J Mater Sci (2018) 53:1556–1567

Polymers

Hydroxyethyl cellulose/alumina-based aerogels as lightweight insulating materials with high mechanical strength

Carolina Simón-Herrero[1], Amaya Romero[1], José L. Valverde[1], and Luz Sánchez-Silva[1,*]

[1] *Department of Chemical Engineering, University of Castilla La Mancha, Av. Camilo Jose Cela 12, 13071 Ciudad Real, Spain*

Received: 19 June 2017
Accepted: 14 September 2017
Published online: 10 October 2017

ABSTRACT

Alumina aerogels reinforced with hydroxyethyl cellulose (HEC) have been successfully synthesised using an environmentally friendly freeze-drying method. Alumina aerogels are materials with interesting properties, such as low density, high-temperature stability, high porosity and high surface area, which can be used in several industrial applications. It is necessary to add one or more supporting materials, such as carbon nanofibres and a fibrous second phase such as cellulose, to the matrix to reinforce the mechanical properties of the aerogels. In this study, the influence of the HEC-to-aluminium tri-sec-butoxide (ASB) solution mass ratio on the morphological, mechanical and thermal properties of the synthesised aerogels and its impact on the thermal insulation properties of the resulting materials were evaluated. The apparent density of the hydroxyethyl cellulose-reinforced alumina-based aerogels increased with the amount of HEC. Thus, compact structures with a small pore size were obtained when increasing HEC/ASB solution mass ratio. The incorporation of HEC into the ASB matrix led to an increase in the mechanical properties in terms of the Young's modulus. Thermal stability of samples varied as a consequence of the HEC addition. Thus, the second decomposition stage shifted to lower temperatures with HEC incorporation. In addition, all synthesised aerogels showed low thermal conductivities. The remarkable physical characteristics of the hydroxyethyl cellulose-reinforced alumina-based aerogels prepared herein and the successful synthesis suitable for scale-up make them a good candidate for construction applications.

Introduction

Aerogels are porous and three-dimensional network solid materials with unique properties, such as a low density and dielectric constant, high surface area and porosity, and extremely low thermal conductivities (0.044 and 0.051 for the type of aerogels synthesised in this work) [1–6]. Consequently, these materials can be used as thermal insulators [7] and in optical (solar windows), acoustic, mechanical (filters), electrical and aerospace applications [8, 9].

Address correspondence to E-mail: Marialuz.sanchez@uclm.es

DOI 10.1007/s10853-017-1584-6

The used energy in the building sector represents a significant portion of the world's energy demand. Consequently, there is considerable interest in improving the energy efficiency of buildings [10]. The need for thermal insulation of residential and non-residential buildings has led to a number of developments in the construction field to fulfil energy regulation requirements [11]. In this regard, insulating materials with low thermal conductivities have been, and continue to be, developed in order to reduce the energy consumption of architectural constructions [10, 12]. Although a large variety of traditional thermal insulation materials, such as mineral wool, expanded polystyrene, extruded polystyrene, cellulose, cork and polyurethane, are known, new materials with better insulating properties, such as vacuum insulation panels, gas-filled panels and aerogels, are currently being investigated [10]. In addition, the development of thermal insulators materials using renewable raw materials (kenaf, sheep wool, hemp, flax) has been carried out. These materials show moisture sensitivity, which could influence on the thermal insulation properties. To solve this problem, hydrophobic surface treatments are necessary [13–15]. In spite of the interest of researchers and industries in natural fibrous thermal insulations, aerogels are considered as the best products to be used as building insulating materials due to their exceptional properties. Furthermore, thin and lightweight walls can be produced using aerogels as insulating materials.

In previous works, [16, 17] CNF-reinforced polymer aerogels (carbon nanofibre-reinforced polymer aerogels) were successfully synthesised by means of a freeze-drying method. Freeze drying is one of the most innovative techniques and provides a highly porous material with a well-controlled aerogel structure. This method has several advantages in comparison with other drying methods. The final product obtained is stable and has a high porosity and a final moisture content of less than 5 wt%. Furthermore, lyophilisation is performed at low temperatures, thus meaning that the stability of the obtained product is high and the loss of volatile substances is low. Furthermore, there are no oxidation problems as the process is conducted under vacuum. In addition, the effect of freeze-drying conditions on the properties of synthesised aerogels was studied [18]. The control of pore size and morphology is often the most critical factor as regards obtaining adequate materials for insulating applications. The internal structure can be tuned by varying the preparation conditions, such as freezing temperature, freezing time, freezing rate, solids loading, particle size, solvent type and freezing direction [19].

The synthesised aerogels in our previous works showed low thermal conductivities and were superinsulators [16, 17]. However, the mechanical properties of these materials are to be improved. In this sense, the synthesis of organic aerogels doped with reinforcement materials could be an interesting alternative, resulting in product that could be used commercially.

Alumina aerogels are nanoporous materials with interesting properties, such as low density, high-temperature stability, high porosity and high surface area that make them useful in several industrial applications [2, 20]. Moreover, they are better insulating materials at high temperatures than silica aerogels [20]. Alumina aerogels are usually prepared by means of a sol–gel method using hydrated alumina salts or aluminium alkoxides as precursors [20, 21]. Moreover, the synthesised aerogels using aluminium alkoxides showed better thermal stability at high temperatures than those synthesised using hydrated alumina salts [21]. The preparation of alumina aerogels from aluminium alkoxides is difficult due to the complex chemical route that must be followed [20, 21]. Thus, Zu et al. [20] have described the synthesis of alumina aerogels from aluminium tri-sec-butoxide in the absence of complexing agents. This method is based on the use of nitric acid to control the hydrolysis and condensation rates of the aluminium alkoxide [20]. To improve the mechanical properties of the aerogels, it is necessary to add one or more supporting materials, such as carbon nanofibres and a fibrous second phase such as cellulose, to the matrix to reinforce the mechanical resistance of the final product [22, 23].

