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ARTICLE

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The effect of temperature on the electrical and thermal conductivity of graphene-based polymer composite films

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Abstract

In this work, we studied the effect of temperature on the electrical, thermal, and mechanical properties of graphene-based poly(vinylidene fluoride-cohexafluoropropylene) composites. Graphene-based polymer composites (PC-Gn) with various graphene content were prepared using solution mixing and molding process. The physical, chemical, and mechanical properties of the PC-Gn composites were investigated using different characterization techniques includdifferential scanning calorimetry, scanning electron microscopy, ing potentiostatic electrochemical impedance spectroscopy, and dynamic mechanical analysis (DMA). DMA results showed that the strength of obtained PC-Gn composites increased with higher graphene wt%. The in-plane electrical and thermal conductivity values were measured over a temperature range from 25 to 125°C using a four-point probe electrical conductivity system and optothermal Raman technique, respectively. Our results showed that temperature had a noticeable effect on the in-plane electrical and thermal conductivity values for PC-Gn where both values gradually decreased by the increment of temperature. We believe that by increasing temperature, the vibration of composite particles became more severe, which increased the system's anharmonicity and strongly reduced the lifetimes of electrons and phonons in the composite. Further analysis, including electrochemical analysis, was also done on all composite films showing that our process produced highly conductive films that potentially can be used in many electrochemical applications in the future.

K E Y W O R D S

applications, conducting polymers, thermal properties

1 | INTRODUCTION

Graphene, a one-atom-thick two-dimensional honeycomb network of carbon atoms, has a very large specific surface area of $2600 \text{ m}^2/\text{g}$ and very high mechanical, thermal, and electrical properties.¹ The in-plane thermal conductivity of a single layer of graphene is very high and is around 3080-5150 W/mK at room temperature.²

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The ultimate strength and Young's modulus can reach up to 130 GPa and 1 TPa respectively for a free-standing graphene monolayer.³ Besides, the electrical conductivity (EC) for a single defect-free graphene layer can reach the value of $10^7 - 10^8$ S/m. However, polymers are electrical insulators, and their thermal conductivity value is in the range of 0.1-0.5 W/mK, which is very low. Researchers have used graphene,⁴ reduced graphene oxide,^{5–8} carbon nanotubes⁹ to enhance the thermal and EC values of polymers.^{10–13} The formation of multiple interconnected conductive graphene networks within the polymer composites enhances the transfer of electrons and phonons.¹⁴ The direction of electron/phonon transport depends on the orientation of graphene flakes within the polymer composite.¹⁵ To fabricate a graphene-based polymer composite (PC-Gn) with high conductivity, the number of effective conductive channels should be increased.¹⁶ This can be achieved by (a) dispersing graphene particles with a larger size, larger aspect ratio, and lesser defects; (b) better alignment of graphene particles within the matrix of polymer; (c) enhancing the interface between the matrix and the graphene filler.^{17,18}

Conductive PC-Gn composites can replace metals in many applications including electronics, sensors, biomedical devices, and batteries.^{19–22} However, these composites are much more sensitive to temperature than metals and it is very important to understand the dependence of their thermal and EC values on their temperature. The mismatch between the expansion coefficients of polymer and conductive filler can disrupt the conductive network at high temperatures hence decreasing the conductivity value of the composites.²³ Besides, the operating temperature has a significant effect on the characteristics of the interface between the polymer matrix and the graphene filler and, as statistically more voids and disconnections between the graphene fillers are generated by increasing the temperature which eventually affects the thermal and EC values of the composites obtained.24

Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) has excellent chemical stability, mechanical properties, and interesting piezoelectric properties, which make PVDF-HFP polymer composites widely used in many applications including filtration, ionic conductivity, and wastewater treatment.²⁵ Thus, it is important to study the effect of high temperature on PC-Gn that can be used in many applications where high temperature is a critical problem like in polymer heat sinks, miniaturized electronic devices, sensors, batteries, and supercapacitors.7,21,26 For example, graphene-based composites can be used in Lithium-ion batteries for electric cars which demand an efficient and effective way to conduct heat since it is subject to the rise in temperature during usage.²⁷ Therefore, it is important to study the thermal conductivity of graphene-

based composites at high temperature since they can be ideal candidates for thermal management because of their high-thermal conductivity. To the best of our knowledge, the influence of temperature on thermal and EC values of Gn-PC has not been thoroughly investigated before. Temperature has a significant effect on the electrical and thermal properties of graphene-based composites, in addition to the interface between the polymer matrix and the graphene filler. Therefore, there is a huge need to know the influence of temperature on electrical/thermal conductivity and mechanical properties of graphene-based composites that can be used in different industries.^{28–30} This study aims to shed more light on this topic and open the door for using Gn-PCs in challenging applications at elevated temperatures including electronic devices, batteries, and heat sinks.7,26,31

