

Effect of Thermal Fatigue on the Mechanical Properties of Epoxy Matrix Composites Reinforced with Olive Pits Powder

G. C. Papanicolaou, A. F. Koutsomitopoulou, A. Sfakianakis

Department of Mechanical and Aeronautics Engineering, Composite Materials Group, University of Patras, GR-26500, Patras, Greece

Received 24 January 2011; accepted 4 March 2011

DOI 10.1002/app.35092

Published online 3 October 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: This study is focused on the investigation of the effect of thermal shock cycling on the mechanical properties of cellulose based reinforced polymer composites. Polymer composites reinforced with olive pits powder at different filler-volume fractions were manufactured. An increase in the bending modulus on the order of 48% was achieved. On the other hand, results showed that the bending strength remained almost unaffected from the amount of filler introduced. Next, the effect of thermal shock cycling on the mechanical behaviour of the thus manufactured composites was investigated. Theoretical predictions for

both the properties variation with number of thermal shock cycles applied as well as with filler-volume fraction were derived using the residual properties model (RPM) and the modulus predictive model (MPM), respectively. Predicted values were compared with respective experimental results. In all cases, a fair agreement between experimental findings and theoretical predictions was found. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 67–76, 2012

Key words: composites; mechanical properties; modeling; natural reinforcement; thermal fatigue

INTRODUCTION

Over the past few decades, polymer composites reinforced with natural fillers have received great attention for academic and industrial purposes.¹ There is a wide variety of different types of natural fillers which can be used to reinforce polymers such as non-wood natural fillers and/or wood fillers. Typical non wood natural fillers are the flax, kenaf, sisal, jute, and hemp.

Natural fibers and fillers and especially lignocellulosic fibers extracted from plants as reinforcements in a polymer matrix have many advantages comparing to synthetic fibers such as glass fibers. Natural fillers and in particular olive pits have a relatively low cost and are environmentally friendly because of their renewable and biodegradable characteristics. Another very important characteristic of all natural reinforcements is their low density which makes the natural composites very popular in many engineering applications because of the reduction of the weight of the final product.^{1,2}

In this study, a relatively unknown and non-traditional, as reinforcement, filler in epoxy–matrix com-

posites was investigated. Olive pits, are part of the soil waste which are produced by the processing and extraction of olive oil in the olive mills and are extensively used in Greece as well as in Southern Europe. A very common use of olive pits which have high combustion power, equivalent to hard wood, is as wood briquettes to generate heat or power.³

MATERIALS AND EXPERIMENTAL PROCEDURE

Materials

Olive pits were obtained from local olive production without having further any physical or chemical modification treatment. They were cleaned and washed to be separated from their impurities, produced during the extracting olive oil process. Then, they were placed in an oven at 50°C for 24 h to remove moisture. The dried olive stones were grinded by a planetary mill (Fritsch, Planetary Mono Mill pulverisette 6). The residues at successive stages of the cleaning procedure applied are shown in Figure 1.

The mean diameter of olive stones produced by the grinding procedure was 10–30 μm, whereas the density of the olive pits fillers was 0.6 g/cm³.

In this current study, the epoxy system used as matrix material was the resin RenLam CY219 combined with a curing agent HY 219 at a ratio 2 : 1 by weight. Polymer resin and olive pits were carefully mixed in

Correspondence to: G. C. Papanicolaou (gpapan@mech.upatras.gr).



Figure 1 The residues at successive different stages of the cleaning procedure applied.

proper quantities to achieve uniform distribution of the fillers into the matrix. Then, the mixture was placed in a vacuum chamber for 5–6 min to reduce the amount of entrapped air. The mixture was then poured in a proper metallic mould ($240 \times 170 \times 2$ mm) and subsequently cured in an oven at 50°C for 14 h.

Static mechanical tests

Pure epoxy resin specimens and polymer matrix composites reinforced with olive pits at different volume fractions of the filler particles ($V_f\% = 7, 14, 27,$ and 44 of olive pit's powder) were manufactured. A series of static three-point bending experiments in an Instron 4301 loading machine of 10 kN loading capacity, were performed at room temperature to investigate the mechanical properties of the manufactured composites. In all cases, a constant crosshead speed of 1 mm/min was applied. As shown in Figure 2, the specimens had a total length of 100 mm and a gauge length of 63 mm.

Scanning electron microscopy

The morphological characteristics of the olive pits powder as well as the cross section surface of the

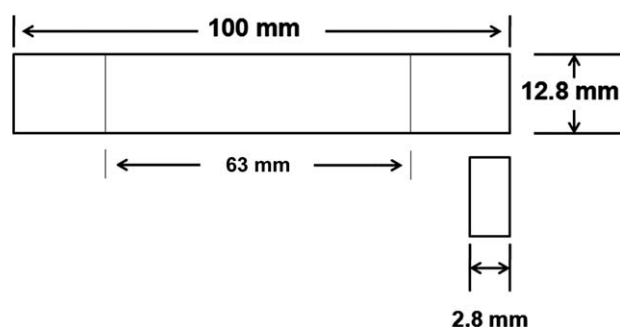


Figure 2 Specimen dimensions.