Cellulose is a polysaccharide consisting of D-anhydrogluco-pyranose units linked by β-(1-4)-glycosidic bonds that form networks that are reinforced by hydrogen bonding as a result of the high content of hydroxyl groups. Thus, it is an interesting supporting material due to its ability to form a strong and a three-dimensional framework [24]. Furthermore, cellulose is the most abundant renewable natural polymer on the planet and is biodegradable and biocompatible [25]. Hydroxyethyl cellulose (HEC) is a water-soluble biopolymer with a low charge

density that has found several uses due to its hydrophilic properties [26, 27]. Sehaqui et al. [28] synthesised nanofibrillar/hydroxyethyl cellulose aerogels and demonstrated that the ductility of the materials could be increased by adding a ductile cellulose-derived matrix (HEC). Therefore, HEC was used in this work as a reinforcing agent.

The aim of this study is to develop hydroxyethyl cellulose/alumina-based aerogels by means of a sol–gel method using a freeze-drying process to dry the wet gel. Furthermore, the influence of the hydroxyethyl cellulose/aluminium tri-sec-butoxide solution (HEC/ASB) mass ratio on the textural, thermal and mechanical properties has been evaluated as well as its impact on the thermal insulation properties of the resulting materials.

Experimental

Materials

Aluminum tri-sec-butoxide (97%), hydroxyethyl cellulose (80–125 cp, 2% H_2O) and nitric acid (1 M) were supplied by Sigma-Aldrich Co., Ltd., and used as received. Nitric acid was dissolved in water to obtain a 0.2 M solution. Water was purified by distillation followed by deionization using ion-exchange resins.

Preparation of hydroxyethyl cellulose/alumina-based aerogels (CAAs)

Hydroxyethyl cellulose/alumina-based aerogels were prepared by following a procedure based on that reported by He et al. [29]. Figure 1 shows a schematic illustration of the experimental synthesis of these materials using a freeze-drying method (Table 1 lists the samples studied).

Aluminum tri-sec-butoxide (ASB) was mixed with deionised water at an ASB/deionised H_2O molar ratio of 1/80 at 70 °C. Appropriate volumes of nitric acid (0.2 M) were added to the ASB solution to adjust the pH at 2–3. The solution was then heated to 80 °C under vigorous stirring for 5 h to obtain the hydrosols. A quantity of hydroxyethyl cellulose (HEC) (from 0 to 100 wt%) was then added to the hydrosol solution to obtain the wet gel, which was poured into the trays of the laboratory freeze dryer (Lyoquest-85, Telstar Co. Ltd) to synthesise the aerogels. After an exhaustive analysis of the operating conditions of freeze-drying process (freezing time, vacuum pressure, freeze-drying temperature and drying time), aerogels were obtained. Once wet gel was introduced into the freeze-drying trays, it was frozen for 6 h at −60 °C and, then, sublimated under vacuum for 45 h.

Characterisation of hydroxyethyl cellulose/alumina-based aerogels (CAAs)

The morphology and pore distribution of the aerogels were measured using a Phenom-ProX scanning electron microscope supplied by Phenom World. This equipment has an energy-dispersive X-ray spectroscopy (EDS) probe to determine the average composition of the aerogels.

The internal structure of the aerogels was analysed using X-ray microtomography (SkyScan 1275, Bruker). Furthermore, porosity characterisation was performed using CT-Analyser. The thermal conductivity of hydroxyethyl cellulose-reinforced alumina-based aerogels was measured using KD2 Pro Thermal Properties Analyser (Decagon Devices).

The pore size distribution and density of the aerogels were analysed using a Mercury Porosimeter (QuantachomePoremaster), which is an automatic pore size analyser. The sample was cut with a dimension of 1 × 3 cm ($w \times h$), and it was introduced into the cells of the porosimeter. The methodology is based on the mercury injection under pressure, and the mercury volume registration is related to the pore size distribution. The porosimeter allows to determine the size and pore distribution between 950 μm and 6.4 nm by means of pressure generation system, in which the pressure rank varies between vacuum and 33000 psi.

Dynamic mechanical measurements were carried out in order to determine the Young's modulus by means of stress–strain analysis (compression mode) using a DMA 1 STARe System (Mettler Toledo). The DMA was operated with a force ranging from 0 to 2 N and a force rate of 0.05 N/min.

Thermogravimetric analysis (TGA) was carried out to study the thermal behaviour of the aerogels synthesised. A thermal analyser (Mettler Toledo TGA/DSC 1 STARe System) was used at a heating rate of 10 °C/min to perform the combustion and pyrolysis processes. Combustion was carried out under an air atmosphere and pyrolysis under a nitrogen atmosphere using a gas flow of 100 NmL/min.

