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Ultralight Graphene Oxide/Polyvinyl Alcohol aerogel for broadband and tuneable acoustic properties

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Abstract

An ultralight Graphene Oxide/Polyvinyl Alcohol (GO/PVA) aerogel is proposed as a new class of acoustic materials with tuneable and broadband sound absorption and transmission loss. The interaction between GO sheets and PVA molecules are exploited in our environmentally friendly manufacturing process to fabricate aerogels with hierarchical and tuneable porosity embedded in a honeycomb scaffolding. The developed aerogels show an enhanced dissipation of sound energy, with an extremely low density of 2.10 kg m^{-3} , one of the lowest values ever reported for acoustic materials. We have first experimentally evaluated and optimized the effects of composition and thickness on the acoustic properties, namely sound absorption and sound transmission losses. Subsequently, we have employed a semi-analytical approach to evaluate the effect of different processing times and find the relationships between the acoustic and non-acoustic properties of the materials. Over the 400 – 2500 Hz range, the reported average sound absorption coefficients are as high as 0.79 for low density aerogels, while the average sound transmission losses can reach 15.8 dB for higher density aerogels. We envision our subwavelength aerogel-based design, tailored at achieving optimal acoustic performance, as a novel lightweight material for advanced engineering applications.

Introduction

The development of innovative acoustic materials has been of huge interest in the past decades with porous absorbers being extensively studied and adopted for several engineering applications¹. Examples of common porous absorbers are cellular foams²⁻⁴ and fibrous materials⁴⁻⁶, showing good sound absorption abilities in a medium frequency range (i.e., 800 – 2000 Hz). Recently, metamaterials have been considered for the same purpose, exploiting geometrical factors to tune the acoustic behaviour over specific frequencies^{7,8}. Cellular absorbers can be distinguished in organic, hybrid, or inorganic, according to their chemical composition⁴, with a recent growing interest toward the use of carbon-based materials^{9,10}. Particularly, Graphene Oxide (GO) can be considered as an ideal candidate for the engineering of novel aerogels, due to its peculiar chemical structure consisting of a two-dimensional (2D) lattice of sp^2 hybridized carbon atoms with oxygen functionalities¹¹. The main advantages of GO are its capability to form stable suspensions in water¹² and to be templated in various assemblies such as aerogels¹³ with low cost and environmental friendly processes. GO has been heavily examined for applications as water treatment¹⁴, energy storage¹⁵, composite reinforcements¹⁶, EMI shielding¹⁷, and thermal insulation with fire-retardancy¹⁸, whereas newly acoustic related properties have been disguised only recently^{10,19,20}. Nine et al.¹⁹ developed a hybrid foam with GO supported by Melamine where it promoted an increase in the air-flow resistivity and tortuosity leading to a sound absorption coefficient of 0.6 over 800 Hz with a sample thickness of 26 mm. Similarly, Oh et al.¹⁰ fabricated a directionally antagonistic Graphene Polyurethane aerogel with a broadband absorption coefficient over 0.6 above 1000 Hz with a sample thickness of 30 mm. An example of carbon-only foam is found in Lu et al. work²⁰, where a bubbled GO solution was freeze casted and thermally reduced obtaining a Bubbled Graphene

Monolith showing a normalized absorption coefficient of 0.9 in the 800 – 6300 Hz range with a sample thickness of 30 mm and a density of 7.5 kg m⁻³. Moreover, to the best of our knowledge, no reports have been published discussing the acoustic behaviour of functionalised GO aerogels based on semi-analytical models relating non-physical and sound properties, nor describing how to optimise sound absorption and/or transmission losses.

