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An advanced multipurpose dental adhesive system

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Abstract—An advanced dental adhesive system, composed of acrylic monomers and coupling agents, characterized by high tensile bond strength, enhanced durability, and biocompatibility was developed. The adhesive composition is curable chemically (self curing) or by visible light.

This adhesive composition can be used for bonding to various substrates such as dentin, enamel, precious and nonprecious alloys, 'fresh' and 'set' amalgam, porcelain, and dental composite. Thus, the developed liquid adhesive composition could be considered as a universal dental adhesive.

Keywords: Dental adhesive; acrylic; amalgam; UV curing.

1. INTRODUCTION

A variety of dental bonding agents (DBAs) have been formulated and commercialized for adhesion to complex dentin surfaces. Based on universality and shrinkage resistance, DBAs could be categorized into four generations as follows:

First generation

The first adhesive material in dentistry was methylmethacrylate (MMA), polymerized with tri-*N*-butylborane [1]. The tensile adhesion strength to dentin obtained in this case was only 2–3 MPa. Other active agents used were [2]: glycidyl methacrylate (GMA) and *N*-phenylglycine (NPG), and 2-hydroxyethylmethacrylate (HEMA).

Surface treatment involves mainly phosphoric acid etching [3], while adhesion is obtained by the adhesive infiltration into the dentin structure resulting in mechanical interlocking and enhanced strength, and reduced bond deterioration to hydrolysis.

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Second generation

A new group of dental adhesives [4, 5] was offered either for enamel or dentin, or exclusively for dentin. Bisphenylglycidylmethacrylate (BisGMA) and tetraethylglycidylmethacrylate (TEGDMA) adhesives were responsible for ionic bonding to calcium (in hydroxyapatite of the tooth structure). However, these bonding systems were sensitive to water environment and thermocycling. Tensile adhesion strength obtained by the second generation of DBAs was 6–9 MPa.

The pretreatment used can be divided in two major categories: either a pretreatment of smear layer by mild agents, or a complete removal of smear layer by acids. The mild agents used are chlorophosphate esters and phosphate esters [6]. The resultant bond exhibits good hydrolytic stability, higher bond strength and reduced microleakage compared to the first generation adhesives.

Third generation

The third generation of DBAs evolved as a result of a major development in the adhesive technology and a better understanding of the structure, organization and the physiological function of the smear layer and its role as a diffusion barrier. The materials developed and used were: *N*-tolyglycineglycidylmethacrylate (NTG-GMA) [7]; maleic acid/2-HEMA system [8]; 4-methacryloxyethyltrimellitate (4-META) [9], etc. It was demonstrated that the multifunctional molecules of coupling agents such as 4-META were responsible for obtaining good adhesion between the curing polymer system and any hydrophilic surface. Bond strength obtained for these compositions was in the range of 10–18 MPa.

Fourth generation

The fourth generation of DBAs was the result of the quest for a simple multipurpose adhesive system which was compatible with enamels, dentin, various alloys, amalgam, porcelain and dental composites, and had a bond strength in the range of 20 MPa. For good adhesion, the adhesive had to penetrate successfully through the smear layer, but should not significantly affect the hydroxyapatite of the tooth material. Furthermore, the polymerization shrinkage had to be minimized for enhanced durability, and the refractive index values of the composition had to be in the range 1.54–1.59 for aesthetic considerations. An additional requirement was to develop an adhesive bond which was hydrolytically stable since humidity adversely affects most bonding agents.

The following three commercial systems currently meet these requirements: Fenure (DENMAT) [10]; All-Bond (Bisco) [11] and Scotch Bond (3M) [12]. 4-META based systems could also be included in this category due to their high bond strength to a variety of substrates [9].

The need still exists for a universal non-specific bonding agent, which will widen the possibilities for simpler design and greater adhesion strength. Consequently the present work was aimed at developing a dental adhesive, suitable for the restoration of lost and damaged tooth structure, which meets the following general requirements: high bond strength to different surfaces, durability, biological compatibility and good handling and setting characteristics suitable for use under clinical conditions.

