Characterization the mechanical properties of Sustainable poly(methyl methacrylate) biopolymer

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ABSTRACT

Denture materials must have robust mechanical properties to withstand high pressures within the mouth. The present study investigates the mechanical properties, including the tensile, hardness, and impact of a new denture composite made of poly(methyl methacrylate) (PMMA) and reinforced with eggshell (ES) powder. The new PMMA (PMMA-EC) was manufactured by mixing different ratios of ES (1 to 7% wt.) with 5% (wt) of Chitosan (CS) (as antibacterial). The new composite was tested for the tensile, hardness, and impact, and the results were compared with those of the traditional PMMA-EC (containing only 5% chitosan). Additionally, a Scanning Electron Microscopy (SEM) was used to examine the dispersion of ES in the material. The results of this study indicated that adding 1% of ES powder did not affect the mechanical properties of the composite. However, increasing the ratio of ES powder to 5% achieved the best improvement in the mechanical properties of the new composite, while increasing the ES ratio by more than 5% caused a considerable decrease in the mechanical strength. Generally, the tensile, hardness, and impact of the new denture composite were examned, respectively.

Keywords: PMMA; eggshell, Chitosan; tensile strength; surface microhardness, impact strength

1. Introduction:

Huge quantities of chicken eggs are consumed daily, and, as a result, a significant amount of eggshells (ES) is wasted with the domestic solid wastes, which contributes to the deterioration of the environment and also exerts an extra load on the local authorities. The wasted ES must be recovered and recycled to minimize its impacts on the environment and economy [1]. Many studies confirmed the recyclability of the ES due to its chemical composition, which is mainly (about 95%) made up of calcium carbonate ($CaCO_3$) in the form of calcite. The latter can be utilized as a bio-filler to strengthen other polymeric matrices [2, 3]. Thus, it is considered a renewable, widely available resource with low cost and unique chemical composition. The investigation of bio-filler reinforced biopolymer composites has increasingly become the focus of many studies [2, 3]. Therefore, this study aims at recycling the ES in manufacturing a new type of poly(methyl methacrylate) (PMMA).

In dental applications, acrylic resin, PMMA is widely used for fabricating dentures because of its high biocompatibility, reliability, dimensional stability, tasteless, odourless, tissue friendliness, and low toxicity, high tooth adhesion, insolubility in bodily fluids, relative ease of manipulation, and colour stability. However, the impact strength, which is a vital property of any denture base, of PMMA is relatively low, which limits its widespread usage [4, 9, 10]. The geometry of denture bases is complicated, and stresses can be focused on notches, causing fractures in the denture base. The PMMA denture base is usually subjected to a lot of stress within the mouth as a result of the forces exerted during chewing [1, 5, 7]. Several investigations have been done to address the issues of PMMA by adding seashells [4, 11], aluminium oxide [12, 13] and nitrile rubber particles with zirconia [11, 14]. Other studies utilized Chitosan (CS) because it is a biopolymer with antibacterial and hemostatic characteristics. Thus, CS is gaining popularity in the field of dental materials research. CS is mostly produced from chitin by N-deacetylation, making it non-toxic, biocompatible, and biodegradable material. Many researchers have combined CS with PMMA polymer to produce composites with good biological characteristics [1, 10, 15].

Pradhan and Sahoo (2017) studied the effects of eggshell (nano-CaO) as a bio-filler on the tensile and compression strengths and thermal stability of CS grafted PMMA using various percentages (from 0.1 to 0.9%) of nano-CaO and found the best percentage of nano-CaO was 0.35%. Al-Hareb et al. (2015) studied the mechanical properties of the denture base made from nitrile butadiene rubber (NBR) with two types of ceramic fillers (Al_2O_3 and YSZ). The results showed that the mean impact strength and fracture toughness significantly improved at mixing ratios: 7.5% NBR, 2.5% $Al2O3$, and 2.5% YSZ. Al-Hotan et al. (2021) studied the influence of three types of fillings (ZrO_2 nanoparticles, TiO_2 nanoparticles, and E-glass fibre) on the flexural strength and surface hardness of heat-cured PMMA. The filers were added at various weight percentages (1.5, 3, 5, and 7%). The results showed that the optimum filler percentage (3–5% ZrO_2, 1.5% TiO_2, and 3–7% E-glass fibre) increased the flexural strength of PMMA. Gad et al. (2019) examined the effects of hybrid reinforcing of PMMA with various ratios of zirconium oxide nanoparticles (nano-ZrO_2) and glass fibres (GFs) on the flexural impact strengths of the denture base. 160 specimens were made from heat-polymerized acrylic resins using the water bath method, with the following nano-ZrO2/GF concentrations: 0-5%, 4-1%, 3-2%, 2.5-2.5%, 2-3%, 1-4% and 0-5%. The optimum flexural strength (94.05±6.95 MPa) and impact strength (3.89 ±0.46 kJ/m^2) were obtained with PMMA reinforced with 2.5% of nano-ZrO_2 and 2.5% of GF [17].

