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Flexural Modulus and Strength of Cold Cured Poly(methylmethacrylate) Reinforced with TiO_2 Nano Particles

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Abstract: *The most significant disadvantage of cold cured poly (methyl methacrylate) - PMMA is its poor mechanical properties, mainly in flexure. The aim of this work is to explore the modulus and flexural strength of modified cold cured PMMA modified with low TiO_2 addition, which can also have antibacterial properties. Commercial cold cured PMMA resin, consisting of powder and liquid components, were modified by adding 0.05%, 0.2%, and 1.5 wt. % 20 nm hydrophobic TiO_2. The specimen's flexural modulus and strength were tested, while heat properties were determined with DSC analysis. SEM and EDX were used to study fracture surfaces of tested specimens. In all modified specimens, an increased flexural modulus and flexural strength were recorded. In all specimens, the appearance of agglomerates was noted. Glass transition temperatures also increased, as the result of the appearance of polymer chains with reduced mobility around nanoparticles. 0.2 % of 20 nm TiO_2 nanoparticle content proved to be the most efficient in increasing flexural modulus and strength.*

Keywords: *Cold cured poly(methyl methacrylate), nano TiO_2, flexural modulus, flexural strength*

1.Introduction

Titanium dioxide (TiO_2) nanoparticles are a widely used material applied in different areas due to its convenient properties: it is non-toxic, chemically stable, and possesses an efficient photocatalytic and antibacterial effect [1,2]. Also, in material science, it was applied as a filler, aimed at increasing mechanical properties of certain types of polymers, such as epoxy, in some cases, as a replacement for rubber beads and glass with increased stiffness, strength and toughness without decreasing its thermo-mechanical properties [3]. Furthermore, the introduction of TiO_2, as well as other titanium-oxides, such as TiO and Ti_2O_3, have shown to be efficient in increasing the number of nucleation sites for intragranular acicular ferrite in weld metals, through the mechanisms of increased nucleation rate and ferrite grain retarded growth [4-7]. Finally, TiO_2 nanoparticles found a new application as an enhancer of coated electrodes in welding technology, benefiting from its relatively high melting/solidification temperature, also representing an inoculant causing a refined grain size in the weld metal [8-11]. TiO_2 found wide applications in dentistry as well, being used as a reinforcement for dental composites [12,13]. Furthermore, TiO_2 reinforced nanocomposites subjected to light represent a very effective antimicrobial agent due to its photocatalytic effects and the release of free radicals [14]. They have several antimicrobial effects, including affecting the cell wall structure [15].

In this paper, TiO_2 nanoparticles were applied as a reinforcement for a cold cured poly/methyl-methacrylate) denture relines resin, due to the inherent low mechanical properties of this type of polymer when it is cold cured. Namely, this material is used as a denture reline resin and for denture repair [16]. It is provided in the form of powder and liquid. These are mixed, after which the radical polymerization commences. Due to limited mixing time, an increased unconverted monomer content is present [17,18]. An unconverted monomer acts as a microvoid, which weakens the material. Therefore, cold - cured

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PMMA has lower mechanical properties compared to hot polymerized PMMA used for denture base [19,20].

The application of added nanoparticles reduces the mobility of polymer chains near nanoparticle. An array of well-distributed nanoparticles throughout the material can cause the formation of a reinforcing field increasing the material's mechanical properties [21].

This work is aimed at determining general mechanical performance by testing bend strength and modulus. Nanoparticle levels were kept at very low levels to hinder agglomeration and an unwanted drop in mechanical properties [22-25]. This way, it is believed that a more uniform nanoparticle dispersion and distribution can be obtained, thus increasing mechanical properties [25, 26]. The main novelty this work offers is the application of TiO_2 nanoparticles in relatively low loadings, of which, the minimal is considerably lower compared to the works by Alamgir et al. [27]. Similarly, other authors applied even higher loadings: Alhareb et al. [28] used 5% microparticle loading, while Ayad et al. [29] applied 5 and 15 % particle contents.

