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INFLUENCE OF SURFACE MODIFICATION TO MECHANICAL AND THERMAL PROPERTIES OF NANOMODIFIED ACRYLIC DENTAL RESIN

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This paper investigated the processing and characterization of dental nanocomposites based on poly(methyl methacrylate) (PMMA) matrix reinforced with zirconium dioxide (ZrO_2) nanoparticles were prepared by *in-situ* free radical polymerization. Surface functionalization of ZrO_2 was performed by using silane coupling agents with vinyl and methacryloxy organo-functional groups. FTIR spectrometry was employed in order to characterize functionalized surface of zirconium oxide and to evaluate chemical interactions between the fillers and matrix in nanocomposites. Micro Vickers hardness showed significant improved resistance to indentation of dental nanocomposites when modified nanoparticles were employed. Obtained SEM images showed that silane coupling agents enabled effective dispersion of nanoparticles in matrix. Thermal properties of nanocomposites were analyzed by differential scanning calorimetry (DSC). Low energy impact test was performed in order to determine the mechanical properties of nanocomposites.

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1. Introduction

Polymer-inorganic particle nanocomposites have garnered considerable interest since they can improve properties such as optical, thermal, mechanical, and chemical, as a result of the inorganic contribution to the polymer matrix [1]. When inorganic materials are incorporated into the organic matrix, called polymer-based nanocomposites, it represents a new class of biomaterials with improved performance compared to than their mono phase counterparts [2]. Interest in the research of bionanocomposites has been increased mainly through polymer/ceramic/metal interaction and modifications in formulation, and their use has been marked in particularly dentistry [3]. There is interest in developing dental composites reinforced with nanosized particles with near-zero volumetric shrinkage during curing and highly translucent and radiopaque post curing [4–11]. Other desired properties of the nanocomposites include high strength, good fracture toughness, and excellent wear resistance [9].

Acrylic resin polymethayl methacrylate (PMMA) has been the most popular material for the dental composites with many advantages such as good aesthetics, accurate fit, stability in the oral environment, easy laboratory and clinical manipulation, and inexpensive processing. But this material has low fracture resistance for dental applications [12, 13].

Because of their obvious improvement in hardness, wear resistance, and thermal shock resistance, zirconium dioxide or Zirconia (ZrO_2) is technologically promising ceramic material of the current generation [14]. Zirconia shows very good optical properties leading to god transparency and tailoring refractive index of composites [15].

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The advanced composite research is focused on producing a material that has perfect filler–resin interface and improvement in filler packing, optimization in filler levels, and development of hybrid filler phases [16, 17].

The role of coupling agents is to modify the interfacial properties between nanoparticles and polymer matrix due to its ability to attach the nanoparticles in one side while favoring the dispersion in the other side. A coupling agent controls the interface properties, which results in the improved mechanical properties and optical properties of nanocomposites [18, 19]. Silanes are a large group of organic compounds that essentially contain silicon (Si) atom or atoms. The organic functional part can polymerize with an organic matrix. Silanes could be monofunctional, bifunctional or trifunctional according that how many atoms Si they contain (where Si atom is surrounded with three alkoxy groups in the molecule) [20].

The aim of this work was to compare influence of Vinyltris(2-methoxyethoxy)silane (VTMOEO) and 3-Methacryloxypropyltrimethoxysilane (MEMO) silane on the thermal and mechanical properties of obtained nanocomposites. The series of samples was processed with modified an unmodified nano Zirconia.

2. Experimental

Commercial denture material „Biokril“, Galenika AD, Beograd, Serbia, was used as polymer matrix. It is a two component system, including powder and liquid. The powder consists of: PMMA polymer and initiator benzoyl peroxide (BPO). The liquid consists of: MMA monomer and small content of ethileneglycol- di-metacrilate (EGDMA) used as chemical activator. The Biokril“ powder was characterized [21]: M_n = 1.27x10^5 g/Mol, MW= 3.82x10^5 g/Mol, with a polydispersity, PI = 3.01, content of MMA was 4.3 mass%. As reinforcement nanopowder ZrO_2 (Zirconia) 100nm, Sigma Aldrich, was used. Vinyltris (2-methoxyethoxy) silane (VTMOEO) and 3-Methacryloxypropyltrimethoxysilane (MEMO) – Dynasylane, Evonik Industries and toluene, hexane (Sigma Aldrich) was used for surface modification of Zirconia.

