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# Synthesis of silica-polybutadiene hybrid aerogels: The effects of reaction conditions on physical and mechanical properties

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ABSTRACT

The aim of this study was to synthesize a novel organic-inorganic hybrid aerogel using silane functionalized polybutadiene latex nanoparticles to enhance their physical and mechanical properties by varying the synthesis conditions. The effect of silica sol concentration, pH of the mixture during gelation and silane grafting degree of polymer latex on the structure, morphology and compression strength properties of the aerogels were studied. The silane-modified rubber particles were combined with Tetraethoxysilane (TEOS) as silica precursor by two step acid-base catalyzed sol-gel process followed by drying in ambient pressure condition. The monolithic hybrid aerogels with different polymer latex content (0–70 wt.%) were prepared. The aerogels containing up to 30 wt.% of polybutadiene latex showed lower densities (ranging from 0.19 to 0.24 g/cm$^3$) and higher surface areas (from 763 to 461 m$^2$/g) with negligible volume shrinkages after drying. Increasing in polymer latex content (>30 wt.%) resulted in lower surface area along with a sharp decrease in the porosity as evaluated by Nitrogen adsorption/desorption. The aerogel samples with compression strength varying from 262 to 14,450 kPa were obtained. It was found that increasing the silane grafting degree of polybutadiene latex improved the compression strength properties >3× (from 262.4 to 853.6 kPa), without decreasing in porosity.

## 1. Introduction

Silica aerogels are a kind of hyperporous nanostructure material with desired properties, such as low density and high specific surface area, low thermal conductivity and low dielectric constant. The unique properties of these materials make them convenient for manufacturing of thermal and acoustic insulation materials, catalyst supports, adsorbents, sensors, supercapacitors and fuel cells [1–4]. However, the potential applications of silica aerogels have been restricted because of fragility, brittleness and hydrophilicity [5,6].

Silica aerogels as the most studied aerogels have pearl-necklace-like structure of secondary particles, which in turn are comprised of primary particles. The secondary particles connect together through the neck region. The inter-particle neck regions are the weak points of this structure. As the bead-like structure of colloidal silica aerogels breaks under force, the primary particles remain intact and the secondary particles lose contacts with one another [1,7]. To improve the mechanical properties of silica aerogels, it has been focused on developing low density aerogels with more elasticity/flexibility which can be able to absorb shock energy during bending or compression [7].

Some attempts have been made to synthesize hybrid aerogels with flexibility using organic modified silane precursors [8–11] The presence of unhydrolysable groups in these networks reduces the network connectivity, resulting in more elastic and flexible materials [7,12,13]. It was observed that the building blocks comprised of organic elastic bridging groups could give rise to strong aerogels with more flexibility rather than native silica aerogels [12,13]. Also, such structural reinforcement has been achieved by a combination of the organic modified precursors and flexible alkyl-bridged silsesquioxanes [5,14]. Compounding of silica aerogels with different polymers [15–17], foams [18,19] and organic aerogels [20] are another ways which have been carried out in various procedures. Moreover, incorporation of different fibrous supporting materials such as nanofibers [21], woven/nonwoven polymeric fibers [22–24] in the silica network structure has been performed to strengthen the mechanical properties of silica aerogels.

It has been shown that introducing a polymer into the fragile structure of silica aerogel can also strengthen its structure. Leventis et al. focused on the interface and represented that the strength of silica aerogels could be improved by making the inter-particle necks wider. It has been achieved by addition of a polymer conformally on the secondary particles. When an inter-particle crosslinker reacted with the surface, the bulk structure of silica aerogel network would be reinforced by preserving the mesoporous structure [1,3]. In this approach, the silica network structure needs to be modified by appropriate functional group. If surface silanol groups of silica particles react with a di or tri-

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isocyanate [1,3,25], urethane groups will be formed. The silica particles can also be decorated with amine groups to react with polyfunctionalized epoxy [26], isocyanates [27–29] and cyanoacrylate [30]. Polystyrene crosslinked aerogels [13,31] can also be synthesized using styrene functionalized silica structure, which are less hydrophilic and more robust than pure silica aerogel. Recently, crosslinking with polymer has been exerted on the organic-modified structure of silica aerogels to obtain more flexibility and elastic behavior [32,33]. However, such reinforcement is along with the increase in density and the decrease in surface area.

