

# Effects of Water Sorption at Different Temperatures on Permanent Changes in an Epoxy

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## Synopsis

Crosslinked epoxy resins, tetraglycidyl 4,4'-diamino diphenyl methane cured with 4,4'-diamino diphenyl sulfone, were soaked in water at either 25°C or 70°C for varying lengths of time. The infrared spectra and DSC thermograms were obtained for samples that were soaked, or soaked and dried. There was a monotonic decrease in exothermic reaction energy with water content. The glass transition was also lowered, although samples soaked at 70°C showed a leveling in the  $T_g$  around 115°C. When the soaked samples were dried, the exothermic reaction energy showed near reversibility for samples soaked at 25°C while the 70°C samples were highly irreversible. IR of the latter samples showed that the 70°C water soaking resulted in reaction of some of the unreacted epoxide groups that remained after the initial cure.

## INTRODUCTION

Structural composite materials derived from epoxy resins and fibrous reinforcements such as graphite and fiber glass filaments have become highly important in the field of commercial and military aircraft and space systems. Several workers<sup>1-3</sup> have documented the detrimental effects of sorbed moisture on epoxy composite properties. There are generally two distinct categories of water related deterioration of epoxies: (1) mechanical losses due to moisture induced plasticization and (2) losses due to moisture-induced mechanical damage, specifically microcracking or crazing.<sup>1,4</sup> Losses due to moisture induced plasticization generally tend to be reversible. The plasticization of epoxy has been well documented.<sup>1,5,6</sup> Deterioration in the properties due to mechanical damage, chemical reactions, or chain scissions is irreversible. Reported here are the effects of water sorption and removal at different temperatures on the properties of an epoxy.

## EXPERIMENTAL

The epoxy samples used in this study were prepared with Ciba Geigy MY 720 Araldite epoxy resin, which consists mainly of tetraglycidyl 4,4'-diamino diphenyl methane (TGDDM). The curing agent was Ciba Geigy Eporal hardener which consists of 4,4'-diamino diphenyl sulfone (DDS). The resin and the hardener were used without further purification.

Mixing and curing of the resin and hardener were described earlier.<sup>7</sup> Disc-shaped samples were prepared for differential scanning calorimetry (DSC) measurements using silicone rubber molds. The silicone rubber molds

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containing the prepolymer mix (20–30 mg) were placed 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. These cured time-temperature conditions are referred to as Standard-II cures. The molds were then taken out of the heated desiccator and allowed to cool to room temperature under vacuum. The samples were disc shaped with flat bottoms that fit snugly in DSC-2 sample pans.

The cured samples were soaked in distilled water at 25°C as well as 70°C for different lengths of time and scanned on a DSC at 20°C/min. from –33°C to 307°C. Two sets of cured samples were soaked in distilled water at 25°C and 70°C for 820 h and 775 h, respectively. These samples were then dried in a vacuum desiccator at 30°C and 70°C, respectively, for different lengths of time and scanned on the DSC at 20°C/min. A Perkin-Elmer Model DSC-2C with a data station was used. All measurements were made in a nitrogen atmosphere.

Cured epoxy films for IR investigations were formed by pressing the prepolymer mix between two smooth Teflon surfaces and curing under a nitrogen atmosphere in a vacuum desiccator as described above. These films were found suitable for transmission IR study and were run on a Perkin-Elmer IR Model 281-B Spectrometer.

## RESULTS AND DISCUSSION

Typical DSC thermograms of dry, soaked (500 h) at 70°C, and soaked (820 h) and then dried (96 h) at 70°C samples are shown in Figure 1. As has been previously reported,<sup>7,8</sup> there remains a significant fraction of unreacted epoxide in the epoxy resin following the cure cycle employed here. In a DSC scan, an exothermic reaction will be seen when the glass transition is

