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The Effect of Tapioca on Morphological and Mechanical Properties of Metakaolin–Zirconia Geopolymer for Dental Restorative Nanocomposite

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Composite is one of the direct dental restoration materials, which is consisted of three main components such as matrix, filler, and coupling agent. Metakaolin and zirconia are potential alternatives as dental restoration materials. This study aims to determine the characteristics of synthesized metakaolin–zirconia geopolymer nanocomposite with the addition of tapioca as a template. The study is a pure experimental laboratory investigation. The sample is fabricated by means of both the synthesis of metakaolin, zirconia, alkali activator, chitosan and the addition of tapioca of 0.4% v/v, 0.8% v/v, and 1.6% v/v. Alkali solution consisting of NaOH and Na_2SiO_3 is used to activate the geopolymerization of metakaolin. Nanocomposite characteristics with variations of the addition of tapioca template are then evaluated for its hardness and microstructure. Synthesis of metakaolin–zirconia geopolymer nanocomposite with the addition of tapioca template is successful, and it has a mean hardness value, which has met the hardness value used for dental composite restoration and has the best attachment to artificial teeth. The best hardness value is of 51.70 VHN achieved by the addition of 1.6% v/v tapioca to geopolymer. The resulting SEM images of all samples show a mean particle size of 100 nm indicating that the size is suitable for dental restoration with the value of 5–100 nm.

Композит є одним з безпосередніх зубних реставраційних матеріялів, який складається з трьох основних компонентів, таких як матриця, наповнювач і зчіпний аґент. Метакаолін і двоокис Цирконію є потенційними альтернативами в якості реставраційних матеріялів зубів. Дане дослідження спрямовано на визначення характеристик синтезованого метакаолін-цирконійового геополімерного нанокомпозиту з додаванням тапіоки як шаблону. Дослідження є чистим експериментальним лабораторним дослідженням. Зразок виготовляється шляхом синтези метакаоліну, двоокису Цирконію, лужного активатора, хітозану та додавання 0,4% об./об., 0,8% об./об. та 1,6% об./об. тапіоки. Розчин лугу, що складається з NaOH і Na_2SiO_3, використовується для активації геополімеризації метакаоліну. Нанокомпозитні характеристики з варіяціями додавання шаблону тапіоки потім оцінюються на предмет його твердости та мікроструктури. Синтеза метакаолін-цирконійового геополімерного нанокомпозиту з додаванням шаблону тапіоки є успішною, а він має середнє значення твердости, що відповідає значенню твердости, яке використовується для реставрації стоматологічного композиту, і має найкращу прихильність до штучних зубів. Найкраще значення твердости — 51,70 VHN, що досягається додаванням 1,6% об./об. тапіоки до геополімеру. Одержані СЕМ-зображення всіх зразків показують середній розмір частинок у 100 нм, що вказує на те, що розмір підходить для реставрації зубів зі значенням 5–100 нм.

Key words: tapioca, metakaolin, zirconia, dental restoration, nanocomposite, hardness.

Ключові слова: тапіока, метакаолін, двоокис Цирконію, зубна реставрація, нанокомпозит, твердість.

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1. INTRODUCTION

Dental restoration aims to restore the integrity of the tooth surface, thereby restoring the function of the tooth as an organ of mastication and aesthetics [1]. Some of the filling materials used in dental restorations are composites and glass ionomer cement (GIC) [2]. Composite filling materials are more often used for dental restorations, because their mechanical function is better than of other filling materials; besides that, composites also have good aesthetic value with a colour that resembles teeth [3].

Composite resin consists of several components, namely the resin matrix, filler, and coupling agent. In addition, it has initiators to activate the hardening mechanism such as photoinitiator [4]. Based on their size, it can be classified into composites made of small particle fillers, microfillers, and nanofillers. Composites with nanofiller or nanocomposites have better performance than other materials, because they have a smooth surface structure, high mechanical properties and can be homogeneously dispersed in a polymer matrix [5, 6]. Various modifications of filler materials continue to be developed to obtain nanocomposites with high mechanical properties [7].

Synthesis of geopolymers can be done by using natural resources on Indonesia such as metakaolin and zirconia. Geopolymer is an inorganic polymer material based on aluminosilicate, which is activated by strong alkaline solution. Mechanical properties such as compressive strength, hardness, and modulus of elasticity are of important consideration to use geopolymers for structural application [8]. Aside from its high mechanical properties, it can be used as composite material because of its acid resistance [9].

