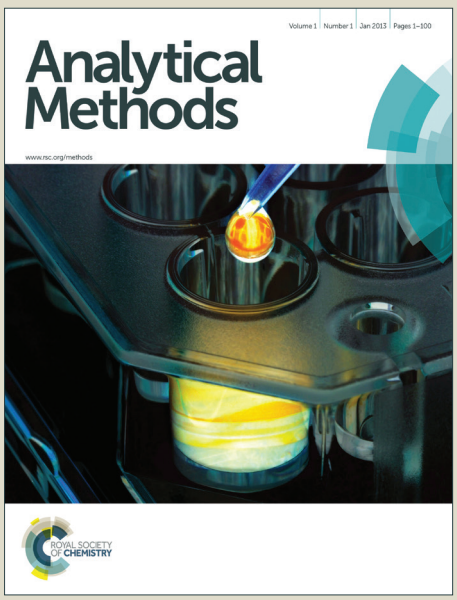
Analytical Methods

Accepted Manuscript



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Ultrasonication-assisted Rapid Determination of Epoxide Value in Polymer Mixtures Containing Epoxy Resin

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Abstract

Relatively long time is required to determine the epoxide value of an epoxy resin or epoxy compound by chemical analysis (titration) method, including the commonly used hydrochloric acid - acetone method which may refer to as hydrochloric acid -acetone-standing method, because the mixture of epoxy resins or epoxy compounds, hydrochloric acid and acetone must be left on standing in the dark for at least 30 min. In this study, ultrasonication was first introduced in this method aiming to rapidly determine the epoxide value of an epoxy resin by accelerating the dissolution of epoxy resin in acetone solvent as well as the reaction between epoxide groups and hydrogen chloride. Further study of this approach was then carried out to determine the epoxide values of a series of epoxy resin/polyethylene glycol mixtures. This new approach which may refer to as hydrochloric acid-acetone-ultrasonication method provides a much faster and more accurate measurement on epoxide value of an epoxy resin (within 2 min.) or its mixture with polyethylene glycol (PEG-4000, within 5 min.), compared to the hydrochloric acid-acetone-standing method. Ultrasonication

method may be readily extended to other chemical analysis (titration) methods.

Keyword：Epoxide value，Hydrochloric acid-acetone method，Ultrasonication

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1. Introduction

Epoxy resins have been a very important class of thermoset polymer materials and found its wide applications in coatings, adhesives, composites, functional polymeric materials such as chelating resin, etc., due to its attractive properties such as low shrinkage, solvent and chemical resistance, good mechanical and electrical properties, etc.

Epoxy resins are low molecular weight pre-polymers or higher molecular weight polymers which normally contain at least two epoxide groups. These epoxide groups are very active and may have simple reaction with various crosslinking agents, such as amines, hydroxyls, carboxyls, etc., to produce materials with different properties. Therefore, it is crucial to control or to know the epoxide content during production of epoxy resins or formulation of a specific product involving epoxy resins in which various crosslinking agents in stoichiometric proportions are required.

Epoxide content is commonly expressed as the epoxide equivalent weight (EEW). The EEW is defined as the weight in grams of an epoxy resin containing one mole equivalent of epoxide (g/mol), i.e., one gram-equivalent of epoxy. Therefore, the EEW is one-half the average molecular weight of a diepoxy resin (an epoxy resin with

two end epoxide groups) and one-third the average molecular weight of a triepoxy resin (an epoxy resin with three end epoxide groups)[1]. Epoxide content is also identically commonly expressed as the epoxide value (number) in industry, which is the number of epoxide equivalents in 1 kg of resin (eq./kg), or customarily 100 grams of resin (eq./100g) as used in this study.

Chemical and spectral analyses are commonly used in determining the epoxide equivalent weight, along with pyrolysis gas chromatography[2] and gel permeation chromatography (GPC)[3]. In spectral analysis, techniques such as infrared (IR)[4-6], near-infrared (NIR)[7] and nuclear magnetic resonance spectroscopy (NMR)[1,3,8] are frequently applied. Unfortunately, they work effectively only when the system contains just one compound. Analytical disturbance occurs when the absorption band which is assigned to determine the epoxide equivalent weight overlaps with other bands from multiple compounds. Besides, high-cost instruments and/or facilities are needed when spectral analysis or analytical techniques such as pyrolysis gas chromatography and GPC are used. Furthermore, the methods determining epoxide equivalent weight involving such expensive instruments may not be applicable for the real-time monitoring of a reaction between epoxy resin and other materials in industry or a lab when short sampling interval is required.

