Original

Fundamental Study on the Coating Ability of Cyanoacrylate Adhesives to Hydroxyapatite Pellet and Surface of Extracted Teeth

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Abstract: Cyanoacrylate adhesive is used worldwide as instant glue because of their one-drop-curing properties. Medical cyanoacrylate adhesive exhibits high adhering strength; its safety for use has been established from its clinical application, use in the living body, and oral use. A hydroxyapatite pellet (HAP) coated with cyanoacrylate adhesive was left in pH 4.0 phthalate standard solution and the concentration of eluted calcium ion was measured. The concentration of eluted calcium ion were 0.4 mM (HAP coated with a cyanoacrylate adhesive) and 6.2 mM (control study of HAP), respectively. This result indicates that the coating with a cyanoacrylate adhesive can inhibit the elution of HAP even in acidic conditions. Cyanoacrylate adhesive was applied to the extracted teeth in the presence of artificial saliva, and the thickness of the adhered area was observed. The thickness of the cyanoacrylate adhesive adhered to the extracted tooth has slightly decreased until the 5th day. The thickness has hardly changed until the 31st. This result shows that the cyanoacrylate adhesive was not removed from the tooth surface in the presence of artificial saliva.

Key words: Cyanoacrylate adhesive, Instant glue, Hydroxyapatite pellet, Dental treatment

Introduction

The primary constituent of instant glue is α -cyanoacrylate (CA), in which one α -hydrogen in acrylate ester is replaced by a CN base. Conversely, it is a compound with the structural formula of $\text{CH}_2=\text{C}(\text{CN})\text{COOR}$. The industrial manufacturing procedure of the aforementioned monomer was developed in 1949 by Goodrich Inc.¹⁾; at that time, there was no demand or interest regarding CA. However, subsequently, Eastman Inc. of the USA coincidentally discovered during a research on synthetic fibers that CA possesses excellent ability to bond glass. The number of CA-based studies increased further, revealing that it adheres strongly and instantaneously to almost all substances with the exception of inactive resins, such as polyethylene and Teflon. This resulted in the global emergence of cyanoacrylate adhesive as instant glue²⁾.

Subsequently, applied research on the medical application of instant glue was performed from the 1960s³⁾. For example, the CA spray was used to suppress the bleeding of wounded soldiers who were transported to hospitals during the Vietnam War. Moreover, it was used for the suturing of the skin, blood vessels, etc., during surgical procedures. Even in the veterinary domain, it was used to repair bones, skin, and turtle shells³⁾. In addition, during the 1960s, in Japan, cyanoacrylate was reportedly used in minor oral surgeries, to protect the wound area of extracted teeth by performing hemostasis in the endodontic treatment area⁴⁾.

Instant glue hardens rapidly when the cyanoacrylate monomer,

which is the primary constituent, reacts with moisture on the surface of binding materials, and subsequently polymerizes into a polymer. Consequently, the binding materials adhere strongly⁵⁾. The following are the advantages of instant glue: it achieves quick results at normal temperatures; it is a one-component solvent-free adhesive; the hardened substance has satisfactory transparency; it exhibits high adhering strength; its safety for use has been established from its clinical application, use in the living body, and oral use; furthermore, there is adequate moisture in the mouth⁶⁾. On the basis of the above-mentioned points, cyanoacrylate adhesive is hypothesized to stop the progression of caries and likely improve the symptoms of dentine hyperesthesia. Recently, we reported that an effectiveness of cyanoacrylate adhesive was shown for dentine hyperesthesia and wedge-shaped defect in clinical research⁷⁾. The purpose of this study is fundamental research for dental clinical application of cyanoacrylate adhesive. We investigated the bonding ability of a cyanoacrylate adhesive to hydroxyapatite pellets (HAPs), which simulate tooth surface enamel in an aqueous solution, and to the surface of extracted teeth in the presence of artificial saliva.

Materials and Methods

This study was performed after approval by the directors of the nursing facilities and Ethics Committees of Osaka Dental University (Approval number 111074).

Cyanoacrylate adhesives

Aron alpha (Daiichi-Sankyo: Tokyo, Japan) cyanoacrylate adhesive, which is an instant medical glue, was used. It came as ethyl 2-cyanoacrylate, which is a cyanoacrylate, in a 0.5-g tube, and it contained polym-

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Figure 1. Coating effect of the cyanoacrylate adhesive against the acid-induced elution of calcium ions from hydroxy apatite pellets. The bars represent mean $\pm$ standard error, $n = 5$, and ** $p < 0.01$ (paired t test).

Figure 2. Changes in the thickness of the cyanoacrylate bonding agent that adhered to the tooth surface in artificial saliva.

Figure 3. Observation of the cyanoacrylate adhesive that adhered to the tooth surface in artificial saliva. The cyanoacrylate adhesive was adhered in the rectangle part. (a) Before cyanoacrylate adhesive was applied; (b) Day 1 post-application; (c) Day 3; (d) Day 5; (e) Day 9; (f) Day 14; (g) Day 20; (h) Day 25; (i) Day 31.

Figure 4. Polymerization of the cyanoacrylate compound. (a) Alkyl- α -cyanoacrylate monomer; (b) Alkyl- α -cyanoacrylate polymer.

ethylmethacrylate as an additive.

