

# Water Sorption Characteristics of Epoxy Resin–UHMPE Fibers Composites

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**ABSTRACT:** Specimens of epoxy resin reinforced with ultrahigh-modulus polyethylene (UHMPE) fibers were immersed in water, and their swelling characteristics were recorded at various temperatures. In addition to an estimation of the response of those composite, the above study aimed at the exploration of the role of the fiber–matrix interface on the water sorption. Therefore, specimens containing original, calendered, and corona-treated fibers were tested. UHMPE fibers were found to limit the extent of sorption due to the nonhydrophilic character of polyethylene. However, specimens with poor interfacial properties, such as those with the original, untreated fibers, showed enhanced sorption since their surface area is drastically increased. As expected, the raise of temperature has a positive contribution to water sorption, and, furthermore, it seemed to affect the interface between epoxy and calendered fibers. On the other hand, the increase of filler volume fraction leads to a decrease in the amount of water uptake. The water transport in the neat epoxy resin specimens is rather diffusion-controlled, and this behavior was also recorded for the composite specimens reinforced with original UHMPE, which presented the maximum absorption. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 747–755, 1998

**Key words:** ultrahigh-modulus polyethylene; fiber; composite; water sorption; interface

## INTRODUCTION

High-performance fiber composites have been gaining wide use in many applications due to their excellent performance characteristics. However, it is well established that absorbed moisture can have undesirable effects on the properties of such materials. In order to fully utilize the potential of composite materials, their behavior during and after exposure to high-humidity environments at various temperatures must be investigated.

During its service, a composite material containing fibrous reinforcement will absorb mois-

ture from its surroundings. Moisture substantially affects the properties of polymer–matrix composites.<sup>1</sup> Two possible mechanisms, as follows, have been suggested for the explanation of this effect occurring in most composite systems: matrix plasticization or degradation of the fiber–matrix interface.<sup>2,3</sup> Water absorbed by epoxy matrix composites plays the role of plasticizer, as evidenced by the reduction in the matrix glass transition temperature,  $T_g$ .<sup>4,5</sup> This effect is usually reversible when water is removed, but exposure to water at elevated temperatures can produce irreversible effects, which can be attributed to matrix chemical degradation and the attack on the fiber–resin interface, as well as expansion and microcracking of internal voids.

