



Evaluation of opto-mechanical properties of UV-cured and thermally-cured sol-gel hybrids monoliths as a function of organic content and curing process

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ABSTRACT

We fabricated sol-gel monoliths using a fast sol-gel (FSG) technique with either UV-curing or thermal-curing, producing highly dense, stable monoliths in a short time. This paper focuses on the preparation and the characterization of different FSG compositions as a function of the inorganic-organic molar-ratio and curing-mechanism. The fabrication of the monoliths was based on three precursors, tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMS), and methacryloxypropyl-trimethoxysilane (MAPTMS). Three series of FSG monoliths with different material compositions were synthesized. The organic content in the final monoliths varied from 17 to 52 weight percent (wt%). We established the range of precursor's molar-ratios that permit formation of stable low-organic content optical monoliths by UV-curing. The physical properties of the monoliths formed under different curing conditions were examined. The refractive-index increased with increased thermal-curing temperature and for combined thermal and UV-curing. On the other hand, the coefficient of thermal expansion (CTE) increases with the organic content for thermally-cured samples and decreases for UV-cured samples, due to full crosslinking. Additional important physical properties for sol-gel applications such as weight-loss, porosity and adhesive strength are also presented. The results obtained give guidelines for fabricating useful optical monoliths with lower CTE using a UV-curing process for applications such as optical bonding and encapsulation.

1. Introduction

Sol-gel technology can be treated as a “tool kit” for preparation of glassy and ceramic materials including organic-inorganic hybrid materials. The process includes three main steps; the formation of a sol, gelation of the sol and removal of the solvent [1,2]. The sol-gel process enable the growing of a three-dimensional glass-like network with controlled properties depending on the composition and process conditions. Sol-gels have been used in various applications such as miniature lenses [3], protective and functional coatings [4]; anti-reflection [5], anti-scratch [6], fog and contamination coatings [7]. Sol-gels are also used as ceramic powders [8], in fabrication of optical fibers [9], matrices for cosmetic products [10], insulation [11], and protective materials in space and aviation technology [12]. Several investigations have shown that the synthesis conditions; H₂O:Si molar ratio (r value), catalyst type and concentration, solvent, temperature and pressure have a large impact on the final product's properties [1,2]. Using the “classical” sol-gel process the cross-linking and coarsening of the network occur at room temperature. The process can take months and results in

30–90% shrinkage.

A specific kind of sol-gel process is the fast sol-gel (FSG) method which was introduced by Haruvy and Webber in 1991 [13]. The FSG method uses a combination of organically modified alkoxides with traditional alkoxides as precursors. The process allows fabrication of a viscous sol-gel resin within a few minutes, which can be solidified by thermal-curing in several hours or by UV-curing in a few seconds [14]. The method is based on the following principles: elimination of the common solvent, blocking of at least one constituent of the Si(OR)_x siloxane monomer, applying a low H₂O:Si ratio (r) and performing the process at an elevated temperature and pressure in a closed vial. The FSG process proceeds at low pH value and low H₂O:Si ratio, $r = 2$. It should be noted that, although full hydrolysis of the precursor requires 4 H₂O molecules ($r = 4$), since H₂O is a by-product of the process (2 molecules) and the reaction proceeds in a closed reactor vial, $r = 2$ should be sufficient. These conditions drive the reaction initially to a linear polymerization and only afterwards to cross-linking. The lack of common solvent and continuous elimination of liquid during the process avoids the high shrinkage and the tendency to develop cracks. As is

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common for classical sol-gel, properties can be tailored by using different ligands in the precursors. FSG has several applications; waveguide fabrication [15], micro-structured replicas [16], optical bonding, macro-scale devices and encapsulation [17]. Using the FSG method, optical waveguides with widths and thicknesses that range from a few micrometers up to hundreds of micrometers can be fabricated.

In 2009, Gvishi and co-workers published studies characterizing the FSG [2]. The materials they formulated exhibited very high transparency in the visible and near IR range. FSG resins with refractive indices that vary from 1.4 up to 1.5 (measured at 589 nm) were fabricated without decreasing the optical bonding properties of the materials. Pokrass et al. [18] investigated the effect of the organic material content (methyl group) on the thermo-optic coefficient of organic-inorganic hybrid glasses made by the FSG process. Their findings have established that the refractive index for a family of materials is linearly dependent on the methyl group content, C_M (wt%) and decreases as the concentration of methyl group increases. In a recent publication Pokrass and coworkers doped the FSG with Carbon-nanotubes (CNT) [19] to create silica-like material exhibiting exceptional electrical & thermal conductivity, mechanical strength, and nonlinear optical properties, which can be used as optical devices.

