Interactions of water with unsaturated polyester, vinyl ester and acrylic resins

Sang-Baek Lee* and T. J. Rockett†
Department of Chemical Engineering, University of Rhode Island, Kingston, RI 02881, USA

and R. D. Hoffman
Research Laboratory, Aristech Chemical Company, 1000 Tech Center Drive, Monroeville, PA 15146, USA

Moisture diffusion in unsaturated polyester, vinyl ester and acrylic resins exposed to various relative humidities and temperatures was investigated. The effects on water uptake of the type and amount of initiator, the post-curing treatment and specimen thickness were evaluated. A weight loss during exposure was observed in some resins; the true equilibrium water content and the diffusion coefficient could not be determined for these polymers. Absorption–desorption–reabsorption (ADR) experiments were conducted to determine the true equilibrium water contents and diffusion coefficients. These ADR experiments also show whether a resin exhibits a continuous weight loss during long term water exposure, a phenomenon associated with degradation of the polymer network, or whether the loss is caused only by the release of residual species. The water diffusion behaviour for polymers containing disc cracks was compared with the behaviour of polymers without disc cracks. Diffusion coefficients and saturation values are given for orthophthalic polyesters, isophthalic polyesters, vinyl ester and acrylic resins at 65°C and a 75% relative humidity.

(Keywords: water; diffusion; polyester; vinyl ester; acrylic; resins)

INTRODUCTION

The understanding of water–polymer interactions in polymeric composite materials is critical to the prediction of their behaviours in applications where they are exposed to water or a moist environment. Water diffusion in a polymer is one of the limiting factors in the use of fibre-reinforced polymer composites[1-3]. Water absorption has been reported to change mechanical properties: blisters, disc cracks and delaminations have been observed[4-10]. An investigation of the causes of such phenomena requires a thorough knowledge of water sorption characteristics. Diffusion coefficients (D) and equilibrium water content (saturated water content or equilibrium solubility, M_∞) are fundamental properties measured during water absorption studies. Recent reports on diffusion coefficients and equilibrium water contents of polyester resins show a wide range of values. Much of the sorption data which has been reported is for resins of poorly defined composition.

In many water absorption studies, cast resins are dried above room temperature to remove moisture or residual materials inside the polymers, but because the cast resin is also post-cured at the drying temperature, the properties of as-cast resins cannot be obtained by this procedure[4,5,11]. A knowledge of sorption properties of as-cast resins is needed for many polymeric composite applications, especially in the boat building industry. Water diffusion in as-cast and post-cured resins is compared in this study.

Several studies have indicated that the weight gain curves for polymers immersed in water show a decrease after reaching a maximum. Springer et al. explained the weight loss phenomena in unsaturated polyester as the loss of resin particles associated with the development of surface cracks[1]. Abeysinghe et al. discussed four possible mechanisms to account for a weight loss: diffusion of residual volatiles; chemical scission of the ester group (hydrolysis); diffusion of residuals induced by disc cracks; and leaching[12]. It is very important to know whether a polymer undergoing a weight loss is suffering permanent network degradation or whether it is losing residual materials. Network degradation can result in lower mechanical properties. A loss of low molecular weight residuals may not only produce surface tensile cracks but may be disastrous in some cases, e.g. the loss of a toxin from a fibre in a closed building or the loss of residual to a packaged food. Therefore, for a given polymer that shows a weight loss, it is important to differentiate a loss of residuals from a loss caused by network degradation.

The objective of this study is to measure water sorption as a function of temperature and water partial pressure in orthophthalic and isophthalic polyesters, vinyl ester and acrylic resins. During this work the weight loss phenomenon was also observed for some polymers to an extent which precluded the direct determination of D and M_∞. A technique was developed to assess the weight loss

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Table 1 Initiators used in curing

Initiator	Peroxide (%)	State	Active oxygen (%)	Other ingredient
BPO	40	Emulsion	2.56	Diisobutylphthalate (60%)
BPO	50	Paste	3.3	Tricresyl phosphate (50%)
MEKP	60	Liquid	9.0	Dimethylphthalate (40%)

and determine the absorption parameters. The values obtained at 65°C are reported here; values from the work at 30°C, 40°C and 90°C are given elsewhere[13]. After absorption, resins were desorbed to measure the amount of absorbed water and remove any remaining residual materials. The desorbed samples were exposed to moisture again for reabsorption. The absorption–desorption–reabsorption (ADR) test is an effective analytical probe for studying water–polymer interactions.

EXPERIMENTAL

Materials

The four materials tested were a general purpose unsaturated orthophthalic polyester resin with a 3:2 molar ratio of phthalic anhydride to maleic anhydride, and an unsaturated isophthalic polyester prepared using a two-stage cooking process (both crosslinked with styrene monomer); a vinyl ester of the ester-linked bisphenol-epoxy type; and a cast acrylic sheet. Two frequently used room temperature curing systems were used with the polyester and vinyl ester resins, i.e. methyl ethyl ketone peroxide (MEKP)/cobalt naphthanate (CN) and benzoyl peroxide (BPO)/N,N-dimethylaniline (DMA). The compositions of the initiators are given in *Table 1*.