2. Materials and methods

The material used in this study was cold cured PMMA denture reline resin Simgal (Galenika, Zemun, Serbia). It is consisted of powder and liquid, with the mixing ratio of 2:1 in weight. The liquid component was modified with AEROXIDE T805 21 nm TiO_2 (Evonik, Essen, Germany), having a specific surface area of 35-65 m^2/g. These nanoparticles were used as received, having the surface layer of dimethyl(dipropyl)silane ($C_8H_{20}Si$) The following loadings, for the addition into the liquid phase were used: 0.05; 0.2 and 1.5% wt. %. The control liquid specimen was untreated. To obtain the desired amount of nanoparticles, the analytical balance was used (Adventurer Pro Ohaus, Parsippany, NJ) with an accuracy of 0.0001 g. The mixing was done by using a magnetic stirrer MM-530 (Tehtnica, Zelezniki, Slovenia) for 10 min and the Vevor PS-20A ultrasonic bath. To determine the size of the particles in the liquid phase, Zetasizer Nano ZS (Malvern Instruments, Malvern, UK) analyzer was used, with MMA liquid component used as a suspension agent (refractive index 1.412 at 20°C; viscosity 0.6 cP at 20°C). Liquid components were mixed with powder component and the obtained mixture was poured into square Al-alloy molds. Afterward, the specimens were mechanically cut with emulsion liquid cooling. The desired shape and dimensions of specimens were obtained with abrasive papers, on a metallographic rotational grinder. All tested specimens had a prismatic shape and the dimensions of 6 x 2.5 x 45 mm.

To evaluate mechanical properties, a flexural modulus of elasticity and flexural strength were determined, in accordance with the Equations (1) and (2). Both mechanical properties were tested by using Toyoseiki AT-L-118B (Toyoseiki, Tokyo, Japan) universal machine. Three-point bending test was used, with 40 mm distance between the supports, with the distance between the supports of 40 mm and with the crosshead speed of 50 mm/min.

$$E = \frac{\Delta F l^4}{4 \Delta d b h^3} \qquad (1)$$

where E is the modulus of elasticity [GPa], l is the distance between the supports [mm], Δd is the displacement range [mm] for a testing load range ΔF [N], b is specimen width [mm] and h is specimen height [mm].

$$\sigma = \frac{3 F l}{2 b h^2} \qquad (2)$$

where σ is the flexural strength [MPa], F is maximum force [N], l is the distance between the supports [mm], b is specimen width [mm] and h is specimen height [mm].

Five specimens were used for each test. After mechanical testing, a one-way analysis of variance (ANOVA) followed by Tukey’s test with the significance value of $P<0.05$ was applied. The tests were performed using Minitab 16 software.

Differential scanning calorimetry (DSC) analysis was performed on Q20 (TA Instruments, New

Castle, DE) device was applied, in the temperature from 60 to 160^{o}C, with a scan rate of 10°C/min. Fracture surfaces were examined by JSM-6460LV (JEOL, Tokyo, Japan) scanning electron microscope (SEM), operating at 25 kV. The specimens were coated with gold, using the SCD-005 (Bal-tec/Leica, Wetzlar, Germany) device. To examine fracture surface morphologies, energy-dispersive X-ray spectroscopy (EDX) was used (Oxford Instruments INCA Microanalysis system).

3. Results and discussions

The size distribution of particles in the liquid component is shown in Figure 1 reveals certain differences between the three mixtures. It can be seen that the peak that refers to 0.2% nanoparticles is narrower and indicating towards a smaller particle size. That means, when TiO_2 nanoparticles are mixed with the liquid phase, the smallest particles containing nanoparticles are obtained with 0.2% loading. The liquid, as such is subsequently mixed with the powder phase.

The results depicting flexural modulus and strength of unmodified and modified materials, along with standard deviations and the results of statistical analysis are shown in Figures 2 and 3, respectively. It can be seen that all modified specimens have improved both flexural modulus and flexural strength compared to the unmodified specimen. However, statistically, only specimens modified with 0.2 and 1.5% TiO_2 were significantly different from the unmodified specimen in flexural modulus. In flexural strength, only 0.2% TiO_2 loading proved to be statistically different than the control specimen. Therefore, the highest mechanical properties tested were obtained with 0.2% of TiO_2.

The results of DSC analysis of unmodified and modified specimens are shown in Figure 4. Glass transition temperatures (Tg) in all three nanoparticle modified PMMA materials are higher than in the unmodified specimen. The highest Tg was observed in specimens modified with 0.05 and 0.2% TiO_2. An increased Tg can be explained by the immobilization of polymer chains near nanoparticles, indicating that the overall volume of the immobilized polymer chains is higher in these specimens.

