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ABSTRACT

Glass-ionomer (GI) fillers are added to restorative materials, but it is unclear if they truly react with these materials. This TEM study evaluated the existence of the GI phase in a conventional GIC (ChemFlex), a resin-modified GIC (Fuji II LC), a compomer (Reactmer Paste), a compomer (Dyract AP), and a composite (Spectrum^{TPH}), before and after water uptake. Wafers were stored at 100% RH for 24 hrs, or in water for 7 or 84 days. ChemFlex glass particles were surrounded by 300-nm-thick silica gel layers. In Fuji II LC, we found thinner hydrogel layers (100 nm) that became thicker upon water storage. No appreciable change occurred in Reactmer Paste. Only a very thin hydrogel layer occurred in Dyract AP, and none was seen in Spectrum^{TPH} after water storage for 84 days. We conclude that the variable extent of the GI phase is determined by differences in the resin composition of the restoratives.

KEY WORDS: glass ionomer, hydrogel, resin matrix.

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The Glass-ionomer Phase in Resin-based Restorative Materials

INTRODUCTION

A spectrum of tooth-colored restorative materials is available that represents the amalgamation of resin-based composite technology with that of water-based glass-ionomer cements (GICs) (McLean *et al.*, 1994). Glass-ionomer reaction in conventional GICs is typified by the partial dissolution of non-silanized, basic fluoro-aluminosilicate glass (FASG) fillers by polyalkenoic acids, forming siliceous hydrogel layers on the surfaces of the glass particles (Nicholson, 1998). Reactions of metallic ions leached from the glass particles with the carboxylic functional groups of polyalkenoic acids further result in the formation of a polysalt matrix within the set cement (Maeda *et al.*, 1999). Ion exchange *via* this glass-ionomer phase is important in terms of chemical adhesion to tooth structure and fluoride release (Sennou *et al.*, 1999). Although this water-dependent acid-base reaction can occur during the initial mixing and setting stages in resin-modified GICs (RM-GICs), the process is tempered by the incorporation of photopolymerizable moieties into these materials (Kakaboura *et al.*, 1996). Continuous formation of the glass-ionomer phase can be expected for up to 7 days (Wan *et al.*, 1999), due to the rapid rate of water sorption caused by the hydrophilic nature of the polymerized resin matrix (Cattani-Lorente *et al.*, 1999b).

By contrast, polyacid-modified resin composites (compomers) are anhydrous, and the glass-ionomer phase can be formed only upon water uptake into the resin matrix. Water sorption in compomers is much less and slower compared with RM-GICs (Small *et al.*, 1998), due to the copolymerization of unsaturated acidic monomers with other comparatively more hydrophobic resins such as urethane dimethacrylate (Cattani-Lorente *et al.*, 1999a). Surface modification of the glass particles *via* silanization to enhance filler-matrix coupling may result in an interim delay in the ion-leaching process (Dupraz *et al.*, 1996). The extent to which this glass-ionomer phase occurs in a compomer is currently unknown.

A recent addition to the continuum of hybrid materials is a novel class of anhydrous resin-based restoratives that uses pre-reacted glass-ionomer (PRG) technology (Roberts *et al.*, 1999). Known as "giomers" in the Japanese market, these materials incorporate fillers that are produced from the complete or partial reaction of ion-leachable glasses with polyalkenoic acids. In the fully pre-reacted type (F-PRG), the remaining soft, siliceous hydrogel is freeze-dried, ball-milled, and silanized to form PRG fillers. Unreacted FASG particles, silica particles, and fumed silica are included to optimize the physical properties of this material. Since PRG fillers are already pre-reacted, acidic resin monomers are not necessary for *in situ* acid-base reactions. A hydrophilic monomer, hydroxyethyl methacrylate

(HEMA), is included with urethane dimethacrylate to produce a resin matrix that is conducive to water uptake and ion exchange. It is postulated that this PRG phase promotes sustained fluoride release *via* ligand exchanges within the ion-rich hydrogel, without disrupting the integrity of the filler-matrix interface that was speculated to occur in materials such as compomers (Roberts *et al.*, 1999).

