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SYNTHESIS OF PMMA/ZnO NANOPARTICLES COMPOSITE USED FOR RESIN TEETH

SINTEZA PMMA/ZnO NANODELCEV KOMPOZITOV ZA IZDELAVO ZOB IZ UMETNIH SMOL

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Wear resistance is one of the most important physical properties of the artificial teeth used in acrylic dentures. The goal of this research was to synthesize a new composite material made of matrix Poly-(methyl methacrylate)-PMMA with different percentages (2 % and 3 % of volume fractions) of zinc-oxide nanoparticles (ZnO NPs) as reinforcing elements, to improve its mechanical properties. The dynamic mechanical behaviour of this composite was studied through the DMA method in comparison to the pure PMMA supported by the characterization of their microstructures. Then the wear resistance was analysed on the samples, which were prepared in the form of teeth. In this context their vertical height loss was measured after 100,000 chewing cycles on a chewing simulator, before and after the artificial thermal ageing. Investigations showed that the PMMA/ZnO NP composites dampened the vibrations better than the pure PMMA, which could be assigned to the homogenous distribution of ZnO NPs in the PMMA matrix. It was found that the mean vertical height loss for the pure PMMA teeth was significantly higher (more than 4 times) compared to composite teeth made with ZnO NPs. Introducing the thermal artificial ageing led to the finding that there was no effect on the height loss by the composite material with 3 % of volume fractions of ZnO NPs. Based on this it was concluded that PMMA/ZnO NPs composites showed improved in-vitro wear resistance compared to acrylic-resin denture teeth, so this new composite material should be preferred when occlusal stability is considered to be of high priority.

Keywords: poly-(methyl methacrylate)–PMMA, zinc-oxide nanoparticles, composite, resin teeth

Odpornost proti obrabi je ena izmed najbolj pomembnih fizikalnih lastnosti umetnih zob pri akrilnih protezah. Cilj te raziskave je bil sintetiziranje novega kompozitnega materiala, izdelanega iz matrice poli-(metil meta akrilata) – PMMA z različnimi volumskimi odstotki (2 % in 3 %) nanodelcev cinkovega oksida (ZnO NPs), uporabljenimi kot ojačitveni element za izboljšanje mehanskih lastnosti materiala. Dinamično mehansko obnašanje teh kompozitov smo raziskali z metodo DMA v primerjavi s čistim PMMA, ter s karakterizacijo njihovih mikrostruktur. Nato je bila analizirana odpornost proti obrabi na vzorcih, ki so bili pripravljeni v obliki zob. Izmerjena je bila njihova navpična izguba višine po 100.000 žvečilnih ciklih na žvečilnem simulatorju, pred in po umetnem toplotnem staranju. Preiskave so pokazale, da so PMMA/ZnO NPs kompoziti bolje blažili vibracije kot čisti PMMA, kar lahko pripišemo homogeni porazdelitvi ZnO NPs v PMMA matrici. Ugotovili smo, da je bila povprečna navpična izguba višina za čisti PMMA zob znatno višja (več kot 4×) v primerjavi s kompozitnimi zobmi z ZnO NPs. Umetno toplotno staranje ni imelo učinka na izgubo navpične višine zoba iz kompozitnega materiala s 3 volumskimi % ZnO NPs. Na podlagi tega smo sklenili, da imajo kompoziti PMMA/ZnO NPs izboljšano in vitro odpornost proti obrabi, v primerjavi z zobno protezo iz akrilne smole, zato naj bi imel ta novi kompozitni material prednost pri uporabi, kadar je potrebna okluzalna stabilnost.

