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Mechanical properties of isocyanate crosslinked resorcinol formaldehyde aerogels

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ABSTRACT

In this study, in order to improve the mechanical properties of resorcinol-formaldehyde (RF) aerogel, synthesis of crosslinked aerogel using hexamethylene diisocyanate (HDI) as a crosslinking agent was investigated. The crosslinking was performed using exitu and in situ methods at two different concentrations of catalyst. The effects of the crosslinking and the catalyst concentration on the morphology and the mechanical properties of RF aerogels were evaluated by different analyzes. The Fourier Transform Infrared Spectroscopy (FTIR) confirmed the reaction of HDI isocyanate groups with resorcinol hydroxyl groups. The Scanning Electron Microscope (SEM) and Atomic Force Microscopy (AFM) results indicated changes in the morphology and thickening of the necks. For the crosslinked aerogels, compared to the native samples, a decrease of the compressive modulus and about five times increase in the compressive stress were obtained. Moreover, an improvement of the impact strength and a reduction in the hardness were observed.

1. Introduction

Aerogels are a special type of open-cell foam materials with high porosity, low density and high surface area [1]. Due to these unique properties, they have attracted great attentions in the recent decades and turn out to be a good choice for many applications in aerospace, electronics, military and optics industries [2]. Despite the above mentioned features, these materials have some drawbacks which have confined their engineering and industrial applications. Since 1932, when Kistler synthesized first aerogel, many attempts have been done to enhance the mechanical properties of aerogels including compression [3,4] and bending strengths [5,6]. Generally, there are some methods to improve the mechanical properties of aerogel which involve the modification of aerogel using rubbers [7,8], preparation of aerogel composites [9–12], tuning sol-gel parameters [13], and crosslinking of aerogel using epoxy [14,15], polystyrene [16] and isocyanates [17].

Hajizadeh et al. [7] investigated the fracture behavior of novalac aerogel. Due to NBR modification, an increase in toughness and density and a decrease in the pore size and pore volume were obtained. Shahzamani et al. [8] assayed the effects of hydroxyl-terminated polybutadiene (HTPB) resin on the mechanical properties of phenolic aerogels and observed a change of the fracture behavior and a reduction in the compressive modulus. TDI was used as a connecting agent between hydroxyl group of HTPB and phenol.

Meador et al. [14] examined the mechanical properties of the epoxy crosslinked silica aerogels. The crosslinking included two steps: the modification of silica aerogel by amine and then, the reaction of the modified silica aerogel with epoxy. Di, tri, and tetra-functional epoxy were used, however, tri functional epoxy induced the best mechanical properties. In comparison to the native aerogel, the density was increased by a factor of 2–3 and the bending strength was enhanced more than 2 orders of magnitude. The crosslinking of silica aerogel using polystyrene were studied by Nguyen et al. [16]. The improved elastic behavior and the reduced surface area were obtained.

Resorcinol–formaldehyde (RF) aerogel, the most well-known organic aerogel, is prepared by sol–gel polycondensation of resorcinol and formaldehyde [18,19]. This aerogel shows the higher mechanical properties in comparison to the silica aerogel [20] and has many applications because of its unique properties [18]. The synthesis parameters of RF aerogel include the molar ratio of resorcinol to catalyst (R/C), resorcinol to formaldehyde (R/F) and resorcinol to solution (R/S). A decrease in R/C and an increase in R/F and R/S can enhance the mechanical properties [21]. Léonard et al. [13] studied the mechanical properties and the shrinkage of RF aerogel in different ratios of R/C and observed the higher mechanical properties and shrinkage in lower R/C ratios. Tuning of the sol-gel parameters is not sufficient to modify RF aerogel mechanical properties, so applying the other methods is required to improve these properties. Another way to alter the mechanical properties is crosslinking of the aerogels using isocyanates.

As illustrated in Fig. 1, the aerogel structure is comprised of the

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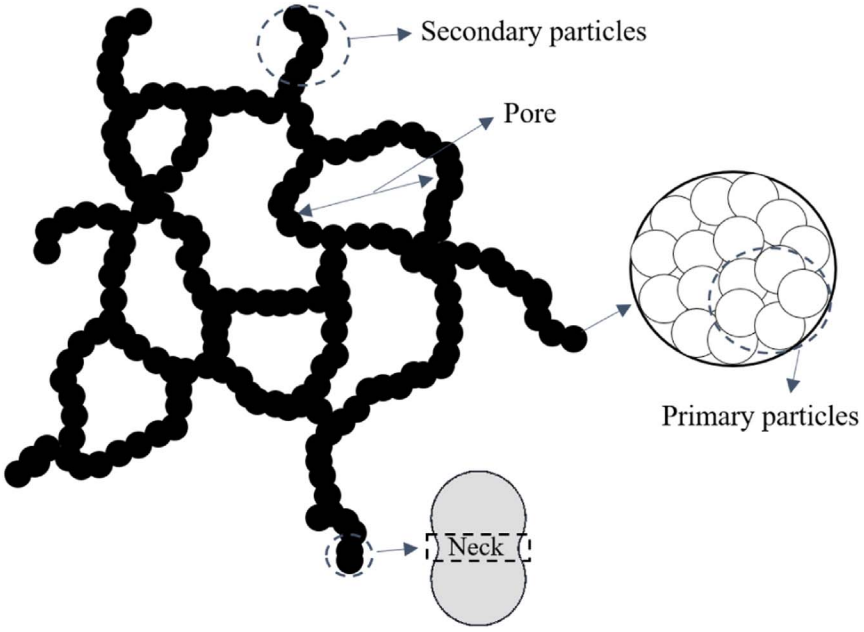

