

Fire Resistance of Hybrid Building Materials

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ABSTRACT: In this work, an experimental procedure was conducted to investigate the effect of weight content of short E-glass fibers on the degradation of flexural properties of a hybrid building material, when exposed to a direct gas (propane/butane) flame for varying time intervals. This experimental procedure is aiming on one hand to define the role that E-glass fibers play on the degradation of the flexural properties of the materials tested, as well as to provide a sufficient quantity of experimental data which will allow to quantitatively predict the observed degradation of the aforementioned properties due to exposure to direct gas flame using the Residual Property Model (R.P.M.) developed by the first author and already successfully applied to a number of different materials subjected to a combination of different damage sources. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: matrix; fibers; reinforcement; degradation; modeling

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INTRODUCTION

Polymer matrix composites have been used for repair and strengthening purposes in the building industry for a quite long time. Their mechanical behavior and properties, in combination with their low weight, as well as their excellent corrosion durability make them an excellent choice for such applications. However, when exposed to certain environmental conditions a rapid degradation of their mechanical properties can be observed. Conditions such as UV radiation, excessive humidity or exposure to elevated temperatures can be responsible for such degradation.

As a result, much research has been conducted on the field of modeling and limiting the degrading effects these damage sources have on polymer matrix composites. A quite large amount of these research works is dealing with the elevated temperatures and fire exposure conditions, since they are common in a large number of applications ranging from aerospace to building industry. Studies have been made on the mechanical behavior of FRP's under simultaneous compressive loading and fire in order a thermo-mechanical model to be developed^{1,2} and the failure modes to be identified.³ Moreover, different types of FRP's such as carbon FRP's used for reinforcing concrete structural members have been tested under fire and mechanical loading conditions on large scale experiments in order to investigate the effect of the reinforcement on the behavior of the structural members.^{4,5} Other tests held, tested polymer composite's

response under other than static loading, such as impact, after exposed to fire.⁶ The effect of fire exposure on specimens made of polymer composite on the microstructure of the material has also been studied.⁷ Modeling of the temperature distribution in the composite as well modeling of fire-induced damage is also of high interest.^{8,9}

In this work, epoxy resin and fine marble sand are mixed in a 20–80%, respectively, by weight ratio to formulate a hybrid polymer matrix. The matrix was then reinforced with 5 and 10% short E-glass fibers. Half of the specimens manufactured were tested on three-point bending test. The rest of them were also tested on three-point bending test but prior to that they were exposed to a direct gas (propane/butane) flame for various time intervals. The effect of reinforcement content on the degradation of the flexural properties of the material manufactured is quantified and discussed. Additionally, the data derived from the experimental procedure were used to calibrate the RPM model¹⁰ to simulate the degradation of the flexural properties of the material when the damage source is considered to be the direct gas (propane/butane) flame.

MATERIALS AND METHODS

A hybrid matrix reinforced with different amounts of short glass fibers constitutes the material manufactured and tested in the present investigation. The materials used for the manufacturing of the hybrid matrix were epoxy resin reinforced with fine

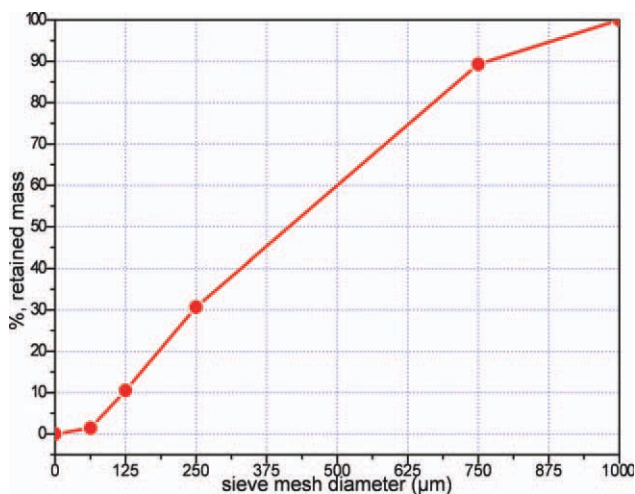


Figure 1. Grading curve of the marble sand. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

marble sand mixed in a composition consisting of 80% by weight marble sand and 20% by weight epoxy resin.

The resin used was an epoxy resin based on bisphenol-A organic compound. Bisphenol-A is reacting with epichlorohydrin, using NaOH as catalyst, forming a prepolymer having on each of its two ends one epoxy group. When diamine is added to the prepolymer, cross-linking is initiated as each molecule of diamine connects to four molecules of the prepolymer, forming long and interconnecting chains. The density of the epoxy resin used is 1065.00 kg/m^3 .