Ključne besede: poli-(metil meta akrilat)-PMMA, nanodelci cinkovega oksida, kompoziti, zobje iz umetnih smol

1 INTRODUCTION

Teeth loss in the human population is associated with numerous problems such as chewing difficulties, alteration of speech and facial expressions, which all leads to de-socialization. According to the Oral Health-Healthy People 2010: Objectives for Improving Health 26 % of the US population and 33 % of the Central Europe population aged between 65 years and 74 years are toothless; but some dramatic data and a wide variation in edentulism prevalence among adults aged 50 and above was found in the following countries: 48.3 % in Ireland, Malaysia 56.6 % and Netherlands 65.4 %, which indicates an international problem.[1–3]

The problems of toothless people in the region of the Balkan peninsula and South-Eastern Europe are usually solved with a complete or partial acrylic denture, which is the easiest and the cheapest solution, because more than 90 % of these patients are in a bad financial situation and incapable of buying dental implants and hybrid bridges above them. With an acrylic denture the wear resistance represents one of the most important physical properties because, in the case that the material has excessive wear, that might cause loss of the vertical dimension of occlusion (VDO) which is associated with decreased occlusal forces, loss of masticatory efficiency, improper tooth relationship, and fatigue of masticatory muscles.[4] Recently, a study examined how VDO can

affect brain function in complete denture wearers, and also measured occlusal forces when there is a change in VDO in which electroencephalograms were used.[5] Many authors have pointed out the necessity of creating complete new dentures, or relining of the denture base, which is not a simple procedure and presents financial pressure for the patients.[6] So, finding the new combination of materials with improved mechanical properties, which include better wear resistance, would be helpful for many reasons for those patients.

Many basic researches based on polymer materials represent the challenge. One of these are made of supramolecular polymers as a new high-tech material.[7,8] Over the past two decades a great effort has been made by the community of researchers for the synthesis and utilization of nanomaterials in the field of medical materials.[9] Using fine nanoparticles as reinforcing elements could improve the functional properties of conventional materials such as PMMA, which has been used for dentures since 1937. The ZnO NPs are small objects that behave as an entire unit regarding their transport and properties. The introduction of ZnO NPs represents a new approach in dentistry by the production of a denture, because they could decrease the level of residual monomer and, besides this, they also have antimicrobial activity. This was shown in recent studies.[10,11] Namely, ZnO NPs are environmentally friendly materials in the nanometre size range, and could be synthesized in a wide range of particle shapes and structures.[12–14] ZnO in bulk form is a largely inert, white powder compound that has a very broad application, from the chemical industry through cosmetic and medical products. In dentistry they have an important place as a medicament for healing injures after periodontal surgical treatment, in the cementation of temporary, as well as definitive, crowns etc. ZnO is also a biocompatible material that exhibits antimicrobial properties against gram-negative as well as gram-positive bacteria.[15] A recent study also investigated, proved and determined the minimal inhibitory concentration of ZnO NPs against *Candida Albicans*.[16]

Nanostructured materials with unique and fascinating properties motivate scientists tremendously to explore and understand their formation and growth processes and following the critical volume in several studies we tried to find the right percentage of ZnO NPs in a PMMA matrix which could advance the properties of this new composite, because increasing the percentage of added NPs could downgrade some of them.[17,18]

According to the presented state-of-the-art study, the aim of this research was:

(i) To synthesize a composite PMMA/ZnO NPs material, to test its mechanical properties, and evaluate the developed microstructures;

(ii) To investigate the wear resistance of resin teeth in a chewing simulator with two combinations, before and after thermal artificial ageing. This investigation included not only the classical testing samples, but also the real model of the shapes of first upper molars (testing resin teeth) and showed possible practical applications in dentistry.

2 EXPERIMENTAL PART

2.1 Materials for composite PMMA/ZnO NPs

Commercially available ZnO nanopowder (purity 99.99 %, density 5.606 g/cm^3, insoluble in water, formula weight 81.37, melting point 1975 °C) was purchased from Interdent (Belgrade, Serbia). The average size of the ZnO NPs was 30 nm and they were in the form of a sphere. The typical shape and morphology of characteristic ZnO NPs are shown in **Figure 1**, which was made on a transmission electron microscope (TEM).

PMMA matrix (polymethylmethacrylate powder with benzoyl-peroxide, pigments and for a liquid-methylmethacrylate HQ 60, ethylene glycoldimethacrylate, methylmethacrylate composite) was distributed by Galenika (Belgrade, Serbia). This material was used for Biogal® acrylic teeth (Galenika, Belgrade, Serbia) and has already passed through the applied ISO Standards.

