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The bad news: those who handle orthodontic sealants, adhesives and restoratives are exposed to cancer.

The good news: with the modern means of today, sometimes it can be cured.

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Introduction.

In the United States, of the approximately 50,000 new cases of head and neck cancer diagnosed annually, over 60% are locoregionally advanced (stages III and IV). According to the American Cancer Society, 11,000 people died from head and neck cancer in 2004. These cancers arise throughout the upper aerodigestive tract and can lead to genetic alterations, such as mutations in the p53 tumor suppressor gene. Aside from smoking and drinking alcohol, factors that may play a role include viral infection, occupational exposure, radiation, dietary factors and genetic susceptibility.

Fate's irony

After publishing a long warning about the cancer generated by resins and polymers, Prof. CG Matasa, editor of this newsletter, got it himself. His warnings were given in a full chapter, "Orthodontic polymers: a present danger?," in *Risk Management*

in *Orthodontics*,¹ and contained in a series of related articles.²⁻⁹ Although Claude spent two decades of his life performing chemical research (involving, among other things, explosives and poisons, see www.matasa.net/papers_chem.html), they did not lead to cancer. In contrast, his exposure during the following three decades to the "mild" chemicals used in dentistry did. Not only did he caution against the toxic ingredients commonly used in orthodontics, but he dedicated part of his research to the detection of the resins and polymers that leach in aqueous environments, finding simple ways to detect them^{6a,6b} (Fig. 1).

What he may not have taken into account, however, is that leaching also occurs in air, and the vapors released may be even more harmful.

Diagnosis. After complaining of throat pain, Claude was subjected to computed tomography (CT) and then to positron emission tomography (PET) for diagnosis. The latter method is more effective because many cancer cells are highly metabolic and rapidly consume the radioactive glucose derivative injected into the patient before the exam. Areas of high glucose uptake are dramatically displayed in the scan imagery, as opposed to the anatomic imagery of CT or MRI, which cannot detect active, viable tumors. The ensuing biopsy confirmed the existence of squamous cell carcinoma, stage III, both as a large mass ($2.4 \times 2.7 \times 4.4$ cm, that extended from the base of the tongue to the right oropharyngeal wall), and as foci in the neck with corresponding lymph node metastases.

Treatment. Treatment was started in October 2006 at the Sylvester Comprehensive Cancer Center, which serves as a hub for cancer-related research, diagnosis and treatment at the University of Miami Leonard M. Miller School of Medicine, and it lasted 6 weeks.

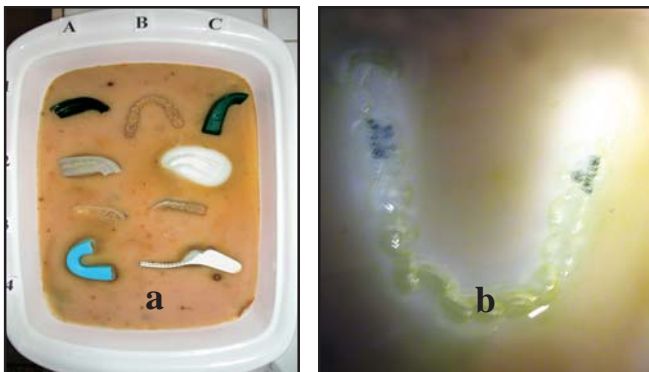


Fig. 1. Discoloration auras generated in a gel containing potassium permanganate. Its decomposition is proportional to the ingredients leached by retainers (a) or aligners (b)

Concomitant exposure to radio- and chemotherapy was recommended. For the first, intensity-modulated radiation therapy (IMRT), a recent variation of 3-dimensional conformal radiation therapy (3D-CRT) was used. The way IMRT x-rays are controlled has been found to potentially decrease damage to normal body tissues and therefore have fewer long-term side effects.

The basic components of the chemotherapy treatment, administered together once a week, were Cisplatinum and Imclone's Erbitux (cetuximab). Cisplatinum, as its name indicates, is a metal coordination complex capable of producing inter- and intrastrand DNA cross-links, whereas Erbitux is a monoclonal, anti-epidermal, growth-factor receptor (EGFR) antibody.

