Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 79 (10) 1295–1307 (2014)
JSCS–4665
UDC 678.82+661.183.8+678.046+665.93:678.017:539.12
Original scientific paper

The effect of the size and shape of alumina nanofillers on the mechanical behavior of PMMA matrix composites

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(Received 21 January, revised 31 March, accepted 2 April 2014)

Abstract: Composites with the addition of alumina nanofillers show improvement in mechanical properties.Poly(methyl methacrylate), PMMA, was used as a matrix and two different types of nanofillers having extremely different shapes were added into the matrix to form the composites. The reinforcements were based on alumina nanoparticles having either a spherical shape or whiskers with a length to diameter ratio of 100. The influence of the size and shape of the alumina fillers and the loading on the mechanical properties of the prepared composite were studied using nanoindentation measurements and dynamic mechanical analysis. It was observed that both alumina whiskers and spherical alumina nanoparticles added in the PMMA matrix improved the mechanical properties of the composites, but the improvement was significantly higher with reinforcement by alumina whiskers. The concentration of the reinforcing spherical alumina nanoparticles and alumina whiskers in the PMMA matrix varied up to 5 wt. %. The best performance was obtained by the addition of 3 wt. % of alumina whiskers in the PMMA matrix in terms of the mechanical properties of the obtained composite.

Keywords: polymer composite; particle shape; nanoindentation; dynamic mechanical analysis.

INTRODUCTION

Poly(methyl methacrylate) (PMMA) has been used in a wide range of fields and applications, such as for rear-lights and instrument clusters of vehicles, and appliances and lenses for glasses. PMMA in the form of sheets affords panels for building windows, skylights, signs, displays, sanitary ware, LCD screens, furniture and many other applications where transparency is an important factor.[1] PMMA is prepared by an addition reaction that requires the presence of an ini-

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doi: 10.2298/JSC140121035B

tiator, such as benzoyl peroxide that is decomposed by either heating or the addition of a chemical activator such as dimethyl-*p*-toluidine that can serve in an autopolymerization reaction.[2,3] PMMA polymer based materials are used as bone cement. The pure resin does not have sufficient strength and is reinforced using oxide particles or other fillers in order to obtain the material that could be used under load bearing conditions.[4,5] Another use of PMMA based resins is in dentistry for different applications, such as denture basis, orthodontic appliances, and provisional restorations.[6]

The addition of fillers in the form of alumina nanoparticles having different shapes and sizes into a polymer that serves as a matrix improves the mechanical behavior of the obtained composite material. The main problems encountered with addition of nanoparticles are mixing and uniform distribution of the nanoparticles in the matrix material because nanoparticles tend to agglomerate.[7–11] There are several techniques of enabling a good dispersion of nanoparticles and these include: direct mixing of polymer and nanoparticles, *in situ* polymerization in the presence of nanoparticles, and simultaneous *in situ* polymerization and nanoparticles formation.[12] The main candidate materials for addition as nanofillers into a polymer matrix are fine nanoparticles of oxides, such as silica,[13] titania,[14] zirconia[15] and alumina.[16] The addition of oxide nanoparticles into a polymer matrix for preparation of bulk composites and films was the topic of a large number of research publications.[17] Ultrasonication was reported to be an effective method to obtain a homogeneous dispersion of nanofillers in the monomer.[18]

The shape of the fillers also influenced an improvement of the mechanical properties of composites.[17–21] It is well known that shape is very important when describing the flow properties of powder particles.[22–24] As much as the particle shape is important in flow characteristics of fillers, it is also of importance in interactions with a composite matrix that determine the performance of composite materials on the macro scale.

The focus of the present research was a study of the influence of the shape and quantity of the alumina nanofillers in a PMMA polymer matrix on the mechanical properties of the obtained composite material. Composites based on a PMMA matrix with the addition of alumina nanofillers of different shapes, *i.e.*, spherical alumina nanoparticles and alumina whiskers, were prepared. The mechanical behavior of the obtained composites was studied using the dynamic mechanical analysis (DMA) and nanoindentation techniques. The shape of the fillers and their distribution in the composite were studied by scanning electron microscopy. The dimensions of the reinforcements were measured using image analysis techniques.

