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A fundamental study of fissure sealant in dental application: *in vitro* adhesive tensile strength

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In order to develop the sealing of pits and fissures in human enamel, a polymethylmethacrylate (PMMA) cylinder was bonded to a flattened one and to the labial enamel surface of young bovine teeth subjected to acid-etched treatment. An increase in adhesive tensile strength occurred for methyl-α-cyanoacrylate, one of the alkyl-cyanoacrylate adhesives tested. A larger significant difference in the release of fluoride was found in each cyanoacrylate adhesive containing 11 kinds of fluoride compounds. The value of the adhesive tensile strength at the interface of the PMMA–acid-etched bovine enamel depended on the cyanoacrylate adhesive type and the conservation conditions.

1. Introduction

Dental pits and fissures were sealed by a fissure sealant, and the bonding between resin and enamel was found to be an important factor on the adhesive tensile strength by a coating of the enamel surface [1]. Alkyl-α-cyanoacrylate adhesives have been used as a surface dressing after oral surgical procedures in humans [2], and the adhesives with the general formula $CH_2{=}C(CN){-}COOR$ have been used as tissue adhesives in dental practice [3–5]. They were tested in pulp capping as a component of the filling material [5–7]. Of these adhesives methyl-α-cyanoacrylate adhesive is the best-known because of the tissue receptivity [6], and cyanoacrylates such as butyl, isobutyl, ethyl, propyl and hexyl have been tried in animal studies [5, 7, 8]. As a result, butyl and isobutyl cyanoacrylates inhibited the growth of certain oral bacteria, and a spray of the cyanoacrylates did not stimulate the growth of anaerobic bacteria [5]. A clinical difference was observed in the duration of bonding of the adhesive applied for caries prevention to the pits and fissures of deciduous and permanent teeth [9]. The safe and effective application of the adhesives as a fissure sealant in the dental field would be of interest to increase the adhesivity at the interface of human enamel. Concerning the bonding of an acrylic resin to bovine enamel surface, pretreatment with a 50% phosphoric acid solution was used [10]. The surface treatment of enamel or dentin with certain inorganic acids increases the retention of some resin restoratives [11, 12].

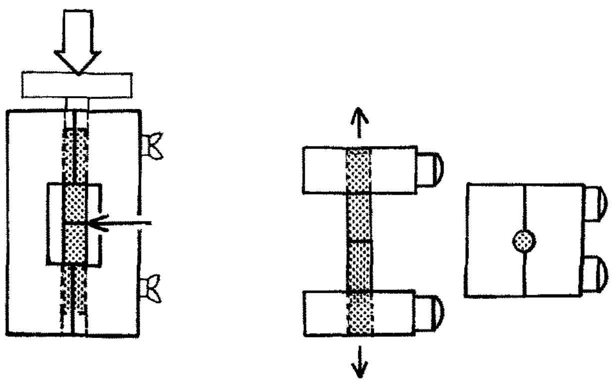
The present *in vitro* study on the adhesive tensile strength was undertaken to evaluate the effect of cyanoacrylate monomers. The findings were applied to strength, using cyanoacrylates containing fluoride compounds, e.g. the interfacial tensile strength between the polymethylmethacrylate (PMMA) and PMMA and also between PMMA and acid-etched bovine enamel. The adhesives were also tested concerning the fluoride concentration in a distilled water in relation to the adhesive tensile strength.

2. Materials and methods

2.1. An adhesive tensile test

The test specimens for tensile testing were prepared by adhering two acrylic PMMAs (diameter 6 mm × 25 mm) as illustrated in Figs 1a and b. The monomers ($CH_2{=}C(CN){-}COOR$) used were ethyl-α-alkyl cyanoacrylate adhesive (denoted as Ethyl; $R{=}CH_3CH_2$), methyl-α-cyanoacrylate (Methyl; $R{=}CH_3$), isopropyl-α-cyanoacrylate (Isopropyl; $R{=}(CH_3)_2CH$) and ethoxy ethyl-α-cyanoacrylate (Ethoxy; $R{=}CH_3CH_2O{-}CH_2CH_2$) (Taoka Chemical Co., Osaka, Japan). The commercial cyanoacrylate adhesives contained hydroquinone (1000 to 2000 p.p.m.) and stabilizer SO_2 (15 p.p.m.), and the SO_2 content in the first three of the above was removed mechanically in order to compare them with the adhesives having no SO_2 content.