2.2 Measurement of ZnO nanoparticles' size distribution and zeta potential in water and MMA

Because of the frequent problem with agglomeration among nanoparticles, especially ZnO NPs in water, we used the DLS technique to confirm or deny this fact indirectly and compare them with ZnO NPs in suspension with MMA. Initially, ZnO NPs powder (0.05 g) with water and MMA monomer (15 mL by volume in both cases) was mixed through magnetic stirring for the time duration of 45 min. The size distributions and surface charge of the nanoparticles were determined with a Malvern Zetasizer Nano ZS (Malvern Instruments Ltd., U.K.) by the DLS technique. The suitable parameters for ZnO NPs Absorption: 0.1 and Refractive index: 2.0. were chosen according to [19].

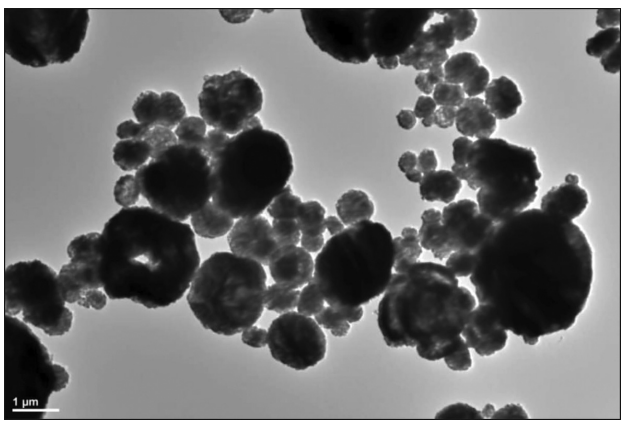

Figure 1: Micrograph of shape and morphology of characteristic ZnO NPs (TEM, 10 000×)

2.3 Preparation of samples

Samples were made in two shapes: Lamina (dimension: 45 mm × 3 mm × 7 mm) for characterization of the new composite and then in the form of the first upper molar for direct potential use in dentistry.

The ZnO NPs in the PMMA matrix were mixed with PMMA powder and then free radical chain polymerization was performed of MMA monomer in bulk. The new composite was synthesized at the selection of the appropriate technological regime, which started in the moment of adding monomer liquid PMMA/ZnO NPs powder for 1 h and 45 min at 100 °C. The procedure for both samples followed by shaping the samples firstly in wax, then duplicated and changed in to the pure PMMA, PMMA filled with 2 % of volume fractions and 3 % of volume fractions of ZnO NPs. The volume % were chosen according to our previous experiences and based on [7,16,18]. All samples in the form of the first upper molar were identical in form, plan parallel and highly polished. They were prepared for a wear test in a chewing simulator. Schematic presentations of the composite PMMA/ZnO NPs synthesis and their corresponding testing are shown in **Figure 2**. A list of samples' names, their mixing ratio PMMA/ZnO NPs and technical descriptions are given in **Table 1**. PMMA1 was chosen for a comparison with the new composites.

2.4 Characterization

Thermo-mechanical properties were examined using a Perkin Elmer DMA 8000 dynamic mechanical analyser. The TT_DMA software, Version 14310, was used for the evaluation of the results. The viscoelastic properties of the samples were analysed by recording the storage modulus (E'), loss modulus (E'') and loss factor (tan δ) as a function of temperature. The height of the peak of the loss factor determined the damping behaviour – with decreasing peak height the damping behaviour was increasing. For the analyses of test samples, the DMA instrument was operated in the dual cantilever mode. The viscoelastic analyses were carried out on samples with dimensions of approximately 42 mm × 5 mm × 2 mm. The samples were heated at 2 °C/min from room temperature to 180 °C under an air atmosphere. A frequency of 10 Hz and amplitude of 20 μm were used.

