Original Article

The Effect of Titanium Dioxide Nanoparticles on the Polymerization Percentage of two Dental Bonding Agents

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Abstract

Aims: To test the immediate and one day post-cure polymerization percentage of two bonding agents incorporated titanium oxide nanoparticles in comparison to the control (non-incorporated) bonding agents. **Materials and Methods**: 32 bonding samples in Potassium Bromide discs were prepared for Fourier transform infrared analysis (FTIR), and distributed as following, i.e., GA: 8 bonding samples of non-incorporated Ambar universal (Control), GB: 8 bonding samples of 4%-incorporated Ambar universal, GC: 8 bonding samples of non-incorporated G-Premio Bond universal (Control), GIV: Eight bonding samples of 4%-incorporated G-Premio Bond universal. Equal amount (45µL) of each bonding agent was placed on potassium bromide disc, the solvents was evaporated by a gentle air steam, and then a second potassium bromide disc was mounted over the first one and pressed softly to form a thin bonding film. Finally, the potassium bromide discs containing the bonding were placed in the demountable cell holder and mounted into the sample chamber of the spectrometer. FTIR spectra was then recorded for each bonding before, immediately after, and one day after polymerization to measure the polymerization percentage. **Results**: The study results showed significantly higher polymerization percentage values (i.e., Immediate and one day after polymerization) for the 4%-incorporated in comparison to the control groups for both bonding agents. G-Premio bond universal (i.e., both control and incorporated) revealed significantly higher polymerization percentage than Ambar universal**. Conclusions**: Incorporation of titanium dioxide nanoparticles at 4% into the universal bonding agents significantly increased their polymerization percentage in comparison to their control non-incorporated bonding agents.

Keywords: Polymerization Percentage, Universal Bonding Agents, Titanium Dioxide Nanoparticles, FTIR Analysis.

Introduction

The terminology "multi-modal" or "universal bonding" pertains to a novel cohort of dental bonding systems that have lately been introduced to the market. These systems have been designed to facilitate the utilisation of several adhesion tactics by doctors, including the etch-and-rinse, self-etch, and selective enamel etching procedures. The proliferation of nanoparticles in various applications has been greatly facilitated by the advancements in nanotechnology. These applications include electronics, antimicrobial materials, cosmetics, sunscreens, and drug delivery systems. Titanium dioxide nanoparticles are produced on a global scale in significant quantities and find application across several industries. The nanoparticles demonstrate distinct physicochemical characteristics in comparison to their fine particle counterparts, and this disparity possesses the capacity to alter their bioactivity. Titanium dioxide nanoparticles have been utilised in dental applications due to their capacity to improve the mechanical characteristics of biomaterials while maintaining their biocompatibility. The aforementioned commitment is the driving force for the advancement of this particular substance. Previous studies have employed titanium dioxide nanoparticles to augment the antimicrobial properties of dental composites and bonding methods. The enhancement of the dental composites' binding was successfully achieved. The term "polymerization percentage" is employed to quantify the extent to which the carbon-carbon double

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bonds (C=C) present in the monomers involved in dental bonding systems are transformed into carbon-carbon single bonds (C-C) during the photo-polymerization process.[1-3] Achieving optimal mechanical, physical, and biocompatibility properties necessitates a significant level of polymerization for enhancing the bonding.[4,5]

Various methodologies have been employed to assess the degree of polymerization shown by dental bonding agents. Vibrational spectroscopies, such as infrared and Raman spectroscopies, are the most commonly employed techniques in scientific research. Fourier Transform Infrared Spectroscopy (FTIR) is well recognised as a reliable and widely accepted method for determining the polymerization degree. This technique utilises infrared vibrational spectroscopy to achieve accurate measurements. According to Moraes *et al.*[6], it can be inferred that... Infrared electromagnetic radiation is employed in order to examine the molecular structures, chemical functional groups, and chemical interactions of various inorganic and organic materials.

The objective of this in vitro investigation was to assess the impact of incorporating a colloidal dispersion of titanium dioxide nanoparticles into two universal adhesive systems on the degree of polymerization of the bonding agent's polymer network. This assessment was conducted immediately after polymerization and one day later using Fourier transform infrared spectroscopy.

