PVA/ nanoclay/ graphene oxide aerogels with enhanced sound absorption properties

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Abstract

Aerogels based on a ternary system of polyvinyl alcohol (PVA), nanoclay and thermally reduced graphene oxide (trGO) have been synthesised at pilot plant scale using an environmentally friendly freeze-drying method. In the present work, the influence of the trGO addition on the physical, thermal and acoustic properties of the resulted aerogels has been evaluated. The trGO incorporation into the PVA/ nanoclay matrix resulted in pore diameter decrease. In addition, trGO addition allowed to improve thermal stability of the aerogels. On the other hand, the introduction of the trGO resulted in improvements of the sound absorption coefficient of the aerogels. This process opens new opportunities to produce materials with exceptional properties as thermal insulators (resulting values of the thermal conductivities ranging from 0.0255 to 0.0289 W/m·K) with enhanced sound absorption properties.

Keywords: *building insulation; reduced graphene oxide; freeze-drying, sound absorption coefficent, nanoclay*

1. Introduction

Energy consumption in the building industry is a very important part of the total energy demand of an industrialized country [1]. Thus, one of the most important goals in the construction of future buildings is the reduction of the energy consumption through their cycle life [2].

Thermal insulation materials are materials that retard the rate of heat flow as a consequence of their high thermal resistance. The use of insulation materials in buildings has several direct advantages such as acoustical comfort improvements and increasing of both energy savings and buildings lifetime; and indirect ones such as: conserving natural resources and decreasing of pollutants emissions. Furthermore, proper design and installation of thermal insulation materials can prevent vapour condensation and flame immigration in case of fire [3]. These materials have to fulfil not only thermal characteristics but also acoustic requirements for sound insulation since noise is recognised as a serious health hazard [4] and a less controlled environmental pollutant [5]. Noise exposure may cause numerous physiological and psychological effects. The frequency range for human hearing is from 20 Hz to 20000 Hz.

To mitigate the noise, several techniques classified as passive (based on noise reduction by energy absorption) and active methods (based on noise reduction by reducing source strength or modifying acoustic field) have been developed [4]. Medium and high frequencies require the use of sound absorption materials. These materials absorb most of the sound energy striking them and reflect very little [7]. It is known that porous materials present very good behaviour as sound absorption materials [7, 8]. When porous materials are exposed to incident sound waves, the air particles at the surface and within the pores of the materials are forced to vibrate and lose part of their original energy due to some of the energy of the air particles is converted into heat. This behaviour is due to the energy loss (thermal and viscous) occurs in boundary layers in the vicinity of the pore walls. In this regard, aerogels, as very high porous and high surface area materials, are being considered as promising materials to be used in noise reduction [9, 10].

Due to their non-toxicity and biodegradability, polyvinyl alcohol (PVA) based composites have shown great interests in many fields [11] despite of their relatively high flammability [12]. The common solution to improve the flame retardancy of PVA is the incorporation of flame retardants into the polymeric matrix by physical mixing or chemical reactions. Chlorinated and brominated flame retardants have been the most widely used additives to improve the flame retardancy of polymers. However, these flame retardants must be replaced with non- halogenated compounds due to the high toxicity of the products generated during fire. In this regard, nanoclays, which own high surface area in a well-dispersed nanocomposite, could be good candidates to overcome this issue since they can improve barrier properties which effectively impedes mass and heat transfer [13, 14, 15]. Furthermore, nanoclays also promote the formation of chars, which are insulators and act as a barrier to flame propagation.

On the other hand, the mixing of a water soluble polymer solution into the clay dispersion allows to get better mechanical properties of the resulting materials. In addition, it is also known that the addition of fillers as nanoclays leads to the creation of more paths into the aerogel structure for passing sound waves which allows the material to absorb more sound [16].

In addition, the negative effect of the moisture on the acoustic absorption properties of the aerogel can be reduced by incorporating additives. In this sense, thermally reduced graphene oxide (trGO) could be a good candidate due to the occurrence of polar functional groups on the oxidized graphene layers generated during the reduction process, which could adsorb water molecules existing in the surroundings [17, 18]. Furthermore, trGO could help to create optimal air-flow resistance and tortuosity into the aerogel that could improve the acoustic absorption [17], and enhance the thermal stability of the polymer matrix of the material [19].

Finally, the internal structure influences considerably their acoustic properties. Previous works studied the effect of the morphological properties on the acoustical behaviour of materials. The heterogeneities scales and the presence of sorption in nanometric pores resulted in a decrease of the effective low frequency sound speed [20]. Furthermore, it was demonstrated that sorption effects occurring in pores modify the macroscopic mass balance and this modification accounts for by the dynamic compressibility of the saturating fluid, resulting in a lower sound speed and higher sound attenuation in the material [21].

