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IMPROVING MECHANICAL PROPERTIES OF POLYMERIC MATERIALS USING OXIDE NANOPARTICLES

Elena Emanuela HERBEI
“Dunarea de Jos” University of Galati, Romania
e-mail: elena.valcu@ugal.ro

ABSTRACT

This paper investigated the effect of zirconium oxide (ZrO_2) and titanium oxide (TiO_2) on the morphology and mechanical properties of poly (methyl methacrylate) (PMMA) blends. Composites of PMMA (5/95 wt%) with ZrO_2 and TiO_2 were prepared by modified sol-gel reaction and then the composites were integrated by compression. The dispersion of ZrO_2 and TiO_2 nanoparticles in the polymer matrix was investigated after deposition as thin films, using optical microscope. It was studied also the transparency and the band gap of thin films of the individual compounds and of the mixed zirconia composites. It was observed that the dispersion of ZrO_2 nanoparticles was relatively good with low ZrO_2 content, but the aggregates of ZrO_2 particles in a polymer matrix increased with increasing the ZrO_2 content. The Vickers hardness test on PMMA and ZrO_2-PMMA showed that the value of hardness increases as the percentage of ZrO_2 increases. The adding of zirconia nanoparticles showed that the composites can be used in fabrication of different application as metal protection, dental materials, abrasion resistant materials, transparent protection due to the hardness tests.

KEYWORDS: zirconia nanoparticles, composites, PMMA, Vickers hardness

1. Introduction

Inorganic nanoparticles-polymeric composite has gained considerable interest due to their special properties as mechanical, thermal resistance, corrosion resistance, low density, easy processing, thermal conductivity, dielectric properties and transparency as a result of the inorganic contribution to the polymer matrix.

Polymethylmethacrylate (PMMA) is one of the most commonly used materials due to its desirable characteristics, such as excellent aesthetic properties, ease of handling and repair, accurate reproduction of surface details, lack of toxicity, and cost-effectiveness [1, 2].

When inorganic nanoparticles oxides as ZrO_2 and TiO_2 are incorporated into organic matrix, called polymer-based nanocomposites, it represents a new class of materials with improved performance compared to their mono phase counterparts [3].

In recent years, several investigations have focused on improving the mechanical properties of PMMA acrylic resins by adding functionalized nanomaterials, such as bio-ceramic nanoparticles, due to their special characteristics [4].

The functionalization agents used for these applications are organo-silica based precursors, used to improve the connection and to create new chemical bonds between the inorganic and organic compounds.

Zirconia (ZrO_2) is considered a bio-ceramic material that has been widely used for various dental applications, electronic application such as crowns and bridges, implant fixture “screws” and abutments, and orthodontic brackets [5]. Zirconia nanoparticles are used also for a high flexural strength (900 to 1200 MPa), hardness (1200 HV), and fracture toughness (9-10 MPa m1/2) [6].

Titanium oxide nanoparticles (TiO_2) is a material that has a high transparency, characterized by wide band gap and high electrical resistivity at room temperature. Also, TiO_2 is a non-toxic and exhibits good chemical, thermal and mechanical stability. In view of its properties, TiO_2 based thin films have wide range of applications. Anatase and rutile phases of tetragonal structure are the most important compounds of TiO_2 that can be used in obtaining composites using different polymer matrix for improving hardness and also for antibacterial properties [9].

Usually increased hardness of the material is strongly correlated to density of thin film. The hardness is, therefore, dependent not only on the material type, but also on its crystalline structure and crystallites size [7].

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The hardness of the thin films is usually many times smaller than that of the bulk. However, it was found that for thin films with dense structure the hardness is higher, and for nanomaterials it is possible to achieve the hardness even greater as compared to the bulk [8]. This is because the hardness of the material increases when the grain size decreases with the maximum in the nanometre range (Hall-Petch effect) [8]. Results of the research presented in the literature show that oxide materials, which are composed from crystallites of a single nanometres in size, exhibit completely different properties than the bulk material of the same chemical composition [10].

The purpose of this study is to evaluate the effects of zirconium oxide and titanium oxide nanoparticle addition at low concentrations (up to 10%) to a commercially available PMMA matrix on selected mechanical properties such as hardness behaviour, morphology and optical properties.

2. Experimental details

2.1. Dispersion preparation

The ZrO_2 (50 nm), TiO_2 (100 nm) nanoparticles and PMMA (495 kw) used for the preparation of dispersion were purchased from Sigma Aldrich and MICRO CHEM, respectively. For the functionalization of nanoparticles, trimetoxysilylpropyl methacrylate agent was used, in absolute ethanol as solvent, for 6 hours. After the reaction of functionalization, the nanoparticles were cleaned in isopropanol and water to eliminate the agent excess. ZrO_2-PMMA and TiO_2-PMMA dispersion with 5/95 wt% ratios were prepared (Figure 1a). Then a part of the dispersion was introduced in crucibles up to 200 °C to eliminate the water and alcohol traces (Figure 1b).

The schematic representation of the dispersion preparation is presented in Figure 2.

