Effect of Surface Treatment on Electrical Properties of Polydimethylsiloxane Based Triboelectric Nanogenerator

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Abstract

This research investigated the effect of surface treatment on electrical properties of flexible triboelectric nanogenerator (TENG). Polydimethylsiloxane (PDMS) was used as triboelectric layer. The PDMS pads were prepared by simple casting method and the effect of surface treatments by heat and acid was examined. Physical morphology of treated samples were investigated by scanning electron microscope (SEM). Electrical properties were measured under continuous periodic knocking. The results revealed that the heat-treated PDMS-based TENG showed the outstanding output voltage. The maximum output voltage of heat-treated based TENG reached approximately 9 V, which was over 4 times larger than those of normal PDMS based TENG. The research demonstrated the feasibility to utilize PDMS-based TENG as an energy harvesting device and presented a cost-effective method for producing high-efficiency PDMS based TENG.

Keywords: triboelectric, surface treatment, polydimethylsiloxane, nanogenerator
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1. Introduction

Environmental mechanical energy is one of the most attractive energy sources for powering small electronics. Recently, the triboelectric nanogenerator (TENG) has attracted considerable attention, which can harvest mechanical energy caused by mechanical motion in our daily life including wind, rain, vehicle and human movement. It has potential applications in wireless systems [1, 2], portable electronics [3-5] and active sensors [6-8]. The principle of the TENG is based on triboelectricfication and electrostatic induction [7]. The triboelectrification is the phenomenon that material becomes electrically charged when two different materials are pressed and rubbed together [7].

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Nowadays, flexible electronic devices have become a novel trend and more attention has been paid to this area to support the revolution of wearable devices. Polydimethylsiloxane (PDMS) elastomer has been considered as one of the most appropriate materials for TENG applications due to its flexibility, transparency, lightweight, non-toxicity, easy fabrication and high electronegativity [9-11].

In the past few years, much work has been done to improve the conversion efficiency of TENG, including optimizing its structure and material [10, 12-14]. Recently, Chen *et al*. [10] reported an enhancing performance of TENG by filling high dielectric nanoparticles into sponge PDMS film, which gives over 5-fold power enhancement compared with the nanogenerator based on the pure PDMS film. However, there have been a few related studies on surface treatment. The interface could significantly influence the electric performance of the triboelectric materials [11, 15]. For example, Yun *et al.* [11] reported the base-treated PDMS surfaces by sprinkling of NaOH solution. The resulting TENG generated voltage of 10.4 V and current of 179 nA is almost 3-fold larger than those of fresh PDMS.

In this work, we demonstrated a cost-effective method for producing high-efficiency PDMS based TENG. This research investigated the influence of chemical and physical treatment on electrical properties of PDMS-based TENG. The PDMS pad was chemically modified by acetic acid to create carboxyl groups on the surface. These chemical treatments devoted to enhance the charge density on the surface while the physical treatment is exposed by heat during the curing process to create an elastic porous PDMS. This research presented the simple preparation process of the TENG, which makes it easy to be upgraded for large-scale production and cost savings.

2. Materials and Methods

Electric properties of PDMS-based TENG was improved by employing chemical and physical treatments. The PDMS pads were prepared by a simple casting method. First, 10 ml PDMS solution (Sylgard 184, Dow Corning) was mixed with 1 ml curing agent. Then, the mixture was cast on plastic substrates and kept under room temperature for 24 h. For chemical treatment, the prepared PDMS pads were immersed in concentrated acetic acid for 24 h. After acetic acid treatment, the sample was rinsed several times with DI water. In the preparation of physical treated PDMS, a mixed PDMS solution was cast onto substrates and then cured at 100 ˚C for 2 h. After drying, the elastic porous PDMS was formed. Finally, the prepared PDMS pads were collected for the test. The effective surface area of the PDMS pads was 3 cm x 3 cm and 1 mm thickness. The chemical bonds of treated PDMS were examined using Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer Spectrum GX FT-IR spectrometer). The morphology of PDMS was characterized by scanning electron microscope (SEM, Zeiss EVO MA1).

In this experiment, the TENG was fabricated with PDMS pad and aluminium (Al) tape. For electrical characterization, a conductive Al tape was applied as both common electrodes and another tribo-material to produce opposite sign mobile charges. The dynamic tester was used to control the cyclic contact of the two plates of the TENG. The PDMS and Al parts of a TENG were attached to the lower fixed part and upper movable part of the dynamic tester, respectively. The output voltage was characterized using an oscilloscope (Trektronix) during the continuous periodic knocking.

