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The role of an anaerobic accelerator in dental adhesives

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Abstract—A dental adhesive system was developed to yield a high bond strength to different substrates, enhanced durability, biocompatibility, and absence of interfacial microleakage. Such a system can be cured chemically (self-curing) or by visible light. Based on the assumption of an anaerobic character of the system's polymerization, the effect of the addition of an anaerobic accelerator (saccharin) on the curing mechanism was studied. Subsequently, the composition of the developed adhesive system and its curing conditions were evaluated and optimized. The developed adhesive compositions demonstrate high and durable bonding to dentin, enamel, porcelain, base and precious alloys, and amalgam, and can be used in different adhesive systems.

Keywords: Dental adhesive; acrylic; anaerobic accelerator.

1. INTRODUCTION

The variety of dental bonding systems (DBSs) which have been formulated and commercialized in the last 20 years have been systematically categorized by Eliades *et al.* [1].

Research and development efforts in adhesive dentistry are currently directed towards the development of multipurpose DBSs (which serve also for dental restorative purposes) for mineralized dental tissues. Such systems should have the ability to bond to enamel, dentin, filling composite, amalgam, alloys, and porcelain, and to achieve clinically acceptable bond strength retention by micromechanical and/or chemical bonding mechanisms in addition to restoration capabilities to prepared enamel and dentinal tooth structure.

Effective interfacial bonding requires complete wetting of the adherent surfaces by the adhesive, the attainment of a durable bond strength, and compatible matching of

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the inherent strength of the dental and restorative components of the bonded joint system. Materials science has contributed much in the pursuit of this goal [2].

Outstanding adhesion performance has been reported for bonding systems, such as All-Bond 2 (Bisco), which consists of NTG–GMA (*N*-tolylglycine–glycidylmethacrylate) and BPDM (biphenyldimethacrylate) [3], and glutaraldehyde/HEMA (hydroxyethylmethacrylate), commonly known as GLUMA [4, 5].

4-META (4-methacryloxyethyl trimellitate)-based systems can also be included in the category of the best DBSs, due to their universality, high bond strength to various substrates, and sufficiently high durability [6, 7].

Dental adhesive systems are basically composed of acrylate/bisacrylate or methacrylate monomers, fillers, different activators, and adhesion promoters. They are polymerized via free radical mechanism in the presence of hydroperoxides (mainly benzoyl peroxide) and aromatic amine (or suitable photosensitizers). The free radicals generated initiate methacrylate polymerization. Both chemically and photochemically initiated curing compositions are available. Modern DBSs demonstrate a sufficiently high bond strength: 25–30 MPa to cast alloys [7], 15–20 MPa to enamel [8], and 22–25 MPa to dentin [9].

It is well known that the hardening of the surface resin is obtained either through chemically initiated polymerization or through a photoinitiated one and it always requires temporary protection from oxygen, which acts as a curing inhibitor [10]. As a result of polymerization inhibition by oxygen, a surface layer containing incomplete polymerized resin is left (in some cases, a composite resin overlay is needed for forming an effective bonding [1]). Consequently, adhesive systems commonly used for dental bonding comprise mixtures of acrylic/methacrylic esters that remain in liquid form upon exposure to air, but harden in the absence of oxygen, and thus they belong to the category of anaerobic adhesives.

A number of alternatives exist for the anaerobic curing of DBSs; however, all of them contain the following basic components: methacrylate esters as monomers, benzoyl peroxide as an initiator of free radicals, and aromatic amines or imides (or their mixture) as accelerators.

The expression 'anaerobic' characterizes rapid curing in the absence of air and in the presence of metal ions. This process requires a low activation energy and takes place at or below room temperature. Most anaerobic adhesives require a free-radical polymerization mechanism.

The system investigated and developed in the present study consists of an acrylic resin, tertiary amine, benzoyl peroxide, and suitable photosensitizers [11, 12]. In the course of the investigations a new DBS was developed, containing *o*-benzoic sulfimide (saccharin), a well-known anaerobic accelerator [13, 14].

The aim of the present study was to investigate the anaerobic curing mechanism of multipurpose dental adhesive systems, suitable for the restoration of lost or damaged tooth structures.