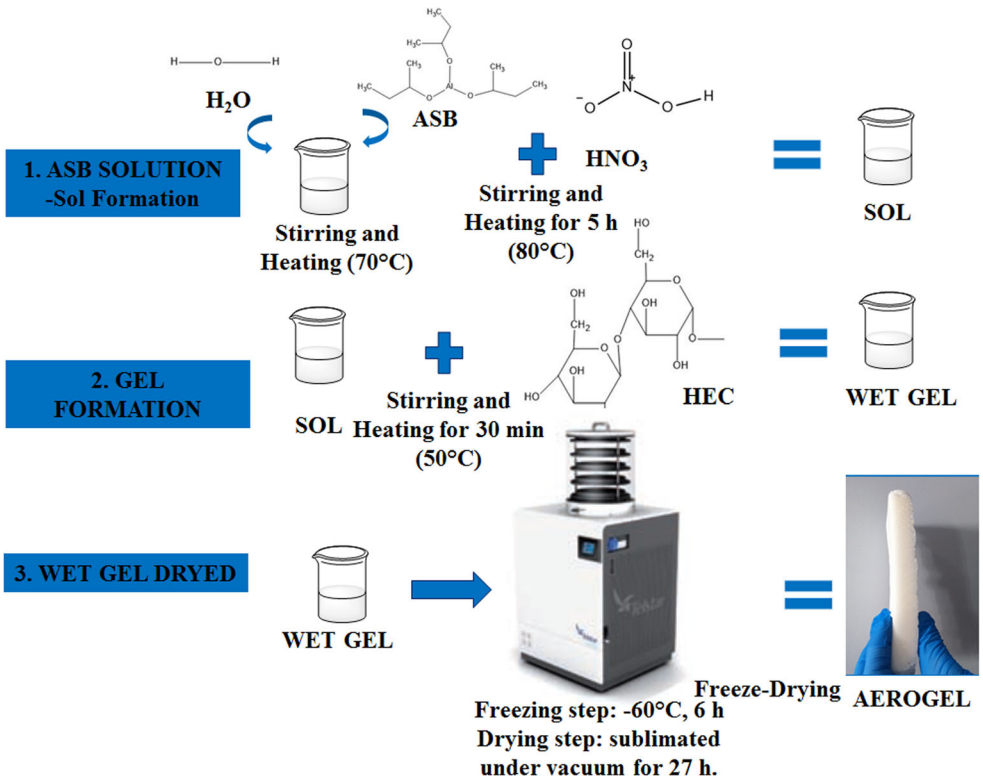

Figure 1 Experimental synthesis of hydroxyethyl cellulose/alumina-based aerogels.

Table 1 Denomination of obtained hydroxyethyl cellulose/alumina-based aerogels

Sample	HEC/ASB solution × 100 (%)
CAA0	0
CAA5	5
CAA10	10
CAA15	15
CAA20	20
CAA30	30
CAA40	40
CAA50	50

Results and discussion

Synthesis of hydroxyethyl cellulose/alumina-based aerogels

Hydroxyethyl cellulose/alumina-based aerogels were successfully obtained by means of the procedure depicted in Fig. 1. It is necessary to optimise the operating conditions of the freeze-drying process before studying the effect of HEC/ASB solution mass ratio on the properties of the aerogels. Thus, CAA20 was selected as example sample to optimise the freeze-drying method. CAA20 with undesirable characteristics was obtained initially, as shown in Fig. 2. This fact was attributed to the freeze-drying conditions used. As reported in several recent studies, [18, 30, 31] operational parameters such as freezing conditions and operation time have a marked effect on the internal structure of the materials obtained.

Therefore, several experiments were carried out varying the operation conditions of freeze-drying process until aerogels with the appropriate appearance and physical properties were obtained (Fig. 3). As can clearly be seen from the SEM micrograph of the aerogel (Fig. 3b), the porous structure is the result of the whole drying of the gel. Similarly, the aerogel structure is non-ordered and highly porous. In addition, bridges formation due to the hydroxyethyl cellulose presence is also observed [28].

A mercury porosimetry analysis was carried out in order to analyse the pore size distribution (PSD) of the resulted aerogels (Fig. 4). These materials are very porous and have a monomodal wide PSD. The vertical coordinates means the mercury volume that is introduced into the pores of the sample. Figure 4

Figure 2 CAA20 sample obtained with non-desirable properties after 15 h of sublimation under vacuum.

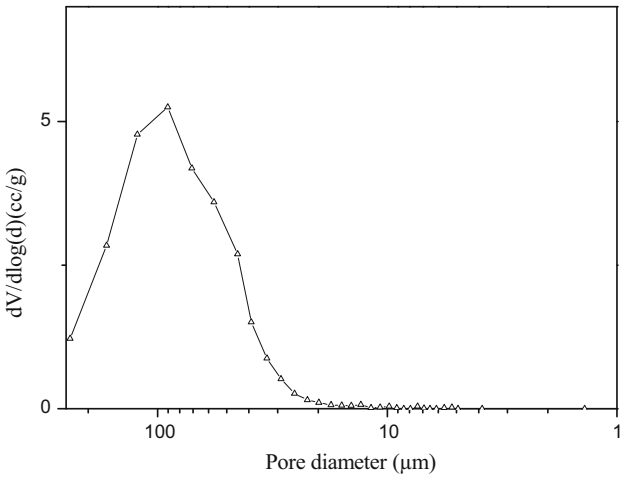

Figure 4 Pore size distribution of CAA20 sample synthesised successfully.

shows the PSD of a sample with pores of different sizes, but the pores that take up more volume are those measures 100 μm of diameter. Furthermore, these materials show low thermal conductivities (0.048 W/m K). Therefore, they are appropriate candidates to be used as building insulation materials.

As the building industry requires aerogels to exhibit adequate mechanical properties, reinforcing agents such as HEC were subsequently added to the matrix in order to enhance its mechanical characteristics. In addition, the effect of the incorporation of different amounts of HEC was evaluated to determine the optimal value for producing aerogels with improved physical and mechanical properties in comparison with conventional aerogels.

Effect of HEC/ASB solution mass ratio on the morphological properties of aerogels

Figure 5 shows the pore size distribution of the synthesised hydroxyethyl cellulose/alumina-based aerogels obtained using different HEC/ASB solution mass ratios. It can clearly be seen that the amount of HEC had a significant effect on the porosity of the resulting aerogels, the higher the HEC/ASB solution mass ratios, the smaller the pore diameters were. Likewise, the peak height of the PSD profiles decreased and the peak width increased with increasing HEC/ASB solution mass ratio. The peak height (intruded volume into the pores sample) of the PSD decreased with the addition of HEC due to its incorporation into the matrix resulted in small pores and compact structures.

In addition, all samples showed a monomodal PSD, with pore sizes ranging from 5 to 250 μm. These findings can be attributed to the presence of HEC in the ASB matrix. According to He et al. [29], HEC fibres restrain ice-crystal growth during the freezing process. Furthermore, the HEC excess fills the ASB network pores [28]. Thus, compact structures are formed when increasing the amount of HEC into ASB matrix due to crosslinking of the long HEC fibres. These findings are in good agreement with the SEM micrographs shown in Fig. 6.

