JOURNAL OF MATERIALS SCIENCE 16 (1981) 75–83

The anomalous lowering of the glass transition of an epoxy resin by plasticization with water

PAUL PEYSER, WILLARD D. BASCOM
Naval Research Laboratory, Washington, DC 20375, USA

The validity of the assertion that 6 to 7 wt% absorbed water lowers the glass transition, T_g, (~ 250° C) of a highly cross-linked, high temperature epoxy resin (NARMCO 5208) by 100 to 150° C was investigated by a number of thermoanalytical techniques. This plasticization is of significance to the use of organic matrix composition skins on supersonic aircraft which experience a sudden "thermal spike", and supposedly a sudden loss in modulus. The study was complicated by the loss of water above 100° C during the tests and the decomposition of the polymer at about the temperature of its apparent glass transition. No glass transition could be observed by differential scanning calorimetry and the thermal mechanical analyser gave inconclusive results. The dynamic mechanical analyser gave a clear indication of a glass-like transition at about 250° C which was reversible, reappearing upon cooling and reheating. This transition could not be related to the decomposition of the sample. Absorption of 7 wt% water broadened and lowered the transition by about 50° C. However, after studying the rate of change of the modulus of the resin from the plasticized state to the dry state it was concluded that the absorbed water lowers T_g by only 50° C and not the 100 to 150° C claimed by others. Moreover, the mechanism of this apparent glass transition differs from that of a normal T_g, and may involve the breaking of hydrogen bonds.

1. Introduction

Tetrafunctional epoxies based on the tetraglycidyl ether of methylene dianiline and diaminodiphenyl sulfone (e.g. NARMCO 5208) are being used as a matrix resin in graphite fibre composites in aerospace construction. It has been reported that the dry resin has a glass transition, T_g, at about 250° C and that the absorption of 6 to 7 wt% water lowers the T_g by more than 100° C due to plasticization [1–3]. We considered such a large plasticization effect to be highly unusual and set out to either confirm or disprove it. The problem is a serious one since composite fuselages on supersonic planes can be subjected to a thermal spike which will increase the temperature of the resin by more than 150° C at a rate greater than 30° C min^{-1}. If the resin had absorbed water, the rapid heating would not provide time for the composite to dry and thus the upper use temperature would be much less than 250° C. If this proposition proves to be correct, it represents a significant limitation on the use of high temperature matrix resins in advanced airframe construction.

To address this problem special techniques must be used to measure the glass transition of a water-plasticized resin since the loss of water above 100° C must be minimized. Browning's [1] technique was to use a large size sample and measure the deflection of the sample (under oil) under three point bending and at a 2° C min^{-1} heating rate in a heat distortion apparatus. Post-heat measurements showed that the weight loss was less than 10%. McKague, Reynolds and Halkias [2] used small flat specimens mounted vertically in a thermal mechanical analyser and determined T_g as the temperature at which a probe penetrated the sample while heating at a rate of 20° C min^{-1} (22% weight loss at 149° C). They claim that their vertical mounting eliminated erroneous effects due to drying out of the surface

0022–2461/81/010075–09$02.90/0

of their specimens, but their method increases the possibility of error due to bending or buckling of the sample. Both the above methods tend to show a lowering of the modulus for the water-plasticized resin at about 150° C below its normal T_g but do not necessarily indicate that this is the precipitous drop in modulus that would occur at a T_g.

Augl [3], using a torsion braid apparatus, measured a gradual decrease in modulus while heating the wet sample at 30° C $\min^{-1}$ as compared to the dry sample which showed a sharp drop in modulus at ~ 250° C, its apparent T_g. One possible interpretation of Augl's results is that if the resin were heated even faster, so that the water was not lost, the T_g of the resin may have been lowered by 150 to 200° C due to plasticization by water.

Some confusion exists as to the T_g of dry NARMCO 5208. Browning [1] measured a T_g of ~ 180° C with his heat distortion apparatus. He also measured the NARMCO 5208 spectrum in a Rheovibron and found a minor peak at about 170° C which he attributed (incorrectly) to the T_g and a major peak at ~ 250 to 300° C which he ignored. McKague *et al.* [2] and Augl [3] measured a T_g at ~ 250° C.

2. Experimental procedure

NARMCO 5208 obtained from the Narmco Corporation was cured according to the following schedule: 20 h and 93° C followed by 3 h at 121° C followed by 2 h at 149° C followed by 2 h at 177° C followed by 4 h at 200° C. Samples were placed above water in a desiccator and the amount of water absorption was determined by weighing.

