MICROSTRUCTURE AND SURFACE FREE ENERGY OF LIGHT-CURED DENTAL COMPOSITES AFTER THEIR MODIFICATION WITH LIQUID RUBBER

Monika Sowa[1] , Agata Przekora[2] ,
Krzysztof Pałka[1]*

[1] Lublin University of Technology,
Faculty of Mechanical Engineering,
Nadbystrzycka 36, 20-618 Lublin, Poland
[2] Medical University of Lublin,
Independent Unit of Tissue Engineering
and Regenerative Medicine,
Chodzki 1, 20-093 Lublin, Poland
*e-mail: k.palka@pollub.pl

Abstract

The use of liquid rubber as a component of light-cured dental composites is one of the methods of increasing their fracture toughness. It also reduces polymerization shrinkage and offers the potential to lower water sorption. The aim of the study was to evaluate the miscibility of liquid rubber in composite matrix resins as well as changes in the wettability and surface free energy (SFE) values of commercial light-curing composites after their modification with liquid rubber. The research materials were Flow Art and Boston (Arkona) light-cured composites and resin mixtures used in their production. Liquid rubber Hypro 2000X168LC VTB (Huntsman Int.) was used as a modifier. The solubility of liquid rubber was assessed under light microscopy. The contact angle and SFE measurements were made on a DSA30 goniometer (Kruss) using water and diiodomethane. It was found that the liquid rubber solubility depended mainly on the viscosity of the resin, which was related to the amount of BisGMA. The resulting mixture showed good temporal stability without larger domains. The curing process released the liquid rubber as a separate phase formed as spherical domains. The morphology of these domains was homogeneous and their size did not exceed 50 µm in diameter. The presence of liquid rubber in modified composites increased their hydrophobicity and reduced the surface free energy value. The obtained properties might help to reduce the formation of bacterial biofilm on dental fillings.

Keywords: dental composite, solubility, liquid rubber, wettability, surface free energy

Introduction

Light-cured polymer-ceramic composites used in dentistry are among the most commonly used biomaterials in the human body. Currently, dental composites account for about 70% of all dental fillings [1]. These materials, made of a polymer matrix reinforced with organic or inorganic mineral or mixed particles of various sizes and shapes, are characterized by good mechanical properties and Young's modulus close to the value of tooth tissue [2]. Since the invention of the BisGMA monomer by Rafael Bowen in 1962, they have become the main direction of development in conservative dentistry, gradually replacing amalgams, silicon cement, and noble metal fillings [3]. The widespread use of composites based on light-curing resins is primarily implied by their good wear resistance, which determines their durability, moreover, the ease of forming and application, or the natural color-matched to the teeth [1].

The properties of dental composites result from their composition. Their matrix is a mixture of methacrylate resins, most often BisGMA, BisEMA, TEGDMA, and UDMA. The size of the reinforcement particle has been reduced over the years until it reached nanometric dimensions to achieve better properties [4]. Apart from changes in the amount and shape of particles and their surface treatment, alterations were also made in the structure or chemistry of the monomer used and the dynamics of the polymerization reaction [5]. Despite many years of development, light-cured dental composites are still not free of disadvantages. Their durability is limited under *in vivo* conditions, which results in a relatively short period of replacement of the filling and causes additional loss of tooth tissue. Despite the improvements, several clinically negative effects of using light-cured composite fillings are still observed, e.g., marginal leakage [6], discolorations [7], cusp fractures [8], unbonding, lack of marginal integrity [9], secondary caries [10,11], postoperative sensitivity or pain [12]. These effects are often associated with polymerization shrinkage stress [9], although there is little clinical evidence to support a clear relationship between these effects [13]. As a result, the above-mentioned disadvantages cause the unwavering interest of the scientific community for medical, technical, and economic reasons.

Research is constantly underway to improve the properties of composites. There are many methods of boosting their mechanical properties, including the use of spherical-shaped reinforcement particles [14], whiskers [15], or glass fibers [16]. Along with the increasing proportion of the ceramic reinforcing phase, a decrease in polymerization shrinkage and an increase in the hardness and strength of these composites were observed, however, most often at the expense of fracture toughness [17]. Reduction of polymerization shrinkage can be achieved, among others, by controlling the proportions of the matrix components [18] and its modification with liquid rubber [19]. The potential increase in the fracture toughness of composites is also possible due to the modification of matrix resins by introducing liquid rubber [20-23]. These modifiers may be, for example, low molecular weight butadiene [24] and butadiene-styrene rubbers [22]. Recent work has also shown an increase in the strength of resins for dental applications due to the use of polybutadiene/bisphenol A copolymers [22]. Poly(butadiene-acrylonitrile-acrylic acid) terpolymer with methacrylate functional groups with good solubility in BisGMA resin caused a 25% increase in fracture toughness and an increase in hydrolytic resistance [21]. This solution uses a copolymer made with the use of acrylic acid, which is, unfortunately, a toxic component also showing a carcinogenic effect [25].