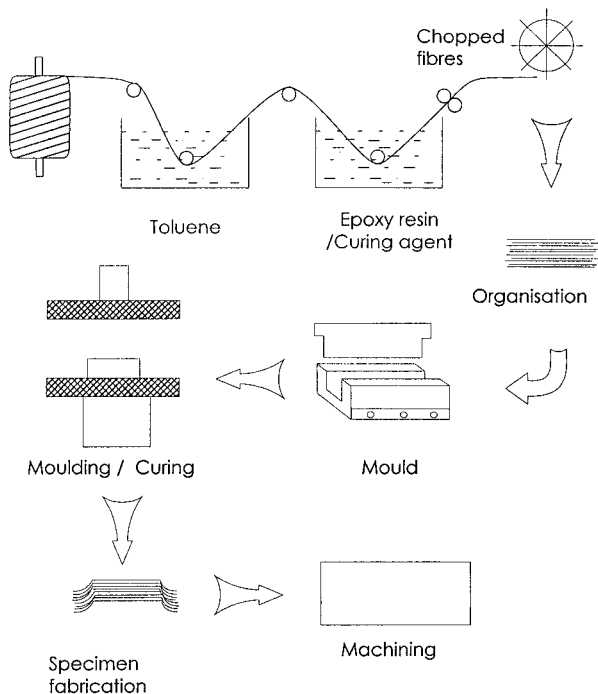
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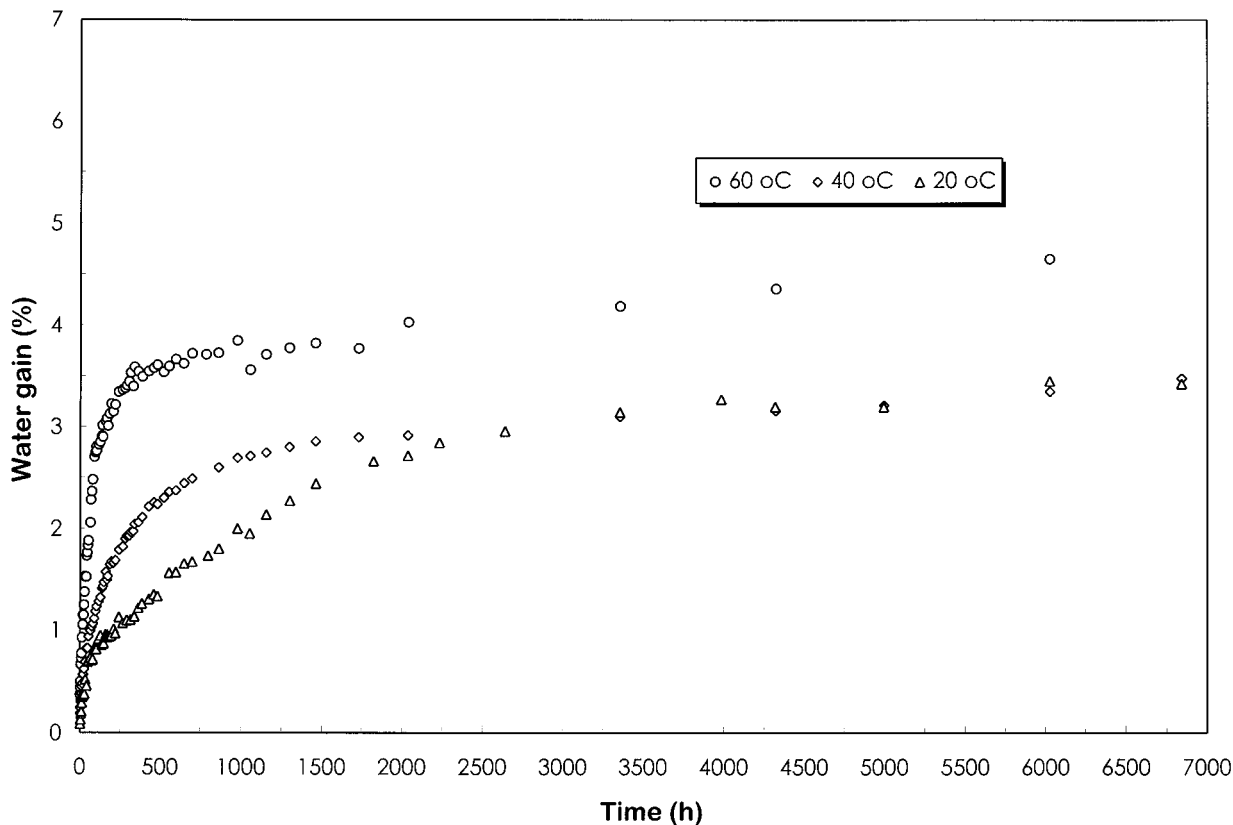
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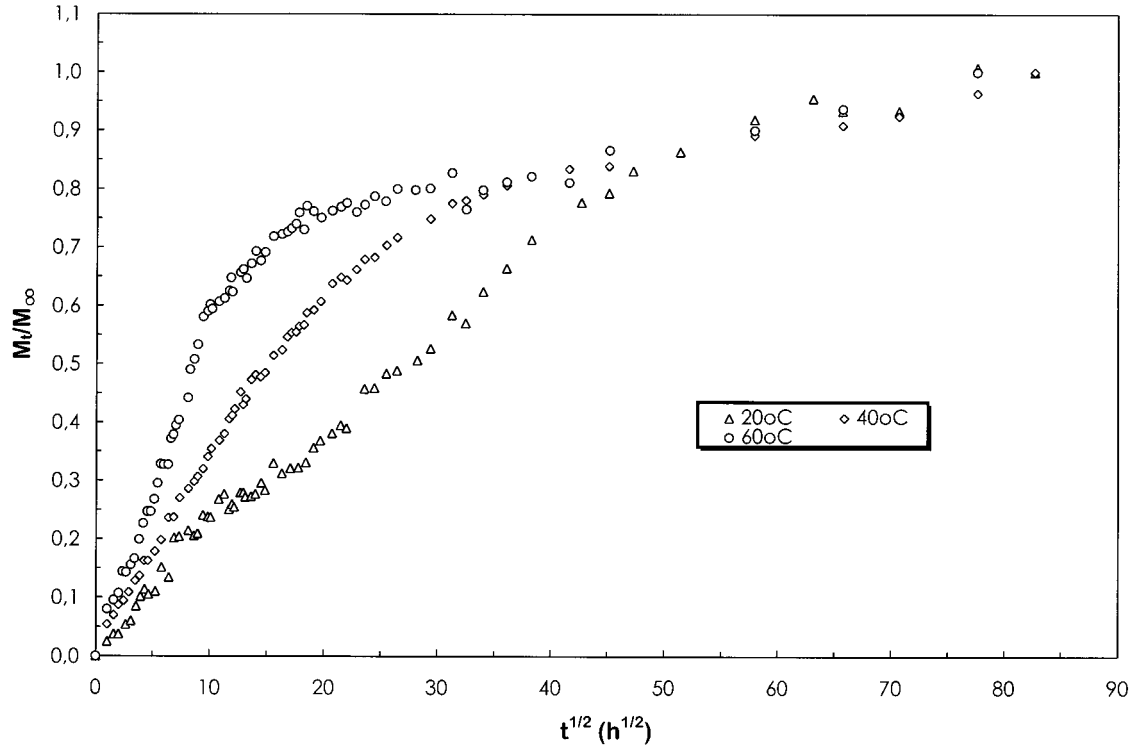
**Figure 1** Complete line for the preparation of epoxy specimens reinforced with UHMPE fibers.

