Adhesive Monomers to Dental Ceramics. III. Influence of Surface Treatment on Effective Adhesion of Calcium Metaphosphate Ceramic with *N*-(Vinylbenzyl)iminodiacetic Acid

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SYNOPSIS

Influence of surface treatment of calcium metaphosphate ceramic was analyzed in detail to achieve high adhesion in an aqueous environment with *N*-(vinylbenzyl)iminodiacetic acid as a novel dental adhesive monomer. The adhesion strength was enhanced greatly by alkali etching of the ceramic surface, although the adhesion profile varied with etching conditions. Scanning electron microscopy, electron probe microanalysis, and roughness evaluation indicated that high adhesion was closely associated with the formation of fine irregularity on the surface that was rich in Ca. *N*-(Vinylbenzyl)iminodiacetic acid was thus confirmed to be a suitable adhesive monomer for the ceramic in dentistry in terms of strength and durability when the ceramic surface was properly etched. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Esthetic dentistry is becoming increasingly important, and many kinds of new materials and techniques have been developed to make fabrication of toothlike restorations possible.[1-3] Calcium metaphosphate ceramic is one of the most promising materials for esthetic restorations, because it is processed easily by a casting technique like metals and is close to teeth in both appearance and physical properties. It is thus expected to have quite high potential for clinical uses.

In spite of the widely accepted importance of ceramics in clinical dentistry, adhesion of ceramics has remained difficult. Our recent studies[4,5] demonstrated that some carboxyl-containing adhesive monomers attained strong and durable adhesion for calcium metaphosphate ceramic treated with alkali. In this study we evaluated *N*-(vinylbenzyl)iminodiacetic acid as a novel carboxyl-containing adhesive monomer and examined how the alkaline treatment affected the ceramic surface and bonding properties to achieve clinically sufficient adhesion in the aqueous environment.

EXPERIMENTAL

Adhesive Monomer *N*-(Vinylbenzyl)iminodiacetic Acid

To a solution of 13.3 g (0.1 mol) of iminodiacetic acid and 6.6 g (1.65 mol) of sodium hydroxide in 200 mL of 50% methanol was added 15.3 g (0.1 mol) of chloromethylstyrene (*meta* : *para* = 60 : 40) dropwise with stirring at 60°C. After one-half the chloride was added in 30 min, 6.6 g of sodium hydroxide was added, and dropping of the chloride was further continued. After the addition was complete, the mixture was heated at 60°C for 30 min. The methanol was then distilled under diminished pressure to reduce the volume to two-thirds of the original. The solution was extracted with ether, and the aqueous phase was acidified to pH 2.5 with hydro-

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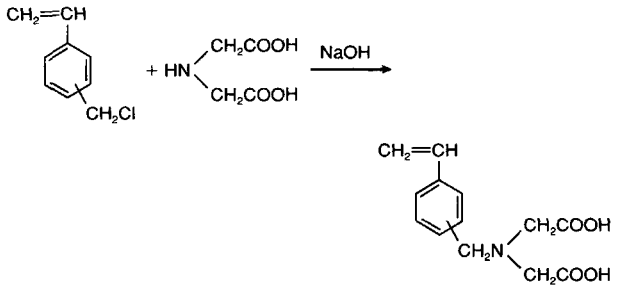
Journal of Applied Polymer Science, Vol. 60, 1821–1825 (1996)
 CCC 0021-8995/96/111821-05



Scheme 1

chloric acid to give a precipitate. It was collected by filtration and recrystallized from 10% methanol to give 5.1 g (20%) of white crystalline product that was a mixture of meta and para isomers (25:75) as determined by high performance liquid chromatography and IR spectroscopy: mp > 200°C (dec); IR(KBr) 1710 (C=O) and 1630 cm^{-1} (C=C).

ANAL. Calcd for $C_{13}H_{15}O_4N$: C, 62.64%; H, 6.07%; N, 5.62%. Found: C, 62.38%; H, 6.09%; N, 5.61%.

Adhesive

The adhesive used here consisted of two components: a powder and a liquid. The powder component was made of α quartz of 4-μm particle size containing 1.0 wt % benzoyl peroxide as the polymerization catalyst. The liquid component was a mixture of methyl methacrylate and 2,2-bis(4-(2-hydroxy-3-methacryloyloxypropyl)phenyl)propane (2:3 by weight) containing 0.5 wt % adhesive monomer and 1.2 wt % *N,N*-diethanol-*p*-toluidine as the cocatalyst for polymerization. Equal amounts of the two components were mixed for 30 s to form the adhesive just before use.

