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Impact Strength, Flexural Modulus and Wear Rate of PMMA Composites Reinforced by Eggshell Powders

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K E Y W O R D S

PMMA composite, eggshell powder, impact strength, flexural modulus, wear rate.

A B S T R A C T

In the present study, the impact strength, flexural modulus, and wear rate of poly methyl methacrylate (PMMA) with eggshell powder (ESP) composites have been investigated. The PMMA used as a matrix material reinforced with ESP at two different states (including untreated eggshell powder (UTESP) and treated eggshell powder (TESP)). Both UTESP and TESP were mixed with PMMA at different weight fractions ranged from (1-5) wt.%. The results revealed that the mechanical properties of the PMMA/ESP composites were enhanced steadily with increasing eggshell contents. The samples with 5 wt.% of UTESP and TESP additions give the maximum values of impact strength, about twice the value of the pure PMMA sample. The calcination process of eggshells powders gives better properties of the PMMA samples compared with the UTESP at the same weight fraction due to improvements in the interface bond between the matrix and particles. The wear characteristics of the PMMA composites decrease by about 57% with increases the weight fraction of TESP up to 5 wt.%. The flexural modulus values are slightly enhanced by increasing of the ESP contents in the PMMA composites.

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1. Introduction

The combination of two or more materials to achieve superior properties by formed of composite materials from those of their constituents. Polymer matrix composites consist of a matrix as polymer resin combining with filler as the reinforcement medium [1]. A composite material can have excellent and unique property due to it was a combination of the most desirable properties of the components. Polymer matrix composites reinforced by particles are widely used, resulting in the simple of the preparation methods and it has a lower cost than polymers reinforced with fibers [2].
Chicken eggshell has represented as waste material worldwide. It was considered as one of the environmental problems, particularly in those countries where the egg product industry is well widened [3]. The eggshell wastes can be made a good bio-filler or reinforcement medium in many composites

due to its lightweight, availability and chemical composition. However, the eggshells don't have of any economic value, but generally; it is rich in many minerals [4].
The eggshells material considered as a source of the calcium, and there are many experiments have been done to demonstrate the positive effects of the eggshell as a component in various products. The eggshell materials can be utilized as the low cost of filler materials and relatively simple preparation methods for the fabrication of different products [3,5].
Eggshell waste is potentially considered an appropriate candidate for an environmental filler material for reinforcing bio-polymeric composites for enhancing its heat stability and the mechanical properties [6]. The chemical composition of eggshell material consists of 94 wt.% of calcium carbonate in the form of calcite and 6 wt.% of other organic compounds such as calcium phosphate, magnesium car-bonate, collagen and other proteins [5,7]. Therefore, using eggshell powder can be a natural source of calcium carbonate ($CaCO_3$). Filling of thermoplastics materials with $CaCO_3$ can be useful for many applications. In general, these fillers can improve the mechanical properties of the composites [6,8].
This work aims to study the effect of the eggshell powder (ESP) additions as bio-fillers on the impact strength, flexural modulus and wear rate of the poly methyl methacrylate (PMMA) matrix composites. Furthermore, this study examines the influence of the calcination process for eggshell powder on the mechanical properties of the PMMA/ESP composites. The produced PMMA bio-polymer composite can be useful for developing denture base properties, when the strengths are required at a low cost.

2. Experimental Work

I. Preparation of Materials

The matrix material used in this study is self-curing base resin poly methyl methacrylate (PMMA). PMMA powders and monomer are mixed relative to the percentage of a mixture which equals (60:40). The polymeric PMMA was supplied from Otto Bock Company. The PMMA material has a density of 1.18 g/cm^3.
The used eggshell (ES) in this work was the white color type. It was obtained from local sources. Broken ES is cleaned and boiled in tap water at 100ºC for 5 minutes, and then dried in the fresh air. ES was crushed and ground by the porcelain ball mill. The particle size of prepared eggshell powder was about 0.5 µm. Figure 1 reveals the particle size distribution of prepared ESP.
The ESP was used as reinforced materials in two status types: (1) untreated eggshell powder (UTESP) (after grinding); and (2) treated eggshell powder (TESP) by heating it at 750ºC for 1 hour in an electric furnace. Figure 2 shows the used eggshells in this work. The ESP was then examined by X-ray diffraction (XRD) as shown in Figure 3. The XRD patterns reveal that ESP composed of calcium carbonate, which presented all diffraction peaks are characteristics in calcite ($CaCO_3$) phase according to JCPDS card no. (05-0586). Figure 3-b shows that the XRD pattern of TESP has more crystallization than the XRD of UTESP in the Figure 3-a, and this is due to the calcination process of ESP.

