Influence of moisture absorption on the flexural properties of composites made of epoxy resin reinforced with low-content iron particles

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Abstract. In this work, the effect of moisture absorption on the mechanical properties of particulate composite materials is studied. Moisture absorption constitutes a main parameter affecting the thermomechanical behaviour of composites, since it causes plasticization of the polymer matrix with a concurrent swelling. In the present work, the influence of water absorption on the flexural properties of particle-reinforced composites was thoroughly investigated. It was found that during the process of moisture absorption there exists a variation of the flexural properties closely related to the degradation of the mechanical behaviour of the composite, as well as the percentage amount of moisture absorbed. Experiments were carried out with composite made of epoxy resin reinforced with low-content iron particles. The variation of ultimate stress, breaking strain, deflection, elastic modulus and Poisson ratio due to water absorption was examined.

Keywords. Particulates; composites; moisture absorption; flexural properties.

1. Introduction

Particulate composites are composites reinforced with particles, where all dimensions show the same order of magnitude. They are produced from a matrix, usually polymer, into which a suitable pulverized substance has been dispersed.

Evidently, such composites are not usually considered as ‘precious’ since they cannot reach the strength and stiffness of fibre-reinforced composites and therefore they are not used in high-tech applications, such as aircraft and space constructions. During the last years, significant progress has been achieved in applications with various types of fibres and other types of matrix such as metal matrix or ceramic matrix, which can serve for example at high temperatures. Thus, from this point of view this material cannot be characterized as a new since epoxy resin and iron particles are not ‘modern’ materials.

However, this type of composite can be used in various applications that do not need high stiffness and strength. On the other hand it can serve as a material for basic research, given that the results of an experimental research work carried out with particulate composites in hygrothermal conditions may be compared to experimental data that will be carried out with new materials in the future, whenever it is possible. Various thermomechanical properties of particle-reinforced composite materials are strongly impressed by moisture absorption [1]. Many composite materials of this type have been formed in order to increase the thermal conductivity and the thermal expansion coefficient and to

decrease the damage of the matrix. Thus, metallic powder as inclusion in a matrix of thermosetting epoxy results in the creation of a composite material that is more ‘powerful’ and resistant and easier transfer of heat and electricity than in the matrix alone. It is known that the addition of copper particles in epoxy resin augments the electrical conductivity of the resin very much. Also, the existence of particles increases the viscosity. Generally, particles with small dimensions augment this aforementioned property more, although this observation does not constitute a general rule. In addition, the thermal stability is enhanced by the presence of particles. Besides, the resistance to compression is increased on adding metal particles, due to their stiffness. The same result is obtained for the impact resistance. The surface hardness, the friction resistance and the quality of mechanical machining are improved by the incorporation of metal particles in epoxy resin. Meanwhile, the inclusions, which generally diminish the degree of contraction, effectively increase the adhesion ability of the epoxy resins. Yet, the particulates, the majority of which have higher density than that of the resin, increase the density of the composites. Thus, their existence considerably diminishes the overall cost of the composite. Finally, as to the resistance to moisture, the particulates generally reduce the diffusion speed of water in the composite. Also, the particulates participate in the corrosion of polymers when they contact metals. Ions that possibly exist in a resin with amine can transport currents and thus favour the corrosion. Epoxy resin hardened with amine has less conductivity than that of the resin reinforced with particulates.

This increment is due to the ability of particulates to release ions. On the other hand, it seems that the main shortcoming of particulates is that they decrease the tensile strength and the ultimate strain, at normal temperatures, as well as the bending strength. Yet, although they augment the tensile modulus and bending modulus this increase is not as significant as that obtained by fibres. Apart from these, absorbed moisture brings on plasticization of the polymer matrix with a simultaneous swelling and decrease of its glass transition temperature, which is referred to as T_g [2–5]. Thermal expansion and swelling of a composite due to temperature and moisture variations influence significantly the mechanical properties of its constituents, through residual stresses between the fibre and matrix [6]. Moreover, incorporation of fillers into polymeric matrices leads to changes in their glass transition temperature T_g [7], probably because of the immobilization by absorption of polymer segments close to the surface of the filler particles [8]. Some discrepancies were also detected in the determination of the effect of the filler content on T_g . Some authors have found a linear relationship between increasing filler content and increasing T_g [8], whereas others have found that T_g is not affected appreciably by the filler content [9–11].

In previous research works carried out in Strength of Materials Department of NTUA, it was found from dilatometric [12] and calorimetric measurements [13] that T_g values of metal-filled epoxy composites were strongly dependent on the filler volume fraction and, in some cases, a decrease with the amount of filler was pointed out. Also, a parameter that affects the position of transition temperature in thermal measurements is the heating rate. Considerable differences were observed in differential scanning calorimetry (DSC) measurements depending on the heating rate [13,14]. Furthermore, moisture diffusion characteristics in epoxy components are crucial factors for predicting the mechanical response and durability of epoxy components in a given environment [15]. The second Fick's law of diffusion may be successfully applied to evaluate sorption and desorption of moisture in epoxy composites [16–19].

On the other hand the mechanical properties of epoxy composites depend, amongst others, on the nature of filler and matrix, the strength of the bond between fillers and the surrounding matter of matrix or their mutual adhesion efficiency, the filler content, the size and size distribution of the fillers, the shape of the inclusions, the fabrication method and the conditions of use. Concerning the latter, it is well known that immersion of composite materials into aqueous environments results in a degradation of their thermomechanical properties. This phenomenon is related to the moisture-induced plasticization and/or micromechanical damaging such as interfacial damage [20] and matrix cracking [21,22].