Materials and Methods

Preparation and Incorporation of Titanium Dioxide Nanoparticles into the Bonding Agents

This work made use of a patented process devised by Cave and Mundell[7], and titled "COATING METAL OXIDE PARTICLES" for the purpose of preparing a colloidal suspension of titanium dioxide nanoparticle.

Following the preparation of the colloidal suspension, 4% by mass of this suspension was incorporated into two universal bonding, namely, Ambar universal and G-Premio Bond universal (Table 1), and then each bonding bottle was shacked in spiral agitation motion by a mechanical mixing device (Vortex-Mixer; Labnique Inc., USA) for 2 minutes at a speed of 3000.

Table 1: Chemical composition of the universal bonding agents used in this study.

Materials	Composition	pH value
Ambar universal	10-Methacryloyloxydecyl dihydrogen phosphate (10-MDP), bisphenol-A di-glycidyl methacrylate (Bis-GMA) (10–25%), 2-hydroxyethyl methacrylate (HEMA) (10-15%), ethanol (10-25%), water (20%), initiators (1-5%).	3.2
G-Premio Bond universal	Bisacrylamide-1 (25–50%), 10-Methacryloyloxydecyl dihydrogen phosphate (10-MDP) (10–25%), bisacrylamide-2 (2.5–10%), 4-dimethylamino benzonitrile (0.1–1%), Dipenta-erythritol pentacrylate-phosphate (PENTA), Isopropyl alcohol (10–25%), water (20%)	2.5

Grouping

A total of thirty-two bonding samples were prepared using Potassium Bromide (KBr) discs for the purpose of conducting polymerization percentage by FTIR. These samples were subsequently distributed in the following manner:

GA: Eight bonding samples of non-incorporated Ambar universal (Control).

GB: Eight bonding samples of 4% incorporated Ambar universal.

GC: Eight bonding samples of non-incorporated G-Premio Bond universal (Control).

GD: Eight bonding samples of 4% incorporated G-Premio Bond universal.

Preparation and Testing Procedure for Samples

In order to assess the polymerization percentage of the bonding agents, an equal volume (specifically, 45 µL) of each universal bonding agent was applied onto a KBr cell window with dimensions of 30 x 3 mm. This was done using the demountable cell holder of the FTIR spectrometer. Subsequently, a controlled flow of air was employed to facilitate the evaporation of solvents present in the bonding agents for a duration of 30 seconds. Following this, a second KBr cell window was carefully positioned above the initial one and applied with gentle pressure, resulting in the formation of a thin bonding film.[8] Subsequently, the KBr cell windows that encompass the bonding are inserted into the demountable cell holder, which is subsequently affixed to the sample chamber of the FTIR spectrometer manufactured by Shimadzu, USA. The absorbance peaks of the bonding agents that had not undergone polymerization were subsequently measured using the transmittance mode. The measurements were conducted at a resolution of 4 cm-1, with a scan range spanning from 400 to 4000 cm-1.[4,9] Subsequently, the bonding agents were subjected to light-curing using an LED light-curing unit (Elipar, USA) with a light intensity of 1200 mW/cm2 for a duration of 20 seconds.

This process was carried out through the KBr cell windows, which possess complete transparency to enable optimal light penetration. Subsequently, Fourier Transform Infrared (FTIR) spectra were promptly acquired subsequent to the completion of the bonding process. Subsequently, the KBr cell windows housing the cured bonding agents were placed in light-protected containers and stored in an incubator set at a temperature of 37 °C. After a period of one day, the FTIR spectra were once again recorded, as documented in Moharam *et al.*[8].

The polymerization percentage was determined by evaluating the absorbance band intensities of aliphatic C=C bands (peak at 1636-1638 cm-1) and the internal

reference of aromatic C=C bands (peak at 1606-1608 cm-1) (Figure 1 A, B). These measurements were taken before, immediately after, and one day after curing for each bonding specimen. The calculation of the polymerization percentage was performed using the equation provided in Cadenaro *et al.*[10].

Polymerization percentage%= 1- ([C aliphatic/C aromatic]) / [U aliphatic/ U aromatic]) x100

in which 'C' refers to cured, and 'U' refers to uncured monomers.