EXPERIMENTAL

The spherical aluminum oxide nanoparticles were declared to have a diameter of less than 50 nm and were obtained from Aldrich. The alumina whiskers were also commercially

available from Aldrich, and they were characterized by diameters of 2–4 nm and lengths of 200–400 nm. This enabled the use of very different alumina fillers with the spherical alumina nanoparticles having a length to diameter ratio of 1, while this ratio was approximately 100 for the alumina whiskers.

Mecaprex KM, PRESI (Grenoble, France) is a two-component autopolymerizing acrylic resin. The first component consists of KM powder (PMMA powder containing dibenzoyl peroxide (DBPO) initiator) and the second contains KM liquid monomer (methyl methacrylate monomer (MMA) with *N*,*N*-dimethyl-*p*-toluidine activator). Spherical alumina nanoparticles or alumina whiskers were added to the KM liquid. The mixture was sonicated for 60 min and KM powder was dispersed in the mixture. The mixing was realized by hand during 2 min and the mixture was poured into a form having dimensions suitable for dynamic mechanical analysis (DMA) and nanoindentation testing. The form was covered with a glass cover to ensure that the surface of the specimen remained smooth. A PMMA/MMA mass ratio of 0.75 was used as this ratio minimizes shrinkage, as suggested by the manufacturer (PRESI) and as previously reported in the literature.[18] The monomer was polymerized at 25 °C. The instruction for use given by the producer says that the polymerization is complete in 20 min at a temperature between 20 and 23 °C. However, the obtained composites were then additionally exposed to a temperature of 37 °C for 30 days in order to obtain a stabile composition of the polymer matrix before the samples were mechanically tested.[25] The compositions of the PMMA/alumina whiskers and PMMA/alumina spherical nanoparticles composites prepared for analysis in this study are summarized in Table I. The samples prepared using the spherical alumina nanoparticles as fillers are denoted as P1, P3 and P5 for contents of 1, 3 and 5 wt. % of the filler, respectively. The samples using alumina whiskers as fillers were denoted as W1, W3 and W5 for contents of 1, 3 and 5 wt. % alumina whiskers, respectively.

TABLE I. The compositions of composite specimens prepared using the PMMA as the matrix and alumina spherical nano particles and alumina whiskers as fillers

Sample description	Sample	Quantity particles/whiskers, g	MMA+initiator mass, g	PMMA Mass g
PMMA without filler	PMMA	–	2.290	1.710
PMMA with 1 wt. % spherical alumina nanoparticles	P1	0.045	2.540	1.910
PMMA with 3 wt. % spherical alumina nanoparticles	P3	0.135	2.540	1.870
PMMA with 5 wt. % spherical alumina nanoparticles	P5	0.225	2.440	1.830
PMMA with 1 wt. % alumina whisker	W1	0.045	2.540	1.910
PMMA with 3 wt. % alumina whisker	W3	0.135	2.540	1.870
PMMA with 5 wt. % alumina whisker	W5	0.225	2.440	1.830

The mechanical behaviors of neat polymer and PMMA/alumina fillers nanocomposites were studied by DMA – cantilever bending and force control nanoindentation. Scanning electron microscopy was used to study the morphology of the spherical alumina nanoparticles and

alumina whiskers prior to incorporation into the polymer and to study the distribution of the spherical alumina nanoparticles and alumina whiskers in the matrix after polymerization.

Methods of characterization

DMA analyzes. Dynamic mechanical analysis was used to examine the performance of the PMMA matrix composite reinforced using alumina spherical nanoparticles or alumina whiskers and to measure the influence of the shape of the alumina fillers on the behavior of the resulting materials. The data obtained from this analysis included the storage modulus (E'), tangent delta (tan δ) and the glass transition temperature (T_g). The storage modulus reveals the ability of the composite to store elastic energy associated with recoverable elastic deformation. Together with tan δ, the storage modulus describes the behavior of the composite under stress in a defined temperature range. DMA was performed on a DMA Q800 (TA Instruments) under a nitrogen atmosphere in the single cantilever mode. Storage modulus and loss factor (tan δ) were calculated for rectangular specimens of size 35 mm×13 mm×3 mm at a frequency ω = 1 Hz. Temperature range was changed from room temperature to 160 °C at a heating rate of 3 °C min^{-1}.

