

The Effect of Various Types of Coupling Agent Solution on the Surface Wettability of Polyoxymethylene

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Abstract

The purpose of this study was to investigate the effect of various types of coupling agent solutions as a surface treatment of polyoxymethylene (POM) on surface roughness and wettability.

Seventy-five POM specimens were fabricated from polyoxymethylene CAD-CAM blocks and divided into non-treated (control) and 4 coupling agent solutions treated groups (n=15/group): MPS, APS, AAPMS, and Clearfil Ceramic Primer (CCP). Fifteen specimens of each treated group were assessed with a goniometer via sessile drop method and profilometer to determine surface roughness and contact angle; morphological changes in untreated and treated specimens were examined by using scanning electron microscopy and element depositions were analyzed by using energy dispersive spectrometer (EDS). One-way ANOVA was used at $p < 0.05$ for statistical comparison.

POM specimens treated with MPS and CCP resulted in significantly lower contact angle than control, APS and AAPMS groups ($p < 0.05$). No differences in contact angle were measured between MPS ($62.2 \pm 9.9^\circ$) and CCP ($52.1 \pm 13.0^\circ$); and also, between control ($90.8 \pm 4.1^\circ$), APS ($91.1 \pm 5.0^\circ$) and AAPMS ($85.6 \pm 7.3^\circ$). Surface roughness was not significantly different after treatment between groups ($p < 0.05$). EDS analysis showed silica on MPS, APS, AAPMS and CCP. Contrary to phosphorus, that was discovered on CCP only.

The surface roughness of all test groups was similar. POM treated with MPS and CCP exhibited the lowest contact angle.

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Introduction

Metal alloys and polymers have been extensively and consecutively used in dentistry. Since the mechanical properties of metal alloys are superior to polymers, metal alloys have been fabricated more often for a denture.¹ However, the disadvantages of metal alloys are metal allergies and esthetic concerns.² To overcome this problem, polymers have been developed to replace metal alloys.

Polyoxymethylene (POM), a

thermoplastic resin also known as acetal resin, has been widely used in the automotive industry and has become a competitor to metal.² POM is formed as formaldehyde, polymerized into a chain of alternating methyl groups interconnected by an oxygen molecule. Due to its high percentage of crystallinity, POM shows high stiffness, high fatigue resistance, good appearance and thermal stability.^{3,4} Since 1986, owing to its superior esthetics and strength, POM has been used in dentistry as an alternative material for denture base and denture clasp.⁵ Used as a clasp for a removable partial denture, although a previous study indicated POM had lower retention than metal. POM had no deformation while the cobalt-chromium metal clasps were still deformed.⁶ Additionally, the increased thickness and undercut of a POM clasp can gain sufficient retention in clinical use.⁷ Regarding denture base material use, wear resistance, fracture toughness and

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microhardness of POM were higher than polymethylmethacrylate (PMMA) which is a conventional plastic material.^{8, 9} Moreover, previous studies showed that POM had low water and color absorption.^{10, 11} Presently, POM is available in CAD-CAM blanks that are suitable for digital dentistry era.

Due to polymeric materials having low surface free energy and lacking polar functional groups on their surfaces, chemical bond strength to other materials is poor.¹² From the study of shear bond strength of CAD-CAM POM and PMMA to composite by using universal adhesives and air abrasion, POM showed lower shear bond strength than PMMA but was sufficient as a repairing material.¹³