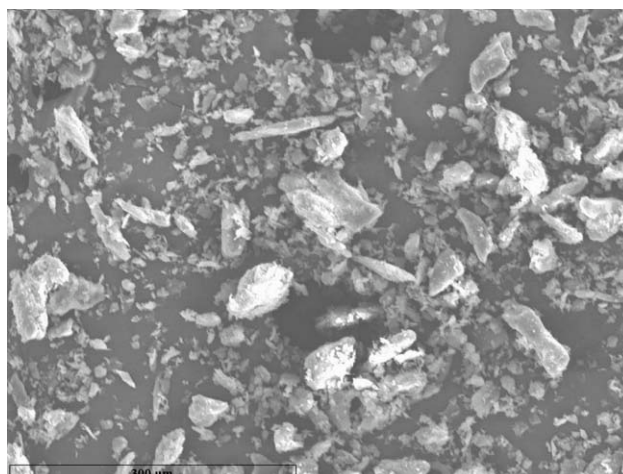


Figure 3 Scanning electron micrograph of olive pits powder.

polymeric matrix composites reinforced with olive pits were observed via scanning electron microscopy (SEM) as shown in Figure 3.

The non-conducting surface of the composites was coated with gold in agar auto sputter coater before subjected to SEM. It is observed from the SEM micrographs of the olive pits powder fractured surface (Figs. 4–6) that the dispersion of the olive pits particles into the polymeric matrix was roughly uniform. Olive pits are cellulose based natural reinforcement having physical and mechanical characteristics similar to those of typical wood and other lignocellulosic fibers extracted from plants (i.e., flax, hemp). This kind of natural filler has higher stiffness comparing to that of polymeric matrix. An increase in the filler content, results in a higher stiffness of the particle-composite. Also, as filler clustering increases, local phase inversions are observed and the fraction of the resin entrapped within the aggregate increases.

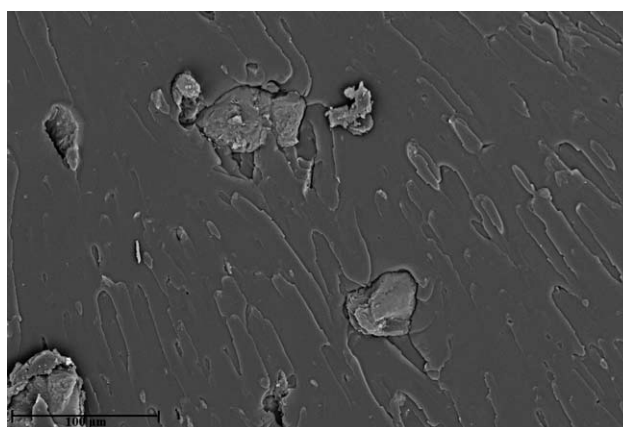


Figure 4 SEM micrographs of cross section of fracture surface of the polymer matrix composites reinforced with 14% by volume olive pits.

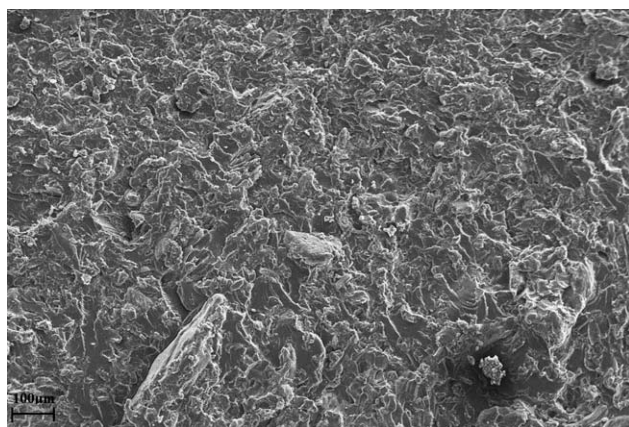


Figure 5 SEM micrographs cross section of fracture surface of polymer matrix composite reinforced with 44% by volume olive pits.

As it is shown in Figures 4–6, in several locations of the inner structure and especially in the interfacial area extended between particle fillers and the matrix no gaps or entrapped air to a great extent can be observed which indicates good inclusion-matrix adhesion. This fact contributes to the good mechanical properties exhibited in the olive pits-polymer composites. According to our experimental results, an increase in bending modulus and a small decrease of the bending strength with filler-volume fraction was found.

Thermal shock

Pure epoxy resin specimens and composites reinforced with olive pits at different volume fractions of the filler particles were induced in thermal shock cycling and the effect on their mechanical characteristics was investigated. Figure 7 shows the thermal shock cycling profile applied. The specimens were exposed to 80°C for 10 min and then they were im-

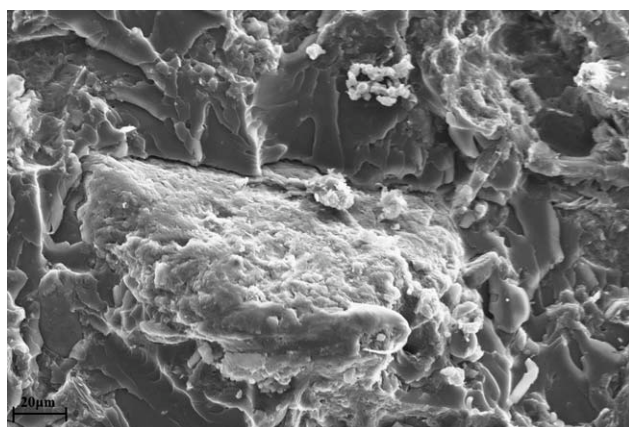


Figure 6 SEM micrographs cross section of fracture surface of polymer matrix composite reinforced with 44% by volume olive pits.