Based on this description, the authors are interested in synthesizing metakaolin–zirconia geopolymer nanocomposites with addition of tapioca as template. The addition of tapioca template solution used in this study was 0.4% v/v, 0.8% v/v, and 1.6% v/v. The hardness value of nanocomposite with metakaolin–zirconia will be tested after curing time of 7, 14 and 28 days. This is to see, if the curing process shows a significant hardness value for the nanocomposite material. The use of these variation aims to produce the smallest particle size in the synthesized nanocomposite using scanning electron microscope (SEM) for morphological evaluation.

2. EXPERIMENTAL

The kaolin was obtained from Bangka Island, Indonesia. It undergoes calcination at 850°C for 6 hours to produce metakaolin. Zirconia was obtained from sol–gel method from $ZrCl_4$ precursor dissolved in aqua dm and NH_3 solution, which was mixed homogenously using magnetic stirrer until its pH reach value of 3. It is a white crystalline oxide ceramic material, which can be used as filler for composite resins, because it improves the mechanical properties of composite and can be used for strengthening as dental restorative materials such as crowns, bridge reinforcements, and composite resin fillers [10]. Zirconia has good mechanical properties, has high strength, is fracture resistant, has good biocompatibility, and its opaque nature can resemble tooth colour, adding to its good aesthetic properties [11].

Chitosan 1% solution was made by dissolving 2 mL of acetic acid and 1 g chitosan powder to 98 mL aqua dm with magnetic stirrer. The addition of coupling agents such as chitosan to dental restorative materials serves to increase the bond between the matrix and filler. Chitosan has non-toxic, biocompatible, bioadhesive, and biodegradable properties [12, 13]. Chitosan has an open amine group (NH), which is positively charged; this serves it as a binder for other materials, which are negative by cloaking or covering the surface of the material. The particle size of the covered material is not getting bigger, and agglomeration or clumping does not occur; so, the particles distributed homogenously are resulting in higher mechanical strength.

Tapioca 0.5% solution was made by mixing 0.5 g of tapioca starch powder to 100 mL aqua dm at 80°C temperature, mixed with magnetic stirrer and cooled to ambient temperature. This material act as a template for nanocomposites for the growth of rod-shaped particles in their morphology. It is composed of glucose monomers, namely, amylose and amylopectin. Amylopectin plays a role in the formation of rods (nanorods), because it has long branched chains that will bind between particles; so, it aims to improve the mechanical properties of nanocomposites [14].

Mix design of this study is presented in Table. Metakaolin, zirconia, and chitosan were weighed as mix design. Tapioca solution of 4, 8, an 16 mL is then added to each mix design homogenously to produce 0.4% v/v, 0.8% v/v, and 1.6% v/v concentration, respectively. The solution was then centrifuged five times and calcined in furnace at 900°C for two hour, resulting in metakaolin–zirconia powder. Next, it is mixed with chitosan and alkali activator solution to produce geopolymer slurry. It was then poured into a cylindrical mould with diameter of 3 mm and height of 6 mm conformed to American Dental Association (ADA) standard. After 24 hours, it was removed from the mould and curing in ambient temperature using plastic wrap. Resulting geopolymer is characterized by XRD.

Mechanical properties of geopolymer are influenced by the curing time: the longer the curing time the harder the material with a standard curing of 28 days [15]. Vickers microhardness experiment was conducted at 7, 14, and 28 days to analyse the effect of curing time to hardness of geopolymer. The instrument used is Vickers microhardness tester with 100 g load. Cylindrical sample was put in object table right below indenter, and the load is applied. Resulting indentation can be seen under microscope and is as rectangular, which has diagonal value (d). The corresponding unit of HV is then the kilogram-force per square millimetre (kgf/mm^2) or HV number:

TABLE. Nanocomposite mix design with different tapioca solution volume.

No.	Code	Metakaolin, g	Zirconia, mL	Tapioca, mL
1	T–0.4	4	6	4
2	T–0.8	4	6	8
3	T–1.6	4	6	16

$$HV = 1.854/d^2 .$$

For the SEM characterization, artificial teeth are immersed in artificial saliva for 24 hour. Geopolymer slurry as above was filled into the cavity of artificial teeth until curing. Because both artificial teeth and geopolymer are not conductive, it was coated with carbon to form conductive layer followed by vacuum treatment. Sample was then transferred into holder and exposed by electrons.

