

## THERMAL ANALYSIS OF AN EPOXIDE RESIN SYSTEM

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TG, DTG, DTA and DSC methods were used to study the curing reaction of diglycidyl ether of bisphenol A and nadic methyl anhydride in the presence of a reactive diluent. DTG plots were used to identify the various stages of weight loss arising from volatilization of components from the resin formulation and pyrolysis of cured resin. DTA and DSC results established the temperatures at which catalysed and thermally activated cure occurred.

The results demonstrate the advantages of combining thermogravimetry and differential thermal techniques to study some factors that affect resin cure and to establish the correct choice of temperature regime and catalyst.

Differential thermal methods (DTA and DSC) have been used in several investigations of epoxide resin systems [1–5]. These techniques can be useful for assessing the amount of cure remaining after various curing regimes and for indicating the temperatures at which curing takes place.

Thermogravimetry (TG and DTG) is used more often as a reliable indicator of thermal stability [2, 4, 5–9], although Lee and Levi [9] suggested that thermal stability as indicated by TG plots can be related to the degree of cure.

Anderson [10] recommended that both DTA and DTG be used to measure pyrolysis of polymers, since thermometric information alone can be misleading, particularly when exothermic and endothermic processes occur simultaneously or when there are pronounced changes in specific heat or thermal conductivity. Results discussed in this paper show that there are similar advantages to be gained by combining thermogravimetric and thermometric techniques to study some factors that affect curing of epoxide resins. TG, DTG, DTA and DSC methods were used to study the curing reaction of the diglycidyl ether of bisphenol A (DGEBA) and nadic methyl anhydride (NMA) in the presence of a reactive diluent.

### Experimental

#### *Materials*

A standard resin formulation (System A) used in most experiments contained the following components in proportions as listed in Table 1:

Epoxide: diglycidyl ether of bisphenol A (DGEBA)

Hardener: nadic methyl anhydride (NMA)

Diluent: tetra methylene glycidyl ether (TGE) with substantial monofunctional component.

Accelerator: triamyl ammonium phenate (TAP)

Flexibilizer: carboxyl terminated butadiene nitrile (CTBN)

Table 1  
Composition of system A

Component	Weight, %
DGEBA	39.0
NMA	46.9
TGE	11.7
TAP	0.4
CTBN	2.0

TG and DTG were applied to resin mix components and cured resin specimens. The curing schedule consisted of heating the resin formulation at 125° for 2 h and then at 160° for 16 h.

#### *Thermal analysis equipment*

TG: Cahn electrobalances (models RG and RH) with hanging Pt sample cups inside quartz furnace tubes. Vertical tube furnaces of our construction were controlled by F & M scientific temperature programmers (model 240).

DTA: Dupont intermediate temperature measuring head controlled by a F & M scientific temperature programmer (model 240). Output was amplified with a custom-built amplifier of our own design.

DSC: Perkin-Elmer differential scanning calorimeter (model DSC-1).

An LSI-11 computer with flexible-disc drives was used to collect, store and process the data. A modified Moseley X-Y recorder (model 135A) served as a function plotter for producing hard copy thermal analysis plots.

DTG plots were calculated from TG data by computing the smoothed first derivative with methods described by Bromba and Zeigler [11] for polynomial smoothing of equispaced data using a recursive digital filter technique.

## **Results and discussion**

### *Thermogravimetric analysis of Mix A*

Figure 1 shows TG and DTG plots for System A heated in nitrogen at 0.5 deg min<sup>-1</sup> and 5 deg min<sup>-1</sup>. There are three stages of weight loss denoted by three DTG peaks. Table 2 lists peak temperatures, weight losses and approximate temperature range for each stage.

