Epoxy/Glass Fiber Nanostructured p- and n-Type Thermoelectric Enabled Model Composite Interphases

George Karalis, Kyriaki Tsirka, Lazaros Tzounis, Christos Mytafides, Lampros Koutsotolis and Alkiviadis S. Paipetis *

Department of Materials Science & Engineering, University of Ioannina, GR-45110 Ioannina, Greece; gkaralis@uoi.gr (G.K.); ktsirka@uoi.gr (K.T.); latzounis@uoi.gr (L.T.); cmytafides@uoi.gr (C.M.); labrkout@uoi.gr (L.K.)

* Correspondence: paipetis@uoi.gr; Tel.: +30-2651-008-001

Received: 9 July 2020; Accepted: 29 July 2020; Published: 3 August 2020

Featured Application: This work proves the thermoelectric principles and efficiency of model composites towards the manufacturing of multifunctional fiber reinforced polymer composites (FRPCs) for large-scale structural applications enabling thermal energy harvesting technology.

Abstract: This experimental study is associated with the modification of glass fibers with efficient, organic, functional, thermoelectrically enabled coatings. The thermoelectric (TE) behavior of the coated glass fiber tows with either inherent p semiconductor type single wall carbon nanotubes (SWCNTs) or the n-type molecular doped SWCNTs were examined within epoxy resin matrix in detail. The corresponding morphological, thermogravimetric, spectroscopic, and thermoelectric measurements were assessed in order to characterize the produced functional interphases. For the p-type model composites, the Seebeck coefficient was $+16.2 \ \mu V/K$ which corresponds to a power factor of $0.02 \ \mu W/m\cdot K^2$ and for the n-type $-28.4 \ \mu V/K$ which corresponds to power factor of $0.12 \ \mu W/m\cdot K^2$. The p–n junction between the model composites allowed for the fabrication of a single pair thermoelectric element generator (TEG) demonstrator. Furthermore, the stress transfer at the interphase of the coated glass fibers was studied by tow pull-out tests. The reference glass fiber tows presented the highest interfacial shear stress (IFSS) of 42.8 MPa in comparison to the p- and n-type SWCNT coated GF model composites that exhibited reduced IFSS values by 10.1% and 28.1%, respectively.

Keywords: Seebeck effect; model composites; SWCNTs; organic thermoelectrics; functional interphases; thermal energy harvesting

1. Introduction

During the last decades, the growing demand for the utilization of lightweight, high-performance structural composite materials has rapidly increased in various commercial sectors, such as the aerospace and automotive industries. Fiber reinforced polymers constitute an extremely interesting field of research due to their potential for the exploitation of additional functionalities. Tailoring or “architecting” the material in relation to both its structural and non-structural services is an inherent ability of advanced composites and is rapidly emerging technology for their next generation. Understanding their mechanical behavior requires the study of the interface, the common physicochemical areas between the distinct phases (reinforcing and matrix materials) \[1,2\]. This is a prerequisite for the design of a composite material, as its behavior is most of the times governed by its interfacial properties \[3\].
The approach of blending nano-scaled reinforcements into the matrix of micro-scale reinforced systems, with a view to enhancing both the matrix dominated properties as well as imparting multifunctionality, has been extensively studied in the last decade. Additional functionalities include both capabilities that relate to structural integrity, such as wear resistance, morphing, or self-healing, as well as non-structural ones, such as inherent structural health monitoring, sensing and actuation, power harvesting, and power storage [4–7].

In an alternative approach, the nanomaterials are deposited directly onto the surface of reinforcing fibers, such as carbon, aramid, and glass fibers (GFs), and this has triggered a new class of functional materials, where the nanoscale functional reinforcement is following the architecture of the microscale reinforcement. This leads to a biomimetic ‘hierarchical’ approach towards multiscale reinforcements with improved wettability, increased adhesion, robust interlocking mechanisms, and enhanced interfacial stress transfer related to the introduction of nanophases such as carbon nanotubes (CNTs) [8–12]. The resultant hierarchical interphases except for the modified mechanical properties also transfuse extra functionalities [13–17].

Du and co-workers presented a synergistic strategy by taking advantage of polyetherimide (PEI) and ZIF-67 to enhance the interfacial strength of carbon fiber (CF) reinforced polyetheretherketone (PEEK) composites via a facile route. After modification, the tensile strength of single CFs showed no deterioration and the interfacial shear strength (IFSS) of the as-prepared modified CF/PEEK model composites revealed an increase of 40.5% [18]. De Luca et al. [19] developed nanostructured ordered “brick-and-mortar” interphases using layer by layer deposition of PDDA/PSS/LDH solution onto the surface of hydroxylated GFs. The resulting anisotropic morphology caused strain hardening phenomena to the produced nanostructured interphases and thus reduced the local stress concentrations arising from fiber breaks and increased the extent of stable fiber slippage. Pozegic et al. presented a scalable method for growing CNTs during either the CF fabrication or the CF surface treatment stage, that could potentially further minimize their damage and offer a suitable replacement for the CF polymer sizing. Moreover, improvements in electrical conductivity in all three directions with significant enhancement in the surface (300%), thickness (450%) and volume (230%) were observed. Additionally, the thermal conductivity was improved by 107% in the through-thickness direction [20]. Another study documented the strongly orthotropic electrical properties of composite materials comprised of hierarchical UD GFs coated with single-walled carbon nanotubes (SWCNTs). The exceptional damage-sensing capability of the SWCNTs hierarchical composites was predicted by simulations and validated experimentally [21].

CNTs dispersed-inks deposition onto fibrous substrates are capable of to convert insulating reinforcing fibers to semi-conductive reinforcements for composites with modified interfacial shear strength (IFSS) and secondary additional properties. The resulting composite materials can be used for a wide range of applications, such as electrostatic charge dissipation, damage sensing, and energy harvesting. Gao et al. reported on the strain, humidity and temperature sensing ability of hierarchical GFs, coated with commercial oxidized CNTs by electrical measurements [22]. Tzounis et al. systematically examined the thermoelectric response of reinforcing fibers coated with CNTs [23], thermoelectric materials based on engineered polymer nanocomposites, and/or polymer/fiber composites [14,24], appropriate for large-scale structural applications with thermal energy harvesting capabilities.

It is common knowledge that energy loss is inevitable during the operation of an engine resulting in a fuel efficiency less than 50%. Most of the wasted energy is in the form of heat. For typical diesel engines, tests from as early as 2009 showed that, the heat lost by the exhaust was approximately a quarter of the energy produced by the utilized fuel [25]. Thermoelectric energy harvesting and pyroelectric energy harvesting exploitation, relying on the temperature change over distance and time, respectively. The aforementioned technologies constitute the two most common thermal energy harvesting methods. Thermoelectric (TE) conversion is a promising technique to recover temperature waste heat as electricity. In general, heat coming from temperature fluctuation in the environment can
be reclaimed as electricity on account of the well-known ‘Seebeck effect’. Thermoelectric materials exhibit the Seebeck effect, in which charge carriers move in response to temperature gradients. The Seebeck coefficient is directly related to the density of states, whereas the electrical conductivity can be limited by electronic and morphological defects. Charge carriers diffuse across the temperature gradient, creating an accumulation of charge and thus a potential difference, $\Delta V$. The magnitude of this effect is described by the Seebeck coefficient ($S$) and is simply the voltage difference divided by the applied thermal gradient $S = \Delta V/\Delta T$. The Seebeck coefficient is further used for the calculation of the power factor ($PF = \sigma \times S^2$), a well-established quantity for comparing the TE performance of different thermoelectric materials. Finally, the overall thermoelectric efficiency for specific temperature range applications of a material is classified by the dimensionless thermoelectric figure of merit, $ZT (ZT = (\sigma \times S^2) \times T/\kappa)$, where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $\kappa$ is the thermal conductivity and $T$ is the corresponding temperature.