A Dupont model 951 thermogravimetric analyser (TGA) (with a 990 control console) was used to measure the weight loss of dry and wet NARMCO 5208 as it was heated at a controlled heating rate.

Differential scanning calorimetric measurements (DSC) were performed on a Perkin–Elmer model DSC-2. The instrument can measure the specific heat of a sample as a function of temperature at a constant heating rate. The glass transition appears as an endothermic change in specific heat. Using special O-ring sealable stainless steel cells obtained from the manufacture it was possible to measure the T_g of water plasticized epoxy resins.

The linear expansion/contraction of dry and wet NARMCO 5208 at a controlled heating/cooling rate was measured on a Perkin–Elmer thermomechanical analyser (TMA).

The mechanical properties of our samples were measured with the Dupont dynamic mechanical analyser (DMA), Model 980 with 990 controller. This instrument vibrates a sample in a bending mode at its natural frequency and records the energy necessary to maintain a constant amplitude of vibration at this frequency (damping). From a knowledge of the geometry of the sample and certain instrument constants it is possible to relate the square of the resonant frequency to the modulus of the sample and to relate the damping to $\tan \delta$, the quantities generally measured by other instruments of a similar type.

3. Results

A major complication arose in our attempt to measure the T_g of NARMCO 5208. The material begins to decompose at a temperature close to that at which the glass transition of the dry material is supposed to occur. In the DSC experiments, decomposition products were collected on the cooling block of the instrument. In the TMA experiments, smoke was often visually detected. In DMA and TGA experiments, decomposition product odours were detected. To obtain meaningful results this decomposition must be recognized and considered in the analysis of the data.

3.1. TGA

Two sets of TGA experiments were run. In the first set (Fig. 1), run on powdered samples, the flow rate of the nitrogen gas and the heating rate were chosen to correspond to a normal TGA run. In the second set (Fig. 2), pieces of NARMCO 5208 similar to those used in the DMA experiments (see below) were run at an unusually high flow rate. In one experiment the sample was wrapped in aluminium foil to retard the loss of water. As expected, these runs were very noisy. These TGA results should be viewed only qualitatively since the actual weight loss of a particular sample depends not only on the heating rate and gas flow but also on the geometry of the sample and heating chamber which could not be exactly duplicated in the TGA as compared to the DMA. However, the following results can be derived from the TGA runs: (1) Even the dry material exhibits a slight weight loss from ~ 100 to ~ 200° C. (2) The dry material begins to decompose significantly above 200° C. (3) The wet material lost all or nearly all of its water above 200° C under heating conditions copying the DMA experiments.

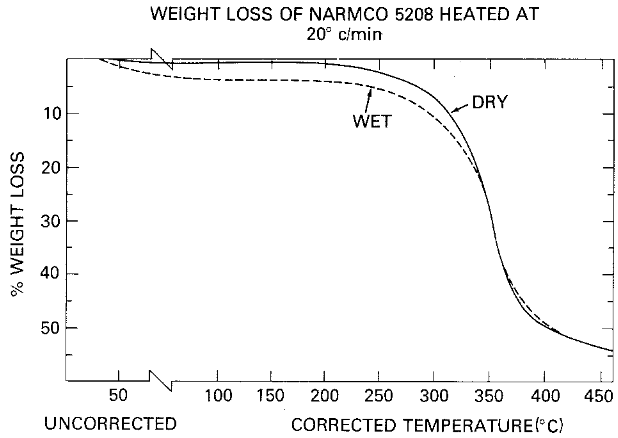

Figure 1 Weight loss of wet (6 wt % water) and dry NARMCO 5208 powders heated at 20° C min^{-1}.*

3.2. DSC

Table I lists the T_g of a series of dry and water-plasticized difunctional epoxy resins measured by the DSC. If these results are extrapolated to predict the maximum change in T_g when water absorption is about 7%, the value obtained for NARMCO 5208, a maximum lowering of about 40 to 50° C is predicted. However, direct attempts to measure T_g on dry or wet NARMCO 5208 proved futile. At first, a *small* change in specific heat similar to that normally observed at a glass transition was measured, but after careful study this endothermic change was attributed to a degassing and decomposition of the material. To prove this point, the following experiment was performed. Dry NARMCO 5208 was heated at 160° C min^{-1} from 77 to 427° C and a straight line indicating no change in specific heat (no T_g) was measured. We reasoned that the degassing and decomposition of NARMCO 5208 would be time dependent but that the sample would respond quickly to a glass transition. Indeed we were able to detect the glass transition of another epoxy resin while heating at 160° C min^{-1} (Fig. 3).