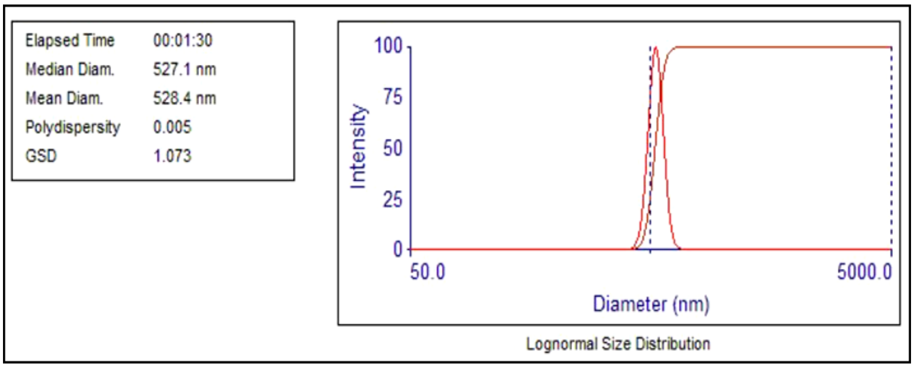

Figure 1: Particle size distribution of the prepared eggshell powders

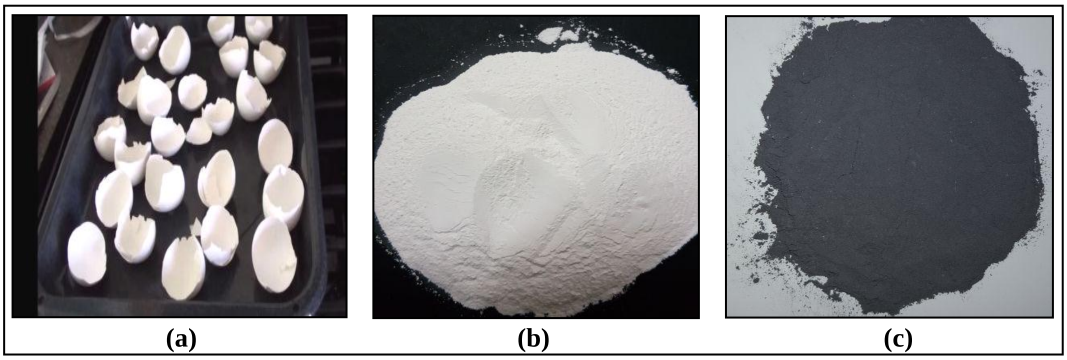

Figure 2: The eggshells (ES) used: (a) broken ES; (b) UTESP; (c) TESP

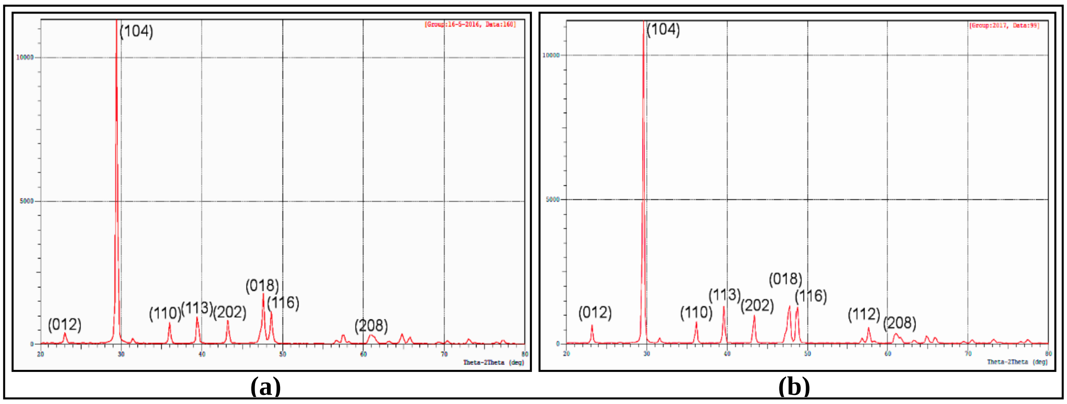

Figure 3: XRD analysis for the ESP: (a) UTESP; and (b) TESP

II. Specimens Preparation

Two types of PMMA/ESP composite samples have been prepared. One of them was PMMA/UTESP composites, and the other was PMMA/TESP composites. Both UTESP and TESP were mixed with the PMMA matrix at different weight fractions of (1, 2, 3, 4 and 5) wt.%. The used mold for preparing the specimens was made from cast iron. The internal walls were coated with a thin layer of Vaseline to avoid sticking the samples on the mold wall. According to the amount of PMMA acrylic resin required for filling the metallic mold cavities, the powders and liquid many changes will take place due to the solution of polymer in the monomer. Weighting the amount of reinforced material (eggshell powder) was by using an electronic balance with an accuracy of (0.0001) digits, depending on the total weight of matrix material (acrylic powder (PMMA)+liquid monomer (MMA)) required for filling the mold cavities by using the theory of rule of mixtures. The acrylic powder (PMMA) and ESP were mixed together at room temperature for 20 seconds using a wooden stick until to get a homogeneous mixture. Then the mixture was poured from one corner into the mold (to avoid bubble formation which causes cast damage) and the uniform pouring is continued until the mold is filled to the required level. The mixture was left in the mold for about 1 hour at room temperature to cure.

III. Testing of Mechanical Properties

Figure 4 shows the prepared samples for the different mechanical tests. The impact strength test of the PMMA/ESP composite samples was carried out on the Izod impact machine to determine the impact energy. According to the standard of (ISO-180), the samples were cut to (80×10×4) mm in dimensions. A V-notch deep of 2 mm has been cut off for providing stress concentration during the impact test. The sample was then placed on the machine and the pendulum was raised and allowed to swing-fall under the gravity hitting the samples. The impact strength (Gc) calculated from the following equation [8]:

$$Gc = \frac{Uc}{A} \qquad (1)$$

Where: Uc: the energy required for sample breaking (KJ); A: the sample cross-section area (m^2).

The wear rate of the pure and reinforced samples was measured by means of a pin-on-disk which consists of rotating disc made of tool steel. The samples were prepared in a cylindrical shape of (10 mm diameter and 15 mm height). The wear characteristics were measured at four constant parameters of 5 N applied load, 2 min period time with sliding speed of 950 rpm, and sliding distance of 60 mm. Wear rates were calculated from careful measurements of weight losses per sliding distance. After installing the sample on the disc with making sure that full contact is occurring between them, the 5 N loads are applied to the sample perpendicularly for 2 min. After running through a fixed sliding distance, the specimen was removed, cleaned, dried and weighed to compute the weight loss resulted from wear. Wear rate can calculate by the difference in weight $\Delta W = (W_1 - W_2)$, and according to the following relationship [8,9]:

$$W.R = \frac{\Delta W}{S.D} \quad (2)$$

$$S.D = S.t \quad (3)$$

Where: W.R: weight sliding wear rate (g/mm); W_1: weight of the sample before testing (g); W_2: weight of the sample after testing (g); S.D: sliding distance (mm); S: speed (mm/min); t: time (min).

The flexural modulus of polymer composite samples was calculated by three-point bending test. According to ASTM D 790-86, the samples were cut in dimensions of (191×13×4.8) mm and then bent using improvised support with a center point load to breaking point. From the slope of the load vs. deformation graph can calculate the flexural modulus (E_f) by the following equation [8,10]:

$$E_f = \frac{F\,L^3}{48\,I\,\delta} \quad (4)$$

Where: F: the fracture load; L: the distance between the two supported points; I: the moment of Inertia; δ: the measured deformation.

