

Use of Solid Residue from Olive Kernel Pyrolysis for Polymer Matrix Composite Manufacturing: Physical and Mechanical Characterization

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ABSTRACT: This study is aiming at the production of carbon material from agricultural residues by pyrolysis and their further use for the production of green polymeric composites. The development of an agricultural-based polymer matrix compatible with olive pits and consequently a fully biodegradable composite system is the future and ultimate goal of the undertaken research. In this study, pyrolysis of olive kernels was conducted at 800°C for 1 h. Furthermore, elemental, proximate, and metal analyses were performed for the raw material and the produced char. The analyses showed that the pyrolytic char from olive kernel is a carbon rich material with significant concentration in metals, which can be further studied as additive for the production of green materials. For that purpose, samples made out of epoxy matrix, reinforced with pyrolytic char from olive kernel at different concentrations, were manufactured and mechanically characterized at three point bending conditions. A maxi-

imum increase of 60% in bending modulus in comparison to the net matrix modulus was achieved. The new material developed in the present investigation is a green composite with an elastic modulus 60% higher than that of the pure matrix. Results were also compared with predictions derived by the application of a theoretical model previously developed by the first author for the evaluation of the elastic modulus in particulate composites taking into account not only the effect of filler-matrix adhesion but also the degree of dispersion of fillers into the matrix. It was found that predicted values as derived from the application of the model were in very good agreement with experimental findings. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2167–2173, 2011

Key words: biomaterials; composites; modeling; mechanical properties; pyrolysis; agricultural residues; olive kernel

INTRODUCTION

Increasing environmental awareness and growing global waste problems in our days has prompt researchers and industry to consider the development of friendly to the environment materials. Fortunately, there is an increasing movement of scientists and engineers who are dedicated to minimizing the environmental impact of using traditional engineering materials. “Green” composites made entirely from renewable resources could offer a unique alternative for those applications where moderate mechanical properties are needed. Green composites are used in many structural applications in the automotive and electronic, but also for packaging, housing, and building industry.

Although the composite system, presented in this work, is not an entirely green composite, it contains a fully biodegradable reinforcing phase. The development of an agricultural-based polymer matrix compatible with olive pits and consequently a fully biodegradable composite system is in our future plans. Olive pit is in fact an agricultural waste, so the cost of using it, is minimum to zero. Furthermore, there are plenty of renewable sources, especially in Mediterranean countries. Olive kernels are the solid residues that come from the olive oil production industry, and constitute one representative agro residue of the agricultural activity in Mediterranean region. Greece is the third in worldwide market share of olive oil production.¹ The amounts of olive kernel produced annually are very high. Other important advantages are the low specific weight, the high specific properties, and the low processing cost.

Combustion, pyrolysis, and gasification of agricultural wastes, appears to be promising technological applications for energy, biofuels, and material production. Combustion is the most applied method but

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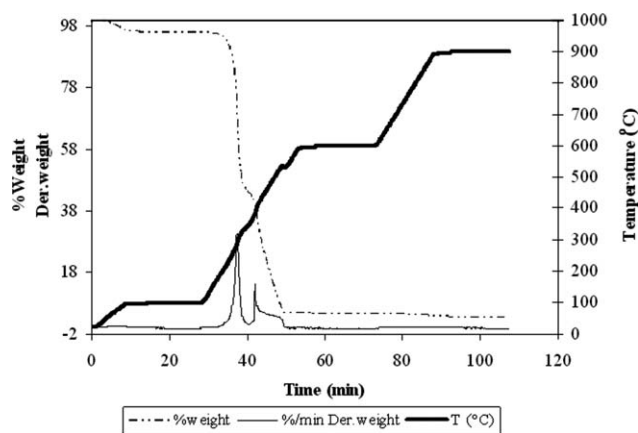


Figure 1 TGA diagram of olive kernel.

concerns about toxic emissions are great. From the other side, gasification and especially pyrolysis are considered CO₂ “neutral” alternative methods for the production of biofuels, H₂ and high added value products, contributing in green houses gases mitigation and atmospheric pollution prevention. When waste biomass is used, these technologies show promising economic viability, particularly if the bio-energy is used locally.² Biomass contains an average of 6% wt H, equal to 0.672 Nm³ of gaseous H₂ produced from 1 kg biomass.³ According to Orecchini and Bocci⁴ for biomasses suitable for thermochemical conversions (woody and cellulosic plant, etc.), it is possible to estimate a hydrogen production of about 65 g of H₂/kg of biomass a total efficiency ~ 40%.

