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Research Article

EFFECT OF SILANE COUPLING AGENT CONTENT ON MECHANICAL PROPERTIES OF HYDROXYAPATITE/POLY(METHYL METHACRYLATE) DENTURE BASE COMPOSITE

Jamal Moammar ALDABIB *

** Lecturer, Baniwalid University, Faculty of Medical Technology, Department of Dental Technology, Bani Walid, LIBYA, e-mail: jamalald71@gmail.com*
ORCID ID: https://orcid.org/0000-0003-2768-760X

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ABSTRACT

In removable prosthodontics, poly(methyl methacrylate) (PMMA) is the most suitable for the construction of denture bases. Intra-orally, the subjected stress intensity during the function accelerate the fracture of acrylic resin denture bases. Extra-orally, fracture occurs when dentures are accidentally dropped on a hard surface. The aim of the current study was to investigate the effect of coupling agent concentration on the mechanical properties of Hydroxyapatite/Poly(methyl methacrylate) (HA/PMMA) denture base composite. The Hydroxyapatite (HA) treated with four different ratios (i.e. 0, 5, 7 and 10 wt%) of 3-(trimethoxysily) propyl methacrylate (γMPS) silane coupling agent was added into the PMMA matrix. The mechanical performance of the composite was evaluated by conducting fracture toughness, flexural and tensile tests. An improvement of 13.83% and 9.62% in the tensile and flexural strength respectively, was achieved. The tensile and flexural modulus of the composite increased by 19.04% and 12.5% respectively. A significant improvement of 29.26% in the fracture toughness was observed at 10 wt% of γ-MPS. 10 wt% of γ-MPS is the optimum amount of coupling agent for obtaining balanced mechanical properties.

Keywords: *Dental Composites; Denture Base materials; Poly (methyl methacrylate); Mechanical Properties; Hydroxyapatite; Silane Coupling Agent.*

1. INTRODUCTION

Coupling agents are able to create a strong interface bond between inorganic and organic materials. In all cases, the coupling agents form a bridge at the interface of both components(Elshereksi et al., 2017a). Therefore, silane coupling agents are more often being used because they are more efficient, easy to spread in the composite and having very good chemical resistance. They are classified as organo-silane compounds which have as a minimum two different types of reactive groups bonded to the silicone in a molecule(Goyal et al., 2006, Šinkovec and Mušič, 2020). The main purpose of using coupling agents is to improve the mechanical properties of nanocomposites by introducing interactions between filler particles and the matrix(Fu et al., 2019).

Using silane coupling agents is a common practice in the construction of dental composite materials (Antonucci et al., 2005). they have been used widely to enhance the bonding strength of the composites' two phases (Elshereksi et al., 2017b). It has been established that isocyanates have the ability to chemically bond to the surface of HA through the reaction of isocyanate with the surface hydroxyl groups of nano apatite (Wang et al., 2011). Therefore, isocyanate and diisocyanate can be used to introduce chemical bonding between HA particles and various polymer materials among them, poly (methyl methacrylate) PMMA(Mei et al., 2019). Similarly, with the hexamethylene diisocyanate, HA filler particles and polymer matrix can be bonded with covalent bond. As a result, the mechanical properties of the composite can be significantly enhanced (Turon et al., 2018).

It was reported that methacryloxy propyl trimethoxysilane (γ-MPS) as a coupling agent considerably increased the tensile, flexural strength, and the hardness of composites for dental applications. Silane coupling agent is more often being used because it is more efficient, easy to spread in the matrix and having very good chemical resistance(Khaje and Jamshidi, 2015, Alrahlah, 2018, Della Bona et al., 2008). The aim of the present research is to study the effect of coupling agent ratio on the mechanical properties of HA/PMMA composite.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1 Powder Components

The powder components consisted of poly(methyl methacrylate) PMMA (Sigma-Aldrich, USA), Hydroxyapatite (HA) (Particle size 5±1 μm, Fluidinova, Portugal) and Benzoyl Peroxide (BPO) (Particle size ≈ 106 μm, MCC, Germany).

2.1.2 Liquid Components

The liquid components consisted of methyl methacrylate (MMA) **(**Aldrich USA**),** 0.0025% of hydroquinone as stabilizer and 10% ethylene glycol dimethacrylate (EGDMA) as cross linking agent **(**Aldrich USA**)**.

