Research on Curing Mechanism of Bisphenol-A Epoxy Resin by DSC

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Abstract: Curing reaction of bisphenol-A epoxy resin were researched by non-isothermal DSC. The experiment result showed that the cured structure were excellent when the proportion between the bisphenol-A epoxy resin DER331 and curing agent DEH622 was 100:30, the reaction heat was 358.53 J/g which is 4 to 9 times higher than the heat released by other different ratios. Initial curing temperature was 36.35°C which is the lowest among all different ratios, curing peak temperature was lower 10°C to 40°C than other proportion. Thus, optimum proportion between the DER331 epoxy resin and the DEH622 curing agent is 100:30.

Introduction

The epoxy resin matrix is epoxy oligomer, and its molecule comprises two or more reactive epoxy groups and cohesive hydroxyl, bisphenol-A skeletal structure which can provide durability and thermostability, methylene with flexibility, and chemical-resistant ether bond [1, 2, 3].The most typical chemical character of epoxy resin is high-reactivity of epoxy groups, which is caused by high deformability of the three-membered ring and polarization of charge. The charge deflection enhances reactivity of oxirane. Electron-rich oxygen atom is attacked firstly when electrophilic reagent approaches, electron-deficient carbon atom is attacked as nucleophilicity reagent approaches, and reaction occurs rapidly [4, 5, 6].

Curing reaction between the epoxy resin and amidogen belongs to typical SN2 nucleophilic addition reaction [7, 8]. Lone pair electrons of N atom attack electron-deficient β carbon atom of epoxy group, and ring-opening addition reaction occurs, as shown in Fig. 1.

Differential scanning calorimetry (DSC) is one of the most effective methods to research epoxy resin curing, including the isothermal method and non-isothermal method. Speculating its curing reaction mechanism by researching heat effect of epoxy resin curing reaction is essential to composite molding process and performance optimization [9].

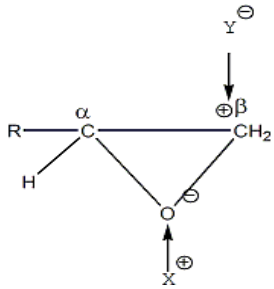

Fig. 1 Epoxy-opened reaction(X- electrophilic reagent; Y- nucleophilic reagent)

We select DER331 bisphenol-A epoxy resin and DEH622 modified amine as the curing agent, and utilize the non-isothermal DSC method to research curing kinetics process and reaction mechanism.

Experiments

Material and formulation

Material

DER331 bisphenol-A epoxy resin, colorless viscous liquid, epoxide equivalent 182-192g/eq., viscosity 11000-14000 cps@25°C, Shanghai Xinzhengxing International Trade Co., Ltd. of Dow Chemical;

DEH622 curing agent, low-temperature rapid amine curing agent, Shanghai Xinzhengxing International Trade Co., Ltd. of Dow Chemical;

Proportion between epoxy resin and curing agent is shown in Table 1.

Number	1#	2#	3#	4#	5#
Proportion	100:10	100:20	100:30	100:40	100:50

Table 1 Experiment proportion between epoxy resin and curing agent (weight of epoxy resin: weight of curing agent)

Experiment instruments and test

Differential scanning calorimeter: DSC-1, Swiss Mettler-Toledo International Inc., nitrogen atmosphere;

Test condition of curing agent dose: 50-260°C, determining the heating rate according to experiment requirements, 10K/min;

Results and discussion

DSC curve in a ratio of 100:10

When the ratio between epoxy resin and curing agent is 100:10, the whole DSC curve is shown in Fig. 2.

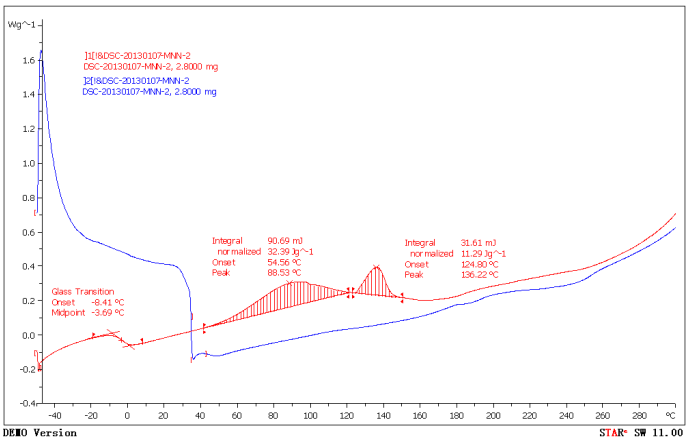

Fig. 2 DSC curve in the ratio of 100:10

Two small continuous exothermic peaks occur, in the first exothermic peak, initial temperature of the curing reaction was 54.56°C, the peak temperature was 88.53°C, total releasing heat is

90.69mJ, and average releasing heat was 32.39J/g, in the second exothermic peak, initial temperature was 124.80°C, the peak temperature was 136.22°C, total releasing heat was 31.61mJ, and average releasing heat was 11.29J/g.

DSC curve in a ratio of 100:50

DSC curve in the ratio of 100:50 appeared one exothermic peak and two endothermic peaks as showed in Fig. 3. The first endothermic peak was probably caused by evaporation of solvent or small molecules, it started to absorb heat at 41.78°C, endothermic heat was 18.46mJ, and average endothermic heat was 3.86J/g; the exothermic peak started to released heat at 48.90°C and peaked at 82.22°C, energy released in the whole exothermic process was 364.51mJ, average releasing heat was 76.26J/g, and the exothermic reaction terminated at about 120°C; the second endothermic peak started from 225.24°C to the peak of 262.64°C, and heat absorbed was 146.73mJ.