Nanoindentation. The nanoindentation test was performed using a Hysitron TI 950 TriboIndenter equipped with *in situ* SPM imaging (Hysitron, MN). The Berkovich indenter has an average radius of curvature of about 100 nm. The tests were performed in the force-controlled feedback mode. The indentation maximum load was set at 4 mN for each tested sample. The loading and unloading times as well as the hold time at the peak force were set to 25 s each. For each loading/hold/unloading cycle, the applied load value was plotted with respect to the corresponding position of the indenter. The resulting load/displacement curves provide data specific to the mechanical nature of the material under examination. All the results were obtained by the Oliver and Pharr method [24] and using an assumed sample Poisson ratio of 0.36 for the calculation of the reduced elastic modulus. Established models were used to calculate the quantitative indentation hardness (H) and reduced elastic modulus values (E) for such data.

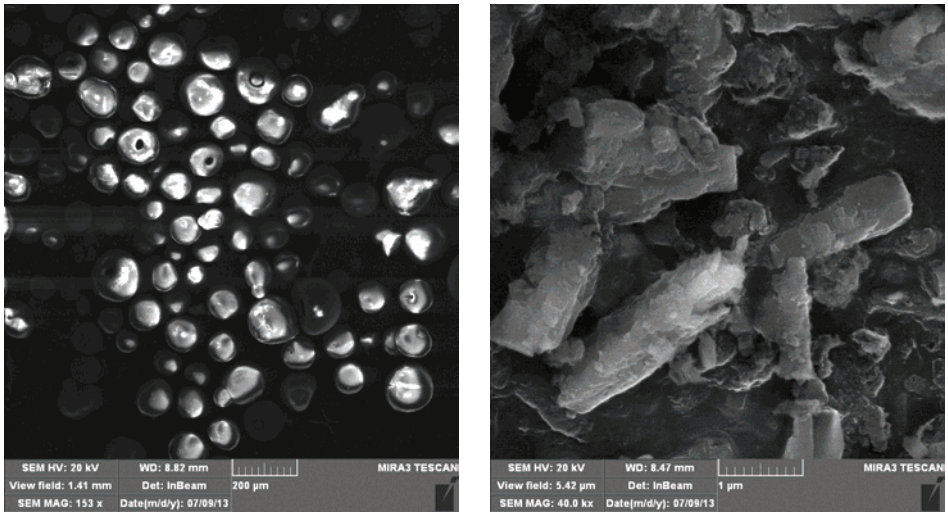
The specimens were polished using alumina paste having abrasive grains of up to 0.02 μm until a flat surface was obtained. The specimens were about 1 mm thick, having dimensions 3 mm×3 mm×2 mm and were placed on the specimen holder in the nanoindenter. Loads of 4 mN were used for the tests. In order to obtain reliable results, 9 indentations were made for each type of sample on random locations.

Analysis of the morphology of the specimens. The morphologies of the alumina nanofillers were examined using a field emission scanning electron microscope (FESEM), MIRA3 TESCAN, operated at 20 kV. The morphology of the PMMA polymer matrix and composites reinforced by the nanofillers were examined using a scanning electron microscope (SEM), Jeol JSM 5800, operated at 20 kV.

RESULTS AND DISCUSSION

Very fine spherical alumina nanoparticles and alumina whiskers tend to agglomerate and they were delivered in their agglomerated form from the producer. The field emission scanning electron microscopy (FESEM) micrographs of the agglomerated spherical alumina nanoparticles and alumina whiskers prior to sonication are shown in Fig. 1. The mean diameter of the spherical alumina nanoparticle agglomerates as received from producer was 87 μm and that for the

alumina whiskers was of 1.1 μm. These values were obtained using image analysis tools applied to the images shown in Fig. 1.



(a) (b)

Fig. 1. The FESEM micrographs of agglomerated alumina nanoparticles and whiskers as received from the producer prior to sonication, a) particles agglomerates having a mean diameter of 87 μm b) whiskers having a mean diameter of 1.1 μm.