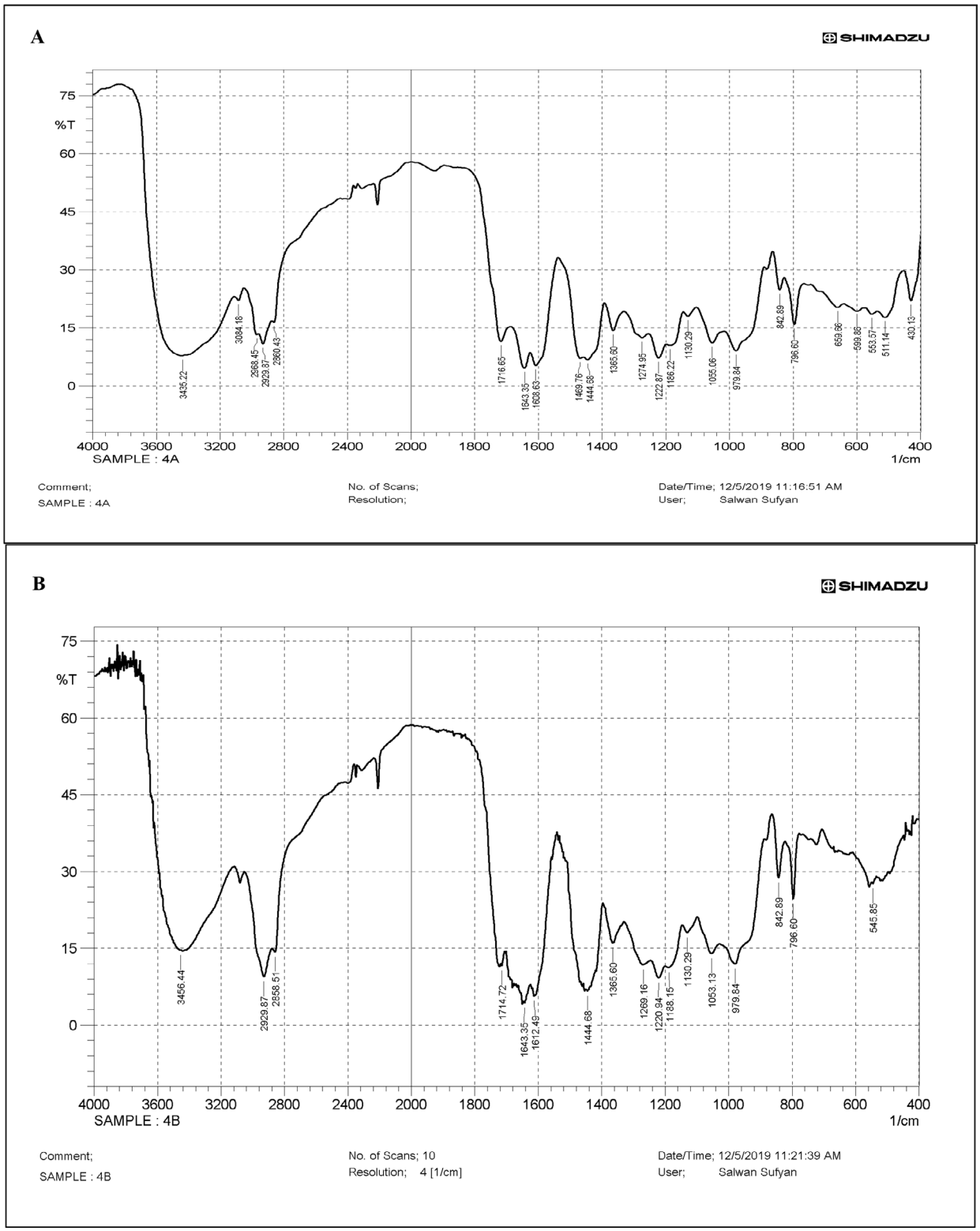

Figure 1: An example FTIR spectra for the dental bonding system (G-Premio bond) (A) before polymerization, (B) after polymerization

