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Mechanical and physical properties of highly eggshell-filled Bis-GMA/TEGDMA for dental application

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Abstract

This study attempts to assess a newly developed eggshell-filled Bisphenol A-glycidyl methacrylate (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) for dental application. Amounts of 30 and 40 wt% of eggshell were filled in Bis-GMA/TEGDMA along with 1% of benzoyl peroxide, followed by the fabrication of rectangular specimens of 20 × 25 × 2 mm for evaluation of physical and mechanical properties. Prior to the fabrication of the composites, the morphology of the eggshell was observed using a field emission scanning electron microscope. The surface roughness and hardness of the specimens were assessed using a surface profilometer and Vickers hardness tester, respectively. The eggshells were irregular in shape with sizes ranging between 5 to 60 µm. The roughness values slightly fluctuated with the incorporation of fillers. The roughest surface was recorded by 40 wt% filled Bis-GMA/TEGDMA with 1.34 µm. On the contrary, the hardness of the composites increased by 37 to 73% as compared to the unfilled Bis-GMA/TEGDMA. With improved mechanical performance as well as physical characteristics that could be further enhanced, eggshell-filled Bis-GMA/TEGDMA could be the next potential substitute for sustainable dental materials, subjected to further investigations.

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1.0 Introduction

Bisphenol A-glycidyl methacrylate (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) are the most commonly used resin for dental restoration. Bis-GMA was introduced in 1963 to replace methyl methacrylate (MMA) monomer in order to improve the physical properties of polymeric resin used in dental restoration (Bowen, 1963). The introduction of Bis-GMA has been a major breakthrough in dental composite for decades. However, its high viscosity affects the handling process. The flowability, mechanical, and physical properties were later improved with the addition of TEGDMA.

TEGDMA acts as a diluent to improve the flowability of the composites hence improving the adherence to the tooth cavity. Nonetheless, polymerisation shrinkage remained a critical issue that needs further improvement. Besides, TEGDMA is also said to inversely affect glutathione levels (GSH) and cell viability as well as cause apoptosis in primary human gingival fibroblast (Janke et al., 2003; Volk et al., 2007).

Besides research on monomer, flowability and its setting process, enormous works have been devoted to modifying the characteristic of dental composites via the introduction of the inorganic filler (Hojati et al., 2013; Dafar et al., 2016). In particular, the effect of particle size, hybridisation of micro and nanofillers, as well as surface modification of filler are among the area that received immense attention.

On the other hand, biowaste fillers are getting considerable attention due to their availability, cost-effectiveness and eco-friendly. The attempt of using biowaste filler in dental materials can be observed in various trials where silica derived from rice husk for example is used to modify the mechanical, physical and antimicrobial properties of glass ionomer cement

(GIC) (Ching et al., 2018). Besides GIC, silica is also used in flowable resin composites to enhance its physical and mechanical performance (Yusoff et al., 2019).

Other than silica, calcium-based materials derived from biowaste have also been a subject of interest. Spherical nanoparticles of calcium carbonate can be obtained from the chemical reaction of cockle shell precursor with hydrochloric acid and potassium carbonate (Hussein et al., 2020), which unleashes its potential in the dental application.

Meanwhile, another source of calcium which tends to be underrated is eggshell. Eggshell is a calcium-rich entity where approximately 95% of the shell corresponds to calcium carbonate. Besides being readily available, the eggshell is easier to be crushed into a finer particle as compared to a cockle shell. While seashell often relates to the toxicity originating from heavy metal pollution such as mercury in the ocean, eggshell is typically safe and proven to be biocompatible (Rohmadi et al., 2021).

To the best of our knowledge, there is no documented study on the direct usage of eggshells for dental application. This study aims to explore the feasibility of eggshells as a potential filler for Bis-GMA/TEGDMA composite for dental application. The surface roughness and hardness of eggshell-filled Bis-GMA/TEGDMA were assessed and the suitability of the developed composites for dental application was discussed.

2.0 Methodology

2.1 Material

In this study, brown eggshell was mainly used. The colour of the eggshell highly depends on the breed of the hen. It should be noted that brown eggshell is generally abundant in Malaysia as compared to white eggshell. The eggshell was obtained from a store in Terengganu. Resins of Bis-GMA (Esstech Inc., USA) and TEGDMA (Esstech Inc., USA) were used as a matrix. Meanwhile, benzoyl peroxide (Sigma Aldrich, USA) was used as a polymerisation initiator.

2.2 Methods

The obtained eggshell was initially cleaned and dried in an oven for 12 hours at 80 °C. The dried eggshell was then grounded into fine particles using a mortar and pestle and finally sieved using a 63 µm metal mesh. For the preparation of composites, the resin matrix of Bis-GMA and TEGDMA were initially mixed at a ratio of 1:1. The composites were then prepared by adding 30 and 40 wt% of eggshell filler to the resin mixture, followed by 1% of benzoyl peroxide (BPO). Unfilled bis-GMA/TEGDMA was also prepared as a control. In this study, a slight modification was made, where BPO was used as an initiator to replace the photoinitiator and co-initiator of camphorquinone (CQ) and 2-(dimethylamino) ethyl methacrylate (DMAEMA). It should be noted that CQ and DMAEMA are among the main components of commercial dental materials. The compound was filled into a rectangular silicone rubber mould with a dimension of 20 × 25 × 2 mm to form specimens. The sample size (n) for the evaluation of hardness and surface roughness per composition were 3 and 5, respectively. The mould with the compound was then placed in an oven at 100 °C for 1 hour to initiate the polymerisation process.