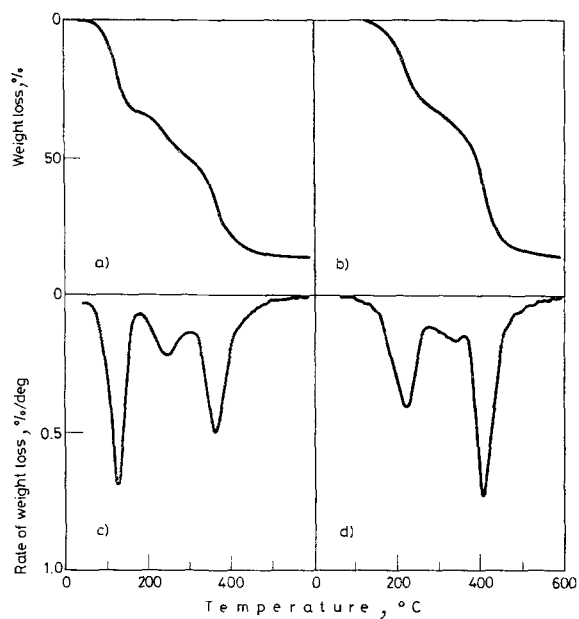


Fig. 1. TG and DTG plots for resin System A heated in nitrogen a: TG, 0.5 deg/min; b: TG, 5.0 deg/min; c: DTG 0.5 deg/min; d: DTG 5.0 deg/min

In Fig. 2, a DTG plot for System A is superimposed on DTG plots for a cured test specimen and each component of the mix; so, by comparing these data with the weight losses of Table 2 and the composition given in Table 1, we identify each stage of weight loss as follows:

Table 2

Thermogravimetric data for System A heated in nitrogen

	Peak temperature, C	Temperature range, C	Weight loss, %
0.5 deg min <sup>-1</sup>			
Stage I	125	50–175	32.7
Stage II	240	175–300	18.7
Stage III	360	300–580	35.6
Char residue			13.4
5.0 deg min <sup>-1</sup>			
Stage I	215	80–270	30.4
Stage II	330	270–360	12.4
Stage III	405	360–580	43.5
Char residue			13.7

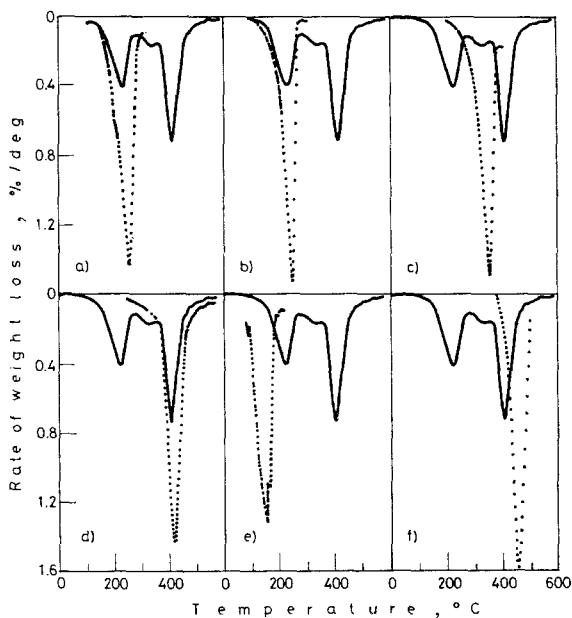


Fig. 2. DTG data for System A and individual components heated in nitrogen at 5deg/min. unbroken trace: System A; broken trace: a: TGE; b: NMA; c: DGEBA; d: cured resin specimen; e: TAP; f: CTBN

- Stage I: Removal of some diluent (TGE) and hardener (NMA), with possible volatilization of some accelerator (TAP)  
 Stage II: Volatilization of unreacted epoxide monomer (DGEBA)  
 Stage III: Pyrolysis of cured resin (including CTBN)

Clearly, volatilization of NMA during Stage I reduces the ratio of anhydride to epoxide groups well below the initial stoichiometry, so that complete cure cannot be obtained during linear heating; the maximum degree of cure achieved prior to Stage III pyrolysis must therefore depend on a balance of curing rates and volatilization rates.

#### *DTA and DSC measurements*

The temperatures at which curing reactions occur can be seen in Fig. 3, which compares DTG, DTA and DSC plots for System A. As noted by others [1, 5], the DTA and DSC plots are dominated by exothermic curing processes which overshadow any endothermic effects from volatilization and decomposition. There are three exothermic steps, with peaks at about 175, 265 and 340°.

If no accelerator is present, the exotherm at 175° does not develop, although DTA and DSC peaks at 265° and 340° are still evident; that is, the peak at 175° arises from the reaction of DGEBA, TGE and NMA catalysed by accelerator TAP.

