

Interrelation between Moisture Absorption, Mechanical Behavior, and Extent of the Boundary Interphase in Particulate Composites

P. S. THEOCARIS, G. C. PAPANICOLAOU, and E. A. KONTOU,
*Department of Theoretical and Applied Mechanics, The National
Technical University of Athens, Zographou, Athens 624, Greece*

Synopsis

The influence of moisture absorption on the extent of the boundary interphase in particulate composites is thoroughly studied. It was found that, during the process of moisture absorption there is a variation of the extent of the boundary interphase, closely related to the degradation of the mechanical behavior of the composite, as well as to the percentage amount of moisture absorbed. An explanation of the observed relationship was advanced, based on a theoretical mechanism of absorption. This study complements a previous one, where the observed degradation of the thermomechanical properties of particulate composites due to moisture absorption was shown to be intimately interrelated with the state and extent of the interphase between fillers and matrix.

INTRODUCTION

One of the usual tests needed for the full characterization of composites is the moisture absorption test. It is well known that moisture absorption is one of the main parameters affecting the thermomechanical behavior of viscoelastic composites.¹ More precisely, the effect of absorbed moisture is in lowering the glass-transition temperature,¹⁻⁶ in addition to the change of the residual stresses, due to matrix swelling.⁷

Although a large number of papers studying the effect of moisture absorption on the thermomechanical behavior of composites may be found in the literature, no work has been done, up to now, on the effect of moisture absorption on the extent of the boundary interphase.

By the term *boundary interphase* is meant the volume of matrix material surrounding each one of the inclusions, which is developed because of the restriction of the segmental mobility of the macromolecules of the polymeric matrix, due to their adsorption into the filler surface. Moreover, this area contains structural microdefects, such as impurities, microcracks, voids, etc., so that one may consider that it is a third infinitesimal phase, developed during the manufacturing of the composite material. This layer, because of its structure, has a different thermoviscoelastic behavior than the other two main phases, and strongly influences the overall behavior of the substance. In addition, the existence of the interphase affects the overall behavior of the composite, because it directly affects the adhesion efficiency between filler and matrix.

In a series of previous papers,⁸⁻¹² the authors have studied extensively the effect of the boundary interphase on the thermomechanical properties of epoxy composites, reinforced either with metallic powders or with glass fibers. In these

investigations some theoretical models have been developed, and theoretical results were compared successfully with experimental findings.

In the present paper we concentrate on studying the variation of the interphase in particulate composites, due to moisture absorption. However, no modeling was developed at this stage of investigation. Moreover, we have undertaken a comparison between the change of the mechanical properties of the composites and the simultaneous change of the interphase-volume fraction during the time of immersion. In order to study the effect of the filler volume fraction, as one of the parameters affecting the overall behavior of composites, specimens with five distinct filler-volume fractions (0%, 5%, 10%, 16%, 20%) were used.

MATERIALS AND EXPERIMENTAL PROCEDURE

The materials were derived from a basic diglycidyl ether of bisphenol A epoxy matrix. As curing agent an 8 phr by weight triethylene-tetramine was added. The epoxy matrix was filled with iron particles of an average diameter of 150 μm . The composites were manufactured in the way described in Ref. 13. Dynamic and thermomechanical properties of the same materials have already been investigated in previous papers.¹⁴⁻¹⁹

In order to measure the percentage weight change, due to moisture absorption, specimens in the form of thin plates were used, in order to achieve a 1-dimensional mode of diffusion. The thickness of these orthogonal plates was in all our tests 0.003 ± 0.0001 m, whereas their width was $w = 0.012$ m and their length $l = 0.050$ m. Before placing the test specimens into the water bath, they were dried in an oven at 50°C until their weight loss was stabilized. The dried specimens were then placed in a high vacuum for 24 h to create full dried specimens, and their weights were measured using an analytical balance.

The specimens afterward were again immersed in a distilled-water bath at a constant temperature of $20 \pm 0.5^\circ\text{C}$. The specimens, thus conditioned in the water, were removed periodically, wiped, air dried for 5 min, and then weighed.

On the other hand, the tensile properties of the materials were determined by using dogbone tension-specimens with standard dimensions at their measuring zone. The elastic moduli and their ultimate strength were measured in an Instron tester with a crosshead speed of 0.5 mm/min.

