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Surface Hydrophilicity of Dental Copolymer Modified with Dimethacrylates Possessing Quaternary Ammonium Groups †

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Abstract

Dental composite reconstructive materials (DCRMs) used in caries treatment possess satisfactory functional properties but lack antimicrobial activity, which may lead to secondary caries. This research aimed to modify the DCRM matrix with urethane-dimethacrylate monomers derived from cycloaliphatic and aromatic diisocyanates bearing quaternary ammonium groups. The diisocyanates used were 1,3-bis(1-isocyanato-1-methylethyl)benzene (TMXDI), isophorone diisocyanate (IPDI), dicyclohexylmethane-4,4′-diisocyanate (CHMDI), and 1,1′-methylenebis(4-isocyanatobenzene) (MDI). As a result, eight modified copolymers were obtained and tested for the surface water contact angle (*WCA*), water sorption (*WS*), and water solubility (*SL*). The *WCA* results indicated predominantly hydrophilic surfaces, while the *WS* and *SL* values were generally satisfactory.

Keywords: photocurable dental resins; quaternary ammonium groups; urethane-dimethacrylate monomers

1. Introduction

The presence of bacteria, moisture, variable temperatures, and nutrient availability in the human oral cavity creates favorable conditions for the development of oral diseases. Oral diseases constitute a major global health problem. The World Health Organization estimates that approximately 3.5 billion people worldwide are affected by oral diseases [1]. The treatment of oral diseases and the development of novel materials for oral applications require addressing numerous challenges resulting from the specific environment of the human mouth.

Dental composite reconstructive materials (DCRMs) used in caries treatment exhibit satisfactory practical properties; however, they lack antibacterial activity [2]. This deficiency may lead to the development of secondary caries, ineffective caries treatment, and degradation of the restorative material itself [3]. Research on DCRM modification primarily focuses on improving the dimethacrylate matrix [4–9]. There are two possible ways to modify the DCRM matrix. Nanoparticles of silver or titanium oxide, as well as chlorhexidine salts, are examples of approaches in which the antibacterial agent is dispersed within the polymeric matrix [5,8,9]. This solution provides satisfactory biocidal properties; however, its effectiveness is limited by the agents' elution. This leads to decreased mechanical properties and long-term antibacterial activity [10,11]. Another possible approach to matrix modification is the incorporation of quaternary ammonium-containing compounds into the dimethacrylate

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network [12–17]. Such an approach eliminates the problem of reduced antibacterial activity caused by the leaching of the antibacterial agent, ensuring stable, long-term properties.

Our research team synthesized eight novel monomers based on cycloaliphatic and aromatic diisocyanates containing quaternary ammonium groups: QA8+TMXDI, QA10+TMXDI, QA8+IPDI, QA10+IPDI, QA8+CHMDI, QA10+CHMDI, QA8+MDI, and QA10+MDI [18,19]. These monomers were introduced into the liquid composition and polymerised to obtain solid copolymers. The water sorption (*WS*) and water solubility (*SL*) of copolymers modified with QA8+IPDI, QA10+IPDI, QA8+CHMDI, QA10+CHMDI, QA8+MDI, and QA10+MDI have been previously reported [19]. The present study aims to characterize the water contact angle (*WCA*) of all eight modified copolymers, as well as the water sorption (*WS*) and water solubility (*SL*) of copolymers containing QA8+TMXDI and QA10+TMXDI.

2. Materials and Methods

2.1. Materials

Methyl methacrylate (MMA), *N*-methyldiethanolamine (MDEA), octyl bromide (OB), and decyl bromide (DB) were purchased from Acros Organics (Geel, Belgium). Toluene, trichloromethane ($CHCl_3$), and dichloromethane (CH_2Cl_2) were obtained from Stanlab (Lublin, Poland). Phenothiazine (PTZ), 1,3-bis(1-isocyanato-1-methylethyl)benzene (TMXDI), isophorone diisocyanate (IPDI), dicyclohexylmethane-4,4′-diisocyanate (CHMDI), 1,1′-methylenebis(4-isocyanatobenzene) (MDI), camphorquinone (CQ), urethane-dimethacrylate (UDMA), triethylene glycol dimethacrylate (TEGDMA), and *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Bisphenol A glycerolate dimethacrylate (Bis-GMA) was obtained from Tokyo Chemical Industry (Tokyo, Japan). Dibutyltin dilaurate (DBTDL) was purchased from Fluka (Charlotte, NC, USA). Magnesium sulfate ($MgSO_4$) and potassium carbonate (K_2CO_3) were purchased from Chempur (Piekary Śląskie, Poland).