3. RESULTS AND DISCUSSION

3.1. XRD Analysis

The x-ray diffraction (XRD) analysis was performed to identify the resulting compound of nanocomposites. Figure 1 shows that there are three major compounds appeared, which are quartz (SiO_2; JCPDS #421401), albite ($NaAlSi_3O_8$; JCPDS #030508) from the geopolymerization; zirconia appears in tetragonal phase (t-ZrO_2; JCPDS #170923). Depending on condensation temperature, geopolymer structure can be either crystalline or amorphous. Albite appeared as amorphous form, because geopolymer is synthesized below 90°C, as higher temperature is prone to form crystalline phases [16–19].

3.2. Vickers Microhardness Analysis

Figure 2 represents the hardness values of each of three geopolymer samples with the addition of tapioca template variations of 0.4%

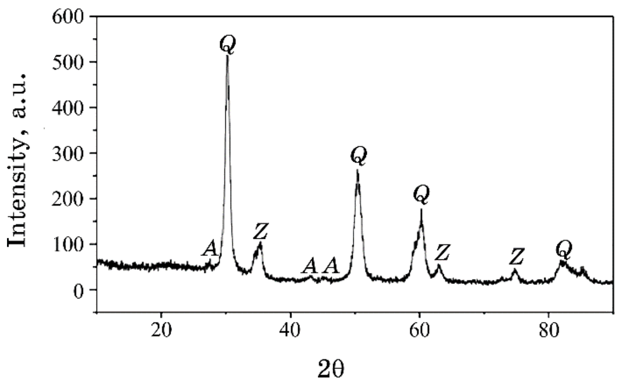


Fig. 1. XRD of geopolymer nanocomposite (note: Q = quartz; A = albite; Z = t-ZrO_2).

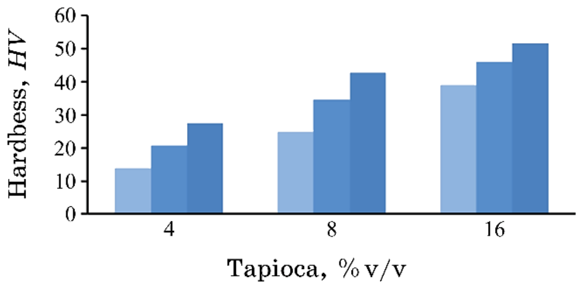


Fig. 2. Vickers microhardness value of geopolymer nanocomposite with tapioca addition.

v/v (*T*–0.4), 0.8% v/v (*T*–0.8), and 1.6% v/v (*T*–1.6) and, followed by curing time, showed different results. Geopolymerization of metakaolin–zirconia nanocomposite was carried out by self-curing. Hardness of these materials depends on the dissolution of Al and Si in alkaline solutions, thus, forming molecules chemically. Alkaline NaOH solution dissociates into Na^+ and OH^- ions in water. The presence of hydroxide ion concentration OH^- in NaOH with an alkaline pH of 14 M can accelerate the reaction through a reagent mechanism with H^+ ions in H_2O (water) molecules; so, the reaction process of dissolving the components in the system becomes faster. Alkali activator solution will increase the stability of the reaction, and the stability of the dimensions of the samples is obtained. Hardness value of resulting geopolymer at 7 and 14 days were lower than at 28 days, because the geopolymerization continues for up to 28 days. Geopolymerization can still continue and gets harder over time [20].

The hardness values of *T*–0.4, *T*–0.8, and *T*–1.6 at 28 days are of 27.50 *HV*, 42.70 *HV*, and 51.70 *HV*, respectively. *T*–0.8 and *T*–1.6 are in the range of hardness of composite restorations for teeth (30–90 VHN) [21]. The value of the composite hardness is increasing due to the good filler distribution, the absence of agglomeration, the ongoing polymerization process, and bonds between the particles. The more interaction between particles increases the mechanical properties of material.

A more homogeneous mixture between the filler and the matrix will result in a high hardness value. Homogeneously dispersed particles will increase polymer absorption on the filler surface; on the other hand, particles, which are not homogeneously dispersed, will cause agglomeration or agglomeration in the matrix [22].

The agglomeration will reduce the surface area; so, it can weaken the interaction between the filler and the matrix and result in a decrease in the physical and mechanical properties of the composite.