Results

The descriptive statistics, which encompass the minimum, maximum, means, and standard deviation values of the polymerization percentage for all groups, have been presented in Table 2 and visually depicted in Figure 2. Both bonding agents that contained 4% incorporation exhibited slightly lower polymerization percentage values compared to their respective control samples immediately after polymerization. After a 24-hour period of curing, the bonding agents that were integrated exhibited slightly higher levels of polymerization percentage values compared to the control group. The G-Premio Bond universal bonding agents, specifically the control and incorporated variants, exhibited higher polymerization percentage values compared to Ambar universal bonding agent, both immediately after curing and one day post-cure. The polymerization percentage mean values of the Ambar universal incorporated at a concentration of 4% immediately after curing were found to be the lowest. On the other hand, the G-Premio Bond universal incorporated at a concentration of 4% and evaluated one day after curing exhibited the highest polymerization percentage mean values.

Table 2: Descriptive statistical results of the polymerization percentage (%) for all groups

Groups	Testing Time	Minimum	Maximum	Mean	Std. Deviation
GA	Immediate	65.45	68.35	67.66	3.42
	One day post-cure	72.95	76.25	74.56	1.41
GB	Immediate	67.55	74.50	72.46	1.51
	One day post-cure	78.55	79.55	77.59	1.11
GC	Immediate	72.45	78.50	76.55	1.64
	One day post-cure	81.65	84.50	80.61	1.77
GD	Immediate	84.55	85.80	79.65	1.65
	One day post-cure	86.65	88.50	86.13	1.46

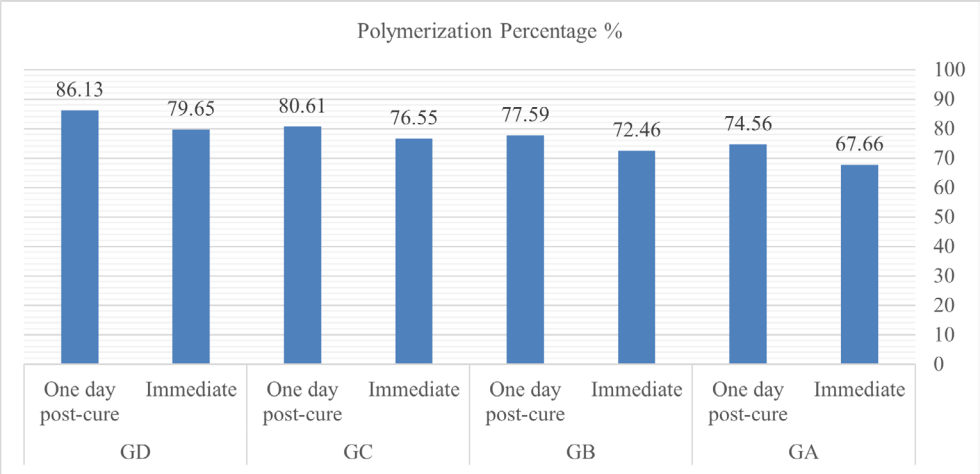

Figure 2: Graph showing the mean values (Immediate, one day post cure) of polymerization percentage of all groups (%).

The findings of the inferential statistics utilizing an independent samples t-test to assess the significance of the disparity between the means of polymerization percentages in two distinct and unrelated groups are displayed in Table 3. The results of this experiment indicate that there were no statistically significant variations observed between the control group and the bonding agents containing 4% incorporation, both immediately and one day after curing. However, significant differences were observed in the polymerization percentage between the Ambar universal and G-Premio Bond universal groups, for both the control group and the group with 4% incorporation, immediately and one day after curing.

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	One day post-cure	81.65	84.50	80.61	1.77
GD	Immediate	84.55	85.80	79.65	1.65
	One day post-cure	86.65	88.50	86.13	1.46

Discussion

The attainment of optimal infiltration and penetration of bonding monomers into demineralized dental substrates, followed by in situ polymerization to achieve a high polymerization percentage, are essential factors to be taken into account in order to build a long-lasting and stable adhesion. The occurrence of inadequate polymerization in dental bonding agents is often associated with decreased adhesive strength to dental substrates, compromised mechanical properties, increased release of monomers, elevated water permeability, resin hydrolysis, and subsequent failure of the bonding restoration.[4,11]

The present study involved the acquisition of Fourier Transform Infrared (FTIR) spectra for the bonding agents that were subjected to a 4% inclusion of titanium dioxide nanoparticles. The spectra were compared with control groups at three distinct time intervals: prior to the curing process, immediately following the curing process, and one day subsequent to polymerization. The aim of this study was to assess the influence of nanoparticles that were included into the bonding agents on the percentage of polymerization. The findings of the study indicated that the inclusion of titanium dioxide nanoparticles resulted in a notable enhancement of both immediate and one-day polymerization values, in comparison to the control groups.