Herein, we present a new class of ultralight and subwavelength acoustic aerogels with high, broadband and tuneable sound absorption and sound transmission loss. The materials are obtained starting from ultra-high shear processing of blends of GO and Polyvinyl Alcohol (PVA) and can be embedded in honeycomb (HC) cores. They exhibit an average sound absorption coefficient up to 0.79 and sound transmission losses up to 15.8 dB over the 400 – 2500 Hz range. Being that PVA is a water-soluble polymer with cross-linking ability, it is an ideal candidate to form homogeneous solutions with GO that would be the precursors for aerogel manufacturing. In addition, PVA is characterized by high chemical resistance, good optical and physical properties²¹, low toxicity²² and high biodegradability²³. The resulting structures, exploiting a hexagonal HC core as scaffolding for its low cost, lightweight, would possess excellent mechanical strength and impact energy absorption ability for use in advanced and structural engineering applications. Due to the presence of PVA, the high shear mixing of GO/PVA blends in water leads to the incorporation of air bubbles, while GO sheets provide stabilization. The following step of freeze-casting guarantees the preservation of the templated structure, while the freeze-drying finally determines the fabrication of the ultralight materials. This process leads to GO/PVA Aerogels (GPA) characterized by a hierarchical and tuneable porosity that enhances the dissipation of sound energy. Digital microscopy, Fourier-Transform Infrared Spectroscopy (FT-IR) and X-Ray Diffractometry (XRD) are used to characterize the physical and chemical properties of the GO/PVA aerogels. The Normal Absorption Coefficient, α , and the Normal Incident Sound Transmission Loss, STL , are measured to determine the acoustic properties of the proposed material, evaluating and optimizing the effects of composition, thickness and processing time. The Johnson-Champoux-Allard (JCA)^{24,25} semi-phenomenological model is applied to analytically study how the acoustic behaviour of the samples obtained with different processing times is related to the non-acoustic properties of the materials.

Results

Formation of ultralight GO/PVA aerogels. Figure 1a shows GO sheets and PVA molecules dispersed in water and their interaction through hydrogen bonds. The oxygen functionalities such as epoxy, hydroxyl and carboxyl groups that are found on GO basal planes and edges²⁶ determine a hydrophilic behaviour and thus the ability of polar solvents, as water, to intercalate between GO interlayers spacings^{11,27} leading to stable suspensions. On the other hand, PVA is hydrophilic and water-soluble as well and is characterized by hydroxyl functionalities²⁸. It is thus expected that when the two components are mixed in solution, homogeneous blends can be obtained with the formation of hydrogen bonds between them^{29,30}. The entrapment of air bubbles in the blends (i.e., the foaming), shown in (Figure 1b), is allowed by the low interfacial tension of PVA, whereas their stability depends on the surface elasticity and on the viscosity of the blends^{31,32}. While in PVA-only blends air bubbles would collapse few instants after the end of the mechanical excitation from the mixer, it was found that the stability is improved by the presence of GO, thanks to both changes in surface elasticity and viscosity in the resulting blends³³. Particularly, with increasing GO amounts, the foaming ability of the blends increases, until a break point where the concentration of solids is high enough to lead to clustering of particles in the bulk and thus destabilizing the foaming³⁴. After a stable hydrogel was obtained, it was possible to maintain the templated structure and to embed it in a Nomex HC core thanks to the subsequent process of freeze drying: the structure is first frozen unidirectionally from the bottom (i.e., cold surface) to the top (i.e.,

surface exposed to the atmosphere), with ice-crystals growing vertically and pushing the bigger and lighter air bubbles upward, and then dried through the process of sublimation thanks to pressure and temperature inside the drying chamber being below the triple point. The resulting structure is pictured in Figure 1c, where a solid aerogel characterized by a hierarchical porosity is presented: a micro-porosity induced by the inherent structure of the blend and the specific freezing process, and a macro-porosity induced by air bubbles previously entrapped. The first, in particular, is generated by the exclusion of particles, polymeric molecules, or a mixture of them, from the nucleation and growth of small ice crystals due to the extremely low temperature (i.e., about $-190\text{ }^{\circ}\text{C}$ thanks to the use of Liquid Nitrogen as freezing medium) to which the solution exposed³⁵.

In the present work, the attention is focused to three blends of different GO:PVA mass ratios: 1:1 in GPA-1, 2:1 in GPA-2 and 3:1 in GPA-3. GO and PVA only aerogels have also been included as reference. Blends having PVA as the more abundant component have been excluded as the resulting aerogels did not possess acceptable cohesion. The variation of PVA amount in the starting blend leads to both macroscopic (Figure 2a-e) and microscopic (Figure 2f-j) differences in the morphology, while good integrity and well defined shapes are observable in all the samples except for pure PVA that shows signs of shrinkage. The GPA-1 sample shows the maximum air bubbles entrapment (Figure 2b) and a bulkier micro-structure (Figure 2g), similar to pure PVA (Figure 2f), while in GPA-3 no bubbles (Figure 2d) and a lighter micro-structure (Figure 2i) similar to pure GO (Figure 2j) are found. Such behaviour is reflected in the density and so the porosity of the aerogels (Table 1) with GPA-1 being the lightest, with a density of 5.11 kg m^{-3} , and the more porous, with a porosity of 99.32%. The change in the structure when different PVA amounts are introduced is also evident by the initial increase in density observed for GPA-2 (7.80 kg m^{-3}), due to high presence of the heavy PVA molecules (33.5 wt%) and a foaming ability compromised by the increased GO sheets concentration (Figure 2h), which is followed by a decrease in GPA-3 (7.59 kg m^{-3}), due to the intrinsically lighter GO assembly.

