Developing of PMMA Bone Cement Performance by Modified TiO$_2$NPs

S K Al-Janabi, M H Al-Maamori and A J Brahi

Department of Engineering of Polymer and Petrochemical Industries, College of Material Engineering, University of Babylon, Iraq

E-mail: stud.sura.kamil@uobabylon.edu.iq

Abstract: Polymethylmethacrylate is considered the most prevalent bone cement base material. Most fractures that occur during function are due to its weakness and lack of mechanical strength. The apparent limitations of PMMA are insufficient ductility, strength, and viscoelastic behavior. The current study aims to strengthen and improve PMMA bone cement properties by adding modified TiO$_2$ nanoparticles (m-TiO$_2$ NPs). Therefore, the silane coupling agent modified the neat TiO$_2$ NPs and then added different ratios (0.5, 1, 1.5, and 2 wt %) to the PMMA bone cement. Fourier transform infrared spectroscopy (FTIR) technique used to investigate the modification process and specify the bonding type between m-TiO$_2$NPs and the PMMA bone cement matrix. The SEM technique is used to study the morphologies of the prepared samples. Properties such as tensile strength, compression strength, modulus of elasticity, and impact strength, were measured. Results proved the successes of TiO$_2$NPs modification by silane coupling agent and the absence of any chemical bonding between this modified filler and other PMMA bone cement ingredients. The mechanical properties increased by m-TiO$_2$NPs addition up to 1 wt% ratio then decreased. The morphology results supported the mechanical properties trends.

Keywords: PMMA bone cement, TiO$_2$NPs, Coupling agent, Mechanical properties.

1. Introduction
Bone has an essential function in ensuring the organs inside the body and offering mechanical support, hematopoesis, and mineral stockpiling. Besides, it can organize with muscular tissue to achieve further developments and react to ecological changes. Enormous segmental bone deformities brought about by extreme trauma, tumor resection, malignancy, or innate maladies must be fixed by bone cement [1]. By and large, bone breaks can be immobilized to take into consideration unconstrained mending after some time. Nonetheless, when bone imperfections are sufficiently massive or basic measured, they cannot recover using normal physiological cycles and require mediation as bone unions cement [2]. Bone cement is one of the most ordinarily utilized items in the orthopedic medical procedure. Among regular signs for its utilization are bone and joint reproductions, all-out joint substitution, fracture obsession, bone diseases treatment, and osteoporotic vertebral cracks [3]. Bone cement depends on Polymethylmethacrylate (PMMA) material, which might be thought of as cement or mortar. It must have the option to retain the powers following up on the joint during development and keep the artificial embed in position. It should likewise be biocompatible; that is, it must not make physical or chemical harm to human tissue.

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A material that meets these prerequisites is Polymethylmethacrylate PMMA. PMMA is regularly known as acrylic bone cement and is generally utilized to embed obsession in different Orthopedic and injury medical procedures. In all actuality, "cement" is a misnomer because the word cement is utilized to portray a substance that bonds two things together. Nonetheless, PMMA goes about as a space-filler that makes a restricted space which holds the embed against the bone and subsequently goes about as a 'grout.' Bone cement has no inherent glue properties; however, they depend somewhat on close mechanical interlock between the unpredictable bone surface and the prosthesis [4]. For example, many nanoparticles, such as TiO2, SiO2, ZnO, Ag, Hydroxyapatite, and carbon nanotube, have been consolidated in various biomaterials to actuate antimicrobial movement and improve mechanical conduct [5]. TiO2 has as of late picked up unmistakable quality attributable to its perceptible high strength, accessibility, white shading, productivity, and minimal effort. Besides, TiO2 NPs are non-poisonous and synthetically dormant and antibacterial activity under a wide arrangement range [6]. Numerous past examinations have indicated that even expansion of low fixations TiO2 NPs can actuate new physiochemical, mechanical properties, bringing about another natural nanocomposite materials with better properties [7]. The agglomeration is one of the challenges for preparing nanocomposite materials of the nanofillers in the polymer matrix, resulting in the composite's insufficient action. Several methods can be used to avoid this problem, using ultrasonic irradiation for dispersion of nanoparticles during the synthesis of inorganic-polymer nanocomposite materials [8]. Also, to guarantee that no chemical holding, improved cooperation between the matrix and filler is not accomplished. It utilized a silane coupling operator to functionalize nano titania fillers to make them more viable with the PMMA grid bioactive PMMA-based bone cement. Even though the silanized nanofiller expanded the cement's mechanical properties, no general improvement of mechanical properties was accomplished credited to the agglomeration of the silanized nano titania particles [9-10]. Khaled (2009) tested the adequacy of utilizing nanotechnology to improve the mechanical properties of PMMA put together bone cement by centering with respect to nanostructured titania (n-TiO2) at first, titania nanofibers (n-TiO2 fiber) and nanotubes (n-TiO2 tube) were brought into a commercial PMMA network with the accomplishment of expanded fracture toughness (KIC), flexural strength and flexural modulus of the subsequent nanocomposites [11]. Ayre (2013) applied novel interdisciplinary ways to deal with PMMA bone cement plan with an end goal to lessen disappointment in solidified joint substitutions. Model cement was consequently evolved, with compositional, mechanical, fatigue, and rheological properties like traditional cement, which empowered two novel radio pacifiers to be tested (anatase TiO2 and yttria-balanced out ZrO2). Silane treating the radio pacifiers upgraded their dispersion, improving the cement's mechanical and fatigue properties [12]. Alrahlah et al. (2018) attempt to assess a polymethylmethacrylate dental replacement base material changed with TiO2 nanoparticles regarding nanomechanical, tensile, compression, creep-recuperation, unwinding, and antimicrobial attachment practices. TiO2 nanoparticles likewise improved the mechanical conduct of PMMA by fundamentally diminishing bacterial adherence with expanding TiO2 proportion [13]. The objectives of the present study are (1) Accomplish of surface modification of TiO2 NPs with silane coupling agents (2) Fabrication of PMMA bone cement/TiO2 nanocomposites; and (3) Studying the effects of m-TiO2 NP on the mechanical properties of the new nanocomposites.

