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ASSEMBLIES OF NANOPARTICLES AS 3D SCAFFOLDS FOR NEW MATERIALS DESIGN: FROM POLYMER CROSSLINKED AEROGELS TO POLYMER MATRIX COMPOSITES

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Introduction

From a materials perspective, nanotechnology furnishes materials with useful macroscopic properties by manipulating matter in the 1-100 nm size regime. Improvements in performance in terms of strength, modulus and wetability are accomplished by, for example, introducing nanoparticles as fillers in plastics [1]. Two issues that usually interfere with optimal materials performance are agglomeration of the nanoparticles and materials compatibility. Agglomeration cancels the advantage of using nanoparticulate matter as dopant, while lack of materials compatibility introduces a discontinuity at the polymer/dopant interface from where failure may begin. Agglomeration is encountered with surfactants that keep nanoparticles dispersed, while materials compatibility is improved by chemical bonding of the filler with the polymer [2]. Overall the criterion for success is enhancement of the materials properties beyond what is obtained by simple mixing nanoparticles in the matrix.

Silica is the most common dopant in use as a filler in plastics. Silica derived through a base-catalyzed sol-gel process consists of interconnected string of nanoparticles dispersed randomly in the 3D space, leaving up to >99% empty mesoporous space between the nanoparticle network. If we consider providing those mesoporous surfaces with functional groups capable of covalent bonding with a polymer formed from monomers introduced in the mesopores, then we can achieve two extreme structures with distinct materials properties: (a) at one end, we may deposit only a thin conformal polymer layer on the nanoparticle network; while, (b) at the other end, we may grow enough polymer to fill the mesopores completely. The first kind of structure emphasizes the materials properties deriving from the porosity, that is lightweight, low thermal conductivity and dielectric constants, and high acoustic impedance. The second kind of structure refers to nanoparticle/matrix polymer composites tackling both issues of dispersion and covalent bonding between matrix and dopant all at once.

Historically, self-supporting 3D dispersions of nanoparticles with a high percent content of interstitial empty space between them have been referred to as aerogels (Figure 1A) [3]. However, despite fascinating materials properties,
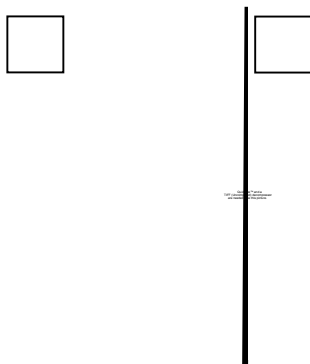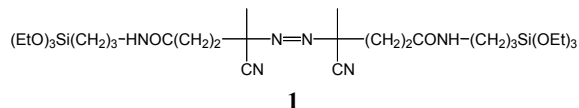

Figure 1. (A) The skeletal framework of a native amine-modified silica aerogels ($\rho_b = 0.190$ g cm^{-3}, porosity = 89 % of empty space). (B) After coating with polystyrene ($\rho_b = 0.457$ g cm^{-3}, porosity = 63 %).

the aerogel perennial problem is their fragility. That has limited their use only in specialized environments, for example as Çerenkov radiation detectors in certain nuclear reactors, as collectors of hypervelocity particles in space (NASA's Stardust program), and as thermal insulators of the electronic boxes aboard all three NASA's Mars rovers (Sojourner in 1997, as well as Spirit and Opportunity in 2004). The aerogel fragility problem is traced to the interparticle necks. By building a conformal polymer coating on the skeletal framework connecting chemically and bridging the nanoparticles reinforces the structure with minimal increase in density. The porosity and the useful material properties derived from it are preserved. The new materials are referred to as polymer crosslinked aerogels [4]. A particularly versatile chemistry that allows linking a variety of polymers onto the surface of silica nanoparticles comprising the 3D skeletal network of typical aerogels involves the amine functionality that can be added by co-gelation of tetramethoxysilane (TMOS) with 3-aminopropyltriethoxysilane (APTES). Crosslinking can be then carried out by reaction with isocyanates, epoxies even styrene by first reaction of surface dangling amines with *p*-chloromethylstyrene (Scheme 1). Figure 1B shows how a typical amine-modified aerogel looks like after crosslinking with polystyrene [5]. The secondary articles are clearly visible, while the fine definition of the primary particles has been erased by the conformal polymer layer. Those materials demonstrate exceptional specific mechanical properties (strength, modulus, energy absorption).