One of the main advantages of the FSG process is the ability to produce optical monoliths without shrinkage and cracks using a UV-curing process [2]. Although UV-curing was applied previously in sol-gel processing it was used mainly in the case of thin film coatings [20–26]. UV-curable sol-gel materials are divided into two categories: UV-curing of the metal ion (Si or Ti) directly using a short wavelength UV-light [20,27], or UV-curing via polymerizable organic species which are introduced as organically modified alkoxides precursors [20]. For the polymerizable organic function one can use groups such as epoxy [27,28], vinyl ether [21] or acrylic resin [22]. The most common precursor used is the organically modified alkoxide acrylic precursor methacryloxypropyl-trimethoxysilane (MAPTMS) [23]. MAPTMS can be used in a dual-cure mechanism (thermal or UV-curing), and in many cases, it is used also as an inorganic-organic coupling agent [24,25]. “Classical” UV-cured sol-gel materials possess high degrees of organic content (> 50%). These UV-cured hybrid sol-gel materials were studied extensively for thin film coating and the influence of precursors on curing behavior, and surface properties were reported [21,26,28]. In contrast, the FSG procedure allows fabrication of monoliths with low organic content by UV-curing [16]. However, since in FSG all the ingredients are added at once and the reactions, hydrolyzation and condensation, occur in a well monitored closed chamber [14], controlling the difference in reactivity of the precursors is crucial to achieve homogeneous monolith. Therefore, in FSG there is a need to define and explain the limitations of the method.

In the current work, we present systematic studies of the opto-mechanical properties of hybrid sol-gel monoliths prepared with dual-cure mechanism (either by thermal or UV-curing). The monoliths are based on three precursors, tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMS), and methacryloxypropyl-trimethoxysilane (MAPTMS) where the organic content in the monolith varied in the range 17–52 weight percent (wt%). To the best of our knowledge, it is the only work which studied the properties of sol-gel monoliths with low organic content prepared by UV-curing process. The results obtained regarding the physical properties of different FSG monoliths provide specific data and guide lines for formation of monoliths with the properties that are required for optical applications.

2. Experimental

2.1. Materials

The materials that were used for the preparation of the FSG are the silane precursors, Hydrochloric acid and Tetrahydrofuran (THF) as a solvent. All precursors (Fig. 1), Tetramethoxysilane (TMOS),

Methyltrimethoxysilane (MTMS) and Methacryloxypropyltrimethoxysilane (MAPTMS), were purchased from Sigma-Aldrich with 98% purity. Hydrochloric acid 0.1 M was also purchased from Sigma-Aldrich. The acid was diluted with di-ionized water to 0.005 M. HPLC grade THF was purchased from Biolab Ltd. For the UV-cured samples photo-initiator IRGACURE 184 from Ciba was used.

2.2. Compositions

We take as our reference FSG a formulation with starting composition of precursors, TMOS:MTMS:MAPTMS with molar ratio 1:4.7:0.8. This FSG was named NR, and is based on the fast sol-gel (FSG) type N (1:5.6:0.4) which was prepared by Gvishi and coworkers [29]. Three different series of FSG were derived from the NR composition. In each set a different precursor is kept in its original quantity while the ratio between the other two changes. A schematic presentation of the series can be seen in Fig. 2. The different compositions and their final organic content (wt%) are listed in Table 1. The final organic content (wt%) in a sample was calculated from the ratio between the organic residual molar weight to the total molar weight of the final molecule.

2.3. Preparation

The NR starting mixture consisted of 84.5 wt% precursors and 15.5 wt% of HCl 0.005 M. 20 g of such a mixture was poured into a glass 50 ml vessel and mixed with a magnetic stirrer. The closed vessel was placed in a glass bowl of water on a heating and stirring stage at 50–55 °C. The water was heated up to 95 °C. After 10 min at 95 °C the pressure in the vessel was released. A vacuum was applied for 30 s using an Alcatel vacuum pump model 2004A, 8 Torr pressure. After this stage, an additional 0.5 wt% (of the total initial weight) of 0.005 M HCl was added. The vessel was closed and returned to the boiling water for an additional 10 min followed by another 30 s of vacuum suction. At this point the sol-gel was highly viscous and about 50% of its initial weight due to loss of water and methanol. Once the sol-gel cooled to about 60 °C a portion of it was directly poured into a polystyrene (PS) Petri-dish for thermal-curing or into a silicone rubber mold for UV-curing. The remaining sol-gel material in the vessel was diluted with an equal weight of THF for later use. Samples for thermal-curing were left at room temperature (RT) for a week and then cured in an oven. Part of the samples was cured at 65 °C for an additional week and part was cured at 150 °C with the following heating procedure. The heating ramp up to 150 °C was 0.1 °C/min. Every 25 °C the samples were left at the set temperature for a half an hour. For UV-curing the photo-initiator, IRGACURE 184 (4 wt%) was added to the sol-gel. UV-curing was performed with a Dymax BlueWave 200 UV lamp. The light-guide was clamped 6 cm above the sample and no special filter was used. Radiation time was set to 120 s. Each sample was exposed to $\sim 9 \text{ J/cm}^2$ in total. General steps of the process are presented in Fig. 3.

2.4. Characterization parameters

The refractive index of samples was measured with an Atago Abbe refractometer, equipped with an Atago WL-3 lamp and Accel 250 LC Cooling/Heating Recirculating Chiller. All the measurements were taken at 589 nm at 25 °C on polished samples. The sample polishing process was performed by Optec Company, Yavne, Israel.

For scanning electron microscopy (SEM) analysis, sol-gel samples were coated with 10 nm of 24 k gold using a coater (model EL45575x, Electron microscopy science), in order to obtain high quality images of the surface. The samples were examined in a FEI quanta 400 SEM with ETD detector at 25 kV under a vacuum of $1.56 \times 10^{-2} \text{ Pa}$. The images were obtained by secondary electrons. The surface documented is the fractal surface of the sample.

The infrared spectra of spin coated sol-gel on NaCl discs were obtained in transmittance mode with a Thermo-Scientific Nicolet is10

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