Materials Science and Engineering C 42 (2014) 161–167

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Synthesis and characterization of hybrid silica/PMMA nanoparticles and their use as filler in dental composites

G. Canché-Escamilla [a,*], S. Duarte-Aranda [a], M. Toledano [b]

[a] Unidad de Materiales, Centro de Investigación Científica de Yucatán A.C. Calle 43 No. 130 Col. Chuburná de Hidalgo, Mérida, Yucatán 97200, Mexico
[b] Facultad de Odontología, Universidad de Granada, Campus Universitario de Cartuja s/n, Granada 18071, Spain

ARTICLE INFO

Article history:
Received 27 November 2013
Received in revised form 23 April 2014
Accepted 13 May 2014
Available online 19 May 2014

Keywords:
Hybrid composite
Nanoparticles
Mechanical properties
Semi-interpenetrating network
Dental composites

ABSTRACT

The effect of hybrid silica/poly(methylmethacrylate) (PMMA) nanoparticles on the properties of composites for dental restoration was evaluated. Hybrid nanoparticles with silica as core and PMMA as shell were obtained by a seeded emulsion polymerization process. Fourier transform infrared spectrum of the hybrid nanoparticles shows an intense peak at 1730 cm^{-1}, corresponding to carbonyl groups ($C{=}O$) of the ester. The thermal stability of the hybrid particles decreases with increasing amounts of PMMA and the residual mass at 700 °C corresponds to the silica content in the hybrid particles. Composites were obtained by dispersing nanoparticles (silica or hybrid), as fillers, in a resin—bis glycidyl dimethacrylate (Bis-GMA)/triethylene glycol dimethacrylate (TEGDMA) (40%/60% (w/w)). The paste was then placed in a mold and polymerized under light irradiation. During the preparation of the composites, with the hybrid nanoparticles, the monomers swell the PMMA shell and after photo-curing, a semi-interpenetrating network (semi-IPN) is obtained around the silica core. The properties of the composites, obtained using the hybrid nanoparticles, depend on the filler content and the amount of PMMA in the semi-IPN matrix. For composites with similar inorganic filler contents, the composites with low amounts of PMMA shell had higher modulus than those in which silica was used as the filler.

1. Introduction

In the last few years, studies of organic–inorganic (hybrid) composites have increased because of their potential applications in different material fields such as plastic and rubber reinforcement, sensors, electronics, energy production, and biomaterials [1–11]. The use of these composites in dental restoration has increased, and they are gaining increasing popularity over metallic dental amalgams because of their advantages such as aesthetic quality, mechanical properties, and easy handling [10]. Composites used in dental restoration consist of a continuous polymeric matrix (based on crosslinked dimethacrylates), reinforced with inorganic fillers that can vary in type, shape, and size [9–11]. The use of nanoparticles in these composites can improve the resin properties such as wear resistance, gloss retention, and modulus and flexural strength [12,13]. However, these properties are greatly influenced by the nanofiller dispersion in the polymeric matrix [14–16]. Because of the very high surface area and surface charge of inorganic nanoparticles, agglomerates form, and thus their dispersion in the polymeric matrix is difficult at high filler quantities [17,18]. These agglomerates can act as stress concentration points and cause failure of the material [19,20]. To achieve a good dispersion of inorganic nanoparticles in the polymeric matrix and improve the interfacial adhesion between the particle and the polymer, synthesis routes whereby inorganic particles are surrounded by the polymer (hybrid particles) have been developed. Emulsion or mini-emulsion seed polymerization has proven effective methods to obtain these particles, and the properties of the nanocomposites can be modified by changing either the constituting materials or the organic–inorganic ratio of the hybrid nanoparticles [21–24]. Although there are numerous studies on obtaining hybrid nanoparticles with silica, one of the most widely used fillers in the preparation of dental composites, as the core [25–29], the use of these hybrid nanoparticles to fabricate dental materials is scarce [11].

