



Article

Physicochemical Properties of Novel Copolymers of Quaternary Ammonium UDMA Analogues, Bis-GMA, and TEGDMA

Marta W. Chrószcz-Porebska ¹, Izabela M. Barszczewska-Rybarek ^{1,*} and Grzegorz Chladek ²

¹ Department of Physical Chemistry and Technology of Polymers, Faculty of Chemistry, Silesian University of Technology, Strzody 9 Str., 44-100 Gliwice, Poland; marta.chroszcz@polsl.pl

² Department of Engineering Materials and Biomaterials, Faculty of Mechanical Engineering, Silesian University of Technology, Konarskiego 18A Str., 44-100 Gliwice, Poland; grzegorz.chladek@polsl.pl

* Correspondence: izabela.barszczewska-rybarek@polsl.pl

Abstract: This study aimed to elucidate the physicochemical properties of copolymers comprising 40 wt.% bisphenol A glycerolate dimethacrylate (Bis-GMA), 40 wt.% quaternary ammonium urethane-dimethacrylate analogues (QAUDMA-*m*, where *m* corresponds to the number of carbon atoms in the *N*-alkyl substituent), and 20 wt.% triethylene glycol dimethacrylate (TEGDMA) copolymers (BG:QAm:TEGs). The BG:QAm:TEG liquid monomer compositions and reference compositions (40 wt.% Bis-GMA, 40 wt.% urethane-dimethacrylate (UDMA), 20 wt.% TEGDMA (BG:UD:TEG) and 60 wt.% Bis-GMA, 40 wt.% TEGDMA (BG:TEG)) were characterized in terms of their refractive index (*RI*) and monomer glass transition temperature (T_{g_m}) and then photocured. The resulting copolymers were characterized in terms of the polymer glass transition temperature (T_{g_p}), experimental polymerization shrinkage (S_e), water contact angle (*WCA*), water sorption (*WS*), and water solubility (*SL*). The prepared BG:QAm:TEG liquid monomer compositions had *RI* in the range 1.4997–1.5129, and T_{g_m} in the range -52.22 to -42.12 °C. The BG:QAm:TEG copolymers had T_{g_p} ranging from 42.21 to 50.81 °C, S_e ranging from 5.08 to 6.40%, *WCA* ranging from 81.41 to 99.53°, *WS* ranging from 25.94 to 68.27 $\mu\text{g}/\text{mm}^3$, and *SL* ranging from 5.15 to 5.58 $\mu\text{g}/\text{mm}^3$. Almost all of the developed BG:QAm:TEGs fulfilled the requirements for dental materials (except BG:QA8:TEG and BG:QA10:TEG, whose *WS* values exceeded the 40 $\mu\text{g}/\text{mm}^3$ limit).

Keywords: quaternary ammonium methacrylate; urethane-dimethacrylate analogue; dimethacrylate-based dental material; photocured copolymer; physicochemical property



Citation: Chrószcz-Porebska, M.W.; Barszczewska-Rybarek, I.M.; Chladek, G. Physicochemical Properties of Novel Copolymers of Quaternary Ammonium UDMA Analogues, Bis-GMA, and TEGDMA. *Int. J. Mol. Sci.* **2023**, *24*, 1400. <https://doi.org/10.3390/ijms24021400>

Academic Editors: Jordi Puiggali and Mary Anne Melo

Received: 2 December 2022

Revised: 3 January 2023

Accepted: 9 January 2023

Published: 11 January 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Over the past three decades, quaternary ammonium methacrylates (QAMs) have attracted the attention of scientists in the field of antibacterial dimethacrylate-based dental composites [1,2]. This is due to the fact that QAMs show high antibacterial activity caused by the presence of quaternary ammonium (QA) moieties in their structures. As the QA moiety contains a positively charged quaternary nitrogen atom, it can adsorb on the negatively charged bacteria cell surface. As a result, the long alkyl chain attached to the quaternary nitrogen can interact with the lipid chains in a cell wall and disturb the cell's electric balance. This causes an increase in the bacteria cell osmotic pressure which leads to its death [3]. What is more, QAMs can be permanently embedded into composite matrices via copolymerization of their double bonds with double bonds of other dimethacrylates constituting the composite matrix [4]. Thus, QAMs may offer long-term antibacterial activity [5,6]. Various QAMs have been described in the literature, including 2-(dimethylamino)ethyl methacrylate derivatives with chloride [7–9], bromide [10–15], and iodide [16,17] counter ions, quaternary ammonium derivative of bisphenol A glycerolate dimethacrylate [18], and fully aliphatic [19] and cycloaliphatic [20,21] urethane-dimethacrylates. Such QAMs represent potential antibacterial components of dental composites because they offer high antibacterial activity against various strains, including

Streptococcus mutans [4,5,10,13–15,18,20,21], *Staphylococcus aureus* [5,18], and *Escherichia coli* [18]. However, the well-known QAMs induce a loss of mechanical properties and an increase in the amount of water absorbed by the material and in residual fraction release [4,5,10,13–15,18,19,21,22]. Nevertheless, the field of antibacterial dimethacrylates has continued to evolve, and there are still many possibilities to design new compounds with chemical structures that are suitable for obtaining dental composites with appropriate physicochemical, mechanical, and antibacterial characteristics.

This study provides insights relevant for preparing bioactive dimethacrylate matrices for dental composite restorative materials. Our proposal is based on the utilization of quaternary ammonium urethane-dimethacrylate analogues (QAUDMA-*m*, where *m* is number of carbon atoms in the *N*-alkyl substituent) (Figure 1) [23]. These compounds comprise a 2,2,4-trimethylhexamethylene diisocyanate (TMDI) core and two methacrylate-terminated wings. The quaternary ammonium groups, each substituted with an *N*-alkyl chain of 8, 10, 12, 14, 16, or 18 carbon atoms, are located in the middle of each wing. Because the QAUDMA-*m* monomers were viscous resins with suitable physicochemical parameters (refractive index (*RI*) from 1.50 to 1.52, monomer glass transition temperature (T_{g_m}) from -31 to -15 °C, degree of conversion (*DC*) from 0.53 to 0.78, experimental polymerization shrinkage (S_e) from 1.24 to 2.99%) [23], we evaluated them in the context of their copolymers with common dental dimethacrylates: bisphenol A glycerolate dimethacrylate (Bis-GMA), urethane-dimethacrylate monomer (UDMA), and triethylene glycol dimethacrylate (TEGDMA) (Figure 1).

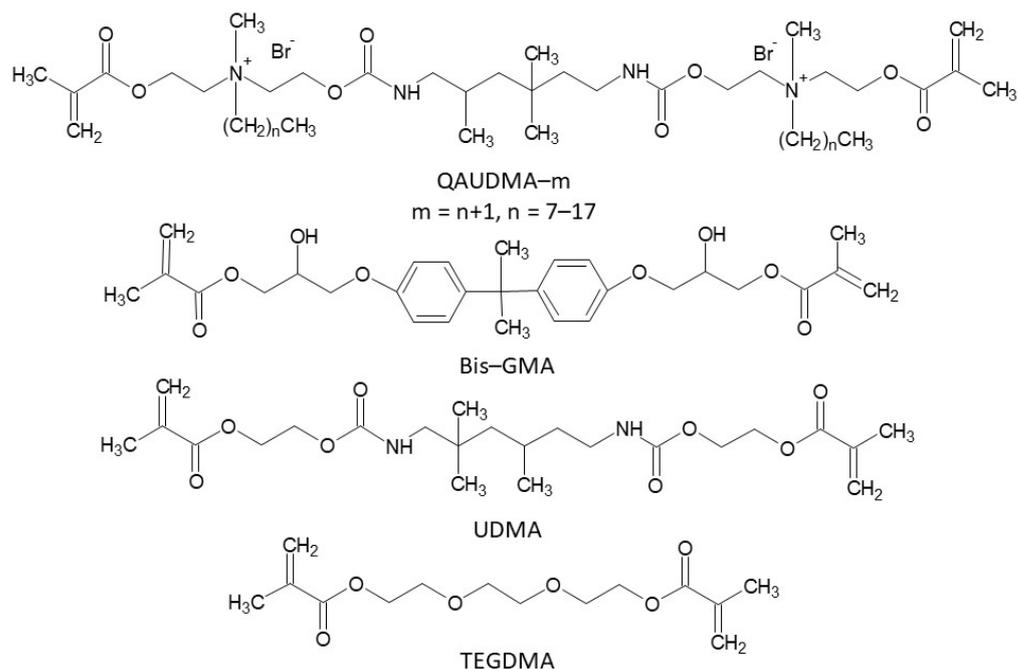


Figure 1. Chemical structures of dimethacrylate monomers used in this study.

