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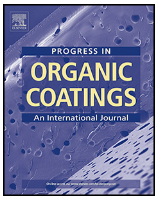

Synthesis and evaluation of new hyperbranched alkyds for coatings

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ABSTRACT

Novel hyperbranched alkyd resins (HBAs) were synthesized by reacting the hydroxyl end-groups of the prepared hyperbranched polyesters, based on 1,3,5-tris(2-hydroxyethyl) cyanuric acid (THECA) as a trifunctional core, with different oil fatty acids, namely, linseed, soya and sunflower oil fatty acids. Resins of different compositions of HBAs were prepared by changing either the fatty acid or the generation of the hyperbranched polyester. Their molecular structures were identified using IR and ^{1}H and ^{13}C NMR spectroscopy. The thermal stability, glass transition temperatures and rheological properties were investigated. All of the alkyd resins exhibited initial decomposition temperature at values >300 °C. The decreased Tg values of LG3, SG3 and SFG3 render them suitable for use as coatings that are applied at ambient temperature. All HBAs show Newtonian behaviour and the viscosity was ranging between 1.2 and 5.2 Pa s. Film properties of the prepared alkyd resins using different driers were determined and it has been found that all samples exhibited good adhesion, bending, impact, ductility, and high gloss, but show low hardness.

1. Introduction

The negative impacts of volatile organic compounds (VOCs) to both the atmosphere and the human health have resulted in increasing research activity focusing on the reduction of VOC levels in coatings and paints. Recently, Europe-wide legislation has placed an upper level of VOC in paint products of 300 g/L. This legislation has effectively eliminated many solvent-borne coatings from the market place and accelerated research work for developing eco-friendly coating formulations, i.e. increased demand for new air-drying solvent-borne coatings, to replace the previous generation of alkyd resin coating technologies [1,2].

Hyperbranched polymers are a class of polymeric materials belonging to the group of macromolecules having highly branched structures and a large number of end groups. The structure of these polymers has a great influence on their physical and chemical properties. Many commercially available chemicals can be used as the monomers in these systems, which should extend the availability and accessibility of hyperbranched polymers with various new end groups, architectures and properties.

Macromolecular architectures including comb-like polymers have been synthesized by Cheng et al. [3] and used to produce low viscosity coatings. They reported that model paint formulations containing up to 40 wt% of the linoleyl-based comb polymers exhibited a dramatic reduction in viscosity (from 35 to 13 Poise at 25 °C) with increasing quantities of polymer added.

Because of their unique behaviour, when compared to linear polymers, hyperbranched polymers contain a greater number of surface functional groups and exhibit lower viscosities rendering them suitable for a wide range of applications, especially for low VOC eco-friendly coatings [4–6]. Reduced coating viscosity lowers the quantity of VOC thinners that are required, whereas curing rates can be increased as a consequence of the high number of surface functional groups present in hyperbranched polymers [7].

Recently, Cheng et al. [1,3,8] synthesized novel hyperbranched polymers featuring oxazoline linear units and studied their application in fast-drying solvent-borne coating formulations. They reported that paint formulations based either on the new hyperbranched polymers or on the blends of them with a commercial alkyd resin resulted in new coatings that cured more rapidly than the control formulation which incorporated only the commercial alkyd resin.

Hyperbranched polyesters are among the most widely studied of the class of hyperbranched polymers [5,9–13]. Their rheological properties, combined with a broad range of possible functional end groups in high amounts, enable good flow, efficient cross-linking, excellent chemical resistance, and good mechanical properties for many different film-forming systems. They are

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being used in a variety of coatings applications, some examples are hydroxyl-functional polymers for coil coatings, powder coatings, and car refinish applications. In addition, hyperbranched polyesters found applications as flow and levelling agents in powder coatings for UV curable coatings and in blends with epoxy resins which enhance the mechanical properties of the cured films [14]. Hyperbranched polyesters modified with caprolactone and with methacrylic anhydride-functional chain ends have been used for the coating of wood and plastic substrates [4].

Alkyd resins are the most widely used polymers for paint and coatings applications [15]. They have good wetting, mechanical properties and durability. One of the factors affecting coating properties is the type of fatty acid or oil used in the alkyd production [16]. Meeting the requirements for high solids and low volatile organic compounds without compromising on the quality of the coating has always been a challenge for scientists. Hyperbranched alkyds provide a solution with their low viscosity at high molecular weights, meeting the stringent requirements of volatile organic contents [7,17–19]. Hyperbranched alkyd resins are hydroxylated hyperbranched polyester modified with fatty acids [15]. Highly branched chains have several advantages compared to the conventional alkyd resins with the same molecular weight, such as lower viscosity, higher gloss, better chemical resistance, and less chemical drying time [20].

Bat et al. [21] studied the synthesis of hyperbranched alkyd resins based on a hydroxylated hyperbranched polyester obtained from dipentaerythritol and 2,2-bis(hydroxymethyl) propanoic acid. The synthesized polyester was first reacted with castor oil fatty acids, then with different amounts of linseed oil fatty acids and benzoic acid. The authors reported that the hardness of the resins increased with fatty acids contents but did not change with benzoic acid content.

Hyperbranched alkyds of different generations based on tall oil fatty acids have been synthesized and characterized by Murillo et al. [22,23]. All synthesized alkyd resins have shown excellent adhesion, flexibility, drying time, gloss, and chemical resistance.