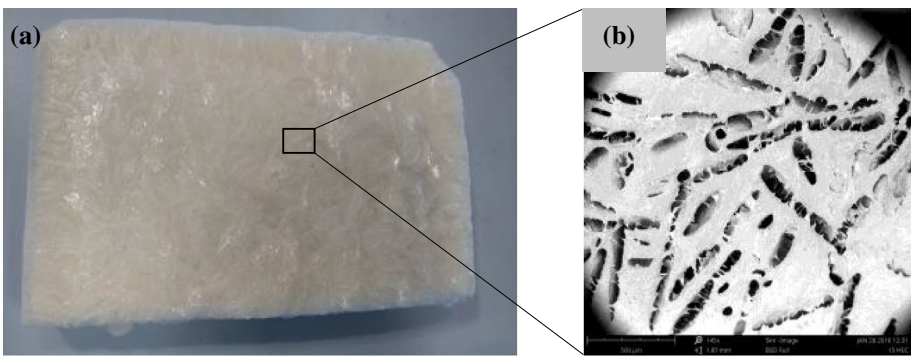

Figure 3 CAA20 sample obtained successfully; **a** image of aerogel; **b** SEM image of the synthesised aerogel.

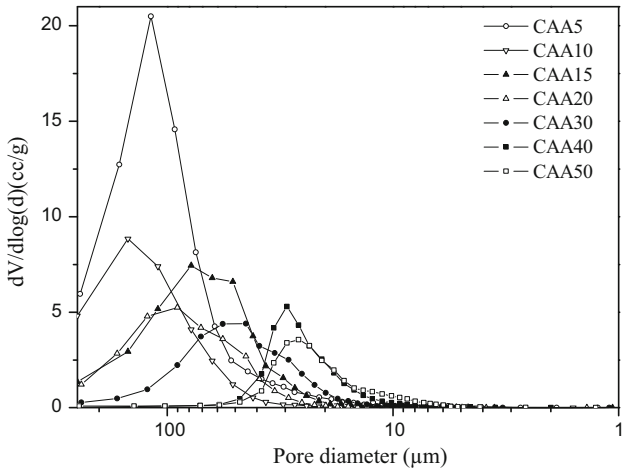

Figure 5 Pore size distribution of cellulose-reinforced-based aerogels.

Figure 6 shows SEM micrographs of synthesised hydroxyethyl cellulose/alumina-based aerogels using different HEC/ASB solution mass ratios. Higher-magnification micrographs were also obtained in order to analyse the pore structure of the synthesised aerogels in detail. The incorporation of HEC has a marked effect on the morphology and pore sizes of the resulting hydroxyethyl cellulose/alumina-based aerogels. Thus, the formation of lamellar porous macrostructures and almost homogeneous structures was observed when the HEC/ASB solution mass ratio was lower than 20%.

Furthermore, the addition of HEC results in a change on the pore morphology to that of a homogeneous spherical pore, whereas the network appears denser in the SEM micrographs. He et al. [29] noted that HEC fibres reinforced alumina lamellas via the ribs between adjacent parallel lamellas, thus resulting in compact structures with small pore sizes.

As shown in Fig. 6, a decrease in the aerogel porosity is also observed at higher HEC concentrations. Thus, samples CAA5 and CAA20 exhibited a flake-like appearance with a PSD from 50 to 200 μm. However, samples CAA30 and CAA50 presented deformed and thicker structures with a small pore size. According to Seanier et al. [24], strong cellulose nanoparticle interactions yield assemblies in both liquid and solid states. The formation of cellulose nanocrystals induces the elimination of some of the macropores, thus aerogels showing networks with small pore sizes.

In order to analyse in detail the internal structure of the synthesised aerogels, X-ray microtomography was carried out for sample CAA20. The volume rendering programme CTvox displays set of reconstructed slices as a realistic 3D object; Fig. 7 shows three orthogonal reconstructed slices through the sample. Sample CAA20 presented a laminar pore structure. In addition, a 3D morphological analysis was performed (Fig. 8). The pore structure of obtained aerogel can be observed in detail, and the resulted porosity of this analysis was 85%.

The textural and structural properties of synthesised aerogels are provided in Table 2. As has been discussed above, the apparent density increased and the mercury volume intrusion and the pore diameter mode decreased with HEC addition.

According to these results, HEC incorporation has a marked impact on the internal pore structure of prepared aerogels using the freeze-drying method.

Effect of HEC/ASB solution mass ratio on the mechanical properties of aerogels

A stress–strain analysis was carried out to determine the relationship between microstructural changes and mechanical properties. The mechanical properties of aerogels are highly relevant for many applications, especially their use in the building industry. The influence of the HEC/ASB solution mass ratio on the mechanical properties of the resulting aerogels was also evaluated. The synthesised aerogels in the absence of HEC could not be tested as they did not form a monolith. This is due to the absence of HEC fibres that enhance the linkage degree of the lamellar structure [29].

Figure 9 presents typical stress–strain curves for the aerogels obtained using different HEC/ASB solution mass ratios. The stress–strain curve for each aerogel is unique and is the result of compressive loading.

Each curve represents the experienced strain when small stresses (from 0 to 2 N) are applied. The elastic or Young's modulus was determined from the slope of the linear part of the stress–strain curve, where an elastic behaviour of the aerogels was observed (Table 3).

The HEC/ASB solution mass ratio has a marked effect on the mechanical properties of hydroxyethyl cellulose/alumina-based aerogels, with the slope of the different curves increasing as the quantity of HEC increases. Consequently, the elastic or Young's

