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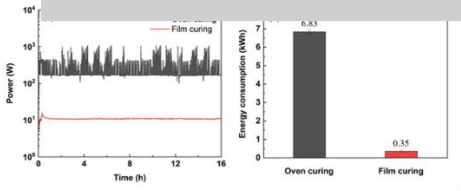
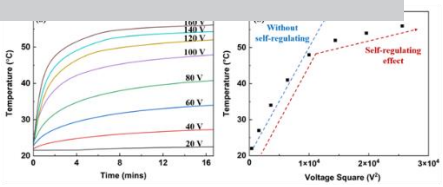


5% energy consumption

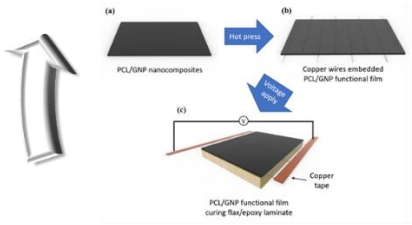
Extremely **energy efficient**

Improved **safety**



Self-regulating at desired temperature

No external controller



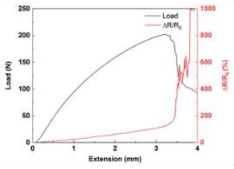
In-situ sensing

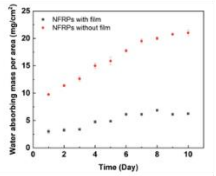
Enhanced water barrier properties

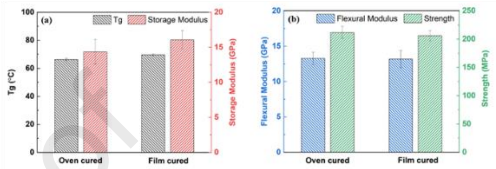
Multifunctional surface layer

No effects on laminates

Tg, modulus and strength remain unchanged







Energy Efficient Out-of-Oven Manufacturing of Natural Fibre Composites with Integrated Sensing Capabilities and Improved Water Barrier Properties

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Abstract:

Bio-based and eco-friendly materials have gained a great amount of attention, thanks to the increased awareness of sustainable development and global environments. The use of natural fibres in composites can reduce greenhouse gas emissions and the carbon footprint compared to many synthetic fibres. However, some challenges and concerns remain in natural fibre-reinforced plastics, such as the high moisture absorption and high energy consumption during their manufacturing stage. To tackle these challenges, this study developed an energy-efficient out-of-oven manufacturing method based on a conductive biopolymer nanocomposite film to fabricate natural fibre-reinforced composites with integrated multifunctionalities throughout their life cycle. The smart nanocomposite layer works as an autonomous self-regulating heating element to cure the laminates at the desired temperature without the risk of overheating. Extremely high energy efficiency has been

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achieved with a significantly reduced energy consumption (a 95 % reduction compared with traditional oven curing), which has been achieved through the direct heat conduction from the surface layer to the laminates. The embedded nanocomposite surface film on the cured laminate subsequently becomes an integrated multifunctional layer, providing integrated real-time deformation and damage sensing capabilities with enhanced water barrier properties to prolong the service life of natural fibre composites.

Keywords: Sustainable manufacturing; Out-of-oven curing; Natural fibre reinforced composites; Damage sensing; Barrier properties

1. Introduction

With the increasing concern for the environment and the necessity of sustainable development in the composite sector, significant efforts have been dedicated to developing eco-friendly and bio-based materials. Natural fibre reinforcements and bio-based resins provide an opportunity to reduce the carbon footprint of structural composites while improving environmental sustainability [1-4]. However, traditional composites manufacturing methods such as autoclave or resin transfer moulding are capital and energy-intensive, and generate a large amount of greenhouse gases during the conventional manufacturing stage, sacrificing the overall sustainability of the system [5].

To achieve improved energy efficiency in composites manufacturing, alternative methods have been explored to cure fibre-reinforced composites, such as microwave [6], infrared [7], ultraviolet [8], induction [9], and frontal polymerization [10]. Zhilyaev *et al.* developed an infrared curing method for fibre-reinforced composites, showing a reduction in power consumption from 154 kWh by conventional curing to 2.8 kWh through infrared curing [7].

Very recently, Sottos' group developed the frontal polymerization curing method for thermoset fibre reinforced polymer composites, which can reduce the curing cycle time and thermal energy consumption significantly in comparison with conventional oven curing [10, 11]. However, most of these innovative methods have certain requirements on the material systems that can be utilised, limiting their wider uses in composites manufacturing. For instance, resistive heating requires intrinsically conductive composite systems to respond to the applied current [12], while microwave methods can result in an uneven curing of the polymer matrix due to hotspots generated by the superposition of electromagnetic waves [6]. Ultraviolet curing can achieve high energy efficiencies for thin composite structures, but face difficulties in penetrating thicker structures [13]. Infrared heating can only induce a weak resonance in the polymer chains, which requires assistance from infrared absorbing materials like carbon fabric [7]. With the increasing demand of natural fibres and bio-resins as sustainable systems for future composites, a universal curing method for non-conductive reinforcing fibres and resin with low energy consumption is still to be developed.

Conduction heating is a curing method in which a heating element is in direct contact with the surface of the composite throughout the cure cycle. This curing method can avoid the unwanted wave superposition and overlapping issues in electromagnetic wave curing, and material selection limitations. In the last few years, flexible in-mould heating films composed of polymer matrix and nanomaterials have been explored as an Out-of-Oven (OoO) curing method due to their rapid heating rate and high energy efficiency. Lee *et al.* used a carbon nanotube (CNT) film as a resistance heating layer to cure carbon fibre prepregs, which reduced the electrical energy consumption by two orders of magnitude with equivalent properties as the conventional curing method [14]. Xu *et al.* applied a non-woven CNT veil as a resistive heating layer to cure fibre reinforced composites with an energy consumption of

only one seventh of an oven curing method [15]. By dispersing CNT into epoxy, Mas *et al.* were able to cure a resin system by applying electric current and reduced energy consumption from 3 MJ in oven curing to 4.5 kJ in Joule heating curing [16]. Utilization of carbon nanomaterials as a Joule heating source has proven to be a highly energy efficient curing method for fibre reinforced composites, although the risks of temperature overshooting remain a great concern during the exothermic reaction of the thermoset curing process, especially for the use of many natural fibres considering their high flammability.