2.1.3 Coupling Agent

The silane coupling agent [3-(methacryloxy) propyl trimethoxysilane] also known as 3-(trimethoxysily) propyl methacrylate (γ-MPS), (Boiling Point ≈ 190°C and Flash Point ≈ 92.22°C, Sigma-Aldrich. UAS).

2.2. Methods

2.2.1. HA Filler Treatment

HA was treated with different ratios (0% wt, 5% wt, 7% wt, and 10% wt) of silane coupling agent (γ-MPS) using a 70/30 acetone-water mixture. The HA powder was added to the liquid mixture (acetone-water-silane) and mixed with stirrer for 4 h, subsequently the mixture was dried in oven at 110°C for 24 h. The procedures were previously described by Kundie et al. (2018a).

2.2.2. Sample Preparation

The treated HA with. 0, 5, 7 and 10 wt% of [3-(methacryloxy) propyl trimethoxysilane] (Aldrich USA) was used as reinforcement filler for the acrylic denture base material. The planetary ball milling technique (PBM) was used to mix powder components the for 30 min. The running speed was set at (150 rpm) and the powder to ball weight ratio (PBR) was 1:10. The milling was stopped every 3 min and continued after 6 min during the run time to avoid the overheating and premature polymerization problems. The powder components were added to the liquid components and mixed in accordance to standard dental laboratory manual (SDL). After reaching the dough stage, the mixture was packed into a stainless steel mold and compression molded at room temperature. The heat treatment process was done at 78°C for 90 min using a water bath. The procedure followed in the current study was according to the conventional technique of the acrylic denture base fabrication.(McCabe and Walls, 2013).

2.3. Mechanical Properties

To evaluate the mechanical performance of PMMA/HA composites in the current study, a total of three tests were carried out. The testing procedures are outlined in the following sub-section.

2.3.1. Tensile Test

A tensile test was carried out according to ASTM D 638-2005 type IV using (INSTRON 5582 10 kN tensile testing machine). The crosshead speed was set at 5 mm/min and gauge length at 50 mm.

2.3.2. Flexural Test

According to the ASTM standard D790-2005, a three point flexural tests was carried out using (INSTRON 5582 10 kN tensile testing machine). The diameter of the loading nose and supports was 20 mm and 10 mm, respectively. The span length was set at 50 mm whilst the crosshead speed at 2 mm/min. The flexural modulus and the flexural strength were calculated using the following equation(Campo, 2008, Hamizah et al., 2012, Kundie et al., 2018a):

$$\text{flexural modulus} = \frac{L^3 m}{4bd^3} \qquad (1)$$

$$\text{flexural strength} = \frac{3PL}{2bd^2} \qquad (2)$$

Whereby, b = specimen width, m = tangent gradient of the initial straight line of load versus deflection curve, d = specimen thickness, P = maximum load, L = span length.

2.3.3. Fracture Toughness

According to ISO 13586:2000, fracture toughness was measured using (SEN-B). The overall length = 80 mm, span length S = 64 mm, thickness, t = 4 mm, notch length a = 4 mm, width w = 20 mm. The crosshead speed of 1.00 mm/min. the values for K_{IC} was calculated using the following equation(Kundie et al., 2018a, Hamizah et al., 2012):

$$K_{IC} = \frac{3PSa^{1/2}Y}{2tw^2} \quad (3)$$

Geometrical correction factor (Y)

$$Y = 1.93 - 3.07\left(\frac{a}{W}\right) + 14.53\left(\frac{a}{W}\right)^2 - 25.1\left(\frac{a}{W}\right)^3 + 25.8\left(\frac{a}{W}\right)^4 \quad (4)$$

whereby: S = span length (mm), w = specimen width (mm), a = notch length (mm), P = load at peak (N), t = specimen thickness (mm).

