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Expanding the portfolio of tribo-positive materials: aniline formaldehyde condensates for high charge density triboelectric nanogenerators

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Abstract

The rapid uptake of energy harvesting triboelectric nanogenerators (TENGs) for self-powered electronics requires the development of high-performance tribo-materials capable of providing large power outputs. This work reports on the synthesis and use of aniline formaldehyde resin (AFR) for energy-harvesting applications. The facile, acidic-medium reaction between aniline and formaldehyde produces the aniline-formaldehyde condensate, which upon an *in-vacuo* high temperature curing step provides smooth AFR films with abundant positively-charged nitrogen and oxygen surface functional groups, endowing AFR with a significantly higher positive tribo-polarity than the existing state-of-art polyamide-6 (PA6). A TENG comprising of optimized thin-layered AFR against a polytetrafluoroethylene (PTFE) film produced a peak-to-peak voltage of up to ~1,000 V, a current density of ~65 mA m^{-2}, a transferred charge density of ~200 μC m^{-2} and an instantaneous power output (energy pulse) of ~11 W m^{-2} (28.1 μJ cycle^{-1}), respectively. The suitability of AFR was further supported through the scanning Kelvin probe force microscopy (SKPFM) measurements, which reveal a significantly higher surface potential value of 1.147 V for AFR as compared to 0.87 V for PA6 and a step-by-step increase of the surface potential with the increase of energy generation cycles. The work not only proposes a novel mouldable AFR synthesis process but also expands with excellent prospects, the current portfolio of tribo-positive materials for triboelectric energy harvesting applications.

1. Introduction

It is well established that the contact charging/electrification phenomena generates an equal and opposite amount of surface charges when two material surfaces are brought into contact, with charges being injected from one material to another. This interfacial charge flow was first empirically established in 1757 by Wilcke [1], and since then materials have been arranged in a specific triboelectric series by Henniker [2] and more recently by the Wang group [3], according to their ability to lose or gain interfacial charge species, thus, classifying them as tribo-positive or tribo-negative materials, respectively. In the case of dielectric materials, these exchanged charges remain on the surface, leading to the formation of uncompensated dipoles, which can be extracted using the metal electrodes as the harvested charge [3]. Indeed, this phenomenon has been used to develop triboelectric nanogenerators (TENGs), which have been utilized to convert various forms of ambient mechanical energy to electrical energy [3–8]. The commonly reported vertical contact mode TENGs typically consist of a combination of dielectric/dielectric or dielectric/metal, with significant differences in their ability to donate (tribo-positive) or accept electrons (tribo-negative). For these TENG systems, the increase in the output power and surface charge density is achieved *via:* (i) judicious selection of tribo-materials [8], (ii) surface micro-/nano-structuring [9,10], surface chemistry modification [11], (iii) charge injection [6] or composites with high-polarization piezoelectric additives [5,7,12] and (iv) physical hybridization of multiple energy harvesting technologies [13]. Except for the judicious use of tribo-materials, the rest of the methods are reliant on expensive equipment and complicated processing steps including lithography etc. which defeats the low-cost advantage of TENGs and may not provide the required stability and reliability. Consequently, the selection of the optimal materials with high electron affinity difference is the simplest and most effective way to improve the performance of TENGs but is currently restricted by the limited choices of existing materials.

With excellent dielectric properties, mechanical robustness and ease of fabrication, both natural and synthetic polymers feature extensively in the triboelectric series and display consistent charge transfer patterns corresponding to specific surface chemical moieties. A preliminary inspection of the chemical structure of these polymers reveals the following material design principles: (i) nitrogen-containing polymers with pyridine, amine and amide groups (e.g. nylon, polyvinyl-2-pyridine), develop the most positive charge ($0.5 - 1.2$ pC cm^{-2}), which is slightly higher than the polymers with oxygen functional (e.g. polyethylene oxide, polyvinyl alcohol) groups, ($0.6 - 1.1$ pC cm^{-2}); (ii) halogenated (i.e. fluoride and chloride) polymers (e.g.