During pyrolysis, biomass is heated in the absence of oxygen, or in a limited oxygen supply.⁵ The pyrolysis process includes a very complex set of primary and secondary reactions involving the formation of free radicals.⁶

The purpose of this study is to investigate whether the use of pyrolysis char from olive kernel, which is a carbon rich material with significant concentration in metals, as an additive for the production of green materials. This study is part of a research carrying out for the development of agricultural-based polymer matrix compatible with olive pits or other agricultural residues for a fully biodegradable composite system. For the objectives of this study, pyrolysis of olive kernels and characterization of the pyrolytic char was performed at the *Biomass Group of the Chemical Engineering Department, Aristotle University of Thessaloniki, Greece*, and the manufacture and mechanical characterization of polymer–matrix composites reinforced with olive kernel pyrolytic char were performed at the *Composite Materials Group of the Department of Mechanical and Aeronautical Engineering, University of Patras, Greece*. In addition, experimental values for the bending modulus were predicted by means of a recently developed by the first author model and a good agreement was found in all cases.

PROCESSES AND MATERIALS

Olive kernel characterization

The agricultural residue used for experimentation was olive kernels. Prior to use, the sample was grounded to desirable particle size (by a small laboratory scale mill) and sieved to powder of <1 mm diameter for enabling running the tests. The ultimate analysis of biomass was carried out using a CHN-LECO 800 Analyser, where the proximate analysis was resulted from the TGA analysis (Fig. 1) using a TA Instruments 2960. The results from the elemental and ultimate analysis of olive kernel are shown in Table I. As it can be observed from the elemental analysis, there is a significant amount of C wt % and H wt % in the raw material, whereas low ash and moisture content is observed.

TGA of olive kernel

TGA was performed in this study to record the weight loss of the raw material from which the ultimate analysis will be resulted. The analytical instrument used in this study was a type of TA Instruments 2960 in which the sample was heated with air according to the following temperature profile: the heating started at 30°C with rate of 10°C/min and remained at 100°C for 20 min. Then, the temperature increased up to 600°C with a rate of 20°C/min, and

TABLE I
Physicochemical Characteristics of Olive Kernel

Ultimate analysis (ww %, dry basis)		Proximate analysis (ww %, dry basis)	
C	48.61	Moisture	4.59
H	6.41	Volatiles	75.56
N	1.57	Fixed C	16.39
O ^a	43.41	Ash	3.46
HHV _b (MJ/kg)	20	LHV _b (MJ/kg)	18
Metal content (mg/kg olive kernel, dry basis)		Ash chemical analysis (ww %, dry basis)	
Zn	28.77	SiO ₂	0.91
Cu	29.87	Fe ₂ O ₃	0.21
		MnO	0.01
		TiO ₂	0.15
Ni	11.54	CaO	0.88
		MgO	0.26
Cr	19.70	SO ₃	0.11
		Na ₂ O	0.28
		K ₂ O	2.00
Mn	26.95	Al ₂ O ₃	9.00
		P ₂ O ₅	0.46
Al	463	L.O.I ^b	85.4
Fe	1236		

^a Calculated by difference.

^b Loss of ignition.

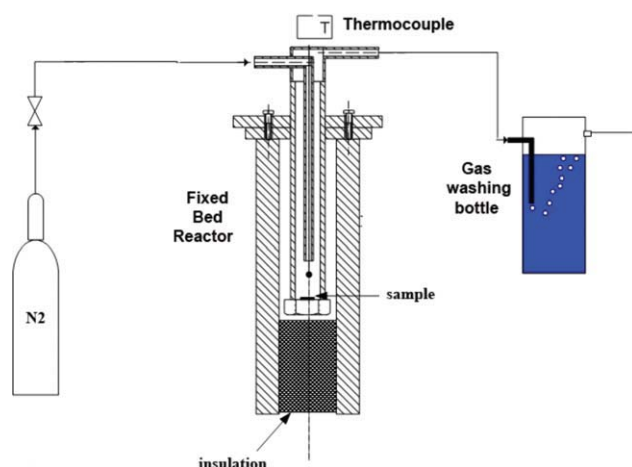


Figure 2 Schematic diagram of experimental set-up of the laboratory fixed bed reactor. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

remained constant for 20 min. With a rate of $20^{\circ}\text{C}/\text{min}$ the final temperature at 900°C was achieved.