3.3. TMA

Under certain conditions and without a critical analysis one can get results from the TMA that

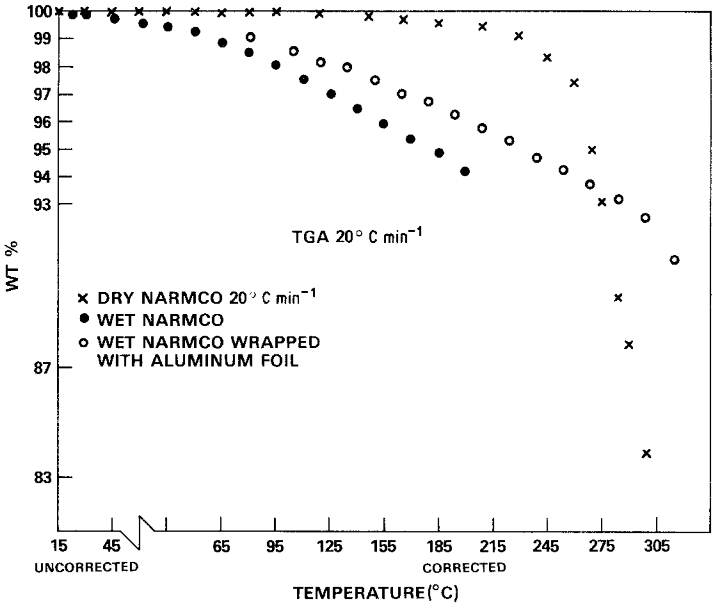

Figure 2 Weight loss of wet (6 wt % water) and dry NARMCO 5208 samples heated at 20° C min^{-1} under conditions copying DMA experiments.*

---

*The uncorrected temperature is that of the thermocouple placed near the sample. The corrected temperature is the approximate temperature of the sample.

TABLE I Glass transition of dry and wet bisphenol-A diglycidyl ether epoxies cured with various curing agents

Curing agent	Water (wt%)	Dry glass transition (K)	Wet glass transition (K)	Extrapolated lowering of the glass transition with 7% water (K)
HHPA*	0.3–0.5	330	327	70–42
DETA†	2.2	401	387	44.5
MPDA‡	3.8	444	425	35

*Hexahydrophthalic anhydride.
†Diethylenetriamine.
‡m-phenylenediamine.

indicate a glass transition in NARMCO 5208. For example, in Fig. 4, after an initial heating, originally wet NARMCO 5208 demonstrates expansion and contraction curves which superficially resemble a glass transition. However, close scrutiny indicated that the change in the coefficient of thermal expansion at the apparent T_g was often enormous compared with a usual T_g where the coefficient changes by a factor of 2 to 4. This occurred even though the water was surely driven off the wet sample after the first heating. The (originally) dry sample did not show this expansion upon heating but only a slight curvature in the dependence of the coefficient of thermal expansion on temperature until at 295° C the sample began burning as evidenced by an increase (beyond the linear heating rate) of the temperature of the thermocouple. Considering the TMA results by themselves one would tend to relate changes in the expansion of the sample more to a decomposition of the sample than to a glass transition.

3.4. DMA

The DMA was uniquely suited to study the present problem. The sample could be heated or cooled at controlled rates of up to 20° C min^{-1} or the temperature could be held isothermally. Small thin samples, 0.01 inch thick, could be used which could be saturated with water in about one month. This apparatus did not require the very thin films which are difficult to make that are required for other DMA instruments. It was also possible, with relative ease, to operate the DMA in a somewhat unusual manner, in a humid atmosphere, as will be presently discussed. The temperature of a sample compared with that of the thermocouple placed near the sample was estimated from the spectrum of polymethylmethacrylate run at various heating and cooling rates and also wrapped with aluminium foil. The temperature in Figs 6 to 11 include this correction. A glass transition would appear as a drastic drop in resonance frequency (modulus) and a simultaneous maximum in damping (tan δ). As such, DMA gave the first clear indication of a T_g-type spectrum with the transition at about 250° C. Moreover, this apparent glass transition was reversible in that it reappeared upon cooling and subsequent reruns. This reversibility is amazing since the sample had clearly decomposed significantly after the first heating as evidenced by its