2.2. Monomer Synthesis

QAUDMA monomers were synthesized via a three-step process (Figure 1), as previously described in the literature [17]. The synthesis involved the transesterification of methyl methacrylate (MMA) with *N*-methyldiethanolamine (MDEA) at a molar ratio of 1.5:1, followed by *N*-alkylation of HAMA with an alkyl bromide (octyl bromide or decyl bromide) at a 1:1 molar ratio. The final step was an addition reaction of QAHAMA-n to a diisocyanate (TMXDI, IPDI, CHMDI, or MDI) at a 2:1 molar ratio. As a result, eight monomers were obtained: QA8+TMXDI, QA10+TMXDI, QA8+IPDI, QA10+IPDI, QA8+CHMDI, QA10+CHMDI, QA8+MDI, and QA10+MDI.

2.3. Copolymer Preparation

The copolymers were obtained via photopolymerization. First, eight experimental monomer compositions were prepared, each consisting of 40 wt.% QAUDMA (QA8+TMXDI, QA10+TMXDI, QA8+IPDI, QA10+IPDI, QA8+CHMDI, QA10+CHMDI, QA8+MDI, or QA10+MDI), 40 wt.% Bis-GMA, and 20 wt.% TEGDMA. The reference composition consisted of 40 wt.% UDMA, 40 wt.% Bis-GMA, and 20 wt.% TEGDMA. The initiating system comprised 0.4 wt.% camphorquinone (CQ) and 1 wt.% *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA). The initiators were introduced into the monomer mixtures, which were then heated to 50 °C under mechanical stirring until complete dissolution of CQ was achieved. The liquid compositions were poured into molds and covered with polyethylene terephthalate (PET) foil. Subsequently, the compositions were irradiated at room temperature for 1 h using a UV–Vis lamp (Ultra Vitalux 300, Osram, Munich,

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Germany). The lamp emitted radiation in the 280–780 nm range with an exitance of 2400 mW/cm^2. Prior to testing, each specimen was polished with fine-grit sandpaper.