First, the physicochemical, mechanical, and antibacterial properties of QAUDMA-*m* copolymers with 40 wt.% TEGDMA (QAm:TEGs) were characterized [24,25]. The uncured QAm:TEGs had appropriate transparency (*RI* from 1.4895 to 1.5001) and molecular mobility (T_{g_m} from -33.82 to -25.84 °C). The QA:TEG copolymers were characterized by low volumetric contraction (S_e from 6.4 to 6.9%), high polymerization efficiency (*DC* from 84.0 to 88.7%), high stiffness (polymer glass transition temperature (T_{g_p}) from 60.33 to 66.32 °C), suitable surface properties (water contact angle (*WCA*) from 82.1 to 98.7°), and high antibacterial activity against *S. aureus* (number of adhered bacteria from 0 (no adhered bacteria) to 4.84 log(CFU/mL), inhibition zone from 6 to 19 mm), and *E. coli* (number of adhered bacteria from 0 (no adhered bacteria) to 3.34 log(CFU/mL), inhibition zone from 6 to 10 mm) [24]. However, they showed excessively high water sorption (*WS* from 116.08 to

148.31 $\mu\text{g}/\text{mm}^3$) and solubility (SL from 12.67 to 52.39 $\mu\text{g}/\text{mm}^3$) [25]. These properties excluded them from potential use as matrices for dental composites.

Therefore, the present study aimed to achieve and characterize the novel copolymers comprising 40 wt.% Bis-GMA, 40 wt.% QAUDMA- m , and 20 wt.% TEGDMA (BG:QAm:TEGs).

Proper functioning and longevity of dental restorations equally depends on the physicochemical properties and mechanical performance. The most important physicochemical properties of dental materials' matrices include (i) DC —which should exceed 0.55 to provide clinical efficacy [26]; (ii) S_e —which should be as low as possible, because the lower the S_e , the narrower the marginal gaps between the reconstruction and adjacent tooth tissue, and therefore, the smaller the area privileged for bacteria growth [27]; (iii) T_{g_p} —which should be higher than 40 °C, ensuring that the material is in a glassy state in a temperature range occurring in the oral cavity [28]; (iv) WS —which should not exceed 40 $\mu\text{g}/\text{mm}^3$ [29], because the excess of water absorbed by the material can cause its swelling and decrease its mechanical properties [30]; and (v) SL —which should not be higher than 7.5 $\mu\text{g}/\text{mm}^3$ [29], because usually, the higher the SL , the lower the mechanical stability of the restoration [31].

Despite the crucial role of the dental composites' physicochemical properties in governing their stability, longevity, and functionality, these aspects are rarely examined. In most cases, studies on dental composite matrices modified with QAMs are only limited to the examination of their antibacterial activity, DC , and mechanical properties.

The aim of this study was the preliminary assessment of the applicability of BG:QAm:TEGs as matrices for dental dimethacrylate-based composites from the perspective of their physicochemical properties. These evaluations were based on measurements of the RI and T_{g_m} of liquid monomer compositions and the T_{g_p} , S_e , theoretical polymerization shrinkage (S_t), WCA , WS , and SL of corresponding copolymers. The DC [32] was also discussed.

2. Results

In this study, eight compositions of dimethacrylate monomers were prepared. Six of them consisted of 40 wt.% Bis-GMA, 40 wt.% QAUDMA- m , and 20 wt.% TEGDMA (BG:QAm:TEGs). For comparison, the 40 wt.% Bis-GMA, 40 wt.% UDMA, 20 wt.% TEGDMA (BG:UD:TEG), 60 wt.% Bis-GMA, and 40 wt.% TEGDMA (BG:TEG) compositions were also prepared. Liquid monomers were characterized in terms of density (d_m), RI , and T_{g_m} , and the corresponding polymers were characterized in terms of density (d_p), S_t , S_e , T_{g_p} , WCA , WS , and SL .

In the BG:QAm:TEG notation, the m still corresponds to the number of carbon atoms in the N -alkyl substituent. Later, C_m is used to denote the length of the N -alkyl substituent in QAUDMA- m and BG:QAm:TEG.

2.1. Properties of Liquid Monomer Compositions

Table 1 summarizes the RI and d_m values of the studied liquid monomer compositions.

The RI of BG:QAm:TEGs ranged from 1.4982 to 1.5129. The BG:QAm:TEGs with C_m of C8 and C10 had lower RI than BG:TEG ($RI = 1.5048$) ($p \leq 0.05$), while BG:QAm:TEGs with C_m from C12 to C18 had higher RI ($p \leq 0.05$). The BG:QAm:TEGs with C_m of C12 and C14 had RI values similar to that of BG:UD:TEG ($RI = 1.5127$; $p > 0.05$), whereas the RI values of the remaining BG:QAm:TEGs were lower than those of BG:UD:TEG ($p \leq 0.05$).

The d_m of BG:QAm:TEGs ranged from 1.099 to 1.154 g/cm^3 and decreased as C_m increased. Specifically, BG:QAm:TEGs with C_m from C8 to C12 had higher d_m values than the reference copolymers ($d_{m\text{BG:UD:TEG}} = 1.115 \text{ g}/\text{cm}^3$, $d_{m\text{BG:TEG}} = 1.102 \text{ g}/\text{cm}^3$) ($p \leq 0.05$), whereas the remaining BG:QAm:TEGs had d_m values similar to the reference copolymers ($p > 0.05$).

Table 1. The properties of studied monomer compositions: the length of the *N*-alkyl substituent in QAUDMA-*m* (C_m), molecular weight (MW), double-bond concentration (x_{DB}), refractive index (RI), and density (d_m). Lowercase letters indicate statistically insignificant differences with a column ($p > 0.05$, non-parametric Wilcoxon test).

Sample Name	C_m	MW (g/mol)	x_{DB} (kg/mol)	RI ¹	d_m (g/cm ³)	
					Average	SD
BG:QA8:TEG	C8	528.74	3.78	1.4997	1.154	0.005
BG:QA10:TEG	C10	535.11	3.74	1.4982	1.142	0.006
BG:QA12:TEG	C12	540.95	3.70	1.5128 ^{a,b}	1.127	0.005
BG:QA14:TEG	C14	546.33	3.66	1.5129 ^{a,c}	1.116 ^{a-d}	0.007
BG:QA16:TEG	C16	551.29	3.63	1.5099	1.113 ^{a,e-g}	0.010
BG:QA18:TEG	C18	555.89	3.60	1.5097	1.099 ^{b,e,h,i}	0.013
BG:UD:TEG	-	389.27	5.14	1.5127 ^{b,c}	1.115 ^{c,f,h}	0.007
BG:TEG	-	429.39	4.66	1.5048	1.102 ^{d,g,i}	0.005

¹ The standard deviation of RI was 0.0001 in each case.

The T_{g_m} of BG:QAm:TEGs ranged from -52.22 to -42.12 °C and decreased as C_m increased. Almost all of the investigated BG:QAm:TEGs had lower T_{g_m} than BG:UD:TEG ($T_{g_m} = -44.89$ °C) ($p \leq 0.05$), except BG:QA10:TEG and BG:QA8:TEG. BG:QA10:TEG had a similar T_{g_m} ($p > 0.05$), whereas BG:QA8:TEG had a higher T_{g_m} ($p \leq 0.05$) compared with that of BG:UD:TEG. All BG:QAm:TEGs had higher T_{g_m} than BG:TEG ($T_{g_m} = -56.45$ °C) ($p \leq 0.05$). Representative differential scanning calorimetry (DSC) thermograms of liquid monomer compositions are shown in Figure 2.