2. Materials and methods

2.1. Materials
PMMA self-curing acrylic powder and the fluid MMA methylmethacrylate were provided from (Sopfadental A Kerr Company) and utilized to create PMMA bone cement as the polymeric matrix of the composite. Titanium oxide nanoparticles powder (TiO2 NPs) gave from (Skyspring Nanomaterials, Inc.USA) of 99.5% and 10-30nm particle size. Benzoyl peroxide BPO as initiator, N, N-Dimethylpara-toluidine DMPT as a quickening agent, and silane coupling agents (3-aminopropyltrimethoxysilane (APTMS) were given from Aarti industries limited Company, India.
2.2. Preparation method

2.2.1. Modification of TiO$_2$ NPs. 0.5 g of TiO$_2$ nanopowder was scattered in 50 ml deionized water by ultrasonication for 15 min. At that point, the silane coupling operator, (3-aminopropyltrimethoxysilane (APTMS) with 25% focuses were included in the scattering. The mixture was continued refluxing at 80°C for 24 h. From that point onward, scattered particles were isolated from dissolvable by rotator (10 min at 10,000 rpm) trailed by washing with ethanol and water on the other hand for in any event two cycles to eliminate extreme silanes. After the cycle was done, the adjusted particles were dried in an oven at 80°C for 24 hr. and cooled at room temperature [14].

2.2.2. Bone Cement Preparation. The bone cement consists of two significant parts; powder and liquid. The cement powder includes PMMA and BPO, while the liquid part is composed of MMA and DMPT. The handling mixing technique was adopted to prepare the samples. The weight ratio of powder to liquid components is 2:1. For the cement dough preparation, weighed amounts of PMMA and BPO powders were first homogeneously mixed, followed by the addition of liquid monomer and mixing. To prepare the composite sample, the m-TiO$_2$ NPs with different percentages were added to the liquid part and dispersed by sonication instrument for 15 min then mixed with the powder part. After mixing, the cement dough was cast using silicon rubber mold and kept for 24 hr. at room temperature.

3. Characterization and testing

Fourier transform infrared spectrometer test is conducted according to (ASTM E1252) using IR Affinity-1 device. FTIR was used to characterize the TiO$_2$ nanoparticles before and after surface modification, neat PMMA bone cement, and PMMA bone cement composites [15]. It is equipped with a room temperature DTGS detector, mid-IR source (4000 to 400) cm$^{-1}$ and a KBr beam splitter. Tensile strength, modulus of elasticity, and compression strength of the modified PMMA bone cement were determined by using a universal testing machine (model WDW 5 E). Test procedure and dimensions of the specimens were according to (ASTM 638) standard. The test is achieved at velocity 5mm/min, and the load is applied until the sample is failed. The data of stress-strain are obtained [16]. Three samples are tested each time, and the mechanical properties are taken as the average. The compression test is conducted according to (ASTM D695) [17] by using the same tensile machine at the cross-head (strain rate) of (5mm/min) and applied a load of (25 KN) until the break of the specimen occurs. The adopted value is the average of three readings. For the impact test, samples were prepared with dimensions of (55×10×4mm) based on ISO Standard 179 [18]; it also utilized without an indented point. Utilizing the Charpy strategy where the example was put evenly. The testing technique incorporated lifting the pendulum to its maximums stature and fixing it immovably where its potential energy would have been changed to dynamic energy. Scanning Electron Microscopy (SEM) test was utilized to review the break surface's morphology for polymeric nanocomposite sample at various amplification. Tests were falter covered with gold in the gadget for good electric conductivity. At that point, take an output for the surface and break the surface of the specimen. SEM gadget of the model (assess S50).

