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Research article

Nanofiber mat-based highly compact piezoelectric-triboelectric hybrid nanogenerators

Ömer Faruk Ünsal¹⁰, Ayşe Çelik Bedeloğlu^{*10}

Department of Polymer Materials Engineering, Mimar Sinan Avenue, Eflak Street, No: 177 Bursa Technical University, 16310 Bursa, Turkey

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Abstract. Studies on energy generation devices for necessary energy needs have been an increasing trend all over the world as the kinds and quantities of consumer gadgets have increased. Researchers have been studying nanogenerators for the last 15 years in response to this demand. The three main reasons for these studies are increased output power, application to consumer items, and mechanical stability. Hybrid nanogenerators, on the other hand, are a method of combining at least two energy conversion mechanisms, hence reducing the need for a single conversion mechanism. In this context, while triboelectric-piezoelectric combination hybrid nanogenerators are the most popular hybrid nanogenerator class, they have several drawbacks, such as non-compact and unstable structures. As a result, for the first time, a small hybrid polymer-nanofiber-based hybrid nanogenerator concept with high output voltage and current is disclosed in this study. A hybrid nanofibrous structure was created using an electrospinning apparatus with double and triple nozzles. As a result of the periodic-compression test, the resulting nanogenerators produced a maximum voltage density of 5350 V/m² and a current density of 5454 A/m². By hand tapping, the resulting master unit was able to light up 119 LEDs and charge a commercial capacitor up to 0.9 V.

Keywords: nanomaterials, smart polymers, hybrid nanogenerator, material testing, nanofiber

1. Introduction

Nanofibers are fine fibers with diameters ranging from a few nanometers to several micrometers that have been used in a variety of applications such as filtration [1], biomedical applications [2–4], energy storage [5, 6], energy harvesting [7], and sensor applications [8], thanks to their large surface area [9]. Electrospinning is a commonly used, acknowledged, and innovative mechanism for producing nanofibers, besides conventional methods such as drawing, extrusion, melt-blown, and centrifugal spinning [10]. The electrospinning mechanism is based on guiding a fluidic polymer (molten or dissolved) through a way from the feeding nozzle to the collector surface by the effect of a high electric field and collecting in fiber form by solidification. Fluidic polymer generates polymer jets under the influence of an electric field, which forms nano-scale fibers on the collector surface [11]. Besides, electrospun nanofiber morphology is directly related to environmental conditions (humidity and temperature), applied voltage, spinning distance, solution concentration, feeding rate, and solvent system [12].

The use of nanofibers as energy materials has grown in importance and popularity over the last two decades. Nanofibers' unique qualifications, such as large surface area, suitability of various organic and inorganic materials to be electrospun, and convenience for surface functionalization of electrospun nanofibers, make them an excellent candidate for energy materials studies [13]. Nanofibrous materials, such as carbon nanofibers, can provide a high surface area requirement for supercapacitor electrodes [14]. Similarly, the gas sensing capability of specified

^{*}Corresponding author, e-mail: <u>ayse.bedeloglu@btu.edu.tr</u> © BME-PT

metal oxides (*e.g.*, SnO_2 , ZnO, In_2O_3 , TiO_2 , NiO, Co_3O_4) dramatically increases in nanofiber form, compared to bulk form, thanks to increasing active surface area [15].

Nanogenerators are another key application for nanofibers. Nanogenerators are devices that can transform mechanical and thermal energy into electricity with piezoelectric, triboelectric, and/or pyroelectric mechanisms [16]. Piezoelectric and pyroelectric systems operate similarly; in both, dipoles are produced in response to a stimulus, and current flow is occurred [17]. This similarity is because pyroelectric materials are a subset of piezoelectric materials. On the other hand, the triboelectric effect is based on the conjunction of triboelectrification and static electrification [18]. When two different materials contact each other, charge transfer is happened according to the triboelectrification mechanism from one to another; the separation of these materials and electrical flow occurs according to the electrostatic induction principle [19]. Furthermore, piezoelectric and triboelectric nanogenerators transform waste mechanical energy into electricity, whereas pyroelectric nanogenerators convert waste thermal energy [20]. Using nanofibers in nanogenerators is a popular method for increasing energy conversion efficiency and improving the mechanical behavior of energy-generating devices. Even if the large surface area of nanofibers is the first of the advantages for the output performance of nanogenerators, such as energy storage and gas sensing applications, the rough surface of nanofibrous mats in nanoscale also makes nanofibers good candidates for energy harvesting applications [21]. Furthermore, while rougher surfaces boost the output power of triboelectric nanogenerators [22, 23], the piezoelectric output power is directly related to the material's surface area [24].

