

Synthesis and modification of acrylic materials used in dental prosthetics

Wojciech Pakaszewski^{1),*} (ORCID ID: 0000-0001-6357-9476), Bogdan Tarasiuk²⁾ (0000-0002-1114-9770), Anna Szabelska¹⁾ (0000-0002-9690-1043), Karolina Młynarczyk²⁾ (0000-0003-3535-5701), Magdalena Jaszek³⁾ (0000-0003-2609-1820), Beata Podkościelna²⁾ (0000-0002-0267-5402)

DOI: <https://doi.org/10.14314/polimery.2025.7.5>

Abstract: Prosthetic composites based on a commercial prosthetic resin (Vertex) or oligomeric methyl methacrylate (OMM) with the addition of zinc oxide (ZnO) were obtained using photochemical and thermal polymerization methods. Fourier transform infrared spectroscopy (ATR-FT-IR) and differential scanning calorimetry (DSC) were used to evaluate the composites. Hardness of the composites increased with increasing ZnO content. The antibacterial activity of ZnO against *E. coli*, *S. aureus*, and *C. albicans* was confirmed.

Keywords: methyl methacrylate; prosthetic materials; zinc oxide; antibacterial properties.

Synteza i modyfikacja materiałów akrylowych stosowanych w protetyce stomatologicznej

Streszczenie: Metodą polimeryzacji fotochemicznej i termicznej otrzymano kompozyty protetyczne na bazie komercyjnej żywicy protetycznej (Vertex) lub oligomerycznego metakrylanu metylu (OMM), z dodatkiem tlenku cynku (ZnO). Do oceny kompozytów zastosowano spektroskopię w podczerwieni z transformacją Fouriera (ATR-FT-IR) i różnicową kalorymetrię skaningową (DSC). Twardość kompozytów zwiększała się wraz ze wzrostem zawartości ZnO. Potwierdzono działanie antybakteryjne ZnO w stosunku do *E. coli*, *S. aureus* i *C. albicans*.

Słowa kluczowe: metakrylan metylu, materiały protetyczne, tlenek cynku, właściwości antybakteryjne.

Poly(methyl methacrylate) (PMMA) has been a fundamental material in prosthetic dentistry for many years, primarily due to its physical, chemical, and aesthetic properties [1, 2]. It is easy-to-process material, characterized by good aesthetics, transparency, and ease of shaping. However, despite its numerous advantages, PMMA has certain limitations, such as brittleness and susceptibility to absorption of oral fluids, which can lead to changes in its mechanical properties and promote microbial colonization [3, 4]. Moreover, this material tends to develop cracks over long-term use. As a result, contemporary sci-

entific research focuses on modifying PMMA to improve its properties and enhance patient comfort and safety.

One of the main directions in PMMA research is increasing its mechanical strength by adding reinforcing materials. The incorporation of glass fibers, aramid fibers, or ceramic nanoparticles into the PMMA matrix allows for the creation of composites with improved mechanical properties, which translates into greater durability of dental prostheses [5, 6]. The use of these reinforcing materials enhances not only flexural strength but also resistance to material fatigue. For example, studies have shown that the incorporation of zirconia (ZrO₂) nanoparticles into PMMA increases its flexural strength and surface hardness [7, 8]. The introduction of alumina (Al₂O₃) nanoparticles has also demonstrated beneficial properties in terms of crack resistance and improved modulus of elasticity [9]. These modifications may extend the lifespan of prostheses, reducing the risk of damage during daily use.

Another crucial aspect is ensuring adequate bond strength between different prosthetic components, such as the denture base and acrylic teeth. Studies have shown that applying methyl methacrylate (MMA) monomer to the surface of an artificial tooth before the polymeriza-

¹⁾ Laboratory of Moder Technologies, Department of Dental Techniques, Medical University of Lublin, ul. Chodźki 6, 20-093 Lublin, Poland.

²⁾ Department of Polymer Chemistry, Institute of Chemical Science, Faculty of Chemistry, Maria Curie-Skłodowska University in Lublin, ul. Gliniana 33, 20-400 Lublin, Poland.

³⁾ Department of Biochemistry and Biotechnology, Institute of Biological Sciences, Maria Curie-Skłodowska University in Lublin, ul. Akademicka 19, 20-033 Lublin, Poland.