As death and serious cardiotoxicity have been observed when combining cisplatin with cetuximab and RT in single-arm trials on patients with locally advanced squamous cell cancer of the head and neck (Claude's case), the related clinical trials of toxicity had to be performed under strict control.¹⁰

Patient's penitence. Claude tolerated the treatment despite such inconveniences as mucositis (along with... dry mouth!), radiation dermatitis, use of an intravenous port for administering drugs, a bruised and swollen tongue and a total loss of appetite (solved by tube feeding). Cramps, restlessness, scars from radiation were just part of it (Fig. 2). After ingesting a nutritive fluid by tube for 2 months, and after the next three months, he still has difficulty eating even soft, mashed or liquefied food. His morale, however, was excellent; despite weakness associated with a weight loss of some 30 pounds, he has continued to perform experiments in his lab and write about them, as witness both the present and past (December 2006) issues of the *Insider*.

Thanks to the excellent care exercised by his physicians, Dr D Jassir (who promptly diagnosed the cancer), Dr AM Markoe (professor of radiation oncology), Dr DS Ernst (associate professor of medical oncology) and Dr DJ Arnold (assistant professor of otorhinolaryngology), by mid-February 2007, 2 months after completion of his treatment, the cancer mass evident in his initial PET scan (Fig. 3) was not evident in Claude's CT-scan, and he looked better (his radiation-reddened face being taken as... suntan).

Risk factors. Cancer is the illness of the century: one out of 5 is its prey. Statistics released by the Edelson Center for Environmental and Preventive Medicine in Atlanta have related common chemicals to cancer:

- 2 million chemicals already synthesized
- 60,000 chemicals in current use
- 4 billion tons dispensed throughout the world yearly

- 2,000 new chemicals each year
- Constant increase in use of toxic heavy metals
- Steady increases in all chronic illnesses (cancer, arthritis, immune diseases, etc.) every year
- Breast cancer, 1950: 1 in 50; 1993: 1 in 9
- Cancer, 1975 – 1993:**
- Increased cancer incidence: 13%
- 5 year survival rate: unchanged
- Death rate increase: 7%

Claude's case raises the question of the influence of his apparently harmless lifestyle on his cancer. Though it has been estimated that the use of tobacco and alcohol account for almost 80% of the head and neck squamous-cell cases,¹¹ these factors could not be accounted for in his case. What he suspects is his inhaling of polynuclear aromatic (benzene-cycles-containing) acrylates during their repeated handling, operations for which he—like many other researchers and practitioners—didn't use a hood.

According to Claude, orthodontists are forced to disregard FDA's guidelines for industry as far as it relates to dental composites¹² because they have no other choice in performing their duties. Major institutions such as the National Institute of Standards and Technology (NIST; Gaithersburg, Md) and the Southwest Research Institute of the University of Texas, San Antonio, which have the means to solve the problem and replace such monomers,⁷ have not yet come up with any solution.

Notably, the FDA's classification of dental cements and composites (ADA/ANSI#66; ISO 7489) indicates that these substances, either directly or through the release of their material constituents, should not (1) produce significant adverse local or systemic effects, (2) be carcinogenic or (3) produce adverse reproductive or developmental defects. The ISO standard (ISO-109993, Part 1) used in Europe is based on a test selection very similar to the Tripartite Guidance used by the FDA.

In the US, Proposition 65—also known as the Safe Drinking Water and Toxic Act of 1986—has no equal anywhere, as it simply states that the *physician* [italics ours] should not use products that are toxic, mutagenic, carcinogenic or estrogenic. According to paragraph 25249.6 of this law (Required Warning Before Exposure to Chemicals Known to Cause Cancer or Reproductive Toxicity), "No person in the course of doing business shall knowingly and intentionally expose any individual to a *chemical known to the state to cause cancer or reproductive toxicity without first giving clear and reasonable warning to such individual.*" Most of the sealants, adhesives, veneers and restor-



Fig. 2. Changes in Claude's skin evolution before, during and after treatment. a. July 2006; b. September 2006 (note scars); c. December 2006; d. February 2007.