2. EXPERIMENTAL

2.1. Adhesive system

The adhesives developed in the course of the present investigation were based on acrylic resins cured chemically or by visible light radiation. This is a new commercial dental adhesive, named H-Q-Bond (Table 1) developed by BJM Lab. Ltd. It is being sold now in Italy ('Dentalica'), France ('Promodontare'), Great Britain ('Scientific-Metalor'), Germany ('Dr. Ihde Dental') and in other countries. It is patented [13, 14] and consists of methylmethacrylate (MMA), crosslinked with a multifunctional agent (trimethylolpropanetriacrylate which is SR-444). An adhesion promoter (glycidoxypropyltrimethoxysilane, Z-6040, Dow Corning) and a comonomer — aliphatic polyester urethane acrylate — are used in addition to demethyl-*p*-toluidine and benzoyl peroxide as initiators of self curing process. Camphorquinone (CQ) and ethyl-4-dimethylaminobenzoate (EDB) are used as photosensitizers for photocuring process. The composition also consists of organic (polymethylmethacrylate, PMMA) and inorganic (silica, metal alloy powder — 70% Ag; 25% Cu; 3% Sn) fillers and curing accelerators [13, 14].

Three different versions are discussed here:

H-Q-Bond (A) consists of MMA, peroxide, amine accelerator, crosslinking agent, PMMA, silica, titanium dioxide, metal powder, and adhesion promoter;

H-Q-Bond (B) consists of MMA, crosslinking agent, PMMA, silica, titanium dioxide, metal powder, adhesion promoter, and photosensitizers;

H-Q-Bond (C) consists of MMA, aliphatic polyester urethane acrylate, adhesion promoter, crosslinking agent and photosensitizers.

Table 1.
Commercial adhesive compositions used

Adhesive composition	Manufacturer	Description
All-Bond	Bisco, USA	Urethane dimethacrylates; Bis-GMA based
Amalgambond	J. Morita, Japan	4-META based
C & B Metabond	J. Morita, Japan	4-META based
Scotchbond multi-purpose	3M, USA	Bis-GMA based
H-Q-Bond:	BJM Lab. Ltd. Israel	Urethane acrylate-based
A	BJM Lab. Ltd., Israel	Chemically cured filled composition
B	BJM Lab. Ltd., Israel	Light cured filled composition
C	BJM Lab. Ltd., Israel	Liquid light cured composition (Liner)

2.2. Test methods

2.2.1. Tensile strength. A rod made of polymethylmethacrylate, 5 mm in diameter, was bonded to different substrate materials (amalgam, dentin, enamel, ceramics, different alloys) using H-Q-Bond adhesives which are brushed on both surfaces. The thickness of adhesive layer thus obtained was in the range 50 μm for liquid adhesive and 150–200 μm for the filled one.

Curing was performed chemically or by irradiation for 40–50 seconds using visible light lamp, Demetrom, Optilux 250, Healthco Israel Ltd.

Following bonding all specimens were kept at room temperature for 24 h and then soaked in water at 37°C for 24 to 1800 h to evaluate their durability after exposure to water.

The tensile strength was determined using an Instron mechanical tester (Zwick 1464) in accordance with ASTM D897. The crosshead speed was 1 mm/min and the number of specimens was 8–10 for each run.

Figure 1 presents the schematic of the tensile adhesion strength tester used.