*) Author for correspondence:

wojciechpakaszewski@gmail.com

T a b l e 1. Amounts of components used to synthesize polymeric composites

| Sample | OMM g | MMA g | H g | BPO g | AIBN g | ZnO g | ZnO % |
|--------|----------|----------|--------|----------|-----------|----------|----------|
| 0 | – | 4.00 | 8.00 | – | – | – | |
| 1 | 8.00 | 4.00 | – | 0.50 | 0.50 | 0.07 | 0.54 |
| 2 | 8.00 | 4.00 | – | 0.50 | 0.50 | 0.14 | 1.06 |
| 3 | 8.00 | 4.00 | – | 0.50 | 0.50 | 0.27 | 2.03 |
| 4 | – | 4.00 | 8.00 | – | – | 0.06 | 0.50 |
| 5 | – | 4.00 | 8.00 | – | – | 0.13 | 1.07 |
| 6 | – | 4.00 | 8.00 | – | – | 0.25 | 2.04 |

tion process increases the bond strength between these materials [10, 11]. Adhesive technology using chemical surface modifications of PMMA allows for better integration of prosthetic components, leading to greater durability in use [12]. This approach enables the achievement of more stable and long-lasting connections between different elements of the prosthesis, which is particularly important in complex prosthetic designs.

The surface of PMMA dentures is prone to biofilm formation, which increases the risk of infections and can cause an unpleasant odor [13, 14]. Therefore, research is being conducted on modifying PMMA surfaces by incorporating antibacterial agents such as silver nanoparticles [15]. Silver nanoparticles exhibit strong antibacterial properties, effectively inhibiting the growth of many pathogens that can colonize denture surfaces. Additionally, copper and titanium dioxide (TiO₂) nanoparticles have also proven effective in reducing bacterial and fungal growth, which may help prevent oral mucosal inflammation in denture wearers. These modifications can increase denture resistance to microorganisms, improving their hygiene and reducing the risk of inflammatory conditions [16]. In addition to silver and titanium-based compounds, zinc oxide (ZnO) nanoparticles have also demonstrated promising antimicrobial effects when incorporated into PMMA matrices.

This study aims to develop prosthetic composites with enhanced antimicrobial resistance. For this purpose, polymeric materials were synthesized based on a commercial prosthetic resin (Vertex) or oligomeric methyl methacrylate (OMM), with zinc oxide (ZnO) incorpo-

rated as a functional additive to impart antimicrobial properties. A combination of photochemical and thermal polymerization methods was used to produce composites with enhanced structural and biological properties. The resulting materials were characterized by using attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR), differential scanning calorimetry (DSC), and Shore D hardness testing. Their antimicrobial efficacy was evaluated against *Escherichia coli*, *Staphylococcus aureus*, and *Candida albicans*.

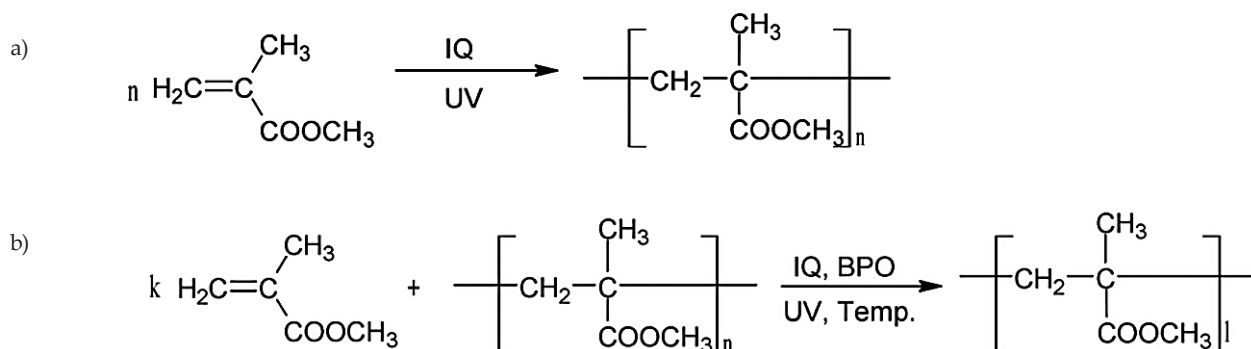
EXPERIMENTAL PART

Materials

Methyl methacrylate (MMA), 2,2-dimethoxy-2-phenylacetophenone (IQ), benzoyl peroxide (BPO), 2,2'-azobis(2-methylpropionitrile) (AIBN), zinc oxide (ZnO) from Merck (Germany). Commercial material for dental prostheses, cold-cured base material for Pour-Type prostheses - Castapress: two components: monomer - methyl methacrylate (MMA), hardener (H) from Vertex-Dental B.V. (The Netherlands).