2.2.1 Morphological observation of eggshell filler

The sieved eggshell filler was observed via a field emission scanning electron microscope (FESEM) (Quanta 450 FEG, Fei, USA). Prior to the observation process, the eggshell filler was dried in an oven for 1 hour. The drying process was performed as the eggshell fillers are hygroscopic and tend to agglomerate once exposed to the room environment. The dried particles were placed on a stub and gold-coated prior to the FESEM observation. The observation was performed at 1000× magnification using a secondary electron at 5 kV.

2.2.2 Determination of surface roughness and hardness of the composites

The surface roughness of the composites was quantified using a surface profilometer (Surfcom Flex, Accretech, Japan). The parameters of the measurement such as cut-off value, evaluation length and speed were set at 0.8 mm, 5 mm and 0.6 mm/s, respectively.

Meanwhile, the hardness of the composites was measured using a Vickers hardness tester (VM 50, FIE, India). The measurement was conducted using a 1 kg load with a dwelling time of 15 seconds.

The hardness value of the composites was determined by the ratio of force (*F*) per unit area (A), following ASTM E 92-82. The details are shown in Eq. (1):

$$HV = \frac{F}{A} = \frac{1.8544F}{d^2} \quad (1)$$

where: d is the diagonal length observed on the specimen after the indentation process.

3.0 Results and discussion

3.1 Filler morphology

The morphology of filler plays a crucial role in determining the mechanical and physical properties of the composites. The morphology of the sieved eggshell was observed via a FESEM and the obtained micrograph is shown in Fig. 1. The particles were generally irregular in shape. Although eggshell with a particle size of less than 63 µm was obtained, the sizes were varied and ranged from approximately 5 to 60 µm.

The shape and size of the fillers are deemed crucial for dental materials. Spherical fillers for instance, can be highly filled in the resin resulting in better mechanical performance (Kim et al., 2002). The enhancement of the mechanical properties of the composites is attributed to the distribution of fillers in the polymer network (Abdullah et al., 2018). While the mechanical and physical properties of dental materials are generally influenced by the usage of fillers with certain shapes and sizes, a similar effect on the biological properties is also anticipated. Besides mechanical and physical properties, the effect of fillers on biological properties such as cytotoxicity and antibacterial properties need to be considered for dental materials. It should be noted that rod shape fillers exhibit higher bacterial inhibition than plate-like fillers (Bakhori et al., 2017). While the antibacterial efficacy of fillers in their individual form is widely reported, the effect of fillers as well as their mechanism of action in composites form remains a challenging issue that needs further exploration.

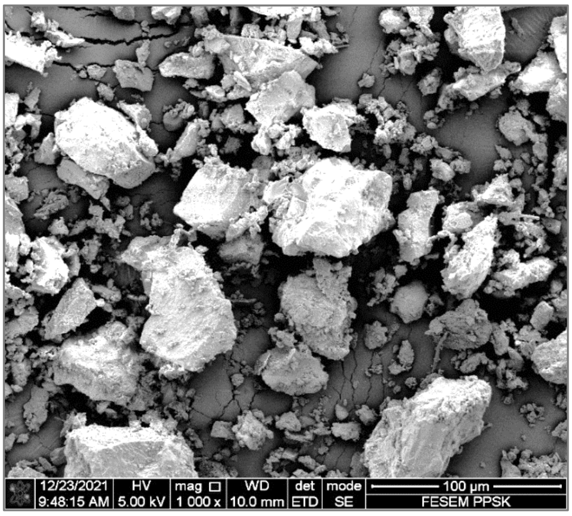

Fig. 1: FESEM micrograph of eggshell at a magnification of 1000×

3.2 Surface roughness and hardness of the composites

Surface characteristics are among the critical factor that contributes to the clinical performance of dental restorative material. In this study, the influence of filler loading on the surface roughness of the composites was assessed. The surface roughness of unfilled and eggshell-filled bis-GMA/TEGDMA is shown in Fig. 2.

The mean surface roughness of unfilled Bis-GMA/TEGDMA was 1.23 µm. The incorporation of 30 wt% of eggshell reduced the surface roughness of the composite by approximately 41%. The roughest surface was recorded by 40 wt% eggshell-filled bis-GMA/TEGDMA. The reduction of roughness value at 30 wt% filler loading could be due to the well dispersion of eggshell filler in the resin matrix. However, the further addition of eggshells caused a sudden increase in roughness value. The increase in the surface roughness of the composites at 40 wt% filler loading is generally expected. The phenomenon might be attributed to the detection and appearance of filler on the surface (Abdullah et al., 2019) of the eggshell-filled Bis-GMA/TEGDMA.

