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The determination of heat of curing accompanied by reactant volatilization using simultaneous thermal analysis (STA)

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Abstract

The curing reaction of a thermosetting system measured by differential scanning calorimetry (DSC) requires a constant sample mass throughout the experiment. If one of the components is a volatile material, the weight loss and heat of volatilization should be taken into account. The simultaneous thermal analysis (STA) method provides simultaneous information of both weight and heat during the reaction. The actual heat of curing can be determined by subtracting the heat of volatilization from the heat of the curing reaction. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Differential scanning calorimetry; Simultaneous thermal analysis; Curing reaction; Thermosetting resin

1. Introduction

The curing reaction for some thermosetting resins may be altered or masked by competitive thermal events, e.g., vaporization of water of condensation or solvent or even volatilization of reactants. It is assumed that when it happens, the net energy change detected by differential scanning calorimetry (DSC) does not yield usable information [1,2].

The curing reaction of the uncatalyzed epoxy-anhydride system has been described by various authors [3–6]. The DSC has been used extensively to monitor and characterize the epoxy thermosetting systems cured by carboxylic acid anhydrides, amines and anionic or cationic catalyst [7]. The influence of the catalyst content has been studied in the cures of DGEBA/diamine/tertiary amine [8] and DGEBA/carboxyclic acid anhydride/tertiary amine [9].

The DSC traces show a multiple peaked exotherm depending on the catalyst type and its content. The uncatalyzed system shows a shoulder on the DSC exothermic peak. This shoulder was attributed to the superposition of two thermal events: the endothermic heat from the weight loss of the hardener and the exothermic heat generated in the curing reaction [9].

This experiment shows the use of simultaneous both weight and heat information during the reaction to obtain the actual heat of curing. This simultaneous information is provided by a simultaneous thermal analyzer (STA) instrument.

2. Materials and instrument

All experiments were performed on rheometric scientific simultaneous thermal analyzer STA 625

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and STA 1500 and also on differential scanning calorimeter DSC-SP. The resin, Araldite F (DGEBA), hardener HY 905 (phthalic anhydride) and accelerator DY 062 (tertiary amine) were supplied by Ciba Specialty Chemicals (UK), Ltd.

3. Results and discussion

Fig. 1 shows the dynamic scanning of resin Araldite F from 50 to 400°C at a ramp rate of 10°C/min. Fig. 1 also depicts that the devolatilization of the resin occurs from 260 to 367°C and the resin starts to degrade after that temperature. The total weight loss after 400°C is 84.7%.

Fig. 2 displays the dynamic scanning of hardener HY-905. The devolatilization of the hardener occurs within 100 to 260°C with a weight loss of 70%.

Fig. 3 illustrates the dynamic scanning of resin and hardener with a ratio of 55 to 45% by weight. The curing reaction starts at 176°C and ends at 325°C with a heat of curing of 306.7 J/g. This is an apparent heat of curing, because the heat of curing should be corrected with the heat of devolatilization of the resin and hardener.

If a curing reaction and a devolatilization process occur simultaneously, one can write

$$\Delta H_c = \Delta H_{ap} - \Delta H_v \tag{1}$$

where ΔH_c is the the actual heat of curing, ΔH_{ap} the apparent heat of curing and ΔH_v the heat of devolatilization.

The correction for heat of devolatilization should be performed into two steps. One is for the hardener and the other for the resin. There are two assumptions should taken into account to calculate the heat of devolatilization:

1. There is no weight loss during the curing reaction. The weight loss observed during the curing reaction is due to the weight loss of hardener and resin.
2. The heat of devolatilization of hardener or resin is proportional to the amount of devolatilized hardener or resin.