2 | EXPERIMENTAL SECTION

2.1 | Materials

Graphene flakes with a specific surface area $\leq 40 \text{ m}^2/\text{g}$, high purity of 98.5%, and lateral average particle size of 7 µm were procured from Graphene Laboratories Inc. (USA). Poly(vinylidene fluoride-co-hexafluoropropylene), abbreviated as PVDF-HFP, with an average molecular weight of 455,000 g/mol, a melting point of 155°C and an average density of 1.77 g/ml at 25°C, and N, N-dimethylformamide (DMF) with a boiling point at 153°C (1 atm) and density of ~0.9 g/ml were obtained from Sigma. A Silicon mold with 16 cubical cavities ($3.5 \times 3.5 \times 3.5 \text{ cm}^3$) was procured from Silikomart (Italy). Phosphate-buffered saline (PBS) (powder, pH 7.4) was purchased from Sigma and it was used to measure the electrochemical impedance of the composites obtained.

2.2 | Graphene-based polymer composites preparation method

PVDF-HFP pellets were dissolved in DMF to make a homogeneous solution. Graphene powder was dispersed in DMF under magnet stirring to prepare the suspension (5 g/L). The mixture was then sonicated for 30 min at 35° C. The polymer solution (20 g/L) and graphene dispersion were heated to 60° C under vigorous stirring and mixed following the recipes reported in Table 1. Then the mixture was poured into the cavities of the silicon mold. Afterward, the mold was then placed inside an oven with proper ventilation at 90° C for 24 h to remove the solvent (DMF) gradually and completely. The thickness of the samples was in the range of 0.2–0.4 mm.

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Sample ID \downarrow	Graphene solution (5 g/L)	Polymer PVDF-HFP (20 g/L)	Graphene (Gn) content in the film (wt%)
PVDF-HFP	0 ml	25 ml	0%
PC-Gn 1%	1 ml	25 ml	0.99%
PC-Gn 5%	5 ml	25 ml	4.8%
PC-Gn 10%	11 ml	25 ml	9.9%
PC-Gn 20%	15 ml	15 ml	20%

TABLE 1 Recipes of graphene-based PVDF-HFP composite (PC-Gn) films with the respective volume used for graphene and polymer solution

Abbreviations: PC, polymer composites; PVDF-HFP, poly(vinylidene fluoride-co-hexafluoropropylene).



2.3 | Graphene-based composite film characterization techniques

The surface morphology for each of the composite films was studied using a scanning electron microscope (SEM-MIRA 3 LMU) from Tescan (Czech Republic) at an accelerating voltage of 20 kV. The thickness of each composite film was measured using the thickness gage MP1 from Brunswick Instrument (UK) with a resolution of 2 µm. The thermal analysis for the samples was performed using a differential scanning calorimeter Q2000 (TA Instruments, USA). The films were studied under a heat/cool/heat cycle in the temperature range from 25 to 200°C with a rate of 10°C/min under nitrogen gas purging. The thermal conductivity values for the PC-Gn samples were measured using optothermal Raman (OTR) spectroscopy as described in our previous publications.^{14,32} A Raman spectrometer with a backscattering configuration and a green laser of an excitation wavelength $\lambda = 532$ nm was used to perform the thermal conductivity measurements. For this measurement, the laser generates energy in a micron-sized region, and the Raman signal, namely the G-peak of the graphene Raman signal, which is a strong function of temperature, measures the temperature in the heated region. By varying the power of the laser, a relationship between the rate at which energy is put in the sample and the temperature gradient established in the studied sample can be measured in a steady-state regime. Then, upon solving the heat diffusion equation across the geometry of the measured sample, the thermal conductivity of the measured sample can be derived, as explained in more detail in a previous publication by the authors.¹⁴ The high-spectral resolution required to observe the displacement of the graphene G-peak was made possible by analyzing the light with a triple monochromator and using a 50 µm slit. A four-point probe system from Ossila (UK) was used to measure the EC for each composite film. The electric current passed between the outer two probes and the change in the voltage was recorded across the inner two probes. The EC for each film was obtained and measured 25 times, and the mean value was reported for each film. Rectangular composite films (length: 15 mm; width: 7 mm) were used for each measurement. The electrochemical performance of the PC-Gn was performed using a three-electrode setup via an electrochemical workstation (Interface 1000, Gamry Instruments, USA). These three electrodes were immersed in the phosphate buffer solution to the same level and cyclic voltammetry (CV) curves (100 mV/s, +/-0.5 V) for all composites were recorded. Electrochemical impedance spectroscopy (EIS) was also measured (100, 20 kHz) for all composite films of areas 0.5 cm² using the three-electrodes system in 1 M PBS. The Ag/AgCl electrode was used as a reference while the Platinum wire acted as the counter electrode.³³ DMA8000 by PerkinElmer was used to get the loss and storage modulus with tan δ (phase shift) curves to study the viscoelastic properties of the composite films obtained. At a constant frequency of 1 Hz, the single cantilever mode was used to test rectangular samples and the temperature was ramped from 30 to 120°C at a rate of 10°C/min.

