



Synthesis and characterization of novel hyperbranched alkyd and isocyanate trimer based high solid polyurethane coatings



R. Balaji Naik*, D. Ratna, S.K. Singh

Naval Materials Research Laboratory, Shil Badlapur Road, P.O. Anand Nagar, Additional Ambernath (East), Dist. Thane, Maharashtra 421506, India

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ABSTRACT

In the present work, hyperbranched urethane alkyd high solid coatings were formulated by mixing hyperbranched alkyd and isocyanate trimer. Initially, a second generation hyperbranched polyol (HBP) was synthesized using dipentaerythritol (DPE) as a core material and 2,2-bis(methylol)propionic acid (BMPA) as a chain extender. This was reacted with varying concentrations of linseed oil fatty acid (LOFA) to make a series of hyperbranched alkyd (HBA) resins. Viscosity and volume solid of the HBA resins were measured. The resins were characterized by Fourier transform infrared (FTIR), and ^{13}C Nuclear magnetic resonance (^{13}C NMR) spectroscopic techniques. The hyperbranched alkyd resins containing varying amount unreacted hydroxyl groups were cured with hexamethylene diisocyanate (HDI) trimer (Desmodur N 3390) depending on their NCO: OH ratio to make hyperbranched urethane alkyd coatings. A series of such coatings were made by mixing HBA/isocyanate trimer (Desmodur N 3390) ratio with respect to the hydroxyl group present on the HBA. The performance of the coated specimens was evaluated by various techniques such as pull-off adhesion strength, tensile strength, abrasion resistance, scratch resistance, flexibility, and impact resistance tests. The weathering properties of the coated specimens were evaluated by UV-Weatherometer. Corrosion resistance of the coated specimens was evaluated by electrochemical impedance spectroscopy (EIS), salt spray, seawater immersion and humidity tests. It was observed that, there exists an optimum coating composition in terms of NCO: OH (HBA: Desmodur N 3390) ratio which showed excellent enhancement in terms of the mechanical, weathering and corrosion resistance properties than remaining coating compositions.

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1. Introduction

Protection of metallic structures against corrosion can be effectively provided by the application of surface coatings. These coatings form an adherent continuous layer on the surface and act as a barrier between the surface and the environment. Selection of coatings and application techniques varies depending on the type of structure to be coated and the environment to be exposed. Surface coatings are broadly classified as metallic, ceramic and organic coatings. Because of availability, ease in application and maintenance, organic coatings have major share as protective systems for structures operating in different environments, such as industrial, marine and underground. Organic coatings are being used in a number of applications, contributing to protection of surfaces against corrosion [1].

The recent trend in the field of organic coatings is to develop coatings with low levels volatile organic compounds (VOCs) [2–8]. The VOCs are added to a coating formulation to reduce the viscosity

of resin for easy processing and uniform application. After application of the coating the VOCs evaporates out causing environmental pollution. There has been a considerable effort in the past years to reduce the VOC content in organic coatings. The risk to human and environmental hazards associated with VOCs, governmental directives, and economic factors are the main driving forces behind this effort. The options available for meeting this requirement on VOCs [3] are powder coatings, thermal spray coatings, water borne coatings, UV curable coatings and high solid coatings. One of the most effective ways to reduce VOCs in organic coatings is to develop coatings by using dendritic/hyperbranched polymers. Over the last few years, syntheses of a large number of dendritic polymers have been reported in literatures [9,10]. They have potential applications in a variety of fields such as commercial coatings, biomedical, foams, catalysis, electrical materials, thermosets and cross linking materials [11].

Recently, dendritic polymers have been produced by a new low cost hybrid synthetic process that generates highly branched, poly-disperse molecules [12]. These materials are called hyperbranched polymers to distinguish them from more perfect mono disperse materials [13,14]. Due to the compact three-dimensional structure of dendritic polymers, these molecules mimic the hydrodynamic

* Corresponding author. Tel.: +91 251 2623184; fax: +91 251 2623004.
E-mail address: balukala.drdo@gmail.com (R.B. Naik).

volume of a sphere in solution and also show low viscosity in the melt, even at high molecular weight, due to the lack of restrictive interchain entanglements [15–17].

Hyperbranched alkyds have been reported as promising resins for development of low VOC or nonpolluting coatings. Bat et al. [18] reported the synthesis of hyperbranched air drying fatty acid based resin having good flexibility, abrasion resistance and adhesion to metal substrate. Johansson et al. [6] reported a high solid coating formulation using highly branched polymers which exhibits higher solubility and low melt viscosity compared to their linear counterparts. Peterson [19] observed that hyperbranched alkyds show significantly lower viscosities and rapid air drying property with enhanced outdoor durability compared to the conventional high solid alkyds.

Polyurethanes [20–26] are known for their excellent physical and mechanical properties. A recently published review [27] indicates the importance of introducing hyperbranched polyurethane for fine tuning properties of polyurethane for high performance applications. Recently Zhang et al. [28] reported the impact properties of polyurethane coatings based on polyester polyol and isocyanate trimers. Thakur and Karak [29] reported that the castor oil based hyperbranched polyurethane as advanced surface coating materials. But a major drawback of polyurethane based resin is high cost of isocyanate and high viscosity of the resin. The problems can be overcome by partially modifying the urethane with alkyd without compromising much on its properties.