The samples were prepared with a powder to liquid ratio of 2:1 in weight. Into a dry and clean glass test container, Simgal liquid was poured and the powder was added until saturation was achieved, lasting no longer than 15–20 seconds (according to the manufactures script). Mixing was performed in 40–45 seconds. After that the solution was processed in an aluminum mold under mechanical pressure with temperature of polymerization 100° C, under water 30 min. The mold was shaped for specimens for impact test (60x60 mm) and tensile test (bone shaped) and all specimens of one series were processed at once. The different Series of samples were prepared: pure thermally polymerized acrylate, and acrylate with different content of unmodified and modified nano-ZrO_2: 1 %wt.; 3 %wt. and 5 %wt.

2.1. Modification of zirconium oxide nanoparticles

5 g of ZrO_2 nanoparticles were dispersed in 150 ml of toluene round-bottom flask equipped with a reflux condenser under the flow of nitrogen. When the boiling point of toluene was achieved, 1 g of silane (VTMOEO/MEMO) was added and the resulting white suspension was stirred and refluxed for 22 h. After completing reaction, the particles were filtrated and washed with hexane to remove the excess of silane. The particles were dried on 40 °C in oven for 12 h and then used in the preparation of nanocomposites [22].

2.2. Characterization of samples

Fourier transforms infrared (FTIR) analysis performed to investigate bonding between ZrO_2 and matrix. FTIR spectra of the samples in KBr discs were obtained by transmission spectroscopy (Hartmann & Braun, MB-series). The FTIR spectra were recorded between 4000 and 400 cm^{-1} wavenumber region at a resolution of 4 cm^{-1}. Thermal analysis of composites was performed on a device for simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in the temperature range from 24˚C to 600˚C (SDT Q600, TA instruments). Morphology of particles and composites were investigated by FESEM (TESCAN MIRA 3) with fracture surfaces sputtered with gold.

Mechanical characterizations of samples were performed by Vickers microhardness tester “Leitz, Kleinharteprufer DURIMET I” using load of 4.9 N. Three indentations were made at each load, yielding six indentation diagonals measurements, from which the average hardness could be calculated. The indentation was done at room temperature. Also, low energy impact test was performed by Puncture Impact testing machine HYDROSHOT HITS-P10. The clamping plates with aperture diameter of 40 mm and clamping pressure of 0.55 MPa were used. The striker with a hemispherical head, diameter 12.7 mm, was loaded with programmable velocity, height and attained a value of depth. In this manner it is possible to control the impact energy. The data for the force, deflection, velocity and energy with time were recorded. The impact speed was set at 1 m/s and load was up to 10 kN. The data were analyzed in terms of load maximum, energy correspond to load maximum and total energy.

3. Results and discussion

The FTIR spectrum of modified Zirconia nanoparticles (Fig. 1a) have peaks in in the 2920-2860 cm^{-1} range, which are assigned to the stretching of the C–H bonds of the silane coupling agents, while the peak at 754 cm^{-1} is attributed to Zr –O stretching vibrations at ZrO_2 nanoparticles. Double bound from silane agents is noticed at 1635 cm^{-1}.

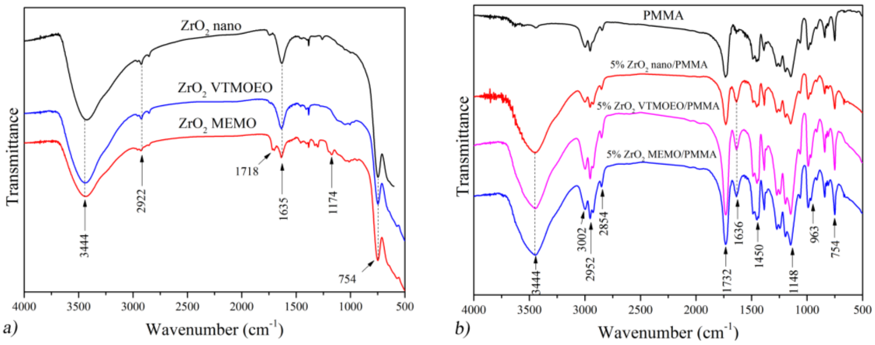


Fig. 1. FTIR spectra of: a) modified of ZrO_2 nanoparticles by VTMOEO and MEMO silane, and b) composites with unmodified and modified ZrO_2 nanoparticles

Characteristic acrylate CH_3 vibration of MEMO silane was observed at 1174 cm^{-1}. Spectrum for VTMEO modified zirconia shows the peaks for both asymmetric Si-O-C stretching of silane and Si-O-Si functionality of siloxane at 1150, 1112 and 1024 cm^{-1}, respectively, [23-26].

