Multifunctional graphene nanoplatelets/cellulose nanocrystals composite paper

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Abstract : We demonstrate a water-based method to fabricate strong, electrically and thermally conductive hybrid thin films (papers) made from the combination of graphene nanoplatelets (GnP) and cellulose nanocrystals (CNC). Unpressed and hot-pressed GnP papers containing CNC ranging from 0 wt% to 25 wt% were prepared. It is found that the GnP is well aligned within the hybrid paper, and a higher degree of alignment is induced by the hot-pressing process. The mechanical properties of the resulting papers increased with increasing content of CNC. The hot-pressed 25 wt% CNC hybrid paper showed the best mechanical properties among all the papers studied and improved the tensile strength by 33% and the modulus by 57% compared to neat GnP paper. Both the highest in-plane and through-plane thermal conductivity

of 41 W/mK and 1.2 W/mK were measured respectively for the hot-pressed 15 wt% CNC hybrid paper. The electrical conductivity decreased continuously with increasing content of CNC but the thin film was still conductive at the highest CNC content in this study. The low-cost, environmental-friendly, thermally and electrically conductive flexible GnP/CNC hybrid papers have a set of properties making them suitable for many potential applications.

Keywords: A. Thin films; B. Electrical properties; B. Mechanical properties; B. Thermal properties.

1. Introduction

Graphene has attracted world-wide attention due to its outstanding mechanical, thermal and electrical properties [1]. Some other novel carbon materials such as carbon nanotubes and helical carbon nanofibers/nanotubes also show good properties. However, their applications are limited by the high fabrication cost and low production rate [2-5]. In contrast, graphene nanoplatelets can be produced at a much lower price by a top-down approach [6, 7]. Recent published research has shown that graphene-based materials are suitable to be used in a wide range of potential applications, such as lithium ion batteries [8], ultracapacitors [9], polymer composites [10, 11], ultra-thin films [12, 13], electronic circuits [14], and transparent and flexible electrodes for displays and solar cells [6, 15].

Graphene can be prepared by employing both top-down (mechanical cleavage or

liquid phase exfoliation) and bottom-up (such as chemical vapor deposition, arc-discharge, chemical conversion, unzipping carbon nanotubes, and epitaxial growth on SiC) approaches [16]. In general, the top-down process starting with natural graphite flakes, which is more suitable for large scale production, and offers significant economic advantages over the bottom-up methods [11, 16]. Research in the Drzal's Group at Michigan State University successfully developed a process that can produce graphene nanoplatelets with thickness ranging from 1 nm to 10 nm and diameters from 300 to 50000 nm [17, 18]. Graphene nanoplatelets (GnP), which consists of a few layers of single layer graphene was produced by either thermal expansion of acid intercalated natural graphite or microwave radiation followed by pulverization using ball milling or ultrasonication [17]. The cost of GnP flakes produced by this method is estimated to be around \$15/lb which makes it is possible for the large-scale application in various fields [19].

Recently, a nanostructured graphene paper which is assembled by well-ordered graphene sheets has attracted increasing attention due to its wild potential application for solar cell, electronic and heat transfer devices [13]. Thin films (papers) of graphene oxide (GO) usually show excellent mechanical properties, however, the lack of electrical and thermal conductive limits their use [20]. Although GO paper can be rendered conductive by thermal annealing, the structure and mechanical properties can be seriously deteriorated after thermal treatment. In addition, the cost of producing single layer graphene sheet is high which limits its applications. The early work in our group showed that papers made from commercially available GnP

exhibited excellent in-plane thermal and electrical properties [21, 22], while the GnP paper is not strong as compared with the graphene oxide or reduced graphene oxide paper. This study reports on the modification of GnP papers and the mechanical, thermal and electrical properties of the resulting materials.