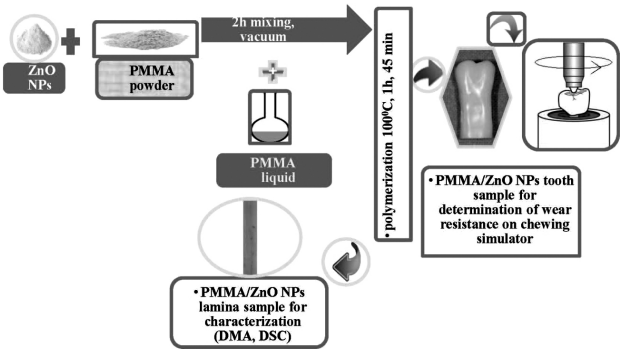

Figure 2: Schematic presentation of synthesis composite PMMA/ZnO NPs and samples for testing

A flash differential scanning calorimeter (Flash DSC) was used for the identification of the glass transition and reorganisation of the polymers for all the samples. Flash DSC works by ultra heating and cooling rates that induce physical transitions and chemical processes. This characterization was very important for dentistry practice because it allowed us to follow the level of polymerization in the residual monomer, which could produce an allergic reaction by the use of the new composite for the resin teeth in removable dentures in the mouths of patients.

2.5 Determination of wear resistance

The wear tests of the samples in the shape of upper first molar were performed in a chewing simulator CS-4.2 economy line (SD Mechatronics, Germany). The simulator has two identical sample chambers and two stepper motors which allow computer-controlled vertical and horizontal movements. The masticatory cycle in this research consisted of three phases: contact with a vertical load of 5 kg, horizontal sliding of 0.4 mm, vertical sliding of 0.2 mm and separating the teeth and machine antagonist. In our investigation, two types of tests were made: before and after thermal artificial ageing including all samples from **Table 1**. The machine was set at 100.000 cycles, which simulated chewing over a period of one year. The loss of substance was measured with an electronic digital calliper – Globathronics GmbH (Germany). Accelerated thermal ageing was carried out by immersing the samples in a water bath at a temperature of 70 °C.[20,21]

Table 1: Composition, mixing ratio and forms of samples for different testing

Samples/ abbreviation	Composition	Mixing ratio	Form for characterization	Form for wear test
PMMA1	Pure PMMA	15 mL MMA + 23.4 g PMMA	Lamina	Tooth model
PMMA2	PMMA/2vol%ZnO NPs	15 mL + 22.93 g PMMA + 0,47 g ZnO NPs	Lamina	Tooth model
PMMA3	PMMA/3vol%ZnO NPs	15 mL + 22.7 g PMMA + 0,7 g ZnO NPs	Lamina	Tooth model

Table 2: Composition and the type of mixing used in the preparation of the solvent with the DLS measurements

Exp. No.	Composition	Methodology	DLS Measurement				
			Run of measurement	Average size range (μm)		Zeta potential (mV)	
1	0.05 g ZnONPs + 15 mL H_20	Magnetic stirring (45 min)	I	3.50	4.01 ± 0.40	–3.45	–3.38 ± 0.81
			II	4.08		–2.35	
			III	4.48		–4.35	
2	0.05 g ZnONPs + 15 mL MMA	Magnetic stirring (45 min)	I	2.28	2.21 ± 0.10	–3.40	–3.48 ± 0.07
			II	2.28		–3.57	
			III	2.06		–3.49	

2.6 Microstructure analysis

Microstructural characterizations of all the samples were carried out with scanning electron microscopy (SEM-Sirion 400 NC and Quanta 200 3D). The specimens, without previous preparation, were broken in an atmosphere of N_2 to minimise the influence of metallographic preparation regarding changes in the structure of the composite. After breaking, the samples were sprayed with Au (Jeol JSM 8310 appliance), which enables the observation of the non-conductive surfaces of the samples with an electron beam. The samples were positioned into the chamber of the microscope and observations were performed with an accelerating voltage of 15 kV.