3. Results and Discussion

The digital photographs of all samples are presented in Figure 1. From the digital photographs, it was found that all PDMS pads have a smooth surface. All samples are very flexible and stretchable [see the inset of Figure 1(a-c)]. As representatively shown for the heat-treated PDMS [Figure 1(c)], an elastic porous structure was formed.

The morphology of all samples was revealed by scanning electron microscope (SEM). Figure 2(a-c) shows top-view of SEM micrographs from normal PDMS, acid-treated PDMS, and heat-treated PDMS, respectively. Figure 2(b) reveals that dipping of PDMS into acetic acid would result in dramatic changes in the surface morphology of PDMS. The surface of the PDMS has become rough and swollen in a circle as seen in Figure 2(b). The average diameter of the swelling area was 3.35±1.14 µm. According to Figure 2(c), it could be seen that the heat-treated PDMS presents a wrinkled surface structure. From a cross-section of SEM image from the heat-treated PDMS [Figure 2(f)], it reveals that the pores are well-formed inside the sample. The average diameter of pores was 2.02±0.47 µm. The formation of this porous structure was probably caused by the boiling effect during the curing process at high temperature above the boiling point of PDMS (>100˚C).

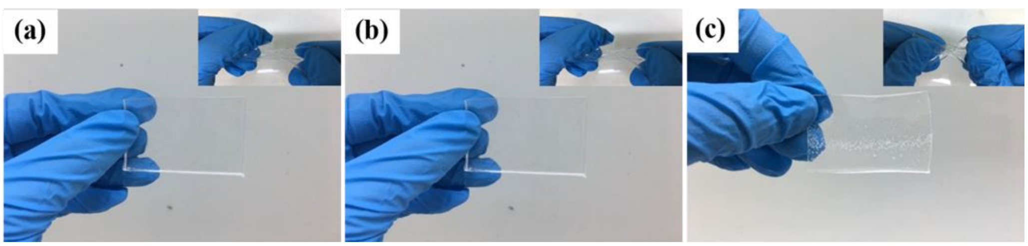

Figure 1. Digital images of (a) normal PDMS, (b) acid-treated PDMS and (c) heat-treated PDMS An inset shows the digital image of PDMS stretched by hand

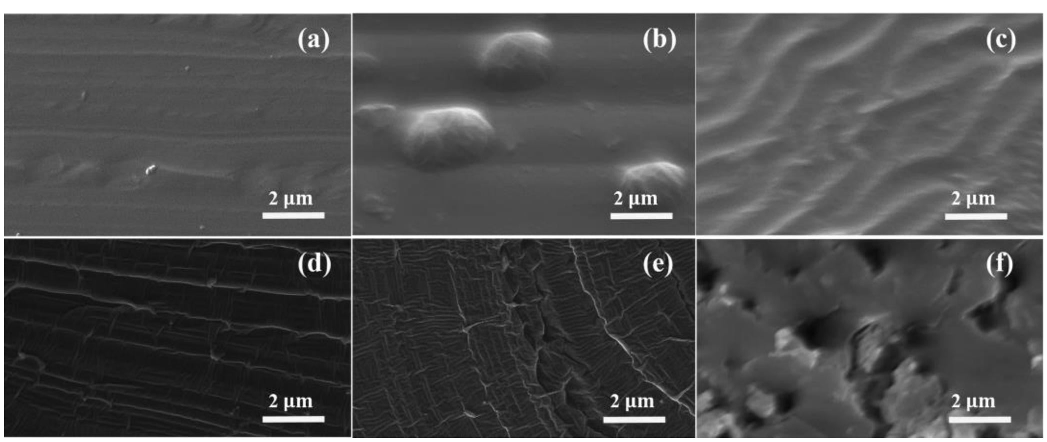

Figure 2. Top and cross-section views of SEM images: (a), (d) normal PDMS; (b), (e) acid-treated PDMS; (c), (f) heat-treated PDMS