2.2.2. Electron microscopy. Scanning electron microscopy (SEM) was carried out using a JOEL-840 microscope.

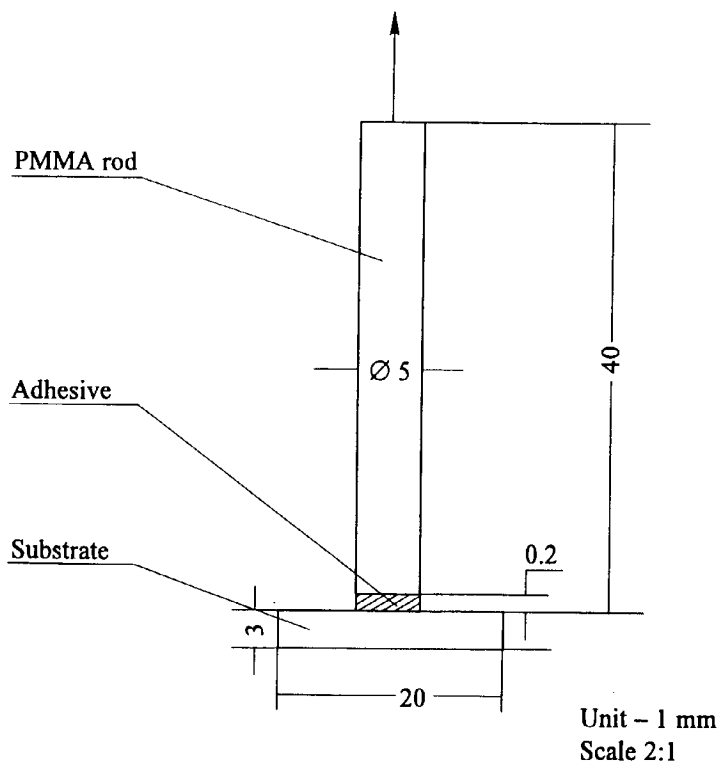


Figure 1. Scheme of tensile adhesion strength measurement.

2.2.3. *Thermal analysis.* Differential scanning calorimetry (DSC) was used (Du Pont Thermal Analyzer 2000) to characterize the curing process of the various dental adhesive compositions.

2.2.4. *Hardness measurement.* Hardness testing was carried out using a Rockwell Hardness Tester (Acco Wilson Instrument, USA) in accordance with ASTM D785-81.

2.2.5. *Compressive strength.* Compressive strength was measured in accordance with ASTM D1621-79 using a Zwick-1464 apparatus.

2.2.6. *Biocompatibility evaluation.* Biocompatibility of the adhesive material was determined in accordance with general histologic examination of the living tissue tolerance to dental adhesive composite [15].

H-Q-Bond (B) adhesive was evaluated in six dogs following creation of cavities in upper teeth.

The control treatment was that of an existing cementing commercial adhesive C & B Metabond (J. Morita, Japan). The cavities were filled with either H-Q-Bond or C & B Metabond, following manufacturers instructions. Also, free and attached gingiva from a tooth without a cavity served as an intact control.

The treated teeth were extracted 6, 14 and 20 days following the fillings. The samples were fixed in 4% phosphate buffered neutral formalin solution, demineralized, dehydrated and embedded in paraffin. Sections of 6 μm were cut and histologically examined.

3. RESULTS AND DISCUSSION

During the course of the work several dental adhesive compositions with sufficiently high values of tensile adhesion strength to different substrates were developed and evaluated. Table 2 presents typical adhesion strength for chemically selfcured (A);

Table 2.
Tensile bond strength of H-Q-Bond adhesive compositions to different substrates

Adhesive material	Tensile bond strength MPa ($\pm 20\%$) substrate					
	Amalgam	Dentin	Perspex	Cr-Ni alloy	Pd-based alloy	Titanium
	'set'					
H-Q-Bond (A)	14.0	9.7	25.0	24.0	12.0	15.0
	15.8					
H-Q-Bond (B)	12.0	8.5	18.7	12.2	12.5	—
	12.8					
H-Q-Bond (C)	13.7	10.0	20.0	12.8	13.0	—
	10.8					

light cured (B), and liquid (C) compositions of the new commercial H-Q-Bond Adhesive.

As can be seen the tensile strength of compositions (A) and (B) is high to 'set' and 'fresh' amalgam. This may be attributed to metal powder incorporated in the adhesive (1% by weight of metal alloy, comprising Ag, Sn, and Cu) in the form of fine particles, generally having a diameter between 5 and 50 μm .

The presence of metal powder in the adhesive composition is responsible for the excellent adhesion even to 'fresh' amalgam. This may be due to the continuous formation of amalgam after restoration, by the metal particles inside the adhesive. It is known [16] that completion of the amalgamization process can take up to a few months.

The time of polymerization of H-Q-Bond (A) adhesive is maintained in between 10–15 min for restoration type compositions. Figure 2 presents a DSC-curve of chemically initiated (composition A) polymerization process under isothermal conditions. The complete polymerization takes 12.0 min.

The durability of the same adhesive composition for bonding to amalgam was evaluated following exposure to water at 37°C for 1800 h. As can be seen in Fig. 3, a sufficiently high level of tensile adhesion strength is manifested following exposure to water.

It is often necessary in restorative practice to cure the adhesive in a minute or less. The H-Q-Bond (B) adhesive could be polymerized to a depth of 1 to 3 mm in only 40–50 s by radiation.

The tensile adhesion strength of this adhesive composition to various materials is high (Table 2) and durability appears to be acceptable after exposure to water for 500 h.

