PRE-PRINT ARTICLE

COPYRIGHT BY COMPOSITES THEORY AND PRACTICE JOURNAL

ISSN: 2299-128X

SELECTED PHYSIOCHEMICAL PROPERTIES OF DIMETACRYLATE RESIN BLEND MODIFIED WITH LIQUID RUBBER

MONIKA SOWA*, KRZYSZTOF PAŁKA

Faculty of Mechanical Engineering, Lublin University of Technology, Nadbystrzycka 36, 20-618 Lublin, Poland

*email: d577@pollub.edu.pl

https://doi.org/10.62753/ctp.2024.01.3.3

Abstract

In the oral cavity environment, light-cured dental composites are susceptible to water sorption. This process can have a detrimental effect on the polymer network over a longer period, thereby causing deterioration of the material properties. This study aims to evaluate the impact of modifying a dimethacrylate resin mixture with liquid rubber on water sorption and the water contact angle. The resin mixture contained BisGMA (20 wt%), BisEMA (30 wt%), UDMA (30 wt%) and TEGDMA (20 wt%). Liquid rubber Hypro 2000X168LC VTB was used as a modifier in quantities of 5%, 10%, 15%, and 20% by weight relative to the resin. Water sorption studies were conducted following the ISO 4049 standard, and water contact angle tests were carried out as well. The percentage change in the water sorption weight after 7 days was approximately 1.6% for the sample containing 5 wt% liquid rubber, while for the sample with the 20 wt% liquid rubber content, this value was approximately 1.9%. The addition of 5 wt% liquid rubber caused the contact angle value to increase by 16.34% after 30 days compared to the first day. In the case of the other samples, such significant differences were not observed. Microscopy was employed to assess the miscibility and morphology of the liquid rubber domains. The study results show that modification with liquid rubber significantly limits water sorption and contributes to increasing the hydrophobicity of the surface, which is significant from a clinical standpoint. In the range of rubber concentrations studied, its solubility in the resin was not found, and for the 5 wt% content, the most uniform distribution of domains was observed. With a larger share of liquid rubber, an increment in the number of domains and their sizes was noted, both before and after polymerization.

Keywords: *dental composite, dimethacrylate resins, liquid rubber, miscibility, wettability, water sorption*

Introduction

Composite materials based on dimethacrylate resins are widely used in dentistry for the restoration of hard dental tissues. They possess excellent mechanical and aesthetic properties, as well as the ability to bond with enamel surfaces; nevertheless, they are continuously being improved to enhance their long-term clinical performance and durability in oral cavity conditions. This is a unique environment where the material is in constant contact with saliva, containing various inorganic and organic compounds, along with a complex of bacterial flora and variable pH [1,2]. In such a complex environment, filling materials can absorb water or

PRE-PRINT ARTICLE
COPYRIGHT BY COMPOSITES THEORY AND PRACTICE JOURNAL
ISSN: 2299-128X
Polish Society of Composite Materials

other liquids, which can significantly impact the degradation of the composite matrix, and as a result, leach out unreacted monomers and loosen the reinforcing particles [3]. The excessive absorption of liquids can have a detrimental effect on the structure and function of the matrix resin as it contributes to the deterioration of the mechanical and physical properties. This leads to a reduction in the durability of the dental filling through cracking and detachment of the reinforcement from the matrix [4].

In dimethacrylate systems, commonly used in dental composites, water sorption primarily depends on their polarity and chain topology. Bisphenol A diglycidyl methacrylate (Bis-GMA) is the most commonly used monomer in dental composites. Due to the presence of bisphenol A, which reduces the degrees of freedom for rotation around the bonds and causes strong hydrogen bonding interactions imparted by hydroxyl groups, this monomer exhibits high viscosity at room temperature [5]. The high viscosity of BisGMA is reduced by adding triethylene glycol dimethacrylate (TEGDMA), resulting in improved usability properties [3,6]. An important characteristic of the TEGDMA monomer is the improvement in the degree of conversion and cross-linking, which results in a smaller number of leached components. However, each of these monomers is relatively hydrophilic [7], as is the case with any molecule containing ether bonds, which translates into a problem of water sorption, leading to progressive degradation [5,6,8]. Krishnan [9] demonstrated that the copolymerization of the TEGDMA monomer with BisGMA resulted in increased compressive strength and microhardness, while the use of a shorter chain ethylene glycol dimethacrylate (EGDMA) derivative yielded greater polymer stability after aging in water. Comparatively, tetraethylene glycol dimethacrylate (TEGDMA) is more hydrophilic than TEGDMA, yet it does not adversely affect the resistance to cracking or solubility in water [10]. In an ideal scenario, polymer networks should be insoluble materials with relatively high chemical and thermal stability. Nevertheless, most monomers used as the base for dental composites absorb water and chemicals from the surrounding environment, releasing components into it [10,11].