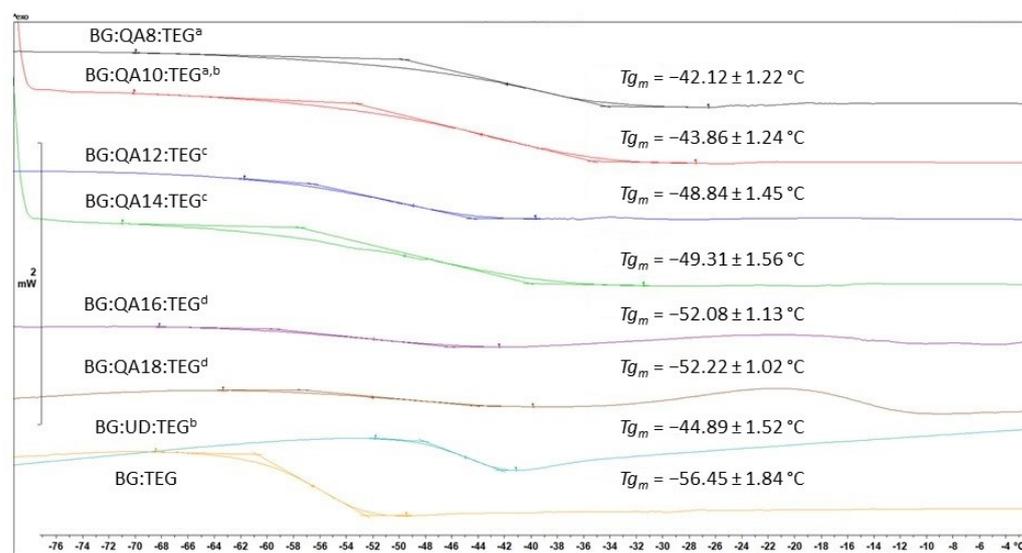


Figure 2. Results of DSC experiments involving the investigated liquid monomer compositions, revealing their glass transition temperatures. Lowercase letters indicate statistically insignificant differences ($p > 0.05$, non-parametric Wilcoxon test).

2.2. Properties of Copolymers

Table 2 summarizes the d_p , S_t , and S_e of the studied copolymers.

The d_p of BG:QAm:TEGs ranged from 1.174 to 1.216 g/cm³ and decreased as the C_m increased. BG:QA8:TEG had a higher d_p than BG:TEG ($d_p = 1.206$ g/cm³) ($p \leq 0.05$), while BG:QA10:TEG and BG:QA12:TEG had d_p values similar to that of BG:TEG ($p > 0.05$). The remaining BG:QAm:TEGs had d_p values lower than those of BG:TEG ($p \leq 0.05$). The BG:QAm:TEGs generally had lower d_p than BG:UD:TEG ($d_p = 1.215$ g/cm³) ($p \leq 0.05$), except for BG:QA8:TEG, which had a similar d_p ($p > 0.05$).

Table 2. The properties of studied copolymers: density (d_p), experimental (S_e), and theoretical (S_t) polymerization shrinkages, and degree of conversion (DC). Lowercase letters indicate statistically insignificant differences with a column ($p > 0.05$, non-parametric Wilcoxon test).

Sample Name	d_p (g/cm ³)		S_e (%)		S_t (%)	DC [32]
	Average	SD	Average	SD		
BG:QA8:TEG	1.216 ^a	0.007	5.08	0.40	9.81	0.59
BG:QA10:TEG	1.208 ^b	0.004	5.48 ^a	0.37	9.60	0.60
BG:QA12:TEG	1.200 ^c	0.002	6.07 ^{a–d}	0.49	9.38	0.61
BG:QA14:TEG	1.189 ^d	0.002	6.14 ^{b,e,f}	0.41	9.18	0.63
BG:QA16:TEG	1.186 ^d	0.005	6.24 ^{c,e,g}	0.54	9.04	0.66
BG:QA18:TEG	1.174	0.004	6.40 ^{d,f,g}	0.48	8.90	0.68
BG:UD:TEG	1.215 ^a	0.002	8.35 ^h	0.23	12.90	0.64
BG:TEG	1.206 ^{b,c}	0.003	8.07 ^h	0.80	11.61	0.68

The S_t of BG:QAm:TEGs ranged from 8.90% to 9.81% and decreased as the C_m increased. All of the studied BG:QAm:TEGs had lower S_t values compared with the reference samples ($S_{tBG:UD:TEG} = 12.90\%$, $S_{tBG:TEG} = 11.61\%$) ($p \leq 0.05$). The opposite relationship was observed for S_e . Specifically, the S_e of BG:QAm:TEGs ranged from 5.08% to 6.40% and increased as the C_m increased. Compared with the reference samples ($S_{eBG:UD:TEG} = 8.35\%$, $S_{eBG:TEG} = 8.07\%$), all of the studied BG:QAm:TEGs had lower S_e ($p \leq 0.05$).

The Tg_p of BG:QAm:TEGs ranged from 42.21 to 50.81 °C and increased as the C_m increased. All of the studied BG:QAm:TEGs had lower Tg_p values compared with the reference copolymers ($Tg_{pBG:UD:TEG} = 55.90$ °C, $Tg_{pBG:TEG} = 61.46$ °C) ($p \leq 0.05$). Representative DSC thermograms of the copolymers are shown in Figure 3.

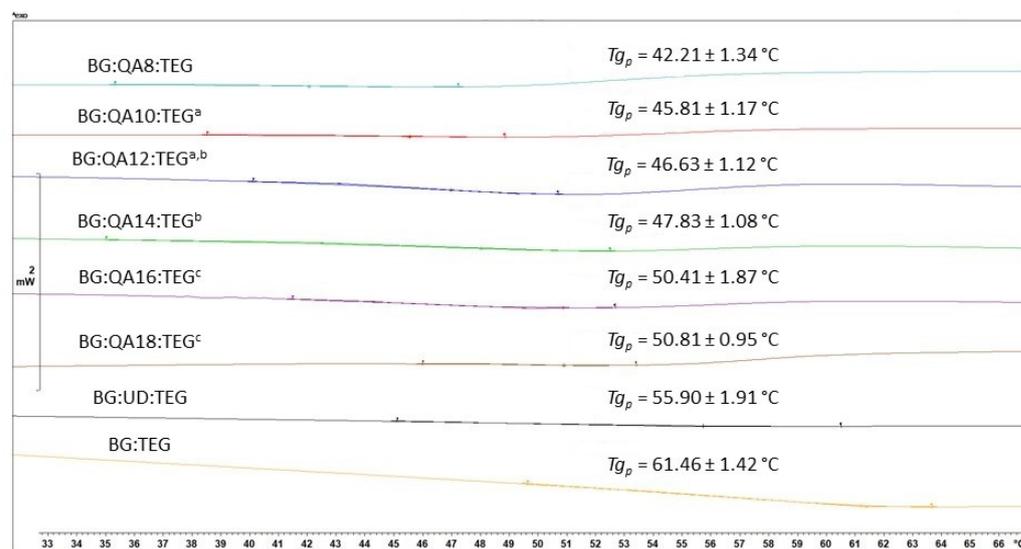


Figure 3. Results of DSC experiments involving the studied copolymers revealing their glass transition temperatures. Lowercase letters indicate statistically insignificant differences ($p > 0.05$, non-parametric Wilcoxon test).

The WCA results are presented in Figure 4. The WCA of BG:QAm:TEGs ranged from 81.41° to 99.53° and increased as the C_m increased. Compared with BG:UD:TEG (WCA = 80.76°), all studied BG:QAm:TEGs had higher WCA values. Almost all of these differences were statistically significant ($p \leq 0.05$), except that for BG:QA8:TEG, which was statistically insignificant ($p > 0.05$). Notably, BG:QA8:TEG had a lower WCA than BG:TEG (WCA = 86.57°), whereas the BG:QAm:TEGs with C_m of C10, C12, and C14 had similar WCA ($p > 0.05$). The remaining BG:QAm:TEGs had higher WCA ($p \leq 0.05$) than BG:TEG.