Figure 1. Schematic illustration of the ultralight GO/PVA aerogels.

Table 1. Physical properties of all samples.

Sample	GO:PVA ratio	Density (kg m ⁻³)	Φ (%)	Weight increment on HC core (%)
PVA	0:1	43.80	96.5	71.55
GPA-1	1:1	5.11	99.32	8.34
GPA-2	2:1	7.80	98.68	12.74
GPA-3	3:1	7.59	98.71	12.41
GO	1:0	5.80	97.77	11.83

Figure 2. Digital Microscopy images and photographs of GO/PVA aerogels. PVA (a, f), GPA-1 (b, g), GPA-2 (c, h), GPA-3 (d, i), GO (e, j). Magnification: x 20 (a-e) and x 500 (f-j).

Another intriguing property of such blends is the possibility to tune the porosity acting on the ultra-high shear processing time. While a processing time of 15 min was kept constant for all the previous blends, as it was found to be the optimum between air entrapment, homogenization and robustness of the resulting aerogel, a tendency of the bubbles to collapse after 5 min of processing was found for the 1:1 ratio blend. More tests were then carried out, with the results summarised in Table 2: an ultralight aerogel characterized by a density of 2.10 kg m⁻³ and a porosity of the 99.72% was obtained precisely with 5 min of processing time. The obtained aerogels are among the lightest acoustic materials reported in literature (see Table S1 of supplementary material), guaranteeing a small weight increment with respect to the HC core (Table 1 and Table 2) that is as little as the 3.43% for the lightest sample.

Table 2. Physical properties of the GPA-1 samples for various processing times.

Processing time (min)	Density (kg m ⁻³)	Φ (%)	Weight increment on HC core (%)
5	2.10	99.72	3.43
10	4.38	99.42	7.16
15	5.11	99.32	8.34
20	7.41	99.23	12.11

Physicochemical characterization. Figure 3a shows the FT-IR spectra of all the manufactured samples. The main features of GO, observable from its spectrum, are: O-H stretching of hydroxyl groups at 3351 cm⁻¹, coupled with the O-H deformation at 1373 cm⁻¹ and the C-OH stretching at 1217 and 1160 cm⁻¹, the C=O stretching of Carbonyl groups at 1718 cm⁻¹, and, at 1033 cm⁻¹, the C-O-C stretching of Epoxy

groups³⁶⁻³⁹. At respectively 3194 and 1615 cm^{-1} , it is also possible to find the stretching and deformation of adsorbed water molecules³⁹. On the other hand, PVA's main features are: O-H stretching at 3307 cm^{-1} , coupled with O-H deformation at 1377 cm^{-1} , the a-symmetric and symmetric stretching of C-H at respectively 2941 and 2911 cm^{-1} , the C-H₂ bending at 1418 cm^{-1} , the C-O-C stretching at 1089 cm^{-1} , and, at 845 cm^{-1} , the C-C stretching⁴⁰⁻⁴². As GO/PVA blends exhibit the features of both the components, with intensities proportional with their relative mass ratios, a thorough mixing between the two and a good stability of the samples can be assumed. Additionally, a shift of the various O-H related features around 3351, 1373, 1217, and 1160 cm^{-1} confirms the formation of hydrogen bonds between GO sheets and PVA molecules^{29,30,43}.