In general, clinicians would aim for dental restorative materials with a maximum surface roughness of 0.2 µm (Bollen et al., 1997). It should be noted that a dental restorative material with a roughness value of more than the threshold of 0.2 µm has a higher plaque accumulation tendency which could lead to tooth decay. In an actual dental restoration process, the restored surface will be further polished to produce a smoother surface.

Besides surface roughness, the hardness of the composite is deemed critical as the dental restorative material is the first entity that encounter the forces during the mastication process. The effect of eggshell loading on the hardness of the Bis-GMA/TEGDMA is shown in Fig. 3. Unfilled Bis-GMA/TEGDMA presented a value of 13.1 HV. The hardness of the Bis-GMA/TEGDMA increased steadily with the increase of filler loading. The hardness of the composites was in the range of 18-22 HV, with 40 wt% eggshell-filled Bis-GMA/TEGDMA recording the highest value of 22.73 HV.

The increment of the hardness value with the addition of eggshell is expected as the filler acts as reinforcement material in the Bis-GMA/TEGDMA matrix. It should be noted that the hardness of commercially available dental composites ranged from 9.6 to 59.9 HV (Beun et al., 2012; Ku et al., 2015). The hardness of the eggshell-filled Bis-GMA/TEGDMA is considered on par with the commercially available dental composites. Although the hardness value of unfilled Bis-GMA/TEGDMA reached the minimum specification of commercial dental composites, it is generally undesirable due to its transparency in nature, which is totally different from the shade of normal human teeth.

As this study aims to assess the feasibility of eggshells as potential fillers for Bis-GMA/TEGDMA composites, a slight modification was made to the methods, where a benzoyl peroxide was used as a polymerisation initiator with the assistance of oven curing to solidify and complete the polymerisation process. It should be noted that commercially available dental composites typically contain CQ which acts as a photoinitiator DMAEMA as a co-initiator (Singh et al., 2017). The polymerisation is initiated by exposing the materials to a blue light-emitting diode (LED) curing unit at a certain duration. Therefore, it is expected that a better hardness value could be achieved if CQ and DMAEMA are used (Yusoff et al., 2019) to initiate the polymerisation process.

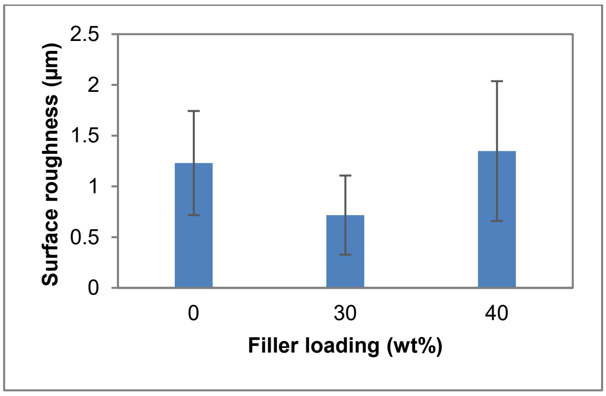

Fig. 2: Effect of filler loading on the surface roughness of Bis-GMA/TEGDMA composites

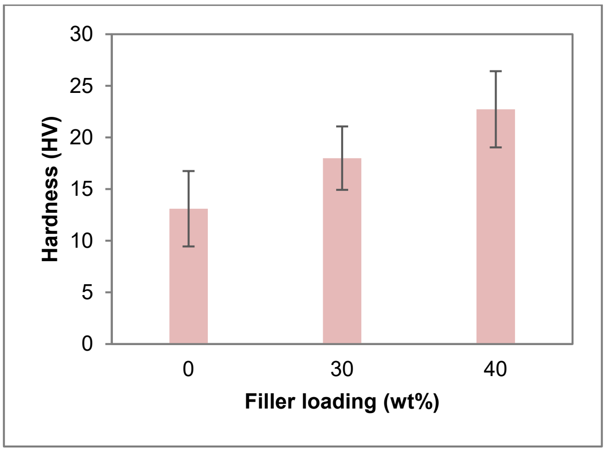

Fig. 3: Effect of filler loading on the hardness of Bis-GMA/TEGDMA composites

4.0 Conclusions

The physical and mechanical properties of highly eggshell-filled Bis-GMA/TEGDMA were successfully assessed. The surface roughness and hardness of Bis-GMA/TEGDMA were affected by the incorporation of eggshells. The surface roughness of the composites was reduced by 40% at 30 wt% filler loading and increased by 9% at the highest filler loading as compared to the unfilled resin. The roughness of the composites was also higher than the threshold for dental restorative materials. However, it can be improved with the introduction of the polishing process. The hardness of the composites increased by 37 to 73% as compared to the unfilled counterpart and met the minimum requirement for dental application. Based on the obtained results, the eggshell-filled Bis-GMA/TEGDMA could be potentially used for dental restorative materials, subjected to further evaluation on aesthetic value such as colour stability as well as other mechanical, physical and toxicity properties.

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