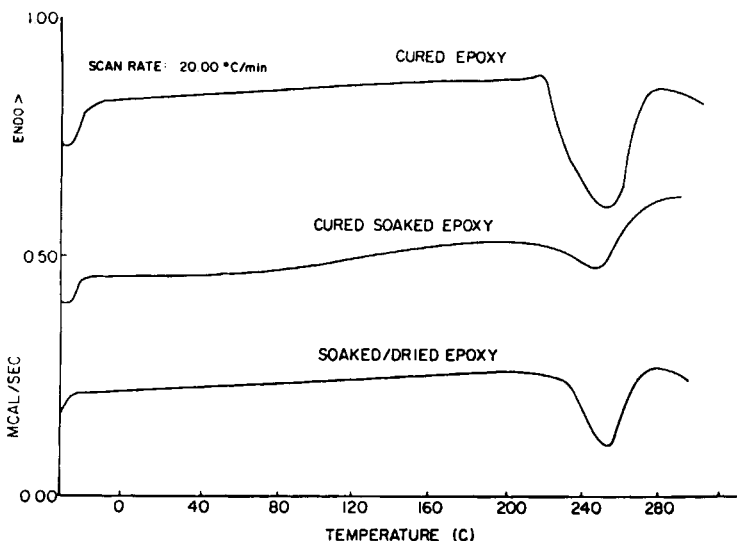


Fig. 1. DSC thermograms of cured dry, soaked (500 h) at 70°C, and soaked (820 h), dried (96 h) at 70°C.

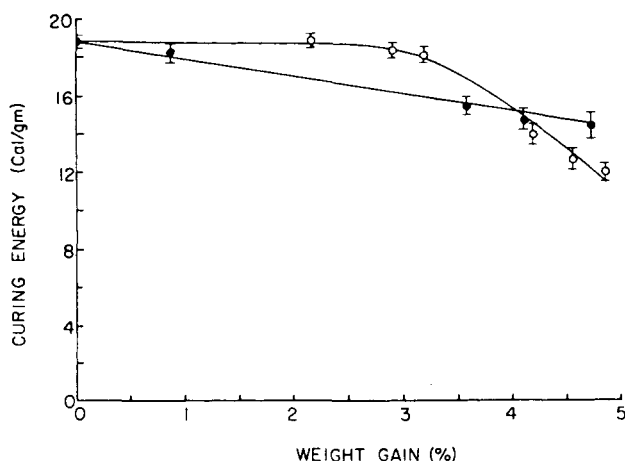


Fig. 2. Plots of curing energy vs. weight gain for cured, soaked [(●) 25°C; (○) 70°C] epoxy samples.

surpassed and the system becomes mobile enough to permit further reactions to occur.

Plots of reaction energy vs. weight gain after the absorption are shown in Figure 2. The data for specimens soaked at 25°C and 70°C are presented in Tables I and II, respectively. The curing energies for the H<sub>2</sub>O-soaked samples are lower than the dry counterpart and decrease monotonically with increase in the water gain. Three factors are responsible for this decrease. First, moisture evolution occurs endothermically. Second, a small amount of the low molecular weight species such as unreacted TGDDM, DDS, and some oligomers leach out during soaking. Leaching out of some species has been observed in the same TGDDM/DDS epoxy system by Yang.<sup>9</sup> Third, water reacts with some of the residual epoxide groups. The latter is especially true for the samples soaked at 70°C. The IR spectra of dry and 70°C-water-soaked samples, shown in Figure 3, confirm that the intensity of the epoxide peak at 904 cm<sup>-1</sup> of the soaked samples has decreased slightly. Illinger and Sprouse<sup>10</sup> using FTIR found earlier that water indeed reacts with the epoxide groups for amine-cured DGEBA systems.

TABLE I  
DSC Results of Standard-II Cured, H<sub>2</sub>O Soaked at 25°C

| Water weight gain (%) | Glass transition temperature (°C) | Curing energy (cal/g) | Curing energy percent of control (%) | Curing peak temperature (°C) |
|-----------------------|-----------------------------------|-----------------------|--------------------------------------|------------------------------|
| 0.0 (Control)         | 236                               | 18.7                  | 100                                  | 266.6                        |
| 0.9                   | 223                               | 18.2                  | 97                                   | 262.7                        |
| 3.6                   | N.C. <sup>a</sup>                 | 15.2                  | 81                                   | 252.7                        |
| 4.1                   | N.C.                              | 14.4                  | 77                                   | 250.7                        |
| 4.7                   | N.C.                              | 14.1                  | 75                                   | 248.7                        |

<sup>a</sup> N.C. = not clearly seen.

