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Original article

The effect of TiO_2 and SiO_2 nanoparticles on flexural strength of poly (methyl methacrylate) acrylic resins

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Abstract

Purpose: TiO_2 and SiO_2 nanoparticles are products of nanotechnology which have been incorporated to acrylic resins (AR) in order to induce antimicrobial properties. However, as additives they can affect the mechanical properties of the final product. The aim of this study was to survey the effects of TiO_2 and SiO_2 nanoparticles on flexural strength (Fs) of poly (methyl methacrylate) acrylic resins.
Methods: Acrylic specimens (Selecta Plus) in size of 5×10 (± 0.2) $\times$ 3.3 (± 0.2) mm were prepared and divided into 7 groups: AR containing nanoTiO_2, SiO_2 and TiO_2 with SiO_2 in two concentration of 1% and 0.5%, in addition to a control group. To prepare nano AR, nanoparticles were added to the monomer. All specimens were stored in 37 °C distilled water and underwent Fs test by universal testing machine (Zwick).
Results: The maximum mean flexural strength (43.5 MPa) belongs to the control group and AR containing 0.5% of both TiO_2 and SiO_2 demonstrated the minimum mean Fs (30.1 MPa). Resins contained TiO_2, demonstrated lower values of Fs than those contained SiO_2 with the same concentration, but the differences were not significant ($P > 0.05$).
Conclusion: Incorporation of TiO_2 and SiO_2 nanoparticles into acrylic resins can adversely affect the flexural strength of the final products, and this effect is directly correlated with the concentration of nanoparticles.

Keywords: TiO_2; SiO_2; Nanoparticles; Acrylic resins; Flexural strength

1. Introduction

The importance of cold-cure acrylic resins (AR) in dentistry is evident. They are widely used in building temporary prosthetic base materials, provisional prosthesis, and orthodontic removable appliances such as retainers and functional appliances. These resins commonly consist of methacrylates, especially poly (methyl methacrylate) (PMMA), poly ethyl methacrylate and additional copolymers [1]. However one of the major problems that patients and dentists commonly faced using these removable acrylic appliances is their potential for plaque accumulation due to surface porosities and food retentive configuration, which in turn increase bacterial activity of cariogenic oral flora [2]. This is especially true about cold cure acrylic resins which suffer more porosity than heat cure ones [3,4]. The consequences will be higher rate of decalcification and dental caries along with marginal gingivitis. In efforts to add antimicrobial activities to dental materials, some nanoparticles (NP) have been applied. TiO_2 nanoparticles have been used as additives to biomaterials in order to induce antimicrobial properties [5,6]. Antimicrobial activities of TiO_2 against *Candida albicans*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Escherichia coli*, *Lactobacillus acidophilus*, etc. have been proved by recent studies [7–10]. This substance demonstrates photo-catalytic properties in presence of photons with wavelength lower than 388 nm by which electrons get

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excited. Free radicals are subsequently formed with such high level of energy that can react with various organic materials and enable their degradation [11]. Along with prominent catalytic effect, other characteristics such as white color, low toxicity, high stability and efficiency as well as availability and low cost [12,13] have made TiO_2 an appropriate antimicrobial additive for use in dental materials. It is advocated that applying inorganic carriers can cause antimicrobial agents to release slowly which enhance the safety and durability of the agent [14]. Among compounds as inorganic carriers such as apatite, zeolite and phosphate, SiO_x is more promising due to its porous structure and adsorption properties. Nano SiO_2 particles possess extremely high surface activity and adsorb various ions and molecules [15]. Thus, the combination of TiO_2–SiO_2 has been investigated in recent studies [16].

On the other hand, mechanical properties of acrylic resins are as much important, and among them all, flexural strength (Fs) has achieved the most attentions. A standard minimal limit has been established for any acrylic resin types' flexural strength by ISO 20795-1(2008) international standard for dentistry base polymers. It has been stated that ultimate flexural strength of any polymerized materials shall not be less than 50 MPa [17]. Thus it is strongly recommended to evaluate the effects of any additive or modifier on mechanical properties of acrylic materials to avoid any deleterious effect which may reduce their strength to below standard level. Nanoparticles as additives can alter the physical properties of the substrates [18]. Among resin based materials nano-TiO_2 has been added in various composition to nanocomposites, to enhance their special characteristics and its effects on overall mechanical properties is mentioned [19,20]. Moreover incorporation of Ti, Zn, or Ce nano-oxides to commercial silicone elastomer has been shown to improve their tensile and tear strength and percent elongation [21]. But about acrylic resins there has been a recent study on the effect of silver nano-particles on their flexural strength which resulted their deleterious effect [22]. Since the potential effects of TiO_2 nano additives on cold-cure acrylic resins has not been discussed in recent investigations, this study was conducted with the purpose of evaluating the effect of TiO_2 and SiO_2 nanoparticles on the flexural strength of poly (methyl methacrylate) acrylic resins. It was hypothesized that adding TiO_2 and SiO_2 nanoparticles to cold-cure acrylic resins with the purpose of imparting self-sterilizing characteristics, can affect the mechanical properties of the final product.