Finally, the glass transition temperature of the composites was measured in a thermal analyzer, combined with a DSC analyzer. Large-diameter aluminum pans, hermetically sealed, were used in all runs. Scans were made at 5°C/min heating rate.

The effect of moisture on the thermomechanical behavior of iron-epoxy composites is reported in Ref. 2.

RESULTS AND DISCUSSION

The physical behavior of a two-phase composite system depends on the combination of several parameters, part of which are filler-dependent, whereas the rest of them are matrix-dependent. Among the first group of parameters, one may include the geometry of the inclusions, their size and the size distribution, their volume fraction, their relative positions, etc., while in the second group

one may include the physicochemical state of the matrix, the degree of polymerization, the crystallinity, the degree of crosslinking, and others.

Except for the above-mentioned parameters, affecting the overall behavior of a composite system, there is also a parameter depending on both filler and matrix characteristics. This parameter is the adhesion efficiency between the two phases, or, in other words, the degree of contact and cohesion, developed on the filler-matrix interface.

The adhesion efficiency between filler and matrix greatly depends, among other things, on the roughness of the filler surfaces. Indeed, the degree of roughness of the two contacting surfaces creates stress concentrations near undulations of surfaces, eventual microcorners, and other anomalies, whose main result is the perturbation of continuity of stresses and displacements at various points of the interface.

Moreover, there is a limitation of the mobility of the matrix chains during polymerization in areas surrounding each one of the inclusions because of their adsorption on the filler surface. This leads to the formation of an interface layer, consisting of a denser material than that of the bulk matrix. The density, as well as the thermomechanical properties, of the interface-layer material is also dependent upon the fineness of the filler. The higher the particle fineness, the greater its influence on the kinetics of polymerization and on the formation of the interface layer.

We have described up to now the formation of the interface layer, which is what we call *boundary interphase*, or simply interphase. Its importance may be seen when we compare the theoretical models, describing the thermomechanical behavior of composites, in the case when the interphase is taken into consideration, to the models in which a perfect adhesion is assumed between filler and matrix. It becomes clear from this comparison that the former models describe better a real situation, whereas the latter refer to an ideal situation, never existing in real composites. Moreover, the comparison between the theoretical predictions, derived from the two models, and the experimental findings shows that there is a better agreement in the case of the model considering the interphase.^{8,10}

Another reason for accepting the existence of the interphase is that, since the immediate vicinity of each inclusion is characterized by the concentration of stresses, impurities, and voids, there is a possibility that microcracks have developed in this area, which may initiate a complete and premature fracture of the composite.²⁰

The purpose of the present paper is limited to investigating the dependence of the interphase zone on the moisture absorption. This dependence is derived from the fact that at the interphase the interaction of the polymer matrix with the surface of the filler particle restricts the mobility of the polymer chains while, at the same time, the average number of intermolecular bonds per unit volume is reduced. Moreover, in the case of moisture absorption, the action of moisture results in the partial disruption of the bonds between filler and matrix and the formation of additional cavities, which would be filled with water. It has been established²¹ that water enters at the interface at a rate of approximately 450 times more rapidly than in the bulk matrix itself, and consequently any absorbed moisture is concentrated preferentially in the interphase.

An evaluation of the interphase-volume fraction may be derived either by

thermal capacity measurements,^{18,22} or by model considerations.^{8,22} We have followed in our tests the former method.

It has been found, from differential scanning calorimetry (DSC) measurements, that polymers exhibit a sudden change in heat capacity Δc_p in their glass transition region, which is progressively reduced, as the filler-volume fraction is increased.¹⁸ This phenomenon is closely related to the existence of the interphase.

More precisely, as the filler-volume fraction is increased, the number of macromolecules, which are in direct contact with the filler surface, and thus characterized by a reduced mobility, is also increased. This means that the volume fraction of the interphase is increased. Consequently, it is possible to measure the increase of volume fraction of the interphase by measuring the value of Δc_p . This is the basic idea of the theory developed in Ref. 22.

The Lipatov theory²² expresses the interphase-volume fraction by the quantity

$$v_i = 3v_f \Delta r_i / r_f \quad (1)$$

where v_i is the interphase-volume fraction, Δr_i the thickness of the boundary interphase, v_f the filler-volume fraction, and r_f the average radius of the filler particles.