The FTIR spectrums of PMMA and composites with unmodified and modified ZrO_2 nanoparticles are presented in Figure 1b). The carbonyl stretching band –C=O at 1735 cm^{-1} did not change and had no relevance to the adhesion process. At about 1636 cm^{-1} there was a characteristic, broad band due to C=C stretching (methacrylate and vinyl groups). In comparison to the hydrolysis spectrum, it did not disappear due to the heat treatment. At 1410–1440 cm^{-1} CH_2 groups and vinyl CH_2=CH– bands were merged together. A vinyl group had also remained. At 1350 cm^{-1} the band was due to the methacrylate group. An intense, merged band of siloxane layer, polymerized silane layer could be seen at ca. 1055 cm^{-1}. A weak signal of the Si–O–Zr vibration was seen at ca. 963 cm^{-1} [26].

The results of DSC analysis are presented in Figure 2. It is obvious that the addition of nano Zirconia improves thermal properties of composites. The glass transition temperature (T_g) of a polymer increased after the addition of inorganic fillers. The particles behaved as functional physical crosslink and thus reducing the overall mobility of the polymer chains, as was already reported [27- 29]. Moreover, modification of interface matrix-Zirconia leads to better thermal stability because the chemical bonding between polymer and particles was established. The modification with MEMO silane was more successful in improvement of thermal properties.

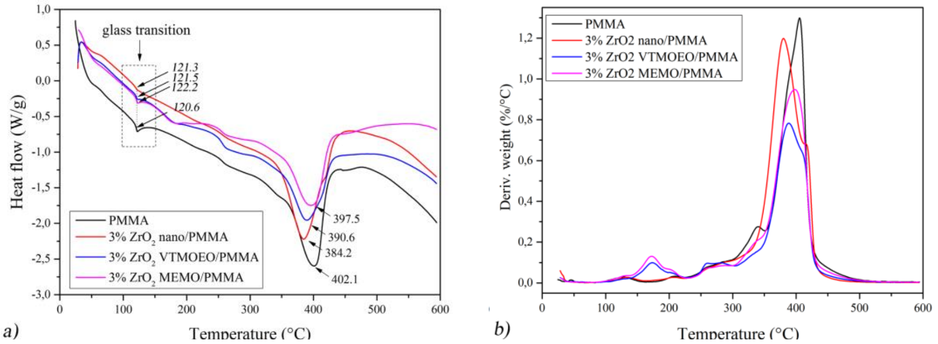
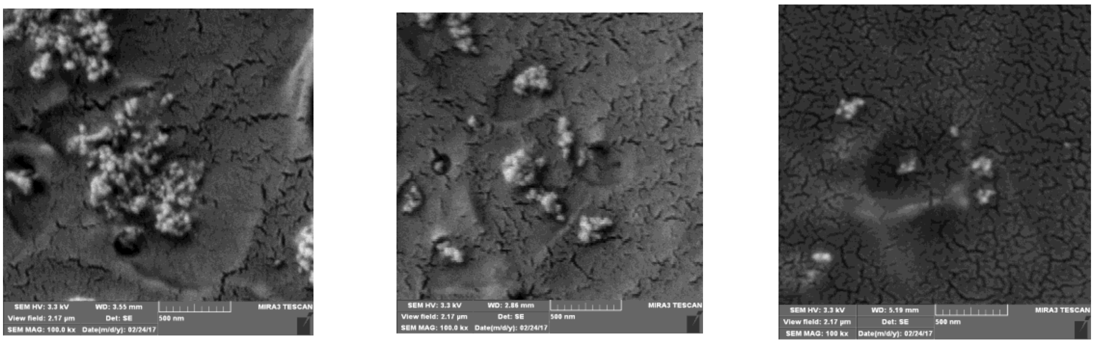


Fig. 2. DSC and DTG curves for PMMA and composites

The FESEM photos of fracture surfaces of composites with unmodified and modified nano particles are presented in Figure 3. A favorable dispersion of particles in nanofibers was achieved and a better deaglomeration of modified particles was obtained. It is obvious that better deagglomeration was achieved with modified nanoparticlees, especially with MEMO silane (Figure 3c). It is seen that the average agglomerate size of the ZrO_2 nanoparticles slightly decreases as the surface modification take place [26].



a) b) c)

Fig. 3. FESEM images of composite fracture: a) PMMA- ZrO_2;
b) PMMA-VTMO ZrO_2; c) PMMA-MEMO ZrO_2

Micro Vickers hardness reflects the uniformity of reinforcement dispersion in composites and effect of cross-linking density on micro-level. Table 1 represents a micro Vickers hardness values for PMMA matrix and composites.

