DENTAL MATERIALS 30 (2014) 632–643

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.intl.elsevierhealth.com/journals/dema

Mechanisms of setting reactions and interfacial behavior of a nano-filled resin-modified glass ionomer

Afshin Falsafi*, Sumita B. Mitra[1], Joe D. Oxman, Tiffany T. Ton, Hoa T. Bui

3M ESPE Dental Products Division, 3M Company, 260-2B-12 3M Center, St. Paul, MN 55144, United States

ARTICLE INFO

Article history:
Received 30 June 2013
Received in revised form
20 November 2013
Accepted 25 February 2014

Keywords:
Glass ionomer
Resin-modified glass ionomer
Nanoionomer
F release
Ketac Nano
Paste-paste system
Setting reaction
FTIR
XPS
Adhesion
SEM

ABSTRACT

Objectives. In order to improve the short-comings of glass ionomers such as polishability and esthetics while preserving their excellent clinical bonding effectiveness, nanofiller technology has been introduced in a paste-paste resin-modified glass ionomer (nano-filled RMGI, Ketac Nano, KN, 3 M ESPE). One objective of this study was to investigate if the introduction of nanotechnology had any significant effect on the setting reaction of the nanoionomer compared to a control RMGI, Vitremer (VM, 3 M ESPE). Another objective was to determine the mechanism of bonding of KN in combination with its primer (KNP) to the tooth.

Methods. Fourier-Transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) analyses were performed on KN and VM during the setting of the GIs. FTIR and XPS were also used to study the reaction of the primer of KN (KNP) with hydroxyapatite (HAP). Shear adhesion to dentin and enamel was measured with KN and compared with several RMGIs and one conventional glass ionomers (CGI). The interfaces were examined with scanning electron microscopy (SEM).

Results. FTIR data show that KN undergoes both acid-base and methacrylate setting reactions of classical RMGIs. XPS and FTIR studies of the interaction KNP with HAP shows the formation of calcium-polycarboxylate bond. Shear adhesion and failure mode of KN to enamel and dentin were similar to the other RMGIs and CGI. SEM images of KN with tooth structure showed a tight interface with a thin but distinct layer of 2–3 microns attributed to the primer. This was also observed for VM but not for the other three materials.

Conclusions. KN showed two setting reactions expected in true RMGIs. The adhesion with dentin and enamel was similar to other glass-ionomers. The formation of calcium-polycarboxylate was also evident. This chemical bonding is a significant factor in the excellent long-term adhesion of these materials.

* Corresponding author at: 260-2A-10 3M Center, St. Paul, MN 55144, United States. Tel.: +1 651 736 3513; fax: +1 651 736 0990.
E-mail address: afalsafi@mmm.com (A. Falsafi).
[1] Present address: Mitra Chemical Consulting LLC, 1952 Nature View Lane, West St. Paul, MN 55118, United States.

http://dx.doi.org/10.1016/j.dental.2014.02.025
0109-5641/

1. Introduction

In spite of the superior adhesive properties and sustained fluoride-releasing characteristics of classical glass ionomers their clinical applications have been limited since their esthetic qualities are not as excellent as those of modern-day composites. In recent years optical properties of many materials have been enhanced by incorporating nanoparticles of 5–100 nm size. The use of nanotechnology in restorative dental composites has greatly improved their esthetics without compromising their mechanical properties and function [1–3]. Hence, with the aim of improving the esthetic properties of glass ionomers, nanotechnology has been introduced to develop a novel nano-filled resin-modified glass-ionomers (RMGI) restorative material and commercialized as Ketac™ Nano (3M™ ESPE™, St. Paul, MN, also known as Ketac™ N100 in some regions). In this class of RMGI restorative material, called a "nanoionomer", the combination of acid-reactive fluoroaluminosilicate glass (FAS glass) and non-reactive nanofillers provides unique characteristics not previously found in traditional conventional or resin-modified GIs [4]. The nanoionomer system utilizes a novel hybrid filler system consisting of synthetic nanomeric and nanocluster surface modified particles of zirconia and silica along with a modified FAS glass filler. For ease-of-use it is formulated as a two-paste system that is delivered either through Clicker™ mixing device and hand-spatulated, or through a direct intraorally deliverable automixing capsule (Quick Mix). An aqueous polycarboxylic acid containing light-cured primer is employed to treat the tooth surface prior to placement and curing of this restorative. While conceptually simple, a viable and successful nanoionomer technical solution was not achieved by simply combining conventional FAS glass particles and nanofillers in a two paste system. The nanoparticles used in composites are inherently incompatible in aqueous solutions and give rise to visually opaque formulations. To overcome this critical limitation and achieve the unique combination of clinically desirable properties, the recently introduced nanoionomer system [Ketac™ Nano (KN)] utilizes a novel hybrid filler system consisting of synthetic nanomeric and nanocluster particles of tailored refractive index and surface functionality along with unique FAS glass filler. A recent publication has shown that the partial replacement of the traditional FAS glass with methacrylate surface-modified nanofillers significantly improved the polish and abrasion resistance of the nanoionomer KN [5,6] as well as the fluoride release and recharge behavior comparable to those exhibited by typical conventional and RMGIs [7]. However, there is little information in the scientific literature on how the setting mechanism and interfacial behavior of the paste-paste nanoionomer compares with those of classical powder-liquid types of conventional and resin-modified glass-ionomers.

