Contents List available at VOLKSON PRESS
New Materials and Intelligent Manufacturing (NMIM)
DOI : http://doi.org/10.26480/icnmim.01.2018.170.172
Journal Homepage: https://topicsonchemeng.org.my/

ISBN: 978-1-948012-12-6

PARTICLE SIZE CONTROLLABLE CATIONIC WATERBORNE POLYURETHANE SIZING AGENTS BASED ON SELF-ASSEMBLED AND SELF-EMULSIFIED TECHNOLOGY

Jing Tian, Weilong Yang, Zhenyu Wang, Chuncai Yang*

Department of Chemistry, Jilin Institute of Chemical Technology, 45 Chengde Street, Jilin City
Corresponding Author Email: 2941883707@qq.com

ARTICLE DETAILS

Article History:

Received 26 June 2018
Accepted 2 July 2018
Available online 1 August 2018

ABSTRACT

A light blue transparent cationic waterborne polyurethane emulsion was prepared by self - assembled and self-emulsified technology. By changing the ratio of hydrophobic and hydrophilic raw materials, the particle size of the waterborne polyurethane emulsion could be controlled as a film former in sizing agents used in the production of carbon fiber，glass fiber and basalt fiber. The polyurethane emulsion was analyzed by Fourier transform infrared analysis, thermogravimetric analysis, particle size analysis and centrifugal stability analysis. Cationic waterborne polyurethane emulsion with a small particle size have good emulsion stability and superior film forming properties prevented it from migrating with water when continuous sized fiber tow is drying. The fibers sized with cationic waterborne polyurethane enhance fiber's heat resistance, dustproof performance, filament tensile strength, wetting and interfacial adhesion with resin matrix as well as suppressing the occurrence of monofilament fracturing and wool yarn, etc.

KEYWORDS

Self-assembled, self-emulsified, particle size controllable, cationic waterborne polyurethane, sizing agent.

1. INTRODUCTION

In recent years, with the emphasis on new materials, the application of fiber and composite materials has gradually increased. However, the research and development of fiber auxiliaries in a world is not perfect, which restricts the application of fiber. Glass fiber is a reinforced material with high strength, low expansion, corrosion resistance, electrical insulation, easy to burn and so on. But its brittleness, wear resistance, easy to take static electricity after friction, poor processing performance, when used as resin matrix reinforced material, the wettablity and adhesive property with resin matrix is poor. Basalt continuous fiber is another kinds of inorganic fiber, which not only has high strength, but also has many excellent properties, such as electrical insulation, corrosion resistance, high temperature resistance and so on. However, the share of basalt fiber reinforced composite product on market have not achieved a great breakthrough because of problems of high performance fluctuation, unclear process route and imperfect standard system. Carbon fiber is the third kinds of inorganic fiber, which has excellent mechanical properties and is regarded as a new material in the 21 st century. Because of its high modulus, high strength, small specific gravity, high temperature resistance, fatigue resistance, corrosion resistance and a series of excellent properties, the composite materials formed with advanced resins in the modern aerospace cutting-edge technology field, sports and leisure products, civil construction, electronic products, medical devices and other fields have a wide range of applications [1,2]. Carbon fiber is a brittle material, in the process of production and processing of carbon fiber composite materials, the fiber strength is reduced due to mechanical friction, which is easy to produce wool yarn and mono-filament fracture. The existence of wool yarn affects the carbon fiber's wettablity with resin matrix and lead to generate lots of pores inside carbon fiber composite materials and thus to affect the mechanical properties of composite materials [3]. In order to improve the filament fracture of carbon fiber, a coating of slurry and sizing agent is often applied on the carbon fiber surface [4,5]. Therefore, the development of new fiber AIDS has become a major concern.

The most important component of fiber auxiliaries is the film forming agent, which is also the key part. The performance of the film forming agent has a great influence on the performance of the auxiliary. It can be said that changing the performance of the film forming agent can affect the performance of the additive [6,7]. Therefore, the film forming agent is now the main research work. Polyurethane (PU) based film forming agent has the characteristics of flexible, flexible membrane, strong bond strength, etc. Due to its good elasticity and strong strength, PU has a good protective effect on the fiber, especially in the chopped fibers and it ensures the integrity of the chopped fiber yarn. This article mainly studies the synthesis, properties and application of cationic waterborne polyurethane emulsion as a film former of sizing agents [8]. The cationic polyurethane modified by hydrophobic and hydrophilic molecular components were intended to optimize the inferfacial wettability and adhesion properties of the fibers with resin matrix [9].