Very recently, Liu *et al.* have successfully developed a Joule heating nanocomposites film by mixing polymer with the conductive particles and used it to cure fibre reinforced composites [17]. Moreover, they demonstrated that intrinsic safety with autonomous temperature control alongside extremely high energy efficiency can be achieved for composites manufacturing. Specifically, by using a conductive polymer composite film with a positive temperature coefficient (PTC) effect as a heating layer for laminate curing, a significantly reduced energy consumption has been achieved with extremely high safety without the risk of overheating. Carbon-based particle/polymer nanocomposites have been proved to have different resistance change ratios according to the temperature [18, 19]. Many modelling works have been carried out to demonstrate the PTC effect, related to the nanoparticle volume fraction, dispersion uniformity, cut-off distance of particles, and the Poison's ratio of the polymer [20, 21]. Due to the mismatch in thermal expansion between matrix and fillers, the electrical resistivity increases drastically when the polymer matrix approaches its transition temperature, leading to a PTC effect within the composite [22, 23]. Therefore, an autonomous and reversible cut-off for Joule heating occurs, which prevents a temperature overshoot [24, 25]. Based on the PTC effect of fabricated conductive polymer composites,

self-regulating heating at desired temperatures can be achieved by Joule heating of the film to cure fibre reinforced thermoset composites.

Apart from the energy efficiency and safety consideration in the manufacturing stage, it is also useful to develop humidity protection for natural fibre reinforced plastics (NFRPs), extending the components' service life to reduce waste and overall environmental impact. It is well acknowledged that the moisture absorption behaviour of natural fibres can lead to the issues such as unwanted degradation, micro-gaps, cracks, voids from swollen fibres and debonding between fibre and matrix [26-28]. Several methods have been developed to modify the interface between fibre and matrix to improve the water barrier property, such as alkali pre-treatment, corona/plasma treatment, and hydrothermal treatment, etc. [29, 30]. Apart from these treatment methods, direct coating of polymer layers such as using polyethylene on natural fibre reinforced plastics (NFRPs) has also been explored to achieve enhanced moisture barrier performance [31]. The introduction of 2D fillers can further enhance the barrier performance, with a reduction of 93% in water permeability (from 181 g/m^2-day to 13 g/m^2-day) at a graphene filler loading of only 0.1 wt.% [32], indicating the potentials of using graphene nanoplatelets inside of polymer films for moisture protection of natural fibre composites.

In this study, a conductive nanocomposite film consisting of graphene nanoplatelets and a biodegradable polymer matrix, polycaprolactone (PCL), has been developed as a thin functional film to provide heat energy on the laminates' surface by Joule/resistance heating. The film has been proved to be an energy efficient and intrinsically safe heating source to cure natural fibre composites without the need of an oven. Compared to other low thermal expansion bio-degradable thermoplastics like PLA or PBAT, we firstly found a relatively large

coefficient of thermal expansion (CTE) bio-degradable polymer of PCL to provide an opportunity to achieve a relatively high PTC intensity in the fabricated nanocomposite film [33], allowing the self-regulating heating to be performed for out-of-oven composites manufacturing. Subsequently, the embedded nanocomposite film can work as a multifunctional layer for deformation and damage sensing, as well as a water barrier layer to protect laminates from moisture penetration, prolonging the service life of natural fibre composites.

2. Materials and methods

2.1 Materials

Polycaprolactone pellets from Ingevity (PCL, Capa™ 6800, M_n = 6900 ± 3500 g/mol, M_w = 112000 ± 5500 g/mol) and graphene nanoplatelets from XG Science (GNP, Grade M, thickness of 6-8 nm and lateral dimension of 25 µm according to the manufacturer) were dispersed in chloroform (Acros Organics, 99+%, CAS: 67-66-3) to fabricate the multifunctional surface nanocomposite film. The natural fibre composites consisted of flax fabrics (EcoTechnilin, FLAXTAPE 110) with an areal weight of 110 g/m^2 and a bio-based epoxy (PRO-SET, M1049 resin with M2049 hardener) with a pre-curing stage at room temperature for 24 hrs followed by a post-curing stage at 55 °C for 16 hours.

2.2 PTC film fabrication and flax/epoxy composites manufacturing

The PTC film was fabricated by a solution casting method. PCL pellets were first dissolved in chloroform overnight with a PCL content of 20 wt.%. Graphene nanoplatelets with a concentration of 10 mg/ml were dispersed in chloroform by a probe sonication (Sonics Vibra-Cell, VCX 500) at 5500 J energy, with a 2 sec on and 2 sec off pulse interval. After the sonication, the two solutions were mixed at a ratio of 63.4 vol.% GNP/chloroform with 36.6 vol.%

PCL/chloroform and magnetically stirred for 10 mins, followed by a degassing step in an ultrasonic bath for 5 mins, before being casted into moulds to obtain the GNP/PCL films. The average amount of chloroform that was used to fabricate one 5.5 wt.% GNP/PCL film with dimensions of 100 × 100 × 0.15 mm^3 was approximately 13.8 ml. It is worth noting that the use of hazardous solvents, such as chloroform, requires a series of precautionary measures before it can be scaled up in a mass production level.

Casted GNP/PCL film with a filler loading of 5.5 wt.% was then compression moulded (Dr. Collin GmbH, Presse P300E) at 110 °C to obtain a rectangular shape with a dimension of 100 mm × 100 mm × 150 µm (Figure 1a). Six parallel copper wires as electrodes were then embedded by compression moulding to the films, with an interval of 15 mm as shown in Figure 1b.

The natural fibre composite laminates with dimensions of 100 mm × 100 mm, consisting of eight layers of unidirectional flax fibre and bio-based epoxy were manufactured by vacuum-assisted resin infusion (VARI). The reference laminate was cured in a convection oven at 55 °C for 16 hours using an aluminium plate as tooling side, while the out-of-oven curing was achieved by applying direct voltage to generate a Joule heating effect from the GNP/PCL surface film on top of the fibre preforms, as shown in Figure 1c. A flat PTFE plate was used as the tooling side for the out-of-oven curing method to prevent excessive heat dissipation. A DC power supply (General Electric Company, EPS 301) was used to apply a voltage of 250 V to the GNP/PCL film to provide a steady-state temperature of 55°C during the 16 hours post curing process. The power consumption of both the convection oven and Joule heating film curing were recorded by a plug-in power monitor (Brennenstuhl®, PM 231 E).