Preparation of Adherent Specimens

Calcium metaphosphate glass (Asahi Glass Co., Japan) having a composition of $49CaO52P_2O_5$ was cast at 1100°C and then crystallized at 700°C for 16 h to form a ceramic adherent specimen measuring 10 × 10 × 3 mm. 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 polished calcium metaphosphate ceramic was then immersed in an aqueous sodium hydroxide solution at a certain temperature for a certain period. The etched specimen was washed well with running tap water and dried with compressed air.

Poly(methyl methacrylate) (PMMA) rods 6 mm in diameter were polished in the same manner.

Adhesion Test

The adhesive was applied to the adherent surfaces of a ceramic plate and a PMMA rod. The rod was set perpendicular to the plate. The adherent specimen was left in water at 37°C for 24 h and then at a thermal cycle of 4°C for 1 min and 60°C for 1 min. This cycle was repeated 1,000, 3,000, 5,000, and 10,000 times. Shear adhesive strength was measured with an autograph (AG-200B, Shimadzu, Japan) at a crosshead speed of 0.5 mm/min. The average strength and standard deviation were calculated from five measurements.

Scanning Electron Microscopy (SEM) and Electron Probe Microanalysis

Carbon-coated ceramic surfaces were viewed with a JXA 8600 scanning electron microscope (JEOL, Japan) operated at an accelerating voltage of 15 kV, and the intensity ratios of the peaks due to Ca and P were calculated to estimate the surface composition.

Surface Roughness

Surface roughness was observed with a surface texture measuring instrument (Surfcom 900A, Tokyo Seimitsu, Japan). Ten points roughness, Rz, was calculated from the roughness profile obtained by tracing a length of 1.5 mm with a contacting needle 1 μm in diameter.

Dissolution Rate of Ca and P

Ten ceramic plates (10 × 10 × 3 mm) were immersed in 50 mL of 6*M* aqueous sodium hydroxide

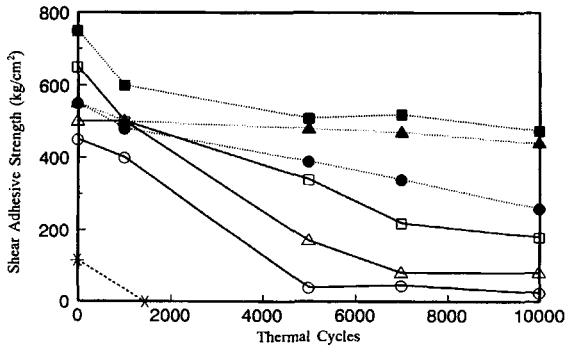


Figure 1 Changes in shear adhesive strengths of the ceramic during repeated thermal cycles of 4°C for 1 min and 60°C for 1 min in water: (*) Polished; etched at room temperature for (○) 1 min, (△) 3 min, (□) 5 min; etched at 80°C for (●) 1 min, (▲) 3 min, (■) 5 min.