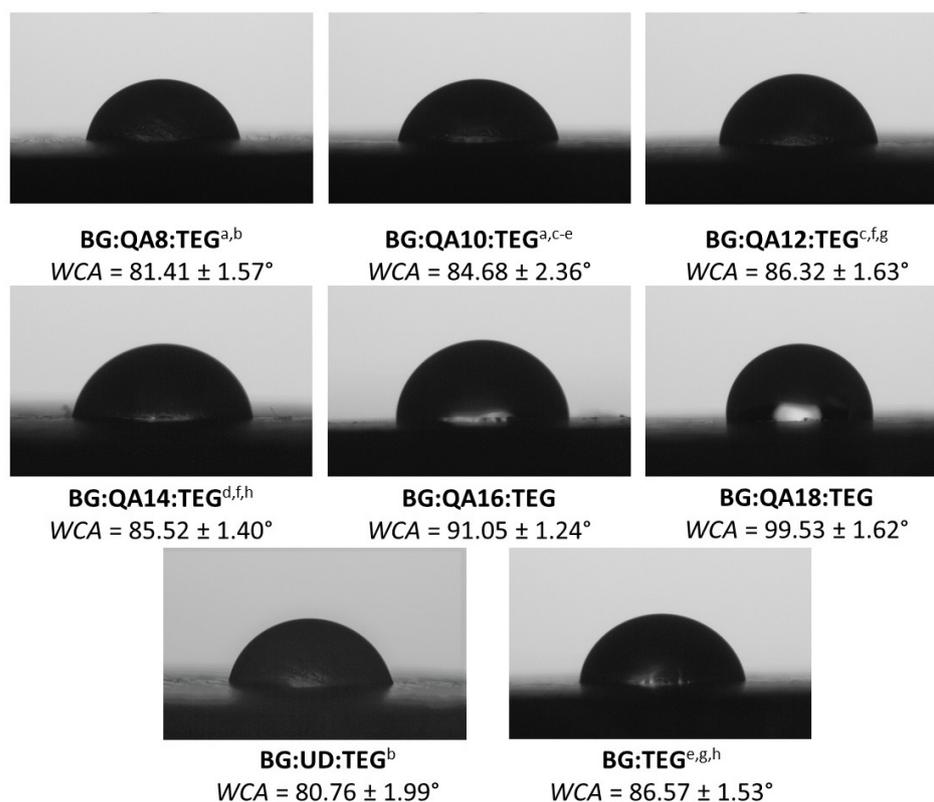


Figure 4. Images captured with the goniometer camera showing droplets of deionized water on the surfaces of the studied copolymers. Lowercase letters indicate statistically insignificant differences ($p > 0.05$, non-parametric Wilcoxon test).

The WS and SL results are presented in Figure 5a,b, respectively.

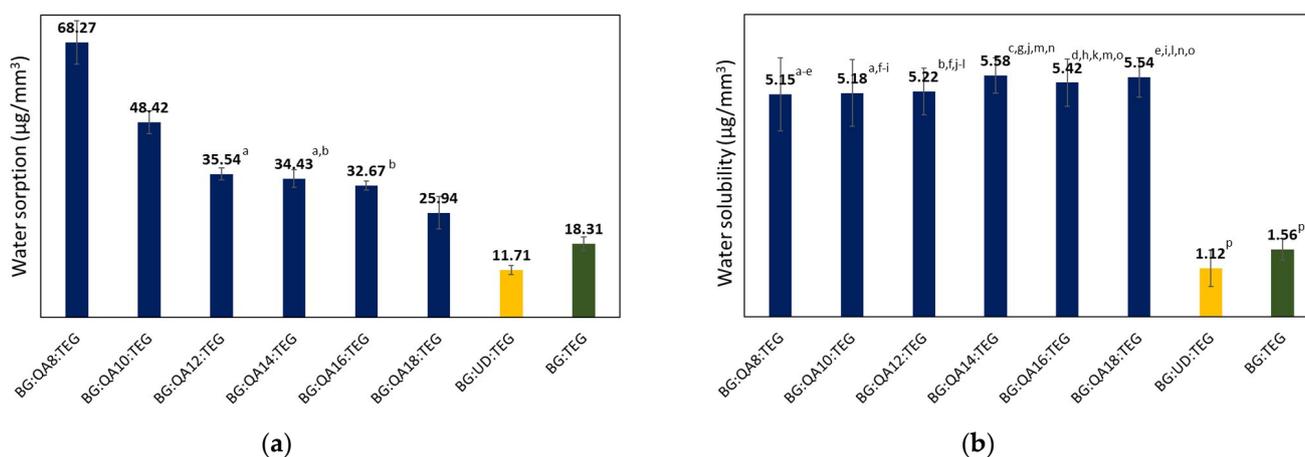


Figure 5. (a) Water sorption and (b) water solubility of the studied copolymers. Lowercase letters indicate statistically insignificant differences ($p > 0.05$, non-parametric Wilcoxon test).

The WS of BG:QAm:TEGs ranged from 25.94 to 68.27 $\mu\text{g}/\text{mm}^2$ and decreased as the C_m increased. All BG:QAm:TEGs had higher WS ($p \leq 0.05$) than the reference copolymers ($WS_{BG:UD:TEG} = 11.71 \mu\text{g}/\text{mm}^2$, $WS_{BG:TEG} = 18.31 \mu\text{g}/\text{mm}^2$). The SL values of BG:QAm:TEGs were similar ($p > 0.05$) and ranged from 5.15 to 5.58 $\mu\text{g}/\text{mm}^3$. Compared with the reference copolymers ($SL_{BG:UD:TEG} = 1.12 \mu\text{g}/\text{mm}^3$, $SL_{BG:TEG} = 1.56 \mu\text{g}/\text{mm}^3$), all of the studied BG:QAm:TEGs had higher SL ($p \leq 0.05$).

3. Discussion

In this study, novel dimethacrylate liquid monomer compositions and their corresponding copolymers consisting of 40 wt.% Bis-GMA, 40 wt.% QAUDMA-m, and 20 wt.% TEGDMA (BG:QAm:TEGs) were prepared, and their physicochemical properties were discussed. It is essential to understand these fundamental properties in order to assess the potential applicability of such copolymers in newly designed dental composite matrices; however, they are rarely studied.

The organic matrix in a dental composite is responsible for the proper functioning and longevity of dental restoration materials. This matrix sticks the filler particles together, transfers stress to those particles, and gives shape to the restoration. Therefore, the matrix should have adequate physicochemical properties and should be stable over the entire desired service time and intraoral temperature range.

3.1. Properties of Liquid Monomer Compositions

The *RI* defines the optical properties of a composite matrix, which should provide similar transparency to enamel [33]. All of the prepared BG:QAm:TEGs met the requirements for dental materials, according to which the *RI* should be within the range from 1.46 to 1.55 [34]. These results suggest that all tested BG:QAm:TEGs have suitable aesthetic properties.

The T_{g_m} of BG:QAm:TEGs ranging from -52.22 to -42.12 °C indicates that all the monomeric systems exist in a liquid state at working temperatures. The T_{g_m} values were analyzed to assess the molecular mobility of liquid monomers; the higher the T_{g_m} , the lower the molecular mobility [35]. The lowest T_{g_m} was recorded for BG:QA18:TEG, which had the highest *Cm*; its T_{g_m} value was 4.23 °C higher than that of BG:TEG and 7.33 °C lower than that of BG:UD:TEG. In contrast, BG:QA8:TEG, which had the shortest *Cm*, was characterized by the highest T_{g_m} ; its T_{g_m} value was 14.33 °C and 2.77 °C higher than those of BG:TEG and BG:UD:TEG, respectively. In general, all of the studied BG:QAm:TEGs were characterized by higher T_{g_m} values than BG:TEG (Figure 2). Relative to the BG:UD:TEG reference, BG:QA8:TEG had a higher T_{g_m} , BG:QA10:TEG had a similar T_{g_m} , and the remaining BG:QAm:TEGs had lower T_{g_m} . These results suggest that the prepared BG:QAm:TEG monomeric systems had lower molecular mobility than BG:TEG. Accordingly, relative to the BG:UD:TEG reference, BG:QA8:TEG showed lower molecular mobility, BG:QA10:TEG showed similar molecular mobility, and the remaining BG:QAm:TEGs showed higher molecular mobility. These distinctions can be explained by differences in the character and the resulting strength of intermolecular interactions between the monomer molecules. Among the two references, BG:UD:TEG had a lower molecular mobility than BG:TEG (i.e., $T_{g_m \text{ BG:UD:TEG}} > T_{g_m \text{ BG:TEG}}$) because of the presence of urethane groups in the UDMA monomer. These moieties are willing to form strong hydrogen bonds with the hydroxyl groups of Bis-GMA, which are also stronger than any other hydrogen bonds occurring in systems comprising Bis-GMA, UDMA, and TEGDMA [36]. Owing to the fact that QAUDMA-m molecules can form strong hydrogen bonds with the hydroxyl groups of Bis-GMA as well as UDMA, all of the BG:QAm:TEG liquid monomer compositions were characterized by lower molecular mobility than BG:TEG. Analysis of the T_{g_m} values further revealed that the *Cm* affects the T_{g_m} . Specifically, T_{g_m} decreased (i.e., molecular mobility increased) as *Cm* increased. This relationship can be attributed to the increasing distance between monomer molecules caused by the increasing *Cm*, which weakens the intermolecular interactions.

