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Polyurethane aerogels synthesis for thermal insulation – textural, thermal and mechanical properties

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ABSTRACT

Polyurethane aerogels were prepared via sol–gel synthesis and dried with supercritical carbon dioxide (CO_2) according to catalyst concentration. The influence of this parameter was investigated, first in order to modify the reaction kinetics, then to study its impact on several characteristics. It was observed that this parameter influences the global shrinkage and the bulk density of the resulting materials. The effect of catalyst concentration on the dry samples was then studied in terms of textural, thermal and mechanical properties, thanks to scanning electron microscopy (SEM), nitrogen (N_2) adsorption, non-intrusive mercury (Hg) porosimetry, thermal conductivity measurements and uniaxial compression tests. Results allowed us to identify correlations between these characteristics and to determine an optimal density range for thermal and mechanical compromise associated with a fine internal mesoporous texture.

1. Introduction

In a context where energy consumption limitation and demand control appear as major environmental and economic issues, it is necessary to reduce primary energy consumption in the building sector. This domain is responsible for a significant portion of global energy consumption, especially due to thermal losses through building envelopes. The use of innovative, performing materials called superinsulating materials is considered as a very most promising market for building retrofit, where it could allow a significant decrease of the energy requirements for existing buildings while maintaining their integrity and architectural quality. These solutions currently exist under two families: vacuum insulation panels (VIP) [1], that exhibit extremely low thermal conductivities but can prove difficult to be handled, and atmospheric pressure super-insulation materials, mainly consisting in light, mesoporous and nanostructured materials called aerogels [2].

Their specific texture is obtained via two main preparation steps. In a first part, the sol–gel synthesis allow the formation of a chemical gel, a tridimensional continuous solid network interpenetrated with a liquid phase, usually in convenient ambient conditions [3]. In a second part, the liquid phase is in most cases extracted in supercritical conditions. This drying method maintains the delicate network characteristics of the aerogels [4]. The use of CO_2 as extracting solvent is now established in the aerogel field thanks to its low critical temperature, non-flammability and low toxicity [5].

In the field of these superinsulation materials at atmospheric pressure, silica aerogels are still considered as the most efficient materials in terms of thermal insulation, with a thermal conductivity as low as 0012 $W\,m^{-1}\,K^{-1}$ in room conditions [6]. These silica-based materials are already commercialized, for instance for interior insulation solutions for building retrofit as well as slim façade insulation for the renovations of historical buildings [7,8]. However, a low thermal conductivity is not the only relevant criteria that insulation materials must fulfill in the building and construction sector, and these mineral aerogels usually appear very fragile in a mechanical point of view, in particular the apparition of dusting leading to thermal performance degradation [9]. In parallel, some organic aerogels currently present very promising thermal performance with a mechanical behavior that seems better than mineral counterparts on the whole. In particular they can stand higher strain and loads at given densities faced with both compression and flexion stress, such as resorcinol-formaldehyde, polyimide or polyurea based aerogels [10–13]. Among these

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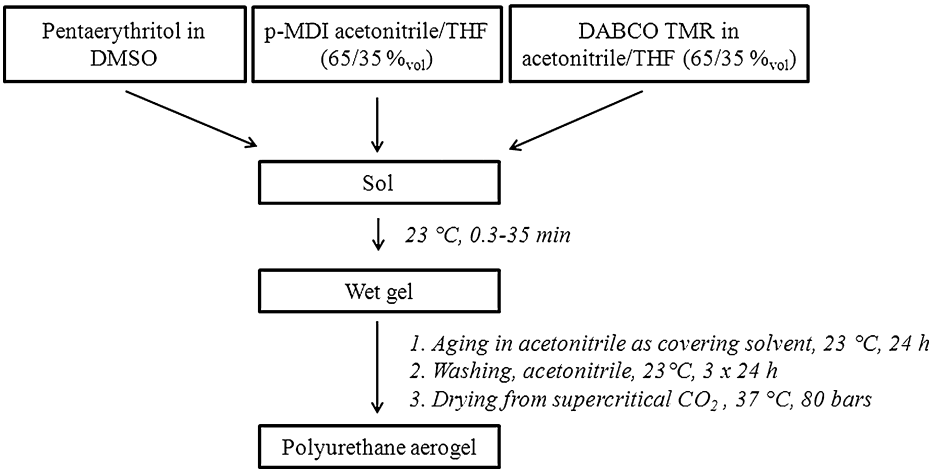

Fig. 1. Preparation of polyurethane from pentaerythritol and p-MDI.

materials, organic aerogels based on polyurethane turn out to be part of the most promising [14,15].