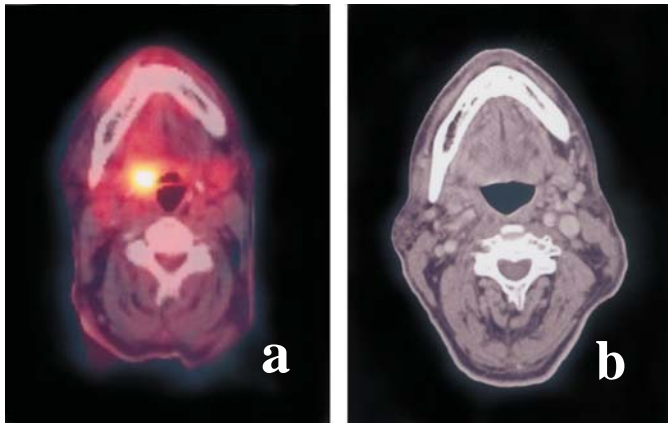


Fig. 3. a. Claude's PET scan, September 2006 (observe white spot (carcinoma)); b. CT-scan, February 2007

atives used today contain bis GMA, an ester of bisphenol A, a polynuclear (polycyclic), aromatic compound and a potential carcinogen to which was dedicated almost all of a chapter ("Here, there and everywhere") in Colborn T, Dumanoski D, Myers JP, *Our stolen future* [preface by Vice President Al Gore], Little, Brown & Co., Boston, and Chelsea Green Publishing, 1996. In Japan, another ester of bisphenol A (a polycarbonate) has been banned from use in plastic bottles from fear of generating cancer. In the US, according to the *Milwaukee Journal's* Sentinel Online: Health and Science, March 2007, the same decision is expected soon. In dentistry, the aromatic components of the dental resins have been found to be mutagenic.^{13,14} Up to 14% of a direct-bonded adhesive can leach out and continue doing so for up to 2 years.^{15,16} Most monomers and oligomers released by the resins were found to be cytotoxic.^{15,16}

Based upon the above, it is not surprising that the growing incidence of head and neck cancer cases¹⁷ [There is no callout for #18.] has been related to the bis GMA content of some dental materials.

Conclusions

We live in a world that is threatened by its own creations. It has been almost a century since K. Yamagiwa found that body penetration or oral absorption of polycyclic aromatic hydrocarbon derivatives leads to cancer; despite this, such compounds continue to be used in medicine. FDA's principle that if its benefits outweigh its risks an agent can be used, doesn't necessarily lead to progress, as the history of bis GMA proves: despite its evident problems, dentistry has been using it for almost half a century.¹⁸

As Claude has shown,¹³ bis GMA, the polycyclic aromatic resin he believes to have generated his condition, seems to have only 1 outstanding advantage: its polymers have exceptional strength. Today's chemistry can synthesize monomers with superior properties starting from liquid crystal (LC) natural products. Hopefully, the Southwest Research Institute, having received a grant of \$3.4 million from the National Institute of Dental Research (NIDR), will develop a material that would be, as they promise, "far superior to anything which currently exists."^{19,20}

Until then, researchers and practitioners alike may still have to suffer or even die from the hazardous products on the market, the use of which is allowed by product-safety agencies.

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“Cyano-” doesn’t always kill you!

A case in point: the cyanoacrylates

How toxic are they?

While we are all familiar with the toxic effects of cyanides from Agatha Christie’s novels, these are produced naturally in the environment by various bacteria, algae, fungi and numerous species of plants. These include beans (coffee, chickpeas and lima), fruits (seeds and pits of apple, cherry, pear, apricot, peach and plum), vegetables of the cabbage family, grains (alfa-alfa and sorghum), roots (cassava, potato, radish and turnip), white clover and young bamboo shoots. Small amounts of the cyanide ion are ubiquitous in nearly all living organisms which tolerate, and even require it, in low concentrations. Upon the cleavage of the glycosidic bond in cyanoglucosides, the most common form found in nature, they yield highly toxic hydrocyanic acid.

In contrast, vitamin B12, or cyanocobalamin, is essential for the formation of red blood cells—preventing anemia—and is responsible for the body’s carbohydrate and energy production. Cyanoacrylates are successfully used as catgut-suture replacement in surgery, as bonding agents in dentistry and orthodontics and for artificial fingernail making; the herbicide dichlobenil (2,6-dichlorobenzonitrile) is considered nontoxic.