More widely accepted in industry, chemical (titration) analysis contains a variety of methods including hydrochloric acid - acetone method[9], hydrochloric acid - pyridine method[9], hydrogen bromide - glacial acetic acid method[10], perchloric acid-tetraethylammonium bromide method[11], etc. These chemical (titration) analysis

methods are based on the stoichiometric addition reaction between hydrogen halide and epoxide group of an epoxy resin or compound which is often dissolved in a solvent.

Among these methods, hydrochloric acid-acetone method receives more attention due to its relatively simple operation process, lower price and lower toxicity of the reagents. Nevertheless, this method which may refer to as hydrochloric acid-acetone-standing method has an obvious disadvantage, namely a long operation circle in which the mixed samples must be placed in the dark for at least 30 minutes[9]. Apparently, this method, as well as the other chemical analysis (titration) methods, is not applicable for the real-time monitoring of epoxide value in the actual production process when the sampling interval is shorter than that. This is one of the two problems occurred recently when we were trying to track the extent of reaction between epoxy resin and polyethylene glycol (PEG) using hydrochloric acid-acetone-standing method. The other problem is that error and consistency of the results were well-below expectation, which we found later was attributed to the fact that the samples were the mixture of epoxy resin and PEG instead of pure epoxy resin. To shorten the test cycle and achieve real - time monitoring, we introduced ultrasonication into hydrochloric acid-acetone-standing method. Correspondingly, the new approach may refer to as hydrochloric acid-acetone-ultrasonication method. A series of experiments with various constituents of epoxy resin/PEG, including pure epoxy resin E-44, mixture of E-44 and low molecular weight PEG (PEG-200) and mixture of E-44 and high molecular weight PEG (PEG-4000), were carried out to test

the efficiency of this new method.

2. Experimental

2.1 Materials and Instrumental

Epoxy resin E-44 was supplied by SINOPEC Assets Management Corporation Baling Petrochemical Branch.. PEG-200 and PEG-4000 were obtained from Hai'an Petrochemical Company, China. The other reagents used were analytical regents, and purchased from Sinopharm Chemical Reagent Co., Ltd.

Hydrochloric acid - acetone solution was prepared based on the volume ratio of hydrochloric acid/acetone, and stored in a glass bottle in case of need.

Mixed indicator was prepared by mixing 0.1% cresol red solution and 0.1% thymol solution at volume ratio of 1:3, and then adjusting pH to neutral with 0.01 mol/L sodium hydroxide aqueous solution.

Ultrasonification instrument was purchased from Shanghai Yuzheng Instrument Co., Ltd.

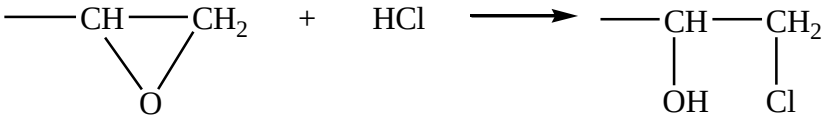
2.2 Procedure

Into a conical flask with ground glass stopper weigh a certain amount of samples (accurate to 0.0001 g). Subsequently, add 10 mL hydrochloric acid-acetone solution into the flask and stopper. The flask was then left in a digital ultrasonification cleaner at room temperature for some time. After dissolution of the samples, 3-5 drops of mixed indicator were added into the flask and the solution was titrated with NaOH standard solution to purple-blue color which does not fade within 5 seconds. Blank

experiment in which no samples were dissolved in the hydrochloric acid-acetone solution was done in the same way. Each set of data was measured three times and the average value was taken as the end result.

2.3 Calculation of epoxide value

Back titrations are used to determine the epoxide value; the excess hydrochloric acid is titrated by NaOH after the addition reaction of epoxide group with HCl.