An efficient thermoelectric material presents a high value of $ZT$, combining high electrical and poor thermal conductor characteristics. The three thermoelectric parameters $\sigma$, $S$ and $\kappa$ are correlated with the intrinsic carrier concentration of the material [26–29]. Thermoelectric energy harvesting is a conventional technique for converting wasted thermal energy into the electrical power by means of thermoelectric element generators (TEGs). A typical TEG device consists of p–n junctions properly interconnected electrically in series and thermally in parallel. When a temperature gradient is established between the hot and the cold side, free electrons and holes are able to move towards specific directions and generate a potential difference proportional to the temperature difference between the p-type and n-type semiconductors. Compared to the traditional TEG devices, high performance flexible TEGs that exploit the nanotechnology advancements are being extensively reported [17,30].

In this study, hierarchical glass fiber tows coated with p-type and n-type SWCNTs as well as reference tows were evaluated in terms of their thermal stability and physicochemical relevance with the epoxy resin. The thermoelectric response of the produced p and n-type epoxy model composites have been assessed for a single pair TEG fabrication. The tow pull-out test was used to determine the quality of interfacial bonding between the epoxy matrix and the nanocoated glass fibers. Fracture morphologies of the pulled-out tows obtained via optical microscopy revealed a cohesive type of failure in all cases, as the epoxy material remained attached on the surface of the tows after the pull-out process.

2. Materials and Methods

2.1. Materials

The 1062 Multi-End Roving (NEG) GFs were employed for this study with a tensile strength of 2300–2400 MPa and tensile modulus of 72 GPa, specifically designed for use with epoxy resin systems in applications that require high mechanical strength and corrosion resistance such as filament wound pipes. The filament diameter is 13.3 ± 0.6 $\mu$m as stated by the manufacturer.

SWCNTs in powder form were provided by OCSiAl (TUBALL, carbon content: >85 wt.%, outer mean diameter of CNT 1.8 ± 0.4 nm, length of CNT > 5 $\mu$m, metal impurities <15 wt.%). SDBS (sodium dodecylbenzenesulfonate, 348.48 g/mol), PEI (Poly(ethyleneimine)) solution ~50% in H$_2$O (Mr 600,000–1,000,000) were purchased from Sigma Aldrich. All chemical reagents were used as received.

RS Pro silver loaded epoxy conductive paste was utilized for the adhesive ohmic contacts.

A commercial low viscosity liquid epoxy resin system was employed, consisting of EPIKOTE Resin 828LVEL (100.0 parts by weight) EPIKURE™, Curing Agent 866 (83.0 parts by weight), and EPIKURE™ Catalyst 101 (1.5 parts by weight). The curing cycle and post-curing included heating at 90 °C for 90 min and at 130 °C for 180 min, respectively.
2.2. Dispersion and Deposition of the TE p and n-Type SWCNTs Inks onto GF Tows

The SWCNTs were dispersed using the UP400S manufactured by Hielscher Ultrasonics tip-ultrasonic probe processor for 45 min at 10 a Watt amplitude to deliver the wave directly into the aqueous solvent. For the p-type TE ink, 2 mg/mL SWCNTs and 5 mg/mL of SDBS were utilized in order to produce a suspension with a proper critical micelle concentration (CMC) and achieve a stable dispersion. Accordingly, for the n-type TE ink, 2 mg/mL SWCNTs and 2 mg/mL of SDBS coupled with 5 mg/mL of poly(ethyleneimine) were used. The notation “p-type and n-type” refers to the type of the charge carriers induced in the two different formulations of the CNTs and does not imply any type of substitutional doping of the CNTs.

Then, the p and n-type TE inks were used for coating of the GF tows via a simple blade coating process. In more detail, 10 cm long single GF tows were cut from the reel, stabilized, and coated towards the creation of homogeneous continuous TE efficient p-type and n-type films onto the GFs. After the coating process, the tows were left to dry on a hot plate at 90 °C for 30 min.

2.3. Manufacturing of Model Composites for Thermoelectrical Characterization

Model composites were prepared and characterized for the study of the effect of the epoxy resin system addition on the thermoelectric response of the coated glass fibers. The coated single GF tows were placed flat onto a pre-cleaned silicon dog-bone shaped mould and secured in place on both sides with an adhesive tape. Then, two thin copper foil electrodes were adjusted tightly on each side of the functional single tows and glued with silver paste on the tow to ensure proper ohmic contacts. Upon drying of the contacts, a well-mixed and degassed epoxy resin/hardener/catalyst mixture was casted in the mould, which impregnated thoroughly the whole GF tow. The system was cured and post-cured following the aforementioned protocol. At least five model composites for each category were fabricated and the mean experimental values with the corresponding standard deviations are presented. The electrical properties and the thermoelectric response of the model composites were measured with the set up that is displayed in Figure 1.

![Figure 1. Manufacturing process of the thermoelectric generator (TEG)-enabled model composites (a) silicon mould utilized for the preparation of dog-bone shaped specimens with copper electrodes placed at both sides ready for the epoxy resin casting and (b) demonstration of the thermoelectric (TE)-enabled p and n-type model composites exposed to temperature gradient.](image)

2.4. Preparation of Model Composite Specimens for Micromechanical Tests

Tests for the interfacial shear strength calculations were performed on single GF tows using a pull-out configuration. These tests were performed in order to evaluate the effects of the nanostructured
coatings on the interfacial mechanical properties between the hierarchical fibers and the epoxy resin system.

For the selected manufacturing process, both uncoated and nanocoated GF tows with a length of 100 mm were pre-impregnated with a thin layer of epoxy resin at 3/4 of their length, using a micro-pipette and were semi-cured until the resin was viscous enough so as not to leak from the impregnated tow.

These epoxy resin semi-cured tows were lowered into the aluminum moulds by using purposely made fixture is presented in Figure 2b. The fixture was designed so as to hold the pre-impregnated tows aligned during the thermal treatment of the resin. Then, 20 g of the resin/hardener/catalyst system were poured into each of the aluminum moulds. Particular attention was paid in order to avoid buckling of the tows and simultaneously maintain the impregnated embedded length in the range of 1–2 mm. Finally, the specimens were cured and post cured according to the recommended curing cycles.

Figure 2. (a) A custom-made blade coating unit for the tows modifications, (b) impregnation of the tows within the epoxy resin mould utilizing the in-house built apparatus for the preparation of the pull-out test specimens, (c) schematic of a pull-out test specimen and (d) photo during the pull-out testing.

