Screening Orthodontic Polymers for Leaching

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It is in the clinician’s interest to select the least hazardous devices and materials among the many offered by manufacturers. The polymer chosen is important; some polymers have been reported to be hazardous, and these are quite often used in direct contact with human tissues. For protection, the clinician could test the material’s extract in water according to an ISO standard, but the tests require sophisticated means and specific knowledge. Its simplified version, however, can be successfully used, since it requires only the observation of the aqueous solution of potassium permanganate, in which the polymer samples were immersed. Initially purple, the solution discolors as the colored ions are reduced, while the released ingredients are oxidized. The faster and more intense the discoloration, the higher the amount of leached ingredients. World J Orthod 2003;4:157-161.

As opposed to those for metabolized medicines, the controls imposed by various governmental agencies on orthodontic devices and materials are low. According to the United States Food and Drug Administration (FDA), dental polymers, including resin-based adhesives and restorative materials (resin or glass-ionomer type), are Class II, and according to ISO, Class IIa, ie, they exhibit a moderate hazard potential. As a result, manufacturers do not feel the need to disclose the ingredients or the procedures used, and journals publish articles that quote commercial names instead of providing specific, scientific information. This lack of information comes as a surprise considering the hazards presented by some polymers and the strict rules governing the matter. Indeed, Title 21 of the Code of Federal Regulations (21 CFR) promulgated by the FDA requires that the compounds for medical devices involving bodily contact must be biocompatible to prevent adverse bodily reactions. Typically, this means exhibiting no cytotoxicity in cell culture tests and/or conformance to the protocols of US Pharmacopeia (USP) Class VI. In addition, the tests required are Ames for mutagenic, carcinogenicity, mucus membrane irritation (hamster’s pouch), and sensitization on guinea pigs.

In the orthodontic specialty, no specific cases have been made public, despite the general outcry against the problems generated by some polymers; this is surprising, since some components have been found to be toxic, mutagenic, carcinogenic, and oestrogenic. These polymer components include the derivatives of bis phenol A, used in both polycarbonate retainers and in bis GMA-containing sealants, adhesives, restorative materials, and veneers, or the phthalate-plasticized vinyls used in retainers. While seldom resulting in a life-threatening condition, the litigious consequences are of major concern; nine major risk-management insurance companies stopped issuing malpractice insurance last year.

Determination of impurities has been the object of two ISO standards, one for a monomer, and the other for water quality. The first requires an expensive spectrophotometer endowed with selectors for continuous variations of wavelength, while the second requires a sophisticated chemical analysis. Fortunately, the color-change exhibited by the strong oxidizing agent used in both cases leads to a simplified method. This process uses diluted, purple solution of potassium permanganate, in which the Mn^{III} ions are reduced to the colorless Mn^{II} ions, while the released ingredients are oxidized.
MATERIAL AND METHODS

Material

To prepare the disclosing solution, 16 mg potassium permanganate ACS reagent grade, 99% (Fisher Scientific, Pittsburgh, PA, USA) is added to 1 liter of distilled water. After mixing, the solution is stored in a closed container for 24 hours. The solution is then placed in an adequate container, either 25-mL capped test tubes or in the dents in a porcelain egg-holder, with the various polymeric products to be tested, such as adhesives, plastic appliances, and elastomeric ligatures. The solution’s discoloration in time is shown in Fig 1. The photographs were taken using a digital Nikon Cool Pix 950 camera.

The reaction proceeds in two ways, according to the pH of the solution. In a neutral environment, the MnVII ions are reduced to manganese oxides (MnIII) that give the solution a brownish tint. By adding a few drops of an acid, such as phosphoric, sulfuric, or hydrochloric (muriatic) to pH 1-2, the color further changes to clear as the manganese is reduced to colorless salts (MnII) (Fig 2). Alternatively, if a reacted solution obtained in a neutral environment is acidified, it will have either a shade of purple (unreacted permanganate) or become clear. The latter indicates a total consumption of the MnVII ions, ie, an excess of leached (and oxidized) ingredients.

Methods

1. The adhesives and restorative materials to be tested were thinly spread on a Teflon surface and cured according to manufacturer recommendations. After curing, the foils were cooled and reduced to particles by using a coffee grinder and weighted to samples of 1 g each. The particles were then immersed in 20 mL of the permanganate solution in 25-cc capped test tubes, in the presence or the absence of phosphoric acid. In alternate tests, the monomers were added as viscous liquids.

2. The retainers were collected from various manufacturers during the 102nd Annual Session of the American Association of Orthodontists, as well as from local drug stores. Due to the resiliency of the rubber-like material, grinding did not result in particles fine enough to expose a large surface area to extraction. As heating would alter the composition, a technique used to disintegrate tissues in biology was used. The samples were first cooled by immersion in stainless steel tea-baskets into liquid nitrogen, and then immediately crushed with a hammer, as shown in Fig 3. One gram of the particles was then placed, along with 5 mL of the acidified potassium permanganate solution (pH 2), in each dent of a ceramic egg-holder platter, and photographed. A second photograph was taken after 24 hours.

