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Ultrahigh dielectric constant and low loss of highly-aligned graphene aerogel/poly(vinyl alcohol) composites with insulating barriers

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ABSTRACT

A novel two-step route to prepare graphene aerogel (GA)/poly(vinyl alcohol) (PVA) composites with exceptional dielectric performance is reported. The composites obtained from the initial unidirectional freeze casting possess a highly-aligned, conducting graphene skeleton with an ultralow density, a high porosity and remarkable thermal stability, showing ultrahigh dielectric constants combined with moderate losses. The losses are significantly reduced by means of PVA barriers introduced between the neighboring conductive main skeletons of the aligned GA/PVA networks in the 2nd freeze casting process. The insulating barriers effectively block the current leakage by removing the transversely interconnected, conductive ligaments. The compaction of barrier-shielded, porous GA/PVA composites yield fully consolidated, solid composites which deliver both exceptional dielectric constants and very stable, low losses. The approach developed here paves the way for rational design and assembly of GA/PVA composites as a lightweight, tunable and high-performance dielectric material, satisfying various requirements for emerging applications.

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1. Introduction

Polymer-based composites with high dielectric constants (ε) and low losses (tan δ) have recently attracted considerable interest for their potential applications in artificial muscles, electromechanical actuators, and next generation capacitors for energy storage [1–3]. Insulating polymers have relatively low dielectric constants ($\varepsilon < 10$), thus achieving both a high ε and a low loss remains challenging [4]. A common approach is to incorporate ceramic fillers with high ε values, such as BaTiO₃ [5,6], Pb(Zr,Ti)O₃ [7,8], and $CaCu_3Ti_4O_{12}$ (CCTO) [9,10], into the polymer matrix to form composites. The dielectric constants of the resultant composites with filler contents over 50 vol% can be ten times higher than that of the neat polymer. However, such a high loading of ceramic fillers is detrimental to the mechanical properties of the composites [11]. An alternative strategy is to fabricate percolative composites by adding conductive fillers, such as metal nanoparticles [12,13], carbon nanotubes (CNTs) [14–17], and graphene

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http://dx.doi.org/10.1016/j.carbon.2017.07.079 0008-6223/© 2017 Elsevier Ltd. All rights reserved. [18–20], into the polymers. The dielectric constants of such composites drastically enhanced as the filler content increased to the vicinity of percolation threshold through the insulator-conductor transition [21]. Among them, graphene/polymer composites exhibited particularly high dielectric constants due to the large surface area and exceptional electrical conductivity of graphene sheets. For instance, a high ε of 7488 was achieved for reduced graphene oxide (rGO)/poly(vinylidene fluoride) (PVDF) composites after Cl-doping of rGO sheets [22]. Taking advantage of the highly aligned and ultralarge rGO sheets, a remarkably high ε of 14,000 at 1 kHz was also reported [23]. These high ε values of the composites, however, are always at the expense of much amplified loss values near the percolation threshold due to the motion of free charge carriers, greatly restricting their practical applications.

To address the aforementioned challenges for conductive filler/ polymer composites, many strategies have been employed with varied successes [22,24–32]. For instance, significant efforts have been devoted to improve the conductivity of fillers and the interfacial adhesion between the filler and matrix through functionalization [22,24]. Although the dielectric constant of the composites was largely enhanced, this strategy failed to suppress the dielectric loss when the filler content was high. A promising strategy to







mitigate the increase in dielectric loss was devised by introducing barriers so that the direct contacts between the conductive fillers were avoided [25–32]. The loss tangent of the fillers with barrier coating was much reduced compared to those without barriers [33,34], indicating the effectiveness of this method. The barriers had a few different forms, including functional groups [28], graphene oxide (GO) [29], metal oxide [30], and insulating polymers, such as poly(vinyl pyrrolidone) (PVP) [25], poly(vinyl alcohol) (PVA) [27], polyhedral oligomeric silsesquioxane (POSS) [26] and polypyrrole (PPy) [31]. For example, Ag particles were coated by PVP shells of different thicknesses, which served as insulating barriers between the conductive Ag cores, giving rise to a high ε and a low loss of the composites [25]. However, it is an enormous challenge to coat thin barriers on graphene sheets compared to the 0-dimensional particles because of many difficulties associated with the reduction of GO and uniform dispersion of coated rGO sheets into the matrix while retaining their large aspect ratios. Consequently, although the dielectric loss of the graphene/polymer composites was reduced after incorporating barriers, their dielectric constants were far below those anticipated from the inherent properties of graphene [27,30].