The tow pull-out experiments were conducted at room temperature using the Universal Testing Machine by Jinan Testing Equipment IE Corporation (Jinan, China) with a 2 kN Load cell. A two-piece metal jig held the epoxy resin mould while the top part was clamped using the appropriate jaw faces. A constant cross-head speed of 5 mm/min was employed for tensile loading to induce the pull out shear force at the tow/resin interphase. Tests were considered successful when the GF tow was completely pulled out from the polymer matrix. The applied load (F) and the corresponding shear strength presented correspond to the average of 8 successful pull-out experiments for each type

\[ \sigma_{\text{IFSS}} = \frac{F_{\text{max}}}{\pi d f l} \]

where \( F_{\text{max}} \) is the maximum load prior to the fracture of the GF tow, \( d \) is the diameter-width of the tow, and \( l \) is the embedded length, including the meniscus, as determined by optical microscopy.

The apparent interfacial shear strength of the functional GF tows and the epoxy resin matrix was calculated and compared with reference uncoated GF tow model composites. The mean values of shear strength presented correspond to the average of 8 successful pull-out experiments for each type
of specimens. Finally, the surface morphology of the pulled-out fiber tows from all categories was studied using an optical stereoscope at low magnification.

2.5. Characterization Techniques

Contact angle measurements were acquired via a commercial automated contact angle goniometer system manufactured by Ossila Ltd (Sheffield, UK).

The morphology of the hierarchical GFs, as well as the reference GFs were evaluated via SEM using the JEOL JSM 6510 LV SEM (JEOL Ltd., Akishima, Japan) with an operating voltage of 3.5 KV.

Thermogravimetric measurements were carried out in the STA 449C analyzer Netzsch-Gerätebau GmbH, Selb, Germany. The experimental procedure included a dynamic step from 25 to 1000 °C with a heating rate of 10 °C/min at ambient conditions to examine the reference and the nanocoated GFs mass loss.

The Labram HR-Horiba scientific micro-Raman system was used. The 514.5 nm line of an Ar + ion laser operating at a power of 1.5 mW at the focal plane was employed for the Raman excitation. An optical microscope equipped with a 50× long working distance objective served both for delivering the excitation light and collecting the back-scattered Raman light. Raman spectra in the range of 90–3500 cm⁻¹ were collected.

In order to determine the basic electrical characteristics, p and n-type bucky paper films were prepared by overnight vacuum filtering of the respective SWCNTs dispersions and four probe sheet resistance measurements were conducted (Table 1). A typical 4-probe technique (Four-Point Probe commercial system manufactured by Ossila Ltd.) was used to calculate the electrical conductivity based on the following formula: \( \sigma = \frac{1}{R \times L/S \times (\ln 2/\pi)} \), where \( R \) is the measured 4 probe sheet resistance, \( L \) is the length, and \( S \) is the cross section of each sample. It should be mentioned that the employed four-point probe system with four equally-spaced, co-linear probes to the material (inter-electrode probe distance/spacing: 1 mm) is capable of delivering currents between 10 nA and 150 mA, and can measure voltages from as low as 100 µV up to 10 V, which results in a sheet resistance measurement range of 3 mΩ/□ to 10 MΩ/□. The values reported are mean values of at least four measurements performed on different samples.

The DC measurements were conducted with a standard two-probe method using the Agilent 34401A multimeter with 6½ digits resolution. Model composites were placed and measured at 25 mm electrode-electrode distance at room temperature and 25% relative humidity (RH).

The voltage output of the model composites was determined using a custom-made setup. The samples were mounted on two metal blocks, which enabled the generation of a temperature difference. For all measurements, the one aluminum block \( T_{\text{cold}} \) was kept at room temperature \((-24 °C)\) via mild water circulation, while the other one \( T_{\text{hot}} \) was heated until 125 °C via calibrated temperature-controlled resistors, allowing for the generation of a temperature gradients. The generated thermovoltage \( \Delta V \) was measured across the electrodes by a multimeter-voltmeter. The temperature of the two blocks was measured with an IR-thermometer (OMEGA OS-VIR50 Dual Laser Video IR Video Thermometer) to verify the temperature difference \( \Delta T \), and the Seebeck coefficient \( S \) was derived from the ratio \( \Delta V/\Delta T \).

3. Results

In this study, organic materials were evaluated as emerging candidates for thermoelectric power generation. Chemical doping was employed for tuning the semiconductive nature of the graphitic material from p-type to n-type. In the literature, the terms p-type and n-type are frequently used to describe which apparent carrier mobility is in larger percentage in a material, rather than the position of the Fermi level [29]. Organic semiconductors can be ambipolar and in some cases the hole and electron mobilities are comparable, but one type of carrier prevails owing to the reactivity of the preferred dopant material to stably tune the initial material [31–33]. Contact angle (CA) measurements and scanning electron microscopy (SEM) were employed in order to assess the specific morphological
characteristics of the produced nanocoated GFs, while their thermal stability was investigated via thermal gravimetric analysis (TGA). Raman spectroscopy (RS) was used to evaluate the quality of and distribution of the SWCNTs deposited on the surface of the GFs under temperature gradients. Finally, the p–n nanostructured interphases were estimated via thermoelectric measurements and micromechanical studies.

3.1. Morphological Measurements of the Coated GFs

Representative contact angle images for each case are represented in Figure 3. Contact angle is a major surface property in terms of assessing the solid liquid interphase. In this study, the static contact angles of the SWCNTs inks onto the GFs as a measure of the surface wetting properties of the coated glass fibers.

The coated glass fiber morphologies were also studied using SEM in order to determine the homogeneity of the coatings and illustrate the specific characteristics of the nanostructuring onto the microscale reinforcing phase. Figure 4a,b illustrates the hierarchical morphology of the coated GFs with homogeneously distributed SWCNTs covering the fiber surfaces for the p- and n-type SWCNT coated GFs, respectively, at two different magnifications.

3.2. Thermogravimetric Analysis of the TE-Enabled GFs

In order to assess the thermal stability of the produced functional hierarchical structures, dynamic thermogravimetric scans were performed from 25 °C to 1000 °C. Thermogravimetric analysis under air atmosphere is very sensitive to the increase of the surface area which promotes the oxidation of the examined material. High thermal stability of these hierarchical structures is critical for the thermoelectric applications that involve high operational temperatures. Figure 5 illustrates the TGA graph of the uncoated and the nanocoated GF tows.
Figure 3. Static contact angle images measured by a goniometer’s software for (a) p-type single walled carbon nanotubes (SWCNTs) dispersion drop let in contact with glass fiber tow and (b) n-type SWCNTs dispersion droplet in contact with glass fiber tow.

The coated glass fiber morphologies were also studied using SEM in order to determine the homogeneity of the coatings and illustrate the specific characteristics of the nanostructuring onto the microscale reinforcing phase. Figure 4a,b illustrates the hierarchical morphology of the coated GFs with homogeneously distributed SWCNTs covering the fiber surfaces for the p- and n-type SWCNT coated GFs, respectively, at two different magnifications.

Figure 4. Scanning electron microscopy (SEM) images depicted surface morphology characteristics at different magnifications of (a) p-type SWCNTs coated glass fiber (GF) tow and (b) n-type SWCNTs coated GF tow.