The morphology of the samples having 3 wt. % of spherical alumina nanoparticles and 3 wt. % of alumina whiskers and of the polymer without reinforcement were examined using a scanning electron microscope (SEM), Jeol JSM 5800, operated at 20 kV, Fig. 2. In Fig. 2b, the micrograph of the sample having 3 wt. % of alumina whiskers is given and in Fig. 2c, the micrograph of the composite having 3 wt. % of the spherical alumina nanoparticles is presented. These images were used to measure the diameters of the alumina spherical nanoparticles agglomerates still visible in the micrograph. The results of measurements presented in Fig. 2c show that the mean diameter of the spherical alumina nanoparticle agglomerates decreased to 0.47 μm in the composite containing 3 wt. % spherical alumina nanoparticles. The main length of the agglomerates of the alumina whiskers visible in the composite was reduced to 0.27 μm. The appreciable reduction in the sizes of the visible agglomerates of the spherical alumina nanoparticle, as well as the reduction in the sizes of the visible agglomerates of the alumina whiskers, indicate that the agglomerates dimensions were reduced and that the spherical alumina nanoparticles and the alumina whiskers that were not agglomerated were well distributed in the polymer, bringing improvements in the mechanical properties.

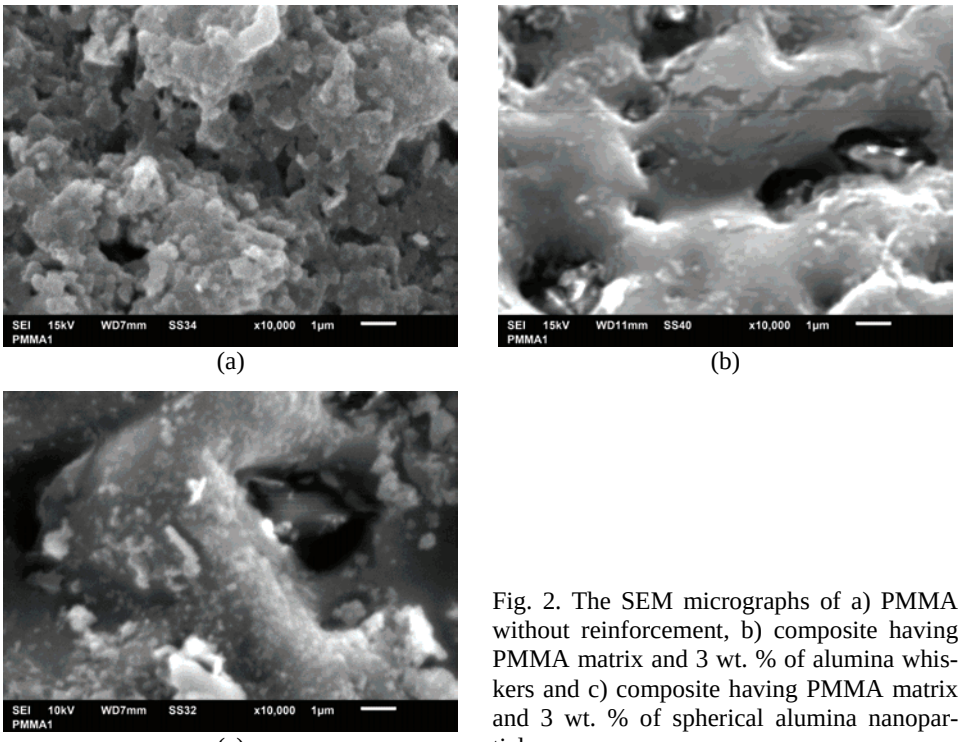


Fig. 2. The SEM micrographs of a) PMMA without reinforcement, b) composite having PMMA matrix and 3 wt. % of alumina whiskers and c) composite having PMMA matrix and 3 wt. % of spherical alumina nanoparticles.

DMA was used to compare the behavior of the pure PMMA to the behavior of the composites with additions of alumina fillers. It was observed that incurporation of both spherical alumina nanoparticles and alumina whiskers resulted in an increase in the values of the storage modulus for the composites in the measured range of temperatures, Fig. 3.

The glass transition temperature T_g can be determined from the DMA results as the maximum of the curve showing the dependence of tan δ *vs*. temperature. The changes of T_g in dependence on the type and quantity of additives are shown in Fig. 4. Composites having 3 wt. % of added alumina whiskers showed an increase in the T_g value of 3 °C, which was the maximum increase observed in specimens prepared within the scope of this research. For samples containing spherical alumina nanoparticles, the largest increase in the T_g value was also observed for the composite with 3 wt. %, but this increase was less significant. This proves that both the spherical alumina nanoparticles and the alumina whiskers were in good contact with the matrix.