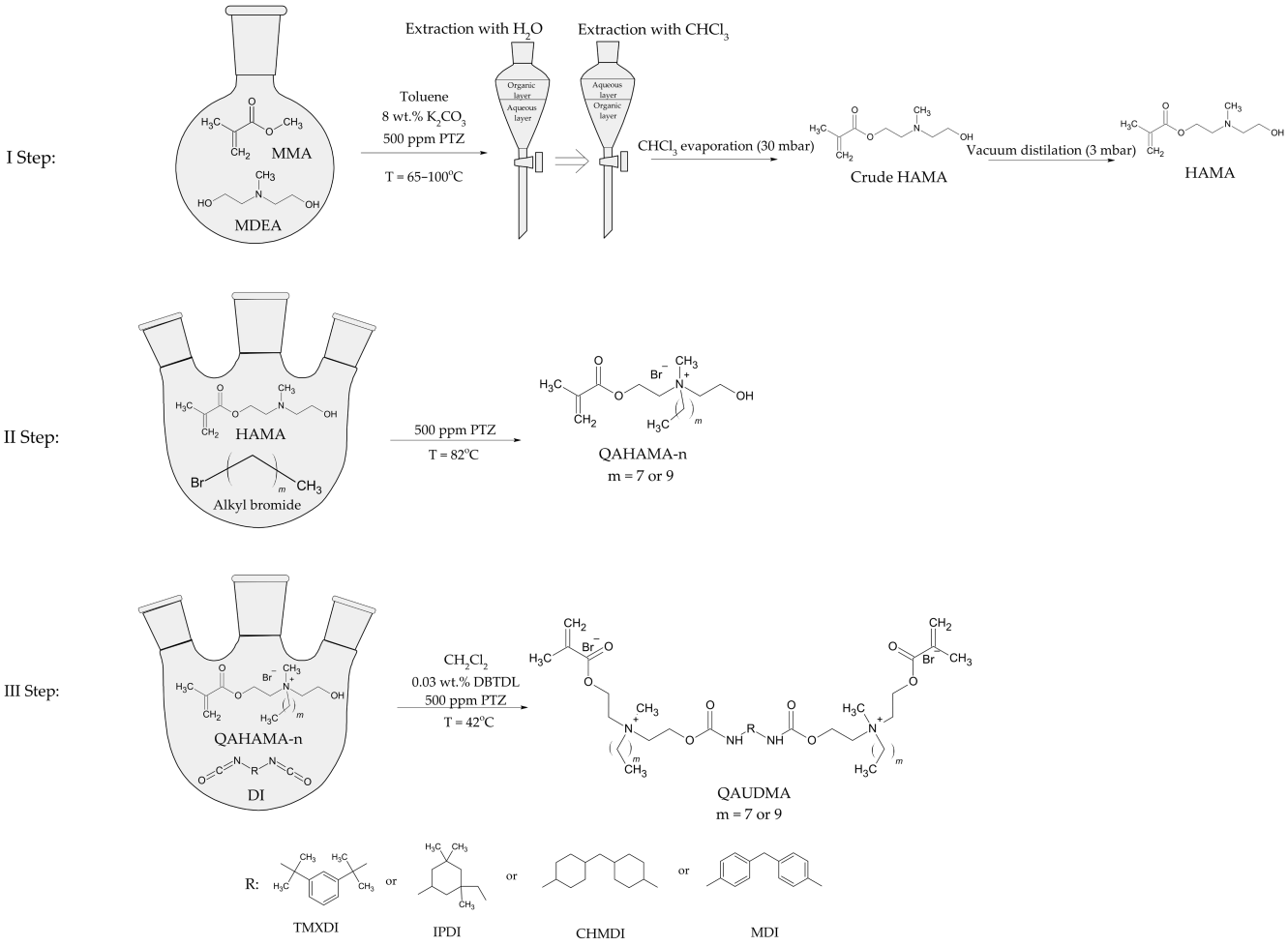


Figure 1. Three-step synthesis route of QAUDMA monomers.

2.4. Water Contact Angle (WCA)

The water contact angles (*WCAs*) of the obtained copolymers were determined using a goniometer (OCA 15EC, DataPhysics Instruments, Filderstadt, Germany). The samples were disk-shaped specimens measuring 15 mm × 1.5 mm (diameter × thickness). Measurements were performed using the sessile drop method with 4 µL of deionised water. The *WCA* was determined immediately after the droplet was placed on the sample surface.

2.5. Water Sorption (WS) and Water Solubility (SL)

The water sorption (*WS*) and solubility *(SL)* of the polymers were determined in accordance with ISO 4049:2019 [20]. Disk-shaped specimens with dimensions of 15 mm × 1.5 mm (diameter × thickness) were dried to a constant mass (m_0) in a laboratory dryer (SLW 53 STD, POL-EKO, Wodzisław Śląski, Poland). The specimens were then immersed in deionised water at room temperature for 7 days. After this period, the samples were removed from the water, gently dried with blotting paper, and weighed to obtain mass (m_1). Finally, the specimens were dried again to a constant mass (m_2). An analytical balance (XP Balance, Mettler Toledo, Greifensee, Switzerland) was used for all weighing steps. The *WS* and *SL* values were calculated using the following equations:

$$WS\left(\frac{\mu g}{mm^3}\right) = \frac{m_1 - m_0}{V}$$

$$SL\left(\frac{\mu g}{mm^3}\right) = \frac{m_0 - m_2}{V}$$

The variables in the equations are defined as follows:
m_0—the initial mass of the dried samples;
m_1—the mass of the swollen samples;
m_2—the mass of the samples after drying following immersion in water;
V—the initial volume of the dried samples.