Fig. 1. Schematic illustration of the primary and secondary particles.

primary and the secondary particles. When the aerogel tolerates impact or compression force, only the secondary particle connections are broken, while the primary particles remain unchanged, therefore, in order to reinforce the aerogel, it is essential to strengthen the neck of the secondary particles. The necks are formed by the connection of the particles during the gelation process. In un-crosslinked aerogel, the secondary particles look like pearl-necklace. When the aerogel is crosslinked using isocyanate, the interparticle necks become thicker so it leads to a stronger aerogel [22]. The crosslinking of the silica aerogels with different types of isocyanate including desmour N3300, desmour N3200 and toluene diisocyanate (TDI) has been investigated and the enhanced stress at break, up to more than 300 times, has been observed [5,6,22]. Due to the presence of hydroxyl groups in resorcinol, isocyanate crosslinking of RF aerogel is possible to strengthen the material and to improve its mechanical properties [23] in the same way as done for silica aerogels.

In this work, the native and isocyanate crosslinked RF aerogels were synthesized by polycondensation of resorcinol and formaldehyde. Two different methods of the crosslinking, including exitu and in situ, were employed. In exitu procedure, the exchanged wet gel was placed in the crosslinking solution, while, in in situ route, the crosslinking agent was added at the time of sol preparation. As a result, in exitu method, the water in the wet gel is removed after solvent exchanging and only the urethane linkages are created through the reaction of resorcinol hydroxyl groups and isocyanate groups of the crosslinking agent. In contrast, in in situ preparation system, due to the presence of water in formaldehyde, urea linkages are also formed, in addition to urethane groups. As reported, urea connections are stronger mechanically than urethane linkages [5]. Thus the in situ synthesized aerogel is expected to be more robust than exitu prepared one, because of the presence of urea groups. Two different concentrations of the catalyst were also applied and the influences of the catalyst concentration were studied. The morphology and the mechanical properties were examined using different analyzes.

2. Experimental

2.1. Materials

Resorcinol (R) (98%, DAEJUNG, Korea), formaldehyde (F) (35%, Ghatran Shimi, Iran) as monomers, hexamethylene diisocyanate (HDI) (Merck, Germany) as crosslinking agent, acetonitrile (ACN) (HPLC grade, DAEJUNG, Korea) as solvent, hydrochloric acid (HCl) (37%, Merck, Germany) as acidic catalyst were purchased and used as received.

2.2. Preparation of native and crosslinked RF aerogels

To synthesize RF aerogel, 5 g of R, 11.7 g of F, 21.9 g of ACN and 0.178 of HCl were mixed and poured into a sealed polypropylene (PP) container. The Gelation process occurred at 70 °C within 15 min. The obtained gel was aged at room temperature for 24 h. Then, the gel was placed in ACN for 48 h in order to exchange the solvent. Finally, the wet gel was dried in the ambient condition.

In exitu method, solvent exchanging of the native wet gel was performed to remove the water and unreacted monomers. The resulted gel was immersed in the crosslinking solution containing 5 g of isocyanate and 60 g of ACN. The sample was maintained at room temperature for 24 h to achieve the equilibrium condition and to obtain maximum penetration of HDI from the crosslinking solution into the wet gel pores. Subsequently, the wet gel was placed in fresh ACN and kept at 70 °C for one day in order to complete the reaction of the diffused isocyanate with hydroxyl group of resorcinol. The drying step was the same as the method used for the native RF aerogel.

In in situ procedure, one solution was consisted of 5 g of R, 11.7 g of F and 11.9 g of ACN and the other solution was comprised of 0.178 g HCl, 10 g ACN and 5 g of HDI. The two solutions were mixed and poured into a mold. The gelation was done at 70 °C within 5 h. The next steps of the process including aging, exchanging and drying were the same as the employed route for the synthesis of the native RF aerogel. The flowchart of the preparation steps is shown in Fig. 2.

The samples with resorcinol to catalyst molar ratio (R/C) of 25 (N-25, Ex-25 and In-25) and R/C molar ratio of 100 (N-100, Ex-100 and In-100) were prepared. “N”, “Ex” and “In” refer to native, exitu and in situ synthesized RF aerogels.

2.3. Characterization

The functional groups and the chemical bonds of the synthesized aerogels were studied by Fourier Transform Infrared Spectroscopy (FTIR) (BRUKER, TENSOR 27, Germany) in the range of 400 cm^{-1} to 4000 cm^{-1} using KBr disk. The samples were dried in a vacuum oven