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EOO-4440-7

Diffusion Mechanisms and Degradation
of Environmentally Sensitive Composite Materials

Progress Report
for period July 1, 1979 - June 30, 1980

Submitted by

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FOREWORD

Much of the progress made this year is summarized in reports COO-4440-4, COO-4440-5 and COO-4440-6. In addition, this progress report (COO-4440-7) describes studies not yet completed or submitted for publication.

ABSTRACT

In this report, progress not previously discussed in reports COO-4440-4 through COO-4440-6 is summarized. Moisture diffusion results in unstressed epoxy samples obtained last year (below 70°C) suggested the presence of a 2-phase structure in the cured epoxy resin. Chemical etching studies initiated this year further confirm the existence of this structure. Also, diffusion results obtained at 95°C demonstrate a reversal in the trend of diffusivity versus crosslink density as observed on the same samples last year. A damage mechanism at this temperature is proposed to explain the results. Initial results on stressed epoxy samples show the inadequacy of the current test fixtures; as a result, new fixtures have been designed to eliminate stress relaxation problems due to swelling and creep of the resin samples during the experiment.

1.0 MOISTURE DIFFUSION IN EPOXY RESINS

During the last year, as described in report COO-4440-2, epoxy resins were formulated in order to change their structure, primarily by altering the molecular weight between crosslink points. The composition and properties are shown in Table 1. Diffusion experiments were conducted so as to gain an understanding between moisture diffusion and epoxy resin structure. Experiments were conducted at various temperatures (Table 2) and equilibrium weight gain as well as diffusivities were determined. Experiments were also initiated to determine the role of an external stress on the diffusion process.

Since the diffusion processes in composite materials are quite dependent upon matrix behavior, these studies on epoxy resins have been continued throughout this year. In addition to studying the compositions shown in Table 1, an epoxy resin manufactured by the 3M Co. and used as a matrix for some of the composites which are being studied, has also been studied as described in report COO-4440-5.

Diffusivity results for compositions E-1, E-2 and E-3 at 95°C are shown in Table 3. Prior to discussing these results, comments must be made concerning the morphology of the epoxy resin network polymer. In order to gain an understanding of the structure, chemical etching experiments were initiated following techniques described by Manson, et al.* Cast epoxy resin samples were etched in either an aqueous solution of Cr_2O_3 or $\text{Cr}_2\text{O}_3/\text{H}_2\text{SO}_4$. After etching, the samples were observed and photographed in an SEM (Figures 1-3). The etching experiments indicated that as the molecular weight between crosslink points increased, the epoxy resin developed a two-phase structure: highly crosslinked shells (less sensitive to etching), surrounding less crosslinked cores. The discontinuous phase size increases with increasing molecular weight between crosslinks.

When the resins were subjected to relatively mild etching conditions, E-1 was not etched, E-2 had fine pores (Fig. 1) accompanied by some etching and E-3 exhibited large pores (Fig. 2). With a more severe etchant, E-1 was unaffected, E-2 exhibited large pores (Fig. 3) and E-3 was uniformly etched resulting in great thickness reduction. Similar conclusions were reached by Manson, et al*. Studies to further elucidate the structure using chemical etching techniques are being continued and additional compositions will be studied using more etchant conditions.

The results shown in Table 3 indicate that at 95°C, the equilibrium weight gains are greater than at lower temperatures (Table 2). The equilibrium weight gain is highest for the E-1 compositions which is similar to the findings at the lower temperatures. The diffusivity increases from E-1 to E-3, which is the reverse of earlier findings at lower temperatures. These results might be explained on the basis of the 2 phase structure. For example, at temperatures below 70°C, the diffusivity decreases with decreasing crosslink density or increasing molecular weight between crosslinks. This may result from the highly crosslinked shells surrounding the less crosslinked cores, thus slowing down water penetration resulting in lower D values. On the other hand, at 95°C, the highly crosslinked shells may crack or craze resulting in easier penetration into the less crosslinked cores and the diffusivities increase in going from composition E-1 to E-3. This latter comment requires additional verification which will be accomplished during the remainder of this study.

*"Influence of Crosslinking on the Mechanical Properties of High Tg Polymers", AFML-TR-77-109, July 1977.