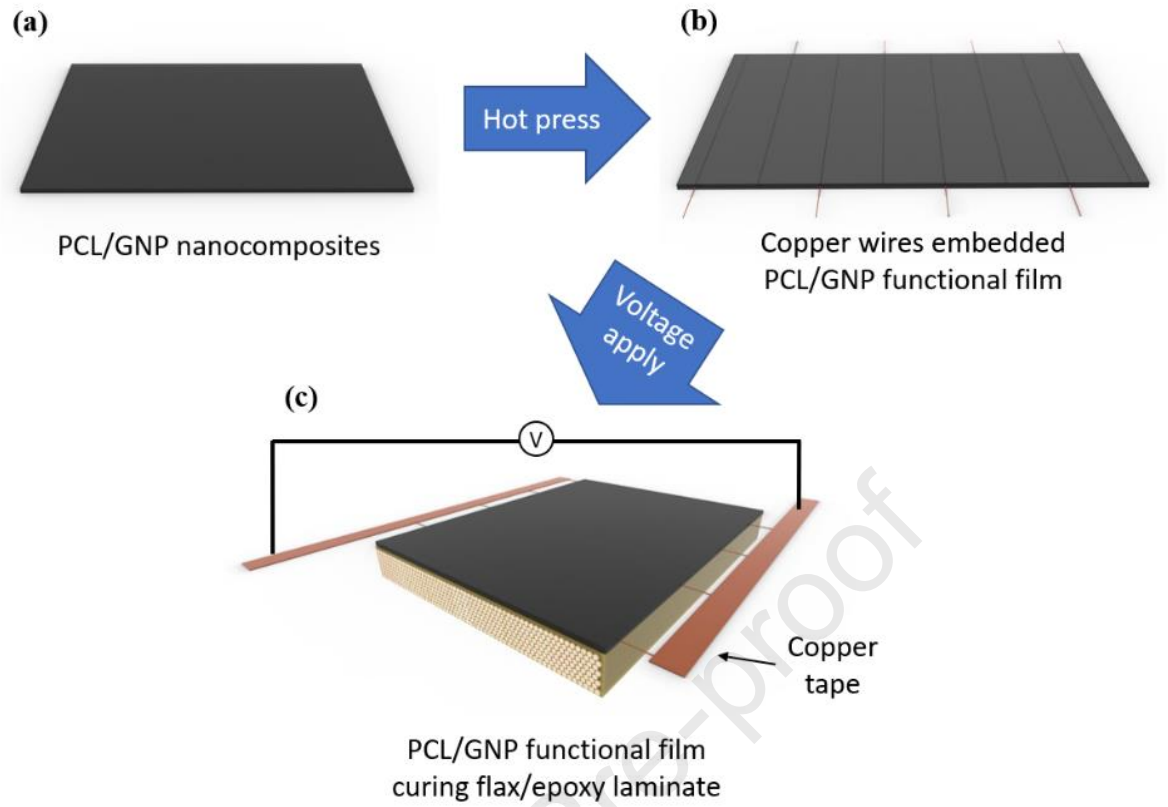

Figure 1 *Schematic illustrations of the manufacturing process: (a-b) Solution casted GNP/PCL nanocomposites were hot-pressed with embedded copper wires as electrodes; (c) The surface nanocomposite film was placed on the surface of natural fibre plies to provide self-regulating heating for laminate curing.*

2.3 Characterization

Thermal expansion of PCL was measured by a dilatometer (Netzsch, 402PC). Pure PCL polymer pellets were hot-pressed in a mould with dimensions of 25 mm × 5 mm × 5 mm and characterised using a heating profile from 30 °C to 55 °C with a heating rate of 3 °C/min.

The electrical conductivity of hot-pressed GNP/PCL nanocomposite film measuring 60 mm × 5 mm and a thickness of 0.15 mm was measured by two-probe method, with a combination of a picoammeter (Keithley 6485) and a DC voltage source (Agilent 6614C). Five specimens were measured to obtain the average value for each filler loading.

Scanning electron microscopy (SEM, Inspect F) was used to examine the morphology of the GNP/PCL nanocomposite films as well as manufactured laminates. PCL films were immersed in liquid nitrogen to obtain the cryo-fractured surfaces, while the film-cured flax/epoxy laminates were polished to reveal the cross-sectional views. Both specimens were gold-sputtered before imaging.

The pyroresistive behaviour of GNP/PCL nanocomposite test coupons with dimensions of 25 mm x 5mm x 1 mm were measured in a small oven at a heating rate of 3 °C/min, with a thermocouple placed close to but not touching the specimens, to measure and record the temperature data (Pico Technology TC-08). Electrical resistance was measured simultaneously by a two-probe method via embedded electrodes on both ends of the specimen.

Dynamic mechanical analysis (DMA, TA Instruments Q800) was used to compare the thermomechanical performance of the NFRPs fabricated by both out-of-oven curing and traditional oven curing methods. The GNP/PCL surface layer was removed before the tests to examine the quality of the laminates. Three-point bending mode was employed with a temperature scan from 30 °C to 90 °C, at a rate of 5 °C/min, a frequency of 1 Hz and a strain of 1 %.

Differential scanning calorimetry (DSC 25, TA Instruments) was used to compare the degree of cure through-the-thickness of the laminates, for both out-of-oven and oven curing methods. A blade was used to remove the GNP/PCL surface layer before testing. Samples were selected from the top, middle, and bottom of the laminate, which were cut into smaller pieces, with a diameter of 0.2 mm. The heating temperature scan profile ramped from 50 °C to 200 °C at a rate of 10 °C/min. The fibre weight was excluded from the sample mass

according to each panel's volume fraction during the calculation of degree of cure. The enthalpy value was selected in a range from 50 °C to 200 °C and calculated through the integrated analysis software from TA Instruments. Neat bio-resin and hardener were mixed and cured by a 48-hour isothermal at 55°C, to provide a value of the enthalpy for the fully cured resin.

The *In-situ* electrical sensing performance of fabricated multifunctional composites was characterised by measuring electrical resistance with a digital multimeter (Agilent 34410A) during three-point bending in an Instron 5566 universal testing frame. The electrical resistance and crosshead displacement data were collected and synchronised with a purpose built LabView program [34]. The chosen test method consisted of 10 loading/unloading cycles at 0.1 % strain, followed by another 10 cycles at 0.2 % strain in a three-point bend configuration with a 1 %/min strain rate.

The flexural properties of the laminates were obtained from the three-point bending test in accordance with ASTM D790-10. Samples were cut using a diamond tipped circular saw to dimensions of 62 mm × 12.7 mm × 3.5 mm. The thickness used for the calculation of flexural modulus and strength was the total thickness of the laminate, including the surface PCL nanocomposite film for OoO specimens.