3. RESULT AND DISCUSSION

3.1 Tensile Properties

Table 1 shows the effect of γ-MPS silane coupling agent amount on the tensile properties of PMMA/HA composite. The tensile strength and modulus increased with increasing the amount of γ-MPS and reached a maximum value of 59.81 MPa and 2.5 GPa, respectively, for the samples treated with 10% of γ-MPS. It can be seen that the treated composites show slightly higher tensile modulus compared with the untreated composite. The presence of silane coupling agent did not only improve the PMMA-HA interaction but also facilitated the dispersion of the HA particles in the PMMA matrix. The improvement in HA dispersion increased the ability of distributing the stresses uniformly in the composite, which led to higher resistance towards deformation leading to higher tensile modulus(Liu and Webster, 2010, Amdjadi et al., 2017). silane coupling agent improves interfacing bond between the inorganic filler and polymer matrix with both strong chemical bond and strong mechanical interlocking that formed between hydroxyapatite and the matrix. Eventually as a result, the tensile strength is improved (Wang and Bonfield, 2001, Marghalani, 2014).

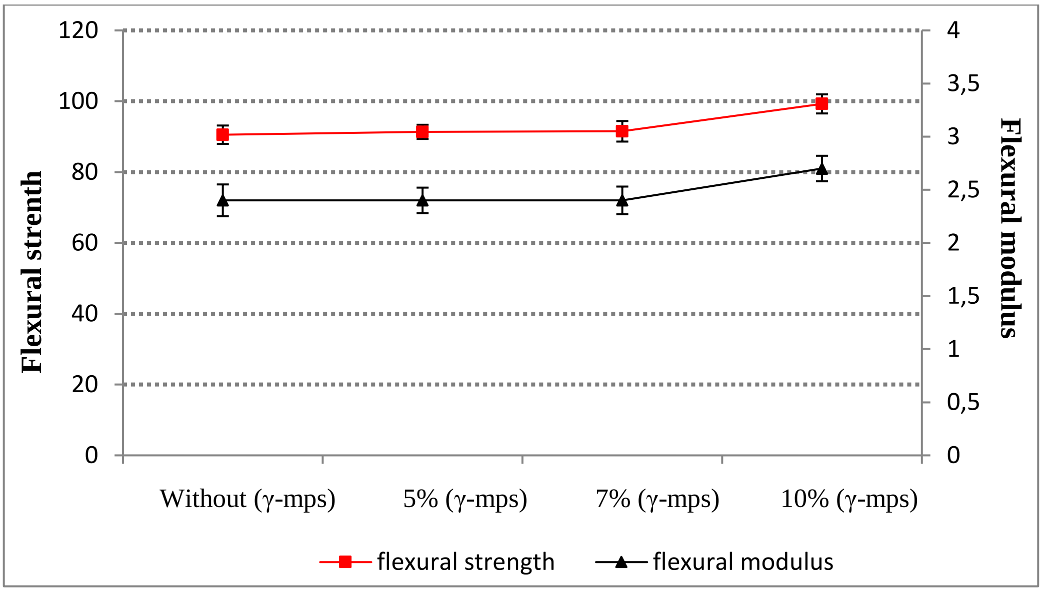
Table 1: The tensile properties of PMMA/ HA 5 wt% as a function of different γ-MPS silane coupling agent concentration.

Content of γ-MPS	Tensile strength (MPa)	Tensile modulus (GPa)
Without (γ-mps)	52.54 ± 1.7	2.10 ± 0.10
5% (γ-mps)	54.88 ± 1.8	2.20 ± 0.09
7% (γ-mps)	55.50 ± 1.6	2.37± 0.06
10% (γ-mps)	59.81 ± 0.8	2.50 ± 0.05

3.2 Flexural properties

Figure 1 shows the effect of the amount of γ-MPS silane coupling agent on the flexural properties of HA/PMMA composites. The flexural strength and modulus rapidly increased with the increasing of γ-MPS amount and reached a maximum value of 99.25 MPa and 2.7 GPa, respectively, for the samples treated with 10% of γ-MPS. This observation is in agreement with the one made by (Tham et al., 2010, Kundie et al., 2018a, Chow et al., 2008). The flexural strength increased as a result the γ-MPS treatment. The silane coupling agent improved the filler-matrix compatibility which led eventually to a better distribution of the stress in the composite thus yielding better composites properties. Synergistic effect was obtained as a result of the silanization of hydroxyapatite which improve the adhesion and interaction between the filler and the matrix. (Sideridou and Karabela, 2009, XAVIER et al., 2015). It can be seen that the flexural modulus is slightly higher for the composite treated with 10 wt% of γ-MPS compared to the other formulations. This can be attributed the strengthened filler-matrix interface which indirectly allows the treated composite to sustain external load and be able to distribute the stress fairly in composite(Marghalani, 2014, Pratap et al., 2019).

