Environmental Effects on Glass Fiber Reinforced Polyester and Vinylester Composites

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ABSTRACT

The effects of environment on glass fiber reinforced polyester and vinylester composites immersed in liquids and in humid air were investigated. Tests were performed at temperatures 23 C and 93 C with the materials exposed to humid air at 50 and 100 percent relative humidities, and to five different liquids: saturated salt water, No. 2 diesel fuel, lubricating oil, antifreeze, and indolene. Changes in weight, ultimate tensile strength, tensile modulus, short beam shear strength, and shear modulus were measured over a six month period, and the effects of the environment on these parameters were assessed.

INTRODUCTION

T HE MAJOR OBJECTIVES of this investigation were to determine the absorption characteristics of glass fiber reinforced polyester and vinylester composites immersed in different fluids, and to evaluate the changes in material strength due to the absorbed moisture. Three different types of materials were tested, these being designated as SMC-R25, SMC-R50, and VE SMC-R25. Brief descriptions of these materials are given in Tables 1 and 2.

Table 1. Descriptions of the Polyester E glass Composites used in this investigation [1, 2, 3]

SMC – R25		
Ingredient	Type	Weight %
Resin	Polyester (OCF E-920-1)	29.4
Filler	Calcium carbonate	41.8
Internal Release	Zinc Stearate	1.1
Catalyst	Tertiary Butyl Perbenzoate	0.3
Thickener	Magnesium Hydroxide	1.5
Pigment	Mapico Black	0.8
2.54 cm Chopped	E-glass (OCF 951 AB)	25.0

SMC – R50		
Ingredient	Type	Weight %
Resin	OCF-E-980 Polyester	32.3
Filler	Calcium Carbonate	16.1
Mold Release	Zinc Stearate	0.8
Thickener	Magnesium Oxide	0.5
Catalyst	TBP	0.3
Inhibitor	Benzoquinone	Trace
2.54 Chopped Class	OCF 433 AB	50.0

Table 2. VE-SMC-R50 paste formulation

Component	Parts
A-SIDE	
XD-9013.03	10
TBPB	1
Camelwite	92
Zinc Stearate	3
B-SIDE	
Derakane* 470-45	100
Maglite D	50
Camelwite	100
Pump 10-14/1 by weight A/B Max viscosity = 6000 cps (90F, RVT, #4 Spindle, 20 rpm)	

*Registered Trademark of Dow Chemical Company

The following parameters were measured during the tests: a) weight change, b) ultimate tensile strength, c) tensile modulus, d) short beam shear strength, and e) shear (flexural) modulus. The measurements were performed over a six month period with the materials immersed in humid air at 50 and 100 percent relative humidities, saturated salt water, No. 2 diesel fuel, lubricating oil, antifreeze, and gasoline (Indolene HO O).

The experimental procedures are discussed in the next section.

Table 3. Nominal dimensions of specimens used in the tests. All units in mm.

Type of Test	SMC-R25			SMC-R50			VE SMC-R25		
	Thickness	Width	Length	Thickness	Width	Length	Thickness	Width	Length
weight change	2.41	12.7	50.8	2.41	12.7	50.8	3.30	12.7	50.8
tensile[a]	2.41	12.7	80.0	2.41	12.7	80.0	3.30	12.7	80.0
short beam shear[b]	2.41	6.35	15.2	2.41	6.35	15.2	3.30	6.35	15.2

a- "Dogbone" specimens. Dimensions given are for gauge section. Total specimen length: 180 mm. Width of grips: 25 mm.

b- With SMC-R50 "baseline" data were also obtained with 8.5 mm thick, 8.5 mm wide, and 50.0 mm long specimens.

EXPERIMENTAL

The weight changes of the materials during immersion were obtained as follows. Before placing the test specimens (Table 3) into the moist environment (humid air or liquids) the specimens were dried in an oven at 66 C until their weight loss became stabilized and no more weight loss was observed. The specimens thus dried were then placed in the appropriate environmental chambers and their weights were measured by weighing them periodically on a Mettler Analytical Balance.