2. EXPERIMENTAL

2.1. Adhesive system

The adhesives developed in the course of the present investigation are based on acrylic resins, which may be cured chemically or by visible light initiation. The composition studied is based on a new commercial dental adhesive, named H-Q-Bond Plus (Table 1), developed by BJM Lab. Ltd. Company. It consists of methylmethacrylate (MMA) crosslinked with a multifunctional agent (trimethylolpropanetriacrylate — SR-444, Sartomer) [12].

An adhesion promoter (glycidoxypropyltrimethoxysilane Z-6040, DowCorning) and a comonomer — aliphatic polyester urethane acrylate — were used in addition to dimethyl-*p*-toluidine (DMPT) and benzoyl peroxide as initiators for the chemical curing process. Camphorquinone (CQ) and ethyl-4-dimethylaminobenzoate (EDB) were used as photosensitizers for the light curing process. The composition also consisted of organic (polymethylmethacrylate — PMMA) and inorganic fillers (silica, metal alloy powder — 70% Ag, 25% Cu, 35% Sn) and an anaerobic curing accelerator — 2,3-dihydro-1,2-benzoiso-thiazol-3-one-1,1-dioxide (*o*-benzoic sulfimide or saccharin).

The developed compositions basically consisted of the following components:

MMA	15.0%
Urethane acrylate aliphatic polyester	10.0%
SR-444	2.7%
Benzoyl peroxide	3.0%
DMPT	0.5%
Z-6040	0.3%
CQ	0.35%
EDB	0.32%
Inorganic fillers	37.0%
Saccharin	0.8%
Organic fillers	30.0%

Based on the above formulation, a few commercial adhesives were developed:

- 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, urethane acrylate aliphatic polyester, crosslinking agent, PMMA, silica, titanium dioxide, metal powder, adhesion promoter, and photosensitizer.
- H-Q-Bond Plus (A) and H-Q-Bond Plus (B) differ from the above materials in that 0.8 wt% (based on total weight) saccharin is incorporated here. In addition to H-Q-Bond adhesives, four commercial adhesives were tested in order to compare their adhesion strengths.

Table 1 summarizes the commercial adhesives studied.

Table 1.
The commercial adhesive compositions studied

Adhesive composition	Manufacturer	Description
All-Bond 2	Bisco, USA	Urethane dimethacrylates; Bis-GMA based
Amalgambond Plus	J. Morita, Japan	4-META based
C & B Metabond	J. Morita, Japan	4-META based
H-Q-Bond Plus	BJM Lab. Ltd., Israel	Urethane acrylate based:
A	BJM Lab. Ltd., Israel	• chemically cured filled composition
B	BJM Lab. Ltd., Israel	• visible light cured filled composition

2.2. *Test methods*

2.2.1. Tensile strength. A rod made of PMMA, 5 mm in diameter, was bonded to different substrate materials (amalgam, dentin, enamel, ceramics, different alloys) using the various adhesives, which were brushed on both surfaces [12]. The thickness of the adhesive layer was around 50 μm for the unfilled resin and 150–200 μm for the filled adhesives. Curing was accomplished chemically or by irradiation for 50 s using an Optilux 250 visible light curing unit from Demetron Research Corporation, Danbury, CT, USA.

Following bonding, all specimens were kept at room temperature for 24 h and then immersed in water at 37°C for 24–4300 h to evaluate their durability in an aqueous environment. The tensile adhesion strength was determined using a Lloyd Mechanical Tester (computer-controlled) in accordance with ASTM D897.

The crosshead speed was 1 mm/min and ten specimens were prepared for each combination of rod and substrate materials.

2.2.2. Shear bond strength (SBS). A device constructed from two identical stainless steel plates, each 3 mm thick, having a cylindrical hole 6 mm in diameter, was fabricated (Fig. 1).

Forty cylindrical samples 6 mm × 6 mm, composed of equal parts of amalgam and composite resin with a layer of bonding material in between, were prepared for each adhesive system. The device was attached to a Universal Testing Machine (Instron Corp., Canton, MA, USA) with a 50 kg load cell and subjected to a continuous increasing tensile force, with a crosshead speed of 1 mm/min.