Adhesion promoters are one way to improve adhesion apart from the mechanical method and have been used to improve the adhesion of polymers.¹² The definition of adhesion promoter is a chemical agent that reacts at the interface of different materials. It could be difunctional or multifunctional monomers or oligomers with more than one functional group that can cause a chemical reaction.^{14, 15} Silane is one of the well-known adhesion promoters in dentistry and industry. Silane creates strong bonding between organic (resins) and inorganic (glasses, metals, and fillers) substances through two functional groups. Apart from utilization as coupling agents in the adhesive application, silane is mostly used to modify the wettability of the substrate because it does not impart chemical activity to the substrate.¹⁶ The increase of wettability in the thermoplastic was due to a covalent bond formation followed by improving bonding through the migration of a coating formulation to the substrate interface.^{17, 18} Thermoplastic has been mostly coupled by aminoalkylsilanes¹⁹, particularly the previous study showed that N-2(aminoethyl)3-aminopropyltrimethoxysilane (AAPMS) was reactive to most thermoplastic in the experiment.¹⁸ In dentistry, acrylate silane and amino silane are used to promote the adhesion of two dissimilar materials. 3-Methacryloxypropyltrimethoxysilane (MPS) is extensively used in clinical commercial silane primers.^{20, 21} For example, Clearfil ceramic primer plus (CCP) which contains MPS and 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP) monomer. The phosphate group in 10-MDP was founded that increased the molecular

polarity of resin cement which is a kind of polymer.²² The coupling agent solutions stated that have the potential to increase the wettability of plastic were chosen in the present study.

The property that indicated the wettability or surface free energy of a material is contact angle.²³ Since there is no study on the wettability of POM to coupling agent solutions, the purpose of this study was to investigate surface roughness and wettability on treated POM surfaces with various types of coupling agent solutions. The null hypothesis was that there were no significant differences in surface roughness and wettability among types of coupling agent solutions.

Materials and methods

Specimen preparation

Table 1 shows the compositions and specifications of the materials utilized in this investigation. Seventy-five square-shaped POM specimens (10x10x2 mm³) were prepared from POM CAD-CAM by using an inLab MC X5 milling machine (Dentsply Sirona, PA, USA).

These specimens were polished using a Grinding & Polishing Machine (MoPao 160E, MEGA Advance, Shandong, China) under running water using 800, 1000, and 2000 grit rotating silicon carbide waterproof abrasive electro-coated paper (K.S.C. engineering co., ltd., Bangkok, Thailand) for 1 min each.

Before surface treatment, all specimens were cleaned using an ultrasonic machine (Ultrasonic cleaner VI, Yoshida dental trade distribution Co., Ltd., Tokyo, Japan) for 10 min followed by air-drying. Specimens were divided into five groups (n=15) which were no surface treatment (control group) and four surface treatment groups: treated with MPS (MPS), treated with 3-Aminopropyltriethoxysilane (APS), treated with N-2(aminoethyl)3-aminopropyltrimethoxysilane (AAPMS), and treated with Clearfil ceramic primer plus (CCP).

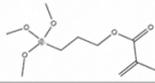
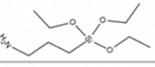
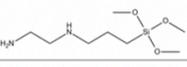
Name		Brand or Cat. No.	Mfg.	Lot. No.
Acetal	99% POM Copolymer	Zirlux®	Henry Schein Inc., New York, US	311684
3-methacryloxypropyl Trimethoxysilane (MPS)	MPS 	KBM 503	Shin-Etsu Chemical, Tokyo, Japan	03999
3-aminopropyl Triethoxysilane (APS)	APS 	KBE 903	Shin-Etsu Chemical, Tokyo, Japan	507147
N-2 (aminoethyl) 3-aminopropyl Trimethoxysilane (AAPMS)	AAPMS 	KBM 603	Shin-Etsu Chemical, Tokyo, Japan	503038
Clearfil ceramic primer plus (CCP)	10-MDP Ethanol (80%) 3-MPS	Kuraray	Kuraray Tokyo, Japan	AV0049
Ethanol	99.7 % Ethanol	RCI LABSCAN	RCI LABSCAN CO.,LTD, Bangkok, Thailand	21020152 (Batch No.)

Table 1. List of materials used.

