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Basic Properties of PMMA Reinforced Using Ceramics Particles of ZrO_2-Al_2O_3-SiO_2 Coated with Two Types of Coupling Agents

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Abstract. In this study, novel composites materials composed of polymethyl methacrylate (PMMA) reinforced ZrO_2-Al_2O_3-SiO_2 filler system were developed. Zirconia-alumina-silica filler system were synthesized through sol-gel technique. Chitosan and trimethoxypropilsilane (TMPS) were used to modify the composites system. The resulting composites material were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and hardness test. SEM images displayed the composites particles in nanometer size with minor agglomeration. The XRD results revealed the presence of cubic and tetragonal phase of zirconia and also monoclinic silica phases in the composites system. These crystallographic characteristic could affect the mechanical properties of the composites. The hardness value for un-modified composites was 15.27 ± 0.25 VHN and for TMPS 19.43 ± 1.89 VHN and chitosan modification 18.75 ± 2.05 VHN, respectively. Therefore, these novel composites materials composed of PMMA reinforced filler system of zirconia-alumina-silica would provide the potential to apply in dental technology.

Introduction

Fixed partial dentures including jacket crown and bridges were commonly prepare from dental porcelain or porcelain-fused to metal. Recently, the development of ceramic nanoparticles as a part of the component in dental materials has gaining interest. The ceramics materials exhibit ideal properties including esthetics, its thermal expansion similar coefficient as tooth structure, good biological and mechanical properties. Restorations process fabricated indirectly in a dental laboratory often require time-consuming procedures, several expensive equipments and highly trained technicians. Several weeks are taken for completion the restorations so that provisional (interim) or temporary restorations must be provided [1]. The provisional crown serves both pulpal and periodontal protection, stabilization of tooth position and maintenance mastication function [2].

Composites is defined as a system that contains two or more distinct constituent or phases. In respect to the dental composite, composites might refer to the filler reinforced polymer matrix materials that commonly used as restorative materials. One of the fillers function is to increase the mechanical properties [3,4]. Recently, the filler particles used are varies in term of chemical composition, morphology and dimensions. One of the most promising filler is silica (SiO_2) which is commonly used due to its excellent mechanical properties and translucency properties. Another type

filler of metal oxides including alumina (Al_2O_3) and zirconia (ZrO_2) were used to prevent crack propagation retention abilities and improving their hardness properties [5]. However, the appearance of both materials is white but not as translucent as silica [6].

Polymethyl methacrylate (PMMA) or acrylic resin is one of the materials candidate which commonly used and widely marketed as temporary restoration material [2,7]. This material has been chosen based on its esthetics, fabrication method, and economic point of view. However, the physical properties improvement are required for special cases such as patient with bruxism or patients with treatment plan which requires long-term use of provisional crown [2,8]. Recently, several methods have been conducted in order to reinforce provisional restorative materials [2]. It has been demonstrated that PMMA could be strengthened through the addition of structural component including metal and ceramic. Those additive components could distributed in the PMMA matrix which further develop a composite structure [9]. Polymers matrix and fillers are the most important component which further define the resulting properties of dental materials [3].

In respect to the dental restoration applications, it is desirable to have a strong bonding interaction among the composites components. One of the strategies that commonly used in order to enhance the interaction is the using of coupling agents. Recently, silane coupling agents has gained interest as coupling agent in dental restoration field. Silane coupling agents, which are synthetic hybrid inorganic-organic compounds, are used to trigger interaction and adhesion between dissimilar materials [10,11]. Functional silanes contain two different functional groups that can react with inorganic materials, for example matrices, and organic materials, for example resins, which is further enhance the mechanical strength, adhesion, resin modification and surface modification of composite materials [12]. Silanization provides the ability of composite to distribute the stress from matrix to the fillers [11]. A silane coupling agent acts as a sort of intermediary between organic materials to inorganic materials. 3-methacryloxypropyltrimethoxysilane (MPTMS) and trimethoxypropylsilane (TMPS) [13] or containing MPS (3-methacryloxypropyltrimethoxysilane) are the silane coupling agents that commonly used for dental composites application [6]. Previous investigation reported the silane coupling agent concentration should generally be around 0,1 – 2% [12, 14]. Chitosan is a polycationic natural copolymer composed of N-acetyl-D-glucosamine ad D-glucosamine. Chitosan contains one amino group and two hydroxyl groups in the repeating glucosidic residue. The active primary amino groups on the molecule being reactive provide sites for a variety of side group attachment employing mild reaction conditions. Chitosan exhibit a nontoxic, biodegradable, and biocompatible characteristics that could be developed for biomedical and pharmaceutical applications [14,15]. Previous investigation used chitosan as a biopolymer coupling agents for wood flour polyvinyl chloride composites to improve interfacial adhesion [16].

In this study, novel composites material composed of polymethyl methacrylate (PMMA) reinforced zirconia-alumina-silica were developed. Systematic characterizations including scanning electron microscope (SEM), X-ray diffraction (XRD) and hardness test have been conducted in order to elaborate the morphology and mechanical properties of the composites.

