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Research

Chemical characterization of silanized silver nanoparticles impregnated in poly (methyl methacrylate) resin: An *in vitro* study

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Abstract

Aim: The intention was to determine the chemical interaction of silanized AgNPs with PMMA by Fourier transform infrared (FTIR) spectroscopy.

Settings and Design: *In-vitro* comparative study.

Materials and Methods: This study is composed of four groups – 0.75% AgNP, 1.0% AgNP, 1.5% AgNP impregnated with PMMA, and nonimpregnated PMMA as control. The chemical nature of silanized AgNPs was studied using FTIR study.

Results: The results showed the appearance of new peak between 1727/cm and 1436/cm, i.e., 1636.476/ cm, 1645.886/cm, and 1646.885/cm, representing the C = C stretch in the experimental groups, i.e., 2, 3, and 4, respectively. This peak confirms that coupling agent has chemically interacted with PMMA.

Conclusion: It can be concluded that the AgNPs coated with the silane coupling agent TMSPM has chemically reacted with PMMA.

Keywords: Denture base resin, silane coupling agent, silver nanoparticles

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Submitted: 22-Apr-2022, **Revised:** 09-Jul-2022, **Accepted:** 13-Jul-2022, **Published:** 29-Dec-2022

INTRODUCTION

Dr. Walter Wright and Vernon Brothers in Philadelphia launched acrylic resins as transparent resin in 1936 and as acrylic powder in 1937. Poly (methyl methacrylate) (PMMA) is of great importance for its superior esthetics, biocompatibility, low cost, solidity in oral environment, convenient processing and repair.[1] It has good mechanical properties such as high hardness, rigidity, discontinuity deformation, and biological properties. However, it has high adhesion of microorganism causing denture stomatitis.

Silver nanoparticle (AgNP) form incorporated in PMMA reduced the adherence and inhibited the growth of microorganism. The properties of silver-impregnated polymer depend on the size, shape, and concentration and its reaction with the polymer matrix. Silver is the

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Quick Response Code:	Website: www.j-ips.org
	DOI: 10.4103/jips.jips_203_22

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How to cite this article: Nayaki VT, Karthigeyan S, Ali SA, Kalarani G, Ranganathan K, Ranganathan A. Chemical characterization of silanized silver nanoparticles impregnated in poly (methyl methacrylate) resin: An *in vitro* study. J Indian Prosthodont Soc 2023;23:45-9.

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most widely used polymer additive due to its antimicrobial properties.

The problem associated with AgNPs is its incapability to homogeneously disperse within the polymer (PMMA) powder causing the agglomeration of nanoparticles, thus preventing its high surface area being realized for antibacterial action.

The dispersibility of AgNPs in polymer matrix is a significant factor which dominates the enhancement ability of properties of the nanocomposites. To increase the dispersibility as well as decrease the agglomeration of AgNPs in polymer matrix, surface modification of AgNPs is the core method.[2]

To overcome this, a silane coupling agent is added to AgNP to enhance its bonding with PMMA. Silane coupling agents upgrade the mechanical properties of composites by easier and better adhesion of inorganic filler particles to the polymer matrix.[3]

Silane coupling agents act in the interphase region between organic and inorganic substrate and act as bridging, bonding, and to improve adhesion between two dissimilar materials.[4] Silane coupling agent bears alkoxy silane groups and a large number of functional groups which ensure good compatibility between the reinforcing element and the polymer matrix [Figure 1].

In this study, a silane coupling agent named 3-(trimethoxysilyl) propyl methacrylate (TMSPM) containing a alkoxy hydrolyzable group that reacts with hydroxyl group present on the surface of AgNPs was tried.

The coupling agent trimethoxymethylsilane cannot be used as there is no linker and an organofunctional group that reacts with functional group present in the heat cure denture base resin. The TMSPM with two functional groups (C = C and O–C = O) can work more effectively and interact more strongly with hydroxyl groups on the surface of nanoparticles. The intention of this modification was to enhance the hydrophobic property of nanoparticles as compared to the noncoated ones, leading to improved dispersion and interaction of modified nanoparticles in a resin matrix, thus uplifting AgNP properties.

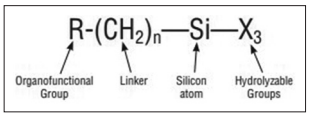


Figure 1: Structure of silane coupling agent

MATERIALS AND METHODS

This was an *in vitro* study done to characterize the chemical interaction of silanized AgNPs impregnated in denture base resins with that of the control group.

Study groups

For this study, four groups were formed and, in each group, one acrylic resin sample was made of AgNP-impregnated PMMA resin.