Coupling agent solution pretreatment

Ethanol was diluted to 70 vol% ethanol solution by a mixture of 99.7 vol% and deionized water (ETH). To initiate and regulate the hydrolysis of alkoxy silanes, particularly MPS24, the pH of ETH mixed with MPS was regulated to 4.5 by titrating with 99.9% acetic acid and measured with a pH meter (MP225 General Purpose GLP pH /mV / T Meter, Mettler-Toledo International, Greifensee, Switzerland). Due to amino silane could be hydrolyzed by moisture in the atmosphere, no adjustments to APS or AAPMS were required. According to previous studies, MPS, APS, and AAPMS were combined with ETH to achieve a 2 vol % concentration. 25, 26 A hundred-milliliter polyethylene cups with a cover were used to store these solutions and allowed silane to hydrolyze for 5 minutes. Then, 10 microliters of coupling agent solution were dropped into each specimen using a micropipette (Biohit Proline, Biohit, Helsinki, Finland), followed by thoroughly spreading the solution using a microbrush and left untouched according to the normal silane application in dentistry. The specimens were air-dried for 10 seconds using a dental unit triple syringe.

Surface roughness measurement

Five specimens were randomly selected from each group and measured before surface treatment to confirm the surface roughness after polishing using a profilometer (Sulitest-402, Mitutoyo, Kanagawa, Japan) equipped with a

contact stylus gauge. The equipment was calibrated with a standard reference specimen before being adjusted at 0.1 mm/s. For each specimen, the procedure was repeated three times with a 2 mm difference in the measurement track. The mean roughness average (Ra) for each specimen was recorded and calculated for the mean Ra value of each test group. After surface treatment, all 75-specimens were measured using the same procedure. The mean difference of Ra value was calculated by the Ra value after surface treatment minus the mean Ra value before surface treatment of each test group.

The sessile drop method for contact angle measurement

The contact angle measurement device (Contact angle goniometer, CMU-PHYS-nanolabs, CMU-PHYS, Chiangmai, Thailand) was used to determine the degree of wettability of each group's surface (n=15) using the sessile-drop technique at room temperature. Using a needle, 10 microliters of deionized water were poured into the center of the specimen. The static contact angles were photographed with a digital camera on a device after exactly 5 seconds. The captured images were determined by ImageJ software (Java 1.8.0_172, U.S. National Institutes of Health, MD, USA) from the average angle from both ends of the drop. The mean contact angle for each tested group was recorded.

Microstructure observation of the surface

Each group's surface structure topography (n=1) was sputter-coated with gold and examined using a scanning electron microscope (JSM-5910LV, JEOL, Massachusetts, USA) at a magnification of x1000.

Element deposition analysis

After investigating the surface structure topography, the same specimens were analyzed by a scanning electron microscope (SEM) with an energy dispersive spectrometer (EDS) (JSM-5910LV, JEOL, Tokyo, Japan). For each specimen, the principal electron energy beam was set at 15 keV and the center of each specimen was examined.

Statistical analysis

Data were statistically analyzed with software (IBM SPSS Statistics 17, SPSS Inc., IL,

USA). After using Shapiro–Wilk and Levene's tests to determine normality and homoscedasticity ($p > 0.05$), the contact angle and mean difference of Ra values were submitted to a one-way ANOVA model ($p = 0.05$).

Results

The surface roughness values before coupling agent solutions pretreatment were normal distribution and no significant difference among all groups. Both surface roughness and contact angle values of all groups were normally distributed. Therefore, they were parametrically evaluated with one-way ANOVA. Table 2 shows the means and standard deviations of surface roughness and contact angle after coupling agent solutions application. For surface roughness, the mean difference of the Ra value of POM treated with various types of coupling agent solutions was $0.0028 (\pm 0.02) \mu\text{m}$. The Ra values were not significantly different among all groups of specimens ($p > 0.05$), whereas contact angle values showed a significant difference ($p < 0.05$). Dunnett T3 analysis showed MPS and CCP were significantly lower contact angle than other groups ($p < 0.05$) while there was no difference among APS, AAPMS, and control. Contact angle images of deionized water on each specimen group were shown in figure 1. The SEM images of all groups were similar and seem slight homogeneous abrasions as seen in figure 2.