The other component of the hybrid matrix that was manufactured and tested was marble sand. Plain marble sand was used which is a byproduct of processing bulk pieces of marble. Marble mainly consists of calcite, a calcium mineral form of CaCO_3 . It is a white-colored material with density approximately equal to 2700.00 kg/m^3 . Figure 1 shows the grading curve of the marble, its maximum grain diameter ($1000.00 \mu\text{m}$), while one can observe that 60% out of the mass of the material consists of grains with diameter size ranging between $250 \mu\text{m}$ and $750 \mu\text{m}$.

Hybrid matrix was reinforced with short ($L = 3 \text{ mm}$) E-glass fibers at two by weight concentrations, namely 5 and 10%. The density of E-glass fibers is equal to 2540.00 kg/m^3 while their diameter is $14 \mu\text{m}$.

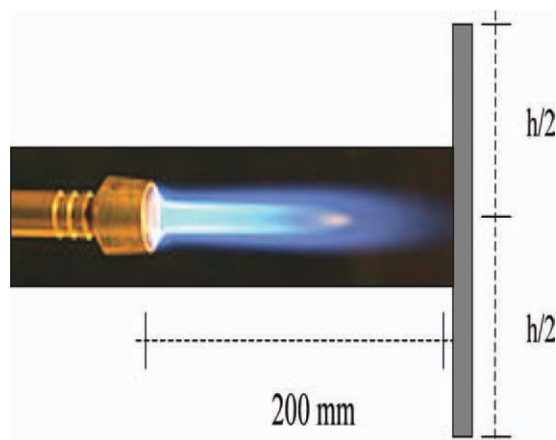


Figure 2. Schematic representation of the experimental apparatus used for flame exposure of the specimens. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

All detailed data concerning compositions of the manufactured and tested specimens are shown in Table I.

Manufacturing the hybrid matrix was conducted by following a standardized procedure. First, fine marble sand was set in an oven over a period of 24 h at a temperature of 50°C in order all the excessive humidity to be removed, permitting improved adhesion conditions between epoxy resin and marble sand particles.

Next step was mixing, which started by the homogenization of the solid ingredients (marble sand and fibers), and then the liquid part (resin) along with the proper amount of diamine was added.

Mixing time (including homogenization) was kept constant and equal to 5 min. The air that was added in the mass of the composite due to mechanical mixing was removed by setting the mixture into a vacuum chamber for a time period of 5 min.

Degassing phase was decided to be as low as 5 min due to the fact that the 80% wt marble sand—20% wt epoxy resin hybrid matrix was quite viscous, making casting into the moulds a time-consuming and difficult to succeed procedure. On the other hand, due to the fact that crosslinking procedure starts immediately after mixing diamine with resin, longer degassing times would reduce the time available for completing casting, since pot time of the epoxy compound is constant and limited.

Table 1. Overview of Compositions Manufactured and Tested

Hybrid matrix composition		Composite composition					
		Epoxy resin		Marble sand		Glass fibers	
		Weight fraction	Volume fraction	Weight fraction	Volume fraction	Weight fraction	Volume fraction
80% (wt) marbles sand 20% (wt) epoxy resin	Composition 1	0.20	0.3879	0.80	0.6121	0.00	0.0000
	Composition 2	0.19	0.3720	0.76	0.5869	0.05	0.0411
	Composition 3	0.18	0.3558	0.72	0.5613	0.10	0.0829

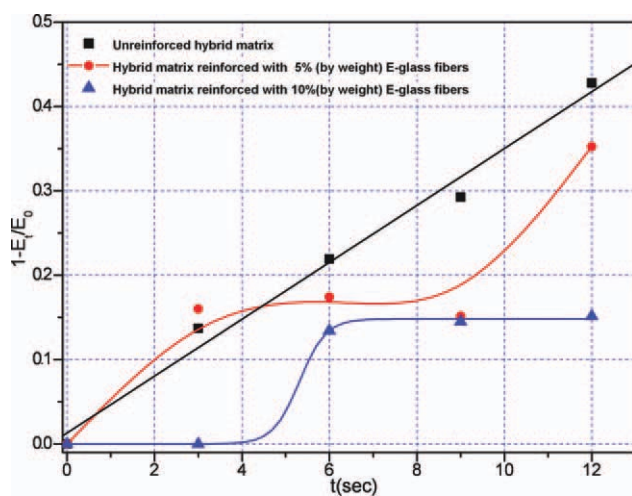


Figure 3. Variation of stiffness degradation with exposure time for various by weight contents of reinforcement. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Casting of the mixture was conducted into metallic open moulds, and curing process was initiated by setting the moulds into an oven at a temperature of 50°C for a 24 h time period. Specimens' dimensions were 100.00 mm long, 12.90 mm wide, and 3.00 mm thick.