In general, tapioca contains amylose as much as 20–27% and 77–80% amylopectin [23]. This shows that, with increasing concentration of tapioca (v/v), it will increase amylose content and amylopectin in the composite mixture. Water-soluble amylose results in an increase in hardness, because amylose will bind to each other with the binding matrix, and amylose will also undergo retrogradation to maintain a structure that can increase hardness. The colour produced in the composite sample has also fulfilled the aesthetic need, which is similar to the colour of the tooth; so, it is hoped that this composite material can be considered as an alternative material for dental restorations that can be applied in the field of dentistry.

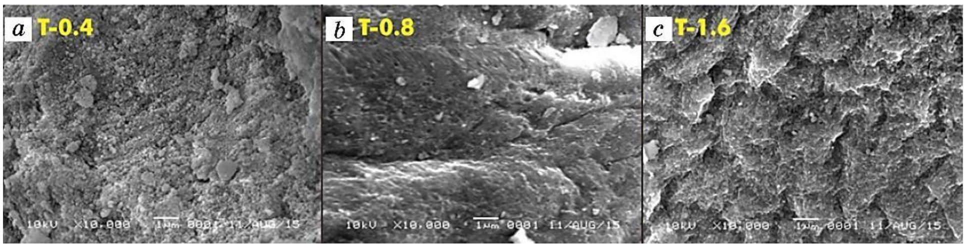
3.3. SEM Analysis

Figure 3 shows the SEM results of metakaolin–zirconia powder with the addition of tapioca template of 0.4% v/v, 0.8% v/v, and 1.6% v/v after calcining at 900°C for two hours. Figure 3, *a* shows that the resulting powder was agglomerated, while Figure 3, *b* shows the formation of rod-like structures. Figure 3, *c* shows more rod-like structure (nanorods). Increase in tapioca content results in more templates for rod-like structure; this shows that tapioca can be used as rod-particle growth medium.

Figure 4 shows the SEM results of *T*–0.4, *T*–0.8, and *T*–1.6 with alkali activator in geopolymer nanocomposites. Figure 4, *a* shows the resulting bonds of nanocomposite filling, and artificial teeth is less than perfect with the occurrence of cracks in between that causes the actual attachment surface not visible between the filling material and the tooth. The distribution of the filler formed is uneven, because the resulting powder was still agglomerated and has not been well dispersed. Figure 4, *b* shows the distribution of the filler formed uneven because the resulting powder is still agglomerated that can narrow the contact surface area between the filler and the matrix. Figure 4, *c* shows the best bonding between artificial teeth and nanocomposite filling. The resulting images reveal almost no gaps between the filling material and the teeth. The distribution of the filler formed is quite homogenously.

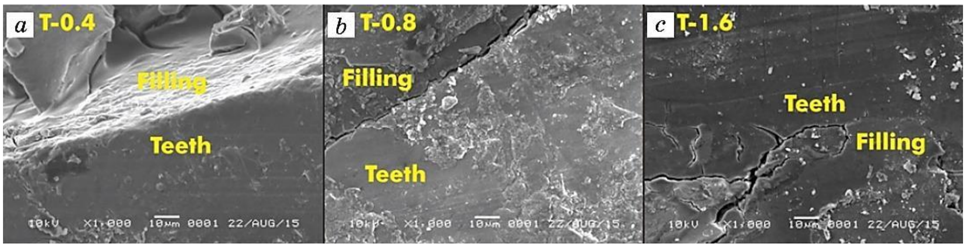
Figure 5 shows the SEM images of geopolymer nanocomposites at higher magnification (×20000) to disclose the particle size of nanocomposites. It shows the differences in distribution and size of the formed particles. Figure 5, *a* has a smooth surface with particles sticking together. Resulting nanoparticles are ranged from 45 to more than 200 nm.

Figure 5, *b* demonstrates the formed small nanoparticles (17–40 nm), which have uneven distribution; it also reveals that there are still larger nanoparticles (127–190 nm). Figure 5, *c* has the best



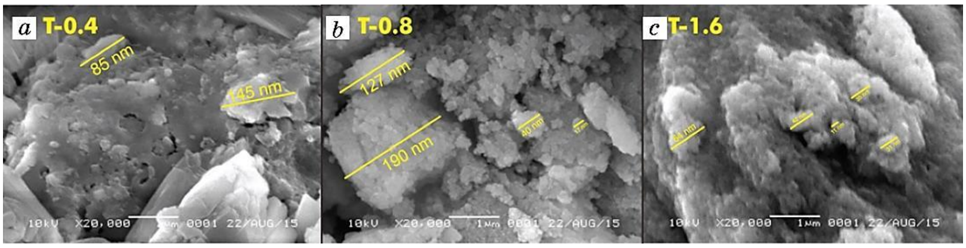
a *b* *c*

Fig. 3. SEM images: *a*) *T*–0.4; *b*) *T*–0.8; *c*) *T*–1.6. All images are at magnification ×10000.