Epoxide value was calculated by the following formula:

$$\text{Epoxide value } (EV) = \frac{(V_0 - V) * N}{W * 10}$$

where, V_0 is the volume (mL) of NaOH standard aqueous solution consumed by hydrochloric acid-acetone solution with no dissolved sample, V is the volume (mL) of NaOH standard aqueous solution consumed by hydrochloric acid-acetone solution with dissolved sample, N (mol/L) is the concentration of NaOH standard aqueous solution, W is the mass (g) of the sample.

The standard error can be obtained by:

$$\text{Error} = \frac{EV\text{-}EV_0}{EV_0} * 100\%$$

where, EV is the measured epoxide value and EV_0 is the theoretical epoxide value.

3 Results and Discussion

3.1 Determination of the epoxide value of the epoxy resin E-44 by hydrochloric acid-acetone- ultrasonication method

Before the determination of epoxide value of the epoxy resin E-44 by hydrochloric acid-acetone-ultrasonication method, the epoxide value of E-44was first obtained by the commonly used hydrochloric acid-acetone-standing method. The experimental conditions were as follows: the volume ratio between hydrochloric acid/acetone was set as 1:40, the molar concentration of the aqueous solution of NaOH was 0.15M, the sample used for each measurement was about 0.3g, and the mixture of sample with 10 mL hydrochloric acid-acetone solution was left in dark for 30min, all as required by the standing method itself.[9] The obtained epoxide value (0.4751) is taken as the theoretical one (a constant) and will be compared with that obtained by the ultrasonication method.

Interestingly, it was found that it only took less than 1 min. for E-44 to be dissolved in hydrochloric acid – acetone solution under the assistance of ultrasonication. It is also of note that the escaped amount (0.42% for 2min. and 0.67% for 5min.) of HCl (and acetone) is negligible under the experimental conditions. Fig. 1 shows the epoxide values of the same sample exposed to continued ultrasonication for different time after the dissolution of the sample, and the errors were listed in Table 1.

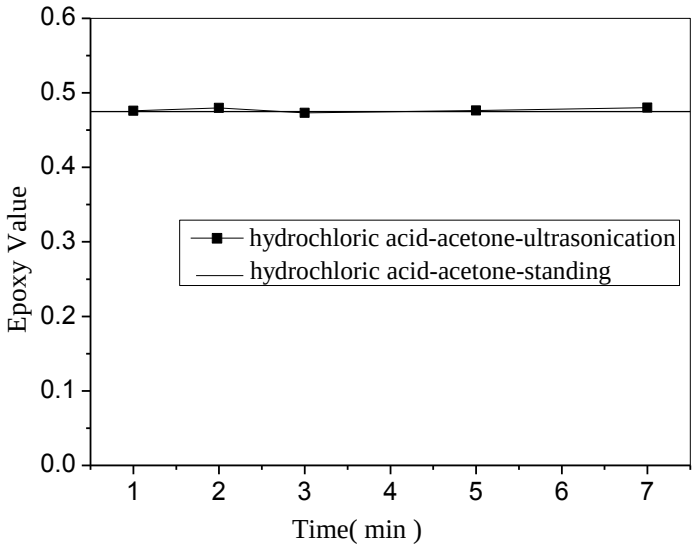


Fig.1 Effect of continued ultrasonication time after the dissolution of the sample on the epoxide value determined.

As seen from Figure 1 and Table 1, the results obtained from hydrochloric acid-acetone-ultrasonication method excellently meet with the value from hydrochloric acid-acetone-standing method, with less than 1% of error for experiments carried out within 5 minutes. This demonstrates that ultrasonication-assisted method successfully gave out remarkably accurate results within a much shorter time ($\leqslant$ 2 min.). With this encouraging result, we are moving to the determination of the epoxide value of a mixture containing epoxy resin and PEG-200.