The XRD patterns of samples are shown in Figure 3b. In GO pattern, at 10.80° it is possible to find its characteristic peak associated to the (001) carbon crystallite phase⁴⁴ and at 42.45° the (100) reflection related to the longitudinal dimension of the structural elements⁴⁵. The introduction of increasing PVA amounts in the blends affects the (001) peak causing its reduction in intensity and sharpness. This indicates a lower degree of crystallinity and a possible decrease of crystallites size. Moreover, a shift toward lower 2θ values (7.92°, 7.07° and 5.45° in GPA-3, GPA-2 and GPA-1, respectively) can also be observed. According to Bragg's law⁴⁶, such behaviour indicates that the interaction between PVA molecules and GO sheets leads to a more expanded structure with a resulting interplanar distance d between GO layers increasing from 8.19 Å of pristine GO to 11.15, 12.4 and 16.20 Å (for PVA inclusion of 25, 33.5 and 50 wt%, respectively). PVA main reflection (i.e., the (101) peak appearing at 19.36°)⁴⁷ is instead not visible in spectra of GO/PVA aerogels, meaning that its phase is completely amorphous.

Figure 3. Physicochemical characterization of GO/PVA aerogels: (a) FT-IR spectra and (b) XRD patterns. Features attributable to GO are denoted in black (●), while those relative to PVA in red (●).

Optimization of the acoustic properties. The aim is to optimize the sound insulating performances over a broad range of frequencies while obtaining robust, thin and lightweight materials. The working mechanism of cellular absorbers consists of the dissipation of sound energy by viscous and thermal losses: the first are due to the friction generated by the contact of air molecules with pore walls, while the viscous fluid flow of air within the pores causes the second. Accordingly, we expect the acoustic properties of the aerogels fabricated with different initial composition, thicknesses and processing time, to reflect the changes in their physical properties observed in the previous sections of the study.

We start to optimize the structure for weight, sound absorption and transmission performances by varying the initial composition of the fabricated aerogels, with three different GO:PVA mass ratios and using pure GO and PVA as reference while keeping a thickness of 25 mm. Figure 4a compares the effect of adjusting the composition on the Normal Absorption Coefficient, α , measured following the standard

test method ASTM E1050⁴⁸. Detailed experimental procedure can be found in Supplementary Information (SI). As PVA inclusion increases, there is a flattening and shifting of the absorption curves to the left of the pristine GO and PVA curves. Figure 2 highlights that the macro and microstructure of GPA-3 and pure GO are similar; this provides evidence for the similarities in the sound absorption curves of these aerogels. The shifting and flattening of the absorption curves as the PVA inclusion is reduced helps to provide higher absorption at lower frequencies (i.e., below 1000 Hz) and lower absorption at higher frequencies (i.e., above 1000 Hz). The key sound absorption properties (i.e., value of α at 500, 1000 and 2000 Hz), reported in Table 3, confirms that GPA-1 and GPA-2 have a higher absorption coefficient at 500 Hz (0.41 for both) and 1000 Hz (0.70 and 0.75, respectively) than GPA-3 and pure GO. The last two outperform at 2000 Hz, with α equal to 0.99 for both. The increase in absorption at lower frequencies can be related to the change in the physical structure of the aerogel: for example, GPA-1 exhibits much larger voids within its macrostructure (Figure 2) when compared to GPA-3. These larger voids result in a reduction in absorption at higher frequencies while improving absorption at lower frequencies, with a behaviour that can be linked directly to an increase in porosity and a reduction in flow resistivity, as discussed in the following section. The average sound absorption coefficients, $\bar{\alpha}$, were also calculated over a 400 – 2500 Hz range to investigate the overall absorption performances. The values for GO/PVA and pure GO aerogels are all between 0.72 and 0.77, with pure PVA performing the worst with $\bar{\alpha}$ equal to 0.54 (Table 3).

The effects of the composition on the Sound Transmission Loss, STL , measured according to the standard test method ASTM E2611⁴⁹ (see SI for more details), are shown in Figure 4b. Key and average values are summarised in Table 3. As PVA is included, the average $\overline{STL}$ only slightly increases from 4.6 dB of pure GO and PVA to 4.9 dB of GPA-3. However, as the presence of PVA increases, the $\overline{STL}$ reaches much higher values of 12.4 and 13.2 dB in GPA-2 and GPA-1, respectively. Such behaviour is expected as, accordingly with equation (1), where R is the reflection coefficient, from which the coefficient α is estimated, low absorption is attributed to a structure with high reflection and thus with higher transmission losses.

$\alpha = 1 - R ^2$	(1)
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Figure 4. Effects of GO/PVA aerogels composition on acoustic properties: **(a)** sound absorption and **(b)** sound transmission.