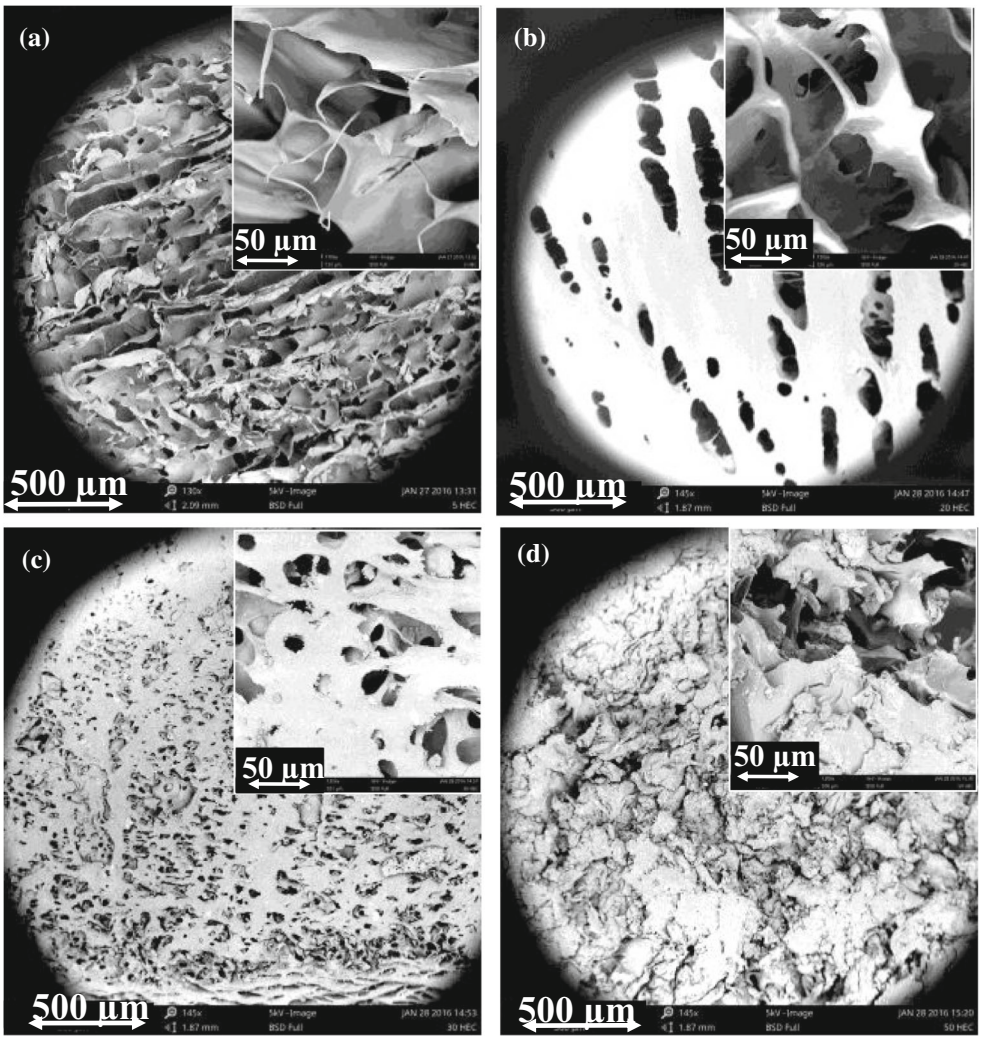

Figure 6 SEM micrographs of samples synthesised using different percentage of HEC. **a** CAA5; **b** CAA20; **c** CAA30; and **d** CAA50.

modulus undergoes a marked increase from 0.014 to 0.209 MPa (Table 3).

The obtained results demonstrate an effective mechanical enhancement with the addition of HEC, leading to a relatively strong alumina skeleton.

Effect of HEC/ASB solution mass ratio on the thermal properties of aerogels

The thermal stability of hydroxyethyl cellulose/alumina-based aerogels synthesised using different HEC/ASB solution mass ratios was evaluated by means of TGA analysis (pyrolysis and combustion processes, Fig. 10a, b, respectively). The insets in Fig. 10a and b show pyrolysis and combustion processes, respectively, for the aerogel synthesised in the absence of hydroxyethyl cellulose (sample CAA0).

Figure 10a shows the weight loss curves obtained through pyrolysis of synthesised aerogels using different HEC/ASB solution mass ratios. As can clearly be seen, these aerogels show different thermal decomposition profiles depending on the amount of HEC incorporation. Moreover, samples CAA10, CAA20 and CAA50 exhibit three thermal decomposition stages. The first stage (25–200 °C) is associated with a small weight loss due to dehydration. This study revealed that these samples contain around 2.5–5 wt% of water, which is evaporated upon heating to 100 °C. The second stage, which ranges from 200 to 400 °C (200–350 °C for samples CAA20, CAA50 and 200–400 °C for CAA10), represents the main weight loss in the pyrolysis process and is due to the decomposition of the HEC groups, which start to degrade at temperatures above 220 °C [29]. The

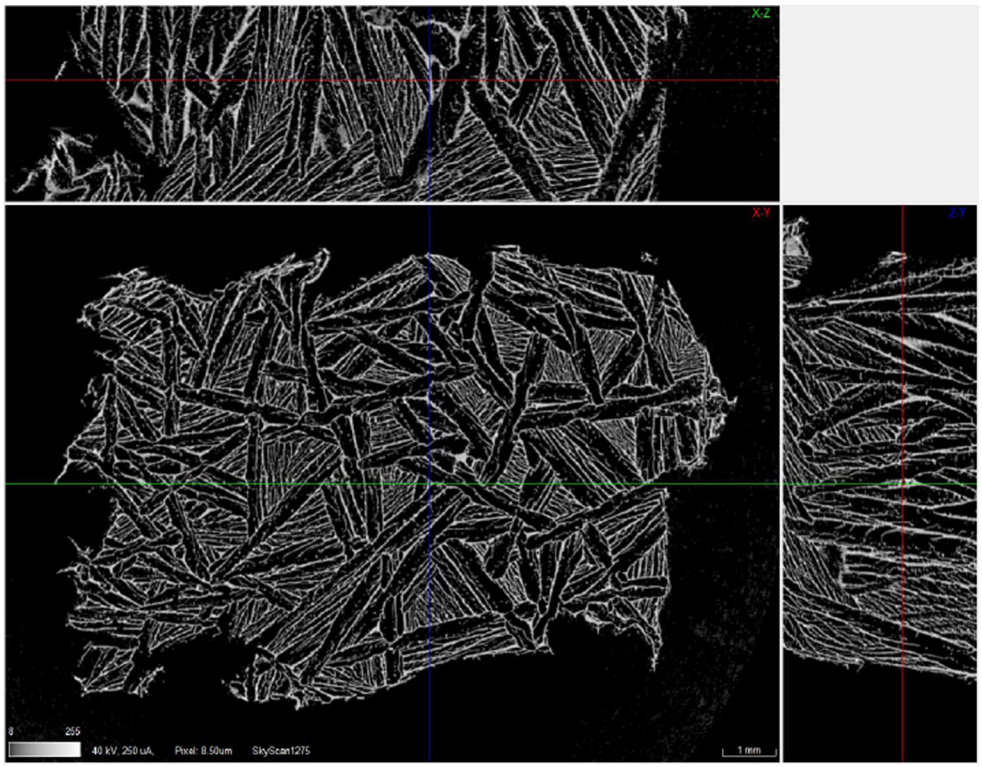

Figure 7 Three orthogonal reconstructed slices through the sample CAA20 (from DataViewer).