Degradation of the resin and the leaching of inorganic fillers can lead to surface changes in the material, which not only reduces its functionality but also affects the aesthetics of the fillings and the health of the patient. Rough material surfaces are more susceptible to bacterial deposition, which promotes the development of periodontal diseases and discolorations [13]. Since no material utilized for the restoration of hard dental tissues is perfect, the search continues for new solutions that meet the high demands placed on these materials. The focus is mainly on modifying the chemical composition of polymer materials (matrix). Minimizing the susceptibility of materials to water sorption seems to be one of the key actions that can ensure the desired durability of filling materials.

This study aims to determine the effect of modifying a mixture of dimethacrylate resins with liquid rubber on water sorption and the contact angle. The research also aims to evaluate the solubility and morphology of the liquid rubber in the experimental mixture of resins. The innovative aspect of the research involves the development of advanced modifications to resin blends with the objective of enhancing their fracture toughness and reducing water sorption, shrinkage, and polymerization stress. These modifications are

PRE-PRINT ARTICLE
COPYRIGHT BY COMPOSITES THEORY AND PRACTICE JOURNAL
ISSN: 2299-128X
Polish Society of Composite Materials

crucial for improving the durability and effectiveness of dental fillings. Furthermore, a non-carcinogenic liquid rubber (free acrylonitrile acid) was employed as the modifier, possessing vinyl functional groups that facilitate the formation of a stable bond with dimethacrylate resins.

Materials and Methods

The material used in the research was an experimental mixture of resins consisting of BisGMA (20 wt%), BisEMA (30 wt%), UDMA (30 wt%), and TEGDMA (20 wt%). The composition of the mixture was determined based on the mechanical properties of the components and preliminary studies [14,15]. The mixture was supplemented with 1 wt% photoinitiator (camphorquinone), co-initiator (2-dimethylaminoethyl methacrylate, DMAEMA), and inhibitor (butylated hydroxytoluene, BHT). All the resins and additives were purchased from Sigma-Aldrich Chemicals (Munich, Germany) (Table 1). To the thus prepared resin mixtures, liquid non-nitrile rubber Hypro 2000X168LC VTB (Huntsman International LLC, Salt Lake City, UT, USA) was added in the following contents (by weight): 0% (reference), 5%, 10%, 15%, 20%. The methodology for the water sorption studies followed ISO 4049. Five samples of each material were prepared for the study with the following dimensions: 15 mm in diameter and 1 mm in thickness, polymerized using a LED lamp of the intensity 1350 mW/cm^2. The samples were dried to a constant weight and then incubated in distilled water at a temperature of 37±1°C for 7 days. During this period, daily weight measurements of the samples were taken. The water contact angle (CA) was studied by means of the sessile drop method (2µl ultrapure water droplets dosed at a 0.16 ml/min. flow rate) using static contact angle measurements on a Kruss DSA25E goniometer equipped with a CCD camera. Samples for the CA studies were prepared in the same manner as for water sorption. The experiments were performed at room temperature (22°C) 24 h after polymerization of the composites. The solubility and morphology of the liquid rubber were assessed using optical light microscopy (Eclipse MA200, Nikon, Tokyo, Japan) with an external yellow light source. A drop of the material was placed on a basic glass slide, covered with a coverslip, and the first photos were taken. Then the resin was polymerized, and micrographs were taken again.