3.2. Properties of Copolymers

The polymerization shrinkage (*S*) was determined to be a factor influencing the restoration shrinking [37]. This phenomenon results from double-bond polymerization, whereby the van der Waals forces between the monomer molecules are replaced by much stronger covalent bonds. As a result, the entire system shrinks, and marginal gaps are formed between the tooth filling and adjacent tissue [38]. The higher the *S* value, the greater

the marginal gap; therefore, the S should be as low as possible to enable optimal restoration implantation. In addition, the narrow space between the restoration and the tooth tissue creates an environment that is extremely conducive to bacteria colonization, which can lead to secondary caries or gum inflammation [27].

The S_t can be calculated considering that (i) shrinkage results from the polymerization of the methacrylate group and (ii) the reduced molar volume of methacrylate groups is equal to $22.5 \text{ cm}^3/\text{mol}$ [39]. The S_t values of all studied BG:QAm:TEGs were lower than those of the reference copolymers and decreased as C_m increased (Table 2). The highest S_t was recorded for BG:QA8:TEG, which was 15.50% and 23.95% lower than those of BG:TEG and BG:UD:TEG, respectively. In contrast, BG:QA18:TEG had the lowest S_t , which was 23.34% and 31.01% lower than those of BG:TEG and BG:UD:TEG, respectively. Thus, all tested BG:QAm:TEG liquid monomer compositions theoretically shrink less than the reference compositions. In addition, increasing the C_m reduced the degree of shrinking because increasing the MW of the QAUDMA- m decreased the x_{DB} (Table 1).

In practice, S_t is always higher than S_e because polymerization is never complete. The S_e was calculated according to the d_m (Table 1) and d_p (Table 2). Similar to S_t , the S_e values of BG:QAm:TEGs were lower than those of the reference copolymers owing to the higher MW of BG:QAm:TEG monomer systems. In contrast to S_t , the S_e values of BG:QAm:TEGs increased as C_m increased (Table 2). The highest S_e was recorded for BG:QA18:TEG, which was 20.69% and 23.35% lower than those of BG:TEG and BG:UD:TEG, respectively. The BG:QA8:TEG had the lowest S_e , which was 37.05% and 39.16% lower than those of BG:TEG and BG:UD:TEG, respectively. These relationships can be explained based on the DC . Table 2 indicates that the DC values of BG:QAm:TEGs increased as C_m increased; therefore, S_e also increased.

The T_{g_p} is related to the stiffness of dimethacrylate polymer networks that create the dental composite matrix; the higher the T_{g_p} , the stiffer the polymer network [40]. The T_{g_p} values of BG:QAm:TEGs were lower than those of the reference copolymers and increased as C_m increased (Figure 3). The reduction in BG:QAm:TEG stiffness in comparison to the reference copolymers can be attributed to the presence of long N -alkyl chains that act as pendant groups and loosen the polymer network structure. The lowest T_{g_p} was recorded for BG:QA8:TEG, which was $19.25 \text{ }^\circ\text{C}$ and $13.69 \text{ }^\circ\text{C}$ lower than that of BG:TEG and BG:UD:TEG, respectively. In contrast, BG:QA18:TEG had the highest T_{g_p} , which was only $10.65 \text{ }^\circ\text{C}$ and $5.09 \text{ }^\circ\text{C}$ lower than that of BG:TEG and BG:UD:TEG, respectively. Considering the target applications of these materials (dental restorations), the T_{g_p} should be higher than the maximum intraoral temperature to ensure that the material will be in a glassy state, with stable mechanical properties over the entire range of working temperatures [28]. For this reason, the T_{g_p} should not be lower than $40 \text{ }^\circ\text{C}$ because the temperature of the oral cavity during a fever usually does not exceed $39 \text{ }^\circ\text{C}$ [41]. Therefore, it can be concluded that the C_m did not negatively affect the T_{g_p} to a significant extent because the T_{g_p} values of all studied BG:QAm:TEGs were higher than $40 \text{ }^\circ\text{C}$.

The WCA was measured to assess the hydrophilicity of the copolymer surfaces. Common dental composite fillers [42,43] and dental tissues [44] are both highly hydrophilic. Therefore, the higher the matrix hydrophilicity, the greater its ability to physically bond with the filler and tissue adjacent to the restoration. The hydrophilicity can be expressed according to the WCA , i.e., if $WCA < 90^\circ$, the surface is hydrophilic, and if $WCA > 90^\circ$, the surface is hydrophobic [45]. The WCA values of the studied BG:QAm:TEGs increased as C_m increased. As shown in Figure 4, increasing the C_m from C8 to C14 caused only a slight increase in WCA , which remained lower than 90° . Therefore, the surfaces of these polymers could be classified as hydrophilic. Further lengthening the C_m to C16 and C18 significantly increased the WCA , thereby changing the nature of the surface from hydrophilic to hydrophobic. These results suggested that the main factor influencing the WCA was the length of the N -alkyl substituents. The trend observed for WCA is consistent with published reports, which indicate that the hydrophobic character of the alkyl chains increases with their length [46]. The slower increase in WCA among BG:QAm:TEGs with

C8 to C14 relative to those with C16 and C18 was attributed to the dominant influence of the hydrophilic quaternary ammonium group [47] in the BG:QAm:TEGs with shorter C_m . In the remaining BG:QAm:TEGs, the hydrophobic nature of the *N*-alkyl chains played a key role. The lowest WCA was recorded for BG:QA8:TEG, which was 5.96% lower than that of BG:TEG and 0.80% higher than that of BG:UD:TEG. The BG:QA18:TEG was characterized by the highest WCA, which was 14.97% and 23.24% higher than that of BG:TEG and BG:UD:TEG, respectively. These results confirm that the surfaces of all studied BG:QAm:TEGs were less hydrophilic than that of BG:UD:TEG. Compared with BG:TEG, only the surfaces of BG:QA16:TEG and BG:QA18:TEG were more hydrophobic, whereas the remaining BG:QAm:TEGs were more hydrophilic.

Dental materials are constantly exposed to moisture, which results in their swelling due to water absorption [30]. This can compensate for the decrease in material volume caused by polymerization [48]. However, excessive WS leads to excess swelling, which may deteriorate the restoration's mechanical properties, and in extreme cases, cause mechanical damage [49]. Therefore, according to the standard, ISO 4049, the WS of dental materials should not exceed $40 \mu\text{g}/\text{mm}^3$ [29]. The WS values of the studied BG:QAm:TEGs were higher than those of the reference copolymers and decreased as C_m increased. The lowest WS was recorded for BG:QA18:TEG, which was 41.67% and 121.52% higher than that of BG:TEG and BG:UD:TEG, respectively. The BG:QA8:TEG was characterized by the highest WS, which was 272.86% and 483.01% higher than that of BG:TEG and BG:UD:TEG, respectively. The BG:QAm:TEG copolymers with C_m from C12 to C18 met the requirements for dental materials because their WS values were lower than $40 \mu\text{g}/\text{mm}^3$. The high WS of studied BG:QAm:TEGs can be explained based on several factors. The most influential factor is likely the presence of two quaternary ammonium groups in the QAUDMA-*m*, which are primed to absorb water [20]. Additionally, as the MW of QAUDMA-*m* increased (i.e., with increasing C_m), the molar ratio of QAUDMA-*m* in the BG:QAm:TEG decreased; therefore, the proportion of hydrophilic quaternary ammonium groups in the BG:QAm:TEGs decreased, thereby reducing the WS. The reduction in WS as the C_m increased can be explained by the increasing hydrophobicity of the longer *N*-alkyl chains [46]. It is also possible that the longer *N*-alkyl chains can shield the positively charged quaternary nitrogen ion, thus limiting its ability to absorb water [50].