On the other hand, other researchers have studied the effect of morphological properties of materials on the sound absorption characteristics of materials [22]. It was observed that material comprehensive sound absorption (NRC) improved with the increase on the air flow resistivity until a certain value, when NRC start to decrease. This behavior was due to the material internal pores were more tortuous and smaller. However, the air flow resistivity did not increase noticeably because of the pores obstruction, resulting in a decrease of the sound absorption [22].

The aim of the present work was to develop aerogels based on a ternary system (PVA, nanoclay and trGO) using a freeze-drying process at pilot plant scale to be used as sound absorption materials. Furthermore, the influence of the trGO addition on the properties of PVA/nanoclay aerogels was analysed in detail.

2. EXPERIMENTAL

2.1. Materials

Polyvinyl alcohol (10–98, Mw 61,000 g/mol) of analytical grade was supplied by Fluka Chemical Co. Hydrophilic bentonite nanoclay was supplied by Sigma-Aldrich Co., Ltd. Thermally reduced graphene oxide (trGO) was obtained according to the procedure described by Lavin-López et al. [23]. Water was purified by distillation followed by deionization with ion-exchange resins.

2.2. Preparation of PVA/nanoclay/trGO aerogels at pilot plant scale

A solution of polyvinyl alcohol in deionized water (2.5 wt. %) at 81ºC was prepared under mechanical stirring. A solution of nanoclay (3 wt. % related to the total amount of polymer) was prepared using an ultrasonic bath at room temperature for 1 h. Different amounts of the trGO suspensions were prepared by sonication (from 0.05 to 0.5 wt. % related to the amount of polymer + nanoclay) and, subsequently, slowly added to the nanoclay suspension. The trGO/nanoclay suspension was stirred and then added to the PVA solution under vigorous stirring. After that, the mixture was poured into the trays of the freeze-drying pilot plant (dimensions of 14.5 cm (long) x 15 cm (high) x 2 cm (wide)), frozen and finally sublimated under vacuum until its complete drying. Table 1 listed the aerogels prepared in this work.

2.3.Characterization of PVA/nanoclay/trGO aerogels

The morphological structure of the aerogels was analysed using a Phenom-ProX scanning electron microscope (SEM) (Phenom World) provided with an energy dispersive X-ray spectroscopy (EDS) probe to determine the average composition of the aerogels. To analyse in detail the pore size of the aerogels, a mercury porosimeter (Quantachrome Poremaster) was used. The mercury intrusion into the pores of the materials when a sufficient pressure is applied was registered as a function of increasing pressure, allowing the generation of their pore size distribution.The measurements were carried out with a pressure range of 0.2 to 30,000 psia, being able to analyse a pore size distribution with pore size range from 1,100 to 0.0064 µm.

Thermal conductivity measurements were carried out using a KD2-PRO thermal conductivity analyser (Decagon Devices). The thermal stability of the synthesized aerogels was measured by using thermogravimetric analysis (TGA) in a thermal analyser (Mettler Toledo TGA/DSC 1 STARe System) under a nitrogen atmosphere (100 NmL/min) with a heating rate of 10 ºC/min under.

The acoustic characterization of the aerogels here prepared was carried out in a traditional impedance tube (Brüel & Kjær) equipped with two microphone locations and a digital frequency analysis system for evaluating the sound absorption coefficient for normal sound incidence (ISO 10534-2) [24]. The environmental parameters of the laboratory (atmospheric pressure, air temperature and relative humidity) were measured before starting each test. Acoustic tests for each sample at the same and different positions inside the tube were repeated at least five times.

3. RESULTS

3.1. Morphological properties of the PVA/nanoclay/trGO aerogels.

The physical aspect of both faces (top and bottom) of the PVA/nanoclay/trGO aerogels looked different (Figure 1). The darker colour observed for the bottom face was due to the larger concentration of trGO in that face. SEM analyses were carried out to study the effect of the trGO incorporation on the morphological characteristics of both faces of the resulting aerogels. Figure 2 shows SEM micrographs for both faces of the aerogels for the samples with the maximum and minimum percentage of trGO (samples 0.05GONPVA and 0.5GONPVA, respectively). As seen from Figure 2a and 2c (Top face), both samples showed a layered structure, typical of PVA/clay aerogels. SEM micrographs of the bottom face of both samples (Figure 2b and 2d) showed more compact structures as a consequence of the higher concentration of trGO. Likewise, magnifications of Figure 2b and 2d showed that sample 0.5GONPVA seemed to be more compact due to it presented a higher concentration of trGO. EDS microanalysis was carried out to corroborate the presence of trGO into the polymeric matrix doped with nanoclays. Figure 2e depicts the obtained results for the sample with the lower trGO amount (sample 0.05GONPVA). Silicon was detected as a consequence of the silicon oxide present in nanoclay. Furthermore, the presence of carbon and oxygen were related to the presence of both PVA and trGO.