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FIGURE 1 SEM images for composite films for various graphene wt%: (a) PVDF-HFP (b) PC-Gn 1% (c) PC-Gn 5% (d) PC-Gn 10% (e) PC-Gn 20% (f) cross-sectional view for PC-Gn 20%. Gn, graphene; PC, polymer composites; PVDF-HFP, poly(vinylidene fluoride-co-hexafluoropropylene); SEM, scanning electron microscope

3 | RESULTS AND DISCUSSION

Figure 1 shows the SEM micrographs of the samples listed in Table 1. Graphene flakes across the top surface of the composite films seem to be uniformly distributed. The surface of the copolymer PVDF-HFP film shown in Figure 1a was smooth, and it appeared to conglomerate because of the spherulitic structure of neat PVDF-HFP.³⁴ For PC-Gn 1% as shown in Figure 1b, some graphene flakes appeared on the surface of the composite surrounded by the polymer matrix that appeared in dark black. As the concentration of graphene filler increased in the composite (more graphene wt%), more graphene flakes could be visually detected on the surface of the films. These flakes were mainly dispersed in-plane across the polymer composites obtained and some are shown in a bright color indicating that these flakes are a bit tilted. The distribution of graphene flakes on the surface of the films was relatively uniform (Figure 1c-e). Graphene

flakes appeared to be distributed along the surface of the composite films with higher graphene wt%. Graphene flakes were seen overlapping for PC-Gn 5%, PC-Gn 10%, and PC-Gn 20% as shown in Figure 1, and in the cross-sectional image for PC-Gn 20% where graphene flakes are seen stacked on top of each other.

Figure 2 shows the differential scanning calorimetry (DSC) thermograms of the PC-Gn films. A heating/ cooling/heating process is very necessary to identify crystallization and melting peaks for semi-crystalline composite PC-Gn that may shift due to the difference in the composition of the polymer composites.³⁵ For a neat PVDF-HFP copolymer the melting temperature is ~155°C provided by the supplier. After adding 1 wt% of graphene and from the DSC diagrams in Figure 2a, PC-Gn 1% film exhibited an exothermic peak showing an average crystallization temperature (T_c) at 128.5°C and an endothermic average peak (T_m) at 154.7°C which is associated with the melting temperature of the crystalline

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FIGURE 2 DSC diagrams of composite films: (a) PC-Gn 1% (b) PC-Gn 10% (c) PC-Gn 20%. DSC, differential scanning calorimetry; Gn, graphene; PC, polymer composites [Color figure can be viewed at wileyonlinelibrary.com]

phase of the PVDF-HFP copolymer.^{34,36} This result agrees with the melting temperature value that was found by thermal gravimetric analysis (TGA) that was done by the authors in a previous publication.¹⁸ The thermal stability of polymer composites is an important parameter that can be obtained from the TGA analysis.³⁷ Previous analysis showed that the initial degradation temperature of the polymer composites was not affected by the addition of graphene filler up to 20 wt%.¹⁸ However, the carbon ash remaining of the polymer composites depended on the initial graphene content (%).¹⁸ With increasing graphene content (wt%), both peaks become broad for PC-Gn 10% and PC-Gn 20% as seen in Figure 2b,c. This agrees with previous studies, where graphene flakes serve as an effective nucleating agent for PVDF-HFP composites and they encouraged the meltcrystallization rates of the composites.38

