Application of Functional Monomers for Dental Use (Part-9) Syntheses of Succinoxy Methacrylates and Their Adhesion to Polished and Etched Tooth Surfaces.

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Four kinds of succinoxy methacrylates (2-succinoxypropyl methacrylate (2SPrM), 2-succinoxyethyl methacrylate (2SEM), 2-succinoxy-3-phenoxypropyl methacrylate (SPPM), and 2,2-bis-(4-(2-succinoxy-3-methacryloxypropoxy)-phenyl)-propane (Bis-SGMA)) were synthesized to improve the adhesive property of dental resins to tooth structure. Also the relations between concentration or chemical structure of these monomers and their adhesive property to polished and etched tooth surfaces were investigated.

The highest adhesion to unetched enamel surface after standing at room temperature and after soaking in water was obtained with Bis-SGMA (50 mol%), and SPPM (40 mol%).

The highest adhesion to unetched dentin surface after standing at room temperature and after soaking in water was obtained with 2SEM (55-65 mol%).

The highest adhesion to etched enamel and dentin surfaces was obtained with SPPM (40 mol%), and Bis-SGMA (15-25 mol%).

Key Words: Synthesized Monomers, Adhesive Strength, Bonding Agent

INTRODUCTION

In a previous paper,¹⁾ four kinds of succinoxy alkylene methacrylates with different lengths of the alkylene group were synthesized, and the relation between the structure of these monomers and their adhesion to the polished and etched tooth surfaces was investigated. The results showed that the average adhesive strength after standing at room temperature increased with decreasing carbon atoms in the alkylene group but the decrease in adhesive strength of these monomers with short alkylene groups was enhanced by immersion in water. Therefore, it was presumed that the adhesive strength of succinoxy alkylene methacrylates with short alkylene groups after immersing in water is improved by addition of a hydrophobic group such as phenyl or methyl groups to the alkylene group. In the present investigation, three kinds of succinoxy alkylene methacrylate derivatives containing different hydrophobic groups were synthesized and their adhesion to the polished and etched tooth surfaces was investigated.

MATERIALS AND METHODS

1. Preparation of monomers

1) Preparation of 2-succinoxypropyl methacrylate (2SPrM)

In a 500 ml round-bottomed flask fitted with a reflux condenser were placed 250 ml of tetrahydrofuran (THF), 15 gr of pyridine, 25 gr (0.25 mol) of succinoyl anhydride and 22 gr (0.15 mol) of 2-hydroxypropyl methacrylate. The mixture was heated to 55–60°C for 15 to 24 hours. The mixture was cooled to room temperature and then the solvent was evaporated under vacuum pressure. The residue liquid was dissolved in 200 ml of benzene and filtered when necessary.

The mixture was next cooled with ice and acidified to pH 3–pH 4 with cold 5% hydrochloric acid. The separated upper layer was washed with dilute acid and water, and then extracted three times with dilute sodium carbonate solution. After washing several times with cold ether, the combined extracts cooled with ice were acidified to pH 3–pH 4 with cold 5% hydrochloric acid. The precipitate was dried over anhydrous sodium sulfate.

2SPrM was isolated by column chromatography on silica gel and identified by elemental analysis, IR spectroscopy and NMR spectroscopy (Table 1).

2) Preparations of 2-succinoyl ethyl methacrylate (2SEM), 2-succinoyl-3-phenoxypropyl methacrylate (SPPM) and 2,2-bis-(4-(2-succinoyl-3-methacryloxypropyloxy)-phenyl)-propane (Bis-SGMA).

The preparation of 2SEM was reported previously.¹⁾ SPPM and Bis-SGMA were prepared by the reaction of 2-hydroxy-3-phenoxypropyl methacrylate synthesized by the method of Masuhara,²⁾ and commercial 2,2-bis-(4-(2-hydroxy-3-methacryloxypropyloxy)-phenyl)-propane isolated by column chromatography,³⁾ respectively, with succinoyl anhydride according to the method described above, but the synthesis of Bis-SGMA was carried out at 60–65°C for more than 24 hours, and SPPM (mp. 52–54°C) was purified by recrystallization from ether.

