

Adhesive Monomers to Dental Ceramics. I. Evaluation of *N*-Substituted 3-Amino-2-Hydroxypropyl Methacrylates as Adhesives for Calcium Metaphosphate Crystalline Glass-Ceramic

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SYNOPSIS

N-Substituted 3-amino-2-hydroxypropyl methacrylates have been evaluated as adhesives for calcium metaphosphate crystalline glass-ceramic, a potential esthetic dental restoration material. Although the adhesion to the ceramic was found to be much more difficult and dependent on the kinds of substituents than that of tooth enamel, monomers having a carboxyl group showed specifically high adhesive tensile strength. The strength tended to decrease as the hydrophobicity and molecular bulkiness increased. Surface treatment of the ceramic, especially with sodium hydroxide, proved effective in terms of both strength and durability for the carboxyl-containing monomers. Scanning electron microscopy analysis confirmed the importance of surface irregularity due to the alkaline treatment.

INTRODUCTION

Esthetics in dentistry is becoming increasingly important in recent years, and many new techniques and materials to fabricate tooth-like restorations are being developed. Among these materials, certain ceramics¹⁻³ are highly attractive for practical uses in many respects, but the potentials have not been fully explored owing to the brittle nature. To use ceramics as dental restorative materials under continual occlusal load, it is necessary to bond them steadily to tooth.^{4,5}

Strong adhesion of ceramics is difficult in most cases, and thus several procedures have been examined for treatment of ceramic surfaces with chemicals such as silane coupling agents^{6,7} and hydrogen fluoride.^{8,9} The adhesion, however, has not been improved much, although the acid etch technique¹⁰ is an accepted clinical procedure for enamel. Furthermore, no studies have been done on

the elucidation of desirable monomer structures for the adhesion of ceramics.

In view of the importance of development of high-performance dental adhesives useful for ceramic materials, we have focused our attention on the effective adhesion of calcium metaphosphate crystalline glass-ceramic. This ceramic is expected to have high potential in clinical applications because of similarities of the composition, appearance, and physical properties¹¹ to those of tooth and the characteristic high tractability for tailored fabrication. Here, we report the structural influence of a series of *N*-substituted 3-amino-2-hydroxypropyl methacrylates on the adhesion and also effectiveness of surface treatment with sodium hydroxide.

EXPERIMENTAL

Adhesive Monomers

N-Substituted 3-amino-2-hydroxypropyl methacrylates were prepared from glycidyl methacrylate and substituted amines as reported elsewhere.¹²

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Table I Composition of the Primer

	Composition A (%)	Composition B (%)
Methyl methacrylate	82.0	82.6
Poly(methyl methacrylate)	16.4	16.5
Dimethyl- <i>p</i> -toluidine	1.6	—
Benzoyl peroxide	—	0.9

Evaluation of Adhesion

Bonding Agent

A 5 w/w % monomer solution in ethanol was prepared as bonding agent.

Preparation of the Primer

Composition A and B shown in Table I were mixed for 30 s to form the primer just before use.

Preparation of Adherent Specimens

Calcium metaphosphate crystalline glass-ceramic (CMP, Asahi Glass Co. Ltd., Japan) was cast at 1100°C to form a plate measuring 10 × 10 × 3 mm and then crystallized at 700°C for 16 h. After polishing the surface with emery papers of up to no.

600 in running water, it was washed with water, cleaned with acetone, and dried. The surface-treated CMP was then immersed in 3 mol/L aqueous sodium hydroxide solution at room temperature for 30 min. The etched plate was washed well with running tapwater and dried with compressed air. A poly(methyl methacrylate) (PMMA) rod of 6 mm in diameter was polished in the same manner.

Adhesion Test

A bonding agent was applied to the adherent surfaces and dried with compressed air. Surfaces were then coated with the primer mixture. A PMMA rod was set perpendicular to the surface. The adherent specimen was allowed to stand at room temperature for 24 h or left in water at 37°C for a certain period. Adhesive tensile strength was measured with an autograph (AG-200B, Shimadzu Mfg., Japan) at a crosshead speed of 0.5 mm/min. The average value and standard deviation were calculated from the data for five specimens. Control strength was measured similarly without applying the bonding agent.

RESULTS AND DISCUSSION

For practical adhesion of dental ceramics to tooth, silane coupling treatment of the surface has been most commonly carried out, and similar attempts

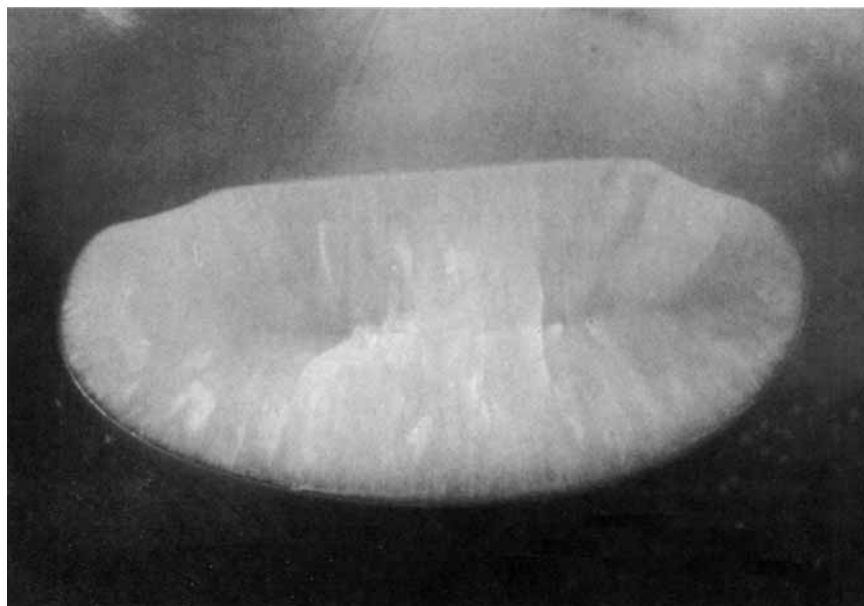


Figure 1 Micrograph of a cross-section of CMP showing crystalline and glass phases (magnification × 20).

are being made for crystalline glass-ceramic recently developed.¹³ Although these procedures are somewhat effective in some cases, it is still difficult to achieve high adhesion. We have thus far discussed

the structural factors of monomers influencing the adhesiveness to enamel and showed high possibilities of a series of 2-hydroxypropyl methacrylate derivatives.^{12,14} So, to elucidate the role of substituents

Table II Adhesive Tensile Strength of *N*-Substituted 3-Amino-2-Hydroxypropyl Methacrylates between CMP and PMMA

Compound No.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{COOCH}_2\text{CH}(\text{OH})\text{CH}_2-\text{R} \end{array}$	Tensile Strength (kg/cm ²) ^a
1		<i>m</i> - 66.2 ± 11.3
2		<i>p</i> - 76.6 ± 16.6
3		35.4 ± 10.2
4		39.1 ± 8.5
5		15.1 ± 3.1
6		11.3 ± 3.3
7		<i>m</i> - 50.3 ± 18.2
8		<i>p</i> - 56.0 ± 22.3
9		21.7 ± 6.6
10		13.4 ± 7.2
11		<i>m</i> - 102.8 ± 36.2 (0) ^b
12		<i>p</i> - 90.0 ± 8.6 (0) ^b
13		<i>m</i> - 104.3 ± 23.3 (0) ^b
14		<i>p</i> - 92.4 ± 17.3 (0) ^b
Control		22.2 ± 9.6

^a Determined after standing for 24 h at room temperature in air.

^b Determined after standing for 24 h at 37°C in water.

Table III Adhesive Tensile Strength of Monomers containing a Carboxyl Group for Sodium Hydroxide-Etched CMP

Compound No.	Tensile Strength (kg/cm ²) ^a		
	24 h	2 Weeks	3 Months
11	135.1 ± 18.6	104.6 ± 17.9 (147 ± 21) ^b	93.9 ± 22.0 (144 ± 36) ^c
12	168.0 ± 16.0	110.0 ± 18.4 (51 ± 19) ^b	108.7 ± 17.5 (58 ± 18) ^c
13	147.0 ± 41.0	105.7 ± 27.0 (131 ± 39) ^b	112.5 ± 20.6 (152 ± 16) ^c
14	146.2 ± 30.0	99.8 ± 15.2 (57 ± 12) ^b	109.8 ± 15.2 (64 ± 8) ^c
Control	44.6 ± 6.8	0 (50 ± 23) ^b	0 (39 ± 25) ^c

^a Determined after standing at 37°C in water.

^b Tensile strength for phosphoric acid-etched bovine enamel after standing for 2 weeks (2 months) at 37°C in water.

in adhesion of ceramic materials, these monomers have been evaluated in terms of adhesion strength toward CMP. CMP, like tooth enamel, is a calcium phosphate material with a basic composition of 49CaO52P₂O₅. A microscopic photograph of CMP (Fig. 1) showed that it consisted of both crystalline and glass phases, and the crystalline rods are oriented toward the surface. The structure is quite similar to that of enamel, in which the enamel crystalline rods also grow toward the tooth surface.

For rapid evaluation of adhesiveness, the tensile strength was measured after 24 h at room temperature, and the results are summarized in Table II. The substituents greatly affected the adhesion of CMP, and the values varied from 11.3–104.3 kg/

cm², the control value being 22.2 kg/cm². The monomethyl substituted aniline derivatives (1 and 2) showed modest adhesive tensile strength, but dimethyl (3) and diethyl (4) derivatives are quite poor in adhesion. The monomers having a phenyl (5) or chloro (6) substituted aniline moiety and a naphthalene (9) or anthracene (10) ring showed very low values, even lower than the control value. The monomer having ethoxycarbonyl group (7 and 8) also exhibited modest strength. This indicates that adhesiveness to CMP tended to decrease as hydrophobicity and molecular bulkiness of the substituents increased. The highest adhesive tensile strengths, 90.0–104.3 kg/cm², were observed for monomers 11–14, probably as a result of the interaction between the carboxyl group and calcium ions of CMP. Consequently, only those containing a carboxyl group showed high adhesion, indicating that the adhesion of CMP is much more difficult and dependent on the structure of substituents than that of enamel.

The adhesive strength in water at 37°C was then examined with these four monomers. The strength, however, turned out to decrease rapidly on standing and became practically zero in 24 h (Table II). All specimens were observed to fail in adhesion at the CMP–adhesive interface, again suggesting the inherent difficulty of CMP adhesion in aqueous environment. Some possible reasons of low adhesiveness are as follows: (1) CMP is not providing considerable wetting with adhesives; (2) functional groups, probably associated with adhesion, are not readily accessible on the surface; and (3) total surface area is insufficient.

Surface treatments of CMP were thus examined with various aqueous acids and bases to enable adhesion in aqueous environment. CMP was first

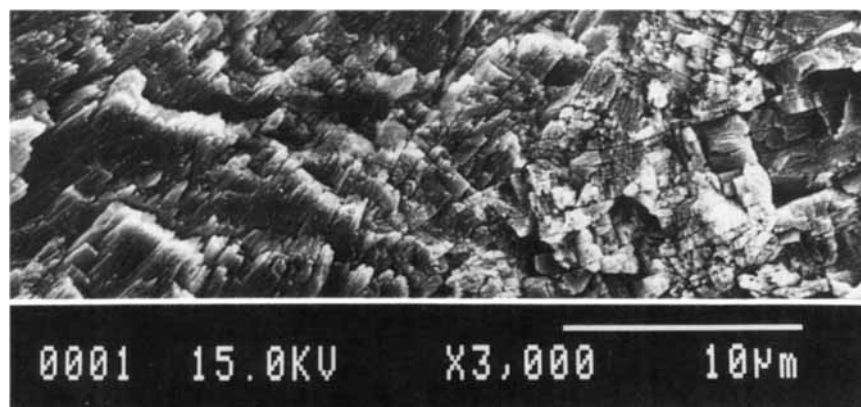


Figure 2 SEM of sodium hydroxide-etched CMP.

treated with acids including phosphoric acid, hydrofluoric acid, hydrochloric acid, nitric acid, and ethylene diaminetetraacetic acid, but only nitric acid showed considerable improvement. Bases such as sodium hydroxide and amines were then used, and sodium hydroxide was confirmed remarkably effective as shown by the high adhesion values listed in Table III. The treatment with sodium hydroxide is noteworthy in that it not only made possible adhesion in water but also improved the strength to a level similar to that for phosphoric acid-etched enamel. In the control experiments, the strength was low in the initial stage and became zero in 2 weeks even after sodium hydroxide treatment.

The scanning electron micrograph of CMP exposed to sodium hydroxide solution (Fig. 2) showed the presence of surface irregularity. This is presumably due to selective dissolution of the CMP surface; the glass phase is easily etched, while the crystalline one was left unaffected. The quite high adhesion attained through the etching is considered to be attributable to a marked increase in the total surface area and accompanying anchoring effect, and also to some sort of interaction of the carboxyl groups with the new surface formed on the material. The importance of the presence of carboxyl groups for CMP adhesion is thus confirmed, and monomers 11-14 are anticipated as potential high-performance dental adhesives for CMP, as well as tooth enamel.

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