2.2.3. Thermal analysis. Differential scanning calorimetry (DSC) was carried out using a DuPont Thermal Analyzer 2000 to characterize the curing process of various dental adhesive compositions.

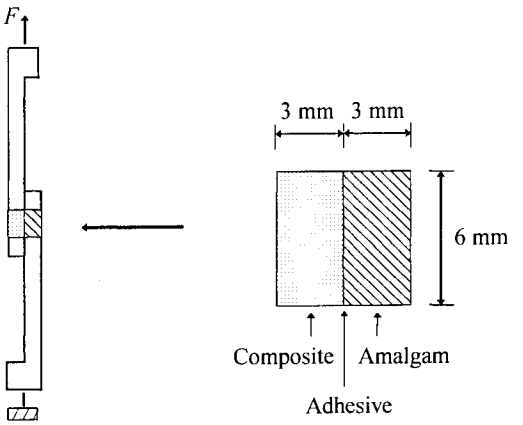


Figure 1. Schematic diagram of a specimen for shear bond strength measurement.

Specific heats and activation energies of the curing processes were determined by generating multiple DSC scans at various heating rates (2, 3, 5, and 10°C/min).

2.2.4. Biocompatibility evaluation. The biocompatibility of dental adhesive materials is a prerequisite for any dental procedure. The tolerance of gingival tissue to the H-Q-Bond Plus adhesive was tested in dogs [15]. The results from H-Q-Bond Plus were compared with those obtained from Super Bond (SB) from Sun Medical Co., Japan.

Twelve subgingival cavities were performed on the teeth of six dogs. One cavity in each dog was filled with H-Q-Bond Plus and the other with SB, prepared in accordance with the manufacturer's instructions. In addition, untreated teeth served as normal intact controls.

All the treated teeth were extracted 6, 14, and 20 days following the fillings. The samples were fixed in 4% phosphate-buffered neutral formalin solution and subsequently demineralized with RDO solution (DuPage Kinetic Lab. Inc., Plainfield, IL, USA), dehydrated, embedded in paraffin, and cut at a thickness of 6 μm [16]. The sections were histologically examined.

3. RESULTS AND DISCUSSION

The adhesives developed here are based on acrylic resins cured chemically or by light initiation and consist of methacrylic and acrylic monomers, a multifunctional crosslinking agent, aliphatic polyester urethane acrylate, different initiators, accelerators, organic and inorganic fillers, and metal powder (Ag–Cu alloy), manufactured under the brand name H-Q-Bond Plus [12].

Polymerization is initiated by free radicals and proceeds by addition to double bonds, provided a high rate of oxygen interaction with radicals of the growing chain is realized. The kinetics of the polymer chain growth can be described by the following

equations:

$$\begin{aligned} &M^{\bullet} + O_2 \longrightarrow MOO^{\bullet}, \\ &MOO^{\bullet} + M \xrightarrow{K_1} MOOM^{\bullet}. \end{aligned} \tag{1}$$

The major impact of oxygen on free radicals comes from its ability to quench the superfluous initiating radicals at the beginning of polymerization. Such quenching is kinetically controlled and is followed by hydrogen abstraction from a monomer, polymer, or solvent to give an unreactive hydroperoxide:

$$MOO^{\bullet} + HR' \longrightarrow MOOH + R'^{\bullet}.$$

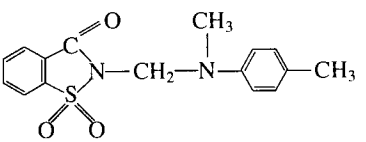
When the levels of oxygen in the system are sufficiently depleted, oxygen also acts as a chain transfer agent, provided that transfer interaction is relatively minor and diffusion-controlled. Furthermore, oxygen begins to deactivate polymerization and the polymer chain grows according to the equation

$$\sim M^{\bullet} + M \xrightarrow{K_2} \sim MM^{\bullet}. \tag{2}$$

Because of oxygen inhibition, temporary surface protection is required for proper conversion [14]. The effect of oxygen inhibition on the polymerization process is governed by the ratio of polymer chain growth in oxygen absence/presence, K_2/K_1. The values of this ratio are 1.2 for styrene, 72 for methylmethacrylate, and 1200 for methacrylate [17].

