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A new trend for development of mechanically robust hybrid silica aerogels

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ABSTRACT

In this study, a mechanically robust silica aerogel has been successfully prepared based on the integration of a crosslinker in the poly (butyl acrylate) grafted silica network *via surface - initiated reversible addition fragmentation chain transfer* technique. Substantial improvements regarding the compressive strength with only a slight difference in aerogel physical properties have been achieved.

1. Introduction

Silica aerogels are interesting, highly porous and low dense materials that were being used for almost three decades in a number of high-performance applications [1,2]. Thermal insulation, particularly in Space exploration, construction and building sectors, is the most promising area of the aerogel applications [3]. However, development of such highly porous free standing aerogel monoliths with a density less than air is practically impossible, except for materials with very tenuous and fragile structures [2]. To this end, most of the studies to afford strong aerogels with a capability of enduring compressive loads up to several hundred of kilograms or stresses up to few MPa, follow the hybridization of the silica aerogels network with various crosslinkers or polymers [4]. Although the density increases, at least, two folds and parts of the active surface area is lost, the crosslinking of the silica aerogels in the "necks" (connection points) of the silica network can provide robust materials with capability to comply with most of the technical applications needs [4,5]. In the majority of these studies, the polymerizations on the silica surface/network connections were conducted during the post gelation stage. However, there is a possibility of performing the polymerization during the sol-gel reaction or after supercritical drying through gas phase deposition [2,5–7].

Very recently, by using the *surface initiated reversible addition fragmentation chain transfer* (SI-RAFT) technique, we were able to grow well-defined polystyrene and poly (butyl acrylate) from the initiator attached to the silica surface [8]. Interesting results regarding the mechanical properties were achieved with only a minimum increase on the density. Also, the control on the molecular weight of the polymer on the surface allowed to establish a structure-property relationship between this property and the performance-related aerogel properties.

It is known that the crosslinking of silica surface has led to the better result in terms of mechanical strength, thus we decided to exploit the crosslinking reaction of ethylene glycol dimethacrylate (EGDMA) with butyl acrylate (BA) on the silica surface, according to the schematic SI-RAFT crosslinking mechanism indicated in Fig. 1. The integration of EGDMA crosslinker in the silica network has previously given rise to promising results regarding the flexural strength and modulus of silica aerogels compared to the growth of linear polymers [9].

2. Experimental procedure

2.1. Materials

Tetramethyl orthosilicate (TMOS) (98%), anhydrous methanol (99.5%), toluene (99%), tetrahydrofuran (THF, ≥ 99.9%), 3-(mercaptopropyl)trimethoxysilane (95%), 1-propanethiol (98%), carbon disulfide anhydrous (> 99%), benzyl chloride (99%), sodium methoxide (25 wt% solution in methanol), butyl acrylate (BA,

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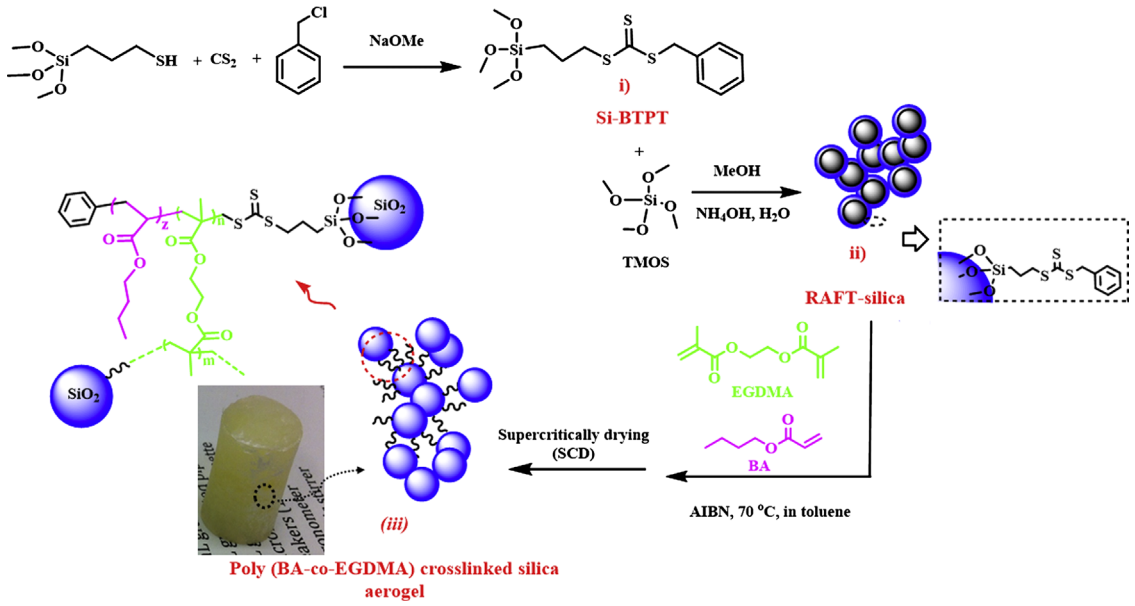

Fig. 1. Process for preparing aerogels with the surface initiator RAFT-silica and using the SI-RAFT process to prepare poly (BA-co-EGDMA) crosslinked silica aerogels.