Olive kernel is a lignocellulosic biomass which is typically composed by cellulose, hemicellulose, and lignin. The lignin is relatively more thermally stable than hemicellulose and cellulose.⁷ When lignocellulosic materials are pyrolysed, lignin is responsible for the char production.⁸ Under ordinary heating rate the hemicellulose pyrolysis is completely up to 350°C and cellulose pyrolysis between 250 and 500°C .⁷ Olive kernels have shown relatively high amount of lignin, which leads to high char yield.

Figure 1 shows that there are two main peaks during the increase of temperature from 100 to 600°C in the TGA analysis of olive kernel. In the spectrum of temperature up to 100°C , moisture content is vaporized. In the temperature range from 100 to 500°C two peaks are depicted Figure 1: The first peak is due to the light volatiles decomposition (hemicellulose and cellulose), and the second is attributed to the heavy volatiles (lignin) decomposition. After 500°C char oxidation occurred.

Pyrolysis of olive kernel

The pyrolysis experiments were performed in a batch, laboratory scale, and fixed bed reactor, as shown in Figure 2. The experimental facility consists of four main parts: (a) the downdraft fixed bed reactor, which operates at atmospheric pressure (b) the N_2 providing section, (c) the gas cleaning section, and (d) the temperature control section. The reactor was constructed by a 316-stainless steel tube and is surrounded by an individually controlled electric heater that aims at supplying heat for start-up and counter heat losses during reactor's operation. The biomass feeding is batch performed manually after appropriate dismantling of the reactor tube. The amount of sample used was approximately 30 g in each experiment.

The experimental procedure was as follows: The reactor was placed vertically into the furnace and heating was turned on by setting the controllers at the selected operating temperature of 800°C (heating rate $\sim 27^{\circ}\text{C}/\text{min}$), after inert atmosphere was achieved. To ensure slow pyrolysis, the sample was left 60 min at 800°C . When the reactor was cooled down the char residue was weighted. The produced gas passed through the cleaning system and then was left in the atmosphere. The next experiment was performed after thorough cleaning for eliminating possible memory effects and tar fouling dangers. Figure 3 shows the raw material before pyrolysis and the obtained char, whereas Figure 4 shows the SEM analysis of the char.

The conversion of olive kernel by slow pyrolysis reached the 74%. Thus, having an initial mass of 30 g, the char that was collected after the experiment was about 7–8 g.

Pyrolysis char characteristics

The ultimate analysis of the pyrolytic char is shown in Table II. It is shown that the carbon percentage in the pyrolytic char is ~ 66.98 wt %, and the hydrogen ~ 1 wt %. Metal analysis was also conducted to the solid product/char (Table I), and showed that the

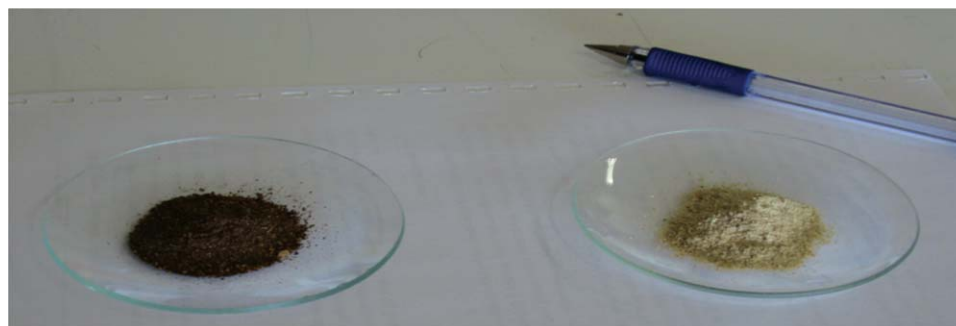


Figure 3 Raw material before pyrolysis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

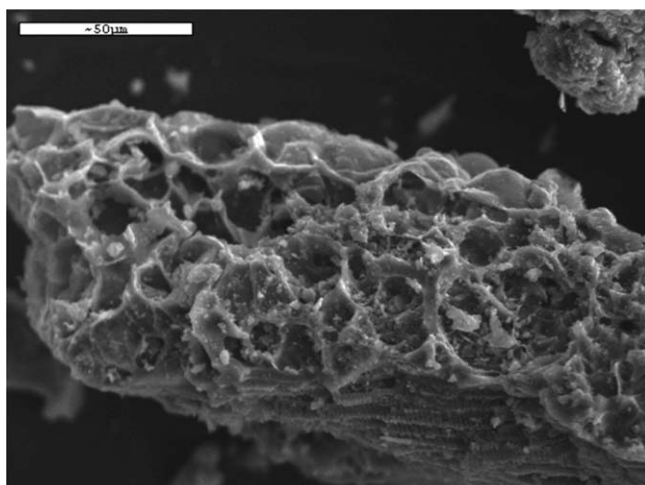


Figure 4 SEM analysis of pyrolysis char (800°C and 1 h).