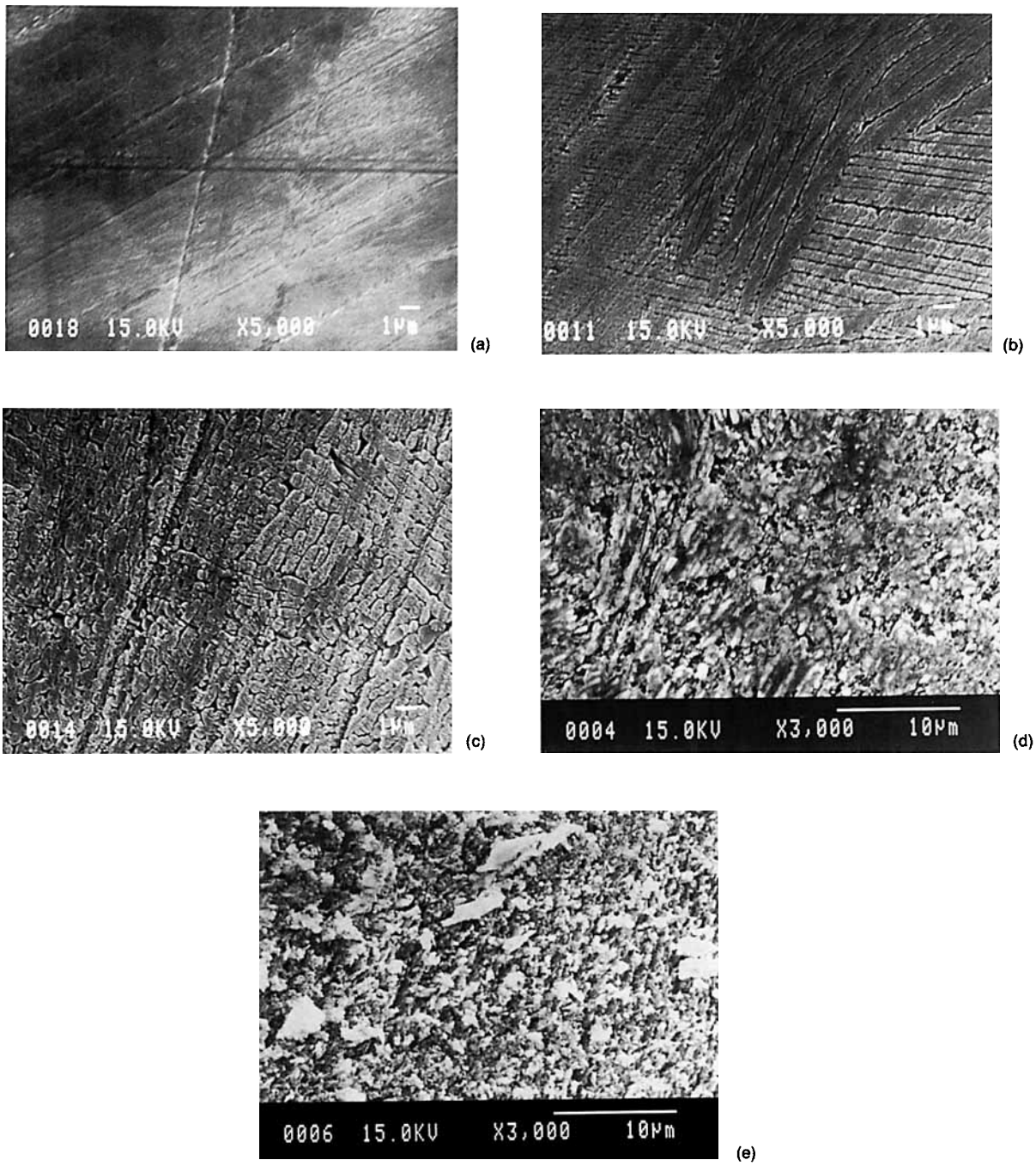


Figure 2 SEM micrograph of (a) polished calcium metaphosphate ceramic and calcium metaphosphate ceramic etched at (b) room temperature for 1 min, (c) room temperature for 5 min, (d) 80°C for 1 min, and (e) 80°C for 5 min.

solution at room temperature for 5 min. The amounts of eluted Ca and P were 0.69 $\mu g/cm^2$ (0.0173 $\mu mol/cm^2$) and 92.6 $\mu g/cm^2$ (2.99 $\mu mol/cm^2$) as determined by atomic absorption spectroscopy and the phosphovanadomolybdatate method,[6] respectively.

RESULTS AND DISCUSSION

Our previous studies[4,5] with various adhesive monomers indicated that high adhesion to calcium metaphosphate ceramic can be accomplished when the monomers have carboxyl groups at appropriate po-

Table I Surface Properties of Calcium Metaphosphate Ceramic Etched with Sodium Hydroxide

Etching Conditions		Surface Properties	
Temp. (°C)	Time (min)	Ca/P[a]	Rz[b] (μm)
—	—	1.27 (1.00)	0.48 (1.00)
rt	1	1.30 (1.02)	0.71 (1.47)
rt	3	1.33 (1.04)	0.53 (1.10)
rt	5	1.32 (1.03)	2.68 (5.56)
80	1	1.58 (1.24)	1.30 (2.70)
80	3	2.21 (1.73)	4.45 (9.23)
80	5	2.06 (1.62)	12.99 (26.94)

rt, room temperature.

[a] Peak intensity ratios determined by EPMA. Values in parentheses are ratios relative to the control value.