3. Results and Discussion

I. Impact Test

The impact strength results of PMMA/ESP composites for all samples that were prepared in this work are shown in Figure 5. This figure illustrates the effect of various types of the ESP (UTESP and TESP) on the impact strength of PMMA composites.

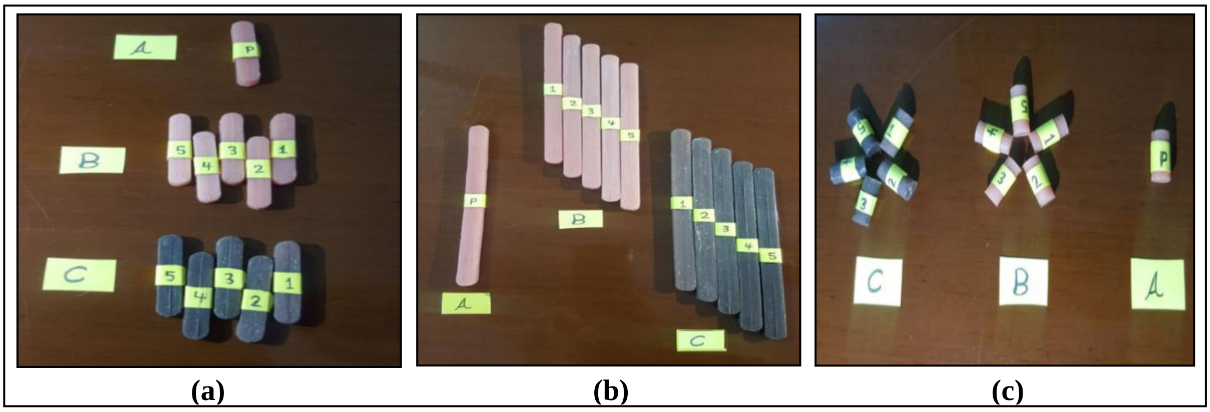

Figure 4: The prepared composite samples for: (a) impact test, (b) bending test, and (c) wear test. A-sample is a pure PMMA; B-samples for PMMA/UTESP composites; and C-samples for PMMA/TESP composites.

It can be seen that the addition of ESP leads to an increase in the impact strength of pure PMMA and reach a maximum value at the addition of 5 wt.% for both ESP additions types (UTESP and TESP). The increase in impact strength of composites was about twice the value of the pure PMMA sample. The impact strength is the energy required to break the sample. The energy absorbed in the PMMA samples is found to enhance by increasing the ESP percentages. The ESP reinforcing particles are believed to absorb part of the delivered energy and prevent the formation of the fractures in the PMMA matrix. In addition, the increase in impact strength might be ascribed to the gradual enhancement of the PMMA crosslinking with the addition of ESP. This finding comes into agreement with previous studies [6,8,11]. Furthermore, the TESP additions enhanced the impact strength of the composite material more than UTESP additions. This is due to the calcination process of ESP increases the calcite ($CaCO_3$) effectively by increasing its crystallinity as shown in the TESP XRD analysis. Furthermore, this process leads to remove most of the organic materials and impurities that can be existed in the ESP [12]. This leads to improve in the interface bond between the PMMA matrix and the ESP particles.