The dual action of absorbed water as a plasticizer and a crazing agent as well deteriorates, in a different way, the physical and mechanical integrity of the epoxy matrix material. This is because plasticization process is indeed a

reversible procedure compared with microcavitation damage, which is a permanent one. Especially, for the latter it was found that water absorption influences the adhesion efficiency between filler and matrix as well as the extent of boundary interphase developed in the area surrounding each inclusion [23]. The concept of boundary interphase and its effect on the overall thermomechanical properties of epoxy composites has been described and studied in a series of previous papers [12,13,23,24]. This area has been developed because of the restriction of the segmental mobility of the macromolecules of the matrix due to their adsorption onto the filler surface and is featured by structural micro-defects such as impurities, microcracks, voids, etc. as well as by concentration of stresses. In the case of water absorption, the action of water results in the partial disruption of the bonds between filler and matrix and the formation of additional cavities, which could be filled with water. Weitsman and Guo [25] established a correlation between fluid-induced damage and anomalous fluid sorption in polymeric composites, whereas Hiel and Adamson [26] studied the thermal expansion and swelling of cured epoxy resin used in composite materials due to temperature and moisture variations that typically occur in a launch environment. In this significant work it was shown that constitutive equations for moisture absorption and moisture-induced dimensional changes can be obtained by means of an internal variable method on the basis of irreversible thermodynamics theory. Moreover, Bera *et al* [27] investigated the effects of thermal shocks and thermal spikes of hydrothermal behaviour of composites. Blikstad *et al* [28] studied the long-term moisture absorption in fibre-reinforced composites. Apicella *et al* [29] investigated the environmental degradation of the electrical and thermal properties of organic insulating materials, whereas Apicella and Nicolais [30] investigated the environmental ageing of epoxy resins. Verpeest and Springer [31] evaluated the moisture absorption characteristics of aramid epoxy composites. Cai and Neitsan [32] examined the non-Fickian moisture diffusion in polymeric composites. Woo and Piggott [33] studied the water absorption of resins and composites. Meanwhile, Weitsman [34] thoroughly studied the moisture transport in fibre-polymer composites. Besides, Xiang and Jones [35] investigated the thermal-spike-enhanced moisture absorption in carbon fibre composites. Moreover, Park and McManus [36] worked on thermally induced damage in composites, whereas Popineau *et al* [37] studied the free/bound water absorption in an epoxy adhesive.

In the recent years, a remarkable extent of research work has been carried out towards the determination of mechanical properties of advanced particle and fibre composite materials in moisture conditions. In particular, Ozdemir and Mengeloglu [38] investigated the adhesion strength in a category of particulate composite panels made from wood flour and recycled polyethylene, and proposed a method to reduce the water absorption and thickness swelling of the panels. Also, the variation of fundamental mechanical properties such

as tensile, flexural and impact strengths of a large class of polyester hybrid composites reinforced with randomly oriented natural fibres was thoroughly examined by Athijayamani *et al* [39]. In addition, the elastic modulus of laminate composites, whose panels were made by coconut fibre particles using castor oil polyurethane adhesive, was determined by a three-point bending test [40]. In this significant study, the specimens were soaked in water for a period of 2 and 24 h. Besides, the influence of moisture absorption on the flexural properties of vinyl ester matrix–glass particle synthetic foams was investigated by Tagliavia *et al* [41]. In this work the flexural properties are identified through three-point bending tests conducted on four types of synthetic foam compositions containing micro-balloons of 220 and 460 kg m⁻³ true particle density in 30 and 60 vol% of particles. A one-dimensional Fickian model is used to identify the diffusion parameters from short-term moisture absorption of neat vinyl ester resin and synthetic foams. On the other hand, Alok *et al* [42] obtained an amendment of tensile strength and flexural properties of epoxy resin composites in water, compared with non-reinforced samples. These workers used shell powder of several particle sizes and contents to reinforce the matrices, a fact that amplifies the interfacial bonding between filler and matrix and reduces the number of micro-voids, resulting therefore in a decrement of the water absorption. In this study, long-term water immersion method was used to determine the absorption behaviour of the samples. The conditioned composite samples were placed in a beaker with water at 23 ± 1°C. At the end of 24 h one of the samples was removed from the water at a time, all surface water wiped off with a dry cloth, weighed immediately and then replaced in the water; this procedure was repeated every 24 h for 7 days and the data were recorded. Concurrently, Bhaskar and Singh [43] investigated experimentally the influence of water absorption on the compressive strength of natural filler particulate composites (coconut shell particle). The effects of water absorption were observed after 24 h of soaking. In this work, the water absorption capacity was found to have its maximum value for 30 wt% of coconut shell particle. The maximum compressive strength investigated was 88.0 MPa. The optimum combination was 30 wt% reinforcement of 200–800 µm coconut particle in terms of water absorption and compressive strength. Hamim and Singh [44] discussed the effect of hygrothermal ageing on the mechanical properties of fluorinated and non-fluorinated clay–epoxy nanocomposites. Specifically, these researchers determined the extent of permanent degradation of fracture and flexural properties due to the hygrothermal ageing by drying the epoxy and their clay–epoxy nanocomposites after moisture absorption. This study was conducted to elucidate the effect of moisture absorption on the mechanical properties of clay-reinforced epoxy polymers. Fracture toughness, flexural strength and flexural modulus were determined for two different clay–epoxy nanocomposites following the ASTM standards. The effects of hygrothermal ageing and subsequent redrying on

