ISSN: 2414-1895 DOI: 10.6919/ICJE.202212_8(12).0025

Progress in Synthesis and Modification of Waterborne Alkyd Resin

Chang Xu[1], Lin Wu[2], Ying Liu[1], Ao Chen[1], Ya Hu[1,2,*]

[1] Key Laboratory of Hubei Province for Coal Conversion and New Carbon Materials, School of Chemistry and Chemical Engineering, Wuhan University of Science and Technology, Wuhan 430081, China

[2] Academy of Green Manufacturing Engineering, Wuhan University of science and technology, Wuhan 430081, China

[*]Email: huya@wust.edu.cn

Abstract

Alkyd resin has strong anti-corrosion resistance, good adhesion and good workability of paint film, and is widely used in paints, coatings, adhesives, ships and other fields. Solvent-based alkyd resins bring serious environmental hazards. Waterborne alkyd resins can greatly reduce VOC emissions by using water as the dispersion medium, which is of great significance to the research of waterborne alkyd resins. Firstly, the synthesis method of waterborne alkyd resin is reviewed, and the research progress and evaluation method of waterborne alkyd resin modification are also introduced. Finally, the development trend of waterborne alkyd resins is prospected.

Keywords

Waterborne Alkyd Resin; Synthesis; Modification; Progress.

1. Introduction

The concept of alkyd resin was first proposed by Kienle in the United States, which refers to polyester resin formed by condensation polymerization of polyols, polyacids and fatty acids as the main raw materials. Its raw materials are widely sourced and do not rely on non-renewable energy sources such as petroleum, and has good adhesion and high gloss, alkyd resin-based coatings have the advantages of low price, hard coating film, good water resistance and weather fastness, etc., and is the largest class of coatings produced in China[1].

With the growth of China's economy, people's awareness of environmental protection has gradually increased. The state has issued a large number of laws and regulations to control VOC emissions in the paint industry, solvent-based coatings are limited. Researchers began investigating alkyd systems with low or zero volatile organic compounds (VOCs) [2]. Compared with traditional solvent-based waterborne alkyd resins, waterborne alkyd resins reduce VOC emissions, and to avoid the use of organic solvents caused by the environmental pollution problems, in the field of coatings also have a very wide range of applications, not only can be used as wood, metal and other surface primers, topcoats and single-layer coatings, but also can be used for railways, ships and other metal materials corrosion resistance coating and protection[3,4,5]. Therefore, it is very important to study the waterborne properties of alkyd resin.However, there are many problems in waterborne alkyd resin, such as slow drying of paint film, poor water resistance and poor storage stability of resin, Therefore, the technical modification research of waterborne alkyd resin has great practical application significance.

ISSN: 2414-1895 DOI: 10.6919/ICJE.202212_8(12).0025

2. Synthesis of Waterborne Alkyd Resins

Waterborne dispersive resin refers to a resin molecule without hydrophilic groups, or with a certain hydrophilic group. This resin is insoluble or not completely soluble in water, but it can be dispersed in water by certain preparation or processing methods to form a dispersion with water as the medium.Most of the traditional alkyd resins are solvent-based, while the waterborne alkyd resins use water as a solvent or dispersing medium. Therefore, the waterborne alkyd resin is the key to synthesize waterborne alkyd resin. There are usually two methods: external emulsification and internal emulsification [6,7].

Internal emulsification means that the molecular chain of the resin contains a certain amount of hydrophilic components that can neutralize salts, but cannot be completely dissolved in water.In the preparation of aqueous dispersions of resins, there is no need to add another emulsifier; it is a method of using a small amount of hydrophilic components contained in the molecular chain itself, and then forming a stable water-dispersing emulsion by mixing with water, stirring, etc. This method does not need to add co-solvents, so in the preparation of waterborne coatings, adhesives and other products used in the waterborne resin, self-emulsifying waterborne dispersion resin occupies the vast majority, nearly ten years, a variety of resins of self-emulsifying waterborne technology, especially the research and development of multi-hybrid waterborne resins is very rapid. Without the addition of surfactants, by introducing nonionic hydrophilic groups (hydroxyl groups and ether groups) in the resin molecular chain, the hydrophilicity of the alkyd resin is enhanced, dispersed in water, and an aqueous alkyd resin is obtained.

At present, there are three main preparation methods: salting method, nonionic group method and zwitterionic intermediate method [8,9].

(1) Salting method

The salt forming method is to introduce the carboxyl group into the chain segment of the polyester resin, and neutralize the salt with amine to obtain an aqueous polyester resin. Vikash [10]et al.useddimethylpropionic acid as internal emulsifier, successfully introduces carboxyl group into the fatty acid chain, and neutralizes by adding triethylamine to get carboxylate type waterborne alkyd resin, which has good comprehensive performance. Xiang Tao [11]et al. take linoleic acid, phthalic anhydride and trimethylolpropane as raw materials, established the quantitative relationship between formula parameters and raw material dosage through formula design and calculation, and uses trimellitic anhydride as an aqueous monomer, successfully introduces carboxyl groups on the fatty acid chain, and gives waterborne alkyd resin after adding triethylamine.

(2) Non-ionic group method

The two main non-negative ionic groups are hydroxyl and ether groups. In order to obtain good water solubility of alkyd resin, non-negative ionic groups can be introduced in alkyd resins and diluted with water to synthesize waterborne alkyd resins. Shui[12]et al. use butyl acrylate, methyl methacrylate, and alkyd resin as raw materials, by introducing the non-ionic monomer N-hydroxymethyl acrylamide (HAM) and the cationic monomermethacryloxyethyltrimethyl ammonium chloride (DMC), successfullysynthesized waterborne acrylate alkyd resin with excellent comprehensive performance and studied the effect of different HAM's amounts on emulsion and coating properties.

(3) Zwitterionic intermediate method

By synthesizing zwitterionic copolymers, a new type of waterborne coating is prepared without amine or formaldehyde. For these two ionic copolymers, both amines and carboxylic acids are connected to the resin by covalent bonds. Ma Baifeng[13]et al. synthesized a highly stable water-soluble alkyd resin. Cotton oleic acid, TMP (trimethyl phosphate), PA (polyamide) are heated and dehydrated for polymerization according to the formula amount. When the acid value of the system reaches 10~20mgKOH/g, the polycarboxylic acid is added for polymerization, and when the system acid value reaches 60~80mgKOH/g, the aqueous alkyd resin with excellent anticorrosion performance, strong impact resistance and fast drying is obtained.

ISSN: 2414-1895 DOI: 10.6919/ICJE.202212_8(12).0025

3. Waterborne Alkyd Resin Modification Method

Waterborne alkyd resin generally has a slow drying speed, storage stability and poor water resistance of the paint film and many other deficiencies, in order to overcome these shortcomings, and further improve the comprehensive performance and cost-effectiveness of waterborne alkyd resin coatings, domestic and foreign scholars have conducted a series of studies on the modification of waterborne alkyd resin, including acrylic modification, styrene modification, polyurethane modification, silicone modification, epoxy resin modification, etc.

(1) Acrylic modified

Acrylic resin has the advantages of weather fastness, light resistance, heat resistance, good corrosion inhibition, etc., and acrylic modified alkyd resin can make up for the lack of weather fastness and hardness of alkyd resin. Two methods of acrylic modification of waterborne alkyd resin include esterification method and Copolymerization[14]. Chen Anqiang[15]et al.synthesized a new waterborne alkyd-acrylic acid composite dispersion, the waterborne alkyd paint preparedin this way has the characteristics of low VOC content, excellent water resistance and mechanical properties, which solves the technical problem of poor water resistance of waterborne alkyd resin. Wang Zhaohui[16]et al.used acrylic monomers to modify epoxy-modified alkyd resin, and prepared an excellent waterborne acrylic-modified epoxy alkyd resin. The waterborne acrylic modified epoxy alkyd resin prepared from this method is designed as the film-forming material, and the experimental results show that the acrylate monomer can improve the weather fastness, water resistance and salt spray resistance of the coating.

(2) Styrene modification

The cost of modifying alkyd resin with styrene is lower than that of modifying with acrylic and polyurethane. It combines the advantages of fast drying, high hardness and good water resistance of styrene with the advantages of good flexibility of alkyd resin, strong pigment bearing capacity and simple and mature process.Xu Xiaoxun[17] et al. first used maleic anhydride instead of some diacids in alkyd resin to make alkyd resin oligomers,and then the carbon-carbon double bond of maleic anhydride was copolymerized with the carbon-carbon double bond of styrene and acrylate, so as to achieve the purpose of modifying alkyd resin. Yang Lifeng[18]et al.mixed styrene, acrylic monomer, silicone monomer, etc. and grafted them into alkyd resin molecule, prepared a high-gloss self-drying waterborne acrylic modified alkyd resin for waterborne coatings.The results show that thewaterborne acrylic modified alkyd resinhas the characteristics of high gloss, self-drying at room temperature, strong water resistance and excellent adhesion.

(3) Polyurethane modified

Polyurethane molecules contain a large number of strongly polar aminoester bonds and urea bonds, and have strong intermolecular and intramolecular hydrogen bonding forces, making it have good wear resistance and excellent chemical resistance.It modifies alkyd resins and introduces the excellent properties of polyurethane into alkyd resins to improve the mechanical properties, weather fastness and chemical resistance of alkyd resins.Gooch[19]et al.used acrylic monomers (methyl methacrylate, butyl acrylate and acrylic) to polymerize with polyurethane modified alkyd resin emulsionto synthesize polyurethane modified acrylic-alkyd emulsion. The emulsion exhibits excellent storage stability. OuCanbin[20]et al.use soybean oil, trimethylolpropane, phthalic anhydride as raw material, and synthesizes alkyd polyol oligomers by alcohol esterification, and then continuously react with isophorone diisocyanate (IPDI), 1,4-butanediol, etc.,polyurethane modified waterborne alkyd resin was synthesized, which overcame the problems of poor drying performance, poor storage stability and poor mechanical properties of waterborne alkyd resin, and the surface and thermal stability of the resin were excellent.

(4) Silicone modification

Alkyd resins modified by silicones have excellent weatheringfastness, chemical resistance, heat resistance, electrical insulation and flame retardancy. Li Penghao[21] et al. synthesized silicone

ISSN: 2414-1895 DOI: 10.6919/ICJE.202212_8(12).0025

oligomers with methyltriethoxysilane (MTES) and tetraethyl orthosilicate (TEOS) as the main raw materials, and then modified the alkyd resin with silicone oligomers, and finally a waterborne alkyd resin with concentrated particle size distribution, good storage stability and good thermal stability was obtained.

(5) Epoxy modification

Epoxy resin coatings have excellent alkali resistance, chemical resistance, high hardness, wear resistance and good adhesion. The use of epoxy resin modified waterborne alkyd resin, in addition to retaining the excellent gloss retention and flexibility of alkyd resin, but also has good adhesion performance and chemical resistance of epoxy resin, improving the adhesion and corrosion resistance of alkyd resin. Wang Zhen [22]et al.Synthesized high solid content, fast drying, high hardness, good salt spray resistance and cost-effective epoxy modified waterborne alkyd resin, epoxy modified waterborne alkyd resin compared with ordinary alkyd resin in terms of chemical resistance has been greatly improved, compared with ordinary waterborne alkyd resin, it has a very highcost performance, especially its anti-corrosion performance is outstanding, in industrial coatings have great application potential. Ma Yangmin[23]et al.used peppercorn seed oil as raw material, modified by epoxy resin, and prepared waterborne alkyd resin by polyesterification reaction. The modified resin has good chemical resistance, physical properties and thermal stability.

4. Performance Evaluation and Testing

Based on the research of waterborne alkyd resins, many researchers synthesize waterborne alkyd resins from different raw materials. In view of some limitations in the performance of waterborne alkyd resins, researchers at home and abroad have conducted a lot of modification studies on alkyd resins [24]. It also tests the properties of alkyd resins and the coatings applied. Choe[25]et al.evaluate the performance of the modified resin based on its gloss, pencil hardness, impact strength, alkali resistance and thermal stability.Pan Xiaoou and other researchers used water resistance, adhesion, stability, viscosity, acid number, etc. as the evaluation technical indicators of waterborne alkyd resins[26].After they made a varnish of waterborne amino alkyd resin, they tested the properties of the paint film such as acid resistance, alkali resistance, salt resistance, hardness and flexibility, and the results showed that the properties of the synthesized alkyd resin have been greatly improved.According to the literature, the acid number is detected according to GB/T 6743-2008; Storage stability is tested according to GB/T 21782.8-2008; The drying time is tested according to GB/T 1728-1979; Impact resistance is tested according to GB/T 1732-1993; Gloss according to GB/T 9754-2007 test; The hardness of the pencil is tested according to GB/T 6739-2006 [27].