Table 3. Key and average sound absorption and transmission properties for GO/PVA aerogels with different composition. ^A The average was calculated in the 400 – 2500 Hz range.

Sample	Peak		500 Hz		1000 Hz		2000 Hz		Average ^A	
	Freq (Hz)	α	α	STL (dB)	α	STL (dB)	α	STL (dB)	$\bar{\alpha}$	$\overline{STL}$ (dB)
PVA	2339	0.99	0.15	2.1	0.25	3.9	0.87	5.65	0.54	4.6
GPA-1	1734	0.85	0.41	9.4	0.70	12.8	0.85	14.57	0.74	13.2
GPA-2	1970	0.89	0.41	8.3	0.75	11.7	0.89	13.75	0.77	12.4
GPA-3	1827	1.00	0.15	2.7	0.56	4.3	0.99	5.86	0.74	4.9
GO	2244	1.00	0.15	2.5	0.51	4.1	0.99	5.51	0.72	4.6

GPA-1 was chosen as the optimum aerogel composition as it provided high absorption and high transmission losses while being the lightest aerogel (5.11 kg m⁻³). Figure 5a compares the effect of adjusting the thickness on α for the chosen composition. It is clear to observe that the increase in aerogel thickness improves sound absorption at lower frequencies. As the sample increases in thickness, it outperforms the thinner samples at lower frequencies achieving an absorption coefficient of 0.62 at 500 Hz and 0.96 at 1000 Hz, compared to 0.41 and 0.13 at 500 Hz, and 0.7 and 0.26 at 1000 Hz for 25 mm and 12.5 mm thick samples, respectively. Figure 5b provides similarly expected results, in that the STL increases as the thickness of the sample increases: from 6.2 dB for 12.5 mm to 15.7 dB for 37.5 mm, a substantial increase for a 25 mm added thickness. Key and average α and STL values are summarised in Table 4.

Figure 5. Effects of thickness on acoustic properties of GPA-1 samples: (a) sound absorption and (b) sound transmission.

Table 4. Key and average sound absorption and transmission properties for the GPA-1 samples with different thicknesses. ^A The average was calculated in the 400 – 2500 Hz range.

Sample	Peak		500 Hz		1000 Hz		2000 Hz		Average ^A	
	Freq (Hz)	α	α	STL (dB)	α	STL (dB)	α	STL (dB)	$\bar{\alpha}$	$\overline{STL}$ (dB)
12.5 mm	2500	0.86	0.13	5.0	0.26	6.2	0.67	6.49	0.46	6.2
25 mm	1735	0.85	0.41	9.4	0.70	12.8	0.85	14.57	0.74	13.2
37.5 mm	948	0.95	0.62	11.3	0.96	15.0	0.73	17.36	0.79	15.7

The next step in optimizing the GO/PVA aerogels was to evaluate the effect of processing time and of, consequently, porosity on sound absorption. This was carried out by creating four new samples with varying levels of porosity and a constant thickness of 25 mm, as outlined in “Methods” and reported in Table 2. Figure 6a shows that as porosity increases, so does the average absorption coefficient of the proposed structure over the inspected frequency range. Particularly, the heaviest aerogel (obtained with 20 min of processing time and resulting in 7.41 kg m⁻³ of density and 99.23% of porosity) has an average absorption of 0.68, while the lightest (5 min, 2.10 kg m⁻³ and 99.72%) increases to 0.79. The key and average values of those samples are summarised in Table 5. Figure 6b follows on from previous results that, due to increased reflection, lower absorption provides a higher transmission loss. As the aerogel becomes more rigid and dense, the transmission loss increases; in other words, as the density of the cellular material increases, we move towards the condition of having a solid and rigid structure which would have very low transmission and low absorption (i.e., high reflection), accordingly with equation (1). Values reported in Table 5 shows that the $\overline{STL}$ sharply increases from 7.3 dB (2.10 kg m⁻³) to 15.8 dB (7.41 kg m⁻³).

Figure 6. Effects of processing time on acoustic properties of GPA-1 samples: (a) sound absorption and (b) sound transmission.

Table 5. Key and average sound absorption and transmission properties for the GPA-1 samples obtained with different mixing times. ^A The average was calculated in the 400 – 2500 Hz range.

