

Dimensional Changes in Glass-Filled Epoxy Resin as a Result of Absorption of Atmospheric Moisture*

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Synopsis

The absorption of water from selected, constant relative humidity atmospheres by glass-filled or reinforced epoxy resin was studied. Four groups of samples were prepared: unfilled epoxy, epoxy filled with glass microspheres, epoxy reinforced with transverse unidirectional glass fabric, and epoxy reinforced with longitudinal unidirectional glass fabric. The absorption and dimensional change rates were measured and formulated in an exponential expression. From the ratio of relative absorption to relative length change, the "hygro-elastic coefficient" was defined.

INTRODUCTION

Atmospheric moisture is absorbed by and diffuses through glass-filled or reinforced epoxy resin (GRP) in proportions and at rates which depend upon the materials used, the proportions and manufacturing methods. Opinions are divided as to the mechanism and values of the coefficients of absorption and diffusion,¹⁻³ but there is broad agreement that diffusion rates along the fiber of GRP are greater than transverse. Concentrations of absorbed water may be located in cavities and microvoids along the length of the glass fibers^{1,2,4} or in unreacted resin distributed as microdefects.⁵⁻⁷ Byron et al.⁸ and Blahnic³ presented expressions of the coordinate-time dependence of absorbed moisture.

According to Jost⁹ and to Garanina,² the rate of absorption of water by polymeric sheet is a function of the quantity already absorbed. Until this reaches about 60% of the equilibrium value in water, the following expression is satisfactory:

$$Mt = M_{\infty}[(4/h)(Dt/\pi)^{1/2}] \quad (1)$$

where Mt is the quantity of water absorbed at any time t , M_{∞} is the absorption at equilibrium, h is the thickness of the sample, and D is the diffusion constant. As absorption proceeds, a second expression becomes more suitable:

$$Mt = M_{\infty}[1 - (8/\pi^2) \exp(-D\pi^2t/h)] \quad (2)$$

Chi-Hung and Springer¹⁰ give another expression, namely,

$$Mt = M_{\infty}\{1 - \exp[-7.3(Dt/4h^2)^{0.75}]\} \quad (3)$$

which is claimed to give more-realistic results.

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Weight and dimension changes have been studied by different techniques and on different specimens. Usually the absorption has been measured in water and at elevated temperature in order to achieve faster rates of absorption than from the atmosphere. This, however, has been at the cost of a small but highly significant transfer of material from the GRP to the water.^{1,2,11-18} Such leaching does not occur when absorption from the atmosphere takes place.^{3,10,19}

The present research was confined to the study of the absorption of water from the atmosphere at different relative humidities, and its effect on dimensional and weight changes.

EXPERIMENTAL

The studies were carried out on four specially prepared samples. These were (a) an unfilled DGEBA epoxy resin (Epon 828) cured with a blend of MDA and MPDA (Shell curing agent Z). This was the basic sample for comparison and subsequently called the "reference"; (b) the reference resin filled with glass microspheres, CPO-2 Code 3000, by Potters Ballotini, coated with A-1100 silan—"microspheres"; (c) the reference resin reinforced transversely with glass fibers (Clark-Schwebel Unidirectional Fabric 1543, treated with silane coupling agent CS-273)—"transverse"; and (d) the reference resin reinforced longitudinally with glass fibers as in (c)—"longitudinal."

A ratio of DGEBA to curing agent of 5:1 was used, mixed at 80°C, and degassed for 10 min at 5–15 Torr. After casting, the reference and microsphere samples were cured in sequence for 1 hr at 80°C, 1 hr at 100°C, and 2.5 hr at 150°C. The samples were then allowed to cool gradually to room temperature.

Some additional details relating to the preparation of the samples follows: (a) The density of the microspheres is given as 2.47 g/cm³. The samples contained 47.7% by weight of glass. (b) The fabric used consisted of 90% *E* glass fibers in the web and 10% in the woof. The samples had five layers of glass fabric which gave 72.8% by weight in the final sample. In this case, the curing was carried out in sequence for 2 hr at 80°C under a pressure of 10 atm and 2 hr at 160°C. The samples were then allowed to cool under pressure; at 100°C, pressure was removed.

The curing schedules for the two sets of samples were different to accommodate an industrial press cure schedule. It is believed that they are sufficiently close not to create differences in the molecular structures of the crosslinked polymers.

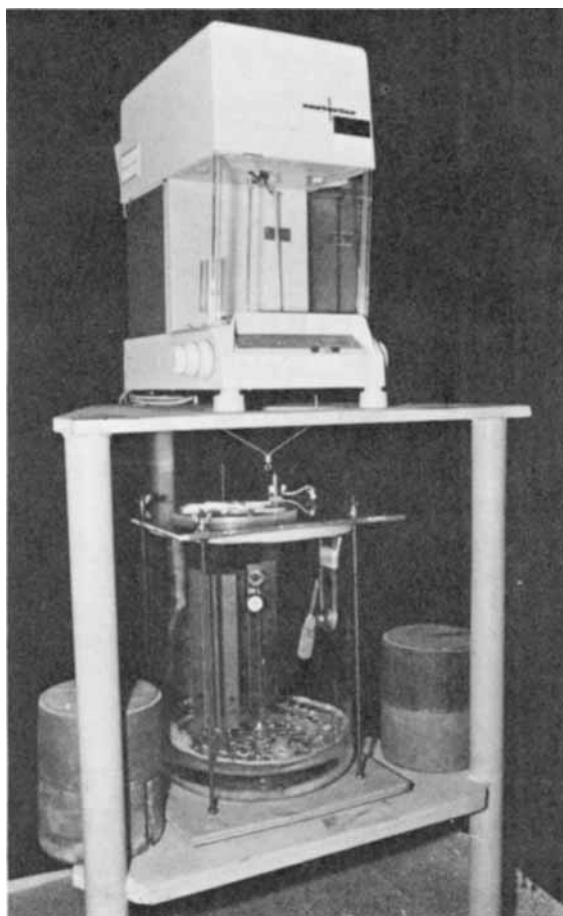
Rectangular samples were cut from the sheets to the following sizes: the reference samples 201 × 19 × 2.4 mm; the microsphere samples 141 × 19 × 2.4 mm; and the fabric-reinforced samples 201 × 20 × 2 mm. Naturally, the transverse and longitudinal samples were cut from the same sheet in different directions. A total of 64 samples were prepared, 16 replicates in each group.

Constant relative humidity atmospheres over saturated salt solutions were obtained in 20 l. Pyrex containers equipped with well-sealed aluminum covers. The salts were selected from the International Critical Tables,²⁰ to give constant relative humidity (RH) values over a range of temperatures about 20°C; (97%–98%) RH was obtained using K₂SO₄; 75% RH using NaCl; and 44% RH using K₂CO₃. The use of salts for 20% RH was not desirable, and aqueous sul-

phuric acid at a density of 1.48 g/cm^2 was substituted as specified in reference 21. A uniform vapor pressure was maintained by a fan which gently circulated the air inside the container. The containers were kept at $20^\circ \pm 2^\circ\text{C}$ and the relative humidity inside was checked with a small hair hygrometer with 5% accuracy.

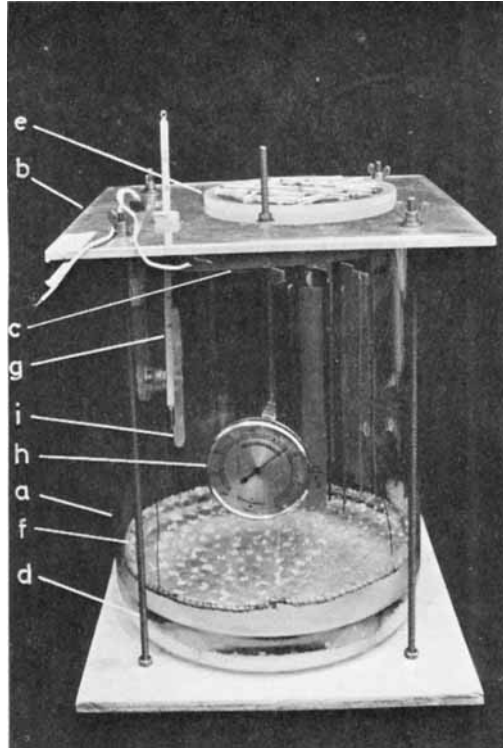
Figure 1 shows a photograph of a container with the samples inside being weighed. The samples were suspended by fine copper wire going through small holes in the aluminum cover and could be weighed at the desired intervals with good accuracy without disturbing the atmosphere surrounding them. The analytical balance indicated 10^{-5} g .

Dimensional changes were measured in a jig (Fig. 2), designed for this purpose, by means of which changes of length could be measured to an accuracy of $\pm 5 \times 10^{-5} \text{ in}$. It was necessary to remove samples from the conditioning containers for measurement which was made in a room at $20^\circ \pm 2^\circ\text{C}$ and $(50 \pm 5)\% \text{ RH}$. The period of immersion and frequency of weighing of the samples was sufficient to bring them almost to equilibrium and to enable rapid changes to be observed.



(a)

Fig. 1. (a) Container and analytical balance.



(b)

Fig. 1. (b) Container assembly: *a*, glass container; *b*, container cover; *c*, rubber gasket; *d*, constant humidity solution; *e*, sample holder; *f*, plastic net; *g*, thermometer; *h*, hygrometer; *i*, ventilator.

Table I indicates the sequence in which the measurements were made. The samples were coded according to Table II, and all graphs, etc., are similarly marked.

RESULTS AND DISCUSSION

Following preparation and machining to size, the samples were dried in air at 80°C. Calculations of absorbed moisture and dimensional changes were based on the initial weight w_0 and length l_0 of the dried samples. The average value of absorbed moisture and of changes in length was calculated from the data of four similar samples at one humidity. The standard deviation of absorption

TABLE I
Schedule of Tests

0	20	40	60	80	100	120	140	160	180	200	DAYS				
0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	WEEKS
1	5	8	10	12	14	16	17	18	19	20	21	22	23	TEST NO.	

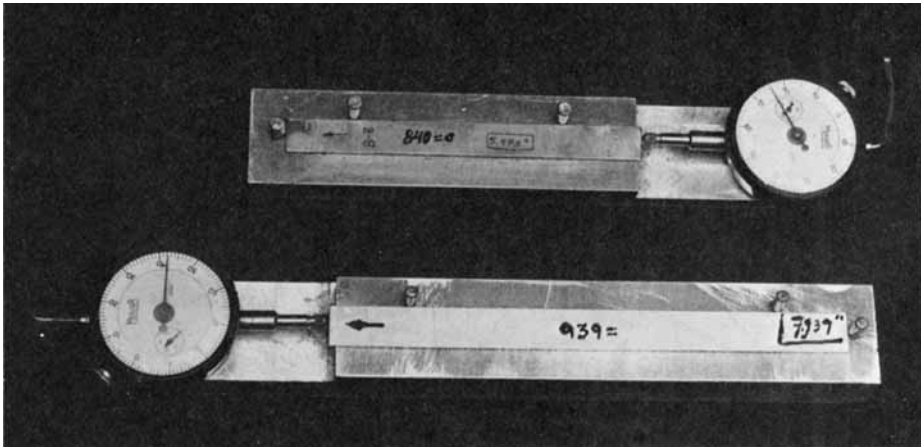


Fig. 2. Length measuring device.

measurements never exceeded 2.5%, and that of the length changes never exceeded 1%. Measurement of weight and length were made daily at the early stages of absorption, and at longer intervals as equilibrium was approached. Typical curves are given in Figures 3 and 4 for samples with transverse reinforcement. Comparison of the various samples for absorption and length increase at 75% RH are given in Figures 5 and 6.

An attempt was made to fit the result to the Garanina² expression

$$Mt = M_{\infty} [HK(t)^{1/2}] \quad (4)$$

where Mt stands for the absorption after t days, and M_{∞} for the maximum absorption. H and K are the relative humidity and an empirical constant, respectively. A plot of Mt/H vs $t^{1/2}$ should give a straight line, and it was found that this holds fairly well until absorption of approximately 75% of the maximum value is reached.

The slope of the line is in fact KM_{∞} and it was found that this was identical for all the samples tested within the above range.

Another correlation attempted was

$$Mt = M_{\infty}(1 - e^{-\lambda t}) \quad (5)$$

where λ is an inverse time constant. It was found that curve fitting was quite accurate except for the first few days, and that the calculated value of M_{∞} can

TABLE II
Code of Samples

Sample	20% RH	44% RH	75% RH	97% RH
reference	A	E	I	M
microsphere	B	F	J	N
transverse	C	G	K	O
longitudinal	D	H	L	P

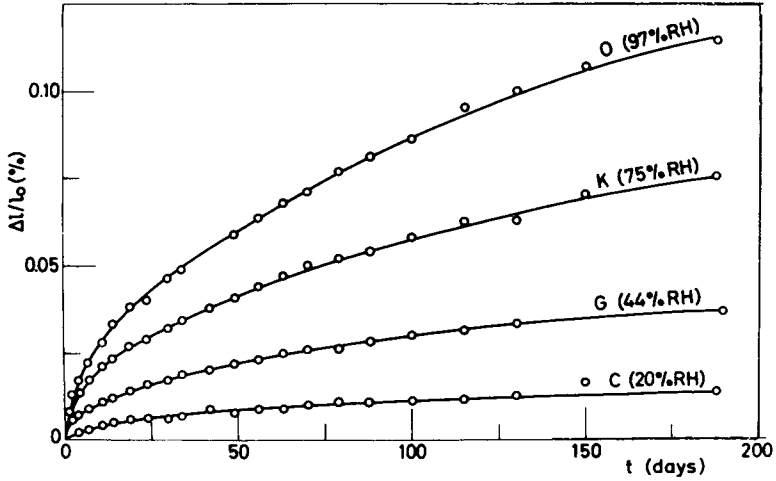


Fig. 3. Relative length changes as a function of time and R. H. in transverse samples.

be relied upon. The results of this computer calculation²² are given in Table III and in Figures 7 and 8 for microsphere, transverse, and longitudinal samples.

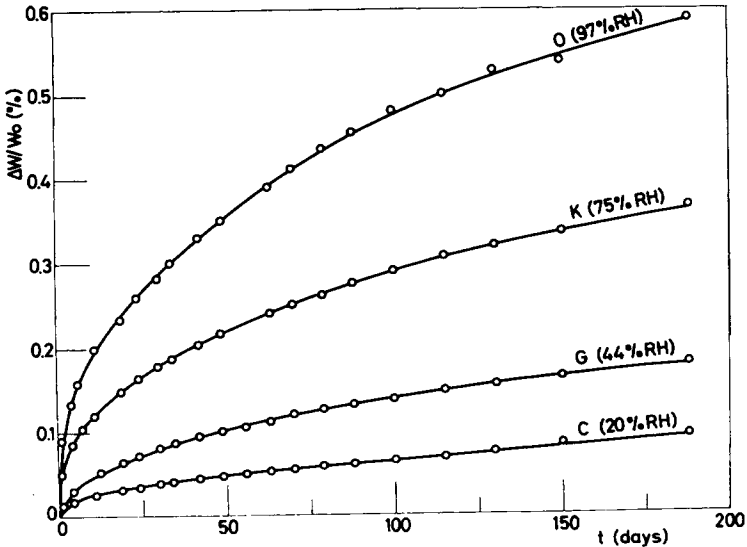


Fig. 4. Relative weight changes as a function of time and R. H. in transverse samples.

TABLE III
Coefficients M_∞ and λ for the Exponential Formula for the Rate of the Absorption

RH	Sample	M_∞	λ	Sample	M_∞	λ	Sample	M_∞	λ
20%	A	0.503	0.0212	B	0.249	0.0209	C	0.0877	0.0131
44%	E	1.00	0.0215	F	0.436	0.0237	G	0.1854	0.0139
75%	I	1.515	0.0226	J	0.745	0.0244	K	0.3165	0.0189
97%	M	2.05	0.0249	N	1.248	0.0244	O	0.5128	0.0197

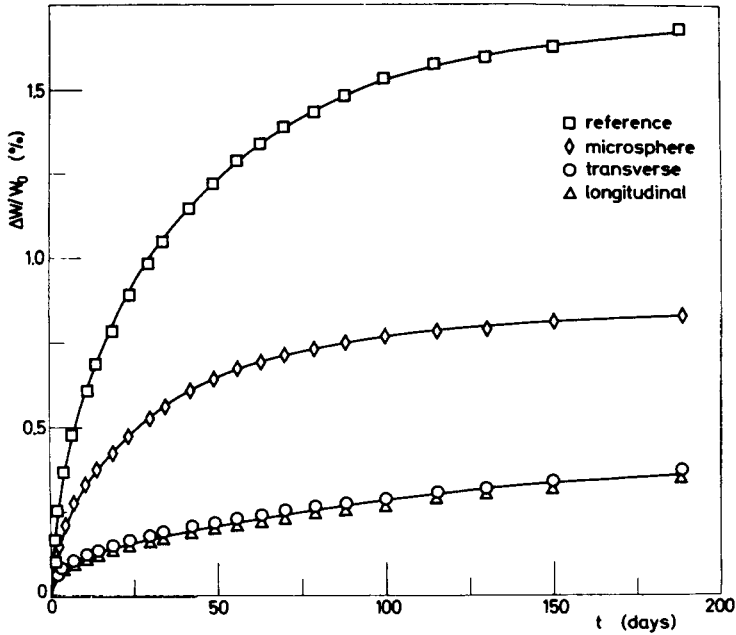


Fig. 5. Relative weight changes in □, reference; ◇, microsphere; ○, transverse; and △, longitudinal samples in 75% RH.

It can be seen from the last data that the equilibrium absorption of water is proportional to the relative humidity, Figure 9, but that the presence of glass restrains absorption, when calculated on the basis of the epoxy resin content alone.

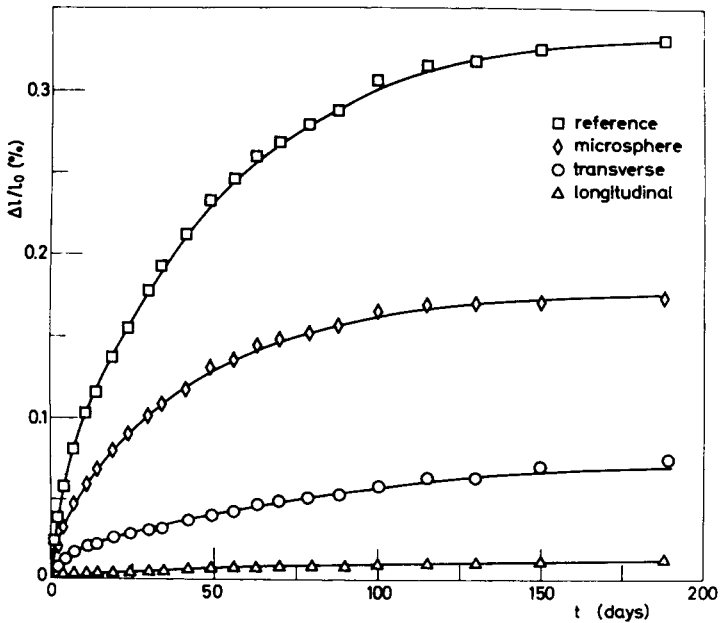


Fig. 6. Relative length change in □, reference; ◇, microsphere; ○, transverse; and △, longitudinal samples in 75% RH.

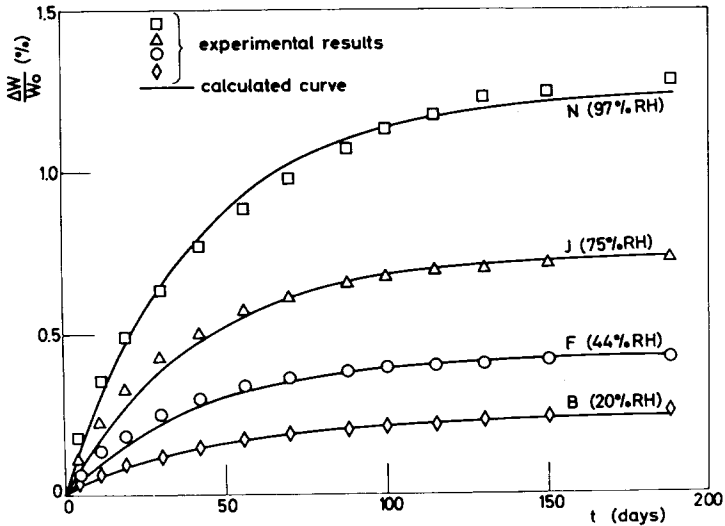


Fig. 7. Rate of water absorption in microsphere samples.

When plotted against changes of length, the relative absorption is seen to vary linearly in Figures 10-13, but that the constants of proportionality are different for various configurations of the filler. A "parameter of performance" was derived, identified by

$$\eta = \frac{(\text{relative length change})/(\text{epoxy content by volume})}{(\text{relative weight change})/(\text{epoxy content by weight})}$$

and this was calculated for the four cases studied:

Configuration	η	Standard deviation
reference	0.209	0.011
microsphere	0.183	0.008
transverse	0.127	0.005
longitudinal	0.022	0.002

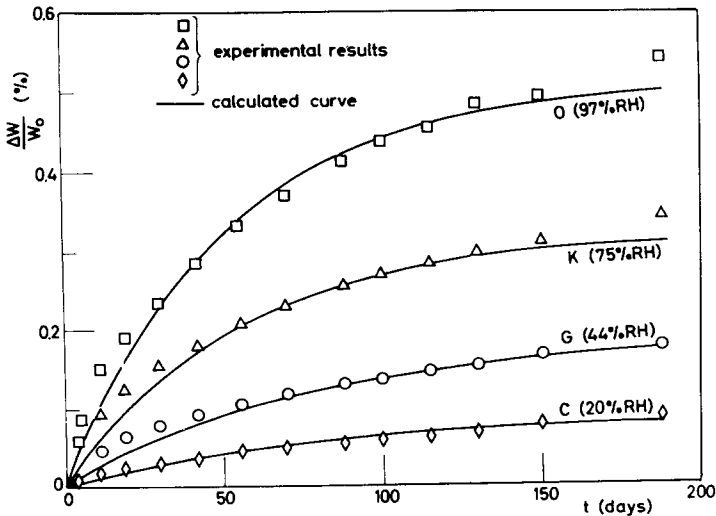


Fig. 8. Rate of water absorption in transverse and longitudinal samples.

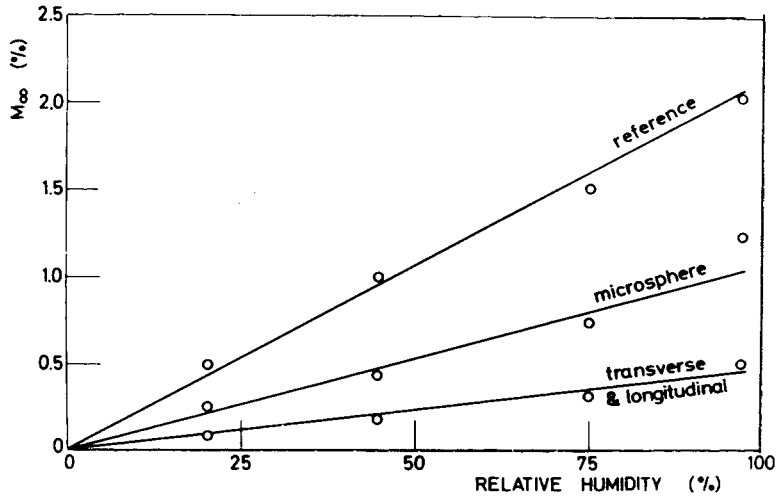


Fig. 9. The variation of M_{∞} as a function of the RH in the different material families.

It is obviously seen that the relative effect of filler configuration is considerably greater than in absorption.

This "parameter of performance" has similar meaning to that of the coefficient of thermal expansion in that it defines changes of length per unit absorbed weight and may be called "the hygroelastic coefficient."

It was observed during the initial stages of this study that the straight lines relating the relative absorbed weight to the relative change in length cut the coordinate axes, whereas it would have been expected that they should pass through the origin. In fact, lines of reference, microsphere and transverse samples cut the relative weight axis above the origin at points generally proportional to the RH, whereas the lines for the longitudinal samples cut it below the origin.

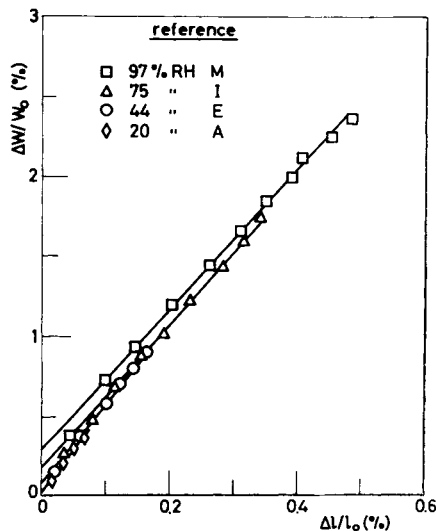


Fig. 10. Relative weight change vs relative length change in reference samples: □, 97% RH, M; Δ, 75% RH, I; ○, 44% RH, E; and ◇, 20% RH, A.

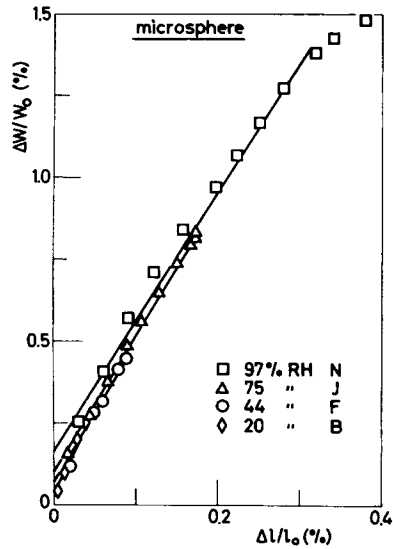


Fig. 11. Relative weight change vs. relative length change in microsphere samples: \square , 97% RH, N; Δ , 75% RH, J; \circ , 44% RH, F; and \diamond , 20% RH, B.

These observations may lead to the following conclusions: (a) Moisture deposits occur initially on the samples surface, and in the early stages do not effect geometrical changes, but add to the weight. (b) Changes in length are enhanced by slippage between the matrix and the fiber.

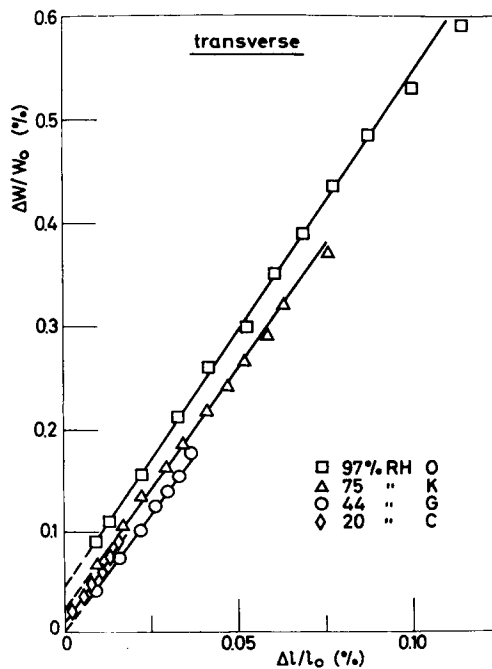


Fig. 12. Relative weight change vs relative length change in transverse samples: \square , 97% RH, O; Δ , 75% RH, K; \circ , 44% RH, G; and \diamond , 20% RH, C.

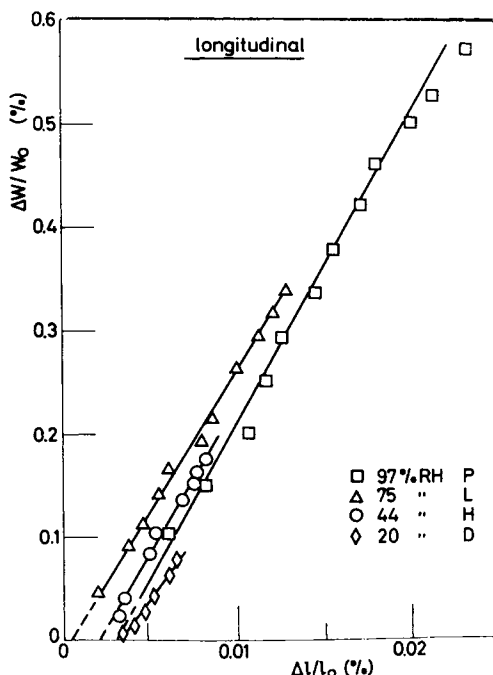


Fig. 13. Relative weight change vs relative length change in longitudinal samples: \square , 97% RH, P; Δ , 75% RH, L; \circ , 44% RH, H; and \diamond , 20% RH, D.

CONCLUSIONS

The following conclusions may be drawn from the observations:

(1) Relative water absorption of glass reinforced epoxy can be satisfactorily described by an exponential function of time. This representation is simple compared with many of the expressions quoted in the references, and it is valid for almost the whole range of the water absorption.

(2) The maximum (equilibrium) absorption is proportional to the relative humidity of the ambient atmosphere, but its value is determined by the type of reinforcement.

(3) There is a proportionality between weight increase and linear dimensional change. The constant of proportionality is highly dependent on the nature of reinforcement. The proportionality indicates that the same mechanism controls water penetration into samples with the same reinforcement at all levels of ambient humidity.

(4) A material parameter called the "hygroelastic coefficient" η , may be defined which characterizes dimensional changes due to moisture absorption. In composite structures, this coefficient is analogous to the coefficient of thermal expansion.

References

1. I. G. Romanekov and Z. P. Machavariani, *Sov. Plast.*, **4**, 49 (1967).
2. S. D. Garanina, Y. V. Zherdev, A. Y. Kovolev, V. A. Goryushkin, and Y. D. Avrasin, *Kolloid. Z. Polym.* **32**(4), 508 (1970).
3. R. Blahnik and V. Preiningerova, *Plaste Kautsch.*, **18**, 501 (1971).
4. I. G. Romanekov, *Sov. Plast.*, **2**, 74 (1967).

5. V. G. Raevskii, E. A. Zhivova, R. M. Vasenin, and V. Ye. Gul, *Polym. Sci. USSR*, **12**, 9 (1970).
6. R. E. Cuthrell, *J. Appl. Polym. Sci.*, **12**, 1263 (1968).
7. Z. Rigbi, *Polymer Networks: Structural and Mechanical Properties*, 1971, 261.
8. R. Byron Pipes, J. R. Vinson, and T. W. Chou, *J. Compos. Mater.*, **10**, 129 (1976).
9. W. Jost, *Diffusion in Solids, Liquids, and Gases*, Academic, New York, 1952.
10. Chi-Hung Shen and G. S. Springer, *J. Comp. Mater.*, **10**, 2 (1976).
11. H. Lee and K. Neville, *Handbook for Epoxy Resins*, McGraw-Hill, New York, 1967.
12. R. C. Wyatt and K. H. G. Ashbee, *Fiber Sci. Technol.*, **2**, 29 (1969).
13. W. Krolkowski, *SPE J.*, **20**, 1031 (1964).
14. A. Blaga and R. S. Yamasaki, *J. Mater. Sci.*, **18**, 654 (1973).
15. K. H. G. Ashbee and R. C. Wyatt, *Proc. R. Soc. London, Ser. A*, **312**, 553 (1969).
16. O. Ishai and A. Mazor, "The Effect of Environmental Loading History on Mechanical Behavior of Fiber Reinforced Polymeric Composites," First Interim Report, Department of Mechanics, Technion-Israel Institute of Technology.
17. T. C. Koshy, P. N. Govindarajan, and D. K. Banerjee, "Effect of Natural and Artificial Weathering on Flexural Properties of G.R.P." *S.P.I. 29th.*, Sec. 2-B, 1-6 (1974).
18. D. I. James, R. H. Norman, and M. H. Stone, *Plast. Polym.*, **36**, 21 (1968).
19. S. Gazit, "Hygroelastic Behaviour of Glass Reinforced Plastics," Research Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Mechanics, Technion-Israel Institute of Technology, 1976.
20. *International Critical Tables*, McGraw-Hill, New York, 1926, Vol. 1, p. 67.
21. *Handbook of Chemistry and Physics*, 51st Ed., Robert Weast (Ed.), Chemical Rubber Co., Cleveland, Ohio, 1970-1971, D-40, F-7.
22. *GMD, Biomedical Computer Programs X-Series Supplement*, W. J. Dixon (Ed.), University of California, Berkeley, 1969, pp. 177-186.

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