The presence of liquid rubber in the matrix of dental composites, in addition to potentially reducing shrinkage and improving mechanical properties, may also have a positive effect on the hydrophobic and biological properties. Work [26] on bone cement with a modified poly(ethyl methacrylate) matrix with n-butyl(PEMA-nBMA) reinforced with hydroxyapatite showed a reduction in water sorption. In addition, such a modification of the cement matrix reduced the value of the modulus of elasticity and increased its plasticity, which favors the reduction of contact stresses and limits cracking. The hydrophobicity of dental composites enhances protection against hydrolytic degradation [27], bacterial film formation [28], and the resulting biodegradation [29].

This study aims to evaluate the miscibility of liquid rubber in composite matrix resins as well as changes in wettability and the value of surface free energy (SFE) of commercial light-curing composites after their modification with liquid rubber.

Materials and Methods

The variety of dental work requires the use of materials of different viscosities. Therefore, two groups of dental composites were tested: flow type and condensable composites. Commercial light-cured composites Flow-Art (flow type) and Boston (condensable) produced by Arkona Laboratory of Dental Pharmacology in Nasutów were used as control materials. Flow-Art is a micro-hybrid composite consisting of a dimethacrylate organic matrix (BisGMA, UDMA, TEGDMA, EBADMA), reinforced with inorganic particles in the amount of approx. 60% by weight. (barium-aluminum-silicon glass, pyrogenic silica) and additional substances (photoinitiator, co-initiator, inhibitor, stabilizers, pigments). Boston is a micro-hybrid light-cured composite. Its matrix is the same mixture of resins as in the case of Flow-Art but with different proportions of components, thanks to which this resin has a lower viscosity, and therefore it is optimized for mixing with a higher amount of reinforcement. The reinforcement of the Boston composite consists of 78 wt% barium-aluminum-silica glass and pyrogenic silica. The composition of the above-mentioned commercial composites is proprietary by the manufacturer and, for confidentiality reasons, it is not presented in detail here.

All composites were made by Arkona based on Polish patent no. 238167.

The research material consisted of analogous composites (flow and condensable type), in which the matrix resin was modified with liquid rubber in an amount of 5% by weight to the resin. Synthetic nitrile-free polybutadiene rubber Hypro 2000X168LC VTB (CAS 68649-04-7; Huntsman International LLC, USA) was used [30]. The liquid rubber was characterized by a relatively light color (4 on the Gardner scale), which did not affect the shade of the final product. The following samples marks were used:
- F – Flow Art composite,
- FM – Flow Art composite modified with liquid rubber,
- B – Boston composite
- BM – Boston composite modified with liquid rubber

For the miscibility tests, resin blends used in commercial Flow-Art and Boston materials containing a package of additional ingredients (initiator, stabilizer, inhibitor) were used. The following resin designations were used:
- resin F - the resin used in the Flow-Art composite, and
- resin B - used in the Boston composite.

The viscosities of these resins, determined at 23°C, were 12 Pa·s for resin F and 7 Pa·s for resin B. The portions of the resins were mechanically mixed with the rubber in predetermined weight proportions in a darkened room, preventing the material from curing. Evaluation of the miscibility and stability of the mixture was performed with a light microscope (Eclipse MA200, Nikon, Japan). Undissolved liquid rubber formed a separate phase in the liquid resin mixture. The samples were placed on a microscopic glass slide with spacers at the edges to ensure a resin layer thickness of 20 µm. Having covered the slide with the applied sample with a coverslip, the desired thickness of the specimen was obtained. Observations were made in the yellow-transmitted light. The first images were taken immediately after mixing the resin with the rubber, while the next images after 1 and 24 h, securing the material against curing. The final images were taken after curing with a LED lamp with an intensity of 1400 mW/cm^2 for 20 s (Cromalux LED 1200, Mega-PHYSIK GmbH & Co., Germany). After curing, the presence of the second phase was also observed.

The composite samples for the contact angle Θ and surface free energy (SFE) γ_S measurements were prepared as discs of 15 mm in diameter and 1 mm in height according to the ISO 4049 standard. The measurements mentioned above were carried out using the sessile drop technique on a DSA30 goniometer (Kruss, Germany) using type I ultrapure water (obtained from Milli-Q® system, Merck Millipore) and diiodomethane (Sigma Aldrich Chemicals) as polar and non-polar liquid, respectively. The liquid droplets were dosed at 2 µL. The samples were tested 24 h after polymerization (dry stored) as well as after 24 h incubation in distilled water as simulations of the oral environment to evaluate changes in surface properties under the influence of the aqueous environment. Surface free energy and its components, polar γ_S^P and dispersion γ_S^D, were determined based on the Owens-Wendt method [31]. For each type of the material, four samples were prepared and at least five measurements were taken (N > 20).

The results were assessed for statistically significant differences between the mean values using the Student's t-test for independent samples, with the Statistica software (TIBCO Software Inc.) at the significance level α <0.05.

Results and Discussions

The microscopic observation of the resins without modification showed their complete homogeneity, with no inclusions or foreign phases present. The curing process did not change the morphology of these resins either.