Sample	Peak		500 Hz		1000 Hz		2000 Hz		Average ^A	
	Freq (Hz)	α	α	STL (dB)	α	STL (dB)	α	STL (dB)	$\bar{\alpha}$	$\overline{STL}$ (dB)
5 min	1885	0.97	0.29	5.5	0.72	6.7	0.97	8.00	0.79	7.3
10 min	1952	0.93	0.36	5.8	0.69	7.3	0.93	9.13	0.77	8.0
15 min	1735	0.85	0.41	9.4	0.70	12.8	0.85	14.57	0.74	13.2
20 min	2284	0.81	0.38	13.7	0.62	16.3	0.80	16.11	0.68	15.8

Semi-phenomenological analysis. To further investigate the effects of processing time and the resulting differences in the macroscopic structure (i.e., variations of physical properties as those previously observed in density and porosity) on the acoustic behaviour of the GO/PVA aerogels, we performed a semi-phenomenological analysis following the Johnson-Champoux-Allard (JCA) equivalent fluid model for porous materials^{24,25}. The model relates some physical parameters of porous materials, the so-called “non-acoustic properties”, to sound propagation through the absorbent thanks to the calculation of the effective density, ρ_e , and the effective bulk modulus, K_e (see SI for more details). Particularly, the non-acoustic properties are: porosity, ϕ ; flow resistivity, σ ; tortuosity, α_∞ ; viscous, Λ , and thermal, Λ' , characteristic lengths. Detailed information on how those properties were measured can be found in the supplementary material. Briefly, porosity was evaluated using the density of the aerogels as expressed in equation (3), flow resistivity was indirectly determined from impedance tube measurements according to equation (S9)⁴⁹⁻⁵¹, tortuosity was experimentally derived from equation (S10) using an ultrasonic time-of-flight method⁵², and finally viscous and thermal characteristic lengths were obtained applying an inverse identification method^{53,54}.

Figure 7a shows the comparison between the modelled absorption curve and the experimental results for GPA-1 structures obtained with different processing times. The JCA model was fitted to the actual results considering three experimentally derived parameters (ϕ , σ and α_∞) and two unknown parameters (Λ and Λ'). The resulting sound absorption coefficient predicted curves have an average error < 1% when compared to the experimental results, and thus suggest that the experimentally derived and the fitted values provide a good estimation of the non-acoustic properties of the developed aerogels. The analysis of those parameters helps in the understanding of the acoustic behaviour of the aerogels. As processing time increases, physical properties change (as density and porosity with an increasing and decreasing trend, respectively) together with the other non-acoustic properties (such as flow resistivity, tortuosity and the viscous and thermal characteristic lengths). The complex interactions between these parameters provide for the shift in the sound absorption of the aerogel. While the positive effect of the porosity, observed in the previous section, is trivial, as it is directly proportional to the volume of air available to sound waves⁵⁵, we have to take into account that the non-acoustic properties are not independent (i.e., a change in one parameter will cause a change in the others). It is interesting to observe the trend of the average absorption coefficient which appears to be inversely proportional with the flow resistivity, as depicted in Figure 7b. Particularly, the best performing sample shows $\bar{\alpha}$ equal to 0.79 corresponding to a σ of 33,981 N s m⁻⁴ (5 min sample) and the worst performing one has $\bar{\alpha}$ equal to 0.68 corresponding to a σ of 81,900 N s m⁻⁴ (20 min). The flow resistivity is a measure of the resistance offered by the porous material to an airflow and can thus give an idea of the extent of sound energy dissipation due to boundary layer effects within the material⁵⁵. However, if the resistivity is too high the sound wave incident to the material would meet a relatively high impedance surface⁵⁶ leading to high reflection due to the impedance mismatch and thus low absorption. This is in agreement with equations (1) and (S2) and with STL values previously