Dynamic mechanical analysis (DMA) is a common method used to study the viscoelastic mechanical properties of polymer composite materials. These mechanical properties are important to study the bonding between the filler and the matrix in any composite material. Using rectangular composite film samples, the storage modulus, loss modulus, and loss factor $(\tan \delta)$ were measured across a temperature range between 30 and 120°C as shown in Figure 3. The storage modulus sudden decrease indicates the transition between the glassy and the rubbery states of the polymer composite or the presence of molecular motion/rotation in the polymer composite. This is accompanied by having also a peak in the tan δ curve that is calculated as the ratio between the viscous and the elastic portion of the composite. Therefore, there was no sudden drop in the modulus for any of the composite films for the temperature range between 30 and 120°C since the temperature range studied is beyond the glass transition temperature for the copolymer matrix PVDF-HPD which is \sim -35° C.³⁹ However, the presence of graphene flakes improves the stiffness of these composites since the storage modulus is higher with increasing graphene wt%. At the temperature of 30°C, the storage modulus was 680 MPa for pure PVDF-HFP, the storage modulus increased to reach 1230 MPa with an increase of nearly 80% for PC-GN 20% as shown in Figure 3f. As graphene wt% increases in the composite, the mobility of the chains of PVDF-HFP copolymer is restricted due to the presence of these graphene flakes fillers making these composites

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FIGURE 3 Storage modulus, loss modulus and tan δ curves from dynamic mechanical analysis (DMA) for the following films (a) PVDF-HFP (b) PC-Gn 1% (c) PC-Gn 5% (d) PC-Gn 10% (e) PC-Gn 20% (f) variation of storage modulus and loss modulus as a function of graphene content at T = 30°C. Gn, graphene; PC, polymer composites; PVDF-HFP, poly(vinylidene fluoride-co-hexafluoropropylene)

more brittle.¹⁸ Also, the loss modulus for all composites decreased with higher temperature as shown in Figure 3. As the temperature continues to increase above the glass transition temperature, the molecular frictions in the composites are reduced, thus less energy is dissipated which causes the loss modulus to decrease. Also, there were no peaks for the loss factor (tan δ) curve which indicates that there is no major motion/rotation of the main

chain backbone for the copolymer composite at the temperature range between 30 and 120°C. Therefore, DMA results showed that there was no major molecular motion/rotation in the composites for the temperature range between 30 and 120°C and there was a good integration between the filler (graphene flakes) and the polymer matrix (PVDF-HFP) which is compatible with the studies that the authors published before.¹⁸

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FIGURE 4 (a) Electrical conductivity (EC) as a function of graphene content (wt%) across a temperature range between 25 and 125°C for PC-Gn 1%, PC-Gn 5%, PC-Gn 10%, and PC-Gn 20% composite films (b) EC for PC-Gn 20% as a function of temperature (c) EC of all composites at 25°C. Gn, graphene; PC, polymer composites [Color figure can be viewed at wileyonlinelibrary.com]

Figure 4 shows the EC values of PC-Gn films as a function of temperature from 25 to 125°C. Enhanced EC was achieved with higher graphene wt% in the composites where graphene composites with 20 wt% achieved the highest EC 4445 S/m at 25°C and this EC corresponds to a major improvement from the EC for pure PVDF-HFP.³² PVDF-HFP, like other polymers, is an electrical insulator with a very low EC which is around 10^{-14} (S/m), and this obtained EC value of the composites corresponds to a huge enhancement of 17 orders of magnitude making these composites comparable to conductive metals.³⁰ This improvement is attributed to many factors including (a) using pure conductive fillers of graphene flakes (i.e., graphene with 98.5% purity), (b) the dispersion of the graphene flakes across the polymer composites as shown in the SEM images in Figure 1, (c) the good integration between the polymer matrix PVDF-HFP and graphene flakes as shown in DMA results in Figure 3, (d) graphene flakes were stacked on top of each other due to the slow gravitational settling of the graphene in PVDF-HFP matrix during the slow solvent evaporation process.14,18

The value of the EC dramatically increased after adding 1 wt% of graphene flakes. The conductive graphene flakes form multiple conductive channels within these fabricated graphene-based PVDF-HFP composites, thus improving the conductivity of these composites with increasing graphene wt% based on a percolation model^{15,18,40} Statistically, more conductive pathways can be generated by the addition of graphene flakes. Thus, the chance of overlapping between the flakes would be also higher with higher graphene wt% which can be estimated by a percolation model.¹⁶ As for the effect of temperature on the EC of the composites obtained, both electrons and phonons exist in a carbon-based material. The trend of a decreasing conductivity is attributed to the fact that with increasing temperature, the probability of electronphonon interaction increases rapidly, resulting in electrons being scattered by phonons at high temperatures which causes this decrease in the EC at high temperatures for graphene-based PVDF-HFP composites. Similar to metals. the value of EC of PC-Gn decreased with the increase of temperature. The lower conductivity is due to electron scattering resulting in a sharp decrease in the mean free path of electrons.⁴¹ Graphene flakes were aligned in a plane creating conductive channels where electrons were able to pass across the polymer matrix that has a very low conductivity value.³² The energy of carbon atoms is at a low level when the temperature is low; however, they acquire more energy and start to vibrate across their mean positions when the temperature increases.²⁴ Therefore, the EC of the films is expected to decrease with temperature due to the collision activity of free electrons and carbon atoms in graphene. Moving electrons tend to collide easily with oscillating atoms thus reducing the conductivity of the composite films obtained for all graphene-based composites at high temperatures.²⁰ This analysis agrees with previous studies that showed that high-temperature affects the electrical properties of composites and the characteristics of the interface between the graphene fillers and the polymer matrix.42-44