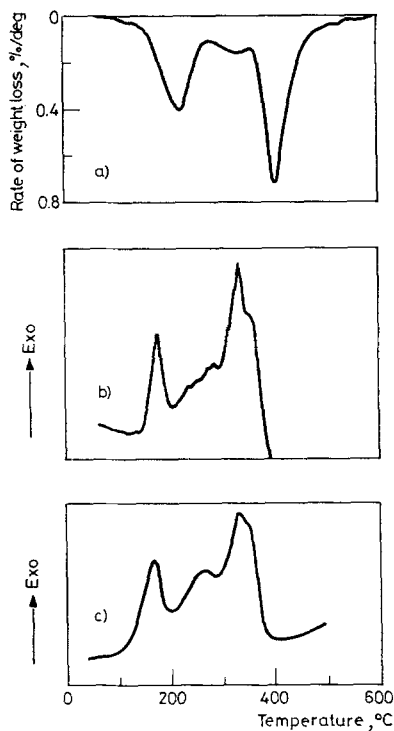


Fig. 3. Thermal analysis data for System A heated in nitrogen at 5deg/min. a: DTG; b: DSC; c: DTA

We conclude, therefore, that the broad 265° exotherm is due to a thermally activated curing reaction.

Exothermic reactions between 300 and 450° which have been observed for a number of epoxide systems [1, 4] including DGEBA-NMA, are identified with isomerization of epoxide groups and homopolymerization of epoxide monomer; so we can attribute the 340° exotherm of Fig. 3 to these reactions, since TG and DTG data show that at 270° an excess of monomer must be present in the mixture.

#### *Effect of isothermal heating on thermal properties of Mix A*

From the results described, it follows that resin cure during linear heating can be increased by isothermal pretreatment, provided that the isothermal temperature and time are chosen so as to (a) minimize volatilization of NMA and (b) induce sufficient catalytic cure to increase resin mix viscosity and establish a diffusion barrier to removal of volatiles during subsequent linear heating.

Some effects of isothermal heating are illustrated by the DTG plots of Fig. 4 and the data of Table 3. Clearly, heating at 75° for 16 h and 40 h substantially

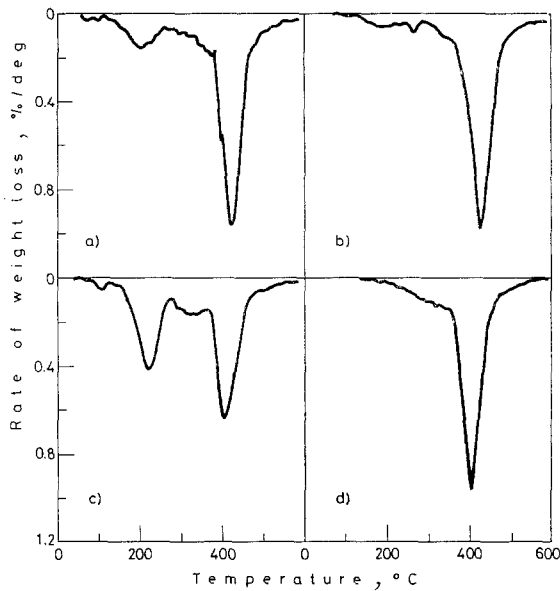


Fig. 4. DTG plots for System A heated in nitrogen at 5 deg/min. Effect of isothermal pretreatment. a: 16 h at 75°; b: 40 h at 75°; c: 2 h at 90°; d: 2 h at 120°

reduces Stage I volatilization of NMA and TGE. The extent of cure is thus enhanced so that less epoxide monomer remains above 270°, as shown by a diminished Stage II peak. An increased magnitude of the Stage III peak reflects the greater degree of cure. Similar effects are obtained by heating 2 h at 120°, whereas 2 h at 90° is ineffective in promoting cure (Fig. 4 c, d). Thus, to effect a satisfactory cure in formulations such as System A, a temperature regime must be chosen with care, taking into account those factors that may affect mass transfer of volatile components (e.g. furnace atmosphere and geometry, thermal gradients, gas flow, sample size and sample geometry).