the mechanical properties of these polymer nanocomposites were investigated. After removing the free water by drying, the irreversible effect or the permanent damage due to hygrothermal ageing on the clay–epoxy nanocomposite systems was determined. Irrespective of the clay reinforcement type, all the studied properties degraded due to hygrothermal ageing. Also, Hossain *et al* [45] investigated the effects of wood properties on the behaviour of wood-particle-reinforced polymer composites. It was found that water absorption of both pure polyester and wood-particle-reinforced composites increased with time. Nevertheless, the overall water absorption behaviours of the composites are dependent on the density of the wood used. Water absorption test of the developed composites was carried out according to ASTM D570 at ambient temperature. To do this, specimens were immersed in water bath for 4 weeks at ambient temperature. After a week, these samples were taken out from the water bath, water was wiped off by tissue paper on both sides of the surfaces and they were reweighed. Again, these test samples were reimmersed in the water bath. Furthermore, a detailed study for the effect of moisture absorption behaviour on the mechanical properties of basalt-fibre-reinforced polymer composites was performed by Pandian *et al* [46]. In this experimental work, the composites samples contained woven basalt, short basalt and alkali- and acid-treated basalt fibres. Next, water absorption tests were conducted by immersing specimens in water at room temperature for different time periods till they reached their saturation state. The tensile, flexural and impact properties of water-immersed specimens were determined and compared to those of dry samples as per the ASTM standard. Finally, Pan and Zhong [47] introduced a novel micromechanical model for predicting the overall mechanical degradation of natural-fibre-reinforced composites induced by moisture absorption. The natural fibre is hydrophilic in the humid environment with remarkable swelling deformation and mechanical degradation, which can be described by a damage variable. By means of a modified Mori–Tanaka method with a damage variable, the modulus loss of the composites was obtained. The theoretical predictions are in good agreement with experimental results, where the sisal fibres were formulated as randomly oriented straight inhomogeneities with a circular cylindrical shape. Further numerical examples for unidirectional-circular-cylindrical-fiber-reinforced composites show that a stiffer matrix can suppress the moisture absorption and the mechanical degradation of the composites, which suggests an effective way to reduce the overall mechanical degradation of the composite.

In this paper, the action of moisture absorption on the flexural properties of composites consisting of epoxy resin reinforced with low-content iron particles at ambient temperature was investigated as a continuation of this research field. The variation of flexural stress, flexural strain, maximum deflection, elastic modulus and Poisson ratio was examined, since it is known that the weak points of the particulate composites are mainly these aforementioned properties.

2. Theoretical considerations

The density ρ of a composite material can be theoretically evaluated by the rule of mixtures as follows:

$$\rho_c = \rho_f U_f + \rho_m U_m, \quad (1)$$

where the terms ρ_c , ρ_f , ρ_m denote the composite, filler and matrix density, respectively, and U_f , U_m denote filler and matrix volume fraction.

The per-cent moisture content $M(t)$ of the composite or per-cent weight gain may be defined as the difference in weights of the moist W_m and dry W_d materials, normalized to W_d , according to the following relationship:

$$M(t) = \frac{W_m - W_d}{W_d} \times 100\%. \quad (2)$$

A series of measurements of moisture content of sample materials was carried out at various time intervals.

In order to verify the validity of the respective Fickian diffusion theory [18], the experimental values of $M = f(t)$ were used to estimate the diffusivity D of the material for various rates of U_f in a direction perpendicular to the lateral faces of the samples, which was determined by the following equation [18]:

$$D = \pi \left(\frac{h}{4M_m} \right) \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2, \quad (3)$$

where the term h is the thickness of the sample, M_m is the maximum moisture content for each case and the quantities M_i , $i = 1, 2, 3$ are the moisture content at discrete times t_i sequentially.

The values of diffusivity D determined via Eq. (3) can be inserted in the following equation to obtain the time-dependent coefficient $G(t)$:

$$G(t) = 1 - \exp \left(-7.3 \left(\frac{Dt}{s^2} \right) \right), \quad (4)$$

where the term s is the thickness of specimen for samples exposed on both sides to the same environment, while it is equal to $2h$ for samples insulated on one of their faces.

The values of the time-dependent coefficient may now be substituted back into the simple relation expressing the instantaneous value of the moisture content of the composite material during both absorption and desorption according to diffusion theory developed [18]:

$$M = G(M_m - M_i) - M_i, \quad (5)$$

where the term M_i now denotes the initial moisture content of the sample and $M(t)$ is the percent moisture content of the composite.

3. Experimental

3.1 Materials, tests and experimental layout

The devices and instruments that have been used to carry out the experiments are located in Strength of Materials Lab of NTUA and are briefly described as follows.

As can be seen in figure 1, a bath device that is appropriate for maintaining a constant-temperature environment till 120°C , in which the specimens are soaked in distilled water and has been lent to the authors by the Water Analysis Lab of Chemical Engineering School of NTUA, has been mobilized in order to conduct the procedure of hydro-absorption.

A thermoscale of company type Kern RH 120-3 with an accuracy of ± 0.001 g, where the specimens were placed to measure the weight change of samples during hydro-absorption, can be seen in figure 2. The thermoscale was used in the drying process of the samples at 80°C . The instrument contains a special device to print the results of specimen weight reduction.

The thermomechanical properties of the constituent materials are presented in table 1.

The specimens used in this work have as matrix a system based on a diglycidil ether of bisphenol A (DGEBA) resin (Epikote 828) as prepolymer, with an epoxy equivalent of 185–192, a molecular weight between 370 and 384 and a viscosity of 15000 cP at 25°C .