Water vapour transmission tests were performed according to ASTM E96, as illustrated in Figure S6b. Neat PCL film and 5.5 wt.% GNP/PCL film with the same thickness of 150 µm were prepared by the aforementioned compression moulding process. Test dishes were filled with water and sealed by either the PCL or GNP/PCL testing film. The dishes were placed in a desiccator with a sustained relative humidity of 5 % and measurements were made each day to record the weight loss of each specimen.

The water absorption test was performed by recording the weight of FRP samples embedded in a hydrophobic polyisobutylene tape surround (Easy Composites Ltd, ST150 Vacuum Bagging Gum Tape), with an exposed surface of either the GNP/PCL film, or the bare FRP surface, as shown in Figure 8a. The top water layer on the sample surface was removed every 24 hours to record the weight difference, before being replenished. The water absorption samples had a water contact surface area of 2 cm × 4 cm and a thickness of 3.5 mm.

3. Results and discussion

3.1 Electrical and pyroresistive properties of GNP/PCL nanocomposites

An appropriate conductive filler concentration is vital to achieve efficient Joule heating and a self-regulating heating function, as well as subsequent electrical sensing properties. Figure 2a shows the percolation curve of GNP/PCL nanocomposites. According to percolation theory [35], electrical conductivity σ is equal to:

$$\sigma = \sigma_0(\rho - \rho_c)^t \quad (1)$$

where ρ is the filler concentration, ρ_c is a specific filler volume fraction known as the electrical percolation threshold, σ_0 is a pre-exponent constant, and t is an exponent which represents the dimensionality of conductive filler network [36-38]. The volume percentage (vol.%) was calculated from the weight fraction (wt.%) that was used in the experiments. The pre-exponent constant (σ_0) and the exponent (t) were obtained from the linear fitting by taking the logarithm of both sides of equation (1), as shown in the inset plot of Figure 2(a). Accordingly, a percolation threshold of 2.29 vol.% (~ 4.12 wt.%) was obtained by putting the linear fitting result (σ_0 and t) back into Equation (1).

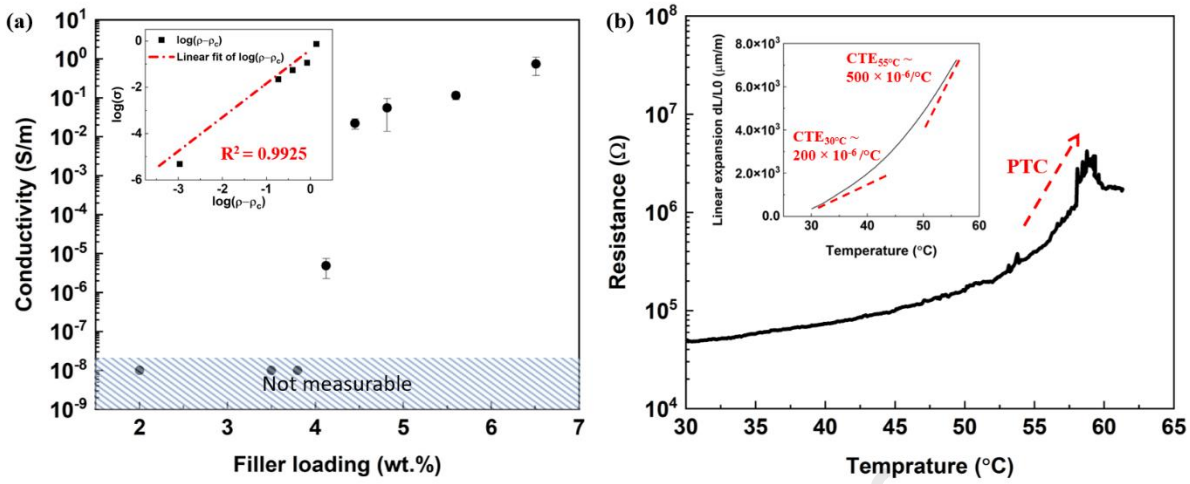

Figure 2 *(a) Percolation curve of GNP/PCL nanocomposites, with linear fitting according to equation 1 (inset). (b) Temperature dependent resistance curve of 5.5 wt.% GNP/PCL specimen with inset of thermal expansion performance of biopolymer PCL. The coefficient of thermal expansion (CTE) of PCL at 55 °C is more significant than that at 30 °C, providing an opportunity to expand the conductive network at 55 °C in GNP/PCL nanocomposites for self-regulated heating. The resistance of GNP/PCL composite shows a relatively sharp increase before the melting point of PCL, where the matrix thermal expansion separates the conductive filler network.*

The positive temperature coefficient effect describes the increase of electrical resistance when the specimen is subject to rising temperature. During the thermal expansion of the polymer matrix, especially around the phase transitions such as glass transition, softening, or melting, the conductive filler network will be disrupted, providing an autonomous cut off during Joule heating and setting a safety limit for Joule heating. Although a filler loading well above the percolation threshold is favoured for Joule heating effect, a filler loading above but closer to the percolation threshold is expected to have a more significant resistance change upon heating, benefiting the self-regulating heating performance of the GNP/PCL nanocomposite layer. In addition, a filler loading close to the percolation threshold will also facilitate the associated electrical sensing properties, as excessively high filler loadings will

lead to a sacrificed sensitivity [39, 40]. A GNP filler loading of 5.5 wt.% was chosen to fulfil both requirements, ensuring sufficient heating as well as a decent PTC intensity of GNP/PCL nanocomposites (see *Figure S1* for PTC intensity at different filler loadings). Apart from the GNP/PCL nanocomposites fabricated by the solution casting method, we have also demonstrated that melt-compounded GNP/PCL nanocomposites provide a good PTC intensity with a GNP loading of 10 wt.% (Figure S2), should the melt-processing methods be favoured for the chosen application.

A good PTC performance with a clear increase in resistance upon increasing temperature has been observed, as shown in Figure 2b. The resistance increased gradually from room temperature upon heating, followed by a clear change in slope when the temperature reached 50 °C, with a sudden jump near the melting point (58 °C) of PCL. Such a change in resistance can be attributed to the thermal expansion behaviour of PCL polymer, as shown in Figure 2b inset. As a comparison, the thermal expansion of both PCL and another biodegradable polymer, PLA, has also been displayed in Figure S3. By comparing the data plots, it is seen that PCL can achieve a higher PTC intensity due to its higher thermal expansion value. According to the definition of CTE, the slope of the expansion curve is the CTE value of the material at a specific temperature. From 30 °C to 55 °C, the thermal expansion rate of the PCL polymer starts to show a clear change in slope. The CTE valued increased from 200×10^{-6} /°C at 30 °C, with a clear change in slope (from around 45 °C) and reached the highest value (~ 500×10^{-6} /°C) when the temperature approached the melting point (58 °C) of this semi-crystalline polymer. A CTE value of approximately 500×10^{-6} /°C at 55 °C indicates a relatively large thermal expansion, which PCL possesses, providing an opportunity to break the nanoscale conductive network in GNP/PCL composites. This is in good agreement with the measured resistance values which start to increase when the temperature rises above 45 °C

and showing a clear jump when approaching the melting temperature. It is worth noting that as the heating continued and went beyond the melting point, a negative temperature coefficient (NTC) effect has also been observed, shown in Figure 2b, which can be attributed to the GNP network rearrangement and agglomeration due to the significantly reduced matrix viscosity [41].

