



Contents List available at VOLKSON PRESS

New Materials and Intelligent Manufacturing (NMIM)

DOI : <http://doi.org/10.26480/icnmim.01.2018.107.109>Journal Homepage: <https://topicsonchemeng.org.my/>

ISBN: 978-1-948012-12-6



SYNTHESIS AND CHARACTERIZATION OF EPOXY-MODIFIED WATERBORNE UNSATURATED POLYESTER AND THEIR USE IN FIBER SIZING AGENTS

Zhenyu Wang, Weilong Yang, Xu Feng, Jing Tian, Feihong Jia, Jianhua Li, Chuncai Yang*

Jilin Institute of Chemical Technology Chengde Street, Jilin, China.

*Corresponding Author's email: 2941883707@qq.com

This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited

ARTICLE DETAILS

ABSTRACT

Article History:

Received 26 June 2018

Accepted 2 July 2018

Available online 1 August 2018

Epoxy-Modified Waterborne unsaturated Polyester (WUP) were synthesized by phthalic anhydride, dipropylene glycol, maleic anhydride, epoxy resin, methyl tetrahydro phthalic anhydride and triethylamine. The chemical structures of the WUP products were characterized by Fourier transform infrared spectroscopy (FT-IR). The thermal properties of the WUP were examined by thermogravimetric analysis (TGA). TGA showed that the WUP had good thermal stability. The particle size of WUP sizing agents was characterized by Laser Particle Size Analyzer. The emulsion morphology and aggregation state were evaluated by scanning electron microscopy (SEM). The SEM confirmed that the particle size of WUP sizing agents was Nano-sized and monodisperse microspheres. The excellent properties of WUP confer it with potential applications as sizing agents in glass fiber and carbon fiber.

KEYWORDS

Unsaturated polyester, epoxy modification, emulsion, sizing agent.

1. INTRODUCTION

Fiber-reinforced composites have been widely used due to their light weight, high strength and excellent impact resistance [1]. However, composite materials also have certain drawbacks for example poor interfacial adhesion between the fiber and the resin matrix [2]. For resin-based composites, the interface has a direct effect on the properties of the composite [3]. Because the surface energy of glass fiber is low and has no binding functional group, inadequate strong bonding strength between the resin and the fiber [4-7]. Therefore, in the drawing process of glass fiber production, it is necessary to coat the surface of the glass fiber with a layer of surface treatment agent, a sizing agent, sizing not only increases fiber-matrix adhesion, but also improves tow handling and helps decrease damage to fibers during fabrication [8-9]. It will also increase the surface energy of the fiber, making it better bonded to the resin.

At present, there are two methods for producing polyester emulsions: external emulsification and self-emulsification. External emulsification method needs emulsifier and high speed agitation [10]. Self-emulsification is the introduction of hydrophilic groups, which allows the entire molecular chain to form an amphiphilic polymer that can act as an emulsifier, thus avoiding the addition of emulsifiers and the film former will be prevented from migrating with the emulsifier during subsequent fiber drying [11]. Polyester emulsions can be classified into anionic, cationic and non-ionic depending on the type of hydrophilic chain extender used.

This article uses esterification reaction of phthalic anhydride, dipropylene glycol, and maleic anhydride etc, to make polyester, when acid number reach the calculated value, epoxy resin is added to extend the polyester chain and produce hydroxyl groups. In the next step methyl tetrahydrophthalic anhydride is added to take a carboxylation reaction and also free carboxyl groups are generated. In the last step triethylamine and deionized water is subsequently added to neutralize acid and the emulsion finally was formed. On the basis of the results, the WUP sizing agents could self-emulsify, self-assembly and self-stabilize itself.