As a curing agent, 8% triethylenetetramine hardener (TETA) per weight of the epoxy resin was employed. The epoxy matrix was filled with iron particles with average diameter of $150\ \mu\text{m}$. The thermomechanical behaviour of the same composite materials was previously investigated [12,13], while the effect of the water absorption at ambient temperature on their tensile properties was also examined in a series of previous publications [23,24].

Figure 1. Device used for moisture experiments.

Figure 2. Device used for the measurements of moisture absorption.

Table 1. Thermomechanical properties of the constituent materials.

Item	Epoxy resin	Iron
<i>Lame constants:</i>		
λ (GPa)	3.34	112
μ (GPa)	1.30	81
Young's modulus, E (GPa)	3.53	210
Bulk modulus, K (GPa)	4.21	167
Poisson's ratio, ν	0.36	0.29
Density, ρ (kg m ⁻³)	1.19E3	7.8E3
Tensile strength (MPa)	65	—
Coefficient of thermal expansion (°C ⁻¹)		
< 123	65E-6	15E-6
> 123	168E-6	—
Glass transition temperature, T_g (°C)	123	—

The materials were produced as follows. The prepolymer was treated up to 30°C to decrease viscosity; proper amounts of curing agent and 150 µm metal (iron) powder were subsequently added and the mixture, after being stirred thoroughly, was put in a vacuum cleaner for about 15 min for degassing. Later, it was cast into a rectangular plexiglas mould of suitable form and capacity with dimensions $(250 \times 10^{-3}) \times (150 \times 10^{-3}) \times (10 \times 10^{-3})$ m³ and coated

with silicon oil to prevent adhesion of the mixture. The latter was then sealed so that it was possible to rotate it in space in order to prevent the settling of iron powder and to obtain as uniform a final product as possible. Pot life of the matrix material at the ambient temperature of 20°C was slightly decreased by the presence of the particles; it only took 20–25 min for the mixture to gel, after which no more rotating was necessary. The moulding was removed 24 h later and the casting was subjected to thermal processing, consisting of a temperature rise at 5°C h⁻¹, maintained constant at 100°C and finally dropped to ambient at 1°C h⁻¹.

In this manner, complete polymerization of the matrix material was obtained and consequently the properties of the final product did not exhibit any storage dependence. The test pieces, which had prismatic shape, were machined from each casting with dimensions of $190 \times 13 \times 10$ mm³, according to ASTM D 790. The density was measured by weighting specimens of known volume and compared to theoretical values given by Eq. (1). For the percent weight change due to moisture absorption, according to ASTM D 570, before placing the test specimens into the waterbath 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 fully dried specimens and their weights were measured in an analytical balance. Next, the specimens were immersed in a distilled water bath at the constant temperature of 20°C; changes in temperature were controlled to less than $\pm 0.5^\circ\text{C}$. The specimens conditioned in water were then removed periodically, wiped, air dried for 5 min and then weighed. In order to measure the fracture stress, fracture strain, elastic modulus and Poisson's ratio of the particulate composite in comparison to the corresponding features of matrix material, four-point bending experiments were carried out with an Instron-type testing machine at room temperature. Four specimens of each material were tested at a crosshead rate of 2 mm min⁻¹.

In order to obtain the load–strain diagrams for each material, strain gauges (KYOWA type, gauge factor $k = 1.99$, gauge length (l) = 2 mm) were used.

In table 2, the type, size and shape of the samples are illustrated.

3.2 Data presentation

The strain was calculated with the aid of the following relationship:

$$\varepsilon = \frac{2\mu \cdot 10^{-6}}{k}, \quad (6)$$

Table 2. Specimen characteristics.

Type of specimens	Shape of specimens	Length (mm)	Width (mm)	Thickness (mm)
DGEBA epoxy resin:				
Iron-particle-filled epoxy resin	Prismatic	190	13	10

where μ is the digital converter reading and k the gauge factor.

The maximum normal stress in the outer fibres occurs between the two central loading points that define the load span. This stress can be calculated for any point on the load–deflection curve by

$$\sigma_{\max} = \frac{PL}{bd^2}, \quad (7)$$

where P is the load at a given point in this region, b the width of the beam and d its thickness.

The flexural strength is equal to the maximum stress in the outer fibres at the moment of fracture. It is calculated using Eq. (7) by setting the variable P equal to the load at the moment of fracture, i.e.,

$$\sigma_F = \frac{P_F L}{bd^2}, \quad (8)$$

where σ_F is the stress at failure and P_F is the fracture load.

The maximum strain at the outer fibres may be calculated as follows:

$$\varepsilon_{\max} = \frac{4.70 f_{\max}}{L^2} d \quad (9)$$

where $f_{\max}$ denotes the maximum deflection of the centre of the beam at the moment of fracture.

The tangent modulus of elasticity is the ratio within the elastic limit of stress to corresponding strain and can be calculated by drawing a tangent to the steepest initial straight line portion of the load deflection curve as follows:

$$E_B = \frac{0.21 L^3 m}{bd^3} \quad (10)$$

where E_B is the tangent modulus of elasticity in bending and m the slope of the tangent to the initial straight line portion of the load–deflection curve.

4. Results and discussion

It may be said that the influence of absorbed water molecules on the mechanical properties of polymers may either be harmful or beneficial. The enhancement of the mechanical properties can be attributed to the increased mobility of the polymer chains due to absorbed water molecules, which results in an orientation of polymer chains in the direction of applied stress. The arising question is that under what conditions water results in a degradation or in an enhancement of the mechanical properties. Figure 3 presents the variation of the composite density ρ_c with respect to the filler content, which is calculated according to the theoretical expression given by Eq. (1), along with the experimentally measured values. As these two sets of values of density are in good agreement, it

Figure 3. Density of the composite vs. filler content.