Moreover, according to the same theory, the thickness of the boundary interphase Δr_i , appearing in relation (1), is given by

$$\left(\frac{\Delta r_i + r_f}{r_f} \right)^3 - 1 = \lambda_i \frac{v_f}{1 - v_f} \quad (2)$$

in which λ_i is expressed by

$$\lambda_i = 1 - \Delta c_{p_{\text{fil}}} / \Delta c_{p_{\text{unf}}} \quad (3)$$

where $\Delta c_{p_{\text{fil}}}$ and $\Delta c_{p_{\text{unf}}}$ are the changes in the specific heat for the filled and the unfilled polymers.

From DSC tests, the temperature and humidity dependence of the specific heat c_p of iron-epoxy composites was extensively studied in Ref. 2. From these tests we present in Figure 1 a representative DSC curve for a typical filler concentration $v_f = 0.10$. From this figure the sudden change Δc_p of c_p , appearing at the zone of the glass-transition temperature with varying time of immersion into the water, can be evaluated. From the same figure it is also shown that Δc_p increases with increasing time of immersion. The variation of Δc_p with time of immersion of the specimens into distilled water for various filler-volume fractions is presented in Figure 2. In this figure, each data point is the mean statistic value derived from 10 tests. All the measurements were characterized by a high accuracy and repeatability, and the scattering of results was kept in general within experimental error, which was of the order of $\pm 1\%$ at maximum and of $\pm 0.6\%$ at average.

From this figure it may be observed that, in general, Δc_p is a linear increasing function of time. Moreover, as the filler-volume fraction is increased, a reduction of the sudden change in heat capacity is observed in the glass transition region. This phenomenon may be explained by the fact that, at higher filler-volume fractions, there appears an increase of the macromolecules absorbed along the

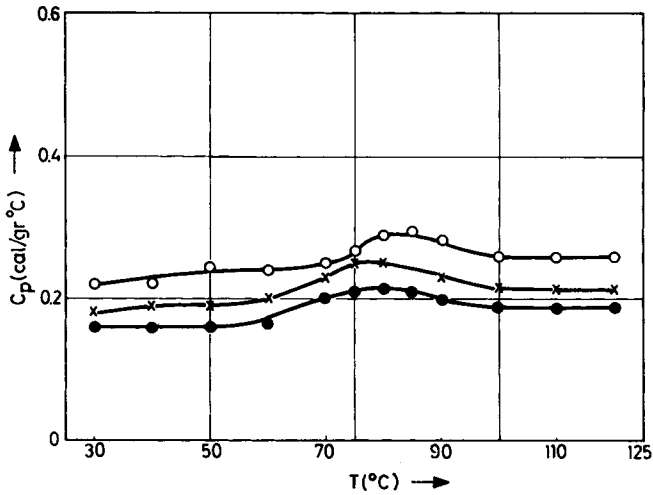


Fig. 1. Variation of c_p with temperature and time of immersion (days) [(O) 10; (X) 72; (●) 172] into distilled water for a filler-volume fraction $v_f = 0.10$.

filler surface, and they are, therefore, characterized by a reduced mobility.

In addition, the rate of increase of Δc_p is decreased as the filler-volume fraction is increased. This phenomenon may be explained by the fact that, as the filler-volume fraction is increased, the free volume decreases and an equilibrium is reached at a shorter time of immersion. This reduction of the time of equilibrium is better shown in Figure 3, where we followed the standard procedure, used by many authors (see, for example, Ref. 23), by plotting the percentage weight change of specimens with different filler-volume fractions as a function

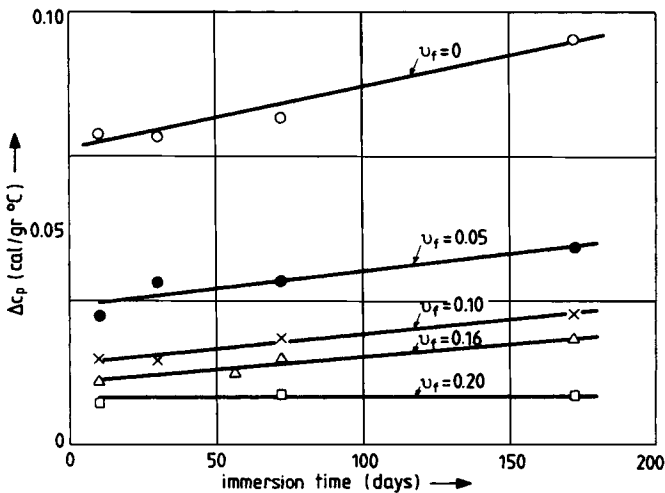


Fig. 2. Variation of Δc_p with time of immersion into distilled water for various filler-volume fractions.