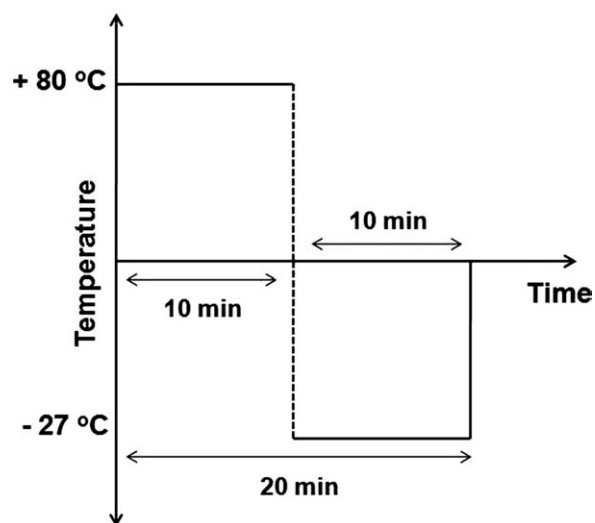


Figure 7 The thermal shock cycling profile applied.

mediately placed in a freezer at -27°C temperature for the same length of time. During tests, samples were removed regularly, every 10 cycles, from the thermal cycling process to evaluate their mechanical properties changes as a function of the number of thermal shock cycles.

THEORETICAL BACKGROUND

Before presenting the modulus predictive model (MPM) and its application for the modulus prediction of the composites manufactured and tested, it is important to preliminary analyze some of the parameters affecting the mechanical behavior of particulates and, which have been taken into account for the development of the model.

Many studies have been conducted on the mechanical properties of particulate polymer composites. Particles when used as fillers modify the physical and mechanical properties of polymeric matrices and there are many factors that result to the complex behavior of these systems.⁴ The mechanical properties of particulate composites are affected by a number of parameters such as the particle size, particle volume fraction, the filler-matrix interfacial adhesion bond, and the degree of mixing that defines the extent of dispersion of fillers into the polymeric matrix.⁵ The latter is a critical factor that influences in a great extent the mechanical properties of particulate composites.⁶ When fillers are not well dispersed in a polymer matrix, then micro-voids and aggregates are likely to be present into the composite resulting in a highly non-homogeneous stress field with localized stress concentration points.⁷ In literature, the experimental data for particulate composites vary significantly and universal findings are hard to find.⁵

Effect of particle stiffness

For high stiffness fillers, we can select some phenomena of physicochemical character. Here, filler practically cannot be deformed, and this influences deformation condition and mechanical behavior of the polymer matrix. In filled specimens, the matrix deformation increases essentially with increase in filler concentration at constant deformation of specimen. The increase in matrix deformation leads to growth of its deformation rate, which in turn increases modulus too.

Effect of particle–matrix interphase

As an essential cause of increase in modulus with filler concentration can be named the increase in polymer part in a form of surface layers at the interface with solid (between filler and particles). In such thin films, the polymer is subjected to bulk deformation. It is known that bulk modulus is much higher than shear modulus, and therefore the increase in polymer fraction in surface layers leads to a general increase in modulus of the filled system.⁵ It was shown^{8,9} that in surface layer the molecular mobility of chains and segments are diminished as a result of conformation restrictions. The existence of such a hard layer may be considered as another cause of modulus increase as a result of apparent increase in particles size. At constant filler amount, it is equivalent to an increase in filler concentration.

Effect of particle–matrix bond strength

The behavior of particle loaded polymers may vary greatly with changes in bond strength between filler particles and polymeric matrix. Particle–matrix debonding constitutes one of the key damage phenomena in particle-reinforced composite materials. This is especially the case in composites consisting of a soft polymeric matrix reinforced by stiff particles. This damage process plays a key role in the initiation and propagation of cracks in composites, as the crack front tends to propagate through the voids generated by the dewetting of the particles embedded in the polymeric matrix. When the reinforcement volume fraction is high, the damage process taking place at the micro scale is strongly affected by the complex interaction between neighboring particles.

- a. Very weak bond strength: For very weak (or zero) bond strength, the filler–polymer bond fails immediately upon straining, and small holes (or vacuoles) are created next to a particle. Since there is no physical reinforcement, the material is weak and highly extensible. This statement is valid for brittle matrices like epoxies.

- b. Very high bond strength: Alternatively, if the bonds are strong, the filled material exhibits a relatively high modulus with considerable reduction in the ultimate elongation. This statement is valid for brittle matrices like epoxies.
- c. Adhesive bond of intermediate value: It is in those systems where the adhesive bond is of intermediate value, however, that the problem of localized failure appears. As the specimen undergoes loading, the weakest bond strengths are first exceeded. The filler particles are then released, transmitting a higher stress to the neighboring polymer–particle bonds. The effect observed is that of a line of released particle perpendicular to the direction of strain. If the applied load occurring after this phenomenon does not exceed the bond strength of the remaining intact bonds, the polymer along this line experiences very high strain and eventually fails.^{10,11}

Effect of high filler content

In the literature, most theoretical calculations for the elastic properties of particulate filler composites have been limited to those with an overall filler content of <0.5 . This is because for composites with low filler content (<0.50), particles can be safely assumed to be randomly dispersed within the resin; thus all the resin acts as the continuous phase.¹² It is believed, however, that with an increase in the filler content, the probability of filler clustering increases, leading to local phase inversions where the fraction of the resin entrapped within the aggregate increases.¹³ For composites with overall filler content >0.5 , one may deduce two possible composite microstructures in addition to that where particles are randomly dispersed. In the first case, the resin is completely entrapped within the filler aggregates or clusters, with particles touching each other. In the second type of microstructure, the composite contains a mixture of regions of resin entrapped within particle clusters. In principal, such composites would consist of regions with randomly dispersed particles, but with each region containing a different volume of filler.¹⁴

Effect of strain magnification

Strain magnification occurs when a sample of a deformable matrix containing essentially non-deformable particles is subjected to an elongation or compression. Barring the deformation of voids, the total sample deformation has to be accommodated by the matrix; hence the strain in the matrix is larger than the measured overall strain.