Coating effect of the cyanoacrylate bonding agent toward the acid-induced elution of calcium ions from hydroxy apatite pellets

HAPs are pellets that were molded into circular shape and sintered have until date been used as representative enamel in fundamental experiments⁸⁾. The drops of the cyanoacrylate adhesive were applied to coat the entire surroundings of the 10 mm $\times$ 10 mm $\times$ 2 mm apatite pellet APP-100 (HOYA Technosurgical, Tokyo, Japan); subsequently, the HAP was left to stand for 24 h. To this HAP, we added 10 mL of a pH 4.0 phthalate standard solution (Kishida Chemical Co., Ltd, Osaka, Japan) and left the mixture to stand for 1 week at room temperature. Subsequently, 10% aqueous ammonia solution was added to the reaction solution to make it basic. Upon adding three drops of the indicator, namely, eriochrome black T (Tokyo Chemical Industry Co., Ltd, Tokyo, Japan), to the reaction solution, it turned into a bluish light purple solution. This solution was titrated using 0.02 M ethylene diamine tetra-acetic acid solution (Kishida Chemicals), and the endpoint was the complete change in the color of the solution.

Experiment on the bonding ability of the cyanoacrylate adhesive to extracted teeth in the presence of artificial saliva

Cyanoacrylate was applied to cover the crown of the extracted maxillary second premolar. After 24 h, the extracted tooth was added to 30 ml of Salivhet aerosol (Teijin Pharma Limited, Tokyo, Japan) in 50 ml of screw tube bottle and left to stand at 37°C. To measure the thickness of the cyanoacrylate adhesive, the tooth was picked out from the solution and taken the photo images by using Illuminated magnifier (LED-100AS, Keiyo Magnifier Co., Ltd., Chiba, Japan). The thickness of the cyanoacrylate adhesive was measured by the magnified photo images.

Results

The concentration of calcium ions in a solution coated with a cyanoacrylate adhesive was 0.4 mM, whereas that in a solution not coated with a cyanoacrylate adhesive was 6.2 mM in Fig. 1. Consequently, it is clear from the control study that in pH 4.0 phthalic acid conditions, HAP elutes calcium ions. Meanwhile, with coated HAP, even under acidic conditions, barely any elution could be seen.

The time course of the thickness of the cyanoacrylate adhesive on the maxillary second premolar was shown in Fig. 2. The thickness of cyanoacrylate adhesive has decreased until the 5th day. However, the thickness has hardly changed until the 31st.

Fig. 3 shows photo images of changes over time of the cyanoacrylate adhesive that adhered to the tooth surface in artificial saliva. From the 5th day, some cracks were seen on the surface, and after that, the surface was slightly deteriorated. However, there was no significant change the overall appearance of cyanoacrylate adhesive.

Discussion

The double-bond of cyanoacrylate has significant reactivity because cyanoacrylate has both electron-withdrawing cyano and ester groups at a double-bond site (see Fig. 4). Therefore, a water molecule, which is a weak nucleophile, acts as an initiator for the addition reaction of cyanoacrylate. Cyanoacrylate reacts even with the small amount of moisture in the air, forming a polymer. The properties of the preparation are that it is a colorless transparent liquid, which when applied to the living body rapidly bonds with even small amount of moisture, causing it to harden and thereby bonding to the teeth⁹⁻¹²⁾. This chemical reaction can be generated in the mouth regions where moisture is abundant¹³⁾.

In this fundamental study, we investigated whether cyanoacrylate adhesive bonded with HAPs, which is a constituent of enamel. As a result, the coating with cyanoacrylate adhesive inhibited the elution of HAP even in acidic conditions. These findings show that cyanoacrylate binds tightly to HAP and that the cyanoacrylate-coating is stable in acidic solutions.

Moreover, we investigated whether cyanoacrylate adhesive bonded with the crown part of extracted tooth in the presence of artificial saliva for certain duration. As a result, the thickness of cyanoacrylate adhesive has slightly decreased until the 5th day. However, the thickness has hardly changed and the bonding between cyanoacrylate adhesive and extracted tooth was maintained until the 31st. This result indicated that cyanoacrylate adhesive barely separate from enamel part even in the presence of chemical factors such as saliva in the mouth. Since the chemical interaction between the cyanoacrylate adhesive and enamel part is weak due to the cyano and ester groups of cyanoacrylate, the main bonding mechanism of cyanoacrylate adhesive to the tooth surface is considered to be the mechanical bonding which called anchor effect⁹⁻¹²⁾. The anchor effect is explained as the bonding agent is poured into pores or crevasses of the material surface, and when it hardens bonding is established. This could be more effective for the bonding with porous materials such as dentin or caries lesions¹⁴⁾.

The physical contact to the coated cyanoacrylate adhesive is a major factor in adhesion to the tooth surface, thus, it is necessary to investigate the effect of physical factors of adhesion for long term use. However, this study showed that cyanoacrylate adhesive adhered to the tooth well under the conditions where there is no physical contact with cyanoacrylate adhesive. Furthermore, our research group has already confirmed that the cyanoacrylate adhesive is appropriate for the suppression of caries progression, dentin hyperesthesia, and secondary caries⁷⁾. Therefore, we expect that cyanoacrylate adhesive may be used as a temporary first aid for caries lesions in dental clinical use in the near future.

Conflicts of Interest

The authors declare no conflict of interest.

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