reported (Table 5). Correspondingly, the other parameters also need to be examined. The tortuosity is a measure of the complexity of the propagation path of sound waves through the material, where more complex paths usually leads to higher sound absorption, while viscous and thermal characteristics lengths are related to the pore-microgeometry and describes viscous effects at medium and high frequencies and the thermal losses at high frequencies, respectively⁵⁵. The tortuosity variation, shown in Figure 7c, except for the 15 min sample having the highest value of 2.57, is within a relatively small range of 1.31 and 1.66 (in the 5 and 10 min samples, respectively). Nevertheless, it is crucial to observe how the increasing processing time leads to an increase of the viscous characteristic length from the minimum value of 29 μm to the maximum of 97 μm for the 5 and 20 min samples, respectively. Λ is defined as “the surface-to-pore volume ratio of the pore-solid interface”²⁴ and is thus proportional to the microscopic dimensions of the pores. Smaller values lead to increased viscous effects and thus to an improved dissipation of sound energy, explaining the acoustic behaviour pictured in Figure 7d. The detrimental effect of the processing time on α could consequently be attributed to the coalescence of the micro-pores due to the protract mixing. Finally, the variation of Λ' is within the relatively small range between 154 μm , for the 5 min sample, and 202 μm for the 10 min one, and its effect over the observed frequency range of 400 – 2500 Hz is at any rate limited (Figure 7d).

Figure 7. Semi-phenomenological analysis of GPA-1 samples with different processing times: (a) comparison between semi-analytical model predictions (solid lines) and experimental measurements (markers) of the Sound Absorption Coefficient; (b) Flow Resistivity, (c) Tortuosity, (d) Viscous and Thermal Characteristic Lengths affected by processing time with Average Absorption Coefficient trend.

Discussion

In conclusion, we have proposed a novel ultralight aerogel for the design of thin and light materials with excellent acoustic properties. We have exploited the chemical properties of GO/PVA blends and a specific environmentally friendly manufacturing process to embed the aerogels in structural HC cores. The resulting material is characterized by a hierarchical and tuneable porosity, up to the 99.72%, and with density as low as 2.10 kg m^{-3} in one of the proposed samples. The physicochemical characterization has demonstrated the effects of the composition on the physical properties of the material, the existence of hydrogen bonds between GO sheets and PVA molecules and the ability of the two components to form a homogeneous and expanded structure. We have also evaluated the effects of composition on the acoustic properties of the proposed material, showing that the GPA-1 sample, obtained from a blend where GO and PVA are present in equal amounts, exhibits the best trade-off between sound absorption and sound transmission losses (with average values over the 400 – 2500 Hz range of 0.74 and 13.2 dB, respectively) and weight (with a density of 5.11 kg m^{-3}). We have demonstrated that the acoustic performances of GPA-1 samples positively respond to increase in thickness, with both $\bar{\alpha}$ and $\overline{STL}$ values sharply rising from, respectively, 0.46 and 6.2 dB, for a 12.5 mm thick structure to 0.79 and 15.7 dB for a 37.5 mm thick structure. Moreover, for the latter the peak in absorption shifts to a frequency as low as 948 Hz with a value of 0.95. Finally, for the same composition we have studied, the effects of the processing time with an experimental and semi-analytical approach. The complex relationship described by the JCA model between the non-acoustic physical properties and the acoustic properties of the materials allowed to optimise the sound absorption for the lightest aerogel (with $\bar{\alpha}$ and density of 0.79 and 2.10 kg m^{-3} , respectively) and the transmission losses for the heaviest material (with $\overline{STL}$ and density of 15.8 dB and 7.41 kg m^{-3} , respectively). With their extremely low weight, sub-wavelength thickness, tuneable sound absorption and transmission properties, and inherently high specific mechanical performances, we envision the proposed aerogel-based structure for the development of acoustic materials in structural engineering applications requiring high sound absorption and/or sound transmission losses as well as excellent mechanical stiffness and strength. Additionally, the inherent potential of GO to unlock multifunctional features as EMI shielding and fire-retardancy may prompt advanced applications in the aerospace and power generation industries.

Methods

Materials. GtO powder was supplied by Xiamen TOB New Energy, PVA (98-99% hydrolyzed, medium molecular weight) was purchased from Sigma Aldrich. Deionized MilliQ® water was used throughout all the experiments. All the chemicals were used as received without further treatment or purification.