2. EXPERIMENTS

2.1 Experimental materials and equipment

Phthalic anhydride (Jiuding Chemical); dipropylene glycol (Macklin reagent); maleic anhydride (Jiuding Chemical); epoxy resin (Nantong Xingchen); methyl tetrahydrophthalic anhydride, (Wengjiang reagent); triethylamine, (Adamas reagent); acetone (Tianjin Dongfang Chemical); deionized water (Laboratory homemade), electric-heated thermostatic water bath (Gongyi Yuhua Instrument), glass reaction flask, electronic balance (Shanghai Hanyu Hengping), FT-IR (Shimadzu, Japan), thermogravimetric analysis (TA Corporation), laser particle size analyzer (Brook, USA), cryo-scanning electron microscope (Tescan GAIA3), high-speed centrifuge (Anhui Zhongke Zhongjia Instrument)

2.2 Synthesis of Epoxy Modified Anionic Polyester Emulsion

The synthesis of epoxy-modified anionic polyester emulsions is carried out in three steps. A certain proportion of phthalic anhydride, dipropylene glycol and maleic anhydride are added to reaction flasks for esterification to form carboxyl-terminated unsaturated polyesters. The acid value is adjusted between 30-50 mg KOH/g. Epoxy resin and catalyst are added to trigger the reaction at 100~115°C. After the acid value reaches 5 mg KOH/g, methyl tetrahydrophthalic anhydride is added for further carboxylation reaction and also to form carboxyl groups. The amphiphilic polymer was finally emulsified into a nano-sized emulsion by adding triethylamine and deionized water with stirring.

2.3 Emulsion Characterization

The FT-IR spectra were recorded by the Shimadzu Japan instrument with KBr pellets. The background spectrum of the KBr pellet was subtracted from the sample spectrum. Particle size and distribution of sizing agents were analyzed by laser particle size analyzer (Brook, USA). Emulsion stability of the sizing agents was tested by high-speed centrifuge (Anhui Zhongke Zhongjia Instrument), 10 ml sizing agents was placed into a centrifuge tube and centrifuged 20 or 30 min at 3000r/min. The thermogravimetric analysis (TGA) data were recorded on TA Corporation

instrument under an N_2 atmosphere from room temperature up to 500°C at heating rate of 10°C/min. Morphology and distribution of the emulsion was examined with the Tescan GAIA3.

3. RESULTS AND DISCUSSION

3.1 FT-IR spectra

Figure 1 shows the FT-IR characterization of synthetic epoxy-modified anionic polyester emulsions. It can be seen from the spectrum that the strong absorption peak $C=O$ at 1723 cm^{-1} and the strong absorption peak near 1287 cm^{-1} have all proved that unsaturated polyesters were synthesized, and $-CH_2$ was found near 2930 cm^{-1} . Absorption peaks confirmed the presence of methylene groups. No characteristic peak of the epoxy resin was observed near 915 cm^{-1} 832 cm^{-1} , indicating that the epoxy rings were involved in the reaction.

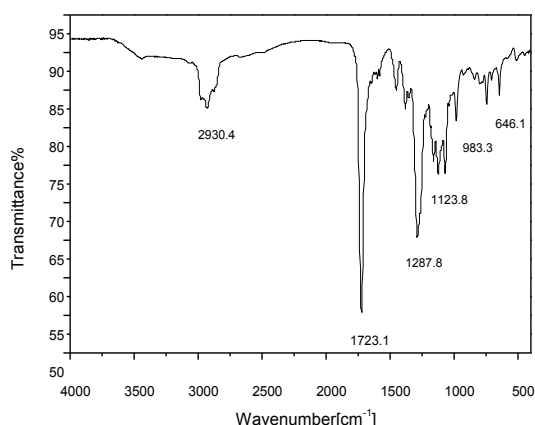


Figure 1: FTIR spectra of WUP sizing

3.2 Characterization of particle size of WUP emulsion

The particle size of the emulsion will affect the stability of the emulsion.