To date, evidence of the existence of a glass-ionomer phase in hybrid restorative materials has been established through the use of chemical analytical techniques (Eliades *et al.*, 1998). Ultrastructural evidence of this phase is lacking, apart from that reported by Hatton and Brook (1992) in conventional GICs. Therefore, the objective of this study was to examine, with the use of transmission electron microscopy (TEM), the ultrastructural manifestation of the glass-ionomer phase in a RM-GIC, a giomer, a compomer, and a resin composite, before and after water uptake. Comparisons were made with the ultrastructure of a conventional GIC.

MATERIALS & METHODS

Material Selection and Preparation

For each of the restorative materials, 2-mm-thick wafers were prepared between 2 glass coverslips. Their compositions are summarized in the Table (Appendix, www.dentalresearch.org).

ChemFlex (Dentsply, DeTrey, Konstanz, Germany), a high-strength conventional GIC, was used as the positive control. It was hand-mixed at the power-liquid ratio of 3.8:1 recommended by the manufacturer. A thin layer of unfilled resin was applied to prevent desiccation of the material during the initial setting stage. Two chemically cured (*i.e.*, acid-base reaction) samples were stored in a humidifier at 100% relative humidity (RH) for 24 hrs.

Fuji II LC (GC Corp., Tokyo, Japan), a dual-cured RM-GIC, was hand-mixed for 20 sec, immediately light-cured for 40 sec from both sides, and then further protected with a layer of light-cured bonding resin as described above. Two samples were aged at 100% RH for 24 hrs. The protective resin layers were removed from another 2 samples that were then stored in de-ionized water at 37°C for 168 hrs for the delayed acid-base reaction to stabilize (Wan *et al.*, 1999).

Reactmer Paste (Shofu Inc., Kyoto, Japan), a giomer, was spread as a 2-mm-thick layer between 2 glass coverslips and light-cured for 40 sec from both sides of the sample wafer. This material incorporates calcium-containing F-PRG fillers. Two samples were aged at 100% RH at 37°C for 24 hrs. Two other samples were stored in de-ionized water for 168 hrs, similar to the RM-GIC group.

Dyract AP (Dentsply, DeTrey), a compomer, was prepared in a manner similar to that used for the giomer group. Two samples were aged at 37°C, 100% RH, for 24 hrs. Since the material is anhydrous and requires water uptake for the formation of the glass-ionomer phase, 2 more samples were stored in de-ionized water at 37°C for 84 days.

Spectrum^{TPH} (Dentsply, DeTrey), a resin composite with ion-leachable glass fillers, but relatively hydrophobic resin matrix components, was used as the negative control. Two samples were prepared in the same manner as for the compomer group. The other two samples were aged similarly for 84 days.

TEM Preparation

Samples were sectioned into 2 mm x 2 mm blocks by means of a slow-speed saw equipped with a diamond-impregnated disk (Isomet, Buehler Ltd., Lake Bluff, IL, USA) under water lubrication. The blocks were supported with cold-cured polymethacrylate in a flat bullet-type TEM mold. From the surface 0.3 mm of the blocks, 90- to 100-nm-thick sections were prepared by means of an ultramicrotome (Ultracut S, Leica, Vienna, Austria) and a diamond knife (Diatome, Bienne, Switzerland). The sections were collected on single-slot, carbon- and formvar-coated copper grids (Electron Microscopy Sciences, Fort Washington, PA, USA). Unstained sections were further coated with carbon and examined by means of a TEM (Philips EM208S, Eindhoven, The Netherlands) operating at 100 kV.

RESULTS

Variable manifestations of the glass-ionomer phase were observed in the 5 materials. Fig. 1 illustrates the extremes of the restorative material spectrum. The micromorphologic appearance of the ionomer matrix and filler particles of a conventional GIC (ChemFlex; positive control) is shown in Fig. 1a. "Seed-like" inclusions were retained within the silica gel layers after depletion of ions from the surface of the glass particles (Fig. 1b). In contrast, this siliceous hydrogel layer, which is indicative of the existence of a glass-ionomer phase in resin-based restorative materials, was absent from the glass fillers in the resin composite (Spectrum^{TPH}; negative control), even upon water storage for 84 days (Fig. 1c).