Sample fabrication. The fabrication process is schematized in Figure 8. GtO was dispersed in water (8 mg mL^{-1}) and exfoliated to form a GO suspension through probe sonication (Dr. Hielscher GmbH UP100H, with an amplitude of the 80% and continuous pulse) for 40 minutes under constant magnetic stirring and in an ice bath to ensure a homogeneous process with controlled temperature. A PVA solution (5 wt%) was obtained dissolving the raw polymer in water: the system was heated up to $90 \text{ }^{\circ}\text{C}$ on a hot plate with continuous magnetic stirring until the solution became clear. Blends of GO and PVA (GO/PVA) were then obtained with ultra-high shear mixing (Ultra-Turrax T25, IKA) at 20,000 rpm for 15 minutes in a typical blend, or with varying processing times for porosity optimization purposes, of the two aqueous solutions in proper amounts so that the designed mass ratio between the two materials would be reached.

The composite structure was obtained with unidirectional freeze casting of the blends in a Nomex honeycomb core with the aid of a silicone mould having an Aluminium plate as base directly placed on a

cold copper heat sink immersed in Liquid Nitrogen. Frozen samples were finally freeze dried (LTE LyoTrap Mini) for 96h, leaving the GO/PVA aerogel embedded in the Nomex core. Samples consisting of pure GO suspension and pure PVA solution were also manufactured as reference.

Figure 8. Schematic illustration of the fabrication process.

Physicochemical characterization. The consequences of the composition of the starting blend on the morphology of the aerogels were evaluated with digital microscopy (Keyence VHX 6000). Fourier-Transform Infrared Spectroscopy (FT-IR, Perkin-Elmer Frontier FTIR Spectrometer) was instead chose for the evaluation of the chemical structure with a liquid nitrogen cooled MCT detector from 400 to 4000 cm^{-1} . The crystalline structure of the blends was finally analysed with X-Ray Diffractometry (XRD, STOE STADI P) in a range of $2\theta = 4 - 50^\circ$ at room temperature using a $\text{Cu-K}\alpha$ generator with 1.54 Å of wavelength. XRD data were additionally processed to calculate the interplanar distance d between GO layers using Bragg's law⁴⁶ as expressed in equation (2), where λ is the radiation wavelength and θ is the reflection angle of the (001) phase.

$d = \lambda / 2 \sin \theta$	(2)
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The density of the samples, ρ_s , was calculated from their weight and volume. The porosity, ϕ , of each sample was calculated as expressed in equation (3), where ρ_{GO} and ρ_{PVA} are the density of bulk GO (0.26 g cm^{-3}) and PVA (1.25 g cm^{-3}), respectively, while w_{GO} and w_{PVA} are the mass percentages of the two components in the blend.

$\phi = \left(1 - \frac{\rho_s}{w_{GO}\rho_{GO} + w_{PVA}\rho_{PVA}} \right) \times 100$	(3)
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Author contributions

M.M. and M.R. designed the project. M.R. performed and analyzed most of the experiments under the guidance of G.M.F. G.M.F. performed the semi-phenomenological analysis under the guidance of M.R. M.R. wrote the manuscript with G.M.F. contributions on the discussion of the acoustic properties and the semi-phenomenological analysis. M.M revised the whole manuscript. All the authors reviewed the manuscript and agreed to the final version of the manuscript.

Additional Information

Competing interests. The authors declare no competing interests.

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Figures

Figure 1

Schematic illustration of the ultralight GO/PVA aerogels.

Figure 2

Digital Microscopy images and photographs of GO/PVA aerogels. PVA (a, f), GPA-1 (b, g), GPA-2 (c, h), GPA-3 (d, i), GO (e, j). Magnification: x 20 (a-e) and x 500 (f-j).

Figure 3

Physicochemical characterization of GO/PVA aerogels: (a) FT-IR spectra and (b) XRD patterns. Features attributable to GO are denoted in black (▣), while those relative to PVA in red (▣).

Figure 4

Effects of GO/PVA aerogels composition on acoustic properties: (a) sound absorption and (b) sound transmission.

Figure 5

Effects of thickness on acoustic properties of GPA-1 samples: (a) sound absorption and (b) sound transmission.

Figure 6

Effects of processing time on acoustic properties of GPA-1 samples: (a) sound absorption and (b) sound transmission.

Figure 7

Semi-phenomenological analysis of GPA-1 samples with different processing times: (a) comparison between semi-analytical model predictions (solid lines) and experimental measurements (markers) of the Sound Absorption Coefficient; (b) Flow Resistivity, (c) Tortuosity, (d) Viscous and Thermal Characteristic Lengths affected by processing time with Average Absorption Coefficient trend.

Figure 8

Schematic illustration of the fabrication process.

Supplementary Files

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