Preparation of a polymeric material based on methyl methacrylate

0.1 g of 2,2-dimethoxy-2-phenylacetophenone was dissolved in 8 g of methyl methacrylate. The resulting solution was stirred vigorously at 25°C and exposed to eight Philips UV-A lamps for 10 min. The reaction mass


Fig. 1. Synthesis reaction of oligomeric methyl methacrylate (a) and oligomeric and monomeric methyl methacrylate (b)

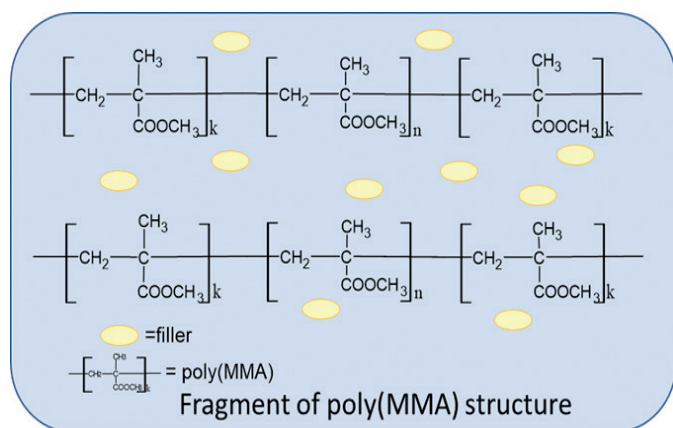


Fig. 2. Proposed fragment of a polymeric composite

was then heated at 40°C for 30 min and irradiated with UV lamps for 1 min. To the oligo(methyl methacrylate) (OMM) thus obtained, monomeric methyl methacrylate (MMA), benzoyl peroxide (BPO), 2,2'-azobis(2-methylpropanitrile) (AIBN) thermal polymerization initiators, and zinc oxide (ZnO) powder were added. The mixture was stirred gently at 25°C for 15 min until a homogeneous mixture was obtained and then heated at 50°C for 20 min to deaerate. The polymerization of the composition was conducted under UV lamps for 20 min and then heated at 80°C for 2 h.

The commercial polymer material was prepared in accordance with the manufacturer's procedure, with the addition of ZnO. In the first step, methyl methacrylate with hardener and zinc oxide were mixed. The composition was stirred gently at 25°C for 15 min until a homogeneous mixture was obtained, followed by heating at 50°C for 20 min to deaerate. The composition was polymerized by heating at 80°C for 2 h [17]. The composition of the polymeric material is shown in Table 1.

The scheme for preparing oligomeric methyl methacrylate (OMM) and oligomeric and monomeric methyl methacrylate is presented in Figure 1.

In Figure 2, a proposed fragment of a polymeric composite is shown.

Methods

UV spectroscopy

TL-K 40W/10-R UV-A Philips lamps emit UV-A in a spectral distribution wavelength of 315 to 380 nm: UV-A radiation 0Hr (IEC) 8.0 W.

FT-IR spectroscopy

ATR-FT-IR spectra were recorded by applying a Bruker Tensor 27 FTIR spectrometer (Germany) in the attenuated total reflectance (ATR) technique. Each spectrum was received in the wavelength range 600–4000 cm⁻¹ in absorbance mode. The spectral resolution was 4 cm⁻¹, and 32 scans were completed for each spectrum.

DSC analysis

Calorimetric analysis was performed using a Netzsch DSC 204 calorimeter (Selb, Germany) in dynamic mode. Scanning was performed at a heating rate of 10°C/min in the temperature range of 25–500°C under an argon atmosphere (30 cm³/min). The sample mass was 7–10 mg. An empty aluminum crucible was used as a reference sample.

Hardness

The hardness of the composites was measured by the Shore D method on a Zwick 7206/H04 hardness tester (Ulm, Germany). The readings were taken after 15 s at a temperature of 23°C.