Glass-ionomer phases were readily observed for both the RM-GIC (Fuji II LC) and giomer (Reactmer Paste). Large electron-dense glass fillers up to 5 μ m were found in Fuji II LC (Fig. 2a). In specimens that were examined after 24 hrs of aging, 50- to 100-nm-thick siliceous hydrogel layers were present on the surfaces of these glass fillers. Phase separation of the resin matrix

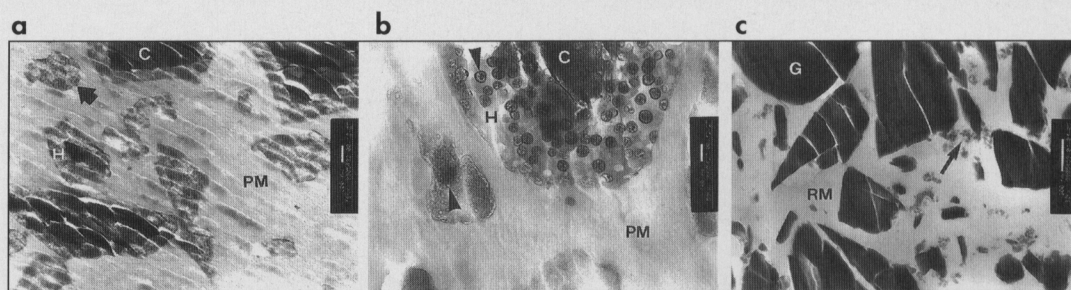


Figure 1. TEM micrographs of ChemFlex (GIC group-positive control) and Spectrum^{TPH} (Composite group-negative control), illustrating the ultrastructural manifestations of the glass-ionomer phase at the two opposing ends of the spectrum of tooth-colored restorative materials that contain ion-leachable glass fillers. (a) A low-magnification view of ChemFlex after 24 hrs of storage at 100% RH. Chatters created by the diamond knife across both the fillers and matrix reflect the brittle nature of the set cement. Siliceous hydrogel layers (H) from 150 to 300 nm thick could be seen around the remnant glass cores (C). Smaller glass particles completely reacted with the polyalkenoic acid, forming "fully reacted" hydrogels (arrow) within the polyalkenoate matrix (PM). Bar = 300 nm. (b) A high-magnification view of ChemFlex. "Seed-like" inclusions (arrowheads) were present within the hydrogel layer (H) as well as in the glass core (C). PM, polyalkenoate matrix. Bar = 100 nm. (c) A higher-magnification view of Spectrum^{TPH} taken from a specimen that was stored in de-ionized water for 84 days. No glass-ionomer phase was evident. G, glass fillers; RM, resin matrix. Arrow: fumed silica clusters. Bar = 300 nm.

