GEPP-TIS-437

MASTER

AGING IN CTBN MODIFIED EPOXY RESIN STOCKS

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ABSTRACT

The cause of degradation in the glass transition temperature (T_G) of a partially crystallized polymer was investigated. Sample epoxy resin filled capacitors were cured at 90°C for 24 hours, then stored at room atmospheric conditions. These showed typical degradation in T_G after storage for one month. One set of epoxy resin castings was stored at room atmosphere and another set was stored in a dry box at 0% relative humidity and 27°C. The samples at room atmospheric conditions showed typical degradation in T_G, while the T_G for those stored in the dry box increased. Further tests were then made on epoxy resin castings at various curing temperatures and times at both room atmosphere and 0% humidity. Resulting data indicated that absorption of moisture during storage was the predominant cause of T_G degradation, with stress relaxation another, though smaller, contributing factor.

CONTENTS

ILLUSTRATION

TABLES

INTRODUCTION

It had been observed in tests at Sandia Laboratories, Albuquerque, (SLA), that while post curing at temperatures higher than the cure temperature raised the glass transition temperature (T_G) of a partially crystalline polymer, this change was temporary and degraded with time to its original level. This was attributed to stress relaxation. Defect analysis at the General Electric Neutron Devices Department (GEND) had revealed a similar degradation of T_G with time, but this degradation appeared to be due to moisture absorption. In an attempt to determine the primary cause of this degradation, two series of tests were initiated: (1) post curing capacitors and (2) T_G studies versus time and relative humidity.

CAPACITOR STUDIES

To assess post cure T_G variability, one capacitor was initially tested. The data shown in Table I appears to support the stress relaxation hypothesis.

TABLE I Glass Transition Temperature Data on a Capacitor after Post Cure and Aging.

		T_G (TMA*)	Change in T_G
Initial	8-17-78 Tested	74°C	-
Post Cured	8-17-78 Tested	85°C	+11°C
Retested	8-22-78 Tested	83°C	+ 9°C
Retested	After 2 Months	79°C	+ 5°C
Retested	After 4 Months	82°C	+ 8°C

On the basis of these tests, ten additional capacitors were evaluated. These were all produced by the GEND production facilities during the period November 1976 to February 1977 and post cured from September to November 1978. The data are tabulated in Table II.

*Thermal Mechanical Analyzer

Table II Glass Transition Temperature of a Series of Capacitors Produced by Manufacturing

Capacitor Number	GLASS TRANSITION TEMPERATURE - °C Initial	After Post Cure (90°C for 24 hours)	After One Month Storage at R.T.
1127	78	80	76
1128	78	78	83
1142	76	81	72
1154	82	81	83
1155	81	84	85
1159	81	84	85
1160	82	86	82
1161	80	82	82
1143	77	84	-
1152	78	85	-
Average +	79.3	82.5	81.0
Sigma	±2.2	±2.5	±4.6

As may be seen, the effect of the post cure was not as great in the initial tests,and after aging one month some samples showed a significant reduction in T_G while others evidenced no change.

Since these tests did not control the aging environment, the changes could have been due to moisture pickup at least in part. To assess this, a controlled experiment was generated, the results of which will be discussed in a following section.

HUMIDITY AGING STUDIES

Concurrent with the capacitor testing, a program to evaluate the effects of humidity during room temperature aging was also initiated. Six different castings were employed: three prepared from CTBN*/Epon** 828/DEA*** stocks and three from CTBN/Epon 828/DEA/GMB**** stocks. The six specimens were divided into

*carboxyl-terminated butadiene acrylonitrile
**Trademark, Shell Chemical Co.
***Diethanolamine
****Glass Micro Bubbles - Trademark, 3M Company

two groups (1) stored at room atmospheric conditions, and (2) stored in a dry box at 0% relative humidity @ 27° C. T_G was measured at 30-day intervals. The data are tabulated in Table III.