Table 1 Standard errors of the epoxide values determined at different ultrasonication time after the dissolution of epoxy resin E-44

Ultrasonication time	Average EV	Error (%)
1 min	0.4758	0.15
2 min	0.4796	0.95
3 min	0.4732	-0.39
5 min	0.4762	0.23
7 min	0.4801	1.05

3.2 Determination of the epoxide value of E-44 in its mixture with PEG-200 by hydrochloric acid-acetone-ultrasonication method

PEG-200 was chosen here because it has a relatively small molecular weight and it can dissolve in hydrochloric acid-acetone solution along with E-44 at room temperature. In the mixture of epoxy resin and PEG-200, the mass percentage of epoxy resin is 13.85 wt%. The theoretical epoxide value would be 0.06580 (0.4751 × 13.85%). The effect of volume ratio of HCl/acetone was discussed. The volume ratio of HCl/acetone varied from 1:30, 1:40, and 1:60 to 1:80. The concentration of NaOH standard aqueous solution was 0.15 mol/L, and the mass of the sample was about 1.5g. It took less than 1 min. for the mixture to be dissolved in hydrochloric acid – acetone solution under the assistance of ultrasonication. Fig. 2 shows the epoxide values of the same sample exposed to continued ultrasonication for different time after its dissolution. The errors were listed in Table 2.

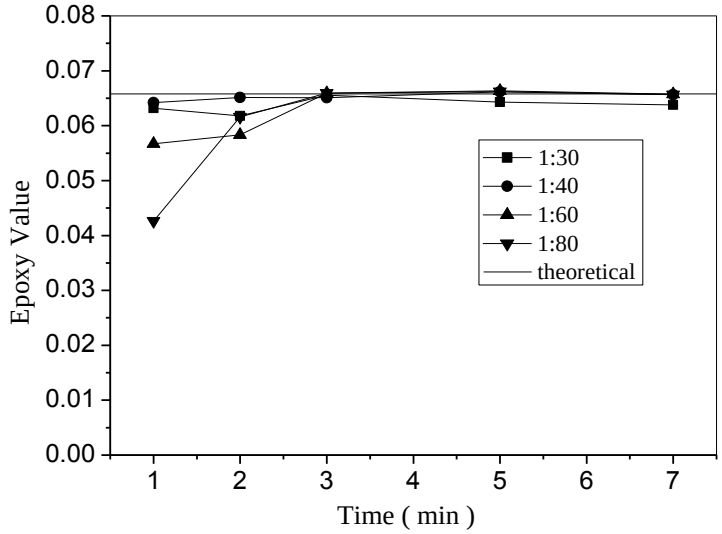


Fig.2 Effects of the hydrochloric acid/acetone ratio and ultrasonication time on

the epoxide value after the dissolution of E-44/PEG-200 mixture

Table 2 Standard errors of the epoxide values determined under different hydrochloric acid/acetone ratio and at different ultrasonication time after the dissolution of E-44/PEG-200 mixture

Ultrasonication time		Hydrochloric acid/acetone ratio			
		1:30	1:40	1:60	1:80
1min	Average EV	0.06319	0.06422	0.05669	0.04261
	Error (%)	-3.96	-2.41	-13.85	-35.24
2min	Average EV	0.06177	0.06515	0.05834	0.06161
	Error (%)	-6.13	-0.99	-11.34	-6.37
3min	Average EV	0.06554	0.06509	0.06593	0.06591
	Error (%)	-0.40	-1.08	0.20	0.16
5min	Average EV	0.06428	0.06614	0.06636	0.06620
	Error (%)	-2.31	0.52	0.85	0.61
7min	Average EV	0.0638	0.06566	0.06574	0.06566
	Error (%)	-3.04	-0.22	-0.09	-0.22

It can be found from Fig. 2 and Table 2 that there are large errors for the epoxide values determined within the first two minutes after the dissolution of the sample. After three minutes, the standard errors are lower than 1%, except for the case when hydrochloric acid/acetone = 1:30, in which the excess percentage of HCl is 300%. There are probably two reasons behind the case when hydrochloric acid/acetone = 1:30. One is the larger volatilization of HCl during ultrasonic dispersion, and the other is the longer titration time required when more excess amount of hydrochloric acid was used. Both will result in the loss of HCl, which leads to the reduced amount of NaOH required. As a result, the calculated epoxide value is lower than the theoretical one. This may explain why one always finds a negative error in table 2 when hydrochloric acid/acetone = 1:30.