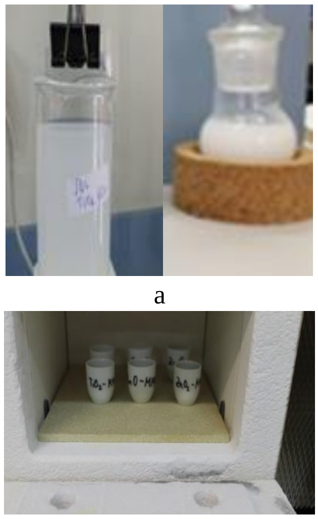

Fig. 1. *The ZrO_2-PMMA and TiO_2-PMMA resulted dispersion obtained by sol-gel modified reaction (a) and the thermal treatment of dispersion (b)*

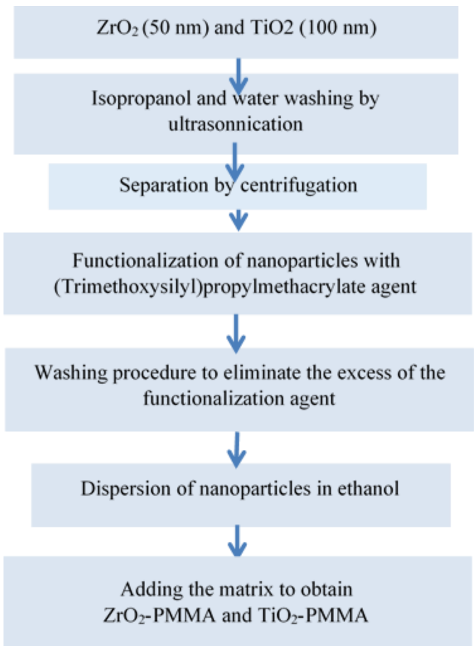

Fig. 2. *Schematic representation of modified sol-gel procedure for obtaining ZrO_2-PMMA and TiO_2-PMMA dispersion*

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2.2. Thin films fabrication

The glass substrates for deposition were cleaned with a standard procedure: washed in water for three times, dipping in isopropanol for 1 minute and cleaning with water, dried with nitrogen stream and heated on hotplate for 5 minutes at 120 °C. For film preparation, the glass substrates were dip coated in ZrO_2-PMMA and TiO_2-PMMA dispersion for 20 seconds in air atmosphere, with controlled speed. The films were thermally treated on hot plate at 120 °C for 30 minutes after they have been cleaned on the back side with alcohol.

3. Results and discussion

Results of optical microscopy investigations revealed that the thin films prepared by dip-coating process were smooth and their surface consisted of visible grains (Fig. 3).

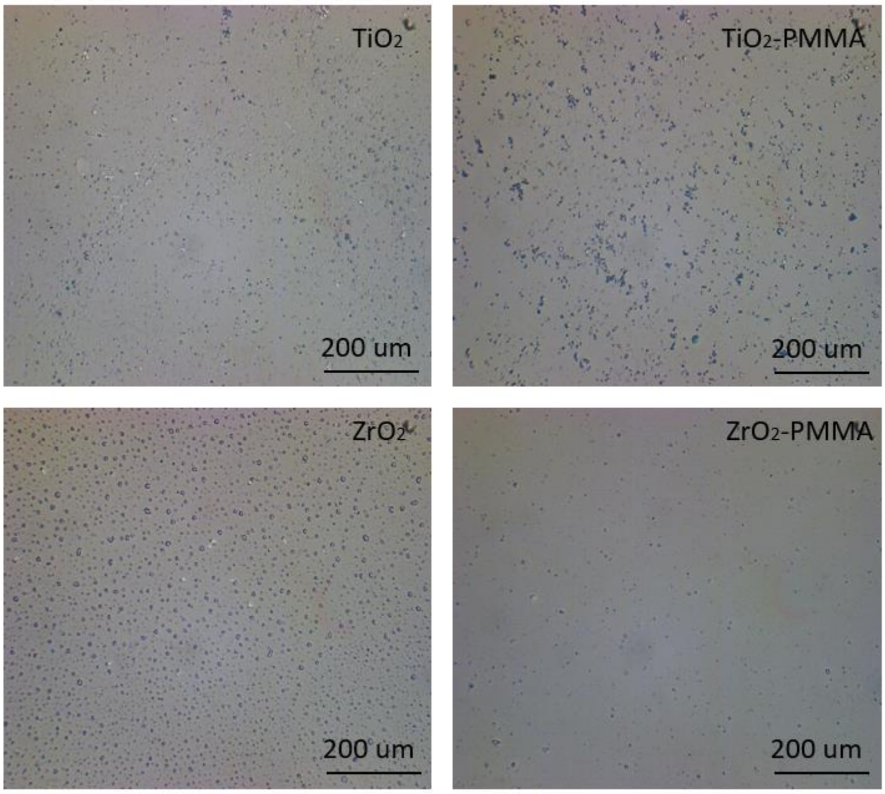

***Fig. 3.** Optical microscopy for thin films*

Optical microscopy images of thin films obtained showed the agglomeration of TiO_2 and ZrO_2 nanoparticles. The embedded nanoparticles in polymer matrix showed a homogenous layer for zirconia oxide nanoparticles than titanium oxide nanoparticles. This is due probable to the electrostatic forces that appears between the TiO_2 nanoparticles.