In Fig. 2 a schematic diagram of the adhesion test between an acrylic cylinder (diameter 6 mm × 18 mm) and acid-etched bovine enamel, e.g. incisors obtained from young cattle at a local abattoir, is shown. The adhesive planes of the acrylic cylinder and bovine enamel were polished by 600-grit emery paper to



(a) (b)

Figure 1 (a) Metal mould employed to apply a load to the adhesion of PMMA to PMMA at the interface during specimen preparation. (b) Apparatus for adhesive tensile testing.

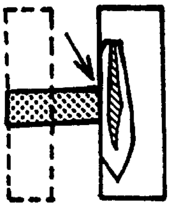


Figure 2 Adhesion of PMMA to bovine enamel which was etched (the bovine enamel was set into the modelling compound as illustrated).

obtain a flat surface. Before adhering, the bovine enamel tested was etched by 50% phosphoric acid [10, 11], because the unetched one had a low adhesive tensile strength (less than 5 kg cm^{-2}). After setting two acrylic cylinders in the apparatus (Fig. 1a), a 1 kg load was applied for 10 min. For acrylic cylinder–acid-etched bovine enamel adhesion no external load was applied (Fig. 2). All specimens were stored in a distilled water bath at 37° C for 1 day or 1 week before testing (wet condition). In addition, the acrylic cylinder–acrylic cylinder adhesive specimens were kept in an incubator at 37° C (dry condition). After this treatment the adhesive tensile test was carried out using an Autograph DCS-500 (Shimadzu Co., Kyoto, Japan: crosshead speed 0.5 mm min^{-1}; chart speed 5 mm min^{-1}; full scale 100 kg).

2.2. Fluoride concentration

In Table I the 11 kinds of fluoride compounds used are indicated. The alkyl-α-cyanoacrylate adhesives containing fluoride compounds were tested as follows: (1) fluoride ion solubility and (2) adhesive tensile testing of PMMA–bovine enamel. In the measurement of fluoride ion in distilled water (50 ml) at 37° C for 1 day from one upper surface the PMMA plate (10 mm × 10 mm × 2 mm) where the mixture was coated after mixing 14 mg powder (fluoride) and 140 mg (methyl-α-cyanoacrylate) at room temperature for 1 min. The other planes were coated with nail varnish for the fluoride measurement. The measurement of fluoride was done by digital ionanalyser (model 810 A; Orion Research Inc., Chicago, USA) with fluoride electrode 96-09, and the pH was checked with the above one with pH electrode 91-03. The pH was adjusted by adding 10^{-3} M NaOH to 10 ml distilled water to obtain optimum pH (6 to 7) for the calibration curve (Fig. 3). In the adhesive tensile testing in (2) the method was carried out as described in Section 2.1.

TABLE I Fluoride compounds in methyl-α-cyanoacrylate adhesive used for adhesive tensile test and fluoride solubility

Fluoride compound	Solubility in H_2O	Manufacturer
AlF_3	Partly solved	Wako
BiF_3	Not solved	Mituwa
CaF_2	Partly solved	Wako
KF	Solved	Kishida
$NaBF_4$	Solved	Wako
NaF	Partly solved	Wako
Na_2FPO_4	Solved	Hanawa
Na_2SiF_6	Partly solved	Kishida
PbF_2	Partly solved	Kishida
SnF_2	Partly solved	Kishida
ZnF_2	Partly solved	Hanawa

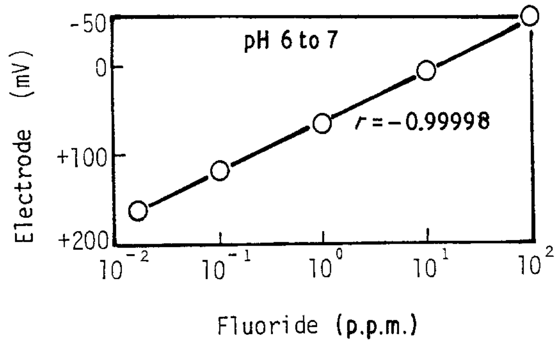


Figure 3 Calibration curve to obtain the fluoride concentration from the recorder reading.

3. Results

Fig. 4 shows the adhesive tensile strength of PMMA–PMMA when four types of alkyl cyanoacrylates were used. The interfacial strength is a quantity which may depend on the type of alkyl cyanoacrylate and the conservation conditions. The value showed a larger adhesive tensile strength for ethyl-α-cyanoacrylate than for the others.