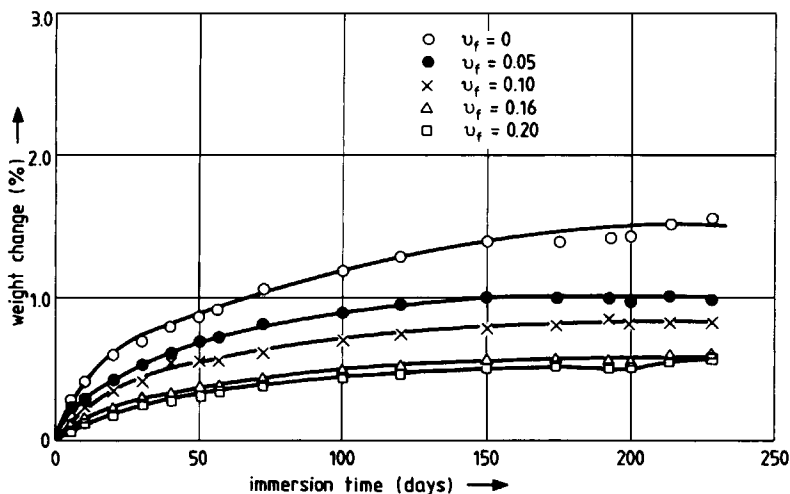


Fig. 3. Variation of the % weight change due to moisture absorption vs. time for different filler-volume fraction v_f : (O) 0; (●) 0.05; (×) 0.10; (Δ) 0.16; (□) 0.20.

of time of immersion. From this figure it may be observed that at 150 days of immersion, although all of the composite specimens have reached their equilibrium, the pure-matrix specimen has only absorbed the 93.3% of its final equilibrium value. All weight change vs. immersion-time curves in this figure present an asymptotic tendency, reaching an equilibrium value after 200 days of immersion.

These experimental values of moisture-content as function of time were used in Ref. 12 for the evaluation of the diffusivity D of the materials. Moreover, a satisfactory coincidence between experimental values and theoretical ones was found in this paper, which were derived from the assumption that the moisture diffusion was a "Fickian" one.

It is well known that moisture absorption causes degradation of the mechanical properties of polymeric composites. As will be described below, the degradation observed is closely related to the variation of the extent of the boundary interphase with the time of immersion.

Figures 4 and 5 show the variation of both the experimental values of the ratio of the moduli E_c of the composites normalized to the respective moduli E_m of the matrix and that of the thickness Δr_i of the boundary interphase with time of immersion, as it is derived from eq. (2). It is obvious from these figures that at the initial period of immersion, extending to about 60–70 days, a slight increase of the ratio E_c/E_m is observed followed by a subsequent decrease. Moreover, at the same time, Δr_i has an inverse behavior, that is, a decrease of Δr_i is observed, followed by a subsequent increase.

This kind of behavior may be explained, if one considers the following mechanism: As is shown in Figure 3, during the initial period, moisture is absorbed by the specimens with a decreasing moisture absorption rate and finally an equilibrium is reached. In addition, since the area surrounding each one of the inclusions is characterized by voids, microcracks, and other defects, which create a preferential diffusion path,²⁴ it is obvious that, at the initial time interval of immersion, absorbed moisture occupies the empty spaces available in the in-

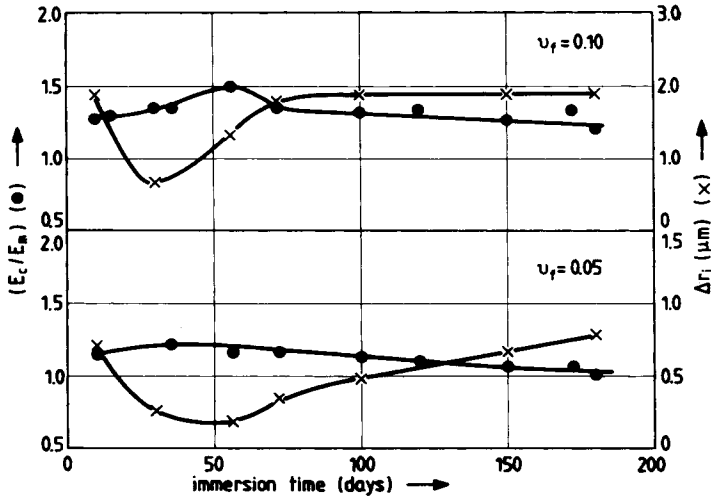


Fig. 4. Variation of both the experimental values of the relative moduli E_c/E_m of the composites and that of the thickness Δr_i of the boundary interphase with time of immersion for various filler-volume fractions.