There is extensive research ongoing to utilize graphene in batteries and supercapacitors for their superior electrical and electrochemical properties.^{45–47} There



FIGURE 5 (a) CV, (b) CSC, (c) EIS for PVDF-HFP, PC-Gn 1%, PC-Gn 5%, PC-Gn 10%, and PC-Gn 20% composite films. CSC, chargestorage capacity; CV, cyclic voltammetry; EIS, Electrochemical impedance spectroscopy; Gn, graphene; PC, polymer composites; PVDF-HFP, poly(vinylidene fluoride-co-hexafluoropropylene) [Color figure can be viewed at wileyonlinelibrary.com]

 TABLE 2
 Charge-storage capacity (CSC) for different materials used as electrodes

Electrode material	CSC (mC/cm ²)	Reference
Iridium oxide	1–5	Shin et al. ⁵¹
Platinum	0.05-0.15	Green et al. ⁵²
Tantalum/Ta ₂ O ₅	0.5	Cogan et al. ⁵³
Titanium nitride	1	Cogan et al. ⁵³
PC-GN 20%	9	This article

are many promising applications for graphene-based electrodes for both electrochemical double-layer capacitors and rechargeable lithium-ion batteries.⁷ Thus, the electrochemical analysis was obtained for all PC-Gn films to study their performance as an electrode material, their electrochemical impedance under typical aqueous conditions, and their potential application in batteries.^{27,48}



FIGURE 6 Thermal conductivity (TC) values for PC-Gn films as a function of temperature. Gn, graphene; PC, polymer composites [Color figure can be viewed at wileyonlinelibrary.com]

Figure 5a shows the CV curves for all the composite films of interest with CV curves for PVDF-HFP, PC-Gn 1%, PC-Gn 5% composites shown in the inset of the figure.

Neat PVDF-HFP did not show any current density value across the voltage range between -0.4 and 0.4 V. By adding graphene to PVDF-HFP, the composites became conductive and the CV curves for PC-Gn 10% and PC-Gn 20% showed a typical rectangular behavior depicting an excellent super capacitive behavior.⁴⁹ The CV curves become quasi parallelograms at the extreme voltages, which could be due to the intrinsic resistance of the stacked graphene flakes. The presented CV curves are in agreement with the previously reported CV curves of graphene electrodes.^{49,50} Figure 5b shows how the charge-storage capacity (CSC) (Area under the curve for the CV curve) increases significantly with increasing the percentage of graphene weight % in these composites. In comparison to other materials used as electrodes as shown in Table 2, PC-Gn 20% composite has higher charge storage capacity than Iridium oxide, platinum, tantalum/Ta₂O₅, and titanium nitride which show the potential of these composites. These electro-chemical properties for PC-Gn allow researchers to use this material in next-generation batteries, super-capacitors, and bio-interfaces.^{54,55} Figure 5c shows the Electrochemical impedance (EIS) of all composite films. The impedance values dramatically decreased after adding just 1 wt% of graphene. The impedance continued to decrease for 5, 10, and 20 wt% of graphene but with a smaller factor, which could also be explained by the percolation transition behavior in conductive polymer composites.¹⁸ The decrease in the amplitude of the impedance spectrum following the addition of the graphene flakes can be related to the presence of conductive graphene channels on the surface of the composites, which are confirmed in the SEM images in Figure 1 complementing also the results of the EC measurements in Figure 4. Neat PVDF-HFP had a very high impedance in the range of $10^8 \Omega$ but adding even 1% of graphene in the matrix would drop the value by nearly half as shown in Figure 5c. Additionally, the reduced impedance makes these graphene-based composites suitable for many applications in the future because it allows for a higher signal-to-noise ratio (SNR) in any bio-potential recording.53

