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An investigation on synthesis of alkyd resin with sorbitol

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ABSTRACT

Sorbitol, as an abundant, cheap and renewable resource, is considered as a potential raw material for the manufacture of alkyd resin. In this study, the kinetics on preparation of alkyd resin using phthalic anhydride, sorbitol and soya bean fatty acid as raw materials is investigated. Three kinds of sorbitol based alkyd resins (SAR) samples having fatty acid content (OL_f) of 42% (SAR1), 52% (SAR2) and 62% (SAR3) were prepared with phthalic anhydride, sorbitol aqueous solution and soya bean fatty acid using fatty acid method. Kinetic studies showed that the initial and latter stages of the reaction follow a second-order rate law. The second-order rate constants were found to be of the order of 10^{-5} g/mg KOH/min. Molecular weight and polydispersity index were determined by GPC and end-group analysis. The number average molecular weight of the alkyd resins ranged from 1435 to 1626 and the weight average molecular weight ranged from 3041 to 3648. A large polydispersity index was found in a range from 2.12 to 2.24. The varnish of alkyd resin SAR1 containing 50% 200# solvent gasoline and 1.25% cobalt naphthenate (drying agent) by weight dried faster than the others. The physical and chemical film properties of the sorbitol based alkyd resins were determined and compared with standard alkyd resins. The results showed that the performance of alkyd resin having fatty acid contents (OL_f) of 42% (SAR1) was almost the same as the standard alkyd resins. It could be a choice binder for alkyd resin paint and helpful to reduce production cost.

1. Introduction

Alkyd resins are a class of polyesters that are synthesized by polymerization of three kinds of monomers: polyols, polybasic acids, fatty acids or triglyceride oils [1]. Due to their compatibility with many polymers and the extremely wide formulating latitude, alkyd resins are extensively used in surface coatings, where they act as a binder [2]. Other uses of alkyd resins include adhesive [3], ink [4], caulks and plasticizers.

The formulation compositions of alkyd resins and the variations during preparation have significant effect on their application properties of alkyd resins. Hence, it is important to investigate the kinetics in the preparation of alkyd resins to understand the physical characteristic changes of the reaction. The kinetics in the preparation of alkyd resins is usually measured by end-group analysis. Up to now, the reaction kinetics for the synthesis of alkyd resins using phthalic anhydride, glycerol and triglyceride oils have been widely investigated. Aigbodion and Okieimen studied the reaction kinetics in the preparation of rubber seed oil alkyds and the results showed that the initial reaction rates followed a second order kinetics [5]. Deviations were observed at the later stage of the reactions. Afterwards, they also utilized the African locust bean seed oil to prepare the alkyd resins, and came to the similar conclusions [6]. Kumar et al. explored the kinetics in the synthesis of the alkyd resin by using non-edible jatropha seed oil [7]. Ataei et al. studied the synthesis of palm oleic based alkyds prepared by employing fatty acid method and found that the number average molecular weight of the synthesized alkyd resins ranged from 980 to 2070 [8]. Without exception, the researches mentioned above found that in the preparation of the alkyd resins, the initial reaction rates followed a second order kinetics and thereafter deviated from it. The second order rate constants were found to be of the order of 10^{-5} g/mg KOH/min. However, heated controversy exists over this topic. Ekpa and Isaac drew different conclusions when they studied on the synthesis of coconut, soybean and palm kernel long oil alkyd resins [9]. The results showed that the three types of alkyd resins followed a second order kinetics at the latter stage of reactions, rather than the onset stage. Igwe and Ogbobe obtained similar observations in the study of alkyd resins formation using melon seed, linseed and rubber seed oils [10].

Apart from the triglyceride oils mentioned above, some other oils, such as karawila (*Momordica charantia*) seed oil [11], Albizia benth oil [12], tung oil [13], are used to synthesized or modified alkyd resin. However, novel polylols are rarely used to prepare

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Table 1
Formulation compositions of the alkyd resin samples.

Ingredients	Alkyd resin samples		
	SAR1	SAR2	SAR3
OL_f (%)	42	52	62
Soya bean fatty acid (g)	114.0	150.0	134.0
Phthalic anhydride (g)	74.0	66.0	40.0
Sorbitol aqueous solution (g)	160.0	145.8	91.4

alkyd resin. Sorbitol, also referred as D-glucitol, is a type of polyol containing six hydroxyl groups [14]. It tends to form inner ethers at high temperature. Sorbitol is a cheap and renewable resource, the production is very huge, especially for sorbitol aqueous solution. It is considered as a potential raw material for the manufacture of alkyd resin since sorbitol has many similar properties to glycerol [15].

Up to present, there are no reports on kinetics of the preparation of alkyd resins using sorbitol. The present study aims to investigate the kinetic behavior of polyesterification during the preparation of sorbitol based alkyd resins. Acid value, extent of reaction (P_A) and average degree of polymerization ($\overline{DP}$) are measured by end-group analysis. The alkyd resins were synthesized by employing fatty acid method and the molecular weight of the synthesized alkyd resins was characterized by gel permeation chromatography (GPC).