Here, we present for the first time a novel, efficient method to introduce barriers into the graphene aerogel (GA)/PVA composites that possess highly aligned conductive networks prepared by unidirectional freeze casing. Extremely stable and low loss tangents are achieved by creating insulating PVA barriers between the aligned conductive networks, while maintaining high ε values. The dielectric performance of the composites can be tailored by controlled compaction so as to satisfy different requirements for new applications. The present approach opens up totally new processing routes to fabricate composites with exceptional dielectric performance.

2. Experimental

2.1. Preparation of GA/PVA composites with aligned porous structure

GO was synthesized via the modified Hummers method [35–37] using natural graphite (supplied by Asbury Graphite Mills), and the size distributions and the functional groups of GO are given in Fig. S1 (Supporting Information). GA/PVA composites with an aligned porous structure were fabricated through unidirectional freeze casting (see Fig. S2) of rGO/PVA dispersion which was prepared as follows. 1.0 g PVA (99+% hydrolyzed, Mw ~89,000-98,000, Aldrich) was dissolved in 20 g deionized (DI) water at 100 °C for 1 h. After cooling down to room temperature (RT), GO dispersion was added into the PVA solution at a weight ratio of graphene to PVA ranging from 0.5 to 5 wt%. The mixture was stirred using a magnetic bar for 1 h, followed by sonication for 15 min to uniformly disperse GO sheets in the PVA solution. Hydrazine solution of three times the GO weight was added into the mixture to in situ reduce GO at 90 °C for 12 h in an oil bath. The pH value of the mixture was maintained at ~10 using ammonia solution during the in situ reduction process. The obtained rGO/PVA mixture was subsequently freeze cast using a custom-made apparatus, as shown in Fig. S2b [38], followed by freeze drying under vacuum for 48 h to form GA/PVA composites with an aligned porous structure. To further augment the dielectric properties of the composites, additional barriers were applied onto the internal micro-walls of composites. The as-fabricated composites were immersed into a PVA aqueous solution with concentrations ranging from 6.25 to 25 mg/mL for 3 h at RT for full infiltration, which were subsequently subjected to another run of unidirectional freeze casting and freeze drying to form final composites with insulating barriers.

2.2. Characterization

The GA/PVA composites were examined on a scanning electron microscope (SEM, JEOL 6390F) using secondary electron beams at an acceleration voltage of 20 kV, and transmission electron microscopy (TEM, IEOL 2010) at an acceleration voltage of 200 kV. For the TEM measurement, the fully compacted GA/PVA composites were mounted in an epoxy resin and thin sections of below 100 nm in thickness were ultramicrotomed and collected using a copper grid. The X-ray diffraction (XRD) measurements were carried out using an X'pert Pro (PANalytical) diffractometer with Cu K α 1 (λ = 0.154 nm) radiation. The Fourier transform infrared spectroscopy (FTIR, Bio-Rad FTS 6000) was used to evaluate the interfacial interactions of the composites in the near-infrared region (500–4000 cm⁻¹), collecting attenuated total reflectance (ATR) spectra. Differential scanning calorimetry (DSC) was used to measure the glass transition temperatures, Tg, of PVA and GA/PVA composites on a DSC Q2000 instrument (TA Instruments) in a nitrogen atmosphere. The samples were heated from RT to 180 °C at a heating rate of 10 °C/min and cooled down to RT. The data obtained from the second heating cycle were plotted from which T_g was determined according to the specification ASTM E1356. The thermal degradation behaviors were measured on a thermogravimetric analyzer (TGA, Q5000, TA instruments) at a ramp rate of 10 °C/min in a nitrogen atmosphere. The Raman spectroscopy (Reinshaw MicroRaman/Photoluminescence System) was used to characterize the aligned graphene structure of the composites. He-Ne laser with a wavelength of 632.8 nm was used in all experiments. The AC conductivities and the dielectric properties of the composites with different filler contents were measured using an impedance/gain-phase analyzer (Hewlett Packard 4149A) in the range of frequencies from 100 Hz to 40 MHz. The samples were placed between two parallel plate electrodes, and the electric field was applied along the transverse to alignment direction. The dielectric constant, ε , was calculated using the following equation:

$$\varepsilon = Ct/A\varepsilon_0 \tag{1}$$

where *C* is capacitance, $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m is the permittivity of vacuum, *t* and *A* are the thickness and the cross-sectional area of materials.

