Advanced Materials Research *Online: 2012-12-13*
ISSN: 1662-8985, Vols. 610-613, pp 494-497
doi:10.4028/www.scientific.net/AMR.610-613.494

Preparation of waterborne epoxy resin emulsion

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Keywords: Epoxy resin, Self-emulsification, Water solubility

Abstract. Waterborne epoxy resin was prepared through introducing hydroxyl and carboxyl groups in the main chain of epoxy resin with the bisphenol epoxy resin, toluene diisocyanate and 2,2-dimethylol propionic acid by self-emulsification. Analyzed the structure of products via Fourier transform infrared spectrometer, then to test the water-soluble and stability. And the best conditions of reaction were determined through studying the influence of material ratio, reaction time and reaction temperature to products. The result shows that the synthesized waterborne epoxy resin has favorable stability and water-dispersion.

Introduction

The performance of epoxy resin is excellent， as a result of the existing of epoxy group, hydroxy and ether bond, which is widely applied to electron, machinery, transportation, building etc. However, epoxy resin is viscid solid or liquid, and it contains the relatively long nonpolar molecular main chain, so it is dissolved in organic solvents, such as alcohol, ketone and aromatic hydrocarbon, rather than water. As we know, many organic solvents pollute the environment badly because they are poisonous, volatile, inflammable and explosive. In the recent years, as health awareness and environmental consciousness gradually improve, products with non-volatile or low-volatile organics are concerned and researched widely.

In this paper, waterborne epoxy resin was prepared through introducing hydroxyl and carboxyl groups in the main chain of epoxy resin molecular with the bisphenol epoxy resin, toluene diisocyanate and 2,2-dimethylol propionic acid by self-emulsification. As a result, the waste of resources and environment pollution are avoided.

Experimental

Materials. Epoxy resin E-44, industrial products, LanXing New Material Wuxi Resin Corporation. Toluene diisocyanate, analytically pure, HongSheng Chemical Plant. 2,2-dimethylol propionic acid, analytically pure, GuangTuo Chemical Plant. Absolute ethyl alcohol, analytically pure, FuYu Fine Chemical Plant. Dibutyltin dilaurate, Chemical pure, GuangFu Chemical Industry Research Institute. N, N-Dimethylethanolamine, analytically pure, KeMiOu Chemical Plant. Dibutylamine, analytically pure, GuangFu Chemical Industry Research Institute.

Techniques. 28.4g E-44 and a certain amount of anhydrous alcohol were added in three necked flask with agitator, spherical condenser pipe and thermometer, then stirred till E-44 dissolved. After that, 15mL TDI and a spot of DBTDL were added. Make them reacting under low temperature. A period of time later, temperature was adjusted to around 50°C, then 13.4gDMPA was added in batches. After reacting for some hours, anhydrous alcohol was removed by the vacuum distillation. Add a certain amount of N, N-Dimethylethanolamine in the products to neutralize them to pH 7.0. Last, with stirring continuously, waterborne epoxy resin emulsion was prepared by adding dropwise of distilled water.

Performance Test.

Infrared Spectrum

The structures of the products were characterized qualitatively by IR. Sampling preparation: KBr wafer; the determination range was from 4000 to 400cm^{-1}; the resolving power was 8cm^{-1}.

Determination of isocyanato-content

Isocyanato-content was determined by di-n-butylamine method, then calculated the conversion rate of isocyanato.

Determination of the particle size

Emulsion was diluted with water to a certain concentration, then determined particle size distribution by laser particle size analyzer.

Determination of water solubility and stability

Some modified epoxy resin was added dropwise of distilled water with stirring continuously, then observed the dispersion. Placing statically for some time, observed whether it was stratified or precipitated.

Results and discussion

Infrared spectrum analysis

In Fig. 1, the FTIR spectra of E-44 and modified epoxy resin in the near range is presented. In the FTIR spectra of E-44 and modified epoxy resin, 913cm^{-1} and 830cm^{-1} assign the characteristic absorption peak of epoxy group. In the FTIR spectra of E-44, the wave number of 3485cm^{-1} indicates the vibration of -OH which in the main chain of epoxy resin molecular. However, in the FTIR spectra of modified epoxy resin, the absorption peak of 3380cm^{-1} resulted from the incoming hydroxyl; the wave number of 1693cm^{-1} indicates the vibration of C=O, and the strong peak at 913cm^{-1} answer for non-plane wagging vibration of hydroxyl, so carboxyl groups exists in the modified epoxy resin. In the FTIR spectra of modified epoxy resin, 3290cm^{-1} assign the characteristic absorption peak of N-H, and 1330.55cm^{-1} assign the characteristic absorption peak of C-N. These data explain that the hydroxyl and carboxyl groups exist in the main chain of epoxy resin.

