ELSEVIER

Progress in Organic Coatings 55 (2006) 330–336

PROGRESS IN ORGANIC COATINGS

www.elsevier.com/locate/porgcoat

Synthesis and characterization of hyperbranched and air drying fatty acid based resins

Erhan Bat[a,b,*], Güngör Gündüz[b], Duygu Kısakürek[c], İdris M. Akhmedov[c]

[a] *Atılım Üniversitesi, Malzeme Mühendisliği Bölümü, Ankara, Turkey*
[b] *Orta Doğu Teknik Üniversitesi, Kimya Mühendisliği Bölümü, Ankara, Turkey*
[c] *Orta Doğu Teknik Üniversitesi, Kimya Bölümü, Ankara, Turkey*

Received 5 August 2005; accepted 13 January 2006

Abstract

In this research four hyperbranched resins having fatty acid residues were synthesized. Dipentaerythritol, which was used as the core molecule of the resins, was twice esterified with dimethylol propionic acid. This resin was then esterified with the castor oil fatty acids. The hydroxyl group present in the ricinoleic acid which constitutes almost 87% of the castor oil fatty acids was then reacted with linseed oil fatty acids and benzoic acid. The linseed fatty acids were incorporated into the structure to esterify 0, 15, and 70% of the ricinoleic acid on mole basis. These resins were named as HBR-1, 2, and 3. A fourth resin (e.g. HBR-4) was synthesized by the incorporation of '15% linseed fatty acids + 55% benzoic acid'. The chemical characterization of the resins was achieved by FTIR spectroscopy and the thermal properties were determined by DSC. The physical and the mechanical properties of the resins were determined. The hardness value of the resins was measured as 24, 27, 25, and 68 Persoz for HBR-1, 2, 3, and 4, respectively. The viscosity of the resins was measured as 17.3, 9.7, 5.8, and 17.5 Pa·s at a shear rate of 200 s^{-1}. The increase in the amount of the linseed fatty acids increased the hardness, and decreased the viscosity of the resins. All resins showed excellent adhesion, gloss, and flexibility.

Keywords: Hyperbranched; Dendrimer; Castor oil; Ricinoleic acid; Air drying; Linseed oil

1. Introduction

There is a strong tendency to shift to organic volatile free resins and paints in the last 2 decades. The volatile organic compounds (VOC) are toxic to plants and animals, and also found to be responsible for global warming and photochemical ozone creation [1,2]. Environmental concerns, the governmental directives, technical and economic factors have stimulated research to develop environment friendly coatings having very low VOC content or no VOC at all [1,2]. Different alternatives have been developed to substitute the paints containing organic solvents. However, the gloss performance that can be achieved with solvent based paints such as alkyd systems could not be attained with any other resin. The application of high solids alkyd paint systems is a promising method of producing low VOC high gloss coating systems. This method provides a considerable decrease in the VOC content of the coatings compared to conventional alkyd coatings [3]. High solids alkyd coatings also have economic and technical benefits. Improved hiding power can be obtained together with significant reductions in costs [2]. In order to develop a high solids alkyd the viscosity of the resin should be acceptably low without compromising other properties; unfortunately they usually have high viscosities. There are several theoretical options to lower the viscosity such as increasing oil length, use of reactive diluents, and narrow molecular weight distribution [2].

Low molecular weight resins which have unsatisfactory properties such as slow drying and sagging are obtained when the oil length is increased. The increase in unsaturation causes loose packing of molecules which in turn leads to a reduction of the intermolecular action. Increasing the oil length also decreases the number of hydrogen bond forming groups (except castor oil). A reactive diluent decreases the viscosity of a coating. During drying it actively participates in drying reactions and is converted to an integral part of the film [3–5]. Very high and low molecular weight molecules prevent the

---

* Corresponding author. Tel.: +90 312 210 26 16; fax: +90 312 210 12 64.
E-mail address: erhanbat@gmail.com (E. Bat).

0300-9440/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.porgcoat.2006.01.005

formation of a homogeneous network and thus have negative effects on overall film properties. However, dendrimers and highly branched chains have a narrower molecular weight distribution, and thus they have lower viscosity at the same molecular weight compared to linear counterparts [2].