After complete oxygen depletion from the reaction system, transfer to the anaerobic polymerization mechanism takes place [18]. To evaluate the possibility of such anaerobic curing, a well-known anaerobic accelerator, saccharin [13, 14, 19], was added to the composition, containing DMPT accelerator.

The use of saccharin and DMPT results in a substantial acceleration of polymerization initiation. Although each of these components by itself is an accelerator, their combination has a strong synergistic effect [18]. It has been suggested that a charge transfer complex is formed by the combination of these materials [19–21] and that the decaying products of the complex are effective catalysts for the acrylic polymerization. A recent investigation [13] concluded that a new complex compound, named 'aminal', is formed:



This complex appears to be an excellent reducing agent for metal ions (present in such adhesive systems). These reduced metal atoms generate, in turn, active radicals by reacting with peroxides and yield rapid and complete curing [18, 19].

For a detailed investigation of the H-Q-Bond Plus polymerization with the addition of saccharin, thermal analysis by DSC was carried out. To obtain the kinetic

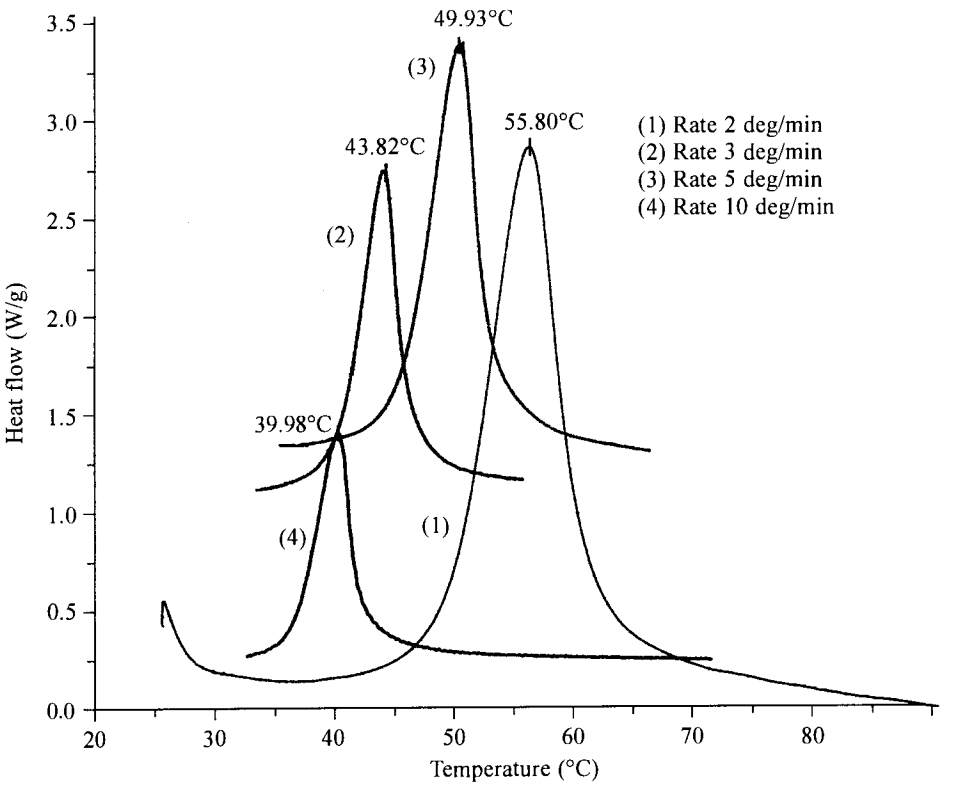


Figure 2. Multiple DSC scans of H-Q-Bond Plus (A) cured at various heating rates (2, 3, 5, 10°C/min).

parameters, multiple DSC scans were generated at various heating rates (2, 3, 5, and 10°C/min, Fig. 2.)

From the variation of the exotherm peak temperature, T_{exo}, with the heating rate, φ, the activation energy, E_a, was determined, using the following relationship [22]:

$$\frac{d\ln(\varphi)}{d(1/T_{exo})} = -\frac{E_a}{R} - 2T_{exo},$$

where R is the gas constant (1.987 kcal/mol per K).