2. EXPERIMENTAL REAGENTS AND INSTRUMENTS

2.1 Experimental reagents

Polypropylene glycol, industrial purity, molecular weight 1000 (Jiangsu Hai'an Petrochemical Plant). Polytetrahydrofuran glycol(PTMG), industrial purity, molecular weight 2000 (Guangdong Zhongpeng Chemical Co., Ltd.). 1 , 4-butanediol / 1 ,6-hexanediol, analytical pure (Shanghai Titan Technology Co., Ltd.). Toluene 2,4- diisocyanate(TDI)/ Isoflurone diisocyanate(IPDI), reagent grade (Jining HuaKai Resin Co., Ltd.). N-methyldiethanolamine: analytical purity (Guangdong Wengjiang Chemical Reagent Company). Glacial acetic acid, analysis pure (Tianjin Damao chemical reagent factory). Diethanolamine, analytical pure (Tianjin Yongda Chemical Reagent Co., Ltd.). Epoxy resin, industrial grade (Hongmaofa Chemical Raw material Distribution Office, Heping District, Shenyang). Octadecyl Acrylate, reagent Grade (Qingdao Renas Polymer material Co., Ltd.). Oleic Acid, analytical Pure (Tianjin Daimao Reagent Co., Ltd.). N-Methyl pyrrolidone (NMP), analytical pure (Tianjin Yongda

Chemical Reagent Co., Ltd.). Acetone, reagent Class (Tianjin Outer Ring Chemical Co., Ltd.).

Intermediate 1: made in laboratory from the reaction of epoxy resin and oleic acid.

Intermediate 2: made in laboratory from the reaction of octadecyl acrylate and diethanolamine.

2.2 Experimental and analytical testing instruments

Heating sleeve, reaction kettle 250ml / 500ml, agitator, thermometer, dispersion tray, oven,4A molecular sieve, Fourier Infrared Spectrometer, ZetaPlusLaser Particle size Analyzer, TA Thermogravimetric Analyzer, HC3018 High Speed centrifuge, PerKinEimer DSC4000.

3. SYNTHESIS OF CATIONIC WATERBORNE POLYURETHANE

3.1 Basic principles of synthesis

By optimizing the hydrophilic and hydrophobic molecular structure design of cationic waterborne polyurethane, a series of polyurethane film forming agents were developed. The film forming agent can be formulated into sizing agents with coupling agents, lubricant, antistatic additives, etc. The sizing agents were used in the production of carbon fiber, basalt fiber and fiberglass. The cationic waterborne polyurethane emulsion synthesized in this article is of the characteristics of self - assembly, self - emulsification and particle size control. The series of experiments are used to optimized sizing agent's compatibility with carbon fiber, basalt fiber and glass fiber to enhance the fiber's wetting and adhesion with resin matrix.

3.2 Synthesis step

The synthesis method of cationic waterborne polyurethane emulsion with self-emulsification and controllable particle size is as follows:

(1) Several polyether or polyester polyol, small molecular diols, intermediate 1 or intermediate 2 and NMP were added to the reactor. In the inert gas atmosphere, the mixture was stirred to 120 °C for 2 hours.

(2) After moisture removal, the temperature dropped to between 35°Cand 40°C, the diisocyanate was added slowly, and then gradually increased reaction temperature to 70°C~ 72°C. The dibutylamine titration method was carried out for determining if isocyanante reaction reached the calculated value.

(3) Lowering reaction temperature to 35°C~ 40°C, adding solvent acetone to reduce viscosity, then adding diethanolamine as a chain extender, reacting in the presence of dibutyltin dilaurate as catalyst for a few hours until the titration results of isocyanate reached the calculated value. Adding acetic acid as salt forming agent to neutralize reaction. Finally waterborne polyurethane emulsion was prepared by adding distilled water and emulsifying under stirring.

3.3 Six samples of cationic waterborne polyurethane emulsion

Synthesis of six samples were outlined as follows: Sample 1 and sample 2 were made by using 70% 1, 4-butanediol and 70% 1, 6-hexanediol mixing with 30% polypropylene glycol (MW 1000) in mole respectively. Sample 3 and sample 4 were prepared similarly with sample 1, but intermediate 1 and intermediate 2 were separately added about 20% in weight replacing partial mixture of 1,4-butanediol and polypropylene glycol. Sample 5 and sample 6 were synthesized by using polypropylene glycol and polytetrahydrofuran glycol individually. The other reaction reagents such as diisocyante, chain extender and salt forming agent were same in the preparation of six samples.