The temperatures of the environmental chambers were controlled by heaters and were kept within ± 1 C. Hundred percent relative humidity was maintained by keeping water in a closed, half-filled container. The temperatures of the water and the air above the water (where the specimens were located) were regulated by separate heaters. At 50 percent relative humidity and 23 C the specimens were kept in an air-conditioned, temperature controlled room. At 50 percent relative humidity and 93 C the specimens were mounted above the surface of a water-ethylene glycol mixture. The temperatures of both this liquid mixture and the air above it were regulated by heaters. In all the tests the relative humidity of the air was measured with Abbeon Hygrometers.

The data are presented in terms of percent weight change which is defined as:

$$M = \frac{\text{weight of specimen} - \text{weight of dry specimen}}{\text{weight of dry specimen}} \times 100 \qquad (1)$$

The tensile and shear properties of the materials were determined in the following manner. The specimens, described in Table 3, were immersed in the appropriate environment for a predetermined length of time. The strength and the modulus were then measured at room temperature using an Instron. The cross head speed was 5 mm/min for the tensile tests and 1 mm/min for the shear tests.

The tensile modulus was estimated from the load-deflection curve. The shear strength and the shear (flexure) modulus were measured by the three point short beam method. The arrangement described in the ANSI/ARTM-D2344-76 standard was used in these tests (Fig. 1). The apparent shear strength and the shear modulus were calculated from the expressions [4, 5]:

$$\tau = \frac{(0.75)(P)}{(b)(h)} \tag{2}$$

$$E_s = \frac{(P)(S)^3}{4(d)(b)(h)^3} \tag{3}$$

where τ is the shear strength, E_s is the shear (flexure) modulus, P is the breaking load, b and h are the width and thickness of the specimen, respectively, d is the deflection at the center point, and S is the span between the supports.
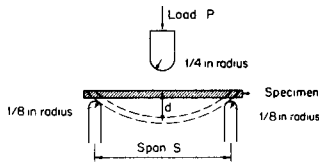
Figure 1. Schematic of apparatus used in the short beam shear tests.

RESULTS

Tests were performed with specimens immersed in humid air and in five different liquids at 23 C and 93 C. The test conditions are summarized in Table 4.

The weight changes, as well as changes in tensile and shear properties, are presented as functions of time and temperature in Figs. 2 to 22. Each point in these figures is the average of five data points. For weight change all five data points were generally within ± 15 percent. The spreads in the mechanical properties data are indicated by error bars.

Weight Change

At every test condition the weights of the specimens increased at first and then leveled off for some length of time. The data indicated that both the initial rate of weight increase and the value at which the weights leveled off depend on (a) the material, (b) the temperature, and (c) the environment (relative humidity of air or