3.2 Self-regulating heating performance of GNP/PCL nanocomposites

To avoid temperature overshoot and associated safety concerns during the exothermic reaction of the curing process, self-regulating heating based on the PTC effect of conductive polymer composites can provide an autonomous solution for a safe composites manufacturing. A reliable heating function that can regulate the temperature without overshooting is crucial for this method. Figure 3a shows the temperature of GNP/PCL film with different voltages applied from 20 V to 160 V. With an increasing voltage applied, a higher heating rate can be observed from the curves, with temperatures reaching 40 °C within 2 mins at voltages above 100 V. The rapid temperature increase is attributed to the increasing power input to the system. With further increase in applied voltage from 100 V to 160 V, the temperature started to show a stabilising trend with a reduced heating rate. This is due to the increased resistance of the film at elevated temperatures (as shown in Figure 2b), restricting the electric current flowing inside of nanocomposites, hence limiting further temperature increase by Joule heating. Once the temperature reaches the self-regulating temperature (around 55 °C), a relatively stable temperature profile can be observed even with a significantly higher voltage applied (up to 160 V). The obtained self-regulating heating capability of the film can be attributed to the thermal expansion of the polymer matrix (as

shown in CTE curve in Figure 2b inset) with the disruption of the conductive network, confirming the reliable and safe heating performance of 5.5 wt.% GNP/PCL nanocomposite films to be used in composites manufacturing. A power density of 0.107 W/cm^2 (7.13 W/cm^3) at a steady-state temperature of 55 °C has been achieved based on the current GNP/PCL film, which is lower than most of reported values at similar steady-state temperature in the literature for nanocomposite heaters [42].

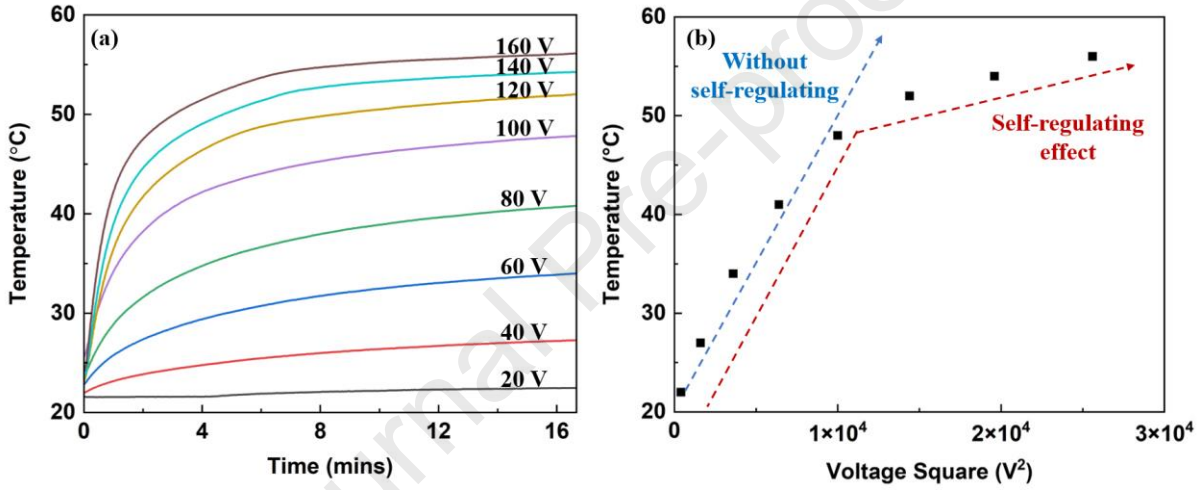

Figure 3 *(a) The heating profiles of GNP/PCL film at various applied voltages. The steady-state temperature tended towards the self-regulating temperature above 120 V. (b) A plot showing the steady-state temperature of GNP/PCL film with the square of the applied voltage, with the non-linear part from 45 to 60 °C reflecting the self-regulating phenomenon of the film.*

Figure 3b shows a steady-state temperature range from 55 °C to 58 °C when plotted against the square of the applied voltages. According to Joule heating theory, the material temperature should have a linear relationship with the voltage square, according to Equation (S1) [43-45]. However, a clear non-linear change with a reduced slope of the curve can be observed above 45 °C, with the temperature of the GNP/PCL film becoming stable when

approaching 55 °C due to the increased resistance hence a reduced heating, further confirming the self-regulating performance.

3.3 Energy consumption during laminate curing

To examine the energy efficiency of the out-of-oven manufacturing method via a self-regulating heating layer, real-time power consumption and temperature were monitored and recorded throughout the curing process for both out-of-oven and traditional oven methods and presented in Figure 4a and Figure S4. Compared with the energy consumption of oven curing (6.83 kWh), a significantly reduced energy consumption based on current self-regulating heating film has been achieved, with only 0.35 kWh consumed, which is 5 % of the total for the oven curing process (Figure 4b). Such a great reduction in energy consumption is mainly attributed to the efficient heat transfer from the surface nanocomposite film, which was attached onto the natural fibre laminates directly, providing a conduction heating source for laminate curing. In contrast, during convection oven curing, the energy needs to heat up the air within the oven first before the laminates can be heated. Due to the low thermal conductivity and the large heat capacity of the air, a large portion of energy is wasted in heating the air, making the whole process energy inefficient. It is also worth noting that the self-regulating heating function of the PTC film could also reduce the Joule heating rate based on increased resistance if the temperature reaches the steady-state temperature range of 55-58 °C during the exothermic curing process, leading to an increased safety level when compared to other Joule heating materials.