4. EXPERIMENTAL RESULTS AND DISCUSSION

4.1 FT-IR spectral analysis

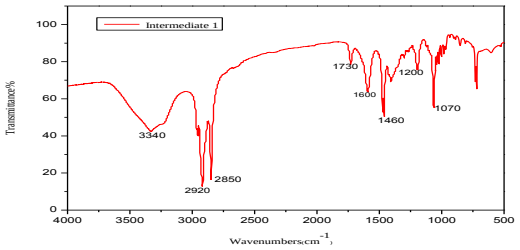

Figure 1: FTIR spectra of Intermediate 1

In figure 1, Absorption peak near 3340cm-1 and 1070cm-1 was -OH and C-O of secondary alcohol, absorption peak near 2920cm-1 and 2850 cm-1 was C-H of CH3 and CH2 individually, C=O absorption peak near 1730cm-1 and C-O absorption peak near 1200cm-1 confirmed that intermediate 1 was an ester , and absorption peak near 1630cm-1 proved that intermediate 1 contained C=C double bond of chain segment of oleic acid, while no characteristic peaks representing acid(COOH) and epoxy ($H_2C\overset{O}{\frown}CH_2$) was observed. All strong absorption peaks in figure 1 indicated that intermediate 1 was synthesized successfully.

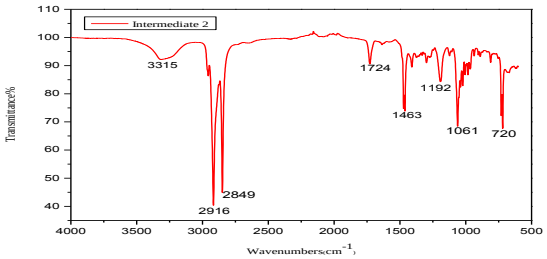

Figure 2: FTIR spectra of Intermediate 2

In figure 2, Absorption peak near 3315cm-1, 1463cm-1 and 1061cm-1 was -OH and C-O of primary alcohol. Absorption peak near 2916cm-1 and 2849 cm-1 was C-H of CH3 and CH2 individually, C=O absorption peak near 1724cm-1 and C-O absorption peak near 1192cm-1 confirmed that intermediate 2 was an ester. The absorption peak near 3350~3310cm-1, 1580~1490cm-1 and 1350~1280cm-1 representing secondary amine and 1630cm-1 C=C absorption peak were missing, which indicates that the intermediate 2 had been synthesized.

4.2 Characterization of particle size of cationic waterborne polyurethane emulsion

Table 1: Particle size and polydispersity

Sample	particle size	polydispersity
	D(nm)	D1/2
1	31.1	0.156
2	38.8	0.302
3	27.6	0.215
4	25.9	0.229
5	39.4	0.180
6	270.9	0.196

It can be seen from Table 1 that the particle size of sample 2 is larger than sample 1 because 1,6-hexanediol is more hydrophobic than 1,4-butanediol. The particle size of Sample 3 and sample 4 do not change much compared with sample 1 because intermediate 1 and 2 was not added enough. The particle size of sample 6 is much larger than sample 5 because polytetrahydrofuran glycol is much more hydrophobic than polypropylene glycol. In summary , the particle size of cationic waterborne polyurethane emulsion could be adjusted to meet the requirements of sizing agents by optimizing the molecular design of hydrophobic and hydrophilic chain segment.

4.3 The thermal stability study of Cationic waterborne polyurethane

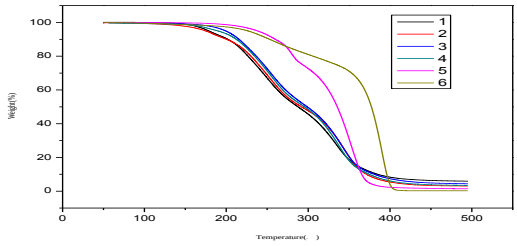

Figure 4: Thermogravimetric analysis

It can be seen from figure 4 that sample 5 and sample 6 have better heat resistance because chain segment containing polypropylene glycol and polytetrahydrofuran glycol has better heat resistance. Sample 3 and 4 has improved heat resistance compared with sample 1 because intermediate 1 and 2 replaced 20% mixture of 1,4-butanediol and polypropylene glycol in sample 1.

The heat resistance of polyurethane materials can be optimized by molecular design and the structure of macromolecules. Because the thermal resistance of polyether is better, the more polyether glycol added, the better the softness and heat resistance of polyurethane has.