Following a 24-hour curing period, the control groups demonstrated a statistically significant rise in the mean polymerization percentage values. Additionally, the bonding agents that were integrated displayed a discernible increase in comparison to both their initial findings and the control groups. The increase in polymerization percentage values found during a 24-hour period can be attributed to the process known as "post-polymerization" or "dark cure." This behaviour occurs in bonding monomers during the initial 24-hour post-curing phase and is similar to what is observed in composites. The occurrence of this phenomenon can be attributed to the existence of free radicals and unreacted monomers that become trapped inside the resin matrix quickly after the commencement of light curing. After the discontinuation of light exposure, there is an ongoing production of free radicals, which can be enhanced by the inclusion of titanium dioxide in the incorporated entities. These antioxidants engage in interactions with oxygen radicals, thereby neutralising them and preventing their scavenging of free radicals. The findings of this investigation provide evidence that the continual creation of free radicals[12] can result in an augmentation of the degree of polymerization following the curing process.

The results obtained in this investigation demonstrate a resemblance to the findings reported by Al-Saleh *et al.*[13] in their research, wherein they observed a marginal decrease in the initial polymerization % upon the addition of titanium dioxide nanoparticles. Nevertheless, the bonding agents that were integrated exhibited sustained or even improved bond strength values over a 6-month period of water ageing, in comparison to the initial results. The observed outcomes were attributed to the interaction between the incorporated titanium dioxide and reactive oxygen species that are produced during the degradation mechanism. This interaction facilitates the ongoing liberation of unreacted bonding monomers and photo-initiators, resulting in a postponed polymerization mechanism. The phenomenon of continuous polymerization results in an increase in bond strength over a 6-month ageing period. Moreover, the research results suggest that while there were slight modifications in the nano-leakage pattern, there was a decrease in the buildup of silver nitrate deposits when employing bonding agents including titanium dioxide nanoparticles. The observed results can be ascribed to the prolonged polymerization process of the bonding chemicals that were infused with nanoparticles.

The research findings eventually indicate that G-Premio Bond universal had significantly higher average values for immediate and one day post-cure polymerization percentage in both the control and integrated groups, when compared to the Ambar universal groups. The observed disparities in the results can be ascribed to the differences in the chemical compositions of the two bonding agents. According to the producers, G-Premio Bond universal is produced utilising a unique chemical composition that is devoid of hydroxy ethyl methacrylate (HEMA) and is an adhesive based on acetone. The chemistry employed in this study involves the utilisation of bis-acrylamide copolymers to facilitate the crosslinking of the bonding monomer components, which encompass both hydrophilic and hydrophobic properties. Through the process of polymerization, the technology significantly inhibits the phase separation of monomers by promoting increased crosslinking. According to Ahmed *et al.*[14], the bonding mechanism is dependent on a range of photo-initiator systems, including 4-dimethylamino benzonitrile. The system in question exhibits the ability to undergo intramolecular chain transfer upon exposure to light, which has the potential to result in an elevated degree of polymerization.[14] Ambar Universal is composed of a blend of conventional Bis-GMA/HEMA and 10-MDP copolymers, along with a photopolymerization system consisting of Camphorquinone and tertiary amine. This formulation results in a lower degree of polymerization compared to G-Premio bond.

Conclusion

The inclusion of 4% titanium dioxide nanoparticles in universal bonding agents resulted in a notable enhancement in the polymerization percentage values immediately after curing and one day after, when compared to the control groups. The G-Premio Bond universal exhibited notably higher percentages of polymerization immediately and one day after curing for both the control and incorporated groups, in comparison to the Ambar universal bonding groups.

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