4. Results and discussions

4.1. FTIR results

Figure 1 investigates the modification process of TiO$_2$ NPs by APTMS coupling agent. From spectra of both neat and modified TiO$_2$ NPs, the peaks below 700 cm$^{-1}$ were assigned to Ti-O and Ti –O –Ti bonding of titania. For neat titania, peaks between 3400 and 3200 cm$^{-1}$ and the low-intensity peak at 1640 cm$^{-1}$ refer to the stretching vibration of absorbed water and surface hydroxyl groups (OH). After surface modification of titania by organosilane (Figure 1b), the asymmetrical and symmetrical extending vibration of the C–H bond in methylene bunch was seen at 2928 and 2870 cm$^{-1}$ individually. Moreover, the pinnacle relating to the Si-O-Si bond was seen at around 1040 cm$^{-1}$ showing the buildup response between silanol gatherings. The N-H twisting vibration of essential
amines (NH$_2$) was seen as broadband in the locale 1605–1560 cm$^{-1}$, and another low power top on the shoulder of titania top at 1140 cm$^{-1}$ was doled out to the C-N bond. The presence of these groups showed that amine utilitarian gatherings in organosilane were joined onto the adjusted molecule surface and the achievement of alteration measure [14].

![Figure 1](image1.png)

Figure 1. FTIR spectra for (a) neat TiO$_2$ (b) modified TiO$_2$.

Figure 2 shows the FTIR spectrum of PMMA and its composites with TiO$_2$ NPs. All the characteristics vibration bands of PMMA composites are reserved in the infrared spectrum of the prepared composites samples. For slick PMMA, absorption groups were seen at 2993, 1730, and 1420 cm$^{-1}$, which are trademark groups for PMMA. The band at 3100 cm$^{-1}$ could be doled out to the extending vibration of Ti–OH and O–H framed by the C=O of PMMA. The expansion of TiO$_2$ in PMMA did not change the composite's functional groups as no new retention groups were watched [16]. Also, it can be noticed that no new peaks appeared after the reinforcing by the m- TiO$_2$ NPs, and there was no shifting in any of these peaks. That means there are only physical interactions between composite constituents, which gives a good indicator about the miscibility state between these constituents and the absence of any residual monomer or by-product that may cause toxicity, allergy, and inflammation of the human body [19].

![Figure 2](image2.png)

Figure 2. FTIR spectrum for neat PMMA and its composites with modified TiO$_2$ NPs.
4.2. Tensile results

The modulus of elasticity and tensile strength for (PMMA) reinforced with TiO$_2$NPs in different ratios (0, 0.5, 1, 1.5, and 2wt. %) are shown in Figures 3 and 4, respectively. Results show some fluctuations in tensile strength and a general increment in the elastic modulus. At the lowest ratio, 0.5 wt. %, the tensile strength decreased due to the phase separation, while at the highest ratio; 2wt% it decreased due to the agglomeration state. The tensile strength reached its maximum value (35.95MPa) at the 1 wt. % addition, which means that this ratio represented the critical fracture volume for the filler component. Beyond this ratio, the tensile strength decreased linearly due to beginning of agglomeration tendency among TiO$_2$ NPs due to the growing of electrostatic forces with TiO$_2$ addition. This behavior weaken the overall physical interactions between the nanoparticles and PMMA matrix, which requires only low tensile stresses for the failure to occurs [20]. The elastic modulus (figure 4) generally increased as TiO$_2$ NPs increased and reached its highest value (2.5 GPa) at 1wt. % ratio. This finding provides another indicator of the 1wt. % ratio represents the optimum reinforcing ratio, and the agglomeration negative effects appear beyond this ratio. At 1 wt.% ratio, the tensile strength improved by 20%, while the elastic modulus by 75% indicates that the new bone cement can resist severe service conditions and bear additional external tension loads [21].