For each fiber weight fraction (namely 0, 0.05, and 0.10) and for each flame exposure time (namely 0, 3, 6, 9, and 12 s), a total number of 12 specimens were manufactured. Three-point bending tests were executed according to ASTM D790-99 standard.

Glass fibers content was limited to 10% wt due to the fact that, as already has been studied and reported in a previous publication,¹¹ for glass fibers' concentrations greater than 10% wt the mixture becomes too viscous to handle it into the mould while at the same time the resulted composite showed a brittle and degraded behavior.

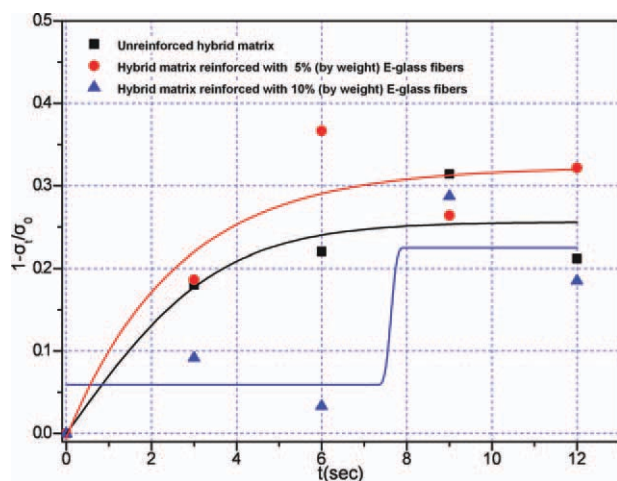


Figure 4. Variation of flexural strength degradation with exposure time for various by weight contents of reinforcement. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

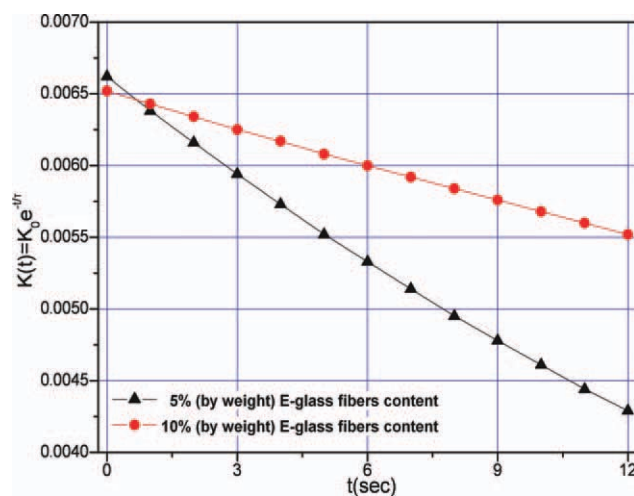


Figure 5. Degradation of adhesion coefficient with time of exposure to flame. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For the fire resistance experiments, specimens were exposed to a gas (propane/butane) flame targeting the center of the specimen, coming from a portable gas torch. The temperature of the flame tip was around 1900°C as measured by means of a short wavelength infrared radiation pyrometer. The distance between the nozzle of the torch and the center of the specimen was kept constant and equal to 200 mm. Figure 2 shows the experimental device that was used. Specimens of each composition were exposed to flame for time intervals of 3, 6, 9, and 12 s. Due to specimen's small thickness, longer exposure times led to uncontrolled combustion and decomposition of the specimen. For that reason maximum duration of exposure time interval was 12 s.

A data acquisition system was used to monitor data and to transform force-displacement curves onto stress-strain curves from which both flexural modulus and strength values were accurately determined as the mean of the six values that were derived from each of the six specimens. The tensioned face of the specimen during three-point bending test was always the burned one.

RESULTS AND DISCUSSION

Physical Interpretation of the Results

Figures 3 and 4 show the results of the experimental procedure. Figure 3 depicts the variation of stiffness degradation with exposure time for the three compositions that were manufactured and tested, namely the unreinforced 80% wt marble sand—20% wt epoxy resin hybrid matrix and the reinforced with 5% wt and 10% wt glass fibers.

Stiffness degradation of the unreinforced hybrid matrix exhibits a linear pattern. Degradation starts immediately after the specimen is exposed to fire and continues to increase with a steady rate for the complete range of exposure periods, ending up to a value of 45% of the stiffness value of the pristine material at 12 s.