The way in which composite materials absorb water depends upon many factors, such as temperature, fiber volume fraction, orientation of reinforcement, fiber nature (that is, permeable or impermeable), area of exposed surfaces, diffusivity, and surface protection. Moisture penetration into composite materials is conducted by 1 major mechanism, namely, diffusion. This mechanism involves direct diffusion of water into the matrix and, to a much lesser extent, into the fibers. The other common mechanisms are capillarity and transport by microcracks. The capillarity mechanism involves flow of water molecules along the fiber–matrix interface, followed by diffusion from the interface into the bulk resin. Transport of moisture by microcracks involves both flow and storage of water in microcracks or other forms of microdamage.<sup>6</sup>

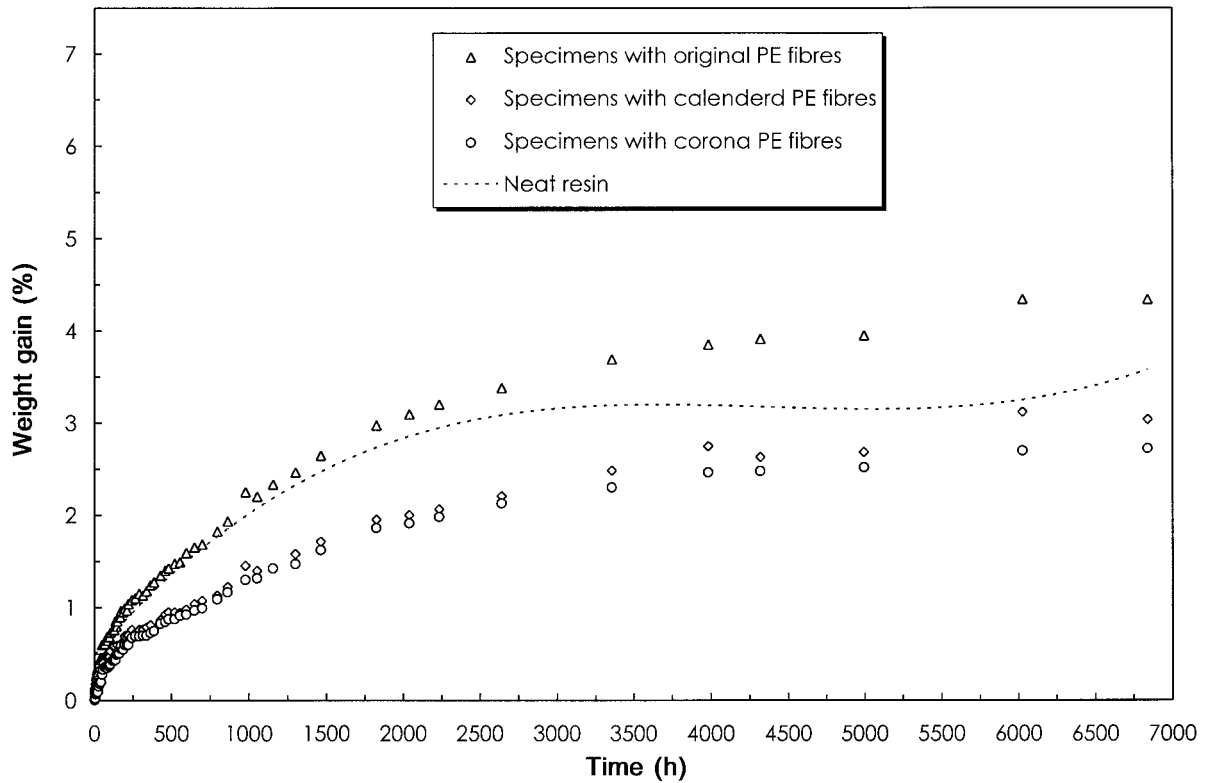
Although many investigators have studied epoxy systems reinforced with various fillers, such as jute,<sup>7</sup> glass fibers,<sup>8</sup> carbon<sup>9</sup> and aramid,<sup>5,10–13</sup> little attention has been paid on the adhesive bonding between the reinforcing fiber and the epoxy matrix. This parameter might be very im-