4.4 Emulsion stability of cationic waterborne polyurethane

Six samples were stored at room temperature for one year and observed no precipitation or stratification. Emulsion stability was also studied by centrifugation for 30 minutes at 3000r/min, the testing results of six samples shown in figure 4a and 4b had no change before and after centrifugation, indicating that and emulsion stability of cationic waterborne polyurethane is stable.

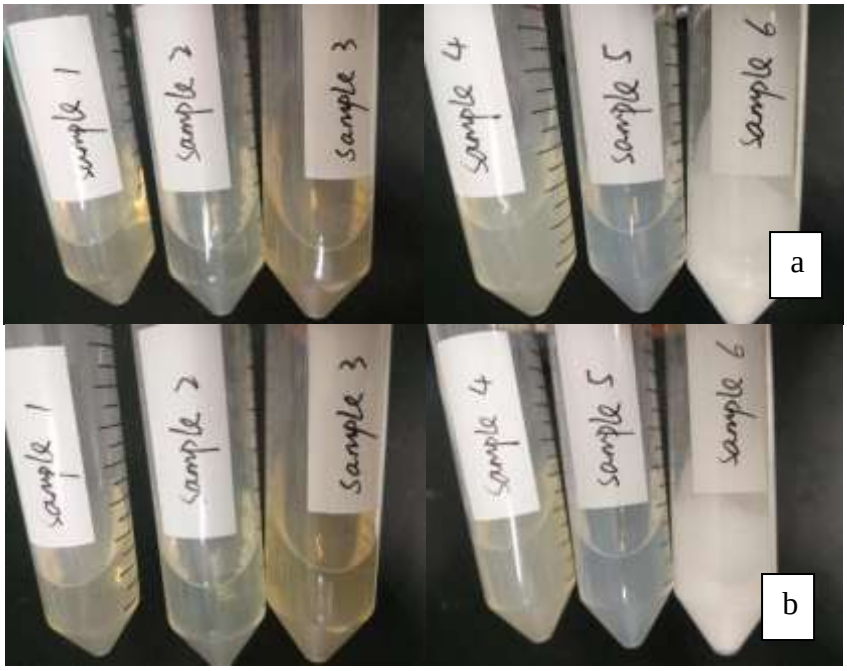

Figure 4: a) Before centrifugation, indicating that and emulsion stability of cationic waterborne polyurethane, b) After centrifugation, indicating that and emulsion stability of cationic waterborne polyurethane

5. CONCLUSION

In this article a series of cationic waterborne polyurethane emulsion were prepared based on self-emulsion and self-assembly technology. The particle size of polyurethane emulsion had been controlled within 25nm to 280nm and its hydrophobic-hydrophilic properties were tailored based on molecular structure design, which makes it suitable for film former of sizing agents applied for different kinds of inorganic fibers, for example sample 1 was much high hydrophilic and appropriate for film former of sizing agent used in production of glass fiber and basalt fiber; the sample 3 and 4 were much high hydrophobic , therefore better compatible with carbon fiber. The emulsion stability and thermal stability of six series of polyurethane emulsion had been studied and confirmed that cationic waterborne polyurethane emulsion synthesized in this paper was suitable fiber auxiliary as well. In the later article, the physical and mechanical properties of sized fiber and its composite with resin matrix will be reported separately.

REFERENCES

[1] Chen, D., Shujing, Z. 1995. Study and present situation of carbon fiber [J]. Industrial Textiles, (1), 23.

[2] Ogawa, H., Shima, M. 1983. Emulsion type sizing agent for carbon fibers process and its preparation, and method for using Same: US ,US 4420512[P], 12-13.

[3] Liu, H., Xiangsheng, W., Hueqing, S. 2016. Anhui chemistry. Research Progress of sizing Agent for carbon Fiber [J]. 2 (24), 11.

[4] Guan, R. 2002. Study on carbon fiber sizing agent [D]. Taiyuan: master thesis of Shanxi Institute of Coal Chemistry, Chinese Academy of Sciences .

[5] Xu, Y. 1992. Carbon fiber sizing agent [J]. Industrial textiles, 10 (4), 18-20.

[6] Tian, J. 1992. Female, graduate student, Jilin institute of chemical engineering, research field is glass fiber / basalt fiber infiltrating agent, carbon fiber sizing agent.

[7] Yang, W. 1992. Male, graduate student, Jilin institute of chemical engineering, research direction is carbon fiber amino modified finish.

[8] Wang, Z. 1994. Male, graduate student, Jilin institute of chemical engineering, research direction is carbon fiber amino modified finish.

[9] Yang, C. 1964. Male, expert of "thousand people" program specially hired by the state, special professor of Jilin Institute of Chemical Technology.