The atomic polarization of macromolecular structures is another key factor for piezoelectric nanofibers. The most well-known piezoelectric polymer is polyvinylidene fluoride (PVDF). PVDF also has several derivatives with different piezoelectric-ferroelectric capabilities (different copolymers such as poly(vinylidene fluoride-*co*-trifluoroethylene)). According to the conformation of macromolecules, vinylidene fluoride-based polymers mainly have three crystalline phases: non-piezoelectric α -crystalline phase, piezoelectric β -crystalline phase, and piezoelectric γ -crystalline phase [25]. This also implies that the β - and γ -crystalline phases have a direct

and beneficial influence on the output performance of nanogenerators. Both the quick drying of polymer jets and the influence of the electrical field in the electrospinning process provide a high piezoelectric β-crystalline phase ratio to PVDF and its derivatives [26, 27]. Aside from these characteristics, one of the most frequent approaches for developing piezoelectric materials or piezoelectric nanogenerators is various nanoparticle loadings in polymer nanofiber or distinct surface modifications such as coatings on nanofibers [28]. Graphene, carbon nanotube, conductive polymers, and metal nanoparticles are the most prevalent conductive materials that carry produced electricity from polymer chains to contact electrodes [29-32]. Piezoelectric nanoparticles (wurtzite crystals or perovskite crystals) are another materials group that is frequently employed in the creation of energy-generating nanocomposite triboelectric or piezoelectric nanogenerators [33-35]. Although triboelectric and piezoelectric nanogener-

ators are intriguing, superior energy technologies for the future, they have some drawbacks, such as lowscale current or voltage output [36], fatigue strength [37], and issues caused by incompact architectures such as low durability, contamination, etc. [38]. Triboelectric nanogenerators, on the other hand, generate relatively large voltages in reverse with ultra-low current levels. In this regard, this kind of complementary shortcomings of different energy harvesting principles can be overcome by hybridization methods [39]. Piezoelectric-triboelectric hybrid nanogenerators (HNG) are devices that use static electrification and piezoelectricity principles to convert energy and boost output power values by a synergistic effect [40]. The combination of these two methods addresses two major flaws: the low current problem of triboelectric devices and the low voltage problem of piezoelectric devices [41–43]. Furthermore, because all nanogenerators are layered structures (energygenerating layers, top and bottom electrodes, circuit components, nanofillers, protective layer, etc.) may become mechanically unstable with time [44–46]. These issues must be explored and resolved, even using hybrid systems.

As a result of all these drawbacks and opportunities, the compact structure of a piezoelectric-triboelectric hybrid nanogenerator based on the all-hybrid nanofiber (HNF) concept was developed, and its properties were investigated in this study. The friction zone between two polymers was enhanced by utilizing the

nanofibrous nature of nanofiber mats, as the increased friction area would improve the device's output voltage. In the case of non-functional polymer preference in the HNF mat, an HNF-based nanogenerator would be a triboelectric nanogenerator with low current output. Due to its piezoelectric properties, PVDF was used as a functional part of HNF in this regard; thus, the HNF-based device became a hybrid nanogenerator. The duel-fed electrospinning method was used to create hybrid nanofibrous mats. During the electrospinning process, PVDF and thermoplastic polyurethane (TPU) were fed at equal rates and concentrations, resulting in PVDF/TPU hybrid nanofibers. The relationship between nanofiber morphology and electro-mechanical energy conversion performance using a periodic compression test is investigated in the first part of this study by varying electrospinning solution concentrations.