Figure 6 represents the in-plane thermal conductivity values obtained for all the composite films at a temperature range between 25 and 125°C using the OTR method. The PC-Gn samples with higher graphene content had higher TC values. This can be attributed to the increase in thermal transport capacity (phonons movement) due to the proper alignment of graphene flakes in-plane across the composite films.^{14,18} Proper orientation of the graphene flakes within composite films would supply a direct path of lower thermal resistance for phonons to travel.^{15,40} The TC values gradually decreased by increasing the temperature for all the samples and this was more pronounced for the samples

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with higher graphene content. The highest value of inplane TC (~26 W/mK) was obtained for PC-Gn 20% at 25°C. This value decreased to 23 and 19 W/mK at temperatures 100 and 125°C, respectively. Thermal conductivity in any material is governed by phonons and electrons movement, therefore the thermal conductivity value of the material is divided into two main parts: $k = k_e + k_p$ where k_e is the thermal conductivity due to electrons movement and k_p is thermal conductivity induced from atom interactions and collisions (phonons). Based on Wiedermann-Franz law, we can estimate the thermal conductivity due to movement of electrons:

$$k_e = L_0 \sigma_e T$$

where the thermal conductivity due to electrons (k_e) is the product of the Lorentz constant ($L_0 = 2.44 \times 10^{-8} W\Omega/K^2$), EC (σ_e), and temperature (T). Thus, for our polymer composites, the highest value for in-plane EC was 4445×10^3 S/m at a temperature of 25°C, therefore the resulting electronic thermal conductivity would be eliminated since it is around 3×10^{-2} W/mK and it is less than 2% of the thermal conductivity of the material. Therefore, phonons are the main carriers of heat for these composites. However, phonons can be scattered through several mechanisms including phonon-impurity scattering, Umklapp phonon-phonon scattering which happens mainly in crystalline materials, phonon-electron scattering, and phonon-boundary scattering. The graphene we used was 98.8% pure and the thermal measurements were performed at room temperature and above so that the rate of phonon-impurity scattering was minimized because in the measured temperature range phononimpurity scattering is unlikely. With increasing temperature, the phonon-phonon scattering rate is expected to increase which may be the reason behind this decrease in the thermal conductivity values of these composites as shown in Figure 6. As thermal conductivity is related to establishing a thermal pathway in the polymeric matrix that allows phonons to transport more efficiently and reducing phonon scattering mechanisms.¹⁸ This analysis is compatible with previous studies that attributed the observed dependence of thermal conductivity on temperature to the severe vibration of composite fillers at high temperatures, which strongly impeded the movement of both electrons and phonons across the composite films decreasing the in-plane thermal conductivity values.^{17,18} Also, graphene weight % affects the temperature dependence of thermal conductivity of obtained polymer composites. For a low weight of graphene, the thermal conductivity of the composite film is weakly temperature-dependent, indicating that the scattering of phonons by mass fluctuation and boundaries are the dominant phonon scattering mechanisms in the measured

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film (as these scattering processes are temperature-independent).⁵⁶ However, as the weight of graphene increases, the temperature dependence of thermal conductivity increases, indicating a predominance of phonon–phonon scattering processes, which are temperature-dependent. However, the in-plane thermal conductivity for PC-Gn 20% at T 125°C remains higher than the thermal conductivity of PC-Gn 10% at T 25°C, which shows that more conductive channels were established with higher graphene content (wt%) allowing these composites to have higher in-plane thermal and electrical conductivities as shown in Figures 6 and 4, respectively.

4 | CONCLUSION

We fabricated a series of highly conductive graphenebased PVDF-HFP composites (PC-Gn) by dispersing and orienting graphene flakes in the polymer matrix through a solution mixing and molding process. SEM results showed that graphene flakes were dispersed in-plane across composite films. DSC thermal analysis showed that the graphene fillers serve as an effective nucleating agent for PVDF-HFP composites and thus promoted the overall melt-crystallization rates of the composites to a certain graphene wt%. DMA analysis showed that there is good integration between graphene fillers and the polymer matrix, in addition to the fact that adding more graphene filler (wt%) will make the composite stronger but more brittle which complemented the results that were published by the authors before. The in-plane electrical and thermal conductivity values of the PC-Gn decreased linearly by increasing temperature. The polymer composites remained conductive even at a temperature as high as 125°C. For a low weight of graphene, the conductivity of the composite film is weakly temperature-dependent, indicating a high rate of scattering of phonons by mass fluctuation and boundaries. However, as the content of graphene increases in the film, the temperature dependence of thermal conductivity increases, indicating a predominance of phonon-phonon scattering processes, which are temperature-dependent. The graphene-based PVDF-HFP composites also showed promising electrochemical performance in a wide temperature range. Consequently, PC-Gn can be used in several applications such as smart textiles, wearable sensors, and batteries in the future.