pyrolysis results demonstrate that this second decomposition stage shifts to lower temperatures when increasing the amount of HEC (the initial decomposition temperatures of CAA10, CAA20 and CAA50 were 250, 240 and 220 °C, respectively). This fact can be explained by the contribution of the HEC groups, which decreases the thermal degradation temperature [32, 33]. This temperature is lower than the thermal degradation one for cellulose due to the destruction in the crystalline region. The final stage (350–500 °C; 350–450 °C for samples CAA20, CAA50 and 400–500 °C for sample CAA10) can be attributed to the degradation of alumina, as shown in the inset of Fig. 10a. Finally, at the end of this stage, the weight loss becomes almost constant above 500 °C. As shown in Fig. 10a, the incorporation of HEC increased the pyrolysis residue [32].

Figure 10b shows the combustion process for samples obtained using different HEC/ASB solution mass ratios. The analysed samples show different thermal properties depending on the HEC amount. Therefore, samples CAA10, CAA20 and CAA50 present four thermal decomposition stages. The first stage, which occurs in the range 25–200 °C, corresponds to the loss of water. The second stage, which ranges from 200 to 350 °C and is characterised by a major weight loss, involves the intramolecular dehydration of HEC. The third stage (350–540 °C; 350–420 °C for samples CAA10, CAA20 and 350–540 °C for sample CAA50) corresponds to the decomposition of HEC and alumina, as shown in the inset of Fig. 10b. The differences observed can be attributed to the effects of the HEC groups. Finally, the last decomposition stage (420–600 °C; 420–500 °C for samples CAA10, CAA20 and 540–600 °C for sample CAA50) corresponds to an oxidation process. At the end of this stage, the weight loss becomes almost constant above 500 °C, for samples CAA10 and CAA20, or 600 °C, for sample CAA50. In addition, the residue is principally attributed to alumina and the oxidised residues [29].

It has been demonstrated that the HEC/ASB solution mass ratio has an important effect on the thermal stability of samples and that the second decomposition stage shifts to lower temperatures when increasing the quantity of HEC. Thus, the most stable aerogel was sample CAA10, having an initial decomposition temperature of 250 °C. Hydroxyethyl

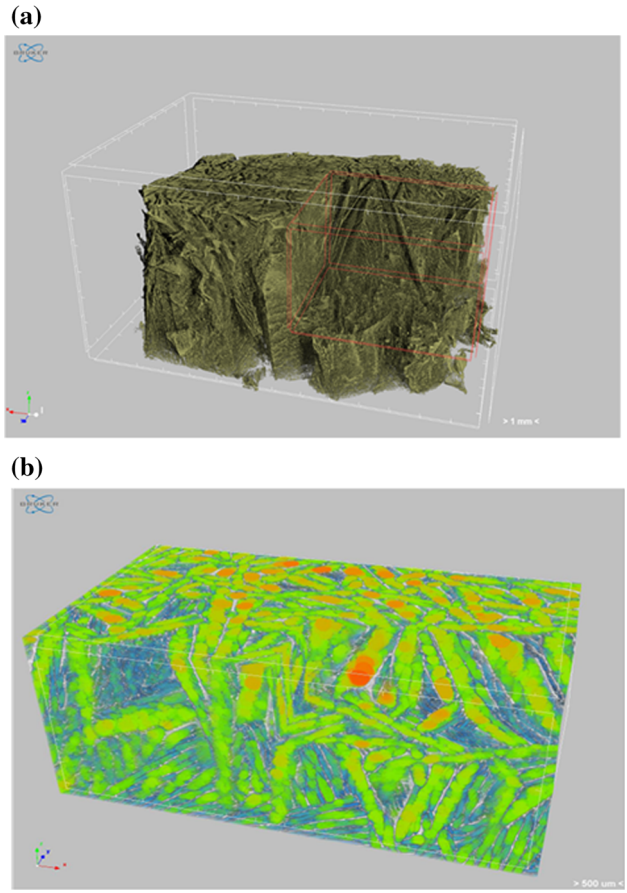

Figure 8 **a** 3D analysis of CAA20. Volume rendering image of the volume of interest (VOI) (from CTvox); **b** volume rendering image of the VOI with the structure separation data added in colour (from CTvox).

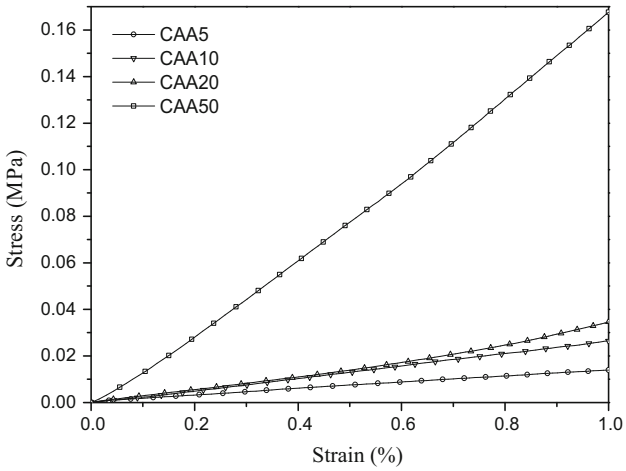

Figure 9 Stress–strain of samples synthesised using different percentages of HEC.