Because of its flexibility and insulating qualifications, TPU was chosen as a counter-material to PVDF, which also allows the HNF mat generated to be employed in smart textile applications. Thereby, optimum morphology, optimum polymer concentrations with the other words, were determined as the main result of the first chapter of the study. In second chapter, graphene oxide (GO) was simultaneously electrosprayed onto the collector, during the HNF mat fabrication and a third feeding nozzle was used to feed the GO solution during fabrication. The requirement for conducting additional material arises from the need for charge transmission in the nanofibrous web from fibers to electrodes. In order to obtain electrically more conductive HNF mat, GO reduction was performed by wet chemical method. Fourier transform infrared spectroscopy (FT-IR), four-probe resistivity analysis, and scanning electron microscopy (SEM) were used to analyze reduced GO-HNF (rGO-HNF) mats. The rGO-HNF mats were then sputtered with a thin coating of gold and sandwiched between two aluminum tapes. The isolation of sandwiched structure was provided by silicone resin coating. Finally, the resulting HNGs were electromechanically analyzed using compression test, demonstrating the utility of our 'master device'.

2. Materials and methods

2.1. Materials

Polyvinylidene fluoride (PVDF) (Alfa Aesar, Germany), thermoplastic polyurethane (TPU) (Ravago, Turkey), dimethyl formamide (DMF) (ISOLAB Chemicals, Germany), acetone (Sigma-Aldrich, France), graphite (Fischer Chemicals, U.K.), sulfuric acid (H₂SO₄) (95-98%, ISOLAB Chemicals, Germany), phosphoric acid (H₃PO₄) (Sigma-Aldrich, Switzerland), potassium permanganate (KMnO₄) (Yasin Teknik, Turkey), hydrogen peroxide (H₂O₂) (ZAG Kimya, Turkey), ethanol (ISOLAB Chemicals, Germany), hydrochloric acid (HCl) (37%, Carlo Erba, France) and hydrazine hydrate (N₂H₄) (50– 60%, Sigma-Aldrich, Switzerland) were purchased.

2.2. Methods

2.2.1. HNF mat-based hybrid nanogenerators *Production of TPU/PVDF hybrid nanofibers*

TPU and PVDF electrospinning solutions were prepared with varying polymer concentrations (5, 7, 9, 11, 13, and 15% by weight) in DMF:acetone (37.5%:62.5% acetone by weight) solvent system under 40 °C with continuous stirring overnight. TPU and PVDF solutions prepared with the same polymer concentrations were electrospun simultaneously to manufacture the HNF mats. Spinning parameters were the same for each HNF mat production process; 36 kV voltage, 175 mm spinning distance, 1.75 ml/h feeding rate, and 500 rpm collector drum rotating speed. HNF mats were named as HNF-5, HNF-7, HNF-7, HNF-9, HNF-11, HNF-13 and HNF-15.

Fabrication of HNF-based hybrid nanogenerators

HNF mats were detached from aluminum foil, which was used as the substrate during the electrospinning process. Then, the front and back surfaces of HNF mats were coated with gold by the magnetic sputter to have integrated highly conductive flexible preelectrodes. The gold-coated area was 2.0×4.0 cm for each sample. Then, the gold-coated HNFs were sandwiched between two conducting aluminum tapes, and electrical contact wires were mounted onto aluminum tapes as top and bottom electrodes. The resulting device structure was coated with silicone resin to insulate the aluminum tapes and provide mechanical stability to the nanogenerator device. PVDF/ TPU HNF-based nanogenerators were named HNG-5, HNG-7, HNG-9, HNG-11, HNG-13 acetone solvent system with 13% concentration was determined as the optimum HNF mat for hybrid nanogenerator device. Therefore, 13% PVDF and TPU solution was used in the second part of the work and HNG-15.

2.2.2. Fabrication of rGO-HNF-based hybrid nanogenerators

Production of GO-TPU/PVDF hybrid nanofibers (GO-HNF) and their reduction

Triple-fed electrospinning method was used to produce GO-HNF nanofibers. TPU and PVDF solution in DMF:acetone solvent system with 13% concentration was determined as the optimum HNF mat for a hybrid nanogenerator device. GO was synthesized with the top-to-bottom principle by the literature [47]. In the triple-nozzle electrospinning process, two polymer nozzles belonged to polymer solutions and the polymers were electrospun simultaneously. The third nozzle was used for GO dispersion and GO was electro-sprayed onto the collector drum simultaneously, with the polymer solutions. For the preparation of the GO dispersion, the determined amount of GO was first sonicated into the determined 20 ml of deionized (DI) water for one hour. Then, 40 ml of 2-propanol (IPA) was added to the GO-water dispersion, and the resulting GO/water-IPA dispersion was used for the electro-spraying solution. The spinning voltage and collector drum rotation speed were the same as in the previous section. However, the spinning distance was 130 mm for polymer feeding nozzles and 80 mm for GO dispersion. The GO feeding nozzle was fastened with a clamp at the back side of the drum. The feeding rates for polymer solutions and GO were 1.75 and 7 ml/h, respectively.