Antimicrobial properties

A modification of the disk-diffusion method was used to assess the antimicrobial activity of the tested composites. Reference strains of the bacteria *Escherichia coli* (ATCC 25922), *Staphylococcus aureus* (ATCC 25923), and the fungus *Candida albicans* (ATCC 10231) from the collection of the Department of Biochemistry and Biotechnology of the Maria Curie-Skłodowska University in Lublin were used. The samples of composites were cut into 10×10 mm pieces and sterilized with UV light for 30 min. Agar plates with Mueller-Hinton medium were prepared. Glucose was also added to the medium in which *C. albicans* were cultured. Young (24 hours for the bacteria and 48 hours for the fungus) cultures of microorganisms were prepared at a concentration of 1.5 · 10⁸ CFU/mL. 200 µL of inoculate was applied to agar plates and thoroughly spread on the surface. Composite samples were placed on the plates prepared in the described way. The control sample was a composite without filler (zinc oxide). The plates were placed in a laboratory incubator at 37°C for 24 h for the bacteria and 48 h for the fungus. After this time, the composite samples were removed. The inhibition of microbial growth was visually assessed, and the zone of inhibition was measured.

RESULTS AND DISCUSSION

FT-IR analysis

The ATR-FT-IR spectra for Vertex-derived materials are shown in Fig. 3. The presented curves contain characteristic absorption bands for the base material – poly(methyl methacrylate) (from Vertex). The main bands observed in all samples are: 1723 cm⁻¹ – an intense band corresponding to the carbonyl group (C=O) typical of acrylic esters, 1434 cm⁻¹ and 1266 cm⁻¹ – deformation and stretching vibrations of C–H and C–O bonds, 986 cm⁻¹, 840 cm⁻¹ and 750 cm⁻¹ – bands characteristic of skeletal vibrations and functional groups present in the

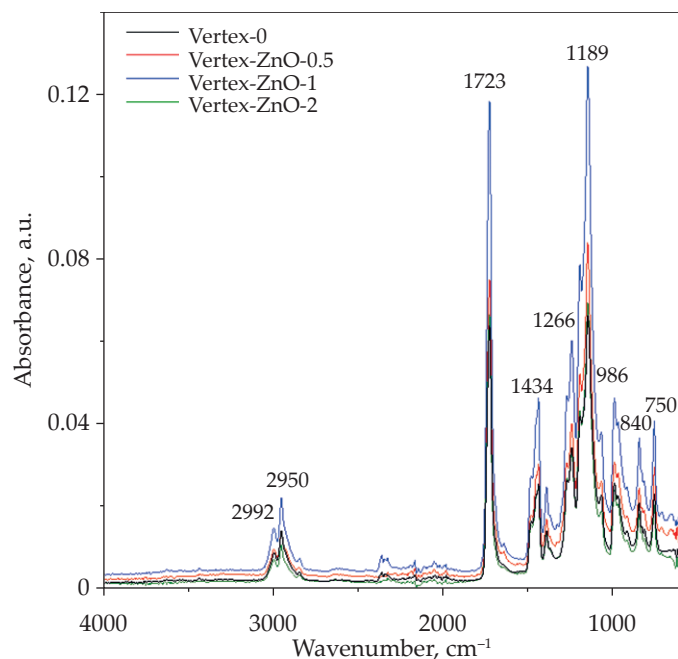


Fig. 3. ATR-FT-IR spectra

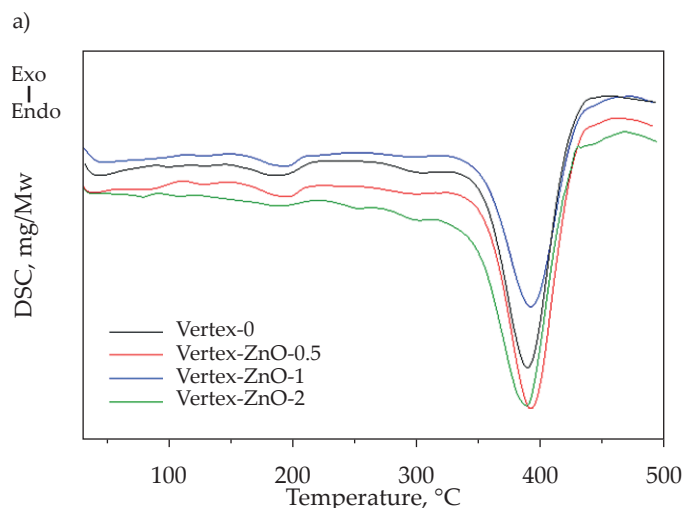
MMA structure, 2950 and 2992 cm^{-1} – stretching bands of CH_3 and CH_2 groups.