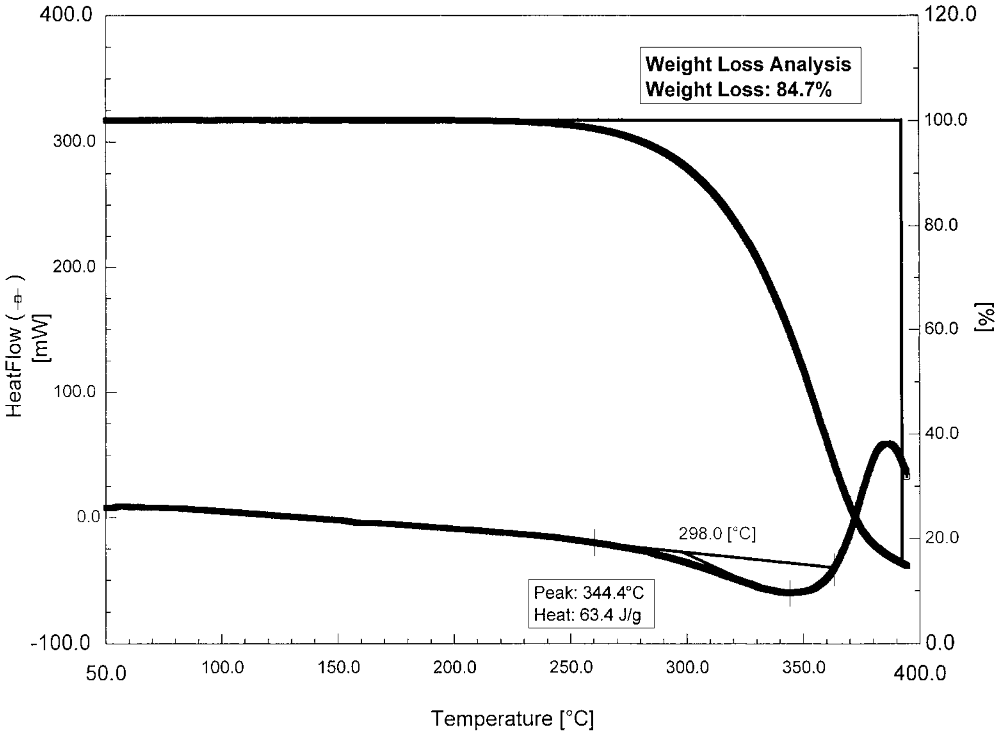

Fig. 1. Dynamic scanning of Araldite F, 10°C/min.

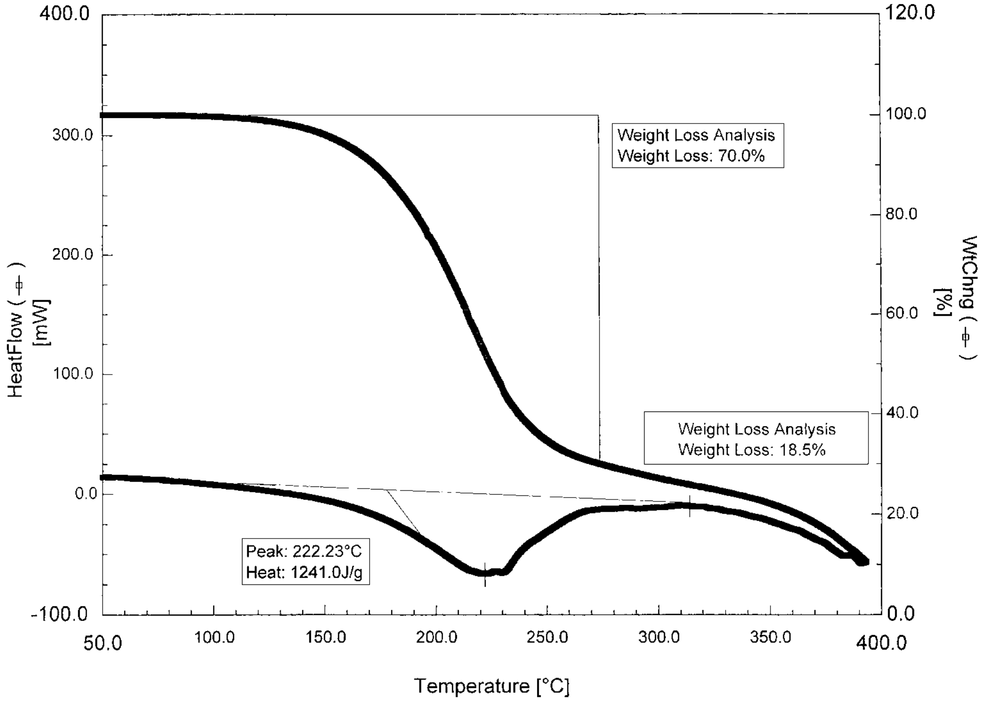

Fig. 2. Dynamic scanning of hardener HY-905, 10°C/min.