In the same context, the purpose of this study is to manufacture PMMA reinforced with ES and CS powder.

2. Materials And Methods

2-1 Materials

The cold-cured PMMA used in this study was supplied by Shanghai New Century Dental Materials Co.Ltd, China. The used PMMA has two components; the first component is a Monomer liquid, which is colourless, combustible, with a pleasant acrid odour. The second component is a pink powder.

ES was collected from local places in Babylon city Iraq. Firstly, ES was carefully cleaned with tap water and detergent to eliminate any unwanted elements, such as dust, solid dirt, chicken faeces, and the internal membrane of the ES. Then, clean ES was washed with deionized water and kept in the laboratory to dry before grinding them using a 150 W coffee grinder with a capacity of 70 g for 15 minutes to create a fine powder, as shown in fig (1).

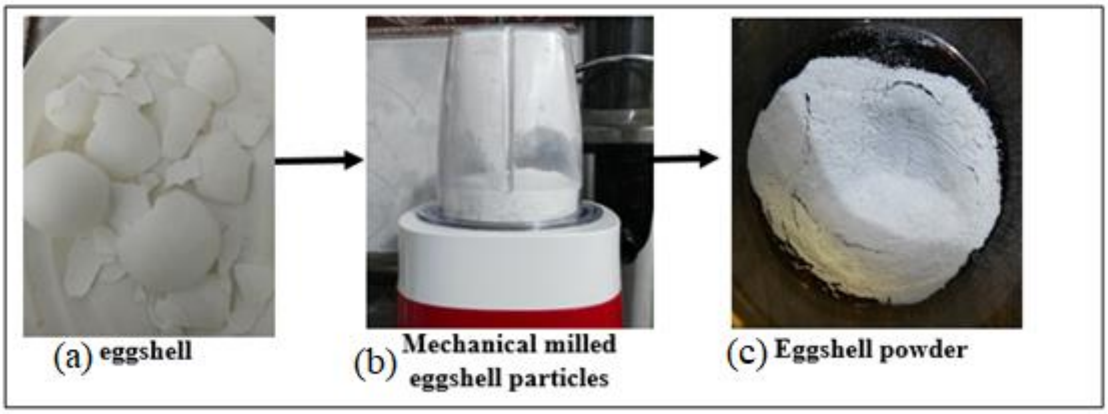

Fig. 1. Preparation of ES powder; a) natural ES, b) Grinder, and c) ES powder.

2-2 Manufacturing of PMMA biocomposites

The powder of PMMA was combined with the different ratios of ES powder (0%, 1%, 3%, 5%, and 7% by weight) and 5% of CS [18]. Mortar and pestle were manually used to smash the materials thoroughly. The materials combination was progressively added to the recommended amount of MMA monomer (17g: 1 ml) in a beaker and continuously stirred until a dough-like mixture was produced. The preparation steps were done in an ice water bath because of hot weather and the exothermic nature of the reaction. The final mixture was poured into greased moulds (75 x 50 x 3 mm) and (75 x 50 x 4 mm) to produce the composites sheets. Then, the sheets were mechanically cut to prepare the standard specimens. Table 1 shows the composition of different powder reinforced composites

Table (1): Composition of different powder reinforced composites.

ES percentage (%)	CS percentage (%)	PMMA powder percentage (%)	MMA Liquid percentage (%)
0	5	47.5	2.79
1	5	47	2.76
3	5	46	2.7
5	5	45	2.64
7	5	44	2.58

2-3 Mechanical properties

After one hour the composite sheet hardened, it was demoulded and stored at room temperature. The specimens with dimensions of 75 × 50 × 3 mm were used for the tensile tests that were carried out in accordance with ASTM D638-03) [1]. The sample was subjected to the tensile force until it failed, and a stress-strain curve was obtained. The impact strength of specimens, with dimensions of 80 x 10 x 4 mm, was tested using an Izod pendulum impact testing device in compliance with ISO 179-1:2010.