The effects of mixing resins with liquid rubber and their time stability are shown in FIG. 1. The components formed a homogeneous system immediately after mixing. Over time, spherical domains of rubber with diameters ranging from less than 1 µm to approx. 10 µm were released from the system. For resin B (with lower viscosity), rubber dissolution was initially observed, followed by the release of domains. Additional studies revealed that the solubility limit of liquid rubber in this resin was about 4%. After the liquid rubber was mixed with resin F, which was characterized by a higher viscosity, the domains of a slightly larger size than those released in resin B were observed. After 24 h in resin F, the formation of larger domains was observed by joining the smaller precipitates. In both resins, the morphology of the liquid rubber showed a homogeneous distribution over the entire volume.
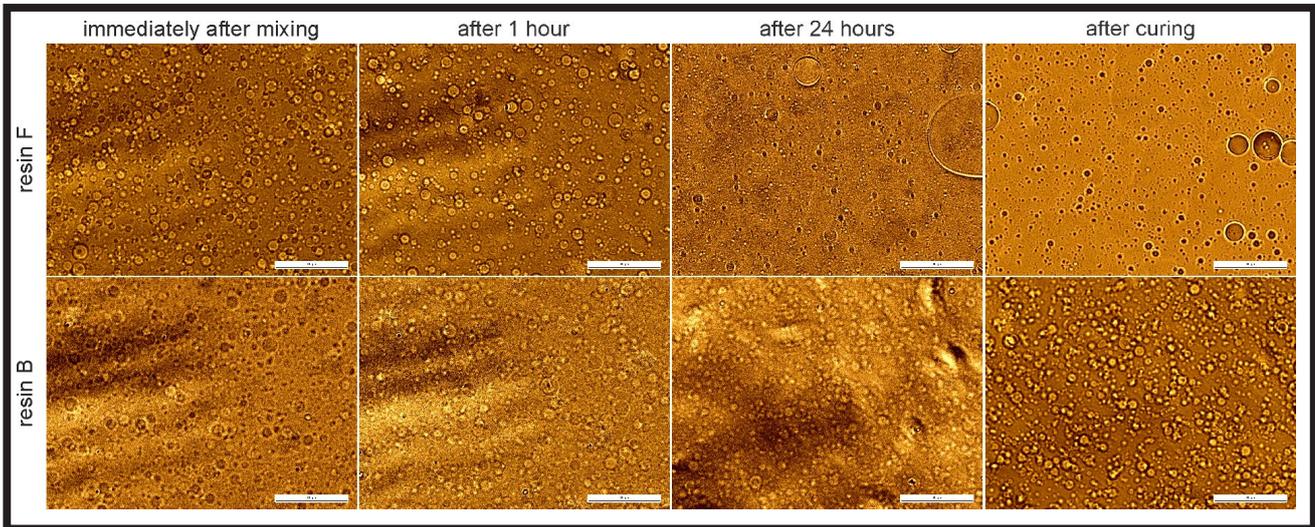
FIG. 1. Solubility and morphology of liquid rubber domains in the tested resins (scale bars 100 μm).
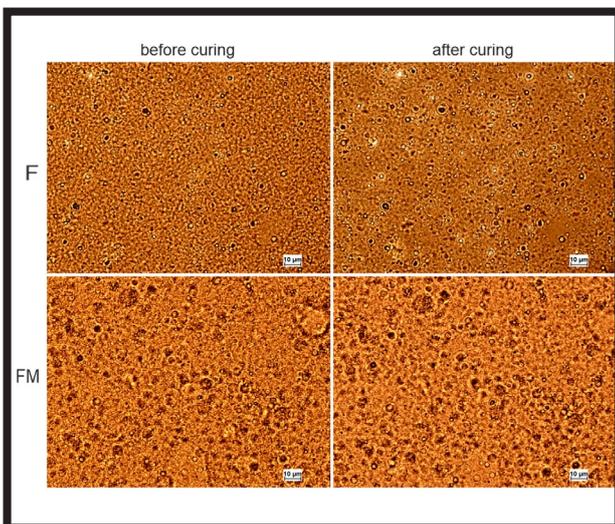

FIG. 2. Microstructures of F and FM composites before and after curing.
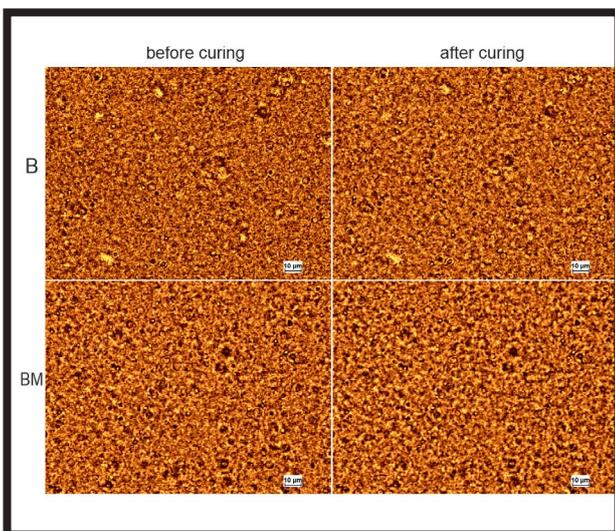

FIG. 3. Microstructures of B and BM composites before and after curing.

The mixture of liquid rubber in the resins, especially those with higher viscosity, did not show satisfactory stability as the domains of large size were formed. It was observed in two-component systems (resin - liquid rubber), while in multicomponent systems (resin - liquid rubber - ceramic particles) higher stability was noted, as a result of higher size reduction of the domains due to mixing and blocking their movement in the presence of particles.