polyvinylchloride, polytetrafluoroethylene (PTFE)) develop the most negative charge (-1.6 – -2.8 pC cm^{-2}); and (iii) the hydrocarbons contribute almost nothing to the tribo-polarity[14–16]. In the first ever report of an empirical triboelectric series by Henniker, it was reported that the series itself showed no correlation with the dielectric constant or the dipole moment but was dependent on a determinant property linked to molecular constitution especially that of the surface [2]. While it is relatively more easy to associate the halide groups (-I, -Br and -F) with the tribo-negative behaviour owing to their high electronegativity; the tribo-positive behaving polymers were observed to be hydrophilic, with high dielectric constants and highly polar with nitrogen and oxygen surface functional groups [17]. In their report, Ohara et al. [18], have reported on the triboelectrification of Langmuir-Blodgett films wherein various polar groups (-COOH, -CONH$_2$, -CONHC$_6$H$_5$, -COOCH$_3$, -CH$_2$OH and -CH$_2$NH$_2$) were bonded to the same type of hydrocarbon chains (CH$_3$(CH$_2$)$_{16-}$). It was observed that the electrification between the monolayers and glass by taking the polarity and the magnitude was as following: (+) -CH$_2$NH$_2$, -CH$_2$OH, -COOH, -CONHC$_6$H$_5$, -CONH$_2$, -COOCH$_3$ (-) with the local dipole moments of the atomic groups being 0.30, 0.26, 0.01, -0.20, 0.17 and 0.34D, respectively. From their data, it seems that there is a direct correlation between the magnitude of the dipole moment with the atomic groups and their corresponding electron density [18]. Similarly, in their work, Shinohara et al reported that for the triboelectric series incorporating the p-substituted styrene polymers, the modified polymers with electron-releasing groups are situated on the positive side, while the electron-attracting polymers are located on the negative side [19]. More importantly, in the case of polymers with nitrogen atoms in polar groups, those with a high electron density on the nitrogen atoms are charged positively, while those with a low electron density were charged negatively [19]. For instance, polymers with an amino group such as poly(p-dimethylaminostyrene) and poly(p-aminostyrene) and those possessing a carbonyl group such as poly- (methylmethacrylate) and poly(vinyl acetate) charged positively when measured against a metal. The presence of lone pair of electrons on the nitrogen atom (in amino groups) was considered to affect the triboelectrification greatly and corroborates the fact that the electronic and chemical surface state of polymers greatly affects the triboelectric behaviour [19]. Thus, the ranking for polymers tends to be determined by their inherent chemical bonding, which affects the molecular constitution of the contact interface and hence the interfacial charge transfer. As polyvinylidene fluoride (PVDF) and PTFE are among the best performing tribo-negative materials, only a few improvements have been brought to these materials such as fluorinated polydimethylsiloxane [20], plasma-treated PTFE [21] and fluorinated ethylene propylene [22]. However, not much attention has been paid to the selection of tribo-positive

materials, which are equally crucial for enhancing the surface charge density and subsequent power density of TENGs. In our previous work, we had introduced the use of flat-surfaced PEO as a tribo-positive material which is capable of providing a high surface charge density of nearly 160 $\mu C\ m^{-2}$ against PDMS [8]. In comparison, the PA6/PDMS based TENGs showed a charge density of 110 $\mu C\ m^{-2}$ only, therefore establishing the superiority of PEO over PA6. However, there is a need to expand the range of available tribo-positive materials further.

Henniker et al. have reported that condensation products of aniline formaldehyde reactions with abundant amide groups acquire the most amount of positive contact charge [2]. The aniline–formaldehyde condensates are thermo-reactive products of chemical interaction between aniline hydrochloride and formaldehyde in an acidic solution and can be synthesized as linear or cross-linked condensation polymers by varying the molar ratio of aniline to formaldehyde during polymerization [20–23]. The cured aniline formaldehyde resins (AFR) have shown to be an effective inhibitor of corrosion on mild steel in acidic medium by forming a protective layer of -C=N- on the metal surface [24,25]. Similarly, by adding an excess of epichlorohydrin, a new type of epoxy was synthesized with applications in casting, adhesives and encapsulation of semiconductor devices [26,27]. The cured AFR resins being chemically resistant to alkalis have been widely used for electro-technical plastics and as components for radio- and high-frequency electrical engineering owing to their excellent electrical insulation properties which outperform the melamine-, urea- and phenol-formaldehyde based resins [20,21]. However, their use has become quite restricted owing to the difficult moulding process and have fallen out in favour of melamine-type resins. Also, the room-/high-temperature synthesis leads to fast reaction kinetics causing the resinous product to have a random porous structure and with the fast-thermosetting properties, the application scenarios of pristine AFRs have been quite limited.