Table 4. Summary of Test Conditions

|	Temperature		Duration of Test
Substance	23 C	93 C	
humid air 50% rel. hum.	x	x	6 months
humid air 100% rel. hum.	x	x	6 months
saturated Nacl-water solutions	x	x	6 months
No. 2 diesel fuel	x	x	6 months
Sunoco 10-W-40 lubricating oil	x	x	6 months
antifreeze (ethylene glycol- water mixture, 50%-50% by volume)	x	x	6 months
indolene HO O	x	x	6 months
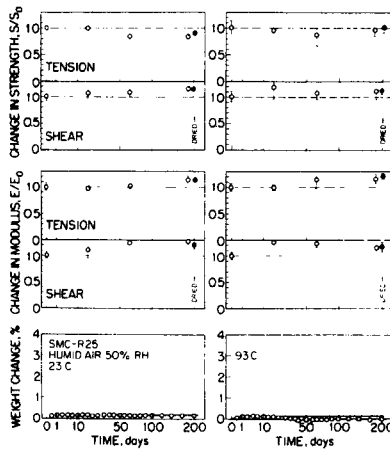
Figure 2. *Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. ---- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. — Fick's law solution.*
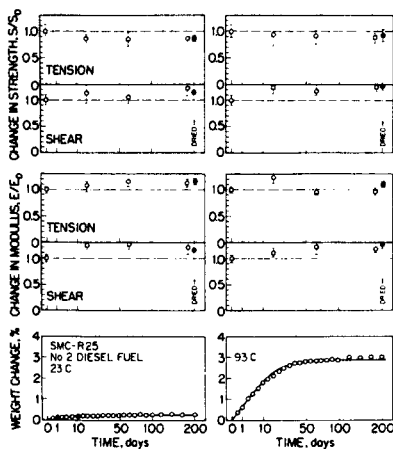
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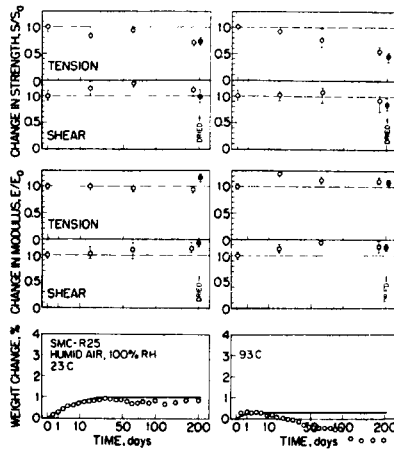
Figure 3. Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. — "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. — Fick's law solution.
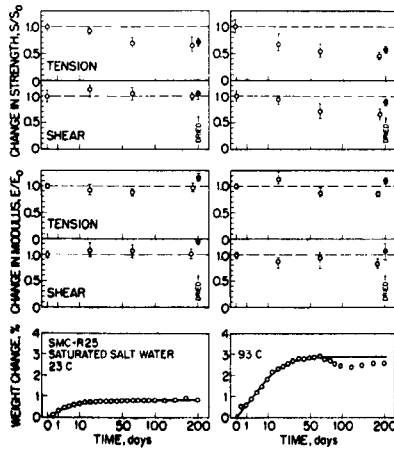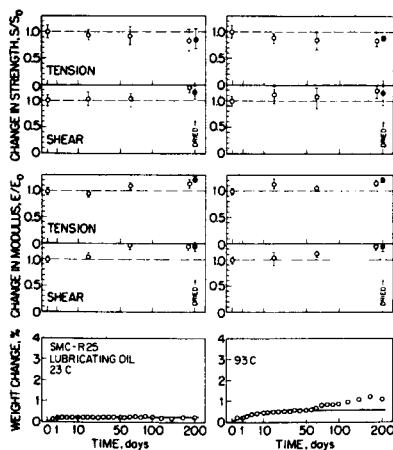

Figure 4. Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. — "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. — Fick's law solution.

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Figure 5. *Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. --- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. — Fick's law solution.*
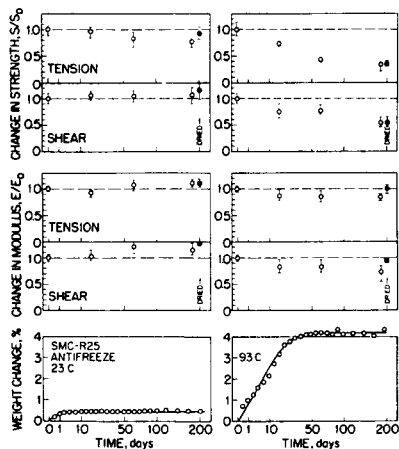

Figure 6. *Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. --- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. — Fick's law solution.*