In a methyl-α-cyanoacrylate adhesive the effect of the conservation conditions on the strength was small compared with the effect for other adhesives. Fig. 5 shows the effect of stabilizer SO_2 on the adhesive tensile strength of PMMA–PMMA in three types of alkyl cyanoacrylates such as Ethyl, Methyl and Isopropyl. The methyl-α-alkyl cyanoacrylate did not show a large change due to removing the stabilizer SO_2 from the adhesive. Therefore, all alkyl cyanoacrylates containing SO_2 as a stabilizer were used for the interfacial adhesivity between PMMA and acid-etched bovine enamel.

Fig. 6a shows the adhesive tensile strength of PMMA–acid-etched bovine enamel when an external load was applied or not applied in adhering it as shown in Fig. 1a. The methyl alkyl cyanoacrylate adhesive had a larger adhesive tensile strength (about 150 kg cm^{-2}) than the other alkyl cyanoacrylate monomers such as Ethyl, Isopropyl and Ethoxy. In Fig. 6b the adhesive tensile strength under conditions conserved in distilled water (1 day or 1 week) is shown. A value of adhesive tensile strength above 100 kg cm^{-2} was found for methyl-α-cyanoacrylate. Table II shows the amount of ion release (mg cm^{-2}) in distilled water in coating each cyanoacrylate containing 11 kinds of fluoride compounds. Fluoride from fluoride

TABLE II Fluoride release into distilled water for 1 day at 37° C

Fluoride compound	Fluoride (mg cm^{-2})
AlF_3	4.2×10^{-3}
BiF_3	3.3×10^{-3}
CaF_2	5.5×10^{-3}
KF	2.8×10^{-3}
NaF	4.7×10^{-3}
$NaBF_4$	5.3×10^{-3}
Na_2FPO_4	2.8×10^{-3}
Na_2SiF_6	5.5×10^{-3}
PbF_2	4.2×10^{-3}
SnF_2	49.5×10^{-3}
ZnF_2	27.5×10^{-3}

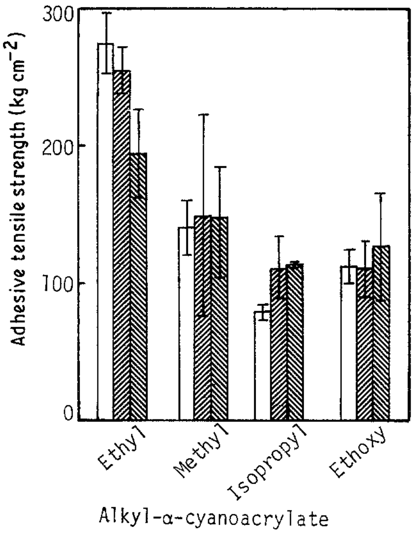


Figure 4 Adhesive tensile strength for the PMMA–PMMA interface when Ethyl, Methyl, Isopropyl and Ethoxy were used. (□) 1 h in an incubator, (▨) 1 day in distilled water and (▧) 1 week in distilled water.

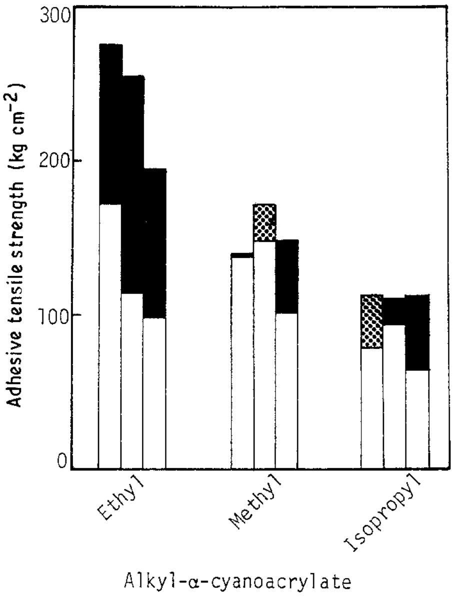


Figure 5 Comparison of adhesive tensile strength for PMMA to PMMA in using cyanoacrylates with and without a stabilizer. (In turn from left to right for each cyanoacrylate, 1 h in an incubator, 1 day in distilled water and 1 week in distilled water; the increasing value for the latter one (■) and the decreasing value for the latter one (▩).)

compounds such as SnF_2 and ZnF_2 after coating methyl-α-cyanoacrylate was released easily to a large degree. In Figs 7a and b the adhesive tensile strength is shown for methyl-α-cyanoacrylate containing the 11 kinds of fluoride compounds in Table I. The dotted line shows the average adhesive strength in using alkyl cyanoacrylate without fluoride compounds (see Fig. 4). The value tends to increase with the coating of methyl-α-cyanoacrylate containing KF, $NaBF_4$, Na_2FPO_4, Na_2SiF_6 and PbF_2, but the value was decreased by coating them to the interface between PMMA and acid-etched bovine enamel (most of the adhesive agents showed a value of about $100\,kg\,cm^{-2}$, except AlF_3 and SnF_2).