Flory presented the condensation reactions of AB_x monomers, which yield highly branched structures without gelation in the early 1950s [6–11]. Highly branched structures were claimed to possess poor mechanical properties due to lack of entanglements. Therefore, almost no effort was spent on this field until late 1970s [6,10]. Tomalia and Frechet presented the divergent synthesis of poly(amidoamine) polymer in 1984 and used the term 'dendrimer' for the first time [10]. Kim and Webster were first to use the term 'hyperbranched' after the one-step synthesis of the first hyperbranched polyphenylenes [11–13]. These highly branched polymers were named dendritic polymers and were accepted as the fourth major class of polymeric architecture. Dendritic polymers consist of three major subgroups: dendrimers, hyperbranched polymers, and dendrigrafts. Dendritic polymers offer unique properties such as high solubility, lower solution and melt viscosity compared to their linear analogues owing to their special architecture [7,11]. Their globular shape eliminates the entanglements leading to Newtonian behavior. Different end groups can be incorporated into the structure of dendritic polymers to adjust polarity and tune other properties. Dendrimers require repetitive isolation and purification steps which make them costly to produce on large scale. However, hyperbranched polymers can be synthesized in one step which makes them attractive for large volume applications [5,14]. Since hyperbranched polymers are statistically branched they are polydisperse. The use of hyperbranched polymers in several coating applications has been presented in the literature [5,15].

Hyperbranched alkyd-like resins have been studied previously in order to obtain low viscosity resins with rapid air drying [3,15–17]. The common part in these works is that the hydroxyl groups at the outer periphery of a hyperbranched polyester were modified with different fatty acids. In this research, a hyperbranched polyester was synthesized starting with dipentaerythritol, dimethylol propionic acid (DMPA), and castor and linseed oil fatty acids. The synthesized polyester was first reacted with castor oil fatty acids. It was then reacted further with different amounts of the linseed oil fatty acids and benzoic acid. Internal functionalization of the alkyd-like resins has thus been accomplished by this route. Four different resins have been characterized in terms of their chemical structure. Their mechanical and the physical properties were determined.

2. Experimental

2.1. Materials

Linseed oil (Betek Boya), castor oil (Akzo Nobel Kemipol), sodium hydroxide (Merck), sodium chloride (commercial grade), magnesium sulfate (commercial grade), and sulfuric acid (Aldrich) were used to produce the fatty acids. Dipentaerythritol and DMPA were kindly supplied by Perstorp AB, Sweden. Nitrogen (Oksan) was used as the blanketing atmosphere in the esterification reactions. *p*-Toluene sulfonic acid (Merck) and toluene (Best Kimya) were used as catalyst, and solvent, respectively. Isopropyl alcohol (Volkan Boya) and potassium hydrogen phthalate (Merck) were used in acid value determination. Cobalt napthenate (Volkan Boya) and lead napthenate (Volkan Boya) were used as driers.

2.2. Production of the fatty acids

The fatty acids of linseed oil and castor oil were produced to use as reactants in the synthesis of hyperbranched resin. The oils were first saponified with sodium hydroxide. For this purpose oil, NaOH and ethanol (50%) were placed in a reactor equipped with a mechanical stirrer. The mixture was left to react under reflux at 80 °C until a homogeneous mixture was obtained. The homogeneous mixture was then poured into a saturated NaCl solution in order to separate organic and inorganic phases. This two-phase mixture was filtered through a filter paper under vacuum. The soap was dissolved in distilled water and reacted with stoichiometric amount of sulfuric acid at room temperature. After the reaction, the produced fatty acids (top layer) were separated by using a separatory funnel. The acids were washed with water several times to remove any remaining glycerol and other water soluble impurities. It was then centrifuged to separate water and saturated fatty acids which are solid at room temperature. Dried and ground $MgSO_4$ was added to further remove water and the remaining suspended saturated fatty acids.

2.3. Synthesis of hyperbranched resins

A five necked flask equipped with a mechanical stirrer was used as reactor. The procedure of synthesis of hyperbranched polyester (HBP) from trimethylol propane and DMPA given by Malmström et al. [18] was followed in our synthesis. Dipentaerythritol was used as the core molecule and DMPA as the chain extender. The reaction was carried out at 140 °C under nitrogen atmosphere in the presence of catalyst (e.g. *p*-toluene sulfonic acid) which was 0.4% of DMPA. Water coming out as the condensation product was removed by nitrogen and azeotropic distillation with toluene. The reaction scheme of the synthesis of the HBP is given in Fig. 1. The HBP was then reacted with the castor oil fatty acids which are mainly ricinoleic (87%), linoleic, and oleic acids at 220 °C. The HBP modified with the castor oil fatty acids only is designated as hyperbranched resin-1 (HBR-1).

HBR-1 was further reacted with linseed oil fatty acids and benzoic acid in different amounts to synthesize other three resins HBR-2, 3, and 4. The acid value of the resins was determined in order to monitor the extent of reaction.

The schematic representations of the resins are given in Fig. 2. Since the reactions did not go to completion, and some side reactions might have occurred the figures are not perfect but nearly ideal representations of the resins. The composition of the resins on mole basis is given in Table 1.