Cellulose is the most abundant renewable organic material with annual production of over 7.5×10^{10} tons [23]. Recently, attention has been directed to nanosized cellulose (fibrils and whiskers) because of their exceptional high specific strength and modulus, low density, chemical versatility, renewable 'green' nature, and their relatively low cost [24-26]. Chun et al. [27] utilized cellulose powders as the starting material and fabricated cellulose nanofiber paper with a vacuum filtration method, the tensile modulus and strength of the prepared cellulose paper can be as high as 6.4 GPa and 55 MPa respectively. Sen et al. [28] fabricated 0.1-0.5 wt% graphene nanoplatelets-cellulose composite films by a solution casting method. The 0.25 wt% graphene nanoplatelets/cellulose composite film produced 0.8 GPa in tensile modulus and 22.6 MPa in strength, an increase of 45% and 31% respectively. The highest electrical conductivity of $5.1 \times 10^{-3} \text{ S cm}^{-1}$ was obtained at 0.50 wt% graphene loading. Si et al.[29] prepared graphene oxide-bacterial cellulose (GO/BC) nanocomposites with a GO content of 0.19, 0.29, and 0.48 wt%. The 0.48 wt% case showed the best mechanical properties with an increase of 38% in tensile strength and 120% in tensile modulus. A relatively low electrical conductivity of $1.24 \times 10^{-9} \text{ S cm}^{-1}$ was noted due to the partial reduction of GO to rGO during the sample preparation. Soheilmoghaddam and coworkers [30] successfully prepared green hybrid films

through regenerating cellulose/exfoliated graphite nanosheets in ionic liquid. The tensile strength and Young's modulus of the prepared nanocomposites were increased by 97.5% and 172% respectively after the incorporation of 0.75 wt% and 1 wt% graphite nanoplatelets, and oxygen barrier properties and water absorption resistance were also improved as compared to the pure cellulose film.

Cellulose nanocrystals (CNC) are fibrillar in nature and have a diameter of around 5 nm and their length can vary depending on their source and method of preparation [31]. In this work, we first formed GnP dominated-CNC (wood pulp) composite papers, and investigated the morphology, mechanical, electrical and thermal properties of the unpressed and hot-pressed papers.

2. Experimental

2.1 Exfoliated Graphene Nanoplatelets (GnP)

Graphene nanoplatelets (GnP) was produced by thermal expansion of acid intercalated graphite compounds (Asbury Mills, NJ), followed by pulverization in isopropanol using ball milling and ultrasonication to produce the desired aspect ratios. GnP was heat treated in a furnace at 400 °C for 2 hrs before use to remove any impurities remaining after the particle fabrication procedure. GnP-5 refers to the graphene nanoplatelets with an average diameter of around 5 μm and a thickness less than 10 nm. Only GnP-5 flakes were used in all the experiments of this paper and GnP mentioned throughout the paper means GnP with an average diameter of 5 μm .

2.2 Cellulose nanocrystals (CNC)

Aqueous cellulose nanocrystals in the never-dried state were obtained in a slurry with a cellulose content of 6.2 wt% produced from wood pulp by the University of Maine (Orono, Me). The as received cellulose nanocrystals are rod-like particles with dimensions of approximately 5 nm in diameter and 150-200 nm long (<http://umaine.edu/pdc/cellulose-nano-crystals/>).

2.3 Exfoliated graphene nanoplatelet paper and GnP/CNC hybrid paper preparation

The suspension of CNC was diluted in water to approximately 1 mg/ml and dispersed using shear mixing (Ultra Turrax T25 basic, IKA Werke GmbH & Co. KG, Germany) for 5 min at 13,500 rpm. Polyethyleneimine (PEI) which works well for dispersing GnP was purchased from Aldrich (branched, Mw= 25,000) and used as received.

GnP powders were dispersed in water at a concentration of ~1 mg/ml with the aid of PEI (GnP:PEI:Water = 2:1:2000, by weight) by high energy ultrasonication for 3 min at a true power output of 120 W. The solution was then stirred overnight to ensure sufficient interactions between GnP flakes and PEI. A variety of cellulose nanocrystals (1 mg/ml) were slowly added to 50 ml of the above mentioned solution with continual stirring to produce mixtures with CNC content ranging from 5 wt% to 25 wt%. The mixed solution was vigorously stirred for 24 h, and GnP/CNC hybrid papers were prepared by filtration of the obtained solution through a 0.22 μm pore size PVDF membrane (Millipore). The films were not rinsed to avoid affecting the GnP alignments of the resulting papers. After filtration, the GnP/CNC paper on the membrane was dried at room temperature for 24 h then carefully peeled off. This

paper was identified as ‘as-made’ in later discussions. The as-made papers were then further vacuum dried at 70 °C for 24 h. The GnP paper without any CNC was also prepared by the same method. These papers are identified as ‘unpressed’. The as-made papers that were compressed in a dual platen press under 65 MPa at 125 °C for 30 min were identified as ‘hot-pressed’.