3. Results

3.1. Water Contact Angle (WCA)

Table 1 shows the water contact angles of the synthesized QAUDMAs compared with the reference copolymer. The measured *WCA* values provide information on the surface wettability of the materials, which is influenced by their chemical composition and molecular structure. Differences in wettability among the tested samples indicate variations in surface properties resulting from the incorporation of QAUDMAs into the copolymer.

Table 1. Water contact angles (*WCA*) of QAUDMA copolymers compared with the reference copolymer.

Copolymer	*WCA* (°)	
	AVG	**SD**
Experimental copolymers		
40(QA8+TMXDI)	68.08	3.99
40(QA10+TMXDI)	71.18	3.99
40(QA8+IPDI)	57.06	3.25
40(QA10+IPDI)	65.92	4.77
40(QA8+CHMDI)	65.82	3.74
40(QA10+CHMDI)	68.94	4.37
40(QA8+MDI)	73.43	3.56
40(QA10+MDI)	87.50	5.27
Reference copolymer		
40(UDMA)	74.07	2.24

Five copolymers: 40(QA8+TMXDI), 40(QA8+IPDI), 40(QA10+IPDI), 40(QA8+CHMDI), and 40(QA10+CHMDI), showed lower *WCA* values (57.06–68.94°) compared to the reference sample, which exhibited a *WCA* of 74.07°. The *WCA* values of 40(QA10+TMXDI) and 40(QA8+MDI), 71.18° and 73.43°, respectively, were comparable to that of 40(UDMA). Only the surface of 40(QA10+MDI) showed lower hydrophilicity compared to 40(UDMA), with a *WCA* of 87.50° versus 74.07°, respectively.

3.2. Water Sorption (WS) and Water Solubility (SL)

Table 2 presents the water sorption (*WS*) and water solubility (*SL*) results for the modified copolymers and the reference copolymer. These parameters provide insight into the interaction of the materials with water and their dimensional and chemical stability in aqueous environments. The results for 40(QA8+IPDI), 40(QA10+IPDI), 40(QA8+CHMDI), 40(QA10+CHMDI), 40(QA8+MDI), and 40(QA10+MDI) have been published previously [19].

All QAUDMA copolymers exhibited higher water sorption (*WS*) and water solubility (*SL*) compared to the reference copolymer. The *WS* values were at least twice those of the reference, ranging from 9.34 to 14.00 $\mu g/mm^3$, whereas the *WS* of 40(UDMA) was 5.85 $\mu g/mm^3$. Similarly, *SL* values were at least two times higher than those of 40(UDMA), ranging from 2.62 to 7.68 $\mu g/mm^3$ compared to 1.13 $\mu g/mm^3$ for the reference.

Table 2. Water sorption (*WS*) and water solubility (*SL*) of QAUDMA copolymers compared with the reference copolymer.

Copolymer	*WS* (μg/mm^3)		*SL* (μg/mm^3)	
	AVG	**SD**	**AVG**	**SD**
Experimental copolymers				
40(QA8+TMXDI)	10.46	0.68	5.63	0.57
40(QA10+TMXDI)	9.34	0.21	5.87	0.35
40(QA8+IPDI) [1]	14.00	1.61	2.70	0.29
40(QA10+IPDI) [1]	13.18	1.02	2.62	0.26
40(QA8+CHMDI) [1]	13.75	1.32	2.94	0.21
40(QA10+CHMDI) [1]	11.79	0.14	3.08	0.20
40(QA8+MDI) [1]	11.67	0.32	7.68	0.48
40(QA10+MDI) [1]	11.63	0.47	6.61	0.53
Reference copolymer				
409(UDMA) [1]	5.85	0.49	1.13	0.04

[1] Taken from [19].

4. Discussion

As part of this study, eight copolymers modified with monomers containing quaternary ammonium groups were synthesized. The monomers were based on aromatic and cycloaliphatic diisocyanates. The modified copolymers were characterized in terms of water contact angle (*WCA*), water sorption (*WS*), and water solubility (*SL*).