TABLE III Glass Transition Temperature of CTBN/Epon 828/DEA Systems Aged under Various Storage Conditions

Specimens	Storage Conditions	Glass Transition Temperature - T_G Initial	30 Days	60 Days	90 Days
#1 CTBN/Epon 828/DEA	Room Atmospheric	81° C	75°C	77°C	77°C
#2 CTBN/Epon 828/DEA	"	76° C	70°C	70°C	70°C
#3 CTBN/Epon 828/DEA	"	76° C	74°C	75°C	76°C
	Average	77.6° C	73.0°C	74.0°C	74.3°C
	Sigma	+2.9° C	+2.7°C	+3.6°C	+3.8°C
#1 CTBN/Epon 828/DEA	Dry Box @	78° C	87°C	87°C	86°C
#2 CTBN/Epon 828/DEA	27°C @	79° C	86°C	88°C	87°C
#3 CTBN/Epon 828/DEA	0% R.H.	79° C	86°C	87°C	86°C
	Average	78.6° C	86.3°C	86.8°C	86.7°C
	Sigma	+0.6° C	+0.6°C	+0.8°C	+0.7°C
#1 CTBN/Epon 828/ DEA/GMB	Room Atmospheric	77° C	70°C	72°C	70°C
#2 CTBN/Epon 828/ DEA/GMB	"	76° C	70°C	71°C	71°C
#3 CTBN/Epon 828/ DEA/GMB	"	78° C	75°C	76°C	77°C
	Average	77.0° C	71.7°C	73.0°C	72.7°C
	Sigma	+1.0° C	+2.9°C	+2.7°C	+3.8°C
#1 CTBN/Epon 828/ DEA/GMB	Dry Box @ 27°C @	78° C	83°C	82°C	83°C
#2 CTBN/Epon 828/ DEA/GMB	0% R.H.	78° C	82°C	82°C	84°C
#3 CTBN/Epon 828/ DEA/GMB	"	78° C	82°C	84°C	82°C
	Average	78.0° C	82.3°C	82.7°C	83.0°C
	Sigma	+ -	+0.6°C	+1.1°C	+1.0°C

Both the unfilled and GMB filled specimens show the same pattern depending on the environment. Those stored at room atmospheric showed a 3-5° C loss in T_G. The degradation occurred within the first month and appeared to plateau after that. Those aged under dry conditions evidenced a 4-8° C increase in T_G. Again the change occurred within the first month and then showed a continued slight increase with time. This definitely does not appear to be a stress relaxation phenomenon, but rather a solvation effect. Since SLA has been discussing the setting up of a long term aging program possibly involving in-line process control specimens, the definition of the storage conditions appears to be vital to ensure reproducible results.

CONTROLLED AGING OF POST CURED SPECIMENS

In order to more clearly determine the causative effect of the T_G changes noted, a controlled experiment was initiated. A CTBN/Epon 828/DEA (10/90/12) stock was employed. One set was cured for 16 hours @ 71° C and the other was cam cured as follows: 2 hours to raise the temperature from room temperature to 54° C + 1.5 hours @ 54° C + 54° C to 71° C in 1.5 hours + 16 hours @ 71° C. Half of the specimens were post cured for 24 hours @ 90° C. A set was then stored at room atmospheric and the other at 27° C 0% R. H. The glass transition temperature and moisture content were measured initially and at one-month storage intervals. The data are shown in Table IV.

As may be seen, the predominant causative agent for the degradation of the glass transition temperature appears to be moisture. The cure does not seem to have any significant bearing on the initial T_G, but drying the samples produced a marked increase in the T_G which appeared to plateau after about a one-month storage time. Conversely, increased moisture caused a loss of T_G which again seemed to plateau at the one-month interval. However, after post curing, dry storage only gave an average increase of +1.3° C compared to the non-post cured increase of +3.5° C. Moisture pickup caused a -9.5° C change as opposed to the normal -3.7° C. The change in slope of the post cured T_G vs. moisture content curve in Figure 1 combined with the greater loss of T_G in the wet samples and essentially lack of change in the dry all indicate a second degrading reaction is occurring. This would support the stress relaxation hypothesis.

TABLE IV Moisture Content and Glass Transition Temperature of CTBN Modified Epoxy under Various Humidity Conditions

Cure	Humidity	Glass Transition Temperature							
		%H_2O	Initial	%H_2O	After 1 Mo. Storage	%H_2O	After 2 Mos. Storage	%H_2O	After 3 Mos. Storage
16 Hrs. @ 71°C	0%	0.25	68°C	0.05	72°C	0.03	90°C	0.04	72°C
Ramp	0%	0.20	67°C	0.04	71°C	0.03	70°C	0.04	71°C
16 Hrs. @ 71°C	Room Atmospheric	0.25	68°C	0.43	65°C	0.54	63°C	0.60	64°C
Ramp		0.20	67°C	0.44	65°C	0.52	62°C	0.54	64°C
16 Hrs. @ 71°C+ Postcure	0%	0.15	78°C	0.04	78°C	0.03	81°C	0.04	78°C
Ramp + Postcure	0%	0.13	78°C	0.04	80°C	0.03	80°C	0.04	79°C
16 Hrs. @ 71°C+ Postcure	Room Atmospheric	0.15	78°C	0.44	74°C	0.62	68°C	0.60	68°C
Ramp + Postcure		0.13	78°C	0.32	65°C	0.56	68°C	0.54	68°C