Table 1 Elemental analysis, IR and NMR data of synthesized monomers

2SPrM				SPPM				Bis-SGMA			
elemental analysis											
C		H		C		H		C		H	
found	calc'd	found	calc'd	found	calc'd	found	calc'd	found	calc'd	found	calc'd
54.10	54.09	6.78	6.60	60.67	60.71	6.07	6.00	62.01	62.35	6.51	6.22
¹ H-NMR (ppm)											
CH ₃	1.2, 1.3	(3H)		CH ₃	1.9	(3H)		CH ₃	1.6	(6H)	
CH ₃	1.9	(3H)		CH ₂	2.7	(4H)		CH ₃	1.9	(6H)	
CH ₂	2.7	(4H)		CH ₂	4.1, 4.2	(2H)		CH ₂	2.7	(8H)	
CH ₂	4.1, 4.2	(2H)		CH ₂	4.4, 4.5	(2H)		CH ₂	4.1, 4.2	(4H)	
CH	5.1–5.5	(1H)		CH	5.3–5.7	(1H)		CH ₂	4.4, 4.5	(4H)	
CH ₂ =5.6, 6.3		(2H)		CH ₂ =5.6, 6.3		(2H)		CH	5.3–5.7	(2H)	
				C ₆ H ₅	6.8–7.5	(5H)		CH ₂ =5.6, 6.3		(4H)	
								C ₆ H ₄	6.8–7.3	(8H)	
IR(cm ⁻¹)											
COOH		3300–2500		COOH		3300–2500		COOH		3300–2500	
C=O		1720		C=O		1720		C=O		1720	
C=C		1640		C=C		1640		C=C		1640

2,2-bis-(4-(2-succinoxy-3-methacryloxy propyloxy)-phenyl)-propane (Bis-SGMA)

2) Amount of water sorption

Synthesized monomers with BPO (0.5 wt %) were polymerized in teflon molds with ends covered with teflon plates at 110°C for 24 hours. Before polymerizing SPPM, however, it was melted and placed in the teflon mold.

The specimens (8.5φ × 0.5 mm) of the obtained polymer disks were immersed in water at 37°C and the amount of water sorption was determined from difference in weight before and after immersing the specimens.

3) Adhesive strength

1) Preparation of bonding agents

Mixtures of synthesized monomers (2SEM(20–80 mol %), 2SPrM(20–80 mol %), SPPM (10–40 mol %), and Bis-SGMA(10–50 mol %)) with 1,4-butylene glycol dimethacrylate (BGDMA) and 100 mol % synthesized monomers (2SEM and 2SPrM) were prepared for use as bonding agents, and BGDMA was used as a control. Because the solubility limit of SPPM with BGDMA was about 40 mol % and the viscosity of mixture containing more than 50 mol % of Bis-SGMA was too high to use as a bonding agent, the maximum concentration of SPPM and Bis-SGMA was 40 and 50 mol %, respectively.

The bonding agents were supplied as two liquids. One contained the monomer or comonomer and BPO(1.5 wt %), and the other contained ethanol, p-toluenesulfonic acid sodium salt(3 wt %) and p-tolydiethanol amine(1 wt %).

2) Treatment of bovine enamel and dentin surfaces

Treatment of enamel and dentin surfaces were carried out according to the previously described method.⁴⁾

The enamel and dentin surfaces finally polished with 1000-grit alumina powder or treated with 37% phosphoric acid solution for 1 min. were used as adherends.

3) Preparation of specimens

Preparation of specimens was carried out according to the previously described method.⁴⁾

4) Measurement of tensile adhesive strength

The adhesion of each bonding agents to the unetched tooth surfaces were measured after standing at room temperature for 10 min. and after immersing in water at 37°C for 24 hours, but to the etched tooth surfaces, measurements were made only after immersing in water at 37°C for 24 hours.

The adhesive strengths were determined as described previously.⁴⁾

RESULTS

The amount of water sorption was reduced by addition of hydrophobic group and decrease was larger for SPPM and Bis-SGMA, which contain a phenyl group (Table 2).

