

The effect of silane-SiO₂ nanocomposite coating on provisional restorative materials in surface hardness

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Objective: To examine the influence of silane-coating material in surface hardness of provisional fixed prosthodontic material and compare the changes in surface hardness after thermocycling.

Materials and Methods: Fifty specimens, fabricated from four commercial provisional restorative materials (GC Unifast Trad™, Major C&B dentine, Protemp™ 4, Luxatemp® star) and a silane coating provisional restorative material (GC Unifast Trad™ coated), were allocated for control condition and thermocycling condition. Surface hardness of the sample from each group was determined using Vicker's surface hardness. The silane coating provisional restorative material was characterized by Fourier-transform infrared (FTIR) spectrometer. The surface morphologies of specimens from each group were observed under scanning electron microscope (SEM). The results were analyzed using two-way ANOVA statistical analysis.

Result: In control condition, hardness of GC Unifast Trad™ coated was significantly higher than that of GC Unifast Trad™. In addition, hardness of GC Unifast Trad™ coated was not significantly different than that of Luxatemp® star. In thermocycling condition, hardness of GC Unifast Trad™ coated was significantly higher than that of GC Unifast Trad™. Moreover, hardness of GC Unifast Trad™ coated was not significantly different than that of Protemp™ 4.

Conclusion: The surface of acrylic resin coated with silane-SiO₂ nanocomposite film exhibits higher hardness compared to conventional acrylic resin and hardly different from bis-acryl composite resin. Even though, after thermocycling condition, the hardness of acrylic resin coated is still close to bis-acryl composite resin.

Keywords: provisional restorative material, silane surface coating agent, surface hardness

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Introduction

Provisional prosthetic restorations provide biological, mechanical, and esthetic requirements before permanent prostheses were done. Provisional restorations were used as diagnostic tools in cases with alteration of abnormal occlusal planes and changes in vertical dimension. In case of oral rehabilitation, provisional restorations were used in verifying vertical dimension for relatively long periods of time (6–12 weeks) as the purpose of monitoring patient comfort and satisfaction and to allow for any necessary adjustments [1, 2].

Interim restorative materials for crown and fixed partial denture were commonly divided into four groups depending on resin compositions. Polymethyl methacrylates (PMMA) was originally used as material for provisional restoration. Recently, bis-acrylate composite resins are more commonly used in direct provisional prosthetics in an oral cavity [3].

In case of using long-term provisional restorations, wear of restorations is an important issue to evaluate occlusion by losing of occlusal contact following by reduced occlusal clearance. The indicator of density is surface hardness that identifies wear resistance and surface degradation [4].

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Hardness is lower in polymethyl methacrylates compared to bis-acrylate composite resins [5].

Recently, dental glazes and coating materials were created to improve some mechanical properties such as altering roughness, changing surface energy, and reducing degradation of material surface.

In dental applications, the silanes were used for many purposes. Silane has an important role that provide adhesion at interface and added the SiO₂ nanoparticles to the strength of the film [6].

Oral conditions alter the mechanical properties of the temporary restorations that were found decreasing in hardness after being stored in water [5]. In addition, changes in intraoral temperature are affected by routine activities such as eating, drinking, and breathing. This situation may change its physical properties and its durability [7].

The aim of this study was to evaluate the hardness of a new modified PMMA provisional restorative material compared to 4 commercially available provisional restorative materials. The null hypothesis of this study was that the surface modification of the PMMA provisional restorative material with the thin film coating would not affect the hardness.

Materials and methods

Two commercially PMMA provisional restorative materials (GC Unifast Trad™, Major C&B dentine) and two commercially bis-acryl provisional restorative materials (Protemp™ 4, Luxatemp® star), commonly used in prosthodontic treatment, were selected for investigation. The types, manufacturers, and compositions of the materials used for the experiments are listed in Table 1.

An epoxy mold was used to prepare 5 mm x 10 mm x 2 mm bar shaped specimens according to EN ISO 4049:2009 and the

manufacturer's instructions. Each specimen was polished using a polishing machine and wet abrasive paper discs with a grit of 600, 800, 1,000, and 2,000. One of four commercially provisional restorative materials (GC Unifast Trad™) was selected for coating with silane-SiO₂ nanocomposite film.