The impact strength of the un-notch specimen was measured as a function of the number of joules of energy absorbed when the specimen was breaking [18]. Surface microhardness was measured using specimens with dimensions of 12 x12 x 3 mm and a digital Vickers hardness tester, in accordance with ASTM E 384-89 [14]. One side of the specimen was polished and subjected to 30 g for 30 seconds to obtain Vickers values. All experiments were repeated three times, and the average value was determined for each specimen [12].

3. Results and discussion

3.1. Mechanical properties

Denture tensile strength is important in determining how well a resin will perform under mastication/chewing stress [1, 16]. Previous researches have discovered that changes in the particle/fibre ratio can influence the tensile strength of PMMA resins [1, 14, 16]. This work found that including ES fillers into the PMMA matrix increased the tensile strength compared to the control specimen, where it was noticed the tensile strength of the new PMMA samples increased from 4.764 to 4.234 and 8.286 MPa when the ES ratio increased from 1% to 3% and 5%, respectively. However, increasing the ES ratio to 7% decreased the tensile strength to 6.02 MPa. Figure 2 clearly shows that adding more than 7% ES powder makes the composite brittle due to higher crosslinking density. The results of this investigation comply with the results of earlier studies that evaluated the influence of ES powder on the tensile of PMMA dentures, such as the results in Pradhan and Sahoo [1].

The Vickers microhardness (HV) of all specimens are illustrated in Figure 3, which shows that adding ES powder improved the hardness. Although there was no significant change in the hardness at low ratios of ES powder (1%), adding 3% of ES powder increased the hardness up to 13.53HV.

The maximum durability was 15 HV that achieved by adding 5% of ES powder, which is larger than the durability of a composite with 3% of ES.

Figure 5 clearly shows that adding more than 7% of ES powder resulted in a substantial decrease in hardness. The increase in filling content improves the surface hardness to achieve the optimum level. This conclusion is consistent with earlier studies that demonstrated adding the ES powder in PMMA enhanced the denture base surface hardness [17]. This can be explained by the fact that the agglomeration of the composite is decreased when the optimum filler level of the matrix is attained using magnetic stirrers and speed mixers [14, 19].

The impact strength result of PMMA-chitosan was low when compared to the reinforced PMMA-chitosan matrix with ES filler (1, 3, 5%). The impact strength of the reinforced PMMA steadily increases as the ES filler content increases up to 5%. The addition of 1, 3, and 5% of ES powder increased the impact strength from 4.556 to 6.023 and 7.87, while increasing the ES powder ratio to 7% decreased impact strength to 5.34 MPa, as shown in figure 4. This result is consistent with the findings of Spasojevic et al. (2015) and Alhareb et al. (2015).

The uniform dispersion of ES powder at its optimum concentration (5%), Figure 5b, has been enhanced when proper powder mixing is made using Mortar and pestle. Milling the PMMA, CS and ES powder results in greater ES particles dispersion and enhanced mechanical properties. The composite containing 7% ES powder has more micropores, which resulted in a reduction in mechanical properties. The SEM images of the failure surface of the composite with 1, 3, 5% of ES powder, Figure 3b, indicates a homogeneous distribution of particles gradually increases with the ES ratios. Also, the images revealed an excellent adhesion between the ES particles and the PMMA matrix, and no microvoids were formed. As a result, ES powder strengthens the PMMA. Figures 5b, 5c, and 5c demonstrate the presence of filler particles within the microspores, and some MMA monomer remains unreacted in the polymer resin after polymerization. It should be mentioned that the unreacted monomer in the polymerized resin, which undergoes further polymerization at the active sites, may also account for the improvement in mechanical characteristics of the 5% ES composite. When the filler amount is increased to 7%, the filler content per unit volume also increases, resulting in poor adhesion between the ES particles and the PMMA matrix. As a result, high ratios of ES powder create weak spots within the matrix, and the stresses will increase in these weak locations, resulting in a decrease in strength. According to Figure 5e, increasing the ES powder by more than 7% promoted agglomeration and altered the shape of the composites, resulting in greater stress at the interface. As a result, the filler particles are poorly bonded. It should also be mentioned that the ES particles act as barriers to cracks that explain why the fracture surface is non-smooth and not straight. Extra additions of ES powder decrease the remaining monomer, resulting in a drop in mechanical property values. This is because the filler has relatively poor compatibility with the matrix that cause a lower matrix's capacity to disperse the energy applied [6, 7, 11]. The mechanical characteristics of the PMMA denture base were also changed by the CS addition (5%) [20]. The presence of ES powder was altered by adding calculated CS ratios to the PMMA denture base material. The effect of the SC particles is to improve energy absorption during the application of fracture stress that reduces the crack propagation and acts as an antibacterial agent in the mouth to minimize inflammation. Another case of the reduction in mechanical properties was produced by increasing concentrations of the crosslinking agent with an increase in filler content [7].