3.2. Thermogravimetric Analysis of the TE-Enabled GFs

In order to assess the thermal stability of the produced functional hierarchical structures, dynamic thermogravimetric scans were performed from 25 °C to 1000 °C. Thermogravimetric analysis under air atmosphere is very sensitive to the increase of the surface area which promotes the oxidation of the examined material. High thermal stability of these hierarchical structures is critical for the thermoelectric applications that involve high operational temperatures. Figure 5 illustrates the TGA graph of the uncoated and the nanocoated GF tows.

Figure 5. Thermogravimetric measurements of uncoated GFs, coated GFs with p-type and n-type SWCNTs, respectively.

3.3. Spectroscopic Measurements of the TE-Enabled GFs

The Raman spectra of the p-type SWCNTs coated GF and the n-type SWCNTs coated GF were acquired at ambient conditions (room temperature–RT), as well as at temperature gradients of 50 °C and 100 °C by performing measurements at 75 °C and 125 °C, respectively. The respective results are presented in Figure 6. A linear baseline was subtracted from the spectra of the p-type and the n-type SWCNTs coated GFs.
analysis under air atmosphere is very sensitive to the increase of the surface area which promotes the oxidation of the examined material. High thermal stability of these hierarchical structures is critical for the thermoelectric applications that involve high operational temperatures. Figure 5 illustrates the TGA graph of the uncoated and the nanocoated GF tows.

**Figure 5.** Thermogravimetric measurements of uncoated GFs, coated GFs with p-type and n-type SWCNTs, respectively.

### 3.3. Spectroscopic Measurements of the TE-Enabled GFs

The Raman spectra of the p-type SWCNTs coated GF and the n-type SWCNTs coated GF were acquired at ambient conditions (room temperature—RT), as well as at temperature gradients of 50 °C and 100 °C by performing measurements at 75 °C and 125 °C, respectively.

The respective results are presented in Figure 6. A linear baseline was subtracted from the spectra of the p-type and the n-type SWCNTs coated GFs.

**Figure 6.** (a) Experimental set-up used to study the Raman spectra of p-type SWCNTs coated GFs and n-type SWCNTs coated GFs at room temperature, as well as at ΔT of 50 °C and 100 °C and (b,c) Raman spectra of the p-type and n-type SWCNTs coated GFs at ambient and at temperature gradients of 50 °C and 100 °C, respectively.

### 3.4. Thermoelectric Response of the Model Composites

In Table 1 the TE properties of both p-type and n-type bucky paper films are presented. The conductivity and the TE response introduced from the coating can be attributed to the nanoparticle-based networks deposited onto the fiber surfaces creating the electron transport pathways. In fact, the electrical conductivity and the Seebeck coefficient values can be explained more precisely if we consider the existence of a continuous self-assembled layer with thickness (t) onto the fiber surface with electrical conductivity (σ) stemming from the electrostatic interactions [34].

More analytically, when the anionic surfactant (SDBS) is added to distilled water it tends to ionize and give a negative charge to the created micelles which include the dispersed de-aggregated SWCNTs. Conversely, the positively charged free silanol particles from the glass fibers surface interact with the ambient oxygen groups result in non-covalent bonding of the CNTs [35]. The resistivity (ρ) of an epoxy coated GF tow along the longitudinal direction is given by the formula: $\rho = A \times R/L$ (A: circular cross section area). Executing this equation, the coated GF tows with SWCNTs (p and n-type) consist of a highly conductive continuous network and could be assumed approximately as a tubular-like geometry resistor ($V = \pi r^2 L$) with electrical conductivity of $\sigma = (4L)/\pi d^2$ [23]. The average diameter ($d = r/2, r$: radius) was ~1654 µm for p GF tows within the epoxy resin and ~1600 µm for the n-type GF tows within the epoxy resin, measured via a calibrated optical microscope. The electrical resistance (R) was measured along the length (L) via a two-probe method. It should be mentioned that the nanoparticle-based layers for both p-type and n-type SWCNTs coatings onto GFs possess lower electrical conductivity values in comparison to the aggregated and highly dense structure of the corresponding bucky paper films form, as presented in Table 1. Furthermore, the bulk thermoelectric properties of both p- and n-type bucky paper films were studied. The positive measured values of the Seebeck coefficient correspond to the p-type semi-conducting behavior and the negative to the n-type, respectively.
The hierarchical GF tows model composites were evaluated in terms of their thermoelectric response as presented in Figure 7.

**Figure 7.** (a) schematic illustration of a p-n junction between the model composites created by interconnecting in series the p-type and n-type model composites by a copper foil at the hot side (125 °C), while at the cold side (~24 °C) the copper electrodes were attached with the multimeter for a 2-probe measurement, graphs of (b) electrical resistance-electrical conductivity, (c) Seebeck coefficient-Power factor and (d) ΔV vs. ΔT curves for the coated p and n-type TE model composites.

### 3.5. Study of the Nanostructured Interfacial Mechanical Properties

Apart from the thermoelectric functionality, the interfacial shear strength of the hierarchical GFs was also measured by tow pull-out tests and compared to the interfacial properties of the reference uncoated GF tows. While the influence of the CNTs on the interfacial bonding of the GF with epoxy resin is usually determined by measuring the interfacial shear strength through single fiber fragmentation [2] or pull-out tests [36,37], the pull out test configuration was deemed as more appropriate for this study and was used to quantify the quality of interfacial bonding between the epoxy matrix and the nanocoated glass fibers which were used in this study.

Figure 8a shows the results of apparent interfacial shear strength (IFSS) measurements, which is indicative of the stress transfer efficiency of the interphase. As can be observed, the uncoated glass fiber tows (REF GF) exhibited the highest interfacial shear strength, i.e., 42.8 ± 0.9 MPa. Comparatively, the p-type SWCNTs coated GF model composites exhibited lower interfacial shear strength values at 38.5 ± 1.5 MPa, that is a 10.1% decrease in comparison to the uncoated GFs. For the n-type SWCNTs
coated GF model composites the interfacial shear strength was about 30.8 ± 3.4 MPa, which corresponds to a 28.1% reduction compared to the uncoated GF tows.

![Figure 8](image_url)  
**Figure 8.** (a) Interfacial shear strength values for the p-type and the n-type TE model composites compared to the reference one, (b) fractography images for the respective three examined categories.

Optical stereoscopic images indicate the failure modes of the model composites after the pull-out testing. Representative fractographic images of the pulled-out tows are shown in Figure 8b.

4. Discussion

4.1. Surface Structure and Wettability of the Coated GF Tows

The good wetting of the glass fiber tows by both the p and n-type SWCNTs ink droplets is indicative of the inherent hydrophilic behavior of the glass fibers, which promotes the forming of a uniform SWCNTs film on the GFs and is a measure of the level of adhesion. In Figure 3, images are shown for each case, captured just after the drop was suspended onto the surface of the glass fibers and also 60 s later to evaluate the progression of the wetting. For the GFs coated with p-type SWCNTs the average contact angle was found to be ca. 56.47° and for the n-type 52.39°.

As was observed in the SEM study (Figure 4), both the p- and n-type SWCNTs films formed on the GFs are satisfactorily uniform and dense exhibiting an interconnected network of SWCNTs which fully cover the surface. Some SWCNTs agglomerates are barely visible. The observed SWCNT–SWCNT junctions are impart the high values of electrical conductivity to the films, which alter the inherently dielectric behavior of the GF tows.

