- Paul SJ, Pliska P, Pietrobon N, Scharer P. Light transmission of composite luting resins. Int J Periodontics Restorative Dent 1996; 16:164–173.
- Arikawa H, Fujii K, Kanie T, Inoue K. Light transmittance characteristics of lightcured composite resins. Dent Mater 1998; 14:405–411.
- Lee YK, Lim BS, Kim CW. Effect of surface conditions on the color of dental resin composites. J Biomed Mater Res 2002; 63:657–663.
- Johnston WM, Ma T, Kienle BH. Translucency parameter of colorants for maxillofacial prostheses. Int J Prosthodont 1995; 8:79–86.
- 12. Johnston WM, Reisbick MH. Color and translucency changes during and after curing of esthetic restorative materials. Dent Mater 1997; 13:89–97.
- Lee YK, Lim BS, Powers JM. Color changes of dental resin composites by a salivary enzyme. J Biomed Mater Res 2004; 70B:66–72.
- Larsen IB, Freund M, Munksgaard EC. Change in surface hardness of BisGMA/ TEGDMA polymer due to enzymatic action. J Dent Res 1992; 71:1851–1853.

- International Organization for Standardization. CIE standard colorimetric observers. ISO/CIE 10527:1991(E).
- International Organization for Standardization. Dentistry—polymer-based filling, restorative and luting materials. ISO 4049:2000(E).
- 17. International Organization for Standardization. Dental materials—determination of color stability. ISO 7491:2000(E).
- Gurdal P, Akdeniz BG, Hakan Sen B. The effects of mouthrinses on microhardness and color stability of aesthetic restorative materials. J Oral Rehabil 2002; 29:895–901.
- Paravina RD, Ontiveros JC, Powers JM. Curing-dependent changes in color and translucency parameter of composite bleach shades. J Esthet Restor Dent 2002; 14:158–166.
- Campbell PM, Johnston WM, O'Brien WJ. Light scattering and gloss of an experimental quartz-filled composite. J Dent Res 1986; 65:892–894.
- 21. Lindqvist L, Bartfai T, Berg JO, Blomlof L. In vivo and in vitro studies of inhibitory effects of restorative dental materials on salivary esterases. Scand J Dent Res 1980; 88:229–235.

- Nakamura T, Saito O, Mizuno M, Tanaka H. Changes in translucency and color of particulate filler composite resins. Int J Prosthodont 2002; 15:494–499.
- Miettinen VM, Narva K, Vallittu PK. Water sorption, solubility and postcuring of glass fiber reinforced polymers. Biomaterials 1999; 20:1187–1194.
- Buchalla W, Attin T, Hilgers RD, Hellwig E. The effect of water storage and light exposure on the color and translucency of a hybrid and a microfilled composite. J Prosthet Dent 2002; 87:264–270.
- Brodbelt RH, O'Brien WJ, Fan PL, Frazer-Dib JG, Yu R. Translucency of human dental enamel. J Dent Res 1981; 60:1749–1753.

Reprint requests: Yong-Keun Lee, DDS, PhD, Associate professor, Department of Dental Biomaterials Science, College of Dentistry, Seoul National University, 28 Yeongeon-dong, Jongro-gu, Seoul, Korea; e-mail: ykleedm@snu.ac.kr ©2005 BC Decker Inc

COMMENTARY

CHANGES IN TRANSLUCENCY OF RESIN COMPOSITES AFTER STORAGE IN SALIVARY ESTERASE

Stephen C. Bayne, MS, PhD*

The authors have tackled an interesting research issue, that of long-term degradation of dental composites caused by salivary esterase interactions. There are two key points to emphasize in considering this issue: (1) What are all possible events that may be involved with resin composite changes over time? (2) What is the relative importance of the salivary esterase contribution to those changes?