The above results indicate that very good analytical result can be obtained using hydrochloric acid-acetone-ultrasonication method when the continued ultrasonication time after the dissolution of the mixture is longer than three minutes and the hydrochloric acid/acetone ratio ≥ 1:40. In other words, the reliable epoxide value of the E-44/PEG-200 mixture may be obtained within 3 minutes of ultrasonication.

3.3 Determination of epoxide value of E-44 in its mixture with PEG-4000 by hydrochloric acid-acetone-ultrasonication method

In this measurement, epoxy resin E-44 accounts for 10 wt% of the mixture and the theoretical epoxide value is 0.04751 (0.4751 × 10%). Due to the much larger molecular weight of PEG-4000 compared to PEG-200, dissolution of the PEG-4000 sample along with E-44 in acetone took much longer time, i.e., about 5 min. When the volume ratio of hydrochloric acid/acetone was 1:60, the concentration of NaOH aqueous solution was 0.15 mol/L. When the volume ratio was 1:100 or 1:120, the concentration of NaOH aqueous solution was set as 0.08 mol/L. The mass of the sample was about 1.5 g. Fig. 3 shows the epoxide values of the same sample at different time of ultrasonication after its dissolution, and the errors were listed in table 3.

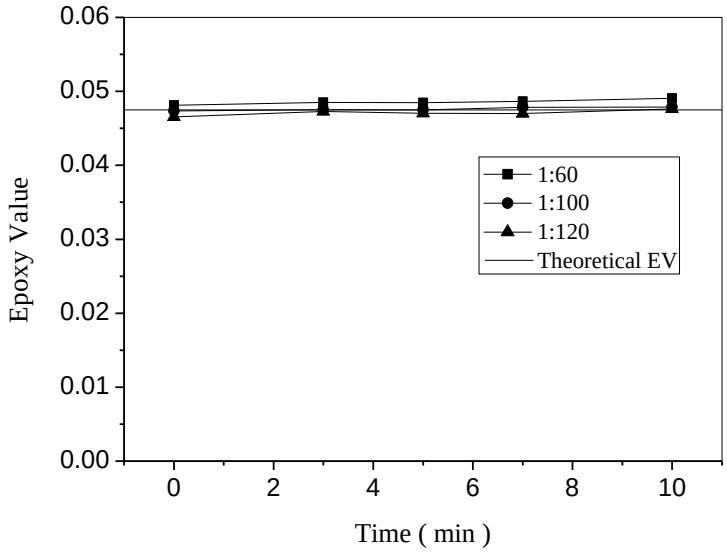


Fig.3 Effects of the hydrochloric acid/acetone ratio and ultrasonication time on the epoxide value after the dissolution of E-44/PEG-4000 mixture

Fig. 3 and Table 3 show that when the volume ratio of hydrochloric acid/acetone is 1:60, i.e., the excess percentage of HCl is 200%, the error of measurement is the largest. When the volume ratio of hydrochloric acid/acetone is 1:120 and the excess percentage of HCl is 50%, the error of measurement is smaller than that when the hydrochloric acid/acetone ratio is 1:60, but much larger than that when the hydrochloric acid/acetone ratio is 1:100 for the first 5 min. Only when the volume ratio of hydrochloric acid/acetone is 1:100 and the excess percentage is about 80%, the measured epoxide value is most close to the theoretical epoxide value and the errors in different time are less than 1%. It can be concluded that a total of 5 minutes is also enough to obtain a reliable epoxide value for the mixture of E-44 and PEG-4000 when the hydrochloric acid/acetone is 1:100.