Coupling agent solutions	Surface Roughness (μm)	Contact angles (degree, °)
	Mean difference (SD)	Mean (SD)
Control	0.0041 (0.02) ^A	90.8 (4.1) ^B
MPS	-0.0003 (0.02) ^A	62.2 (9.9) ^A
APS	0.0079 (0.02) ^A	91.2 (5.0) ^B
AAPMS	0.0005 (0.02) ^A	85.6 (7.3) ^B
CCP	0.0015 (0.01) ^A	52.1 (13.0) ^A

Table 2. The average and standard deviations of surface roughness and contact angle after coupling agent solution application.

Different letters are for post hoc test. Means with the same letter in each row are not significantly different at $p < 0.05$.

From element deposition analysis as shown in table 3, the results found Silica (Si) in all specimen groups. However, phosphorus (P) was detected only in CCP.

Element	Atomic%				
	Control	MPS	APS	AAPMS	CCP
N	17.05	21.13	19.29	11.20	13.63
Si	0.07	4.31	8.70	10.81	14.22
Au	82.88	74.56	72.01	78.00	72.01
P	-	-	-	-	0.14

Table 3. The atomic percentage of elements that was found on POM specimen's surface after being treated with various types of coupling agent solutions.

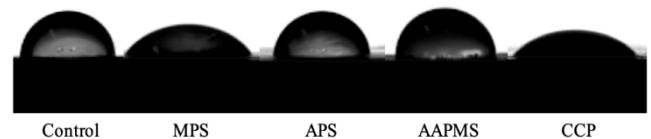


Figure 1. Contact angle image of deionized water on POM treated with various types of coupling agent solutions.

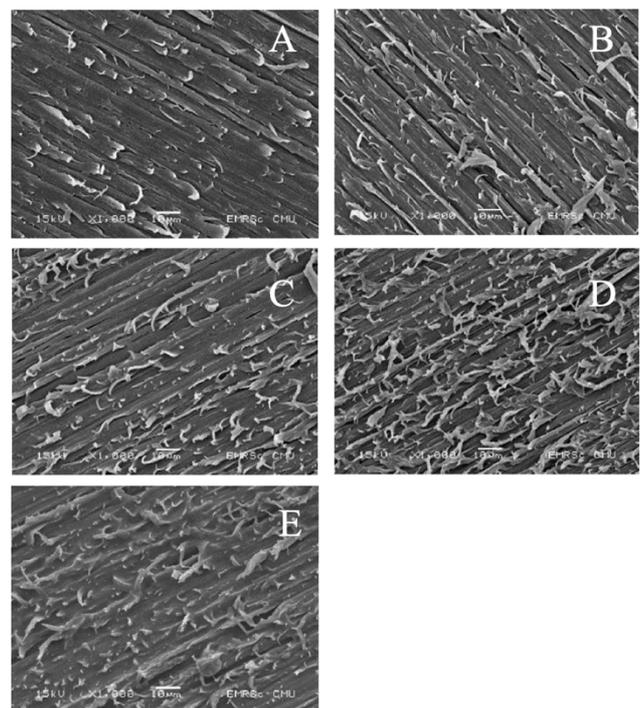


Figure 2. SEM images at 1000x magnification after coupling agent solutions pretreatment. (A) control, (B) MPS, (C) APS, (D) AAPMS and (E) CCP.

Discussion

The present study investigated the influences of various types of coupling agent solutions on wettability through contact angle on deionized water and surface roughness on POM surfaces. Thus, regarding the surface roughness,

the null hypothesis was accepted. But, regarding the contact angle, the null hypothesis was rejected.