The storage moduli for composites having a PMMA matrix and spherical alumina nanoparticles or alumina whiskers as reinforcements are compared to the values for the unreinforced PMMA in Fig. 5. The composite containing 3 wt. % of

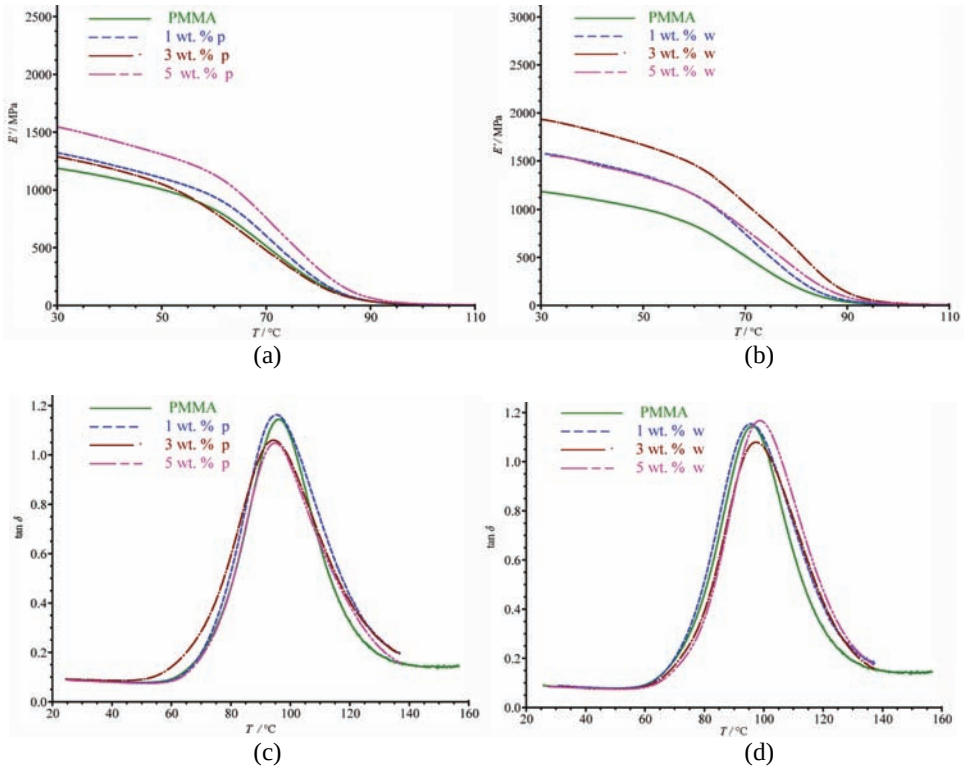


Fig. 3. Changes in the storage modulus (a and b) and tan δ (c and d) for the PMMA matrix composites reinforced with spherical alumina nanoparticles (a and c) and alumina whiskers (b and d).

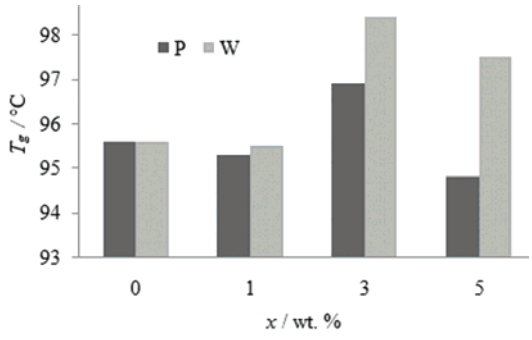
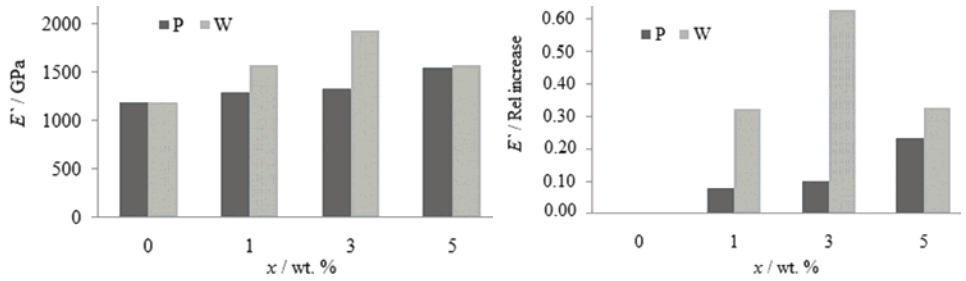