Leachability of the residual monomers to water (*SL*) is another parameter that should be controlled when considering materials for dental applications. The *SL* should be as low as possible because excessive leaking decreases the restoration's lifetime and promotes the deterioration of its mechanical properties [31]. Therefore, according to the standard, ISO 4049, the *SL* of dental materials should not exceed $7.5 \mu\text{g}/\text{mm}^3$ [29]. The *SL* values of the studied BG:QAm:TEGs were higher than those of the reference copolymers and were unaffected by the C_m . The lowest *SL* was recorded for BG:QA8:TEG, which was 230.13% and 359.82% higher than that of BG:TEG and BG:UD:TEG, respectively. In contrast, BG:QA14:TEG had the highest *SL*, which was 257.69% and 398.21% higher than that of BG:TEG and BG:UD:TEG, respectively. However, all of the studied BG:QAm:TEGs met the requirements for dental materials because their *SL* values were lower than $7.5 \mu\text{g}/\text{mm}^3$. The significantly higher *SL* of BG:QAm:TEGs can be explained by the presence of quaternary ammonium groups in QAUDMA-*m*. As previously stated, these groups have a high affinity to water; therefore, they can easily migrate through the polymer network with water.

4. Materials and Methods

4.1. Chemicals and Reagents

The QAUDMA-*m* analogues were synthesized from 2-(methacryloyloxy)ethyl-2-hydroxyethylmethylalkylammonium bromides (QAHAMAs) TMDI (Tokyo Chemical Industry, Tokyo, Japan). The QAHAMAs were synthesized from *N,N*-(2-hydroxyethyl)methylaminoethyl methacrylate (HAMA) and alkyl bromides with chain lengths of 8, 10, 12, 14, 16, or 18 carbon atoms (all purchased from Acros Organics, Geel, Belgium). The HAMA was synthesized from methyl methacrylate (MMA; Acros Organics, Geel, Belgium) and

N-methyl-diethanolamine (MDEA; Acros Organics, Geel, Belgium). All syntheses were performed following the procedures described in a previous report [23]. Camphorquinone (CQ), 2-dimethylaminoethyl methacrylate (DMAEMA), Bis-GMA, TEGDMA, and UDMA were purchased from Sigma-Aldrich, St. Louis, MO, USA and used as received.

4.2. Sample Preparation

In total, eight compositions of dimethacrylate monomers were prepared, six of which comprised 40 wt.% Bis-GMA, 40 wt.% QAUDMA-*m*, and 20 wt.% TEGDMA (i.e., BG:QAm:TEGs). For comparison, compositions of 40 wt.% Bis-GMA, 40 wt.% UDMA, 20 wt.% TEGDMA (i.e., BG:UD:TEG), and 60 wt.% Bis-GMA, 40 wt.% TEGDMA (i.e., BG:TEG) were also prepared.

The homogenous mixtures of monomers were enriched with a photoinitiating system comprising 0.4 wt.% CQ (initiator) and 1 wt.% DMAEMA (accelerator). The mixtures were poured into Teflon disc-like molds (diameter \times thickness = 15 mm \times 1.5 mm), covered with a PET film, and subjected to irradiation with a UV-Vis lamp (Ultra Vitalux 300, Osram, Munich, Germany, 280–780 nm wavelength range, radiation exitance = 2400 mW/cm²) for 1 h at room temperature.

4.3. Refractive Index

The RI of the liquid monomer compositions was determined according to the standard, ISO 489:1999 [51], using a DR 6100T (Krüss Optronic, Germany) refractometer. Briefly, 2 mL of each liquid monomer composition was placed on the refractometer plate, and the measurement was performed at 20 °C.

4.4. Density and Polymerization Shrinkage

The d_m was determined according to the standard, ISO 1675 [52], using a 1 mL pycnometer. The d_p was determined using an analytical balance (XP Balance, Mettler Toledo, Greifensee, Switzerland) equipped with a density determination kit, which operated on the basis of Archimedes' principle.

The S_e was calculated using Equation (1),

$$S_e(\%) = \left(1 - \frac{d_m}{d_p}\right) \times 100 \quad (1)$$

where d_m is the liquid monomer composition density, and d_p is the copolymer density.

The S_t was calculated using Equation (2),

$$S_t(\%) = \left(\frac{f \times \Delta V \times d_m}{MW}\right) \times 100 \quad (2)$$

where f is the methacrylate functionality ($f = 2$), ΔV is the decrease in molar volume attributable to the polymerization of one mole of methacrylate ($\Delta V = 22.5 \text{ cm}^3/\text{mol}$ [39]), d_m is the liquid monomer composition density, and MW is the liquid monomer composition molecular weight.

4.5. Glass Transition Temperature

The T_{g_m} and T_{g_p} were determined using a differential scanning calorimeter (DSC 3, Mettler Toledo, Greifensee, Switzerland) according to the standard, ISO 11357-2:2020 [53]. Briefly, 2 mg of sample were placed in a standard aluminum crucible and heated in air within the temperature range from -90 to 200 °C, with a heating rate of 10 K/min.

The T_g was taken as the midpoint of the transition region.

4.6. Water Contact Angle

The WCA was determined using an OCA15EC goniometer (Data Physics, Filderstadt, Germany) via the sessile drop method. Briefly, 4 μL of deionized water were dropped on the surface of disc-shaped copolymer samples (diameter \times thickness = 15 mm \times 1.5 mm).

4.7. Water Sorption and Solubility

The WS and SL were determined according to the standard, ISO 4049 [29], using disc-shaped copolymer samples (diameter \times thickness = 15 mm \times 5 mm).

Initially, the samples were dried at 100 $^{\circ}\text{C}$ in a conditioning oven until they reached a constant weight (m_0), which was usually achieved after 72 h. Then, samples were placed in glass vials containing distilled water and stored for seven days at room temperature. Next, samples were removed from the water, blotted dry, and weighted (m_1). Finally, the samples were once again dried to a constant mass (m_2) at 100 $^{\circ}\text{C}$ in a conditioning oven. Sample weights were measured using an analytical balance (XP Balance, Mettler Toledo, Greifensee, Switzerland) with 0.01 mg accuracy.

The WS and SL were calculated using Equations (3) and (4), respectively,

$$WS (\mu\text{g}/\text{mm}^3) = \frac{m_1 - m_0}{V} \quad (3)$$

$$SL (\mu\text{g}/\text{mm}^3) = \frac{m_0 - m_2}{V} \quad (4)$$

where m_0 is the initial mass of the dried sample, m_1 is the mass of the swollen sample, m_2 is the mass of the dried sample after storage in water, and V is the initial volume of the dried sample.

4.8. Statistical Analysis

The experimental results reported herein were expressed as an average of five measurements and presented with the associated standard deviations (SD). The data were analyzed and compared using the non-parametric Wilcoxon test with a significance level (p) of 0.05 using Statistica 13.1 software (TIBCO Software Inc., Palo Alto, CA, USA).

5. Conclusions

The physicochemical properties of six dimethacrylate-based compositions comprising 40 wt.% Bis-GMA, 40 wt.% QAUDMA- m , 20 wt.% TEGDMA, and their corresponding copolymers mainly depended on the length of the N -alkyl substituent. It was observed that: (i) Tg_m decreased with increasing Cm , whereas the opposite trend was observed for Tg_p , (ii) S_e increased with increasing Cm , (iii) hydrophobicity (determined from WCA) increased with increasing Cm , and (iv) WS decreased with increasing Cm . Only RI and SL were unaffected by the Cm .

In relation to the properties of the reference copolymers, the following conclusions were drawn. All liquid BG:QAm:TEG monomer compositions had suitable RI and Tg_m . Moreover, all studied BG:QAm:TEG copolymers were characterized by low S values and Tg_p values higher than 40 $^{\circ}\text{C}$, suggesting that they would have stable mechanical properties over the working temperature range of dental restorations. The surfaces of two of the BG:QAm:TEGs adopted a hydrophobic character (BG:QA16:TEG and BG:QA18:TEG), whereas the remaining BG:QAm:TEGs had hydrophilic surfaces. All of the studied BG:QAm:TEGs had higher SL than the reference copolymers; however, the obtained SL values did not exclude their use as matrices of dimethacrylate-based dental composites. Only BG:QA8:TEG and BG:QA10:TEG did not fulfill the WS requirements because their WS values were higher than 40 $\mu\text{g}/\text{mm}^3$; this feature would prevent their use as matrices for dental composites.

