Thermogravimetric Analysis of Water-Epoxy Interaction

Introduction

Epoxies are among the most important commercial plastics. Epoxy resin-graphite fiber composites are widely used in aerospace applications because of their high strength-to-weight ratio. A deficiency of epoxy resins, however, is the loss of mechanical properties at elevated temperature, which is enhanced as a result of moisture absorbed from high-humidity environments. Several workers[1-4] have documented the plasticizing effect of sorbed water on epoxy. Epoxies that have been soaked in water for extended periods of time show additional reaction of the oxirane rings. The examination of the interaction of water and an epoxy during water sorption and desorption using thermogravimetric analysis (TGA) is reported here.

Experimental

Cross-linked epoxy resin samples were made using Ciba-Geigy MY720 Araldite epoxy resin (tetraglycidyl-4,4'-diaminodiphenylmethane; TGDDM) cured with Ciba Geigy eporal hardener (4,4'-diaminodiphenylsulfone; DDS). The resin and the hardener were used without further purification.

Resin mixing and storing procedures have been described earlier.[3] Disk-shaped samples were prepared for TGA using silicone rubber molds with cavities of diameter of 0.2 mm and depth of approximately 0.5 mm. A prepolymer mix of curing agent dissolved in the resin (3–5 mg) was placed in each cavity of the mold. The mold and contents were heated in a vacuum desiccator and held under partial vacuum in a nitrogen atmosphere at 150°C for 1 h. The temperature was then raised to 177°C and held for 5 h. The molds were then taken out of the heated desiccator and allowed to cool to room temperature under vacuum.

Individual samples were weighed, soaked in distilled water at 25 or 70°C for different times following soaking, scanned on a TGA at 20°C/min in a nitrogen atmosphere from 25 to 325°C, and then immediately cooled back to 25°C. Rapid degradation was observed above 325°C. TGA measurements were also made on two sets of cured samples that were soaked at 25 and 70°C for 750 and 675 h, respectively, and then dried for different times in a vacuum desiccator at 30 and 70°C, respectively. A Perkin Elmer Model TGS-1 thermobalance and a Perkin Elmer strip chart recorder were used.

Results and Discussion

Typical TGA heating thermograms of a dry and a soaked (200 h at 70°C with a weight gain of 4.5%) cured resin are shown in Figure 1. The TGA dynamic weight loss data of soaked samples are presented in Tables I and II. Plots of weight gain in water versus dynamic weight loss at 325°C are shown in Figure 2. The dynamic weight loss at 325°C is about 1.2% for the dry samples and increases with water content. The increase in dynamic weight loss is obviously due to water evolved as the sample is scanned. This makes the T_g appear broader, a phenomenon also observed by Thompson et al.[6]

The T_g was measured independently by differential scanning calorimetry (DSC) and reported elsewhere.[3] For the control samples, the T_g was about 236°C (scan rate of 20°C/min) and decreases with moisture content. It was also noted that the T_g of samples soaked in water at 70°C remained significantly depressed even after most of the water was removed.

Samples containing water have a smaller net dynamic weight loss (after accounting for the water pickup) than the dry (control) samples. For the dry samples the weight loss was 1.16%, and for samples soaked at 25°C and with 5.20% weight gain, the dynamic weight loss was 5.27%, a difference of only 0.07%. For samples soaked at 70°C with 5.30% weight gain, the dynamic weight loss was 5.33%, a difference of only 0.03%.

At least three factors should be considered for the difference in the net dynamic weight

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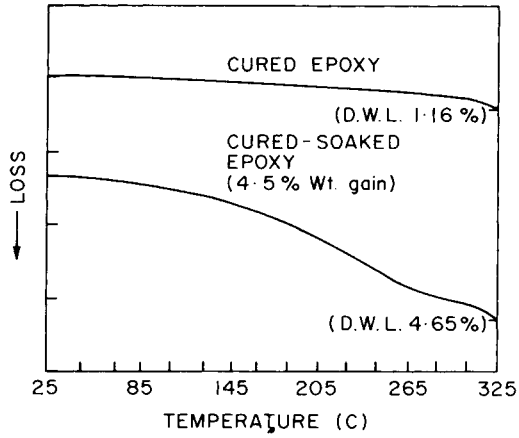

Fig. 1. TGA thermograms of a dry-cured epoxy soaked in water (200 h at 70°C, 4.5% weight gain).

loss of the soaked samples compared to the control. First, it takes 15 min for the samples to reach 325°C at a heating rate of 20°C/min. Apparently, this is not sufficient time for all the water to diffuse out of the system.