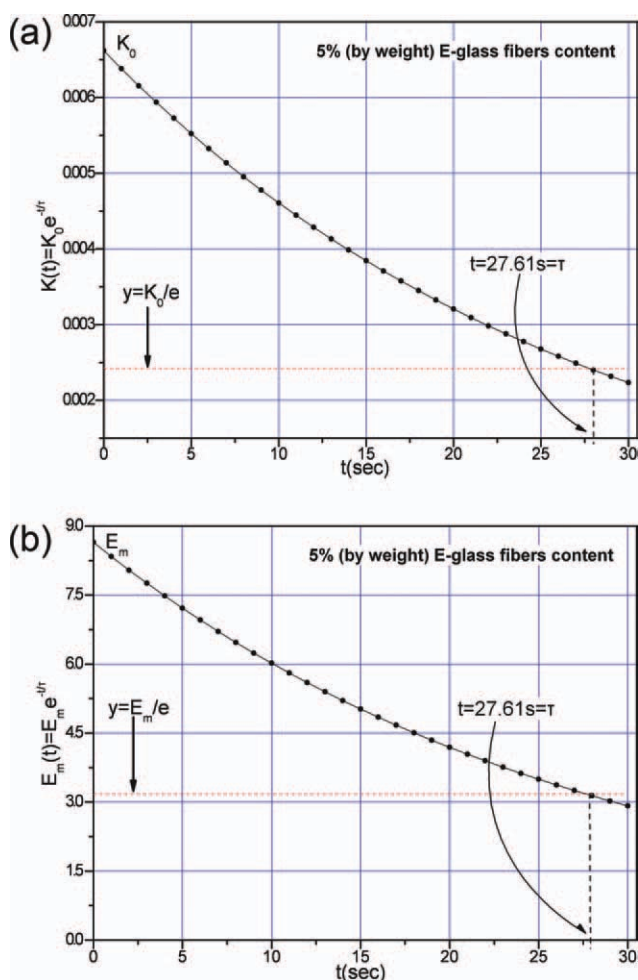


Figure 6. (a) Variation of adhesion coefficient $K(t)$ with exposure time according to Eq. (6). (b) Variation of stiffness $E_m(t)$ of the hybrid matrix with exposure time according to Eq. (5). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

On the other hand, when 5% wt short E-glass fibers are added to the hybrid matrix, degradation of stiffness follows a different pattern. For the first 3 s of exposure time, stiffness is degrading rapidly with a rate comparable to the rate exhibited by the unreinforced material at the same exposure time period. When exposure time exceeds 3 s, degradation reaches a plateau value equal to the 16% of the value of the pristine material. This value remains constant until exposure time exceeds 9 s. After this time point, degradation's rate increases again and at 12 s of exposure reaches a value of about 35% of the value of the corresponding pristine material.

The same nonlinear behavior is observed for the case of the hybrid matrix reinforced with 10% wt short E-glass fibers. The graph of stiffness degradation is the same as the one for the 5% wt glass fibers reinforced hybrid matrix, displaced on the time axis for a time period of 4 values. More specifically, no degradation is observed for a time period of ~ 4 s. Between 4 and 6 s of exposure time, degradation increases with a rapid rate and reaches a plateau value corresponding to the 14% of the value of the pristine material. No further degradation was observed

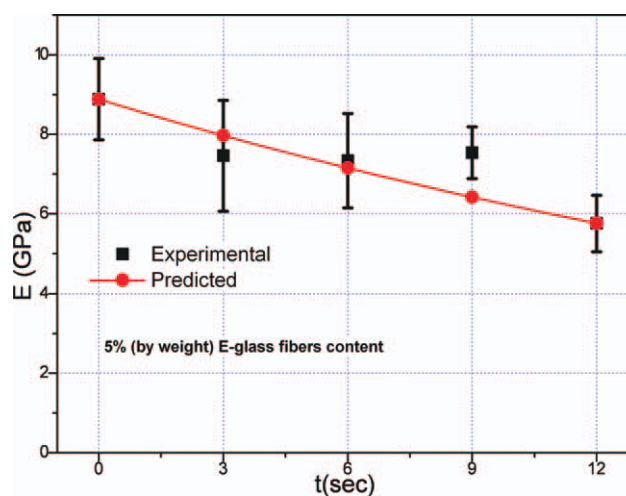


Figure 7. Measured and predicted values of stiffness for the 5% wt short glass fibers reinforced hybrid matrix with exposure time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

until the maximum exposure time of 12 s utilized in the experiment was reached.