Statistical significance was considered at the probability of $p<0.05$ using Statistica software (TIBCO Software Inc.).

PRE-PRINT ARTICLE

COPYRIGHT BY COMPOSITES THEORY AND PRACTICE JOURNAL

ISSN: 2299-128X

Polish Society of Composite Materials

Table 1. Characteristics of components of the materials used in the study

Material	Manufacturer	CAS	Molecular weight [g/mol]	Density [g/cm³]	Viscosity	Boiling point [°C]	Specific gravity [g/cm³]	Glass transition temperature [°C]
resin BisGMA	Sigma-Aldrich Chemicals (Munich, Germany)	1565-94-2	512	~1.2	600-800 Pa·s (25°C)	>200	N/A	N/A
resin BisEMA	Sigma-Aldrich Chemicals (Munich, Germany)	41637-38-1	540-650	~1.1	200-400 mPa·s (25°C)	>200	N/A	N/A
resin UDMA	Sigma-Aldrich Chemicals (Munich, Germany)	72869-86-4	470	~1.1	1500-3000 mPa·s (25°C)	~200-220	N/A	N/A
resin TEGDMA	Sigma-Aldrich Chemicals (Munich, Germany)	109-16-0	286.32	1.08	7-12 mPa·s (25°C)	~245	N/A	N/A
liquid rubber Hypro 2000X168LC VTB	Huntsman International LLC, Salt Lake City, UT,USA	68649–04–7	4 450	N/A	100 Pa·s (27°C)	N/A	0.929	-80
Photoinitiating system (CQ : DMAEMA)	Sigma-Aldrich Chemicals (Munich, Germany)	10373-78-1 2867-47-2	322.41	N/A	N/A	~102	1.08	N/A

Results and Discussion

The average results of the weight change measurements (in percentage) in the water sorption test are presented in Fig. 1, approximating the data with the function $f(x)=a+be^{-x}$. A dynamic increase in the weight of the samples was observed in the first three days of incubation in water. During the subsequent period, the rate of growth diminished, and the weight of the samples did not change by more than 0.1 mg over 24 hours. The largest weight changes were recorded for the sample containing 20 wt% liquid rubber (2.099%), while the samples with the 10 wt% and 15 wt% liquid rubber contents exhibited similar weight change values compared to the 0 wt% control sample. The sample containing 5 wt% liquid rubber was characterized by the smallest weight change.