Secondly, some low-molecular-weight polymer species should be leached out during soaking. Yang[7] used tetrahydrofuran (THF) to extract low-molecular-weight species from thin films of the same TGDDM-DDS system. Using high-performance liquid chromatography, he identified unreacted TGDDM, DDS, and some oligomeric species in the extract. Fisher et al.[8] found that little weight loss occurred (approximately 1–2%) after soaking thin films (approximately 10–20 m) for several hundred hours in water followed by drying. However, the samples in this study were much thicker (1–2mm), and no net weight losses were observed for samples first soaked, then dried.

Third, some of the absorbed water may be strongly bound or chemically reacted with the resin. Fuller et al.[9] used nuclear magnetic resonance (NMR) to study the molecular interactions between water and TGDDM-DDS epoxy resins. As absorption increases, a line much narrower than the line associated with the matrix protons begins to appear. However, this line does not account for all the water. They concluded that the water sorbed by the resin and detected by proton NMR does not act as free water but that it is more mobile than water in a crystalline state. Moy and Karasz[10] reported similar NMR results. They noted that the first fraction of a percentage of water absorbed in the TGDDM-DDS system was both rotationally and translationally hindered and had a characteristic line width indistinguishable from the matrix

TABLE II
TGA Dynamic Losses of Cured, Soaked at 70°C, Epoxy Samples

No. of hours soaked	Weight gain (%)	Dynamic weight loss (%)			
		100°C	150°C	177°C	325°C
0	0.0	0.05	0.14	0.24	1.16
25	2.9	0.10	0.61	1.01	3.89
46	3.2	0.15	0.73	1.16	4.35
70	3.8	0.21	0.92	1.46	4.81
240	4.9	0.19	0.83	1.39	5.00
360	5.1	0.21	0.85	1.49	5.18
500	5.1	0.23	0.90	1.46	5.21
770	5.3	0.23	0.97	1.62	5.33

TABLE I
TGA Dynamic Losses of Cured, Soaked at 25°C, Epoxy Samples

No. of hours soaked	Weight gain (%)	Dynamic weight loss (%)			
		100°C	150°C	177°C	325°C
0	0.0	0.05	0.14	0.24	1.16
25	1.8	0.12	0.44	0.69	2.35
60	2.9	0.13	0.56	0.89	3.51
310	4.9	0.17	0.89	1.42	5.08
385	4.9	0.19	0.87	1.42	5.12
455	5.0	0.20	0.89	1.44	5.13
530	5.1	0.20	0.96	1.47	5.19
825	5.2	0.20	0.92	1.51	5.27

protons. In another study using infrared spectroscopy, Fuller et al.[11] showed that water absorbed by the resin is involved in chemical exchange between hydrogens of water and those on the epoxy. Lawing[12] also found similar results with NMR and observed that, with increase in the temperature, the mobility of the water hydrogen increases.

Illinger and Sprouse[5] found, by using difference infrared (IR) spectra, that water reacts with oxirane rings. A decrease in the epoxide band (915 cm^{-1}) was observed. Using IR, Netravali et al.[3] also detected a decrease in the epoxide band when the epoxy films were exposed to water for long times. Therefore, the data suggest that the strongly bound water is not easily evolved.

TGA data were obtained on samples that were soaked for an extended period and then dried for varying times. Data are shown in Table III for samples that were soaked at 25°C for 750 h, then dried at 30°C. Similar data are shown in Table IV for samples soaked at 70°C, then dried at 70°C. Plots are shown in Figure 3 of net weight gained versus dynamic weight loss. Samples that were dried for more than 25 h following soaking showed virtually no dynamic weight losses until the temperature surpassed 177°C (the resin cure temperature). Further, the net weight loss at 325°C after accounting for the increases weight due to water was 0.79 and 0.42% for the samples soaked at 25 and 70°C, respectively, compared with 1.16% for the dry control. This supports the contention that additional reaction of the polymer has been induced by the presence of water (thus cross-linking a higher fraction of the oligomers present)

