



## Novel waterborne hyperbranched acrylated-maleinized alkyd resins

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### ABSTRACT

Different waterborne hyperbranched acrylated-maleinized alkyd resins (HBRAAM) were synthesized by modifying a hyperbranched alkyd resin (HBRA) with three different butylmethacrylate–maleic anhydride copolymers (BMA–MA) in the presence of p-toluenesulfonic acid (PTSA). The HBRAAM resins were characterized by using infrared analysis, iodine value, hydroxyl value, vapor pressure osmometry (VPO), dynamic light scattering (DLS), acid value, rheological analysis, differential scanning calorimetry, adhesion, flexibility, drying time, gloss, hardness and chemical resistance to solvents. The iodine value and hydroxyl value decreased with the amount of BMA–MA copolymer employed in the synthesis. Infrared analysis, VPO, and hydroxyl values allowed us to conclude that the reaction between HBRA resins and BMA–MA copolymers occurred. The viscosity of the HBRAAM resins was between 50.5 and 468 Pa.s. All HBRAAM resins presented good properties of adhesion, flexibility, drying time, gloss, hardness and chemical resistance.

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### 1. Introduction

The polyol polyester with a high number of OH groups present in the periphery of the molecule [1–4], can be modified in order to obtain materials with specific applications. Hyperbranched alkyd resins are polyol polyesters modified with fatty acids [5]. The hyperbranched alkyd resins are a good alternative for obtaining environmentally friendly coatings since they can be synthesized with high solid content and low viscosity due to its high packing structure. Furthermore they exhibit several advantages; such as lower time for chemical drying, and higher gloss and chemical resistance than conventional alkyd resins (linear structure) [6]. Despite the fact that hyperbranched alkyd resins can be obtained with less volatile organic compounds content (VOCs) than conventional alkyd resins, they still continue producing VOCs, which are toxic and responsible for global warming and photochemical ozone creation [7]. Therefore it is necessary to develop water-borne hyperbranched alkyd resins with good properties for the coating industry.

Alternative methods to produce more environmentally friendly resins (water borne) consist in modifying hyperbranched alkyd resins with polar groups to interact with water. Studies of the copolymerization of maleic anhydride with acrylic monomers for increasing the hydrophilicity of conventional alkyd resins have

been done [8–12]; grafting of maleic anhydride in polymers for obtaining specific interactions between polymers has also been done [13–16].

Solvent based conventional acrylated-maleinized alkyd resins were synthesized by modifying an alkyd resin conventional with butylmethacrylate (BMA)–maleic anhydride (AM) copolymers. The resins exhibited low solvent resistance, good adhesion and flexibility, the drying time were in the range 12–26 h and the hardness increased with the content of maleic anhydride [8].

Water-borne conventional acrylated-maleinized alkyd resins were synthesized by Saravari et al. [9], employing ratios of 15 and 40% of BMA–AM copolymers with respect to a conventional alkyd resin. They obtained a heterogeneous mixture for 15% BMA–MA copolymer content; this behavior was due to an overwhelming excess of hydroxyl groups. For the 40 wt% of BMA–MA copolymers, gelatins were formed, which was attributed to the hydroxyl/carboxyl that was around 1. These resins were obtained with a solid content of around 34.75 wt%; they exhibited yellow color, good adhesion, good flexibility, and good resistance to water and hydrochloric acid. The film resins did not cure very well after air drying for 10 days at room temperature, this phenomenon was attributed to the presence of water and diethanolamine, which inhibited the oxidation and crosslinking. The films only dried at 190 °C and the drying times were between 90 and 120 min.

Aigbodion et al. [10] synthesized water-borne conventional maleinized-alkyd resins by modifying conventional alkyd resins with phthalic anhydride. The resins were obtained with a 30 wt% solid content and presented good resistance to 0.1 M sulfuric acid solution, sodium 5 wt% chloride solution, and water. But it

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presented bad resistance to 0.1 M sodium hydroxide solution, and the color of the resins was dark brown. They found that iodine value decreased with the BMA–MA copolymer content, which was endorsed to the formation of free radicals.

Akbarinezhad et al. [11] modified conventional alkyd resins with acrylic copolymers (methylmethacrylate butylmethacrylate, acrylic acid, and methacrylic acid) to obtain waterborne alkyd resins. The emulsions presented good hydrolytic stability; they used tri ethyl amine (TEA) and diethanolamine (DEA) as neutralization agents. TEA produced a higher reduction of stability than DEA; they concluded that this behavior was probably due to the formation of hydrogen bonding between the hydroxyl groups present in DEA and water.

So far, all studies have been mainly focused to obtain conventional alkyd resins, but studies of hyperbranched alkyd resins (HBRA) are still scarce despite the fact that it has been demonstrated that hyperbranched alkyd resins present better properties than conventional alkyd resins, with the exception of its hardness [5]. The literature did not present reports of waterborne hyperbranched alkyd resins obtained by modifying HBRA with BMA–MA copolymers and subsequent neutralization with DEA. In this work hyperbranched acrylated-maleinized alkyd resins (HBRAAM) with different ratio of HBRA and BMA–MA copolymers were synthesized by an esterification reaction between acid groups derived of maleic anhydride and OH groups of hyperbranched alkyd resins. The effect of the proportions of BMA–MA copolymers employed on the synthesis of the HBRAAM resins and MA content in the copolymers, in the structural, hydrolytic and films properties of the HBRAAM resins is studied.