TABLE II  
DSC Results of Standard-II Cured, Soaked at 70°C Epoxy, Samples

| Water weight gain (%) | Glass transition temperature (°C) | Curing energy (cal/g) | Curing energy percent of control (%) | Curing peak temperature (°C) |
|-----------------------|-----------------------------------|-----------------------|--------------------------------------|------------------------------|
| 0.0 (Control)         | 236                               | 18.7                  | 100                                  | 266.6                        |
| 2.2                   | 232                               | 18.8                  | 101                                  | 266.9                        |
| 2.9                   | N.C. <sup>a</sup>                 | 18.1                  | 97                                   | 264.4                        |
| 3.2                   | N.C.                              | 17.9                  | 96                                   | 259.4                        |
| 4.2                   | 116                               | 13.7                  | 73                                   | 247.0                        |
| 4.6                   | 116                               | 12.4                  | 66                                   | 247.1                        |
| 4.9                   | 117                               | 11.7                  | 63                                   | 246.6                        |

<sup>a</sup> N.C. = not clearly seen.

The glass transition temperature ( $T_g$ ) and the curing peak temperature also decrease with increasing water content. Interestingly, above 4.2% water gain, no further lowering of  $T_g$  is seen for samples soaked at 70°C. Earlier, Browning<sup>1</sup> observed similar behavior for the TGDDM/DDS epoxy system. This was taken as evidence of microcracking. Water could cluster in the microcracks in bulk form and would not contribute towards further plasticization. However, there is no indication of any clustered, freezable water observed in the thermogram (Fig. 1) as indicated by the absence of an endothermic peak for the melting of ice near 0°C. This implies that microcracks, if present, are not big enough for water to penetrate, freeze, and be detected by the DSC. Broadline NMR spectra of a soaked epoxy in earlier studies<sup>5,11,12</sup> also failed to show clustered water, although highly mobile water species were observed. It is possible, however, that there is a distribution of freezable cluster sizes so that the effective melting point is spread over a range of temperatures.

Data for the samples soaked at 25°C and 70°C and then dried at 30°C and 70°C, respectively, are presented in Tables III and IV. Plots of curing energy vs. water gain are shown in Figure 4. The samples soaked at 25°C and dried at 30°C had 0.4% net weight gain even after 400 h of drying under vacuum,

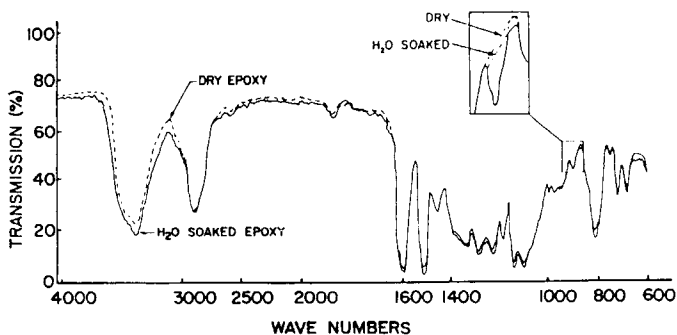


Fig. 3. IR spectra of cured, dry, and water-soaked (70°C, 340 h) epoxy samples.

TABLE III

DSC Results of Standard-II Cured, Soaked at 25°C, for 820 h and Dried at 30°C in Vacuum

| No. of hours dried | Weight change (%) | Glass transition temperature (°C) | Curing energy (cal/g) | Curing energy (%) | Curing peak temperature (°C) |
|--------------------|-------------------|-----------------------------------|-----------------------|-------------------|------------------------------|
| Dry <sup>a</sup>   | 0.0               | 236                               | 18.7                  | 100               | 266.6                        |
| 5                  | 4.1               | N.C. <sup>b</sup>                 | 14.5                  | 78                | 247.2                        |
| 48                 | 3.0               | N.C.                              | 16.5                  | 88                | 249.2                        |
| 120                | 1.4               | 186                               | 17.5                  | 93                | 255.1                        |
| 165                | 1.1               | 201                               | 17.5                  | 94                | 257.3                        |
| 300                | 0.6               | 211                               | 17.3                  | 93                | 258.6                        |
| 400                | 0.4               | 220                               | 17.4                  | 93                | 259.6                        |