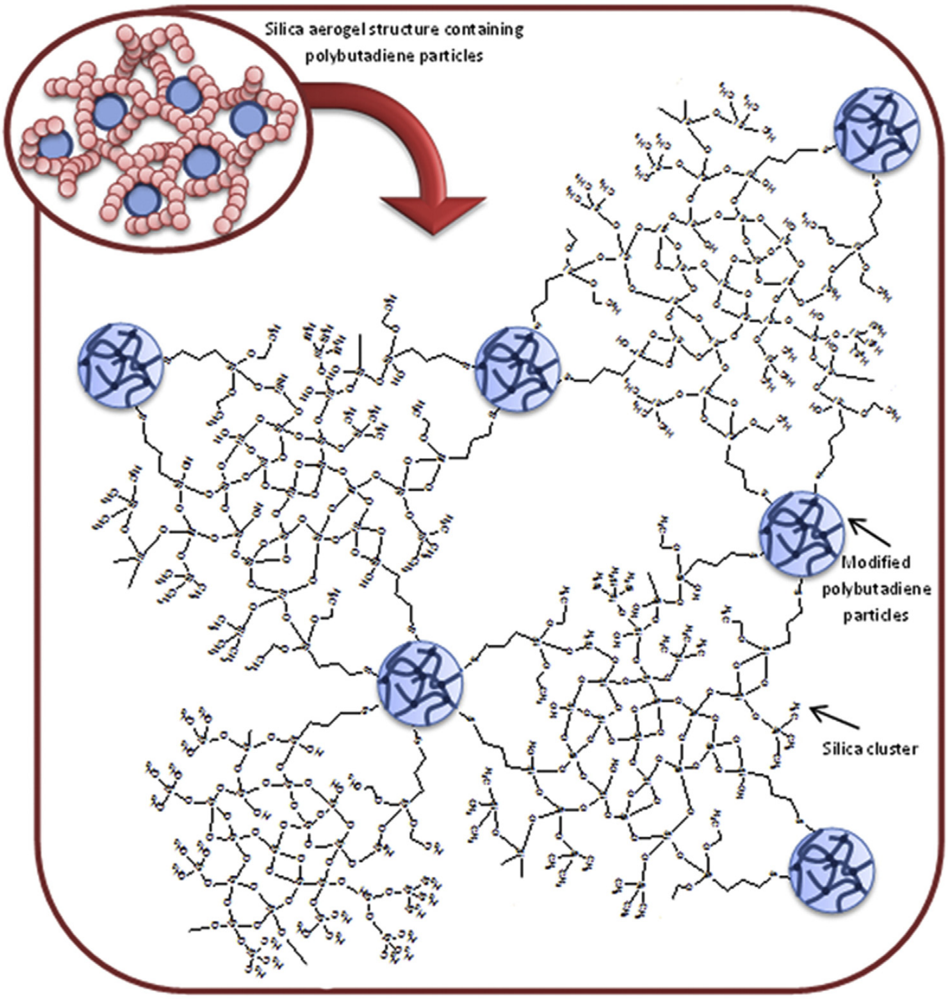
Another technique that affects mechanical properties of silica aerogels is co-hydrolyzing and co-condensation of the inorganic precursor with functionalized polymer nanoparticles. The crosslinked core-shell triethoxysilyl-modified polybutyl methacrylate particles with low glass transition temperature, have been cohydrolyzed with Tetraethoxysilane as silica precursor [34,35]. The resulting hybrid aerogels remained brittle but were able to absorb much higher energy rather than pure silica aerogels [34–36]. Evans et al. patented [37] a novel method for using rubber material in silica aerogel structure to obtain more flexibility under supercritical drying conditions. It was claimed that introduction of rubber particles in silica network could improve the flexibility of silica aerogels [37]. This method presents a great advantage for inorganic-organic hybrid aerogels, because it can be used on preformed commercial latex. In this kind of aerogel, the modified rubber particles minimize the connectivity of clusters. This reduction of the crosslink density in the silica network may result in softness or flexibility. Moreover, they can act as impact modifiers and hinder crack propagation in the nanostructured materials.

In the present work, this latter method was used to synthesize a new hybrid aerogels using silane modified polybutadiene nanoparticles through ambient pressure drying. The chemical structure of synthesized hybrid aerogel is shown in Scheme 1. The effect of modified latex particles on the microstructure and physical properties such as density, volume shrinkage, porosity and pore size distribution of these hybrid aerogels were determined. Since synthesis conditions and polymer particles play a key role in determining the mechanical properties of these hybrid aerogels, the influence of silica sol concentration, pH of mixture during gelation and silane degree of grafting on compression strength of silica-polybutadiene hybrid aerogels were also evaluated.

## 2. Experimental

### 2.1. Material

Polybutadiene latex (PBL) used in this work (~40 wt.% solid cont., particle size ~90 nm as measured with dynamic light scattering (DLS), pH = 8.5) was supplied from a Petrochemical Company in Iran. Silane coupling agent namely, bis[3-(triethoxysilyl) propyl] tetrasulfide (TESPT, Si69) was received from Evonik Degussa Company, Belgium. Tetraethylorthosilicate (TEOS, 98%), Hexamethyldisilazane (HMDZ, 98.5%), Ammonium Hydroxide (25%) and oxalic acid were supplied from Merck Company. 2-Propanol and n-Hexane (from Arman Sina



**Scheme 1.** Schematic representation of silica-polybutadiene hybrid aerogels.