In this work, hybrid nanoparticles, consisting of silica nanoparticles coated with an acrylic shell, were synthesized by emulsion polymerization. The dispersion of the hybrid nanoparticles in the matrix and the effect of the silica/acrylic shell content ratio on the mechanical properties of dental composite materials were evaluated.

2. Experimental

2.1. Materials

Aerosil OX-50 fumed silica nanoparticles with an average diameter of 40 nm were obtained from the Evonik Industries AG. The nanoparticles were used as received. The following reactants were obtained from Sigma-Aldrich Química SL (Toluca, México) and used as received—methyl methacrylate (MMA) and hexadecyltrimethylammonium

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[*] Corresponding author. Tel.: +52 999 9428330.
E-mail address: gcanche@cicy.mx (G. Canché-Escamilla).

http://dx.doi.org/10.1016/j.msec.2014.05.016
0928-4931/

bromide (CTAB) were used as monomer and surfactant, respectively, to prepare the hybrid silica/PMMA nanoparticles by seeded emulsion polymerization; potassium persulfate (PPS) was used as the thermal initiator. The following reactants were obtained from Sigma-Aldrich Química SL (Madrid, Spain) and used as received—bis[4-(2-hydroxy methacryloxypropoxy)phenyl]propane (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) were used as resin; and camphorquinone (CQ, 97%) and ethyl 4-dimethylaminobenzoate (4EDMAB, 99 + %) were used as photoinitiator system. Silica or hybrid nanoparticles (with different silica/PMMA content ratios) were obtained and used as fillers to prepare nanocomposites with different mass fractions of inorganic fillers.

2.2. Synthesis and characterization of hybrid nanoparticles

The hybrid silica/acrylic nanoparticles were obtained using seeded emulsion polymerization. The silica nanoparticles were added to an aqueous solution of CTAB at 2%, and stirred for 30 min. The nanoparticle suspension was sonicated for 2 h at 50 °C. The dispersion was added to a jacketed reactor equipped with a stirred, reflux condenser, and N_2 inlet. The MMA was added and the temperature was raised to 70 °C. The initiator, PPS, was then added to the system, and the reaction was maintained for 3 h for the polymerization of the PMMA. The hybrid nanoparticles were recovered by precipitation and washing with methanol to remove the surfactant. The particles were then dried at 80 °C overnight in an oven. The monomer conversion was calculated by the weight increment of the silica nanoparticles. Two silica/MMA ratios (50/50 and 70/30) were chosen to grow a 3–6-nm-thick PMMA shell with varying silica/PMMA ratios.

The morphology of the hybrid nanoparticles was analyzed by electron microscopy, using a JEOL 6360 LV scanning electron microscope (SEM) and a JEOL 2100F High Resolution Transmission Electronic Microscope (HRTEM). The samples were prepared by diluting the latex particles in water and a drop of the diluted latex solution was deposited on a graphite tape or on a grid. For SEM analysis the samples were coated with a thin layer of gold, to improve the contrast, using an ion sputtering Delton vacuum instrument (LLC II). Uncoated particles were used to determine the particle size of silica and hybrid nanoparticles. Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA) were used to evaluate PMMA formation. FTIR analysis was performed on a Nicolet Protégé 460 Magna IR spectrometer using the KBr pellet technique. Spectra were recorded in the 4000–400 cm^{-1} region with a resolution of 4 cm^{-1} and an average of 100 scans. TGA analysis was performed in the range of 30–700 °C using a TGA7 PerkinElmer thermal analyzer. 5 mg of sample and a heating rate of 10 °C min^{-1} in nitrogen atmosphere were used. The molecular weight of the PMMA, obtained by the extraction of hybrid particles with chloroform, was determined by GPC using an Agilent HPSEC 1100 chromatographer with refractive index detector. Measurements were carried out with THF as solvent and 1 ml/min flow rate using a ZORBAX PSM 1000S HSPEC column. The molecular weight was determined from the retention time using a calibration curve derived from monodisperse standard polystyrene (PS) obtained from Polymer Laboratories.