Figure 4. Moisture absorption vs. (a) time and (b) filler content.

is evident that no appreciable voids exist in the mass of the composite specimens.

The experimental data of moisture content for various values of the filler content U_f with respect to time, which were calculated using Eq. (2), are plotted in figure 4a. Each of these data points corresponds to the average value of four specimens. The values of M determined using Eq. (5) are also plotted in the same figure by continuous lines. It can be observed that there is a satisfactory coincidence between theoretical and experimental values, indicating the validity of the theory.

Table 3. Moisture absorption with respect to time for three classes of specimens.

U_f	m (%)							
	0 day	10 days	20 days	30 days	50 days	90 days	130 days	280 days
0	0	0.08	0.13	0.17	0.20	0.29	0.43	0.71
	0	0.09	0.15	0.18	0.22	0.32	0.44	0.73
	0	0.09	0.14	0.17	0.21	0.35	0.43	0.71
	0	0.1	0.15	0.17	0.22	0.31	0.46	0.75
	0	0.08	0.14	0.17	0.21	0.32	0.43	0.71
	0	0.06	0.14	0.16	0.20	0.31	0.43	0.74
0.1	0	0.09	0.13	0.15	0.19	0.29	0.42	0.71
	0	0.08	0.14	0.17	0.21	0.32	0.42	0.72
	0	0.07	0.13	0.16	0.20	0.33	0.41	0.71
	0	0.06	0.12	0.15	0.21	0.31	0.44	0.73
	0	0.07	0.12	0.17	0.20	0.32	0.43	0.71
	0	0.08	0.13	0.16	0.19	0.31	0.42	0.72
0.15	0	0.08	0.12	0.14	0.18	0.27	0.41	0.70
	0	0.07	0.13	0.16	0.20	0.32	0.42	0.72
	0	0.06	0.11	0.17	0.19	0.31	0.40	0.71
	0	0.05	0.12	0.13	0.21	0.31	0.42	0.70
	0	0.06	0.11	0.15	0.19	0.32	0.43	0.71
	0	0.07	0.13	0.16	0.17	0.31	0.41	0.70

From the shapes of isothermal absorption curves plotted in figure 4 one may observe that initially each one of them is linear with time up to 0.15% weight gain and this suggests that in this initial time interval the absorption process constitutes a controlled diffusion. However, as time proceeds, the specimens are filled with moisture, leading to a decrease in moisture absorption rate after the formation of a slight cusp in the diagram. As the equilibrium moisture content is approached there is a slight decrease in the absorption rate at about $t = 150$ days, but the equilibrium is not achieved even after 280 days. Such an anomalous behaviour has been also reported for other polymer diluents systems [48,49,51]. A thorough explanation of this kind of behaviour was given by Appicella *et al* [52], according to which the anomalous behaviour shown in highly humid environments could, in principle, be due to an effective concentration dependence of the diffusion coefficients.

Moreover, any damage induced in the epoxy resin, or epoxy composite, can cause deviations from the Fickian diffusion and accelerate moisture absorption. As to the influence of the filler content on the moisture absorption behaviour, one may note from figure 4a that as U_f increases the absorbed moisture decreases and also the linear variation of weight gain with respect to time slides to lower values. This may be explained by a 'transport model' for systems in which sorbed molecules can be divided into two populations, one formed by completely immobilized molecules and the other by freely diffusing molecules [30]. Also, it is known that as the filler content increases, the free volume decreases and the equilibrium is reached faster.

In table 3 the moisture content with respect to time for three classes of specimens with filler content of 0, 0.1, 0.15 is presented. Each class contains six samples. Thus, in figure 4b the variation of moisture absorption against filler volume fraction is illustrated for different times, i.e., 10–280 days.

On the other hand, the area surrounding each one of the inclusions as previously stated is characterized by voids, microcracks and other defects, which result in an anomalous moisture absorption behaviour. Since this kind of irregularities is more pronounced for high filler contents, it is reasonable to assume that at high filler volume fractions the behaviour will be more anomalous. Another explanation could be that moisture initially enters rapidly into the specimen, filling the microcracks that exist on the surface and inside the material [53]. However, after a few hours of exposure to the moisture, resin particles are actually lost into the water. Thus, there is a simultaneous loss of material and a weight gain due to the moisture absorption. The weight of the specimen increases if the weight gain is greater than the material loss, whereas in the opposite case, the weight of the specimen decreases. As a result of this mechanism, the measured weight change of the specimen does not always correspond to the moisture content of the material. At this point, it should be also emphasized that such a behaviour is more pronounced at high temperatures. Impurities in fluids or differences in material composition may also contribute to the differences in the weight change [54].

In figure 5a–c the stress–strain diagrams of the particulate composite for $U_f = 0, 0.10$ and 0.15 are illustrated for normal conditions, i.e., without moisture absorption, after

Figure 5. (a–c) Stress–strain diagrams for normal conditions at different filler contents.

bending experiments. Similarly, in figure 6a–c the same diagrams appear for 280 days, i.e., for almost moisture saturation conditions. In these two series both longitudinal and transverse strains are traced in order to obtain the elastic modulus and the Poisson ratio of the material. It can be observed that the addition of iron particles decreases the elastic modulus of the material as the slope of the load vs. longitudinal strain curve diminishes, in all cases. As is well known when water is absorbed by a polymeric material, hydrogen bonds of hydroxyl group are broken, resulting in an increased segmental motion, i.e., rotation of chain segments. Moreover,

Figure 6. (a–c) Stress–strain diagrams for saturation conditions at different filler contents.

due to the migration of water molecules from one group to another, small amounts of water may have a large effect on the mechanical properties of the material. A point that is worth mentioning is that the addition of the filler influences the material and renders the matrix less ductile as can be observed from the more linear behaviour of the strain curves, especially in the moisture saturation conditions.