raw material has high content of Fe. The low heating value of the char as a biofuel was ~ 19 MJ/kg, calculated by eq. (1) using the % wt of C, H and from the elemental analysis of the char.

$$\text{LHV} = 0.34\%C + 1.4\%H - 0.1\%O \text{ [MJ/kg]} \quad (1)$$

GREEN POLYMERIC COMPOSITES PRODUCTION

Manufacturing procedure

Polymer composite formulations were prepared by mixing pyrolytic char of olive kernels with an epoxy resin (RENLAM CY 219 with RENLAM HY 5161 as a hardener). Pyrolytic char of olive kernels and resin were carefully mixed for 30–40 min, to achieve uniform distribution of grains in the matrix. Proper amounts of the curing agent were then added. The olive-resin mixture was then placed in a vacuum pump for 3 min to reduce voids in the composite. Subsequently, the mixture was poured in Plexiglas molds (90 mm \times 95 mm \times 3 mm) of suitable capacity. Next, the filled molds were placed in an oven for the curing phase. The following curing process was applied: temperature was raised at 5°C/h from ambient to 50°C and maintained constant for approximately 24 h. As shown in Figure 5, the particle shape was irregular with a mean maximum diameter 100–200.

Static mechanical tests

Bending measurements^{9–16} were carried out with a conventional Instron type tester (INSTRON 4301), at room temperature. Specimens with a gauge length of 63 mm were tested at a constant strain rate of 1 mm/min. The repeatability of results confirms the good manufacturing conditions of the specimens and the appropriate selection of the curing processing conditions. The samples were cut out from the

cured block and their final dimensions were approximately 90 ± 0.01 mm, 12 ± 0.01 mm wide and 2.85 ± 0.01 mm thick.

MODELING

Mechanical behavior of polymer composites reinforced with particles is complex mainly because it is affected by a great number of parameters, such as: (1) particle stiffness, (2) particle–matrix interphase,^{9,11} (3) particle–matrix bond strength, (4) filler concentration,¹¹ (5) particle agglomeration,^{17,18} (6) strain magnification, (7) dewetting,^{19–21} (8) particle distribution,¹¹ (9) crazing,^{22,23} and (10) degree of mixing.

Filler particles act as stress concentrators and a non-uniform stress field is obtained in a stressed sample. In addition, since any deformation of a polymeric matrix results in nonuniform straining in the vicinity of a filler particle, the localized behavior is nonhomogeneous. Therefore, models analogous to those used for the unfilled polymers would be expected to yield only approximate correlations. In addition, physical interaction between particles amplifies the complexity of the already intricate response behavior of the filled polymer, especially at high filler loadings.²⁴

A semiempirical two-parameter equation describing the moduli of particulate systems has recently been formulated by Papanicolaou as follows:

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

where E_c , E_m , and E_f are the composite, the matrix, and the filler moduli, respectively; V_f is the filler-volume fraction, k is the adhesion coefficient that can be experimentally determined from a single tensile test of a specimen loaded with particles at very low filler-volume fraction, and λ is a coefficient related to the degree of agglomeration of the filler particles and which can be experimentally determined from a single tensile test of a specimen with high filler-volume fraction.

It is important to say that both k and parameters vary in the range 0–1, both having a clear a physical meaning:

More precisely, $k = 0$ corresponds to no-adhesion condition, while $k = 1$ corresponds to filler-matrix perfect addition. In addition, $\lambda = 1$ means perfect

TABLE II
Ultimate Analysis of Pyrolysis Char

Ultimate analysis (% ww, dry)	
C	66.98
H	0.96
N	1.56
O ^a	30.5

^a Calculated by difference.