Thus, a set of dynamic curves, obtained by using varying heating rates, enables the construction of a plot of ln φ versus $1/T_{exo}$, where the slope is equal to E_a/R. The activation energy can be calculated when $E_a/R \gg 2T_{exo}$ (Fig. 3). In addition, specific heats were determined using DSC at a heating rate of 3°C/min and isothermal condition curves ($T = 37$°C; Fig. 4) for each composition were examined [22].

The influence of saccharin incorporation on the activation energy and the heat of polymerization is shown in Figs 5 and 6, respectively. The increase of accelerator (saccharin) concentration up to 0.8% (by weight) reduced the activation energy of curing (Fig. 5). Further addition of saccharin (up to 1 wt%) resulted in an increase of the E_a values to their initial range.

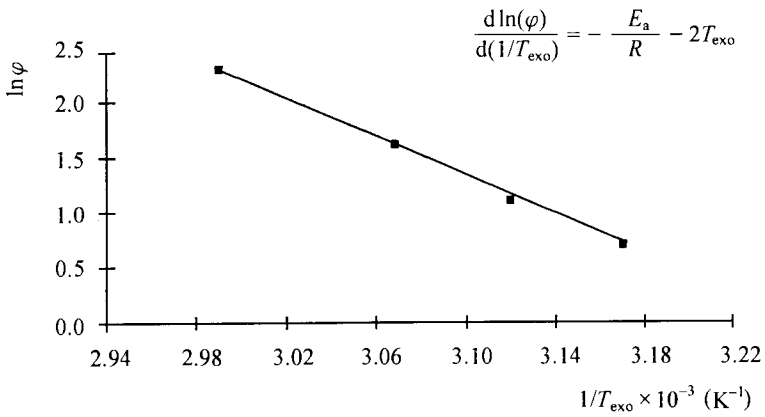


Figure 3. Activation energy for the H-Q-Bond Plus (A) curing process.

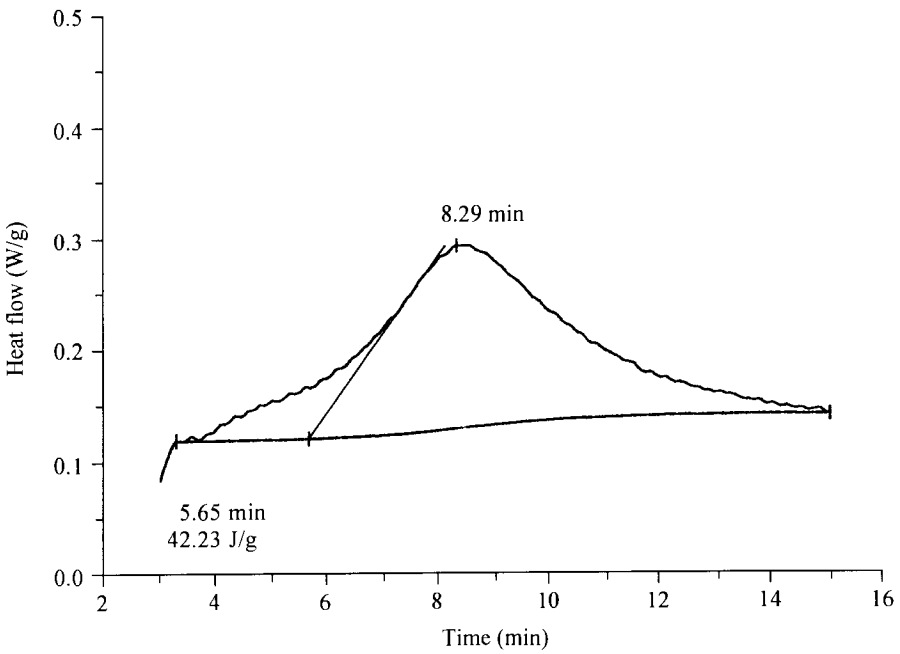


Figure 4. DSC isothermal curve (37°C) for the polymerization of H-Q-Bond Plus (A) adhesive.

The relationship between the heat of reaction (ΔH) and the accelerator content (Fig. 6) correlates well with the one for E_a versus the accelerator content (Fig. 5). The heat of polymerization increases with the addition of saccharin up to 0.8 wt%, whereas further increase of saccharin results in a decrease of the heat of polymerization.