4.2. Thermal Stability of the Produced Coated GF Tows

Thermogravimetric analysis was used in order to characterize the thermal stability of the SWCNTs coated GFs in comparison to the reference GFs.

As depicted in Figure 5, a minor mass loss in the order of almost 0.05% was observed for the reference GFs as well as for the n-type SWCNTs coated GFs above 100 °C and up to 241.5 °C and 213.2 °C, respectively. The p-type SWCNTs coated GFs depicted a similar behavior at that temperature range losing, however a slightly higher amount of its mass, namely 0.28% up to 175.3 °C. This mass loss is attributed to the evaporation of residual moisture for all the samples and is observed to be increased in the p-type SWCNTs coated GFs due to the increased amount of carboxy moieties. At higher temperatures, between about 241.5 °C and 539.2 °C the reference GFs lost 0.7% of their mass due to the combustion of the silane type sizing [38–40]. Then, the mass of the E-glass fibers remained almost constant without considerable weight loss up to 1000 °C.

The thermal degradation of the p-type and the n-type molecular doped SWCNTs is a multistage process due to the existence of the various functional groups that are absorbed on their surface or are interacting with it. The functional chemical groups as moieties that SWCNTs contain are in general decomposed during the second temperature range that spans from roughly 200 °C to 500 °C. In more detail, the p-type SWCNTs exhibited the typical decomposition behavior of pristine SWCNTs that are
inherently p-doped by a small amount of adsorbed oxygen containing groups. The oxygen-based moieties promote the electron withdrawing process from the CNT electron-rich back-bone, effectively introducing holes as main charge carriers (p-doping). The p-type SWCNTs coated GFs lost ca. 1% of their mass up to 373 °C that can be attributed to smaller in size oxygen containing functional groups like hydroxy and ether moieties. Another 1.35% mass loss was observed up to 531 °C that can be due to larger oxygen containing moieties like carboxyl and ester moieties [41]. The initial mass loss of SDBS molecules is owing to burning with the presence of oxygen (330–450 °C) and the burning of the SDBS continued to occur above 800 °C [42]. Overall, due to the fact that the SDBS concentration is lower (2 mg/mL) in the n-type SWCNTs coatings, this may also explain the loose of less weight compared to the p-type SWCNTs coatings (5 mg/mL). The observed loss amount is in agreement with the percentage of SDBS and CNTs that were used for the preparation of the inks. Additionally, any amorphous carbon that might be present into the SWCNTs coating would also be combusted at this temperature range. A further 0.7% mass loss occurred up to 756 °C that can be attributed to the combustion of the SWCNTs. Afterwards, the mass of the underlying GFs remained almost stable up to 1000 °C, with only a small amount equal to a further 0.24% being decomposed up to 1000 °C maybe on account of some possible remaining percentage of catalyst particles due to the production process of the CNTs [43].

A slightly different behavior was presented by the n-type SWCNTs coated GFs. The decomposition of the nitrogen containing moieties that are included in the PEI molecules, which are entangled in between the CNT network, was responsible for the 0.53% mass loss from 213 °C up to 368 °C. A further 1% mass loss was observed up to 626 °C that is attributed the total decomposition of the SWCNTs. Afterwards, the mass of the underlying GFs remained almost stable up to 1000 °C, with only a small amount equal to a further 0.24% being decomposed up to 1000 °C maybe on account of some possible remaining percentage of catalyst particles due to the production process of the CNTs [43].

4.3. Raman Analysis of the TE-Enabled GF Tows

The p-type and the n-type SWCNTs coatings onto the GFs possess all the expected vibrational modes commonly encountered in graphitic materials. More specifically, the most prominent band of the spectrum of SWCNTs was the graphitic or G band with \( E_{2g} \) symmetry located at about 1590 cm\(^{-1} \). The radial breathing mode, which is a unique phonon mode of SWCNTs was also observed at the 120 cm\(^{-1} \) to 140 cm\(^{-1} \) region. Another disorder-induced band appearing in the first order spectrum of the SWCNTs is the D band, at about 1340 cm\(^{-1} \). The D band is caused by either amorphous carbon or \( sp^3 \) carbon atoms at defect sites on the CNT sidewalls [44]. Furthermore, the 2D peak dominated the second order spectrum of the SWCNTs coatings. This band was located at about 2685 cm\(^{-1} \). This overtone results from a double resonance process and is a symmetry allowed band which requires two phonons to be completed [45,46].

As can be seen in Figure 6b,c, no changes were observed in the Raman spectra of both the p-type and the n-type SWCNTs coatings onto the GFs when they were subjected to temperature gradients of 50 °C and 100 °C, apart from minor positive frequency shifts of all vibrational modes which were attributed to the increased temperature. This result indicates that the hierarchical GFs which are coated with the organic SWCNTs inks of both p-type and n-type TE behavior are chemically and structurally stable.

4.4. Evaluation of the Model Composites Thermoelectric Efficiency

The electrical resistance as well as the electrical conductivity of the prepared model composites are presented in Figure 7b. The p-type SWCNTs coated GF model composites exhibited electrical resistance of 127.2 ± 2.9 Ohm, which corresponds to electrical conductivity of 1.097 ± 0.05 S/cm, while for the n-type SWCNTs coated GF model composites showed very similar values i.e., 95.6 ± 1.1 Ohm and 1.561 ± 0.023 S/cm, respectively. The high electrical conductivity of the coated GFs is a key parameter for thermoelectric performance, since it can facilitate the flow of the thermally induced charge carriers upon being exposed to a temperature difference. Additionally, as aforementioned, low thermal conductivity
is also desirable for the sustainability of the thermoelectric effect. In the case of the SWCNT interphase, it may also be postulated that the infusion of the thermally insulating epoxy molecules reduces thermal conductivity, thus further enhancing thermoelectric performance. More analytically, this mechanism creates a barrier at the SWCNTs junctions and prevents the direct physical contact between them resulting in reduced thermal energy transport. [23,29].

The Seebeck coefficient (\( S = \Delta V/\Delta T \)) was derived from the slope of \( \Delta V \) vs. \( \Delta T \) curves by linear fitting. Figure 7c shows the Seebeck coefficients of the p and the n-type model composites. For the p-type model composite, the Seebeck coefficient was found to be +16.2 ± 6 \( \mu V/K \) corresponding to a power factor of 0.02 \( \mu W/m-K^2 \) and for the n-type −28.4 ± 4 \( \mu V/K \) corresponding to a power factor of 0.12 \( \mu W/m-K^2 \).

As was observed, the p-type SWCNTs coated GF model composites exhibited slightly lower values of Seebeck coefficient compared to the corresponding bucky papers. This can be attributed to the high nitrogen amount of the hardener within the epoxy system, acting as a n-dopant [32]. On the other hand, for the n-type SWCNTs coated GF model composites the Seebeck coefficient values remain almost identical.