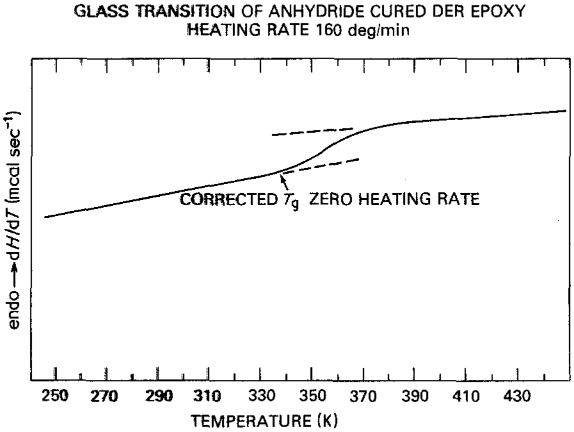

Figure 3 Glass transition of HHPA cured DER epoxy measured at a heating rate of 160° C min^{-1}.

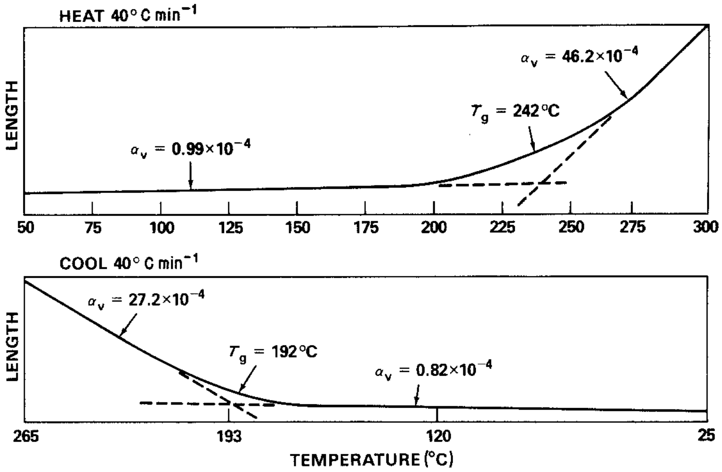

Figure 4 TMA of originally wet NARMCO 5208 after first heating. Heating rate 40° C min^{-1}. Note large change in coefficient of volumetric (× 3 linear) thermal expansion α_v at transition.

darker brown colour and increased brittleness. (The increased brittleness may be due to increased cross-linking or the loss of low molecular weight plastisizing components.) Many cooling runs were lost because the sample broke. Although we tried, we could not relate this apparent T_g simply to a decomposition reaction. In one experiment we held the temperature isothermally in the middle of a heating run at a point where the modulus begins to drop drastically. We reasoned that if this drastic drop was due to decomposition, it would continue at a lower temperature but at a slower rate. Except for a slight drop in modulus due to the temperature of the sample catching up with that of its environment and the thermocouple, the modulus did not continue to drop as it does in the complete T_g run. In another experiment we coated an aluminium sample with a room temperature cured epoxy and attempted to obtain a T_g-like spectrum in the DMA as the epoxy decomposed at high temperatures. Such a spectrum was not, however, obtained.

While the glass-like transition observed in the DMA could not be related directly to the decomposition of the sample and was measured upon cooling as well as heating, the transition was effected by the high temperature of the transition. As previously mentioned, an attempt was made to correct for the thermal lag of the system and specify the temperature of the sample by calibration with polymethylmethacrylate. As can be seen from Figs 6 and 7, at 5° C min^{-1} the correction was fairly successful in that the corrected heat and cool curves for NARMCO 5208 were quite similar. However, at 10 and 20° C min^{-1} the cool curve showed a correction transition temperature

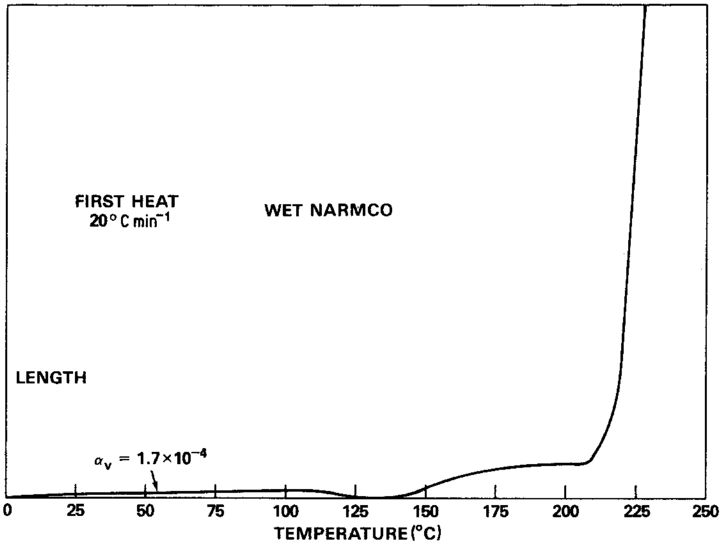

Figure 5 TMA of wet (7 wt% water) NARMCO 5208. Heating rate 20° C min^{-1}.