**Figure 2** Weight gain in specimens of neat epoxy resin at various temperatures.



**Figure 3** Percentage of water uptake as a function of the square root of time for epoxy specimens.



**Figure 4** Water sorption in reinforced specimens, at 20°C ( $V_f = 0.48$ ).

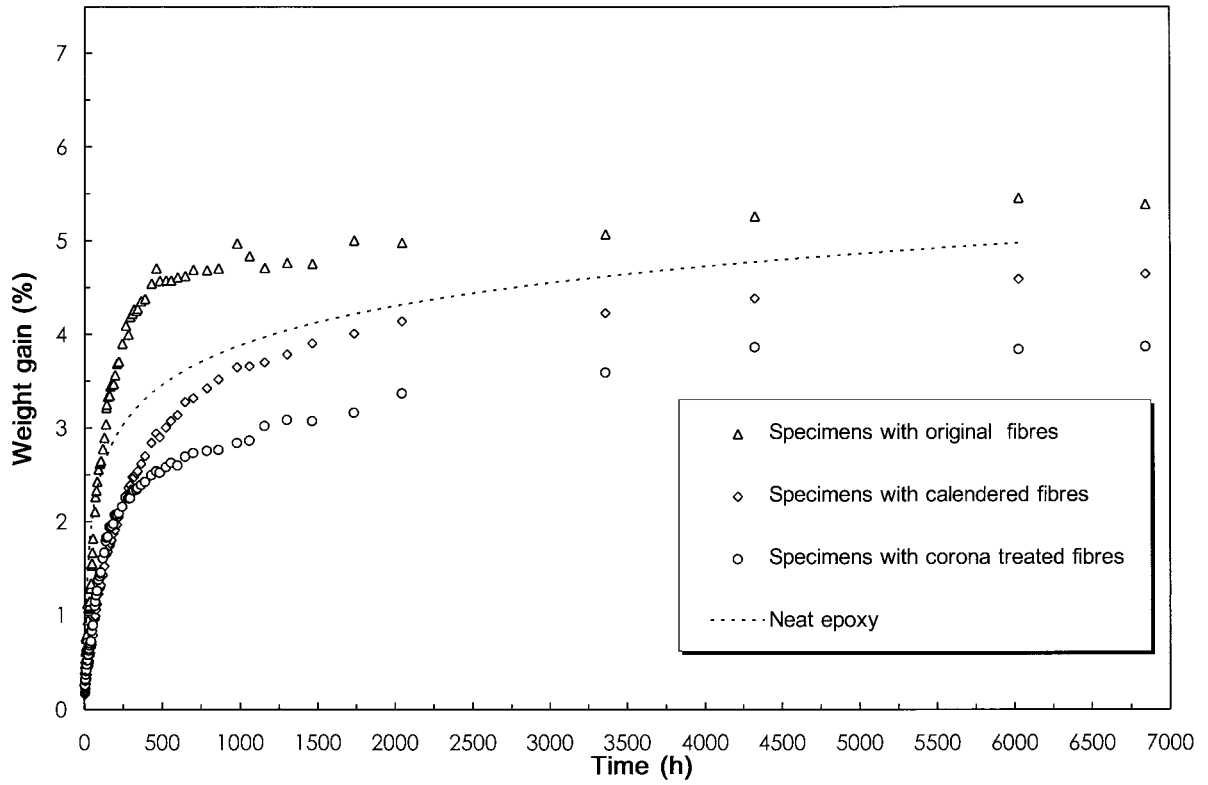


Figure 5 Water sorption in reinforced specimens, at 40°C ( $V_f = 0.48$ ).

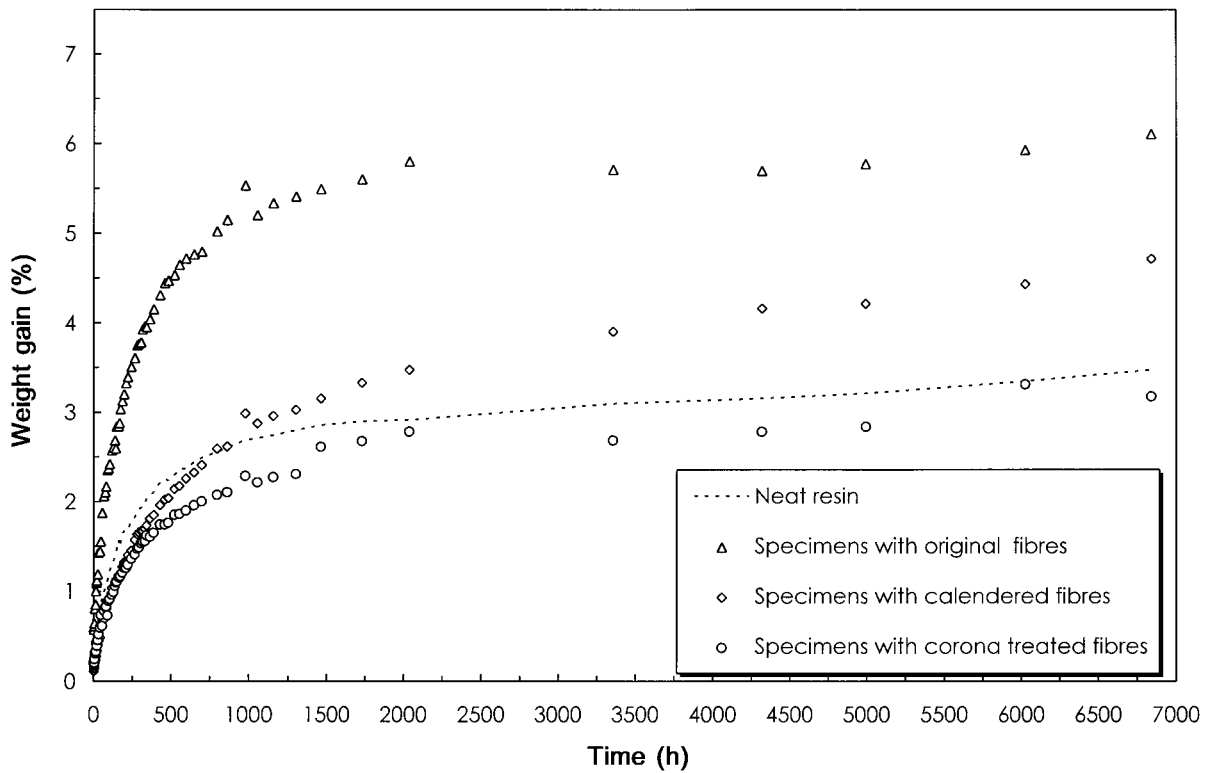
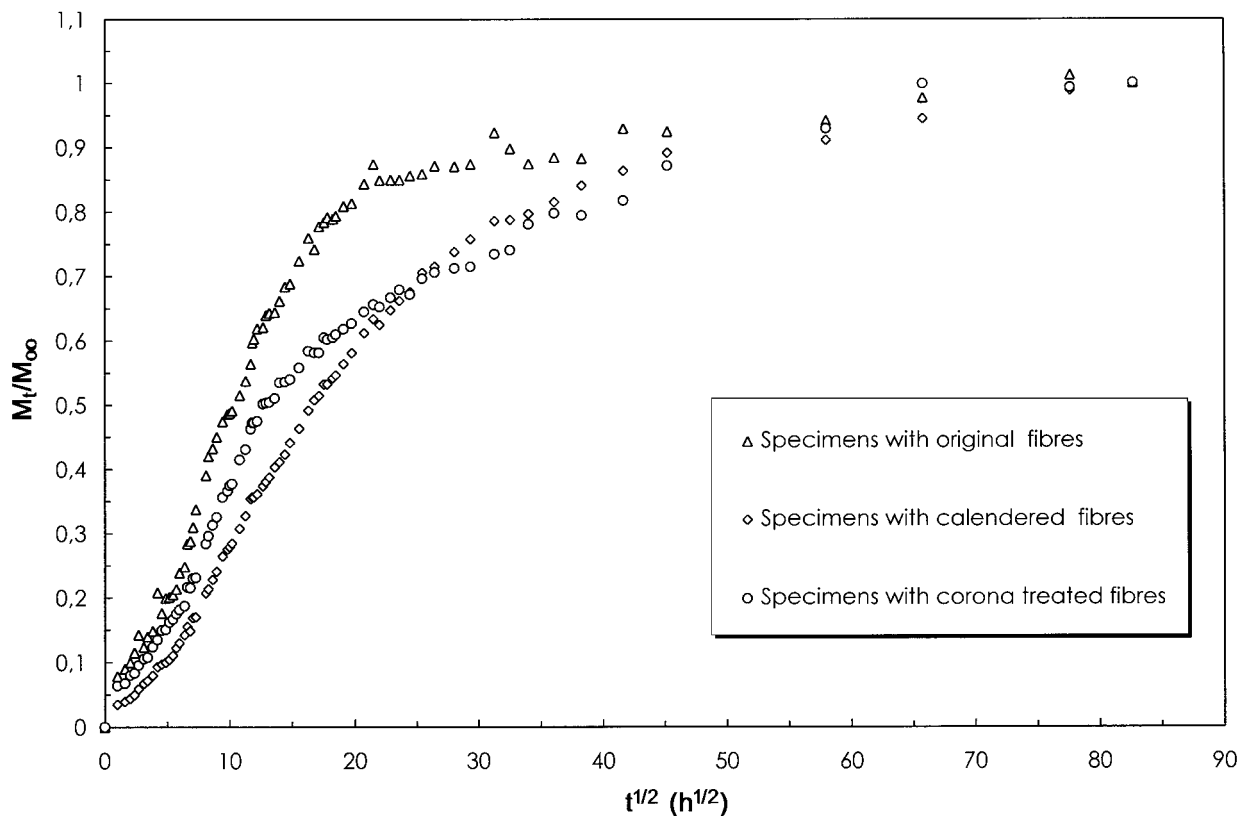