In this section, the GO amount in the nanofiber mat was determined by GO:polymer ratio by weight (0.08, 0.24, 0.40, 0.56, 0.72%). GO electro-spraying solutions were prepared in line with these ratios. Produced nanofiber mats were subjected to a wet chemical process to chemical reduction of GO flakes in the nanofibrous structure. Therefore, the nanofibers were immersed in 0.5 M hydrazine hydrate solution in DI water, and reduction was maintained overnight under reflux at 75 °C. The resulting nanofibers were named as rGO-HNF-008, rGO-HNF-024, rGO-HNF-040, rGO-HNF-056, and rGO-HNF-072, respectively.

Fabricating rGO-HNF-based hybrid nanogenerators

The fabrication procedure for rGO-HNF-based hybrid nanogenerators was the same as the HNF-based hybrid nanogenerators. rGO-HNF mats were coated with gold and sandwiched between two aluminum layers, and the resulting structure was coated with silicone elastomer for insulation and mechanical stability of HNG-008, HNG-024, HNG-040, HNG-056, HNG-072.

2.2.3. Characterization

To characterize the HNF and HNF-based nanogenerators, all TPU/PVDF HNFs and rGO-HNF mats were analyzed morphologically with SEM (Gemini 300, Carl Zeiss; Oberkochen, Germany). The morphology, fiber diameter, and bead formation characteristics of nanofibers were considered to determine the optimum HNF samples. Besides, an energy dispersive X-ray spectrum (EDS) analysis was performed for different fibers in an HNF sample to prove the existence of both PVDF and TPU fibers, separately. Fiber diameters were measured with ImageJ software from SEM images and mean fiber diameters were obtained.

Furthermore, differential scanning calorimetry (DSC) (DSC25, TA Instruments, Delaware, USA) analysis was performed on PVDF powder, TPU granules, and HNF mats. The presence of both polymers on hybrid nanofibers and crystalline phase determination of PVDF nanofibers were demonstrated by FT-IR analysis (Nicolet iS50, Thermofischer Scientific, Massachusetts, USA).

rGO-HNF mats were subjected to a volumetric high electrical resistivity test to see the rGO effect on the nanofiber mat with Keithley 6517B high resistivity meter and Keithley 8009 test fixture (Solon, Ohio, USA). HNF-based nanogenerators and rGO-HNFbased hybrid nanogenerators were characterized electromechanically, with an oscilloscope (1102B, GWInstek, New Taipei, Taiwan)) and a periodic compress test apparatus, which was a modified version of the device developed in our previous work [28]. All electromechanical tests were performed at a frequency of 4.2 Hz. At least 3 of each nanogenerator (HNF or rGO-HNF based) were produced and electromechanically characterized.

3. Results and discussion3.1. HNF-based hybrid nanogenerators3.1.1. SEM Analysis

As a result of SEM analysis, mean fiber diameters linearly increased with increasing polymer concentrations (Figure 1a). Figures 1b–1d show the EDS analysis of hybrid nanofibers. In Figures 1c and 1d, while detected fluorine signals create the shape of PVDF nanofibers, nitrogen signals could not form



Figure 1. a) Graph of mean fiber diameter *vs.* solution concentration of HNFs and b) image of hybridized EDS mapping of N and F atoms, c) image of EDS mapping of F atoms, and d) image of EDS mapping of N atoms.

the TPU nanofibers due to the smaller nanofiber diameter of TPU. Therefore, fluorine-containing PVDF nanofibers and nitrogen-containing TPU nanofibers could be described by elemental analysis.