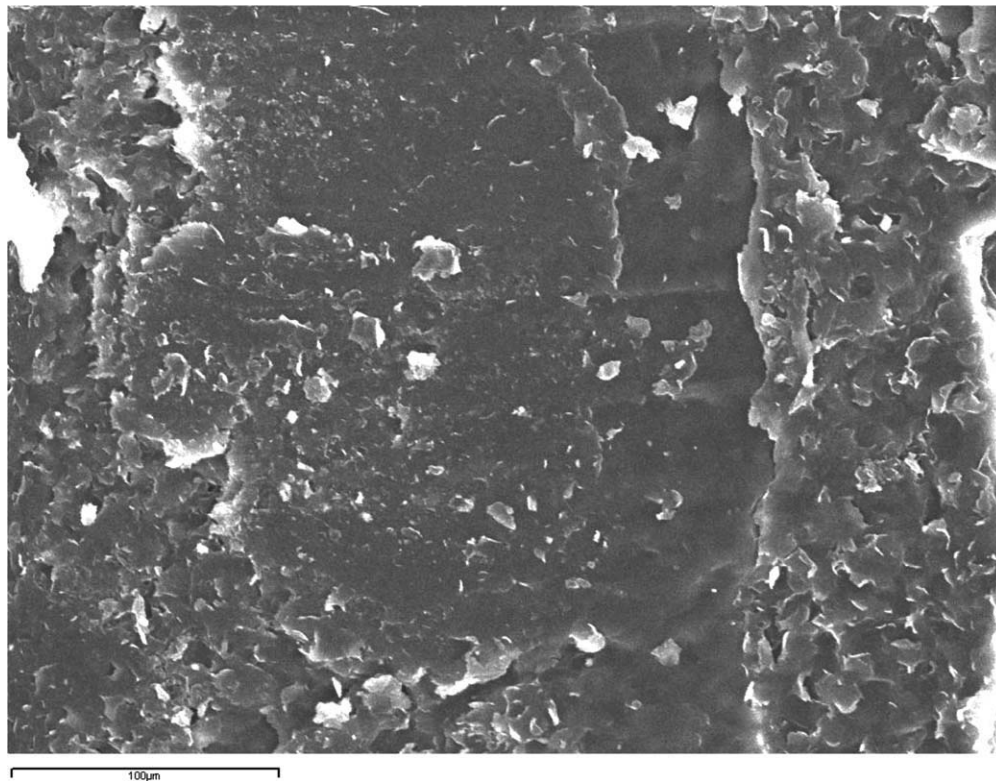


Figure 5 SEM micrograph of resin reinforced with 18% V_f filler reinforcement.

particle distribution (no agglomeration) within the matrix, while values within the range of $0 < \lambda < 1$ correspond to respective degree of agglomeration.

The degree of adhesion, k , is determined at low filler volume fractions since at low V_f there is no agglomeration and the reinforcing effect is mainly affected by the filler-matrix degree of adhesion. In contrary, the agglomeration parameter is determined at high filler-volume fractions, since at high filler loadings, agglomeration is more likely to exist and the composite mechanical behavior is dominated by the formation of aggregates.

In addition, as it is clear from the abovementioned equation,

- (a) For $k = \lambda = 1$ (i.e., for perfect adhesion and uniform particle distribution), the predictive equation gives the linear rule of mixtures.
- (b) for $k = \lambda$, a linear variation of E_c with V_f is depicted.
- (c) for $k \neq \lambda$ a parabolic variation is depicted.

RESULTS

Mechanical testing results

The variation of the flexural strength of the composite under investigation with the filler weight fraction is shown in Figure 6. Each value represents the

average from three different specimens. Maximum strength initially decreases with the volume fraction until 10% of reinforcement and this is followed by a subsequent increase remaining always lower than respective strength of the unreinforced material. The observed behavior can be attributed to the

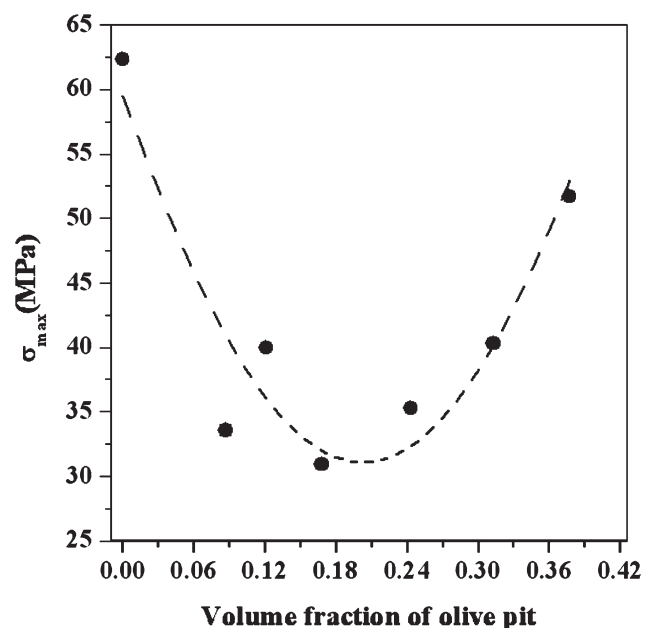


Figure 6 Maximum bending strength as a function of the volume fraction of reinforcement.