Upon loading, at a critical strain level, the particles separate from the matrix causing dewetting.

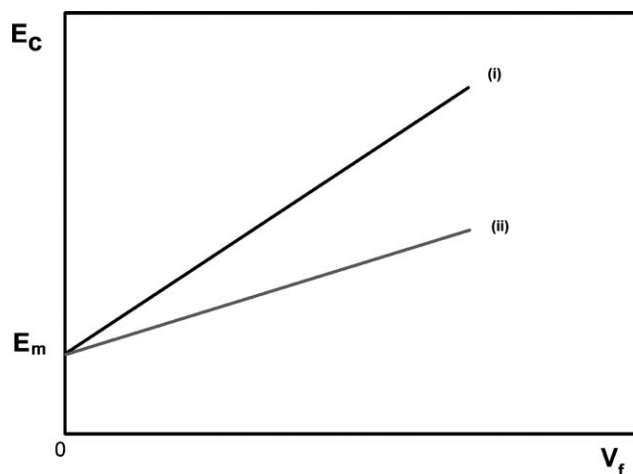


Figure 8 Schematic representation of modulus variation with the filler-volume fraction for (i) perfect adhesion and dispersion (law of mixtures) and (ii) perfect adhesion with agglomerations (linear behavior).

This introduces volume dilatation and results in non-linearity in the stress–strain behavior. However, for well bonded particles, cavities and cracks may form entirely within the matrix.¹⁵

Effect of the degree of mixing

The properties of a given particle loaded polymer depend on the degree of mixing of the filler. The degree of mixing is defined as the extent of homogeneity for the dispersion of given filler in the polymer matrix. So far, no methods exist to deal with the effects of degree of mixing on the properties of filled polymers. Therefore, trial and error methods are still used in designing polymer compositions for achieving the required properties. A good degree of mixing will enhance the properties of filled polymers.

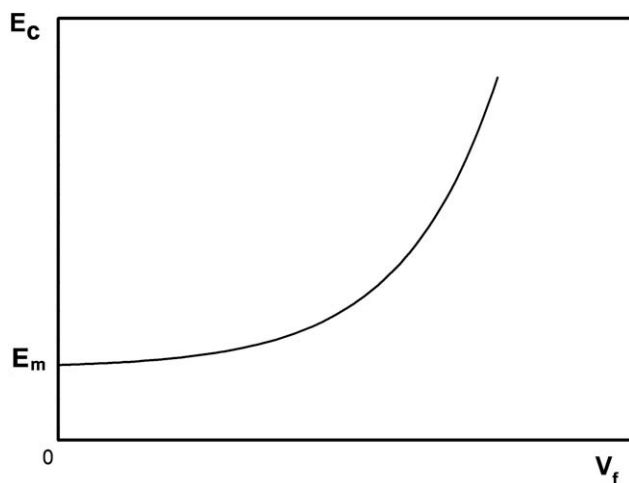


Figure 9 Schematic representation of modulus variation with the filler-volume fraction in the case of low degree of adhesion and high degree of dispersion.

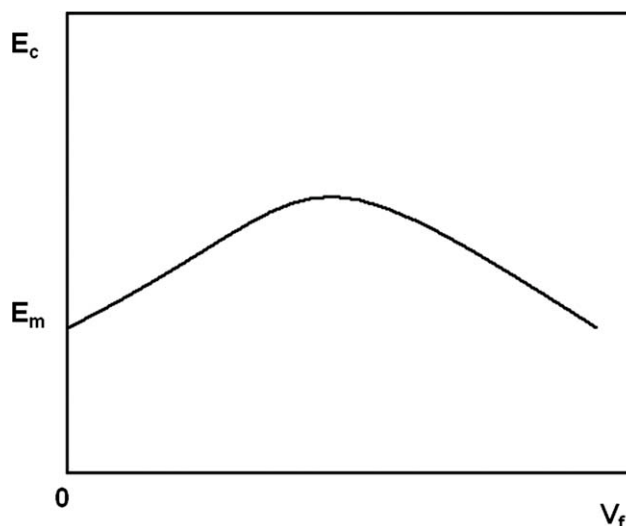


Figure 10 Schematic representation of modulus variation with the filler-volume fraction in the case of high degree of adhesion and low degree of dispersion.

Mechanically mixing particulate composite constituents can lead to different properties. This is because the dispersion of the particles within the polymeric matrix depends on the mixing time period.⁶

MODULUS PREDICTION MODEL FOR PARTICLE-FILLED POLYMER

MPM for particulate composites is a semi-empirical model developed by the first author and is used to predict the modulus variation with filler-volume fraction. It is based on the assumption that the main parameters affecting the modulus variation of particulates, are the filler concentration, the particles' degree of dispersion and the strength of adhesion bond between fillers and the polymer matrix as shown in qualitative diagrams (Figs. 8–10).

As it will be analyzed in the sequence, depending on the specific combination of the above parameters, the following four main cases can be distinguished: (1) For perfect matrix-reinforcement adhesion bond and ideally homogeneous filler dispersion, the modulus variation with filler-volume fraction is linear following the “rule of mixtures” [Fig. 8(i)]. (2) For degrees of adhesion and dispersion of equal value the modulus variation with filler-volume fraction is again linear corresponding to lower modulus values in comparison to those predicted by the rule of mixtures [Fig. 8(ii)]. (3) For low degree of adhesion and high degree of dispersion the elasticity modulus behavior is not linear following a non-linear variation shown in Figure 9. (4) Finally, for high degree of adhesion and low degree of dispersion, the variation of elasticity modulus with volume fraction is shown in Figure 10.

