



Optimized synthesis and properties of surfactant-free water-reducible acrylate-alkyd resin emulsion



Liyun Liang^{a,*}, Caie Liu^a, Xiao Xiao^a, Shi Chen^b, Aiqiong Hu^c, Jun Feng^c

^a School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, China

^b School of Computer Science and Technology, Wuhan University and Technology, Wuhan, China

^c Wuhan Twin Tigers Coating Co., Ltd, Wuhan, China

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ABSTRACT

In this work, a modified alkyd resin (basic alkyd resin) was synthesized using maleic anhydride (MAH) to replace part of phthalic anhydride (PA) to achieve the target product acrylate-grafted-alkyd hybrid resin. The resin was then dispersed in water to form water-reducible emulsion. The properties were examined, including the extent of neutralization of final emulsion, ratio of MAH/PA in basic alkyd resin, mole ratio of basic alkyd resin to modified vinyl monomers, mole ratio of vinyl monomers (MMA/St/AA) on water dispersion stability of emulsion, particle size, drying time and mechanical properties. The optimal synthesis conditions produced a final emulsion particle size of 81.1 nm with good storage stability, hydrolytic stability and shorter drying time. The optimized synthesis conditions were identified as 80% neutralization, 1:0.8 mole ratio of basic alkyd resin to modified monomers, 4:3:2 modified monomers MMA/St/AA and 0.18 mole ratio of MAH/PA.

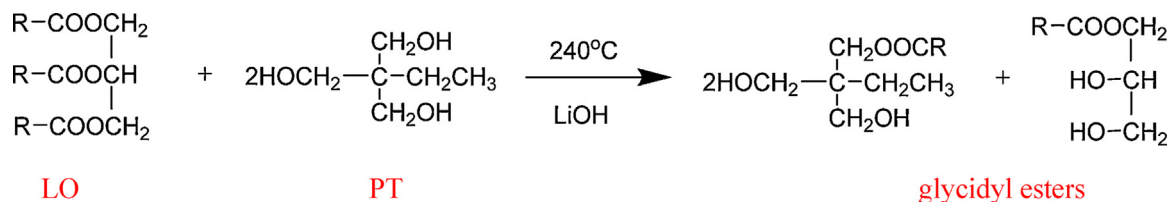
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1. Introduction

Alkyd resin is known as one of the most important binders in the coating industry. It is advantageous due to its independence from oil resources, ability to provide high gloss and efficient auto-oxidative curing at room temperature. However, traditional alkyd resin coatings are a large consumer of organic solvents, which is becoming increasingly limited due to rigorous environmental regulations issued around the world. As a result, researchers have increasingly recognized the potential of waterborne alkyd resin due to its lower VOCs (volatile organic chemicals) and ease of cleanup with water. Until now, the literature has reported only two primary approaches to obtain waterborne alkyd resin. In the one method, several hydrophilic monomers are induced into alkyd formulation to form a main alkyd chain, alkali is added for neutralization and the chain is dispersed into water to obtain water-reducible alkyd resin. The hydrophilic monomers utilized in this method include: 1,2,4-benzenetricarboxylic anhydride, trimethylolpropane (TMP) [1,2], maleic anhydride [1,2], low molecular weight polyethylene glycol (PEG) [3,4] and low molecular weight polyacrylate [5]. These hydrophilic monomers are known to react with other monomers to prepare alkyd resin by their $-\text{COOH}$ groups or $-\text{OH}$ groups. In the

second method, hybrid acrylic-alkyd emulsion is prepared through emulsion and mini-emulsion polymerizations [6–8]. Emulsion and mini-emulsion polymerizations are carried out in the presence of alkyd resin, which is dissolved in solvent or dispersed in water before synthesis. In order to disperse in water, the acid value of final alkyd resins should range from 5 to 40, while the hydroxyl value should range from 150 to 300 before polymerization [7]. Acrylate and derivatives are commonly used to modify alkyd resin to produce acrylate-alkyd hybrid resin with emulsion polymerization [6,9]. Acrylate resin is particularly known for its quick curing and color retention [10]. The acrylate-alkyd hybrid resin thus provides excellent compatibility between acrylate and alkyd resins and has excellent mechanical properties, such as pencil hardness, adhesion and water resistance [8]. To their disadvantage, each method has presented a very common side reaction in ester bond hydrolysis in basic synthesis. On the other hand, the use of surfactant and co-surfactant in emulsion and mini-emulsion polymerizations [11,12] provides higher hydrophilic properties and decrease water resistance. In recent years, there have been various attempts [5,13] to develop waterborne alkyd resin with good water dispersion and high hydrolytic stability. However, results for water resistant properties in the films remained disappointing. This was attributed to excess carboxyl groups in the side chain of waterborne resins; in addition to a small amount of low molecular weight polyacrylate remaining unreacted in the system, leading to prolonged drying time. More recently, a method was reported using MAH to

* Corresponding author. Tel.: +86 27 87558172; fax: +86 27 87543632.
E-mail address: liyun.liang@mail.hust.edu.cn (L. Liang).