The optical properties of zirconia oxide nanoparticles thin films show a good transparency of 91% for PMMA thin films which decrease to 85% for thin film of ZrO_2-PMMA. The sample containing TiO_2 shows a value of 80% in transparency, due to the size of nanoparticles which is 100 nm, and due to the agglomeration of nanoparticles created by the electrostatic forces. The optical transmittance of thin films obtained are presented in Figure 4.

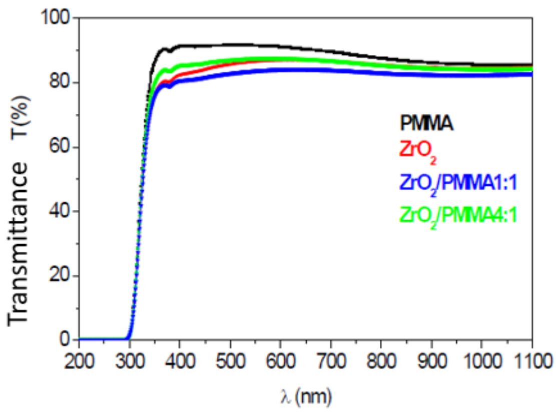

***Fig. 4.** Optical transmittance for ZrO_2 and ZrO_2-PMMA thin films*

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Micro Vickers hardness reflects the uniformity of reinforcement dispersion in composites and effect of cross-linking density on micro-level. Micro Vickers hardness values for PMMA matrix and ZrO_2-PMMA composites presented in the Figure 5 a and b. Vickers hardness number of the surface was calculated using the following formula: HV = 1.8544 F/d^2, where F is the load applied by the indenter and d is the mean diameter of the engraved diamond-shaped indent.

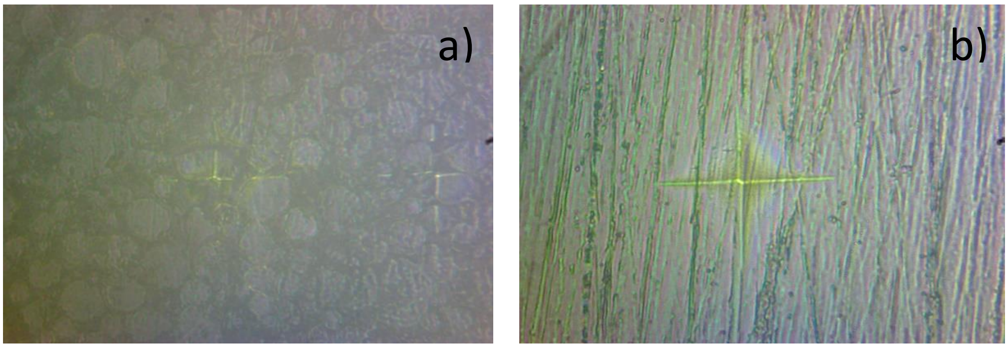

Fig. 5. *Micro-hardness test for PMMA (a) and ZrO2-PMMA (b)*

An addition of zirconia nanoparticles improved micro hardness by 40% of PMMA sample due to the uniformity of the nanoparticles in the polymer matrix and to the good dispersion of nano-ZrO_2. The improvement of the hardness is due probably to the nano size particles which helps in filling the matrix interstitially. Also, the strong adhesion formed between the functionalization agent on the surface of the nano-ZrO_2 and PMMA matrix improves the mechanical properties of nanocomposites [11, 12]. The values of Vickers hardness are presented in Table 1.

Table 1. *Micro Vickers Hardness*

Compounds	Diag. med [mm]	F (kgf)	HV 0.02/30 [kg/mm^2]	HV med
PMMA	0.044842495	0.02	18.44494211	**19.07212**
	0.04489842	0.02	18.39902108	
	0.04386418	0.02	19.27688264	
	0.04288455	0.02	20.16763708	
ZrO_2-PMMA	0.025765125	0.02	55.8717566	**41.62146**
	0.031756295	0.02	36.77876806	
	0.030916775	0.02	38.80328224	
	0.032538365	0.02	35.03203614	

4. Conclusion

Surface functionalization of nano ZrO_2 and TiO_2 was performed by using silane coupling agents with methacryloxy organo-functional groups, and after that nanoparticles was embedded in PMMA matrix. Three-layer polymer-nanoparticle oxide films with thicknesses less than 1 μm were deposed and obtained.

ZrO_2 and TiO_2 oxide nanoparticles were incorporated into organic PMMA matrix.

Obtained images of optical microscopy showed that the embedded nanoparticles in polymer matrix are homogenous, for zirconia oxide nanoparticles than titanium oxide nanoparticles.

Micro Vickers hardness of ZrO_2 and ZrO_2-PMMA samples was determined and showed improved hardness of the samples with zirconia oxide nanoparticles on micro-level.

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