3. Results and discussion

3.1. Aligned porous structure of GA/PVA composites

Aligned, hierarchical porous structures are important for enhanced dielectric performance of nanocomposites [23]. In this study, the preferential orientation of GA/PVA skeletons was achieved via unidirectional freeze casting of rGO sheets/PVA dispersion where the large temperature gradient rapidly drove the growth of ice crystals, which in turn expelled the surrounding materials in one direction [38-40]. The high degree of alignment and the relatively simple process make the unidirectional freeze casting technique ideally suited to fabrication of an aligned, porous graphene structure compared to other methods, such as self-alignment [23,41], flow-induced alignment [42,43], and forced alignment by magnetic or electric fields [44,45]. Fig. 1a gives the detailed fabrication process of aligned GA/PVA composites. As one of the most important steps of the synthesis process, a stable and uniform dispersion precursor is required. A stable and homogeneous colloidal dispersion of rGO/PVA (see Fig. S2a) was obtained through in situ chemical reduction of GO in PVA aqueous solution using hydrazine [46,47]. The rGO/PVA dispersion was freeze cast unidirectionally using the custom-made apparatus (Fig. S2b) [38].



Fig. 1. (a) Schematic illustration of highly aligned, porous GA/PVA composites fabricated by simultaneous unidirectional freeze casting and cryo-polymerization; and SEM images of aligned, porous GA/PVA composites taken at (b) a low magnification with a digital image in inset, and (c,d) a high magnification. (A colour version of this figure can be viewed online.)

Freezing of the dispersion is the most pivotal stage during freeze casting because the morphology of ice crystals determines the resulting microstructure of the composites, and several processing parameters such as temperature gradient and freezing rate determine the inner structure and integrity of the composites [48]. Here, liquid nitrogen was chosen to create a high degree of supercooling at the bottom surface of rGO/PVA dispersion, while the top surface was kept at RT. Hence, a large temperature gradient was generated between the bottom and top surfaces, i.e. -196 °C to RT, forcing the ice crystals to grow vertically. The GA/PVA composite skeletons were in situ formed vertically between the rapidly advancing ice fronts, while the PVA was in situ cryo-polymerized under the supercooling condition, as illustrated in Fig. 1a. Cryo-polymerization, a polymerization process occurring below the melting temperature of the solvent, is based on the formation of a polymeric structure in a semi-frozen system where solvent crystals act as porogens [49]. The porogens served as sacrificial template and provided an ideal platform for the freeze cast structure. After eliminating the oriented ice crystals by freeze drying, freestanding GA/PVA composites with a highly aligned and interconnected porous structure were formed.

The GA/PVA composites shown in Fig. 1b–d exhibit a highly aligned, anisotropic structure, possessing a high porosity of ~94% and an ultralow density of 72.3 mg/cm³. The side view presents vertically aligned and continuous GA/PVA main skeletons, which are bridged by ribbon-like short ligaments in the transverse direction, forming a 3D freestanding porous architecture. These ligaments were formed during freeze casting where small amounts of rGO sheets and PVA were entrapped by the rapidly advancing ice fronts, connecting the adjacent, vertical main skeletons [38]. In contrast, the top view of the composite shows closely-packed pores without any preferred orientation (Fig. 1d).