#### *Effect of accelerator on resin cure*

Figure 5 compares the DTG and DSC plots for System A with plots obtained for a similar formulation (System B) in which 1-methylimidazole (1-MI) was used as accelerator. These data show that 1-MI is the more effective accelerator: increased rates of catalytic cure inhibit volatilization during Stage I; volatilization of DGEBA is likewise reduced and the Stage III peak is much greater than for System A. The difference in catalytic effect is reflected in the respective DSC plots (Fig. 5 c, d). Replacement of TAP by 1-MI gives a greater amount of catalysed cure as shown by the substantial increase in the exotherm at 175°, with the absence of a peak at 380° confirming that very little epoxide monomer remains above 270°.

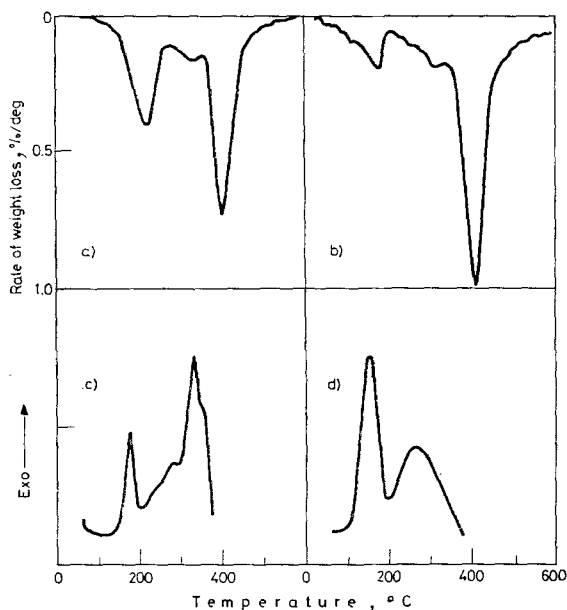


Fig. 5. DTG and DSC data for System A and System B heated in nitrogen at 5deg/min; System A (TAP accelerator). a: DTG c: DSC, System B (1-MI accelerator) b: DTG d: DSC

These results indicate that for epoxide systems similar to System A, volatilization of components may lead to substantial variations in the properties of cured resin samples. In particular, we can expect the mechanical properties of a cured resin to be affected by:

- (i) changes by volatilization in the amount of monofunctional reactive diluent, leading to differences in the degree of cross linking;
- (ii) presence of excess epoxide monomer within the cured resin matrix; and
- (iii) presence of homopolymerized epoxide.

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ZUSAMMENFASSUNG — Die Härtung des Diglycidäthers von Bisphenol A und nadic methyl anhydrid in Gegenwart eines reaktiven Verdünnungsmittels wurde durch TG, DTG, DTA und DSC untersucht. Die verschiedenen Stadien des durch die Verflüchtigung von Komponenten der Formulierung und bei der Pyrolyse von gehärtetem Harz eintretenden Gewichtsverlustes wurden an Hand von DTG-Kurven identifiziert. Die Temperaturen, bei denen die katalytische und thermisch aktivierte Härtung einsetzt, wurden durch DTA- und DSC-Messungen ermittelt. Die Ergebnisse zeigen die Vorteile auf, die kombinierte thermogravimetrische und thermometrische Techniken bei der Untersuchung einiger die Harzbildung beeinflussender Faktoren und bei der Wahl der richtigen Temperaturverhältnisse und des Katalysators aufweisen.

Резюме — ТГ, ДТГ, ДТА и ДСК методы были использованы для изучения реакции отверждения дифенилового эфира эпигидринового спирта и метилового ангидрида адипиновой кислоты в присутствии реакционноспособного разбавителя. Графики ДТГ были использованы для идентификации различных стадий потери веса, возникающих вследствие выделения летучих компонент при образовании резин и при пиролизе отвержденных резин. Результаты ДТА и ДСК измерений позволили установить температуры, при которых происходят каталитические и термические процессы отверждения. Проведенные исследования показали преимущества комбинированных термогравиметрических и термометрических методов для изучения некоторых факторов, затрагивающих процесс отверждения резины, а также позволили установить правильный выбор температурного режима и катализатора.