DATA AVAILABILITY STATEMENT

No. Research data are not shared.

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REFERENCES

- G. Jo, M. Choe, S. Lee, W. Park, Y. H. Kahng, T. Lee, *Nano*technology **2012**, 23, 112001.
- [2] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan,
 F. Miao, C. N. Lau, *Nano Lett.* **2008**, *8*, 902.
- [3] D. G. Papageorgiou, I. A. Kinloch, R. J. Young, Prog. Mater. Sci. 2017, 90, 75.
- [4] Z. L. Hou, W. L. Song, P. Wang, M. J. Meziani, C. Y. Kong, A. Anderson, H. Maimaiti, G. E. Lecroy, H. Qian, Y. P. Sun, ACS Appl. Mater. Interfaces 2014, 6, 15026.
- [5] A. L. Ahmad, U. R. Farooqui, N. A. Hamid, Polymer 2018, 142, 330.
- [6] P. Kumar, F. Shahzad, S. Yu, S. M. Hong, Y. H. Kim, C. M. Koo, *Carbon N. Y.* **2015**, *94*, 494.
- [7] B. Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, *Adv. Mater.* **2010**, *22*, 3906.
- [8] P. Kumar, M. K. Yadav, N. Panwar, A. Kumar, R. Singhal, *Mater. Res. Express* 2019, *6*, 115604.
- [9] Z. Han, A. Fina, Prog. Polym. Sci. 2011, 36, 914.
- [10] W. E. I. Lin, R. Zhang, C. P. Wong, *Electron. Mater.* 2010, 39, 268.
- [11] L. Lv, W. Dai, A. Li, L. Cheng-Te, Polymers 2018, 10, 1201.
- [12] A. Li, C. Zhang, Y.-F. Zhang, Polymers 2017, 9, 437.
- [13] X. Huang, Z. Yin, S. Wu, X. Qi, Q. He, Q. Zhang, Q. Yan, F. Boey, H. Zhang, *Small* **2011**, *7*, 1876.
- [14] A. Tarhini, A. R. Tehrani-Bagha, M. Kazan, J. Appl. Polym. Sci. 2020, 137, 48927.
- [15] X. Shen, Z. Wang, Y. Wu, X. Liu, Y.-B. He, Q. Zheng, Q.-H. Yang, F. Kang, J.-K. Kim, *Mater. Horizons* **2018**, *5*, 275.
- [16] A. Aryanfar, S. Medlej, A. Tarhini, B. A. R. Tehrani, Soft Matter 2021, 17, 5258.
- [17] A. Henry, Ann. Rev. Heat Trans. 2014, 17, 485.
- [18] A. A. Tarhini, A. R. Tehrani-Bagha, Compos. Sci. Technol. 2019, 184, 107797.
- [19] L. Liao, Y. C. Lin, M. Bao, R. Cheng, J. Bai, Y. Liu, Y. Qu, K. L. Wang, Y. Huang, X. Duan, *Nature* **2010**, *467*, 305.
- [20] G. Kaur, R. Adhikari, P. Cass, M. Bown, P. R. Gunatillake, Soc. Chem. 2015, 5, 37553.
- [21] Z. Song, T. Xu, M. L. Gordin, Y.-B. Jiang, I.-T. Bae, Q. Xiao, H. Zhan, J. Liu, D. Wang, *Nano Lett.* **2012**, *12*, 2205.
- [22] M. S. Ergoktas, G. Bakan, P. Steiner, C. Bartlam, Y. Malevich, E. O. Yenigun, G. He, N. Karim, P. Cataldi, M. Bissett, I. A. Kinloch, K. S. Novoselov, C. Kocabas, *Nano Lett.* **2020**, *20*, 5346.
- [23] A. Király, F. Ronkay, Polym. Test. 2015, 43, 154.
- [24] X. Xia, G. J. Weng, J. Zhang, Y. Li, Acta Mech. 2020, 231, 1305.
- [25] H. C. Bidsorkhi, A. G. D'Aloia, G. De Bellis, A. Proietti, A. Rinaldi, M. Fortunato, P. Ballirano, M. P. Bracciale, M. L. Santarelli, M. S. Sarto, *Mater. Today Commun.* **2017**, *11*, 163.
- [26] J. J. Yoo, K. Balakrishnan, J. Huang, V. Meunier, B. G. Sumpter, A. Srivastava, M. Conway, A. Leela, M. Reddy, J. Yu, R. Vajtai, P. M. Ajayan, *Nano Lett.* **2011**, *11*, 1423.
- [27] G. Shi, S. Araby, C. T. Gibson, Q. Meng, S. Zhu, J. Ma, Adv. Funct. Mater. 2018, 28, 1706705.