3.2. Interfacial interactions and thermal properties of GA/PVA composites

Fig. 2a shows the XRD patterns of GO, rGO, PVA, and GA/PVA composites with 2 wt% graphene. The neat GO sheets had a typical XRD diffraction peak at $2\theta = 8.3^{\circ}$, corresponding to a d-spacing of 1.06 nm, while that of neat PVA was observed at $2\theta = 19.7^{\circ}$. The interlayer distance of rGO reverted to 0.37 nm ($2\theta = 23.9^{\circ}$), indicating the most of oxygenated functional groups on GO were eliminated, and the much broader peak with a reduced intensity suggests mono- or few-layer rGO sheets [50]. The GA/PVA composite showed only one diffraction peak resembling that of PVA, while the peak corresponding to rGO completely disappeared. The above observations signify that the rGO sheets were fully exfoliated and uniformly dispersed in the PVA matrix [51]. The FTIR spectra shown in Fig. 2b present significant analogy between the neat PVA and the GA/PVA composites with different graphene contents. The only exception is the downshift of -OH stretching bands from 3369 to 3359 cm^{-1} as the graphene content was increased to 5 wt%. The -OH stretching bands located at $3000-3600 \text{ cm}^{-1}$ are sensitive to hydrogen bonds, indicating substantial hydrogen bonds between the residual oxygenated functional groups on rGO sheets and the hydroxyl groups on PVA chains [52,53].

Thermal stability of the as-prepared composites was characterized using TGA, as shown in Fig. 2c. Both PVA and GA/PVA composites exhibited a three-step weight loss. The first small weight loss (<10%) took place below ~200 °C, which is mainly ascribed to the removal of adsorbed moisture and decomposition of evaporative oxygenated functional groups in the samples [54,55]. The second large weight loss at 200–350 °C is attributed to degradation of PVA matrix, whereas the third weight loss taking place at 400–500 °C arises from the decomposition of the remainders [56]. The temperatures corresponding to 50% weight loss, T_{50%}, of the GA/PVA composites with 2 and 5 wt% graphene were 33



Fig. 2. (a) XRD patterns of GO, rGO, PVA, and 2 wt% GA/PVA composites; (b) FTIR spectra, (c) TGA, and (d) DSC curves of neat PVA and GA/PVA composites with different graphene contents. (A colour version of this figure can be viewed online.)

and 54 °C higher than that of the neat PVA, respectively. Such significant increases in $T_{50\%}$ are a testament to enhanced thermal stability because the mobility of polymer chains at the GA/PVA interfaces was suppressed by the strong hydrogen bonds between the composite constituents [57], as confirmed by the FTIR analysis. The DSC scans in Fig. 2d present that the T_g of the composites containing 2 and 5 wt% graphene increased by remarkable 11.8 and 29 °C, respectively, compared to the neat PVA. This finding confirms that the polymer chains were severely constrained by the presence of rGO sheets with hydrogen bond interactions.

3.3. Dielectric properties of GA/PVA composites

The electrical conductivity and dielectric properties of the composites are presented in Fig. 3. The dependence of AC conductivity of the composites with different graphene contents on frequency is shown in Fig. 3a. For graphene contents lower than 2 wt%, the composites presented a typical dielectric behavior, similar to the neat PVA, where the AC conductivity increased almost linearly with frequency. At filler contents above 2 wt%, the conductivity increased significantly, especially at a low frequency domain where they remained almost constant regardless of frequency [58]. Thus, the percolation threshold of the composites is estimated to prevail between 2 and 4 wt%, equivalent to 0.066 and 0.136 vol%, respectively, according to the densities of the constituents and the porosity [59]. Fig. 3b and c shows the frequency-dependent dielectric constant and loss of the composites. As expected, the neat PVA exhibited low ε values of below 10 over the whole frequency range of 100 Hz to 40 MHz, consistent with the literature value [60]. The dielectric constant surged by more than one order of magnitude after adding only 0.5 wt% graphene, and raised to a less extent with further increase in graphene content. The enhanced dielectric constants were always at the expense of similar increases in loss, which is ascribed to the motion of free charge carriers resulting from the formation of continuous conductive networks. The interfacial polarization, also known as the Maxwell-Wagner-Sillars (MWS) effect, can explain the entrapment of free charges at the interface of the insulating PVA and the conductive rGO sheets, which played an important role in enhancing the dielectric constant in this study [23]. Both the dielectric constant and loss were higher in the low-frequency region than in the high frequencies due to the relaxation arising from the interfacial polarization [22]. In the low-frequency region, the alternation of the field is slow and the induced dipoles can align themselves with sufficient time in response to the applied electric field, leading to enhanced interfacial polarization.