terphase region, leading to a plasticization of the interphase material. Thus, at this period the interphase shrinks, because of the stresses exerted on it from the bulk matrix. However, the decreasing of the interphase thickness leads to a better adhesion between filler and matrix and consequently to an increase in the ratio E_c/E_m .

Next, as the time passes, absorbed moisture plasticizes the bulk matrix, and thus the interphase is expanded. The increase of the interphase thickness leads to a weaker bonding of the two main phases and consequently to a respective decrease of the value of the ratio E_c/E_m .

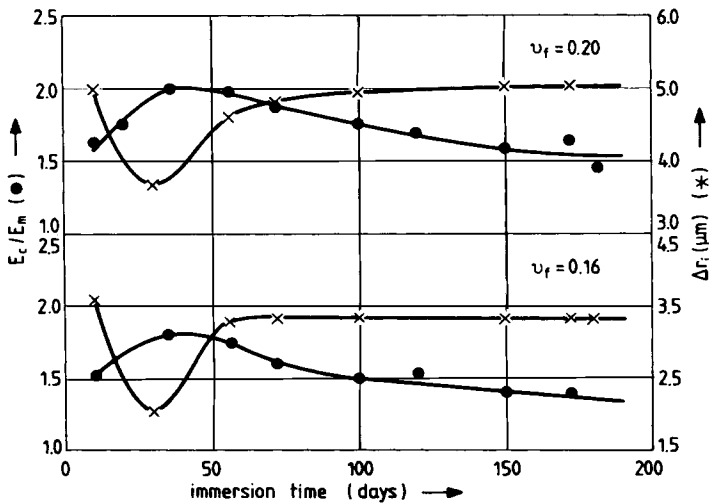


Fig. 5. Variation of the experimental values of the relative moduli E_c/E_m of the composites and the thickness Δr_i of the boundary interphase with time of immersion for various filler-volume fractions.

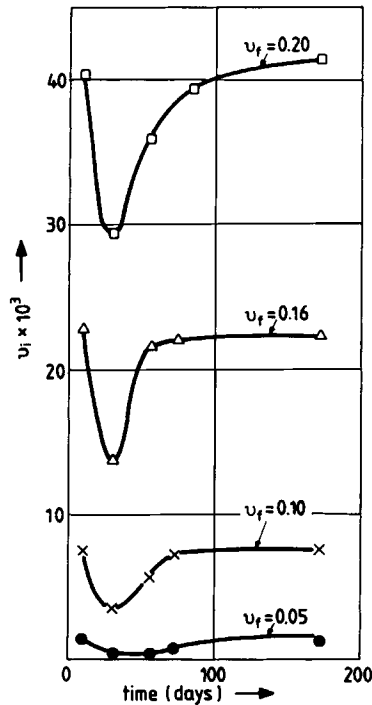


Fig. 6. Dependence of the interphase-volume fraction on the time of immersion for various filler-volume fractions.

Finally, as the equilibrium is reached, both E_c/E_m and Δr_i take again their initial values and remain constant for the rest of the time of immersion.

The variation of the thickness Δr_i of the boundary interphase is proportional to the variation of the interphase-volume fraction.

Figure 6 shows the dependence of the interphase-volume fraction v_i , on the time of immersion, as was calculated from eq. (1). From these diagrams we observe that, during the initial period of immersion there is a strong variation of v_i with time, this variation being analogous to the respective variation of Δr_i . Moreover, the higher the filler-volume fraction, the stronger the variation of v_i observed.

CONCLUSIONS

The effect of moisture absorption on the extent of the boundary interphase was investigated. It was shown that during the initial period of absorption there is an inverse change of the ratio E_c/E_m as compared with the respective change of the thickness Δr_i of the boundary interphase. The observed inverse change was explained by means of an absorption mechanism related to the real structure of particulate composites. It was also proved that the observed variation of the extent of the boundary interphase with moisture affects the mechanical degradation of composites.

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Received January 25, 1983

Accepted May 16, 1983