Mercury porosimetry analysis was carried out to evaluate the textural properties of the synthesised aerogels (3 measurements per face). Table 2 shows the average values of textural properties of the synthesised aerogels. It was observed that the average pore diameter decreased when the trGO concentration in the samples was increased.

3.2. Thermal properties of the PVA/nanoclay/trGO aerogels.

Thermal conductivity analysis was carried out to determine the thermal properties of the synthesised aerogels. Table 3 lists the thermal conductivity values for all the samples. The presence of trGO did not have a clear influence over the thermal conductivity, which is opposite to some results reported elsewhere for trGO-based composites [25]. This behaviour could be attributed to the small amount of carbonaceous nanomaterial in the polymeric matrix. Average measurement of the thermal conductivity for all the samples here prepared ranged from 0.0255 to 0.0289 W/m·K, thus demonstrating that PVA/nanoclay/trGO aerogels are suitable candidates to be used as building insulation materials due to their low thermal conductivity values [26, 27].

Thermal stability is a very important factor that has to be considered in building insulation materials. Figure 3 shows the weight loss curves for samples NPVA, 0.05GONPVA and

0.5GONPVA as a function of the temperature. TGA data, including the decomposition temperatures at 10% weight loss ($T_{d10\%}$), at 50% weight loss ($T_{d50\%}$) and the weight loss at 100ºC, are listed in Table 4. All samples presented three decomposition steps, typically associated to the presence of PVA. The first one, which occurred in the range of 25-100°C, was associated to the loss of water. The second decomposition stage, which ranged from 230-500°C, represented the main weight loss in the pyrolysis process and was due to the dehydration and chain scissions reactions of PVA and degradation of residual acetate. Finally, at the end of this stage, the weight loss became almost constant above 500ºC [28]. As shown in Table 4, the incorporation of trGO resulted in a reduction of water content from 2 wt. % for sample NPVA to 0.9wt. % for sample 0.5GONPVA due to the increased hydrophobicity of aerogels as a consequence of the trGO presence [17, 18]. The $T_{d10\%}$ and $T_{d50\%}$ values increased as a consequence of the growing presence of trGO in the aerogel (the higher the trGO content in the aerogel, the higher the thermal their thermal stability of the aerogel were). The enhanced thermal stability of the aerogels was attributed to the high aspect ratio of trGO that prevented the emission of small gaseous molecules during thermal degradation [29]. According to the obtained results, the best thermal stability was obtained with sample 0.5GONPVA.

3.3. Influence of the graphene oxide amount on acoustic properties of the graphene oxide/ nanoclay- based PVA aerogels.

Sound absorption coefficients of PVA/nanoclay/trGO aerogels were measured in order to know their capability of being used as thermal and acoustic insulation materials in buildings. The sound absorption coefficient is defined as the ratio of the absorbed energy by a material to the incident energy [30]. The higher the value of this ratio, the better the absorption is [6]. It is well known that the material thickness plays an important part in the capacity for sound absorption of a given material. According to some authors, the higher the values of material thickness, the higher the value of the sound absorption at frequencies in the range from 100 to 2000 Hz is [6, 30]. Note that the present research has not been focused on the study of the influence of the material thickness on the sound absorption coefficient. That means that it remained constant.

On the other hand, the morphology of the pores in porous materials has an important influence on the value of sound absorption [7]. Porous and fibrous materials are the most efficient acoustic ones [17]. Porous materials have cavities, channels or interstices so that sound waves are able to enter through them. Closed pores are isolated from their neighbours and are less efficient than open pores in absorbing sound energy. However, open pores have continuous channels of communication with the external surface and have a great influence on the sound absorption. The air particles at the surface and within the pores of the material are forced to vibrate and lose part of their original energy due to some of the energy of the air particles is converted into heat [7]. Figure 4 shows the frequency-dependence of sound absorption coefficients for samples NPVA and 0.5GONPVA when they were exposed to incident sound waves. Results showed a better acoustic behaviour of the bottom face of the sample, probably as consequence of the morphology of its pores, with a sound absorption peak at 580 Hz.