The dielectric properties of the composites obtained at 1 kHz are summarized in Fig. 3d. The highest dielectric constant achieved was 5720 at a graphene content of 5 wt% (or 0.172 vol%), equivalent to almost 1150 times that of the neat PVA. Such a high dielectric constant is a reflection of several ameliorating features of the GA/ PVA composites, including (i) the excellent exfoliation and uniform dispersion of rGO sheets in the aqueous PVA solution during the *in situ* reduction process on a nanoscopic scale and (ii) the highly aligned GA/PVA skeletons obtained through unidirectional freeze casting on a microscopic scale. Full exfoliation and dispersion of rGO sheets in the polymer matrix gave rise to enlarged interfacial areas and thus high dielectric constants. The continuously aligned GA/PVA main skeletons separated by air can serve as numerous



Fig. 3. Electrical conductivity and dielectric properties of GA/PVA containing different rGO contents: (a) AC conductivity; (b) dielectric constant; (c) dielectric loss; and (d) summary of dielectric properties of composites at 1 kHz. (A colour version of this figure can be viewed online.)

microscale capacitors (see inset of Fig. 3b). The 3D network of the composites containing numerous capacitors can hold an extremely large capacity to store electric charges, leading to a high ε value of the composites.

3.4. Morphologies and dielectric properties of compacted GA/PVA composites with barriers

Similar to other conductive filler/polymer composites, the significant enhancement of dielectric constant of GA/PVA composites with increasing graphene content accompanied a concomitant increase in dielectric loss. In an effort to reduce the dielectric loss of GA/PVA composites, a completely new, two-step process was developed to create PVA insulating barriers on the aligned conductive skeletons, as illustrated in Fig. 4a. The composites with a graphene content near the percolation threshold of 2 wt% were chosen to ensure both high dielectric constants and low loss values. The additional process involved (i) the infiltration of PVA solution into the porous structure of GA/PVA composites and (ii) the 2nd run of unidirectional freeze casting to apply PVA barriers on GA/PVA main skeletons. The ice crystals grew along the vertically aligned porous columns existing between the GA/PVA main skeletons on which a PVA barrier was applied. Fig. 4b presents the SEM image of the composites with barriers prepared using PVA concentration of 25 mg/mL (GA/PVA-25 PVA). It is seen that the aligned main skeleton of the original GA/PVA composites remained intact, with a PVA barrier successfully coated on the adjacent aligned micro-walls. Fig. S3 presents the SEM images of the composites without, and with barriers prepared using PVA concentrations ranging from 6.25 to 25 mg/mL, showing the barriers becoming thicker with increasing PVA concentration.

The aligned GA/PVA composites with barriers were characterized using polarized Raman spectroscopy. The Raman intensity of carbon materials is sensitive to polarization angle and a prominent resonance was obtained in the alignment direction [46]. An obvious difference in intensity of Raman spectra was revealed along the two orthogonal directions of the GA/PVA-25PVA composite (Fig. 4c): a large intensity ratio ~2.83 of the Raman G-band in the alignment direction (G_{ll}) to that transverse to it (G_1) indicates highly aligned graphene structure [61]. Fig. 4d shows the G_{II}/G_1 ratio of the GA/PVA composites with different degrees of barrier concentration. The large increase in G_{II}/G_{\perp} ratio by almost 50% after barrier coating is likely due to the damaged GA/PVA ligaments in the transverse direction (see Fig. 1c) by the advancing ice crystals during the 2nd unidirectional freeze casting (Fig. 4a). The G_{II}/G_1 ratio, however, remained almost constant with increasing barrier concentration, suggesting similar degrees of aligned graphene structures. The above observation also implies that the improved alignment by barrier coating mainly depended on the processing parameters in the 2nd unidirectional freeze casting process, such as the freezing rate [38,48], whereas the PVA concentration only determined the thickness of barriers without disrupting the graphene skeletons. The fast freezing rate generated using the custom-made apparatus in this study (Fig. S2b) led to rapidly advancing ice fronts that effectively removed the transverse conductive ligaments only to maintain the longitudinal skeletons with enhanced orientation.