Moreover, SEM images clearly showed that very high polymer concentration and very low polymer concentration in electrospinning solutions distorted fiber morphology (Figure 2). In electrospinning processes, microfibers are formed in places due to the high concentration of polymer in solution spinning. Average diameters of 5, 7, 9, 11, 13, and 15% were 120.32, 138,12, 162.20, 268.88, 277.11 and 337.57 nm, respectively.

Although the concentration was not very high in HNF-5, HNF-7, and HNF-9, spinning solutions with low concentration resulted in a half film/half nano-fiber structure. Since low polymer concentration means high solvent content, nanofibers formed in the collector drum were re-dissolved with non-vapor solvents, resulting in a semi-filmy structure [48–50].

3.1.2. FT-IR and DSC analyses

FT-IR analysis showed the bonds in the molecular structures of TPU and PVDF, the macromolecular

conformation of PVDF chains in nanofiber form, and the presence of both polymers in HNF samples. Figure 3a shows the FT-IR spectrum of PVDF nanofiber, TPU nanofiber and HNF. In PVDF nanofiber, at 441, 509, 839, 1229, and 1273 cm⁻¹ vibrational peaks prove the formation of piezoelectric γ - and β -crystalline phases of PVDF chains in electrospinning process [51]. In the FT-IR spectrum of TPU nanofibers, vibrational peaks at 1066 cm⁻¹, between 1133–1219, at 1529, at 1596, at 1725, and at 3326 cm⁻¹ represent C–N stretching, C–O stretching, N–H deformation, C–C stretching, C=O stretching of urethane groups, and N–H stretching vibrations, respectively [52–55].

DSC analysis was performed with a TA Instrument DSC25, between -50 to 210 °C with a 5 °C/min heating rate under a nitrogen atmosphere, and all DSC analyzes were performed on the single or hybrid nanofibers to determine the melting behaviors of polymers (Figure 3b). According to literature [56], TPU melting peak around 160–170 °C with a weak intensity (1.67 J/g for this study) is an expected result. The glass transition temperature (T_g) peak was also observed at 57 °C for TPU nanofiber. The peak



Figure 2. SEM images and fiber diameter distribution graphs of a) HNF-5, b) HNF-7, c) HNF-9, d) HNF-11, e) HNF-13, and f) HNF-15.

at 55 °C in the PVDF thermogram indicates the upper glass transition temperature of the α -crystalline phase of PVDF [57] and low α -crystalline phase content with 1.18 J/g enthalpy. PVDF curve also gave the melting point at 159 °C with 49.78 J/g melting enthalpy. In the DSC curve of the HNF sample, all these peaks appeared almost at the same points, as expected. However, due to the decreased PVDF content in the hybrid sample, the melting enthalpy decreased to 24.11 J/g compared to the neat PVDF nanofiber sample.

FT-IR analysis was also used for the β -phase content of HNF, PVDF nanofiber, and PVDF powder. β -phase content of samples was calculated with Equation (1):

$$F(\beta) = \frac{A_{840} + A_{1274}}{1,26(A_{766} + A_{976} + A_{1240}) + (A_{840} + A_{1274})}$$
(1)

where $F(\beta)$ is the β -phase fraction, A_{840} , A_{1274} , A_{766} , A_{976} , and A_{1240} are the absorption values at 840,



Figure 3. a) FT-IR spectra of PVDF nanofiber, TPU nanofiber, and HNF; b) DSC curves of PVDF nanofiber, TPU nanofiber, and HNF; c) absorption peaks of β - and α -crystalline phases.

1274, 766, 976, and 1240 cm⁻¹. The absorption peaks at 840 and 1274 cm⁻¹ are the β-phase peaks, while the 766, 976, and 1240 cm⁻¹ are the α-phase peaks. However, the peak point can be varied for a few units because of differences in FT-IR device configurations. Therefore, the absorbance signals of β- and α-crystalline phases are shown in Figure 3c. The 1.26 is the ratio of β- and α-absorbance coefficients, which are $7.73 \cdot 10^4$ and $6.13 \cdot 10^4$ cm²/mol, respectively [58]. β-phase content of PVDF powder, PVDF nanofiber, and HNF were calculated as 28.66, 55.64, and 45.08%, respectively. According to the results, the electrospinning process clearly enhanced the β-phase fraction in samples.

