

## NOTES

*Mass-Spectrometric Thermal Analysis of Impurities in Epoxy Resins*

## INTRODUCTION

Mass-spectrometric thermal analysis (MTA) has been widely applied to thermal decomposition of various substances.<sup>1</sup> We have made an attempt to apply MTA to analysis of residual solvents and impurities of epoxy resins, and some interesting results have been obtained. It is a new application of MTA to polymers. Epoxy resins are applied to encapsulation of various electronic parts and components. In the application, the impurities and their state in the resin are very important characters. The method would be useful for this application; the analysis of hydrochloric acid is especially interesting. In this note, we report these results.

## EXPERIMENTAL

Materials used are epoxy resins cured with aliphatic amines; epoxy resin is Epon 827 (Shell Chemical Co.), and amines are ethylenediamine (EDA) of E.P. grade, purchased from Wako Pure Chemical Industries, Ltd. and decamethylenediamine (DMDA), purchased from Aldrich Chemical Co., Inc.

Epoxy resin and DMDA are mixed in such a way that the number of active hydrogen atoms of the amine is equal to the number of the epoxide group, while twice that amount of active hydrogen is combined for EDA-cured resin. They are left for more than 24 hr to be cured at room temperature. Then the undercured resin is postcured at about 140°C for more than 24 hr. Powdered sample is obtained by filing the resin.

The MTA apparatus utilized is described elsewhere.<sup>2</sup> Briefly, the sample is heated at a constant rate of the sample container put beneath the ionization chamber of a time-of-flight mass spectrometer of the Bendix type. The pressure is less than  $10^{-5}$  torr. The volatilized products are analyzed immediately. Ionization voltage is 20 eV to prevent severe fragmentation, while 70 eV is utilized for the assignment of the spectrum, and 8–15 mg of the powdered sample is used.

## RESULTS AND DISCUSSION

Typical mass spectra are reproduced in Figures 1 and 2. In the temperature range from 40° to 140°C, ions of mass number ( $M/e$ ) 92, 91, 65, and 39 are observed. The ion of  $M/e$  92 is a parent ion of toluene, and the others are its fragment ions.<sup>3</sup> The ions of  $M/e$  60 and 30 are also found for EDA-cured resin, and they are a parent ion of ethylenediamine and its fragment ion, respectively. On the other hand, quite different ions are found in a high-temperature range from 100° to 290°C, that is, the ions of  $M/e$  36, 38, and 35. These are parent ions and fragment ion of hydrogen chloride.<sup>3</sup> Similar mass spectra are observed in the same temperature ranges for the DMDA-cured resin, but the unreacted curing agent is not detected. Thus, on heating, the residual solvent of the epoxy resin and the unreacted curing agent are volatilized first in the low-temperature range, and hydrogen chloride is then volatilized in the high-temperature range.

The MTA curves, which are plots of the ion currents versus temperature, for DMDA-cured resin are shown in Figure 3, and its dependence on the heating rate is seen in Figure 4 for  $M/e$  36. The plot of the logarithm of the heating rate against the reciprocal absolute peak temperatures gives a straight line, as seen in Figure 5. From the

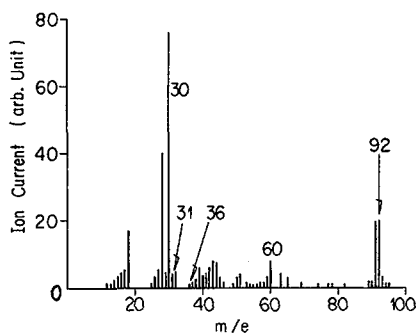


Fig. 1. Typical mass spectrum of EDA-cured resin observed at 70°C for heating rate of 1°C/min and ionization voltage of 70 eV.

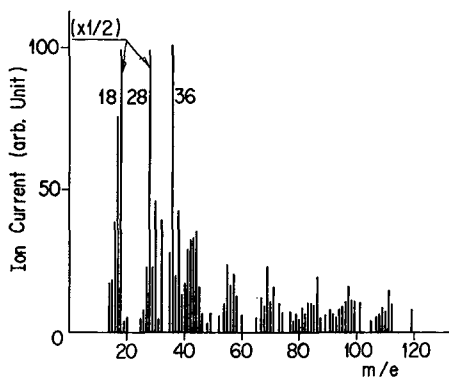


Fig. 2. Typical mass spectrum of EDA-cured resin observed at 190°C for heating rate of 1°C/min and ionization voltage of 70 eV.