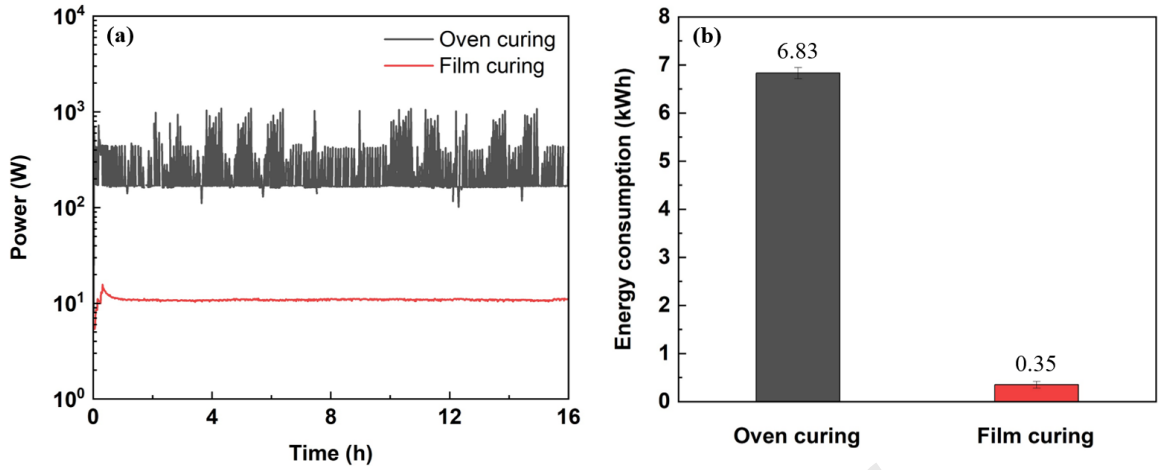

Figure 4 *(a) Real-time power consumption of oven curing and OoO film curing, and (b) the total energy consumption showing that the Joule heating film can achieve a significantly enhanced energy efficiency with conduction heating over the traditional convection oven.*

3.4 Thermomechanical, flexural properties and morphologies of natural fibre laminates

Although the main aim of this work is to develop an energy efficient composites manufacturing process, it is essential that the original performance of the composite system is maintained. Therefore, the thermomechanical properties of flax/epoxy laminates cured by the out-of-oven surface nanocomposite films were directly compared to the same flax/epoxy system cured by traditional convection oven method. The effect of both curing methods on the mechanical and morphological properties of the flax/epoxy laminates were systematically characterised. Figure 5a presents the thermomechanical performance of the laminates measured by DMA tests. Between the two methods, no obvious difference can be found in the obtained glass transition temperature (T_g) of the specimens, while a slightly higher average value of the storage modulus was obtained from the film cured specimens. This is believed to be due to the slightly higher fibre volume fraction of 28.6 % in the film cured panel, compared to the fibre volume faction of 26.5 % for the oven cured panel. From the three-point bending results in Figure 5b, similar values of both flexural modulus and strength were

obtained from the panels cured by two different methods, although a slightly higher thickness value (including surface film) was used to calculate the modulus and strength. DSC results in Figure S5 also proved that there is no obvious difference in the degree of cure between laminates. Clearly, no detrimental effects on the thermomechanical or mechanical properties were introduced by the out-of-oven curing method, confirming the effectiveness of current sustainable manufacturing method for natural fibre composites.

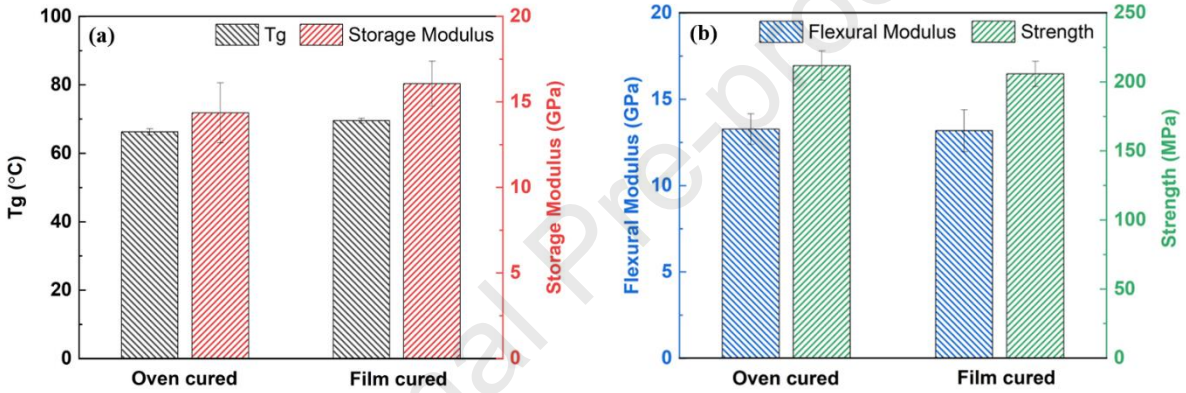

Figure 5 *Thermomechanical and flexural properties of natural fibre composites cured by the traditional oven and current out-of-oven curing methods: (a) glass transition temperature and storage modulus measured from DMA; (b) flexural modulus and strength measured from three-point bending. Similar values were obtained from two curing methods, indicating the feasibility and effectiveness of using out-of-oven manufacturing for natural fibre composites.*

The morphologies of the nanocomposite surface layer, flax/epoxy laminates, as well as the interface between surface layer and laminates have been examined under SEM. Figure 6a shows the cryo-fractured surface of GNP/PCL, with an in-plane orientation of graphene nanoplatelets attributed to the compression moulding process during the film fabrication. The polished surfaces of the cured specimen are shown in Figures 6b and 6c, with the

GNP/PCL film firmly attached to the flax/epoxy laminate, even after various polishing steps. Figure S7 and S8 also confirmed the good flexibility and attachment of GNP/PCL film to the laminates' surface. It also remained attached to the laminates after the three-point bending mode damage sensing test. This strong attachment can be attributed to the relatively large surface free energy of PCL leading to a good wetting of the resin [46]. No obvious voids were found in the laminates cured by GNP/PCL films, as confirmed from cross-sectional view of the specimens in Figure 6c. Fracture surfaces of the laminates after three-point bending tests have also been examined, with very similar fracture morphologies between the two manufacturing methods. Evidence of interfacial debonding between flax fibres and epoxy matrix were observed in both oven cured (Figure 6d) and film cured laminates (Figure 6e), indicating the panels cured by different curing methods have similar failure mechanisms during the mechanical test.

