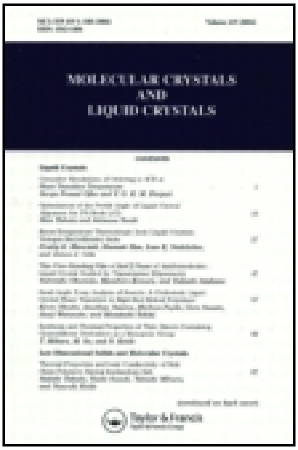

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Compression and Aging Properties of Experimental Dental Composites Containing Mesoporous Silica as Fillers

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Porous fillers can be used to obtain micromechanical interlocking between the filler particles and polymer matrix. Micromechanical interlocking in dental composites can overcome the traditional problem of hydrolysis associated with silane coupling. Such an interlocking could also enhance the overall performance of dental composites. In the current study, mesoporous silica was used as fillers to obtain experimental composites. Light curable dental resin (BisGMA/TEGDMA) was used as polymer matrix. The mechanical (compressive) and aging properties of these experimental composites were investigated. The results demonstrated that mesoporous fillers improved the mechanical and aging properties of experimental dental composites.

Keywords: aging test; compression testing; dental composites; dental filler; hydrolysis; mesoporous

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INTRODUCTION

Dental resin composites are being used extensively today to restore carious lesions or structural defects in teeth. The composites are usually comprised of an inorganic filler phase (such as silica or zirconia particles) dispersed in a cross-linked polymer matrix. Despite recent advances in resin-based restorations, these composites still lack durability when compared to dental amalgams. Previous studies suggest that weak bonding and insufficient interactions between the filler particles and the polymer matrix might be responsible for the poor mechanical properties [1] and lack of wear resistance [2]. Silane treatment of the filler surface is usually employed to enhance the mechanical properties of dental composites. Silane treatment enhances interfacial bonding by providing covalent bonds between the filler and the matrix of the dental composite [2]. However, hydrolysis of silane coupling between the filler and resin in oral environment might significantly reduce the mechanical properties of dental composites over time [3].

The limitations of silane coupling agents can be overcome by improving the bonding between filler particles and the matrix of dental composite through micro-mechanical interlocking of the two phases [4,5]. In the absence of chemical bonding, there is no concern about hydrolytic de-bonding at the filler-polymer matrix interface. Micromechanical bonding can be achieved by introducing the polymer matrix into the pore channels of inorganic fillers. Silica-polymer nanocomposites with interpenetrating networks have been made before in a number of ways [6]. For dental applications, it is more practical to first prepare a mixture of monomers present within preformed porous inorganic filler and polymerize the mixture *in situ* i.e., within the tooth cavity. Mesoporous fillers also possess the potential to have less volume shrinkage compared to the inorganic–organic hybrid nanocomposites made *in situ* by sol-gel process [7,8].

Microporous silica fillers (average pore size around 1.5 nm) have been tested as potential reinforcing agents in dental composites and have been shown to improve wear resistance [9]. Luo *et al.* [9] showed that the wear resistance depended on the nature of the pore structure present in those fillers. Mesoporous materials possess pore sizes in the range of 2 to 50 nm [10] and have been investigated for a number of potential applications. In this work, we explored the use of mesoporous (or more generally nanoporous) silica as fillers to prepare experimental dental composites. For the synthesis of the experimental dental composites, a classic dental resin system, i.e., bis-phenol-A bis-(2-hydroxypropyl) methacrylate (BisGMA)/tri(ethylene glycol) dimethacrylate (TEGDMA), was selected. The mesoporous silica fillers were prepared using the nonsurfactant-templated sol-gel method, which was developed in our laboratory [11,12]. The mesoporous fillers were then heat-treated at different temperatures. The mechanical (compressive) and aging properties of these mesoporous filler based experimental dental composites were investigated. In addition, the effect of mesoporous filler heat treatment on the compressive modulus of the composites was studied.