FTIR is used to verify the effect of surface treatment of the PDMS as shown in Figure 3. For all samples, the spectrums showed multiple peaks in the range of 1000 to 4000 cm^{-1}, which correspond to the vibrations of PDMS functional groups. The absorption bands around 1400 and 1200 cm^{-1} correspond to the vibration of $–CH_3$ and the C-H stretching vibration was detected at 2950 cm^{-1} [16]. Peaks of around 700 and 1250 cm^{-1} indicated the Si-CH_3 stretching vibration [17]. A peak at 875 cm^{-1} corresponds to the Si-OH stretching vibration [17]. The multicomponent peaks of Si-O-Si stretching vibration were detected in a range of 930-1200 cm^{-1} [16]. Peaks of around 1100 cm^{-1} indicated the Si-O stretching vibration [17]. The Si-C and Si-$(CH_3)_2$ peaks were evidenced in the region of 825-865 cm^{-1} and 785-815 cm^{-1}, respectively [16]. After acetic acid treatment, the C=O stretching vibration of carboxyl (-COOH) functional groups was detected at around 1500 [18]. Moreover, the peak intensities of the CH_3 around 2800 cm^{-1} became more obvious, which correspond to the vibrations of acetic acid functional groups. These results revealed that the COOH functional groups were introduced onto the PDMS surface after surface treatment. Carboxylic groups were attached to the PDMS surface by formed H-bond, as shown in Figure 4. In another set of experiments, the heat-treated PDMS was investigated. The IR spectrum revealed that the spectrum has not been changed after heat treatment. The spectrum exhibited multiple absorption peaks in the region of 1000 to 4000 cm^{-1}, which corresponds to the vibrations of PDMS functional groups.

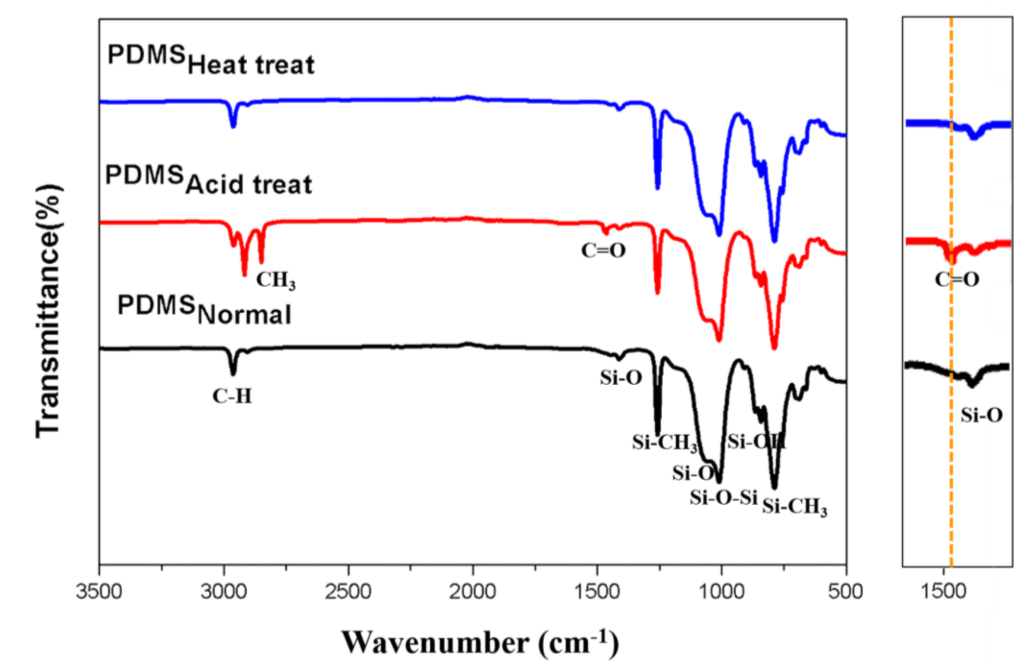

Figure 3. FT-IR spectra of the normal PDMS, acid-treated PDMS and heat-treated PDMS. Insets show FTIR spectra at high magnification.

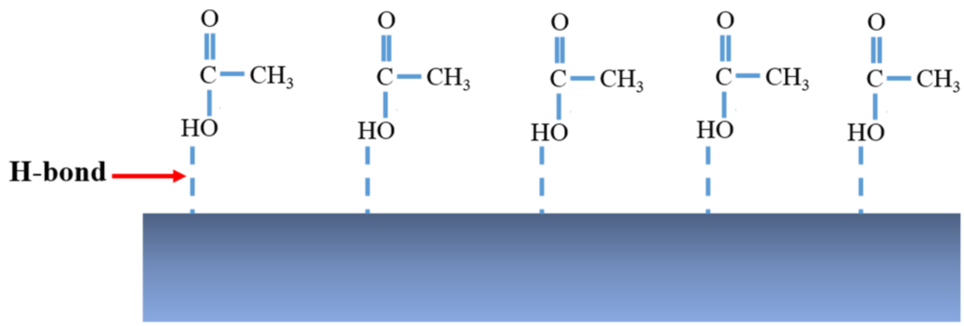

Figure 4. Schematic diagram of the effect of acid treatment which introduce the functional COOH groups onto the surface of PDMS