2. Materials and methods

The sample size was established according to ISO 20795-1(2008) for comparing the flexural strength of samples with the standard level [17]. To do that, a pilot study was conducted with 5 samples in each study group to determine the mean number of specimens required for strength comparison tests.

Acrylic specimens in size of 5 × 10 (±0.2) × 3.3 (±0.2) mm were prepared. To have a smooth surface without porosity, with sharp edges and by considering setting shrinkage of acryl, a larger metal mold (54 × 14 × 7.3 mm) was built and a negative silicon impression was made. Acrylic liquid (Selecta Plus, Dentsply Company, Addlestone, UK) containing TiO_2 nanoparticles (Degussa Company, Krefeld, Germany) or SiO_2 nanoparticles (Degussa Company) in two concentration of 0.5% and 1% were prepared. To achieve the above concentrations, 0.02 and 0.04 g of nanoparticles were added to each milliliter of acrylic monomer respectively. The particle size was 21 nm for TiO_2 nanoparticles and 20 nm for SiO_2 ones. Nano particles were made by milling method. The powder and liquid of acrylic resins were mixed with the ratio of 4 g to 2 ml but a sonication of 1 h for TiO_2 and 2–3 min for SiO_2 containing monomers preceded mixing. To prepare AR containing nano TiO_2–SiO_2, TiO_2 and SiO_2 nanoparticles were mixed with the weight proportion of 1 to 1. A control group containing no nanoparticles was also prepared. The study groups are illustrated in Table 1.

Table 1
The mean flexural strength of study groups in MPa.

Study groups	Number of specimens	Mean flexural strength (MPa)
1. Control group (without nanoparticles)	11	43.5 (±3.44)
2. 0.5% TiO_2	10	37.3 (±2.69)
3. 1% TiO_2	11	34.6 (±3.17)
4. 0.5% SiO_2	10	39.0 (±2.63)
5. 1% SiO_2	10	36.9 (±3.58)
6. 0.5% TiO_2 and 0.5% SiO_2	11	30.1 (±2.19)
7. 1% TiO_2 and 1% SiO_2	11	32.4 (±3.41)

Prior to flexural strength tests, the specimens were stored in 37 °C distilled water for 50 ± 2 h to stimulate oral environment. The acrylic specimens were inserted in universal testing machine (ZWICK Z250, Zwick Roell Group, Herefordshire, UK) with no delay (Fig. 1). The initial applied force was zero followed by a gradual increase with the rate of 25 ± 1 ml/min.

The amounts of flexural strengths in MPa were calculated according to the formula below:

$$\sigma = \frac{3 \cdot F \cdot I}{2 \cdot b \cdot h2}$$

F = the maximum applied force in Newton; I = the distance between the supporter arms of the machine in mm, accurate to ±0.01 mm; b = the width of the specimens in mm, measured immediately prior to water storage; h = the height of the specimens in mm, measured immediately prior to water storage; as it was mentioned, the amount of I, b and h were 50 mm, 10 mm and 3.3 mm respectively.

Statistical analysis was done by one way ANOVA applying SPSS 16 software package (IBM Company, New York, U.S.). Since the hypothesis of equal variances was rejected by Levene test (P = 0.035), Tamhane's test was applied as a post hoc test to compare the results of each two groups.

3. Results

Seven study groups, each contained about 11 specimens, with different concentration of nanoparticle in specimens were tested. In three groups one sample was lost during the procedure and final results were according to data of 74 acrylic specimens.

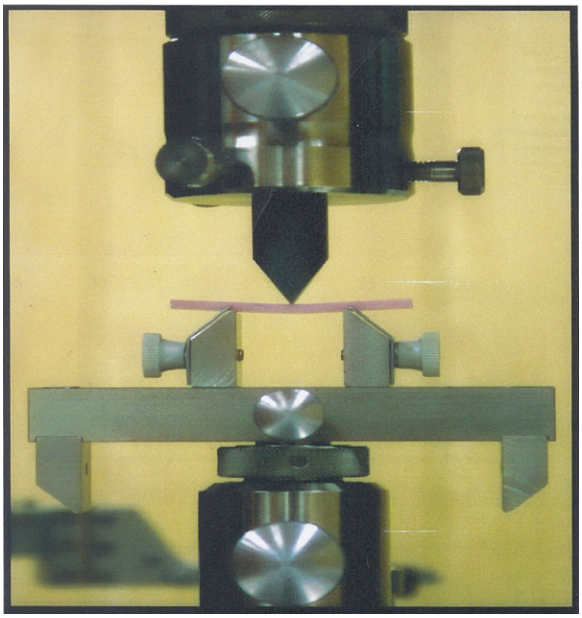

Fig. 1. An acrylic resin specimen in the universal testing machine (ZWICK Z250).