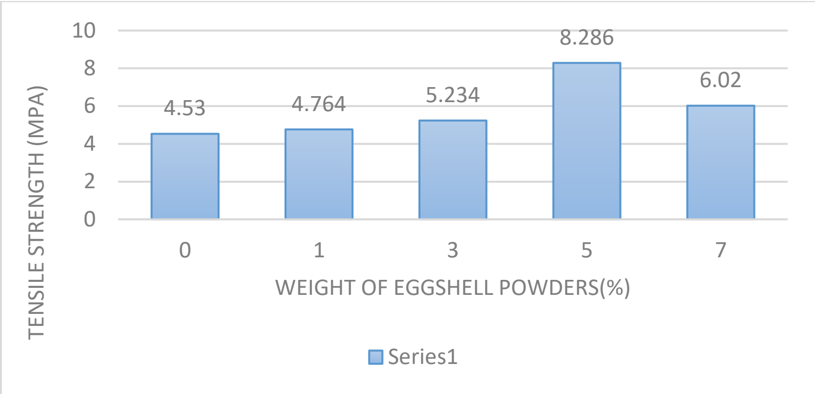

Fig.2: Effect of addition ES powder on tensile strength values of the composites.

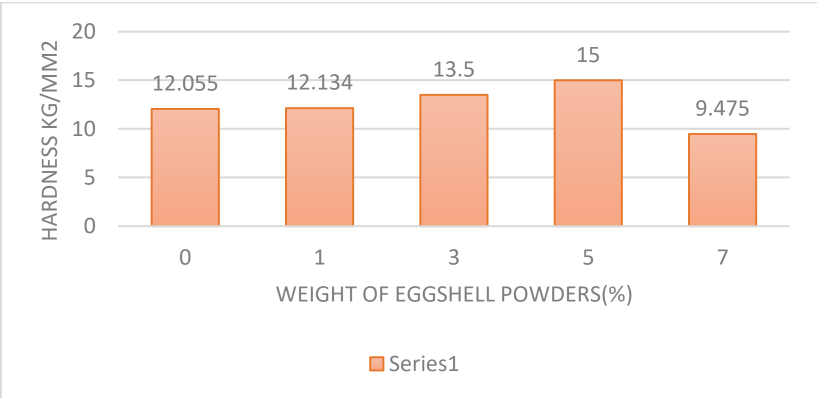

Fig.3: Effect of addition ES powder on hardness values of the composites.

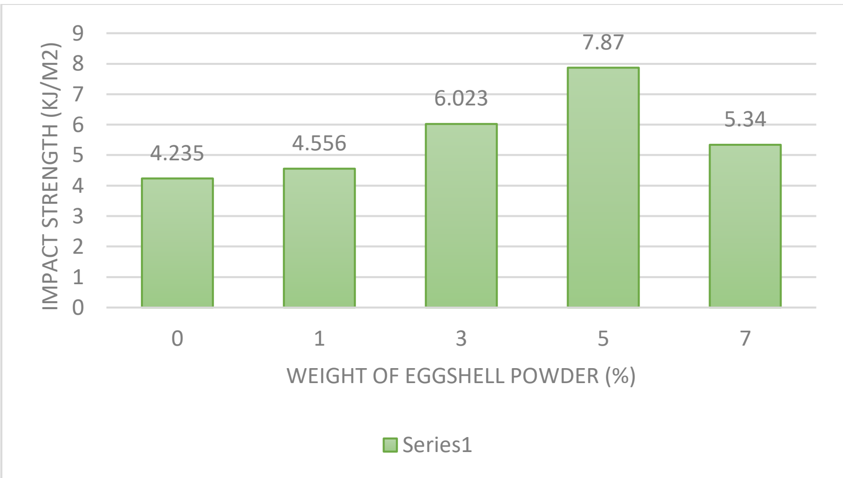

Fig.4: Effect of addition ES powder on impact strength values of the composites.