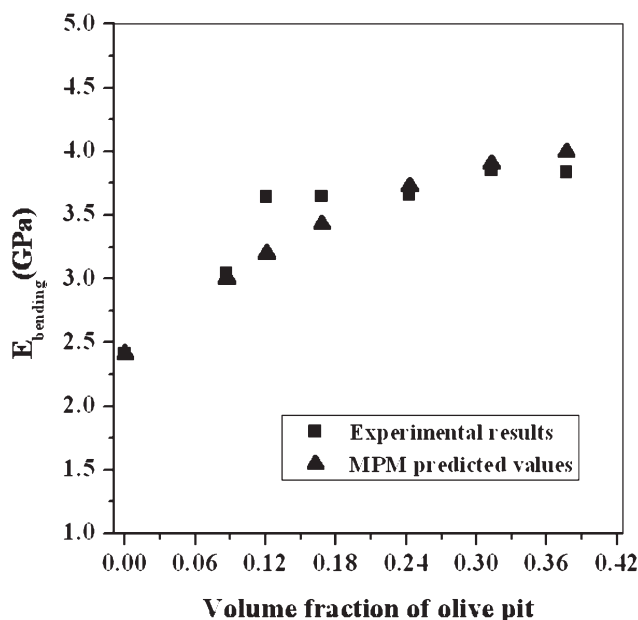


Figure 7 Comparison between experimental and theoretical results for maximum bending modulus as a function of the volume fraction of reinforcement.

simultaneous existence of two antagonistic phenomena. The first phenomenon is the bad degree of adhesion exhibited between reinforcing particles and the polymer matrix resulted in the creation of interfacial voids which, in turn, leads to a decrease in strength when compared with respective values for the pure resin. On the other hand, the addition of filler results in a partial reinforcing effect which is stronger as the filler concentration increases. The simultaneous existence of both phenomena leads to the observed in Figure 6 variations.

Figure 7 depicts the variation of the bending modulus with the volume of pyrolytic char of olive kernels. It can be observed that bending modulus is increasing continually reaching a saturation level at 0.313 V_f and then it remains almost constant. The initial rate of increase is high and then it is lowered tending to zero as the curve reaches the plateau. Composites' modulus is increasing because of the presence of the reinforcement (pyrolytic char of oil practically cannot be deformed, and this influences deformation condition and mechanical behavior of matrix-resin, the matrix deformation increases essentially with increase in pyrolytic char of oil concentration at constant deformation of specimen, and this increases the modulus); however, at the same time, as the percentage of pyrolytic char of olive kernels is increased, the number of aggregates is increasing too (which decrease composites' modulus) and as a result the modulus of the composite remains almost equal. What is most important is that at 0.377 V_f of reinforcement, an increase on the order of 60% in bending modulus in comparison with the unrein-

forced resin is achieved representing the highest percentage of improvement observed. However, even for only 0.087 V_f of olive particles the observed improvement in modulus is significant (27% in comparison with the pure resin).

Modeling results

In this article, the above-mentioned model has been applied for the materials considered (with $k = 1$ and $\lambda = 0.1$) and the results are shown in Figure 7. As it is clear a fair agreement between experimental values and predicted ones is observed.

CONCLUSIONS

In this article, polymer–matrix composites reinforced with olive kernel pyrolytic char were manufactured and mechanically characterized. The new material developed in this investigation is a green composite with an elastic modulus 60% higher than that of the pure matrix. The influence of particle-weight fraction (0–25%) on the bending behavior of the particulate composites manufactured was thoroughly studied. Even with filler loadings on the order of 5% wt olive particles, a 27% increase in the bending modulus was obtained. As a result, the produced polymer composite exhibits an excellent performance in combination with the fact that it is environmentally friendly of very low cost composite.

In addition, a recently developed by the first author model was applied for the prediction of the bending modulus of the composites developed. A good agreement between experimental findings and predicted values was found in all cases.

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