Figure 7d depicts the generated thermovoltage upon exposure to various values of \( \Delta T \), for both p and n-type SWCNTs coated GF model composites. More specifically, the TE voltage of the in-series electrical and the in parallel thermal connection between the p-type and the n-type model composites creating a p–n junction are being displayed. As can be observed, within the studied temperature range, the generated voltage increased linearly with increasing temperature, \( R^2 > 0.98 \) for all cases. The measured voltage output was 4.46 ± 0.3 mV with a device resistance of 235.5 ± 2.5 Ohm at 100 °C \( \Delta T \). The maximum output of the p–n model composites TEG device was calculated 0.02 \( \mu W \) at a temperature difference of 100 °C, according to the following equation \( P_{\text{max}} = \Delta V^2/4 \times RTEG \) [24]. The derived maximum output power density of the device (p–n model composites pair) was 0.016 \( \mu W/cm^2 \).

Overall, the relatively high values of the electrical resistance were directly related to the area of the evaluated coated GF tows. It is expected that by increasing the area of the thermoelement (in this case the single coated GF tow), the electrical conductivity could be significantly increased while the Seebeck coefficient would not be affected as it is an inherent material property and is independent of the geometry of the evaluated specimen. To further elaborate on this statement, when the cross-sectional area of the coated substrate is increased, by increasing the thickness of the CNT coating on the GF substrate, its electrical resistance is reduced. Generally, the electrical resistivity of the CNTs films decreases as the thickness of the coatings is being increased. The property of the electrical resistivity highly depends on carrier concentration and carrier mobility, while the electrical resistance depends on the resistor shape geometry and the specific material. Electrical resistivity is an intrinsic property of a conductive film which is directly proportional to the total resistance \( R \), an extrinsic quantity that depends on the length and cross-sectional area of the corresponding film. Larger cross section areas present lower values of electrical resistance. In the case of SWCNTs, changes within the conductive network due to thickness optimization are able to positively impact the electrical conductivity. Both cases are true until the bulk resistance value is reached, thereby no further increments in electrical conductivity can be achieved. There also exists an optimal area that produces the highest possible thermoelectric values, as it is able to host the highest possible electron flow/current under a fixed \( \Delta T \). Therefore, since the Seebeck coefficient is a material property, the power factor of the coated GFs can be optimized by combining the most appropriate substrate dimensions and coating thickness. This is of the utmost importance for the exploitation of the nanomaterial coated reinforcements as thermoelectric elements in composite structures.

### 4.5. Evaluation of Interfacial Shear Strength

Tow pull out testing as opposed to single fiber pull-out testing was the preferred methodology for assessing the stress transfer between the nanocoated tow and the matrix, as it resulted in a more realistic measurement of the interfacial shear strength. Moreover, it was possible to effectively reduce...
the errors associated with the handling of single fiber filaments, which typically requires extremely careful manipulation due to their small size and brittle nature [47,48]. Several trials were performed with different specimen designs in order to consider all the different aspects that are involved in the particular test. Since the tow pull out process is not a standard test [49,50], preliminary tests were performed to optimize parameters such as the embedded length and the resin pre-impregnation process before insertion in the matrix.

Fracture morphologies of the pulled-out tows obtained via optical microscopy reveal a cohesive type of failure in all cases, since epoxy material remained on the tow surface after the pull-out process. In general, the GF tow was covered by a cone of resin and as such it was detached from the matrix. In the case of the n-type tows, a mixed type of failure mode was observed, whereby fiber/matrix-to-matrix failure was also present. The fiber-to-matrix failure, whereby the GF tow was completely detached from the resin, was not observed in any of the tested specimens. As should be noted, the persistent presence of cohesive failure within the matrix suggests that measured values were an underestimate of the true IFSS. This was also suggested during the process of experimental optimization where it was observed that small embedded length and low values of pull out force correlated more with fiber to matrix failure than cohesive failure.

In conclusion, it can be assumed that the presence of surfactant for the dispersions of both SWCNTs inks affected negatively the IFSS when a commercial epoxy resin was used as a matrix. Further studies could be performed oriented to optimize the coating process and simultaneously assess the effect of the surfactant existence on the interfacial shear strength [51,52]. As is well known, a strong interface provides efficient stress transfer but promotes brittle failure, whereas a weaker may promote energy dissipation and thus improve toughness. Balancing these conflicting requirements by engineering composite interphases to improve optimal strength and toughness values remains a great challenge.

5. Conclusions

The scope of this research study was to introduce and evaluate functional interphases between modified GFs with p and n-type SWCNTs model epoxy composites. Efforts were devoted to the morphological inspection as well as the evaluation of the structural changes that might be caused by the functional nanocoated GFs in the presence of temperature gradients. The thermal stability of the nanocoated GF tows was investigated through thermogravimetric analysis (TGA). Additionally, the chemical and structural stability of the TE nanoparticle-coated GF tows were studied by Raman measurements at elevated temperatures. The Raman spectra of p-type SWCNTs coated GFs and n-type SWCNTs coated GFs were acquired at ambient conditions, as well as at temperature differences of 50 °C and 100 °C by performing measurements at 75 °C and 125 °C. The results indicated that both the p-type and n-type TE enabled GF tows are chemically and structurally stable. The effect of the integration of the modified nanocoated GFs into a conventional epoxy resin was evaluated. The TE performance of the functional GF tows was only slightly affected by the resin encapsulation. Both p and n-type SWCNTs model composites exhibited a combination of high electrical conductivity and Seebeck coefficient. N-type model composites exhibited higher electrical conductivity compared to the corresponding p-type, due to their higher intrinsic electrical properties, as measured on SWCNTs bucky paper films. Moreover, the n-type model composites exhibited excellent behavior as thermoelectric materials with remarkably high values of Seebeck coefficient very close to the properties of the bulk SWCNTs material. An epoxy-based TEG model composite was manufactured to demonstrate the potential application of the technology in a TE generator, using a pair of alternating p- and n-type junctions interconnected in series via a metallic junction. The interfacial shear strength for both p and n-type TE enabled model composites was assessed by tow pull-out tests. The presence of SDBS as surfactant for the dispersion of the SWCNTs affected negatively the IFSS when epoxy resin was used as a matrix leading to a slight reduction of the IFSS values for both systems comparatively to the reference one. Finally, the fractographic study of the tested samples revealed that the matrix-to-matrix failure was more dominant than fiber/matrix-to-matrix failure, indicating strong interfacial adhesion.
Further optimization of the thermoelectric performance which involves the increase of both the electrical conductivity and the Seebeck coefficient could be achieved via doping of SWCNTs, use of different types of SWCNTs and creating efficient p–n heterojunctions for the fabrication of TEG module devices. The generation of thermoelectricity using structural engineering materials that are routinely exposed to high temperatures will represent a breakthrough in multifunctional materials, rendering them an attractive technology for aerospace and automobile applications.

**Author Contributions**: G.K.: conceptualization, methodology, validation, writing, visualization; K.T.: formal analysis, review and editing; L.T.: conceptualization, review and editing; C.M.: validation; L.K.: validation; A.S.P.: review and editing, supervision and project administration. All authors have read and agreed to the published version of the manuscript.