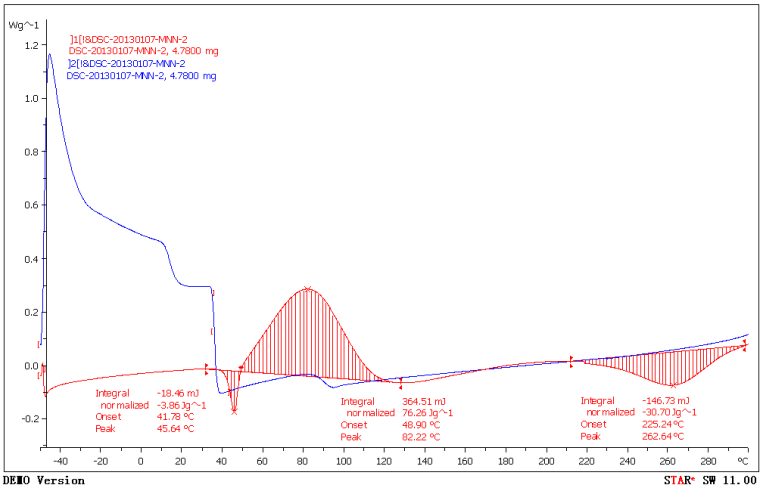

Fig. 3 Epoxy resin and curing agent in the ratio of 100:50

DSC curve in a ratio of 100:30

Compared with the two previous curves, the curve in the ratio of 100:30 was changed obviously, and the exothermic peaks were merged into a large one. Initial temperature of the exothermic peak was 36.35°C, and the exothermic peak temperature was 83.11°C. The exothermic peak shape conformed to the typical Gauss distribution law, and it indicated that the curing reaction rate also should conform to the characteristic of the Gauss distribution. The total releasing heat was 1326.57mJ, the average releasing heat was 358.53J/g, and average reaction rate was obviously accelerated. The secondary heating and cooling test were carried out to the cured compounds, the color of curve was blue, the glass transition plateau occurs at about 40°C, went on heating up, the temperature also presented the slightly upward trend compared with curve in the ratio of 100:10. It indicated its thermal stability was improved.

Conclusions

Among all the ratios,The curing reaction was carried out completely when the ratio was 100:30. The reaction heat was 358.53J/g which is 4-9 times higher than the heat released from other ratios. And the initial curing temperature was also the lowest, and it was 10-40°C lower than the initial reaction temperature of other ratios. The difference of curing peak temperature was relatively small,

and the temperature difference ranges from 1°C to 7°C. Thus, optimum proportion between DER 331 epoxy resin and DEH622 curing agent is 100:30.

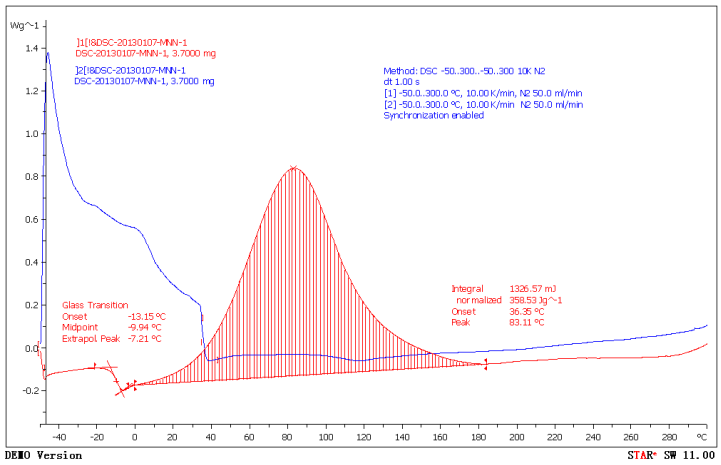

Fig. 4 Oxygen resin and curing agent in the ratio of 100:30

References

[1]Sun Manling, The Application Principle and Technology of Epoxy Resin [M]. Beijing: China Machine Press, 2003, 5-8.

[2]Hu Yuming, Wu Liangyi. Curing Agent [M]. Beijing: Chemical Industry Press, 2004, 112-115.

[3]Chen Ping, Liu Shengping, etc. Epoxy Resin and Application [M]. Beijing: Chemical Industry Press,2011.

[4]Liu Guangye, Zhao Juan, Research Development of Composite Damping Materials [J].Plastics Science and Technology, 38(6): (98-101)

[5]Zhang Ming, An Xuefeng, Tang Bangming, Yi Xiaosu. Cure kinetics and TTT diagram of a bicomponent high performance epoxy resin for advanced composites [J].Acta Materiae Compositae Sinica, 2006,(01):17-25.

[6]Li Heng, Wang Dehai, etc. Research of Epoxy Resin Curing Kinetics and its Application [J]. Fiber Reinforced Plastics/Composites, 2013(4):43-50

[7]Zhu Aishi, Zheng Chuanxiang, etc. Review of Matrix Solidification and Forming Processes of Composite Materials [J], Journal of Zhejiang University of Science and Technology, 2008,20(4):269-273.

[8]Ma Nannan, Zhao Juan, etc. The Characterization of Epoxy Value by Infrared Spectroscopy Method Combined with Chemical Analysis [J].Fiber Reinforced Plastics/Composites, 2013 (5):3-6

[9]Vyazovkin S.Thermal analysis [J]. Anal Chem, 2008, 80 (12):4301