Preparation of silanized silver nanoparticles

AgNPs of size 10–20 nm (Amnium Technologies, Pune) and a coupling agent TMSPM (Sigma Aldrich) were used. One hundred milliliters of ethanol aqueous solution (70 vol%) was prepared using 99.8 vol% ethanol and deionized water (30 vol%). The pH of ethanol was maintained at 4.8. Five milliliters of ethanol was added to 5 ml of coupling agent, and this mixture was then added to 5 g of AgNPs. The mixture was then placed in magnetic stirrer for 20 min and sonicated in probe sonicator apparatus for 20 min, and left to dry at room temperature for 14 days.[5]

Preparation of experimental groups

For the fabrication of experimental groups, a specified percentage of AgNPs (0.75%, 1.0%, and 1.5%) and polymer is ball milled for 1 h to achieve homogeneous mixing.

Preparation of mold space

Steel dies of size 10 mm × 2 mm were prepared according to the dimension quoted by Ramakrishna Alla in the year 2019.[6] Vernier caliper was used to measure the dimension of the dies. The standardized steel dies of 10 mm × 2 mm thickness were used to prepare the mold space for acrylic samples. The dental flask was filled with dental plaster and coring was done using putty elastomer and the dies were pressed and closed for 5 min.

Preparation of experimental group

For the fabrication of discs in the experimental group, the polymer containing the silanized AgNPs and unmodified monomer were proportioned at 3:1 ratio in a porcelain jar. Once the dough stage is formed, the polymer containing the silanized AgNPs and monomer mixture were then packed in the molds and placed under mechanical press for 10 min. The heat-curing cycle of 74°C for 90 min and at 100°C for 30 min was followed. After curing, the flasks were bench cooled and the disks which were formed were trimmed and polished.

Fourier transform infrared study

Samples were tested by Fourier transform infrared (FTIR) spectrophotometer to determine if the functional groups

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present in the silane coupling agent have been coupled to PMMA resin by scrutinizing characteristic vibrations of functional groups.

RESULTS

Fourier transform infrared–chemical interaction study

To study the chemical interaction of AgNPs coated with TMSPM with that of PMMA, FTIR study was done for both control group and experimental groups.

The peaks from 2956.350/cm to 2921.475/cm represent methylene stretch (C–H), the peaks from 1727.186/cm to 1719.858/cm represent the carbonyl stretch (C = O), the peaks from 1646.885/cm to 1636.476/cm represent TMSPM substituted stretch (C = C), the peaks from 1436.865 to 1433.961 represent C–H deformation, the peaks from 1387.157/cm to 1375.267/cm represent CH_3 deformation, the peaks 1271.418/cm, 1238.620/cm, 1139.415/cm, and 985.859/cm represent C–O stretching, and the peaks 680.096/cm–670.086/cm represent the presence of AgNPs[7] [Figures 2-5 and Table 1].

DISCUSSION

This is an *in vitro* study done to characterize the chemical interaction of silanized AgNPs impregnated in denture base resins with that of the control group.

In this study, it was found that the coupling agent added to the AgNPs has chemically interacted with the PMMA when compared to the control group. Earlier, the same procedure was done using titanium nanoparticles; however, no studies have been reported on AgNPs.

FTIR method is nondestructive, faster than older techniques, sensitive, and precise with simultaneous quantification of many compounds. FTIR detects functional groups, and a molecule's covalent bonds will selectively absorb the radiation of specific wavelength which changes the vibrational energy in the bond. When FTIR study was done to study the characterization of silanized AgNPs impregnated in PMMA, the results showed the appearance of new peak between 1727/cm and 1436/cm, i.e., 1636.476/cm, 1645.886/cm, and 1646.885/cm, representing the C = C stretch in the experimental groups, i.e., 2, 3, and 4, respectively. This peak confirms that TMSPM has chemically interacted with PMMA. This new peak between 1727/cm and 1436/cm was absent in the control group. The peaks 670/cm and 681/cm confirm the presence of AgNPs.