2.4 Characterization

An environmental scanning electron microscopy (ESEM, Philips Electroscan 2020) with energy dispersive spectrometer (EDS) equipment at accelerating voltage of 20 kV was used to image the fracture of the cross section of both the unpressed and hot-pressed papers. The distribution of GnP/CNC in solution was examined using an Olympus optical microscope (BX-51M). Transmission electron microscope (TEM) analyses were conducted on a JEM 2100F STEM/EDS electron microscope at 200 KV, and the samples were prepared by drop casting on carbon-coated copper grids followed by solvent evaporation in air at room temperature.

Raman spectroscopy was carried out using a Micro Raman spectrometer (Renishaw, system 100, UK) in the range of 500 to 3500 cm^{-1} . The excitation wavelength was 785 nm from He-Ne laser with a laser power of 28.2 mW at the sample surface. Results are the average of at five Raman measurements per group.

Mechanical properties of the papers were measured under controlled air conditions of 23 °C and 50 % relative humidity by a Dynamic Mechanical Analyzer (DMA, Q800, TA instruments). GnP based papers with different thickness were cut with a razor blade into rectangular strips of 30 mm in length and 6.6 mm in width for

measurements. The dimensions were measured by calipers, and the thickness of each type of paper was measured with a digital micrometer. The samples were gripped using a film tension clamp with a clamp compliance of about $0.25 \mu\text{m N}^{-1}$. After the specimens were clamped, the length between the clamps was read from the DMA instrument. All tensile tests were conducted in controlled strain rate mode with a preload of 0.01 N and a strain ramp rate of $0.1\% \text{ min}^{-1}$. Measurements were made on at least three specimens for each type of paper.

The in-plane electrical properties of the GnP based papers (unpressed and hot-pressed) were tested with a Keithley 2400 SourceMeter. The samples were prepared with rectangular strips of approximately $32 \times 12.6 \text{ mm}^2$. The dimensions were obtained with calipers, and the thickness was measured with a digital micrometer. Four electrode pins were pressed to the paper surface with a spacing of 1 cm for the measurements. The electrical conductivity is then calculated according to equations (1) and (2).

A two point method was employed to measure the through-plane electrical resistivity (R), and the sample dimension is the same as the specimens for in-plane electrical properties measurement. In order to eliminate the effect of contact resistance, strips of adhesive copper foils were used. The through-plane electrical conductivity was obtained from the following equation (3). The results are based on data collected from five specimens and the standard deviations were calculated.

$$\rho = \frac{VWT}{IL} \quad (1)$$

$$S_1 = \frac{1}{\rho} \quad (2)$$

$$S_2 = \frac{T}{RLW} \quad (3)$$

where ρ = Electrical resistivity ($\Omega \text{ cm}$), S_1 =In-plane electrical conductivity (S cm^{-1}), S_2 =Through-plane electrical conductivity (S cm^{-1}), V = Voltage measured by the voltmeter (V), I = Current measured by the ammeter (A), W = The width of the sample (cm), T = The thickness of the sample (cm), L = The distance between the two points where the voltmeter measures the voltage (cm).