- [28] R. Yan, J. R. Simpson, S. Bertolazzi, J. Brivio, M. Watson, X. Wu, A. Kis, T. Luo, A. R. Hight Walker, H. G. Xing, ACS Nano 2014, 8, 986.
- [29] J. Chen, B. Liu, L. Yan, Results Phys. 2019, 14, 102363.
- [30] P. Kumar, S. Yu, F. Shahzad, S. M. Hong, Y. H. Kim, C. M. Koo, *Carbon N. Y.* **2016**, *101*, 120.
- [31] S. Afroj, N. Karim, Z. Wang, S. Tan, P. He, M. Holwill, D. Ghazaryan, A. Fernando, K. S. Novoselov, ACS Nano 2019, 13, 3847.
- [32] A. Tarhini, A. Tehrani-Bagha, M. Kazan, B. Grady, J. Appl. Polym. Sci. 2021, 138, 49821.
- [33] M. L. Khraiche, W. B. Phillips, N. Jackson, J. Muthuswamy, *Microsyst. Technol.* 2017, 23, 3671.
- [34] W. Ma, H. Yuan, X. Wang, Membranes 2014, 4, 243.
- [35] G. Wu, X. Xu, X. He, Y. Yan, Polymers 2018, 10, 133.
- [36] Y. Laxmayyaguddi, N. Mydur, A. Shankar Pawar, V. Hebri, M. Vandana, G. Sanjeev, D. Hundekal, ACS Omega 2018, 3, 14188.
- [37] X. He, Y. Wang, Ind. Eng. Chem. Res. 2021, 60, 1137.
- [38] C. Yu, D. Li, W. Wu, C. Luo, Y. Zhang, C. Pan, J. Mat. Sci. 2014, 49, 8311.
- [39] L. F. Malmonge, J. A. Malmonge, W. K. Sakamoto, *Mater. Res.* 2003, 6, 469.
- [40] J. Du, H. Cheng, Macromol. Chem. Phys. 2012, 213, 1060.
- [41] O. Kahveci, H. Tecer, Mater. Res. 2018, 22, 1.
- [42] L. C. Costa, F. Henry, J. Non-Cryst. Solids 2011, 357, 1741.
- [43] C. D. Rio, M. C. Ojeda, J. L. Acosta, M. J. Escudero, E. Hontan, L. Daza, J. Appl. Polym. Sci. 2001, 83, 2817.
- [44] H. Nakano, K. Shimizu, S. Takahashi, A. Kono, T. Ougizawa, Polymer 2012, 53, 6112.

Applied Polymer_WILEY 1 of 11

- [45] I. Ahmad, J. McCarthy, A. Baranov, Y. Gun'ko, *Materials* 2015, 8, 5953.
- [46] Q. Wu, Y. Xu, Z. Yao, A. Liu, G. Shi, ACS Nano 2010, 4, 1963.
- [47] J. K. Lee, K. B. Smith, C. M. Hayner, H. H. Kung, Chem. Commun. 2010, 46, 2025.
- [48] V. Singh, D. Joung, L. Zhai, S. Das, Prog. Mater. Sci. 2011, 56, 1178.
- [49] K. Krishnamoorthy, A. Ananth, Y. S. Mok, S. J. Kim, Sci. Adv. Mater. 2014, 6, 349.
- [50] M. M. M. Ahmed, T. Imae, Phys. Chem. Chem. Phys. 2016, 18, 10400.
- [51] S. Shin, J. Kim, J. Jeong, T. M. Gwon, G. J. Choi, S. E. Lee, J. Kim, S. B. Jun, J. W. Chang, S. J. Kim, *Sens. Mater.* 2016, 28, 243.
- [52] R. A. Green, K. S. Lim, W. C. Henderson, R. T. Hassarati, P. J. Martens, N. H. Lovell, L. A. Poole-Warren Proc. Ann. Int. Conf. IEEE Eng. Med. Biol. Soc. EMBS. 2013, 15, 6957.
- [53] S. F. Cogan, Ann. Rev. Biomed. Eng. 2008, 10, 275.
- [54] T. Sattar, Top Curr Chem., 2019, 377, 10. https://doi.org/10. 1007/s41061-019-0235-6
- [55] G. A. Silva, M. L. Khraiche, Discov. Med. 2013, 15, 357.
- [56] A. Gupta, G. Chen, P. Joshi, S. Tadigadapa, P. C. Eklund, *Nano Lett.* 2006, 6, 2667.

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