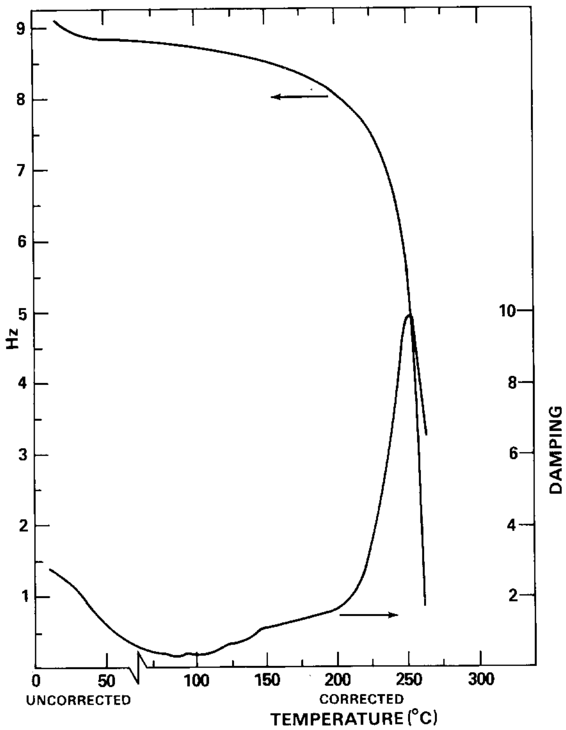

Figure 6 DMA of dry NARMCO 5208 heated at 5° C min^{-1}.*

lower than the heat curve, Fig. 8. Moreover, a gradual lowering of the transition temperature occurred as the sample was rerun again and again. (Therefore, any cross-linking, tending to increase T_g, that may have occurred was overshadowed by a decomposition.) After a few runs, however, the cool transition was similar to the heating one even at 10 and 20° C min^{-1}, Fig. 9. For the first heating, the (corrected) temperature of the transition increased by about 25° C as the heating rate doubled from 5 to 10° C min^{-1} and from 10 to 20° C min^{-1}. At times a new peak appeared at about 150° C after the first run. Note that this occurred on a dry sample and was no doubt related to the decomposition of the sample. The DMA of dry NARMCO 5208 with a heating rate of 20° C min^{-1} is shown in Fig. 10.

The modulus drop and maximum damping in wet (7% water) NARMCO 5208 were broadened and the apparent T_g was lowered by about 50° C as would be expected from a water-plasticized polymer (Fig. 11). When the sample was rerun, the original properties of a dry sample were again obtained. An indication of a maximum in damping at a much lower temperature, 100 to 150° C, was detected in some tests on the wet sample and this gave credence to the point of view that the T_g of water-plasticized NARMCO 5208 can be lowered by as much as 150° C (if it had retained all its water). However, this small maximum also occurs in dry NARMCO 5208 which had gone through many runs. This maximum is therefore probably related to a different molecular structure resulting from the decomposition of dry NARMCO 5208 and water assisting this decomposition.

3.5. DMA rate studies

Let us now analyse these results in more detail. From our TGA experiments it is certain that, for the first run on the wet sample, almost all of its water had been lost by the time we measured an apparent T_g. Why then do we not obtain the spectrum of dry NARMCO 5208 towards the end of the test, particularly since we do indeed obtain this spectrum in subsequent retuns? The answer is that the loss of water from wet NARMCO 5208