MATERIALS AND METHODS

Materials

The chemicals ethanol, 3-methacryloxypropyltrimethoxysilane (MPS) and tetraethyl orthosilicate (TEOS) were obtained from Aldrich, St. Louis, MO. Bis-phenol-A bis-(2-hydroxypropyl)methacrylate (BisGMA), tri(ethylene glycol) dimethacrylate (TEGDMA), tertiary amine dimethylaminoethyl methacrylate (DMAEMA) and camphorquinone (CQ) were obtained from ESSTECH (Essington, PA) and was used as received. Silica particles were obtained from Lancaster Synthesis Inc., Pelham, NH and were used after heating at 100°C to remove moisture.

Preparation of Mesoporous Filler

Nanoporous silica fillers were prepared following similar literature procedures via hydrochloric acid-catalyzed sol-gel reactions [13] of tetraethyl orthosilicate (TEOS) in the presence of fructose molecules, which served as the nonsurfactant template [11,12]. In a typical procedure, TEOS (104 g), water (36 g), ethanol (69 g) and HCl solution (2 M, 0.25 ml) were refluxed at 60°C for half hour and was then cooled to room temperature. A fructose solution of desired weight percent (10–50% in water) was added to this mixture and on standing gelled within 12 h. The gelation time can be shortened to a few minutes by adding 3 ml of 0.25 M NaOH. Upon gelation at room temperature, the container was covered with parafilm containing 12–15 pinholes to allow for slow evaporation of solvents and reaction by-products. After 24 h, the silica gel system was placed in a vacuum oven at 70°C for drying until it reached a constant weight. After drying, the monolithic silica was crushed into fine powder using a mortar and pestle and the fructose template was removed by Soxhlet extraction with deionized water for 2–3 days. The whole process took about 6 days to get the final product. The silica fillers (irregular shaped particles) were divided into three parts and heat-treated at three different temperatures (i.e., 200, 500, and 800°C) for 4 h. The Brunauer-Emmett-Teller (BET) surface area and pore volume [14,15] were determined using a surface area and pore size analyzer (Micromeritics ASAP 2010, Norcross, GA) at −196°C. Prior to the measurements, the samples were degassed at 100°C under vacuum for 6–7 h. For each measurement, 0.1–0.2 gram sample was used. Nitrogen adsorption isotherms were determined before and after heat treatment of mesoporous silica.

Preparation of Experimental Composites

Light curable resin was prepared by mixing 50 weight % bisphenyl A glycidyl dimethacrylate (BisGMA) and 50 weight % triethylene glycol dimethacrylate (TEGDMA). Camphorquinone (0.5 weight %) and 2-(dimethylamino) ethyl methacrylate (DMAEMA) (0.5 weight %) were used as photoinitiator and accelerator respectively. Two different types of experimental composites were made 1) with mesoporous silica fillers without silane treatment and 2) with silane (MPS) treated silica fillers (1.5 micron) [16]. The light curable composite mixtures were then placed in an ultrasonic bath to remove entrapped air. In the case of mesoporous filler based composite mixtures, a combination of vacuum, vibration and ultrasonic treatment was applied to remove the entrapped air from the pores. The composite mixtures were then placed in cylindrical glass molds. The composite mixtures were then polymerized in a light-curing unit (Triad II, Dentsply International, York, PA) for six minutes. The composite cylinders were removed from the glass molds immediately after light curing and post-cured for 24 h at 37°C.

Evaluation of Mechanical Properties

Post cured experimental composites containing mesoporous and silica fillers were tested in compressive mode to find the compressive strength and modulus. The compression test specimens were cut according to the ASTM standard (length to diameter ratio = 2:1) using a diamond saw. Compressive tests were performed using a servo-hydraulic machine (MTS Mini-Bionix 2, Eden Prairie, MN). A cross-head speed of 1 mm/min was used. The compressive strengths were calculated using the following equation:

$$\sigma = \frac{F}{A}$$

where σ = compressive strength, F = maximum failure load and A = cross-sectional area of the specimen.