This study focuses on an organic aerogel based on polyurethane matrix, that was already presented in previous articles [16,17]. The aim of the present work is to study the main properties of a polyurethane aerogel in order to reach an efficient thermal-mechanical compromise. The materials were prepared through sol–gel synthesis and supercritical drying in CO_2 in a new reaction medium.. The effect of one key formulation parameter, the catalyst concentration, was studied in terms of textural, thermal conductivity and mechanical characteristics. The two latter have been especially investigated in connection with the evolution of bulk density.

2. Experimental

2.1. Materials

Pentaerythritol was purchased from Alfa Aesar, (purity > 98%). Poly-(diphenylmethane-isocyanate) (p-MDI) commercialized under the name of Lupranat M20S was gracefully provided by BASF Polyurethane. It consists in a blend of monomers and oligomers derived from 4,4′-methylenebis(phenylisocyanate), mainly 4,4′ diphenylmethane diisocyanate with 2,4′ diphenylmethane diisocyanate and 2,2′diphenylmethane diisocyanate isomers. Tris(dimethylaminomethyl)-phenol commercialized under the name of DABCO TMR was gracefully provided by Air Products. Dimethylsulfoxide (purity 99%) and tetrahydrofurane (purity > 99%) were purchased from Alfa Aesar, acetonitrile (purity > 99.8%), and acetone (purity 99%) were purchased from Fisher Scientific. The extracting fluid for supercritical drying, liquid CO_2 (purity 99.7%) was purchased from Air Liquide. Chemicals and CO_2 were used as received.

2.2. Gels synthesis

The polyurethane gels were synthetized through a two-step condensation reaction. The aerogel preparation is summed up in Fig. 1, with the quantities presented in Table 1 for the preparation of 100 ml of initial sol.

Three solutions were prepared separately at ambient temperature under magnetic stirring with a magnetic bar (500 rpm): pentaerythritol was dissolved in DMSO at 100 g l^{-1}, p-MDI was diluted in a mix of acetonitrile and THF (35:65%$_{vol}$) at 44 g l^{-1}, and DABCO TMR was diluted in a mix of acetonitrile and THF (35:65%$_{vol}$) at a concentration in solution varying from 17 to 110 g l^{-1}. The three solutions were then mixed together with respectively 9.2; 86.1; 4.7%$_{vol}$ at ambient temperature under magnetic stirring (500 rpm) for 20 s, and poured in PET molds in presence of molecular sieves from Sigma–Aldrich.

Table 1
Quantities of reagents for the preparation of a 100 cm^3 polyurethane gel (before shrinkage).

	mmol	g
p-MDI	14.6	3.7
pentaerythritol	6.3	0.9
DABCO TMR	[0.27–1.77]	[0.07–0.47]
Acetonitrile	553.9	22.7
THF	666.5	48.0
DMSO	121.5	9.5

This specific solvent mixture was chosen in order to reach a specific Hildebrand solubility parameter of 21.7 MPa$^{1/2}$, identical to the solubility parameter used in previous studies [17]. The choice of acetonitrile as the main solvent through all the preparation steps (including washing steps) was made in the perspective of a coupling process between polyurethane and functionalized silica gels, as described in [18,19]. In addition, the use of dimethylsulfoxide is crucial to a proper dissolution of pentaerythritol [20] and the use of tetrahydrofurane merely balances the global solubility parameter.

Regarding the molar ratio between the two reactants $n_{\text{p-MDI}}/n_{\text{pentaerythriol}}$, it is kept constant at 2.3 throughout the study. The average functionality is 2.7 isocyanate groups in p-MDI and 4 hydroxyl groups for pentaerythritol, and respective molar concentrations are 146 and 63 mmol l^{-1}. This leads to an excess of isocyanate groups over the theoretical amount needed for the reaction, with an isocyanate index of 1.55, ensuring the complete reaction of —OH groups and the complete cross-linking of the system via urethane bonds. The remaining —NCO groups could also theoretically lead to the formation of secondary allophanate network in certain conditions [21]. The molar DABCO TMR concentration ($C_{DABCOTMR}$) in the sol is varied between 2.7 and 17.7 mmol l^{-1}.

2.3. Supercritical drying

After the sol–gel transition, the samples were covered with acetonitrile in order to avoid premature evaporative drying, and kept at ambient temperature for washing and aging purpose. The solvent was washed three times with fresh acetonitrile in order to remove THF, DMSO and other unreacted chemicals from the open porosity of the gel. The gels were then placed in an autoclave with