Vodnik *et al*. in 2009 studied the characterization of AgNP in PMMA. When IR measurements were done to check if chemical bonding has occurred, the results of the study showed that there was a weak and physical interaction between the polymer matrix and nanofiller particles.[8]

Kassaee *et al*. in 2010 studied the characterization of AgNPs in PMMA using FTIR study for pure PMMA and PMMA stabilized AgNPs. The results were similar which

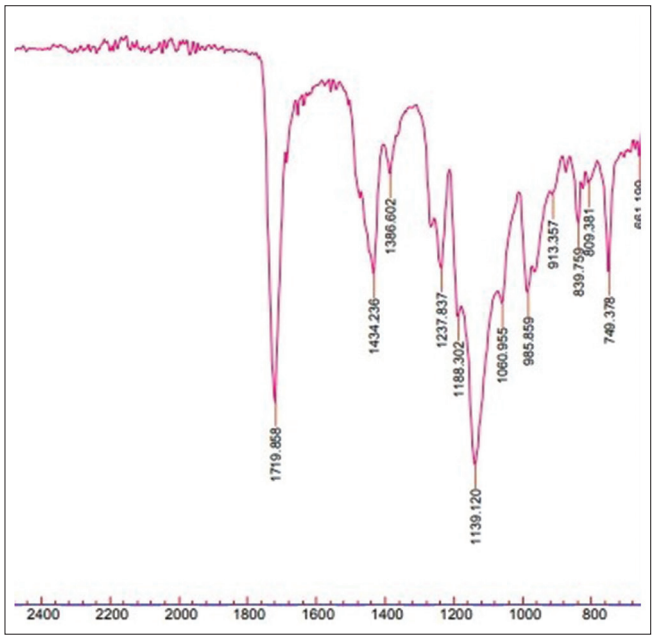


Figure 2: FTIR Group I – Control group. FTIR: Fourier transform infrared

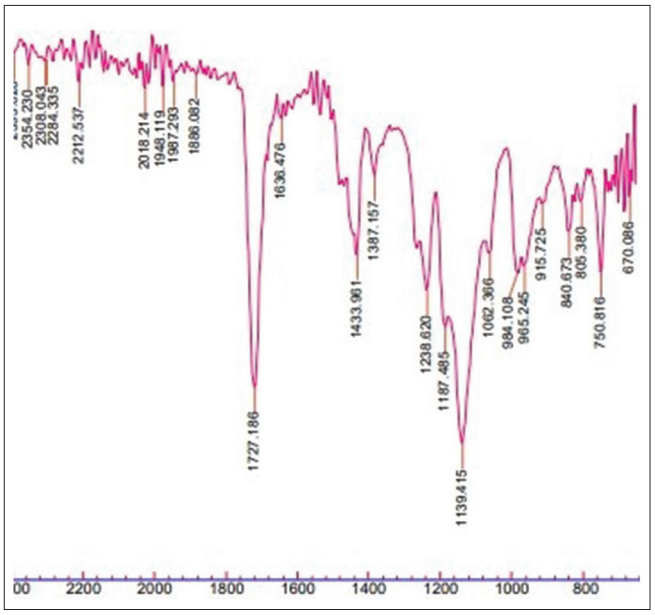


Figure 3: FTIR Group II – 0.75% AgNP impregnated in PMMA. FTIR: Fourier transform infrared, AgNP: Silver nanoparticle, PMMA: Poly(methyl methacrylate)

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Table 1: Spectral wavelength of functional groups

Wave number (per cm)	Functional group	Groups			
		I. Control	II. 0.75% AgNP	III. 1.0% AgNP	IV. 1.5% AgNP
2956.350-2921.475 (C–H)	Methylene stretch	Present	Present	Present	Present
1727.186-1719.858 (C=O)	Carbonyl stretch	Present	Present	Present	Present
1646.885-1636.476 (C=C)	TMSPM substituted stretch	Absent	Present	Present	Present
1436.865-1433.961	C-H deformation	Present	Present	Present	Present
1387.157-1375.267	$-CH_3$ deformation	Present	Present	Present	Present
1271.418, 1238.620, 1139.415, 985.859	C-O stretching	Present	Present	Present	Present
680.096-670.086	AgNP	Absent	Present	Present	Present