Figure 7. Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. -- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. — Fick's law solution.
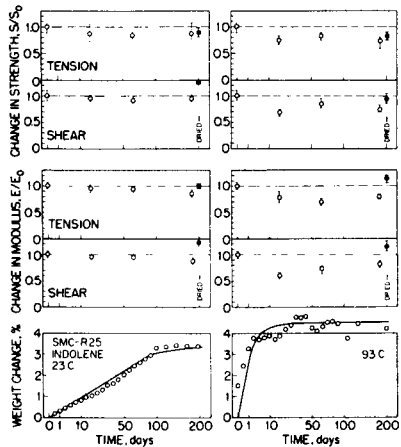

Figure 8. Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. --- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. — Fick's law solution.
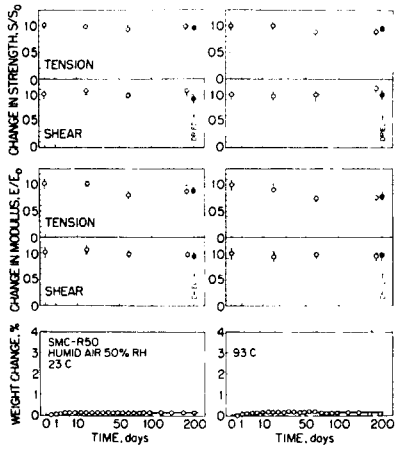
Figure 9. *Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time.* ---- *"baseline" data.* ● *specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data.* — *Fick's law solution.*
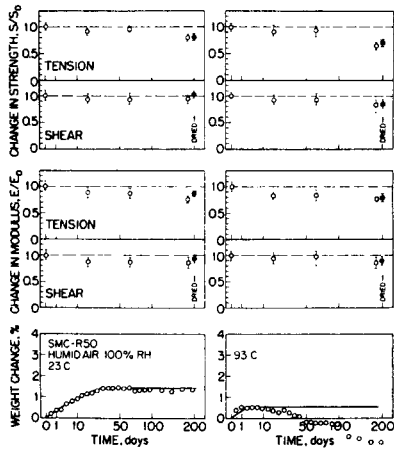

Figure 10. *Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time.* ---- *"baseline" data.* ● *specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data.* — *Fick's law solution.*
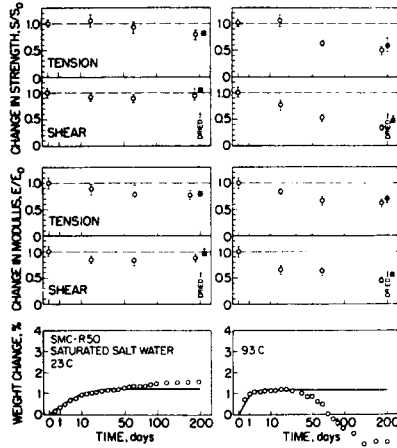
Figure 11. Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. ---- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. ― Fick's law solution.

Figure 12. Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. ---- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. ― Fick's law solution.
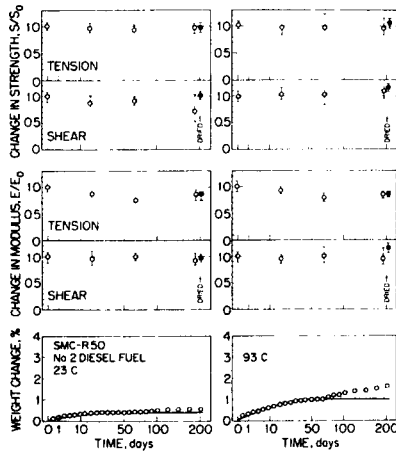
Figure 13. *Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. ---- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. ─── Fick's law solution.*
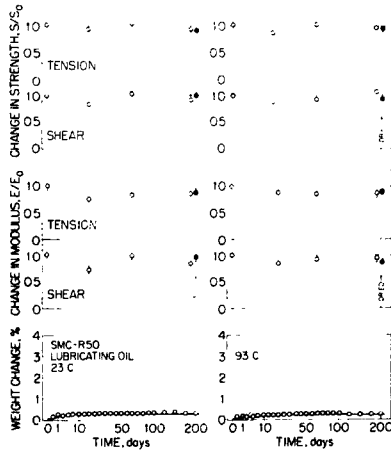