Scheme 1. Formula of alcoholysis reaction.

modify the rubber seed in the preparation of a water-soluble alkyd [14]. Changes in the amount of MAH have thus been highlighted as a key factor in altering physico-chemical and chemical resistance properties. On the other hand, there has been one report of a latent oxidatively functional (LOF) acrylic monomer being used to offset decreases in the double bonds of the alkyd chain while grafting acrylic acid into alkyd resin [9]. Although measures can be taken to prevent decreases in the double bond of waterborne alkyd resin, catering to exact design parameters of *K* (the esterification degree of alkyd resin), *OL* (oil length), *R* (alcohol excess) of alkyd resin has proven to be highly problematic in preparing waterborne resins. The alkyd resin system has a strong tendency to transform to gel during the reaction if the design parameters are not controlled. Moreover, little experimental data is available on the drying time of coating film; although waterborne alkyd resins have shown good dispersion properties in water [15]. In this work, a basic alkyd resin was designed and synthesized using the $-\text{COOH}$ group monomer MAH to replace a part of phthalic anhydride (PA), thus increasing latent oxidatively functional groups, such as double bonded MAH at the side chain of alkyd resin and finally synthesizing an acrylate monomer to provide the MAH modified alkyd resin. The new method aimed to improve water resistance, drying time and the compatibility properties of waterborne alkyd resin. The most important properties of alkyd resin are achieved through the auto-oxidation curing process, which has been changed in the preparation of waterborne alkyd resin as acrylic monomers graft the alkyd chain. High gloss and other advantageous properties in coatings are dependent upon the degree of the auto-oxidation curing process. The drying time of acrylate-alkyd resin emulsion is known to be greatly influenced by the curing process; as such, drying time can be used as a measure of efficiency for the auto-oxidation curing process. This paper examines the effects of neutralization on final emulsion, mole ratios of basic alkyd resin and modified monomer, mole ratios of vinyl monomers (MMA:St:AA), ratios of MAH:PA, water dispersion stability of emulsion and mechanical properties. Following optimized synthesis, the final modified waterborne alkyd resin demonstrated good hydrolytic stability, shorter drying time and enhanced mechanical properties.

2. Experimental

2.1. Materials

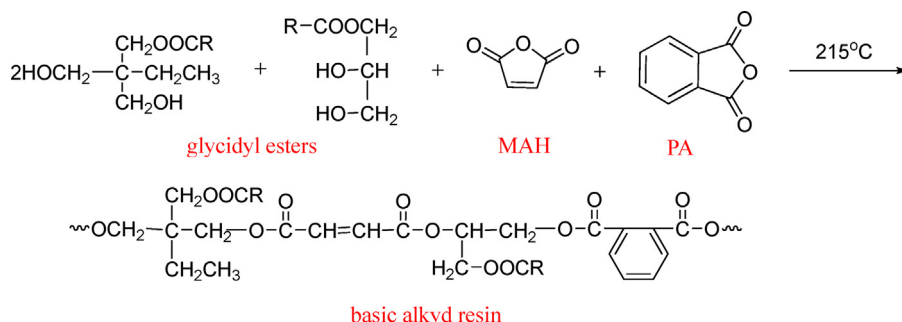
The technical grade reagents methyl methacrylate (MMA), acrylic acid (AA), styrene (St), maleic anhydride (MAH), azoisobutyronitrile (AIBN), LiOH, xylene, toluene, methanol n-butanol, ethylene glycol monobutyl ether and triethylamine were purchased from Sinopharm Chemical Reagent Co., Ltd (China). The industry grade reagents cobalt octoate, magnesium octoate and lead octoate driers, linseed oil (LO), phthalic anhydride (PA) and pentaerythritol (PT) were supplied by Wuhan Twin Tigers Coating Co., Ltd (China). The technical grade reagent trimethylolpropane (TMP) was purchased from Shanghai Nuotai Technology Co., Ltd (China). All were used without further treatment or purification.

2.2. Preparation of waterborne acrylic-alkyd resin

Step 1 (Alcoholysis): LO, TMP, PT and LiOH were poured into a 500 ml four neck, round bottom glass reactor equipped with a mechanical stirrer, condensator, thermometer and nitrogen protector. The mixture was slowly heated until the mixture melted, after which mechanical stirring began. The reaction temperature was maintained at 240°C for 40 min until the production of the alcoholysis products: glycidyl esters. The reaction formula is shown in Scheme 1.

Step 2 (Esterification): A lower temperature of 140°C was used with PA, MAH and xylene in the glass reactor. A water/oil separator was added and the mixture was heated to 180°C . Here, the xylene was employed as an azeotropic solvent. Following heating for 1.0 h at 180°C , the mixture was slowly heated to 215°C and maintained at this temperature for 1.5–2.0 h. The redundant xylene was then distilled from the system by vacuum distillation and the temperature was decreased to 120°C . Finally, the polycondensation reaction occurred when the acid value was between 16 and 20 mgKOH g^{-1} . The esterification process is shown in Scheme 2.

Step 3 (Preparation of side chain grafting acrylated-alkyd resin emulsion): The temperature from the final stage of step 2 was reduced to 100°C . One quarter of total initiator AIBN containing



Scheme 2. Synthesis of basic alkyd resin introducing MAH in main chain.

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