AgNP: Silver nanoparticle, TMSPM: 3-(trimethoxysilyl) propyl methacrylate

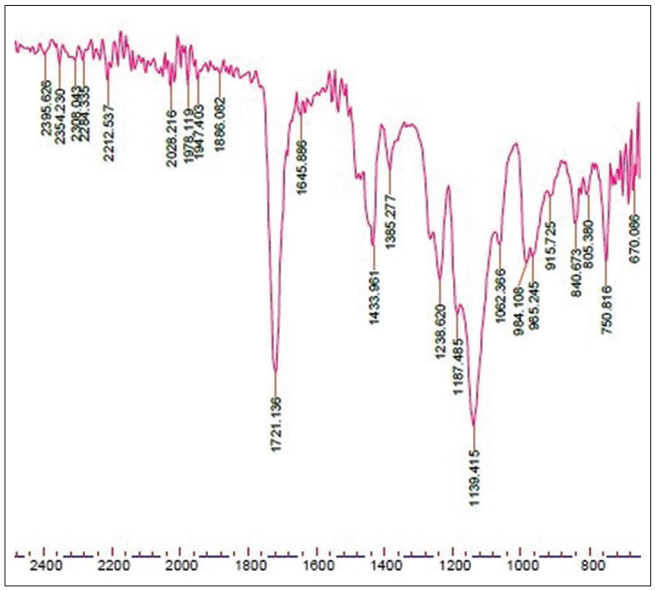


Figure 4: FTIR – Group III –– 1.0% AgNP impregnated in PMMA. FTIR: Fourier transforminfrared , AgNP: Silver nanoparticles, PMMA: Poly (methyl methacrylate)

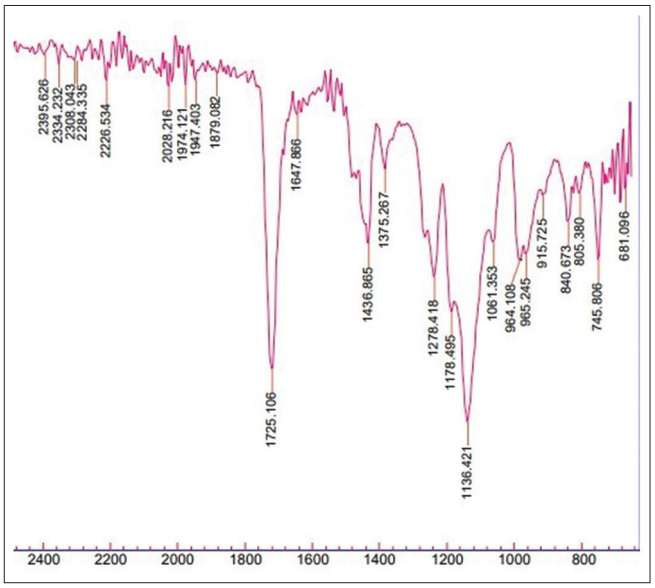


Figure 5: FTIR - Group IV –– 1.5% AgNP impregnated in PMMA. FTIR: Fourier transforminfrared , AgNP: Silver nanoparticles, PMMA: Poly (methyl methacrylate)

states that the bond is physical and not chemical between nanoparticles and resin matrix.[9]

A study by Siddiqui *et al.* in 2015 prepared AgNPs by dissolving $AgNO_3$ silver nitrate in dimethylfuran solvent and compared. Characterization of the control group with experimental groups was evaluated by FTIR study that showed no appearance of peaks 1724/cm and 1436/cm, indicating that the reaction between AgNPs and resin is physical.[10]

In this study, we have attempted to coat the AgNPs with silane coupling agent TMSPM.

On heating, the initiator benzoyl peroxide is converted to free radicals that cleave the double bond present in methyl methacrylate and in silane coupling agent TMSPM to single bond. The silane group present in the coupling agent joins with the inorganic filler and forms the matrix.

This reaction was confirmed by the appearance of peaks at 1636.476/cm, 1645.886/cm, and 1646.885/cm in the FTIR study representing the C = C stretch.

Biofilm formation and bacterial growth are common in dentures. The addition of AgNPs in PMMA significantly inhibits the growth of *Candida albicans* in denture stomatitis.[11] However, achieving full utilization of AgNPs in PMMA has remained a concern due to agglomeration and prevention of dispersibility of the material. To improve its dispersibility when incorporated in PMMA, an attempt was made to coat the AgNPs with a silane coupling agent.

Hence, in contrast to the above-cited studies, the AgNPs coated with the coupling agent TMSPM formed a chemical bond with the heat-polymerized denture base resin in our study. Therefore, it is expected to improve its dispersibility and prevent agglomeration. Since it is chemically reacted, it can be a part of denture base resin leading to less agglomeration and availability of more silver for antimicrobial action.

CONCLUSION

Thus, from the findings of the present *in vitro* study, it was concluded that the silane coupling agent TMSPM

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used to coat the AgNPs has chemically reacted with the AgNP-impregnated PMMA and this can prevent the agglomeration between AgNP and PMMA.

Limitations

This is an *in-vitro* study, future studies on *in vivo* study is recommended.

The color of AgNPs causes discoloration to denture base resin.

This study was limited to only one strain of fungus.

Future recommendations

Studies on mechanical properties of PMMA such as surface hardness and abrasion resistance with larger sample size is recommended.

Financial support and sponsorship

Nil.

Conflicts of interest

There are no conflicts of interest.

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