Figure 14. *Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. ---- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. ─── Fick's law solution.*

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Figure 15. Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. --- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. — Fick's law solution.
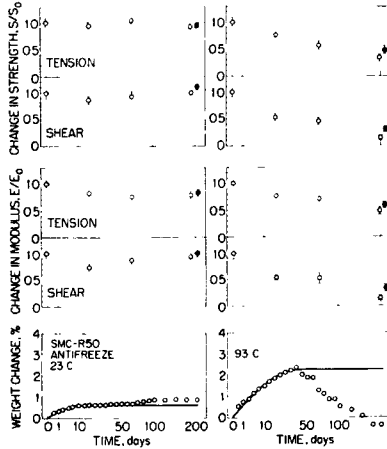

Figure 16. Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. ---- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. — Fick's law solution.
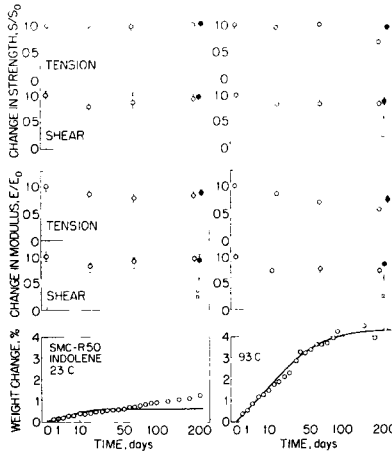
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Figure 17. Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. --- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. —— Fick's law solution.
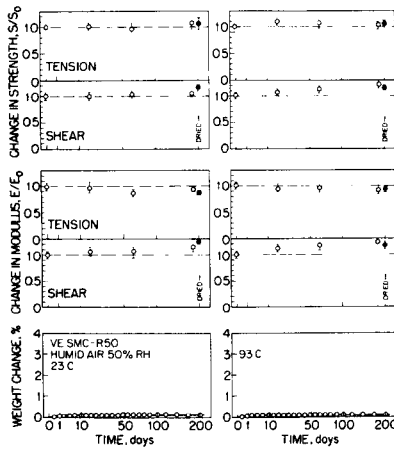

Figure 18. Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. --- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. —— Fick's law solution.

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Figure 19. Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. ---- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. — Fick's law solution.
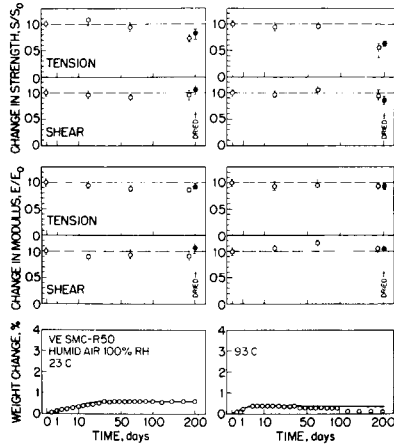

