

Water Transport in Thermosetting Polyester, Vinyl Ester and Acrylic Resins

Lee Sang-baek*, T. J. Rockett**

열경화성 폴리에스터, 비닐에스터와 아크릴 수지에서의 물의 이동

李相白*, 톰 로켓트**

Introduction

The understanding of water diffusion in polymers is critical to the prediction of their behavior in applications where they are exposed to water or moist environments. Water diffusion in a polymer is one of the limiting factors in the use of fiber reinforced polymer composites (Springer, Sarder and Tung 1981). Water absorption has been reported to change mechanical properties; blisters, disk cracks, and delaminations have been observed (Apicella et al 1983, Ellis and Found 1983, Shen and Springer 1981). An investigation of the causes of such phenomena requires a thorough knowledge of water sorption characteristics. Diffusion coefficient and equilibrium water content (saturated water content or equilibrium

solubility M_{∞}) are fundamental properties measured during water absorption study. D and M_{∞} are well known for many polymers (Delasi and Whiteside 1978, Moy and Astarita 1979). For unsaturated polyester, however, the literature values widely vary and chemical compositions are often not specified. Even when specified, the wide chemical composition range of materials used today means that the sorption properties must be evaluated by chemical type.

Commercial fabrications are often multilayer composites - e.g., a gelcoat, a skincoat, and a backup glass fiber filled resin. To compute the transient and equilibrium water concentration in a composite, it is necessary to determine the relation between partial pressure and water content for each component in the structure so that the concentration change at the interface can be assessed.

* Dept. of Chemical Engineering, College of Engineering

** Dept. of Chemical Engineering, University of Rhode Island

Experimental Procedure

Materials

Table 1 lists the composition of the two polyesters, an orthophthalic and an isophthalic

polyester used in this study. The third material was a vinyl ester resin (Dow Derakane 411-45) and the fourth was a cast acrylic sheet. The polyester resins were promoted with N,N-diethylaniline and cured with 2% of benzoyl peroxide, Lupersol ATC (Pennwalt Corp., 8.7% active oxygen minimum).

Table 1. Composition of Polyesters. Data is given as mole per cent anhydride in a molar ratio 1 : 1 with total glycol.

	Mole %	
	Orthophthalic	Isophthalic
Propylene Glycol	84	110
Diethyl Glycol	22	-
Phthalic Anhydride	60	-
Maleic Anhydride (M.A)	40	50
Isophthalic Anhydride	-	50
Styrene/M.A molar ratio	2.20	1.03

Preparation of Samples

Polyester sheets were cast between glass plates separated to a sheet thickness of 0.5~1.0mm. Half of the casting was post-cured at 100°C for 1 hour. The sheets were cut into one inch squares and stored in a desiccator at room temperature. The acrylic was from biaxially oriented cast sheet.

Testing Procedure

The experiment exposes many samples to various partial pressures at normal or elevated temperatures. The bottom of a desiccator was filled with water or salt solution to control the partial pressure; the samples were placed on a rack above the liquid, and the desiccator was placed in a oven at the desired temperature, the

samples were removed periodically and weighed to the ± 0.0001 gram.

Results and Discussion

Sorption Data

Fig.1 shows absorption data for the isophthalic polyester at three test temperatures 28.5°C, 38.5°C, and 65°C, several partial pressures, and for as-cast and post-cured samples. Each curve represents the change in weight during absorption at the water partial pressure set by the solution in the desiccator. At 65°C the sample loses weight after reaching a maximum; this loss is greater in the as-cast sample. The orthophthalic polyester loses some weight at 38.5°C and more 65°C. The vinyl ester resin also loses weight. Only the acrylic resin

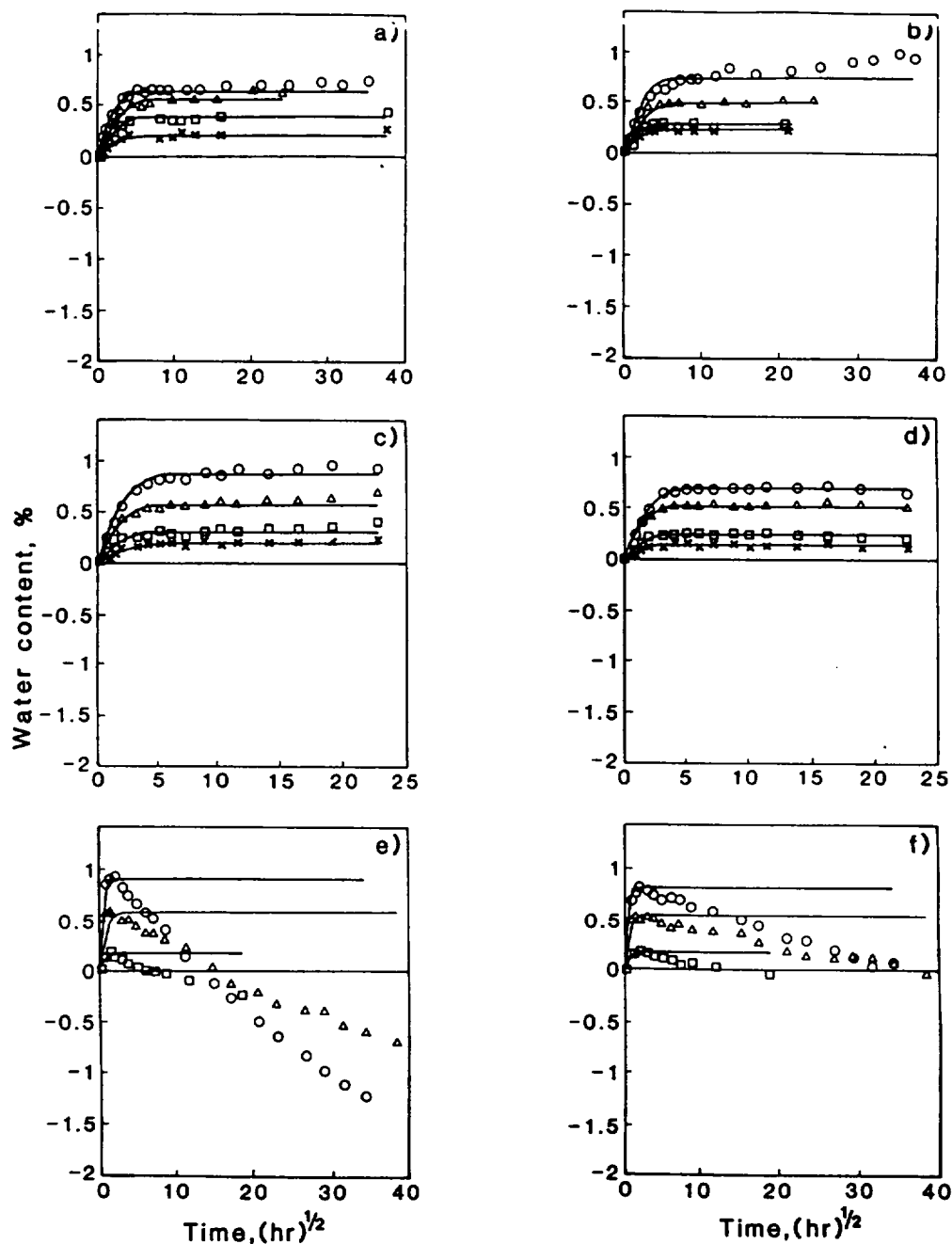


Fig 1. Water absorption curves for isophthalic polyester at three temperatures and various partial pressures. a) as cast at 28.5°C b) post cured at 28.5°C key (partial pressure, mmHg) : ○, 30; △, 23; □, 16; ×, 10; ---, Fick's law solution. c) as cast at 38.5°C d) post cured at 38.5°C key : ○, 51; △, 38; □, 26; ×, 16; ---, Fick's law solution. e) as cast at 65°C f) post cured at 65°C key : ○, 188; △, 139; □, 53; ---, Fick's law solution.

does not lose weight at 65°C. The weight loss is caused by outgassing of volatile residuals. High partial pressure and 65°C, for all samples except the acrylic, produces erratic data after saturation due to disk cracking and osmotic swelling. Steel (1967) and Ashbee (1967) described this behavior. The absorption curves in Fig.1 e) and f) are not drawn after these effects begin because it no longer reflects absorptive diffusion of water molecules.

Diffuion Coefficients

Table 2 lists the diffusion coefficients

Table 2. Diffusion coefficients ($D \times 10^9$, cm^2/sec) at 28.5°C, 38.5°C and 65°C and various partial pressures

Temperature (°C)	28.5				38.5				65			
Relative humidity (%)	32	52	75	100	31	50	75	100	18	28	75	100
Partial pressure of H ₂ O (mm Hg)	10	16	23	30	16	26	38	51	33	53	139	188
Orthophthalic resin, as cast	0.81	0.60	0.66	0.63	1.52	1.49	1.58	1.36	9.58	11.2		16.2
orthophthalic resin, post cured	0.62	0.71	0.57	0.54	1.07	1.22	1.24	1.02	17.5	9.51	16.3	16.4
Isophthalic resin, as cast	0.84	0.91	0.74	1.39	1.15	2.10	1.79	1.66	9.36	6.97	19.1	17.1
Isophthalic resin, post cured			0.85	0.97	2.73	3.05	2.88	2.00	13.4	12.9	15.0	144.4
Vinyl ester resin	2.05	2.68	2.36	1.39	4.03	3.89	3.08	2.44	39.3	30.6	25.5	18.0
Acrylic	1.36	1.02	0.76	0.50	1.75		1.45	0.99	9.54	3.44	6.91	5.34

Treatment of Diffusion Data

M_t was evaluated by fitting data points in the linear region to a least squares straight line. Uncertainty in values of M_∞ were treated as follows: for experiments that lost weight after saturation, M_∞ was taken to be the maximum weight; for experiments with slight positive deviation from constancy, the D value was calculated using the best fit zero-slope line. Values in Table 2 are averaged values from two or three replicate experiments.

calculated using the solution of Fick's second law (Cracnk 1975) :

$$\frac{M_t}{M_\infty} = \left(\sqrt{\frac{D}{\pi}} \frac{4}{h} \right) \sqrt{t}$$

where D is the diffusion coefficient, h is the sample thickness, M_∞ is the weight of the polymer and water in the polymer at equilibrium saturation, t is time and M_t is the weight of sample and the absorbed water at time t. From the absorption curves, such as those in Fig.1, values of M_t , M_∞ and t were taken.

Interpretation of Diffusion Data

If the diffusion coefficient is not a function of concentration (or stresses induced by concentration changes), then the values for a given temperature at all partial pressure should be constant. The two polyesters do not consistently increase or decrease with partial pressure suggesting that diffusivity is independent of concentration. Diffusion values for both vinyl ester and the acrylic decrease with increasing partial pressure. For acrylic, D is

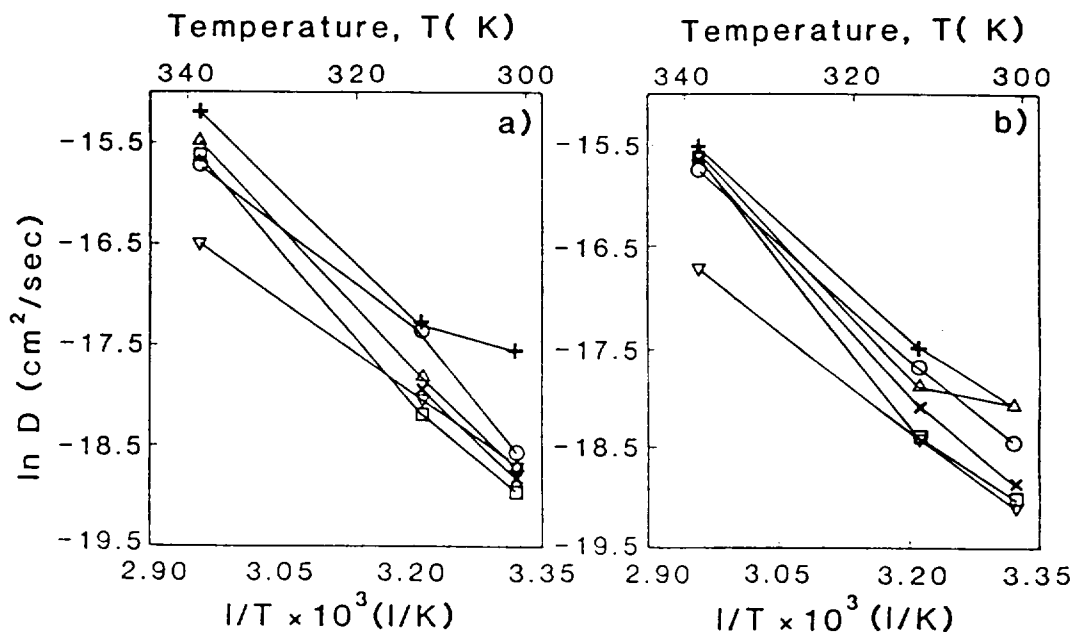


Fig 2. Diffusion coefficients as a function of temperature. a) 75% relative humidity. b) 100% relative humidity. key: \times , orthophthalic (as cast); \square , orthophthalic (post cured); Δ , isophthalic (as cast); O, isophthalic (post cured); +, vinyl ester; ∇ , acrylic.

reported to depend on concentration. (Barrie and Platt 1963)

Under identical conditions, water diffuses most rapidly through vinyl ester, moderately through isophthalic and most slowly through orthophthalic polyester resin. The greater separation of ester linkage in the vinyl ester and isophthalic polymer structures may explain this finding.

Effect of Post-Curing

Post-curing changes the diffusion coefficient for the unsaturated polyesters. It is difficult to generalize the changes because of weight loss observed at 65°C. However, post-curing slows the movement of water through the orthophthalic polyester resin at the lower temperatures. Post-curing reduces the diffusion

coefficient of isophthalic polyester resin at 28.5 °C and 65°C but higher values were found for the 38.5°C tests.

Activation Energy for Diffusion

An activation energy of diffusion is calculated from the Arrhenius equation. Fig.2 shows that only the acrylic gives a reasonably straight line with a value of 11.7 Kcal/mole. This deviation reflects the diffusion coefficient deviation at high temperature due to weight loss. The other method is required to determine the accurate diffusion coefficient at high temperature.

Equilibrium Water Concentration (M_{∞})

Table 3 lists the equilibrium water concentration for the six polymers at the three

fits with residual squared values of greater than 99%. Variables were tested for statistical significance; no statistical dependence was found for post-curing of the orthophthalic polyester resin. No dependence on temperature was found for the isophthalic polyester, vinyl ester and acrylic. The absorption isotherms are shown in Fig.3.

Phase Diagram for Polymer Absorption

The data is replotted in the form of a phase diagram in Fig.4. The solubility limit of water in the polymer separates the single phase polymer-water solid solution from the two phase region of liquid water and saturated polymer. The dashed lines represent the superimposed water iso-bars, giving the saturation value of the polymer at all temperatures and partial pressures. If a polymer, after saturation, is heated or cooled so that it falls into two phase region, water clusters will form in the polymer.