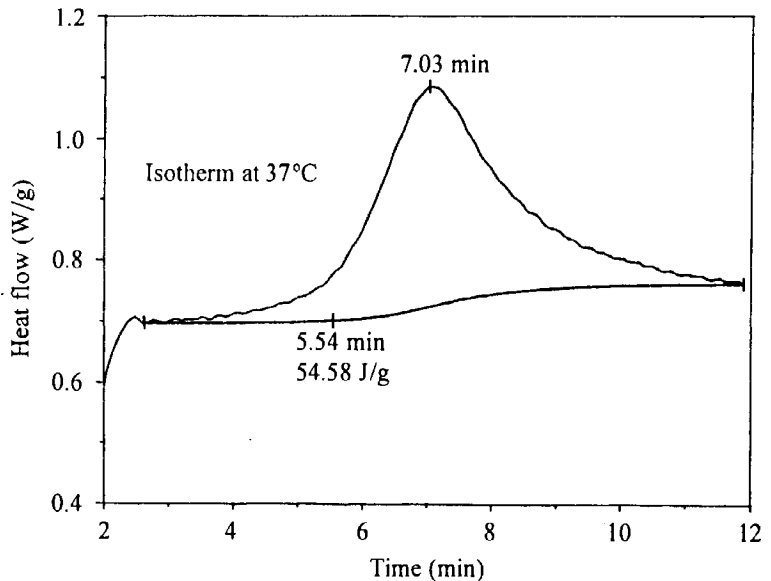


Figure 2. DSC isothermal curve for curing of H-Q-Bond (A) adhesive.

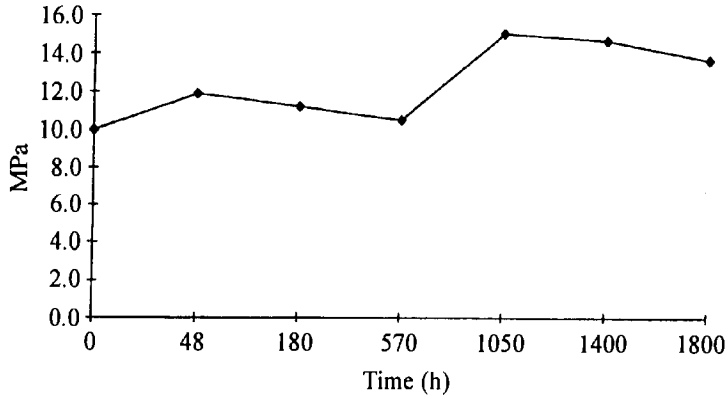


Figure 3. Durability of H-Q-Bond (A) adhesive to amalgam.

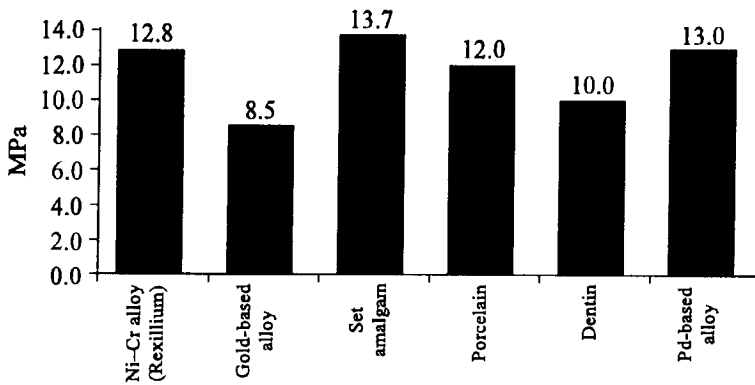


Figure 4. Tensile adhesion strength of H-Q-Bond (C) adhesive to different substrates.

Liquid H-Q-Bond (C) composition could also be polymerized to a depth of 1 to 3 mm in 35 s by visible light radiation. This composition could be used as a liner (bottom layer) and adhesive as well. Figure 4 depicts values of tensile bond strength of this composition to different substrates. Its bonding capability is sufficiently high for practical purpose.

Adhesion of H-Q-Bond materials to dentin is also appreciable. As can be seen in Fig. 5, adhesion strength of composition (A) exceeds those of commercially available dental adhesives.

Compressive strength and hardness tests were carried out for the adhesive H-Q-Bond (B) composition and compared to commercial material, based on Bis-GMA. The results are presented in Table 3. The hardness and compressive strength values of H-Q-Bond (B) are higher than those of All-Bond adhesive.

