DENTAL MATERIALS 31 (2015) 789–798

Available online at www.sciencedirect.com

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Formation of functionalized nanoclusters by solvent evaporation and their effect on the physicochemical properties of dental composite resins

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ARTICLE INFO

Article history:
Received 14 October 2014
Received in revised form
20 January 2015
Accepted 9 April 2015

Keywords:
Nanoclusters
Solvent evaporation method
Functionalized silica nanoparticles
Composites
Restorative materials
Dental resins
Silane coupling agents

ABSTRACT

Objective. The aim of this work was to study the effect of silica nanoclusters (SiNC), obtained by a solvent evaporation method and functionalized by 3-methacryloxypropyltrimethoxysilane (MPS) and MPS + octyltrimethoxysilane (OTMS) (50/50 wt/wt), on the rheological, mechanical and sorption properties of urethane dimethylacrylate (UDMA)/triethylenglycol dimethacrylate (TEGDMA) (80/20 wt/wt) resins blend.

Methods. Silica nanoparticles (SiNP) were silanized with MPS or MPS + OTMS (50/50 wt/wt) and incorporated in an UDMA-isopropanol mix to produce functionalized silica nanoclusters after evaporating the isopropanol. The effect of functionalized SiNC on resins rheological properties was determined by large and small deformation tests. Mechanical, thermal, sorption and solubility properties were evaluated for composite materials.

Results. The UDMA/TEGDMA (80/20 wt/wt) resins blend with added SiNC (ca. 350 nm) and functionalized with MPS showed a Newtonian flow behavior associated to their spheroidal shape, whereas the resins blend with nanoclusters silanized with MPS + OTMS (50/50 wt/wt) (ca. 400 nm) showed a shear-thinning behavior due to nanoclusters irregular shape. Composite materials prepared with bare silica nanoclusters showed lower compressive strength than functionalized silica nanoclusters. MPS functionalized nanoclusters showed better mechanical properties but higher water sorption than functionalized nanoclusters with both silane coupling agents, MPS and OTMS.

Significance. The solvent evaporation method applied to functionalized nanoparticles showed to be an alternative way to the sinterization method for producing nanoclusters, which improved some dental composite mechanical properties and reduced water sorption. The shape of functionalized silica nanoclusters showed to have influence on the rheological properties of SiNC resin suspensions and the mechanical and sorption properties of light cured composites.

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http://dx.doi.org/10.1016/j.dental.2015.04.001
0109-5641/

1. Introduction

Dental composites have displaced dental alloys in restorative dentistry due to their superior esthetic qualities, tooth like appearance, workability and light curing setting. However, composites show some disadvantages such as volumetric contraction, low adhesion to natural dental pieces and less wear resistance [1–3]. A number of reinforcing materials and changes in resins chemical nature have been used to improve resins composites performance. Recently, nanoparticles have been used as reinforcing material due to better mechanical properties of composite materials obtained with them in comparison to bare polymer matrixes or polymers reinforced with microfillers [4,5], and the generation of translucent dental materials, which are not feasible with reinforcing particles sizing more than 200 nm. However, nanoparticles can only be used at a relatively low concentration (<10 wt%) in order to produce resins composites with manageable viscosities and in a non-aggregated state [6–8]. The final polymerized composite material, at this low nanoparticles concentration, shows low mechanical properties that are unacceptable for dental restorative materials. Therefore, it is necessary to increase particles concentration in the system at values above 60 wt% to achieve adequate mechanical properties of composite materials [9]. This increase in particles concentration can be obtained by adding microparticles (with diameters above 1 μm) into the resin system. In such nano-microparticle system (so called microhybrid), the nanoparticles can fit in the interparticle gaps created between adjacent microparticles, which allows high particle packing at relatively low viscosity [5,9]. However, compact microparticles show deficiencies in the reinforcement of soft matrixes [4,10]. As an alternative, nanoparticle aggregates, or nanoclusters (ca. 1 μm), have been introduced into the dental restorative market during the last decade to replace compact microparticles [11–13]. The porous structure of the nanocluster induces a higher connectivity with the polymeric matrix, which improves the dissipation of mechanical stresses that are applied to the dental composite. Trade marks such as Filtek Supreme Body and Filtek Supreme Translucent use a mix of nanoclusters and nanoparticles to produce the mechanical and esthetical properties expected by patients [13,14]. These nanoclusters are usually produced by a partial sinterization of silica nanoparticles at high temperatures (>500 °C) [15]. The sintered silica nanoclusters can be subsequently functionalized with silane groups anchored to silica particles to improve surface–polymer matrix interaction, or to provide a more hydrophobic material with higher resistant to hydrolysis on a wet mouth environment. Silane coupling agents such as 3-methacryloxypropyltrimethoxysilane (MPS) and octyltrimethoxysilane (OTMS) (Fig. 1) have been used to obtain covalent bonds between the polymeric matrix and the functionalized particles, and to increase nanoparticle surface hydrophobicity, respectively [16–20]. Moreover, the increase in particle surface hydrophobicity could induce changes in the rheology of the resin composite before polymerization. In this way, the viscoelastic properties of the resin composite can be adjusted to improve its handling during application in the dental piece to reproduce its anatomy. The OTMS has been used for this purpose, instead of MPS, because it induces a high increase in the viscosity and hydrophobicity of the system due to its long carbon chain. However, some investigations have shown that OTMS can decrease the mechanical properties and increase the water sorption of dental polymers when used in large amounts [18,19].