The mean flexural strength of each group in MPa is illustrated in Table 1. The results revealed that none of the study groups even the control one, could reach the standard level of ISO:2008 for flexural strength which is 50 MPa [17]. As can be seen in Table 1 the maximum mean flexural strength (43.5 MPa) belongs to the control group and acrylic resins containing 0.5% of both TiO_2 and SiO_2 demonstrated the minimum mean Fs (30.1 MPa). The Fs decreased as the concentration of nanoparticles of TiO_2 and SiO_2 increased. Acrylic resins contained nano SiO_2 demonstrated higher values of Fs compared with those contained nano-TiO_2 with equal concentration but the differences were not significant ($P > 0.05$). According to the results of one way ANOVA and the Tamhane's post hoc test, the only significant differences, were among control group and 0.5% TiO–SiO_2 group ($P = 0.007$) and among control group and 1% TiO–SiO_2 group ($P = 0.045$) (Table 2). The maximum difference was between group 1 (without any nanoparticles) and group 6 (containing 0.5% TiO_2 and 0.5% SiO_2) and the minimum difference was between group 5 (1% SiO_2) and group 2 (0.5% TiO_2).

4. Discussion

Microbial plaque adheres to acrylic resin appliances with a wider adhesion area than to natural teeth [23] and mechanical methods have been shown ineffective in eradicating microorganisms completely [24]. Chemical antimicrobial agents are with the drawback of converting to harmful or carcinogenic products [7]. Accordingly, many researches have been devoted to the development of efficient and harmless processes that incorporate self-sterilizing agents in AR materials [25]. Among them all, the antibacterial properties of nanoparticles especially TiO_2 NP incorporated into matrix of polymeric materials have achieved much attention in recent dental material research [6,13,26]. This study was conducted to test the effects of TiO_2 (and SiO_2 as its carrier) on mechanical properties of the final acrylic product.

Table 2
Differences among mean flexural strength of study groups.

Study groups	Study groups	Mean difference (MPa)	Standard error	*P* value
1	2	6.18	3.67	0.912
	3	8.96	3.22	0.227
	4	4.50	4.25	0.999
	5	6.66	3.08	0.625
	6	13.41*	2.84	0.007*
	7	11.06*	3.11	0.045*
2	3	2.77	3.18	1.000
	4	−1.67	4.22	1.000
	5	0.48	3.04	1.000
	6	7.23	2.80	0.420
	7	4.88	3.07	0.951
3	4	−4.45	3.83	0.998
	5	−2.29	2.40	1.000
	6	4.45	2.17	0.710
	7	2.11	2.52	1.000
4	5	2.15	3.73	1.000
	6	8.90	3.53	0.455
	7	6.56	3.75	0.898
5	6	6.75	1.97	0.067
	7	4.40	2.34	0.800
6	7	−2.34	2.02	0.998

Study groups: 1, control group; 2, 0.5% TiO_2; 3, 1% TiO_2; 4, 0.5% SiO_2; 5, 0.1% SiO_2; 6, 0.5% TiO_2 and 0.5% SiO_2; 7, 1% TiO_2 and 1% SiO_2.
* Significant difference ($P < 0.05$).

Based on our obtained flexural strength values, incorporation of nano-sized TiO_2 and SiO_2 at concentrations of 0.5% and 1% by weight into AR adversely affected the mechanical properties of the polymerized material and flexural strength values decreased with increase in concentration of TiO_2. These findings are consistent with Shibata et al.'s study [27] and also Sodagar et al.'s [22] on addition of silver nanoparticles to AR and can be attributed to the effect of nano-sized oxides on the internal structure of polymerized PMMA. It has been demonstrated that flexural strength would drop by addition of extra additive to AR since it acts as impurities [25,28]. Dispersion of TiO_2 NP in PMMA matrix adversely affects degree of conversion which in turn leads to increase in the level of residual unreacted monomer that acts as plasticizer [27]. It is noteworthy that the content of nano additives is of critical importance. Even in modified polymeric materials to which TiO_2 NP addition reinforced the matrix such as silicon elastomer [21] or nano composites [20], when NP exceeded a particular percentage −2.5 wt% as for example in elastomer matrix or 0.4 wt% in a nanocomposite, an opposite trend was observed and the value of tensile strength decreased in the elastomeric material [21] and solubility increased in the dental composite [20].

Incorporation of NP causes these particles to agglomerate and aggregate. The agglomerated compounds can act as stress concentrating center in the matrix and adversely affect mechanical properties of the polymerized material [21].