All the above cases can be described by the following single equation:

$$E_c = (\lambda - k)E_f V_f^2 + k(E_f - E_m)V_f + E_m \quad (1)$$

where k is the adhesion coefficient between fillers and the polymer matrix and λ is the dispersion coefficient of the fillers into the polymer matrix.

More precisely:

- $k = 0$ corresponds to zero adhesion
 - $k = 1$ corresponds to perfect adhesion
 - $\lambda = 1$ corresponds to perfect dispersion
1. For $k = \lambda = 1$ (i.e., for perfect adhesion and dispersion), eq. (1) reduces to the well known rule of mixture:

$$E_c = E_f V_f + E_m(1 - V_f) \quad (2)$$

2. For $k = \lambda \neq 1$ (i.e., for the same degree of non-perfect adhesion and dispersion), eq. (1) reduces to the linear expression:

$$\begin{aligned} E_c &= k(\lambda - k)E_f V_f^2 + E_m \Rightarrow E_c \\ &= E_f(kV_f) + E_m(1 - kV_f) \end{aligned} \quad (3)$$

This is an expression similar to that of the rule of mixtures and where the quantity kV_f could be considered as the "effective filler-volume fraction."

3. For k (i.e., for low degree of adhesion and high degree of dispersion), then:

$$E_c = (\lambda - k)E_f V_f^2 + k(E_f - E_m)V_f + E_m \quad (4)$$

with $\lambda - k > 0$, so that the modulus variation with V_f is parabolic with a graph of the shape shown in Figure 9. This type of variation has the following physical meaning: Initially, as the filler volume fraction increases, due to the low degree of particle adhesion, a slow increase in modulus is observed. On the other hand, due to the high degree of dispersion, aggregation does not exist in a high extent so that the filler-matrix contact area increases with increasing filler-volume fraction leading to a continually increasing modulus. Thus, the overall behavior observed is characterized by an initial slow increase in modulus, followed by a subsequent increase with a higher rate.

4. For $\lambda > k$ (i.e., for high degree of adhesion and low degree of dispersion) then:

$$E_c = (\lambda - k)E_f V_f^2 + k(E_f - E_m)V_f + E_m \quad (5)$$

with $\lambda - k < 0$ so that the modulus variation with V_f is parabolic with a graph having the shape shown in Figure 10. This type of variation has the following physical meaning: As the filler

volume fraction increases, due to the low degree of particle dispersion, aggregation becomes a parameter of crucial importance leading to a reduction of the total filler-particle contact area. Thus, at low filler loadings and due to the high degree of adhesion an initial increase in modulus is observed. However, as the filler-volume fraction increases, high degree of agglomeration is observed due to the low degree of dispersion, leading to a total reduction of the filler-particle contact area. Thus, the overall behavior observed is characterized by an initial increase in modulus up to a certain limit, followed by a subsequent decrease of its value.

Steps to be followed for the application of the MPM

For the application of the MPM to real particulates, it is assumed that at too low filler-volume fractions, the parameter that mainly affects the modulus variation with filler-volume fraction of the polymeric matrix particulate is the degree of filler-matrix adhesion, k . This assumption is based on the fact that at very low filler-volume fractions, a low degree of agglomeration is expected to be present into the material. Thus, the degree of adhesion, at too low filler-volume fraction, can be obtained from eq. (1) if we let $(\lambda - k)E_f V_f^2 \rightarrow 0$, then:

$$k = \frac{E_c - E_m}{(E_f - E_m)V_f} \quad (6)$$

In this study, the low filler-volume fraction was taken as $V_f = 0.07$ and the degree of adhesion value found was $k = 0.357$.

The second assumption made was that the degree of adhesion, k , depends only on the, the manufacturing procedure followed and the specific materials' combination in the composite as well as their mutual compatibility, being independent on the filler-volume fraction. Thus, once its value is known, it remains constant.

Next, the degree of dispersion λ can be calculated at a relatively high filler-volume fraction where a low degree of dispersion is expected to exist, leading to a high degree of agglomeration. Thus, the degree of dispersion is given by:

$$\lambda = \frac{(E_c - E_m) - k(E_f - E_m)V_f}{E_f V_f^2} + k \quad (7)$$

In this case, the high filler-volume fraction was taken as $V_f = 0.44$ and the degree of dispersion found was $\lambda = 0.335$.

THERMAL SHOCK CYCLING

Thermal shock cycling is a factor that affects the physical and mechanical characteristics of composites resulting to degradation and reduction of their properties.¹⁶ Thermal shock cycling is a process that can result the initiation and the propagation of cracks in composites produced by cycling or periodic temperature changes. Besides the cavities and the cracks that form within the matrix during thermal shock cycling process, changes in geometry and the physical characteristics of composites might occur. Thus, localized stress concentration arises due to the heterogeneous nature of composites and the different mechanical characteristics and coefficients of thermal expansion of the components.¹⁶ Because of the mismatch in shrinkage between the particles and the matrix the composite generally experiences a state of thermal residual strain that result to crack propagation.¹⁷

Several degradation mechanisms affect the reduction of properties of the induced to thermal shock cycling composites. The resistance on thermal shock cycling depends on the properties of the different components, the number and duration of the thermal cycles as well as the temperature range of each cycle. Moreover, the polymeric matrices degrade through physical and chemical changes due to reaction of their molecular components with the environment.¹⁸ Under thermal shock cycling conditions, these mechanisms result in properties degradations causing by the induced thermal residual stresses.¹⁸ In addition, oxidation of the epoxy-resin also involves a weight loss and a density increase and as a consequence some shrinkage of polymeric matrix. Another crucial factor that affects the thermal degradation of composites is the bond strength between the polymer matrix and the filler.