Preparation of samples

Polyesters and a vinyl ester were cast at room temperature between glass plates separated to a sheet thickness of 0.5–1.3 mm. The sheets were cured at 26°C for 48 h before the glass was removed. A mylar sheet prevented the resin from sticking to the glass and was easily peeled from the sheet. Half of the casting was post-cured. The sheets were cut into 25.4 mm squares. The acrylic resin used in this study was cut from biaxially oriented cast sheet. If the samples were not used immediately they were stored in a vacuum desiccator.

Testing procedure

During the experiments, samples were exposed to vapour containing various water partial pressures (relative humidities) at 30°C, 40°C and 65°C. The bottom of a desiccator was filled with water or a salt solution to control the water partial pressure; the samples were placed on a rack above the liquid. The desiccator was placed in an oven at the desired temperature. The samples were removed periodically and weighed to ±0.0001 g. After absorption, the absorbed samples were placed in a vacuum or over P_2O_5 for the desorption experiments. The decrease of weight was monitored periodically. The reabsorption testing was carried out in the same manner as the absorption tests.

Weight change measurements were duplicated using a Cahn electrobalance (model no. 2000) which was connected to a computer through an I/O interface. The results of the continuously weighed samples were

compared with the weight measurements made after periodic removal from the environmental chamber to determine if any differences resulted. No differences were observed. The data from the interrupted desiccator experiments are just as reliable as the data from continuous electrobalance experiments.

RESULTS AND DISCUSSION

Water absorption measurements

The per cent weight change during water sorption was determined as follows:

$$wt\%(t) = \frac{W(t) - W(0)}{W(0)} \times 100 \qquad (1)$$

where $wt\%(t)$ is per cent weight change at time t, $W(t)$ is the weight of the polymer sample and absorbed water at time t, $W(0)$ is the dry polymer weight at time zero. *Figures 1* and *2* show the per cent weight change curves during absorption as a function of the square root of time for four polymers at 30°C/75% r.h. and 65°C/75% r.h., respectively. Data are not presented for 100% r.h. because difficulties are encountered in collecting data as a result of the tendency of water to cluster in some resins and from disc cracking in other resins[14]. Some polyester and vinyl ester resins show a weight loss after reaching a maximum, especially at 65°C. Acrylic does not lose weight. The water saturation values were taken as the maximum in the weight gain curves. In some cases these values are not the true M_∞ because of the weight loss and are reported as observed values in the absorption column of *Tables 2* and *3*.

Without a weight loss, resins show Fickian diffusion behaviour. From the solution of Fick's second law of diffusion, the diffusion coefficient was calculated as follows[15]:

$$D = \Pi \left(\frac{kl}{4M_\infty} \right)^2 \qquad (2)$$

where D is a diffusion coefficient, k is the slope of the linear region of the per cent weight change *versus* square root of time plots, l is the thickness of the sample and M_∞ is the equilibrium water content. The true diffusion parameter, D cannot be obtained for a polymer which shows a significant weight loss because, as shown in equation (2), the value is dependent upon M_∞. Since these observed values are smaller than the true values the calculated D will be inflated. These values are listed in *Table 4*, in the absorption column, for comparison with the other values. *Figures 1c* and *2a* show a slight increase in solution level after an apparent equilibrium has been reached. This could be the result of a relaxation of the structure caused by swelling stresses or a shift in the glass transition temperature.

As expected, the saturation values increase with temperature as do the diffusion coefficients. Weight loss
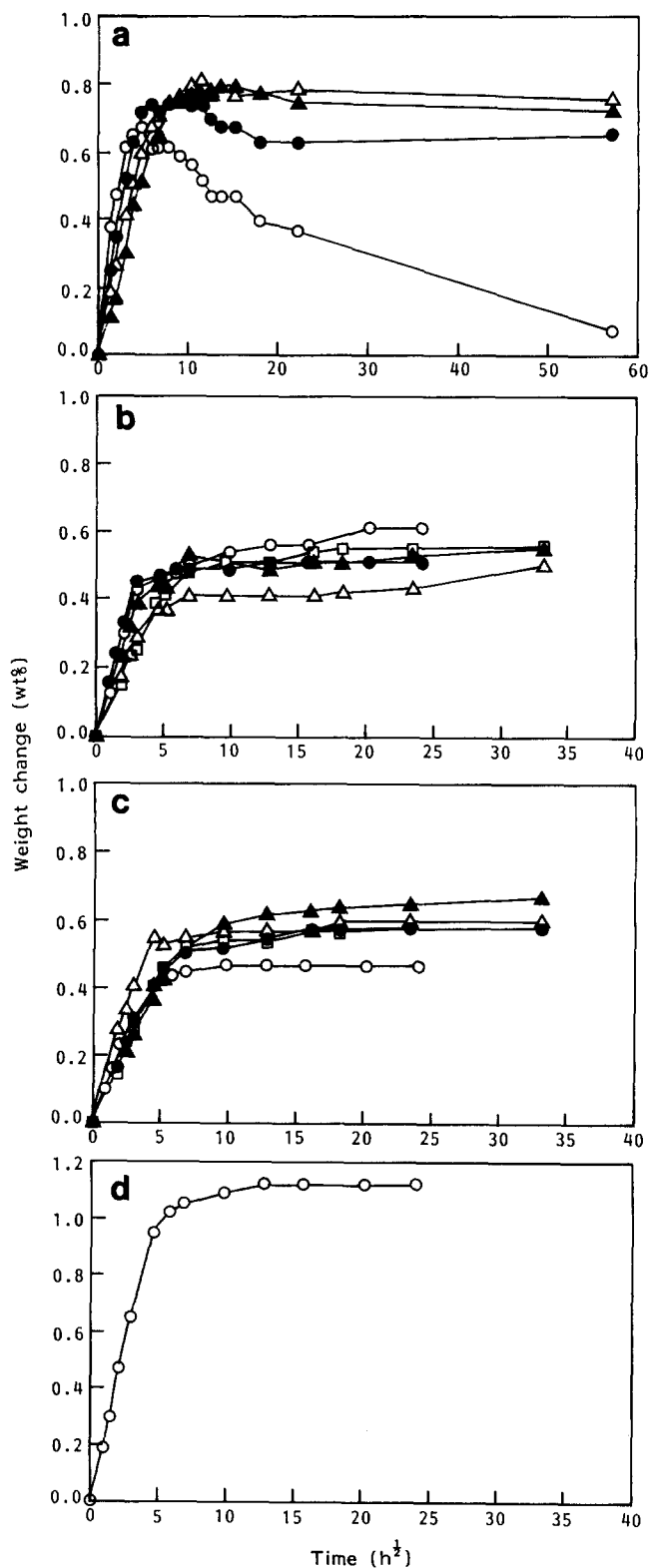
Figure 1 Weight change as a function of time$^{1/2}$ of polymers exposed to 30°C/75% r.h. (a) Orthophthalic polyester: ○, BPO 1%/DMA 0.3% as-cast (AC); ●, post-cured (PC); △, MEKP 1%/CN 0.3%/DMA 0.05% AC; ▲, PC. (b) Isophthalic polyester: ○, BPO 2%/DMA 0.3% AC; ●, PC; △, MEKP 0.5%/CN 0.3%/DMA 0.05% AC; ▲, PC; □, MEKP 4%/CN 0.3%/DMA 0.1% PC. (c) Vinyl ester: ○, BPO 2%/DMA 0.3% AC; ●, MEKP 0.5%/DMA 0.05%/CN 0.3% PC; △, MEKP 2%/CN 0.3%/DMA 0.1% PC; ▲, MEKP 4%/CN 0.3%/DMA 0.1% AC; □, PC. (d) Acrylic cast sheet

Figure 2 Weight change as a function of time$^{1/2}$ of polymers exposed to 65°C/75% r.h. (a) Orthophthalic polyester: ○, BPO 1%/DMA 0.3% as-cast (AC); ●, post-cured (PC); △, MEKP 1%/CN 0.3%/DMA 0.05% AC; ▲, PC. (b) Isophthalic polyester: ○, BPO 2%/DMA 0.3% AC; ●, PC; △, MEKP 0.5%/CN 0.3%/DMA 0.05% AC; ▲, PC; □, MEKP 4%/CN 0.3%/DMA 0.1% PC. (c) Vinyl ester: ○, BPO 2%/DMA 0.3% AC; ●, MEKP 0.5%/DMA 0.05%/CN 0.3 PC; △, MEKP 2%/CN 0.3%/DMA 0.1% PC; ▲, MEKP 4%/CN 0.3%/DMA 0.1% AC; □, PC. (d) Acrylic cast sheet

tendencies increase dramatically at 65°C. MEKP yields cured resins more resistant to weight loss than those cured with BPO. If a resin shows a weight loss, it is more pronounced in the as-cast state than in the post-cured state.
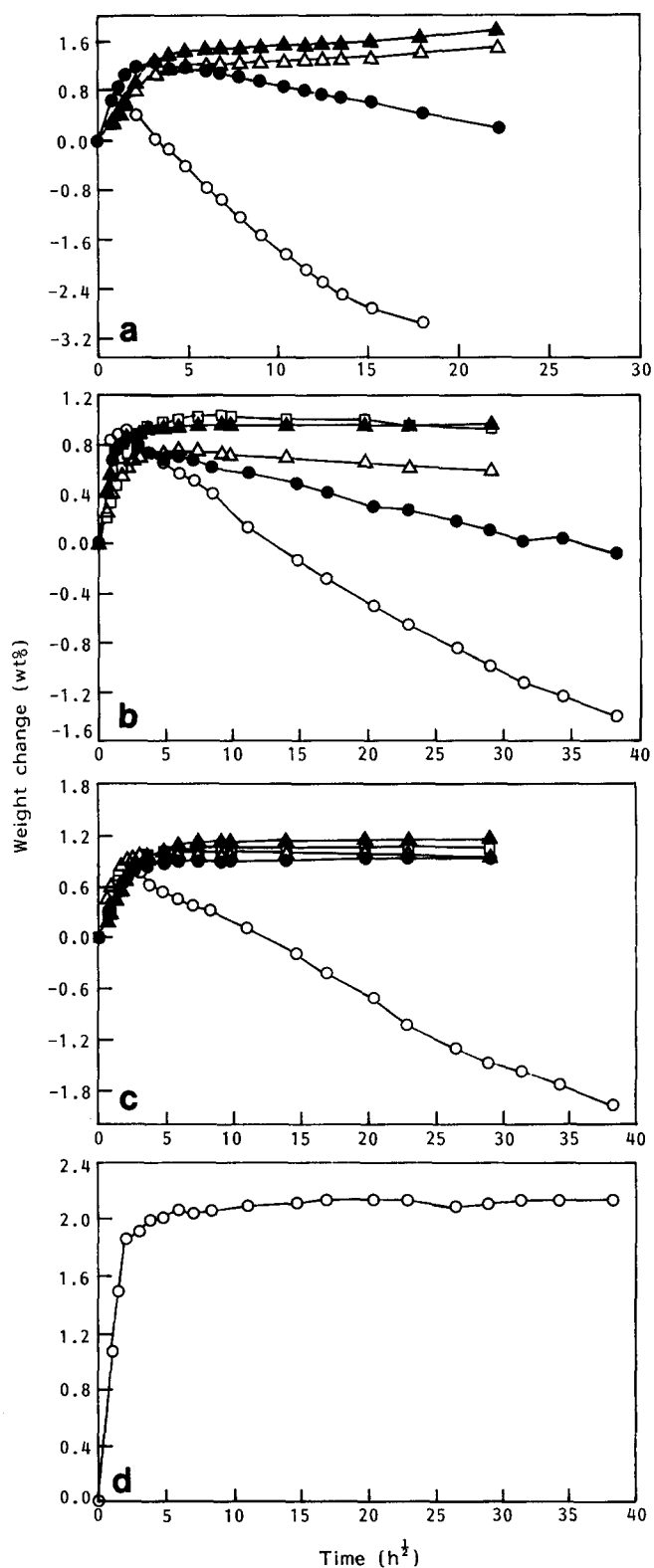
Absorption-desorption-reabsorption (ADR) measurements

To find the true equilibrium water content (M_∞) and the accurate D values of samples which showed a weight

loss, the following procedure was used. The absorption runs were continued until the weight loss rate became zero (see point 1 in *Figure 4*). The samples were then placed in a vacuum and the desorption curves were determined. At point $W(d)$ in *Figure 4*, reabsorption was begun. *Figures 3–5* show the actual weight change and the per cent weight change curves for the four polymers subjected to ADR tests at 65°C and 75% r.h. for

absorption and reabsorption and to vacuum for desorption. The orthophthalic polyester (*Figure 3*), isophthalic polyester (*Figure 4*) and vinyl ester (*Figure 5* with the acrylic curve) were cured with 2% BPO (paste type)/0.3% DMA. No cracking, crazing or deformation was observed on any of these samples after absorption, desorption or reabsorption. The M_∞ and D values extracted from these curves are given in *Tables 2*

Table 2 Per cent weight change and total weight loss at 65°C/75% r.h. during absorption–desorption–reabsorption (ADR)

Resin[a]	Weight change (%)			Total weight loss (%)	
	A	D	R	After desorption	After redesorption
Ortho AC	0.67	0.82	0.61	5.39	6.37
Ortho PC	0.68	0.88	0.67	1.88	2.67
Iso AC	0.58	0.68	0.66	2.09	2.23
Iso PC	0.52	0.59	0.61	1.01	1.11
VE AC	0.49	0.72	0.64	4.13	4.35
Acrylic	1.19	1.06	1.17	0.00	0.02

[a] Ortho, orthophthalic polyester; iso, isophthalic polyester; VE, vinyl ester; AC, as-cast; PC, post-cured

Table 3 Per cent weight change and total weight loss at 65°C/18% r.h. during absorption-desorption-reabsorption (ADR). The values in vacuum and P_2O_5 represent the 'dry loss' results

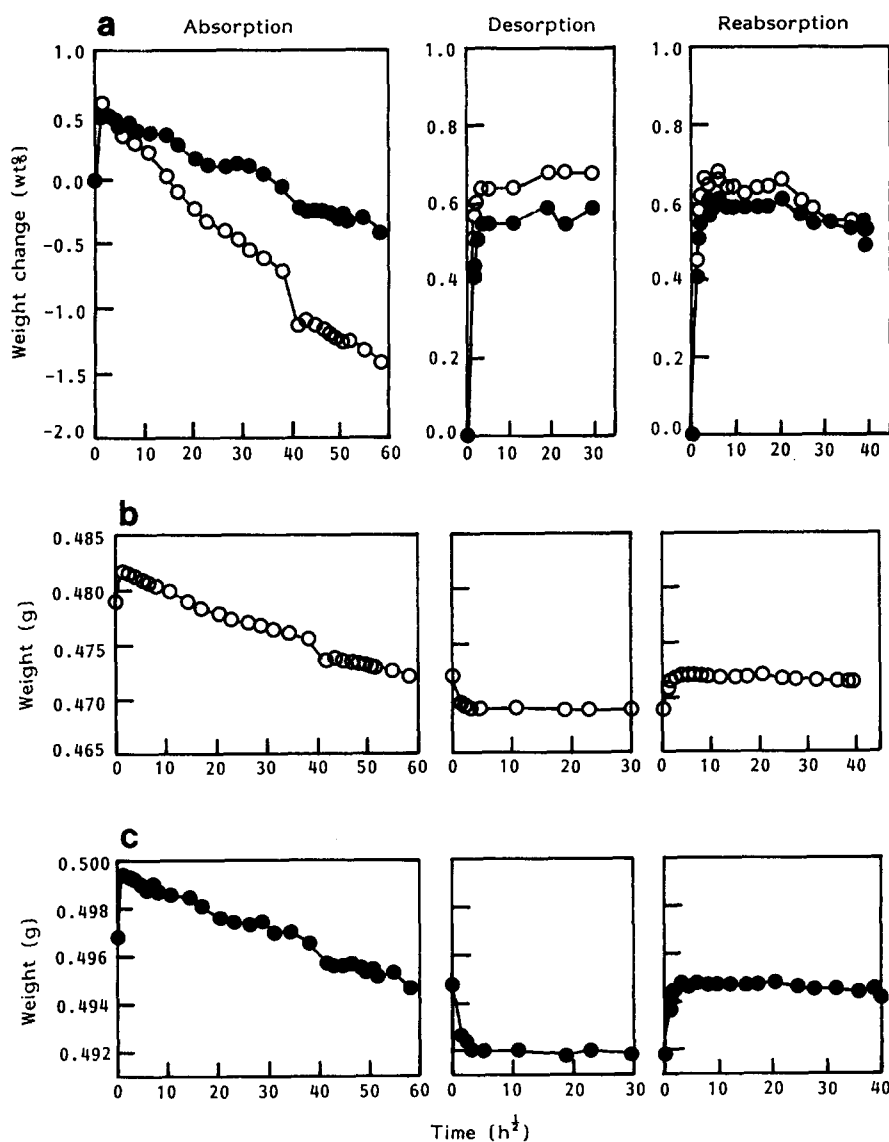| Resin[a]	Weight change (%)			Total weight loss (%)		
	A	D	R	After desorption	Vacuum	P_2O_5
Ortho AC	0.11	0.21	0.16	3.75	2.21	2.09
Ortho PC	0.13	0.18	0.16	1.28	0.77	0.91
Iso AC	0.14	0.16	0.13	1.22	0.66	0.48
Iso PC	0.11	0.13	0.12	0.73	0.52	0.39
VE AC	0.05	0.17	0.10	3.49	2.82	2.46
Acrylic	0.18	0.23	0.21	0.02	0.05	0.07

[a] See *Table 2* for abbreviations

Figure 3 (a) Per cent weight change of orthophthalic polyester during ADR at 65°C/75% r.h.: ○, BPO 2%/DMA 0.3% as-cast; ●, post-cured. (b) Actual weight change during ADR of as-cast; (c) actual weight change during ADR of post-cured

and *4*. Identical experiments were made at 65°C and 18% r.h. and these 'dry' values are given in *Table 3*.

The total weight loss after desorption was calculated as follows:

$$\text{wt loss } \% = \frac{W(0) - W(d)}{W(0)} \times 100$$

where $W(0)$ is the initial dry polymer weight at time 0 and $W(d)$ is the weight of the polymer after desorption as shown in *Figure 4*. The total per cent weight loss used here is the best measure of weight loss. If a polymer does not show a weight loss during absorption and desorption, the initial weight of the polymer and the weight after

Table 4 Diffusion coefficients $((\text{cm}^2\text{s}^{-1}) \times 10^8)$ at 65°C/75% r.h. from absorption (A), desorption (D) and reabsorption (R)

Resin[a]	A	D	R
Ortho AC	13.4	2.95	3.22
Ortho PC	13.1	3.39	3.29
Iso AC	14.4	4.99	6.17
Iso PC	12.8	4.35	5.93
VE AC	22.5	5.83	5.29
Acrylic	5.10	4.38	4.07

[a] See *Table 2* for abbreviations

desorption will be the same and the per cent weight loss will be zero (see the ADR curves for acrylic in *Figure 5c*). The weight losses in vacuum and over P_2O_5 (water partial pressure is less than 2×10^{-4} mmHg)[16] are also shown in *Table 3*. The weight losses at 65°C are affected by the amount of water that has diffused into the polymers. *Tables 2* and *3* show that the total weight losses increase as the relative humidity increases from 0 (in vacuum) to 18% and 75%. Similar effects on the diffusion of organics in polymer caused by absorption of water vapour have been reported[17,18].