Coating solution was prepared by mixing 7.5 g of methyl trimethoxysilane (MTMS) with 0.9 mL of acetic acid and 8.1 g of SiO₂ nanoparticles, following with 10.5 mL of solvent. The specimens were cleaned using isopropanol 30s. The hard-coating solution was applied to the pretreated specimens by motorized dip coater at a withdrawal speed of 30 cm/min. Next, the coated specimens were subjected to evaporate the solvent in coating solution by preliminary curing in temperature of 65°C for 20 minutes and heating treatment at 110°C for 2 hours [6, 8].

The GC Unifast Trad™ coated specimens were characterized with a Nicolet 6700 Fourier-transform infrared (FTIR) spectrometer (Thermo Scientific).

There were two conditions of test specimens: control condition and thermocycling condition made in a thermocycling machine and consisted of 5,000 cycles at 5 and 55 °C with a 30-second dwell time.

Five specimens from each group were evaluated with a Vickers hardness tester (Microhardness Tester FM-700; Future-Tech Corp). The diamond indenter was pressed into the specimens under a load of 1 N and with a loading time of 15 seconds. Three indentations were created and measured on each specimen under a microscope. The mean values of 15 indentations in each group were calculated.

Hardness data were normally distributed according to Shapiro-Wilk test. The hardness data were analyzed using two-way analysis of variance at $\alpha=0.05$. Bonferroni test was used to reveal which groups differed.

Table 1 Specification of tested samples groups

Material	Types	Methacrylate	Compositions
GC Unifast Trad™	Methacrylate	GC America, Illinois, USA	Powder: Methyl methacrylate and Ethyl methacrylate copolymer Liquid: Methyl methacrylate, butylated hydroxytoluene, hydroquinone
Major C&B dentine	Methacrylate	Major, Moncalieri (TO), Italy	Unfilled acrylate polymer based on polymethyl methacrylate.
Protemp™ 4	Bis-acryl	3M ESPE, Seefeld, Germany	Base paste: Dimethacrylate(BisEMA6), Silane treated amorphous silica, Reaction production products of 1,6-diisocyanatohexane with 2-((2-methacryloyl)ethyl]6-hydroxyhexanoate and 2-hydroxyethylmethacrylate (DESMA), Silane treated silica Catalyst paste: Ethanol, 2,2'- [(1-methylethylidene) bis (4,1-phenyleneoxy)] bis-, diacetate, Benzyl-phenyl-barbituric acid, Silane treated silica, Tertbutyl peroxy-3,5,5-trimethylhexanoate
Luxatemp® star	Bis-acryl	DMG, Hamburg, Germany	Glass filler in a matrix of multifunctional methacrylates; catalysts, stabilizers and additives. Free of methyl methacrylate. Total filler volume: 44 w% = 24 vol% (0.02 to 1.5 µm)

Result

The FTIR spectrum of both GC Unifast Trad™ and GC Unifast Trad™ coated had Carbon (C)-hydrogen (H) stretching that was observed at approximately 2984.1-2947.4 cm⁻¹. Carbon (C)=oxygen (O) stretching at 1720.3 cm⁻¹ and C-O

stretching at 1140.4 cm⁻¹ were showed in GC Unifast Trad™ specimen. and a silicon-oxygen-silicon peak was remarked in the phase of 996.6 cm⁻¹ that present hard coating film on GC Unifast Trad™ coated specimen (Figure 1).

Means and standard deviations of hardness in control and thermocycling conditions are shown in Table 2.