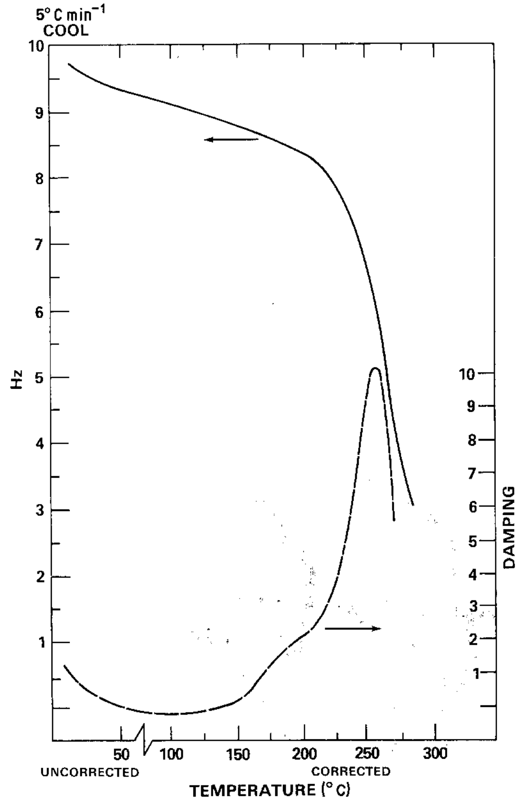

Figure 7 DMA of dry NARMCO 5208 cooled at 5° C min^{-1} after a 5° C min^{-1} heat up.*

---

*The uncorrected temperature is that of the thermocouple placed near the sample. The corrected temperature is the approximate temperature of the sample.

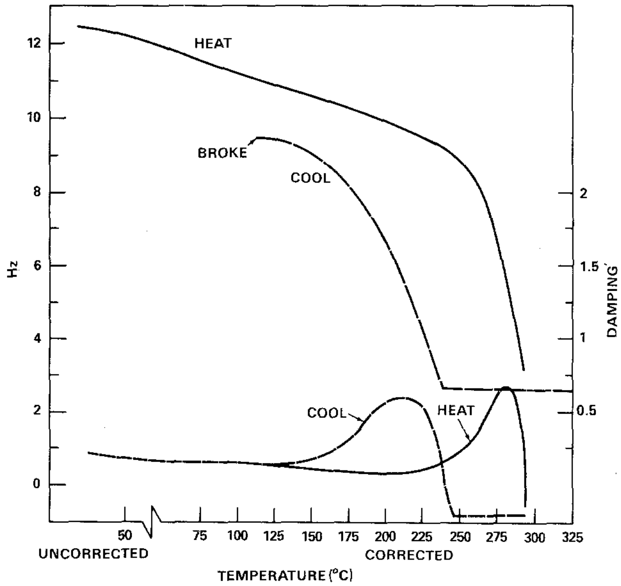

Figure 8 DMA of dry NARMCO 5208 heated at 10° C min^{-1} and then cooled at 10° C min^{-1}. Solid line heating. Broken line cooling.*

is not instantaneous, i.e. it is time dependent. This can be illustrated by stopping the run on a wet sample in the middle of the apparent T_g modulus drop, holding the temperature constant, and measuring the slow increase in modulus to that of dry NARMCO 5208, (see Fig. 12). Realizing that there is a time dependence in the change from a plasticized to unplasticized state, it can now be argued that the spectrum of water-plasticized NARMCO 5208 that was measured at a 20° C min^{-1} heating rate (with only a 50° C drop in apparent T_g) is characteristic of wet NARMCO 5208 measured at any rapid heating rate. To justify this point of view, the following experiment was performed. A wet sample containing 7% water was weighed and heated at 20° C min^{-1} in the DMA up to 175° C. The DMA chamber was kept humid by placing water in small quartz containers surrounding the sample. No drastic drop in modulus was noted during the 20° C min^{-1} heating.

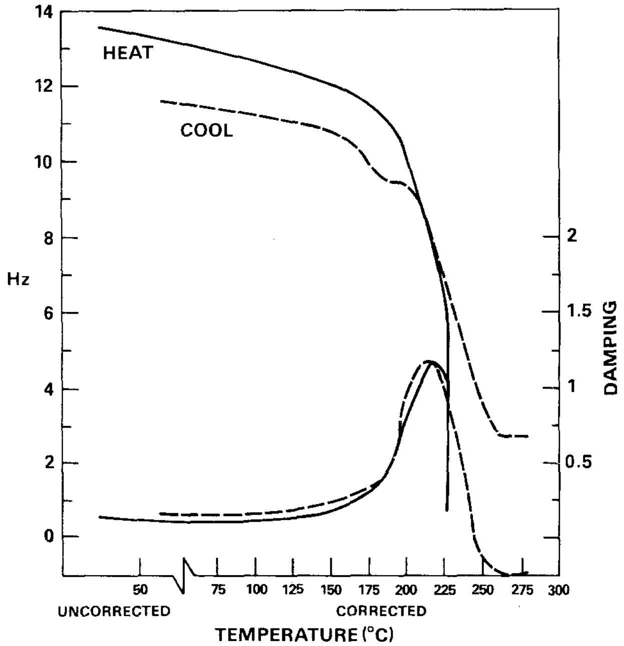

Figure 9 DMA of dry NARMCO 5208 after a few previous heatings to above the transition temperature. Heating and cooling rates 10° C min^{-1}. Solid line heating. Broken line cooling.*

---

*The uncorrected temperature is that of the thermocouple placed near the sample. The corrected temperature is the approximate temperature of the sample.