The microstructure of flow-type composites before and after polymerization is shown in FIG. 2. In the case of a composite without modification, fine reinforcement particles were visible, including translucent ceramic particles visible due to illumination. The material microstructure was homogeneous, the reinforcement was evenly distributed without clusters or agglomerates. Polymerization did not change the appearance of the microstructure. The composites after modification with liquid rubber also showed homogeneous structure without the clusters of reinforcement particles. However, after the modification, the composite microstructure changed, i.e. a large number of round (probably spherical) domains (marked with arrows in the figure) with a diameter of approx. 1-2 μm appeared.

The reinforcement particles located inside the domains were also observed as a result of good wetting and compatibility of liquid rubber with silica reinforcement [30]. The curing process caused the formation of "shells" resulting from a change in optical properties, as well as possible deformation of the rubber due to the polymerization shrinkage of the resin. Comparing the domains before and after curing, it could be stated that there were no noticeable differences in their sizes, yet their optical properties changed - after curing they were much darker. In some areas, the domains were not visible before curing. However, after curing, round rubber domains were revealed due to the release of the second phase or the domains being pushed out of the deeper layers of the composite, in consequence of viscosity changes during curing or polymerization shrinkage.

The microstructure of the condensable composite B (FIG. 3) showed high uniformity of ceramic phase dispersion; there were no clusters and agglomerates. Larger particles as brighter spots were visible. The curing process, similarly to the case of composite F, did not significantly change the appearance of the microstructure. In composite B, there were also visible "shells" formed around the reinforcement particles, caused by changes in the optical properties of the resin due to the generated stresses and polymerization shrinkage, and changes in the resin viscosity during polymerization.

Images of liquid drops on the surface of tested materials, which were the basis for the measurement of the contact angle and SFE, are shown in FIG. 4, and after the 24 h incubation in water, in FIG. 5.

The results of the contact angle measurements together with the value of the surface free energy and its components: dispersion and polar, are presented in TABLE 1 and FIG. 6.

The results of the measurement of contact angles for composite surfaces were consistent with those obtained by Rüttermann S. et al. [32]. All the tested materials showed hydrophilic surface properties ($\Theta < 90°$ [19]). Modification of both types of composites significantly increased the water's contact angle, but it still remained at a level below 90°. The reasons for the hydrophobicity increase of the rubber-modified composites should be seen in the change of surface topography (increased roughness), as well as in physicochemical factors. Bis-GMA resin, as the main component of the composite' matrix, has polar hydroxyl groups [33], while liquid rubber is non-polar [34], which will increase the contact angle.

Following the presumptions contained in the article [35] it was found that the increase in the micro-roughness of the composites surface after modification may result from a different morphology of the reinforcement in the matrix due to the presence of liquid rubber whose properties are different from the properties of the rest of the resin matrix. Nanosized particles may preferentially be placed in the rubber domains, thus causing changes in the micro-roughness. Such a location of the reinforcement particles in the rubber domains was confirmed by additional microscopic observations (not presented here).

After the incubation, a statistically significant reduction in the water's contact angle value was observed for the FM material, while the BM became significantly more hydrophobic. Lower values of contact angles after incubation in water indicated an increase in hydrophilicity, which might be related to the formation of bridged hydrogen bonds between the absorbed water and the composite surface [32].
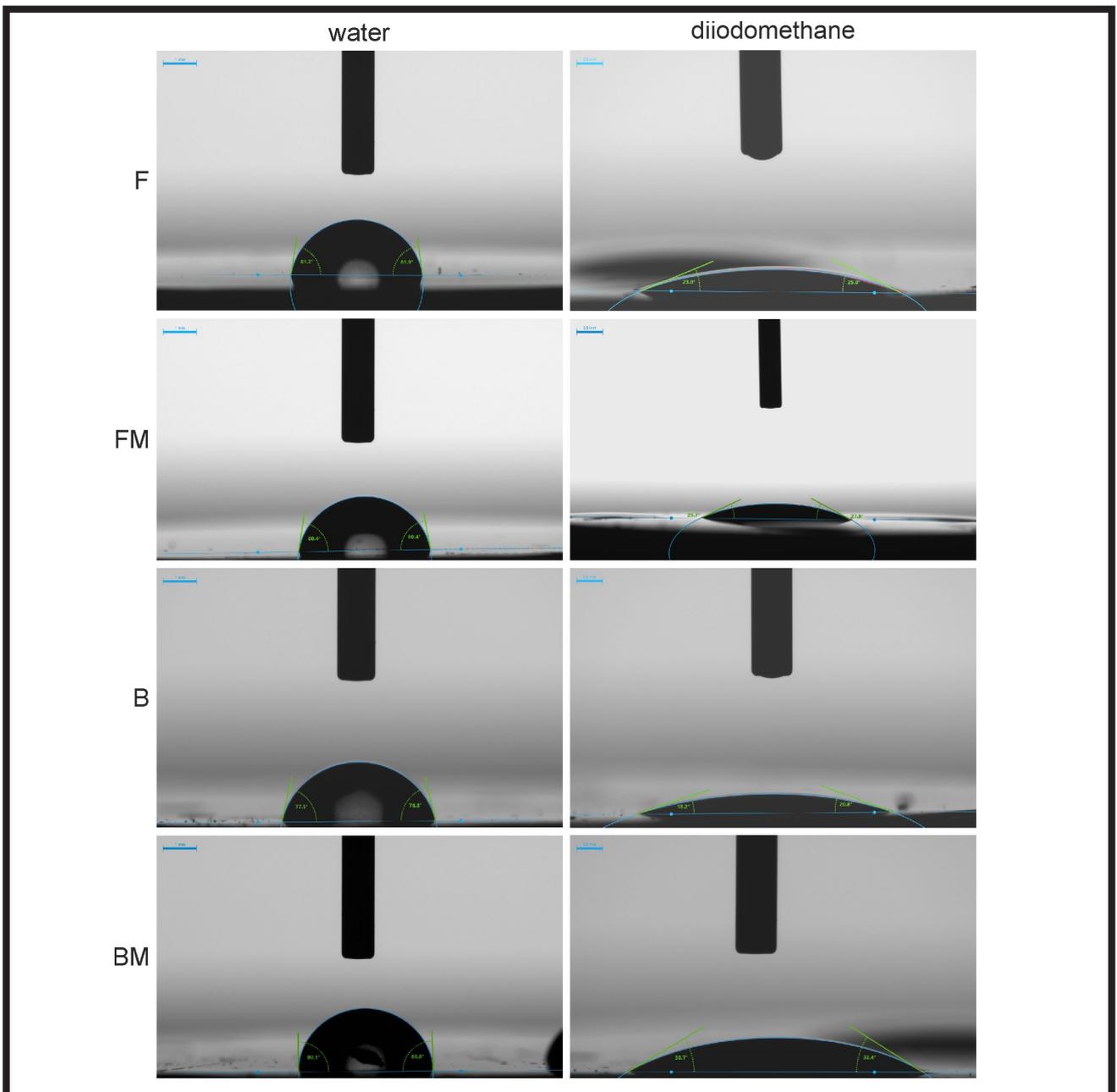