3. The elastomeric ligatures, chains, or separate modules were cut to a weight of 1 g and immersed, as shown above, in the acidified solution of potassium permanganate. The color changes were photographed.
RESULTS

Adhesives, restorative materials, and monomers

The array of marked test tubes shown in Fig 4 contained the following minced polymeric material suspended in neutral potassium permanganate: 0, None (Control); 1, Fuji Ortho LC, compomer (GC America, Chicago, IL, USA); 2, PQT, adhesive (Ultradent, South Jordan, UT, USA); 3, Perma Quick, adhesive (Ultradent); 4, Light Bond, sealant (Reliance, Itasca, IL, USA); 5, LCR, adhesive (Reliance); 6, Light Bond, adhesive (Reliance); 7, Quick Cure, adhesive (Reliance); 8, Bond Lock, adhesive (Reliance); 9, Bond Fast, adhesive (Reliance); 10, Phase II, adhesive (Reliance); 11, Maximum Cure, sealant (Reliance); 12, Advantage, adhesive (Ortho-Organizers, San Marcos, CA, USA); 13, Jet, self-curing resin (Lang Dental, Wheeling, IL, USA); 14, Ketac-Cem, glass ionomer (ESPE, Seefeld, Germany); 15, Maxibond, adhesive (Ortho-Source, North Hollywood, CA, USA); 16, Genie, liquid-powder adhesive (Lee Pharmaceuticals, South El Monte CA, USA).

As the reaction was too slow in a neutral environment, phosphoric acid (pH 2) was added in all subsequent experiments, as recommended in the ISO standard for testing water. The polymeric materials tested were, in part, the one presented above, to which some precursor monomers were added, as shown in Fig 5: 0, Control; 1, Jet; 2, LCR; 3, PQT; 4, Perma Quick; 5, Light Bond; 6, Ketac-Cem; 7, Maximum Cure; 8, Ethoxylated bisphenol A dimethacrylate monomer (adhesive precursor, Sartomer, West Chester, PA, USA); 9, Bis GMA monomer (adhesive precursor, Rohamere, Rohm & Haas, Philadelphia, PA, USA).

The reaction was faster this time, reducing the test time to a few minutes. During the previous experiment, a brown-black precipitate was formed, while in the second experiment, the samples were clean and the solution became clear.

Retainers

The minced appliances were exposed to the same conditions as in the previous experiment, and were photographed before and at 24 hours, as shown in Fig 6: 1, Night Guard, grinding protector (Walgreens, Deerfield, IL, USA); 2, Essix "A", retainer (RainTree Essix, Metairie, LA, USA); 3, Ortho Tain, retainer (Ortho-Tain, Winnetka, IL, USA); 4, Tru-Tain, retainer (Tru-Tain, Rochester, MN, USA); 5, Therabite, wafer
Elastomeric ligatures

Several elastomeric chains and modules were exposed to the conditions described above, and photographed before and at 12 and 24 hours, as shown in Fig 7: 1, Adenta, chain (Adenta, Gilching, Germany); 2, Ortho Arch, chain (Ortho Arch, Schaumburg, IL, USA); 3, OSE, chain (OSE, Gaithersburg, MD, USA); 4, Ortho-Source, chain (Ortho-Source); 5, Dynaflex, chain (Dynaflex, St Louis, MO, USA); 6,Ormco, chain (Ormco, Orange, CA, USA); 7, Tiger, chain (Tiger, Columbus, IN, USA); 8, OSE, modules (OSE); 9, A-Co, modules (Ormco); 10, H. Schein, modules, yellow (Henry Schein, Melville, NY, USA); 11, H. Schein, modules, silver (Henry Schein).

DISCUSSION

While differing in speed, some oxidation-reduction reaction took place in all cases, as shown by the discoloration of all the samples except the control. In a neutral environment, the reaction is slow and the discoloration more difficult to assess due to the suspended particles of manganese oxides; therefore, an acid environment was preferred. In an acid environment, the reaction is faster and the shades vary between clear and purple.

Among adhesives, restorative materials, and sealants, the unfilled samples (sealants) showed, as expected, the fastest color changes. Interestingly, the cold cure Jet, from which unreacted methyl
methacrylate presumably could be easily released, leached less than most samples. Fuji's compomer was found to leach more reducing ingredients than the resin-based adhesives.

With the exception of the mouthguards, designed for short wear and based upon plasticized polyvinyl chloride, the retainers tested did not show any alarming leach. The least leaching among these was seen in the C+ retainer from Raintree Essix, which contains, or is based upon, polypropylene, a polymer known for low water solubility.

Some of the elastomeric ligatures leached more visibly than the others. This may be because these are sometimes used to release fluoridation agents, instead of being sealed, and, therefore, are less affected by the oral environment.

While not all the released ingredients significantly reduce the properties of the device or are harmful to the patient, some can generate problems, as in the case of plasticizers or the derivatives of bis-phenol A. Lower amounts of leaching indicate a better cure and safer product (a higher molecular weight of the polymer and a denser cross-linking).

**CONCLUSION**

Sealants are a short-term product in the oral environment, while adhesives and restorative materials remain in place for a longer period of time. Some plates and retainers may have to be repeatedly replaced (Invisalign, for example, may be replaced up to 40 times), raising the possibility of significant release of various ingredients. While these released ingredients have been reported to be toxic, mutagenic, carcinogenic, and oestrogenic, but until now there has not been a readily accessible method of assessment.

The sophisticated ISO method to detect organic impurities is so sensitive that it is currently used to assess tap water. However, the simplified method presented here uses do-it-yourself means to indicate the degree to which a polymer leaches oxidizable, organic matter. By indicating the degree of leaching, the method allows manufacturers to optimize their polymer-containing products and the clinician to select the least harmful ones.

**REFERENCES**