Contact angle (Θ) is measured by a drop of liquid on a plane, between a plane of the solid-liquid surface and a plane of the liquid-gas surface, as a result of equilibrium of adhesion and cohesion force. This method is an excellent indicator of a substrate's relative hydrophobicity or hydrophilicity, as well as an inverse wettability assessment.^{16, 27} The surface of all specimens was polished with 2000-grit silicon carbide abrasive paper to standardize the surface roughness which subsequently eliminate the physical aspect of wettability. Molded POM has a smooth surface with low surface polarity and surface tension (38 mJ m^{-2})²⁷ which affects poor wettability. To improve surface properties, physical and chemical treatment can be used to improve coating adhesion. Acid solutions such as phosphoric acid, acid ammonium sulfate, and oxidant solutions such as a mixture of chromic and sulfuric acids can react to the surface of POM, followed by increasing roughness. However, since the preparation conditions are excessively aggressive, the physio-mechanical characteristics of POM may be compromised. Adding functional modifiers such as carbonyl, hydroxyl, amide, and methacrylate compound groups could overcome this issue.²⁸

The present study focused mainly on silane use for modifying the wettability of substrate. There are two reactive groups of silane coupling agents attached to the silicon atom:



R, a nonhydrolyzable side, usually forms a chemical bond with organic materials such as synthetic resins. X, a hydrolyzable side, generally methoxy or ethoxy, reacts with the various forms of hydroxyl groups in inorganic substrate followed by methanol or ethanol releasing,^{18, 19} especially methoxy groups which can react with hydroxy-functional polymers.¹⁸

Typically, the substituent polarity is related to the relative hydrophobicity or hydrophilicity of the silane. Because of the low critical surface tension of silane, MPS (28 mN/m), APS (35 mN/m) and AAPMS (33.5 mN/m) are silane hydrophobic.^{17,29} In general, the hydrophilicity of a surface increases in the following order: non-polar polar, no hydrogen

bonding polar, hydrogen-bonded, hydroxylic and ionic.¹⁶ It can be assumed that the POM surface became more hydrophilic due to the hydroxyl group of the hydrolyzable side, which is created after hydrolysis and condensation reaction of silane. The rate of hydrolysis and condensation reaction depends on the steric and inductive effects and polarity of the organofunctional group.³⁰ According to MPS, APS, and AAPMS have different molecular weights and structures. Regarding the steric hindrance effect, MPS and AAPMS have a methoxy group as the end group that is smaller than the ethoxy group from APS.³¹ Therefore, when the nucleophile hits the core silicon atom, this would decrease the steric repulsion resulting in decreasing the activation energy of the transition state and increasing the rate of hydrolysis.²¹ Which corresponds to the lowest contact angle of MPS. On the other hand, both APS and AAPMS did not affect contact angle, it can be assumed that the occurrence of hydrolysis was less for amino silane on POM surfaces.

Additionally, the functional group on the nonhydrolyzable side of silane may form the covalent bond by reaction with completed polymer or copolymerized with the monomer for a thermoplastic.¹⁹ Methacryloxy functional silane (MPS) which typically reacts to substrate by copolymerization with a covalent bond.³² While, amino-functional silane (APS, AAPMS) reacts to substrate by a hydrogen bond with nitrogen inside the molecule.³³ According to the weaker bond of a hydrogen bond than a covalent bond, this could be the cause of the lower wettability of MPS. Moreover, the selection factors of solvent for the polymer are the polymer-silane reactivity, compatibility, and the polymer-silane solubility parameters. The solubility parameter concept is usually used as a screening tool for the prediction of compatibility of polymer and solvent systems.¹⁸ The previous study showed that alumina treated with MPS created the highest bond strength to PMMA because of the lesser difference of the Hildebrand solubility parameter of MPS.²⁰ Hildebrand solubility parameter of MPS (9.48) and POM (8.3) that calculated from Hansen solubility parameter with the same experimenter and method are the closest compared to other coupling agents.^{34,20} This can be concluded that POM is the most compatible with MPS.

The CCP group exhibited a lower contact angle than the MPS group. The additional component apart from MPS is 10-Methacryloyloxydecyl dihydrogen phosphate (10-MDP) which has a similar structure as MPS: a similar polymerizable side and phosphate group as a hydrophilic side instead of a hydroxy group. The phosphate group in 10-MDP has an increased molecular polarity of resin cement that helps to attract water.²² EDS analysis showed P only in the CCP group that was assumed as a phosphate group. Likewise, more water attraction from more phosphate in the coupling agent solution can be inferred.³⁵

The influence of the degree of surface wettability on the enhancement of bond quality is both a physical and chemical interaction.³⁶ Treated POM surfaces showed similar surface roughness and surface characterization to untreated POM surfaces. Thus, the physical properties of a material's surface were unchanged, which could infer that the important role of increasing the wettability surface of treated on POM surface was not from the physical interaction of the material but chemical interaction indeed.