2.7 Statistical analysis

The statistical analysis included all the parameters involved in the laboratory tests and it was performed in the statistical package SPSS® 17.0. Multivariate linear regression analysis was used to determine the predictors of differences between the analysed groups of samples. The threshold value for accepting the working hypothesis was set at $p < 0.05$.

3 RESULTS AND DISCUSSION

3.1 Macroscopic view

A macroscopic view of both samples' shapes confirmed the homogenous structure of PMMA and PMMA/ZnO NPs. There was only an acceptable difference in colour. Adding ZnO NPs to the mixture with PMMA gave a brighter colour as the percentage of nanoparticles grew. This could be solved in the future by the addition of proper pigment, which results in a similar colour as in the teeth or oral mucosa, which are replicated in resin teeth and denture bases.

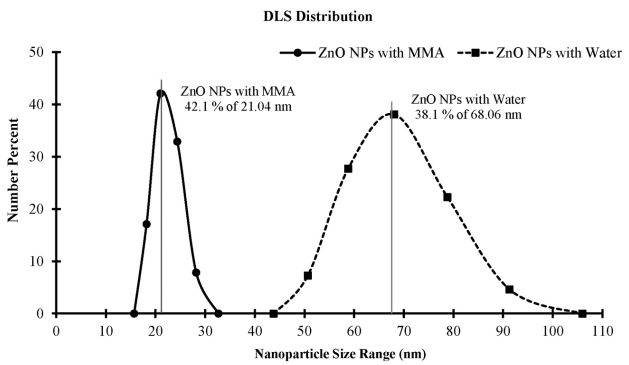

Figure 3: Number vs. size distribution curve of ZnO NPs with MMA and water

3.2 Size distribution and zeta-potential by DLS

The statement of the homogeneous distribution of ZnO NPs in samples was also confirmed by DLS measurement of the results, which are shown in **Table 2**. In ZnO NPs with MMA suspension, the average particle size was 2.21±0.10 μm, while 42.1 % of the particles were in the size range of 21.04 nm, whereas in ZnO NPs with water suspension, the average particle size was 4.01±0.4 μm, while 38.1 % of the particles were in the size range of 68.06 nm. Therefore, the average size of the particles was greater in ZnO NPs with water suspension with more presence of larger-sized clusters of particles. Distribution of ZnO NPs in MMA suspension was homogenous, which showed additionally the insolubility of ZnO NPs in water. ZnO NPs with MMA had a sharp and narrow intensity vs. size curve, as compared to ZnO NPs with water; thereby, it can be stated that there is a higher degree of agglomeration in the ZnO NPs with water suspension (**Figure 3**). The present study showed how it is possible to predict, simulate and characterize the composite material, which is aimed for use in dentistry. The DLS technique could confirm indirectly that ZnO NPs in an MMA suspension give a smaller agglomeration, which was also proven through the calculated large hydrodynamic diameters. ZnO NPs which have a zeta-potential between minus 30 mV and plus 30 mV show a tendency for coagulation. Therefore, ZnO NPs suspensions with water were unstable solutions and showed the tendency of agglomerate, while adding MMA in the ZnO NPs did not show much difference in the stability of the suspension as compared with the water. The samples in our work were made by mixing first ZnO NPs nanopowder and PMMA powder matrix in vacuum, at room temperature for 2 h then adding MMA, which reduced the aggregation among ZnO NPs. This may allow us to prepare homogenous nanocomposites with organic matrices without additional surface modification. The chosen average ZnO NPs size showed

that is of vital importance for the final properties of the new developed composite PMMA/ZnO NPs since it affected the UV-vis absorption and thermal stability. During the synthesis it was found that smaller ZnO NPs showed a higher degree of agglomeration, which is in accordance with the literature.[22–24]

3.3 Determination of properties

The results obtained by the DMA (**Figure 4**) showed the following results. The difference in the elastic modulus at low temperatures which may be due to a slight decrease in the cross linking of PMMA by adding ZnO NPs. At elevated temperatures, the incidence of chain transfer increased (at termination). With chain transfer, the propagating polymer radical reacts with another molecule by proton abstraction and this leads to branching and cross-linking.