WCA measurements were performed using deionized water. The results showed that the surfaces of both the reference and all modified copolymers were hydrophilic, with all *WCA* values below 90° [21]. The *WCA* of 40(UDMA) was 74.07°. The main factors influencing *WCA* were the type of diisocyanate in the modifying monomers and the length of the N-alkyl substituent. Copolymers containing monomers based on cycloaliphatic diisocyanates exhibited lower *WCA* values (57.06–68.94°) compared to copolymers with aromatic diisocyanates (68.08–87.50°). Regarding the N-alkyl substituent, copolymers with an 8-carbon chain showed lower *WCA* values than those with a 10-carbon chain. A clear example of the influence of both the diisocyanate core and the length of the N-alkyl substituent is provided by copolymers containing CHMDI and MDI cores. Both diisocyanates have similar structures—CHMDI contains two cycloaliphatic rings, while MDI contains two aromatic rings. For 40(QA8+MDI), the *WCA* was 73.43°, and for 40(QA10+MDI), it was 87.50°. In the case of 40(QA8+CHMDI) and 40(QA10+CHMDI), the *WCA* values were 65.82° and 68.94°, respectively.

All modified copolymers exhibited higher *WS* and *SL* values than the reference copolymer. The *WS* values of the modified copolymers ranged from 9.34 to 14.00 μg/mm^3, while the *WS* of 40(UDMA) was 5.85 μg/mm^3. The *SL* values of QAUDMA copolymers ranged from 2.62 to 7.68 μg/mm^3, compared to 1.13 μg/mm^3 for 40(UDMA). According to ISO 4049, the *WS* and *SL* of dental materials should not exceed 40 μg/mm^3 and 7.5 μg/mm^3, respectively [20]. Thus, the *WS* values of all copolymers were satisfactory, while *SL* values were acceptable for all copolymers except 40(QA8+MDI), which had an *SL* of 7.68 μg/mm^3. The same factors that influenced *WCA* also affected *WS* and *SL*. Copolymers containing aromatic rings exhibited lower *WS* values (9.34–11.67 μg/mm^3) compared to those with cycloaliphatic rings (11.79–14.00 μg/mm^3). In contrast, *SL* values were higher for copolymers with aromatic diisocyanates (40(QA8+TMXDI), 40(QA10+TMXDI), 40(QA8+MDI), 40(QA10+MDI); 5.63–7.68 μg/mm^3) than for those with cycloaliphatic diisocyanates (40(QA8+IPDI), 40(QA10+IPDI), 40(QA8+CHMDI), 40(QA10+CHMDI); 2.62–3.08 μg/mm^3). The length of the N-alkyl substituent also influenced *WS*: copolymers

with longer substituents exhibited lower *WS* values. For example, *WS* was 10.46 μg/mm^3 for 40(QA8+TMXDI) and 9.34 μg/mm^3 for 40(QA10+TMXDI).

5. Conclusions

The study aimed to modify a dental copolymer using previously synthesized and characterized monomers containing quaternary ammonium groups derived from aromatic and cycloaliphatic diisocyanates. As a result, eight novel copolymers, along with a reference copolymer, were obtained via photopolymerization. The modified copolymers were evaluated in terms of water contact angle (*WCA*), water sorption (*WS*), and water solubility (*SL*). *WCA* measurements indicated that all copolymers possessed hydrophilic surfaces. *WS* values were satisfactory according to ISO 4049 [20], and *SL* values were also within the acceptable range for all copolymers, except for one sample. The main factors influencing these properties were the type of diisocyanate used during synthesis and the length of the N-alkyl substituent. Our further research will focus on the full characterization of the properties of modified copolymers. We will determine their physicochemical properties, such as the degree of conversion, glass transition temperature, and polymerization shrinkage, as well as mechanical properties, including hardness and flexural strength. A key aspect of the modified copolymers is their potential application as a matrix for DCRM; therefore, antibacterial activity and cytotoxicity will also be evaluated. All of the above-mentioned characteristics will be published in the future as part of a much broader characterization of the copolymers.

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