PRE-PRINT ARTICLE
COPYRIGHT BY COMPOSITES THEORY AND PRACTICE JOURNAL
ISSN: 2299-128X

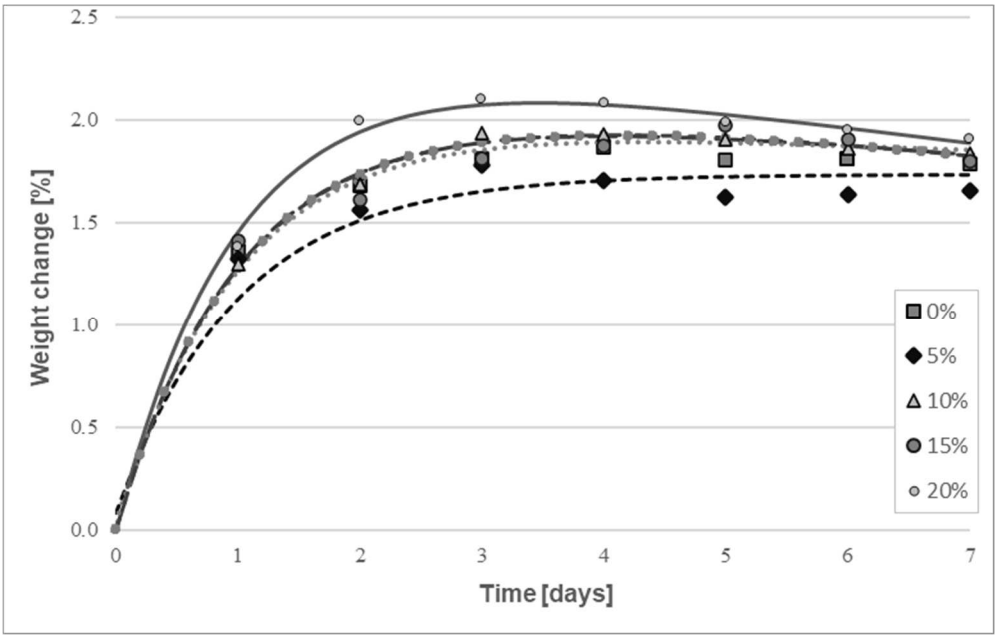

Fig. 1. Weight change percentage in water sorption process

The study results indicate a limitation of water sorption following modification with liquid rubber, especially in the initial stage of the test. For the sample containing 5 wt% liquid rubber, the smallest propensity for water sorption was observed compared to the other samples. In the case of the sample with the 20 wt% liquid rubber content, the observed increased water sorption capacity may result from the limited solubility of liquid rubber in the resin matrix, as shown by microscopic analysis (Fig. 3). The emergence of free spaces, diverse domains of liquid rubber and other defects in the material structure facilitates water penetration, leading to the destruction of polymer network connections, resulting in increased water sorption by the material [15,16]. Despite the hydrophobic nature (Fig. 2) of the sample with the 20 wt% liquid rubber content, reduced water sorption was not observed. In the 5 wt% material, an even distribution of liquid rubber domains was found, characterized by a uniform material structure, in which no free areas conducive to increased water sorption were observed. The analysis of liquid rubber miscibility (Fig.3), contact angle (Fig.2), and water sorption (Fig. 1) showed that water sorption is reduced in the case where the material is characterized by a uniform structure after modification with liquid rubber. The percentage increases in weight of the samples modified with 5 wt% and 20 wt% liquid rubber present statistically significant differences when comparing the results to the control sample (Table 2).

PRE-PRINT ARTICLE

COPYRIGHT BY COMPOSITES THEORY AND PRACTICE JOURNAL

ISSN: 2299-128X

Table 2. Results of t-test with respect to reference sample for water sorption. Statistically significant differences at p<0.05

Day	Liquid rubber content [wt%].			
	5%	10%	15%	20%
1	0.0075	0.0534	0.0524	0.0155
2	0.0077	0.0512	0.0596	0.0146
3	0.0075	0.0852	0.0546	0.0145
4	0.0080	0.0512	0.0602	0.0150
5	0.0081	0.0546	0.0561	0.0153
6	0.0081	0.0514	0.0501	0.0153
7	0.0215	0.0512	0.0781	0.0439

Water sorption in composite materials is a diffusion process that mainly occurs in the resin matrix [18], and the hydrophobicity of the material [19], which can be evaluated by the contact angle, affects water sorption. In the analyzed case, this translates into the susceptibility of composite materials to water sorption and the potential for bacterial film formation on their surface, significant from the perspective of clinical success. The results of the contact angle measurements for the studied materials are presented in Fig. 2. Higher water contact angle values were observed for the materials modified with liquid rubber and the differences in the results obtained in relation to the control sample are statistically significant.