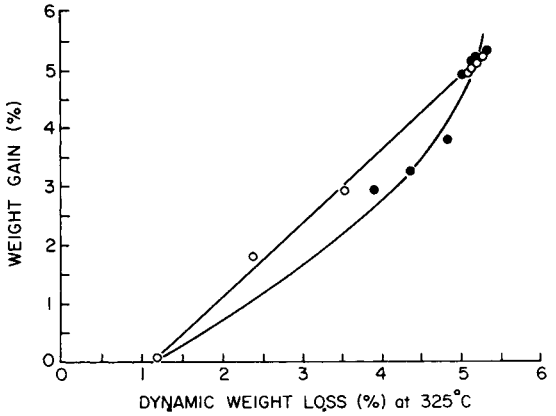

Fig. 2. Plots of weight gain in water (%) versus dynamic weight loss (%) at 325°C of cured epoxy soaked either at 25°C (○) or at 70°C (○).

TABLE III
TGA Dynamic Weight Losses of Cured, Soaked at 25°C for 750 h, and Dried at 30°C in Vacuum

No. of hours dried	Weight gain (%)	Dynamic weight loss (%)			
		100°C	150°C	177°C	325°C
Dry[a]	0.0	0.05	0.14	0.24	1.16
6	3.0	0.00	0.03	0.58	3.75
24	1.7	0.00	0.05	0.18	2.52
50	0.7	0.00	0.00	0.06	1.62
75	0.6	0.00	0.00	0.04	1.41
150	0.2	0.00	0.00	0.01	0.99

[a] Dry control sample.

and that some of the water is strongly bound to the resin. The lower net dynamic weight loss of samples soaked at 70°C compared with samples soaked at 25°C suggests that after soaking at the higher temperature the reaction with water occurs more readily.

Conclusion

As samples of water-soaked, cured epoxy are scanned on a thermogravimetric analyzer, sorbed water diffuses out. The net dynamic weight loss after accounting for the water loss is less, however, than for samples not previously exposed to water. It is proposed that this is due to two primary factors. First, insufficient time is available for the water to completely diffuse out during the experiment. Second, some water either reacts or is strongly bound to the epoxy. In addition, some weight loss should occur in the water-soaked samples because of extraction of oligomeric species. The data, however, are not sufficient to quantify the contribution of each factor.

The soaked epoxy samples cannot be dried completely even after 150 h at 30°C or 95 h at 70°C under constant high vacuum. the samples soaked at 70°C show a lower net weight loss than those soaked at 25°C and dried at 30°C, suggesting a higher extent of reaction in the former samples.

TABLE IV
TGA Dynamic Weight Losses of Cured, Soaked at 70°C for 675 h, and Dried at 70°C in Vacuum

No. of hours dried	Residual weight gain (%)	Dynamic weight loss (%)			
		100°C	150°C	177°C	325°C
Dry[a]	0.0	0.05	0.14	0.24	1.16
2	3.2	0.00	0.14	0.42	3.28
22	1.0	0.00	0.02	0.04	1.22
32	0.5	0.00	0.00	0.00	1.03
45	0.3	0.00	0.00	0.00	0.78
70	0.3	0.00	0.00	0.00	0.70
95	0.2	0.00	0.00	0.00	0.62

[a] Dry control sample.

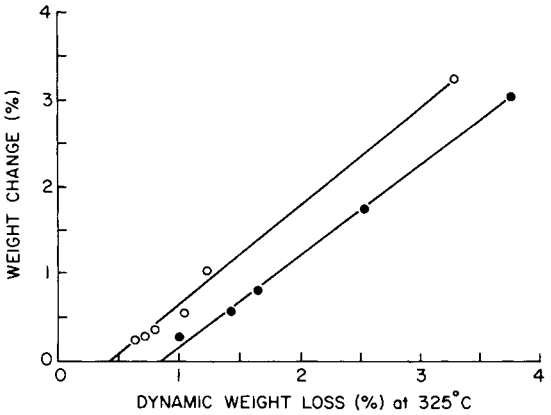

Fig. 3. Plots of residual weight gain (%) versus dynamic weight loss (%) at 325°C of cured epoxy, soaked at either 25°C (○) and dried at 30°C or soaked and dried at 70°C (○) in vacuum.

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