## 2. Experimental

### 2.1. Materials

HBRA resins and BMA–MA copolymers were synthesized in our group. Details of the synthesis procedure and properties (HBRA2) were reported in an earlier publication [17]. The preparation method of the BMA–MA copolymers was by solution polymerization using benzoyl peroxide as an initiator and the composition were the following: BMA–MA 80:20, 65:35 and 50:50. The grafted MA proportions on BMA–MA copolymers were respectively: 13.83, 25.12 and 34.47 wt%.

Xylene, sodium hydroxide, p-toluenesulfonic acid (PTAS), sodium chloride zirconium octoate and hydrochloric acid, were purchased from Sigma–Aldrich and they were used as received. Cobalt and calcium chloride were supplied by Colorquímica and they were used as received.

### 2.2. Synthesis of HBRAAMs

Since HBRA resin was obtained initially from hyperbranched polyol polyester of fourth generation and tall oil fatty acid by esterification reaction [17], some OH groups of polyester remain unreacted. So, they can react with the acid groups of BMA–AM copolymer.

The HBRA resin was mixed with an appropriate amount of BMA–MA copolymers in the presence of an acid catalyst (p-toluenesulfonic acid). Then, the system was heated (150–200 °C) under constant mixing and nitrogen atmosphere. The production of modified HBRA resins was monitored by measuring the acid value. When the value of acid was between 10 and 100 mg KOH/g the temperature was reduced between 60 and 100 °C. In this reaction step, the resin is hydrophobic (Fig. 1). Then a determined amount of DEA was added, to neutralize some of the acid groups of BMA–MA copolymer inserted in the resin. In this step the resin is hydrophilic

**Table 1**  
Composition of the different HBRAAM resins.

HBRAAM resins	BMA–MA copolymer	Percentage of BMA–MA copolymer	Percentage of HBRA
HBRAAM1	80:20	20	80
HBRAAM2	80:20	30	70
HBRAAM3	65:35	20	80
HBRAAM4	65:35	30	70
HBRAAM5	50:50	20	80
HBRAAM6	50:50	30	70

due to the presence of ionic groups (Fig. 2). Finally the respective amount of water for obtaining resins with solid content of 50% was added during one hour to the reactor and then the material was taken out of the reactor. Table 1 presents proportions of the HBRA and BMA–AM copolymers employed in the synthesis of the HBRAAM resins.

### 2.3. Characterization of the HBRAAM resins

The modified percentage of the HBRA resin was measured by analysis of the hydroxyl value according to the ASTM D 4274 standard test method. The determination of the iodine value was done according to ASTM D 1959.

The infrared spectra were collected on a Spectrum one, Perkin Elmer spectrometer. The vapor pressure osmometry analysis (VPO) was carry out to determine the number average molar mass in Knauer vapor pressure osmometer using N,N-dimethyl formamide (DMF) as a solvent in a concentration range of 10.55 and 42.19 g/kg at 100 °C. Benzil was used for calibration. The experiments were repeated five times and the reported data is the average of the five measurements. Dynamic light scattering analysis (DLS) of the solutions of HBRA resins were done on a zetaser Nano Series machine from Malvern Instruments at 633 nm wavelength.

In order to study the hydrolytic stabilization, the HBRAAM resins were stored at 50 °C during 28 days. To determine the acid value, the resins were taken out of the oven and kept at room temperature, and then the sample was diluted with 10 ml of water and titrated with 0.4601 M KOH standard solution using phenolphthalein as an indicator.

MRC 301 rotational rheometer was used to determine rheological properties under steady shear conditions; 25 mm parallel-plate fixtures were used with a constant gap of 1.0 mm for all measurements.

The glass transition temperatures ( $T_g$ ) was determined by differential scanning calorimetry (DSC) in a TA Instrument model Q100 equipped with a refrigerated cooling system. A heating and cooling rate of 30 °C/min, under nitrogen atmosphere was used.

In order to analyze film properties, the HBRAAM resins were mixed with solutions of cobalt chloride (0.6 wt%), calcium chloride (0.6 wt%) and zirconium octoate (1.8 wt%). By using a film applicator, the films were applied on steel surfaces and dried at 25 °C under relative humidity of 40%, the final thickness of the films were 52 μm. The flexibility, adhesion, gloss, drying time and chemical resistance of the films were studied.

The flexibility of HBRAAM resins was done according to ASTM D 522 using a Braive Instruments conical mandrel bending 1510 tester. The adhesion analysis based on ASTM D 3359 was measured using cross-hatch cutter. Specular gloss measurements were performed on leneta (ASTM D 523) substrates at 60° and 85° using an Elcometer. The drying time of the HBRAAM resins was taken, as the time required, for obtaining a tack-free film without remotion or compression of the material from the substrate according to ASTM D 523. Vickers hardness was measured by using the Shimadzu HMV-mIII hardness tester at one load of 100 g. The application time of load was 5 s. The friction coefficient was determined by using

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