The relation between the adhesion of synthesized monomers to the unetched enamel and dentin surfaces, and their concentration is shown in Figures 1 and 2. The adhesion of the bonding agents with 2SEM, and 2SPrM to the unetched enamel surface after standing at room temperature increased up to 55–65 mol% and 35–45 mol%, respectively, but decreased with further increases in the molar ratios of synthesized monomers. However,

Table 2 Amount of water sorption (mg/cm²)

2SEM	4.2
2SPrM	4.0
SPPM	1.5
Bis-SGMA	0.9

Figure 1 Effect of concentration of synthesized monomers on adhesion to bovine enamel and dentin (enamel: dry(○), wet(●), dentin: dry(□), wet(■))

Figure 2 Effect of concentration of synthesized monomers on adhesion to bovine enamel and dentin (enamel: dry(○), wet(●), dentin: dry(□), wet(■))

the adhesion of the bonding agents with SPPM, and Bis-SGMA increased with increasing molar ratios of synthesized monomers. On the other hand, after soaking in water, the adhesion of the bonding agents with 2SEM, 2SPrM, and Bis-SGMA increased up to 65–75 mol%, 75–85 mol%, and 25–30 mol%, respectively, but decreased with further increasing molar ratios of synthesized monomers. However, for SPPM, the adhesion increased with increases in these molar ratios.

The adhesion on the bonding agents except for the bonding agent with 2SEM to the unetched dentin surface after standing at room temperature increased with increasing molar ratios of synthesized monomers. However, for 2SEM, the adhesion increased up to 55–65 mol% but decreased with further increases in these molar ratios. On the other hand, after soaking in water, the adhesion of the bonding agents with 2SEM, 2SPrM, SPPM, and Bis-SGMA increased up to 55–65 mol%, 60–70 mol%, 15–25 mol%, and 25–35 mol%, respectively, but decreased with further increasing molar ratios of synthesized monomers.

The adhesion to the unetched enamel and dentin surfaces was reduced by immersion in water. The relation between the strength of adhesion of synthesized monomers to the etched enamel and dentin surfaces, and their concentration is shown in Figures 3 and 4.

The adhesion of the bonding agents with 2SEM, and 2SPrM to the etched enamel surface increased up to 60–70 mol% and 75–80 mol%, respectively, but decreased with further increasing molar ratios of synthesized monomers. However, the adhesion of the bonding agents with SPPM, and Bis-SGMA increased with increasing molar ratios of synthesized monomers.

The adhesion of the bonding agents with 2SEM, SPPM, and Bis-SGMA to the etched dentin surface increased up to 35–45 mol%, 10–20 mol%, and 15–25 mol%, respectively, but decreased with further increasing molar ratios of synthesized monomers. However, the adhesion of the bonding agents with 2SPrM slightly increased with increases in these molar ratios.

Figure 3 Effect of concentration of synthesized monomers on adhesion to etched bovine enamel (2SEM(○), 2SPrM(●), SPPM(□), Bis-SGMA(■))

Figure 4 Effect of concentration of synthesized monomers on adhesion to etched bovine dentin (2SEM(○), 2SPrM(●), SPPM(□), Bis-SGMA(■))

DISCUSSION

The bonding of a dental resin to both unetched and etched tooth structure was improved by the use of bonding agents with succinoyx alkylene methacrylates as described in the previous paper¹⁾ and also, newly synthesized monomers promoted the bonding of the resin to both unetched and etched tooth structure. The adhesion of the bonding agents with synthesized monomers was greater than that of the control except for the adhesion of the bonding agents with SPPM (30–40 mol %), and Bis-SGMA (50 mol %) to the etched dentin surface as shown by the results in this paper.

Since the amounts of water sorption of newly synthesized monomers containing additional hydrophobic groups decreased, it was expected that the decrease in adhesive strength in water was less than those of the bonding agents with 2SEM. However, the average decrease in adhesive strength of the bonding agents with newly synthesized monomers in water was unexpected. In particular, the decrease became larger with higher molar ratios of SPPM and Bis-SGMA, and also, the adhesion to the etched dentin surface became lower. The adhesive layer thickened with increases in the molar ratios of SPPM, and Bis-SGMA because the viscosity increased and curing time shortened, hence the influence of water on adhesive property of the bonding agents with higher molar ratios of SPPM, and Bis-SGMA became greater.

However, the decrease in adhesive strength at lower molar ratios of SPPM, and Bis-SGMA, which contain a phenyl group was less than those of the other monomers in water and if the concentration of initiator and accelerator in the bonding agent, and the viscosity of the bonding agent are controlled in order to thin the adhesive layer, the decrease in adhesive strength of the bonding agents with SPPM, and Bis-SGMA at higher molar ratios may become less.

Therefore, the hydrophobing of monomer is necessary to inhibit the decrease in adhesive strength in water. Actually, the amount of water sorption was reduced by hydrophobing of monomer.

Also, to enhance the adhesive property of newly synthesized monomers, it is necessary to investigate the effect of both concentration and type of initiator, accelerator,⁵⁾ and diluent on their adhesion.

CONCLUSIONS

The four kinds of succinoy methacrylates were synthesized to improve the adhesive property of dental resins to tooth structure.

The amount of water sorption and the adhesive strengths of these monomers to unetched and etched tooth structure were measured to investigate the relation between chemical structure and the adhesive property.

The amounts of water sorption of SPPM and Bis-SGMA were lower than those of the other monomers.

The highest adhesion to unetched enamel surface after standing at room temperature and after soaking in water were obtained with Bis-SGMA (50 mol %), and SPPM (40 mol %).

The highest adhesion to unetched dentin surface after standing at room temperature and after soaking in water were obtained with 2SEM (55–65 mol %).

The decrease in adhesive strength of the bonding agents with 2SPrM, SPPM, and Bis-SGMA in water was comparable to those of the bonding agents with 2SEM.

The highest adhesion to etched enamel and dentin surfaces were obtained with SPPM (40 mol %), and Bis-SGMA (15–25 mol %).

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討を行った。

その結果によれば、いずれの材料にも時間-温度換算則が適用でき、重ね合わせの良好な合成曲線を作製することができた。パラフィンに、カルナウバワックスを添加した場合、高温側での応力緩和が著しく抑制されるこ

とがわかった。パラフィンにみつろうを添加すると、低温側の弾性率が低下することがわかった。またダンマルは混合物の応力緩和挙動にほとんど影響を与えないことが明らかになった。

溶融 Ni 基合金中の酸素の電気化学的測定

—添加元素としての Cu および Cr の影響—

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溶融 2 元系 Ni 基合金の酸素濃度を固体電解質を用いた電気化学的方法により評価した。そのセルは、 $\text{Pt}|\text{Mo} + \text{MoO}_2|\text{ZrO}_2(\text{MgO})|\text{O}(\text{液体})|\text{Mo}$ である。熱起電力 (EMF) から決定する酸素活性は純 Ni に Cu を添加した時増加した。すなわち、酸素濃度は、その添加量が 1 wt% 以上 30 wt% までの時、純 Ni での値よりも大きく

なった。2 元系 Ni-Cr 合金では、5, 7 および 10 wt% ほど Cr を含有すると、純 Ni よりも大きい酸素濃度を示すように思われ、15 および 20 wt% Cr の添加によって、純 Ni よりもより低い酸素濃度を呈するものと推測できる。

機能性モノマーの歯科的応用 (その 9)

各種 succinoxy methacrylate の合成と無処理および酸処理歯質への接着性

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レジンの歯質への接着性を改善するために、succinoxyethyl methacrylate (2SEM) に各種疎水基を導入した新しい succinoxy methacrylate (sSPRM, SPPM, Bis-SGMA) と 2SEM の 4 種を合成し、歯質への接着性と構造との関係を検討した。合成モノマーと BGDMA から調製した各種 bonding agent を無処理 (最終研磨: サンドペーパー #600) と酸処理 (37%リン酸, 1 分間処理) 牛歯エナメルおよびデンチンに薄く塗布し、その上から即重レジンを填入して作製した接着試料について、

室温に10分間放置後 (Dry: 無処理), 水中浸漬 1 日後 (Wet: 無処理と酸処理) に引張り接着試験を行った。無処理エナメルおよびデンチンへの接着性が Dry で最も優れていたのは、それぞれ Bis-SGMA (50 mol%) と 2SEM (55~65 mol%) であった。Wet では SPPM (40 mol%) と 2SEM (55~65 mol%) であった。酸処理エナメルおよびデンチンへの接着力が最も優れていたのは、それぞれ SPPM (40 mol%) と Bis-SGMA (15~25 mol%) であった。

合着用セメントの硬化後の寸法変化

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現在、市販されている 4 種類の系の合着用セメントについて練和比および試料寸法を変えた場合、硬化後の寸