Table 3 Elastic or Young's modulus of samples synthesised using different HEC/ASB solution mass ratios

Sample	Young's modulus (MPa)
CAA5	0.014 ± 0.003
CAA10	0.029 ± 0.003
CAA20	0.030 ± 0.003
CAA50	0.209 ± 0.003

cellulose/alumina-based aerogels have better thermal behaviour than aerogels obtained in previous works, which initial decomposition temperature was ranged from 180 to 250 °C [17]. A thermal conductivity analysis was also carried out to corroborate the thermal insulation properties of these materials. After performing several measurements in all samples, the thermal conductivity values varied between 0.044 and 0.051 W/m K. These small observed differences could be attributed to the experimental error of the KD2 Pro Thermal Properties Analyser. These small values of thermal

Table 2 Textural properties of samples synthesised using different HEC/ASB solution mass ratios

Sample	Apparent density (g/L)	Hg volume intrusion (cm^3/g)	Pore diameter mode (μm)[a]	Pore diameter mean (μm)[b]
CAA5	106.4	8.51	114.8	92.6
CAA10	180.2	4.29	125.3	4.09
CAA15	203.7	4.24	76.24	1.48
CAA20	257.2	3.07	96.13	1.02
CAA30	330.2	2.58	47.08	0.47
CAA40	447.0	1.58	29.94	0.73
CAA50	496.7	1.38	26.80	0.83

In reference to mercury volume

[a]Pore diameter mode: pore diameter that takes up more volume

[b]Pore diameter mean: pore diameter that takes up a mercury volume equal to total intrusion volume mean

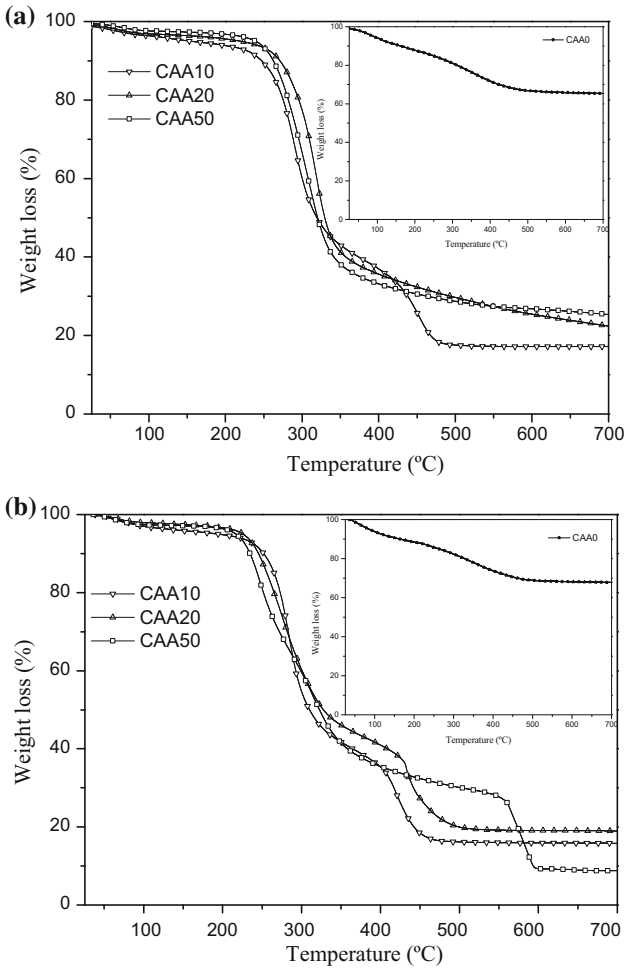

Figure 10 TGA analysis: **a** pyrolysis of samples CAA10, CAA20 and CAA50; inset: pyrolysis of sample CAA0 and **b** combustion of samples CAA10, CAA20 and CAA50; inset: combustion of sample CAA0.

conductivity are similar as those detected in sample synthesised previously, which range varied between 0.03 and 0.06 W/m K [17]. The main trouble when aerogels are used as building insulation arises due their fragility. Therefore, this study has confirmed that HEC could be a potential strengthening material to overcome this drawback. Consequently, the obtained aerogels in this study could be considered for their use as thermal insulating materials in different industrial applications.

Conclusions

Hydroxyethyl cellulose/alumina-based aerogels have been successfully synthesised using an environmentally friendly and low-cost process. The resulting aerogels have a monomodal pore size distribution with the formation of bridges due to the hydroxyethyl cellulose interactions. This reinforcing agent allows the mechanical properties of the aerogels to be improved. Moreover, high HEC/ASB solution mass ratios have been found to result in a higher density and lower porosity and that compact structures with a small pore size are obtained. Furthermore, it has been demonstrated that the incorporation of HEC significantly improves the mechanical properties of the resulting aerogels, which show different thermal behaviours depending on the HEC amount. All samples exhibit low thermal conductivities. These hydroxyethyl cellulose/alumina-based aerogels could, therefore, find potential future applications in the building industry due to their excellent physical and mechanical characteristics and the fact that their synthesis is suitable for scale-up.

Acknowledgements

The present work was performed within the framework of the NANOLEAP project. This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 646397.

References

[1] Bryning MB, Milkie DE, Islam MF, Hough LA, Kikkawa JM, Yodh AG (2007) Carbon nanotube aerogels. Adv Mater 19:661–664

[2] Cao F, Ren L, Li X (2015) Synthesis of high strength monolithic alumina aerogels at ambient pressure. RSC Adv 5:18025–18028

[3] He S, Zhang Y, Shi X, Bi Y, Luo X, Zhang L (2015) Rapid and facile synthesis of a low-cost monolithic polyamide aerogel via sol–gel technology. Mater Lett 144:82–84

[4] Han Y, Zhang X, Wu X, Lu C (2015) Flame retardant, heat insulating cellulose aerogels from waste cotton fabrics by in situ formation of magnesium hydroxide nanoparticles in cellulose gel nanostructures. ACS Sustain Chem Eng 3:1853–1859

[5] Xu X, Zhou J, Nagaraju DH, Jiang L, Marinov VR, Lubineau G, Alshareef HN, Myungkeun Oh (2015) Flexible, highly graphitized carbon aerogels based on bacterial cellulose/lignin: catalyst-free synthesis and its application in energy storage devices. Adv Funct Mater 25:3193–3202

[6] Nemoto J, Saito T, Isogai A (2015) Simple freeze-drying procedure for producing nanocellulose aerogel-containing, high-performance air filters. ACS Appl Mater Interfaces 7:19809–19815