Figure 20. Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. ---- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. — Fick's law solution.
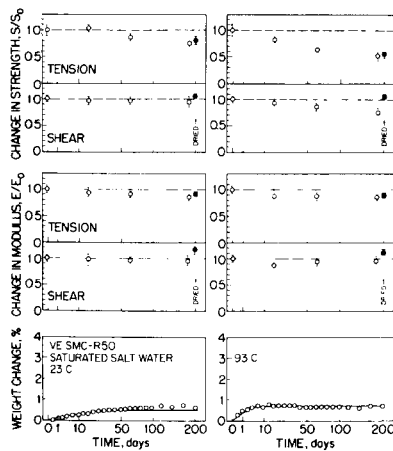
Figure 21. Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. ---- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. —— Fick's law solution.
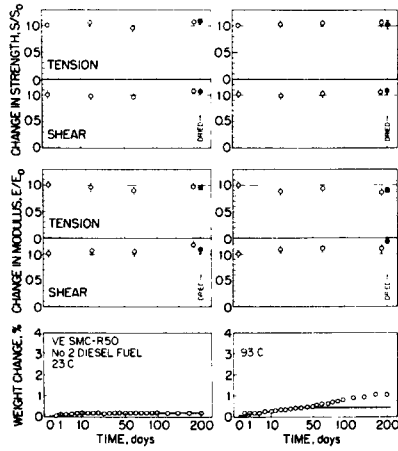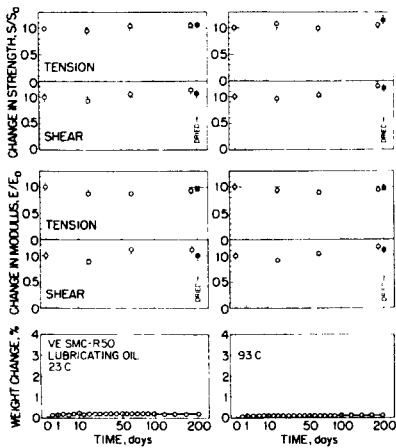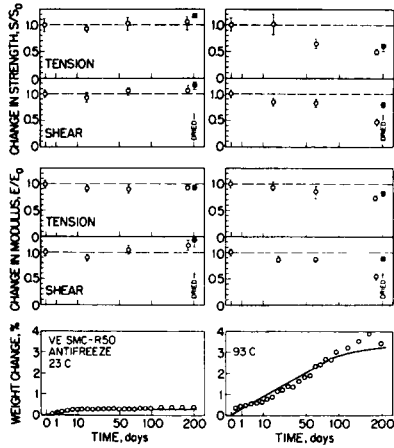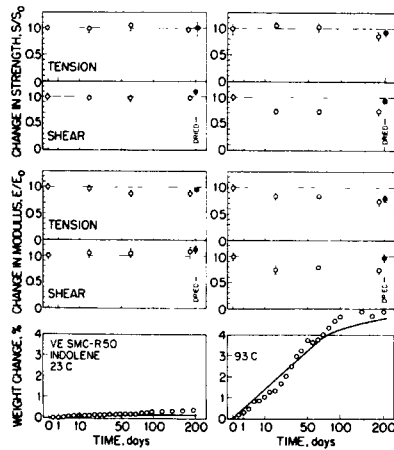

Figure 22. Changes in ultimate tensile strength, short beam shear strength, tensile modulus, shear modulus, and weight as functions of immersion time. ---- "baseline" data. ● specimens tested after 6 months immersion followed by 3 weeks drying. Bars indicate spread in data. —— Fick's law solution.

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the type of liquid used). The data also show that in some instances the weight did not always remain constant after it reached a level value, but kept either increasing or decreasing. This suggests that under some conditions the moisture transport was by a "non-Fickian" process. To assess the conditions under which the absorption was governed by Fick's law, weight changes were calculated by the expression developed for "Fickian" diffusion [6]:

$$M = \left\{ 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{\exp[-2j + 1)^2 \pi^2 (Dt/h^2)]}{(2j + 1)^2} \right\} (Mm - M_i) + M_i \tag{4}$$

In the present tests the initial moisture content M_i was zero. The apparent maximum moisture content (Mm) was taken from Figs. 2 to 22 as the value at which the weight change first seemingly leveled off. The apparent diffusivity was calculated by assuming that the moisture absorption process followed Fick's law. Hence, the apparent diffusivity was calculated from the expression [6]:

$$D = \pi \left(\frac{h}{4Mm} \right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \left(1 + \frac{h}{\ell} + \frac{h}{n} \right)^{-2} \tag{5}$$

where h, ℓ, and n are the thickness, the length, and the width of the specimens, respectively. M_1 and M_2 are the moisture contents at times t_1 and t_2, these times being sufficiently low so that the weight change can still be taken to vary linearly with (time)$^{1/2}$. The Mm and D values did not show systematic variation either with the environment or with temperature. Hence their values are not included here.