Herein, we report on the use of AFR films as tribo-positive material to fabricate high-performance TENGs in combination with PTFE. Relying on a facile low-temperature (~0 °C), acidic-medium condensation polymerization of aniline with formaldehyde, the condensate is fully curable at ~130 °C and can be formed into the required shape with sufficient mechanical rigidity. We demonstrate AFR/PTFE TENG with a peak-to-peak voltage of ~1,000 V, a short-circuit current density of 65 mA m^{-2} (corresponding a charge density of ~200 $\mu C\ m^{-2}$), and energy pulse of ~28.1 μJ cycle^{-1} with an instantaneous power density of ~11 W m^{-2}, all of which are near twice the values reported for PA6/PTFE TENGs. The synthesized AFR is mechanically stable, and the AFR/PTFE TENG shows excellent stability with less than ±5 %

variation in its electrical output over 16,000 contact cycles. In-depth characterization of AFR samples *via* thermal, dielectric, nuclear magnetic resonance and X-ray spectroscopic techniques in conjunction with scanning Kelvin probe force microscopy (SKPFM) surface potential measurements supports the suitability of AFR as a high-performance tribo-positive material. The SKPFM measurements show clearly the significantly higher surface potential value of 1.147 V for AFR as compared to 0.87 V for PA6, thereby expanding the rather small portfolio of high-performance tribo-positive materials for energy-harvesting applications.

2. Experimental

2.1 Materials and characterization

Aniline (>99.5 %), hydrochloric acid (37 %) and aqueous formaldehyde solution (37 wt%, containing 10-15 % methanol as a stabilizer) were purchased from Sigma Aldrich (United Kingdom) and used as such without any further purification. PTFE films (~0.03 mm thickness) for fabricating tribo-negative layers were supplied from the College Hardware, China. The charge injection on PTFE films was carried out using a commercial antistatic gun (Zerostat 3, Milty). Further details on the charge injection process can be found in our earlier work [6].

The curing temperature and thermal behaviour of the synthesized AFR materials were investigated by Differential scanning calorimetry (DSC) system on a TA Instruments DSC Q2000. The samples, approximate weight of 2 mg, were heated at 10 °C min^{-1} from 0-200 °C under a constant 50 mL min^{-1} N$_2$ flow. Vendor provided software was used to assess parameters of glass transition temperature (T$_g$) and onset, maximum curing temperatures. A Hitachi S3400N scanning electron microscope (SEM) was used to study the surface morphology and cross-section of the AFR and PTFE layers. The Fourier transform infra-red (FTIR) spectra of samples were obtained on a Thermo Scientific IS10 Nicolet at a nominal resolution of ±1 cm^{-1} for a total of 128 scans and processed through OMINIC. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher Scientific NEXSA spectrometer using a micro-focused monochromatic Al x-ray source (19.2 W) over an area of approximately 100 microns. Data were recorded at pass energies of 150 eV for survey scans and 40 eV for high-resolution scans with 1 eV and 0.1 eV step sizes, respectively. Charge neutralization of the sample was achieved using a combination of both Ar$^+$ ions and low energy electrons. Depth profiling was accomplished using the instrument's EX06 monatomic ion source operated at 1

keV and rastered over a 3 x 3 mm^2 area at the rate of 0.4 nm s^{-1} (reference Ta$_2$O$_5$) for 2500 s.[1]H Nuclear Magnetic Resonance (NMR) spectra of the cured AFR was obtained in a deuterated dimethyl sulfoxide (DMSO) using a Bruker NMR Spectrometer AV3 HD 500 operated at 600 MHz and processed with a third-party analytical chemistry software. Dielectric measurements were carried out using Dielectric Relaxation Spectroscopy (DRS) technique employing an Alpha analyser supplied by Novocontrol. For this, an AFR sample of ~1 mm thickness was placed between two brass electrodes of 20 mm diameter and inserted as a capacitor in the Novocontrol sample cell. The complex dielectric permittivity was recorded and measured in a broad frequency ranging from 1 to 10^6 Hz. Nanoscale surface potential mapping was undertaken using an Asylum Research MFP-Infinity atomic force microscope in the SKPFM mode, which allows measurement of true surface potential through operation in a two-pass mode. For SKPFM measurements, Pt-coated Si tips (Nanosensors PPP-EFM) with stiffness constant of 2.8 N m^{-1} were used.