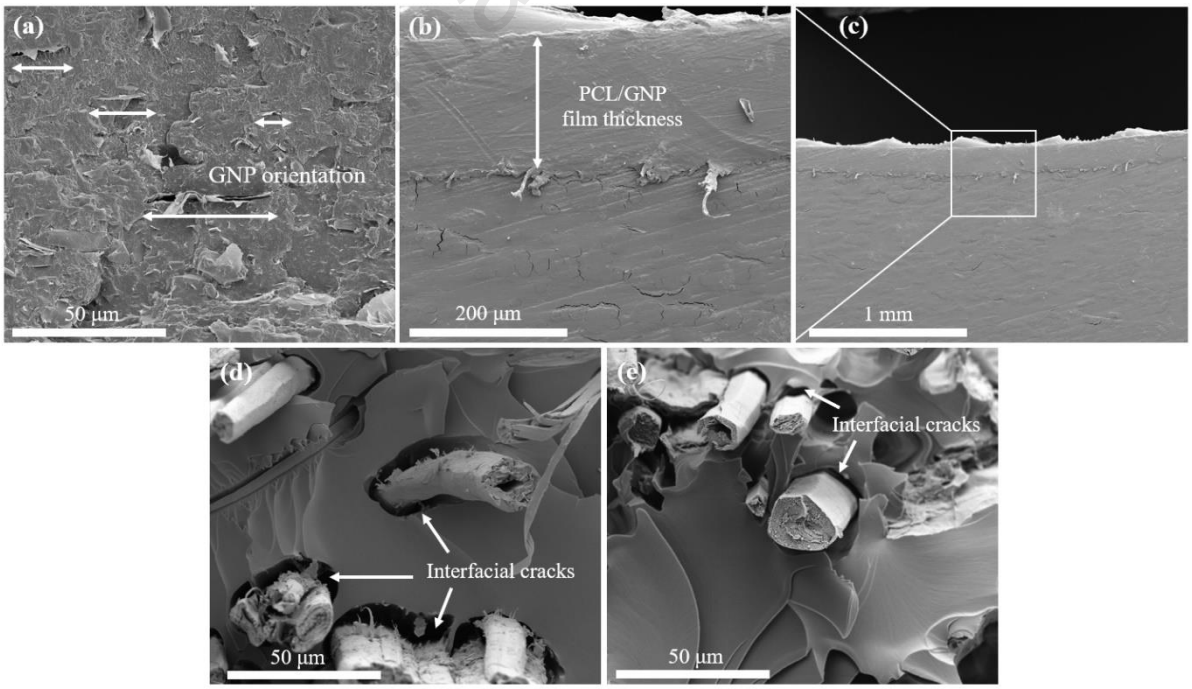

Figure 6 *SEM images of: (a) cryo-fractured surface of GNP/PCL film with an in-plane orientation of GNP within the PCL matrix; (b-c) cross-sectional views of polished flax/epoxy laminate with GNP/PCL film well attached to the laminates after polishing; fracture surface of*

(d) oven cured specimen and (e) film cured specimen after three-point pending tests, showing similar failure mechanisms between two curing methods.

3.5 Real-time deformation and damage sensing

The embedded GNP/PCL surface layer can introduce new functionalities such as deformation and damage sensing based on piezoresistive methods, despite the electrical insulating nature of the natural fibre composites. In three-point bending test, the GNP/PCL film (at the bottom surface as shown in Figure 7b inset) is under tension. Therefore, the resistance of the GNP/PCL film will increase as the number of conductive filler contact points is reduced with increasing strain. By measuring the electrical resistance changes upon loading, deformation and damage of the laminates can be monitored in real time, avoiding excessive deformation or damages to the structure during its service life. The *in-situ* deformation sensing of current multifunctional natural fibre composites has been examined under a three-point bending test, with the functional surface layer positioned at the bottom tensile surface and subject to cyclic loadings at different strain levels (Figure 7a). The relative resistance change of the GNP/PCL surface layer ($\Delta R/R_0$) was used as the sensing signal to detect the deformation of the specimen. Under a very low strain of 0.1 %, the sensing signals showed some changes upon deformation, although the signals also possessed some fluctuations in resistance change and were not ideally correlated to the loading cycles. This can be attributed to the intrinsic low stiffness and high deformability features of PCL matrix (T_g: - 60 °C) at room temperature. Therefore, in the soft polymer matrix, the nanoparticle network will slightly reform and reconnect, which leads to the signal of GNP/PCL films being less sensitive at room temperature. However, a much clearer sensing signal can be found under a strain of 0.2 %, with a good correlation between each cycle of deformation, indicating the feasibility of using

current surface film to detect deformation of the laminates. It is believed with a higher strain level, a more reliable sensing signals can be obtained, although relatively low strains (up to 0.2 %) have been employed in current study to avoid unnecessary damage initiated within the laminates. Furthermore, a slightly reduced resistance between the 1st and 10th loading cycle, as observed in Fig.7a, is believed due to the viscoelastic effect of the nanocomposite layer. With a longer relaxation time (as shown between 0.1 % and 0.2 % strain cycles), the resistance of the film returned to the original level [9], since the elastic deformation is fully reversible after removing the strain.

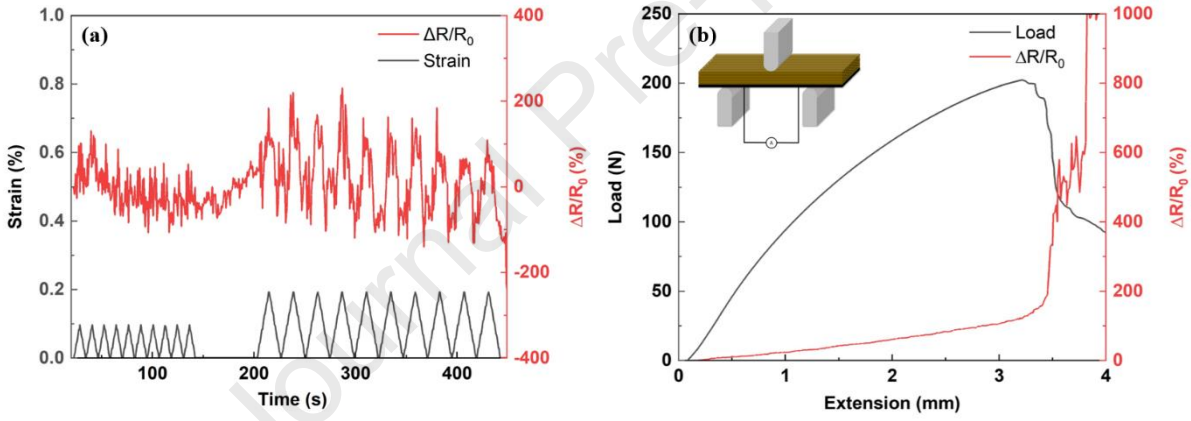

Figure 7 *(a) The real-time deformation sensing signal from the embedded surface layer of natural fibre composites under cyclic three-point bending at different strains; (b) The damage sensing and its illustration of the multifunctional natural fibre composites under three-point bending tests, showing a clear correlation between the sensing signals and load drops.*