If after absorption and desorption a polymer has released all species contributing to the weight loss, the desorption equilibrium water content and reabsorption equilibrium water content should be the same. Post-cured isophthalic polyester resin showed almost identical desorption and reabsorption equilibrium water contents. Orthophthalic polyester resin, especially the as-cast samples, show a lower apparent water content after reabsorption than after desorption, proving that the polymer is still releasing some component after 7100 h (9.5 months). The as-cast cured vinyl ester also showed a small but continuous weight loss throughout the entire test cycle.

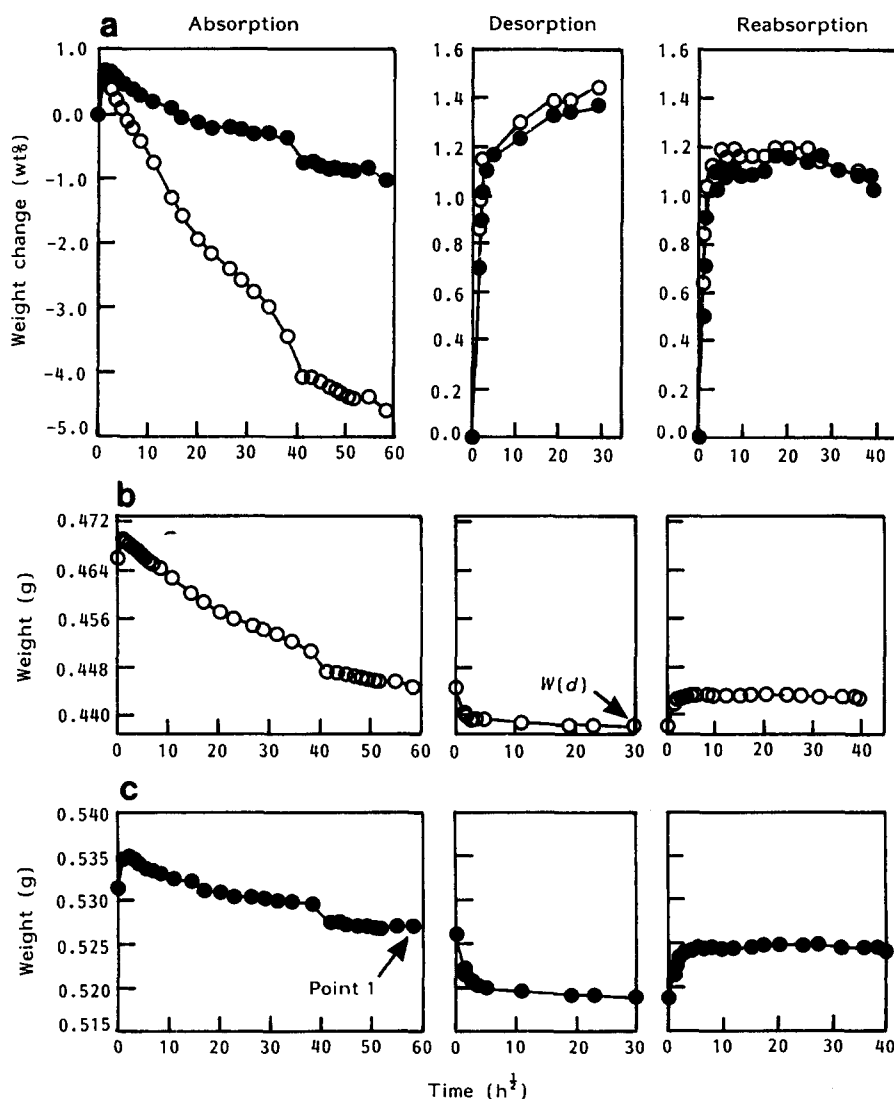Reabsorption samples were placed in vacuum once