The thermal diffusivity of the as-made and hot-pressed GnP based papers was analyzed by the laser flash method (Netzsch 447 NanoFlash) at room temperature. Square samples with a side length of 10 mm and circular samples with a diameter of 25 mm were prepared for the measurement of through-plane and in-plane thermal diffusivity respectively. The size of test specimens was measured using a digital micrometer. The top and bottom surfaces of the samples were coated with graphite to insure uniform heat flow and the thermal diffusivity values (mm^2/s). The specific heat capacity (C_p : J/g K) was measured with DSC (Q2000, TA instruments). The densities (ρ' : g/cm^3) of the samples were collected by dividing the mass over the volume, and the thickness of the finished samples were determined using a digital micrometer. The in-plane and through-plane thermal conductivity were calculated according to equation (4).

$$K = \alpha \times \rho' \times C_p \quad (4)$$

Where K =thermal conductivity (W/mK), α =thermal diffusivity (mm^2/s), ρ' =densities

of the samples (g/cm^3), C_p = specific heat capacity (J/g K).

3. Results and discussions

3.1 Morphological investigation of GnP and CNC

Fig. 1(a) shows a mechanically robust GnP/CNC hybrid unpressed paper. The SEM micrographs of as-received GnP and CNC are shown in Fig. 1(b) and (c). They indicate that the platelet-like GnP has an average diameter of 5 μm and the CNC looks like rice with about 5 nm in diameter and 150-200 nm in length. Fig.1 (d) shows the surface morphology of GnP/CNC hybrid paper containing 20 wt% CNC, and shows that the CNC is coated uniformly on the surface of GnP. The uniform coating is probably attributed to interactions between CNC and PEI present on the surface of GnP.

TEM was employed to further analyze the GnP flakes. Fig. 2(a) represents the typical TEM images of surface of GnP flakes from which we can say that the flakes were composed of a few graphene layers. The inset of Fig. 2(a) shows the corresponding selected area electron diffraction pattern which exhibits a typical six-fold symmetry for graphene [32]. Fig. 2(b) illustrates that the most common thickness of the GnP flakes is about 5 nm. Considering that the interlayer space is 0.336 nm (graphite interlayer distance), this means that most of GnP flakes are composed of about 15 graphene layers. It is also noticed that single layer graphene or two layers of graphene sheets were observed as indicated by the black arrows in Fig. 2(b). Fig. 2(c) and (d) show optical micrographs of the GnP and CNC mixed solution with the lowest (5 wt%) and highest percentage (25 wt%) of CNC. The distribution of

GnP was found to be nearly uniform without segregation after mixing with hydrophilic CNC.

The Raman spectrum of the GnP flakes and hot-pressed GnP paper is shown in Fig. 3 which provides the information about the structure of GnP before and after forming thin film papers. The Raman spectra of all carbon systems have a rather simple set of peaks. As shown in curve 1 of Fig. 3, the main features of GnP flakes display D peak ($\sim 1355\text{ cm}^{-1}$), the G peak ($\sim 1570\text{ cm}^{-1}$) and the 2D peak ($\sim 2710\text{ cm}^{-1}$). The D peak is due to Raman scattering induced by zone-boundary phonons that reflects disordered structures which include defects, edges, disorder, crystal boundaries, symmetry breaking, etc. The sample edges can be always seen as defects [33], and the D band of GnP flakes (curve 1 of Fig. 3) is mainly induced by edges of the disordered GnP flakes. It is noted that the D band of GnP papers ((curve 2 of Fig. 3) is much lower than that of the GnP flakes which is ascribed to the high alignment of GnP. The G peak arises from the stretching of the C-C bond in graphitic materials. The prominent 2D band reflects the stacking structure of graphite, and it is well known to be very sensitive to the number of graphene layers in a flake. The shape of 2D band of graphite is different from the single peak of 2D band of GnP or graphene, usually consists of two peaks with low intensity [33, 34]. As we can see from Fig. 3, there is not much difference between the Raman spectra of GnP flakes and GnP paper in terms of the shape and intensity of 2D band which indicates that the GnP is still in a few layer platelet form.