Figure 7 shows the relationship between the tensile adhesion strength, obtained by bonding H-Q-Bond Plus (A) to Ni–Cr alloy, and the amount of saccharin added. It is evident that a maximum strength is obtained at 0.6 wt% saccharin.

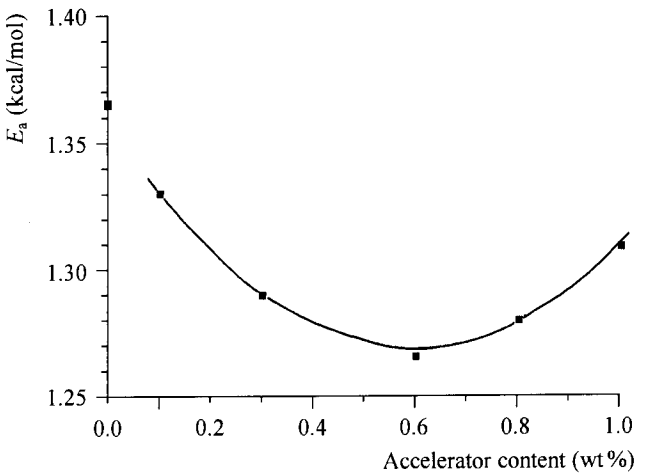


Figure 5. Activation energy of H-Q-Bond Plus (A) curing as a function of the accelerator content.

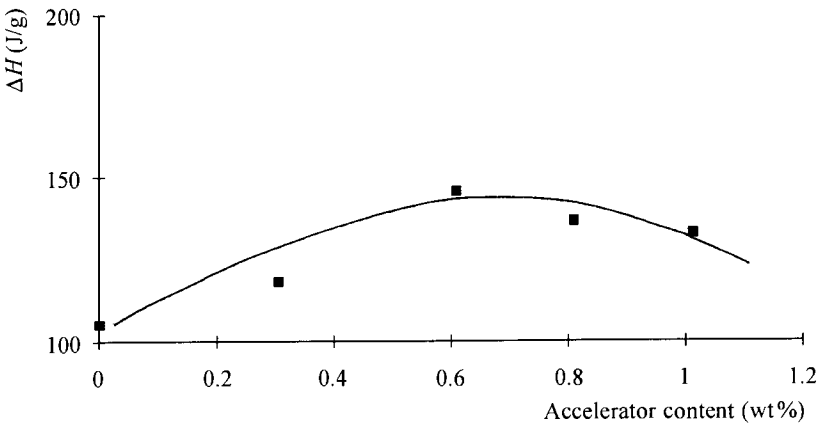


Figure 6. H-Q-bond Plus (A) heat of polymerization as a function of the accelerator content.

It should be noted that the peaks in the curves for activation energy, heat of polymerization, and tensile adhesion strength (Figs 5–7) occur at the same level of saccharin content (0.3–0.8 wt%).

The incorporation of saccharin in amounts exceeding 1 wt% results in an increase of the activation energy and a reduction in the heat of polymerization and tensile adhesion strength. This may be attributed to the excess of free radicals obtained, which may lead to termination reactions (recombination).

From the above results one may conclude that the polymerization time of the developed chemically cured dental adhesives could be shortened to 5 min at oral temperature and to 15 min at ambient temperature with the addition of 0.8 wt% saccharin based on the total composition.

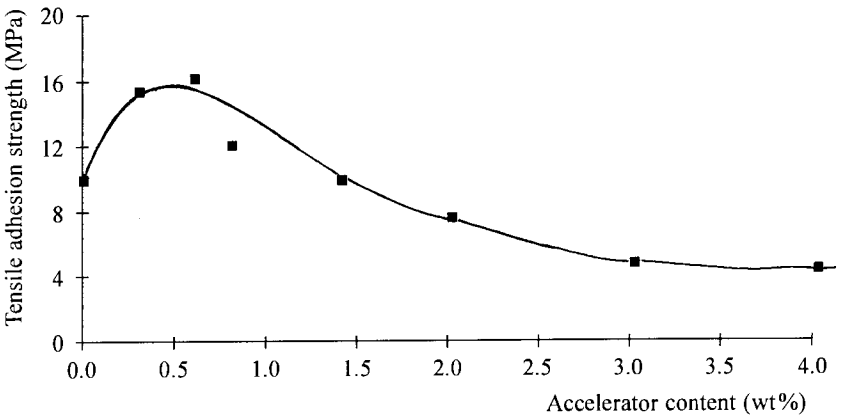


Figure 7. Tensile adhesion strength of H-Q-Bond Plus (A) to Ni–Cr substrate as a function of the accelerator content.