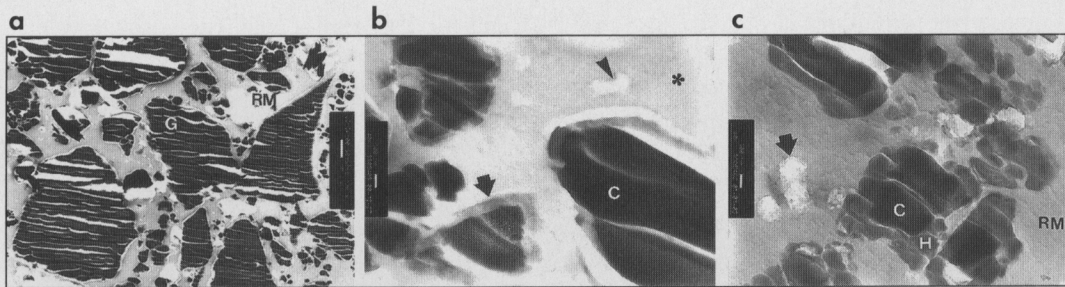


Figure 2. TEM micrographs of Fuji II LC (RM-GIC group). (a) A low-magnification view of the set material after 24 hrs of aging at 100% RH. Unlike conventional GICs, chatters were observed only within the glass fillers (G), reflecting the more resilient nature of the polymerized resin matrix (RM). Filler particles up to 5 μm in diameter could be identified. Bar = 1 μm . (b) A high-magnification view, showing the presence of 50- to 100-nm-thick siliceous hydrogel layers (arrow) around the periphery of the glass filler cores (C). Phase separation could be vaguely discerned within the resin matrix. The mild electron-dense (gray) nature of the major portion of the matrix (asterisk) was probably due to metallic ions that reacted with the polyacid component of the cement. The minor electron-lucent (white) portion (arrowhead) probably contained hydrogels of poly-HEMA. Bar = 100 nm. (c) After a specimen of Fuji II LC was aged in de-ionized water for 168 hrs, 100- to 150-nm-thick siliceous hydrogel layers (H) were formed around the glass cores (C). The gray portion of the matrix (RM) was considerably more electron-dense. Numerous round holes (arrow) may represent voids that remained as HEMA leached out after water sorption. Bar = 100 nm.

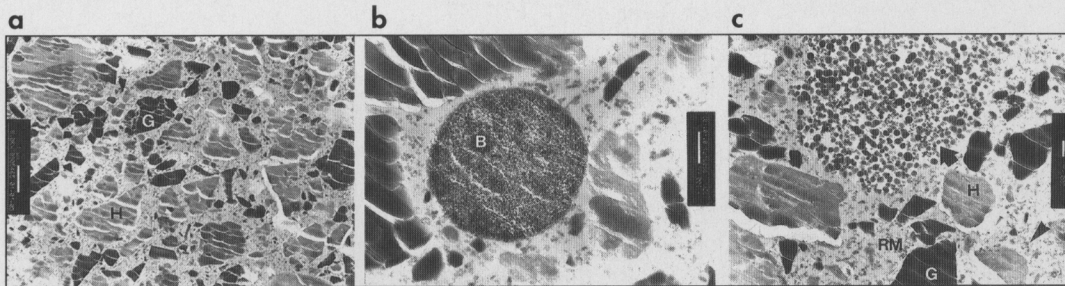


Figure 3. TEM micrographs of Reactmer Paste (giomer group). (a) A low-magnification view of the polymerized material after aging for 24 hrs at 100% RH. Three types of fillers were ubiquitously identified: less electron-dense (gray) F-PRG fillers that consisted predominantly of dehydrated silica gels (H), FASG fillers that were ultrastructurally manifested as electron-dense (black) glass particles (G), and fumed silica clusters. Bar = 1 μm . (b) Another view of Reactmer Paste, showing the occasional presence of conglomerated bodies (B) of small silica particles that were probably created during silanization. Bar = 300 nm. (c) A higher magnification of a specimen after storage in de-ionized water for 168 hrs. In the absence of acidic resin monomers, no siliceous hydrogel layers were formed around the basic FASG glass fillers (G) in the set Reactmer Paste. Partial disaggregation of the conglomerated bodies into individual circular silica particles (arrow) was probably caused by hydrolysis of the silane coupling that encompassed these particles as water diffused into the resin matrix (RM). Arrowhead, fumed silica clusters; H, F-PRG fillers. Bar = 300 nm.

could be vaguely discerned (Fig. 2b). This phenomenon became more distinct after 168 hrs of water storage. Thicker siliceous hydrogel layers (*ca.* 100 to 150 nm) were also seen around the glass fillers (Fig. 2c). In Reactmer Paste, the glass-ionomer phase was present as dehydrated silica gels in the F-PRG fillers. Electron-dense FASG fillers and fumed silica were concomitantly found within the homogenous resin matrix (Fig. 3a). Large, electron-dense, conglomerates of larger silica particles were occasionally observed (Fig. 3b). There were no appreciable ultrastructural changes after 168 hrs of water storage, except for some disaggregation of the conglomerated bodies (Fig. 3c).