The results derived from the experimental procedure show that glass fiber reinforcement reduces the degradation of the stiffness of an epoxy resin-based hybrid building material due to exposure to a gas flame. More accurately speaking, addition of short glass fibers is causing a time-delay of the degradation of stiffness. For by weight fiber content as low as 5% the material showed an initial degradation from 0 until 3 s of exposure time. After that and for the next 6 s of exposure time, the material did not suffer any further degradation of stiffness until exposure time became greater than 9 s. On the other hand, specimens manufactured from hybrid matrix reinforced with 10% by weight short glass fibers suffered no initial degradation for the first 4 s of exposure time. After that, degradation reached a

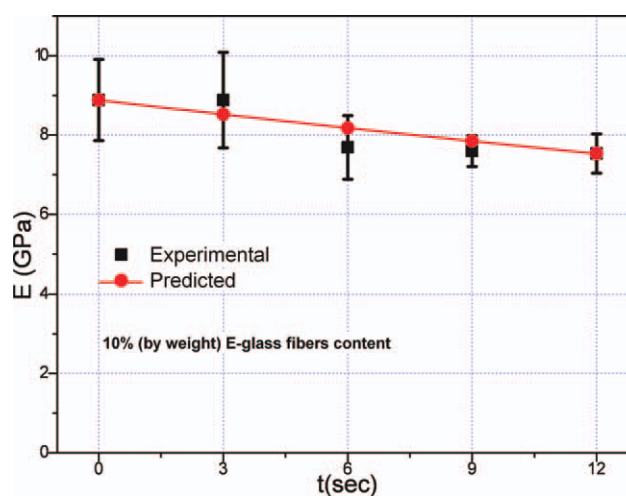


Figure 8. Measured and predicted values of stiffness for the 10% short glass fibers reinforced hybrid matrix with exposure time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

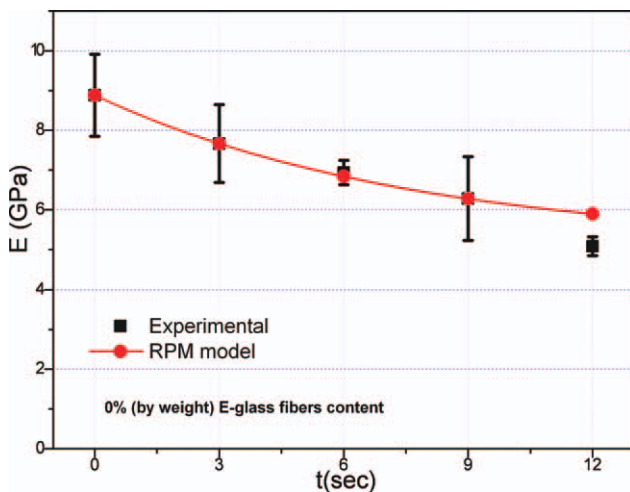


Figure 9. Stiffness variation by means of the RPM model and comparison with respective experimental results for the unreinforced hybrid matrix with fire exposure time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

steady value, close to the one that was measured for the 5% by weight reinforced material, until the end of the exposure time that was considered in the experiment. From Figure 3, we can conclude that addition of 5% more by weight glass fibers caused a delay of 4 s in the manifestation of the same amount of damage on the stiffness of the glass fiber reinforced hybrid matrix material.

Figure 4 shows the variation of the flexural strength degradation with exposure time for the three compositions that were manufactured and tested. Unreinforced hybrid matrix exhibits an exponential rate of degradation from the first moment of exposure to fire. After an exposure time of about 9 s, degradation seems to be reaching a plateau value, which remains

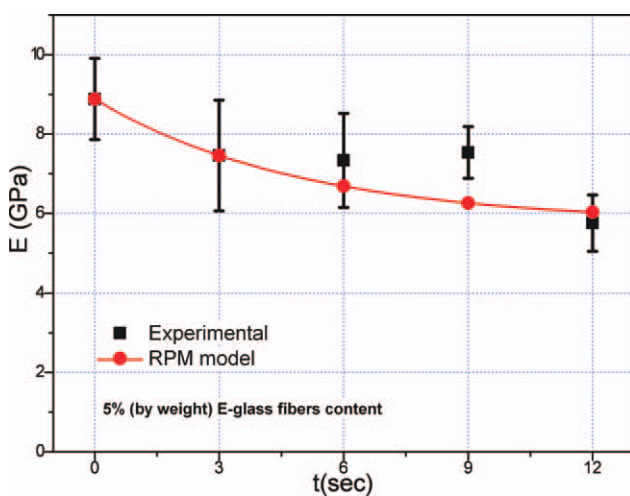


Figure 10. Stiffness variation by means of the RPM model and comparison with respective experimental results for the 5% (wt) short glass fibers reinforced hybrid matrix with fire exposure time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