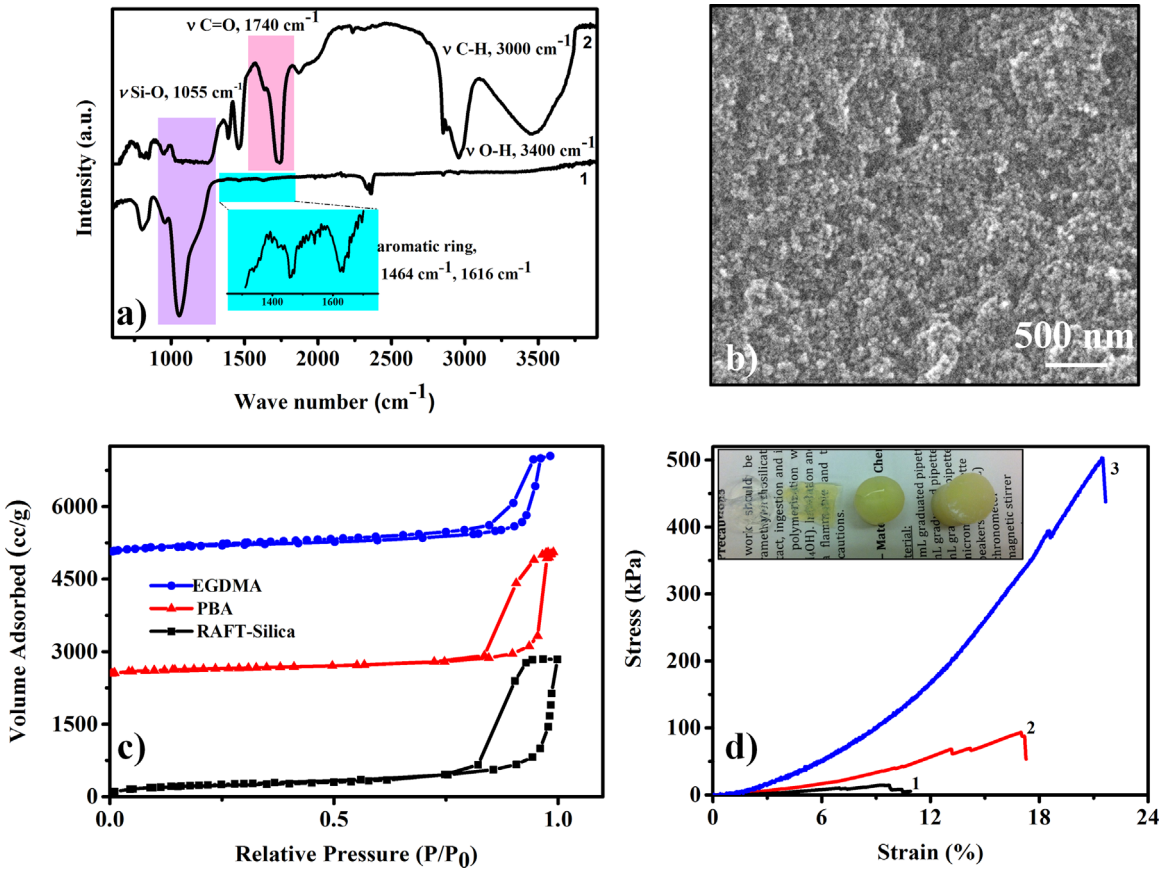

Fig. 2. (a) ATRFTIR of (1) RAFT-silica, (2) PBA-silica, and (3) poly (BA-co-EGDMA) crosslinked silica aerogels; (b) SEM micrograph of poly (BA-co-EGDMA) crosslinked silica aerogel; (c) N_2 adsorption and (d) stress-strain curves of (1) RAFT-silica, (2) PBA-silica and (3) poly (BA-co-EGDMA).

< 99%), ethylene glycol dimethacrylate (EGDMA, 98%), 2,2′- azobisisobutyronitrile (AIBN, 99%) and ammonium hydroxide (NH_4OH, 28–30 wt% aqueous solution) were purchased from Sigma-Aldrich. All reagents were used without further purification. The preparation of *S*-Benzyl *S*′-trimethoxysilylpropyl-trithiocarbonate (BTPT-silica) and RAFT-silica are described in our previous paper [8].

2.2. Characterization

Infrared spectroscopy was conducted with ATR-FTIR (*JASCO FTIR-4100*). The bulk density (ρ_b) was determined by measuring the weight and volume of the samples. He pycnometry (*Accupyc 1330*, *Micromeritics*) was used to measure the skeleton density (ρ_s) and, indirectly, to calculate pore volume and pore diameter of the