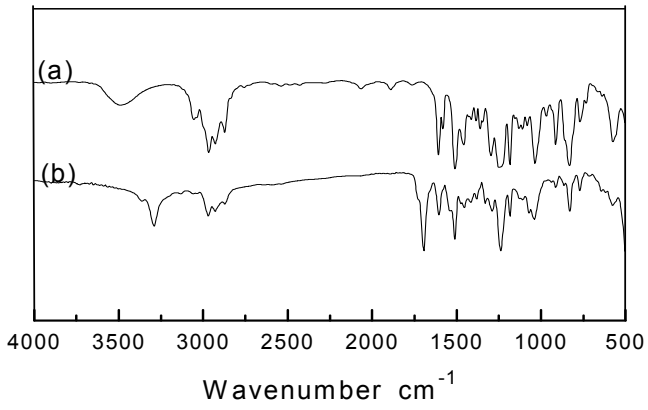

Fig.1 FTIR spectra of E-44 (a) and product (b)

Particle size distribution

In Fig. 2, particle size distribution of waterborne epoxy resin was presented. It shows that the average particle size of products is 240nm.

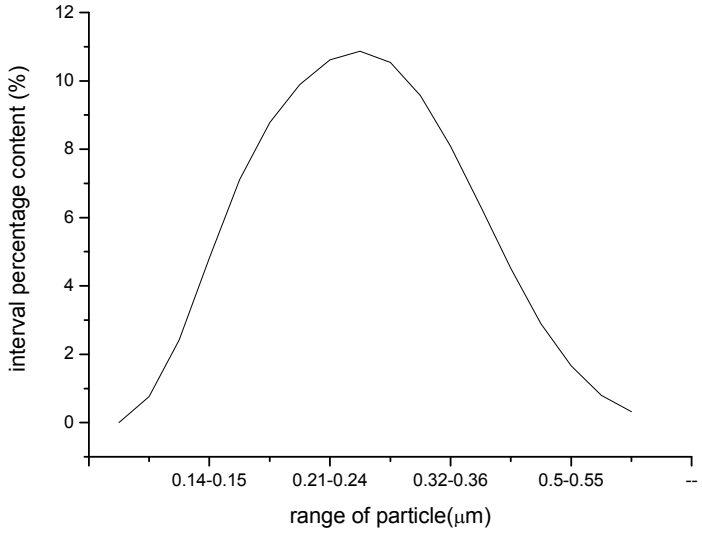

Fig.2 Particle size distribution of product

Water solubility and stability

As hydroxyl and carboxyl groups were introduced in, the synthesized waterborne epoxy resin has favorable water-dispersion. Test results were presented in Table1. V_1 is volume of modified epoxy resin, V_2 is volume of water.

It could be observed that modified epoxy resin has favorable water-dispersion and stability when the volume fraction of water and modified epoxy resin was no more than 3:1.When it is over 3:1, the stability was decreased.

Table 1 Testing results of stability and dispersity

	appearance	stability
1:1	White ropiness emulsion	homogeneous phase for over 3 months
1:2	White ropiness emulsion	homogeneous phase for over 3 months
1:3	White emulsion	homogeneous phase for over 3 months
1:4	White emulsion	homogeneous phase for 17 days
1:5	White emulsion	homogeneous phase for 6 days
1:6	White emulsion	homogeneous phase for 1 days

Discussion on the Synthesis Conditions

The effect of the temperature, time and material ratio on reaction were investigated by orthogonal experiment. Orthogonal experiment and experimental data are presented in Table2.

Through orthogonal experiment we can summarize that temperature has a great effect to experimental results, then time, and last is material ratio. The optimum condition is as follows: reaction temperature was 60°C, reaction time was 5 hours, n(E-44):n(TDI):n(DMPA) was 1:1.2:1.2.

Table 2 Orthogonal experiment and experimental data

Experimental	Temperature(°C)	Time (h)	material ratio	conversion rate of isocyanato (%)
1	40	3	1:1:1	95.1
2	40	4	1:1.2:1	96.6
3	40	5	1:1.2:1.2	98.2
4	50	3	1:1.2:1	91.2
5	50	4	1:1.2:1.2	93.5
6	50	5	1:1:1	94.7
7	60	3	1:1.2:1.2	97.8
8	60	4	1:1:1	96.3
9	60	5	1:1.2:1	97.0
K_{1j}	289.9	284.1	286.1	——
K_{2j}	279.4	286.4	284.8	——
K_{3j}	291.1	289.9	289.5	——
k_{1j}	96.6	94.7	95.4	——
k_{2j}	93.1	95.5	94.9	——
k_{3j}	97.0	96.6	96.5	——
R_i	3.9	1.9	1.6	——

Conclusion

The optimum reaction conditions were investigated by orthogonal experiment, which the proportion of Epoxy resin, Toluene diisocyanate and 2, 2-dimethylol propionic acid was 1:1.2:1.2, react temperature was 60°C, react time was 5 hours. The conversion of isocyanato could be 98%.

The epoxy resin that modified by toluene diisocyanate and 2, 2-dimethylol propionic acid had good water-dispersion. As a result, the waste of resources and environment pollution are avoided.

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