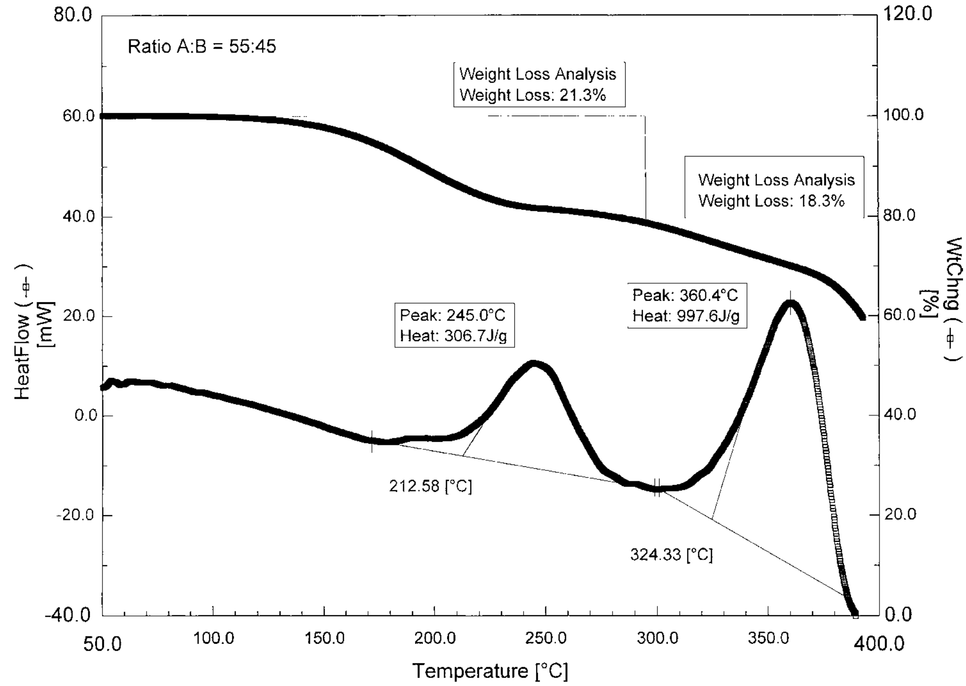

Fig. 3. Dynamic scanning of Araldite F and HY-905, 10°C/min.

The heat of devolatilization of hardener during the dynamic scanning of the hardener can be calculated using the following equation:

$$\Delta H_{\mathrm{v}} = \Delta H_{\mathrm{vr}} + \Delta H_{\mathrm{vh}} \tag{2}$$

where ΔH_{vr} is the enthalpy of volatilization of the resin present (mJ) and ΔH_{vh} the enthalpy of volatilization of the hardener present (mJ), For the expected values.

$$\Delta H_{\mathrm{vr}} = \Delta H_{\mathrm{r}} W_{\mathrm{r}} \tag{3}$$

$$\Delta H_{\mathrm{vh}} = \Delta H_{\mathrm{h}} W_{\mathrm{h}} \tag{4}$$

where ΔH_{r} is the specific enthalpy of volatilization of the resin (mJ/mg), ΔH_{h} the specific enthalpy of volatilization of the hardener (mJ/mg), W_{r} the mass of resin present in mixture (mg) and W_{h} the mass of hardener present in mixture (mg).

Substituting Eqs. (3) and (4) in Eq. (2) and then Eq. (2) into Eq. (1),

$$\Delta H_{\mathrm{c}} = \Delta H_{\mathrm{ap}} - \Delta H_{\mathrm{r}} W_{\mathrm{r}} - \Delta H_{\mathrm{h}} W_{\mathrm{h}} \tag{5}$$

where ΔH_{r} is determined from STA experiment run with only resin (Fig. 1), ΔH_{h} is determined from STA experiment run with only hardener (Fig. 2), ΔH_{ap}, W_{r} and W_{h} are determined from STA experiment on resin and hardener (Fig. 3).

Substituting these values into Eq. (5) yields ΔH_{c}.

The heat of volatilization of the resin can be calculated using similar formulation. The heat of curing after correction for the heat of devolatilization of both resin and hardener is shown in Fig. 4. The corrected heat of curing is 429.0 J/g.

The volatilization of hardener and resin can be prevented with the addition of tertiary amine DY-062. The absence of volatilization is shown in Fig. 5. There is no weight loss up to 350°C and the weight loss after that temperature is due to the degradation of the resin.

The above analysis demonstrated the advantage of STA in correcting the heat of curing of thermosetting system. Another advantage is the determination