In an effort to specifically study the effects of porosity and density of composites on dielectric properties, the composites with PVA barriers were compacted to different degrees by applying compression transverse to the alignment direction. The SEM images of GA/PVA-25 PVA composites with porosities ranging from the original 94% (without compaction) to 0% (after full compaction) are shown in Fig. 5a. The porosities of the composites were calculated based on the equation [62]:



Fig. 4. (a) Schematic of the 2nd run of unidirectional freeze casting to apply PVA barrier; (b) SEM image and (c) polarized Raman spectra for GA/PVA-25PVA; and (d) intensity ratio of Raman G band for GA/PVA composites in the parallel (G₁) and transverse (G₁) directions as a function of PVA concentration. (A colour version of this figure can be viewed online.)

Porosity
$$(P) = \left(1 - \frac{\rho}{\rho_0}\right) \times 100\%$$
 (2)

where ρ_0 (~1.27 g/cm³) and ρ are the densities of the solid and porous GA/PVA composites, respectively. The composites had denser networks with intact, aligned main skeletons as the porosity were reduced after compaction. It is seen from the TEM images of the fully compacted GA/PVA-25PVA (Fig. 5e) that the aligned main skeletons consisted of highly orientated rGO sheets within the PVA matrix. These rGO/PVA composite main skeletons were sandwiched between the PVA barrier layers, effectively preventing their direct contact and thus current leakage. The dielectric properties of the composites with different porosities are given in Fig. 5f and g. The AC conductivity, dielectric constant and dielectric loss all increased with reducing porosity. There were consistent reductions in conductivity and dielectric constant with increasing PVA barrier concentration, confirming the important role of barriers in disconnecting the transverse conductive ligaments. The effectiveness of PVA barriers in reducing the dielectric loss is clearly seen in Fig. 5g. Without the barrier, the dielectric loss surged drastically when the porosity was reduced because of direct contact between the aligned main skeletons when the porous GA/PVA composites were compacted. In the presence of barrier, however, the loss values varied only moderately. The thickness of barriers for composites coated with different concentrations of PVA were examined by analyzing the corresponding SEM images using software Image], and the details are given in Supporting Information. The barrier thickness tended to increase with increasing PVA concentration, and a large average thickness of ~0.36 μ m was achieved for GA/ PVA-25PVA (Table S1). The effect of barrier thickness on dielectric properties of GA/PVA composites was also studied (Fig. S5). Both the dielectric constant and loss values decreased with the increasing barrier thickness. It is confirmed that the composites containing a thick barrier (GA/PVA-25PVA) delivered a low loss below 0.1, which is sufficient for practical applications such as embedded capacitors [63]. This finding suggests that the insulating barriers effectively suppressed the tunneling current between the adjacent aligned conductive skeleton, reducing the current leakage. Thus, an exceptional dielectric constant of over 1000 along with a remarkable dielectric loss of less than 0.08 were achieved simultaneously for GA/PVA-25PVA.

In summary, the dielectric properties measured at 1 kHz of the current composites (GA/PVA-25 PVA) with different porosities are compared with those reported in the open literature for polymerbased composites containing ceramic and conductive fillers, as shown in Fig. 6. To differentiate the dielectric performance of composites containing different types of fillers, Fig. 6a was divided into three regions. Region I represents high performance dielectric materials, where the dielectric constant is high while the corresponding loss is low. The composites located in Region I simultaneously enjoy a high dielectric constant in the order of 100 or above, and a low loss of less than 0.1. The GA/PVA-25PVA composites obtained after compaction possess ideal dielectric properties and belong to Region I. Region II is designated as moderate dielectric materials, where the increases in both dielectric constant and loss are moderate. Polymer composites reinforced with ceramic fillers fit to Region II [64-66]. They deliver very low dielectric loss values due to the insulating nature of ceramic particles, while only moderate increases in dielectric constant are achieved, even with very high filler contents ranging 40-50 vol%. Region III represents the materials with poor dielectric properties regardless of the large increase in dielectric constant, due to the high loss values of well over 0.1, unsuitable for practical applications. Conductive filler/polymer composites containing fillers above the percolation and without barriers [22,34,67] belong to Region III or the boundary between Regions II and III where the interconnected conductive network causes current leakage. However, the application of barrier does not always ameliorate both the dielectric properties of composites and the effect of barriers is