2.3. Nanocomposite preparation

The resin used was a mixture of Bis-GMA/TEGDMA (40%/60% (w/w)), which contained the photoinitiator system (CQ (0.2 wt.%) and 4EDMAB (0.8 wt.%)). The silica or hybrid nanoparticles were mixed manually with the resin until the powder was completely wetted. The resulting paste was smeared over a glass surface with a spatula to produce a semi-transparent film to ensure optimal particle dispersion. Bar specimens were obtained by filling a bronze mold with the non-polymerized material, taking care to minimize trapped air. The upper and lower surfaces of the mold were overlaid with glass slides covered with Mylar sheets to avoid adhesion with the non-polymerized material. The composite assembly was held together with spring clips, and both sides were irradiated (during 90 s with light energy density of 750 mW/cm^2), using a dental photo-curing unit (Bluephase C8, Ivoclar Vivadent). Then, the mold was dismantled and the resulting bar specimen was carefully removed from the bronze mold. Table 1 shows the type of particle used and the filler content.

2.4. Mechanical properties

Mechanical properties were measured in accordance with the ISO 4049-2000 "Dentistry-Polymer-based restorative materials" standard. Prior to flexural testing, bar specimens of 2 mm × 2 mm × 25 mm, as described previously, were stored in distilled water at 37 ± 1 °C in the dark for 5 days prior to flexural testing. The 3-point bending test was then performed on the wet specimens using a universal testing machine (model 5942, Instron) at a cross-head speed of 1 mm min^{-1}. One way ANOVA, of least six measurements, was performed to detect significant difference in the flexural mechanical parameters. A p-value less than 0.005 was considered significant.

For the dynamic mechanical analysis (DMA) testing, bar specimens of 2 mm × 2 mm × 40 mm were prepared. The DMA tests were performed on a DMA7 PerkinElmer dynamic mechanical analyzer using a dual cantilever clamp. A frequency of 2 Hz was applied at an amplitude of 10 μm. A temperature range of 0–180 °C, which covers the mouth temperature and the materials' glass transition temperatures (T_g), was selected. Fracture surface of the specimens, obtained after the flexural test, was observed on a scanning electron microscope (JEOL 6360 LV). The samples were gold sputter coated before SEM observations.

3. Results and discussion

3.1. Hybrid silica/PMMA nanoparticles

Table 2 shows the composition of the hybrid particles obtained in this work. The MMA conversion to polymer was 74 and 65% at corresponding silica/MMA ratios of 50/50 and 70/30. The monomer conversion and morphology of the hybrid nanoparticles depend on the surface chemistry and the size of the inorganic particles, the type and amount of surfactant, and the hydrophilicity of the monomers. In this case, the surfactant adsorbs on the silica surface through ionic interactions between the positively charged surfactant and negatively surface charged silica, forming a hydrophobic interphase that improves the dispersion of the nanoparticles in water [30,31]. The MMA monomer can then diffuse into the hydrophobic layer to form a shell on the nanoparticle following MMA polymerization. The morphology of the silica and hybrid nanoparticles is shown in Fig. 1. The spherical form of the silica nanoparticle was maintained in hybrid nanoparticle. It can be seen in the distribution of size particle results (Fig. 1-d), an increase in average particle size and a shift of the size distribution to larger sizes for hybrid particles in comparison with the original silica nanoparticle. This behavior can be attributed at the formation of the shell of PMMA on silica nanoparticles. The HRTEM micrographs (Fig. 1e and f) confirm

Table 1
Formulation of dental composite materials.

Sample	Type of particle used as filler	Filler content (wt.%)	Relation silica/PMMA in nanoparticle
NCD19	Silica	30	100/0
NCD18	Silica	40	100/0
NCD8	Silica	50	100/0
NCD7	Hybrid A5	40	57/43
NCD10	Hybrid A5	50	57/43
NCD28	Hybrid A10	40	78/22
NCD15	Hybrid A10	51.3	78/22
NCD27	Hybrid A10	60	78/22