In the case that the polymer-filler bond strength is weak, thermal shock cycling might cause strengthening of the adhesion between the polymer and the filler. At heating conditions, additional cross-links might occur and brittle the matrix.

All these mechanisms, causing degradation or not, as mentioned above, affect the properties of the composites not independently to each other. The mechanical behavior of composites induced in thermal shock cycling, is the result of all these mechanics.

The residual property model

The RPM is a model developed by the first author and his group members and can be applied for the description of the residual mechanical properties of materials after damage. RPM gives satisfactory predictions for the residual properties changes irrespectively of the cause of damage and the type of

material considered. There are many causes that can damage a material. Among usual damage sources is water absorption, mechanical, thermal or hydrothermal fatigue, single or repeated impact, existing notches, etc. In this study, the source of damage studied is thermal shock cycling.

The basic assumption of the RPM is that the mechanical degradation of a material, due to a source of damage, follows an exponential decay law. According to RPM, the degradation of a property due to damage will be described by the following equation¹⁹:

$$\frac{P_r}{P_0} = s + (1-s)e^{-sM} \quad \text{with } s = \frac{P_\infty}{P_0} \quad (8)$$

where P_r is the current value of the mechanical property considered, P_0 and P_∞ correspond to the value of the same property for the virgin and the damage saturated (i.e., after too many cycles) material, respectively. In this study, P represents the bending modulus.

Finally, since M is proportional to the number of thermal shock cycles and this, in turn, affects the damage produced in the material tested, it can be considered as a damage function depending on the source of damage. In the case considered in this study, damage function M for thermal shock cycling is given as:

$$M(n, T) = \frac{n \cdot \Delta T}{T_g - T_R} \quad (9)$$

where ΔT is the temperature range of thermal shock cycling, T_g is the glass transition temperature of the material tested, T_R is the room temperature (25°C), and n is the number of thermal shock cycles.

RESULTS AND DISCUSSION

Bending strength

Generally, the strength of particulate polymers decreases with the increase of filler concentration due to the creation of aggregates. However, in our materials this kind of behavior is not really observed; instead a small decrease of the bending strength with filler-volume fraction was found to exist and this is shown in Figure 11.

Application of the MPM

Reinforcing the polymer matrix with olive pits powder, an increase in bending modulus with filler-volume fraction was observed. To show the percentage increase in modulus with respect to that of the pure resin, the variation of the reduced modulus was

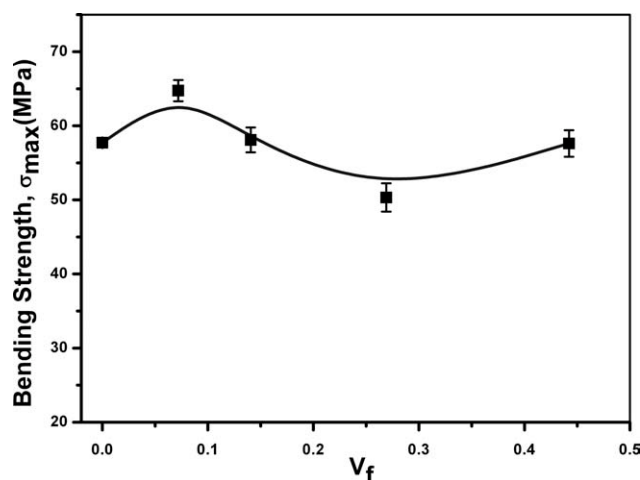


Figure 11 Bending strength as a function of olive pits volume fraction.

plotted against filler-volume fraction and the result is shown in Figure 12. From this Figure, it becomes clear that the bending modulus of the manufactured composites is increasing with particle volume fraction and a maximum increase of $\sim 48\%$ in modulus was achieved at $V_f = 45\%$. Such an increase is important when considering the low cost of the material used as reinforcement.

Next, the MPM was applied for the prediction of the modulus of the composites manufactured and a comparison between predicted values and respective experimental results was made. In this case, as we have stated above, the degree of adhesion and the degree of dispersion were found to be $k = 0.357$ and $\lambda = 0.335$, respectively. The results of comparison are shown in Figure 13. All experimental points represent the mean value of five specimens tested. In general, experimental deviations were $<3\%$ showing an excellent repeatability. As it is observed, there is a fair agreement between the MPM predictions for

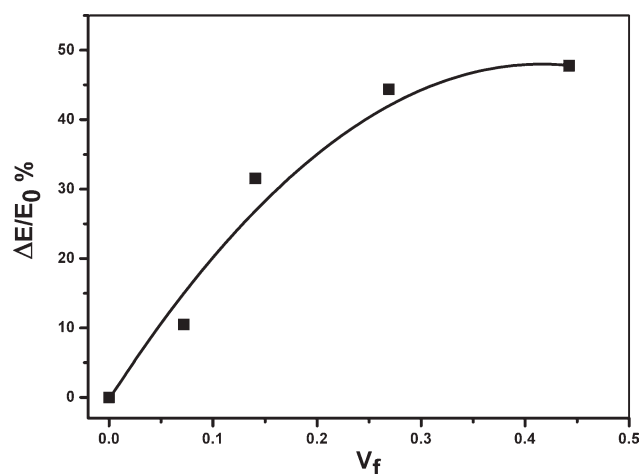


Figure 12 Variation of the reduced bending modulus with filler-volume fraction.