Scheme 1. Aerogels by attaching functional groups on silica.
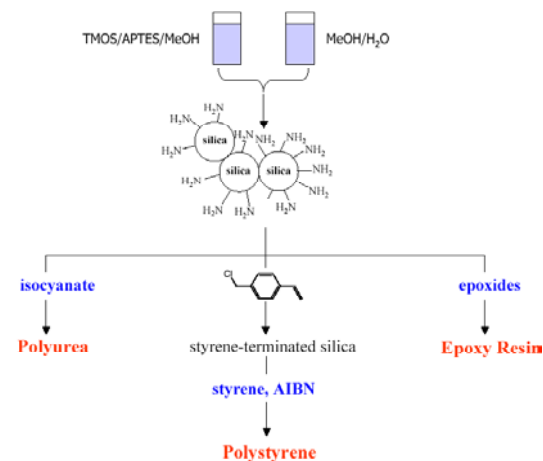
We are not aware of attempts to fill completely the pores of sol-gel derived silica with polymer and explore the properties of the resulting polymer/nanoparticle composites, whereas the totally random distribution and covalently bonding of the nanoparticles with the matrix will be ensured by the morphology and the chemical composition of the inorganic scaffold, respectively. That has been accomplished in the present work by a modification of the Scheme 1 approach, where skeletal nanoparticles are modified with free radical intiators by co-gelation of TMOS with the bidentate free radical initiator **1** [6]. Compound **1** decomposes thermally producing two surface-bound radicals that initiate polymerization of monomer (methylmethacrylate -MMA- in our case) in the mesopores. Depending on the concentration of the monomer in we can move between conformal polymer coatings (polymer crosslinked aerogels), and polymer matrix composites.

$$(EtO)_3Si(CH_2)_3-HNOC(CH_2)_2\underset{CN}{\overset{}{\text{—}}}N{=}N\underset{CN}{\overset{}{\text{—}}}(CH_2)_2CONH{-}(CH_2)_3Si(OEt)_3$$

1

Experimental

Wet gels incorporating **1** were prepared as described recently [6], and they were either dried using supercritical fluid (SCF) CO$_2$ to native aerogels, or they were solvent exchanged with a 1:1 (v/v) uninhibited MMA:toluene monomer solution, followed by heating at 70 ºC for 12 h, solvent exchange with toluene and SCF CO$_2$ drying to yield crosslinked aerogels. In order to obtain silica/PMMA matrix composites, wet gels made with 20 mL of sol in

25 mL syringe molds (syringes from Fisher Scientific, CAT no. 14-817-32, 25 mL, 20 mm inner diameter) were solvent-exchanged with inhibitor-free MMA (5 washes, 100 mL of wash solution each time) in glass jars (from Fisher Scientific, catalogue number 06-414-1A). An interval of 24 h was allowed between washings, with frequent agitation. Finally, gels were heated in the last MMA bath at 70 °C for 12 h. At the end of the 12 h period, MMA surrounding each gel became viscous while the gel was enclosed in a shell of PMMA that extends beyond the original geometric gel boundaries. The monolith was removed from the viscous liquid, air dried on the hood floor for 24 h and subsequently it was heated at 95 °C to complete polymerization.

Results and Discussion

Scheme 2 summarizes the preparation processes outlined in the Experimental, but most importantly it emphasizes the relationship between the three kinds of materials discussed here. Clearly, the sol-gel 3D network of nanopartices comprises the common denominator of all three.

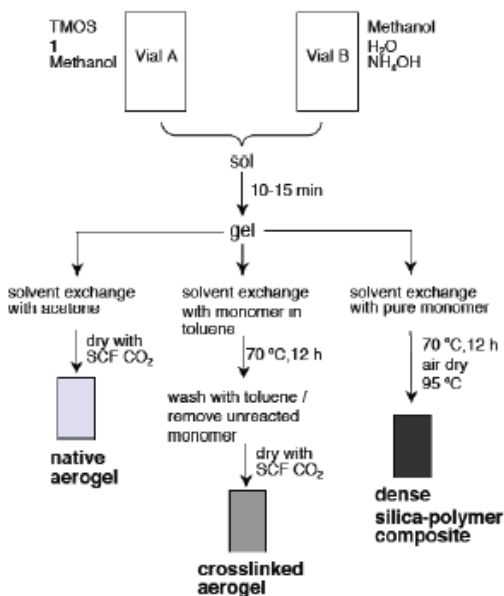**Scheme 2.** Relationship of the three materials considered in this study.