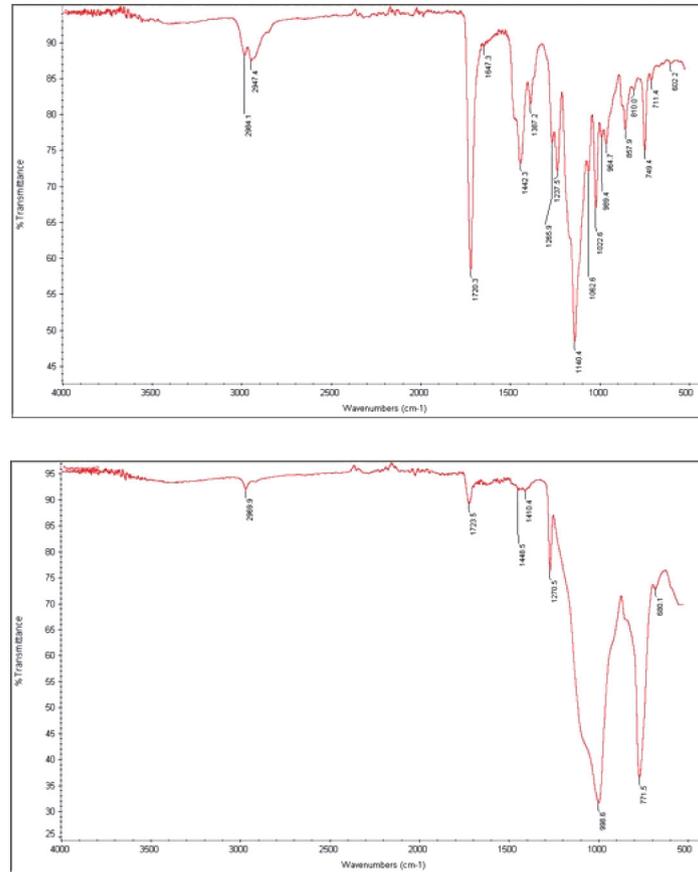


Figure 1 The FTIR spectrum of GC Unifast Trad™ (Top) and GC Unifast Trad™ coated (Bottom)

Table 2 Mean and standard deviation values of hardness of control and thermocycling conditions in each group (n=15)

Material	Mean(SD) in control condition	Mean(SD) in thermocycling condition
GC Unifast Trad™	15.58 (0.96) ^{a,A}	14.24 (0.44) ^{b,A}
Major C&B dentine	17.94 (0.55) ^{a,C}	16.64 (0.91) ^{b,C}
Protemp™ 4	19.63 (0.84) ^{a,D}	17.65 (0.77) ^{b,B,C}
Luxatemp® star	20.52 (1.42) ^{a,D,B}	20.60 (0.20) ^{a,D}
GC Unifast Trad™ coated	21.12 (1.73) ^{a,B}	18.20 (1.05) ^{b,B}

Note: within the same material (horizontal row), means with different superscripts written in lowercase letters were significantly different ($p < 0.05$).; within the same condition (vertical column), means with different superscripts written in uppercase letters were significantly different ($p < 0.05$).

In control condition, hardness of GC Unifast Trad™ coated was significantly higher than hardness of GC Unifast Trad™ ($p < 0.05$). In addition, hardness of GC Unifast Trad™ coated was not significantly different than that of Luxatemp® star ($p > 0.05$).

In thermocycling condition, hardness of GC Unifast Trad™ coated was significantly higher than hardness of GC Unifast Trad™ ($p < 0.05$). In addition, hardness of GC Unifast Trad™ coated was not significantly different than that of Protemp™ 4 ($p > 0.05$).

Comparing control and thermocycling conditions, GC Unifast Trad™, GC Unifast Trad™ coated, Major C&B dentine, Protemp™ 4 were

significantly reduced in hardness ($p < 0.05$), whereas Luxatemp® star was not significantly reduced in hardness ($p > 0.05$).