**Funding**: Co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH-CREATE-INNOVATE (project code: T1EDK-03480).

**Conflicts of Interest**: The authors declare no conflict of interest.

**References**

1. Jin, S.; Young, R.J.; Eichhorn, S.J. Controlling and mapping interfacial stress transfer in fragmented hybrid carbon fibre—Carbon nanotube composites. *Compos. Sci. Technol.* 2014, 100, 121–127. [CrossRef]
2. Paipetis, A.; Galiotis, C.; Liu, Y.C.; Nairn, J. Stress Transfer from the Matrix to the Fibre in a Fragmentation Test: Raman Experiments and Analytical Modeling. *J. Compos. Mater.* 1999, 33, 377–399. [CrossRef]
3. Jin, S.; Young, R.J.; Eichhorn, S.J. Hybrid carbon fibre—Carbon nanotube composite interfaces. *Compos. Sci. Technol.* 2014, 95, 114–120. [CrossRef]
4. Wicks, S.S.; Wang, W.; Williams, M.R.; Wardle, B.L. Multi-scale interlaminar fracture mechanisms in woven composite laminates reinforced with aligned carbon nanotubes. *Compos. Sci. Technol.* 2014, 100, 128–135. [CrossRef]
5. Bekas, D.G.; Paipetis, A.S. Damage monitoring in nanoenhanced composites using impedance spectroscopy. *Compos. Sci. Technol.* 2016, 134, 96–105. [CrossRef]
6. Orfanidis, S.; Papavassiliou, G.; Paipetis, A.S. Microcapsule-based self-healing materials: Healing efficiency and toughness reduction vs. capsule size. *Compos. Part B Eng.* 2019, 171, 78–86. [CrossRef]
7. Foteinidis, G.; Tsirka, K.; Tzounis, L.; Baltzis, D.; Paipetis, A.S. The role of synergies of MWCNTs and Carbon Black in the enhancement of the electrical and mechanical response of modified epoxy resins. *Appl. Sci.* 2019, 9, 3757. [CrossRef]
8. Wu, G.; Ma, L.; Liu, L.; Wang, Y.; Xie, F.; Zhong, Z.; Zhao, M.; Jiang, B.; Huang, Y. Interfacially reinforced methylphenylsilicone resin composites by chemically grafting multiwall carbon nanotubes onto carbon fibers. *Compos. Part B Eng.* 2015, 82, 50–58. [CrossRef]
9. An, Q.; Rider, A.N.; Thostenson, E.T. Electrophoretic deposition of carbon nanotubes onto carbon-fiber fabric for production of carbon/epoxy composites with improved mechanical properties. *Carbon* 2012, 50, 4130–4143. [CrossRef]
10. Mei, H.; Zhang, S.; Chen, H.; Zhou, H.; Zhai, X.; Cheng, L. Interfacial modification and enhancement of toughening mechanisms in epoxy composites with CNTs grafted on carbon fibers. *Compos. Sci. Technol.* 2016, 134, 89–95. [CrossRef]
11. Mosaei, E.; Karimi, M.; Baniadam, M.; Maghrebi, M. Enhancement in mechanical properties of multi-walled carbon nanotube–carbon fiber hybrid epoxy composite: Effect of electrostatic repulsion. *Appl. Phys. A Mater. Sci. Process.* 2016, 122, 1–8. [CrossRef]
12. Tsirka, K.; Foteinidis, G.; Dimos, K.; Tzounis, L.; Gournis, D.; Paipetis, A.S. Production of hierarchical all graphitic structures: A systematic study. *J. Colloid Interface Sci.* 2017, 487, 444–457. [CrossRef] [PubMed]
13. Mueoz, B.E.; Dalton, A.B.; Collins, S.; Kozlov, M.; Razal, J.; Coleman, J.N.; Kim, B.G.; Ebron, V.H.; Selvidge, M.; Ferraris, J.P.; et al. Multifunctional Carbon Nanotube Composite Fibers. *Adv. Eng. Mater.* 2004, 6, 801–804. [CrossRef]
14. Tzounis, L.; Liebscher, M.; Mäder, E.; Pötschke, P.; Stamm, M.; Logothetidis, S. Thermal energy harvesting for large-scale applications using MWCNT-grafted glass fibers and polycarbonate-MWCNT nanocomposites. *AIP Conf. Proc.* 2015, 138, 138–148. [CrossRef]
15. Malakooti, M.H.; Patterson, B.A.; Hwang, H.S.; Sodano, H.A. ZnO nanowire interfaces for high strength multifunctional composites with embedded energy harvesting. Energy Environ. Sci. 2016, 9, 634–643. [CrossRef]

16. Karalis, G.; Mytafides, C.; Polymerou, A.; Tsirka, K.; Tzounis, L.; Gergidis, L.; Paipetis, A.S. Hierarchical Reinforcing Fibers for Energy Harvesting Applications—A Strength Study. Key Eng. Mater. 2020, 827, 252–257. [CrossRef]

17. Liang, D.; Yang, H.; Finefrock, S.W.; Wu, Y. Flexible Nanocrystal-Coated Glass Fibers for High-Performance Thermoelectric Energy Harvesting. Nano Lett. 2012, 12, 2140–2145. [CrossRef]

18. Liu, H.; Zhao, Y.; Li, N.; Zhao, X.; Han, X.; Li, S.; Lu, W.; Wang, K.; Du, S. Enhanced interfacial strength of carbon fiber/PEEK composites using a facile approach via PEI&ZIF-67 synergistic modification. J. Mater. Res. Technol. 2019, 8, 6289–6300. [CrossRef]

19. De Luca, F.; Sernicola, G.; Sha, M.S.; Bismarck, A. “Brick-and-Mortar” Nanostructured Interphase for Glass-Fiber-Reinforced Polymer Composites. ACS Appl. Mater. Interfaces 2018, 10, 7352–7361. [CrossRef]

20. Pozegic, T.R.; Anguita, J.V.; Hamerton, I.; Jayawardena, K.D.G.I.; Chen, J.; Stolojan, V. Multi-walled Carbon Fibre Composites using Carbon Nanotubes as an Alternative to Polymer Sizing. Sci. Rep. 2016, 6, 3734. [CrossRef]

21. Tzounis, L.; Zappalorto, M.; Panozzo, F.; Tsirka, K.; Maragoni, L.; Paipetis, A.S.; Quaresimin, M. Highly conductive ultra-sensitive SWCNT-polycarbonate composites for structural health monitoring. Compos. Part B Eng. 2019, 169, 37–44. [CrossRef]

22. Gao, S.L.; Zhuang, R.C.; Zhang, J.; Liu, J.W.; Mäder, E. Class fibers with carbon nanotube networks as multifunctional sensors. Adv. Funct. Mater. 2010, 20, 1885–1893. [CrossRef]

23. Tzounis, L.; Liebscher, M.; Tzounis, A.; Petinakis, E.; Paipetis, A.S.; Mäder, E.; Stamm, M. CNT-grafted glass fibers as a smart tool for epoxy cure monitoring, UV-sensing and thermal energy harvesting in model composites. RSC Adv. 2016, 6, 55514–55525. [CrossRef]

24. Karalis, G.; Tzounis, L.; Lambrou, E.; Gergidis, L.N.; Paipetis, A.S. A carbon fiber thermoelectric generator integrated as a lamina within an 8-ply laminate epoxy composite: Efficient thermal energy harvesting by advanced structural materials. Appl. Energy 2019, 253, 113512. [CrossRef]