Figure 2 examines the effect of different acid values on the particle size of the emulsion in our designed experiment. It can be seen from the figure 2 that the emulsion particle size obtained by the self-emulsification method is nanoscale, which greatly improves the storage stability. The particle size of the emulsion increases with the acid number decreasing. Because the bigger the acid value, the stronger the hydrophilicity of the polymer chain and the less intermolecular entanglement between the molecular chains, the better dispersion in water, the smaller the particle size [12]. If the endpoint acid value is too high, there are many hydrophilic groups, the emulsion is transparent, and the particle size distribution is very small. However, this state emulsion film has poor water resistance, because the presence of too many carboxyl groups will generate water sensitivity in the membrane. As the acid value decreases, the hydrophilic group decreases, the emulsion becomes milky white, and the particle size becomes large. When the acid value is less than 30, it is difficult to disperse the polyester molecule in water. Therefore, the endpoint acid value should be controlled between 30-40Mg KOH/g.

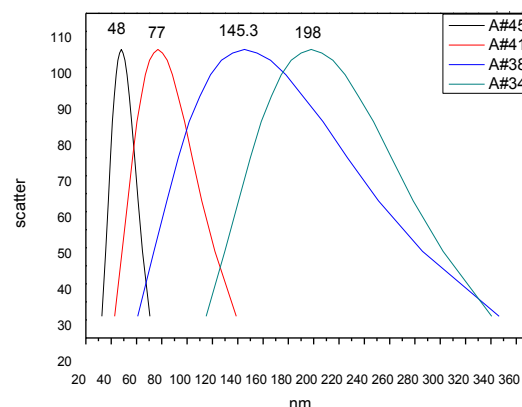


Figure 2: Particle size characterization of emulsion

3.3 Emulsion stability

Table 1: Effect of Different Acid Values on Emulsion Stability

	A#45	A#41	A#38	A#34	A#32
Storage at room temperature for six months	Stable	Stable	Stable	Stable	A little precipitation
3000r/min centrifugation for 20 minutes	Stable	Stable	Stable	Stable	Stable
3000r/min centrifugation for 30 minutes	Stable	Stable	Stable	Stable	A little precipitation

Table 1 shows that the polyester emulsion with the endpoint acid value of 32 will have a little precipitation when stored at room temperature for six months, and there will be a little precipitation when centrifuged at 3000r/min for 30 minutes. The acid value of 34 or more at room temperature storage for six months and 3000r/min centrifugation will not produce precipitation, indicating that the stability of synthetic self-emulsifying agent is very good.

3.4 WUP thermal stability Study

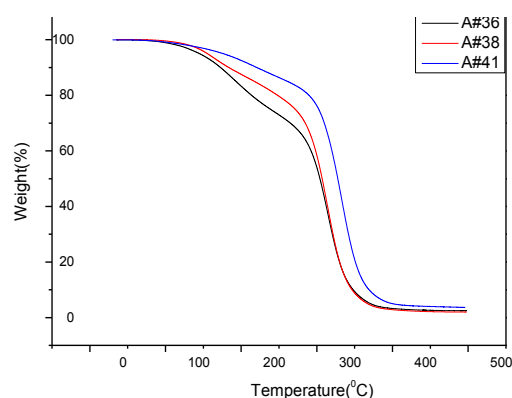


Figure 3: TGA

In order to study the thermal stability of the emulsion polymers, the weight loss test of WUP sizing agents with the acid value of 36, 38, and 41 was analyzed. The results showed that the thermal decomposition can be divided into two stages. The first decomposition temperature is between 130°C and 300°C, the second stage begins to decompose is between 300-400°C. In addition, it can be seen that the thermal decomposition process of different acid values is not same. The effect of the test results indicates that WUP has good thermal stability.