In the present study, attempts have been made to synthesize a hyperbranched alkyd urethane coating. The aim of this work is to obtain both the properties of alkyd and urethane in a single polymer backbone. For this, hyperbranched polyol was synthesized and its hydroxyl groups at the outer periphery were reacted with varying concentration of linseed fatty acid. The remaining free hydroxyl groups of the hyperbranched alkyds were cured with isocyanate trimer in the presence of di-butyl tin di-laurate as a catalyst. The synthesis, characterization of urethane alkyd coating and their properties will be discussed in the present paper.

2. Experimental

2.1. Materials

Linseed oil (M/s Jayant Oil Mill, India), sodium hydroxide, sodium chloride, anhydrous sodium sulphate and hydrochloric acid (S.D. Fine Chem., India) were used to produce the linseed fatty acid. Bis methylol propanoic acid, dipentaerythritol were procured from (Aldrich, Germany). *p*-Toluene sulfonic acid (Merck, India) was used as a catalyst. Xylene (High Purity Laboratory Chemicals Pvt. Ltd, India) was used as a solvent. Methanol and potassium hydrogen phthalate (Aldrich, India) were used for the determination of acid value. Cobalt octoate, and lead naphthenate (Globe products, India) were used as driers. Di-butyl tin di-laurate (DBTL) (Aldrich, USA) was used as a catalyst. HDI trimer (Desmodur N 3390) was obtained from Bayer chemicals, India. All the chemicals were used as received without any further purification.

2.2. Synthesis of hyperbranched polyol (HBP)

The hyperbranched polyol (HBP) was synthesized using dipentaerythritol as a core molecule and BMPA as the chain extender [18]. A typical synthesis of 2nd generation hyperbranched polyol is given below. A mixture of DPE (38 g, 0.15 moles) and BMPA (362 g, 2.7 moles) were taken in a four necked 1000 ml round

Table 1
Composition of different resins.

S. No.	Resins	HBP (mole)	LOFA (mole)	Oil length (%)	Theoretical hydroxyl value
1	HBA-0	1.0	24	75	–
2	HBA-10	1.0	21.6	73	3576
3	HBA-20	1.0	19.6	71	1874
4	HBA-30	1.0	16.8	68	995
5	HBA-40	1.0	14.4	64	672
6	HBA-50	1.0	12	60	480

bottom flask fitted with a mechanical stirrer, a condenser attached with a Dean & Stark apparatus, and a thermometer. Xylene (20 ml) was added as an azeotropic solvent to remove the water, formed during the esterification reaction. The reaction was carried out at 140 °C under nitrogen atmosphere, using *p*-Toluene sulfonic acid as a catalyst. The reaction was continued till theoretical amount of water was collected and acid value [30] attained below 10 mg KOH/g. The reaction scheme for the synthesis of the HBP is given in Fig. 1.

2.3. Synthesis of hyperbranched Alkyd (HBA)

Hyperbranched alkyds with different oil length were prepared from hyperbranched polyol and linseed oil fatty acid [31] with a varying concentration of free hydroxyl groups (10, 20, 30, 40, and 50%) at the outer periphery of HBP. The procedure for the synthesis of a HBA having 30% free hydroxyl group is described below. A mixture of HBP (52 g) and fatty acid (112 g) in mole ratios were taken in a four necked round bottom flask fitted with a mechanical stirrer, a condenser, a thermometer and an inlet for nitrogen. 20 ml xylene was added as an azeotropic solvent to remove water formed during the esterification reaction. The reaction mixture was heated at 220 °C for 4 h and the reaction was continued till the theoretical amount of water was collected. The reaction mixture was then allowed to cool down to room temperature. The condensation product (water) was removed by azeotropic distillation with xylene. The acid value of the resins was determined in order to monitor the extent of reaction. The reaction was stopped when the acid value of the product was less than 10 mg of KOH/g of resin. The reaction scheme of the synthesis of the HBA (30% free hydroxyl group) is given in Fig. 2. Similar procedure was followed to synthesize the HBA resins having varying concentration of free hydroxyl groups with different oil length and named as HBA-0, HBA-10, HBA-20, HBA-30, HBA-40 and HBA-50, respectively, based on their free hydroxyl group on HBP. The compositions of various HBA resins were presented in Table 1.

2.4. Preparation of hyperbranched urethane alkyd (HBUA) coatings

HBUA coatings were prepared by mixing the above synthesized HBA having free hydroxyl groups with isocyanate trimers (Desmodur N 3390) in an appropriate ratio. The HBA obtained from the polycondensation reactions described above were diluted in solvent of xylene and mixed with isocyanate trimer in the presence of catalysts such as of Pb-naphthenate (1.20 g), cobalt octoate (0.5 g) for oxidative curing and DBTL (0.025 g) for isocyanate curing were used for 100 g of the mixed coating. The solid content of the coating was kept at 80–90 wt%. The HBUA coatings were applied on to the burnished mild steel panels, which had been degreased with toluene and burnished with emery paper. The average film thickness of $115 \pm 10 \mu\text{m}$ was maintained in all these coating compositions.

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