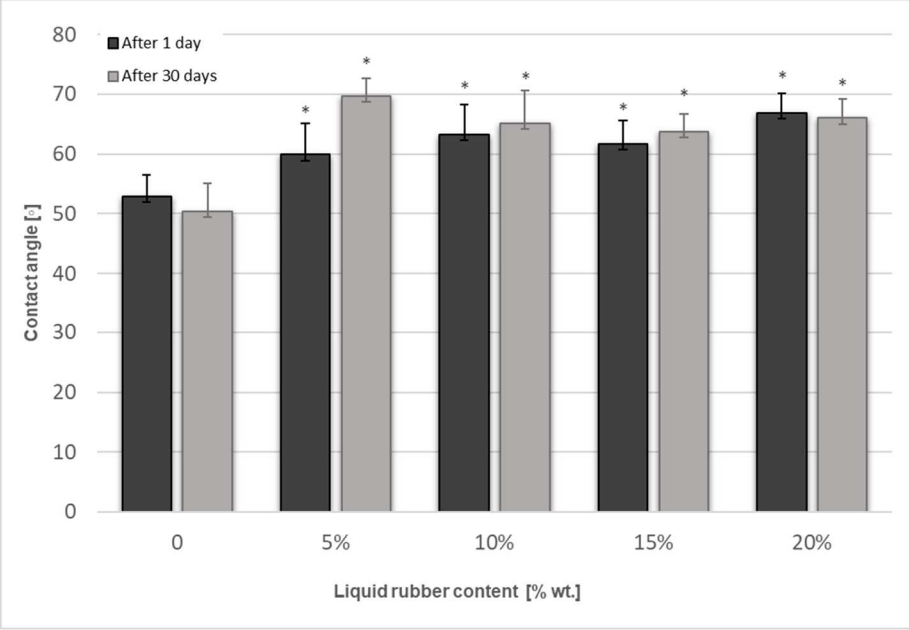

Fig. 2. Results of contact angle measurement (asterisks * indicate statistically significant differences from reference material (p<0.05))

Storing the tested samples for 30 days in distilled water led to an increase in the contact angle for the sample with 5 wt% liquid rubber content. Meanwhile, for the samples with the 0 wt% and 20 wt% liquid rubber contents, a slight decrease in the contact angle was observed compared to the same samples analyzed 24 h after the polymerization time.

The BisGMA resin, as the main component of the composite matrix, possesses hydroxyl groups [20], whereas liquid rubber is nonpolar [21], which favors an increase in the contact angle. In the conducted studies,

PRE-PRINT ARTICLE
COPYRIGHT BY COMPOSITES THEORY AND PRACTICE JOURNAL
ISSN: 2299-128X
Polish Society of Composite Materials

the modification of dental composites with liquid rubber favored their hydrophobicity, which is significant from the standpoint of limiting bacterial colonization in dental fillings. The studies of Gyo et al. [22] show that hydrophobic surfaces have a significantly lower potential for bacterial colonization. Therefore, from a clinical standpoint, filling materials should have good wettability to the binding system to ensure the required adhesion strength, while the outer surface should exhibit low water wettability to prevent bacterial adhesion [23]. The increment in the wettability of the surface of composite materials is an essential factor contributing to the formation of dental plaque on the material surface.

The effects of mixing resins with liquid rubber are shown in Fig. 3. In all the cases, no or only partial solubility of the rubber in the resin was observed. For the 5 wt% liquid rubber content, uniform distribution of rubber domains, ranging in size from 1 μm to about 50 μm, was obtained. As the content of the modifier was increased, a larger number of domains was observed both before and after polymerization. The presence of larger domains was noted for the mixtures containing 15 wt% and above liquid rubber content. Due to the onset of the polymerization process, the increased viscosity and molecular weight of the resin mixture change the solubility conditions for the rubber, causing the formation of visible domains. The polymerization process resulted in the formation of envelopes around the rubber domains, which stems from a change in the optical properties, as well as from possible deformation of the rubber owing to the polymerization shrinkage of the resin. When comparing the domains before and after polymerization (Fig. 3), no difference in their sizes was noted, but the optical properties of the material changed; after curing, the domains were significantly darker and more distinct. In some areas, before curing, the domains were not visible (likely dissolving), but after curing, rounded, more distinct liquid rubber domains were revealed. This was due to the separation of the rubber from the solution as a result of viscosity changes during polymerization. The miscibility of resins with liquid rubber at a specific temperature depends on many factors, including the functional number and molecular weight of the monomer, as well as the dispersion of the liquid rubber.