Materials and Methods

Synthesis of ceramic nanoparticles. Ceramic nanoparticles composed of zirconia-alumina-silica were prepared using sol-gel techniques. Aluminum nitrate nanohydrate, tetraethyl orthosilicate, and zirconium chloride were used as precursors for alumina, silica and zirconia, respectively. Distilled water and 1%w/v chitosan were used as solvent and dispersant, respectively. Briefly, the precursor with the proportion of 10% alumina, 70% silica, and 20% zirconia was employed and mixed homogeneously followed by hydrolysis and condensation process. The as-prepared composites was homogenized using ultrasonic homogenizer. Afterwards, the heat treatment was applied into the composites in two stages. Firstly, the composites was dried at 100°C. Secondly, the composites were calcined at 700°C for two hours in electric furnace (Cress Electric Furnace C1228/935, Carson City, Nevada).

Structure and morphological characterization. X-ray diffraction (XRD, Philips Analytical X-Ray B.V) was conducted to evaluate the crystallographic characteristics. Scanning electron microscope (JEOL JSM-6360-A) was conducted to analyzed the structure, morphology and particle size of composites

Coating process. TMPS and chitosan 4 % were used as a coupling agent. The coupling process was developed based on the Enshu technique with minor modification. Briefly, the composites powder was soaked in coupling agent followed by centrifugation. Furthermore, the powder were dried in *vacuo*. The resulting powder was then crushed and stored in room temperature.

Hardness test. The composites produce were subjected to the hardness test. Hardness could be used as an indicator of wear resistance and strength of materials [17]. These tests are commonly used to assess the mechanical strength of dental composite [11]. Prior to the test, the samples were prepared. Briefly, the wax patterns were made in disc form with 8 mm in diameter and 3 mm in thickness. Gypsum molds were prepared by investing the wax pattern using dental stone in dental flasks then immersed in boiling water. Afterwards, the softened wax was taken out and flushed with boiling water added by detergent to remove any impurities and to facilitate the application of separating medium (cold mold seal). The mold cavities obtained were used for the preparation of test samples. PMMA heat cured resin, polymer and monomer in the ratio of 1:2 by weight was mixed and allowed to reach dough stage and packed in the mold were used as control. The flasks was put in water at room temperature then raised until boiled within 1 hour. After that, the flasks were kept for 1 hour to continue the polymerization. The samples were de-flasked after bench cooling. PMMA with zirconia-alumina-silica coated by coupling agents were prepared with aforementioned procedure, except the coated-zirconia-alumina-silica were mixed with resin then packed in the mold. While the ratio of PMMA:fillers = 1: 2. Prior to hardness test, all samples were store in water bath 37 °C 24 hours. Hardness test was determined using Vickers hardness tester machine, LECO – Japan M– 400–H1/H2/H3. A load of 200 grams was applied to the surface of the samples for 15 seconds (ADA Specification No. 27).

Results and Discussion

Figure 1 shows the SEM image of composites of zirconia-alumina-silica. It showed that the morphology of the particles exhibited granules particles with various particle size. Hybrid composites were formulated using mixed filler systems that contain microfine (0,01-0,1 μm) and fine (0,1-10 μm) particle fillers. This combination system will provide smooth surface and good mechanical properties [3].

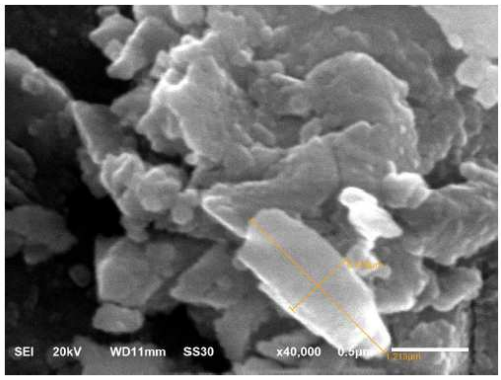

Fig 1. SEM images of ZrO_2-Al_20_3- SiO_2 filler

Figure 2 shows XRD spectra of zirconia-alumina-silica. XRD analysis revealed the formation of cubical (45,3%) and tetragonal (21,2%) phase of zirconia with ~5 nm and ~6-7 nm crystal size, respectively. Monoclinic phase of silica (20,1%) and alumina (13.3%) were also presented in 700°C.

The crystallinity increased with increasing calcination temperature. At high temperature (550 - 700°C) the peaks and intensity of the crystal phase suggest that tetragonal phase coexists with the monoclinic and cubical phase.