In a previous work [24] we synthesized and characterized some aromatic hyperbranched polyesters based on 1,3,5-tris(2-hydroxyethyl) cyanuric acid as multifunctional core. The work was extended [25] and a detailed study on synthesis, identification and modification of some new aliphatic hyperbranched polyesters based on 1,3,5-tris(2-hydroxyethyl) cyanuric acid (THECA) as multifunctional core and 2,2-bis(hydroxymethyl) propionic acid (bis-MPA) as an AB2 type monomer was performed. Modification and methacrylation [26] and evaluation [27] of these aliphatic hyperbranched polyesters as binding agents for heavy metals were also investigated.

Our work with hyperbranched polyesters based on 1,3,5-tris (2-hydroxy- ethyl) cyanuric acid (THECA) as a core is still in progress and represents the objective of this study. Synthesis of low viscosity air drying hyperbranched alkyd resins by modifying the aforementioned hyperbranched polyesters, with different oil fatty acids has been carried out. These prepared resins, which are of interest to the coating industry, will be investigated with respect to methods of preparation, their physical and mechanical properties and advantages over conventional counter parts. Such hyperbranched alkyd resins can be of great potential for different applications.

2. Experimental

2.1. Materials

2,2-Bis(hydroxymethyl) propionic acid (bis-MPA), 1,3,5-tris(2-hydroxyethyl) cyanuric acid (THECA), and p-toluene sulfonic acid (PTSA) were purchased from Sigma–Aldrich, Germany. All driers including Octa-Soligen 155, Borchers Dry 0133 and Borchers Dry 0411 HS were kindly provided as a gift by OMG Borchers GmbH OM Group, Schönebeck, Germany. The oil fatty acids were also kindly supplied as a gift by Oleon GmbH, Emmerich, Germany. All materials in this study were used as received without further purification.

2.2. Methods

2.2.1. Synthesis of hyperbranched polyesters (HBPs)

A series of new aliphatic hyperbranched polyesters was synthesized by the polycondensation of stoichiometric amounts of the monomer bis-MPA, corresponding to each generation with 1 mol of THECA as a trifunctional core [25]. The monomer to core ratio was varied between 3 and 21. The polymerization reaction was carried out in bulk at a maximum temperature of 160 °C. p-Toluene sulfonic acid (PTSA), 0.5 wt% based on bis-MPA monomer, was used as an acid catalyst in all reactions. To obtain several generations of growth, (G1–G3), the procedure was repeated with a stepwise addition of stoichiometric amounts of monomers to the core molecule. The yield of all obtained polymers was found to be above 97%.

The first generation G1 was synthesized according to the following method. THECA (26.124 g, 0.1 mol), bis-MPA (40.239 g, 0.3 mol), (molar ratio 1:3), and a catalytic amount of PTSA (0.2 g) were placed in a three-necked flask equipped with argon inlet. The reaction vessel was evacuated for 10 min, flushed with argon, and then immersed in a preheated oil bath with magnetic stirrer at 160 °C. The reaction mixture was left to react for 2 h under stream of argon. After that a vacuum was applied for another 1 h. The resulting product was collected and identified by ^{1}H and ^{13}C NMR. Yield: 59.6 g (98%); ^{1}H NMR (250 MHz, $CDCl_3$, δ): 1.01–1.16 (CH_3-bis-MPA), 3.44 (CH_2-OH), 3.82 (CH_2-N), 4.1 (CH_2-OR), 4.64 (OH-terminal), 4.94(OH-linear). ^{13}C NMR (62.5 MHz, $CDCl_3$, δ): 17.6 (CH_3), 46.8–50.8 (quaternary C), 58.3–66.1 (CH_2), 149.1 ($N{-}C{=}O$), 172–175 ($C{=}O$).

2.2.2. Synthesis of hyperbranched alkyd resins (HBAs)

Novel hyperbranched alkyd resins (HBAs) were synthesized by reacting the hydroxyl end-groups of the prepared hyperbranched polyesters with different oil fatty acids, namely, linseed, soya and sunflower oil fatty acids. The reaction was carried out in bulk at a maximum temperature of 220 °C. PTSA, 0.5 wt% based on fatty acid, was used as an acid catalyst in all reactions. The reaction of the first generation (G1) of the hyperbranched polyester with linseed oil fatty acids (in molar ratio of 1:5) is presented as an example:

Linseed oil fatty acids (41.1 g, 0.1476 mole), G1 (18.0 g, 0.03 mole) and a catalytic amount of PTSA (0.2055 g) were placed in a three necked flask, equipped with a condenser, thermometer and an argon inlet. The reaction vessel was evacuated for 10 min, flushed with argon, and then immersed in a preheated oil bath with magnetic stirrer at 180 °C. The reaction mixture was further heated to 220 ± 5 °C and maintained at this temperature until the acid value decreased to the desired one (7–17 mg KOH/g). A stream of argon was applied to continuously remove the water formed during the reaction. The acid value was monitored during the reaction and determined by end-group analysis of samples collected at different time intervals.

Yield: 48.4 g (86%); ^{1}H NMR (250 MHz, $CDCl_3$, δ): 0.85–1.2 (CH_3-fatty acid and -bis-MPA), 1.5–2.8 (CH_2 and CH-fatty acid), 4.2 (CH_2-OR), 3.82 (CH_2-N), 5.30 ($-CH{=}CH-$). ^{13}C NMR (62.5 MHz, $CDCl_3$, δ): 14.3 (CH_3), 22.5–31.9 ($CH_3{-}CH_2$, $CH_3{-}(CH_2)_2$ and $-CH_3{-}(CH_2)_3$ – methylene carbons), 34 (CH_2COOR), 128–130 ($-C{=}C-$).

In a similar manner, resins of different compositions of HBAs were prepared by changing either the fatty acid or the generation of the hyperbranched polyester. The yield of all obtained alkyd resins