PRE-PRINT ARTICLE
COPYRIGHT BY COMPOSITES THEORY AND PRACTICE JOURNAL
ISSN: 2299-128X
Polish Society of Composite Materials

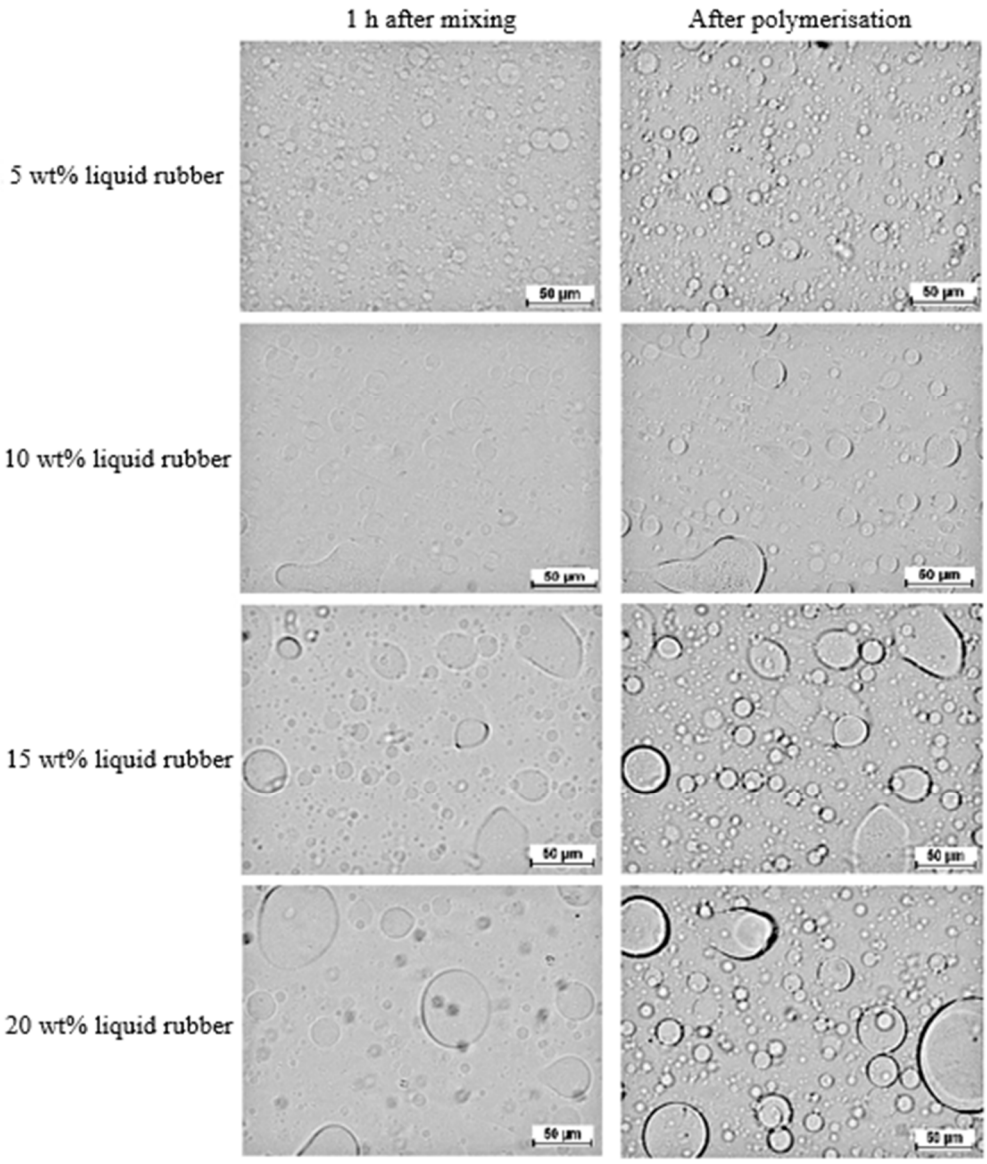

Fig. 3. Solubility and morphology of liquid rubber domains in resin blend

Conclusions

The solubility of liquid rubber Hypro 2000X168LC in a mixture of dimethacrylate resins was limited as a consequence of the composition and viscosity of the resins. The polymerization process resulted in separation of the liquid rubber as a distinct phase in the form of domains. With the 5 wt% content of liquid rubber, the morphology of the domains was uniform and their size remained within the range of 1-50 µm. Further increases in the content of liquid rubber led to growth in both the number and size of the domains before and after curing. The presence of liquid rubber in the dimethacrylate resin mixture raised its

PRE-PRINT ARTICLE
COPYRIGHT BY COMPOSITES THEORY AND PRACTICE JOURNAL
ISSN: 2299-128X

hydrophobicity, which contributes to reducing biofilm formation. The contact angle 24 h after polymerization changed from 52° for the reference sample to 66° for the material containing 20 wt% liquid rubber.