Author Contributions: Conceptualization, I.M.B.-R. and M.W.C.-P.; methodology, I.M.B.-R. and M.W.C.-P.; Investigation, M.W.C.-P.; Statistical analysis, G.C.; Resources, I.M.B.-R. and M.W.C.-P.; Data curation, M.W.C.-P.; Writing—original draft preparation, I.M.B.-R. and M.W.C.-P.; Writing—review and editing, I.M.B.-R.; Visualization, M.W.C.-P.; Supervision, I.M.B.-R.; Project administration, I.M.B.-R. and M.W.C.-P.; Funding acquisition, I.M.B.-R., M.W.C.-P. and G.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Rector’s grant for scientific research and development activities at the Silesian University of Technology, grant number: 32/014/RGJ22/2004.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data supporting the reported results are available from the authors upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Makvandi, P.; Jamaledin, R.; Jabbari, M.; Nikfarjam, N.; Borzacchiello, A. Antibacterial Quaternary Ammonium Compounds in Dental Materials: A Systematic Review. *Dent. Mater.* **2018**, *34*, 851–867. [[CrossRef](#)] [[PubMed](#)]
2. Ge, Y.; Wang, S.; Zhou, X.; Wang, H.; Xu, H.H.K.; Cheng, L. The Use of Quaternary Ammonium to Combat Dental Caries. *Materials* **2015**, *8*, 3532–3549. [[CrossRef](#)] [[PubMed](#)]
3. Kwaśniewska, D.; Chen, Y.L.; Wieczorek, D. Biological Activity of Quaternary Ammonium Salts and Their Derivatives. *Pathogens* **2020**, *9*, 459. [[CrossRef](#)] [[PubMed](#)]
4. Huang, L.; Yu, F.; Sun, X.; Dong, Y.; Lin, P.T.; Yu, H.H.; Xiao, Y.H.; Chai, Z.G.; Xing, X.D.; Chen, J.H. Antibacterial Activity of a Modified Unfilled Resin Containing a Novel Polymerizable Quaternary Ammonium Salt MAE-HB. *Sci. Rep.* **2016**, *6*, 33858. [[CrossRef](#)] [[PubMed](#)]
5. Huang, L.; Xiao, Y.H.; Xing, X.D.; Li, F.; Ma, S.; Qi, L.L.; Chen, J.H. Antibacterial Activity and Cytotoxicity of Two Novel Cross-Linking Antibacterial Monomers on Oral Pathogens. *Arch. Oral Biol.* **2011**, *56*, 367–373. [[CrossRef](#)] [[PubMed](#)]
6. Imazato, S.; Kinomoto, Y.; Tarumi, H.; Ebisu, S.; Tay, F.R. Antibacterial Activity and Bonding Characteristics of an Adhesive Resin Containing Antibacterial Monomer MDPB. *Dent. Mater.* **2003**, *19*, 313–319. [[CrossRef](#)]
7. Li, F.; Li, F.; Wu, D.; Ma, S.; Gao, J.; Li, Y.; Xiao, Y.; Chen, J. The Effect of an Antibacterial Monomer on the Antibacterial Activity and Mechanical Properties of a Pit-and-Fissure Sealant. *J. Am. Dent. Assoc.* **2011**, *142*, 184–193. [[CrossRef](#)]
8. Xiao, Y.H.; Chen, J.H.; Fang, M.; Xing, X.D.; Wang, H.; Wang, Y.J.; Li, F. Antibacterial Effects of Three Experimental Quaternary Ammonium Salt (QAS) Monomers on Bacteria Associated with Oral Infections. *J. Oral Sci.* **2008**, *50*, 323–327. [[CrossRef](#)]
9. Chai, Z.; Li, F.; Fang, M.; Wang, Y.; Ma, S.; Xiao, Y.; Huang, L.; Chen, J. The Bonding Property and Cytotoxicity of a Dental Adhesive Incorporating a New Antibacterial Monomer. *J. Oral Rehabil.* **2011**, *38*, 849–856. [[CrossRef](#)]
10. Antonucci, J.M.; Zeiger, D.N.; Tang, K.; Lin-Gibson, S.; Fowler, B.O.; Lin, N.J. Synthesis and Characterization of Dimethacrylates Containing Quaternary Ammonium Functionalities for Dental Applications. *Dent. Mater.* **2012**, *28*, 219–228. [[CrossRef](#)]
11. Li, F.; Weir, M.D.; Xu, H.H.K. Effects of Quaternary Ammonium Chain Length on Antibacterial Bonding Agents. *J. Dent. Res.* **2013**, *92*, 932–938. [[CrossRef](#)] [[PubMed](#)]
12. Lu, G.; Wu, D.; Fu, R. Studies on the Synthesis and Antibacterial Activities of Polymeric Quaternary Ammonium Salts from Dimethylaminoethyl Methacrylate. *React. Funct. Polym.* **2007**, *67*, 355–366. [[CrossRef](#)]
13. Manouchehri, F.; Sadeghi, B.; Najafi, F.; Mosslemin, M.H.; Niakan, M. Synthesis and Characterization of Novel Polymerizable Bis-Quaternary Ammonium Dimethacrylate Monomers with Antibacterial Activity as an Efficient Adhesive System for Dental Restoration. *Polym. Bull.* **2019**, *76*, 1295–1315. [[CrossRef](#)]
14. Yanwei, Y.; Li, H.; Yan, D.; Hongchen, Z.; Wei, Z.; Jinghao, B.; Jingjing, W.; Yan, L.; Jing, G.; Jihua, C. In Vitro Antibacterial Activity of a Novel Resin-Based Pulp Capping Material Containing the Quaternary Ammonium Salt Mae-Db and Portland Cement. *PLoS ONE* **2014**, *9*, e0112549. [[CrossRef](#)]
15. Li, F.; Weir, M.D.; Chen, J.; Xu, H.H.K. Comparison of Quaternary Ammonium-Containing with Nano-Silver-Containing Adhesive in Antibacterial Properties and Cytotoxicity. *Dent. Mater.* **2013**, *29*, 450–461. [[CrossRef](#)]
16. Cherchali, F.Z.; Mouzali, M.; Tommasino, J.B.; Decoret, D.; Attik, N.; Aboulleil, H.; Seux, D.; Grosgeat, B. Effectiveness of the DHMAI Monomer in the Development of an Antibacterial Dental Composite. *Dent. Mater.* **2017**, *33*, 1381–1391. [[CrossRef](#)]
17. He, J.; Söderling, E.; Österblad, M.; Vallittu, P.K.; Lassila, L.V.J. Synthesis of Methacrylate Monomers with Antibacterial Effects against *S. Mutans*. *Molecules* **2011**, *16*, 9755–9763. [[CrossRef](#)]
18. Makvandi, P.; Ghaemy, M.; Mohseni, M. Synthesis and Characterization of Photo-Curable Bis-Quaternary Ammonium Dimethacrylate with Antimicrobial Activity for Dental Restoration Materials. *Eur. Polym. J.* **2016**, *74*, 81–90. [[CrossRef](#)]