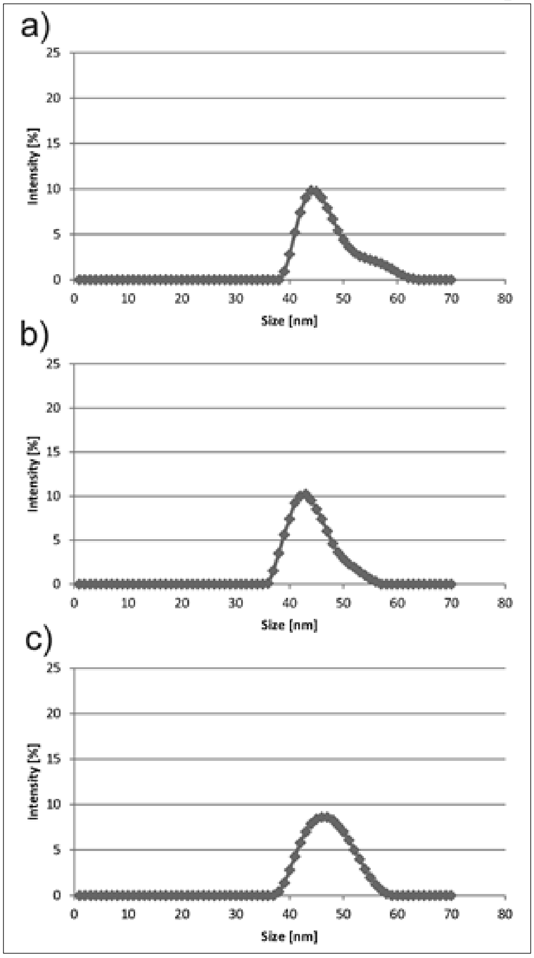

Figure 1. Particle distribution after mixing with liquid phase: a) 0.05 %; b) 0.2 %; c) 1.5 %