3.2 Morphology of GnP-5/CNC hybrid papers

Fig. 4 shows the SEM images of the fracture cross-section of unpressed and hot-pressed neat GnP papers, GnP/(10 wt%)CNC papers and GnP/(25 wt%)CNC papers. Pull out of the GnPs was observed for all of the GnP based papers upon tensile testing. In Fig. 4, the 0 wt% CNC unpressed GnP paper shows that the GnP flakes are in loose contact with each other and form a long continuous phase that is interspersed with large pores ranging in size from 1 μm to 10 μm . In comparison, the unpressed papers with CNC are more compact with better alignment, and the number of pores in the composite papers decreases as the CNC loading increases. After hot-pressing, the GnP flakes are even more closely aligned parallel to each other compared to their unpressed counterparts. The hot-press process eliminates pores inside GnP based papers and decreases the spacing between adjacent GnPs to form denser structured materials.

Table 1 shows the average thickness and density of unpressed and hot-pressed GnP-based papers. The density of the unpressed papers increases with increasing concentration of CNC, The same trend was observed for the hot-pressed papers. As for the thickness of the prepared papers, the thickness of hot-pressed papers increases with increasing CNC fraction. However, the thickness of unpressed papers decreases as the CNC content increased. This interesting phenomenon is related to the hydrophilic CNC that attracts and holds water between the inter-layers of adjacent GnP flakes [26, 35], and capillarity forces assist in the formation of denser papers during the drying process, resulting in thinner papers.

3.3 Mechanical properties of GnP/CNC hybrid papers

Fig. 5(a) shows the paper coupons used in tensile testing. Representative stress-strain behaviors for both unpressed and hot-pressed GnP papers containing 0 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt % and 25 wt% CNC are presented in Fig. 5(b). The data indicate that the unpressed control GnP paper is very weak with an average tensile strength, tensile modulus and elongation of 0.1 MPa, 0.07 GPa and 0.18% respectively. When the CNC is added, the tensile strength, tensile modulus and elongation increased significantly with increasing CNC content, reaching 38 MPa in strength, 10.6 GPa in modulus and 1.5% in elongation for the paper with 25 wt% CNC. The increase is due to the incorporation of CNC which functions to strengthen the GnP paper by bringing the GnP flakes closer during drying process and leads to a more compact structured paper. In addition, the amino groups of the PEI or oxygen groups presented on the surface of the GnP flakes may form hydrogen bonds with the CNC which could also contribute to the improvement of the mechanical properties [30, 36, 37]. The hot-pressed GnP papers display a similar trend in tensile strength, modulus and elongation (with 50.7 MPa, 16.64 GPa and 1.12% respectively for the paper containing 25 wt% CNC). Based on the SEM images (Fig. 4) of the fracture surfaces of both unpressed and hot-pressed papers, increasing interactions between GnP and CNC produce a higher stress at failure with increasing content of CNC, resulting in good mechanical properties.

It should be emphasized that both the tensile strength and tensile modulus of the hot-pressed papers are greater than their unpressed counterparts for the following reasons. First, most pores that have a negative effect on the mechanical properties are

eliminated after hot-pressing resulting in a compact paper with less defects. Second, the GnP flakes alignment which affects the mechanical properties increases with the hot-pressing process [30].

Fig. 6 shows the strain to failure of the unpressed and hot-pressed papers. The strain to failure of the hot-pressed papers with CNC content below 15 wt% is higher than the unpressed ones. As more CNC is added, the elongation of the unpressed papers exceeds that of the hot-pressed ones. It is believed that, for unpressed papers with the CNC content less than 15 wt%, the unpressed samples are very weak, both the strength and modulus are low, and they fail under low stress at low elongations. Hot-pressed samples are stronger than the unpressed samples, and they fail at larger elongations. However, when the CNC fraction exceeds 15 wt%, the strength of both the unpressed and hot-pressed samples becomes greater. The strain to failure is remarkably high considering the porosity [38]. Under the tensile load before failure, GnP flakes in the composites can experience reorientation to become more aligned in the tensile direction if there is space available for doing so. Apparently, because of the porosity, the unpressed papers are able to reorient to a higher degree than their hot-pressed counterparts and hence show greater elongation.