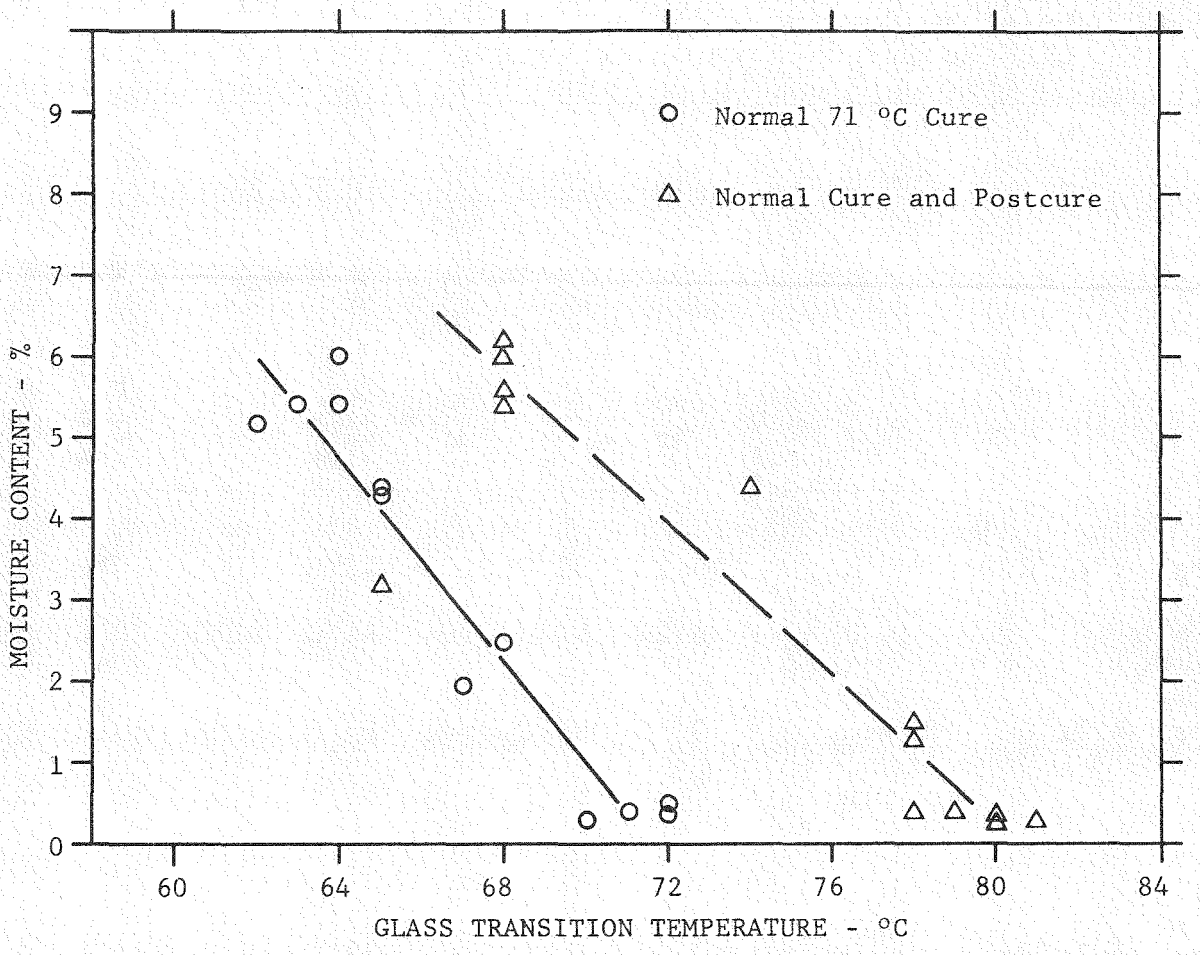

Figure 1. Change in Glass Transition Temperature With Moisture Content in a CTBN/Epon 828/DEA Stock After Normal and Post Curing

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