As with any restorative material, there are quite a few possible intraoral events that can occur along the restoration surfaces. It is convenient to categorize these events in terms of physical, mechanical, chemical, and biologic ones,¹ with salivary esterase effects being considered chemical events. Imagine the restorative surface as schematically portrayed in Figure 1. Although interactions may occur throughout the "bulk restorative material," most likely the external surfaces will be more affected. These surfaces (or interfaces) involve the passage of materials from the outside to the inside and from the inside to the outside. Under most circumstances, surfaces are not clean. They are coated with saliva, other intraoral fluids, absorbed materials (such as stains), and acquired coatings (such as biofilms).

*Professor, Operative Dentistry, University of North Carolina School of Dentistry, Chapel Hill, NC, USA



Physical events at the surface include the adsorption (onto the surface) of things such as food stains, absorption (into the surface), food bolus contents, salivary constituents (including esterase), and gases. All of these are capable of altering the local chemical environment of the restorative material and leading to chemical instabilities. These will be reconsidered shortly.

Mechanical events in the restorative material may arise during placement (and carving, burnishing, finishing, or polishing) or during service. Quite often there is a debris layer associated with placement, but it is assumed that this is lost in days or weeks. Very little is actually known about its thickness or effects. During mechanical loading, it is rare for loads to exceed the elastic limit of restorative materials. Rather, mechanical changes occur by fatigue. Fatigue is the accumulation of very small amounts of plastic deformation (that would otherwise be considered negligible) at loads well below the elastic limit over many cycles of loading. Although there is no well-known value for the loading cycle rate, a rule of thumb is about 1,000,000 loads per year. A key result of fatigue is that plastic deformation is typically displayed as the development of crack systems in the substrate. These cracks, especially along surfaces, can have the effect of increasing the effective surface and accelerating events. Interestingly, although suspected, no superficial crack systems have ever been experimentally revealed in composites.

Chemical events in composites can occur in any of the component phases—resin matrix, filler particles, and silanation. All three have come under more careful scrutiny in recent years. The resin matrix is assumed to be stable under moderately acidic conditions but is perhaps unstable under strongly acidic and moderate to strong basic conditions. The resin matrix can change in chemical composition owing to pH or the presence of other chemicals that could produce competing reactions. Exposure to ultraviolet and other radiation may induce chemical changes as well. Equally important are the effects of other dental treatments such as bleaching, fluoride varnishes, and topical fluorides on the chemical stability of the surface layers.

Obviously, there are quite a few possible reactions. Acrylic monomers tend to undergo depolymerization reactions, side chain scission, and/or monomer decomposition. In previous dental experiments, the generation of surface damage and/or formaldehyde by-products has been demonstrated.^{2–10} Despite a potential hazard from formaldehyde, the con-

centrations are incredibly small and pale in comparison to otherwise huge, naturally occurring environmental exposures to which human beings are routinely and unavoidably exposed. Therefore, this would not be considered a risk per se.

Reinforcing glass filler particles can be degraded as well, but the primary evidence of this seems to be coupled to strongly basic conditions and not to normally mild acidic conditions that are more typical intraorally.^{11,12} All composites are formulated in a way to ensure that there is intimate adaptation of the resin and filler phases. This is normally accomplished by coating the filler particles with a silane coupling agent that increases the wetting of the two phases and provides a means for chemical bridging from the matrix phase to filler particle surfaces.^{13,14}

Although a positive effect of silanation can be demonstrated, the actual structure of the silane coating may not be as simple as imagined. Consider the following: A silane coupling agent is a di-functional molecule that includes a methoxy group capable of reacting with partially hydrated silicon atoms along the filler surface.¹⁵ The other end of the particular silane used in dentistry is acrylic and intended to copolymerize with the resin matrix during composite curing. Under ideal circumstances, the silane should form a monomolecular film that includes highly oriented molecules with their ends in position to allow these reactions. However, it is more likely that this is a complex multilayered film. Silanes are capable of dimerizing, and this generates a di-functional acrylic moiety eliminating the opportunity for a silica surface chemical reaction.¹⁶ These dimers most likely stay associated with the surface films and interfere with effective bridging. The fact that the film is many molecules thick creates a potentially weaker layer than the resin matrix or silica filler. Even if the silane layer is well formed, it is subject to uncoupling in the presence of strong bases.