2.2 Synthesis of AFR

An acidic medium (20 ml, 10 M HCl solution) was first prepared by adding 10 ml deionized water to 10 ml of stock 20 M HCl, and further mixed with 15 ml of aniline. The prepared pale-yellow coloured solution was then cooled down to ~0 °C in an ice bath under constant stirring. Subsequently, 7 ml of formaldehyde was added dropwise slowly into the solution under continuous vigorous stirring, during which the solution gradually became a yellow resinous condensate. Owing to the high viscosity of the condensate, the magnetic stirring bar was removed, and further vigorous stirring carried out manually using a glass rod to ensure a complete reaction. The collected condensate was subsequently washed with copious amounts of distilled water to remove the excess unreacted reactants and by-products.

2.3 Preparation and electrical characterization of TENGs

Conductive aluminium layers as electrodes were attached to two separate glass slides (2×2 × 0.1 cm). The tribo-negative layer was produced by attaching a PTFE thin film, while the AFR acted as the opposite layer. For the tribo-positive layer, the obtained gelatinous AFR condensate was spread out evenly on the surface of the prepared Al electrodes (Fig. 1b(i)), washed with distilled water (Fig. 1b(ii)) and further dried overnight in a desiccator (Fig. 1b(iii)). The samples were then cured under optimal conditions (detailed discussion in the following section) to obtain smooth AFR films on Al substrate (Fig. 1b(iv)). The two layers were assembled to form contact mode TENG devices.

A computer-controlled dynamic fatigue tester system (Popwil Model YPS-1) was used to characterize the TENGs by controlling the contact force (1-100 N), frequency (0-10 Hz) and spacer distance of the two tribo-contact layers. An oscilloscope (Tektronix MDO3022) and a picometer (Keysight B2981A) were connected in parallel or serial, respectively, to test the voltage output and the short-circuit current, respectively. The corresponding charge density was derived from the area under the curve of the measured current density. For all the TENG electrical measurements on picometer and oscilloscope, the Al electrode corresponding to the AFR side was connected to the positive lead, while the PTFE side Al was grounded.

3. Results and discussion

3.1 Material characterization

It is well established that, to achieve maximum cross-linking and ensuing mechanical strength, resins should be cured at the lowest curing temperatures for a longer duration [28]. The aniline formaldehyde condensates are thermosetting resins whose optimal curing conditions were determined using a two-cycle DSC thermal analysis [23]. The thermogram shown in Fig. 1(a) exhibits classic thermoset behaviour. In the first heating run, an exothermic peak was observed at ~120 °C, corresponding to the curing temperature range, while in the second heating run, no further melting/curing peaks were observed except for a glass transition (T_g) peak at ~31 °C. The second DSC run is essential to assess that the samples are fully cured (indicated by the absence of any further curing exotherm) or whether further post-curing was required [23,28]. Correspondingly, the curing process of the AFR resins on Al substrates was performed in a vacuum oven (~120 °C, ~14.5 Psi) for 2 hours to eliminate any residual unreacted aniline, formaldehyde and/or other volatiles entirely with no further post-curing. The curing was performed by turning the AFR deposited side upside down onto a flat PTFE substrate to make flat thin films for TENGs. To obtain AFR samples with varying thicknesses, four different weights (1000g/500g/300g/200g) were added on to the backside. Subsequently, the oven was switched off, and samples were allowed to cool down to room temperature to obtain the hot-pressed AFR thin films on the Al electrode (Fig. 1e (iv)). As observed in the SEM images of Fig. 1(a-d), a significant variation in the surface morphology was observed which can be attributed to the following factors: *in-vacuo* removal of pores and residual moisture content under heating and the simultaneous application of weight to obtain a smooth free-standing film under vacuum conditions. As the AFR condensate is put through its curing cycle, it softens up

The cured AFR sample was characterized by ^{1}H NMR and data shown in Fig. 2(c) with the sharp sextet at δ 2.51 ppm being ascribed to the solvent DMSO. Previous work by Zhang et al. has shown that a reduction in the aniline to formaldehyde ratio in the polymerization reaction has a significant effect on the intensity, area and shape of the peak at δ 5.10 ppm with corresponding changes in the peaks for aromatic rings and methylene groups [25]. The further multiple peaks appear in the range of δ 6.5-7.0 ppm, corresponding to the aromatic rings and amino groups; meanwhile, the peaks in the range of δ 3.55-3.67 ppm correspond to the methylene group (-CH$_2$-) groups connecting the aromatic rings [22,25,29]. The broad peak around δ 5.50 ppm corresponds to the primary and secondary amine protons [22,25,29]. By integration of the ^{1}H NMR signals, the relative molecular ratio of the prepared for aromatic rings, methylene and amino groups were calculated to be 10:4:5 which is similar to those reported by Zhang et al. [25].