In figure 7a–c the flexural stress at failure vs. filler content is illustrated for normal conditions (without moisture absorption) and for 110 and 280 days of moisture absorption, i.e.,

Figure 7. (a–c) Flexural stress at failure vs. filler content.

for almost moisture saturation conditions, respectively. In all cases the stress decreases as filler is added in the matrix material. This means that the addition of iron particles diminishes the stress at failure as well as the ductility of the material. Residual stresses due to swelling and eventual interface degradation due to moisture are mechanisms that possibly induce the flexural stress at failure loss. These mechanisms are most prevalent at room temperature, where the composite is more brittle.

In figure 8 the variation of elastic modulus vs. the filler volume fraction is illustrated. It can be clearly observed that, as stated previously, the modulus increases when iron particles are uniformly added in the epoxy resin matrix and also this modulus decreases as it is exposed more to moisture absorption. It is well known that absorbed moisture causes a reduction of the composite modulus similar to that of the matrix. However, the decrease is more severe for the matrix

Figure 8. Variation of elastic modulus vs. filler content.

Figure 9. (a and b) Variation of Poisson ratio vs. filler content.

than for the composite, as can be observed from this figure. In figure 9a and b the variation of the Poisson ratio vs. filler content is presented for normal conditions and for moisture saturation conditions, respectively. It can be explicitly observed that the Poisson ratio decreases as the filler volume fraction increases and the moisture absorption raises this elastic constant. This may be due to the following phenomenon. It has been noted that an increase in the moisture content of the polymers reduces their glass transition temperature T_g , which is a measure of their flexibility. The lower this value the greater their flexibility. Thus, in a composite the moisture effects are limited to the permeable phase, i.e., the resin, whose flexibility increases as the moisture content is increased; this effect,

Figure 10. Variation of stress at failure vs. filler content for (a) 110 and (b) 280 days.

however, is reflected in an overall increase in the value of Poisson ratio of the composite.

Comparison of the experimental results for flexural stress at failure versus filler content for 110 and 280 days of moisture absorption with theoretical values obtained by Eqs. (11) and (12) of Schrager [55] and Nicolais and Mashelkar [56], respectively, is illustrated in figure 10a and b. It can be observed that there is a difference of about 10% between theoretical and experimental values in both cases. Comparison of the experimental results for flexural strain at failure vs. filler volume fraction for saturation moisture conditions with theoretical values obtained by Eqs. (13) and (15) of Smith [57], Bueche [58] and Ziegel *et al* [59], respectively, is presented in figure 11. It can be undoubtedly observed that there exists a slight discrepancy between the experimental results and theoretical results of Bueche and Smith and a total discord with those of Ziegel *et al*, who assume an almost linear variation instead of a curve.

Load-deflection diagrams for various filler contents are illustrated in figure 12a–c for normal conditions and for moisture saturation conditions in figure 13a–c. It can be observed that the deflections at the middle of the specimens decrease as the epoxy resin is uniformly enhanced by iron particles, in both cases. On the other hand it can be said that the moisture absorption almost does not affect the deflection for each case of particle content since the respective values when compared

Figure 11. Variation of failure strain vs. filler content for 280 days.

to those obtained from dry specimens are too close. This can mainly attributed to the fact that the elastic modulus diminishes as the specimen is exposed to water. It is known that absorbed moisture causes a modulus reduction in parallel with a strength reduction in the composite, which are very similar to those of the matrix. However, the flexural strength loss is more severe for the composite than for the matrix and this is shown in figure 5, where the variation of elastic modulus is plotted vs. filler content. Residual stresses due to swelling and eventual surface degradation due to moisture are possible mechanisms that induce strength loss. The dependence of the fracture strain, the fracture stress as well as the elastic modulus on the time of immersion for different filler contents shows a general decrease as the time of immersion is increased, as may be anticipated. However, there does not seem to be a clear correlation between the losses in flexural strength and the weight change. Hence, a unique relationship between the weight change and the change of these mechanical properties cannot be readily established. An evaluation of the experimental results can yield the following interesting conclusion.

The degradation of the mechanical properties of iron-particle-reinforced epoxy composites due to moisture absorption is more pronounced after immersion for 110 days into water than after immersion for 280 days. This kind of behaviour is due to a combination of several parameters affecting the ultimate mechanical properties of composite materials. Amongst these parameters, one may consider the inhomogeneous distribution of the water molecules in the composite, resulting in craze initiation in the matrix and the formation of water clusters in the polymer. These phenomena may create preferentially high plasticized zones, which would lower local shear stresses and favour cavitations.

Moreover, during the preparation of the specimens, the particles may aggregate to form larger particles often containing holes. On the other hand, in areas where voids exist, these voids originate from holes in the original granular particles and form incomplete contacts amongst particles. These voids and holes formed in the polymeric matrix are

Figure 12. (a–c) Load–deflection diagrams for normal conditions.

Figure 13. (a–c) Load–deflection diagrams for saturation state.

of cardinal importance in determining the degradation of the mechanical response of composite specimens due to moisture absorption.