3.1.3. Electro-mechanical analysis

The contribution of TPU and PVDF hybridized nanofibers in triboelectricity, which is the novelty of this study, was initially investigated using output current and voltage values of HNF and neat PVDF nanofibers with equivalent material amounts. Periodic compression stimuli with equivalent compression force were used to obtain output voltage and current values. The output voltage and current signals of PVDF and HNF-based nanogenerators are shown in

Figures 4a and 4b, respectively. PVDF nanofiberbased nanogenerator had peak-to-peak voltage and current values of 0.82 V and 0.74 A. In comparison to PVDF-based nanogenerators, HNF-based nanogenerators demonstrated approximately three times higher values of 2.32 V and 2.55 A. Further, nanogenerators with different nanofiber morphologies were analyzed electro-mechanically to investigate their energy conversion performance. Voltage and current outputs of nanogenerators showed the nanofiber mat morphology effect on energy conversion rate. As we mentioned above, extremely high or low polymer concentrations caused impaired fiber morphology, thicker fibers and/or semi-film nanofiber mats. It was seen that poor-quality nanofiber mats with poor morphological properties, non-fibrous structure, or extremely thick fibers decrease the output signals of nanogenerators. Voltage and current density graphs of nanogenerators are given in Figures 4c and 4d. Low-concentrated electrospun nanofiberbased nanogenerators HNG-5 and HNG-7 have shown weak output voltage and current densities (peak-to-peak) with 2050 V/m² and 2525 μ A/m² and 1675 V/m² and 2273 μ A/m², respectively. Voltage densities of HNG-9, HNG-11, and HNG-15 were



Figure 4. a) Output voltage and b) output current comparison of PVDF-HNF; c) output voltage density and d) current density graphs of HNGs.

2300, 2350, and 2650 V/m². The current densities of HNG-9, HNG-11, and HNG-15 were 3737, 3030, and 2526 μ A/m². As a result of electro-mechanical characterization, HNG-13 was determined as the optimum sample for the further chapter of this work. Current and voltage densities of HNG-13 were $3182 \,\mu\text{A/m}^2$ and $2900 \,\text{V/m}^2$, respectively. Even though higher output values are expected from smaller fiber diameters, or higher surface area in other words, half film/half nanofiber failed morphology, as described in SEM analysis results, reduced the performance of HNG-5 and HNG-7. Furthermore, the failed morphology was corrected by increasing polymer concentration as fiber diameter increased; as a result, output voltage and current values increased. However, the rise in output performance was reversed at HNG-15 due to thicker fibers and smaller surface areas. In other words, higher concentration polymer solutions solved the film formation problem and provided the desired nanofiber formation, improving the output performance of HNGs. However, higher concentrations also caused thicker nanofibers and smaller surface areas. In this regard, HNG-13 sample was the 'balance point' between nanofibrous morphology and optimum nanofiber diameter.

Here we claimed that the hybrid nanofibrous structures would generate more electrical energy thanks to increasing the contact-separation area compared to contact-separation area of film-based triboelectric devices (Figure 5) [24]. Figure 5a illustrates the piezoelectric polarization behavior of PVDF nanofibers. Nanofibers are electrically polarized as the mechanical force is applied onto fibers. Here, compression stress is delivered to the nanofibers in pressure or stretching form. On the other hand, Figure 5b is the schematic illustration of triboelectrification between TPU and PVDF nanofibers. In the initial condition, PVDF and TPU nanofibers are randomly collected and stand separated from each other. When the compress force is applied to the hybrid nanofibrous mat, two different mechanisms start to work. The first of them is piezoelectricity, which is described in Figure 5a. The second one is triboelectrification between TPU and PVDF nanofibers. Mechanical compression onto nanofibrous mat provides PVDF and TPU nanofibers contact with each other. When the compression force is removed, nanofibers get separated and nanofiber surfaces are electrically charged, according to the triboelectrification mechanism. As the result of electromechanical analysis of HNG-5 to HNG-15, increasing



Figure 5. Schematic illustration of a) piezoelectric polarization mechanism of PVDF nanofibers and b) triboelectrification mechanism of hybrid nanofibers.

nanofiber density in nanofiber mat, with other words increasing contact-separation area nanofiber in the mat, clearly increased the output values of nanogenerators.