The molecular structure of the AFR samples before and after curing was confirmed with FTIR spectroscopy. By observing Fig. 2(d), the bands at ~1,515 cm^{-1} and ~812 cm^{-1} can be assigned to the stretching vibration of the benzenoid framework and the bending vibration of the substituted benzene ring [22,25]. The absorption bands range from 1,630-1,500 cm^{-1}, and 1,350-1,250 cm^{-1} are assigned to -NH and -C-N- vibrations and stretching, respectively; while the bands in the range of 3,500-3,300 cm^{-1} are due to the primary and/or secondary amine functional groups [22,25,30]. The peaks in the range of 1,400-1,300 cm^{-1} indicate the existence of -CH$_2$-N bonding. Stretching vibrations of aromatic protons result with peaks at ~2,900 cm^{-1} and out of plane bending vibrations in the range of 780-650 cm^{-1} [31]. After the curing process, the intensities decrease for the absorption bands at ~3,340 cm^{-1} and ~1,619 cm^{-1}, indicating the presence of lower primary and secondary amine units in the molecular structure, which could lead to the formation of the final product with much lower solubility [22]. Although it is generally recognized that polymer chemical structure cannot be fully identified from the spectral results only, previous work by Zhang et al.[25] have shown that a linear copolymer is formed when an excess of aniline is used (similar to the one used in our work), in which the amino group of aniline unit predominantly exists as primary and/or secondary amine. As mentioned earlier in the experiment section, the yellow residual solution indicates an excess

amount of aniline and the presence of primary and secondary amines can be confirmed by the existence of strong absorption bands at ~1,600 cm^{-1} and ~1,268 cm^{-1} of the FTIR results [22,25], as observed in our samples. The probable reaction mechanism and structures of the synthesized products are proposed by combining all the obtained spectra results, which is shown in Fig. 3[20].

Fig. 2(c) shows the core-level XPS spectra for the carbon, nitrogen and oxygen, while quantification using appropriate relative sensitivity factors reveals the surface composition, carbon (81.5 at.%), nitrogen (8.9 at.%) and oxygen (9.6 at.%). All the high-resolution core-level spectra were fitted using Gaussian components to identify the diverse chemical bonding states present in the AFR samples. The high binding energy asymmetrical C 1s spectrum was deconvoluted into four components centred at 284.8 eV, 285.8 eV, 287.0 eV and 288.7 eV, corresponding to sp^2 bonds, C-N bonds in amino groups and/or amine-sided carbon atoms, C–O groups and C=O groups, respectively apart from the satellite peak at ~291 eV [32]. The N 1s spectra show only a single peak at ~ 399.7 eV, corresponding to the nitrogen bonded to carbon in amino and/or amino and/or amide groups [32,33]. This peak has also been attributed to an overlap of the amine, amide and imide contributions for nitrogen-containing polymers [32,33]. The O 1s spectra show the presence of components at 531.5 eV and 532.9 eV, corresponding to C-O and C=O groups, respectively [32,33]. It should be noted that oxygen is not usually expected in the chemical structure of AFR, but owing to the low-vacuum curing process, surface oxygen is observed which is absent in the bulk of the material (as confirmed from *in-situ* XPS Ar$^+$ sputtering (see Fig. S2, Supporting Information). As discussed earlier, both the nitrogen and oxygen groups can impart tribo-positive functionality to the surface owing to their electron-donating capabilities wherein the nature of the oxygen group (ether, hydroxyl or carbonyl), has only a small effect on the magnitude of the charge. For AFR which has abundant nitrogen and oxygen functional groups, a high tribo-positive behaviour is therefore expected.