Fig. 1: The flexural properties of PMMA/ HA 5 wt% as a function of different γ-MPS silane coupling agent concentration.

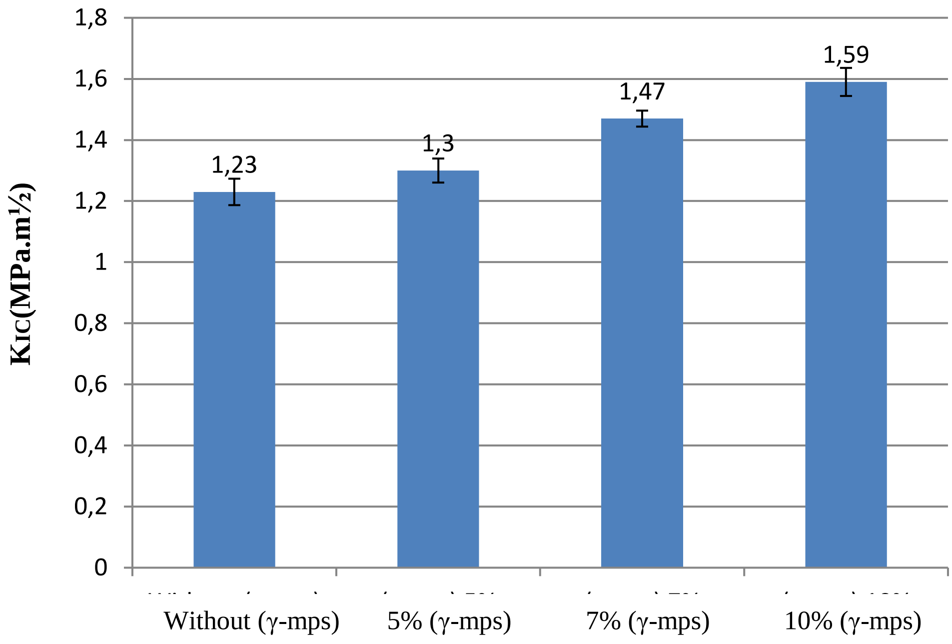


3.3 Fracture toughness

Figure 2 shows the effect of the amount of γ-MPS silane coupling agent on the fracture toughness of PMMA/HA composites. The fracture toughness reached the maximum value of 1.59 MPa.m^{½}, for the samples treated with 10% of γ-MPS. The toughening mechanisms are known to be associated with distribution of the filler particles. The homogenous distribution of the filler allows good plastic deformation which prevents crazing of the matrix resulting in high fracture toughness(Bartczak and Galeski, 2014, Lauke, 2008, Cotterell et al., 2007). The toughening efficiency indirectly depends on the amount of the coupling agent. Enough amount of coupling agent improves the distribution of filler particles (Kundie et al., 2018b, Fu et al., 2008). Homogeneously dispersed filler particles significantly effect the mechanical properties the polymer matrix, mainly in fracture toughness(Nilagiri Balasubramanian and Ramesh, 2018, Li et al., 2019).

If there is poor interfacing between the two phases of the composite result will be premature failure. Therefore, The filler-matrix interlocking is a very important factor (Šupová, 2009). The γ-MPS silane coupling agent can chemically link inorganic and organic materials in composites. The chemical structure of the silane, the silanization process and the silane content play a key role in determination of durability and strength of this interphase bond (Antonucci et al., 2005, Nakatani et al., 2011).

Fig. 2: The fracture toughness of PMMA/ HA 5 wt% as a function of different γ-MPS silane coupling agent concentration.



4. CONCLUSION

The use of silane coupling agent improved the chemical adhesion between the HA filler particles and the PMMA matrix. which led to improved mechanical properties of the denture base material. The unique dual functionality of silane coupling agent have the ability to chemically bridge organic and inorganic materials by creating an adhesive interphase in composites. The strong interfacial bond doesn't only aids the mixing of the two phases but also benefits the overall properties of the composite. It can also resist fracture through improving the stress transferring and distribution between the strong and brittle HA filler particles and flexible acrylic resin matrix.

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