

Cyano- does by far more than kill you...

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Introduction

Commercial cyanoacrylate-containing adhesives have not been widely accepted in orthodontics despite their strength and ability to bond to moist surfaces. Aside from having poor resistance to water, these adhesives have a limited number of possible formulations because of their high reactivity which doesn't lend to stable combinations—important for the long shelf life required in orthodontics.

As shown in Fig. 1, α -cyanoacrylates easily react with weak bases such as traces of alcohols, amines and water and become inactive, a fact that explains the paucity of possible formulations. In the presence of appropriate monomers, cyanoacrylates lead to copolymers that, if properly selected, may combine the best properties of both species.

As a long-lasting cyanoacrylate formulation may prove difficult to achieve, we advance the hypothesis that, for a short time, it is possible to take advantage of their properties if these substances are added not to the adhesive itself but to the substrates to be attached. Three ways to add the cyanoacrylates were tested:

1. Their addition as such
2. Temporarily diluted with a volatile solvent
3. As a solution in a copolymerizable monomer

The following exploratory research was performed in Ortho-Cycle's laboratory and was facilitated by the advices received from Prof. Dr MM Kufinec, Department of Orthodontics, New York University, NY.

Materials & method

The substrates used to bond the brackets were commercial, enamel-coated, 8" x 8" commercial ceramic tiles, etched for about 10 minutes with 50% hydrofluoric acid, rinsed and air-dried, office style. As cyanoacrylates' polymerization is highly sensitive to water saturation of the substrate, the latter's humidity was controlled in some instances by brushing the surface with a solution of water and acetone.

Because the approach was new, a series of preliminary—and often random—experiments were performed each time involving the debonding of from 5 to 10 bonded brackets. By using few samples but a large testing area, we took the value of the debonding forces as the average of the readings.

Following preliminary tests, central incisor brackets from American Orthodontics (Sheyogog, WI; Triple Action™, standard size, 80 mesh) were abandoned because the forces needed to debond them were uncomfortably high and did not lend themselves to the photochemical cure of the adhesive. In contrast, the "mini" upper centrals (Straight Edge™, 100 mesh, TP International, Laporte, IN) which we did use had single tie-wings and a high enough under-the-tie-wing distance to permit their easy attachment required by the debonding test.

We used the two-paste, Phase II™ adhesive system (Reliance, Itasca, Ill) and a visible light curable, fluoride-added single-paste, Light Bond™, also from Reliance. To test adhesive-smear bases for sliding on a vertical surface, several uncured formulations were used, irrespective of if destined for light or chemical cure, as such (parts A or B) or combined.

The bond promoters or primers used were solutions containing a solvent and the commercial form of α (or 2-) ethyl cyanoacrylate sold as Crazy Glue™ (KG), from Toagosei, (Tokyo, Japan). To prepare for the various additions while protecting it from premature polymerization, the monomer had to be squeezed from its polyethylene vials into larger, glass ones under a supernatant n-pentane layer. The solvents added to the cyanoacrylate were methylene chloride, acetone, and triethylene glycol dimethacrylate (TEGDM). The first had to be abandoned because of poor performance. Both

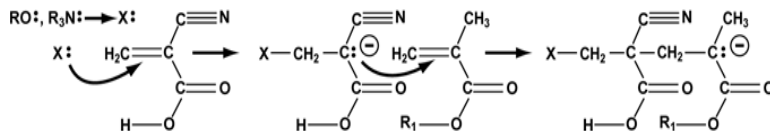


Fig. 1. In α -cyanoacrylates, the CN group strongly attracts electrons rendering the double bond in the vinyl highly susceptible to attacks even by weak bases such as aromatic amines or water. In turn, the carbanion (C⁻) resulted can attack other double bonds: these can be either of the same species, or, for a short time, of another one, such acrylates, as depicted in this sketch were R₁ is an aromatic moiety

acetone and TEGDM were of technical purity as sold by Home Depot and Sartomer (Warrington, PA), respectively.