Figure 6 Water sorption in reinforced specimens, at 60°C ( $V_f = 0.48$ ).



**Figure 7** Water sorption in specimens reinforced with various types of fibers, at 60°C ( $V_f = 0.48$ ).

portant as it controls the interface profile in terms of voids and pores, which greatly affect absorption according to the above mechanisms.

In the present work, the water absorption of composite specimens made of epoxy matrix reinforced with ultrahigh-modulus polyethylene (UHMPE) fibers was studied. Unidirectional composites containing untreated and surface treated fibers with varying fiber volume fraction were examined. In addition, the effect of temperature on the absorption phenomena was investigated. The aim of this work was to record and discuss the response of these composite systems and compare their absorption characteristics with other already studied systems, such as carbon-epoxy and aramid-epoxy. Emphasis was given in the interpretation of results, taking into account the fiber-matrix interface, which significantly differs in the case of treated and untreated fibers.

## EXPERIMENTAL

### Materials

UHMPE multifilament yarns with the trade name Tekmilon® NA 310 were supplied by Mitsui

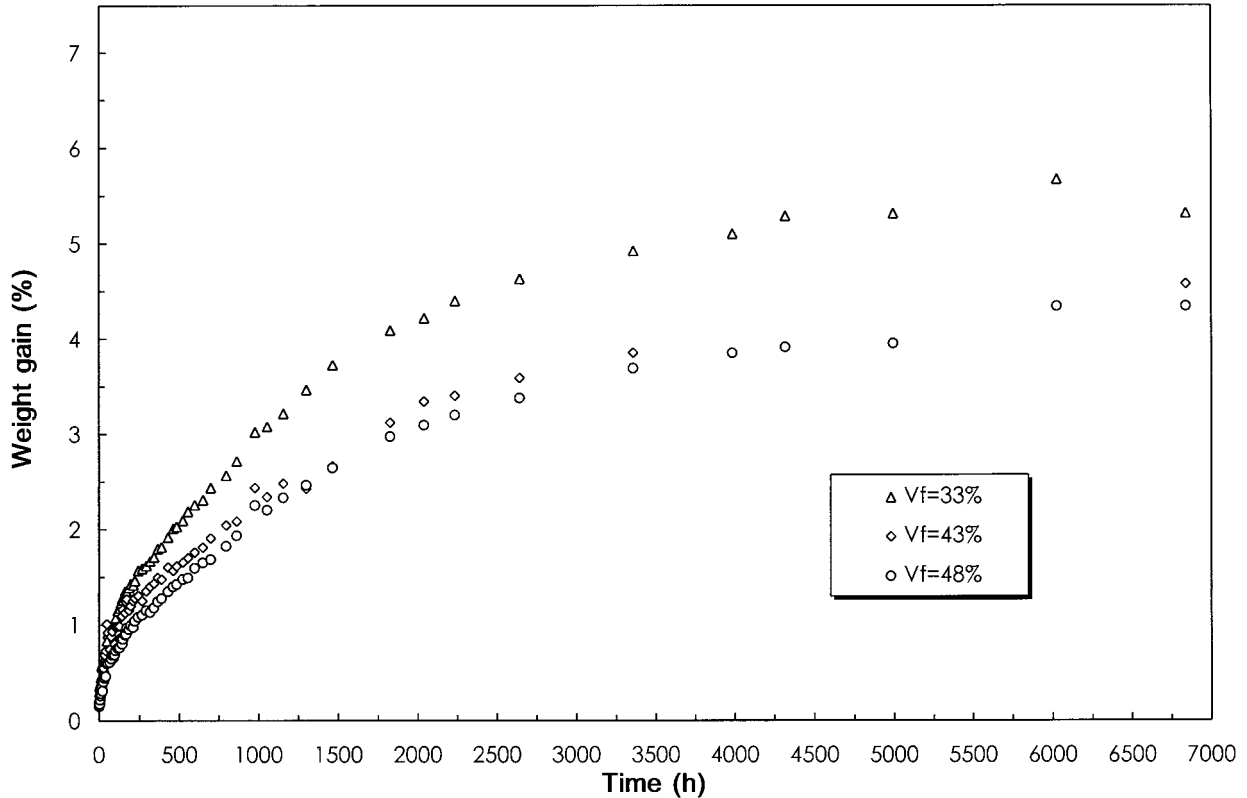
Petrochemicals Industries LTD, Tokyo, Japan. Corona-treated, Tekmilon® NC 310 and fibers calendered at 130°C were also used for comparison. Calendered fibers were prepared by the use of a two-roll mill, as described elsewhere.<sup>14</sup> The preparation process of epoxy systems reinforced with UHMPE fibers is illustrated in Figure 1.

