APPLICATION NOTE

Thermal Analysis

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Use of DSC, DMA and TG-GC/MS in the Study of Epoxy Materials

Introduction

Traditionally approaches to studying the curing of epoxies concentrate on the thermo-chemical[1] and thermo-rheological[2] properties of the material. As changes in the glass transition temperature (Tg) correlate strongly with functional properties[3] like mechanical strength, tribology, permeability, etc, studies on epoxies often rely on techniques like Differential Scanning Calorimeter (DSC) and Dynamic Mechanical Analysis (DMA) to quantify it. DSC also allows one to characterize the degree of cure in a thermoset and to determine the kinetics of the cure[4]. DMA can characterize the rheology profile of the cure[5] as well as the final modulus and Tg values after curing. In many cases, the greater sensitivity of the DMA to the presence of the Tg makes it the preferred method for epoxies studies[6].

In this work we report that even when the curing profiles and final properties of the epoxies are very similar, their suitability for use may be influenced by other factors. Characterization of the materials by Thermo-Gravimetric Analysis (TGA) showed that the materials could exhibit considerable weight loss after curing. These weight losses can be characterized by hyphenated methods like Thermo-Gravimetric Analysis Mass Spectrometry (TG-MS) or Thermo-Gravimetric Analysis-Gas Chromatography Mass Spectrometry (TG-GC/MS).

Our case study is a set of three epoxies used in an electronic assembly. All three materials cure and exhibit proper behavior on curing. One material, however, was found to be associated with significant amount of component failure. This occurred intermittently but reached as high as 30% failure rates when it occurred.

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Experimental

Three samples of commercial epoxies compounds were received as two-part systems containing an epoxy component and a separate amine component. Of these, it was known to cause intermittent failures in manufactured parts used in electronics. To study, curing samples were mixed by weight and loaded at room temperature. For cured specimens, samples were mixed at room temperature and cured at 30 °C in silicon molds. After curing overnight, the samples were removed and post-cured for 8 hours at 100 °C.

DSC studies were performed using a PerkinElmer® DSC8500 with Intracooler 2, Pyris® Software Version 11, and nitrogen purge. Samples of 10-15 milligrams were prepared using 50 microliter pans and run at 10 °C per minute.

The PerkinElmer DMA8000 was used for all DMA studies. Curing was studied using 15 mm diameter parallel plates and cured samples were tested either in the above mentioned plates or in single cantilever mode. All work was done under nitrogen.

For both TGA and hyphenated studies, a Pyris 1 TGA from PerkinElmer was used. A PerkinElemr Clarus® 600 GC/MS was used for both the MS and GC/MS hyphenation. Samples were approximately 10 milligrams under nitrogen at 40 ml/minute for TGA and helium at the same rate for GC/MS. For the GC/MS, sample was collected on the column at 15 °C across the TGA range of interest and then run by standard methods.

Results

A comparison of the curing of the three samples by DSC and DMA showed differences in their behavior on curing. DSC data collected at 10 °C/minute did not show significant variation in the samples. Despite differences in isothermal curing at 30 °C in the DMA profiles, the resulting cured materials showed only minor differences in the final modulus and in the final Tg value, which leads one to suspect the performance of the epoxies in their ultimate use will be the same. An example of the DMA curing curves is shown in Figure 1. for all samples at the end of the cure although times varied. Similarly comparison of the enthalpy of curing and the Tg of the cured materials by DSC showed little difference between samples. Table 1 reports DMA and DSC values.

However, TGA studies immediately following curing showed that sample 3 gave a distinctive weight loss at lower temperatures. This is shown in Figure 2 and tabulated in Table 2.

Analysis of the same specimen after two weeks sitting at room temperature showed the disappearance of the drop. Repeating these experiments with TG-MS and TG-GC/MS showed that the initial weight loss corresponded to a mixture epoxy fragments and low boiling amines. After allowing these samples to sit 2 weeks a room temperature, the weight loss again decreased dramatically and the major component lost below 250 °C was found to be water.

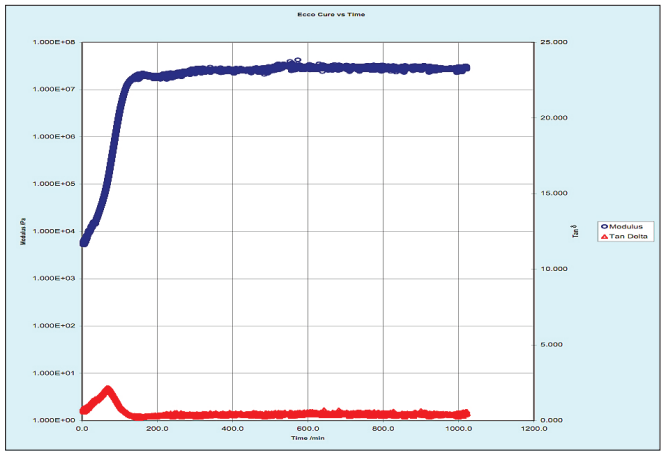

Figure 1. Example of a curing curve for DMA runs.

Sample	DSC Onset in °C	DMA Peak in tan δ (min.)	DMA time to vitrification	Cured Tg by tan δ in °C	E' at 20 °C
A	44.1	8.2	40	62.7	2.1e8
B	45.2	71	140	61.8	9.1e7
C	44.8L	62	325	63.1	1.3e8

Table 1. DSC and DMA Data

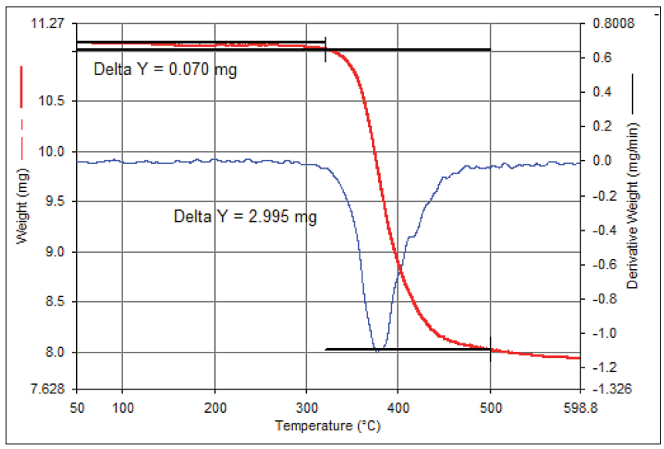

Figure 2. TGA of epoxy showing low temperature weight loss. TG-MS and TG-GC/MS determined weight loss was amine compound.

Sample	%Weight loss to 250°C	%Weight loss to 250 After 2 weeks
A	1.8	.8
B	2.1	.7
C	6.5	.8

Table 2. TGA Data

Conclusion

While epoxies are normally characterized by chemo-rheological and thermo-chemical means, it has been found that these methods may not detect all of the properties affecting use. Volatile compounds can remain in the epoxy for significant periods of time and on heating in operation, redeposit onto parts causing failures. Thermal characterization of epoxies is not enough: hyphenated techniques allow for a fuller characterization of curing systems.

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