Ammonium thiocyanate is used in antibiotic preparations, pesticides, liquid rocket fuels, adhesives and matches. Recently, the federal government has announced ferric ferrocyanide as a recommended treatment for radiation exposure and metal poisoning. Commonly used as a pigment in printing inks, paints and paper dye, it also provides the blue color in cosmetics and orthodontic etching gels. In contrast, some cyanide salts widely used in industry are the highly toxic.

Somewhat less toxic than cyanides, cyanate compounds should also be handled under controlled conditions. Moderately toxic, sodium cyanate is used in organic synthesis, the heat treatment of steel, and as an intermediate in the manufacture of pharmaceuticals.

What renders cyano-compounds toxic?

Although all have in common the cyan group CN, some of the compounds described above (commonly called cyanogens) are highly toxic while others are not. The toxicity of nitriles varies greatly with their molecular structure, ranging from comparatively nontoxic compounds (e.g., saturated fatty acid nitriles) to highly toxic materials, such as α -aminonitriles and α -cyanohydrins, considered as toxic as hydrocyanic acid itself.

In chemical combinations, the cyan functional group consists of a carbon atom joined to a nitrogen atom by a triple bond that can be joined to an atom or another group by a single CN bond. The various toxicities presented above reside in the group’s availability to the various receptors, in other words, to its propensity to debond from the cyanogen. When a cyan group is joined to hydrogen, it forms hydrocyanic acid; with metals it forms solid cyanides, compounds that readily dissociate into the cyanide anion (CN⁻) and cations.

When it is joined to an alkyl or aryl group, CN forms nitriles; the longer the alkyl group (over C₁₂), the less harmful the nitrile.¹ In contrast, having only half as many carbon atoms, benzonitrile (C₆H₅CN) is nontoxic² because of the benzenic cycle’s affinity for electrons. This is important because whenever the cyan

group is conjugated with double bonds (α -position), as in cyanoacrylates (front, next page), the electrons circulate all along the system, reinforcing the bond of the cyan moiety to the rest of the molecule and hindering its dissociation (i.e., lowering toxicity). As a result, α -cyanoacrylates are far less toxic than the alkyl nitriles having the same number of carbon atoms. Cases in point are the complex cyanogens such as sodium nitroprusside or ferric ferrocyanide, which owe their diminished toxicity to similar phenomena.

What are cyanoacrylates?

Esters-monomers, cyanoacrylates are liquids that polymerize when initiated by moisture or certain chemicals because the cyan group is so electrophilic (thanks to conjugation) that a positive charge is induced at the terminal vinyl carbon (C⁺; formulas, next page). Highly reactive, carbanions attack weak bases such as the hydroxyl (OH⁻) in water; this destabilizes the double bond of the vinyl groups and leads to the monomer’s polymerization. The ensuing anionic and additional polymerization chain reaction leads to a very tenacious polymer film that typically immobilizes within minutes and achieves full bond strength in 24 hours.

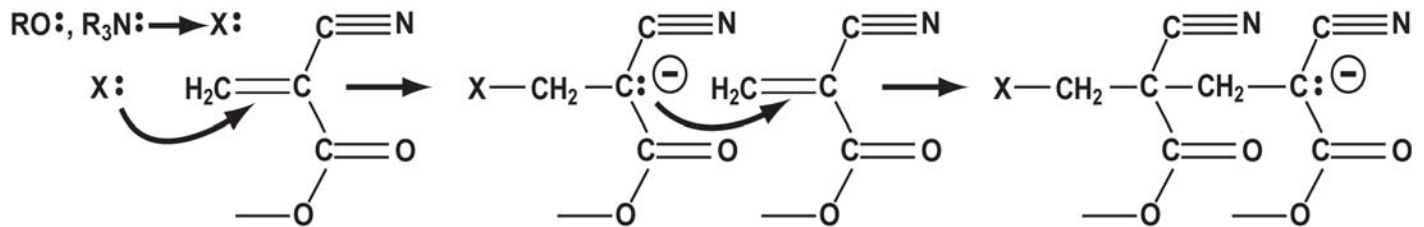
First manufactured in the US in 1949 and used as adhesives in surgery were the lower molecular weight methyl- and ethylcyanoacrylates. Introduced in 1958 as industrial adhesives, both are widely used today in the aerospace and automotive industries as well as in consumer products such as Super Glue™ and Crazy Glue™. In the 1970s, a higher molecular weight or longer alkyl group, representative of this class was introduced; n-butyl-2 (or α)-cyanoacrylate was the first adhesive to unite negligible toxicity to good bonding strength. By the mid-90s an even higher molecular weight representative of this class was introduced, n-octyl-2-cyanoacrylate. Its advantages were high bond strength, microbial barrier, controllable polymerization, fast healing and reduction of pain and infection. In 1998, a purer form received approval from the Food and Drug Administration (FDA) for market release as a topical wound-closure agent. In 2000, the administration approved a brand of n-butyl-2-cyanoacrylate as a liquid embolic treatment system.