[7] Fickler S, Milow B, Ratke L, Schnellenbach-Held M, Welsch T (2015) Development of high performance aerogel concrete. Energy Procedia 78:406–411

[8] Pierre AC, Pajonk GM (2002) Chemistry of aerogels and their applications. Chem Rev 102:4243–4265

[9] Randall JP, Meador MAB, Jana SC (2011) Tailoring mechanical properties of aerogels for aerospace applications. ACS Appl Mater Interfaces 3:613–626

[10] Jelle BP (2011) Traditional state-of-the-art and future thermal building insulation materials and solutions—properties, requirements and possibilities. Energy Build 43:2549–2563

[11] Baetens R, Jelle BP, Gustavsen A (2011) Aerogel insulation for building applications: a state-of-the-art review. Energy Build 43:761–769

[12] Zhu M, Ji R, Li Z, Wang H, Liu L, Zhang Z (2016) Preparation of glass ceramic foams for thermal insulation applications from coal fly ash and waste glass. Constr Build Mater 112:398–405

[13] Kumar A, Staněk K, Ryparová P, Hajek P, Tywoniak J (2016) Hydrophobic treatment of wood fibrous thermal insulator by octadecyltrichlorosilane and its influence on hygric properties and resistance against moulds. Compos Part B Eng 106:285–293

[14] Korjenic A, Petránek V, Zach J, Hroudová J (2011) Development and performance evaluation of natural thermal-insulation materials composed of renewable resources. Energy Build 43(9):2518–2523

[15] Asdrubali F, D'Alessandro F, Schiavoni S (2015) A review of unconventional sustainable building insulation materials. Sustain Mater Technol 4:1–17

[16] Sánchez-Silva L, Víctor-Román S, Romero A, Gracia I, Valverde JL (2014) Tailor-made aerogels based on carbon nanofibers by freeze-drying. Sci Adv Mater 6:665–673

[17] Víctor-Román S, Simón-Herrero C, Romero A, Gracia I, Valverde JL, Sánchez-Silva L (2015) CNF-reinforced polymer aerogels: influence of the synthesis variables and economic evaluation. Chem Eng J 262:691–701

[18] Simón-Herrero C, Caminero-Huertas S, Romero A, Valverde JL, Sánchez-Silva L (2016) Effects of freeze-drying conditions on aerogel properties. J Mater Sci 51:8977–8985. doi:10.1007/s10853-016-0148-5

[19] Liu R, Xu T, Wang C (2016) A review of fabrication strategies and applications of porous ceramics prepared by freeze-casting method. Ceram Int 42:2907–2925

[20] Zu G, Shen J, Wei X, Ni X, Zhang Z, Wang J, Liu G (2011) Preparation and characterization of monolithic alumina aerogels. J Non-Cryst Solids 357:2903–2906

[21] Zu G, Shen J, Zou L, Wang W, Lian Y, Zhang Z, Du A (2013) Nanoengineering super heat-resistant, strong alumina aerogels. Chem Mater 25:4757–4764

[22] Eichhorn SJ, Dufresne A, Aranguren M, Marcovich NE, Capadona JR, Rowan SJ, Weder C, Thielemans W, Roman M, Renneckar S, Gindl W, Veigel S, Keckes J, Yano H, Abe K, Nogi M, Nakagaito AN, Mangalam A, Simonsen J, Benight AS, Bismarck A, Berglund LA, Peijs T (2010) Review: current international research into cellulose nanofibers and nanocomposites. J Mater Sci 45:1–33. doi:10.1007/s10853-009-3874-0

[23] Moon RJ, Martini A, Nairn J, Simonsen J, Youngblood J (2011) Cellulose nanomaterials review: structure, properties and nanocomposites. Chem Soc Rev 40:3941–3994

[24] Seantier B, Bendahou D, Bendahou A, Grohens Y, Kaddami H (2016) Multi-scale cellulose based new bio-aerogel composites with thermal super-insulating and tunable mechanical properties. Carbohydr Polym 138:335–348

[25] Zhai T, Zheng Q, Cai Z, Turng L, Xia H, Gong S (2015) Poly(vinyl alcohol)/cellulose nanofibril hybrid aerogels with an aligned microtubular porous structure and their composites with polydimethylsiloxane. ACS Appl Mater Interfaces 7:7436–7444

[26] Zulkifli FH, Hussain FSJ, Rasad MSBA, Yusoff MM (2014) In vitro degradation study of novel HEC/PVA/collagen nanofibrous scaffold for skin tissue engineering applications. Polym Degrad Stab 110:473–481

[27] Chahal S, Hussain FSJ, Kumar A, Rasad MSBA, Yusoff MM (2016) Fabrication, characterization and in vitro biocompatibility of electrospun hydroxyethylcellulose/poly(vinyl)alcohol nanofibrous composite biomaterial for bone tissue engineering. Chem Eng Sci 144:17–29

[28] Sehaqui H (2011) Nanofiber networks, aerogels and biocomposites based on nanofibrillated cellulose from wood. Ph.D. Thesis, KTH School of Chemical Science and Engineering, Sweden

[29] He F, Sui C, He X, Li M (2015) Facile synthesis of strong alumina-cellulose aerogels by a freeze-drying method. Mater Lett 152:9–12

[30] Patapoff TW, Overcashier DE (2002) The importance of freezing on lyophilisation cycle development. Biopharm 3:16–21

[31] Wang Y, Gawryla MD, Schiraldi DA (2013) Effects of freezing conditions on the morphology and mechanical

properties of clay and polymer/clay aerogels. J Appl Polym Sci 129:1637–1641

[32] Li X-G, Huang M-R, Bai H (1999) Thermal decomposition of cellulose ethers. J Appl Polym Sci 73:2927–2936

[33] El Idrissi A, El Barkany S, Amhamdi H, Maaroufi A-K (2013) Synthesis and characterization of the new cellulose derivative films based on the hydroxyethyl cellulose prepared from esparto "stipatenacissima" cellulose of Eastern Morocco. II. Esterification with acyl chlorides in a homogeneous medium. J Appl Polym Sci 127:3633–3644