In figure 14a and b, photos of a specimen before failure during the four-point bending experiment and also the surface of fractured specimen are illustrated. The large deflection and the failure of the specimen in the first photo and the difference between the two zones or areas after fracture in the second photo, where one of the zones appears 'polished' whereas the second one seems rough, are noteworthy. Low degrees of damage characterize samples conditioned in water at ambient temperature when equilibrated in environments of different relative humidities.

Here, we can point out that the obtained results are not totally in accordance with those obtained from Galperin *et al* [60], who reported their observation that in the system Epoxy 828 with 14.3% TiO_2 the presence of humidity seems to enhance mechanical properties such as tensile strength, ultimate elongation and elastic modulus. On this point the following comments can be made. It is well known that absorbed moisture causes a modulus reduction as well as a strength reduction in the composite, which are very similar to those of the matrix. However, the strength loss is more severe for the composite than for the matrix. The dependence of the ultimate strain as well as the ultimate stress on the time of immersion for different filler contents is usually a decrease

Figure 14. (a) Specimen under four-point bending and (b) fractured specimen.

when the time of water exposure is increased. The void content, the swelling, or the polymerization, the hardening and the curing of the matrix may be the reasons. The results of the aforementioned reference can be explained in this manner. Theocaris *et al* [24] observed a slight increase of the elastic modulus at the first period of immersion into water but this was followed by a subsequent decrease. In our work, only the flexural strain and deflection seem not to be significantly affected by water absorption; it cannot be said that these properties are enhanced by humidity, as claimed in Ref. [60].

The results of this experimental work are synopsized in table 4, which shows a qualitative behaviour of the composite properties when filler content and moisture absorption are augmented.

5. Conclusions

A systematic investigation of the influence of water absorption on the flexural properties of low-content iron particle–epoxy composites was performed in this article. Ambient water conditioning temperature was used during this study, from which the following firm conclusions may be drawn.

Table 4. Influence of moisture absorption and filler content on composite flexural properties.

Property	Particle content	Water absorption
Flexural strength	Decrease	Decrease
Flexural strain	Decrease	Little difference
Flexural modulus	Increase	Decrease
Poisson ratio	Decrease	Increase
Deflection	Decrease	Little difference

- (i) The equilibrium moisture volume fraction is approached faster as the filler concentration is increased.
- (ii) An equilibrium was not achieved even after 280 days of moisture exposure.
- (iii) The flexural strength, the flexural strain and the flexural modulus show in general a decrease, whereas Poisson ratio shows an increase, with the time of immersion.
- (iv) The flexural strength, the flexural strain and the Poisson ratio decrease, whereas the elastic modulus increases, as the filler content is increased.

Finally, it can be said that the degradation of the mechanical properties of iron-particle-reinforced epoxy composites due to moisture absorption is more pronounced after immersion for 110 days into water than after immersion for 280 days. The plasticization and polymer–filler interface failure should play a role on the variation of the mechanical properties of the material.

Also, the results of an experimental research work carried out with particulate composites in hygrothermal conditions may be compared to experimental data that will be carried out with new materials in the future, whenever it is possible.

6. Appendix

6.1 Tensile stress at failure

Schrager formula [55]

$$\sigma_c = \sigma_m e^{-r \cdot U_f}, \quad (11)$$

where σ_c and σ_m denote the composite and the matrix stress at failure, respectively, and r is a constant equal to 2.66, obtained from experiments

Nicolais–Mashelkar formula [56]

$$\sigma_c = \sigma_m \left(1 - 1.21 U_f^{2/3}\right). \quad (12)$$

6.2 Tensile strain at failure

Bueche–Nielsen formula [58]

$$\varepsilon_c = \varepsilon_m \left(1 - U_f^{1/3}\right), \quad (13)$$

where ε_m and ε_c denote the matrix and the composite strain at failure, respectively.

Ziegel formula [59]

$$\varepsilon_c = \varepsilon_m [1 - U_f(1 + \Delta r/R)^3], \quad (14)$$

where Δr is the increase of the radius R of the particles due to existence of an interphase.

Smith formula [57]