a *b* *c*

Fig. 4. SEM images of geopolymer nanocomposite: *a*) *T*–0.4; *b*) *T*–0.8; *c*) *T*–1.6. All images are at magnification ×1000.



a *b* *c*

Fig. 5. SEM images of geopolymer nanocomposite: *a*) *T*–0.4; *b*) *T*–0.8; *c*) *T*–1.6. All images are at magnification ×20000.

morphology among others and shows homogenously distributed nanoparticles (11–64 nm). The particle size of nanocomposite geopolymer with tapioca template addition has met the requirements for nanocomposite particle size for dental-restoration material of 5–100 nm [24].

Metakaolin–zirconia geopolymer was synthesized to produce nanoparticle size, where the formed-nanoparticle size was influenced by the manufacturing process of the synthetic material. Metakaolin and zirconia produce nanoparticle size through a sol–gel process using the bottom up method. Crystal with nanoparticle size is obtained from the construction of chemical atomic structures; so, the nanoparticles will be more easily achieved. The solution is used as a precursor to achieve the desired nanoparticles' size until it goes through the calcination process. Chitosan is also added as a dispersant in the manufacture of sol–gel, which serves to form small nanoparticles' size [25].

Chitosan will coat the surface of the particles before mixing with alkali activator; so, it will prevent contact with other particles, the agglomeration does not occur, and the particles are expected to be homogeneous and well dispersed. Agglomeration is a lump of particles that causes the particles not to be well dispersed and can reduce the mechanical properties of the composite. Fillers have an important role in modifying the properties of nanocomposites, such as increasing hardness and wear resistance [26]. Metakaolin–zirconia powder has nanoparticle size that will expand the surface area, because smaller particle size formed the particles of filler material, which can occupy more area; this explains the improvement of the mechanical properties. Tapioca addition showed a change in each sample with the formation of an irregular form in SEM images. This shows that tapioca is functioning as a growth site or template for particle formation. Tapioca plays a role in binding between particles, which will form a certain pattern, where tapioca can form nanopores, nanospheres, or nanorods [27]. The final stage of making tapioca as a template is through a calcination process, which will degrade or lose the polymer structure.

4. CONCLUSION

The conclusions that can be drawn from the results of this study are as follow.

1. The highest hardness value was of 51.70 VHN achieved by the addition of 1.6% v/v tapioca to geopolymer nanocomposites. Higher the concentration of tapioca used results in increase of hardness value of resulting materials. The hardness value has met the composite restoration hardness criteria range, which is of 30–90 VHN.

2. The best effect of tapioca template on the morphology of synthesized geopolymer nanocomposite with a concentration of 1.6% v/v results in best adhesion between the filling material and the artificial teeth, which was obtained.

3. The results of SEM microstructural characterization of geopolymer nanocomposite with the addition of tapioca template of 0.4% v/v, 0.8% v/v, and 1.6% v/v each have an average particle size of

100 nm. Higher concentration of tapioca results in better distribution and smaller size of nanoparticles.