<sup>a</sup> Dry control sample.<sup>b</sup> N.C. = not clearly seen.

while the samples soaked and dried at 70°C had a net weight gain of 0.2% after 145 h of drying under vacuum; the  $T_g$ 's of the samples soaked at 25°C were almost reversible after drying. However,  $T_g$ 's of the samples soaked and dried at 70°C were much lower than the  $T_g$  of the as-cured sample. It is noted, however, that the DSC trace shows a very weak  $T_g$  for the dried specimens.

The curing energy behaves in a similar fashion. For samples soaked at 25°C, the curing energy is nearly equal to that of dry samples (93%). However, the curing energy for samples soaked and dried at 70°C is only 60% of the original dry samples. These data show clearly that, at moderate temperatures above ambient conditions (e.g., 70°C), water induces further reactions of the resin. This may cause permanent change in the physical and the chemical properties of the epoxy. It is also noted that the maximum in the exothermic peak decreases as a function of H<sub>2</sub>O content. Upon drying, the maximum for both the 25°C and 70°C soaked samples returns to almost the same temperature as the control.

TABLE IV

DSC Results of Standard-II Cured, Soaked at 70°C, for 775 h and Dried at 70°C in Vacuum

| No. of hours dried | Weight change (%) | Glass transition temperature (°C) | Curing energy (cal/g) | Curing energy (%) | Curing peak temperature (°C) |
|--------------------|-------------------|-----------------------------------|-----------------------|-------------------|------------------------------|
| Dry <sup>a</sup>   | 0.0               | 236                               | 18.7                  | 100               | 266.6                        |
| 4                  | 3.2               | N.C. <sup>b</sup>                 | 11.1                  | 59                | 245.7                        |
| 22                 | 1.7               | 104                               | 11.3                  | 60                | 251.5                        |
| 46                 | 0.9               | 116                               | 11.4                  | 61                | 256.7                        |
| 96                 | 0.3               | 123                               | 10.9                  | 58                | 262.1                        |
| 120                | 0.3               | 132                               | 10.9                  | 58                | 262.7                        |
| 145                | 0.2               | 133                               | 11.1                  | 59                | 263.0                        |

<sup>a</sup> Dry control sample.<sup>b</sup> N.C. = not clearly seen.

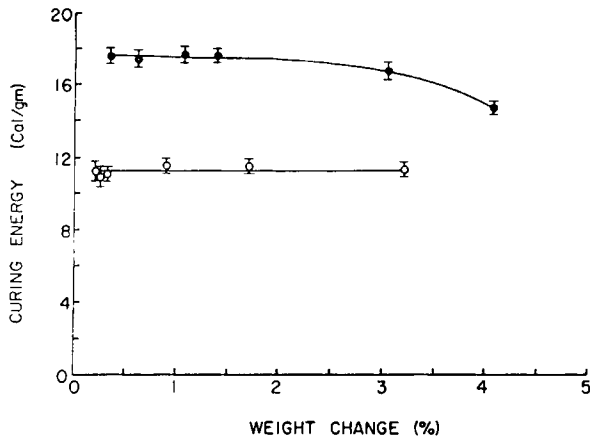


Fig. 4. Plots of curing energy vs. weight change for samples cured and soaked, and then dried for varying times. (● soaked at 25°C, ○ soaked at 70°C).

### CONCLUSIONS

Sorbed water plasticizes the epoxy TGDDM/DDS at ambient temperatures, but the plasticization is mostly reversible. Samples soaked at 70°C show a monotonic lowering of the  $T_g$  up to a weight gain of ca. 4% H<sub>2</sub>O. Additional weight gain does not lower  $T_g$  further. Upon drying, the samples soaked at 70°C show a weak  $T_g$  appreciably lower than the control samples.

It is shown that water causes further reaction of the unreacted epoxide groups, which apparently causes permanent change in the physical and chemical nature of the epoxy.

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