Moreover, the tendency of TiO_2 NP to agglomerate into large particles can also decrease photo catalytic efficacy [13]. Preventing agglomeration has been a main challenge in nanocomposite production. Many efforts have been made to prohibit association of small particles such as applying 3-methacryloxy propyl trimethoxy silane, or MPTS, as coupling agent between nano-sized silica particles and resin [18].

On the other hand, one of the problematic issues in incorporating NP into AR is pertained to lack of chemical bond between inorganic material such as TiO_2 and PMMA. To improve bonding between metal and resin some chemicals such as 4-methacryloxyethyl trimellitate anhydride (4-META) and γ-methacryloxypropyltrimethoxy silane (γ-MPS) have been used [28,29]. Accordingly, we can extrapolated that by finding out more appropriate substances as coupling agent between nano-TiO_2 and AR, alleviating it's deleterious effect on mechanical properties is promising.

It has been also claimed that preparation of TiO_2 nanometer photocatalyst film by a hydrothermal method would enhance the stability of attachment on special substrate [30]. This method leads to production of anatase phase which is preferable to rutile-type structures due to higher photo catalytic activity [31]. However the most photo catalytic activity has been observed when the two phases are mixed with the proportion of 80% anatase plus 20% rutile [30]. Thus in this study the aforementioned nano-TiO_2 composition was utilized. The structure and photocatalysis of TiO_2 NP can be modified by various post-treatments [12]. In Choi et al.'s study, anodic oxidation of NP at 250 V for 3 min in a solution containing 0.04 M β-glycerophosphate disodium salt pentahydrate and 0.4 M calcium acetate, resulted in the formation of anatase peaks [9]. Apparently, electrolyte concentration and voltage play a critical role in the composition and degree of oxide crystallinity [32].

As mentioned previously, nano-SiO_2 can be used as carrier of TiO_2. Based on recent studies, combination of TiO_2–SiO_2 possesses higher thermal stability than pure TiO_2 since prevents transformation of anatase to rutile phase. This enhances photocatalytic activity of nanoparticles due to higher specific surface area, larger pore volumes, higher band gap energy and smaller crystallite structure [33]. According to Wang et al., a chemical bond of Ti–O–Si is formed as SiO_2 and TiO_2 react and this bond is conductive to stability of anatase phase [34]. However, higher photocatalytic activity does not necessarily means higher mechanical properties. As can be seen in the results of this study, the Fs of TiO_2–SiO_2 contained AR is lower than TiO_2 alone (Table 1). In order to enhance photocatalytic activity of the AR without increasing the concentration of nano particles, an appropriate source of UVA irradiation should be applied. To take the advantage of UVA, the patients are advised to keep their acrylic appliances containing TiO_2 for about 1 h in outdoors under sun exposure or under UVA lamps with the intensity of 1 mW/cm^2. For denture base material the patient could be advised to keep their dentures under appropriate irradiation source during night [27].

With regard to acrylic resin composition, just one brand was applied in this study. In our previous experience on the effect of adding silver NP to PMMA from two different manufacturer, the results were conflicting no similar trends in flexural strength values of the two types of AR were observed as the concentration of NP were increased [22]. However, about the effect of TiO_2 nano-oxide, the result of the current study, concur with Shibata et al.'s, although the applied AR were not identical in these two investigations [27]. Moreover, NP concentrations were not similar −1 wt%, 5 wt% and 10 wt% in Shibata's study compared with 0.5 wt% and 1 wt% in ours.

Not to be lost in this discussion is the effect of modification in TiO_2 NP on antimicrobial properties of the final product. It has been demonstrated that deposition of noble metals, such as Ag, Au, Pt and Pd can enhance photocatalytic effect of TiO_2 and improve its bactericidal activities [35–37]; but their effects on physical properties of AR has not received much attention in the literature, and worth further studies. In addition, in order to avoid wasting of nano-TiO_2, some films or fibers with different polymers containing these nanoparticles has been used that can alter the substrate's properties [38,39]. Based on these theories, the effects of adding SiO_2 NP to TiO_2 ones on antimicrobial properties of the acrylic material are under investigation by our research team.

Finally, it should be mentioned that this study was limited to just one brand of AR which was commercially available. Also we could not achieve our goal in retesting the specimens after UVA irradiation, to evaluate the probable effects of TiO_2 photocatalysis on AR strength, or retesting the Fs of AR after some time-intervals to evaluate the effect of aging on mechanical properties of acrylic products containing nano particles, by some executive limitations. Thus longer follow-ups are suggested for further studies on similar issues.

5. Conclusion

Within the limitations of this study, it was concluded that incorporation of TiO_2 and SiO_2 nanoparticles into acrylic resins can adversely affects the flexural strength of the final products, and this effect is directly correlated with the concentration of nanoparticles.

Conflict of interest statement

There are no financial and personal relationships with other people or organizations that can inappropriately influence (bias) their work.

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