Partly, the E modulus increases due to the addition of ZnO NPs, but this increase is minimal. Because of the absence of good interactions between the ZnO NPs and the PMMA matrix, the loss factor increases with the amount of addition of ZnO NPs in the PMMA matrix. ZnO NPs added to the PMMA increased the E modulus and reduced the level of cross-linking. At the same time, the poor interaction between the filler and the matrix results in a less elastic response, which means that the composite of PMMA/ZnO NPs dampen the vibrations better than pure PMMA. With the increasing of the loss factor (tan delta) the damping of the material also increases. In our case, the height of the loss factor peak of the sample PMMA3 was the highest; therefore, the damping of the vibrations of the sample PMMA3 is the highest (**Figure 5**).

Characterization using the DMA method showed that changes in the vibration-damping behaviour of the new composite could mean that at the gingival a more gentle feeling appears, which leads to this material being more friendly to oral mucosa due to vibration damping. This should also be proven through practice. Composite PMMA/ZnO NPs would require longer curing times in comparison with the pure PMMA. Based on this finding it is expected to obtain a better material with the surface modification of ZnO NPs where good interactions between filler and matrix can be formed.

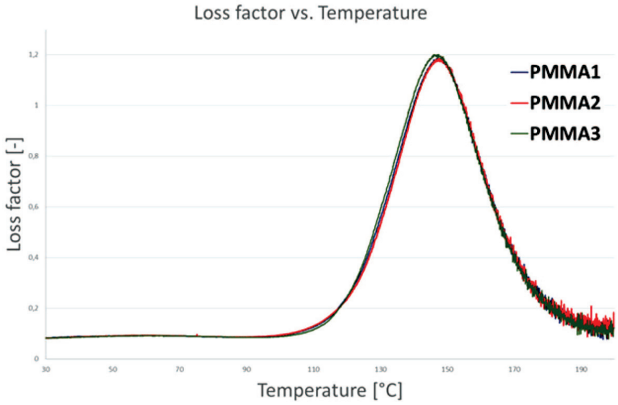

Figure 5: DMA results-loss factor vs. temperature for all samples

From the Flash DSC measurements (**Figure 6**), the lowest glass-transition temperature was measured in the PMMA3 sample (129.6 °C), followed by PMMA2 (131.0 °C) and the highest glass-transition temperature was in the pure PMMA1 (131.1 °C). This fact is also confirmed by the position of the peaks of the loss factor (tan δ), where the lowest glass-transition temperature was measured in the PMMA3 (146.1 °C), followed by PMMA2 (147.2°C) and the highest glass-transition temperature in the pure PMMA1 (147.8 °C). In this context it was found that the degree of cross-linking was reduced by the addition of ZnO NPs. With increasing glass-transition temperature the loss factor decreased, which indicates that the material PMMA3 (tan δ = 1.2003) has the best vibration-damping behaviour, followed by PMMA2 (tan δ = 1.1856). The pure PMMA1 (tan δ = 1.1839) showed the most elastic response. From the height of tan δ it can be concluded that the 3 % addition of ZnO NPs in PMMA is needed to obtain a significant change in the vibration-damping behaviour of the composite. Despite the small differences measured, as well on DMA (E modulus, tan δ) as on Flash DSC (glass-transition temperatures), all the results had the same tendency.