Modeling the Composite Concentration Profiles

The a, b values for the polynomials from equilibrium water content permit the calculation of water concentration profiles in multilayer polymer composites. As water diffuses into the surface, the concentration changes with time according to Fick's second law. At interfaces between two polymers, the partial pressure of the water in polymer 1 must equal the partial pressure of water in polymer 2. As a consequence, the concentration gradient across the interface is discontinuous. Once the relationship is known between the partial pressure (or relative humidity) and the concentration (M_{∞}), the discontinuity can be

calculated. Fig.5 shows the concentration of water in acrylic resin versus the concentration in isophthalic resin at equal activities (P/P_0). Fig.6 shows the concentration profile of water for an acrylic-isophthalic polyester multilayer.

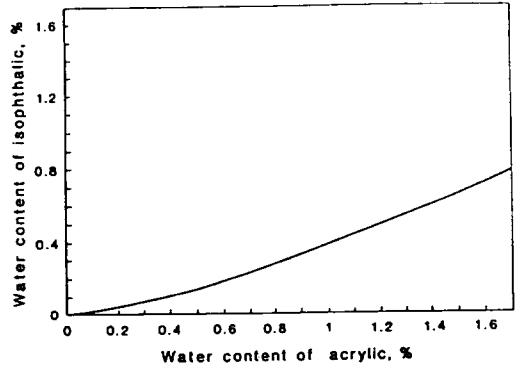


Fig 5. Concentration of water in isophthalic (as cast) and acrylic resins at identical partial pressures.

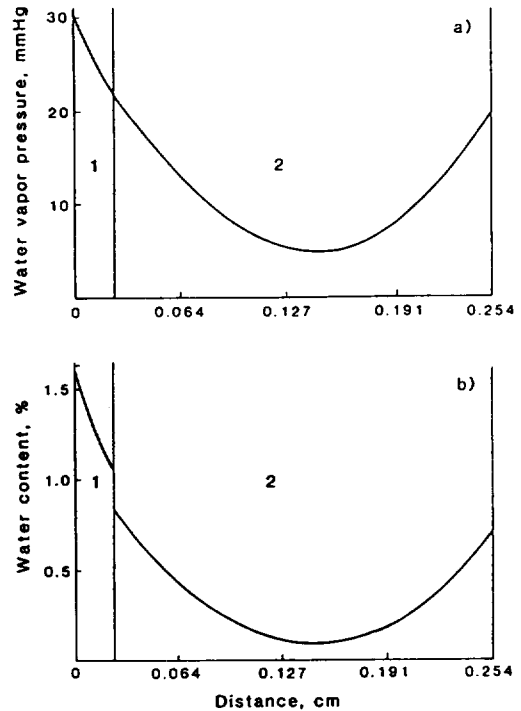


Fig 6. Profiles of a) partial pressure b) concentration in an acrylic(1)-isophthalic(2) resin multilayer.

Conclusions

A study of the absorption of water in six polymeric materials produced diffusion coefficient and saturation values for short time exposure at three temperatures. Disk cracks and weight losses in long term exposure affected diffusion characteristics. The development of modified experiments are required to determine

true diffusion parameters in long term exposure. The calculated activation energies exhibited the influence of weight losses at high temperature on diffusion coefficient. Isotherm curves showed higher increase of solubility near 100% relative humidity. The phase diagrams can give solubility at any temperature and partial pressure. From the relationship between concentration and partial pressure the concentration profile of composite was obtained.

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〈國文抄錄〉

열경화성 폴리에스터, 비닐에스터와 아크릴 수지에서의 물의 이동

오르소프탈릭, 아이소프탈릭 불포화 폴리에스터, 비닐에스터, 아크릴 수지에서의 물의 흡수에 관하여 고찰하였다. 습한 환경에서의 고분자의 무게 변화가 온도와 증기 부분압(상대습도)의 함수로 측정되었다. 흡수물무게 배분율 곡선과 상평형도가 얻어졌다. 확산계수, 물의 고분자에서의 용해도 활성화 에너지가 결정되었다. 다층 복합재료에서의 농도분포도 부분압과 농도의 관계로 유도 되었다.