19. Liang, X.; Söderling, E.; Liu, F.; He, J.; Lassila, L.V.J.; Vallittu, P.K. Optimizing the Concentration of Quaternary Ammonium Dimethacrylate Monomer in Bis-GMA/TEGDMA Dental Resin System for Antibacterial Activity and Mechanical Properties. *J. Mater. Sci. Mater. Med.* **2014**, *25*, 1387–1393. [[CrossRef](#)]
20. Liang, X.; Huang, Q.; Liu, F.; He, J.; Lin, Z. Synthesis of Novel Antibacterial Monomers (UDMQA) and Their Potential Application in Dental Resin. *J. Appl. Polym. Sci.* **2013**, *129*, 3373–3381. [[CrossRef](#)]
21. Huang, Q.; Lin, Z.; Liang, X.; Liu, F.; He, J. Preparation and Characterization of Antibacterial Dental Resin with UDMQA-12. *Adv. Polym. Technol.* **2014**, *33*, 21395. [[CrossRef](#)]
22. Huang, Q.T.; He, J.W.; Lin, Z.M.; Liu, F.; Lassila, L.V.J.; Vallittu, P.K. Physical and Chemical Properties of an Antimicrobial Bis-GMA Free Dental Resin with Quaternary Ammonium Dimethacrylate Monomer. *J. Mech. Behav. Biomed. Mater.* **2016**, *56*, 68–76. [[CrossRef](#)]
23. Chrószcz, M.W.; Barszczewska-Rybarek, I.M. Synthesis and Characterization of Novel Quaternary Ammonium Urethane-Dimethacrylate Monomers—A Pilot Study. *Int. J. Mol. Sci.* **2021**, *22*, 8842. [[CrossRef](#)] [[PubMed](#)]
24. Chrószcz, M.W.; Barszczewska-Rybarek, I.M.; Kazek-K, A. Novel Antibacterial Copolymers Based on Quaternary Ammonium Urethane-Dimethacrylate Analogues and Triethylene Glycol Dimethacrylate. *Int. J. Mol. Sci.* **2022**, *23*, 4954. [[CrossRef](#)] [[PubMed](#)]
25. Chrószcz-Porebska, M.W.; Barszczewska-Rybarek, I.M.; Chladek, G. Characterization of the Mechanical Properties, Water Sorption, and Solubility of Antibacterial Copolymers of Quaternary Ammonium Urethane-Dimethacrylates and Triethylene Glycol Dimethacrylate. *Materials* **2022**, *15*, 5530. [[CrossRef](#)] [[PubMed](#)]
26. Alshali, R.Z.; Silikas, N.; Satterthwaite, J.D. Degree of conversion of bulk-fill compared to conventional resin-composites at two time intervals. *Dent. Mater.* **2013**, *29*, e213–e217. [[CrossRef](#)]
27. Ensaff, H.; O'Doherty, D.M.; Jacobsen, P.H. Polymerization Shrinkage of Dental Composite Resins. *Proc. Inst. Mech. Eng. Part H J. Eng. Med.* **2001**, *215*, 367–375. [[CrossRef](#)]
28. Moraes, J.C.S.; Sostena, M.M.D.S.; Grandini, C.R. The Glass Transition Temperature in Dental Composites. In *Metal, Ceramic and Polymeric Composites for Various Uses*; Cuppoletti, J., Ed.; IntechOpen: London, UK, 2011. [[CrossRef](#)]
29. ISO 4049:2019; Dentistry—Polymer Based Restorative Materials. International Standard Organisation: London, UK, 2019.
30. Bociong, K.; Szczesio, A.; Sokolowski, K.; Domarecka, M.; Sokolowski, J.; Krasowski, M.; Lukomska-Szymanska, M. The Influence of Water Sorption of Dental Light-Cured Composites on Shrinkage Stress. *Materials* **2017**, *10*, 1142. [[CrossRef](#)]
31. Kumar, N.; Sangi, L. Water Sorption, Solubility, and Resultant Change in Strength among Three Resin-Based Dental Composites. *J. Investig. Clin. Dent.* **2014**, *5*, 144–150. [[CrossRef](#)]
32. Chrószcz-Porebska, M.W.; Barszczewska-Rybarek, I.M.; Kazek-Kęsik, A.; Chladek, G. Novel mechanically strong and antibacterial dimethacrylate copolymers based on quaternary ammonium urethane-dimethacrylate analogues. *Dent. Mater.* **2022**, submitted.
33. Meng, Z.; Yao, X.S.; Yao, H.; Liang, Y.; Liu, T.; Li, Y.; Wang, G.; Lan, S. Measurement of the Refractive Index of Human Teeth by Optical Coherence Tomography. *J. Biomed. Opt.* **2009**, *14*, 034010. [[CrossRef](#)]
34. Manappallil, J.J. *Basic Dental Materials*, 4th ed.; Jaypee Brothers Medical Publishers: New Delhi, India, 2015.
35. Véchambre, C.; Buléon, A.; Chaunier, L.; Gauthier, C.; Lourdin, D. Understanding the Mechanisms Involved in Shape Memory Starch: Macromolecular Orientation, Stress Recovery and Molecular Mobility. *Macromolecules* **2011**, *44*, 9384–9389. [[CrossRef](#)]
36. Barszczewska-Rybarek, I.M. Structure–Property Relationships in Dimethacrylate Networks Based on Bis-GMA, UDMA and TEGDMA. *Dent. Mater.* **2009**, *25*, 1082–1089. [[CrossRef](#)] [[PubMed](#)]
37. Schrickler, S.R. Composite Resin Polymerization and Relevant Parameters. In *Orthodontic Applications of Biomaterials*; Woodhead Publishing: Sawston, UK, 2017; pp. 153–170. [[CrossRef](#)]
38. Soares, C.J.; Faria-E-Silva, A.L.; de Paula Rodrigues, M.; Fernandes Vilela, A.B.; Pfeifer, C.S.; Tantbirojn, D.; Versluis, A. Polymerization Shrinkage Stress of Composite Resins and Resin Cements—What Do We Need to Know? *Braz. Oral Res.* **2017**, *31*, 49–63. [[CrossRef](#)] [[PubMed](#)]
39. Watts, D.C. Adhesives and Sealants. In *Biomaterials Science: An Introduction to Materials*, 3rd ed.; Ratner, B., Hoffman, A., Schoen, F., Lemons, J., Eds.; Elsevier Inc.: Amsterdam, The Netherlands, 2013; pp. 889–904.
40. Wang, R.-M.; Zheng, S.-R.; Zheng, Y.-P. Matrix Materials. In *Polymer Matrix Composites and Technology*; Woodhead Publishing: Sawston, UK, 2011; pp. 101–548. [[CrossRef](#)]
41. Walker, H.K.; Hall, W.D.; Hurst, J.W. *Clinical Methods: The History, Physical, and Laboratory Examinations*, 3rd ed.; Butterworths: Boston, MA, USA, 1990.
42. Pratap, B.; Gupta, R.K.; Bhardwaj, B.; Nag, M. Resin Based Restorative Dental Materials: Characteristics and Future Perspectives. *Jpn. Dent. Sci. Rev.* **2019**, *55*, 126–138. [[CrossRef](#)]
43. Farooq, I.; Ali, S.; Al-Saleh, S.; Alhamdan, E.M.; Alrefeai, M.H.; Abduljabbar, T.; Vohra, F. Synergistic Effect of Bioactive Inorganic Fillers in Enhancing Properties of Dentin Adhesives—A Review. *Polymers* **2021**, *13*, 2169. [[CrossRef](#)] [[PubMed](#)]
44. Ayar, M.K. A Review of Ethanol Wet-Bonding: Principles and Techniques. *Eur. J. Dent.* **2016**, *10*, 155–159. [[CrossRef](#)]
45. Purkait, M.K.; Sinha, M.K.; Mondal, P.; Singh, R. Photoresponsive Membranes. *Interface Sci. Technol.* **2018**, *25*, 115–144. [[CrossRef](#)]
46. Gao, Y.; Duan, L.; Guan, S.; Gao, G.; Cheng, Y.; Ren, X.; Wang, Y. The Effect of Hydrophobic Alkyl Chain Length on the Mechanical Properties of Latex Particle Hydrogels. *RSC Adv.* **2017**, *7*, 44673–44679. [[CrossRef](#)]
47. Kowalczyk, I.; Pakiet, M.; Szulc, A.; Koziróg, A. Antimicrobial Activity of Gemini Surfactants with Azapolymethylene Spacer. *Molecules* **2020**, *25*, 4054. [[CrossRef](#)]

48. Feilzer, A.J.; Kakaboura, A.I.; de Gee, A.J.; Davidson, C.L. The Influence of Water Sorption on the Development of Setting Shrinkage Stress in Traditional and Resin-Modified Glass Ionomer Cements. *Dent. Mater.* **1995**, *11*, 186–190. [[CrossRef](#)]
49. Al-Bader, R.M.; Ziadan, K.M.; Al-Ajely, M.S. Water Adsorption Characteristics of New Dental Composites. *Int. J. Med. Res. Health Sci.* **2015**, *4*, 281. [[CrossRef](#)]
50. Yudovin-Farber, I.; Beyth, N.; Weiss, E.I.; Domb, A.J. Antibacterial Effect of Composite Resins Containing Quaternary Ammonium Polyethyleneimine Nanoparticles. *J. Nanoparticle Res.* **2010**, *12*, 591–603. [[CrossRef](#)]
51. *ISO 489:1999*; Plastics—Determination of Refractive Index. International Standard Organisation: London, UK, 1999.
52. *ISO 1675:2002*; Plastics—Liquid Resins—Determination of Density by the Pycnometer Method. International Standard Organisation: London, UK, 2002.
53. *ISO 11357-2:2020*; Plastics—Differential Scanning Calorimetry (DSC)—Part 2: Determination of Glass Transition Temperature and Step Height. International Standard Organisation: London, UK, 2020.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.