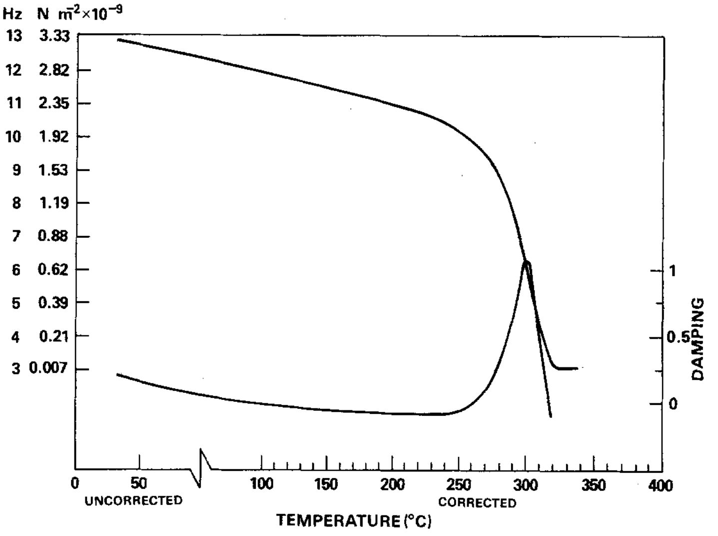

Figure 10 DMA of dry NARMCO 5208. Heating rate 20° C min^{-1}.*

As quickly as possible the sample was cooled and reweighed and the weight loss was 1.4%. The sample was quickly rerun giving the spectrum of a wet sample.

4. Discussion

We are in disagreement with other researchers and conclude that NARMCO 5208 does not loose its stiffness between 100 and 200° C during a thermal spike due to water plasticization.

None of the work by others on NARMCO 5208 has shown a *drastic* lowering of the T_g by water. The results of Browning [1] and of McKague *et al.* [2] only indicate some lowering of the modulus and we confirm these results. Nor do our results differ from those of Augl [3]. We did, however, investigate the matter further and conclude that the mechanical spectra of wet NARMCO 5208 which we and other workers obtained at fast heating rates are in fact indicative of wet NARMCO 5208.

Attempts have been made by Browning [1] and by McKague *et al.* [2] to justify on theoretical grounds, using the Kelley–Bueche equation [4], a drastic lowering of the T_g of NARMCO 5208 by absorbed water. The problem with these calculations is that the T_g of water is assumed to be 4° C instead of −123° C [4] and that the coef-

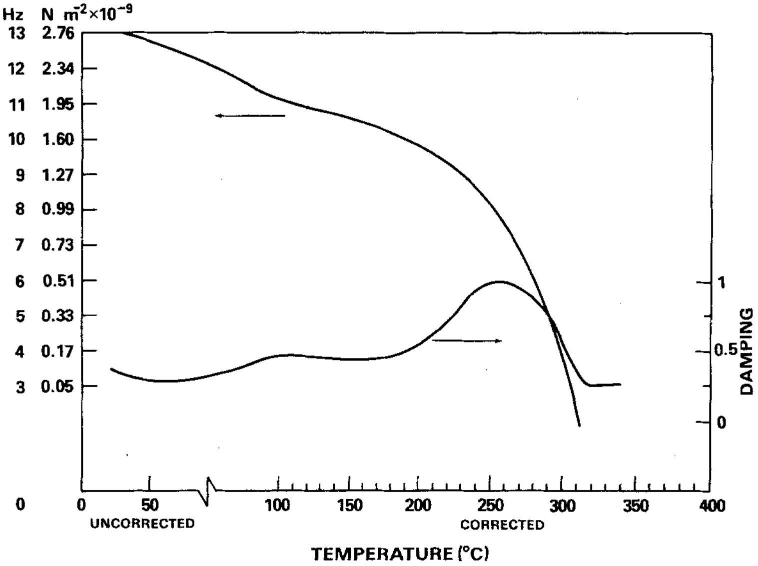

Figure 11 DMA of NARMCO 5208 with 7 wt% absorbed water. Heating rate 20° C min^{-1}.*

---

*The uncorrected temperature is that of the thermocouple placed near the sample. The corrected temperature is the approximate temperature of the sample.