The epoxy resin used for the fabrication of the composite specimens was a two-component system based on diglycidyl ether of bisphenol A (Epikote 828 LV) and an oligomeric amide as hardener (Epilink 175), both obtained from Shell Chemicals Hellas Ltd. (Athens, Greece).

The specimens were rectangular bars with dimensions 100 × 9.5 × 2.4 mm and were prepared by the leaky mold technique according to the procedure described in Tarantili and Andreopoulos.<sup>15</sup>

### Water Sorption Tests

The water absorption was evaluated in terms of the weight increase of composite specimens immersed in water, at various temperatures. The specimens were dried in vacuum at room temperature for 2 days and then weighed and placed in conical flasks containing 250 mL of deionized wa-



**Figure 8** Water uptake in specimens reinforced with various  $V_f$  of original UHMPE fibers, at 20°C.

ter. Specimens reinforced with as-received, calendered, and corona-treated UHMPE fibers were studied. The absorption for each type of specimen was studied at 3 different filler volume fractions and at 3 different temperatures (20, 40, and 60°C). Specimens of neat epoxy resin were also tested for comparison reasons.

## RESULTS AND DISCUSSION

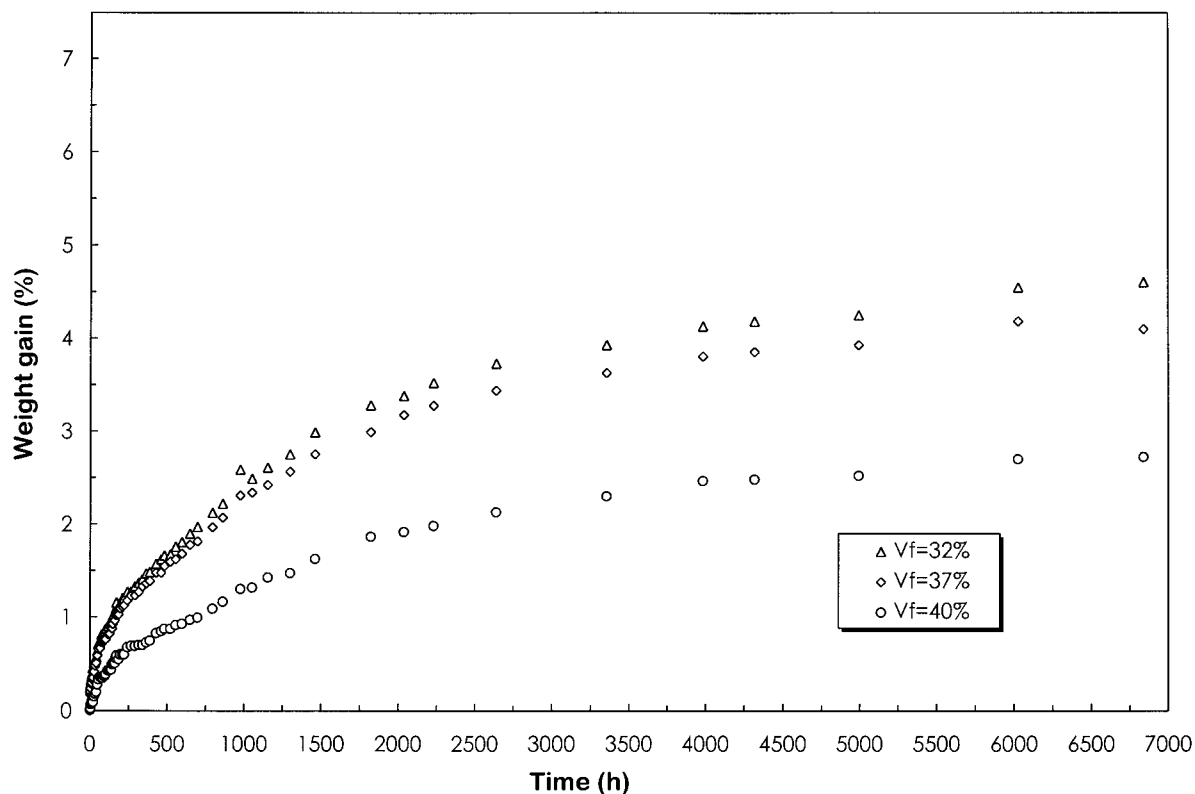
The weight gain of neat epoxy samples immersed at various temperatures is shown in Figure 2. It is clear that water sorption proceeds very quickly in a first stage of a few days. Then the rate of sorption decreases, and equilibrium seems to be achieved. The increase of temperature makes sorption of water by the epoxy resin more enhanced in terms of extent and rate. This can be attributed to higher microcavitation expected to occur at elevated temperature since water solubility is a decreasing function of temperature. For the same reason, equilibrium swelling is achieved

