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Effect of crosslinking density of polymers and chemical structure of amine-containing monomers on the neutralization capacity of dentin adhesives

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ABSTRACT

Objectives. Neutralization of the acidic micro-environment at the tooth/material interface is expected to provide enhanced durability for dental composite restorations. The objective of this study is to explore the effect of amine-containing monomer formulations and the crosslinking density of the resultant polymers on the neutralization capacity.

Materials and methods. The co-monomer system was varied systematically to obtain different proportions of Bisphenol A glycerolate dimethacrylate (BisGMA) and 2-hydroxyethyl methacrylate (HEMA), while maintaining a constant amount of amine-containing methacrylate monomer. A series of amine-containing monomers covering a range of pKa values were examined. Crosslinking density of formed copolymers was controlled by adjusting the weight content of the dimethacrylate monomer BisGMA. Lactic acid (LA) was used as a probe to analyze the effectiveness of the basic polymers to neutralize acid. The neutralization capacity of each amine-containing crosslinked copolymer was characterized by measuring pH as a function of time when the specimens were soaked in 1-mM LA solution, and the results were compared to the control formulations composed solely of BisGMA and HEMA. Polymer surfaces were examined using the methyl orange (MO) assay to quantify the amount of accessible amine groups.

Results. For each amine-containing crosslinked co-polymer, the neutralization capacity is enhanced by decreasing crosslinking density (e.g., by reducing BisGMA concentration in the formulation). In addition, more amine groups were accessible when crosslinking density was decreased. For different amine-containing polymers with the same BisGMA concentration, the neutralization capacity is higher when the amino monomers with higher pKa values were used in the formulations.

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Significance. This is the first time that the neutralization capacity based on crosslinked dental polymers has been studied. The information is important for future development of durable dentin adhesives.

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1. Introduction

Polymer-based composites have become the most common restorative material and are currently used more than twice as often as dental amalgam [1]. These resin composites fulfill many of the requirements for clinical restorative applications, including excellent esthetics. The durability of composite restorations does not, however, match that of dental amalgam [2–6]. The average clinical lifetime of composite resin restorations is just 5.7 years due to recurrent decay or fracture [7]. Recurrent decay has been linked to the failure of the bond between the tooth and composite and increased levels of the cariogenic bacteria *Streptococcus mutans* at the perimeter of these materials [8,9].

The composite is too viscous to bond directly to the tooth; a low-viscosity adhesive is used to connect the tooth to the composite. The adhesive bonds effectively to the acid-etched enamel, but bonding to dentin has been fraught with problems. In vitro and in vivo studies suggest that several factors inhibit the formation of a durable adhesive/dentin bond. One of the important factors is water sorption and hydrolysis of the adhesive polymers [10,11]. Water and saliva are always present in the mouth of healthy patients, and they are expected to penetrate into the free volume spaces between polymer chains. With water penetration, hydrolysis of ester groups in the polymer chains may occur, which shortens the clinical lifetime of polymer-based dental restoratives.

Another important factor is the polymer network structure, which is induced by photopolymerization of methacrylate monomers. Due to the rapid polymerization rate, after polymerization, highly crosslinked networks are formed, which are usually very heterogeneous due to the formation of highly crosslinked regions and loosely crosslinked regions [12–16]. The more heterogeneous a material, the more likely it is to have a significantly weaker structure in the regions of lower crosslinking, increasing the risk of premature failure.

The monomers used in dental restorative materials are particularly critical because polymerization of monomers produces the crosslinked matrix in the resultant polymers. Thus, monomer selection exerts considerable influence on the properties, durability and behavior of dentin adhesives in the wet, oral environment. Much attention and effort has been devoted to developing new adhesive monomers in order to enhance the lifetime of dental composite restorations [11,17–21].

Introducing neutralization capacity by using amine-containing monomers offers a promising approach to enhance hydrolysis resistance. The presence of water promotes the chemical hydrolysis of ester bonds in methacrylate materials

[22–24]. This reaction might be relatively slow at the neutral pH typical of saliva, but excursions in pH, caused by food or cariogenic bacteria that produce lactic acid, may lead to transient acid catalysis [25]. Degradation of methacrylate ester groups produces carboxylic acids, which contain the same functional group that is the culprit in lactic acid-induced decay. Degradation products from ester hydrolysis are more hydrophilic than the parent ester, which further enhances the local ingress of water and hydrolysis. With time, local domains of the methacrylate network may become sufficiently degraded and/or hydrophilic to permit access by esterases that greatly accelerate ester bond hydrolysis.

The chemical and enzymatic degradation of the methacrylate-based matrix could create a low pH environment at the composite/tooth interface because of the low pKa values of methacrylic acid and lactic acid, which are 4.66 and 3.86, respectively [20,26–31]. Furthermore, acidification of the oral microenvironment promotes demineralization of tooth structure at the margin of composite restorations. The increased surface roughness of the demineralized tooth surface creates additional opportunity for adhesion by biofilm, mainly salivary proteins and pioneer pathogenic bacteria, thereby accelerating the degradation process. We proposed that the pathogenic impact of biofilm at the margin of the composite restoration could be reduced by engineering novel dentin adhesives that neutralize the acidic microenvironment and resist biofilm attachment [32]. Integrating basic moieties with an appropriate pKa into methacrylate derivatives provides the opportunity to act as an acid-neutralizing proton sponge and/or buffer to protect against acid-induced degradation.

In our previous work, the neutralization capacity of amine-containing monomers was quantified in a water/ethanol co-solvent system and the effects of solvent environment on pKa were examined [33]. However, to our knowledge, there are no reports of neutralization capacity having been determined for amine-containing crosslinked polymers. As such, it is necessary to determine the correlation between the inter-related properties of neutralization capacity and crosslinking density/chemical structure of amine-containing monomers within crosslinked polymer systems.

The twofold objectives of this work are: (1) to study the crosslinking effect on the neutralization capacity of the polymer, and (2) to investigate the influence of the chemical structure of amine-containing monomers on the neutralization capacity. To our knowledge, this investigation marks the first study on the neutralization capacity of crosslinked dentin adhesives. The results provide important information to enable future development of durable dental restorative materials.

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