3.2. rGO-HNF-based hybrid nanogenerators 3.2.1. FT-IR, SEM, and resistivity analysis of rGO-HNFs

rGO-HNFs were subjected to FT-IR spectrophotometric analysis and spectrums of rGO-coated nanofibers were compared with HNF without graphene. FT-IR analyses showed that the GO coating and its reduction process cannot be seen in the FT-IR spectrum clearly. GO or rGO, even carbon nanotubes, already do not give specific vibrational peaks in FT-IR spectrophotometry due to their high light absorbing nature [59, 60]. Besides, intense PVDF and TPU vibrations, which were clarified in the HNF characterization part, could easily mask the weak vibrational signals of rGO sheets (Figure 6a). SEM analyses were performed on rGO-HNFs to demonstrate the rGO coating on PVDF and TPU nanofibers. t was clearly seen that the rGO sheets successfully wrapped the polymeric nanofibers (Figure 6b). rGO-coated nanofiber surfaces also provided rougher surfaces which is important for the tribo-electrification mechanism. However, the main purpose of rGO coating onto nanofiber surfaces was to assist in the conduction of tribo-electrically generated electricity.

Although this is not a common problem when the nanogenerator studies are checked, short-circuit is the major mistake in the nanogenerator fabrication process. There are two main reasons for this defect on samples; faulty electrode design in the electrode integration step, and relatively high electrical conductivity of the electricity generating layer. The electrode design and application mistakes can be minimized in fabrication step. However electrical resistivity (or conductivity) should be higher than a few hundred of $M\Omega$ as the optimum resistivity value, according to our pre-studies on nanogenerators. We clearly have seen that output-voltage and current is dramatically decreased in short-circuit defected samples due to because electric flow preferred the path with less resistance (Figures 7a and 7b). Although aluminum tapes and copper wires were used as electrodes and electrical contacts, electricity is generated between PVDF and/or TPU polymer chains which are not electrically conductive. Since the resistivity of polymer chains can easily block the electron flow between chain and electrode, current flow can prefer another way in high amounts of conductive-filled structures. For all these observations, the electrical resistivity of rGO-HNFs was measured by four probe method with a Keithley 6517B high resistivity-meter and a Keithley 8009 text fixture. Electrical resistivity measurements have shown that the resistivity was decreased by the increasing rGO amount in HNFs (Figure 7c).

As for the HNF samples, the β -phase fraction of rGO-HNF samples was calculated with Equation (1). β -phase content results of rGO-HNF samples were given in Table 1. In fact, a crystallization agent effect cannot be expected from GO or rGO for rGO-HNFs because of rGO is not doped into the nanofibers. rGO flakes get in between PVDF and TPU nanofibers and GO spray is performed after the solidification of polymers. Therefore, samples could not show a dramatic enhancement or reduction in β -phase content. Although the absorbent behavior of carbon-based materials caused a small drop, maximum of the reduction was about 2% for rGO-HNF-008.

3.2.2. Electromechanical analysis of rGO-HNF-based HNGs

rGO-HNF-based nanogenerators were fabricated and characterized with the same method and test setup. Voltage density values from HNG-008 to HNG-072 were 2475, 3100, 3600, 4600, and 5350 V/m², respectively. On the other hand, current densities for the same nanogenerators were 3485, 4040, 4141, 4848, and 5454 μ A/m², respectively. According to this result, HNG-072 has been determined as the

HNF

rGO-HNF-008 rGO-HNF-024

rGO-HNF-040



Figure 6. a) FT-IR spectra of rGO-HNFs and b) SEM images of rGO-HNF-072.

most efficient nanogenerator. Considering the voltage and current density values, rGO-HNF-based devices have shown dramatic output values compared to HNF without rGO-based nanogenerators (Figures 8a and 8b). The nanogenerators have shown the rGO effect clearly as the result of the electromechanical analysis. Both voltage and current density were proportionally increased with increasing rGO amount in the nanofibrous structure (Figure 8c). According to electromechanical and electrical resistivity tests, rGO addition among the nanofibers formed the pathways to carry the charge to the top and bottom electrodes (Figure 8d). A signal stability test was performed for 5000 s and is given in Figure 9. According to the signal stability test, the proposed HNF-based compact nanogenerator model is successful in fatigue resistance for the first 2000 s.