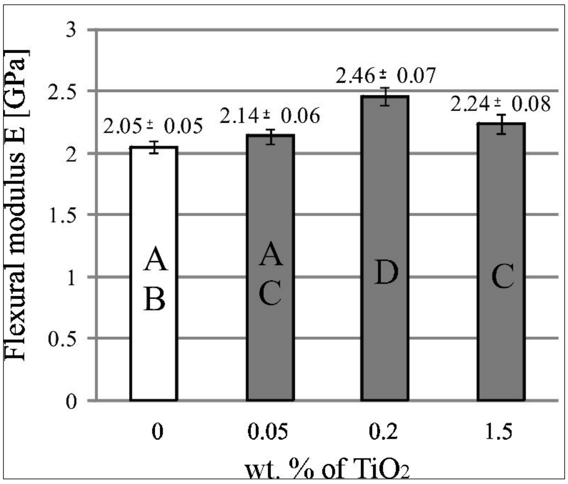

Figure 2. Flexural modulus results

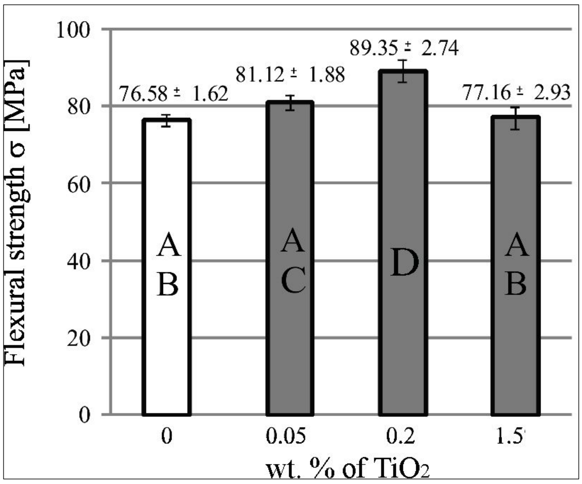

Figure 3. Flexural strength results

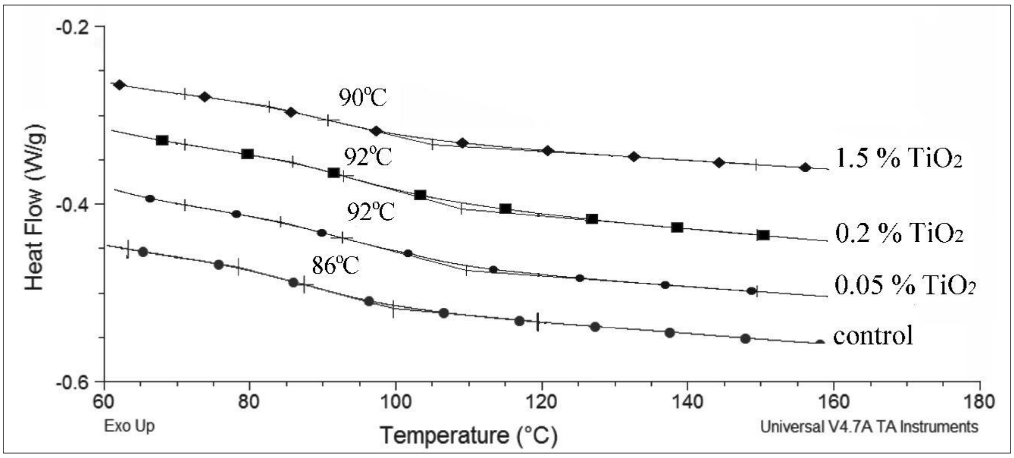

Figure 4. DSC curves of tested materials

Representative fracture surfaces of unmodified specimen and specimens modified with 0.2 and 1.5 % TiO_2. SEM fracture surfaces obtained after the fracture of bend strength specimens testing of unmodified specimens and specimens containing 0.2 and 1.5 % TiO_2 nanoparticles are shown in Figure 5**.** In all specimens, river marks are visible, which extend both through base material PMMA powder particles and between them, throughout the material that was cured during the process of fabrication. In specimen modified with 0.2 % TiO_2, the fracture surface was formed by the crack propagation through both powder particles and cured material surrounding them, Figure 5b. On the other hand, in the unmodified specimen and the specimen modified with 1.5 % TiO_2, the crack propagates mainly between powder particles, indicating that the material between them in considerably less resistant than the material of the primary particles, Figures 5a,c. Such behavior is in accordance with the results of mechanical property testing.

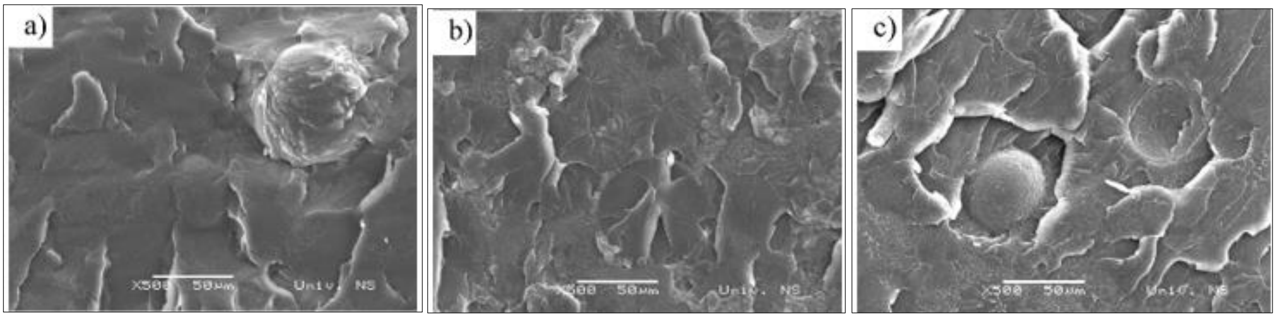

Figure 5. Fracture surfaces: a) unmodified, specimen 0, b) secimen containing 0.2 % nano particles, c) specimen containing 1.5 % nano particles

Another feature of the fracture surfaces is the presence of agglomerates (Figure 6). It can be seen that there is a presence of Ti, which probably comes from the TiO_2 in Spectrum 1. Particles found in this particular area, having a size of several microns can be agglomerates, which form from a larger number of nanoparticles.

The effect of nanoparticle addition on mechanical properties is reflected through the immobilization of polymer chains at the distance of micrometer level around the nanoparticle [21]. If the dispersion of nanoparticles is not optimal, the crack may propagate through the unreinforced material. This may be the result of either the lack of particles (specimen with 0.05% of TiO_2) or the appearance of large agglomerates (specimen with 1.5% TiO_2). The latter, having relatively large agglomerates, where nanoparticles are bonded by weak Van der Waals forces may fracture under load, causing instability in crack propagation, making the material weaker. Similar findings were obtained in the research by Balos et al. [30] and Elshreksi et al. [31].