3.4 Electrical properties of GnP based papers.

Fig. 7 shows the in-plane electrical conductivity of unpressed and hot-pressed GnP-based papers. After hot-pressing, the neat GnP paper showed a significant increase in the in-plane electrical conductivity, reaching up to 270 S/cm. The same trend was also observed for the papers containing CNC, which suggests that the

elimination of the pores inside the papers plays a significant role in the in-plane electrical conductivity. Hot-pressing eliminates most of the large pores causing the GnP flakes to be better aligned and more closely connected, resulting in lower GnP to GnP particle contact resistance and better in-plane electrical conductivity. The in-plane electrical conductivity of hot-pressed papers containing CNC decreases gradually as more insulating CNC fibers are added. Although the addition of CNC decreases the conductivity of the GnP papers, the hot-pressed 15 wt% CNC/GnP hybrid paper still produces excellent in-plane electrical conductivity (as high as ~36 S/cm) which is much higher than the cellulose/graphene or cellulose/CNT composite papers reported elsewhere [25, 28, 39].

Through-plane electrical conductivity of the GnP/CNC based papers were also characterized which is shown in Fig. 8. It is noted that the through-plane electrical conductivity is much lower than the in-plane electrical conductivity for a specific paper, and this was ascribed to the anisotropic inherent conductivity of the GnP [22]. The through-plane electrical conductivity of both hot-pressed and unpressed papers decreases with the increasing content of CNC. This phenomenon was caused by the presence of the CNC that can separate the GnP flakes and leave fewer pathways for cross-plane electron transport, resulting in greater through-plane electrical resistivity. As shown in the Fig. 8, the hot-pressed papers however, display higher through-plane electrical conductivity as compared with the unpressed counterparts. Better orientation of GnP flakes coupled with the dense and compact structure of the hot-pressed papers are believed to improve the through-plane conductivity.

3.5 Thermal properties of GnP based papers

The in-plane thermal diffusivity and in-plane thermal conductivity of GnP based papers are presented in Fig. 9 and Fig. 10. As shown in Fig. 9, the thermal diffusivity of hot-pressed papers is higher than that of the unpressed ones regardless of papers with or without CNC. The benefit of the pressing process was also observed for the GnP only paper which was reported by our group previously [21]. Both the unpressed and hot-pressed papers experienced a slight decrease in the in-plane thermal diffusivity at higher CNC loading (20 wt% and 25 wt%) due to the thermal insulating properties of CNC. The existence of too large a concentration of CNC is likely to prevent the GnP from making contact with each other, and lead to high thermal contact resistance leading to the reduced thermal diffusivity. It is interesting that the unpressed GnP-only paper showed a lower thermal diffusivity than the paper containing CNC as listed in the Fig. 9, while the hot-pressed GnP-only paper showed the highest value ($\sim 50 \text{ mm}^2/\text{s}$) among all the papers. We believe that this is due to the number of pores and the amount of CNC inside the papers. For the unpressed papers, the addition of moderate amounts of CNC could obviously bridge the small gaps between individual nanoplatelets leading to thinner and compact papers with better thermal diffusivity, which is also evidenced by the thickness values listed in table 1 and the SEM images displayed in Fig. 4. As for the hot-pressed papers, most pores inside the papers are eliminated and more CNC leads to lower thermal diffusivity due to the insulating thermal properties of CNC.

The in-plane thermal conductivity of unpressed and hot-pressed papers are shown

in Fig. 10. GnP paper containing 15 wt% CNC showed the best in-plane thermal conductivity (47 W/mK and 73 W/mK for unpressed and hot-pressed paper respectively). The hot-pressed papers all have higher conductivity than their unpressed counterparts which indicates that the moderate amount of CNC benefits the thermal conductivity of the resulting papers due to the combination of optimal CNC content, high heat capacity of CNC, better alignment of GnP flakes and lower amount of pores.

The through-plane thermal diffusivity of the unpressed and hot-pressed papers are presented in Fig. 11, as we can see, the thermal diffusivity decreased gradually with increasing content of CNC. The hot-pressed papers have a lower through-plane thermal diffusivity than their unpressed counterparts.

Consistently, the hot-pressed papers showed lower through-plane thermal conductivities than the unpressed papers (Fig. 12). It is well known that the pores in a paper structure material have a negative effect on thermal properties [40, 41], The highest through-plane thermal conductivity (1.2 W/mk) for GnP/CNC paper was recorded for the 15 wt% CNC content unpressed GnP paper. This composition probably has the balance between the number of pores and the GnP flake contact area, since with the increasing content of CNC, pores decreased while the flake contact area of the GnP/CNC papers increased.