After soaking for 30 days in distilled water, the contact angle changed from 50° for the reference sample to 69° for the material containing 5 wt% liquid rubber. As a result of the water sorption process analysis, it was found that the resin containing 5 wt% liquid rubber exhibited the smallest percentage change in weight compared to the reference sample. Meanwhile, the material with the 20 wt% content of liquid rubber showed the highest water absorption capability, and the materials with the 10 wt% and 15 wt% liquid rubber contents had values similar to the reference resin. Despite the hydrophobic nature of the investigated samples, the uniform structure of the material after modification with liquid rubber has a significant impact on the dynamics of the water sorption process.

Acknowledgments

This research was supported by the NAWA STER Program - Internationalization of the Doctoral School of Lublin University of Technology – IdeaS of LUT.

References

[1] Y. Tanimoto, T. Kitagawa, M. Aida, and N. Nishiyama, "Experimental and computational approach for evaluating the mechanical characteristics of dental composite resins with various filler sizes," *Acta Biomater.*, vol. 2, no. 6, pp. 633–639, 2006, doi: 10.1016/j.actbio.2006.06.006.

[2] K. Okada, S. Tosaki, K. Hirota, and W. R. Hume, "Surface hardness change of restorative filling materials stored in saliva," *Dent. Mater.*, vol. 17, no. 1, pp. 34–39, 2001, doi: 10.1016/S0109-5641(00)00053-1.

[3] C. K. Y. Yiu *et al.*, "Effect of resin hydrophilicity and temperature on water sorption of dental adhesive resins," *Biomaterials*, vol. 27, no. 9, pp. 1695–1703, 2006, doi: 10.1016/j.biomaterials.2005.09.037.

[4] K. Pałka, *Wpływ modyfikacji ciekłym kauczukiem na właściwości światłoutwardzalnych kompozytów stomatologicznych*. Lublin: Wydawnictwo Politechniki Lubelskiej, 2020.

[5] N. R. de Godoy Fróes-Salgado *et al.*, "Influence of the base and diluent monomer on network characteristics and mechanical properties of neat resin and composite materials," *Odontology*, vol. 103, no. 2, pp. 160–168, 2015, doi: 10.1007/s10266-014-0153-6.

[6] C. L. Soles, F. T. Chang, B. A. Bolan, H. A. Hristov, D. W. Gidley, and A. F. Yee, "Contributions of the nanovoid structure to the moisture absorption properties of epoxy resins," *J. Polym. Sci. Part B Polym. Phys.*, vol. 36, no. 17, pp. 3035–3048, 1998, doi: 10.1002/(SICI)1099-0488(199812)36:17<3035::AID-POLB4>3.0.CO;2-Y.

[7] M. Atai, M. Nekoomanesh, S. A. Hashemi, and S. Amani, "Physical and mechanical properties of an experimental dental composite based on a new monomer," *Dent. Mater.*, vol. 20, no. 7, pp. 663–668, 2004, doi: 10.1016/j.dental.2003.08.008.

[8] T. Arima, T. Hamada, and J. F. McCabe, "The Effects of Cross-linking Agents on Some Properties of HEMA-based Resins," *J. Dent. Res.*, vol. 74, no. 9, pp. 1597–1601, 1995, doi: 10.1177/00220345950740091501.

[9] V. Kalliyana Krishnan, K. Manjusha, and V. Yamuna, "Effect of diluent upon the properties of a visible-light-cured dental composite," *J. Mater. Sci. Mater. Med.*, vol. 8, no. 11, pp. 703–706, 1997, doi: 10.1023/A:1018592008152.

[10] D. J. Indrani, W. D. Cook, F. Televantos, M. J. Tyas, and J. K. Harcourt, "Fracture toughness of water-aged resin composite

restorative materials," *Dent. Mater.*, vol. 11, no. 3, pp. 201–207, 1995, doi: 10.1016/0109-5641(95)80019-0.