Figure 4 (a) Per cent weight change of isophthalic polyester during ADR at 65°C/75% r.h.: ○, BPO 2%/DMA 0.3% as-cast; ●, post-cured. (b) Actual weight change during ADR of as-cast; (c) actual weight change during ADR of post-cured
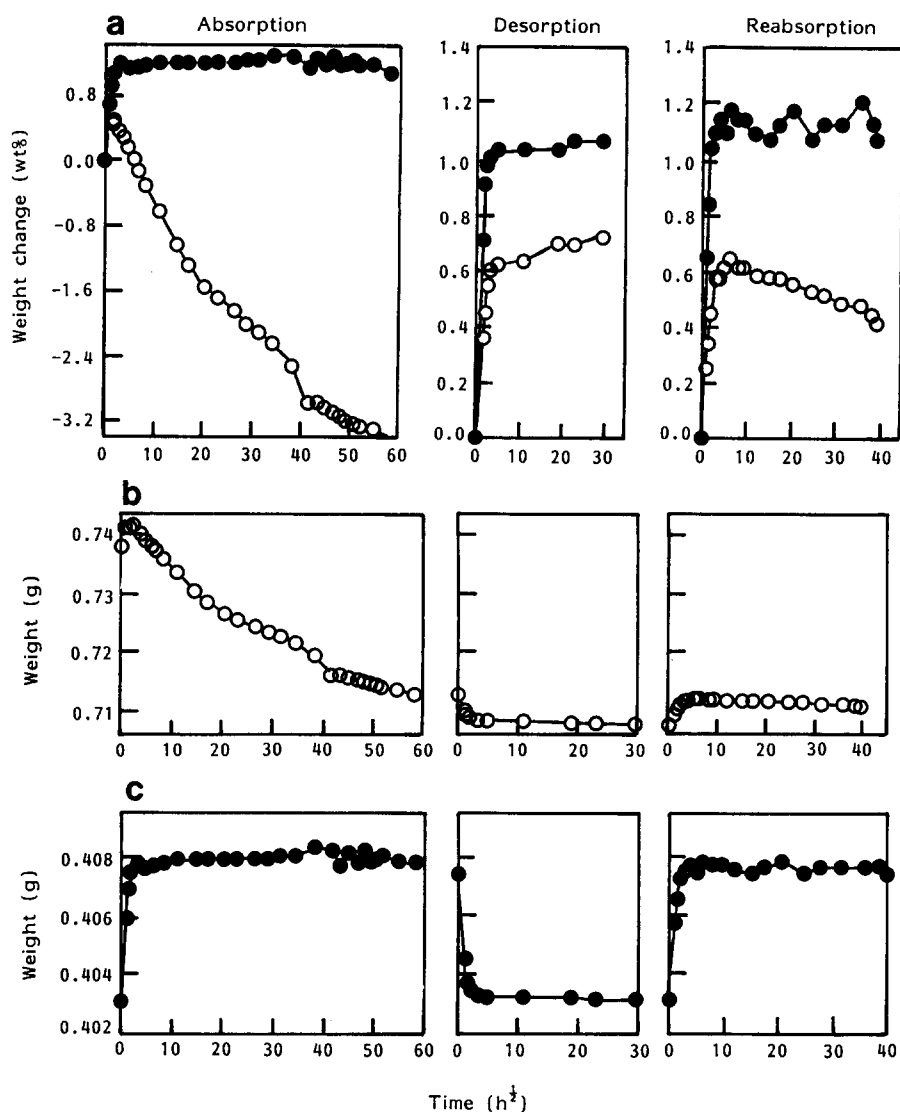
Figure 5 (a) Per cent weight change of vinyl ester and acrylic during ADR at 65°C/75% r.h.: ○, BPO 2%/DMA 0.3% as-cast; ●, acrylic. (b) Actual weight change during ADR of vinyl ester as-cast; (c) actual weight change during ADR of acrylic

again for a second desorption. A difference between the weight loss after desorption and the weight loss after redesorption indicates continued weight loss during reabsorption. This comparison is another way of determining the extent of continuous loss during ADR testing. The results confirm the comparison of M_∞ during desorption and reabsorption. Almost no change occurred in isophthalic polyester, while vinyl ester changes by 0.22 wt%. Orthophthalic polyester shows a substantial change: 0.98 wt% and 0.79 wt% for the as-cast and post-cured state, respectively. The total weight losses after redesorption are listed in *Table 2*.

Table 4 lists diffusion coefficients at 65°C and 75% r.h. for absorption, desorption, and reabsorption. As mentioned above, the diffusion coefficients calculated from the absorption data are much higher than those from desorption and reabsorption data because the *D* of absorption is calculated using the 'observed water content' (column 1 of *Table 2*) which is lower than the true M_∞. The deviation of the diffusion coefficients which is caused by the weight loss helps to explain substantial differences in reported diffusion coefficients of as-cast composites[4,10–12].

Weight loss and the release of residuals

All samples, except acrylic, lost weight under some conditions during ADR testing. Weight loss was increased and the rate was accelerated for a given resin under the following conditions: in the as-cast state; when BPO was used for curing; at high water partial pressures; and at elevated temperatures. Head-space gas analysis was performed using mass spectrographic/gas chromatography to determine the species being lost. Samples of orthophthalic resins were exposed to water vapour at 65°C for 170 h. *Figure 6* shows the results of gas chromatography. Other than water, styrene and ethyl benzene were the only detectable components in the head-space gas. Therefore, the loss of residual styrene and ethyl benzene accounted for all loss during 170 h of absorption. Ethyl benzene, the saturated analogue of styrene, was present in one run in a ratio of 26.3 to 1, styrene to ethyl benzene and in another run, the ratio was 50.6 to 1. A common impurity in styrene, this concentration of 2–4% ethyl benzene in the residuals suggests a concentration of about 20 ppm in the original styrene. Since none of the original ethyl benzene can cross-link with the polymer, its concentration will reach
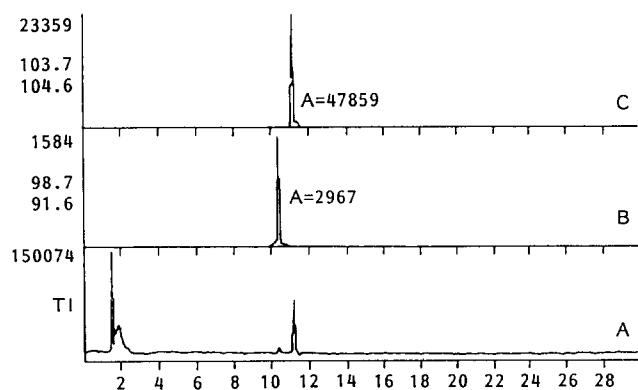
Figure 6 Gas chromatographic peaks for the head-space gases: A, head-space analysis for the gas; B, integrated area for ethyl benzene; C, styrene
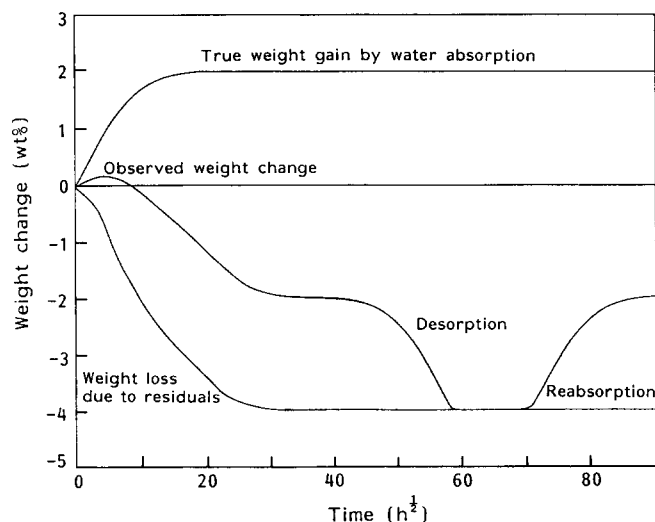

Figure 7 Hypothetical weight change curve resulting from simultaneous water absorption and residual loss from a polymer

a maximum as the free styrene decreases during cross-linking.

If the loss of unreacted residuals accounts for all weight loss during ADR testing the curves should look like the observed weight change curve of *Figure 7*. The weight change during desorption and reabsorption should be identical and of opposite sign. While well cured isophthalic resin shows such behaviour, orthophthalic resin does not (*Figure 3*). In spite of prolonged exposure, the resin has not lost all of the modified species and a weight loss is continuing even in the reabsorption experiment.

While the ADR behaviour of these polymers can be attributed to simultaneous water absorption and residual release, other phenomena can take place during absorption of water (or other solvent species) which can influence the shape of the curves. Post-curing effects at elevated absorption temperatures reduce residuals. If water absorption causes the hydrolysis of network-forming bonds, such as ester linkages, the curves could show delayed or secondary weight gain because the more open polymer structure can hold more water. If degradation is severe, a weight loss could also result from the release of hydrolysis products. Water can plasticize a material and, in the extreme, reduce the glass transition temperature below the absorption temperature. As this process takes place, a weight increase will be seen. Exposure to water, near but below the glass transition temperature, can cause a relaxation (annealing) which

can lead to a reduction in the amount of water the polymer can hold. This drop in saturation can lead to the nucleation of disc crack as reported earlier[14]. Finally, at 100% r.h., internal disc cracking and osmotic processes can lead to weight gains or sudden losses as osmotic blisters grow and then break and lose solution. A totally satisfactory mathematical model has not yet been formulated for the weight change with time because of the independent nature of several of the processes discussed.

CONCLUSION

The moisture diffusion characteristics of orthophthalic, isophthalic, vinyl ester and acrylic resins have been studied. The three ester resins underwent a weight loss during absorption. The weight loss for a given resin was affected by initiator type, the amount of initiator, the post-curing treatment, relative humidity and temperature. MEKP-cured resins showed a smaller weight loss than those cured with BPO. Post-curing reduced weight loss significantly. Higher temperature and relative humidity increases the weight loss rate. The true equilibrium water content and diffusion coefficient could not be obtained during absorption because of the weight loss.

Absorption–desorption–reabsorption experiments were conducted to establish the true diffusion characteristics. BPO-cured orthophthalic resin showed the continuous weight loss which took place during absorption, desorption and was still taking place during reabsorption. MEKP-cured orthophthalic and vinyl ester resins were much more stable, showing only slight loss during reabsorption. Isophthalic resin did not lose weight after desorption. Equilibrium water contents (M_∞) and diffusion coefficients were determined using absorption, desorption and reabsorption data, and the latter are considered accurate values for these polymers.

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