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Short communication

All-polymer hybrid electret fibers for high-efficiency and low-resistance filter media

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**HIGHLIGHTS**
- A new method to enhance electret property without using nanoparticles is reported.
- All-polymer electret PS/PVDF fibers without nanotoxicity are prepared.
- Novel theory describing the electret mechanisms of electrospinning is proposed.
- The resultant electret fibers show competitive air filtration performance.

**GRAPHICAL ABSTRACT**

**ABSTRACT**

A one-step and controllable strategy to prepare all-polymer hybrid electret fibers is reported based on the coupling of polystyrene and polyvinylidene fluoride in electric response. The complementary dielectric properties between PS and PVDF generate dual-system electret charges within PS/PVDF fibers, thereby improving the electret effect. The bi-component all-polymer electret fibers show enhanced electret property and structural continuity, contributing to a N95 protective respirator with high filtration efficiency (99.752%), low air resistance (72 Pa) and long service life. The fabrication of all-polymer electret fibers solves the challenge of nanoparticle toxicity for existing polymer/nanoparticle electret fibers.

1. Introduction

The outbreaks of emerging infectious diseases (EIDs), such as the ongoing Coronavirus Disease 2019 (COVID-19), always take a significant human toll and affect social stability [1,2]. To protect the public from being infected via droplets and aerosols [3], protective respirators are highly demanded. Currently, respirators are mostly composed of micro-sized melt-blown fibers with large pore size (10–20 μm), rendering a low pressure drop thereby satisfying breathing comfort [4]. However, determined by the single filtration mechanism of size sieving, melt-blown filters suffer from low filtration efficiency towards aerosols with small particle size, which is especially poisonous [5]. Currently, increasing the fiber consumption has become a usual strategy to improve the protective ability. However, this strategy causes the sharp increase of pressure drop simultaneously [6].

Electret technology is effective in alleviating the conflict between...
filtration efficiency and pressure drop by endowing fibers with electrostatic effect, which contributes to particle adsorption while generating negligible impact on airflow [7,8]. Compared to the current electret technologies [9,10], electrospinning can achieve the in-situ charging along with the formation of fibers, achieving the one-step production of electret fibers [11,12]. To enhance the electret effect of electrospun fibers, introducing nanoparticles is a state-of-art and common strategy [13–16]. However, this strategy has two drawbacks: the intrinsic nano-agglomeration behavior makes nanoparticles hard to evenly distribute within fibers [11,13]; particles, especially the accumulated ones, can easily detach from fibers and be inhaled, yielding additional threat to human health [17]. The remaining challenge is to develop electrospun fibers with strong electret effect independent of particle charge enhancers.

Herein, we prepare all-polymer hybrid electret fibers by studying the complementarity of electric responses between electrospun polymers. The coupling of electric polarization behaviors of polystyrene (PS) and polyvinylidene fluoride (PVDF) enables the hybrid PS/PVDF fibers to show enhanced electret effect and high porosity. The protective respirator using PS/PVDF fibers as core layer exhibits high filtration efficiency, low air resistance, and long service life.

2. Results and discussion

The premise to design all-polymer electret fibers is the reveal of electret mechanisms while electrospinning polymers with different dielectric properties. A general overview of electrospinning process in Fig. 1a. Under the high voltage, solutions were ejected from a metal needle and evolved into electrified jets, which finally deposited on a collector as solid fibers after being continuously elongated and charged, as well as the simultaneous phase separation [18]. Obviously, electrospinning can in situ endow fibrous assemblies with electret effect during the evolution from solutions to solid fibers, implying that the electret property and structures could be simultaneously tailored by solution properties [19]. PS and PVDF were selected because they belong to the weakly and strongly polar polymers due to their ultralow and ultrahigh dielectric constants, respectively [20,21]. Additionally, they were widely studied electret materials and were easily electrospun. The dielectric property of PS and PVDF was provided in Fig. S1, which also showed the relationship between dielectric property and polarity. The dielectric properties of other commonly used electrospun polymers were provided in Fig. S1 for comparison.

The morphologies of PS and PVDF electrospun fibers (Fig. 1b and c) indicated that fibrous assemblies composed of PS possessed larger fiber diameter and higher porosity (89%) than PVDF (Fig. 1d). The effect of dielectric property on structures was discussed in Supplementary Discussion 1. The electret property of fibers was evaluated by the electric field intensity (E) of single fibers, which was deduced from the tested surface potential of fibrous assemblies (U) (Fig. 1d). Based on the non-contact measuring principle (Fig. 1e), the E were calculated by:
$$\vec{E} = \frac{\lambda}{2\pi \varepsilon_0 L} \frac{\vec{U}}{r^2 + 1 - R L}$$

where $\lambda$ is the charge density of single fiber, $\varepsilon_0$ is the dielectric constant, $L$ is the distance, $r$ and $p$ refer to the thickness and porosity of fibrous membranes, $R$ and $H$ are the radius of testing samples and testing distance, respectively [22]. The detailed deducing process was provided in Supplementary Method 1. PVDF membranes exhibited negative surface potential, implying that dipole charges played a predominant role in PVDF fibers considering that $\vec{U}$ was calculated by:

$$\vec{U} = \vec{U}_s - \vec{U}_d,$$

where $\vec{U}_s$ and $\vec{U}_d$ resulting from space and dipole charges, respectively [23]. The comparison of $\vec{E}$ among different fibers was intuitively visualized by color maps (Fig. 1f). The largest red zones of PS fibers indicated the highest sensibility of electret effect on dielectric property. Namely, synthesizing polymers showing the similar dielectric property with PS could be an effective strategy to acquire electrospun electret fibers with high positive $\vec{E}$. The $\vec{E}$ of PVDF fibers was negative due to the negative surface potential. The electret effect of fibers composed of weakly and strongly polar polymers (typical for PS and PVDF) resulted from the injection of charges into polymer traps and the dipole orientation, respectively (Fig. 1g).