[11] J. P. Santerre, L. Shajii, and B. W. Leung, "Relation of dental composite formulations to their degradation and the release of hydrolyzed polymeric-resin-derived products," *Crit. Rev. Oral Biol. Med.*, vol. 12, no. 2, pp. 136–151, 2001, doi: 10.1177/10454411010120020401.

[12] J. L. Ferracane, "Hygroscopic and hydrolytic effects in dental polymer networks," *Dent. Mater.*, vol. 22, no. 3, pp. 211–222, 2006, doi: 10.1016/j.dental.2005.05.005.

[13] R. R. De Moraes, J. L. M. Marimon, L. F. Jochims Schneider, M. A. C. Sinhoreti, L. Correr-Sobrinho, and M. Bueno, "Effects of 6 months of aging in water on hardness and surface roughness of two microhybrid dental composites," *J. Prosthodont.*, vol. 17, no. 4, pp. 323–326, 2008, doi: 10.1111/j.1532-849X.2007.00295.x.

[14] V. E. S. Gajewski, C. S. Pfeifer, N. R. G. Fróes-Salgado, L. C. C. Boaro, and R. R. Braga, "Monomers used in resin composites: Degree of conversion, mechanical properties and water sorption/solubility," *Braz. Dent. J.*, vol. 23, no. 5, pp. 508–514, 2012, doi: 10.1590/S0103-64402012000500007.

[15] A. Szczesio-Wlodarczyk, M. Domarecka, K. Kopacz, J. Sokolowski, and K. Bociong, "An evaluation of the properties of urethane dimethacrylate-based dental resins," *Materials (Basel).*, vol. 14, no. 11, pp. 1–15, 2021, doi: 10.3390/ma14112727.

[16] R. Brożek, E. Paszyńska, R. Koczorowski, and B. Dorocka-Bobkowska, "Wchłanianie wody przez wybrane materiały polimerowe, stosowane w stałych i ruchomych protezach zębowych — badania eksperymentalne," *Dent. Forum*, vol. 46, no. 1, pp. 25–30, 2018, doi: 10.20883/df.2018.3.

[17] P. K. VALLITTU, "The effect of void space and polymerization time on transverse strength of acrylic-glass fibre composite," *J. Oral Rehabil.*, vol. 22, no. 4, pp. 257–261, 1995, doi: 10.1111/j.1365-2842.1995.tb00083.x.

[18] M. Braden, E. E. Causton, and R. L. Clarke, "Diffusion of Water in Composite Filling Materials," *J. Dent. Res.*, vol. 55, no. 5, pp. 730–732, 1976, doi: 10.1177/00220345760550050501.

[19] H. Øysæd and I. E. Ruyter, "Water Sorption and Filler Characteristics of Composites for Use in Posterior Teeth," *J. Dent. Res.*, vol. 65, no. 11, pp. 1315–1318, 1986, doi: 10.1177/00220345860650110601.

[20] R. B. Cornelio *et al.*, "The influence of bis-EMA vs bis GMA on the degree of conversion and water susceptibility of experimental composite materials," *Acta Odontol. Scand.*, vol. 72, no. 6, pp. 440–447, 2014, doi: 10.3109/00016357.2013.856467.

[21] S. Xu, *Handbook of Epoxy Blends*. 2016. doi: 10.1007/978-3-319-18158-5.

[22] M. Gyo, T. Nikaido, K. Okada, J. Yamauchi, J. Tagami, and K. Matin, "Surface response of fluorine polymer-incorporated resin composites to cariogenic biofilm adherence," *Appl. Environ. Microbiol.*, vol. 74, no. 5, pp. 1428–1435, 2008, doi: 10.1128/AEM.02039-07.

[23] M. Sowa, A. Przekora, and K. Pałka, "Microstructure and surface free energy of light-cured dental composites after their modification with liquid rubber," *Eng. Biomater.*, vol. 2022, no. 164, pp. 9–15, May 2022, doi: 10.34821/eng.biomat.164.2022.9-15.