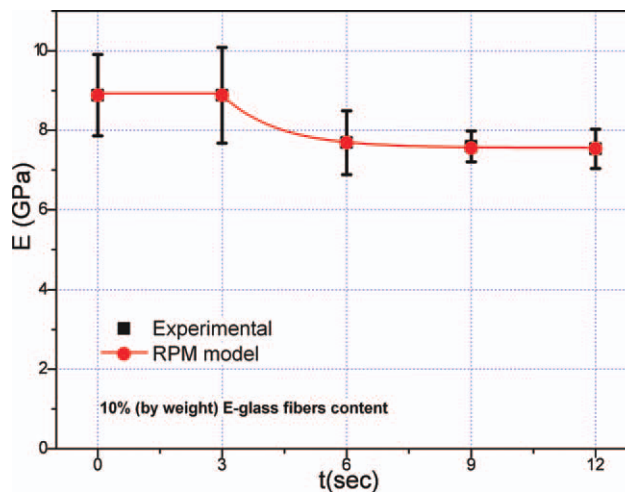


Figure 11. Stiffness variation by means of the RPM model and comparison with experimental results for the 10% (wt) short glass fibers reinforced hybrid matrix with fire exposure time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

almost constant until the end of the maximum exposure time of 12 s.

As far as flexural strength's degradation is concerned, we could conclude that 5% wt glass fiber reinforced composite seems to behave worse than the unreinforced one. A possible explanation would be that addition of 5% wt glass fibers is causing voids to be inserted in the mass of the composite. These voids are expanding when the flame heats the air they contain causing even larger discontinuities to be present in the composite. The amount of fibers is not enough to compensate the loss of load transfer that discontinuities are causing, and for that reason reinforced material exhibits greater degradation values than the unreinforced one.

Hybrid matrix reinforced with 10% wt short E-glass fibers it seems to have a remarkable reinforcing effect since for an exposure period of about 7.5 s no flexural strength degradation was manifested. After exceeding that exposure period, flexural strength degradation increased at a high rate and reached a plateau value of about 18% of the value measured at pristine material specimens. In this case, apparently, the amount of fibers that is added is enough to balance the degradation that would be expected due to the insertion of voids in the mass of the composite.

Modeling the Damage Caused by the Exposure to Gas Flame

In addition to the qualitative interpretation of the experimental results, an attempt was made to formulate a mathematical expression, which would be able to produce a quantitative evaluation of the damage caused by the exposure to the gas flame. A measure of damage degradation is reflected through the expression:

$$D(t) = 1 - \frac{E(t)}{E_0} \quad (1)$$

where $D(t)$ is the time dependent stiffness degradation during flame exposure, $E(t)$ the corresponding stiffness at the same

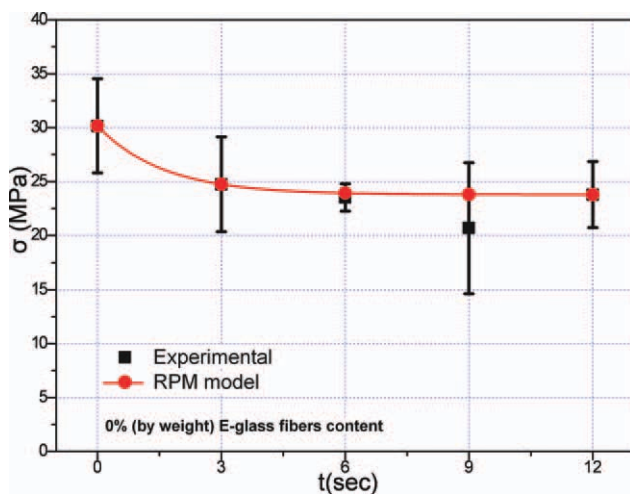


Figure 12. Strength variation by means of the RPM model and comparison with experimental results for the unreinforced hybrid matrix with fire exposure time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

instant of time and E_0 is the stiffness value of the material before exposure to flame.

As it is well known, a preliminary damage is introduced in the material structure during the stage of manufacturing where voids, microcracks, and other defects appear to be present, leading to a premature degradation of the material which is reflected through a degradation of the fiber-matrix adhesion coefficient, and in turn, to a lower value in stiffness, E_{exp} , in comparison to that predicted by the law of mixtures, E_{comp} .