A comparison of tensile adhesion strength of H-Q-Bond (A) to different substrates with that for a variety of commonly used commercial adhesives [17] is presented in

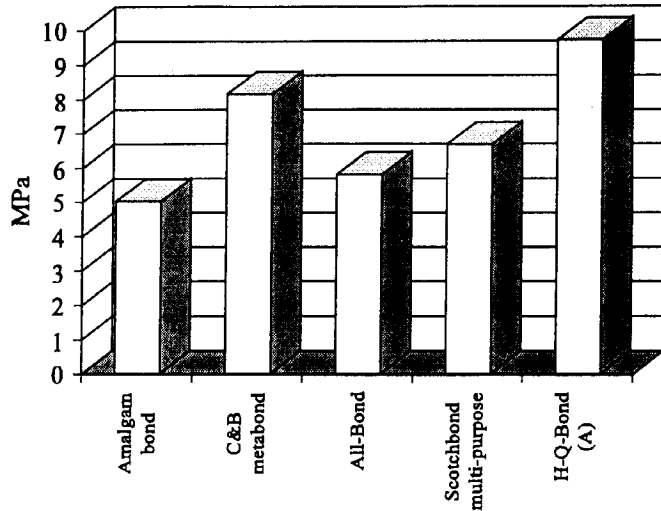


Figure 5. Comparison of tensile adhesion strength to dentin for H-Q-Bond (A) adhesive and a variety of commercial adhesives.

Table 3.
Mechanical properties of photocured filled adhesive compositions

Adhesive material	Hardness, ($\pm 10\%$)		Compressive strength, MPa ($\pm 15\%$)
	Rockwell	Knoop	
Bis-GMA (All-Bond)	44	55	14.08
H-Q-Bond (B)	57	68	28.17

Figs 6 and 7. These values show that for bonding to Ni–Cr alloy and to ‘fresh’ and ‘set’ amalgam, H-Q-Bond (A) exhibits superior adhesion strength compared to the five commercial adhesives studied.

The H-Q-Bond (B) adhesive exhibits tissue compatibility when used as a filling material in dental cavities of a dog. Histologically, the intact controls showed normal histology of a dog gingiva. The results of this experiment [15] clearly indicate the tissue friendliness of this material when used as a filling composition in a dog’s dental cavities.

Sections of these examined teeth were cut and were either stained for light microscope examination or used as such for electron microscopy. Light microscopy (Fig. 8a) showed that in the cavity wall, despite the dissolution of most of the H-Q-Bond (B) filling material during the processing of the samples for histological examination, some of it was still present. This result indicates a strong adhesion developed to the dentin in the cavity wall.

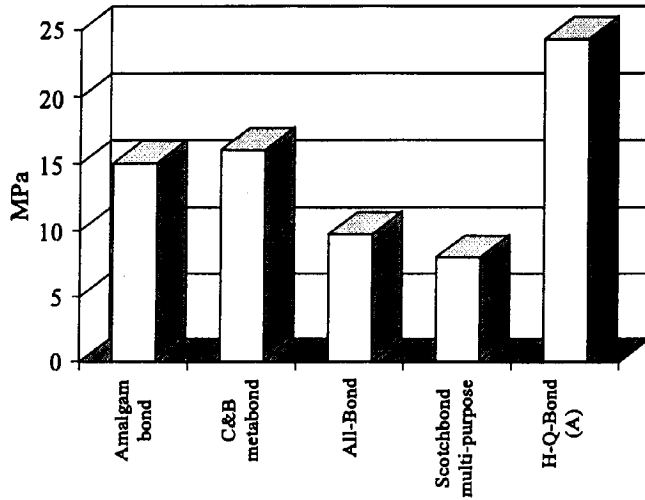


Figure 6. Comparison of tensile adhesion strength to Ni-Cr alloy for H-Q-Bond (A) adhesive and a variety of commercial adhesives.