FIG. 4. Representative images of liquid droplets on the surfaces of the tested materials after curing.
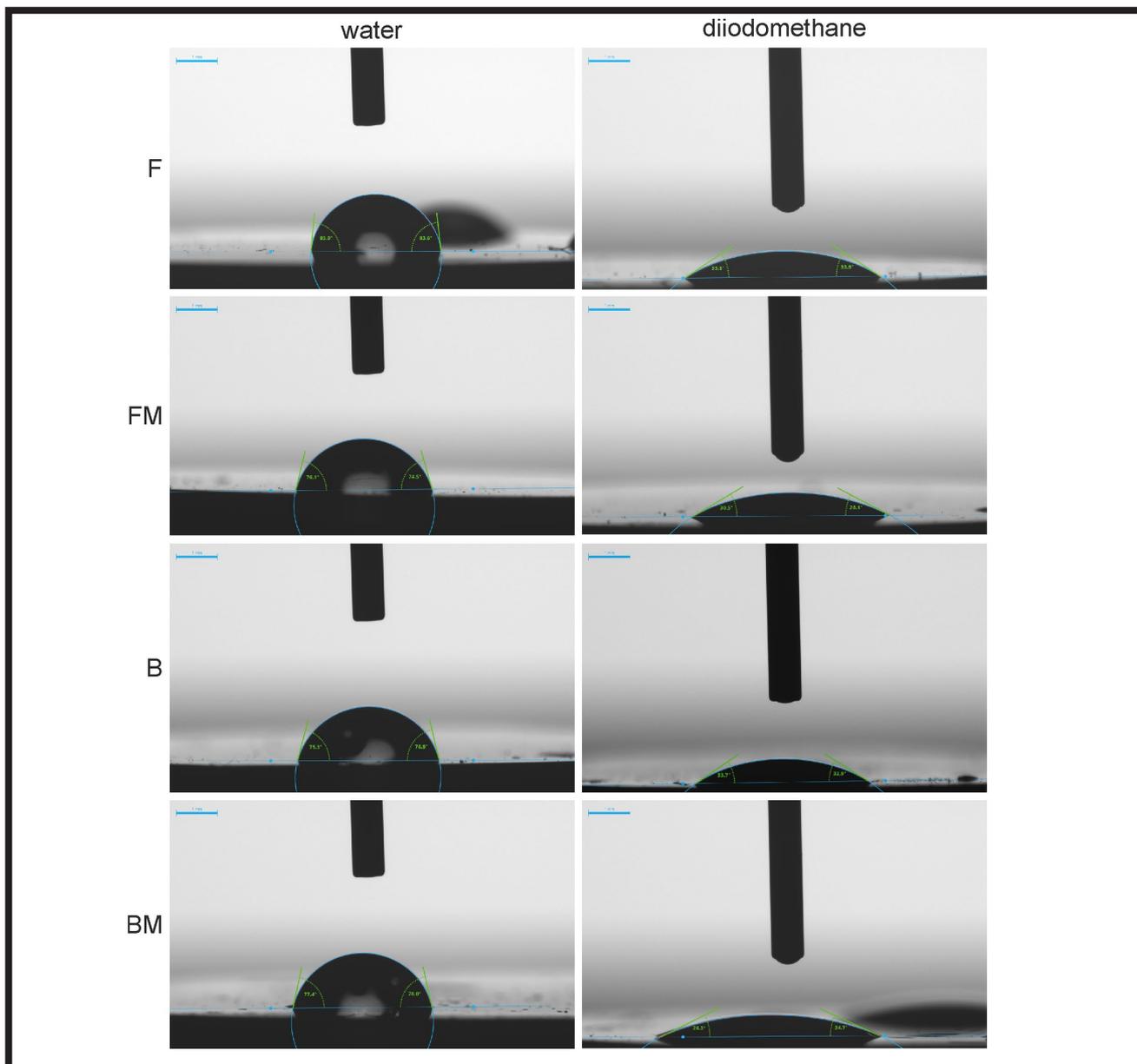
FIG. 5. Representative images of liquid droplets on the surfaces of tested materials after curing and 24 h of incubation in distilled water.