It is worth noting that the electrical and thermal conductivity of GnP paper is highly dependent on the lateral size (or aspect ratio) of GnP [21,42,43]. Larger platelets generally provide better properties, since the network formed by the larger platelets

has fewer particle-to-particle contacts responsible for contact resistance resulting in higher electrical properties. Therefore, the electrical and thermal conductivity of the resulting papers can be tuned by CNC content, compression parameters and lateral size of the GnP.

4. Conclusions

Flexible GnP/CNC hybrid papers with tunable conductivity as well as good mechanical properties were fabricated by simple vacuum filtration of a GnP and CNC mixed water suspension. A continuous conducting network was formed by GnP, and a better layer aligned and denser film can be obtained after hot-pressing. The mechanical properties of the hybrid GnP papers were improved greatly by the incorporation of CNC, and the hot-press process further enhances the mechanical properties by eliminating internal pores and forming better particle alignment. Both in-plane and through-plane electrical conductivity decreased after the addition of CNC, while better electrical properties were recorded after hot-pressing. The hot-press process can improve the in-plane thermal properties up to an optimum addition of CNC loading of 15 wt%, but has a negative effect on the through-plane thermal conductivity due to more CNC-GnP contacts being produced. These flexible, electrically and thermally conductive hybrid GnP/CNC papers with good mechanical properties may be useful in many applications in the packaging, electrical and heat-conducting fields.

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Tables

Table 1. Average thickness and density of hot-pressed and unpressed GnP based papers.

CNC content (Weight %)	Unpressed		Hot-pressed	
	Thickness (mm)	Density (ρ : g/cm ³)	Thickness (mm)	Density (ρ : g/cm ³)
0%	0.123	0.376	0.036	1.135
5%	0.097	0.507	0.038	1.137
10%	0.080	0.722	0.040	1.200
15%	0.072	0.871	0.044	1.282
20%	0.067	0.993	0.048	1.349
25%	0.065	1.124	0.052	1.391

List of figures

Fig. 1: Photograph of (a) mechanical flexible GnP/CNC paper ; SEM images of (b) GnP and (c) cellulose nanocrystals; (d) Surface of GnP/(20 wt%) CNC paper.

Fig. 2: TEM micrographs of (a) the surface of GnP flakes and (b) the cross sectional view of GnP flakes. Optical micrographs of GnP/cellulose nanocrystals solution showing good dispersion (c) 5 wt% CNC and (d) 25 wt% CNC, both of the scale bars are 20 μm .

Fig. 3: Raman spectra of GnP flakes and hot-pressed GnP paper.

Fig. 4: SEM images of unpressed and hot-pressed GnP/cellulose nanocrystals papers with 0 wt%, 10 wt% and 25 wt% of CNC loading, all taken at fractured sample surfaces upon tensile testing; All of the scale bars are 2 μm .

Fig. 5: (a) Photograph of paper strips prepared for tensile testing. (b) Stress-strain curves of GnP based papers; Curves of 1,3,5,7,9 and 11 represent unpressed GnP based papers containing 0 wt%, 5 wt%,10 wt%,15 wt%,20 wt% and 25 wt% CNC respectively, and curves of 2,4,6,8,10 and 12 represent hot-pressed papers containing 0 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt% and 25 wt% CNC respectively.

Fig. 6: Tensile strain of GnP based papers.

Fig. 7: In-plane electrical conductivity of GnP based papers.

Fig. 8: Through-plane electrical conductivity of GnP based papers.

Fig. 9: In-plane thermal diffusivity of GnP based papers.

Fig. 10: In-plane thermal conductivity of GnP based papers.

Fig. 11: Through-plane thermal diffusivity of GnP based papers.

Fig. 12: Through-plane thermal conductivity of GnP based papers.

Fig. 1.

Fig. 2.

Fig. 3.

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Fig. 10.

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Fig. 12.