It is foreseen that US demand for medical and dental adhesives and sealants will grow 8.4% percent annually through 2009; this forecast was based in part on new product development and increasing acceptance of these materials in surgical and consumer settings.³

Is the handling and use of cyanoacrylates risky?

The alkyl 2 (or α)-cyanoacrylates are primarily irritants. Sensory response to cyanoacrylates is reported to occur at approximately 1 ppm, with nose and eye irritation occurring in the 3-to-5 ppm range. No reports on acute cyanoacrylate exposure to humans has been found in the literature. Based on animal experiments, it is presumed that methyl 2-cyanoacrylate is of low toxicity. Also no information was found to indicate that alkyl α or 2-cyanoacrylates are toxic to humans. However, because of their highly reactive nature, skin and eye contact with alkyl 2-cyanoacrylates should be avoided.

Methyl and ethyl α -cyanoacrylates were also noted to cause tissue inflammation. Although not labeled for use by the



FDA, both have been used in Canada and numerous other countries for the past 20 years. Despite their availability and usefulness as sutures, these adhesives have failed to gain widespread popularity because of their application characteristics, variable outcomes and histotoxicity. The last-named trait is related to the byproducts of polymer degradation, length of the alkyl group of the cyanoacrylate and rate at which degradation occurs. In decreasing order, the lowest toxicity is exhibited by n-octyl-2-cyanoacrylate, then by n-butyl-2-cyanoacrylate (approved for medical use in Europe and Canada) and lastly by ethyl- or methyl 2-cyanoacrylate. It is interesting to note that although 2 ethyl 2-cyanoacrylate is a high-volume chemical with production exceeding 1 million pounds annually in the US alone, it is not listed for recognized risks, being only “suspected” of being toxic to the immune and, respiratory systems and to the skin and sense organs.⁴ Its superior homologue, n-butyl-2-cyanoacrylate, is sold in the US as a replacement for bandages and is an acceptable adhesive⁵ in oral surgery. A step forward in rendering the whole class less risky was the introduction of antimicrobial agents into the liquid prepolymer adhesives in order to reduce the risk of infection, having the advantage of being released to the skin over a sustained period.

As far as we know, only 2 such adhesives have yet been launched commercially in the US and Europe: “FH”-Cement,^{6,7} (Tokyo, Japan) and Smartbond (Gestenco, Göthenburg, Sweden). Early attempts to develop cyanoacrylate adhesives before 1990 showed that their strength diminished over time.⁸ After more than a decade, studies found Smartbond unsuitable for use as a bonding agent in routine orthodontic practice,⁹⁻¹⁵ the main reasons being insufficient bond strength, bond failures and decalcification. Among the few advantages was that the Adhesive Remnant Index indicated less residual adhesive remaining on the tooth¹⁶ and the adhesive’s cohesive fracture.¹⁷ While the latter indicates that the adhesive has been strained to its limits, it doesn’t mean that it was at the same time stronger than its competitor, the resin composite. Cyanoacrylate’s adhesion to porcelain has not been found to be better, either,¹⁸ nor was its bond strength after several second bonding/debonding sequences.¹⁹ when compared with competing products. As is expected, however, it bonds better to moist enamel than does its resin counterpart.²⁰

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Cyanoacrylate primers, a way to better bonds?