5. Conclusion

Waterborne alkyd resin has rich sources of raw materials, high coating gloss, strong flexibility, and has been widely used in coatings and other related industries. However, the coating prepared by waterborne alkyd resin has slow drying speed, water resistance, low hardness, solvent resistance and poor corrosion resistance. The current research focuses on optimizing the performance of waterborne alkyd resin by modifying waterborne alkyd resin with a monomer, and the modification method is single. Therefore, new raw materials can be tried or modified to waterborne alkyd resins by monomer compounding. In addition, although the modification can improve a certain performance of the waterborne alkyd resin, it does not play a great role in broadening the application field of the waterborne alkyd resin, so if the basic theoretical research of the waterborne alkyd resin is carried out, it is more conducive to solving its problems from the root.

Acknowledgments

This work was financially supported by the Key Research and Development Program of Hubei Province (Grant No. 2021BAA063 and No. 2020BAB084), National Natural Science Foundation of

ISSN: 2414-1895 DOI: 10.6919/ICJE.202212_8(12).0025

China (Grant No. 61904130), and Key Laboratory of Hubei Province for Coal Conversion and New Carbon Materials (Grant No. WKDM201907).

References

[1] Fu Yuanyuan, Kang Wendong, Wang Yong, et al. Preparation and Application of Two DOPO Derivatives Modified Alkyd Resin[J].Synthetic Resins and Plastics,2016,33(4):5-10.https://doi.org/10.3969/j.issn.1002-1396.2016.04.002.

[2] Quehong Huang et al. Effects of formulation on set-to-touch time of waterborne alkyd resin by uniform design[J]. Progress in Organic Coatings, 2015, 87: 189-196.https://doi.org/10.1016/j.porgcoat.2015. 06.001.

[3] DamirGagro. Waterborne coatings have a good momentum of development[J].China Coatings, 2017, 32(02): 75-76.https://doi.org/10.13531/j.cnki.China.coatings.2017.02.015.

[4] Li Chunlin. A brief analysis of the application of waterborne coatings in rail vehicles[J].Science and Technology Innovation Herald,2017,14(01):89-90.https://doi.org/10.16660/j.cnki.1674-098X.2017.01.089.

[5] H. A. Mohamed. New waterborne paints with different binders and corrosion inhibition application[J]. Journal of Coatings Technology and Research, 2010, 7(1): 85-89.

[6] Chen Jun, Yan Fu'an, Wen Yanxia. Research Progress on Synthesis and Modification of Waterborne Alkyd Resin[J]. Coating Technology and Abstracts,2009,30(01):4-7.

[7] Zhu Qin, Yi Changfeng, Xu Zushun, Hu Xiaoxi, Wang Yun, Shi Haixin. Research Progress on Synthesis and Modification of Waterborne Alkyd Resin[J].China Coatings,2015,30(09):11-16.https://doi.org/10.13531/j.cnki.China.coatings.2015.09.004.

[8] Sun Shichang. Study on the stability and coating performance improvement of alkyd resin emulsion[D].Zhengzhou University,2021.https://doi.org/10.27466/d.cnki.gzzdu.2021.002640.

[9] Mei Ying Zhongyi. Hydration and waterborne coating applications of polyester resin[J].Contemporary Chemical Industry Research, 2017(05):28-30.

[10] Vikash K. Mishra and Kalpesh I. Patel. Synthesis and Characterization of Soya Fatty Acid-Based Self-Emulsifiable Alkyds[J]. Journal of Dispersion Science and Technology, 2015, 36(7): 1036-1046. https://doi.org/10.1080/01932691.2014.950740.

[11] Xiang Tao. Synthesis and properties of modified waterborne alkyd resin[D].Chongqing University,2017.