Based on the above considerations, the following relations are valid^{12,13}:

$$E_{\text{comp}} = E_f V_f + E_m (1 - V_f) \quad (2)$$

$$E_{\text{exp}} = E_f K_0 V_f + E_m (1 - K_0 V_f) \quad (3)$$

where E_{comp} is the Stiffness values calculated by the rule of mixtures before flame exposure, E_{exp} is the Actual stiffness values before flame exposure, E_m is the Stiffness of the hybrid matrix before flame exposure, V_f is the Volume fraction of the reinforcement, K_0 is the Adhesion coefficient between matrix and reinforcement before flame exposure.

Given the values of E_{exp} , E_m , and E_f for a certain filler volume fraction V_f , the value of K_0 can be derived from expression (3) as:

$$K_0 = \frac{E_{\text{exp}} - E_m}{(E_f - E_m) V_f} \quad (4)$$

which represents the value of the glass-fibers-matrix adhesion coefficient before the composite is exposed to the gas flame.

Specimens exposed to flame impact exhibit mechanical degradation due to the following two main reasons: First, it is the resin that suffers thermal degradation on the side of the sample impacted by the gas flame. However, damage is not limited at

the point of impact but merely, due to the high temperature of the flame, temperature increases in an area surrounding the impact point so that material damage spreads in a larger area of both the surface and the bulk of the material under consideration. In these areas, and due to the difference in thermal expansivities of the constituent materials, large thermal stresses develop, which, as a result, lead to debonding of the filler from the resin and to a consequent mechanical degradation of the hybrid composite.

Thus, after exposure to gas flame, both stiffness of hybrid matrix and the adhesion coefficient are both degrading. It is assumed that, for exposure time equal to t seconds, both the stiffness and the adhesion coefficient follow an exponential law of decay:

$$E_m(t) = E_m e^{-\frac{t}{\tau}} \quad (5)$$

and

$$K(t) = K_0 e^{-\frac{t}{\tau}} \quad (6)$$

where: τ : a characteristic time parameter depended on the material structure, the filler-volume fraction, the flame characteristics and the exposure conditions.

If the flame is applied at $t = 0$, then for $t > 0$ expression (4) in combination with expression (5) gives:

$$K(t) = \frac{E(t) - E_m(t)}{(E_f - E_m(t)) V_f} \quad (7)$$

Combining expressions (4) and (7) and taking into account (5) and (6) we finally get:

$$E(t) = \left[\frac{(E_{\text{exp}} - E_m) (E_f - E_m e^{-\frac{t}{\tau}})}{(E_f - E_m)} + E_m \right] e^{-\frac{t}{\tau}} \quad (8)$$

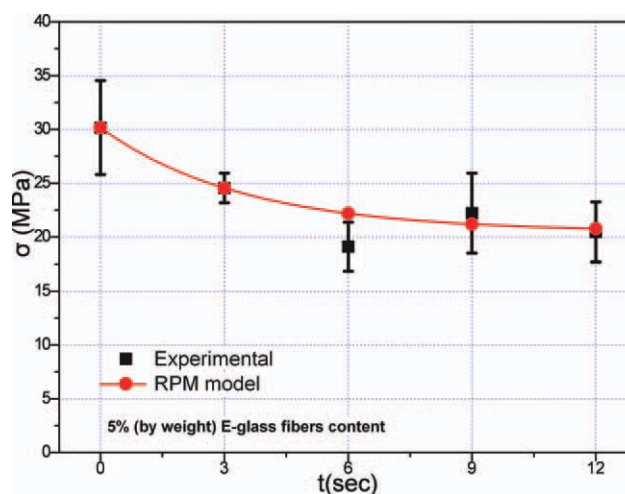


Figure 13. Strength variation by means of the RPM model and comparison with experimental results for the 5% (wt) short glass fibers reinforced hybrid matrix with fire exposure time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