The calculated weight changes are shown as solid lines in Figs. 2 to 21. In most cases the calculated values and the data agree reasonably well until the apparent maximum weight change is reached. Beyond this point the data often deviate from the calculated values, the differences between the measured and the calculated values being more pronounced at the higher temperature.

Once the data deviated from the calculated values the absorption process was "non-Fickian." One reason for this may be that moisture transfer through the resins did not proceed according to Fick's law. Such "non-Fickian" behavior has been observed in the past with rubbers and polymers [7]. Another plausible explanation of the observed non-Fickian absorption process is as follows. Owing to the moist, high temperature environment, microcracks developed on the surface and inside the material. Moisture rapidly entered the material, causing the increase in weight. As the cracks developed, material, most likely in the form of resin particles, was actually lost. In fact, such material loss was frequently observed after a few hours of exposure to the moist environment. As long as the moisture gain was greater

than the material loss, the weight of the specimen increased. Once the weight of the lost material exceeded the weight of the absorbed moisture, the weight of the specimen decreased. Of course, when material was lost, the measured weight change no longer corresponded to the moisture content of the material.

Non-Fickian absorption similar to that observed here was observed with graphite epoxy composites immersed in saturated steam at 150 C. the microcracks formed during these tests were readily apparent on photo-micrographs taken of the specimens [8].

Weight changes of SMC-R25 have been measured previously [9]. The present data agree reasonably well with the earlier measurements, with the exceptions: 100% relative humidity air at 23 C, No. 2 diesel fuel at 23 C and lubricating oil at 23 C. For these conditions the previous data show a one to two percent larger weight change than the present measurements. To ascertain the validity of the present data the weight change measurements were repeated at the above three conditions. The data thus obtained agreed with the present first set of measurements which are given in Figs. 3, 5, 6.

A completely satisfactory explanation for the above noted discrepancies could not be found. Some likely causes for the differences between the present and the previous results can be offered. In the tests with humid air the temperatures in the previous (32 C) and the present (23 C) tests were different. Impurities in the fluids or differences in material composition may also have contributed to the differences in the weight change.

Strength and Modulus

The ultimate tensile strengths, the shear strengths, and the tensile and shear moduli were determined at room temperature immediately after the materials were received (i.e. without the test specimens having been placed in the environmental chambers). The results of these measurements (designated as "baseline" data and identified by the subscript o) are listed in Table 5. All data presented in Figs. 2 to 22 were normalized with respect to the values given in Table 5. As a check on the "baseline" data, a set of the received specimens were dried at 66 C and their properties were then determined. The properties of the "baseline" (as received) specimens (Table 5) and the "dried" specimens did not differ appreciably.

In order to evaluate the effect of specimen size on the short beam shear strength and on the shear modulus, "baseline" data were obtained with two different size specimens (see Table 3). The specimen size did not significantly affect either the short beam shear strength or the shear modulus.

It is noted that for SMC-R25 and SMC-R50, the values given in Table 5 are of the same order of magnitude as reported previously [1] − [3]. The results in Figs. 2 to 22 show that exposure to a moist environment affects both the strength and the modulus of the materials. The change in strength and in modulus depends upon a) the material, b) the temperature, and c) the environment (relative humidity of

Table 5. The Apparent Maximum Moisture Content Mm and the Apparent Diffusivity D.