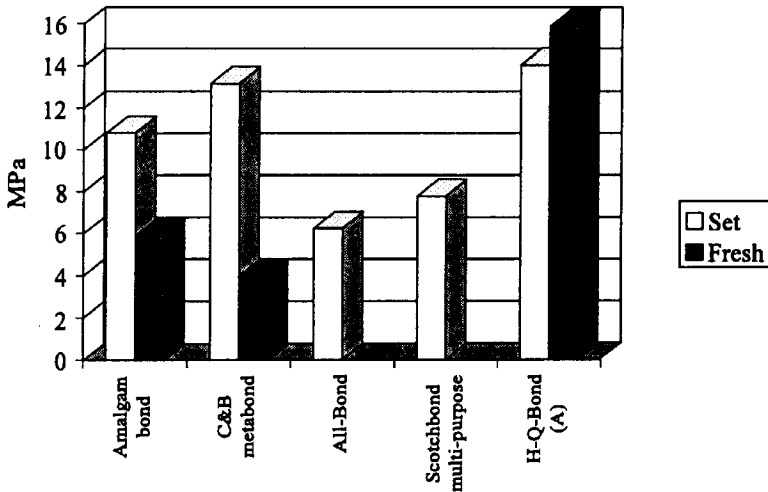


Figure 7. Comparison of tensile adhesion strength to 'set' and 'fresh' amalgam for H-Q-Bond (A) adhesive and a variety of commercial adhesives.

The penetration of the bonding resin into the dentinal tubules, which was found in the best dental adhesives [18], was also observed by SEM. Figures 8b and 9 present SEM pictures of the dentin surface with H-Q-Bond (B) remaining after demineralization of the teeth samples examined.

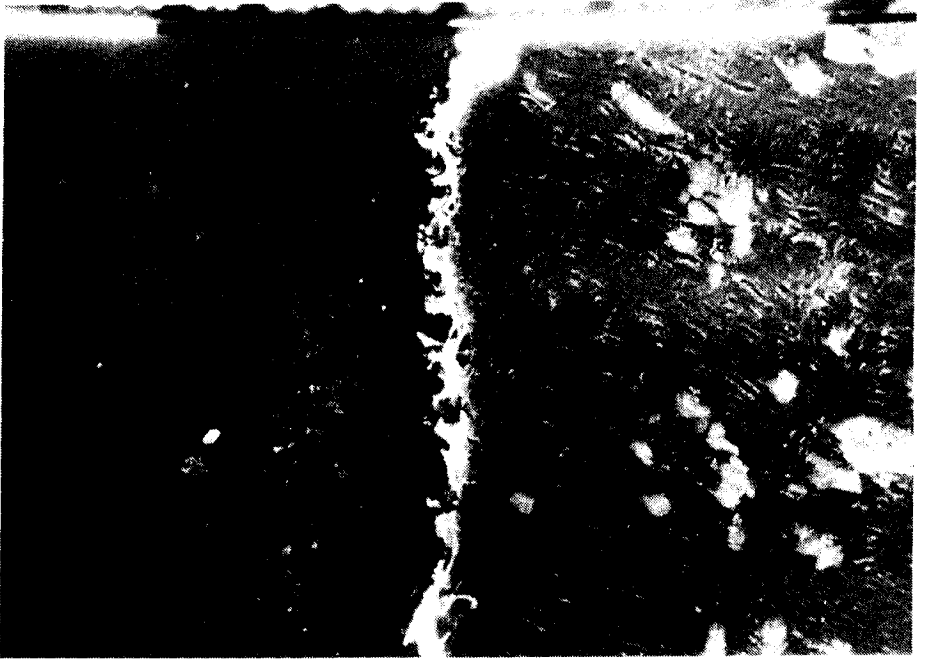


Figure 8(a). Photomicrograph of a cavity wall with H-Q-Bond (B) adhesive. Magnification $\times 125$.



Figure 8(b). SEM picture of a cavity wall with H-Q-Bond (B) adhesive. Magnification $\times 4060$.