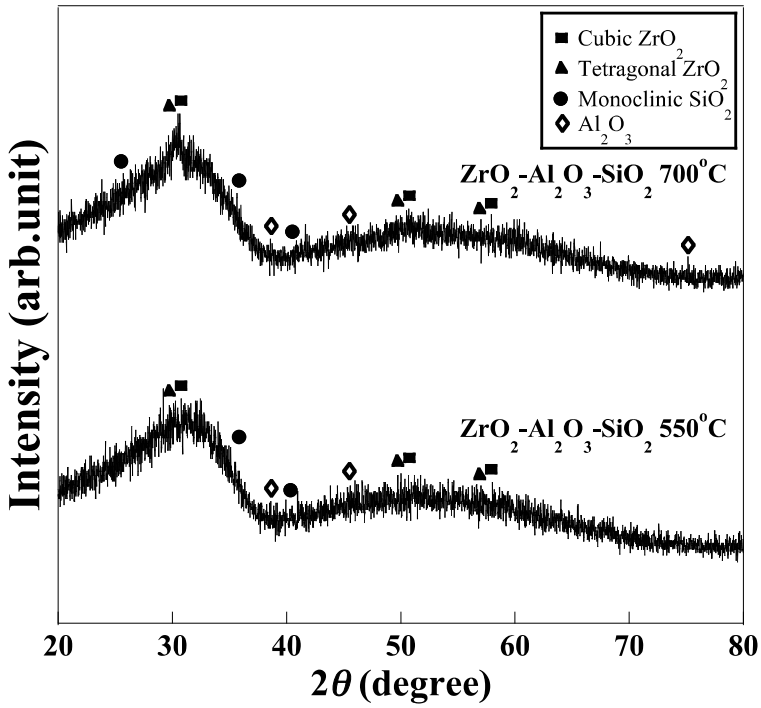

Fig 2. XRD spectra of ZrO_2-Al_2O_3- SiO_2 filler system

Silane/coupling agents have taken an important role besides the fillers. Silanization of the filler surface gives the ability of composite to distribute stress from matrix to fillers [11]. Silane/coupling agents are compounds molecules contain functional groups that bond organic and inorganic materials. A silane/coupling agent acts as a sort of intermediary between organic materials to inorganic materials. The hydrogen bonding allows bonding between organic and inorganic material as well as promoting adhesion by forming chemical bonding with resin. This characteristic makes silane/coupling agent useful for improving the mechanical strength, adhesion, resin modification and surface modification of composite materials [12]. The silane/coupling agent usually used for dental composite is organosilane which are 3-methacryloxypropyltrimethoxysilane (MPTMS) and trimethoxypropylsilane (TMPS) [13] or containing MPS (3- methacryloxypropyltrimethoxysilane) [6].

Silane/coupling agent concentration should generally be around 0,1 – 2% and usually not used higher than 6% [12,14]. Beside organosilane groups, chitosan can be used as dental silane materials, the silicone oxide and bind powders could maintain the granular shapes with cross-linking ability. This material is biocompatible and has chemical properties such as reactive amino group and reactive hydroxyl group available as well. In this present study, the lightweight chitosan was used with the concentration of 4% [14].

Ayad, Badawi and Fatah (2008) found the addition of zirconia treated with zirconat (5% and 15%) increased the transverse strength of acrylic resin but no significant difference was detected for surface hardness [18]. However, Ahmed and Ebrahim (2014) suggested that Zirconium oxide nano-fillers was increased the flexural strength and hardness of the acrylic resins significantly using 7%wt ZrO_2 concentration but did not explain about silanization [19].

Figure 3 shows the Vickers hardness result of this study. The data analyzed with one-way analysis of variance (ANOVA) with α=0,05. It was found that the hardness values of composites modified with TMPS was higher than composites modified with chitosan and un-modified composites. TMPS has the highest hardness result because it contain only hydroxyl groups which is more reactive than other group of silane. In contrasts, chitosan contains a combination of hydroxyl

and amine group [20]. Further studies are awaited using other silanes which more compatible with both polymer matrix and inorganic fillers.

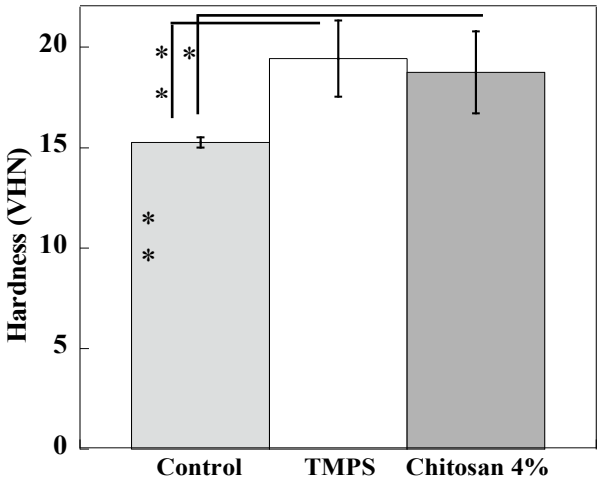

Fig 3. Vickers hardness value of composites system ($p<0.05$).

Conclusions

We fabricated the novel composites of polymethyl methacrylate (PMMA) reinforced zirconia-alumina-silica which could be developed in the dental material technology. SEM images revealed the nano and micro size particles of composites. XRD analysis displayed the cubic and tetragonal phase of zirconia and monoclinic phase of alumina and silica in zirconia-alumina-silica system. This structure might increase hardness properties of PMMA. Hardness test measurement proved that the incorporation of ceramic filler zirconia-alumina-silica could increase the hardness value of the composites. Furthermore, these new composites system could be anticipated to be developed as a dental composites for dental applications.

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