![Figure 3. Tensile strength of polymeric PMMA: TiO$_2$ Nano composite as a function of TiO$_2$ NPs content.](image)

![Figure 4. Elastic Modulus of polymeric PMMA: TiO$_2$ Nano composite as a function of TiO$_2$ NPs content.](image)

4.3. Compression set results

The compression set values for the prepared samples are shown in Figure 5. It can be noticed that the compression sets enhanced by increasing the modified TiO$_2$ NPs content and reached its maximum value (118.4 MPa) at 1 wt. %. That means that 1 wt. % TiO$_2$ NPs give the maximum strength to the PMMA polymeric matrix due to the highest physical interaction density among the composite components. The 1 wt. % TiO$_2$ NPs ratio increases the compression set clearly; by 39.31%, comparing with its initial value (for neat PMMA). This considerable improvement enhances the need to improve and modify the inert surfaces of the neat TiO$_2$ particles and creates new active sites on their surfaces by treatment with silane coupling agents [11].
4.4. Impact strength results

The impact strength property is a function of the absorbed energy within the internal structures of materials. The impact test differs from other mechanical tests because the sample is subjected to fast stress, which leads to real changes in the material responses [22]. Figure 6 shows the relationship between the impact strength and the modified TiO$_2$ NPs content. Two elements constrain the impact quality of the composite sample: initially, by the capacity of the strengthening material to stop split proliferation by absorbing energy, and also by the helpless holding between reinforcing particles and polymer, which cause small spaces and result in crack propagation [23]. Results (Figure 6) showed that the impact strength increased linearly as TiO$_2$ NPs increased up to 1 wt. % ratio reached its upper value, 7.4 kJ/m$^2$ and then declined. This high increment (about 48%) is due to the highest interactions, which create a coherent structure able to absorb the external shocks and dissipate its energy within the entanglement polymeric chains. The entangled state among the polymeric chains creates many voids, attenuating the shock energy and finally protecting from failure beyond the 1 wt. % ratio, the accumulation of TiO$_2$ particles on each other causes the active sites on the filler surfaces to be buried within the composite structure and preventing the interactions from occurring. These interactions are just weak secondary forces, and it will weaken more and more by the presence of any obstacles like filler accumulation.
4.5. Morphology results

Figure 7 monitors the effects of m-TiO$_2$NPs on the morphologies of the PMMA bone cement at 3000X magnification power. The nanocomposite material's structure morphology is affected by a few boundaries, such as the nature of filler, the particle shape, the particle size, filler appropriation, the segments proportions, and the segment soften viscosities, and preparing conditions [24]. There is some homogeneity between the four components of the neat bone cement (figure 7-A): PMMA, BPO, MMA, and DMPT. This sample's roughness is due to the incomplete dissolving of the powdered components in the liquid ones by adding the m-TiO$_2$NPs with 0.5 and 1 wt. % ratios (Figure 7 - B and C), the homogeneity increased, the roughness decreased, and the new material, m-TiO$_2$NPs, appear clearly. These roughly smooth surfaces refer to good miscibility (good compatibility) among the bone cement components, good dispersion of m-TiO$_2$NPs within the bone cement matrix, and high bonding degree, which predicts high mechanical properties high resisting to the failure occurrence. It is also clear from these two figures that most m-TiO$_2$NPs are embedded inside the polymer, going about as an essential aspect of the PMMA bone cement structure, demonstrating a better interfacial grip between its constituents [13]. Beyond the 1 wt. % addition, clear weaknesses appeared in the morphologies stats (figure - 7 D and E), such as micro creaking, inhomogeneity, high roughness, phase separation, delamination, and agglomeration. All these factors predicted a poor interfacial adhesion among the components, leading to bad mechanical properties [25].

![Figure 7](image_url)

Figure 7. SEM image of fractured surface morphology for (A): Neat PMMA, (B): Nanocomposite sample reinforced by 0.5%wt. nTiO$_2$, (C): Nanocomposite sample reinforced by 1%wt. nTiO$_2$, (D): Nanocomposite sample reinforced by 1.5%wt. nTiO$_2$, and (E): Nanocomposite sample reinforced by 2%wt. nTiO$_2$ at 3000X magnifications.
5. Conclusions
In this paper, TiO₂ NPs can be successfully modified by the APTMS coupling agent to increase their surface reactivity. There are no chemical bonds between TiO₂ filler and the PMMA matrix, which enhances the miscibility trend. Generally, modified TiO₂ NPs enhance tensile strength, elastic modulus, compression set, and impact strength up to 1wt% and then decreases that the 1wt% represents the best ratio and morphology results support the mechanical properties.

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