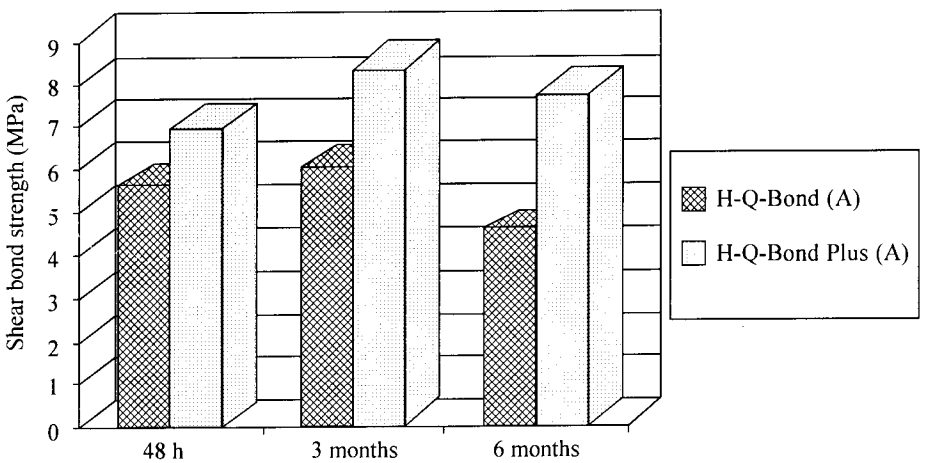


Figure 8. Comparison of the shear bond strength to fresh amalgam of H-Q-Bond (A) and H-Q-Bond Plus (A).

Figure 8 shows the influence of a small amount (0.8 wt%) of saccharin on the shear bond strength between H-Q-Bond Plus (A) and H-Q-Bond compositions and amalgam substrate. Figure 9 presents the durability results for up to 6 months exposure to water at 37°C in terms of the shear bond strength between H-Q-Bond Plus (A) and fresh amalgam in comparison with other commercial adhesives: All Bond 2 and Amalgambond Plus. The results show that the latter adhesives deteriorated with immersion time, whereas H-Q-Bond Plus (A) did not deteriorate significantly. H-Q-Bond Plus (A) undergoes no deterioration and maintains the highest shear bond strength values through a 6-month period, probably because of the slower water absorption.

The multipurpose potential of H-Q-Bond Plus (A) and the contribution of saccharin to the bond strength is shown in Fig. 10. It is evident that the tensile adhesion strength values obtained with this accelerator are significantly higher compared with