$$\varepsilon_c = \varepsilon_m (1 - 1.06U_f^{1/3}). \quad (15)$$

References

- [1] Mc Kague E L, Reynolds J D and Halkias J E 1975 *Life Assur. Compos. Struct. AFML Tech. Rep.* **1** 51
- [2] Fried N 1967 *Proceedings of the fifth symposium on naval structural mechanics* (Philadelphia: Pergamon Press) p 813
- [3] Hertz J 1970 *Proc. Soc. Aerospace Mater. Process Eng.* **3** 9
- [4] Browning C E and Whitney J M 1974 *Fillers and reinforcements for plastics, advances in chemistry series*, No. 134 (USA: Amer. Chem. Soc.) p 137
- [5] Browning C E and Hartness J T 1974 *Proc. Third ASTM STP* **546** 284
- [6] Adamson M J 1980 *J. Mater. Sci.* **15** 1736
- [7] Landal R F and Smith T L 1961 *Am. Rocket Soc. J.* **31** 599
- [8] Kwei T K and Kumins C A 1964 *J. Appl. Polym. Sci.* **8** 1483
- [9] Turner S 1965 *Appl. Mat. Res.* **10** 10
- [10] Van Der Wal C W, Bree H W and Schwarzl F R 1965 *J. Appl. Polym. Sci.* **9** 2145
- [11] Kumins C A and Roterman J 1963 *J. Polym. Sci. A: Polym. Chem.* **1** 527
- [12] Papanicolaou G C, Paipetis S A and Theocaris P S 1977 *J. Appl. Polym. Sci.* **21** 689
- [13] Theocaris P S, Papanicolaou G C and Sideridis E P 1982 *J. Reinf. Plast. Compos.* **1** 50
- [14] Strella S and Erhart P F 1969 *J. Appl. Polym. Sci.* **13** 1373
- [15] Morgan R J and O' Neal J E 1978 *Polym. Plast. Technol. Eng.* **10** 49
- [16] Manson J A and Chin E H 1973 *J. Polym. Sci. C* **1331** 654
- [17] Mc Kague E L, Halkias J E and Reynolds J D 1975 *J. Comput. Mater.* **10** 49
- [18] Shen C H and Springer G S 1976 *J. Comput. Mater.* **10** 2
- [19] Mehta B S, Dibenetto A T and Kardos J L 1977 *J. Appl. Polym. Sci.* **21** 3111
- [20] James D I, Norman R H and Stone M H 1968 *Plastics Polym.* **36** 21
- [21] Ashbee K H, Frank F C and Wyatt R C 1967 *Proc. R Soc. A* **300** 415
- [22] Steel D J 1967 *Trans. Plast. Inst.* **35** 429
- [23] Theocaris P S, Papanicolaou G C and Kontou E A 1983 *J. Appl. Polym. Sci.* **28** 3145
- [24] Theocaris P S, Kontou E A and Papanicolaou G C 1983 *Colloid Polym. Sci.* **261** 394
- [25] Weitsman Y J and Guo Y J 2002 *Compos. Sci. Technol.* **62** 889
- [26] Hiel C and Adamson M 1986 *Compos. Struct.* **6** 243
- [27] Bera T, Mula S, Ray P K and Ray B C 2007 *J. Reinf. Plast. Compos.* **26** 725
- [28] Blikstad M, Siöblom P O W and Johannesson T R 1984 *J. Compos. Mater.* **18** 32
- [29] Apicella A, Egiziano L, Nicolais L and Tucci V 1988 *J. Mater. Sci.* **23** 729
- [30] Apicella A and Nicolais L 1981 *Ind. Eng. Chem. Prod. Res. Dev.* **20** 138
- [31] Verpoest I and Springer G S 1988 *J. Reinf. Plast. Compos.* **7** 2
- [32] Cai L W and Neitsan Y 1994 *J. Compos. Mater.* **29** 130
- [33] Woo M and Piggott M R 1987 *J. Compos. Technol. Res.* **9** 162
- [34] Weitsman Y J 1987 *Int. J. Solids Struct.* **23** 1003
- [35] Xiang Z D and Jones F R 1997 *Compos. Sci. Technol.* **57** 451
- [36] Park C H and McManus H L 1996 *Compos. Sci. Technol.* **56** 1209
- [37] Popineau S, Rondeau-Mouro C, Sulpice-Gaillet C and Shanahan M E R 2005 *Polymer* **46** 10733
- [38] Ozdemir T and Mengeloglu F 2008 *Int. J. Mol. Sci.* **9** 2559
- [39] Athijayamanian A, Thiruchitrambalamb M, Natarajana U and Pazhanivel B 2009 *Mater. Sci. Eng. A* **517** 344
- [40] Fiorelli J, Curtoloa D, Barreroa N, Savastano Jr H, de Jesus Agnolon Pallonea E and Johnson R 2012 *Ind. Crops Prod.* **40** 69
- [41] Tagliavia G, Porfiri M and Gupta N 2012 *Composites Part B* **43** 115
- [42] Singh A, Singh S and Kumar A 2013 *Int. J. Mater. Sci. Appl.* **2** 157
- [43] Bhaskar J and Singh V 2013 *J. Mater. Environ. Sci.* **4** 113
- [44] Hamim S and Singh R 2014 *Int. Scholarly Res. Notices* **2014** Article ID 489453 doi:10.1155/2014/489453
- [45] Hossain M R, Hossain M F and Islam M A 2014 *J. Sci. Res.* **6** 431
- [46] Pandian A, Vairavan M, Jappes W, Jebbas T and Uthayakumar M 2014 *J. Compos.* **2014** Article ID 587980
- [47] Pan Y and Zhong Z 2015 *Mech. Mater.* **85** 7
- [48] Le Grand P G, Kambour R P and Haaf W R 1972 *J. Polym. Sci.* **A2** 1565
- [49] Thomas N A and Windle H 1978 *Polymer* **19** 253
- [50] Nicolais L E 1978 *J. Membr. Sci.* **3** 231
- [51] Apicella A, Nicolais L, Astarita G and Drioli E 1981 *Polym. Eng. Sci.* **21** 18
- [52] Apicella A, Nicolais L, Astarita G and Drioli E 1979 *Polymer* **20** 1143
- [53] Wieth W R and Sladek K J 1965 *Colloid Sci.* **20** 1014
- [54] Springer G C, Sanders B A and Tung R W 1980 *J. Comput. Mater.* **14** 213
- [55] Schragar M 1978 *J. Appl. Polym. Sci.* **10** 2379
- [56] Nicolais L and Mashelkar R A 1976 *J. Appl. Polym. Sci.* **20** 561
- [57] Smith T L 1961 *Rubber Chem. Technol.* **34** 123
- [58] Bueche F 1960 *J. Appl. Polym. Sci.* **4** 107
- [59] Ziegel K D, Frensdorff H K and Fogiel A W 1969 *J. Appl. Polym. Sci.* **13** 867
- [60] Galperin I, Arnheim W and Kwei T W 1965 *J. Appl. Polym. Sci.* **9** 3215