4. Discussion

A tensile test was used to determine the interfacial adhesive strength between PMMA and PMMA and between PMMA and acid-etched bovine enamel. It was found that the bonding strength using an acid-etched technique ranged from 40 to $60\,kg\,cm^{-2}$ as an average value [13, 14]. In this study a larger value than that reported in the literature was obtained for PMMA–acid-etched bovine enamel, as shown in Fig. 7b. The adhesive enamel bond strength for an unfilled resin was $175\,kg\,cm^{-2}$ as a highest value [14], but a mean value of $150\,kg\,cm^{-2}$ in dry conditions such as after 1 day at 37° C in an incubator was obtained for the use of methyl-α-cyanoacrylate adhesive (Fig. 6a). It is apparent from the result that the methyl-α-cyanoacrylate adhesive has a significant effect on the bonding strength (Figs 6a and b).

It is deduced that the CH_3 of the methyl-α-cyanoacrylate may bond easily to the hydroxide on the bovine enamel. As a result the adhesive tensile strength increased as shown in Fig. 6a. On the contrary, the microfil and small-particle restorative resins failed principally by fracture through the bonding of

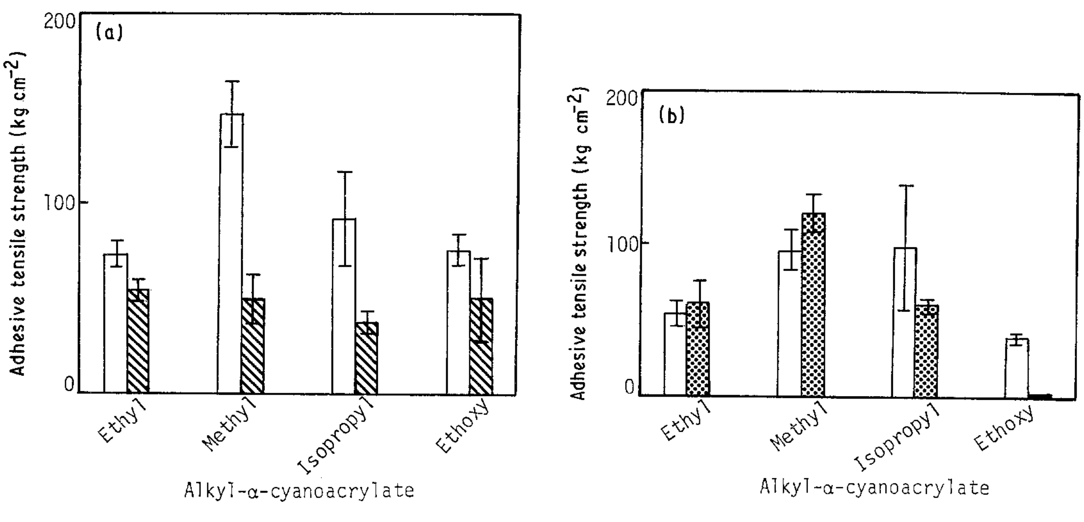


Figure 6 Adhesive tensile strength of the PMMA–acid-etched bovine enamel interface for four types of alkyl cyanoacrylates in loaded (▧) and unloaded conditions (□). (b) Adhesive tensile strength of the PMMA–acid-etched bovine enamel interface for four types of alkyl cyanoacrylates in conservation conditions such as 1 day (□) and 1 week (▩) immersions in distilled water at 37° C.