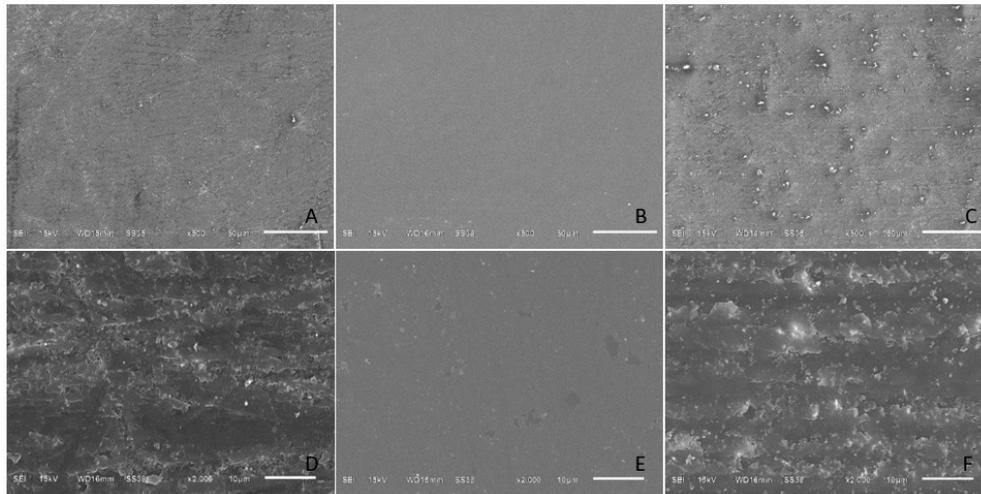


Figure 2 Scanning electron microscope images of specimens (500 magnification). A Top-view image of GC Unifast Trad™. B, Top-view image of GC Unifast Trad™ coated. C, Top-view image of Major C&B dentine. Scanning electron microscope images of specimens (2,000 magnification). D, Top-view image of Top-view image of GC Unifast Trad™ after thermocycling. E, Top-view image of GC Unifast Trad™ coated after thermocycling. F, Top-view image of Major C&B dentine after thermocycling.

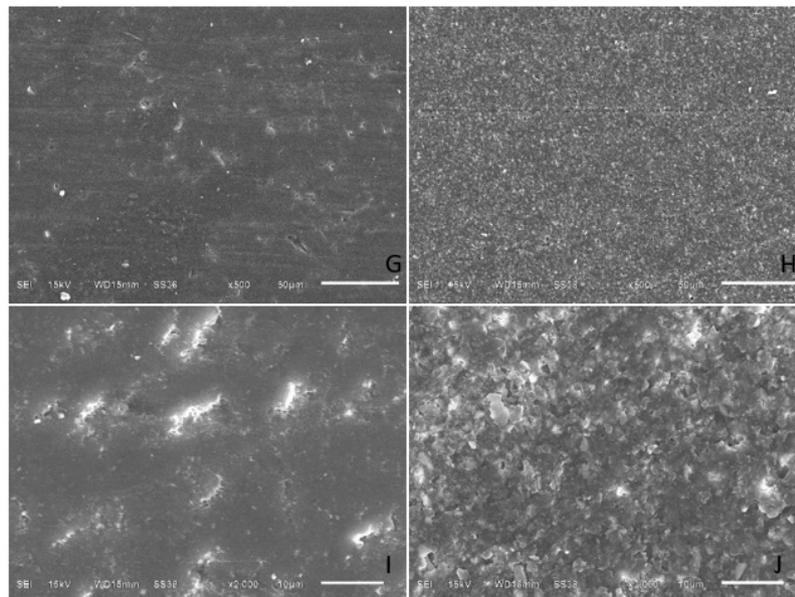


Figure 3 Scanning electron microscope images of specimens (500 magnification). G, Top-view image of Protemp™ 4. H, Top-view image of Luxatemp® star. Scanning electron microscope images of specimens (2,000 magnification). I, Top-view image of Top-view image of Protemp™ 4 after thermocycling. J, Top-view image of Luxatemp® star after thermocycling

Discussion

The null hypothesis that a silane-SiO₂ nanocomposite film would not affect surface hardness of the PMMA provisional restorative material in both before and after thermocycling conditions was rejected.

The provisional restorative materials' mechanical properties in PMMAs and bis-acrylate composite resins were compared. Because of the basic chemical compositions of bis-acrylate composite resins, which are rigid, cross-linked structures e.g., Bis-GMA, TEGDMA, the previous studies demonstrated that bis-acrylate composite resins exhibited better mechanical properties in terms of hardness than PMMAs [9]. The present results confirmed that the hardness in bisacryl groups (Protemp™ 4, Luxatemp® star) was not significantly different ($p>0.05$) and significantly higher than that in PMMA groups (GC Unifast Trad™, Major C&B dentine) ($p<0.05$).

In the other hand, PMMAs contains linear molecules leading to lower rigidity and mechanical resistance [10]. In this study, GC Unifast Trad™ PMMA provisional restorative group was chosen for strengthening with silane-SiO₂ nanocomposite film because GC Unifast Trad™ is commonly used in dental clinics and faculty of dentistry.

Thin hard coating film with silane added with SiO₂ nanoparticles reinforces the strength of the film [6, 11]. The film effects the properties of the film such as hardness, roughness, and texture of the surface, as a result, hardness of GC Unifast Trad™ coated was significantly higher than that of GC Unifast Trad™ ($p<0.05$) [8]. In addition, The FTIR spectrum of the Si-O-Si bonds presented on the coated surface indicating that GC Unifast Trad™ surface was covered by the silane-SiO₂ nanocomposite film.