25. Petsagourakis, I.; Tybrandt, K.; Crispin, X.; Ohkubo, I.; Mori, T. Thermoelectric materials and applications for energy harvesting power generation. Sci. Technol. Adv. Mater. 2018, 19, 836–862. [CrossRef]

26. Snyder, G.J.; Toberer, E.S. Complex thermoelectric materials. Nat. Mater. 2008, 7, 105–114. [CrossRef]

27. Minnich, N.; Dresselhaus, M.S.; Ren, Z.F.; Chen, G. Bulk nanostructured thermoelectric materials: Current research and future prospects. Energy Environ. Sci. 2009, 2, 466–479. [CrossRef]

28. Vineis, C.J.; Shakouri, A.; Majumdar, A.; Kanatzidis, M.G. Nanostructured thermoelectrics: Big efficiency gains from small features. Adv. Mater. 2010, 22, 3970–3980. [CrossRef]

29. Yu, C.; Choi, K.; Yin, L.; Grunlan, J.C. Correction to Light-Weight Flexible Carbon Nanotube Based Organic Composites with Large Thermoelectric Power Factors. ACS Nano 2013, 7, 9506. [CrossRef]

30. Kim, S.J.; We, J.H.; Cho, B.J. A wearable thermoelectric generator fabricated on a glass fabric. Energy Environ. Sci. 2014, 7, 1959–1965. [CrossRef]

31. Tzounis, L.; Hegde, M.; Liebscher, M.; Dingemans, T.; Pötschke, P.; Paipetis, A.S.; Zafeiropoulos, N.E.; Stamm, M. All-aromatic SWCNT-Polyetherimide nanocomposites for thermal energy harvesting applications. Compos. Sci. Technol. 2018, 156, 158–165. [CrossRef]

32. Nonoguchi, Y.; Ohashi, K.; Kanazawa, R.; Ashiba, K.; Hata, K.; Nakagawa, T.; Adachi, C.; Tanase, T.; Kawai, T. Systematic conversion of single walled carbon nanotubes into n-type thermoelectric materials by molecular dopants. Sci. Rep. 2013, 3, 1–7. [CrossRef]

33. Luo, J.; Cerretti, G.; Krause, B.; Zhang, L.; Otto, T.; Jenschke, W.; Ullrich, M.; Tremel, W.; Voit, B.; Pötschke, P. Polypropylene-based melt mixed composites with singlewalled carbon nanotubes for thermoelectric applications: Switching from p-type to n-type by the addition of polyethylene glycol. Polymer 2017, 108, 513–520. [CrossRef]

34. Stamm, M.; Kirsten, M.; Simon, F.; Ma, E. The interphase microstructure and electrical properties of glass fibers covalently and non-covalently bonded with multiwall carbon nanotubes. Carbon 2014, 73, 310–324. [CrossRef]

35. Zhang, J.; Zhuang, R.; Liu, J.; Ma, E.; Heinrich, G.; Gao, S. Functional interphases with multi-walled carbon nanotubes in glass fibre/epoxy composites. Carbon 2010, 8, 2273–2281. [CrossRef]
36. Zhou, J.; Li, Y.; Li, N.; Hao, X.; Liu, C. Interfacial shear strength of microwave processed carbon fiber/epoxy composites characterized by an improved fiber-bundle pull-out test. *Compos. Sci. Technol.* 2016, 133, 173–183. [CrossRef]

37. Padmanabhan, K. Modelling considerations for fibre tow/epoxy matrix interfacial pullout tests. *J. Inst. Eng. Mech. Eng. Div.* 2010, 91, 30–33.

38. Kessler, E.; Gadow, R.; Straub, J. Basalt, glass and carbon fibers and their fiber reinforced polymer composites under thermal and mechanical load. *AIMS Mater. Sci.* 2016, 3, 1561–1576. [CrossRef]

39. Garay, C.; Heck, V.; Zattera, A.J.; Souza, J.A.; Amico, S.C. Influence of calcium carbonate on RTM and RTM light processing and properties of molded composites. *J. Reinf. Plast. Compos.* 2011, 30, 1213–1221. [CrossRef]

40. Rahman, A.S.; Rangari, V.; Jeelani, S. Thermal and Mechanical Properties of Woven Glass Fiber Reinforced Epoxy Composites with Carbon Nanotubes. *Int. J. Eng. Sci.* 2015, 4, 54–61.

41. Wepasnick, K.A.; Smith, B.A.; Bitter, J.L.; Howard Fairbrother, D. Chemical and structural characterization of carbon nanotube surfaces. *Anal. Bioanal. Chem.* 2010, 396, 1003–1014. [CrossRef] [PubMed]

42. King, S.G.; McCafferty, L.; Stolojan, V.; Silva, S.R.P. Highly aligned arrays of super resilient carbon nanotubes by steam purification. *Carbon* 2015, 84, 130–137. [CrossRef]

43. Tzounis, L.; Liebscher, M.; Fuge, R.; Leonhardt, A.; Mchtherine, V. P- and n-type thermoelectric cement composites with CVD grown p- and n-doped carbon nanotubes: Demonstration of a structural thermoelectric generator. *Energy Build.* 2019, 191, 151–163. [CrossRef]

44. Dresselhaus, M.S.; Dresselhaus, G.; Saito, R.; Jorio, A. Raman spectroscopy of carbon nanotubes. *Phys. Rep.* 2005, 409, 47–99. [CrossRef]

45. Ferrari, A.; Robertson, J. Interpretation of Raman spectra of disordered and amorphous carbon. *Phys. Rev.* 2000, 61, 14095. [CrossRef]

46. Tsirka, K.; Karalis, G.; Paipetis, A.S. Raman Strain Sensing and Interfacial Stress Transfer of Hierarchical CNT-Coated Carbon Fibers. *J. Mater. Eng. Perform.* 2018, 27, 5095–5101. [CrossRef]

47. Mulvihill, D.M.; Smerdova, O.; Sutcliffe, M.P.F. Friction of carbon fibre tows. *Compos. Part A Appl. Sci. Manuf.* 2017, 93, 185–198. [CrossRef]

48. Mottershead, B.; Eichhorn, S.J. Deformation micromechanics of model regenerated cellulose fibre-epoxy/polyester composites. *Compos. Sci. Technol.* 2007, 67, 2150–2159. [CrossRef]

49. ASTM D4018-17. *Standard Test Methods Standard Test Methods for Properties of Continuous Filament Carbon and Graphite Fiber Tows*; ASTM International: West Conshohocken, PA, USA, 2017. [CrossRef]

50. Chen, J.; Zhao, Y.; Li, Y.; Yang, Z.; Cheng, M. Effects of Different Testing Conditions on Tensile. In Proceedings of the 20th International Conference on Composite Materials, Copenhagen, Denmark, 19–24 July 2015; pp. 19–24.

51. De Greef, N.; Gorbatikh, L.; Godara, A.; Mezzo, L.; Lomov, S.V.; Verpoest, I. The effect of carbon nanotubes on the damage development in carbon fiber/epoxy composites. *Carbon* 2011, 49, 4650–4664. [CrossRef]

52. Sui, G. Improved interfacial properties of carbon fiber composites by building stress transition layer with carbon nanotubes. *Adv. Polym. Technol.* 2018, 37, 2510–2519. [CrossRef]