To proof the proposed electret mechanisms, stoichiometric calculations associated with polymer traps and group motion were performed. The detailed calculation process of Fig. 2 was provided in Supplementary Method 2. Charge-trapping sites, generally contributed by chemical and physical defects in a pure polymer insulator, are necessary for the injection of space charges [24]. To compare the chemical defects between PS and PVDF under the same weight, their oligomers with the minimum polymerization degrees of 4 and 7 respectively were constructed, donated as PS(4) and PVDF(7). Fig. 2a revealed the overlapping molecular orbitals in PS(4), which could serve as charge trapping sites. PS(4) and PVDF(7) exhibited higher energy of the Highest Occupied Molecular Orbital (HOMO) levels and the Lowest Unoccupied Molecular Orbital (LUMO) levels (Fig. 2b), suggesting holes and electrons tended to be injected into PS and PVDF, respectively [25,26]. The comparison of energy band density between PS and PVDF also indicated that charges were more likely to be trapped within PS (Fig. S2 and Supplementary Discussion 2). Additionally, more charge trapping sites were predicted in PS/PVDF due to the internal rotation of molecular main chain (Fig. 2d and e, Fig. S3). The internal rotation barrier of VDF was an order of magnitude lower than that of styrene, implying that dipole charges were predominant in electrospun PVDF fibers. Detailed discussions could also be found in Supplementary Discussion 3.

The reveal of electret mechanisms linked to the dielectric properties provides a new insight to improve electret property, that is, taking advantages of the synergistic effect of weakly and strongly polarized polymers. Hybrid PS/PVDF fibers with the mass ratios of 16/0 (PS/PVDF-0), 15/1 (PS/PVDF-1), 14/2 (PS/PVDF-2), 13/3 (PS/PVDF-3) were fabricated. Their morphologies displayed negligibly changed fiber diameter (Fig. 3a–c, Fig. S4). However, the surface roughness appeared with the introduction of PVDF (Fig. S5 and Supplementary Discussion 4). The SEM-energy dispersive spectrometer image suggested the charge enhancer of PVDF evenly distributed in fibers (inset of Fig. 3b). The surface potential achieved improved by 36% by introducing 2/16 content of PVDF (Fig. 3d). The contribution of PVDF on electret property was illustrated by Fig. 3e. Charges injected into the matrix PS fibers generated local electric fields exhibiting the same direction with the external electrostatic field; however, the dipole orientation of PVDF generated local electric fields showing the opposite direction with the external one. Different electronic transport capabilities between PVDF and PS rendered the charge accumulation at the interfacial zones instead of being transferred from one to another [29]. Thus, induced charges within PS were generated, which interestingly showed the same direction with the injected charges. As a result, the electret effect of whole fibers was enhanced. PS/PVDF-3 membranes exhibited declined surface potential due to decreased interfacial zones. The highest porosity was achieved by PS/PVDF-2 fibers (94.4%) and porosity exhibited the same variation trend as surface potential. The electric field intensity ($\vec{E}$) around single PS/PVDF-2 fiber was calculated by eliminating the effects of porosity and thickness (Fig. S6). Compared to pure PS, a wider range of scale bar (from $-4.2 \times 10^9$ to $22 \times 10^9$) implied a higher $\vec{E}$ (Fig. 3f). Notably, the electret property was enhanced without relying on toxic nanoparticle as charge enhancers, which has never been reported in the previously developed electrospun electret fibers and melt-
blown electret fibers. The comparison of surface potentials among PS/PVDF fibers and recently reported electret fibers were provided in Tab. S3 and Supplementary Discussion 5.

PS/PVDF-2 membranes exhibited the highest filtration efficiency of 83.726%, improved by 12% than PS/PVDF-0 membranes (Fig. 3g). The pressure drops of various PS/PVDF membranes were extremely low (< 10 Pa), < 0.01% of atmosphere pressure. The filtration efficiency was further increased to meet different protective requirements (Fig. S7). The excellent filtration performance of PS/PVDF fibers was highlighted by comparing with previously reported air filtration materials (Fig. 3h) [13,16,30–32]. Furthermore, a wearable respirator was fabricated by using PS/PVDF membranes as the core functional layer (Fig. 3i). The filtration performance of this respirator was evaluated according to the method proposed by the National Institute for Occupational Safety and Health (NIOSH). Its filtration efficiency (99.752%) met the requirements of N95 respirators for protective function (> 95%). More importantly, its air resistance (72 Pa) was only one fifth of the maximum limit (~320 Pa) in NIOSH standard, ensuring the breath comfort. It also exhibited a long service life (Fig. S8), the detailed information were provided in Supplementary Discussion 6.

3. Conclusions

All-polymer hybrid electret fibers relying on the coupling behaviors of PS and PVDF in electric polarization were fabricated. First, the electret mechanism of electrospinning technology was revealed by focusing on the dielectret property of polymers. The electret effect of electrospun fibers, composed of polymers with ultralow and ultrahigh dielectret constants, came from the injection of charges into polymer traps and the dipoles orientation, respectively. Moreover, hybrid PS/PVDF fibers with structural continuity and enhanced electret effect were obtained, exhibiting high filtration efficiency (99.752%), low air resistance (72 Pa) and long service life. They were promising candidate as the core materials of low-resistance N95 protective masks.

Declaration of Competing Interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://
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