluxed at $300 \pm 5^\circ C$ for 1 h and cooled gradually to R.T. The product was washed with acetone to remove unbound Fe_3O_4 . The prepared $Fe_3O_4@SiO_2$ was collected by a magnet and the supernatant that contain free nano- Fe_3O_4 crystals was dried under vacuum. Controlling silica concentration and the percentage of the iron precursor can greatly affect binding efficiency and the size of nano-magnetite.

2.4. Coating film

Carbon steel panels (20 cm \times 10 cm \times 1 mm) were polished and degreased with SiC paper of standard sizes (180, 320, and 500 grit). The specimens were cleaned with ethanol and propanone and dried before applications. The prepared virgin polymer was applied and cured with common alkyd resin driers via physical and chemical methods called autoxidation. The DCO fatty acid-based alkyd resin (87 wt%) was dissolved in 10% mixture of toluene and turpentine (1:1 by volume). A definite amount of the drying agents were added under continuous stirring as follow: cobalt octoate (0.6 wt% in), calcium octoate (0.6 wt%) and zirconium octoate (1.8 wt%) until a homogenous solution was obtained. The mixture was applied to steel surface by spraying and dried at R.T. After solvent evaporation, the matrix particles coalesced and the coated film was cured by air oxidation of unsaturated linkages. The autoxidation of the alkyd took place as previously studied [29], taking place in six steps, induction, initiation, hydroperoxide formation, hydroperoxide decomposition, cross-linking, and degradation [30].

2.5. Fabrication of hyperbranched alkyd/ $Fe_3O_4@SiO_2$ nanocomposite coatings

The $Fe_3O_4@SiO_2$ hybrid nanofiller was dispersed in a mixture of turpentine and toluene (0.05%, 0.1%, 0.3%, 0.5%, 0.7% and 1% NP loadings.

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