From the result of this study, MPS and CCP may be good adhesion promoters for POM. However, the wettability can be indicated only as a trend of adhesion. Thus, further studies should investigate the bond strength between POM and selected materials. For example, in the clinical use of POM as an RPD framework³⁷, the study of bond strength between POM and PMMA using MPS as a surface pretreatment could lead to a new guideline for surface pretreatment in clinical application.

Conclusions

Within the limitations of this in vitro study, it could be concluded that:

1. MPS and CCP significantly increased the wettability of deionized water on treated POM surfaces.
2. Surface roughness was not affected by any coupling agent.
3. The type of coupling agent significantly influences the degree of wettability of the POM surface.

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Declaration of Interest

The authors report no conflict of interest.

References

1. Becker CM, Kaiser DA, Goldfogel MH. Evolution of removable partial denture design. *J Prosthodont.* 1994;3(3):158-66.
2. Jarvis DL. Polyacetals. *Brydson's Plastics Materials.* 8th ed. ed: Elsevier; 2017. p. 513-26.
3. Karamuk E, Mayer J, Düring M, et al. Biocompatible materials science and engineering. Paper presented at: Proceedings of the 2nd international Conference, 24th and 25th August 1999, 2001; Bolton Institute, UK.
4. Fitton J, Davies E, Howlett J, Pearson G. The physical properties of a polyacetal denture resin. *Clin Mater.* 1994;17(3):125-29.
5. Turner JW, Radford DR, Sherriff M. Flexural properties and surface finishing of acetal resin denture clasps. *J Prosthodont.* 1999;8(3):188-95.
6. Arda T, Arikan A. An in vitro comparison of retentive force and deformation of acetal resin and cobalt-chromium clasps. *J Prosthet Dent.* 2005;94(3):267-74.
7. Tannous F, Steiner M, Shahin R, Kern M. Retentive forces and fatigue resistance of thermoplastic resin clasps. *Dent Mater.* 2012;28(3):273-78.
8. Alagwany A, Diab Fatoh MA, Helal MA, Mahmoud II. Wear resistance evaluation of the thermoplastic acetal resin denture base material—an in vitro study. *J Clin Res Dent.* 2019;2(2):1-5.
9. Kamal M. Evaluation of surface micro-hardness and fracture toughness of conventionally constructed versus CAD/CAM constructed denture base materials—an in-vitro study. *Egypt Dent J.* 2021;67(1-January (Fixed Prosthodontics, Removable Prosthodontics and Dental Materials)):757-65.
10. Arikan A, Ozkan YK, Arda T, Akalin B. An in vitro investigation of water sorption and solubility of two acetal denture base materials. *Eur J Prosthodont Restor Dent.* 2005;13(3):119.
11. Ozkan Y, Arikan A, Akalin B, Arda T. A study to assess the colour stability of acetal resins subjected to thermocycling. *Eur J Prosthodont Restor Dent.* 2005;13(1):10-4.
12. Awaja F, Gilbert M, Kelly G, Fox B, Pigram PJ. Adhesion of polymers. *Prog Polym Sci.* 2009;34(9):948-68.
13. Rosca B, Ramalho S, Sampaio-Fernandes JC, Portugal J. Reparability of two different CAD/CAM polymer materials using a light-cured composite and universal adhesives. *Rev Port Estomatol Med Dent Cir Maxilofac.* 2016;57(4):189-96.
14. Pape PG. Adhesion promoters: Silane coupling agents. *Applied plastics engineering handbook:* Elsevier; 2011. p. 503-17.
15. Licari JJ, Swanson DW. Adhesives technology for electronic applications: materials, processing, reliability: William Andrew; 2011.
16. Arkles B, Pan Y, Kim Y. The role of polarity in the structure of silanes employed in surface modification. *Silanes and other coupling agents;* 2009. p. 51-64.
17. Arkles B. Hydrophobicity, hydrophilicity and silanes. *Paint and*

Coatings Industry; 2006. p. 114.