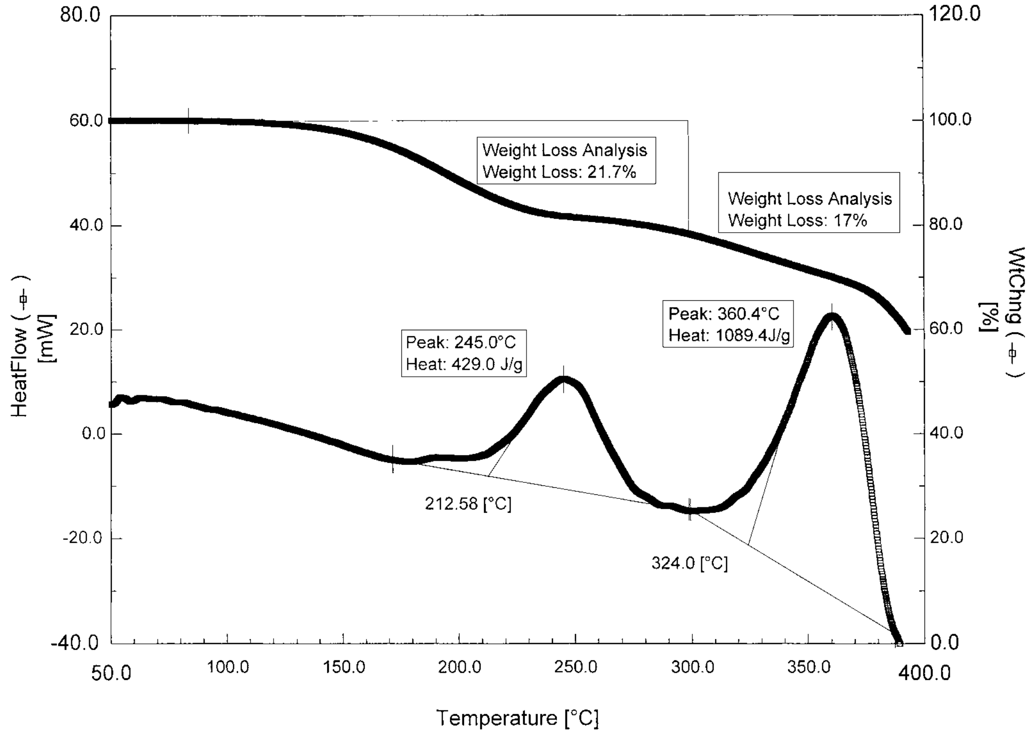

Fig. 4. Dynamic scanning of Araldite F and HY-905 after correction.

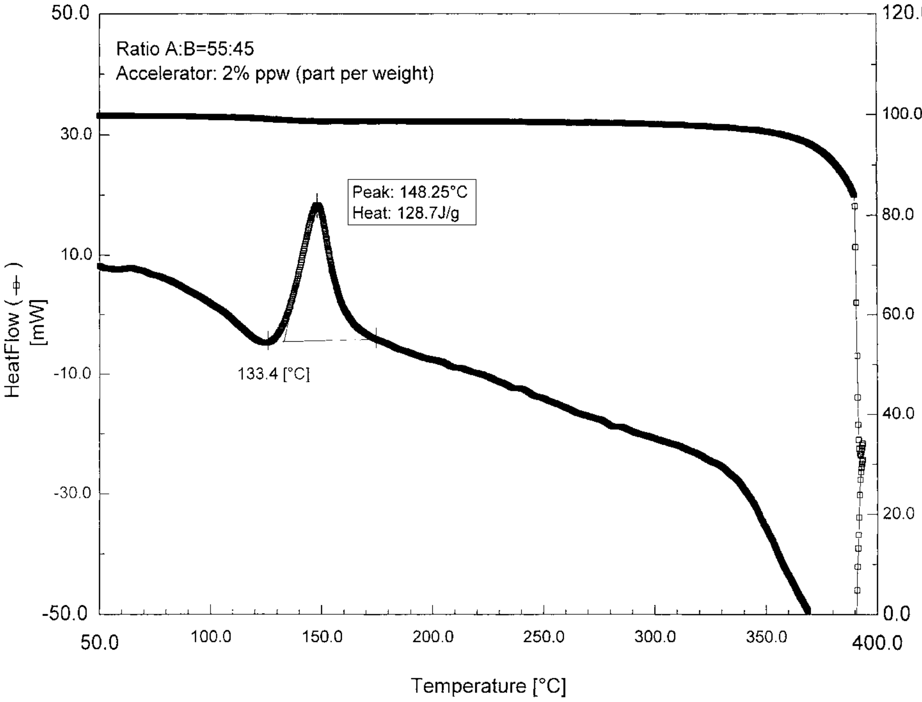

Fig. 5. Dynamic scanning of Araldite F and HY-905 with accelerator DY-062.