For the application of the cured AFR samples in a capacitive type TENG device, it is essential to study their dielectric behaviour. including the variation of the real part (ε'), and the loss tangent tanδ [tan$\delta = \varepsilon''/\varepsilon'$] (where ε'' presents the imaginary part) of dielectric constant with the variation of frequency. It can be observed (Fig. 2(d)) that the ε' of AFR at room temperature decreases from a value of 3.96 at 1 Hz to a value of 3.17 at 1 MHz, similar to those referred to the literature [34]. When the frequency was higher than 10 Hz, tan δ shows values of less than 0.2 in all the frequency window. Especially for frequencies higher than 1 kHz, tan δ presents a

value lower than 0.01. The near-linear increase of tan δ below 1 kHz may be associated with the low-frequency dielectric relaxation, which is accompanied by a corresponding greater increment of ε′ values. This trend of the dielectric parameters matches well with Koop's theory and Maxwell-Wagner model, which describes the interfacial dipoles have less time to orient themselves in the direction of the high-frequency alternating field, thus decreasing the polarization at higher frequencies [35]. However, as the contact-mode TENG is commonly operated in the low-frequency range (1-10 Hz), the effect of variation of the dielectric constant on the TENG output is minimal (see Eqs. 1 & 2) [36].

3.2 Electrical characterization

The measured output performance of the produced AFR/PTFE TENG is shown in Fig. 4. For the short-circuit condition, the transferred charge for the contact-separate mode TENG devices can be theoretically represented by [36]:

$$Q_{sc} = \frac{S\sigma x(t)}{d_0 + x(t)} \tag{1}$$

Where S is the plane contact area, σ is the surface electrification charge density, $x(t)$ is the real-time distance between two contact layers, and d_0 is the effective thickness represented by:

$$d_0 = \frac{d_1}{\varepsilon_1} + \frac{d_2}{\varepsilon_2} \tag{2}$$

Where ε_1 and ε_2 represent the relative dielectric constants of the two contact triboelectric contact layers of thicknesses d_1 and d_2, respectively [36]. Considering the Eq. (1) & (2), the d_1 and d_2 have a profound effect on the produced voltage output and charge density. To explore this parameter, samples of varying thickness on the Al electrodes prepared by controlling the load during the *in-vacuo* hot-press process. With the increase of the pressing load (200g/300g/500g/1000g), the thickness of the AFR films reduced from ~973 μm to ~117 μm. As expected, the output voltage and transferred charge density increased with the reduction in the AFR layer thickness (Fig. 4(a&b)) and the trend was confirmed for all the possible contact-force conditions. For the highest performance, thinner dielectric layers are preferred owing to the better charge induction on the back metal electrodes [36]. Therefore, for further experiments, only samples of ~117 μm AFR samples were considered.

Unlike the piezoelectric energy harvesters, which require operation at their resonant frequencies, the TENG devices are high-efficiency mechanical energy to electrical energy

converters in the low-frequency (1-10 Hz) region [37,38]. As shown in Fig. 4(c, d) the output voltage and current followed this pattern to give maximum voltage output of ~900 V and current density of ~60 mA m^{-2} when the contact forces and spacer distance were fixed as 50 N and 5 mm, respectively, while the short-circuit charge density remained relatively constant at a value of 200 µC m^{-2}. However, for the energy harvesting purpose, the transferred charge density is the most crucial output parameters. It can be observed that the maximum transferred charge density value (~225 µC m^{-2}) was obtained at the working frequency of 5 Hz, which indicated the optimized working condition of the AFR/PTFE TENG.

According to the literature [36,39] and indeed our previous reports [5–8], the impact force and impact frequency are the two most important operating parameters that affect the contact-separation mode TENGs outputs. However, surprisingly, within the contact force range of 20-80 N, the AFC/PTFE device gave a near-constant level of peak-to-peak voltage output (V_{p-p}) of ~1,000 V (Fig. 4(c)), albeit at lower contact forces, this output dropped off fairly quickly (see Fig. S3, Supplementary Information). For the current output shown in Fig. 4(d), although the peak values of the current density increase from ~45 mA m^{-2} to ~65 mA m^{-2}, the effective transferred charge density stays around 200 µC m^{-2}. This relatively constant output, unaffected by the variation of contact force is attributed to the high hardness, flat contact surface and non-variable polarization properties of the cured AFR substrate. The slight variation of the observed current density may arise due to the malleability of the relatively soft PTFE film, which leads to a variation of film thickness at different impact forces and pressures. It should be noted that this value of ~200 µC m^{-2} is similar to the values reported for the TENGs based on liquid metal gallium (~219 µC m^{-2}) [37] but lower than that of soft material and fragmental contacting structure (silicone rubber mixed with nanocarbons) which reach a value of ~250 µC m^{-2} which is considered as the maximum charge density of TENGs working in air environment [38]. Thus, the AFR represents a relatively straightforward material and process for achieving high surface charge density without the need for expensive liquid metals or polymer compounding steps.