The output signals of nanogenerators can be demonstrated by the measurement methods used in this study, or they can be used as an electrical energy source for different systems. In this study, we have used a circuit which consists of 119 serially connected green LEDs to demonstrate the usefulness of our 'master device', HNG-072. Electrical contacts of the nanogenerator connected to a full bridge rectifier circuit for AC-DC transformation and rectified current



Figure 7. Schematic illustration of the flow behavior of a) high resistant HNF-based nanogenerator, b) low resistant HNF-based nanogenerator, and c) results of electrical resistivity measurements.

lighted up most of 119 LEDs by hand tapping (Figures 10a and 10b). We also observed that when

Table 1. β -phase con	itents of rGO-HNFs
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Sample	β-phase content [%]
rGO-HNF-000	45.08
rGO-HNF-008	42.42
rGO-HNF-024	43.46
rGO-HNF-040	43.48
rGO-HNF-056	43.91
rGO-HNF-072	43.45

the analyst touched to the LED circuit, LEDs lighted up brighter (Figure 10c). Moreover, to demonstrate the charging capability of nanogenerators, we used a commercial capacitor (4.7 μ F, 25 V) and the periodical compress test machine (Figure 10d). The voltage value of the capacitor reached 0.9 V in 10 s and the charge was discharged in 25 s (Figure 10e).

A comparison table and graph of voltage, current, and power density values were given in Figure 11 between this work and the other novel approaches to the hybrid nanogenerator concept. According to comparison, it is clearly seen that hybrid nanofiber



Figure 8. a) Output voltage and b) current density graphs of rGO-HNF-based nanogenerators, c) effect of fiber morphology and rGO addition on voltage density and current density and d) energy conversion mechanism of the hybrid nanofibrous mat.



Figure 9. Signal stability of HNF-072 under constant compression force for 5000 s.

mats and conductive particle addition between nanofibers boosted the output values. So that rGO doped HNG devices showed high output current values, which is one of two important points for output power, compared to other works even without any perovskite or wurtzite crystal doping. However, though the output current value is acceptable, voltage density was not high enough compared to other studies. The main reason for low output voltage density values is the all-organic (without perovskite or wurtzite in other words) structure of HNFs. The other reason was the selection of TPU as a counter material to PVDF. TPU was preferred for the compatibility of these nanogenerators to textile applications thanks to its elastomeric behavior and low cost. Similarly, the non-inorganic configuration of nanofibers was preferred to obtain textile-compatible resulting mats.

4. Conclusions

We presented a unique hybridization approach for triboelectric-piezoelectric hybrid nanogenerators in this paper. This innovative nano-scaled hybridization using the dual and triple spinning methods was made possible by the electrospinning process. For energy scavenging, a piezoelectric and a non-piezoelectric



Figure 10. a) Schematic illustration of the full bridge rectifier, b) emitting light by hand tapping of 119 LEDs arranged to write SMR (abbreviation of Smart Materials Research Group) and BTU (abbreviation of Bursa Technical University), c) brighter lighting led by touching LED circuit with hand, d) periodic compress device, e) charge-discharge curve of the commercial capacitor with HNG-072.



Figure 11. a) Voltage density and current density, and b) power density comparisons of this work and novel PVDF nanofiberbased hybrid nanogenerator studies.

polymer were utilized. In the first stage, we investigated the effect of fiber morphology on nanogenerator outputs. Thinner fibers outperformed bulkier fibers due to a more successfully interwoven structure and clear fiber shape. However, the conduction of generated energy in volumetrically central threads constituted an issue in nanofiber-based nanogenerators, particularly in thick nanofiber mats. Later, graphene oxide was employed to provide a channel for electrical flow from the nanofiber mat's center regions to the top and bottom electrodes. To put it another way, two polymers and a GO dispersion were fed into the electrospinning apparatus at the same time, and the GO was chemically reduced to improve electrical conductivity. Consequently, GO addition at 0.72% by weight in the nanofibrous structure enhanced the output voltage by 71.4% and the output current by 84.5%. Furthermore, the proposed hybridization approach lends itself to further development with other polymer and additive combinations for smart wearable electronics.

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