Compressive modulus of the specimens was determined from the slope of a straight line fit to the initial linear portion of the stress-strain curve. The peak slope value was used to calculate the compressive modulus.

Aging Studies

Experimental dental composites containing 35 wt% mesoporous silica fillers (heat-treated at 200°C for 4 h) were aged in water at 37°C for 14 days and 35 days. Some of these composites were not soaked in water and they were used as controls. After drying (by using tissue paper) the specimens immediately after each aging interval, compression testing was performed on the specimens using a servo-hydraulic machine. The results were then compared with in house aging studies conducted on experimental composites containing similar weight percentage silane treated SiO_2 as fillers.

RESULTS

BET Analysis

The surface area of mesoporous silica increased with an increase in weight percent of fructose template (Table 1). The surface area of mesoporous fillers (fructose template weight percent range 30–50 wt%) used in this study varied from 230 m^2/g to 370 m^2/g. The pore size of the mesoporous fillers was approximately 5–8 nm depending on the template content and thermal treatment conditions and the pore volume increased with the template content (Table 1). At 50 wt% fructose concentration, the pore volume was very high (i.e., 0.71 cm^3/g), which is typical of mesoporous materials and is much higher than most of microporous materials.

TABLE 1 BET Analysis of Mesoporous Fillers at Different Fructose Concentration

Fructose weight percentage	Surface area (m^2/g)	Pore volume (cm^3/g)
30%	232	0.47
40%	259	0.51
50%	345	0.71

TABLE 2 Comparison of Compressive Properties of Composites with Different Types of Fillers. The Number of Specimens Tested is Given in Parenthesis

Filler type	Modulus (GPa)	Compressive Strength (MPa)
Neat Resin	2.7 ± 0.1 (6)	274 ± 35 (6)
SiO_2 (40 wt%)	4.5 ± 0.3 (4)	260 ± 28 (4)
Mesoporous (40 wt%, 200°C)	5.4 ± 0.1 (3)	193 ± 9 (3)
Mesoporous (40 wt%, 500°C)	5.7 ± 0.3 (7)	144 ± 6 (7)
Mesoporous (40 wt%, 800°C)	6.0 ± 0.2 (6)	169 ± 4 (6)

Compression Testing

The maximum mesoporous filler loading that can be achieved in these composites was approximately 40 wt%. Above this filler loading, the composite mixture becomes dry due to insufficient resin to wet its surfaces. For comparison purposes, the controls were made with 40 wt% SiO_2. At the same filler loading (i.e., 40 wt%), the composites made using mesoporous fillers had higher compressive modulus compared to composites made using silane treated SiO_2 fillers (Table 2). However, the compressive strength of composites with SiO_2 filler was higher than the composites with mesoporous filler. Mesoporous composites containing the maximum filler loading (approximately 40 wt%) did not have post yield region during compression testing. This implied that mesoporous composites at maximum filler loading were brittle.

Aging Study

Mesoporous filler based composites were soaked in water at 37°C for up to 35 days. They showed no significant difference in compressive modulus between the aged sample and control. However, the compressive strength of mesoporous composites decreased with aging (Table 3). In case of composites with SiO_2 fillers, the compressive modulus decreased as the sample aged but the compressive strength remained almost the same.

Effect of Mesoporous Filler Heat Treatment

The heat treatment temperature of the mesoporous fillers shows an increase in compressive modulus of post-cured composite. The modulus of composites increased when mesoporous fillers with higher heat treatment temperatures were used (Fig. 1).