Both samples NPVA and 0.5GONPVA exhibited good behaviour as sound absorption materials due to their high porosity. It is known that the addition of fillers, such as nanoclays, into the polymeric matrix increases the value of the sound absorption coefficient as a consequence of their large surface area that create more paths for passing sound waves into the sample structure [16]. Moreover, nanomaterials are considered suitable in the field of noise control because they can contribute to improve the acoustic properties of traditional materials without increasing their weight and size [31, 32].

As listed in Table 5, the incorporation of trGO into the PVA/nanoclay matrix resulted in higher values of the sound absorption coefficient regardless the frequency used, which is associated to an increase of the flow resistance and tortuosity increase [17, 22]. As seen in Figure 4, the peak height (maximum value of the sound absorption coefficient) in the frequency-dependence of the sound absorption curve shifted to lower frequencies with increasing amounts of trGO in the aerogel. Summarizing, PVA/nanoclay/trGO aerogels could be considered promising sound absorption materials if compared to other sound absorption materials (Table 6) due to the higher values of the sound absorption coefficients [10, 33].

4. CONCLUSIONS

Aerogels based on a ternary system of PVA, nanoclay and trGO were successfully synthesised using a freeze-drying process at pilot plant scale. The reduced graphene oxide incorporation into the PVA/nanoclay matrix resulted in a decrease of the average pore diameter. Furthermore, the introduction of trGO into the aerogel improved the thermal stability of the final product as a consequence of the high aspect ratio of the former that prevents the emission of small gaseous molecules during thermal degradation. It was demonstrated that the presence of trGO into the aerogel improved the value of the sound absorption coefficients of the aerogels. This process opens new opportunities to produce materials with exceptional properties as thermal insulator (values of the thermal conductivity from 0.0255 to 0.0289 W/m·K) with enhanced sound absorption properties.

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REFERENCES

[1] P. Ricciardi, E. Belloni, F. Cotana, Innovative panels with recycled materials: Thermal and acoustic performance and Life Cycle Assessment, Appl. Energ. 134 (2014) 150–162.

[2] F. Asdrubali, F. D' Alessandro, S.Schiavoni, A review of unconventional sustainable building insulation materials, Sustainable Materials and Technologies 4 (2015) 1–17.

[3] M.S. Al-Homoud, Performance characteristics and practical applications of common building thermal insulation materials, Build. Enviro. 40 (2005) 353–366.

[4] M. Azimi, Noise Reduction in Buildings Using Sound Absorbing Materials, J Archit Eng Tech 6 (2) (2017) doi: 10.4172/2168-9717.1000198

[5] J. Feng, D. Le, S.T. Nguyen, V. Tan Chin Niena, D. Jewell, H. M. Duong, Silica–cellulose hybrid aerogels for thermal and acoustic insulation applications, Colloids and Surfaces A: Physicochem. Eng. Aspects 506 (2016) 298–305.

[6] M. A. Kuczmarski, J.C. Johnston, Acoustic Absorption in Porous Materials, NASA/TM—(2011)-216995.

[7] J. P. Arenas, M.J. Crocker, Recent Trends in Porous Sound-Absorbing Materials, 2010.

[8] M.J. Crocker, J.P. Arenas, Use of Sound-Absorbing Materials, Chapter 57 in Handbook of Noise and Vibration Control (M.J. Crocker, Ed.), John Wiley and Sons, New York, 2007.

[9]C.R. Sangam, Are View of Aerogels Applications in Buildings, IJTARME 2 (4) (2013) 85-90.

[10] K. Wha Oh, Duk Ki Kim, S. H. Kim, Ultra-porous Flexible PET/Aerogel Blanket for Sound Absorption and Thermal Insulation, Fibers and Polymers 10 (5) (2009) 731-737.

[11] C. Li, Y. Li, X. She, J. Vongsvivut, J. Li, F. She, W. Gao, L. Kong, Reinforcement and deformation behaviors of polyvinyl alcohol/ graphene/montmorillonite clay composites, Compos. Sci. Technol. 118 (2015) 1-8.

[12] F. Laoutid , L. Bonnaud , M. Alexandre , J.M. Lopez-Cuesta , Ph. Dubois, New prospects in flame retardant polymer materials: From fundamentals to nanocomposites, Mater. Sci. Eng. **R.** Rep. 63 (2009) 100–125.

[13] H. Kim, J-W. Park, H-J. Kim, Flame Retardant Nano-Composites containing Nano-Fillers, Chapter 1 in Science and Applications of Tailored Nanostructures January 2017.

[14] G. Shan, W. Jin, H. Chen, M. Zhao, R. Surampalli, A. Ramakrishnan, T. Zhang, R. D. Tyagi, Flame-Retardant Polymer Nanocomposites and Their Heat-Release Rates, J. Hazard. Toxic Radioact. Waste, 2015 19(4): 04015006.