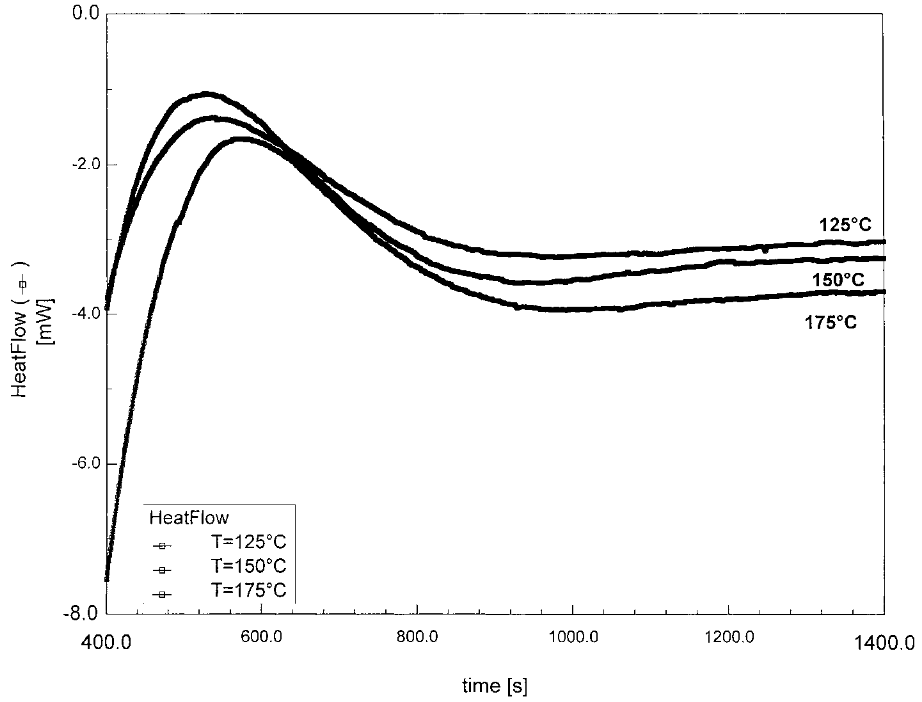

Fig. 6. Isothermal curing reaction at various temperatures.

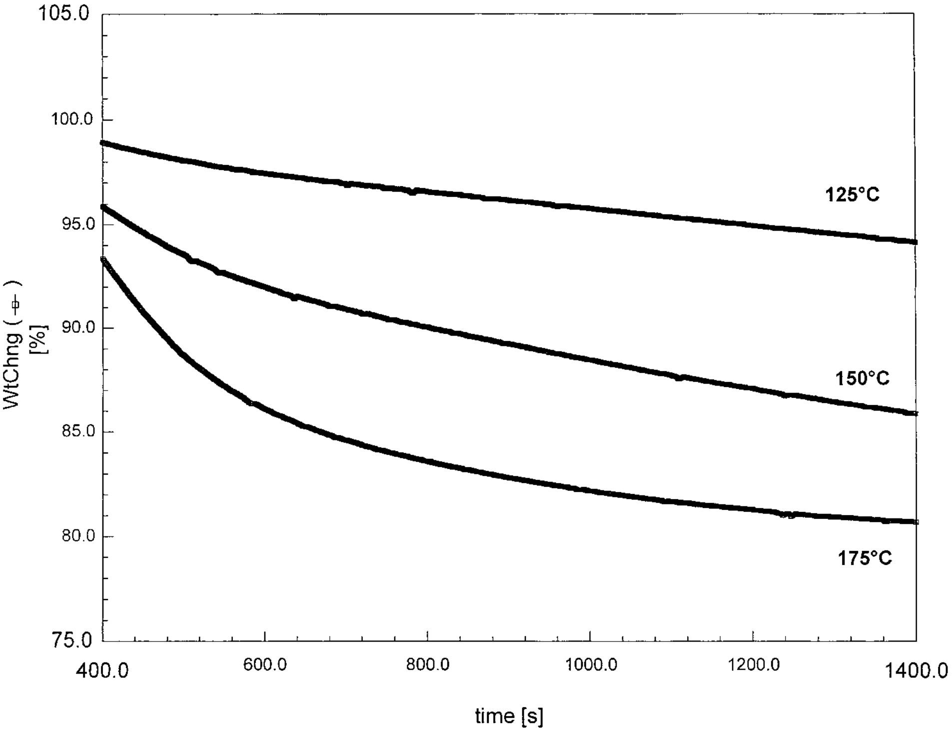

Fig. 7. Isothermal curing reaction at various temperatures.

of the kinetics of curing reaction. The kinetics of curing reaction can be determined by both isothermal and non isothermal method [9,10,11]. The degree of curing at a certain temperature can be also determined simultaneously from both partial heat of curing and the weight loss of hardener and resin during the reaction. Figs. 6 and 7 illustrate three isothermal curing of Araldite F and HY-905 at 125, 150 and 175°C.

4. Conclusions

Simultaneous thermal analyzer can be utilized to perform various thermal analysis of the curing reaction using both heat flow and weight loss data.

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