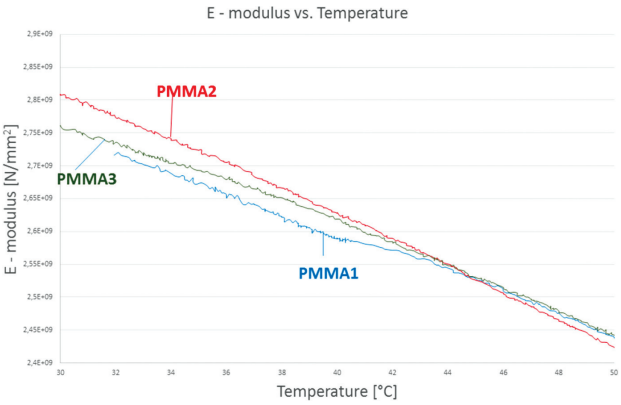

Figure 4: DMA results- diagram E – modulus (N/mm^2) – T (°C) for all samples

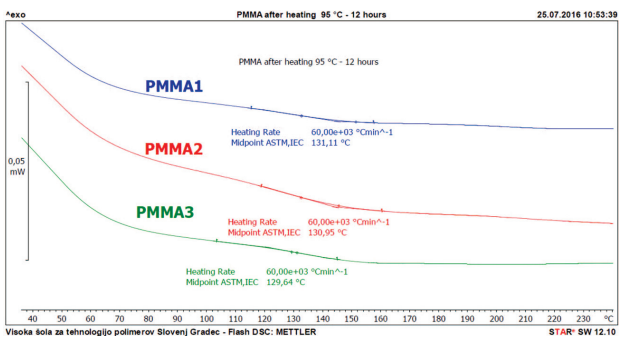

Figure 6: Results of flash DSC analysis for all samples, heating 1.000 °C/s (diagram heat flow (mW) – T (°C))

The difference in the E modulus at low temperatures may have been due to the slight decrease in the cross-linking of the PMMA by adding ZnO NPs. The degree of cross linking by adding ZnO NPs decreased, as shown by the measurements on the Flash DSC and the level of the peak of tan δ. This results, at temperatures up to about 45 °C, in a minimum E modulus in the PMMA3 and a maximum E modulus in the PMMA2 (the difference between the glassy transition of PMMA2 and pure PMMA1 was minimal). Partly, the E modulus increased due to the addition of ZnO NPs, but this increase was minimal. Because of the absence of good interactions between the ZnO NPs and the PMMA matrix, the loss factor increased with the amount of addition of ZnO NPs in the PMMA matrix.

3.4 Wear resistance

The mean vertical dimension of each tooth sample was measured (from the top of the field where the wear test was performed to the bottom) before the artificial chewing action and after. All the samples were subjected to artificial thermal ageing (the samples were in warm water at 70 °C for one month) and, after that, to mechanical ageing on the chewing simulator. The results of mean height loss of the control (PMMA1) and tested group (PMMA2, PMMA3) are shown in **Figure 7**. Recently, a study showed that the median vertical wear of polymer denture teeth, made by different materials, has been reported to be above 0.2 mm after 2 years of observation and, in over 50 % of these, variability of wear. This could be attributed to specific patient factors such as biting force, nutrition habits and other unknown factors. Gender differences were also found in the spatial and temporal parameters of masticatory movement path and rhythm.[25–27] On the other hand, we used the same material and improved these mechanical properties by adding a different percentage of ZnO NPs; we also checked the height loss of the material only after one year of mechanical ageing on a chewing simulator.

The tested PMMA2/3 samples showed a higher wear resistance than the tooth sample PMMA1 by 4 times. Artificial thermal ageing had an effect on the pure PMMA1 and PMMA2, but there was no effect in the group with samples made of PMMA3. There was no statistically significant difference in the loss of height between samples made of PMMA2 with PMMA3. Occlusal wear values of the samples made of pure PMMA1 and PMMA2 after thermal artificial ageing were 2-times as big compared to the samples made from PMMA3. Wear resistance of restorative materials under clinical conditions is a rather complicated phenomenon compared to other mechanical and physical properties of materials.[25] Furthermore, the cause of thermal stability and its effect on the wear resistance of both PMMA2 and PMMA3 samples could be linked significantly. Long-term polymerization at 70 °C, after polymerization at the usual 100 °C for 1 h and 45 min can be recommended, because of its positive effect on the wear resistance of PMMA1 and PMMA2 after artificial ageing (70 °C, one month). PMMA3 had lower height loss before, as well as after, thermal artificial ageing compared to the other samples.