[15] C.Kaynak, H. O.Gunduz, N.A. Isitman, Use of Nanoclay as an Environmentally Friendly Flame Retardant Synergist in Polyamide-6, J. Nanosci. Nanotechnol. 10 (2010) 7374–7377.

[16] R. Gayathri, R. Vasanthakumari, C. Padmanabhan, Sound absorption, Thermal and Mechanical behavior of Polyurethane foam modified with Nano silica, Nano clay and Crumb rubber fillers, International Journal of Scientific & Engineering Research, 4 (5) (2013) 301-308.

[17] M. J.Nine, M. Ayub, A.C. Zander, D.N. H. Tran, B.S. Cazzolato, D.Losic, Graphene Oxide-Based Lamella Network for Enhanced Sound Absorption, Adv. Funct. Mater. 27 (2017) 1703820 doi: 10.1002/adfm.201703820.

[18] Y. Liu, J. Ma, T.Wu, X. Wang, G. Huang,Y. Liu, H. Qiu, Y. Li, W.Wang, J. Gao, Cost-Effective Reduced Graphene Oxide-Coated Polyurethane Sponge As a Highly Efficient and Reusable Oil-Absorbent, ACS Appl. Mater. Interfaces 5 (2013) 10018−10026.

[19] B. Zhang, S. Xu, H. Tang, P. Wu, Crosslinked acetylacetonated poly(vinyl alcohol-co-vinyl acetate) nanocomposites with graphene oxide and reduced graphene oxide: a new way to modify the property of nanocomposites, RSC Adv. 3 (2013) 8372–8379.

[20] H. Karpinski, O. Umnova, R. Venegas, M. Nahil, Acoustical properties of nanoporous activated carbon fibres, J. Acoust. Soc. Am., 141(5) (2017) 3888-3888.

[21] R. Venegas, C. Boutin, O. Umnova, Acoustics of multiscale sorptive porous materials, Physics of Fluids, 29(8) (2017) 08200.

[22] L. Xiangyu, L. Wenfang， J. Xueli， Z. Lingke, Effects of Porosity and Pore Size on Sound Absorption Characteristic of Ceramsite Porous Material, Journal of the Chinese Ceramic Society 39 (2011) 158-163.

[23] M.P. Lavin-Lopez, A. Paton-Carrero , L. Sanchez-Silva , J.L. Valverde , A. Romero, Influence of the reduction strategy in the synthesis of reduced graphene Oxide, Advanced Powder Technology 28 (2017) 3195–3203.

[24] International Standard ISO 10534-2: Acoustics — Determination of sound absorption coefficient and impedance in impedance tubes —

[25]W. Park, J.Hu, L.A. Jauregui, X. Ruan, Y.P.Chen, Electrical and thermal conductivities of reduced graphene oxide/polystyrene composites, Appl. Phys. Lett. 104 113101 (2014).

[26] L. Adityaa, T.M.I. Mahlia, B. Rismanchic, H.M. Ng, M.H. Hasan, H.S.C. Metselaar, Oki Muraza, H.B. Aditiya, A review on insulation materials for energy conservation in buildings, Renew. Sust. Energ. Rev. 73 (2017) 1352–1365.

[27] E. Cuce, P.M. Cuce, C.J.Wood, S.B. Riffat, Toward aerogel based thermal superinsulation in buildings: A comprehensive review, Renew. Sust. Energ. Rev.34 (2014) 273-299.

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

[29] B. W Chieng, N. A. Ibrahim , W. M. Z. W. Yunus , M. Z. Hussein , Y.Y.Then , Y.Y. Loo, Effects of Graphene Nanoplatelets and Reduced Graphene Oxide on Poly(lactic acid) and Plasticized Poly(lactic acid): A Comparative Study, Polymers 6 (2014) 2232-2246.

[30] S Amares, E Sujatmika, T. W. Hong , R. Durairaj, H. S. H. B. Hamid, A Review: Characteristics of Noise Absorption Material, IOP Conf. Series: Journal of Physics: Conf. Series 908 (2017) 012005.

[31] D.V. Bihola1, H N Amin, V. D. Shah, Application of Nano Material to Enhance Acoustic Properties, IJESFT 12 (2015) 001-009.

[32] L. Cao, Q. Fua, Y. Sia, B. Dinga, J. Yua, Porous materials for sound absorption, Composites Communications 10 (2018) 25–35.

[33] F. Asdrubali, S. Schiavoni, K. V. Horoshenkov, A Review of Sustainable Materials for Acoustic Applications, Building Acoustics 19 (4)(2012) 283–312.