Figure 2 shows the microscopic difference between a polymer crosslinked aerogel and the polymer matrix composite. The porosity seen in Figure 2A has been blocked in Figure 2B.
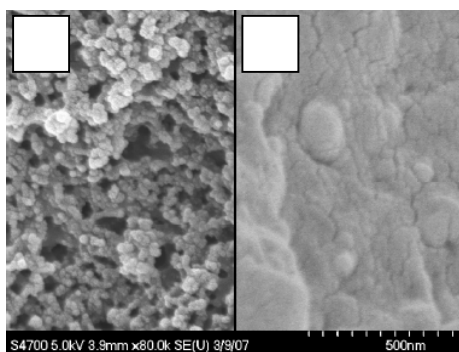

Figure 2. (A) A silica aerogel crosslinked with PMMA according to Scheme 2 ($\rho_b = 0.807$ g cm^{-3}, porosity = 38 %). (B) The same network filled with PMMA formed *in situ* from MMA according to Scheme 2 ($\rho_b = 1.170$ g cm^{-3}).

The behavior under compression of neat PMMA and various silica/PMMA composites is shown in Figure 3. Based on the density of the materials (legends of Figures 2 and 3) we conclude that silica/PMMA composites still include pores (the density of neat PMMA and of

silica/PMMA composite are about equal). Nevertheless, despite that residual porosity, the modulus and yield strength of silica/PMMA are close to those of neat PMMA, but the ductility of the former is clearly better already. Indeed, Figure 4 shows the behavior of neat PMMA versus that of silica/PMMA composite. Both materials show barreling but neat PMMA develops cracks and fails while the composite stays together as one piece. Obviously, randomly distributed nanoparticulated silica, covalently bonded to the polymer helps keep the material together.
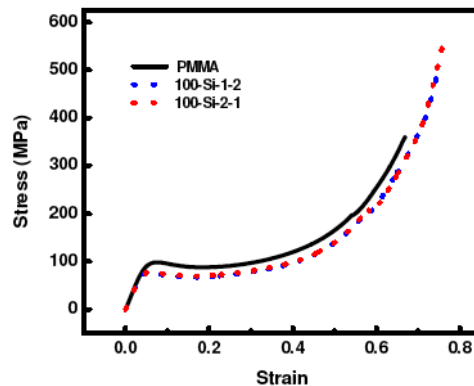

Figure 3. Stress strain data of neat PMMA ($\rho_b = 1.15$ g cm^{-3}) and of silica/PMMA matrix composites ($\rho_b = 1.17$ g cm^{-3}; sample dimensions: length 200 mm; diameter; 20 mm).
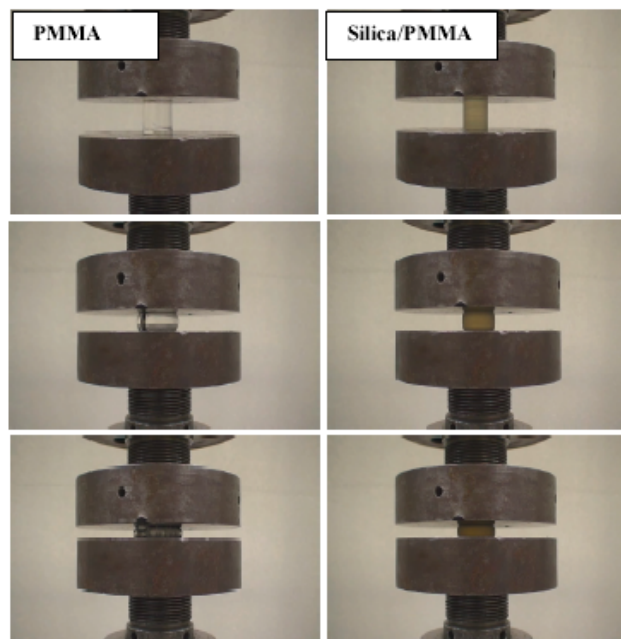

Figure 4. Compression of neat PMMA and of a silica/PMMA matrix composite with microstructure as shown in Figure 2B.

Conclusion

Using preformed 3D dispersions of sol-gel silica nanopartices is a viable approach for improving the mechanical properties of plastics.

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