[12] Shui Xiaojun, Shen Yiding, Fei Guiqiang, Wang Haihua, Zhu Ke. The effect of nonionic monomer HAM on properties of cationic surfactant-free acrylic/alkyd hybrid emulsion[J]. Journal of Applied Polymer Science,2014, 132(5/6). https://doi.org/10.1002/app.41406.

[13] Ma Baifeng,Zhen Weijun,AbulajangYusufu,et al. Synthesis, characterization and properties of waterborne alkyd resin based on cotton oleate[J].Coating Industry,2022,52(3):44-50,56. https://doi.org/10.12020/j.issn.0253-4312.2022.3.44.

[14] ZhangXiaona,ShangYanming,Zhang Rui. Research progress of waterborne alkyd resin and its acrylic modified body[J].Shanghai Coatings,2010,48(08):31-34.

[15] ChenAnqiang,Guo Wen,LiuXianwen,YangPenggang,LiuLanglang,LaiYaodong. Study on the influencing factors of water resistance of new waterborne alkyd/acrylic composite dispersion paint film[J].Coating Industry,2022,52(09):64-69.

[16] Wang Zhaohui,Yong Tao,Yang Jingxia,Zhang Anjie,NiuBinbin. Preparation and Properties of Waterborne Acrylic Modified Epoxy Alkyd Resin[J].Coating Industry,2021,51(07):36-41.

[17] XuXiaoxun,Gong Xian,XuHaiyou. Preparation and Properties of Styrene and Acrylate-Modified Alkyd Resin[J].Coating and Protection,2021,42(10):20-23.

[18] YangLifeng,DongQunfeng,PeiKemei. Preparation and Properties of High-Gloss Self-Drying Waterborne Alkyd Resin[J].Modern Coatings and Coating,2020,23(02):1-4+8.

[19] J. W. Gooch, H. Dong, F. J. Schork. Waterborne oil-modified polyurethane coatings via hybrid miniemulsion polymerization[J]. Journal of Applied Polymer Science,2000,76(1).

[20] OuCanbin. Preparation and properties of silicone-polyurethane modified waterborne alkyd resin[D].South China University of Technology,2016.

ISSN: 2414-1895 DOI: 10.6919/ICJE.202212_8(12).0025

[21] LiPenghao,LiPeili,ZhuGuangjun. Preparation and Properties of Silicone Modified Waterborne Alkyd Resin[J].Modern Industries,2016,36(04):137-140.https://doi.org/10.16606/j.cnki.issn0253-4320.2016.04.033.

[22] Wang Zhen,GanShipeng,HuangHuizi. Preparation of epoxy-modified waterborne alkyd resin and study on its varnish properties[J].Shanghai Coatings,2022,60(03):58-60.

[23] Yangmin Ma, Rui Lei, Yajuan Jiang. Synthesis and characteristics of Zanthoxylum bungeanum seed oil-based alkyd resin modified by epoxy resin and their blends with HMMM[J]. Polymer Bulletin, 2019, : 1-15. https://doi.org/10.1007/s00289-019-02980-z.

[24] Ifijen, IkhazuagbeH.,Maliki, Muniratu,Odiachi, Ifeanyi J.,Aghedo, Oscar N.,Ohiocheoya, Ewanole B.. Review on Solvents Based Alkyd Resins and Water Borne Alkyd Resins: Impacts of Modification on Their Coating Properties[J]. Chemistry Africa, 2022, : 1-15.

[25] Choe Yong-A, Kim Su-Il, Ju Kyong-Sik. Synthesis and characterizations of high oil length alkyd resin with dehydrated castor oil and acrylic pimaric acid[J]. Chemical Physics Letters,2022,805. https://doi.org/10.1016/J.CPLETT.2022.139934.

[26] Wang Yao,DengYuequan,GuoLiqin,Yang Wei,JiangZhengxing. Preparation of Co/Ca Composite Waterborne Alkyd Resin Anti-corrosion Coating[J].Chemical New Materials,2020,48(01):266-269. https://doi.org/10.19817/j.cnki.issn1006-3536.2020.01.050.

[27] SunZhenhong,Yong Tao,YangJingxia. Preparation and Application of Waterborne Low Hydroxyl Value Acrylic Modified Alkyd Resin[J].New Chemical Materials,2022,50(04):267-272+277. https://doi.org/10.19817/j.cnki.issn1006-3536.2022.04.054.