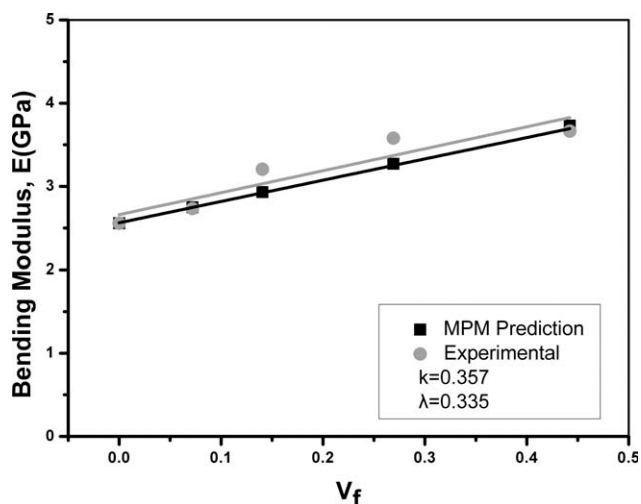


Figure 13 Experimental and predicted values, according to the MPM model, for the bending modulus as a function of filler-volume fraction.

the modulus elasticity and respective experimental results. Thus, the MPM can effectively predict the modulus variation with reinforcement.

Application of the RPM to thermal shock cycling experimental results

The RPM was applied to predict the elasticity modulus variation as a function of the thermal shock cycles number for different filler-volume fractions. Because of their heterogeneous nature and the very dissimilar expansion/contraction behaviour of the two components of the composite, different damage mechanisms developed within the materials resulting in the degradation of their physical and mechanical characteristics.^{16,20}

For the application of RPM, P_∞ obtained from the experimental bending modulus at 200 cycles for the composites with $V_f \% = 7, 14, 27$ of olive pit's powder and 100 cycles for those with $V_f \% = 44$. P_0 obtained from the experimental bending modulus of the virgin composites. The temperature range of thermal shock cycling, ΔT , was 107°C . In Table I, the glass transition temperature of composites reinforced with olive pits powder at different filler-volume fractions.

TABLE I
T_g of Composites Reinforced with Olive Pits Powder at Different Filler-Volume Fractions

Olive pit's powder (V_f)	T_g ($^\circ\text{C}$)
0	77.28
0.07	91.59
0.14	96.81
0.27	100.16
0.44	95.67

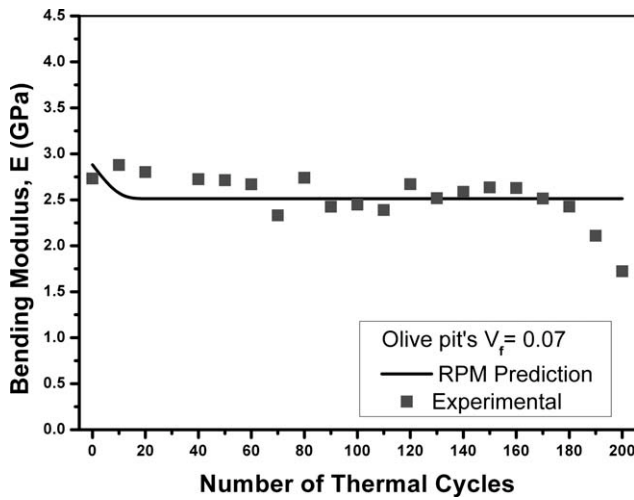


Figure 14 Experimental results and RPM predicted values for bending modulus with the number of thermal cycles for the composites with $V_f = 0.07$.

In Figures 14–17, a comparison between the experimental results and respective RPM predictions for the bending modulus with number of cycles is shown. It can be seen that a fair agreement between experimental results and respective predictions exists in most of cases. Another interesting observation is that in all cases presented, even under such an aggressive environment, the bending stiffness of the materials manufactured remained almost unaffected.

CONCLUSIONS

In this study, the effect of thermal shock cycling on the mechanical behavior of polymer matrix composites reinforced with olive pits powder is investigated. Specimens loaded at different filler volume fractions were manufactured, mechanically charac-

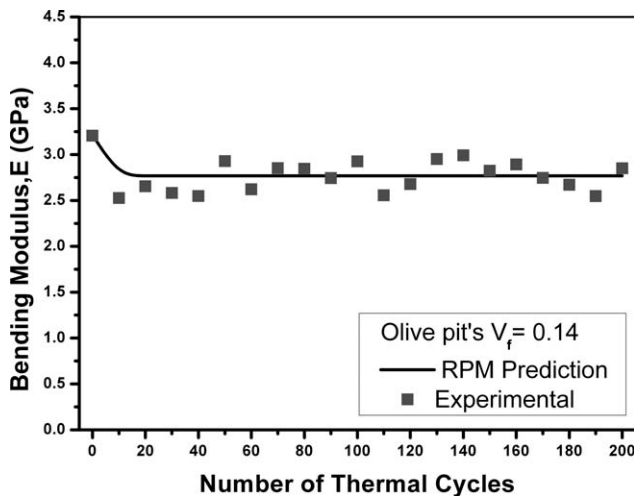


Figure 15 Experimental results and RPM predicted values for bending modulus with the number of thermal cycles for the composites with $V_f = 0.14$.