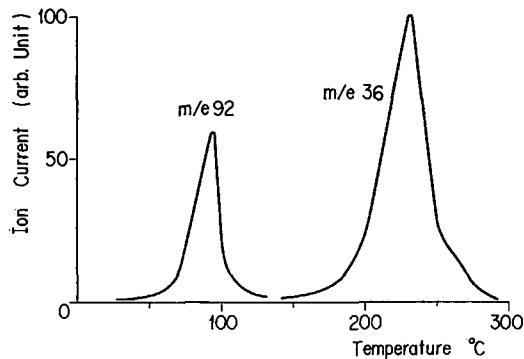


Fig. 3. MTA curve of DMDA-cured resin obtained for heating rate of 2°C/min.

slope and the intercept of the straight line, the activation energy and the preexponential factor of the reaction producing hydrogen chloride are estimated<sup>4</sup> to be 32.2 kcal/mole and 11.3 sec<sup>-1</sup>, respectively. The experimental master curve is drawn in Figure 6 by using the activation energy thus estimated. As is seen in Figure 6, the plots of different heating rates are on the same smooth curve. In Figure 6, the best-fitted theoretical

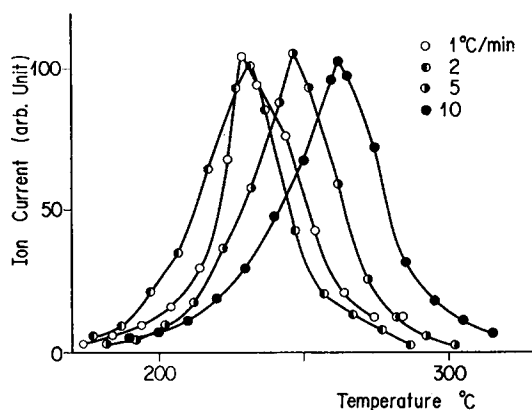


Fig. 4. MTA curves of DMDA-cured resin obtained for various heating rates for  $M/e$  36. The heating rate is indicated in the figure.

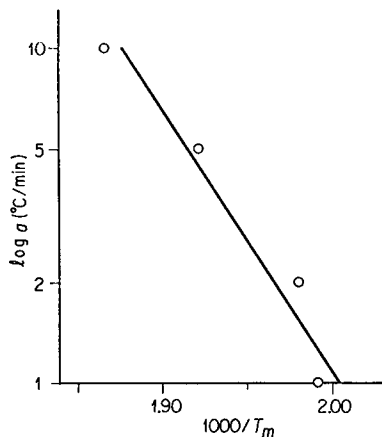


Fig. 5. Plot of logarithm of heating rate vs. the reciprocal absolute peak temperature for  $M/e$  36 of DMDA-cured resin.

curve of the reduced rate of conversion  $dC/dA\theta$  versus the reduced time  $A\theta$  for the reaction of the 1.5th order is also shown as a solid line. The agreement between the experimental master curve and the theoretical curve is very good, and this fact means that the reaction producing hydrogen chloride is a single reaction of the 1.5th order. Since the product is only hydrogen chloride, the integration of the MTA curve gives the conversion. From the conversion and the rate of conversion, the rate constants of the reaction are estimated as a function of the temperature, assuming the reaction to be of the 1.5th order.<sup>4</sup> Arrhenius plots are made for the rate constants obtained for the different heating rates in Figure 7. The straight line is obtained for a large temperature range and for the different heating rates. From the slope and the intercept, the activation energy and the logarithm of the preexponential factor are estimated 32.2 kcal/mole and 12.1 sec<sup>-1</sup>, respectively. These values are in good agreement with those mentioned above. Thus, the order of the reaction, the activation energy, and the preexponential factor are ascertained.