The output power of the AFR/PTFE TENG was tested by connecting various external load resistors in series (operating conditions: 50 N force, 5 mm spacer distance and 5 Hz working frequency. The accurate instantaneous peak power values ($P=I^2 \times R$) can be obtained by measuring the current across each resistor. It can be observed in Fig. 5(a) that the output power of AFR-PTFE TENG was maximized at a load resistance of 100 MΩ, corresponding to a peak power density of nearly 11 W m^{-2}. However, it has been shown that the instantaneous power output is related to not only the amount of charge transferred, but also to the duration of the

charge transfer time. Indeed, such an effect has been applied to design micro/nano-switch structure for developing TENG based applications which require high-magnitude voltage peaks [43]. Therefore, instead of the instantaneous peak power, the energy (E) derived from the area under the power curve of each energy generation cycle at the impedance matching condition is much more representative of the output electric energy characterization. This energy, E, is given by:

$$E = \int_{nt}^{(n+1)t} I^2(t).R_{load}dt \qquad (3)$$

where I stands for the measured current across the load resistance (R_{Load}), n is the number of generation cycle, and t is the time period of each energy generation cycle (0.2 s at 5 Hz working frequency) [44, 45]. At the impedance matching condition (when R_{Load}=100 MΩ), the energy harvested was calculated to be ~28.1 µJ cycle^{-1} (Fig. 5(b)), which is nearly twice that that harvested from a PA6/electrospun-PTFE based TENG reported in our earlier work (~13.8 µJ cycle^{-1}, see Fig S4, Supplementary Information) measured in our previous work [6].

The output stability of the AFR/PTFE TENG was demonstrated by a continuous operation for over 16,000 energy generation cycles at 50 N, 5 Hz condition). As shown in Fig. 5(c, d), the output variation is within the mechanical system error range (±5%) of the contact forces. The continuous stable output demonstrates not only the duration of the tribo-charge on the selected dielectric material surfaces but also the sufficient mechanical strength of the fabricated AFR layer for the long-term energy generation applications. The AFR/PTFE TENG provides enough power to immediately light up 32 chip LEDs without the need for any charge storage (Fig. 5(e)).

3.3   The mechanism for high performance of AFR/PTFE TENGs

Under compressive forces, when the AFR/PTFE surfaces are in contact, equal and opposite triboelectric charges, *i.e.* negative charges on PTFE and positive charges on AFR are generated. Upon the removal of the force, the presence of these opposite charges on the surfaces leads to the formation of the potential between the two metal electrodes, which can drive the electrons through an external circuit until the potential difference is neutralized. Thus, a higher charge density will produce a higher potential difference between the two TENG dielectric surfaces. It is clear that as compared to PA6, the significantly higher tribo-positive nature of the synthesized AFR layer can be further demonstrated by using SKPFM technique.

The SKPFM measurements rely on the matching of tip bias V_{DC} with the contact potential difference between the sample and the probe contact potential difference, V_{CPD}, by nullifying the vibration of the probe, which is initially driven by the electrostatic force, induced on the AFM probe. The relationship between the parameters and measurement conditions are detailed in the Supplementary Information. In the first instance, we have measured the surface potential of the as-prepared cured AFR sample (Fig. 6(a, b). For the pristine AFR sample, this average surface potential ϕ was measured to be 1.147 V which is significantly higher than that of the extensively used tribo-positive PA6, which showed a value of 0.875 V only [8]. A higher contact potential difference, V_{CPD}, implies that the electrons can be easily donated from the surface and the surface will gain a positive charge after contacting with the other materials. Thus, as compared to the PA6, a higher surface potential means that the AFR is more triboelectric positive, thus having a higher ability to donate electrons and explains the significantly higher performance for the AFR/PTFE TENG as compared to the PA6/PTFE TENG. It should also be noted that the average surface potential of AFR is quite close to our earlier reported value for polyethene oxide (1.160-1.266 V) which was shown to be a superior material as compared to PA6 [8]. The surface potential values for AFR are therefore in line with the earlier reports on the correlation between the surface functional groups and the ensuing surface charge on a material [15].