2. Experimental

2.1. Materials

Technical-grade phthalic anhydride, soya bean fatty acid and sorbitol aqueous solution containing 70% sorbitol by weight were used in the synthesis of the alkyd resins without further purification. Technical-grade 200# solvent gasoline and cobalt naphthenate were used in the preparation of alkyd resin varnishes. The standard alkyd resins were synthesized with glycerol and pentaerythritol. The materials used above were obtained from Shandong Changyu Group Co., Ltd. Qilu paint. Ethanol, toluene, xylene, potassium hydroxide, phenolphthalein and potassium hydrogen phthalate were analytical grade chemicals. Distilled water was used throughout the procedures.

2.2. Synthesis of sorbitol based alkyd resins

Three kinds of sorbitol based alkyd resins (SAR) samples having fatty acid content (OL_f) of 42% (SAR1), 52% (SAR2) and 62% (SAR3) were prepared with phthalic anhydride, sorbitol aqueous solution and soya bean fatty acid using fatty acid method. The formulation compositions for the synthesis of alkyd resin samples are given in Table 1. Sorbitol aqueous solution and xylene (used as the azeotropic solvent) were charged into a 500 mL four-neck round bottomed glass reactor fitted with a Dean and Stark apparatus carrying a water-cooled condenser for separating the water evolved from the reaction, nitrogen gas inlet tube, mechanical agitator and thermometer. The mixture was stirred and temperature was raised to 120–150 °C for exporting the water in sorbitol aqueous solution. Then phthalic anhydride and soya bean fatty acid were added in the reactor and temperature was raised to 180 °C for 1.5 h. The mixture was subsequently heated to 240 °C at constant rate of about 1 °C/min and maintained at 240 °C. Samples carried out at regular time intervals were dissolved in an equal volume mixture of toluene and ethanol, and their acid value were determined by titrating the resulting solution with a 0.1 mol/L KOH solution to the phenolphthalein endpoint at room temperature. Progress of the polycondensation reaction was monitored periodically by the acid value of in-process samples.

2.3. Calculation of extent of reaction and average degree of polymerization

The extent of reaction (P_A) and average degree of polymerization ($\overline{DP}$) were calculated from the acid value of in-process samples [16,17]. The extent of reaction (P_A) was calculated using the following relationship:

$$P_A = \frac{C_0 - C_t}{C_0} \quad (1)$$

where C_0 is taken conveniently as the acid value at zero reaction time and C_t is remaining acid value after time t.

The average degree of polymerization ($\overline{DP}$) was calculated with P_A value using the following equation:

$$\overline{DP} = (1 - P_A)^{-1} \quad (2)$$

2.4. Gel permeation chromatography (GPC)

GPC was performed on a Waters 515 HLPC with a Waters 2414 Refractive Index detector for eluate monitoring. HPLC-grade chloroform ($CHCl_3$) was used as eluent at a flow rate of 1 mL/min. Samples were dissolved in chloroform ($CHCl_3$) at around 9 mg/mL. Ten microliters of the solution were injected into the column at a temperature of 30 °C. The calibration of the GPC column was performed with monodispersed polystyrene standards.

2.5. Determination of the film properties of sorbitol based alkyd resins

Samples of the sorbitol based alkyd resin were thinned with 200# solvent gasoline to brush consistency. The alkyd resin varnishes with solid content of 50%, 60% and 77% for samples SAR1, SAR2 and SAR3, were prepared, respectively. 2.5% by weight cobalt naphthenate to alkyd resin was added as drying agent. The resulting solutions were applied by brush on clean mild steel panels and glass panels for determining physical and chemical film properties of sorbitol based alkyd resins respectively. In addition, all coated panels were air-dried for 48 h before the tests and sides of the coated glass panels were protected by molten wax when the chemical resistance tests were carried out. The physical and chemical film properties of sorbitol based alkyd resins were compared with standard alkyd resins prepared from glycerol and pentaerythritol.

3. Results and discussion

3.1. Extent of the reaction and average degree of polycondensation reaction

As a function of polyesterification reaction time, acid value for the in-process alkyd resin samples is plotted in Fig. 1. It can be observed that the acid value decreased as reaction progressed. Compared to the later stages of the reaction, the reduction in acid value is faster at the early stages of the reaction. This pattern of changes in acid value during polyesterification reaction can be explained in two aspects: (1) the number of hydroxyl group decreased as the reaction progressed; (2) the viscosity of reaction mixture at different stages of reaction. At the initial stage of the reactions, the number of hydroxyl group is much large. As the reaction progressed, the number of hydroxyl group gradually decreased. In low temperature region (about 180 °C), the reaction progressed mildly and the increment rate of backbone chain is relatively slow. The primary hydroxyl groups of sorbitol react faster than the secondary hydroxyl groups, and crosslinks and branching which lead to high viscosity of the reaction mixture formed rarely. With the reaction ongoing, the viscosity of the reaction mixture