REFERENCES

1. M. S. Gowd, T. Shankar, R. Ranjan, and A. Singh, *J. Int. Soc. Prev. Community Dent.*, **7**, No. 7: 1 (2017); https://doi.org/10.4103/jispcd.JISPCD_149_17
2. L. Rondrang, *International Journal of Recent Scientific Research*, **11**: 6 (2020); https://doi.org/10.24327/ijrsr.2020.1106.5434
3. E. M. AlHamdan, A. Bashiri, F. Alnashmi, S. Al-Saleh, K. Al-shahrani, S. Al-shahrani, A. Alsharani, K. M. Alzahrani, F. K. Alqarawi, F. Vohra, and T. Abduljabbar, *Appl. Sci.*, **11**, No. 21: 10108 (2021); https://doi.org/10.3390/app112110108
4. A. Kowalska, J. Sokolowski, and K. Bociong, *Polymers (Basel)*, **13**, No. 3: 470 (2021); https://doi.org/10.3390/polym13030470
5. S. Fu, Z. Sun, P. Huang, Y. Li, and N. Hu, *Nano Materials Science*, **1**, No. 1: 2 (2019); https://doi.org/10.1016/j.nanoms.2019.02.006
6. A. D. de Oliveira and C. A. G. Beatrice, *Nanocomposites — Recent Evolutions* (London: IntechOpen: 2018); https://doi.org/10.5772/intechopen.81329
7. O. A. Moskalyuk, A. V. Belashov, Y. M. Beltukov, E. M. Ivan'kova, E. N. Popova, I. V. Semenova, V. Y. Yelokhovsky, and V. E. Yudin, *Polymers*, **12**: 2457 (2020); https://doi.org/10.3390/polym12112457
8. A. Mahmood et al., *Polymers*, **13**, No. 13: 2099 (2021); https://doi.org/10.3390/polym13132099
9. T. A. Aiken, J. Kwasny, and W. Sha, *Mater. Struct.*, **53**: 115 (2020); https://doi.org/10.1617/s11527-020-01549-x
10. A. F. El-Saadany, S. M. El-Safty, U. M. Abdel Karim, and E. R. S. Kenawy, *Tanta Dent. J.*, **16m**, Iss. 3: 149 (2019); https://doi.org/10.4103/tdj.tdj_22_19
11. J. Grech and E. Antunes, *Journal of Materials Research and Technology*, **8**, No. 5: 4956 (2019); https://doi.org/10.1016/j.jmrt.2019.06.043
12. G. A. Martău et al., *Polymers*, **11**: 1837 (2019); https://doi.org/10.3390/polym11111837
13. I. Kozina, H. Krawiec, M. Starowicz, and M. Kawalec, *Int. J. Mol. Sci.*, **22**: 8301 (2021); https://doi.org/10.3390/ijms22158301
14. P. Jha, K. Dharmalingam, T. Nishizu, N. Katsuno, and R. Anandalakshmi, *Starch — Stärke*, **72**, No. 1: 1900121 (2019); https://doi.org/10.1002/star.201900121
15. A. Harmaji and B. Sunendar, *Materials Science Forum*, **841**: 157 (2016); https://doi.org/10.4028/www.scientific.net/msf.841.157
16. T. Bakharev, *Cem. Concr. Res.*, **35**: 1124 (2005); https://doi.org/10.1016/j.cemconres.2004.06.031
17. M. Grutzeck, S. Kwan, and M. DiCola, *Cem. Concr. Res.*, **34**: 949 (2004); https://doi.org/10.1016/j.cemconres.2003.11.003
18. D. Koloušek, J. Brus, M. Urbanova, J. Andertova, V. Hulinsky, and J. Vorel, *J. Mater. Sci.*, **42**: 9267 (2007); https://doi.org/10.1007/s10853-

007-1910-5
19. J. Brus, L. Kobera, M. Urbanova, D. Koloušek, and J. Kotek, *J. Phys. Chem. C*, **116**: 14627 (2012); https://doi.org/10.1021/jp300181q
20. B. Kallesten et al., *IOP Conf. Ser., Mater. Sci. Eng.*, **700**: 012032 (2019); https://doi.org/10.1088/1757-899X/700/1/012032
21. A. Khosla, *Electrochem. Soc. Interface*, **21**, No. 3: 67 (2012); https://doi.org/10.1149/2.F04123-4if
22. S. W. Horstmann, K. M. Lynch, and E. K. Arendt, *Foods*, **6**, No. 4: 29 (2017); https://doi.org/10.3390/foods6040029
23. *Applied Dental Materials* (Eds. J. McCabe and A. Walls) (Oxford, UK: Blackwell Pub.: 2008).
24. *Craig's Restorative Dental Materials* (Eds. R. Sakaguchi, J. Ferracane, and J. Powers) (St. Louis, MO: Mosby Elsevier: 2006).
25. S. Budi, B. A. Suliasih, and I. Rahmawati, *Science Asia*, **46**, No. 4: 457 (2020); https://doi.org/10.2306/scienceasia1513-1874.2020.059
26. S. V. Panin et al., *Materials*, **14**, No. 5: 1113 (2021); https://doi.org/10.3390/ma14051113
27. K. C. B. Naidu, N. S. Kumar, P. Banerjee, and B. V. S. Reddy, *J. Mater. Sci.: Mater. Med.*, **32**: 68 (2021); https://doi.org/10.1007/s10856-021-06541-7