Table 3 Standard errors of the epoxide values determined under different hydrochloric acid/acetone ratio and at different ultrasonication time after the dissolution of E-44/PEG-4000 mixture

Ultrasonication time		Hydrochloric acid/acetone ratio		
		1:60	1:100	1:120
1min	Average EV	0.04813	0.04734	0.04656
	Error (%)	1.30	-0.36	-2.00
2min	Average EV	0.0485	0.04753	0.04729
	Error (%)	2.08	0.04	-0.47
3min	Average EV	0.04848	0.04749	0.04702
	Error (%)	2.04	-0.04	-1.04
5min	Average EV	0.04864	0.04784	0.04699
	Error (%)	2.38	0.69	-1.09
7min	Average EV	0.04905	0.04789	0.04763
	Error (%)	3.24	0.80	0.26

It is of note that, in this study, when the volume ratio of hydrochloric acid/acetone ⩽1:80, the concentration of NaOH aqueous solution was set as 0.15 mol/L, and when the volume ratio ⩾1:100 (i.e., 1:100 and 1:120), the concentration of NaOH aqueous solution was set as 0.08 mol/L. This adjustment was done to ensure that the volume of NaOH aqueous solution consumed is not more than 20 mL during blank experiment, and not less than 5 mL during the measurement with the samlpe, so that higher accuracy of measurement may be achieved.

4. Conclusions

Compared to the hydrochloric acid-acetone-standing method, the hydrochloric acid-acetone-ultrasonication method provides a much faster and more accurate measurement on the epoxide value of a pure epoxy resin (within 2 min.) and the mixture of epoxy resin with polyethylene glycol (PEG-4000, within 5 min.) by

enhancing the dissolution of epoxy resin and its mixture with polyethylene glycol as well as the reaction between epoxide groups and HCl. As a result, real-time monitoring of the reaction between an epoxy resin and other materials such as polyethylene glycol becomes feasible. Ultrasonication-assisted dissolution and reaction may be extended to other chemical (titration) analysis methods.

Acknowledgements

Partial financial support from the National Natural Science Foundation of China (NSFC, No.21074087) and PAPD was kindly acknowledged.

References

1 J. G. Dorsey，G. F. Dorsey，A. C. Rutenberg，L. A. Green. *Anal. Chem.*, 1977, **49,** 1144-1145.

2 X. K. Yang，R. L. Chen. *Chinese Journal of Adhesives*, 1987, (3), 22-23.

3 S. A. Garea，A.C. Corbu，C. Deleanu，H. Iovu. *Polymer Testing*，2006, **25**,107-113.

4 Yu. M. Evtushenko，V. M. Ivanov，B. E. Zaitsev. *Journal of Analytical Chemistry*，2003, **58**, 347-350.

5 Y. S. Zhang，Y. S. You，K. J. Gong，X.W. Tan. *Chemical Analysis and Meterage*, 1995, **4** (1) : 18-21.

6 L. M. Gan. *Coating Industry*, 1984, (4), 47-48.

7 M. Pramanik，S. K. Mendon，J. W. Rawlins. *Polymer Testing*，2012，**31**, 716-721.

8 F. G. Garcia，B. G. Soares. *Polymer Testing*，2003, **22**, 51-56.

9 GB/T 1677-2008 (National Standard of China), Epoxide value Determination of Plasticizer.

10 J. Xiao, J. M. Chen, M. J. Sun, et al. *Thermosetting*，2006, **21** (5), 28-31.

11 GB/T 4612-2008 (National Standard of China), Epoxy Equivalent Determination of Plastic Epoxy Compound.

12 J. Liu，L. Tang，Y. Li. *Leather and Chemicals*, 2012, **29** (1), 26-27, 35.

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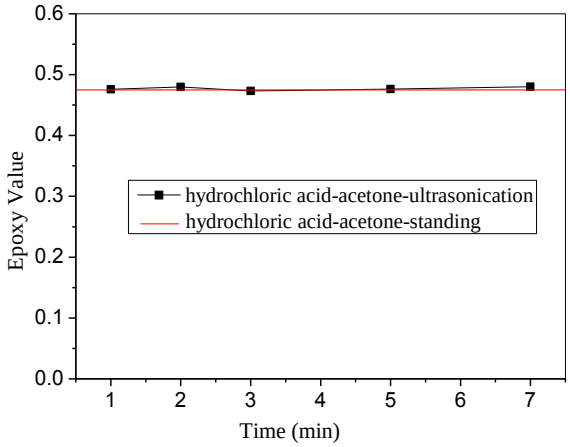

The hydrochloric acid-acetone-ultrasonication method provides a much faster and accurate measurement on epoxide value than the corresponding standing method.