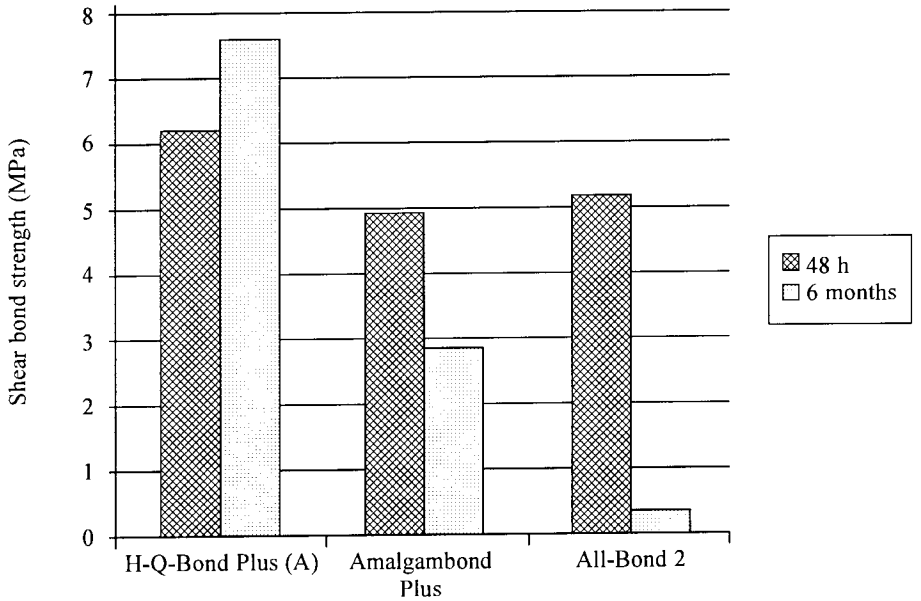


Figure 9. Durability comparison of commercial adhesives: shear bond strength between adhesives and fresh amalgam, measured following immersion in distilled water (37°C) for 48 h and 6 months.

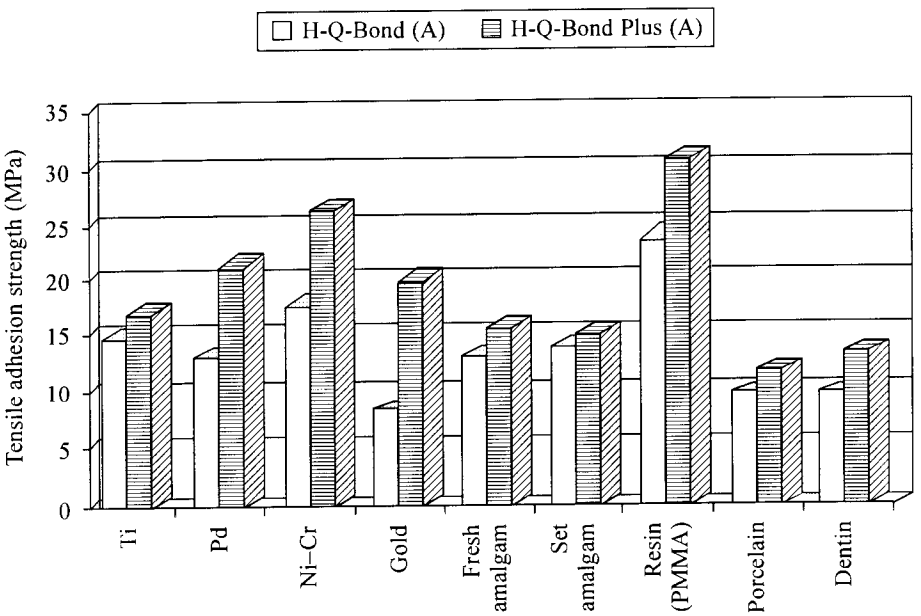


Figure 10. Tensile adhesion strength to different substrates of H-Q-Bond (A) and H-Q-Bond Plus (A) compositions.

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

Adhesive material	Tensile bond strength (MPa) (±20%)					
	Amalgam set/fresh	Dentin	Perspex	Ni–Cr alloy	Pd-based alloy	Titanium
H-Q-Bond Plus (A)	15.0/15.6	14.0	31.0	27.0	21.4	17.0
H-Q-Bond Plus (B)	12.0/12.8	8.5	25.2	19.6	12.8	—

[a]Measured after 24 h in water at 37°C.

the H-Q-Bond (A) composition. The H-Q-Bond Plus (B) composition also results in rather high values of the adhesion strength to different substrates (Table 2).

As for biological characteristics, the histological observations showed at various times examined an inflammatory response in the gingiva in the case of Super Bond-treated teeth, while the H-Q-Bond Plus compositions had no noticeable effect on the gingival tissue [15].

Thus both H-Q-Bond Plus compositions exhibit tissue compatibility ('tissue friendliness') when used as a filling material in the dental cavities of dogs.

4. CONCLUSIONS

Advanced dental adhesive compositions were evaluated for teeth restoration. The effect of addition of an anaerobic accelerator (saccharin) to the adhesive composition was investigated and optimized.

The developed adhesive compositions demonstrate biocompatibility; high and durable bonding to dentin, enamel, porcelain, base and precious alloys, and set and fresh amalgams; and can be used in chemically or visible light curing adhesive systems.

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