Application of the adhesive-smear brackets to the cyanoacrylate-primed substrate took place within 1 minute if KG was used, between 10-20 minutes with acetone and 10 to 60 minutes if TEGDM was used. Approx. 0.05 g of parts A and B of the chemically curable adhesive were first mixed on a cold slab up to 30 seconds while the photochemically curable adhesive was used as such or along with a photochemically curable sealant. The amount of added adhesive was always enough to allow it to flow freely around the base when the bracket was pressed against the substrate. After a partial curing, the adhesive excess was carefully removed after which the cure continued. The brackets bonded with Phase II™ were debonded after 30 to 60 minutes, while the photochemically cured ones after 15-30 minutes. An orientative, preliminary test of the resistance of the acrylate-cyanoacrylate bonds to hydrolysis has been performed by immersing brackets bonded to a ceramic tile in water for 10 days.

Instead of an universal testing machine, a simplified bench bond tester was used¹ (Fig. 2). Inspired by a device we previously described², it replaced the weight of water as a debonding force with stainless steel balls. The system allows measuring the brackets' bonding peel strength when they are attached under a tie-wing by a loop of the tester's wire. To enable the balls to flow evenly, a sand-timer type of arrangement was used: as soon as the tested bracket detached, the direction of the ball flow was manually changed. The small additional weight at the time the container was weighted was small enough to be neglected.

Results

An impressive feature of the systems cyanoacrylate-acrylate adhesive is the abrupt increase in viscosity when the two parts are placed in contact with each other. Thus, a bracket coated with any commercial orthodontic adhesive of today, or even with an uncured sealant, will not slide if kept in place for 5 sec on a vertical substrate if freshly brushed with a cyanoacrylate. The uncured sealants ranged from those destined to be light cured to either part A or B of the chemically curable ones.

The substrates tested were ceramic tiles—both smooth and glazed or acid etched—that were used either dry or after wetting and drying them office-style. All the brackets did not slide, although these ranged from the "mini" Straight Edge to the larger and heavier Triple Action™ centrals.

Results of the experiments are shown in Figure 2. The tests performed on dry ceramic tiles have been colored differently from the ones where the latter were wet and office-style dried. On the abscissa are presented the attachment systems that involve the adhesives Phase II™ and Light Bond™, as such or added with KG, the latter being used alone or mixed with acetone or TEGDM. On the ordinate are shown the forces needed to debond a Straight Edge™ central from an etched tile according to the systems mentioned. It is important to mention that neither the acetone nor the TEGDM solutions with KG were stable; in both cases first thickening (prepolymerization) and then hardening occurred. No measures had been taken to render these solutions more stable by adding weak acids or by

lowering the acetone content of the water (technical acetone's content might even be above 1%).

In the exploratory test of water resistance, the brackets bonded with Phase II™ adhesive to a cyanoacrylate-primed wet tile (KG and TEGDM) exhibited after a 10 days immersion an average debonding force as high as 4,500 g.

Since each experiment involved relatively few debondings (the tests encompassed a rather large domain), a probable interval for the debonding forces needed for each of the attachment systems (grey shaded area) was based upon the most frequent values obtained.

Discussion

As an Internet search demonstrates, the use of cyanoacrylates as primers for other adhesives, as such or in solution, has not yet been described. The only primers used in conjunction with the cyanoacrylate adhesives are intended to promote bonding to polyethylene, polypropylene and other low-energy plastics. The explanation may reside in the fact that moisture, normally found on surfaces exposed to the



Fig. 1. Bench bond-strength tester. A controlled, increasing weight (stainless steel balls) pulls a wire, the end of which can be attached to bracket tie-wings, and various holding devices: 1. Sample tested (brackets bonded to a gold coin). 2. System of pulleys transmitting the force; 3. Container for fallen metal balls. 4 & 5. Sand-timer system working with steel balls. 6. Container for the latter. 7. Scale.

atmosphere, leads to a pre-polymerization that seems to hinder further bonding. As the cyanoacrylate's curing occurs fast, it is logic to assume that its propensity for any further reaction will drop.