TABLE 1. Summary of the measurement results of the contact angle and surface free energy of the tested composites immediately after polymerization and after 24 h incubation in distilled water. The indices at the Θ angles for water and SFE mean statistically significant differences between the determined values.

Composites	F	FM	B	BM
after curing				
contact angle (water) Θ [deg]	78.62 ± 2.48 [1]	81.98 ± 2.74 [1,2]	75.39 ± 1.51 [3]	77.23 ± 1.92 [3,4]
contact angle (diiodomethane) Θ [deg]	23.55 ± 1.64	23.68 ± 3.15	25.26 ± 2.20	20.08 ± 1.24
Dispersive component of surface energy [mJ/m²]	46.66 ± 0.56	46.61 ± 1.07	47.76 ± 0.37	46.06 ± 1.27
Polar component of surface energy [mJ/m²]	2.68 ± 0.71	1.81 ± 0.66	2.91 ± 0.57	3.79 ± 0.53
SFE [mJ/m²]	**49.33 ± 1.27** [a]	**48.42 ± 1.74**	**50.67 ± 0.94** [c]	**49.84 ± 1.74** [e]
after 24 h of incubation In distilled water				
contact angle (water) Θ [deg]	78.24 ± 4.68	78.17 ± 2.10 [2]	75.44 ± 2.32 [3,5]	83.77 ± 3.05 [4,5]
contact angle (diiodomethane) Θ [deg]	33.34 ± 2.54	28.48 ± 2.37	29.97 ± 3.07	27.78 ± 2.69
Dispersive component of surface energy [mJ/m²]	42.78 ± 1.14	44.84 ± 0.94	44.23 ± 0.79	45.12 ± 1.05
Polar component of surface energy [mJ/m²]	3.46 ± 1.53	3.11 ± 0.66	4.12 ± 0.85	1.58 ± 0.69
SFE [mJ/m²]	**46.24 ± 1.67** [a,b]	**47.95 ± 1.61** [b]	**48.36 ± 1.12** [c,d]	**46.70 ± 1.32** [d,e]
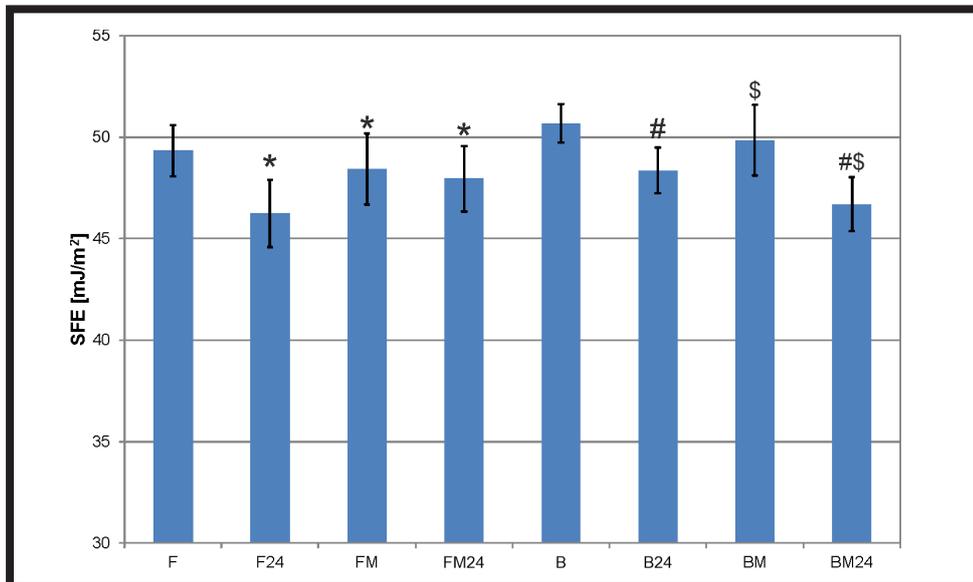
FIG. 6. Summary of SFE measurement results for materials without and after 24 h of incubation in distilled water (the number 24 in the sample designation). The symbols (*) indicate statistically significant differences against material F, (#) - against material B, $ - statistically significant difference between materials BM and BM24.

Higher contact angles might be associated with the existence of strong repulsive forces between the surface and the absorbed water molecules. This could create a thin and even more hydrophobic layer above the surface of the water-saturated material. This layer might be a surface that can be damaged by abrasion but also renewed during the service life of the filling.