within the first 500 h at 60°C, whereas it takes 1000 h at 40°C and more than 2000 h at 20°C.

The percentage of water uptake at equilibrium exceeds 4.5% for swelling at 60°C but it remains lower than 3.5 at a temperature below 40°C. Very interestingly, the ultimate amount of water sorbed by the epoxy samples at 20 and 40°C seems to be the same, which suggests that changes in temperature within range of glassy state for the epoxy have little effect on its swelling capacity. The sorption data for the epoxy specimens are presented in Figure 3 in terms of  $M_t/M_\infty$  versus the square root of time. These expressions were selected in order to examine the applicability of the Fick's law. That is,

$$M_t/M_\infty = 4/\pi [Dt/l^2]^{1/2}$$

where  $M_t$  and  $M_\infty$  are the amount of water sorbed at time  $t$  and equilibrium, respectively,  $D$  is the diffusion coefficient, and  $l$  is the specimen thickness. The above equation is useful for the determination of the diffusion coefficient of materials,

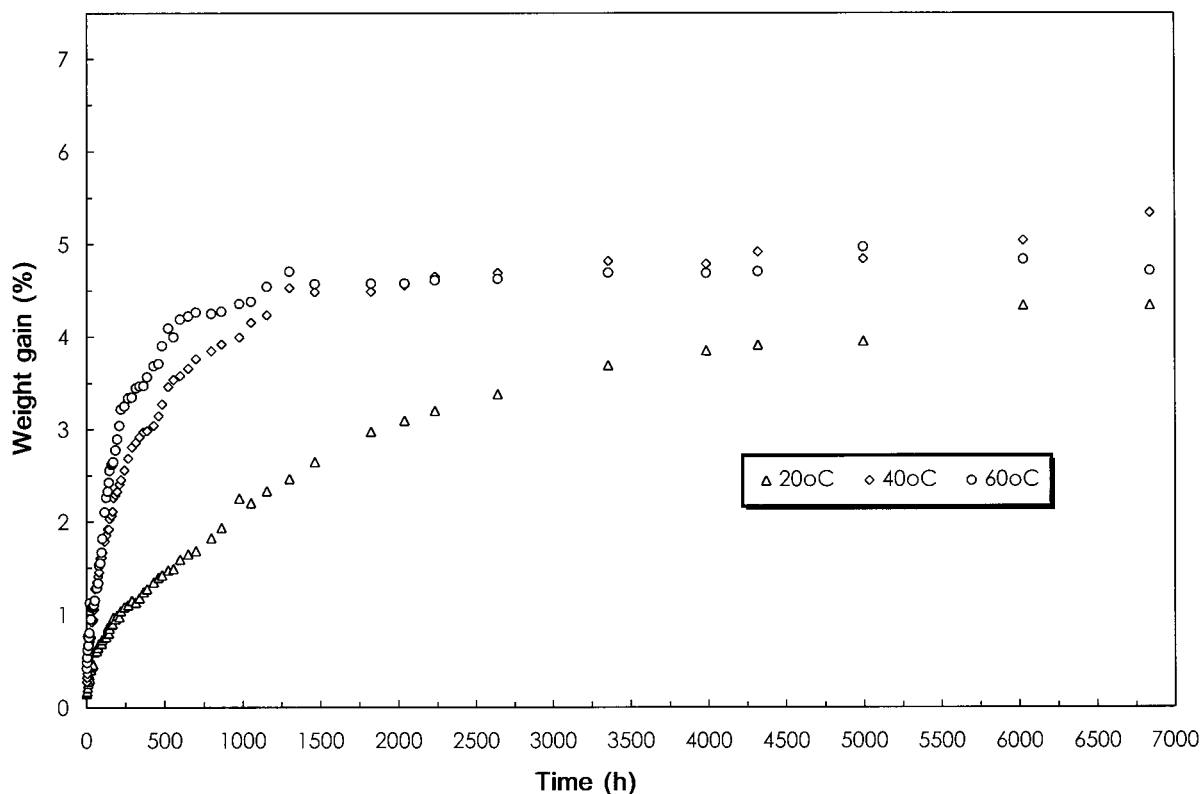


**Figure 9** Water uptake in specimens reinforced with various  $V_f$  of corona-treated UHMPE fibers, at 20°C.

such as membranes, and seems to describe the water uptake of neat epoxy resin at least for the initial stages of sorption. Linear relationship between  $M_t/M_\infty$  and  $t^{1/2}$  means that water transport is diffusion-controlled and has also been reported by many other investigators for neat epoxies or those reinforced with aramid and carbon fibers.<sup>6,12,13,16-19</sup> The curves of Figure 3 become concave for  $M_t/M_\infty$  values ranging from 0.6 to 1, which is again typical for Fickian sorption<sup>6</sup> and probably associated with alterations in the value of the diffusion coefficient beyond this limit.

The water sorption of epoxy specimens reinforced with various types of UHMPE fibers (namely original, corona-treated, and calendered fibers), at a filler volume fraction ( $V_f$ ) of 0.48 can be seen in Figure 4. The swelling process, which took place at 20°C, is again parabolic with time but shows a lower rate compared to the neat resin. This would be reasonable since the presence of reinforcing fibers, at that high  $V_f$ , drastically reduces the mass of the resin and therefore restricts the water uptake. In fact, the epoxy is the only component that absorbs water since polyethylene is nonpolar and cannot retain even

traces of water. Very interestingly, the composite samples containing untreated UHMPE fibers display higher equilibrium swelling, not only compared to those with calendered and corona-treated fibers but also to the neat epoxy resin. This can be attributed to the fact that untreated polyethylene fibers present very poor interfacial characteristics with the epoxy matrix, and, therefore, the interface acts as additional free surface of the specimen and facilitates sorption. On the other hand, the surface-treated UHMPE fibers, which present increased adhesive bonding and do not allow pores and voids on the interface, gave lower equilibrium values. In this respect, specimens reinforced with corona-treated fibers showed minimal sorption, which is in agreement with data obtained from mechanical testing.<sup>16</sup> Figures 5 and 6 illustrate the water sorption of the same as above specimens at temperature 40 and 60°C, respectively. It is clear again that the raise of temperature leads to enhanced sorption in terms of water uptake at equilibrium. Also, composites containing corona-treated fibers display the lowest water sorption, followed by the specimens reinforced with calendered and those



**Figure 10** Water uptake in specimens reinforced with various types of UHMPE fibers ( $V_f = 0.48$ ), at various temperatures.

with original fibers. Interestingly, the specimens reinforced with calendered fibers absorb less than the neat resin at 20°C; whereas at 40°C, they present the same behavior as the neat epoxy resin and further, and at 60°C, they absorb more water. These changes are probably due to the fact that the fiber–matrix interface in those composites is affected by the rise of temperature, and, more specifically, the adhesive bonding is deteriorated. This is consistent to the related result obtained from the investigation of mechanical properties of these composites at room and elevated temperatures.<sup>20</sup>

The dependence of water sorption on the square root of time, at 60°C, for composite specimens reinforced with various types of fibers is plotted in Figure 7. In this case, it is evident that no linear relationship exists, and a rather sigmoid behavior is established. The curves present a single inflection point at about 50% equilibrium sorption, which is reported by J. Crank<sup>21</sup> as one of the typical sorption anomalies.

The effect of the filler volume fraction ( $V_f$ ) on the sorption of water at 20°C, in composites containing original and corona-treated UHMPE fi-

bers can be concluded from the curves of Figures 8 and 9, respectively. In all cases, it is evident that the increase of the fiber content is associated with lower water uptake, and this is due to the completely nonhydrophilic character of polyethylene. It is worthy mentioning that the increase of  $V_f$  from 0.43 to 0.48 does not substantially influence the water uptake in specimens with original fibers; whereas for the corona-treated fibers, an increase in  $V_f$  from 0.37 to 0.40 is accompanied by a decrease in swelling of about 35%. This is again evidence of the better interfacial characteristics between the corona-treated fibers and the epoxy matrix.

Finally, the effect of temperature on the water sorption for specimens containing original UHMPE fibers, at  $V_f = 0.48$ , is presented in Figure 10, which clearly shows the accelerating influence of temperature in reaching equilibrium. The raise of temperature does not strongly affect the water sorption, which suggests that the initially poor interfacial characteristics between the epoxy and original UHMPE, unlike those between epoxy and calendered fibers, are not further deteriorated upon heating.



## CONCLUSIONS

From the above discussion, the following conclusions can be drawn. In general, UHMPE fibers restrict the water sorption in the reinforced epoxy specimens obviously because of the nonhydrophilic character of polyethylene. In the case of poor interfacial characteristics (for example, when the original, untreated fiber is used), the surface area of absorption is increased by the pores and voids of the interface, and, therefore, the water uptake is enhanced. Also, the filler volume fraction was found to have a negative contribution to the extent of water sorption. The raise of temperature up to 60°C is accompanied by an increase of the rate and extent of sorption, whereas some effect on the fiber-matrix interface for the calendered fibers could be considered.

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