For electrical characterization, a conductive aluminium (Al) tape was applied as both electrodes and opposite tribo-material. When PDMS and Al come into contact with an external force, the Al is positively charged and the PDMS is negatively charged owing to its intrinsically different triboelectricity tendency [19]. Figure 5 compares the triboelectric power generation of untreated, acid-treated, and heat-treated PDMS-based TENGs. The output voltage signals were detected in both positive and negative side when the substrate was pressed and released, respectively. The formation of a negative signaled after removing external load due to the reverse-flowing carriers. During periodic contact and separation, the normal PDMS-based TENG generated an output voltage of about 2 V [Figure 5(a)]. After surface treatment with acetic acid for 24 h, the PDMS-based TENG exhibited a significantly enhanced triboelectric voltage [Figure 5(b)]. The output voltage of the acid-treated PDMS reached approximately 5 V, which was over two times larger than those of normal PDMS based TENG. This result can be attributed to two reasons. The first reason is the effect of surface roughness, resulting in larger contact areas compared with the normal PDMS. This result leads to an increase in surface charge density and directly enhances the output signals of the TENG. Another possible reason could be the presence of carboxyl groups on the PDMS surface. This could increase the polar components on the surface of PDMS, which affects the surface charge density. The increasing of surface charge density could enhance the output signals of TENG. Yun *et al*. [11] reported the significantly enhanced triboelectric surface charge of PDMS by sprinkling of NaOH solution. It reveals that the enhanced triboelectric charge is related with an increase of polar bonds in PDMS. Therefore, the acid-treated PDMS could greatly enhance the electric output of TENG when combined with the larger contact areas.

In another set of experiments, the heat-treated PDMS-based TENG showed outstanding output voltage [Figure 5(c)]. The maximum output voltage can reach 9 V, which was almost 4.5 times as high as that in the untreated samples. This result may be due to the pores forming in the PDMS pads that could effectively minimize its thickness [10]. The elastic porous PDMS can

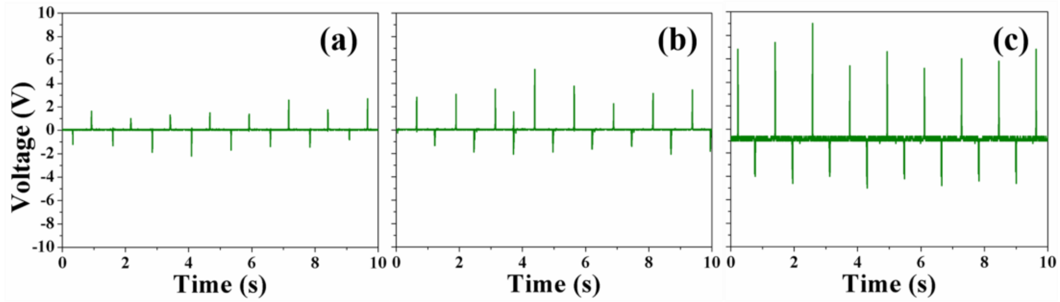

Figure 5. Output voltage of (a) normal, (b) acid-treated and (c) heat-treated PDMS-based TENGs measured with respect to time under an impulsive loading

shrink into minimum thickness which is lower than normal one after an external force was applied. This result leads to an increase in capacitance and the capacitance affects the surface charge density [10]. Therefore, the output signals of the TENG was increased. Moreover, based on the SEM images, the heat-treated sample showed the roughest surface that resulting in larger contact areas. This result also leads to an increase in surface charge density and directly enhance the output signals of the TENG. The triboelectric voltage of heat-treated PDMS-based TENG is higher than those of untreated and acid-treated PDMS-based TENGs.

4. Conclusions

In summary, this research reported the improving electric properties of polydimethylsiloxane based triboelectric nanogenerator by employing physical and chemical treatment. The PDMS pad was chemically modified by acetic acid. The acid-treated PDMS-based TENG revealed a significantly enhanced triboelectric voltage. This improvement corresponded to the increase of surface charge density, which was induced by the carboxyl groups on the sample surface and increase of surface area. While physical treatment is exposed by heat during the curing process. After drying, the elastic porous PDMS was formed. The heat-treated PDMS-based TENG showed better TENG performance than both the normal and the acid-treated PDMS-based TENGs. This result can be attributed to the pores forming in the PDMS pads by heat treatment which could effectively reduce its thickness. This result leads to an increase in capacitance and affects the surface charge density. Therefore, the output signals of the TENG was increased. The output voltage of the heat-treated PDMS-based TENG reached approximately 9 V, which was over 4 times larger than those of normal PDMS-based TENG.

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