Kamonwanon *et al.* [8] found that the microhardness of the silane-SiO₂ nanocomposite film coated acrylic resin artificial teeth was superior to that of the conventional acrylic resin artificial teeth. Similarly, Yodmongkol *et al.* [12] found higher surface hardness in acrylic resin denture base material after coated SiO₂-nanocomposite film. As a result, the findings from the two research that are related to this one.

In scanning electron microscope, thin hard coating thickness is about 2 μm (Figure 4). Comparing to 25-50 μm of commercially surface sealing agents such as Palaseal (Heraeus Kulzer GmbH), Optiglaze (GC Corp Biscover; Bisco Inc.), the thickness of silane-SiO₂ nanocomposite film coating in this study is lesser. Moreover, human natural teeth can usually recognize a range

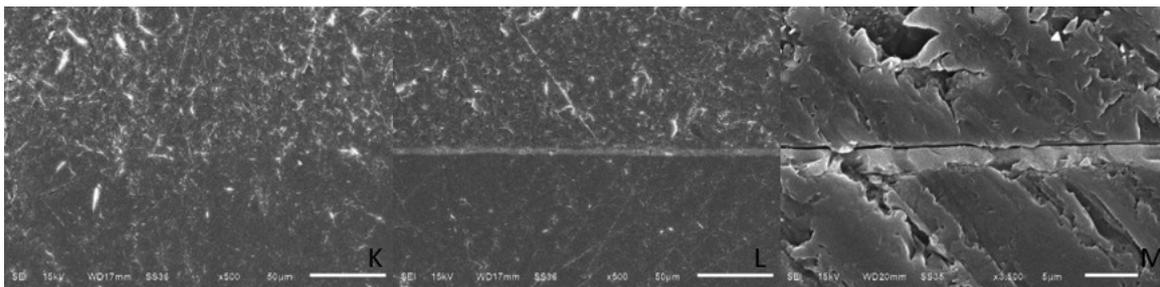


Figure 4 Scanning electron microscope images of specimens (500 magnification). K, cross sectional-view image of GC Unifast Trad™. L, cross sectional-view image of GC Unifast Trad™ coated. Scanning electron microscope images of specimens (3,500 magnification). M, cross sectional-view image of GC Unifast Trad™ coated.

of variation being 8-30 μm [13]. Therefore, GC Unifast Trad™ coated restorations will not disturb perception that become from overcontour or overocclusion.

After thermocycling condition, the water molecules inside the polymeric structure actions plasticizing effect and the reduction in the interchain interactions results in reduced hardness [14]. In addition, when the temporary restorations are submitted to temperature changes inside the oral cavity, the restorative material could undergo fatigue or stress following by decreasing of hardness.

However, polymeric chains with high crosslink density in bis-acrylate composite resins reduce water absorption of the material due to decrease in free space. Therefore, in materials with a denser polymer network, lesser water absorption is observed [15]. In the other hand, PMMAs has linear polymer network structure, the high polarity of its molecules, and the air bubbles engaged in its construction, thus it could absorb more than bis-acrylate composite resins [10, 16]. In thermocycling condition, the presence of cross-linked chain did not affect the hardness values. In case of bis-acrylate composite resins, the hardness was higher than PMMAs. Comparably, the hardness of GC Unifast Trad™ coated in thermocycling condition remained higher than GC Unifast Trad™ because Methyltrimethoxysilane (MTMS) is an alkyl silane that has methyl functional group which reduces surface energy and accounts hydrophobic properties [12].

All types of materials presented surface degradation after thermocycling condition, as shown in scanning electron microscope figures. Protemp™ 4 and Luxatemp® star were found filler leaching when compared to the control condition. In case of GC Unifast Trad™ and Major C&B dentine were found rough surfaces. Whereas GC

Unifast Trad™ coated was found disintegration of the silane coating at the resin-filler interface in some areas.

Additionally, silane-SiO₂ nanocomposite film coating is practical and inexpensive that it can be processed in dental laboratories and dental clinics. However, the method should be developed to be simpler in the further research.

Conclusion

The surface of acrylic resin coated with silane-SiO₂ nanocomposite film exhibited higher hardness compared to conventional acrylic resin and hardly different from bis-acryl composite resin. Even though, after thermocycling condition, the hardness of acrylic resin coated was comparable to bis-acryl composite resin.

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