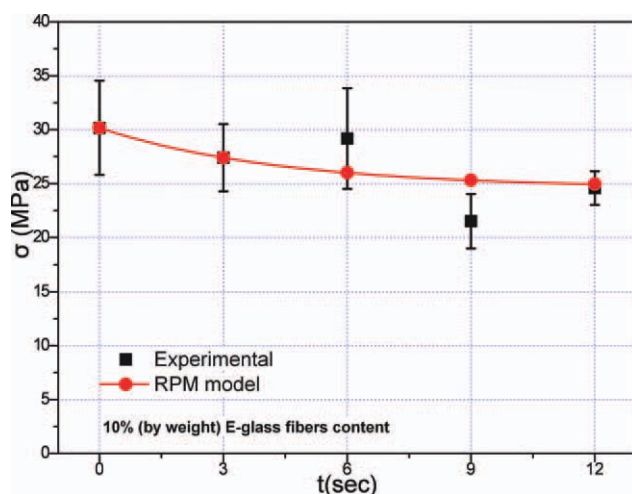


Figure 14. Strength variation by means of the RPM model and comparison with experimental results for the 10% (wt) short glass fibers reinforced hybrid matrix with fire exposure time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which gives the composite stiffness after exposure to flame for a period of t seconds. For each different volume fraction of reinforcement, a value of parameter τ has to be calculated. The experimental values of stiffness under damage saturation conditions were used to calibrate the model by calculating the value of the τ parameter. The τ -values were found 27.61 s and 72.72 s for the 5 and 10% hybrid matrix composites respectively. These values correspond to the time needed for the adhesion coefficient to be reduced to a value equal to $\frac{1}{e}$ of its initial value and/or the time needed for the matrix stiffness to attain a value equal to $\frac{1}{e}$ of its value before exposure to flame.

Figure 5 shows the values of adhesion coefficient $K(t)$ for the two compositions that were manufactured and tested, calculated from relationship (6) using the experimental τ values 27.61 s and 72.72 s for the 5 and 10% by weight short E-glass fibers reinforcement content, respectively.

As mentioned before, the τ -values were calculated using the last experimental point. To verify that these values correlate with the values corresponding to the $\frac{1}{e}$ fraction of the initial values of $K(t)$ and/or $E_m(t)$, respective curves were plotted against time by using the experimentally found τ -values and the time corresponding to their intersection with the horizontal line traced $y = K_0 \frac{1}{e}$ or $y = E_m \frac{1}{e}$ was compared to the experimentally found τ -values [Figures 6(a,b)]. From this comparison, it was deduced a perfect agreement between the experimentally found τ -values and the values of time corresponding to the $\frac{1}{e}$ fraction of E_m and or K .

From the obtained values it is clear that as the amount of reinforcement is increased, there is a delay in stiffness degradation of the material due to the resistance of the existed reinforcement. A second point of interest is that for the application of the model, only one experimental point was used (that one of the maximum degradation observed) and that all parameters introduced in the predictive expression have a clear physical meaning.

Figures 7 and 8 show the values of stiffness, which were experimentally found, along with those calculated using expression (8) for compositions containing 5 and 10% by weight glass fibers, respectively. For both compositions the calculated and the experimental values seem to be in quite good agreement.

Modeling by Means of the R.P.M. Model

The Residual Property Model (RPM)¹⁰ describes the degradation of a material's mechanical property under various types of damage sources such as impact, thermal fatigue, etc. Experimental data from the present experimental work were used to calibrate the R.P.M. in an attempt to model the degradation of flexural properties of the material due to exposure to direct gas flame. The general equation of the model is as follows:

$$\frac{P_t}{P_0} = s + (1 - s)e^{-\lambda N} \quad (9)$$

where:

$$s = \frac{P_\infty}{P_0}$$

P_t is the property value at a specific time point during exposure to flame; P_0 is the property value before exposure to flame (reference value); P_∞ is the property value under damage saturation conditions; λ is the rate of damage development; and N is the duration of damage source activity.

RPM model was applied to both flexural strength and modulus variation with exposure time. Figures 9–11 show the results of the RPM application on material's stiffness, along with the experimental results derived from the previously described experimental procedure for the unreinforced, reinforced with 5% wt short glass fibers and reinforced with 10% wt short glass fibers respectively.

Figures 12–14 also depict the application of the residual property model on the flexural strength of the three compositions manufactured and tested.

As it can be observed from the corresponding figures, for most of the cases tested, RPM model can produce accurate predictions of the measured values, while it can reproduce the overall trend of the property's variation with exposure time.

CONCLUSIONS

- In this work, epoxy resin and fine marble sand are mixed in a 20–80% respectively by weight ratio to formulate a hybrid polymer matrix. The matrix was then reinforced with 5 and 10% short E-glass fibers. Half of the specimens manufactured were tested on three-point bending test. The rest of them were also tested on three-point bending test but prior to that they were exposed to a direct gas (propane/butane) flame for various time intervals.
- In addition to the qualitative interpretation of the experimental results, an attempt was made to mathematically formulate the damage caused by the exposure to the gas flame.
- From the obtained experimental results, it was clear that as the amount of reinforcement is increased, there is a delay in stiffness degradation of the material due to the resistance

of the existed reinforcement. A second point of interest was that for the application of the model one only experimental point was used (that one of the maximum degradation observed) and that all parameters introduced in the predictive expression have a clear physical meaning.

- Finally, the RPM model was applied to predict both flexural strength and modulus variation with exposure time. It was proved that the RPM model can produce accurate predictions of the measured values, while it can reproduce the overall trend of the residual property's variation with exposure time.

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