Cyanoacrylates are neither suitable to make good primers nor other formulations. This can be seen from the limited

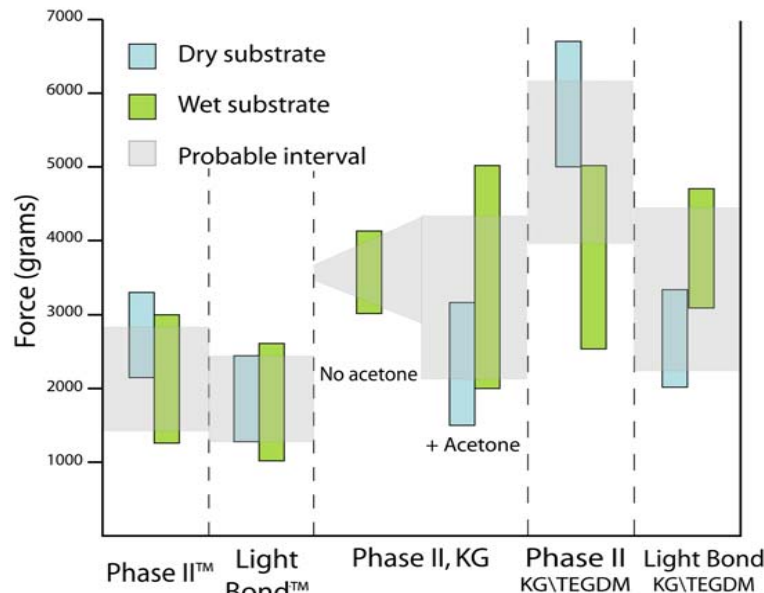


Fig. 3. Force (g) needed to debond (peel) Straight Edge™ "mini" brackets from an etched ceramic tile. Adhesives were Phase II™ and Light Bond™ with or without addition of α -ethyl cyanoacrylate (KG) and/or acetone and TEGDM.

variety of their compounded adhesives offered on the market. Indeed, Smartbond's formula for a direct-bonding orthodontic adhesive is about the same as that used by MRO's (Niles, IL) for bonding similar and dissimilar materials such as metals, rubber, ceramics and wood:

-Smartbond³ contains 85% to 90% α -ethyl cyanoacrylate, 5% to 10% poly (methylmethacrylate), 5% to 10% amorphous silica and 0.1% to 0.5% hydroquinone.

-MRO3 contains unfilled, 60% to 100% α -ethyl cyanoacrylate, 10% to 30% poly (methylmethacrylate) and 0% to 1% hydroquinone.

Acrylic-resin bonding, as we know it today, is exclusively mechanical, being based on the riveting effect exerted by the hardened resin in the enamel prisms. In acrylic-acid bonding, such as it occurs in glass ionomers, the adhesive forms chemical bonds to hydroxy-apatite, but these are known not to be strong enough.

As tested in the present study, the cyanoacrylate-acrylate ability of bonding combines the mechanical strength of the acrylic resins with the glass ionomers chemical affinity to the substrate. This seems to be demonstrated by the strength of the derived bonds: they are not only significantly greater than those obtained with the classical adhesive, be it chemical or photochemical, but also show some resistance to water. While poly-cyanoacrylates are hard and brittle, their in situ copolymerization with acrylic resins may lead to polymers that are suitable for orthodontic purposes

This study presents work performed in a modest laboratory using for testing an inexpensive contraption instead of a complex universal testing machine. To be definitive, the number of experiments should have been by far greater, involving many more lab hours. The results, however, indicate that studies of cyanoacrylates as short-lived primers for acrylates are worth pursuing.

While the systems we explored may not be at this time acceptable for clinical use (only too few clinicians are also amateur chemists), the possibility of combining cyanoacrylates' propensity for chemical bonding and strong affinity for water-saturated substrates—with the strength and "hydrophobia" of the acrylic resins—opens new vistas. Indeed, in-situ combinations between acrylates and cyanoacrylates may provide the latter with a key property, water resistance.

Conclusion

Cyanoacrylates are capable of not only bonding to polar substrates, but for a short while also of copolymerizing with acrylic resins. The latter feature leads not only to stronger bonds, but imparts to the resulting copolymer a controllable solubility that oscillates between water-hate and dissolution in more polar solvents. A stable primer with the proper balance of acrylic resin and cyanoacrylate may lead to both the patient's and clinician's dream, bracket debonding through the adhesive's dissolution. Further research, using widely accepted techniques and instrumentation, should therefore be quite rewarding...

References

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