Introduction

As shown in the preceding article, commercial cyanoacrylate-containing adhesives have not been widely accepted in orthodontics despite their well advertised 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. Cyanoacrylates do not lend themselves to stable combinations—important for the long shelf life required in orthodontics.

Cyanoacrylates react rapidly with weak bases such as traces of alcohols, amines and water, becoming inactive, a fact that explains the paucity of possible formulations. As a long-lasting adhesive formulation may prove difficult to achieve, we advance the hypothesis that it is possible to take advantage of cyanoacrylates' 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 talent and hard work of Dr Nasreddin Terfas, international resident at the New York University, Department of Orthodontics, and by the advices received from Dr MM Kuftinec.



Prof. C G Matasa and Dr. N. Terfas preparing samples

Materials and method

The substrates used to bond the brackets were commercial, enamel-coated, 8" × 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 (Sheyboan, WI; Triple Action™, stan-

dard 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 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 Krazy 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 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



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.

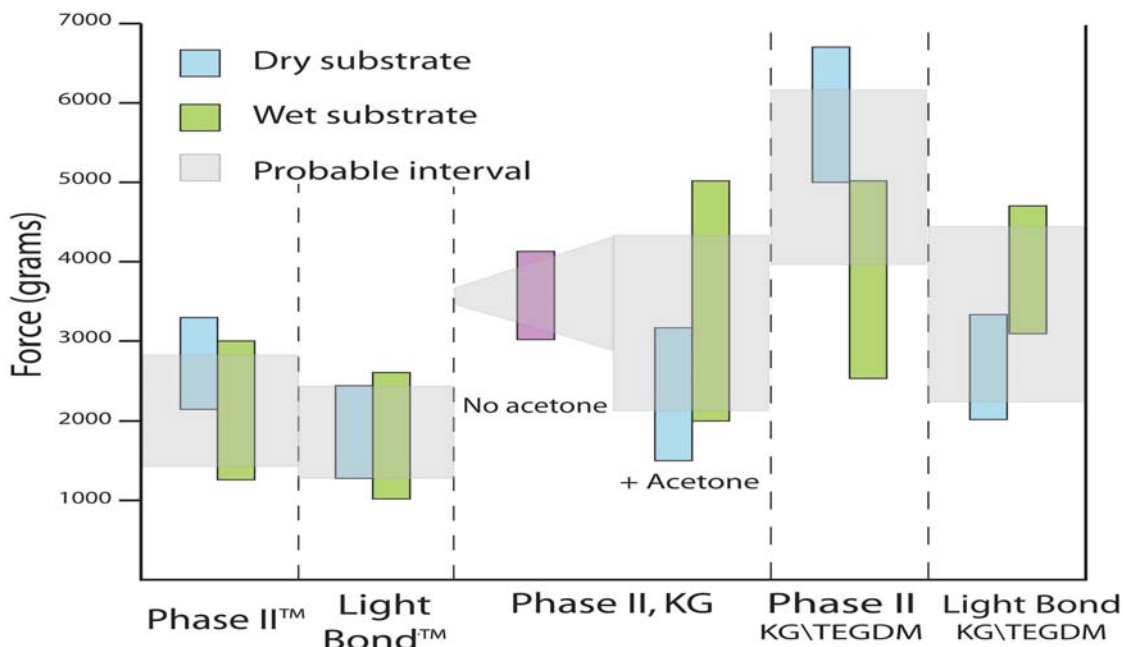


Fig. 2. Force (g) needed to debond (peel) Straight Edge™ “mini” brackets from an etched ceramic tile. Adhesives were Phase II™ and Light Bond™ with or without addition of α -ethyl cyanoacrylate (KG) and/or acetone and TEGDM

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 used (Fig. 1). Inspired by a device we previously described, it replaced the weight of water as a debonding force¹ with stainless steel balls. The system allows measuring the brackets' bonding peel strength when they are attached under a tying 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 these 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 atmosphere, leads to a pre-polymerization that seems to hinder further bonding. As the cyanoacrylate's curing was already underway, it is logic to as-

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sume 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 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:

-Smartbond² 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 bonding seems to combine 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 seems to lead to polymers that are more 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.

Conclusions

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 already accepted techniques and instrumentation, should therefore be quite rewarding...

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