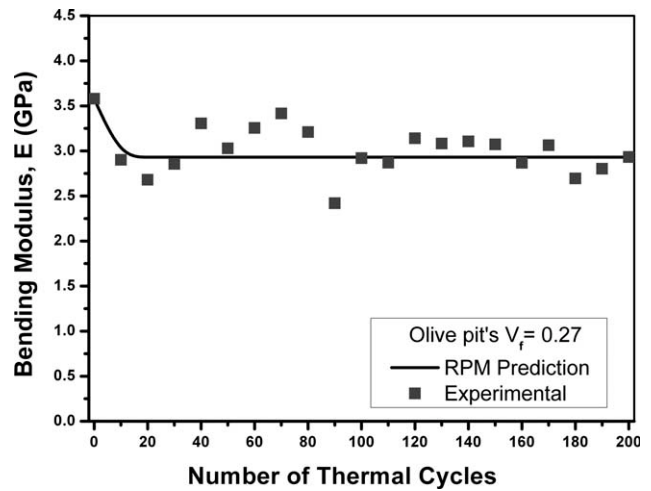


Figure 16 Experimental results and RPM predicted values for bending modulus with the number of thermal cycles for the composites with $V_f = 0.27$.

terized, and tested after having subjected to thermal shock cycling conditions in the temperature range from -27°C to $+80^{\circ}\text{C}$. From the SEM micrographs a good inclusion-matrix adhesion it was observed. Next, the MPM was used for the prediction of modulus variation with filler-volume fraction, and the RPM was used for the prediction of stiffness degradation with number of thermal cycles applied. The main conclusions can be summarized as follows:

1. With filler loading, an increase in the bending modulus on the order of 48% was achieved.
2. A small decrease in bending strength with filler volume fraction was observed.
3. A fair agreement between experimental results and theoretical predictions made through the MPM was found.

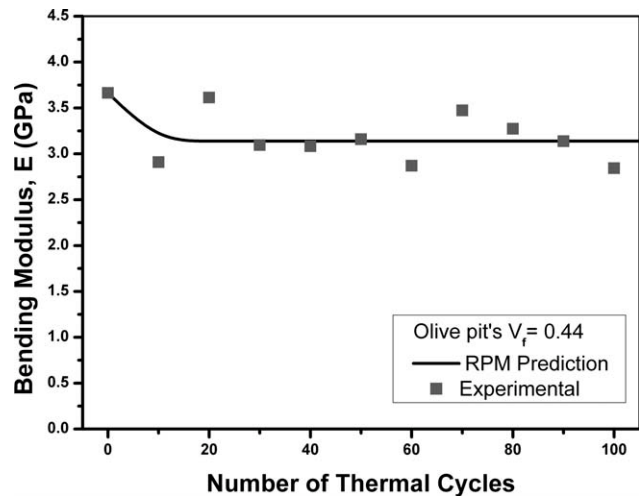


Figure 17 Experimental results and RPM predicted values for bending modulus with the number of thermal cycles for the composites with $V_f = 0.44$.

4. Composite stiffness remained unaffected from the thermal shock cycling duration.
5. Predicted values for the stiffness as derived from the application of the RPM were found in good agreement with respective experimental results.

References

1. Joshi, S. V.; Drzal, L. T.; Mohanty, A. K.; Arora, S. *Compos Part A: Appl Sci Manuf* 2004, 35, 371.
2. Wambua, P.; Ivens, J.; Verpoest, I. *Compos Sci Technol* 2003, 63, 1259.
3. Vlyssides, A.; Barampouti, E.; Mai, S. *Biodegradation* 2008, 19, 209.
4. Fu, S.-Y.; Feng, X.-Q.; Lauke, B.; Mai, Y.-W. *Compos Part B: Eng* 2008, 39, 933.
5. Basaran, C.; Nie, S.; Hutchins, C. S.; Ergun, H. *Int J Dam Mech* 2008, 17, 123.
6. Lee, M. C. H. *J Appl Polym Sci* 1984, 29, 499.
7. Liu, C. T. *Compos Struct* 1997, 39, 297.
8. Lipatov, Y. S.; Babich, V. F.; Rosovizky, V. F. *J Appl Polym Sci* 1974, 18, 1213.
9. Lipatov, Y. S. *Int Polym Sci Tech, Monograph No.2*.
10. Bills, K. W.; Sweeny, K. H.; Salcedo, F. S. *J Appl Polym Sci* 1960, 4, 259.
11. Moloney, A. C.; Kausch, H. H.; Kaiser, T.; Beer, H. R. *J Mater Sci* 1987, 22, 381.
12. Davy, P. J.; Guild, F. J. *Proc R Soc Lond A* 1988, 418, 95.
13. Wu, W.; Sadeghipour, K.; Boberick, K.; Baran, G. *Mater Sci Eng A* 2002, 332, 362.
14. Alberola, N. D.; Mele, P. *Polym Eng Sci* 1997, 37, 1712.
15. Ziegel, K. D.; Frensdorff, H. K.; Fogiel, A. W. *J Appl Polym Sci* 1969, 13, 867.
16. Hancox, N. L. *Mater Design* 1998, 19, 85.
17. Parlevliet, P. P.; Bersee, H. E. N.; Beukers, A. *Compos Part A: Appl Sci Manuf* 2007, 38, 1581.
18. Chung, K.; Seferis, J. C.; Nam, J. D. *Compos Part A: Appl Sci Manuf* 2000, 31, 945.
19. Papanicolaou, G. C.; Kosmidou, T. V.; Vatalis, A. S.; Delides, C. G. *J Appl Polym Sci* 2006, 99, 1328.
20. Humfeld, G. R.; Dillard, D. A. *J Adhes* 1998, 65, 277.