The addition of ZnO in small amounts (up to 2%) does not cause significant shifts or the formation of new bands, which suggests that there are no strong chemical interactions between ZnO and the polymer matrix. A similar observation was made for MMA derivatives.

DSC analysis

The DSC thermograms are presented in Fig. 4.

To evaluate the effect of ZnO particles on the thermal properties of two polymer composites based on methyl methacrylate (MMA) and commercial (Vertex), a differential scanning calorimetry (DSC) analysis was performed. The obtained DSC curves (Figures 4a and 4b) showed the presence of characteristic endothermic peaks associated with the thermal degradation of the materials. In



the case of polyMMA samples (MMA-0, MMA-ZnO-0.5, MMA-ZnO-1, MMA-ZnO-2), the main endothermic peak occurred in the range of 378–392°C. With increasing ZnO content, a small decrease in the degradation temperature was observed. The reference sample MMA-0 (without ZnO addition) showed the highest thermal resistance, while the lowest was shown by the MMA-ZnO-2 sample, containing the highest concentration of ZnO. A similar trend was observed in the Vertex system. The maximum degradation peak temperatures ranged from 390 to 407°C. For Vertex samples, a slight endothermic signal of about 200°C was observed, related to the degradation of additives (c.a. dye).

Hardness

Shore D hardness measurements were conducted to evaluate the influence of zinc oxide (ZnO) as a functional additive on the mechanical properties of polymer composites. All the materials evaluated fall within the range of hard polymers, with Shore D hardness between 81 and 85°D (Table 2). The reference materials Vertex-0 and MMA-0 exhibited hardness of 81 and 82°D, respectively. When ZnO was added at increasing concentrations (0.5%, 1%, and 2%), an overall increase in hardness was observed in both composite systems. Notably, the Vertex-ZnO-2 sample exhibited the highest hardness of 85°D, indicating significant enhancement. Similarly, MMA-

Table 2. Hardness of the tested composites

| Sample | Hardness, °D Shore |
|----------------|--------------------|
| Vertex-0 | 81.0 |
| Vertex-ZnO-0.5 | 81.5 |
| Vertex-ZnO-1 | 83.0 |
| Vertex-ZnO-2 | 85.0 |
| MMA-0 | 82.0 |
| MMA-ZnO-0.5 | 81.0 |
| MMA-ZnO-1 | 82.5 |
| MMA-ZnO-2 | 84.0 |

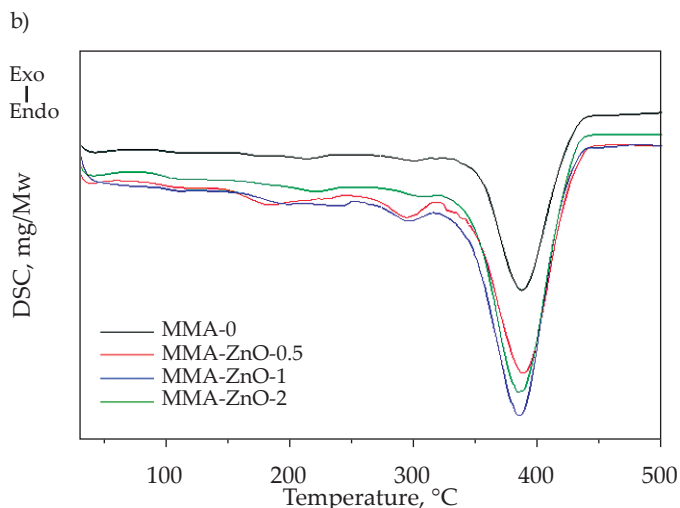


Fig. 4. DSC curves: a) Vertex-derived composites, b) MMA-derived composites

based composites with ZnO demonstrated improved hardness; MMA-ZnO-2 reached hardness of 84°D compared to 82°D for unmodified MMA. These results suggest that ZnO can enhance hardness of the composites, particularly at higher concentrations.