Fig. 5. (a–d) Morphologies of GA/PVA-25PVA composites with different porosities controlled by compaction; (e) TEM images of GA/PVA-25PVA (P = 0%); effects of porosity on (f) AC conductivity and dielectric constant; and on (g) dielectric loss measured at 1 kHz of composites coated with PVA barriers of different concentrations. (A colour version of this figure can be viewed online.)

different depending on the type and dimension of fillers. For example, the thin organic coating applied to 0-D Ag@C spherical particles served as electrical barriers to form a continuous interparticle-barrier network and retained a high constant and a stable low loss [25]. Disappointingly, however, the introduction of barrier on individual 1D CNTs [26,32] or 2D graphene sheets [27] failed to show similar improvements in dielectric properties because of the difficulty to form a continuous barrier on these fillers. Therefore, these composites are actually placed in Region III, similar to the composites without insulating barriers.

To further demonstrate the advantages of barrier, the ratio of dielectric constant to loss was used as a measure of the overall dielectric performance, where a higher 'dielectric ratio' means better dielectric performance [67], and the results are compared with available data, as shown in Fig. 6b. Filler contents corresponding to the highest dielectric ratio were chosen for all composites used in Fig. 6b. It is seen that both the ceramic filler/ polymer composites (Region II) and the conductive filler/polymer composites without barriers (Region III) delivered similar dielectric ratios of below 3000. Among the composites with insulating barriers, those containing CNTs or graphene sheets failed to show any benefits over those reinforced with metal particles like Ag. The

current GA/PVA-25PVA composites with a porosity of 0%, however, delivered an exceptional dielectric ratio of 13,843, the highest among all polymer composites thus far reported. This finding unequivocally supports our claim in that the compacted GA/PVA-25PVA composites with a thick insulating barrier can serve as an ideal material for niche applications including capacitors for energy storage and electromechanical actuators.

4. Conclusion

GA/PVA composites with a highly aligned porous structure were produced by simultaneous unidirectional freeze casting of aqueous rGO/PVA dispersion and *in situ* cryo-polymerization of PVA, followed by freeze drying. The composites delivered an ultralow density, a high porosity and excellent thermal stability. A two-step process was developed for the first time to apply insulating barriers between the aligned networks to remove transversely interconnected ligaments and thus to avoid direct contacts between the neighboring conductive main skeletons. The resulting composites coated with barriers exhibited exceptional dielectric properties. The following can be highlighted from the experimental study:



Fig. 6. Comparison of (a) dielectric constant and loss, and (b) dielectric constant/loss ratio of polymer composites reinforced with ceramic and conductive fillers. ¹AC = amorphous carbon; ²Pl = polyimide; ³PP = polypropylene; ⁴GNP = graphite nanoplatelet. (A colour version of this figure can be viewed online.)

- (i) The GA/PVA composites obtained after the initial freeze casting consisted of highly aligned main skeletons, which were bridged by ribbon-like, short GA/PVA ligaments in the transverse direction. The unique aligned and porous structure was achieved by unidirectional freeze casting, where the PVA matrix assembled together with rGO sheets between the growing aligned ice crystals and cryo-polymerized under the supercooling condition.
- (ii) The GA/PVA composites delivered excellent thermal stability. The $T_{50\%}$ and T_g of composites containing 5 wt% graphene were 54 °C and 29 °C higher than those of neat PVA, respectively. The excellent thermal properties of the composites were aided by the hydrogen bonds formed between rGO sheets and PVA, as proven by FTIR spectra.
- (iii) The fully consolidated, rigid GA/PVA-25PVA composites obtained after the two-step process and compaction delivered tunable dielectric constants ranging from 290 to 1059 with stable, low loss values below 0.08, which satisfy practical applications such as embedded capacitors. The PVA barriers

applied onto the aligned GA/PVA networks effectively avoided direct contacts between the conductive skeletons by breaking the transverse ligaments while the compaction along the transverse direction significantly enhanced the dielectric constant of the composites.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2017.07.079.

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