3.5 WUP Emulsion SEM Characterization

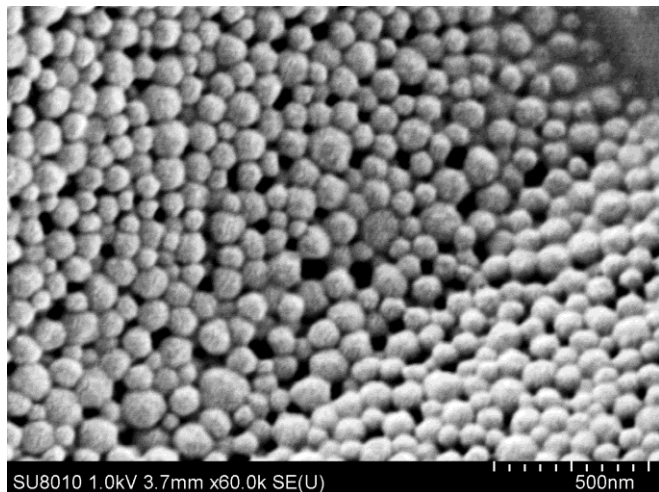


Figure 4: SEM

The electron microscope picture was shown in the figure 4. It can be seen from the figure 4 that the morphology of self-emulsifying polyester sizing agent is irregularly spherical and the diameter of the particles is very small. The average diameter is about 50 nanometers, indicating that the emulsion particles have good stability and good dispersion.

4. CONCLUSION

Synthetic polyester sizing agents in this article are of self-emulsification effect, and the acid value is within a certain range, the emulsion stability is good, and the particle size can be controlled without high speed agitation and external emulsifier.

REFERENCES

[1] Sever, K., Sarikanat, M., Seki, Y., Cecen, V., Tavman, I.H. 2008. Effects of

fiber surface treatments on mechanical properties of epoxy composites reinforced with glass fabric. *Journal of Materials Science*, 43, 4666-4672.

[2] Liu, Z., Tian, Y., Kang, S., Zhang, X. 2012. Synthesis and characterization of novel epoxy-modified waterborne polyurethanes and their use in carbon fiber sizing. *Journal of applied polymer science*, 125, 3490-3499.

[3] Xuang, Y. 2010. *Composite interface*. Beijing: Chemical Industry Press. ISBN : 9787122085733

[4] Haomiao, Y., Peng, H., Peng, W., Cheng, P. 2014. Surface energy of glass fiber and its wetting properties with different resin systems. *Mechanical functional materials*, 38 (10), 50-53.

[5] Feuillade, V., Bergeret, A., Quantin, J.C., Crespy, A. 2006. Relationships between the glass fiber sizing composition and the surface quality of sheet molding compounds (SMC) body panels. *Composites Science and Technology*, 66 (1), 115-127.

[6] Wu, Q., Li, M., Gu, Y., Wang, S., Wang, X., Zhang, Z. 2015. Reaction of carbon fiber sizing and its influence on the interphase region of composites. *Journal of applied polymer science*, 10, 1002.

[7] Chen, P., Yu, Y., Lu, L. 2005. Research progress in the interface of fiber reinforced polymer matrix composites. *Fiber composites*, (1), 53-59.

[8] Mallarino, S., Chailan, J.F., Vernet, J.L. 2005. Glass fibre sizing effect on dynamic mechanical properties of cyanate ester composites I. Single frequency investigations. *European Polymer journal*, 41 (8), 1804-1811.

[9] Zhijian, Z., Jianzhong, Z. 2011. The influence of sizing agent and molding process on the properties of glass fiber. *Glass Fiber*, 4, 18-22

[10] Weimin, Z., Lihong, W., Bingxiang, D. 2000. Zhou Juxing Emulsification of Unsaturated Polyester Resins Thermosetting Resins, 15 (3).

[11] Fangqiang, L.S.F., Hu, Z. 2012. Cai Preparation and Properties of Environmentally-friendly Two-component Aqueous Polyurethane Waterborne Polyester Dispersion Plating and finishing. 36, 22.

[12] Xiangfu, L., Jianfu, C. 2010. Influence of Particle Size of Waterborne Polyurethane Emulsion. *Dye and Dyeing*, 47 (3), 47-49.

ABOUT THE AUTHORS

Zhenyu Wang (1994-) male, graduate student, The main research direction is fiber interface modifier.

Chuncai Yang (1968-) male, Thousand Talents Program Specifically-Invited Expert.