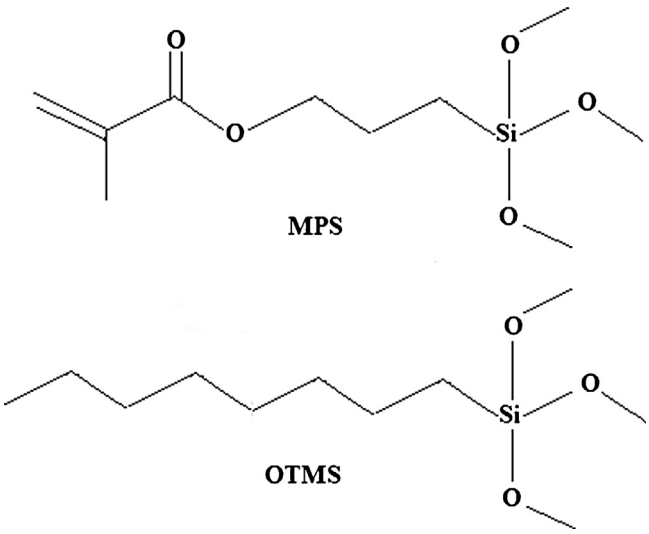

Fig. 1 – Chemical structure of silane coupling agents used in this study, methacryloxypropyltrimethoxysilane (MPS) and octyltrimethoxysilane (OTMS).

The objective of this study was to evaluate the effect of silica nanoclusters, obtained by a solvent evaporation technique and functionalized with MPS and a mixture of MPS + OTMS, on the rheological, mechanical and sorption properties of composite materials.

2. Materials and methods

2.1. Materials

Silica nanoparticle dispersion in isopropanol (30 wt%, diameter between 10 and 20 nm, Lot No. P070302), was supplied by Nissan Chemical Corporation (Houston, USA), 3-methacryloxypropyltrimethoxysilane (MPS) (97 wt%, Lot No. 10146396), ethyl-4-dimethylaminobenzoate (4EDMAB) (99 wt%, Lot No. 10059615) were supplied by Alfa Aesar (Ward Hill, Massachusetts, USA), UDMA monomer (90 wt%, Lot No. 715-36) was provided by Esstech Inc. (Essintong, Pensilvania, USA) and TEGDMA monomer (96 wt%, Lot No. 36296HK), photoinitiator camphorquinone (97 wt%, Lot No. 09003AQ) and octyltrimethoxysilane (OTMS) (96 wt%, Lot No. 000181503) were supplied by Sigma Aldrich GmbH (Deisenhofen, Germany). All materials were used as received without further purification. Monomers structures are shown in Fig. 2.

2.2. Silanization of silica nanoparticles

The isopropanol silica nanoparticle dispersion was heated at 65 °C and stirred during 3 h at atmospheric pressure in reflux. Afterwards, MPS or a MPS + OTMS blend (50/50 wt/wt) was