By contrast, there was no evidence of a glass-ionomer phase in the compomer (Dyract AP) after 24 hrs of aging. Apart from angular glass fillers, this material also contains large silhouettes of monoclinic crystals (Fig. 4a), as well as relatively smooth-edged, electron-dense conglomerated bodies (Fig. 4b). The former probably represented spaces occupied by the crystalline strontium fluoride supplements. The latter were submicron glass fragments produced from ball-milling that were tacked together

into aggregates during the silanization process (Dr. Gordon Blackwell, personal communication). There were far fewer siliceous hydrogel layers (< 200 nm thick) after 84 days of water storage (Fig. 4c). Disaggregation of some of the conglomerated bodies was also evident at this time within the resin matrix.

DISCUSSION

The restorative materials examined in this study all contain ion-leachable glass fillers. Although barium-containing silicate glass in Spectrum^{TPH} does not release fluoride, leaching of other metal ions can occur (Söderholm *et al.*, 1996). The “seed-like” inclusions that are present in ChemFlex and Dyract AP represent segregated regions of fluoride-rich phases within a more continuous glass phase in certain reactive glass compositions (Barry *et al.*, 1979). The variable extent in which the glass-ionomer phase is manifested in this spectrum of resin-based restoratives may be related to the leaching stoichiometry of the reactive glass fillers (De Maeyer *et al.*, 1999), the media of exposure (Bapna and Mueller, 1999; Marks *et al.*, 2000), the influence of silane coupling on ionic transport (Dupraz *et al.*, 1996), and, above all, to the differences in liquid/resin composition in these systems (Mante *et al.*, 1999).

Both conventional and RM-GICs contain non-silanized fillers in water-bound matrices. In a conventional GIC, tartaric and polyalkenoic acids are neutralized within 1 hr of being mixed (Young *et al.*, 2000). Conversely, photopolymerization extensively reduced the acid-base reaction during the early setting stages of RM-GICs (Kakaboura *et al.*, 1996). In Fuji II LC, a polymerizable hydrophilic monomer (HEMA) is added to polyalkenoic acids to form the liquid component. The concentration of HEMA in RM-GIC liquids was found to vary between 18 and 32% (Ikeda *et al.*, 1999). Although continuous formation of the glass-ionomer phase is expected on maturation of the material (Bourke *et al.*, 1992), bound water that is trapped within poly-HEMA hydrogels (Roorda *et al.*, 1988) is unlikely to be available for the delayed acid-base reaction. Perpetuation of the glass-ionomer phase may be enhanced by early rapid water sorption into the hydrophilic matrix (Small *et al.*, 1998). Unlike polymerizable polyalkenoic acids contained in other RM-GICs, HEMA lacks carboxylic functional groups that can interact with metal cations, and polysalt formation in Fuji II LC is probably

restricted to the polyelectrolyte portion of the set cement matrix. Phase separation has been speculated to occur in matrices of RM-GICs that contain separate polymerizable monomers (Wilson, 1990). Although both HEMA and polyalkenoic acids are water-soluble, they may not be mutually miscible, with the possibility of development of an aqueous biphasic system (Cabezas *et al.*, 1990). Phase separation of poly-HEMA may also occur in the presence of a salt solution, forming porous hydrogels (Liu *et al.*, 2000). This may contribute to the susceptibility of RM-GICs to dehydration (Sidhu *et al.*, 1997).

The giomer and compomer examined in this work both contain silanized fillers in anhydrous resin matrices, in which hydrophilic resins co-polymerize with the more hydrophobic urethane dimethacrylate. Water uptake in these materials is thus expected to be less than for RM-GICs, but considerably more than for resin composites (Small *et al.*, 1998). In Reactmer Paste, polyalkenoic acid is replaced by a hydrophilic, non-acidic monomer (HEMA). Minimal acid-base reaction can be expected from the FASG fillers, even upon subsequent water sorption. However, the glass-ionomer phase that is responsible for fluoride release in this material is readily available in pre-reacted form. In Dyract AP, polyalkenoic acid is replaced by a hydrophilic acidic monomer (tetracarboxylic acid butane). Unlike in a giomer, a glass-ionomer phase has to be generated in a compomer by water uptake before fluoride can be released from reactive glass fillers.