The values of the surface free energy γ_s for the tested materials before and after incubation in water, along with the statistically significant differences, are presented in FIG. 6. A statistically significant decrease in the SFE value was noted in the case of composite FM when comparing to F, from 49.33 to 48.42 mJ/m^2. Composite B achieved a higher SFE value compared to F composite, however, similar to BM and FM composites, which indicated the effect of a higher amount of reinforcement. Composite BM showed lower values of SFE than the composite B ones, yet the differences did not show statistical significance. The incubation in water significantly lowered the surface free energy values for all the tested materials. Importantly, in all the tested composites, the dispersion component has a decisive share in the surface free energy value, which means a higher adhesive affinity for non-polar substances. Similar dependencies were revealed by Rüttermann et al. [32]. For FM composite, the value of this component decreased by 32% compared to the F one. On the other hand, an increase in the polar component value was achieved for BM composite.

The obtained results of γ_s presented higher values than those reported in the studies [32,36]. An increase in surface free energy was related to a different composition of resins and reinforcement; it might also suggest the adhesion reduction resulting in a limited formation of a bacterial film.

An increase in the wettability or free energy of the surface of dental fillings is an important factor contributing to the plaque formation on dental materials [37]. Many studies on dental composites wettability indicated that hydrophobic surfaces have a lower potential for bacterial colonization [38]. Thus, the materials for dental fillings should have good wettability to the bonding system to ensure the required adhesion of the joint, while the outer surface should show low wettability to prevent bacterial adhesion.

Thus, the modification of dental composites with liquid rubber favored their hydrophobicity and lowered the surface free energy value. It is particularly important in terms of reducing the possibility of colonization of such modified fillings by bacteria.

Conclusions

The miscibility of Hypro 2000X168LC liquid rubber with the blend of methacrylate resins was limited by their composition and viscosity. However, regardless of miscibility, the curing process released the liquid rubber as a separate phase in the form of spherical domains. The morphology of these domains was homogeneous, and their size did not exceed 50 µm in diameter.

The presence of liquid rubber in modified composites increased their hydrophobicity and reduced the value of surface free energy. The obtained properties might reduce the formation of bacterial biofilm on the dental fillings, while the adhesion to the bonding system might strengthen the bond between the filling and the tooth tissues. A tendency to limit water sorption as a result of liquid rubber modification was also observed.

Acknowledgements

ORCID iD

M. Sowa: https://orcid.org/0000-0001-5784-3701
A. Przekora: https://orcid.org/0000-0002-6076-1309
K. Pałka: https://orcid.org/0000-0003-4920-4613

References

[1] Bociong K., Krasowski M., Domarecka M., Sokołowski J.: Wpływ metody fotopolimeryzacji kompozytów stomatologicznych na bazie zywic dimetakrylanowych na naprężenia skurczowe oraz wybrane właściwości utwardzonego materiału. Polimery/Polymers 61 (2016) 499-508.

[2] Pawłowska E., Loba K., Błasiak J., Szczepańska J.: Właściwości i ryzyko stosowania metakrylanu bisfenolu a i dimetakrylanu uretanu - podstawowych monomerów kompozytów stomatologicznych. Dent. Med. Probl. 46 (2009) 477-485.

[3] Schmidseder J., Stomatologia Estetyczna. Wydawnictwo Czelej 2011.

[4] Garoushi S., Lassila L.V.J., Vallittu P.K.: Influence of nanometer scale particulate fillers on some properties of microfilled composite resin. J. Mater. Sci. Mater. Med. 22 (2011) 1645-1651.

[5] Ferracane J.L.: Current trends in dental composites. Crit. Rev. Oral Biol. Med. 6 (1995) 302-318.

[6] Braga R. R., Hilton T.J., Ferracane J.L.: Contraction stress of flowable composite materials and their efficacy as stress-relieving layers. J. Am. Dent. Assoc. 134 (2003) 721-728.

[7] Priyalakshmi S., Ranjan M.: A Review on Marginal Deterioration of Composite Restoration. IOSR J. Dent. Med. Sci. 13 (2014) 06-09.

[8] Fennis W.M.M., Kuijs R.H., Kreulen C.M., Roeters F.J.M., Creugers N.H.J., Burgersdijk R.C.W.: A survey of cusp fractures in a population of general dental practices. Int. J. Prosthodont. 15 (2002) 559-63.

[9] Ferracane J.L., Mitchem J.C.: Relationship between composite contraction stress and leakage in Class V cavities. Am. J. Dent. 16 (2003) 239-243.

[10] Ferracane J.L.: Models of Caries Formation around Dental Composite Restorations. J. Dent. Res. 96 (2017) 364-371.

[11] Kuper N.K., Van De Sande F.H., Opdam N.J.M., Bronkhorst E.M., De Soet J.J., Cenci M.S., Huysmans M.C.D.J.N.M.: Restoration materials and secondary caries using an in vitro biofilm model. J. Dent. Res. 94 (2015) 62-68.

[12] Celerino I.C.C.M.: Post-operative sensitivity in direct resin composite restorations: Clinical practice guidelines. Int. J. Res. Discov. 1 (2012) 1-12.

[13] Ilie N., Hickel R.: Resin composite restorative materials. Aust. Dent. J. 56 (2011) 59-66.

[14] Kim K., Ong J., Okuno O.: The effect of filler loading and morphology on the mechanical properties of contemporary composites. J. Prosthet. Dent. 87 (1992) 642-649.