Table 1 Results of micro Vikers test and standard deviations

Sample	HV, MPa	St.dev.,MPa
PMMA	195	±2
1% ZrO	225	±11
3% ZrO	242	±5
5% ZrO	259	±1
1% ZrO VTMOEO	253	±6
3% ZrO VTMOEO	286	±17
5% ZrO VTMOEO	297	±2
1% ZrO MEMO	258	±8
3% ZrO MEMO	295	±30
5% ZrO MEMO	310	±12

An addition of Zirconia nanoparticles improved micro hardness by 24%, while employed silane functionalization enabled effective dispersion and cross-linking and thus improvement of HV value of 46.3% and 50.7% for nanoparticles functionalized with VTMOEO and MEMO silane, respectively (Figure 4 and Table 1).

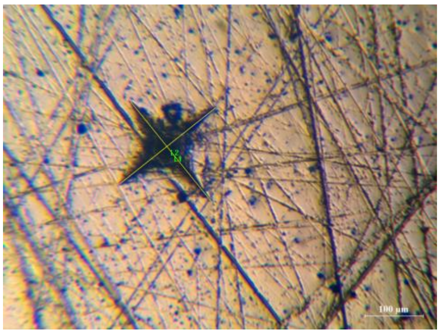
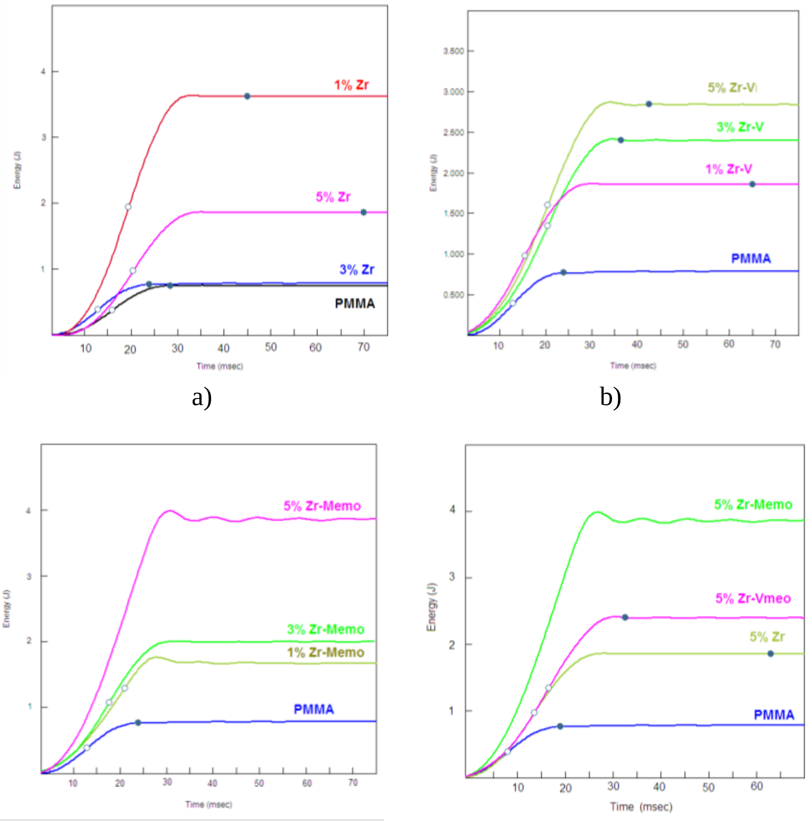


Fig. 4. Indent of PMMA sample

The results of impact test are presented in Figure 5. as Energy-time diagrams. Impact test revealed the improved impact behavior of nano composites with modified particle surface in comparison with pure PMMA. The energy increased as content of nano-reinforcement increase [31]. The maximum absorbed impact energy has shown the composites modified with MEMO silane.



a) b)

c) d)

Fig. 5. Energy-time diagrams from impact test: a) Composites with unmodified ZrO_2 nanoparticles, b) Composites with modified with VTMOEO c) Composites with modified with MEMO, d) Composites with different content of ZrO_2 modified with MEMO

4. Conclusions

Surface functionalization of nano ZrO_2 was performed by using silane coupling agents with vinyl and methacryloxy organo-functional groups, and after that nano ZrO_2 was embedded in acrylic resin. FTIR spectrometry revealed that chemical interactions between the fillers and matrix were established. Obtained SEM images showed that silane coupling agents enabled effective dispersion of nanoparticles in the matrix.

Micro Vickers hardness showed improved resistance to indentation on micro-level. Low energy impact tests revealed that both silane was effective in matrix-reinforcement bonding. But MEMO silane was achieved better dispersion of nano particles. The modification of ZrO_2 led to improved thermal and mechanical properties compared to the nano composites reinforced with unmodified particles.

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