18. Witucki GL. A silane primer: chemistry and applications of alkoxy silanes. *J Coat Technol Res.* 1993;65:57-60.
19. Arkles B. Silane coupling agents: connecting across boundaries: Gelest Inc.; 2014.
20. Chajareenont P, Takahashi H, Nishiyama N, Arksornnukit M. Effects of silane coupling agents and solutions of different polarity on PMMA bonding to alumina. *Dent Mater J.* 2012;31(4):610-16.
21. Lung CYK, Matinlinna JP. Aspects of silane coupling agents and surface conditioning in dentistry: an overview. *Dent Mater.* 2012;28(5):467-77.
22. Ito S, Hashimoto M, Wadgaonkar B, et al. Effects of resin hydrophilicity on water sorption and changes in modulus of elasticity. *Biomaterials.* 2005;26(33):6449-59.
23. Subedi DP, Zajickova L, Bursikova V, Janca J. Surface modification of polycarbonate (bisphenol A) by low pressure rf plasma. *Himalayan J H Sci.* 2003;1(2):115-18.
24. Plueddemann EP. Nature of adhesion through silane coupling agents. Boston, MA.: Springer; 1991.
25. Matinlinna JP, Lassila LV, Vallittu PK. The effect of five silane coupling agents on the bond strength of a luting cement to a silica-coated titanium. *Dent Mater.* 2007;23(9):1173-80.
26. Chen T, Brauer G. Solvent effects on bonding organo-silane to silica surfaces. *J Dent Res.* 1982;61(12):1439-43.
27. Shafrin EG, Zisman WA. Constitutive relations in the wetting of low energy surfaces and the theory of the retraction method of preparing monolayers. *J Phys Chem.* 1960;64(5):519-24.
28. Scaramuzzino P, inventor. Modified polyacetals for decorative applications. US patent US 2004/0228971 A1 2004 Nov. 18, 2004
29. Owen MJ. 3-Methacryloxypropyltrimethoxysilane. *Progress in Silicones and Silicone-Modified Materials;* 2013. p. 47-56.
30. Issa AA, Luyt AS. Kinetics of alkoxy silanes and organoalkoxy silanes polymerization: a review. *Polymers.* 2019;11(3):537.
31. Arkles B, Steinmetz J, Zazyczny J, Mehta P. Silanes and other coupling agents. Ed. KL Mittal, VSP. 1992:91-104.
32. Ishida H, Koenig JL. An investigation of the coupling agent/matrix interface of fiberglass reinforced plastics by Fourier transform infrared spectroscopy. *J Polym Sci B Polym Phys.* 1979;17(4):615-26.
33. Suzuki N, Ishida H. A review on the structure and characterization techniques of silane/matrix interphases. Paper presented at: Macromolecular Symposia, 1996.
34. Hansen CM. Hansen solubility parameters: a user's handbook. 2nd ed. Boca Raton, FL: CRC press; 2007.
35. Carrilho E, Cardoso M, Ferreira M, et al. 10-MDP based dental adhesives: adhesive interface characterization and adhesive stability—a systematic review. *Materials.* 2019;12:790.
36. Della-Bona A. Characterizing ceramics and the interfacial adhesion to resin: II—the relationship of surface treatment, bond strength, interfacial toughness and fractography. *J Appl Oral Sci.* 2005;13:101-09.
37. Teeranuwat P, Jindachua C, Rungsiyakull P, Chajareenont P. Computer-aided design and computer-aided manufacturing fabricated polyoxymethylene used for maxillary removable partial denture framework. *J Int Dent Med Res.* 2022;15(1):306-11.