Another interesting consideration is that the actual volume of silane phase is much greater than might be imagined when examining high-filler composites with small particle sizes. Changing the average filler particle size by a factor of 10 increases the particle surface area by a factor of 10. In highly filled composites, the silane may represent 30 to 40% of the entire organic component of the composite.

Biologic events in composites are associated with interactions with biologic materials such as biofilms.^{17–19} Until recently, there had been a general disregard for the omnipresent effects of biofilms on biologic surfaces. Composites are always covered with biofilms! It appears that composite surfaces are only transiently cleaned by food chewing or prophylaxis but otherwise are always affected by some stage of biofilm formation. Currently there is a rapidly evolving, more-sophisticated understanding of the complex architectures of biofilms in which local conditions of pH, pO₂, and microcirculation may have dramatic influences on the actual diffusion gradients that truly exist along composite surfaces. These may affect diffusion of fluoride as well.

In light of this wide range of possible interactions, one must ask what might be the effect of any of these changes on any of the properties of a restorative material such as a composite. The authors have chosen to examine the effects of esterase-like materials on a single optical property, translucency. There is always some risk in choosing such a narrow focus. Although convenient for a research experiment, it may not reveal the true story of the complex, real interaction. As mentioned earlier, it is presumed that degradation reactions influence surfaces primarily at first. Bulk changes may occur much later or not at all. In that case, it is better to choose metrics associated with surface changes and not bulk changes. Consider this potential situation: If a 1.8 mm (1800 μ m) thick sample disk was affected only to a depth of 45 μ m on top and bottom surfaces, then only 5% ([2 × 45]/1800 = 0.05) of the entire material would be undergoing a change. Therefore, measurement of a bulk property such as translucency would most likely not detect the change unless the instrumentation was extremely precise.

Another challenge for experimentation is that many of the materials in the oral environment have a limited lifetime. Therefore, although their effects will be accumulated on restorative materials over long periods of intraoral service, it may be difficult to practically simulate them and/or accelerate the effects. It is quite complicated to ensure that concentration, pH, pO₂, and other local conditions are maintained during the storage of specimens in test solutions. Another often-overlooked feature of accelerated testing is that true cyclic challenges are replaced by high-strength challenges. For example, instead of examining the effects of pH cycling from 6.8 to 4.5 a few times a day for years, the specimen might be exposed to a pH of 4.5 continually for several days. This may not duplicate any true effects at all. Be cautious in overinterpreting the value of laboratory tests in which presumed simulation has not been demonstrated. The current authors argue that since surface hardness detected changes in concentrated solutions exposed for shorter times, their design is a rational one. However, the previous test that they quoted was focused on surface testing and not bulk testing, so the validity of this design may need to be reconsidered.

Finally, the authors have looked at only a single effect. It is rational to try to simplify the number of variables, but this design may also conceal the true changes. Consider a further option: Could it be that esterase weakens a very thin layer of resin composite and then food bolus wear removes that layer more easily? If this were true, then the real impact of esterase would not be discovered without including wear in the experimental design.

All of these many potential problems point to the need for more controls in experiments of this kind. The authors have posed an interesting issue and attempted to detect a single effect in a controlled way. However, as they also suggest, much more research is needed to understand this interaction and others. It is fair to conclude that we are still far from uncovering potential damage effects of esterase and other mediators on composite restorations. However, it is also fair to suggest that the impact of these changes would not seem to represent any risk to patients based on historical evidence. Restorations normally do not wear out.²⁰ The wear process is self-limiting. If 250 µm (0.25 mm) of a 3 mm wide by 6 mm long restoration were lost over 4 to 5 years, this would only represent 4.5 mm³ of material (1 mm³/yr) and would hardly be considered a health risk.