Figure 7b presents the damage sensing of the natural fibre composites based on the embedded surface layer under three-point bending. With the increasing load, the sensing signals can be observed with a clear increasing trend from the beginning of the test. With the increasing load applied to the specimen, the sensing signals continued to increase, with a

clear jump associated with the load drop (at around 3.3 mm extension). An early warning based on appropriate threshold of sensing signals (associated with the local deformation) can be established to avoid the catastrophic damage of the components, while the failure of the components can be clearly detected by the established sensing system [17, 40, 47, 48]. A good correlation between sensing signals and load curves can be established, providing early deformation signal of 0.2-0.3 % strain before catastrophic failure. It is worth noting that due to the surface position of the current sensing layer, the internal damage such as matrix cracking or interfacial debonding of flax/epoxy laminates cannot be detected by the surface sensing film. Therefore, it is important to set a relatively early safety threshold of the sensing signal. Nevertheless, with a multifunctional surface layer capable to detect deformation as low as 0.2 % strain, the deformation and structural integrity can be monitored in real time without interfering the internal structures of the composite systems.

3.6 Water barrier properties

It is well acknowledged that natural fibre composites can be susceptible to environmental conditions, while many research efforts have been made in improving barrier properties [27]. An in-plane aligned GNP orientation can form tortuous paths to prolong the water molecular cross distance [49]. With orientated GNP within the surface layer (Figure 6c), an improved water molecular shielding performance has been achieved in GNP/PCL specimens.

To examine the water protection ability of current embedded multifunctional surface layer, the water absorbing behaviour of flax/epoxy laminates has been examined. The mass of both reference and out-of-oven cured laminate with GNP/PCL embedded surface layer has been measured, with the top surface of laminates exposed to the same amount of water between

each measurement (as illustrated in Figure 8a). It can be observed that the flax/epoxy laminate covered by the GNP/PCL film has a reduced rate of water absorption compared to the specimen without surface film. Between days 7 and 10, the average amount of water which has been absorbed per unit surface area is reduced from 22 mg/cm^2 without the GNP/PCL film, to 7 mg/cm^2 with the film (Figure 8b). Furthermore, it has been shown that the addition of 5.5 wt.% GNPs to the PCL film results in a 57 % reduction in water permeability compared to a neat PCL film without GNPs (Figure S6). This demonstrates that the GNP/PCL film could be used as a protective shielding layer on natural fibre composites, especially in humid environments to prolong components' service life.

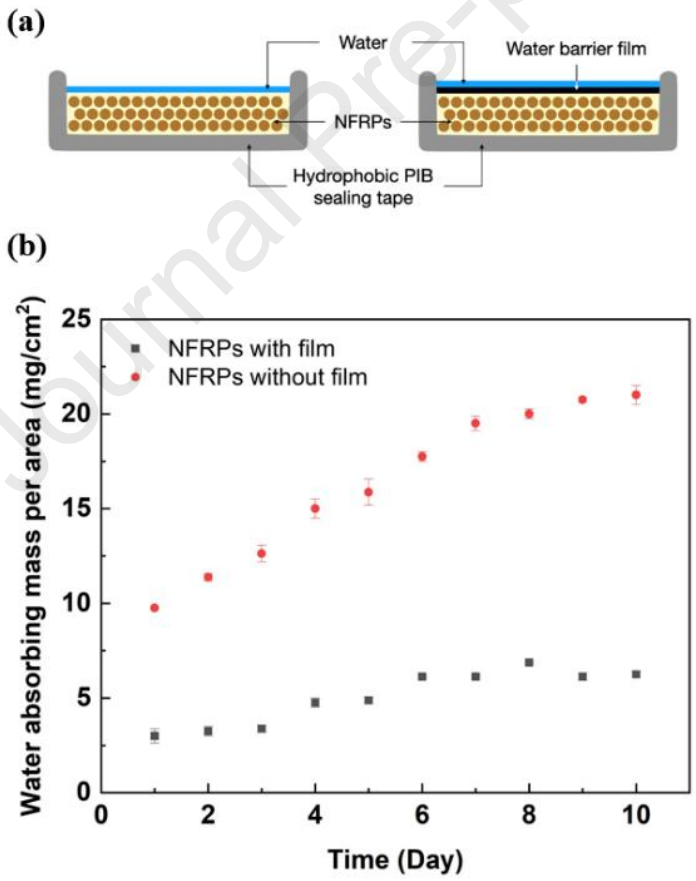

Figure 8 *(a) An illustration of the water barrier property experimental design, showing NFRPs both with and without the GNP/PCL film layer and (b) the mass of absorbed water per unit area of the oven cured and film-cured NFRPs over time. The film cured flax/epoxy laminate has a lower water absorption rate compared to the NFRPs without the film layer.*

4. Conclusions

This study developed an extremely energy-efficient composites manufacturing method for natural fibre composites based on a smart GNP/PCL nanocomposite film. Compared with traditional convection oven curing, a 95% reduction in electrical energy consumption has been achieved via an out-of-oven (OoO) Joule heating method thanks to the more efficient heat transfer by conduction from film to laminate. Based on the PTC effect, the fabricated smart biopolymer layer possesses a self-regulating heating function, providing an intrinsic safety assurance without the risk of overheating, which is exceptionally important for the exothermic reaction of thermoset curing processes.

The developed energy efficient OoO curing method has no detrimental effects on the thermomechanical and mechanical properties of manufactured natural fibre composites, while being fully compatible with existing composite liquid moulding processes, ensuring its feasibility in replacing traditional oven curing with significantly enhanced energy efficiency. In addition, the embedded GNP/PCL surface layer provides real-time deformation and damage sensing functions based on electrical sensing method, with an enhanced water barrier property to prolong the life of the natural fibre composites. This study opens a new arena for sustainable composites manufacturing with a significantly reduced energy consumption and integrated multifunctionalities, without affecting composite internal structures or sacrificing their performance, which can be applied in many composite systems.

However, for any new manufacturing routes, it is also important to recognise the environmental impact of any new materials involved in the process and how the minimise the carbon footprint associated with these new materials. For instance, appropriate recovery

processes should be implemented for the use of organic solvents, ensuring effective reuse of the solvent to minimise the environmental impact. A life cycle assessment should also be carried out for the target applications hence to have a full understanding of the impact.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: