

# Adhesive Monomers to Dental Ceramics. II. Methacrylamide Derivatives Containing Carboxyl and Phenyl Groups for Effective Adhesion of Calcium Metaphosphate Ceramic

SHINYA KITOH,<sup>1,\*</sup> KUNITOMO SUZUKI,<sup>2</sup> TAKAO KIYOHARA,<sup>2</sup> and KEISUKE KURITA<sup>3</sup>

<sup>1</sup>Pharmaceutical Laboratories, Lion Corporation, Odawara, Kanagawa, Japan; <sup>2</sup>Oral Care Laboratories, Lion Corporation, Odawara, Kanagawa, Japan; <sup>3</sup>Department of Industrial Chemistry, Faculty of Engineering, Seikei University, Musashino, Tokyo, Japan

## SYNOPSIS

Twelve methacrylamide derivatives containing carboxyl and phenyl groups have been evaluated as adhesives for calcium metaphosphate ceramic, a promising but hard-to-adhere cast ceramic restoration material. Although methacrylamide monomers having a carboxyl group showed low adhesive tensile strength for the ceramic, contrary to the glycidyl methacrylate derivatives, the monomer having neighboring two carboxyl groups at the phenyl ring exhibited quite high adhesion. Moreover, the monomer proved to retain high adhesion strength for the surface-etched ceramic for a long period of time even in water and would thus be suitable for practical clinical applications. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Recent growing interest in esthetics in dentistry has brought the development of many new techniques and materials to enable toothlike restorations.<sup>1,2</sup> Among restoration materials recently developed, calcium phosphate glass is expected to be potentially one of the most useful materials in clinical applications, since it is castable like metals and has close similarities to natural teeth in terms of appearance, composition, and physical properties.

To elucidate the high potential and overcome the brittle nature of ceramics as dental restorative materials under continual occlusal load, it is necessary to bond them durably to teeth.<sup>3,4</sup> Adhesion of dental ceramics has thus become increasingly important recently. It is, however, particularly difficult, much more difficult than that of tooth enamel, and no effective adhesion has been reported. Most of the attempts to improve the adhesion have been focused on the surface treatment of ceramics with silane couplers<sup>5</sup> or hydrogen fluoride,<sup>6</sup> but adhesion

strength is generally not satisfactory. This suggests the necessity of the development of new types of adhesive monomers, but molecular structures appropriate for high adhesion have not been discussed.

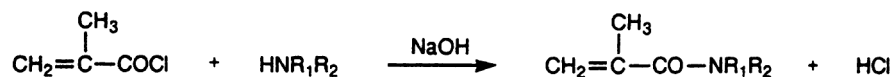
We have been interested in the relationship between the molecular structures of monomers and adhesion of calcium metaphosphate ceramic to open a way to clinical uses and have reviewed the structural influence of a series of *N*-substituted 3-amino-2-hydroxypropyl methacrylates on the adhesion of the ceramic to teeth.<sup>7</sup> High adhesion was achieved with carboxyl-containing monomers in both bond strength and durability. Here, we have evaluated methacrylamides containing carboxyl and phenyl groups with expectation of high-performance water-resistant adhesives for the ceramic.

## EXPERIMENTAL

### Adhesive Monomers

Methacrylamide monomers containing carboxyl and phenyl groups were synthesized from methacryloyl chloride and aniline derivatives in the presence of aqueous alkali (Scheme 1) according to the procedure reported previously.<sup>8</sup> To a mixture of an aniline

\* To whom correspondence should be addressed.



Scheme 1

derivative, sodium hydroxide, and water was added with agitation, over a 30 min period, freshly distilled methacryloyl chloride while maintaining the reaction temperature under 5°C. The mixture was acidified with diluted hydrochloric acid and the product was filtered. It was recrystallized from ethyl acetate.

## Evaluation of Adhesion

### Bonding Agent and Primer

Methacrylamide monomers were dissolved in ethanol to form 5 wt % solutions as bonding agents. The primer was prepared by mixing compositions A and B in Table I for 30 s just before use. Dimethyl-*p*-toluidine was added as the accelerator or co-catalyst for benzoyl peroxide to form the redox system.

### Adherent Specimens

Calcium metaphosphate glass (Asahi Glass Co., Japan) cast at 1100°C to form a plate measuring 10 × 10 × 3 mm was crystallized at 700°C for 16 h. The surface was polished with emery papers of up to no. 600 grit in running water, washed with water and then with acetone, and dried.

For surface etching, polished ceramic plates were immersed in a 3 mol/L aqueous sodium hydroxide solution at room temperature for 30 min. They were washed thoroughly with running tap water and dried with compressed air. Poly(methyl methacrylate) (PMMA) rods of 6 mm in diameter were polished and cleaned in the same manner.

### Adhesion Test

Surfaces of both the ceramic plate and the PMMA rod were coated with a bonding agent, dried with compressed air, and then coated with the primer. A PMMA rod was set perpendicular to the surface of the ceramic plate. 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 a bonding agent.

## RESULTS AND DISCUSSION

One of the most important requirements, and difficulties at the same time, for dental adhesives is to maintain the performance in the presence of water for a long period of time, and we found that glycidyl methacrylate monomers containing a carboxyl group achieved a high bond strength to calcium metaphosphate ceramic (CMP) even in a wet environment.<sup>7</sup> Methacrylamides are expected to be more water-resistant than are glycidyl methacrylates because of the presence of the amide linkage instead of the ester linkage. We discuss here the adhesion of CMP with methacrylamides containing carboxyl and phenyl groups that were shown to provide high adhesion to tooth enamel.<sup>8</sup>

The tensile strength between the CMP plate and PMMA rod was measured first, and the results for 12 monomers, after 24 h standing, are summarized in Table II. The monomers showed varying degrees of bond strength from 18 to 117 kg/cm<sup>2</sup> depending on the molecular structures. No significant differences in strength were observed among *o*-, *m*-, and *p*-isomers of *N*-carboxyphenyl/substituted monomers, i.e., monomers 1–3 and monomers 4–6. The tensile strength of the monomers decreased considerably when the hydrogen atom of the amide linkage was replaced by a methyl group (monomers 4–6) and drastically by a phenyl group (monomer 7). Three  $\alpha$ - and  $\beta$ -amino acid derivatives having a phenyl group (monomers 8–10) also exhibited moderate adhesion. These results indicate that adhesion of the CMP plate is not influenced much by the substitution positions of carboxyl and phenyl

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

**Table II** Tensile Strength of Adhesion Between the CMP Plate and PMMA Rod with Methacrylamides Containing Carboxyl and Phenyl Groups in Air

Monomer	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2=\text{C}-\text{CO}-\text{R} \end{array}$	Tensile Strength (kg/cm <sup>2</sup> ) <sup>a</sup>
1		<i>o</i> - 49.6 ± 13.2
2		<i>m</i> - 45.4 ± 11.8
3		<i>p</i> - 45.1 ± 16.1
4		<i>o</i> - 31.3 ± 14.2
5		<i>m</i> - 39.6 ± 15.3
6		<i>p</i> - 31.3 ± 8.6
7		18.1 ± 6.6
8		58.3 ± 22.3
9		50.6 ± 18.3
10		43.1 ± 15.8
11		62.8 ± 21.3
12		117.6 ± 28.3
Control		22.9 ± 9.6

<sup>a</sup> Determined after 24 h at room temperature.

groups as in the case of the adhesion of tooth enamel.<sup>8</sup> Bulkiness of the substituent also greatly influenced the adhesion of the CMP plate as reported for the glycidyl methacrylate monomers.<sup>7</sup> Consequently, the bond strengths of the monomers having a carboxyl group (monomers 1–10) were lower than

those of the glycidyl methacrylate derivatives having a carboxyl group,<sup>7</sup> and the highest value was only 58 kg/cm<sup>2</sup>.

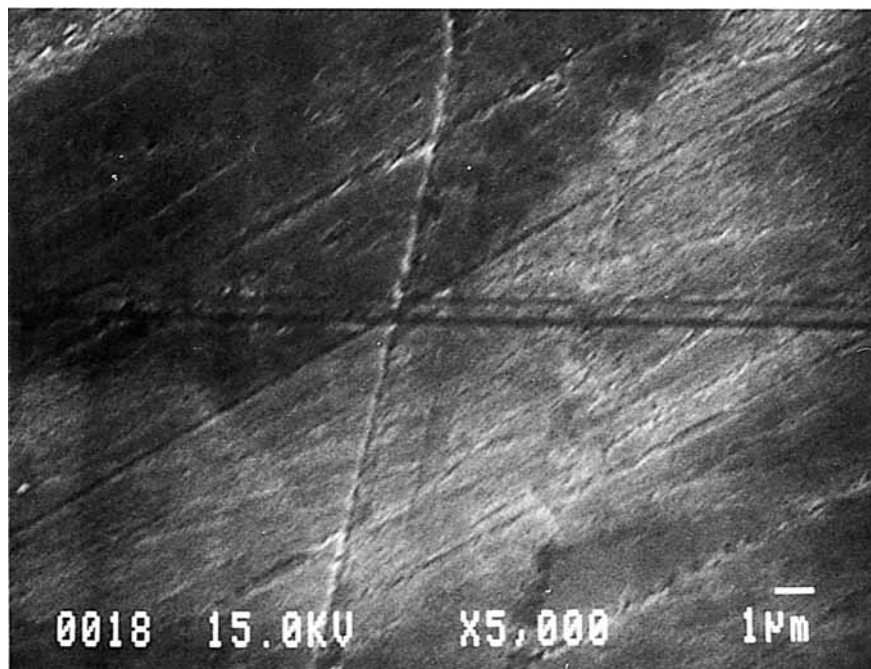
The glass employed here has a basic composition of 49CaO52P<sub>2</sub>O<sub>5</sub> and was crystallized at a 1 : 1 molar ratio of CaO and P<sub>2</sub>O<sub>5</sub> to form a ceramic with mixed crystalline and glass phases. The P<sub>2</sub>O<sub>5</sub> component accordingly becomes rich in the glass phase, and, hence, the ceramic surface is presumed to be polar, implying that monomers with higher polarity would show higher affinity for the surface. As expected, monomers having two carboxyl groups at the phenyl ring (monomers 11 and 12) exhibited high strength, and monomer 12 was confirmed to show a particularly remarkable strength of 117.6 kg/cm<sup>2</sup>. This suggests that the presence of two neighboring carboxyl groups is a key factor for achieving high adhesion where they are supposed to play important roles for promoting favorable interaction with calcium on the ceramic surface as well as for enhancing affinity owing to high polarity.

Monomer 12, the most effective one in air, however, showed an adhesive tensile strength of only 41.3 kg/cm<sup>2</sup> in water after 24 h, again indicating the characteristic difficulty in ceramics adhesion, especially under wet conditions.

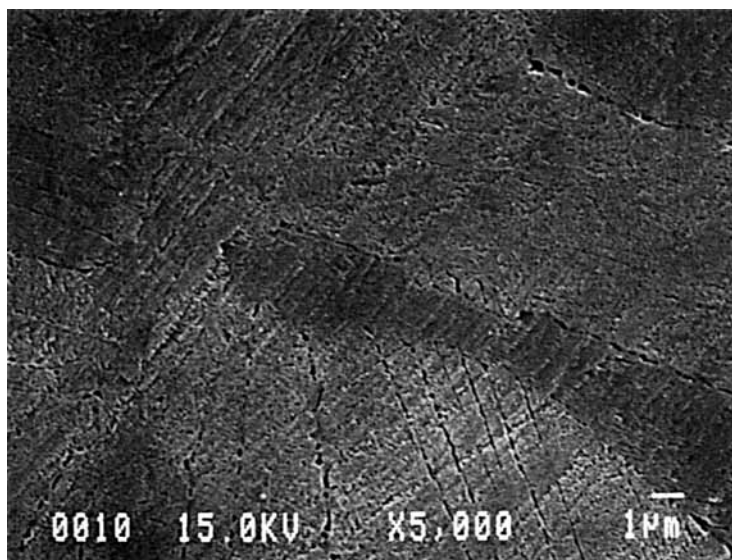
The CMP plate was then subjected to surface treatment to enable high adhesion in water. It was treated with various acids including phosphoric, hydrofluoric, hydrochloric, nitric, lactic, and ethylenediaminetetraacetic acids, and bases such as amines and aqueous sodium hydroxide. The etched surfaces were examined by scanning electron micrography. As shown in Figure 1, etching with alkali created clearer and deeper edges on the surface compared to acid etching and was thus expected to provide effective penetration of adhesives. In adhesion tests with commercial dental adhesives and *N*-(vinylbenzyl)iminodiacetic acid under various etching conditions, aqueous sodium hydroxide solution was actually confirmed to be effective, and the treatment with 3 mol/L sodium hydroxide at room temperature for 30 min turned out to be appropriate.<sup>9</sup> *N*-(Vinylbenzyl)iminodiacetic acid was also confirmed to achieve high and durable adhesion to the ceramic etched under the conditions found, with tensile strength of 171.5 kg/cm<sup>2</sup> after 24 h, 141.6 kg/cm<sup>2</sup> after 2 weeks, and 154.8 kg/cm<sup>2</sup> after 2 months in water.<sup>10</sup>

The CMP plate treated with aqueous sodium hydroxide under such conditions was thus employed for the adhesion test with monomer 12, and the bond strength of specimens kept in water was determined. As listed in Table III, while the strength

(a)



(b)



**Figure 1** Scanning electron micrographs of (a) polished, (b) lactic acid-etched, and (c) sodium hydroxide-etched CMP plate.

of the control experiment was low in the initial stage and became zero in 2 weeks, monomer **12** retained high tensile strength in water for a prolonged period.

The values after 2 weeks and 3 months are considered to be high enough, since they are in the same level as those for the adhesion of phosphoric acid-

(c)

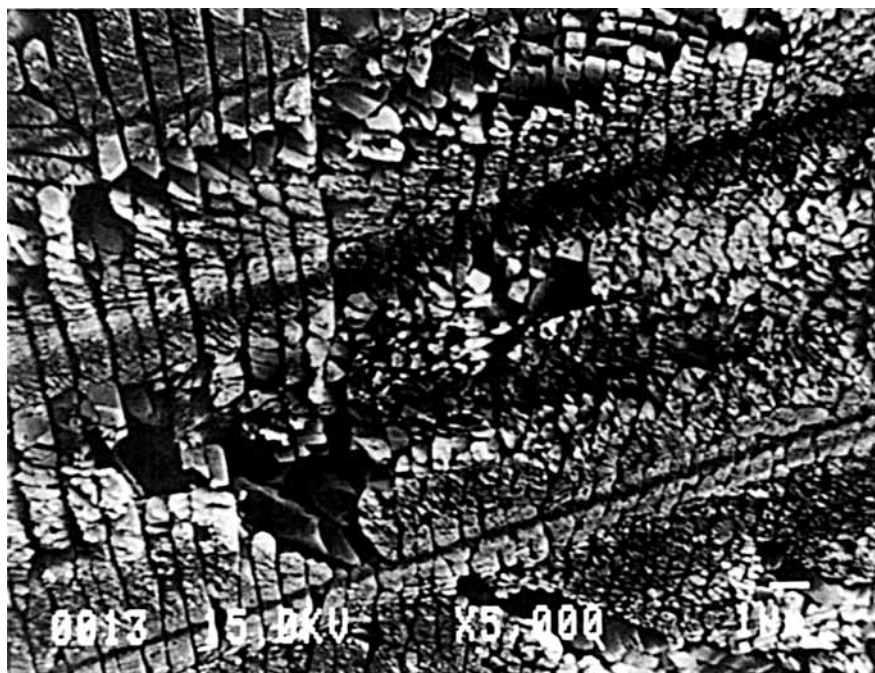


Figure 1 (Continued)

etched tooth enamel.<sup>8</sup> These results confirm that the monomer containing two neighboring carboxyl groups as exemplified by monomer **12** and *N*-(vinylbenzyl)iminodiacetic acid has high potential for practical clinical applications.

**Table III Tensile Strength of Adhesion Between the Alkali-etched CMP Plate and the PMMA Rod with Monomer 12 in Water**

No.	Tensile Strength (kg/cm <sup>2</sup> ) <sup>a</sup>		
	24 h	2 Weeks	3 Months
<b>12</b>	195.8 ± 15.0	127.3 ± 13.8 (121 ± 19) <sup>b</sup>	137.3 ± 32.9 (138 ± 32) <sup>c</sup>
Control	44.6 ± 6.8	0 (50 ± 23) <sup>b</sup>	0 (39 ± 25) <sup>c</sup>

<sup>a</sup> Determined after standing at 37°C in water.

<sup>b</sup> Tensile strength for phosphoric acid-etched bovine enamel after standing for 2 weeks at 37°C in water.

<sup>c</sup> Same as footnote b but for 2 months.

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