REFERENCES

- 1. Bayne SC, Thompson JY. Biomaterials science. Chapel Hill, NC: Brightstar Publishing, 2004.
- 2. Freund M, Munksgaard EC. Enzymatic degradation of BISGMA/TEGDMA-polymers causing decreased microhardness and greater wear in vitro. Scand J Dent Res 1990; 98:351–355.
- 3. Larsen IB, Munksgaard EC. Effect of human saliva on surface degradation of composite resins. Scand J Dent Res 1991; 99:254-261.
- 4. de Gee AJ, Wendt SL, Werner A, Davidson CL. Influence of enzymes and plaque acids on in vitro wear of dental composites. Biomaterials 1996; 17:1327–1332.
- Santerre JP, Shajii L, Tsang H. Biodegradation of commercial dental composites by cholesterol esterase. J Dent Res 1999; 78:1459–1468.
 Jaffer F, Finer Y, Santerre JP. Interactions between resin monomers and commercial composite resins with human saliva derived esterases. Biomaterials 2002: 23:1707–1719
- 7. Finer Y, Santerre JP. Biodegradation of a dental composite by esterases: dependence on enzyme concentration and specificity. J Biomater Sci Polym Ed 2003; 14:837–849.
- 8. Finer Y, Santerre JP. The influence of resin chemistry on a dental composite's biodegradation. J Biomed Mater Res 2004; 69A:233-246.
- 9. Finer Y, Santerre JP. Salivary esterase activity and its association with the biodegradation of dental composites. J Dent Res 2004; 83:22–26.
- Jaffer F, Finer Y, Santerre JP. Mutual influence of cholesterol esterase and pseudocholinesterase on the biodegradation of dental composites. Biomaterials 2004; 25:1787–1793.
- 11. Sarkar NK. Internal corrosion in dental composite wear: its significance and simulation. Appl Biomater 2000; 53:371–380.
- Sarkar NK, Karmaker A, Prasad A, Shih F. Simulation of in vivo degradation of dental composites. J Mater Sci Let 1999; 18:1749–1752.
 Kaas RL, Kardos JL. The interaction of alkoxy silane coupling agents with silica surfaces. Polym Eng Sci 1971; 11:11–18.
- Kaas KC, Kardos JL. The interaction of arkoxy share coupling agents with since surfaces. Folyin Eng Sci 1971, 11:11
 Chen TM, Brauer GM. Solvent effects of bonding organo silanes to silica surfaces. J Dent Res 1982; 61:1439–1443.
- Bayne SC. Light curing variable effects on chain reaction polymerization events. Session 1: the chemistry of polymerization contraction. In: Fundingsland J, ed. 3M Symposium: control of polymerization stress; 2000 June 22–25; St. Paul, MN. St. Paul, MN: 3M. (Available on CD-ROM)
- 16. Antonucci JM, Dickens S, Fowler BO, Xu HHK, McDonough WG. Chemistry of silanes: interfaces in dental polymers and composites. Trans Acad Dent Mater 2003; 17:81–109.
- 17. Fux CA, Costeron JW, Stewart PS, Stoodley P. Survival strategies in infectious biofilms. Trends Microbiol 2005; 13:34-40.
- 18. Berg J. Moving toward a new kind of dentistry. Emerging trends in oral care. Sci Am 2003; (Spec Issue):2–5.
- 19. Costerton JW, Stewart PS. Battling biofilms. Sci Am 2001; 285(1):75-81.
- Wilder AD, May KN, Bayne SC, Taylor DF, Leinfelder KF. Seventeen-year clinical study of ultraviolet-cured posterior composite Class I and II restorations. J Esthet Dent 1999; 11:135–142.

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