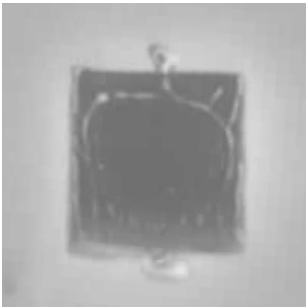
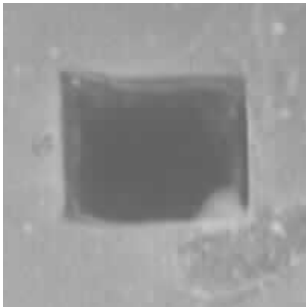
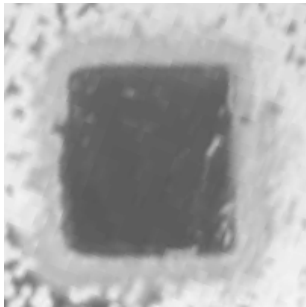
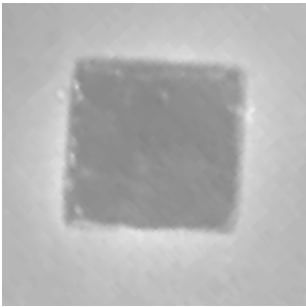
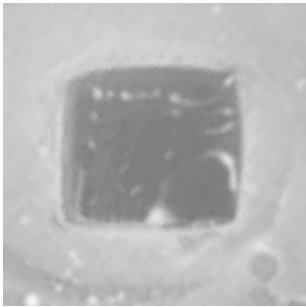
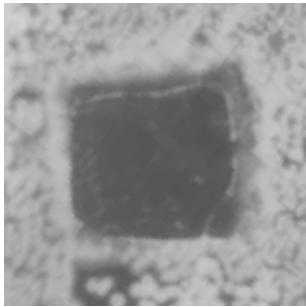
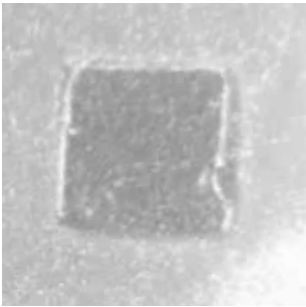
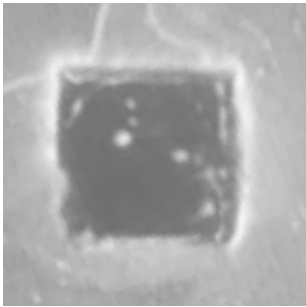
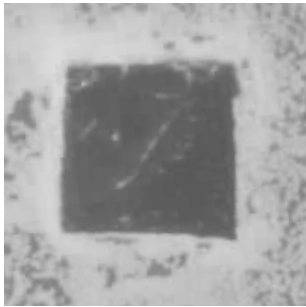
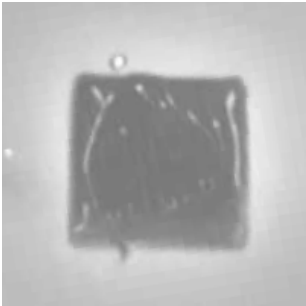
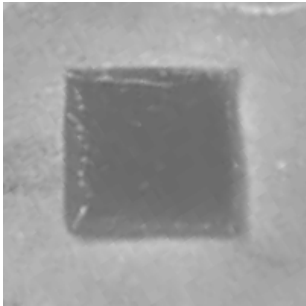
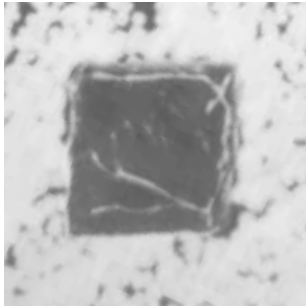
Evaluation of antimicrobial potential

The antimicrobial activity of MMA-derived materials against the pathogenic bacteria *Escherichia coli* and *Staphylococcus aureus* and the fungi *Candida albicans* is sum-

marized in Table 3. The control sample (MMA-0) showed no visible inhibition, confirming the absence of inherent antimicrobial activity. Samples containing 0.5 wt% ZnO exhibited small inhibition zones (1–2 mm), indicating limited antimicrobial potential. In contrast, samples with 1 wt% and especially 2 wt% ZnO showed significantly larger inhibition zones, particularly against *S. aureus* and *C. albicans*. This demonstrates a dose-dependent increase in antimicrobial activity with rising ZnO concentration.