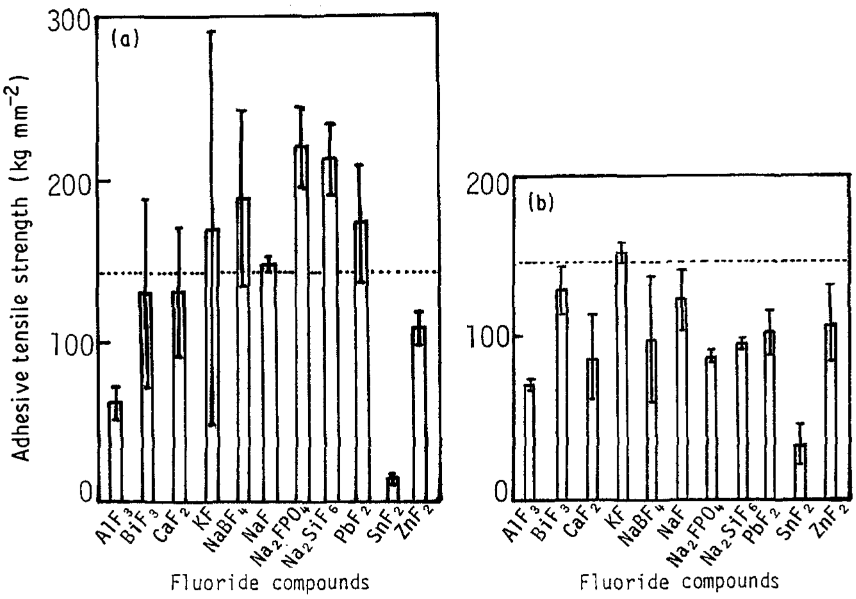


Figure 7 (a) Adhesive tensile strength of the PMMA–PMMA interface in using each methyl cyanoacrylate adhesive containing 11 types of fluoride compounds. (b) Adhesive tensile strength between the interface of PMMA and acid-etched bovine enamel.

resin–resin interface or the resin itself, rather than at the bovine enamel surface [15]. This means that the tensile strength of the restorative resins was obtained rather than the interfacial bonding strength. The PMMA was selected here to evaluate the adhesive tensile strength due to the interface between the PMMA and PMMA and between the PMMA and acid-etched bovine enamel, because the resin had a high value of $352\,kg\,cm^{-2}$ [16].

The appropriate method to obtain the adhesive tensile strength was, as shown in Figs 5, 6a and b, to adhere the interface between PMMA and acid-etched bovine enamel without loading for increasing the adherence to the treated surface, although the applied load was necessary for the PMMA–PMMA (Figs 1 and 4). In the acid-etched treatment, the filamentous tag-like extension of acrylic resin of 15 to 20 μm in length was formed at the interface where the resin contacted on the surface the acid-etched bovine enamel [17, 18]. It is considered that a more intimate contact between them is permitted because of the very small adhesive tensile strength of $< 5\,kg\,cm^{-2}$ as described. The adhesive would rest partially on the enamel surface, with the penetration of the adhesive as evidenced previously by the formation of tags. Thus, the adhesive tensile strength showed a relatively small value compared with that in the PMMA–PMMA interface (Figs 7a and b).

In the *in vitro* study the release of fluoride ion into distilled water was studied to help in the investigation of the uptake of fluoride to human teeth after fluoride-coating as a future study. Human dental pulps contained fluoride, calcium, phosphate, ash and water [19], and especially the fluoride concentration was detected in the range of 70 to 1450 p.p.m. for pulps of different ages. In using fluoride compounds such as SnF_2 and ZnF_2 for the adhesive, the amount of fluoride release was about 8 to 10 times that with the residual ones (AlF_3, BiF_3, CaF_2, KF, NaF, $NaBF_4$, Na_2FPO_4, Na_2SiF_6 and PbF_2; Table II). This means that the solubility in distilled water of SnF_2 and ZnF_2 is larger than that in the residual ones, because they are partly solved in the water (Table I). Therefore, methyl-α-cyanoacrylates could be used in the presence of moisture, such as oral environment, using each methyl-α-cyanoacrylate adhesive indicating higher adhesive strength and fluoride solubility as a fissure sealant to the oral cavity.

Cyanoacrylate adhesives are known to be a chemical tissue adhesive with bacteriostatic properties [2]. It was noted that the methyl-α-cyanoacrylate adhesive had a greater resistance to failure by tensile test than did the other cyanoacrylate adhesives. The release of fluoride in the methyl-α-cyanoacrylate adhesive in distilled water was different among the fluoride compounds investigated, ranging from 3.3×10^{-3} to $49.5 \times 10^{-3}\,mg\,cm^{-2}$. It is supposed that the adhesive agent would not simply rest on the bovine enamel surface and the fluoride in the adhesive agent would penetrate somewhat into the surface.

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