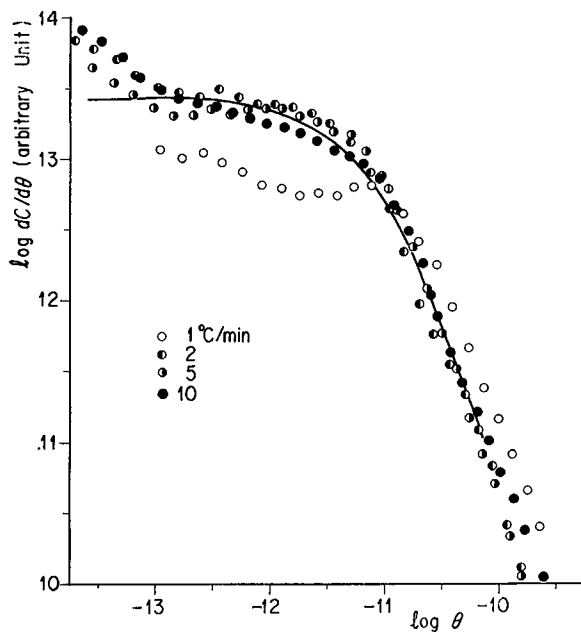


Fig. 6. Experimental master curve of DMDA-cured resin for  $M/e$  36 and theoretical curve for the 1.5th order reaction.

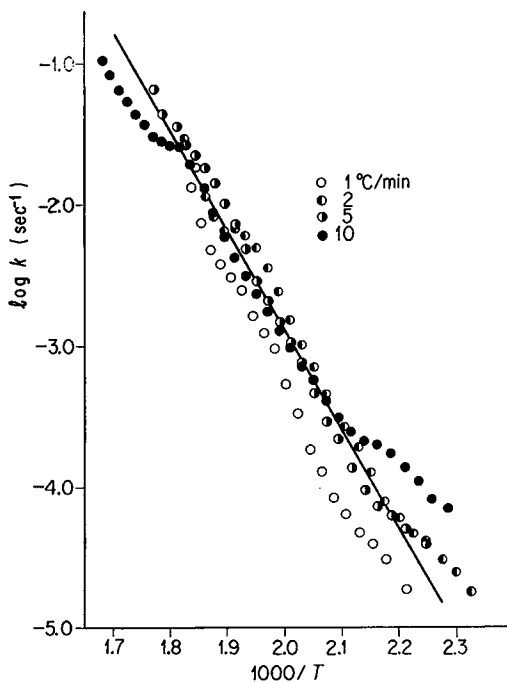
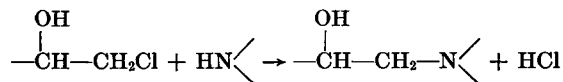


Fig. 7. Arrhenius plot of rate constant  $k$  of the reaction producing hydrogen chloride. The heating rate is indicated in the figure.

The origin of hydrogen chloride is not apparent. However, it is plausible that it was produced during the production of epoxy resin as a byproduct and/or during the curing process as a product of the reaction of the amine with unreacted groups, as follows:



Hydrogen chloride may be combined with amines to form quarternary amine hydrochloride. The mechanism of the 1.5th order reaction is explainable, assuming that the hydrogen chloride is formed by the reaction of the quaternary amine hydrochloride with free chloride ion, the concentration of which is in a steady state between the ionization of other quaternary amine hydrochloride and the backward combination.

Similar plots of the logarithms of the heating rates against the reciprocal absolute peak temperatures are also made for the  $M/e$  92 ion of toluene and the  $M/e$  60 ion of ethylenediamine. Although straight lines are obtained, single experimental master curves cannot be obtained for both ions. From these facts we can deduce that the volatilization of toluene and ethylenediamine is not governed by activation energy of Arrhenius type. It may be plausible that they exist freely in the sample and are volatilized by diffusion within the sample about the glass transition temperature.

As is clearly seen in the results mentioned above, MTA is a promising method for analyzing residual solvents and impurities and for elucidating their state in the sample; hydrochloric acid is not free in the resin, but combined with amines. The methods and the information obtained by them are very useful for characterization of the resins. Nonisothermal kinetics and methods to analyze thermoanalytical data of diffusion are now in progress in our laboratory, and the results of their application of MTA of various epoxy resins will be reported in the near future.

#### References

1. H. L. Friedman, *Thermochim. Acta*, **1**, 199 (1970).
2. R. Sakamoto, T. Ozawa, and M. Kanazashi, *Thermochim. Acta*, to be published.
3. American Petroleum Institute Research Project No. 44, Mass Spectral Data (API).
4. T. Ozawa, *J. Thermal Anal.*, **2**, 301 (1970).

RYUZI SAKAMOTO  
YOSHIO TAKAHASHI  
TAKEO OZAWA

Electrotechnical Laboratory  
Tanashi, Tokyo, Japan

Received October 21, 1971