Fig. 4. Changes in T_g of the PMMA matrix composite materials having spherical alumina nanoparticles or alumina whiskers as additives.

spherical alumina nanoparticles showed the largest increase in the value of the storage modulus (23 %) among the composites prepared with spherical alumina nanoparticles. All the composites having the alumina whiskers as reinforcements showed increases in storage modulus compared to that of pure PMMA. The addition of 3 wt. % alumina whiskers resulted in an increase of 63 %. The addi-

tion of 5 wt. % of alumina whiskers did not improve the storage modulus value more than the addition of 3 wt. % of alumina whiskers and this could be explained by the difficulty in mixing and breakage of the agglomerates when the concentration of alumina whiskers was larger than 3 wt. %. The values of tan δ presented in Fig. 6 are in accordance with observations made for the storage modulus.



(a) (b)

Fig. 5. a) The dependence of E' for the PMMA matrix composite materials having spherical alumina nanoparticles or alumina whiskers as additives; b) relative increase in E' of the composites compared to the PMMA polymer matrix.

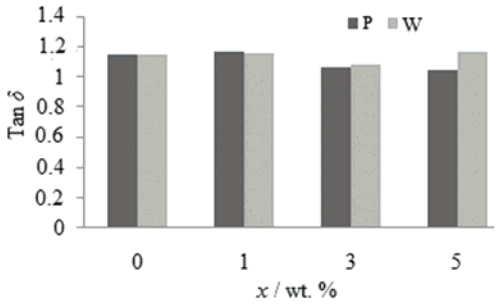


Fig. 6. Dependence of tan δ on the quantity and morphology of the reinforcement by spherical alumina nanoparticles or alumina whiskers as additives in PMMA matrix composite materials.

DMA gave the characteristics of the composite at the macro-level and such properties describe the behavior of the entire specimen under load at different temperatures. The nanoindentation test enabled the properties of the composite to be studied at the nano- and micro-level. From nanoindentation results, it is possible to determine whether the properties have uniform values throughout the specimen and to discuss possible inhomogeneities of the distribution of the reinforcement in the composite.

The obtained results gave insight into the influence of the shape and amount of the alumina fillers added on the obtained mechanical properties of PMMA matrix composite. Data showing the changes of the modulus of elasticity of the PMMA matrix/alumina spherical nanoparticles and PMMA matrix/alumina whisker composites in dependence on the type and amount of alumina fillers added

are given in Fig. 5. It could be seen that both the alumina spherical nanoparticles and alumina whiskers made the composites stiffer compared to the PMMA polymer, even if only 1 wt. % of spherical alumina nanoparticles was added. Addition of spherical alumina nanoparticles into the composition did not dramatically change the values of mechanical properties, modulus and hardness, of the obtained composite. The addition of 3 wt. % spherical alumina nanoparticles resulted in a composite material having properties that had higher values of the modulus of elasticity and hardness as measured using the nanoindentation method. The addition of 5 wt. % of spherical alumina nanoparticles did not improve additionally the mechanical properties of the PMMA matrix composite. The improvement of mechanical properties obtained using 1 wt. % of alumina whiskers gave better properties than the PMMA matrix composite containing the same quantity of spherical alumina nanoparticles. The addition of 3 wt. % of whiskers gave maximum stiffness improvement of the PMMA matrix composite material and the obtained composite had the maximum value of the modulus of elasticity that was improved by 56 % compared to the polymer without reinforcement. The addition of 5 wt. % of alumina whiskers did not further improve the values of mechanical properties measured using the nanoindentation method. From the data presented, the addition of 3 wt. % of alumina whiskers gave the material having the best modulus of elasticity. This is a considerable reinforcement for a small addition of alumina whiskers.

The results of hardness measurement exhibited the same trend as those for the modulus of elasticity for PMMA matrix/spherical alumina nanoparticle composites. The addition of 1 wt. % of spherical alumina nanoparticles gave a slight deterioration in the hardness of the material. The PMMA matrix composite with 3 wt. % of spherical alumina nanoparticles gave the best performance concerning the hardness of the PMMA/spherical alumina nanoparticle composites. The addition of 5 wt. % of alumina whiskers did not improve additionally the hardness of the PMMA matrix composite. The addition of 3 wt. % of alumina whiskers gave an increase in hardness of the material that was 40 % improvement compared to the PMMA polymer without the addition of the fillers.