Besides the understanding of the surface potential of a triboelectric surface, it is equally important to understand the change in the surface potential and the spatial distribution of charges occurring upon the contact between the triboelectric materials. Fig. 6(a-h) showing the SKPFM plots of the topographic height and the surface potential of the AFR sample at various stages of contact with the charge injected PTFE by the ionization gun. It should be noted that the surface potential of the charge injected PTFE sample was too high, leading to channel saturation (±10 V for our system) (see Fig. S5 and Fig. S6, Supplementary Information for the KPFM and electrostatic force microscopy (EFM) images) and even after multiple contact cycles remained too high to be measured, hence, the SKPFM discussion would be limited to the AFR samples alone. In addition, there is no cross-talk between the topographic features and surface potential was observed for the AFR samples.

By employing a method similar to that of Barnes et al. [43], the AFR and PTFE layers were repeatedly contacted/separated with each other for a number of cycles (TENG excited by hand, 1-2 Hz, 5-10 N) and then the surface potential was measured by using SKPFM. The delay between the contact and the completion of the scan was kept to a minimum so that the time-

variant effect on surface potential could be minimized [43]. Due to the lack of metal contacts on the imaging surface (acting as reference points) and the relatively large area of the AFR samples, we could not ensure that the same area was being measured. However, repeated measurements have shown that the surface potential changes observed are consistent throughout the sample. The contact electrification between AFR and PTFE, after a nominal 30 contact cycles, leads to the exchange of charges between the AFR and PTFE and change the average CPD, $V_{CPD(av)}$ of AFR to 1.176 V (Fig 6(c, d)). As the cyclic contact increases to 60 cycles, $V_{CPD(av)}$ has a nominal increase to 1.187 V (Fig. 6(e, f)). This variation of nearly 40 mV is shown in Fig. 6(i), where the surface potential histogram shows a clear upshift of the AFR surface potential. This increase in the $V_{CPD(av)}$ can be considered to arise from a reduction in the overall roughness upon cycling resulting in better microscopic contact.

However, unlike the study by Baytekin et al. [44], for any of the contact cycled AFR surfaces, no mosaic charge distribution could be observed. However, when the AFR and PTFE surfaces were brought in contact for 10 sec, there was a significant shift in the surface potential for the AFR samples from 1.187 V to 1.206 V. However, any further cycling or contacting/rubbing of the AFR and PTFE surface did not affect the surface potential of the AFR visibly, and it remained around the 1.206 V value only. This trend of the upshift in the surface potential of the tribo-positive material is in line with that observed by Baytekin et al. and Barnes et al. [43, 44]. However, their use of soft, high tack PDMS ensures higher conformity of the tribo-surfaces leading to a significantly higher difference in the observed surface potentials (up to 100 mV) [43, 44]. The surface charge density increase on the AFR surface by contact electrification can be calculated using the simple capacitor model [43]:

$$\sigma = \frac{\varepsilon_0 \Delta V_{CPD}}{h} \tag{4}$$

where ε_0 is the vacuum permittivity ($8.854 \times 10^{-12} F/m$), ΔV_{CPD} (+60 mV) is the $V_{CPD(av)}$ change of AFR before and after the contact with PTFE and h is the lift height (10 nm) between the AFM tip and AFR film during the second pass of the SKPFM measurement. The calculated value of 53.12 µC m^{-2} matches quite well with the low-frequency low impact operation of the TENG, which showed a charge transfer value of nearly 53 µC m^{-2} (Fig. S3, Supplementary Information).

4. Conclusions

In summary, a facile approach for the synthesis of highly tribo-positive aniline formaldehyde

resin is proposed. The ease of post-processing and curing steps, in conjunction with its suitable chemical functional groups, dielectric behaviour, and surface morphology makes AFR highly suitable for energy harvesting TENG applications. A thin (~117 μm) flat AFR dielectric film in an AFR/PTFE TENG gave a maximum peak-to-peak voltage of 1,000 V, a current density of 65 mA m^{-2} and a transferred charge density of 200 μC m^{-2}, respectively. With each generation cycle, the AFR/PTFE TENG can harvest ~28 μJ energy to a matched load resistor, which is twice the value of a PA6 tribo-positive layer based PA6/PTFE TENG. The improvement of the performance of the AFR/PTFE TENG is mainly attributed to the high surface potential of AFR (1.147 V) as confirmed by SKPFM. In addition, the AFR/PTFE TENG device was demonstrated to be able to light up 35 LEDs and have a highly stable output for a long test duration of over 16,000 cycles. The work, therefore, provides a simple, cost-effective route for expanding the portfolio of tribo-positive materials for enabling high-performance TENG energy harvesters.

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