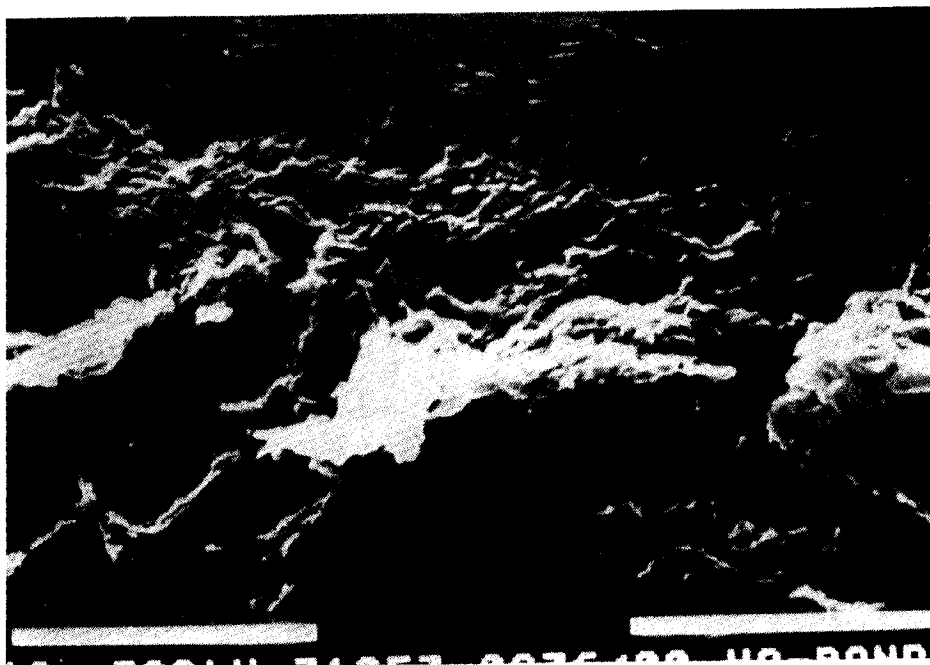


Figure 9. SEM picture of impregnation of dental surface by H-Q-Bond (B) adhesive. Magnification $\times 4580$.

4. CONCLUSIONS

The developed dental adhesive compositions described here can be used for restoring teeth. These adhesives possess strong adhesion to commonly used 'set' amalgam and to just prepared or 'fresh' amalgam. These adhesive compositions can also be successfully used as dental adhesives for procedures like orthodontics, repair of broken porcelain with composite resin, as an adhesive for veneering of crowns, bonding of amalgam to tooth structure, material for core build-up, etc.

The bonding capability of these newly developed adhesives has been shown to be superior to that of commercial materials investigated.

REFERENCES

1. E. Masuhara, K. Kojima, T. Hirasawa, N. Tarumi and T. Kimura, *Rep. Inst. Dent. Mater.*, Tokyo Med. Dent. Univ. **2**, 457-465 (1963).
2. D. N. Misra and R. L. Bowen, *J. Colloid Interface Sci.* **61**, 14-20 (1977).
3. N. Nakabayashi, *Int. Dentistry J.* **35**, 145-154 (1985).
4. G. C. Eliades, A. A. Caputo and G. J. Vougiouklakis, *Dental Mater.* **1**, 170-176 (1985).
5. R. L. Erickson, *J. Biomater. Appl.* **1**, 336-371 (1987).
6. R. S. Mandras, H. Retieff and C. M. Russell, *J. Dent. Res.* **70**, 395, Abs. 1038 (1991).
7. R. L. Bowen and E. N. Cobb, *J. Amer. Dental Assoc.* **107**, 734-736 (1984).
8. G. Eliades, G. Palaghias and G. Vougiouklakis, *Dental Mater.* **6**, 208-216 (1990).
9. N. Nakabayashi, in: *Transactions, International Congress on Dental Materials*, T. Okabe and S. Takahashi (Eds), pp. 70-79 (1989).

10. D. F. Quellet and S. Los, *J. Dent. Res.* **71** (Spec. Issue), 137, Abs. 252 (1992).
11. M. H. Souza, D. H. Retief and C. M. Russell, *J. Dent. Res.* **71** (Spec. Issue), 169, Abs. 511 (1992).
12. E. Asmussen, J. M. Antonucci and R. L. Bowen, *Scand. J. Dent. Res.* **96**, 584–589 (1988).
13. Israel Patent N 107414 Priority date — Oct. 27, 1993.
14. B. Zalsman, H. Dodiuk, I. Eppelbaum and A. Valdman, US Patent No. 5374664, Dec. 20, 1994.
15. S. Shoshan and M. Redlich, Report of histologic examination of H-Q-Bond (B) adhesive. The Hebrew University Hadassah School of Dental Medicine, Connective Tissue Res. Lab., November (1993).
16. E. W. Skinner, R. W. Phillips, *The Science of Dental Materials*. W. B. Saunders Co., Philadelphia (1968).
17. B. Zalsman, H. Dodiuk, I. Eppelbaum and A. Valdman, *J. Dent. Res.* **72**, 775, Abs. N45 (1993).
18. K. Hotta, M. Mogi, F. Miura and N. Nakabayashi, *Dental Mater.* **8**, 173–175 (1992).