A comparison of the nanoindentation curves for the PMMA polymer without the addition of reinforcement and for composites having 3 wt. % of spherical alumina nanoparticles and 3 wt. % alumina whiskers is given in Fig. 7.

Comparison of DMA and nanoindentation results

Both the nanoindentation measurements of the modulus of elasticity and hardness and the DMA measurement of the storage modulus prove that the composite having 3 wt. % of alumina whiskers had the best mechanical properties among the studied composites. The nanoindentation (Figs. 8 and 9) and DMA (Fig. 5) results are in accordance proving that the addition of spherical alumina

nanoparticles was less efficient compared to the addition of alumina whiskers with a very high value of the length to diameter ratio.

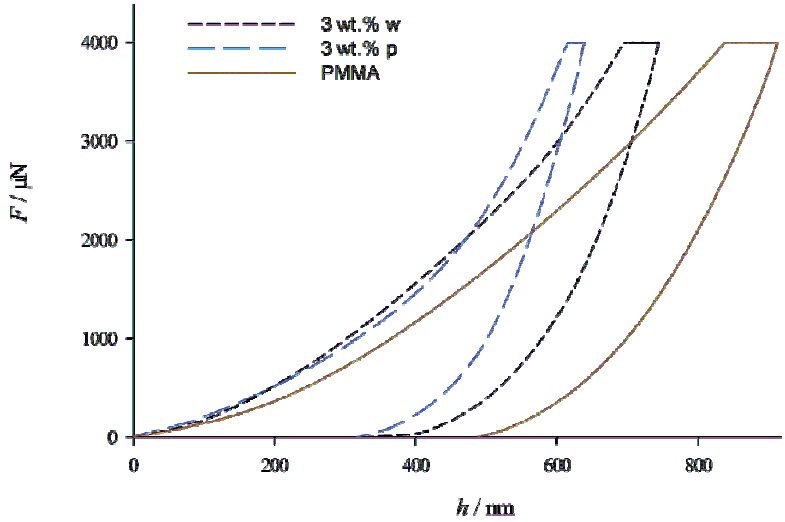


Fig. 7. Nanoindentation curves showing the dependence of the force on displacement for the PMMA polymer and the composite having 3 wt. % of spherical alumina nanoparticles or alumina whiskers.

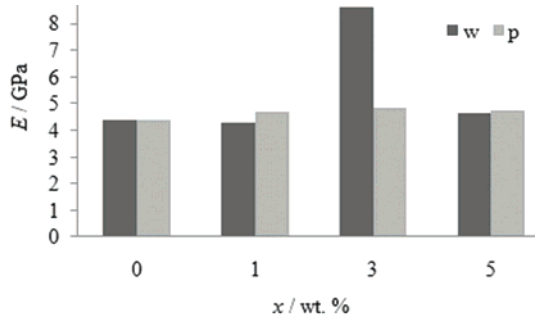


Fig. 8. Dependence of the modulus of elasticity measured during nanoindentation tests for PMMA matrix composite materials containing spherical alumina nanoparticles or alumina whiskers as additives.

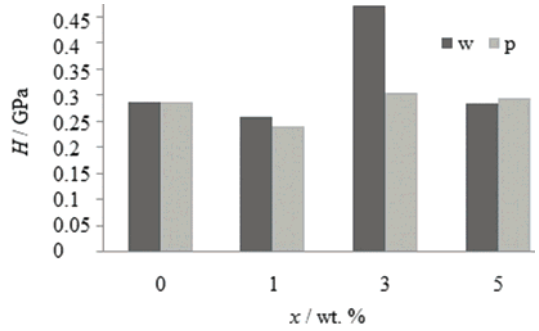


Fig. 9. A summary of the results from the nanoindentation testing of PMMA matrix composite materials containing spherical alumina nanoparticles or alumina whiskers.