Table 1
Summary of Epoxy Resin Compositions and Properties

<u>Materials</u>	<u>E-1</u>	<u>E-2</u>	<u>E-3</u>	<u>E-4</u>	<u>E-5</u>
Epon 828 (%)	86	83.6	83.3	82	91
m-phenylene diamine (%)	14	8.8	6.5	18	9
aniline (%)	-	7.6	10.2	-	-
density (g/cc)	1.210	1.204	1.201	1.207	1.201
T _g (°C)	150	127	113	129	103
M _c (calculated for random reaction)	448	605	874	593*	448

*640, if stepwise reaction

Table 2
Moisture Absorption in Epoxy Resins

	<u>E-1</u>	<u>E-2</u>	<u>E-3</u>	<u>E-4</u>	<u>E-5</u>
D (10^{-9} cm ² /sec)					
25°C	.83	.66	.60	.54	.67
40°C	2.18	1.46	1.50		
55°C	5.53	3.99	3.85		
70°C	10.17	8.95	8.18	6.43	7.49
M _∞ (%)	3.1	2.7	2.5	3.5	3.2

Table 3
Moisture Absorption in Epoxy Resins at 95°C

	<u>E-1</u>	<u>E-2</u>	<u>E-3</u>
k (%/h ^{$\frac{1}{2}$})	0.32	0.33	0.32
M_{∞} (%)	3.29	3.02	2.88
D_x (10 ⁻⁹ cm ² /sec)	83.0	101.6	109.0
D_r (10 ⁻⁹ cm ² /sec)*	62.9	77.0	82.6

* D_r is the one-dimensional diffusion coefficient after correcting for edge effects

Composition E-2
Etchant: Cr_2O_3
Magnification: 30X

Composition E-2
Etchant: Cr_2O_3
Magnification: 300X

Figure 1.

Composition E-2
Etchant: $\text{Cr}_2\text{O}_3/\text{H}_2\text{SO}_4$
Magnification: 30X

Composition E-2
Etchant: $\text{Cr}_2\text{O}_3/\text{H}_2\text{SO}_4$
Magnification: 300X

Figure 2.

Composition E-3
Etchant: Cr_2O_3
Magnification: 30X

Composition E-3
Etchant: Cr_2O_3
Magnification: 300X

Figure 3.

2.0 MOISTURE DIFFUSION IN STRESSED EPOXIES

Prior studies have shown an increased rate of moisture diffusion into epoxy resins when subjected to stress. Our studies last year initiated an investigation of this phenomenon, and this year the same effect is calculated from the results of studies on composites. The continuation of the studies on the effect of stress on moisture diffusion and degradation in epoxies has revealed problems with some of the constant stress fixtures. Because of the low stiffness of the polymer and the relatively large swelling and creep which can occur during the course of a diffusion experiment, particularly at high temperature and stress, significant load relaxation can occur due to the extension of the springs in the test fixture. In fact, load relaxation curves for the fixture when immersed in water at 95°C are shown in Figure 4. As the load relaxes, the rate of moisture diffusion is altered leading to nonlinear weight gain curves. Thus, significant errors could be introduced into the diffusion calculations.

In order to correct for this effect, new constant load fixtures have been designed as shown in Figure 5. These fixtures incorporate an air cylinder mounted on a stainless steel channel to which the specimen is also attached. The channel stands vertically in a water bath and several fixtures can be contained in each bath. Each fixture has its load accurately established by the use of an air regulator which is preset by measuring the load applied by the cylinder piston against a calibrated load cell. The regulator position is then held fixed, a sample is placed on the fixture and the cylinder is pressurized. This fixture results in a compact loading device, which should allow us to maintain the load during sample extension to within a few percent of the original value.

Figure 4. Moisture Diffusion Results for Stressed Epoxy Resin Samples

Figure 5. Constant Stress Fixture for Diffusion Experiments

3.0 FUTURE STUDIES

The following studies are being continued during the last quarter of this contract period (April 1 to July 1):

1. Effect of crosslink density variation on the epoxy resin morphology will be continued to be studied by etching and further microscopy studies.
2. The new test fixtures for constant stress will be used to establish the influence of stress (at 95°C) on diffusivity of compositions E-1, E-2 and E-3 as well as on the 3M epoxy. If time allows, other temperatures will also be considered.
3. Experiments will be initiated to judge the practicality of using the sample length change to measure diffusivity.
4. Further study will be done to determine the role of Poisson's ratio and volume change under stress with respect to the moisture diffusion as a function of stress.

4.0 CONTRACT PERFORMANCE AND PRINCIPAL INVESTIGATOR TIME

At this time, our performance on research goals is in accordance with our proposed research contract goals. The principal investigator has thus far devoted 10 percent of his time to this contract. In the remainder of the contract period, it is proposed that this effort will continue.