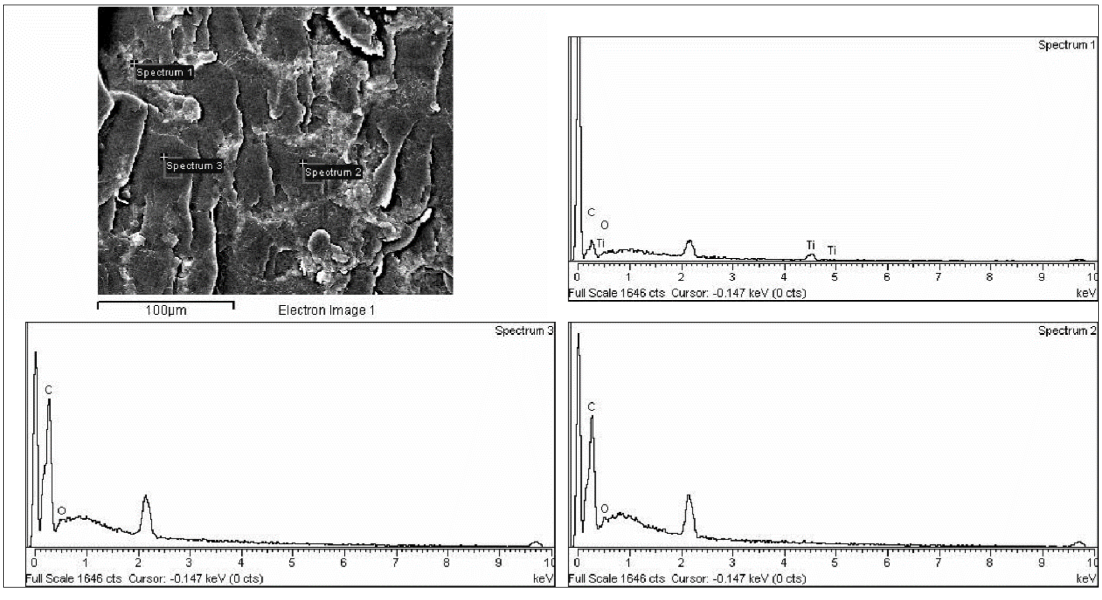

Figure 6. EDX analysis of specimen modified with 1.5 % TiO_2 fracture surface

To better describe the effectiveness of the reinforcement consisting of TiO_2 nanoparticles, the rule of the mixture and the inverse rule of mixtures equations were used [32]. As a reference, TiO_2 modulus of 293 GPa was used [33], while PMMA modulus of the reference specimen 0 was used (2.05 GPa). The results of the calculated modulus are shown in Table 1**.**

Table 1 Calculated values of the modulus and actual values obtained

	Modulus [GPa]		
	0.05 % of TiO_2	**0.2% of TiO_2**	**1.5 % of TiO_2**
Rule of mixtures	2.19	2.63	6.41
Inverse rule of mixtures	2.05	2.05	2.08
Values obtained in this study	2.14±0.06	2.46±0.07	2.24±0.08

It can be seen that the modulus of the specimens containing 0.05 and 0.2% of TiO_2 is closer to the rule of mixture calculated values than in specimen containing 1.5%. This indicates that the reinforcement containing a lower amount of nanoparticles is more effective and it can be predicted much more accurately. Also, the specimen containing 1.5% TiO_2 behaves more like a filler, as in particulate composites, since it is closer to calculated values obtained by the inverse rule of mixtures [34].

In this work, the relatively low TiO_2 nanoparticle content was applied. However, in some of our previous publications, which also studied the effect of relatively low SiO_2 nanoparticle addition to PMMA [16, 30] and flowable dental composite [35], some differences can be observed. Although mechanical properties increase was similar to this study, the maximum strengthening effect was observed at minimal tested nanoparticle loading of 0.05%. A plausible explanation might be related to the nanoparticle size (7 nm) applied in these referenced studies, which refers to the higher effectiveness of smaller particle size. This is related to the larger number of particles within the same loading as with larger 21 nm TiO_2. On the other hand, in all these studies, the highest nanoparticle loading results in the lowest mechanical properties, due to the agglomerate formation and cracking, unstable crack propagation and fracture.

4. Conclusions

According to the presented results, the following conslusions can be drawn:

- The addition of 20 nm TiO_2 nanoparticles can be beneficial to the flexural strength and modulus of PMMA
- The optimal content of nanoparticles in this study is 0.2%, having a statistically significant increase in tested mechanical properties
- There is a significant effect of agglomeration, which is the main reason the highest nanoparticle content of 1.5 % is not as effective as specimens containing a lower amount of nanoparticles.
- The highest nanoparticle content causes the particles to behave more like a filler as in particulate composites, since the obtained values are much closer to the calculated values of modulus by the application of the inverted rule of mixtures, unlike the lowest and medium nanoparticle content, which gives values closer to the calculated values obtained by the application o rule of mixtures.

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