Previous studies on the modification of acrylic resins, including polymethyl methacrylate (PMMA), have

T a b l e 3. Evaluation of the antimicrobial potential of examined composite materials

| Composite | <i>Escherichia coli</i> | <i>Staphylococcus aureus</i> | <i>Candida albicans</i> |
|-------------------------|---|--|---|
| Control sample MMA-0 |  1 mm |  0 mm |  1 mm |
| MMA-ZnO-0.5 |  1 mm |  2 mm |  1 mm |
| MMA-ZnO-1 |  0 mm |  1 mm |  1 mm |
| MMA-ZnO-2 |  1 mm |  1 mm |  0 mm |

focused on improving their mechanical properties and imparting antimicrobial activity through the incorporation of functional nanofillers such as zinc oxide (ZnO), silver (Ag), copper oxide (CuO), or graphene (GO). Santhanam *et al.* [18] found that the addition of ZnO to PMMA at concentrations of 0.4–1.4 wt% led to a significant increase in flexural strength (from 61 MPa to 91 MPa). Similarly, in [19], the use of ZnO/GO nanocomposites in PMMA resulted in improved mechanical strength and over 60% reduction in the number of bacterial colonies, without any cytotoxicity. Other studies have also demonstrated that ZnO effectively limits colonization by *Candida albicans* and Gram-positive bacteria such as *Staphylococcus aureus* [20, 21]. It has also been shown that increasing the ZnO content in the PMMA matrix (e.g., up to 7.5 wt%) enhances both hardness and antifungal properties, as reported in [22, 23].

In comparison to these reports, the present study introduces several notable innovations. First, a unique synthetic approach combining photochemical and thermal polymerization was employed, which may contribute to better cross-linking and a more homogeneous dispersion of ZnO within the composite matrix. The application of oligomeric methyl methacrylate (OMM) as a monomer may positively affect the polymer structure, improving its mechanical resistance and durability. Importantly, unlike many previous studies that focused on a single microorganism, this study evaluated antimicrobial effectiveness against three representative pathogens: *Escherichia coli*, *Staphylococcus aureus*, and *Candida albicans*.

CONCLUSIONS

Polymer composites were synthesized using commercial Vertex resin and oligomeric methyl methacrylate (OMM), with zinc oxide (ZnO) added as a functional additive to enhance antimicrobial efficacy. DSC analysis showed that the addition of ZnO slightly lowered the thermal degradation temperature of both MMA-based and Vertex-based composites. Samples without ZnO exhibited the highest thermal stability, while composites with 2 wt% ZnO exhibited the lowest resistance to thermal degradation. In contrast, the addition of ZnO resulted in a noticeable increase in Shore D hardness, especially at higher concentrations, confirming the reinforcing effect. Furthermore, the antimicrobial activity of the composites significantly increased with increasing ZnO content, with the largest zones of inhibition for *E. coli*, *S. aureus*, and *C. albicans* observed at 2 wt% ZnO. The results confirm that ZnO is an effective multifunctional additive that increases the mechanical strength and antimicrobial resistance of polymeric prosthetic materials.

Authors contribution

W.P. – methodology, writing-original draft, project administration; B.T. – conceptualization, methodology; A.S. – formal analysis, writing-review, and editing;

K.M. – methodology, editing; M.J. – validation, writing-review; B.P. – conceptualization, methodology, formal analysis, writing-review, and editing.

Funding

No funding/no source of financing.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Copyright © 2025 The publisher. Published by Łukasiewicz Research Network – Industrial Chemistry Institute. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY-NC-ND) license (<https://creativecommons.org/licenses/by-nc-nd/4.0/>).