3.5 Microstructure

The microstructure of the fracture surface of the newly developed PMMA2 is shown in micrographs (**Figure 8**), where the visible fracture is brittle. Detailed observation by higher magnification revealed that ZnO NPs (coloured in white) are distributed homogeneously through the PMMA matrix with some small evidence of ZnO NPs' agglomeration (about 1 μm) and signs of de-polymerized dark fields around them. This led to the deteriorated final properties of the composite. In the future, it is necessary to avoid the de-polymerization process by the adequate preparation of ZnO NPs' surface

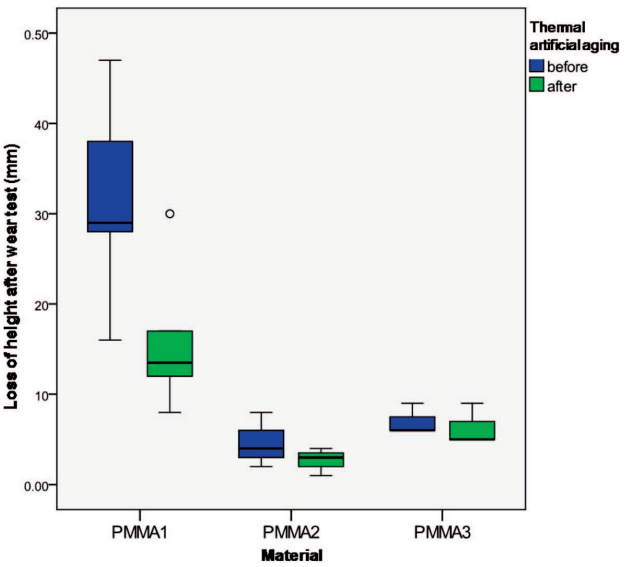

Figure 7: Loss of height of resin teeth after wear test on chewing simulator before and after thermal artificial aging

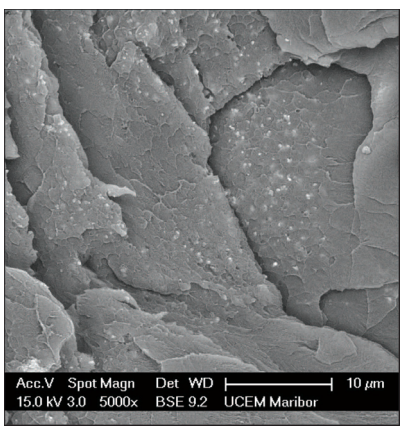

Figure 8: Micrographs of characteristic surface fracture in PMMA2

modification.[23] On the other hand, from the literature it is known that homogeneously dispersed ZnO NPs in the PMMA matrix can be explained by the theory of the different kinds of integration by grafting copolymer chains.[28,29]

4 CONCLUSIONS

Based on the methodology applied in this study, and by considering the obtained results, the following conclusions can be drawn:

- The newly developed composite of PMMA/ZnO NPs has a better vibrations damping effect than pure PMMA1. This could lead to the gingival's more gentle feeling of appearance.
- Composite resin denture PMMA teeth reinforced by the ZnO NPs showed better wear resistance by about 4 times compared to the pure PMMA1.
- The microstructure of PMMA/ZnO NPs consists of a PMMA matrix and homogenously distributed ZnO NPs.
- Combinations of different characterization techniques in the designing of polymer composites reinforced by nanoparticles with in vitro chewing simulation enable the determination of functional composite's behavior in dentistry.

Conflicts of interests

There are no conflicts of interests to declare.

Acknowledgment

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The responsible translator for the English language is mag. Shelagh Hedges, Faculty of Mechanical Engineering, University of Maribor, Slovenia.

Abbreviations:

PMMA – Poly-(Methyl-Methacrylate)(powder)
MMA – Methyl-Methacrylate(liquid)
ZnO NPs – Zinc-Oxide Nanoparticles
DMA – Dynamic mechanical analysis
PMMA2 – PMMA + 2 vol. %ZnO NPs
PMMA3 – PMMA + 3 vol. %ZnO NPs
Flash DSC – Flash differential scanning calorimeter
DLS – Dynamic light scattering
TEM – Transmission Electron Microscope

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