Substance	Temperature $C°$	SMC-R25		VE SMC-R50		SMC-R50	
		M_m %	$D_{x_2} 10^5$ mm²/sec	M_m %	$D_x 10^5$ mm²/sec	M_m %	$D_{x_2} 10^5$ mm²/sec
Humid air, 50%	23	0.17	10.0	0.13	10.0	0.10	30.0
	93	0.10	50.0	0.10	50.0	0.22	30.0
Humid air, 100%	23	1.00	10.0	0.63	5.0	1.35	9.0
	93	0.30	50.0	0.40	50.0	0.56	50.0
Salt water	23	0.85	10.0	0.50	5.0	1.25	15.0
	93	2.90	5.0	0.75	30.0	1.20	80.0
No. 2 diesel	23	0.29	6.0	0.19	5.0	0.45	5.0
	93	2.80	6.0	0.45	10.0	1.00	5.0
Lubricating oil	23	0.25	10.0	0.20	10.0	0.30	10.0
	93	0.60	10.0	0.10	10.0	0.25	10.0
Antifreeze	23	0.45	50.0	0.30	30.0	0.65	20.0
	93	4.25	5.0	3.50	0.8	2.25	10.0
Indolene	23	3.50	1.0	0.25	10.0	0.60	10.0
	93	4.50	40.00	5.00	1.0	4.25	3.0

air, or type of liquid used). The temperature and the environment seem to be the more significant factors. Exposure to saturated salt water, antifreeze, and indolene at 93 C have the most pronounced effect on the mechanical properties. The weight changes were also largest at these conditions, suggesting — as expected — that the amount of moisture absorbed and the material properties are related. However, there does not seem to be a clear correlation between the losses in strength and modulus and the weight change. Thus, a unique relationship between the weight change and the change in properties cannot be established readily.

It is of interest to determine whether or not the changes in strength and modulus are permanent. To answer this question the strengths and moduli were measured of specimens which were immersed for six months in the test environment and then were dried at 66 C for three weeks. These data are represented by solid circles in Figs. 2 to 22. As can be seen, by drying the material, some, but not all, of the losses in strength and modulus are recovered. It appears, therefore, that changes in the material properties are permanent. Drying out the material does not restore either the strength or the modulus to their original values.

An effort was made to determine the cause of the material failure. Towards this end selected tensile specimens were examined by a scanning electron microscrope (Table 6). Photographs were taken of the failure surfaces using 57X and 570X magnifications (Table 7).Unlike metals (which usually fail along a surface normal to the load), the SMC materials tested here failed along a slanted surface as illustrated in Fig. 23. Thus, the failure mechanism could not be discerned on the photographs.

Table 6. Initial Strengths and Initial Moduli of the Materials at 23 C ("baseline" data). Average of Five Measurements.

	SMC–R25	SMC–R50	VE SMC–R50
ultimate tensile strength (MPa)	84	180	165
tensile modulus (GPa)	5.0	8.0	7.0
short beam shear strength (MPa)	18	29	35
shear modulus (GPa)	5.0	7.0	4.0

Table 7. Summary of Tensile Specimens which were Examined by a Scanning Electron Microscope. Two Magnifications were used for Each Photograph (57 X and 570X).

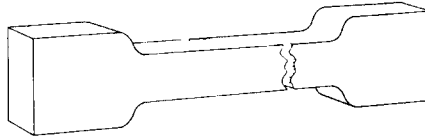|	SMC–R25	SMC–R50	VE SMC–R50
Baseline, as received	x	x	x
Antifreeze 93 C, 18 days immersion	x		
Antifreeze 93 C, 6 months immersion	x	x	x
No. 2 diesel 93 C, 6 months immersion	x	x	x
Indolene HO 0 93 C, 6 months immersion	x	x	x
Saturated salt water 93 C, 6 months immersion	x	x	x

Figure 23. *Typical failure surface in tensile tests.*

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APPENDIX

In a previous paper (ref. 9) we reported apparent diffusivity values for polyester-E glass composites. The values of D given in Table 4 of this paper should be multiplied by 0.046. Also, the first D value for SMC-65 (100% rel. humidity, 32C) should read 1.3 instead of 3.1.