The reactive fluoroaluminosilicate glass in the nanoionomer was comminuted to very fine microparticles and then selectively surface-treated to provide a reactive surface area that is at least three times that of the traditional fluoroaluminosilicate glass in the RMGI, Vitremer™ (VM). Furthermore, unlike nanocomposites wherein the nanoparticles are treated with primarily hydrophobic silanes that bind to the resin matrix, in KN the surfaces of the nanofillers were treated with a mixture of silanes to maintain an optimum hydrophilic/hydrophobic balance that would facilitate water-mediated ion transport [8]. However, it is not immediately evident if these bonded nanoparticles in a two-paste system would influence the setting reactions of the nanoionomer compared to other GIs. With that in mind one of the objectives of this investigation was to see if this technological approach of creating the nanoionomer KN would allow substantial water-mediated acid-base reaction to progress during the setting of nanoionomer comparable to the classical RMGI VM. The evaluation of acid-base reaction kinetics by FTIR has been shown to be an effective tool for the study of conventional glass-ionomers CGI [9,10]. The FTIR technique has also been effectively used to characterize the setting reactions of classical powder-liquid RMGIs, e.g. Vitremer™ (VM) and Fuji® II LC (FIILC) [11–13] whereby it has been demonstrated that significant acid-base glass ionomers setting as well as polymerization of methacrylate groups occur in these materials. Hence, the first objective of the present investigation was to perform an FTIR study in which the setting reactions of the paste-paste nanoionomer, KN, were followed progressively with time after photocuring and compare it to that of VM.

The ionic reaction that takes place in the glass-ionomers is also believed to be the reason why they behave as adhesive bioactive materials [14]. In these water-based materials, migration and exchange of ions such as fluoride, calcium, strontium, etc. take place from and into the material. This ion migration is said to occur across the interface of the bulk material and the tooth structure [15]. Several studies have shown that both CGI and RMGI materials have clinical bonding effectiveness comparable to that of the best performing three-step etch-and-rinse adhesives [16–18]. Some studies have also shown that several RMGIs exhibit superior and more predictable adhesion to tooth structure in comparison to other adhesive strategies (e.g. etch-and-rinse adhesives with three or two steps; self-etch adhesives with two or one steps) although their *in vitro* measured bond strengths may be lower than pure resin-based adhesives [19–22]. The chemical bonding of some RMGI liners to HAP crystals has been demonstrated by X-ray photoelectron spectroscopy (XPS) [23–26] while the ability of these materials to bond micromechanically and form hybrid layers was demonstrated by FE-SEM [27] and confocal microscopy studies [28]. However, such mechanistic studies have not been reported on RMGI filling materials. Nor has the effect of incorporating nanoparticles and nanoclusters in the nanoionomer on its interfacial adhesion behavior been studied in detail. Commercial RMGI filling materials require the use of a pretreatment of the tooth surface prior to the application of the restorative. In some instances the cavity surface is conditioned with a polyacrylic acid solution followed by washing and drying. In other RMGIs the pretreatment (identified by some manufacturers as a primer or a self-conditioner) is provided by the application of a polycarboxylic acid containing solution which remains on the cavity surface and is set through light activation [15]. For KN, an aqueous primer called the Ketac Nano Primer (KNP) is applied to the cavity surface for 20 s and then set in place by light. This material contains a methacrylated polycarboxylic acid (MAP). The