[b] Rz, Ten points roughness. Values in parentheses are ratios relative to the control value.

sitions and the surface is treated with alkali. These results suggested that *N*-(vinylbenzyl)iminodiacetic acid should have high potential as a novel adhesive monomer for the ceramic in clinical applications. This monomer was synthesized from chloromethylstyrene and iminodiacetic acid[7] according to Scheme 1 and was a mixture of meta (25%) and para (75%) isomers.

Tensile strength of the monomer for the polished calcium metaphosphate ceramic was determined first, and it was 114.9 kg/cm^2 in air at room temperature after 24 h and 65.8 kg/cm^2 in water at 37°C after 24 h. The strength for the ceramic etched at room temperature with 3*M* sodium hydroxide for 30 min was, however, as high as 154.8 kg/cm^2 even in water at 37°C after 2 months, indicating the importance of etching for strong adhesion.

To establish optimum etching conditions for reliable and improved adhesion, therefore, the relation between the surface treatment with sodium hydroxide and adhesiveness was examined in detail after repeated thermal cycles at 4°C for 1 min and 60°C for 1 min in water to simulate the actual dental environment. Shear bond strengths of the ceramic etched under various conditions were measured after up to 10,000 thermal cycles, and adhesive profiles are shown in Figure 1. As evident in the figure, the bond strength for the polished surface dropped to zero after around 700 cycles. The etched specimens showed much improved adhesion, and the strength became higher as the etching temperature and time increased. Even after 10,000 cycles, the strength of the surface etched at 80°C was in the range of 260–475 kg/cm^2, although some reductions of the strength were observed, particularly in the initial stage. *N*-(Vinylbenzyl)iminodiacetic acid thus turned out to be a clinically applicable adhesive monomer for dental restoration, because commercially available dental adhesives show shear bond strength of 100–200 kg/cm^2 for the adhesion between tooth enamel and composite resins.[8] Judging from the values of the bond strength and ease of practical manipulation of the surface treatment, etching at room temperature for 3–5 min appeared to be appropriate.

The surface treatment proved to be quite effective, and thus the changes in the surface features were analyzed by electron microscopy in terms of its appearance and composition to elucidate essential factors for improving adhesion. Scanning electron micrographs of the surfaces are shown in Figure 2(a–e). Advanced irregularity was observed on the etched surface compared to the polished one. The surfaces etched at room temperature show clear edges of crystalline phases [Fig. 2(b,c)]. As reported previously,[4] because the ceramic consisted of crystalline and glass phases, the formation of clear edges was probably owing to selective dissolution of the glass phases. In sharp contrast to the etching at room temperature, the etching at 80°C resulted in the disappearance of clear edges. This indicates that both the glass phases and some part of the crystalline phases dissolved simultaneously at elevated temperatures.

The compositional changes of the surface were examined by electron probe microanalysis (EPMA). The relative intensities of the peaks due to Ca and P were measured to elucidate the surface compositions. As listed in Table I, the Ca/P value became higher on etching at higher temperatures and for longer times, indicating the formation of a Ca-rich surface.

In the crystallization process of the glass whose initial composition is $49CaO52P_2O_5$, crystalline parts develop with equivalent molar amounts of CaO and P_2O_5. The ceramic has thus the crystalline phases in addition to the glass phases rich in P_2O_5. When the ceramic was immersed in alkali solution, the glass phases dissolved preferentially. The dissolution rates of Ca and P were hence determined, and, actually, the dissolution of P from the ceramic into aqueous alkali was 173 times faster than that of Ca.

To compare the extent of irregularity of the etched surfaces, the roughness was measured. The values of ten points roughness, Rz, one of the pa-

rameters often used to estimate surface roughness,[9] are included in Table I. Rz increased with etching temperature and time, and the increases in the value were remarkable after 5 min. As Rz increased, adhesion became more and more reliable as evident in Figure 1. Both the SEM observation and roughness measurement have thus proved to be useful tools for the evaluation of surface irregularity that promotes micromechanical bonding.

Consequently, adhesion profiles of the calcium metaphosphate ceramic were dependent on the surface treatment with alkaline solution, and adhesive strength could be improved markedly. The alkaline surface treatment caused the formation of fine irregularity and the concentration of Ca on the surface. These results indicate that both micromechanical bonding due to irregularity and the interaction between the Ca and carboxyl groups of the monomer apparently contribute to effective adhesion. *N*-(Vinylbenzyl)iminodiacetic acid was thus confirmed to be a suitable adhesive monomer for the surface treated ceramic to accomplish high adhesion for clinical applications.

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Received February 10, 1995
Accepted November 23, 1995