Pre-reacted GIC powder incorporated into ceramic-whisker-containing experimental composites has a reported cumulative fluoride release of about 20% of the original GIC (Xu *et al.*, 2000). This decrease may be partially attributed to the presence of silane coupling in the pre-reacted fillers, vs. non-silanized glass particles in the original GIC. The fillers in Reactmer Paste and Dyract AP are both silanized. Filler-matrix coupling enhances the physical properties of these materials, and allows for adequate wetting and dispersion of the fillers within the considerably more hydrophobic resin matrices. The effect of silane coupling on ion transport from reactive glass has not been thoroughly investigated. However, based on a similar study on silane-coated apatite powder, any barrier that exists may be only temporary (Dupraz *et al.*, 1996), and depends on the hydrophilicity of different types of silane (Craig and Dootz, 1996). The very thin silica gel layers that were identified on the surfaces of glass fillers in Dyract AP after water storage for 84 days corresponded well with the relatively low fluoride release reported from this material (Peng *et al.*, 2000). It is further speculated that the strontium fluoride crystals that were present in the material may have contributed to the bulk of the fluoride release. Since these crystals are non-silanized (Dr. Gordon Blackwell, personal communication), elution of fluoride ions can eventually create voids that may result in degradation of the mechanical properties of this material after water sorption. This

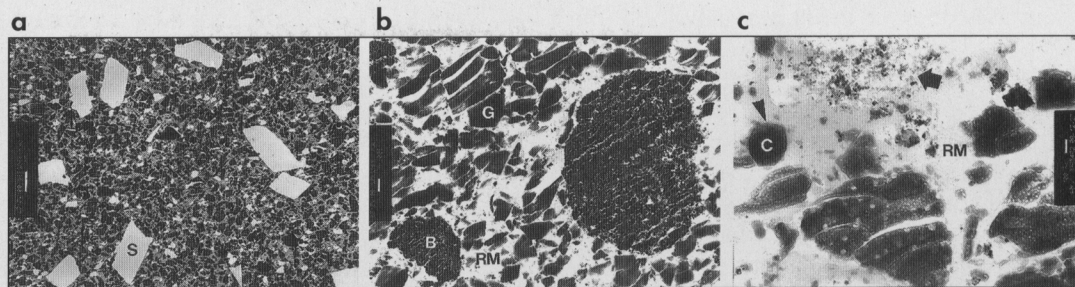


Figure 4. TEM micrographs of Dyract AP (compomer group). (a) A low-magnification view of the polymerized material after 24 hrs at 100% RH. Large, electron-lucent (white) silhouettes of monoclinic crystallites (S), up to 3 μm in length, probably represent spaces occupied by the crystalline strontium fluoride additives. Two types of electron-dense fillers could be identified within the resin matrix: solitary, angular glass fillers that were up to 1 μm in size; and conglomerated bodies with relatively smooth edges (arrowheads) that were up to 1.5 μm in size. Bar = 3 μm . (b) A higher magnification of (a), showing the absence of siliceous hydrogel layers around the solitary glass fillers (G). Conglomerated bodies (B) probably represent submicron glass fragments produced from ball-milling that were tacked together into aggregates during the silanization procedure. RM, resin matrix. Bar = 300 nm. (c) A higher-magnification view of Dyract AP after storage in de-ionized water for 84 days. The formation of the glass-ionomer phase was present but limited, as evident by the very thin siliceous hydrogel layers (arrowhead) that were formed around the glass cores (C). "Seed-like" inclusions similar to those observed in ChemFlex (Fig. 1b) could also be identified within the glass cores. Disaggregation of some of the conglomerated bodies (arrow) was probably caused by the hydrolysis of silane around the submicron glass fragments after water sorption into the resin matrix (RM). Bar = 100 nm.

may not be the case in a giomer, in which the fluoride seems to be more evenly distributed within the F-PRG fillers.

Based on the ultrastructural manifestation of the glass-ionomer phase, Dyract AP is very similar to a resin composite. Unlike a compomer, Reactmer Paste that contains a pre-reacted glass-ionomer phase behaves more like a RM-GIC, and may well deserve a position between the 2 materials within the spectrum of hybrid tooth-colored restoratives.

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