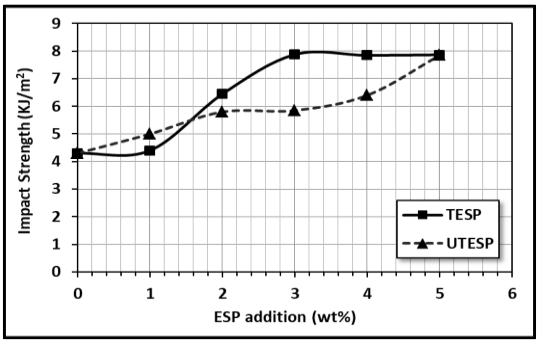

Figure 5: Impact test of PMMA/ESP composites

II. Wear Test

Figure 6 shows the results of wear tests of PMMA/ESP composite samples. This figure reveals that the wear rate of PMMA composites reduced with increasing ESP addition for all specimens. This is because of increasing the ESP content, which composed of calcite that has a higher hardness than the PMMA matrix, and thus can reduce the sliding wear rate. In addition, this behavior might be understood in terms of frictional forces acting between the sliding surfaces. Decreasing in the frictional forces will give rise in wear resistance [9]. It is known that with the increase of load the contact between two surfaces increases, leading to rapid deformation of polymer protrusions because compressive and frictional forces dominate in dry sliding conditions. So, the presence of ESP as reinforcing particles in these protrusions reduces wear rates [8,13]. Also from this figure, it can be noticed that the PMMA/UTESP composite samples have higher values of wear rate than PMMA/TESP samples. This is attributable to good interfacial bonding between the matrix and TESP filler type; which made tough and rigid surfaces of the PMMA matrix resin.

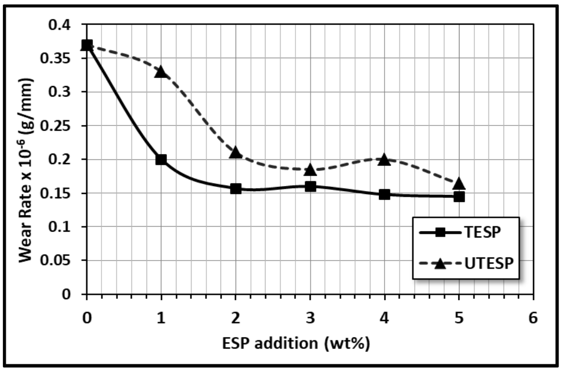

Figure 6: Wear rate of PMMA/ESP composites.

III. Three-Point Bending Test

The results of the flexural modulus obtained from the three-point bending test that carried out on PMMA/ESP composites presented in Figure 7. It can be noticed that the values of flexural modulus were slightly increased with increasing weight fraction of both types of ESP particles in the PMMA composites. This is because to the propagation of the crack can be changed by good bonding between the PMMA matrix and ESP particles. Also, this increase may be due to the fact of the high flexural modulus value of the ESP particles as compared with the PMMA matrix [14]. The values of flexural modulus for the PMMA/TESP composite samples are higher than the PMMA/UTESP composite samples. This behavior is attributed to the nature of ESP particles bonding with the PMMA matrix. The TESP particles might make high interfacial shear strength with PMMA matrix as the formation of cross-links bonding or supra-molecular which prevents the propagation of cracks inside the material. Moreover, the incorporation of the hard particles inside polymers enhances the stiffness of the polymer composites by limited the mobility of matrix chains [10,15].

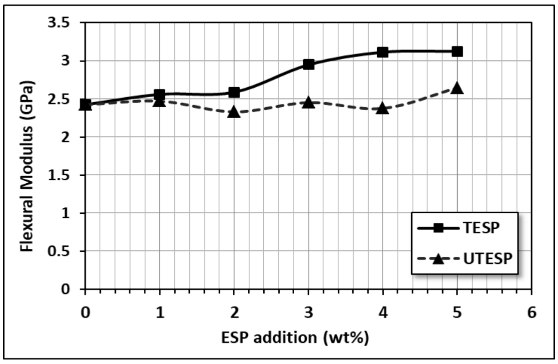

Figure 7: Flexural modulus of PMMA/ESP composites.

4. Conclusion

The mechanical properties of PMMA matrix composites such as impact strength and wear rate are greatly influenced by the ESP addition. The flexural modulus of the composites is slightly enhanced by increasing of the ESP content. The calcination process of eggshell powder, TESP, gives better mechanical properties of the PMMA composite compared with untreated eggshell powder, UTESP, for the same weight fraction. The maximum value of impact strength was when adding 5 wt.% of ESP to the PMMA samples. The increase in impact strength of the composites was about, twice the value of the pure PMMA sample. The minimum value of wear rate was when adding 5 wt.% of ESP to the PMMA matrix composite.

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