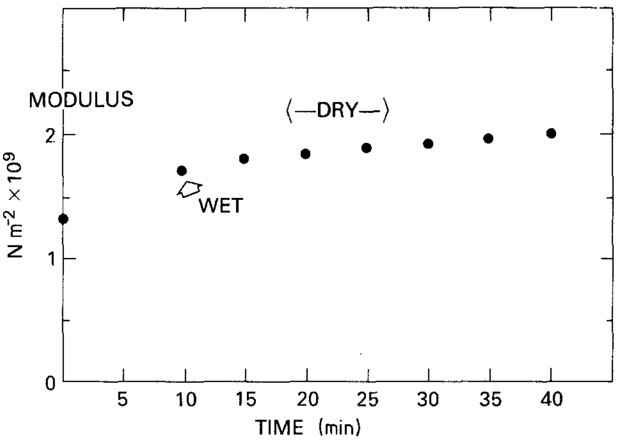

Figure 12 Change in modulus of wet NARMCO 5208 versus time at 230° C.

ficient of thermal expansion for water at 4° C is taken to be 4×10^{-3}, a value orders of magnitude too high [6]. Another calculation by Morgan and O'Neal [7] predicts less than a 20° C lowering of the T_g by 7% absorbed water. Another theoretical equation, derived by Carter and Kebler [8] also predicts a drastic lowering of the T_g of NARMCO 5208 by absorbed water. However, Carter and Kebler make use of an experimentally determined ΔCp (change in specific heat at T_g) as measured by Reynolds [9]. Our results, however, suggest that the use of DSC to determine the T_g for NARMCO 5208 is questionable, and this gives rise to doubt about the determination of ΔCp. Moreover, the value of ΔCp determined by Reynolds is very small, a value which could only be measured on a DSC under ideal conditions where no decomposition of the epoxy is simultaneously occurring.

The "T_g-like" spectra that NARMCO 5208 displays differs from usual glass transitions in the following respects: (1) A significant decomposition occurs in the vicinity of the transition but the high temperature of the transition is little effected by this decomposition. Hence if we are indeed dealing with a glass transition, the high cross-linking necessary for such a high temperature glass transition must still be present. (2) No transition was measured in the DSC. (3) In the TMA we at times found no transition, and at times a transition at ~ 217° C where the change in the ratio of the coefficient of thermal expansion at the transition was very large. (4) Different researchers and different methods of measurement by the same researcher gave more than expected variations in the transition temperature. Hence we have reason to suspect that we are not measuring a glass transition; a transition associated with increased chain mobility. It is possible that we are dealing with a breakdown of the molecular cross-linked structure of NARMCO 5208, possibly H-bonds, which is partially reversible and partially irreversible. From this point of view, the role of water is to assist this breakdown.

5. Conclusions

1. There is no reason to expect absorbed water to degrade the mechanical properties of high temperature tetrafunctional epoxies by an anomalously large amount, as suggested by other workers.

2. The apparent T_g of NARMCO 5208 is anomalous in nature and may be due to bond breaking.

References

1. C. E. BROWNING, "The Mechanism of Elevated Temperature Property Losses in High Performance Structural Epoxy Resin Matrix Materials After Exposures to High Humidity Environments", Ph.D. Thesis, University of Dayton, 1976.
2. E. L. MCKAGUE, Jr, J. D. REYNOLDS and J. E. HALKIAS, *J. Appl. Polymer Sci.* **22** (1978) 1643.
3. J. M. AUGL, "The Effect of Moisture on Carbon Fiber Reinforced Epoxy Composites", 11 NSWC Technical Report, NSWC/WOL/TR 76-149 ADA 039903 (1977).
4. F. N. KELLEY and F. BUECHE, *J. Polymer Sci.* **1** (1961) 459.
5. M. SUGLSAKI, H. SUGA and S. SEKI, *Bull. Chem. Soc. Japan* **41** (1965) 2591.
6. V. STOTT and P. H. BIGG, "International Critical Tables", Vol. 3, edited by E. W. Washburn (McGraw-Hill Book Co., New York, 1928) p. 24.
7. R. J. MORGAN and J. E. O'NEAL, *Polymer Plastic Technol. Eng.* **10**(1) (1978) 49.
8. A. G. CARTER and K. G. KEBLER, *J. Comp. Mater.* **11** (1977) 265.
9. J. D. REYNOLDS, 11 NSWC Technical Report, NSCW/WOL/TR 76-149 ADA 039903 (1977).

Received 15 May and accepted 10 June 1980.