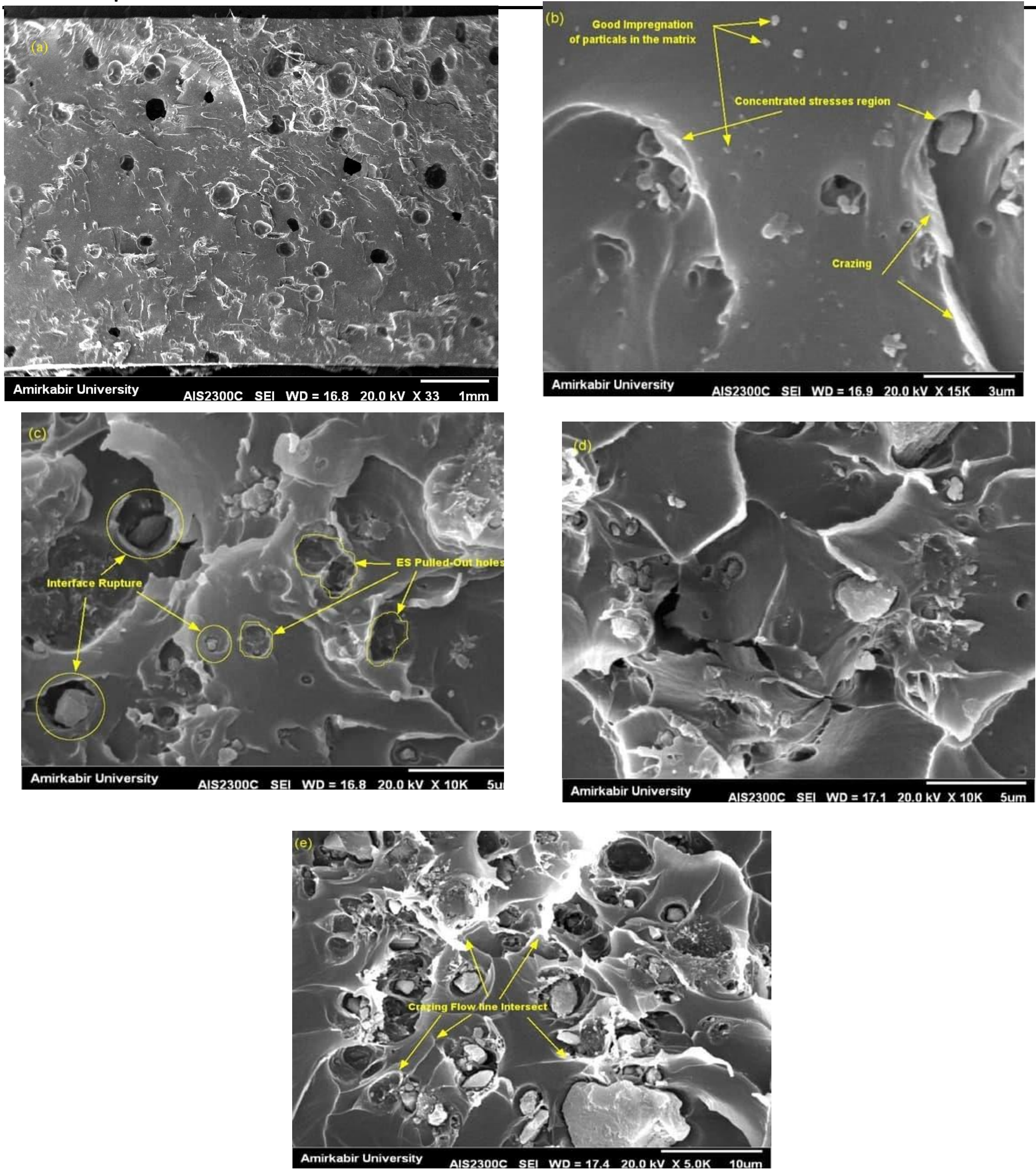

Fig.5: SEM micrographs from the fracture surfaces of PMMA-chitosan copolymer, (a) biocomposite PMMA- Chitosan, (b) biocomposite containing 1% ES, (c) biocomposite containing 3% ES, (d) biocomposite containing 5% ES, and (e) biocomposite containing 7% ES.

4. Conclusion

The results of this study indicated that the addition of ES powder improved the mechanical properties of PMMA base material. The optimum mechanical properties of the PMMA was achieved at a ratio of ES powder of 5%. The major reasons for improving the mechanical characteristics of the PMMA at an ES ratio of 5% are homogeneous dispersion, improved filler matrix interactions, and decreased porosity. However, extra amounts of ES powder (7% or more) could result in a loss in mechanical properties due to the high intensity of the ES powder, which damages the morphology of the composite and increased its porosity.

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