[15] Xu H.H.K., Quinn J.B., Smith D.T., Giuseppetti A.A., Eichmiller F.C.: Effects of different whiskers on the reinforcement of dental resin composites. Dent. Mater. 19 (2003) 359-367.

[16] Elbishari H., Satterthwaite J., Silikas N.: Effect of filler size and temperature on packing stress and viscosity of resin-composites. Int. J. Mol. Sci. 12 (2011) 5330-5338.

[17] Xu H.H.K.: Dental composite resins containing silica-fused ceramic single-crystalline whiskers with various filler levels. J. Dent. Res. 78 (1999) 1304-1311.

[18] Pałka K., Janiczuk P., Kleczewska J.: Polymerization shrinkage of resin mixtures used in dental composites. Eng. Biomater. 154 (2020) 16-21.

[19] Pałka K.: Polymerization Shrinkage of New Dental Composites Modified With Liquid Rubber. Eng. Biomater. 158 (2020) 19.

[20] Lee V.A., Cardenas H.L., Rawls H.R.: Rubber-toughening of dimethacrylate dental composite resin. J. Biomed. Mater. Res. - Part B Appl. Biomater. 94 (2010) 447-454.

[21] Kerby R.E., Tiba A., Knobloch L.A., Schricker S.R., Tiba O.: Fracture toughness of modified dental resin systems. J. Oral Rehabil. 30 (2003) 780-784.

[22] Matsukawa S., Hayakawa T., Nemoto K.: Development of high-toughness resin for dental applications. Dent. Mater. 10 (1994) 343-346.

[23] Palka K., Kleczewska J., Sasimowski E., Belcarz A., Przekora A.: Improved fracture toughness and conversion degree of resin-based dental composites after modification with liquid rubber. Materials (Basel) 13 (2020) 1-13.

[24] Rodford R.A.: Further development and evaluation of high impact strength denture base materials. J. Dent. 18 (1990) 151-157.

[25] Dusek K., Lednicky F., Lunak S., Mach M., Duskova D.: Toughening of Epoxy Resins With Reactive Polybutadienes., in: Riew C.K., Gillham J.K. (Eds.), Advances in Chemistry Series. Advances in Chemistry (1984) 27-35.

[26] Deb S., Braden M., Bonfield W.: Water absorption characteristics of modified hydroxyapatite bone cements. Biomaterials 16 (1995) 1095-1100.

[27] Sadek F.T., Castellan C.S., Braga R.R., Mai S., Tjäderhane L., Pashley D.H., Tay F.R.: One-year stability of resin-dentin bonds created with a hydrophobic ethanol-wet bonding technique. Dent. Mater. 26 (2010) 380-386.

[28] Pałka K., Miazga-Karska M., Pawłat J., Kleczewska J., Przekora A.: The effect of liquid rubber addition on the physicochemical properties, cytotoxicity and ability to inhibit biofilm formation of dental composites. Materials (Basel) 14 (2021) 1704.

[29] Moussa D.G., Fok A., Aparicio C.: Hydrophobic and antimicrobial dentin: A peptide-based 2-tier protective system for dental resin composite restorations. Acta Biomater. 88 (2019) 251-265.

[30] CVC Thermoset Specialties, Hypro ® 2000X168LC VTB. Technical Bulletin. 2019.

[31] Rudawska A., Jacniacka E.: Analysis for determining surface free energy uncertainty by the Owen-Wendt method. Int. J. Adhes. Adhes. 29 (2009) 451-457.

[32] Rüttermann S., Trellenkamp T., Bergmann N., Raab W.H.M., Ritter H., Janda R.: A new approach to influence contact angle and surface free energy of resin-based dental restorative materials. Acta Biomater. 7 (2011) 1160-1165.

[33] Cornelio R.B., Wikant A., Mjosund H., Kopperud H.M., Haasum J., Gedde U.W., Örtengren U.T.: The influence of bis-EMA vs bis GMA on the degree of conversion and water susceptibility of experimental composite materials. Acta Odontol. Scand. 72 (2014) 440-447.

[34] Xu S.A.: Miscibility and Phase Separation of Epoxy/Rubber Blends, in: Parameswaranpillai J., Hameed N., Pionteck J., Woo E.M. (Eds.), Handbook of Epoxy Blends. Springer International Publishing AG (2017) 68-100.

[35] Sumita M., Sakata K., Asai S., Miyasaka K., Nakagawa H., Dispersion of fillers and the electrical conductivity of polymer blends filled with carbon black. Polym. Bull. 25 (1991) 265-271.

[36] Namen F.M., Ferrandini E., Galan J.: Surface energy and wettability of polymers light-cured by two different systems. J. Appl. Oral Sci. 19 (2011) 517-520.

[37] Ono M., Nikaido T., Iked M., Imai S., Hanada N., Tagami J., Matin K.: Surface properties of resin composite materials relative to biofilm formation. Dent. Mater. J. 26 (2007) 613-622.

[38] Gyo M., Nikaido T., Okada K., Yamauchi J., Tagami J., Matin K.: Surface response of fluorine polymer-incorporated resin composites to cariogenic biofilm adherence. Appl. Environ. Microbiol. 74 (2008) 1428-1435.