When comparing the results obtained on reinforcing a PMMA matrix of a composite with spherical alumina nanoparticles to those obtained on reinforcing the same PMMA polymer with functionalized spherical particles, it could be observed that better values of the mechanical properties, *i.e.*, modulus of elasticity and hardness, were obtained using the functionalized silica particles than the values found in the present study.[13] The preparation of the samples in this study was performed according to the instructions obtained from the producer and the specimens were left at a temperature of 37 °C for 30 days. In the previous study, the specimens were heated at 60 °C after the preparation and later up to 110 °C in order to eliminate stress and residual monomer. It is possible that these conditions that included heat treatment of the specimen to eliminate completely the monomer from the composition whereas in the present case when only a temperature of 37 °C was applied for 30 days, complete monomer conversion was not attained. This could be the reason that the small amount of residual monomer was present that served as a plasticizer in the composite.[13] The content of residual monomer and allergic or cytotoxic effects of dentures based on acrylic resins may be related to powder to liquid ratio, storage time, temperature, polymerization method and this will be the subject of a future study. In this paper, the basic research was focused on the influence of size, shape and loading of nanoparticles on the mechanical properties of acrylic polymers.

As has been shown, alumina nanofillers have the possibility to improve the values of mechanical properties of the polymer when added in very small amounts. Similar improvements in the values of the mechanical properties could be obtained using very high loadings of functionalized alumina microparticles. In order to obtain the improvement of the mechanical properties in the same range as those obtained with the addition of 3 wt. % of alumina whiskers, 30 % of functionalized microparticles had to be added to the polymer matrix.[26]

CONCLUSIONS

The PMMA matrix composites were prepared in the presence of spherical alumina nanoparticles and alumina whiskers as reinforcements. Ultrasonication was used to mix the components and to deagglomerate the spherical alumina nanoparticles and alumina whiskers prior to the polymerization of the matrix material. The DMA and nanoindentation techniques were used to characterize the mechanical behavior of the obtained composites. The DMA results showed that the spherical alumina nanoparticles were able to increase the storage modulus of the composite by up to 30 % compared to that of PMMA, while the alumina whiskers led to an improvement in the storage modulus value of 62 %. The T_g of the composite increased by up to 1.2 °C in the presence of spherical alumina nanoparticles and by 3 °C in the presence of alumina whiskers. Among the composites studied containing 1, 3 and 5 wt. % of either added spherical alumina

nanoparticles or added alumina whiskers in the PMMA matrix, the best result in increasing the T_g was obtained using 3 wt. % of added alumina whisker reinforcement. The nanoindentation results for the same set of composite materials containing alumina fillers of different shape in the PMMA matrix, the best results for the modulus of elasticity and hardness were obtained for the specimen reinforced with 3 wt. % of alumina whiskers in the PMMA matrix.

Concerning the influence of the morphology of the reinforcement, better results were obtained using the alumina whisker reinforcement, for which the length to diameter was much more important than for the alumina nanoparticles that were declared as spherical. The increase in all properties, *i.e.*, storage modulus, T_g, measured using the DMA, and modulus of elasticity and hardness measured using the nanoindentation technique, were better in the presence of alumina whiskers than in the presence of spherical alumina nanoparticles. The use of an ultrasonic bath for the homogenization of the composite was satisfactory for the production of the specimens and this was proved by the increase in the mechanical properties measured using the presented techniques.

Acknowledgement. This research has been financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia as a part of the project TR34011.

И З В О Д

УТИЦАЈ ВЕЛИЧИНЕ И ОБЛИКА АЛУМИНИЈУМ-ОКСИДНИХ НАНОПУНИЛА НА МЕХАНИЧКО ПОНАШАЊЕ КОМПОЗИТА СА МАТРИЦОМ ОД ПОЛИ(МЕТИЛ-МЕТАКРИЛАТА)

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Композити са додатком нанопунила показују побољшање механичких својстава у односу на полимерну матрицу. За израду композита, коришћен је поли(метил-метакрилат), PMMA, као полимерна матрица у комбинацији са два нанопунила, потпуно различитих облика. Полимерна матрица је ојачана коришћењем две врсте нанопунила на бази алуминијум-оксида: наночестица сферног облика и игличастих вискерса, који имају однос дужине према пречнику од 100. Утицај величине честица, њихов облик и удео, на механичка својства композита проучавани су помоћу наноиндентационих мерења и динамичко–механичке анализе. Примећено је да и сферне наночестице и вискери побољшавају механичка својства композита, али веће побољшање је постигнуто додатком вискера. Концентрација обе врсте нанопунила, сферних наночестица и вискера је варирана у опсегу до 5 мас. %. Најбоља механичка својства композита су добијена додатком 3 мас. % вискера у полимерну ПММА матрицу.

(Примљено 21. јануара, ревидирано 31. марта, прихваћено 2. априла 2014)

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