REFERENCES

- [1] Vallittu P.K., Lassila V.P., Lappalainen R.: *The Journal of Prosthetic Dentistry* **1994**, 71(6), 607.
[https://doi.org/10.1016/0022-3913\(94\)90446-4](https://doi.org/10.1016/0022-3913(94)90446-4)
- [2] Sakaguchi R.L., Powers J.M.: “Graig’s Restorative Dental Materials”, Elsevier, Philadelphia, 2012.
- [3] Chang C.C., Merritt K.: *Journal of Biomedical Materials Research* **1992**, 26(2), 197.
<https://doi.org/10.1002/jbm.820260206>
- [4] Wang Z., Shen Y., Haapasalo M.: *Dental Materials* **2014**, 30(2), e1.
<https://doi.org/10.1016/j.dental.2013.12.001>
- [5] Yerliyurt K., Korkmaz F.M., Tercan M. *et al.*: *Polymers* **2023**, 15(15), 3211.
<https://doi.org/10.3390/polym15153211>
- [6] John J., Gangadhar S.A., Shah I.: *The Journal of Prosthetic Dentistry* **2001**, 86(4), 424.
<https://doi.org/10.1067/mp.2001.118564>
- [7] Gad M.M., Rahoma A., Abualsaud R. *et al.*: *Dental Materials Journal* **2020**, 39(3), 471.
<https://doi.org/10.4012/dmj.2018-436>
- [8] Alhotan A., Yates J., Zidan S. *et al.*: *Materials* **2021**, 14(10), 2659.
<https://doi.org/10.3390/ma14102659>
- [9] Roato I., Genova T., Duraccio D. *et al.*: *Polymers* **2023**, 15(15), 3186.
<https://doi.org/10.3390/polym15153186>
- [10] Akin H., Kirmali O., Tugut F. *et al.*: *Photomedicine and Laser Surgery* **2014**, 32(9), 512.
<https://doi.org/10.1089/pho.2014.3732>
- [11] Perdigão J., Araujo E., Ramos R.Q. *et al.*: *Journal of Esthetic and Restorative Dentistry* **2021**, 33(1), 51.
<https://doi.org/10.1111/jerd.12692>

- [12] Jagger D.C., Harrison A., Jandt K.D.: *Journal of Oral Rehabilitation* **1999**, 26(3), 185.
<https://doi.org/10.1046/j.1365-2842.1999.00375.x>
- [13] Kazmi S.A.D., Soomro T., Soomro R. *et al.*: *Journal of Basic Microbiology* **2024**, 64(12), e2400460.
<https://doi.org/10.1002/jobm.202400460>
- [14] Imazato S., Kinomoto Y., Tarumi H. *et al.*: *Dental Materials* **2003**, 19(4), 313.
[https://doi.org/10.1016/s0109-5641\(02\)00060-x](https://doi.org/10.1016/s0109-5641(02)00060-x)
- [15] Li F., Weir M.D., Chen J. *et al.*: *Dental Materials* **2013**, 29(4), 450.
<https://doi.org/10.1016/j.dental.2013.01.012>
- [16] Yadfout A., Asri Y., Merzouk N. *et al.*: *International Journal of Nanomedicine* **2023**, 18, 6941.
<https://doi.org/10.2147/IJN.S425702>
- [17] Patent application „Sposób otrzymywania tworzywa polimerowego do ruchomych uzupełnień protetycznych i tworzywo polimerowe otrzymane tym sposobem” P.451298 (2025)
- [18] Santhamer V., Chander N.G.: *European Oral Research* **2020**, 54(1), 31.
<https://doi.org/10.26650/eor.20200063>
- [19] Ruan S., Zhao Y., Chen R. *et al.*: *BMC Oral Health* **2024**, 24, 1013.
<https://doi.org/10.1186/s12903-024-04754-0>
- [20] Sirelkhatim A., Mahmud S., Seeni A. *et al.*: *Nano-Micro Letters* **2015**, 7, 219.
<https://doi.org/10.1007/s40820-015-0040-x>
- [21] Xu M.N., Li L., Pan W. *et al.*: *Frontiers in Microbiology* **2021**, 12, 766138.
<https://doi.org/10.3389/fmicb.2021.766138>
- [22] Mazur M.W., Grudniak A., Szałaj U. *et al.*: *Polymers* **2024**, 16(24), 3512.
<https://doi.org/10.3390/polym16243512>
- [23] Rao S., Nandish B.T., Ginjupalli K. *et al.*: *Trends in Biomaterials and Artificial Organs* **2021**, 35(3), 316.

Received 19 V 2025.

Accepted 20 VI 2025.

2nd Baltic Symposium on Polymer and (Bio)Materials Science

Baltic BioMat

From Materials Design to Advanced Structures

18-19 September 2025
Szczecin, Poland

Nanotechnology Centre
for Research & Education