TABLE 3 The Effect of Aging (in Water at 37°C) on the Compressive Properties of Composites Prepared Using Mesoporous and SiO_2 Fillers

Filler type	Modulus (GPa)	Compressive strength (MPa)
Mesoporous (35 wt%, Control)	5.1 ± 0.3 (5)	171 ± 9 (5)
Mesoporous (35 wt%, 14 days)	5.2 ± 0.6 (7)	126 ± 7 (7)
Mesoporous (35 wt%, 35 days)	5.0 ± 0.3 (4)	113 ± 8 (4)
SiO_2 (40 wt%, Control)	4.5 ± 0.3 (4)	260 ± 28 (4)
SiO_2 (40 wt%, 35 days)	3.5 ± 0.2 (4)	243 ± 32 (4)

DISCUSSION

The results show that the mesoporous filler based composites are extremely promising for the future of dental composites. For dental applications, the variables in mesoporous filler based composites need to be optimized. One of the variables that can be optimized is the filler loading. It is well known that the mechanical properties of composites improve significantly with increase in filler loading. In our current research the filler loading that can be achieved was 40 wt%. Theoretically, filler loading of mesoporous composites can be increased by reducing the surface area of mesoporous fillers. This is because as the surface area of the filler decreases, the amount of resin needed

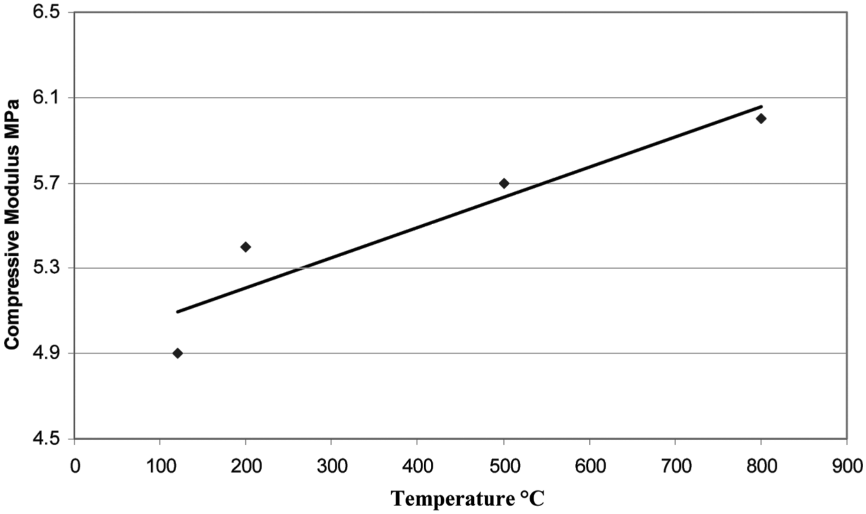

FIGURE 1 The effect of filler heat treatment on the compressive modulus of post cured composites.

to wet the surface decreases. Surface area of fillers can be decreased by using a different template or heating the mesoporous fillers to high temperatures (up to 800°C). Above 800°C, the mesoporous structure totally collapses. Another way of increasing the filler loading is to use a mixture of mesoporous and nonporous silica fillers. Preliminary results on these types of composites are promising and their mechanical properties are superior compared to the composites with mesoporous fillers alone.

The compressive modulus of mesoporous fillers did not show any significant decrease on aging for 35 days. This shows that the mesoporous fillers without a silane-coupling agent are probably more hydrolytically stable compared to silane treated silica, as the silane bonding could undergo hydrolysis under physiological conditions. The reduction in compressive strength of mesoporous composites with aging needs further investigation. The decrease in compression strength could be due to water absorption of sol-gel silica particles. The water absorption problem might be solved by surface chemical modification of mesoporous fillers (e.g., introduction of hydrophobic groups), which is a topic for further investigation.

Curing time needs to be reduced from the current 6 min, in order to use these composites for dental applications. Further study is underway to characterize other mechanical properties of mesoporous composites such as fracture toughness and wear resistance.

CONCLUSIONS

The preliminary results demonstrated that mesoporous fillers do affect the mechanical properties of composites and show promise for use in dental composites. The mesoporous filler based composites had superior compressive properties compared to silane treated silica based composites in terms of their compressive modulus. The micromechanical interlocking may improve the resistance to hydrolytic de-bonding at the filler-matrix interfaces. Further experiments are underway to increase the filler loading and improve the aging properties of mesoporous filler based composites.

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