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Preparation of PVDF with High β-phase for Intelligent Fabrics

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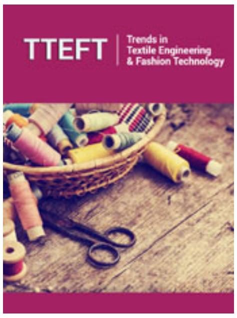

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Abstract

Flexible polyvinylidene fluoride (PVDF) has excellent piezoelectric properties, it has broad application prospects in wearable electronic products and smart fabrics. PVDF fibers or films with high β phase can be obtained by solution casting, electrospinning, stretching and other preparation methods, but they cannot meet the complex shape requirements of wearable products. The PVDF piezoelectric fibers and films prepared by near-electric field 3D printing method not only have high β-phase content, but also do not need to undergo polarization, especially for customized preparation. This provides a new idea for fabricating wearable flexible devices based on intelligent fabrics.

Keywords: Wearable electronic products; Woven fabrics; Piezoelectric polymer

Introduction

With the vigorous development of intelligent industry, there have been a lot of wearable electronic products based on woven fabrics have entered our lives, showed a huge market prospect, but also quietly changed the consumer's consumption concept and lifestyle. For smart fabrics, it is crucial to choose a flexible material with energy conversion function.

Polyvinylidene fluoride (PVDF) is a kind of piezoelectric polymer, compared with the traditional piezoelectric ceramics, it has the advantages of high sensitivity, low density, easy processing, especially good flexibility. So, it is unique in the preparation of light and small, flexible energy conversion devices, and is an ideal material for fabricating wearable flexible devices based on fabric. For example, Chakhchaoui et al. [1] put the PVDF into the knee pads as an energy harvester to generate electric energy through the action of the knee. The knee pad is made of textile woven with PVDF patches, which replaces the traditional knee pad and can be used as an energy harvester. Chiu et al. [2] investigated and developed a PVDF-based wearable sensor capable of monitoring heartbeat and respiration with high fidelity. Chang et al. [3] reported that the PVDF nanofiber generator has a high energy conversion efficiency, which can power wearable smart clothes through human motion, and thus power handheld electronic devices.

The crystal structure of PVDF usually exists in α- β- γ- and δ-phases [4]. Under general crystallization conditions, the α-phase of TGTG is arranged in antiparallel and has no polarity. However, the β-phase with all-trans TTT conformation has fluorine on one side and hydrogen on the other side, which forms a net dipole moment. The directional order of the dipole moment makes its electrical activity reach its strongest, so increasing the content of β-phase is very important to improve the electrical properties of PVDF. The PVDF prepared by the general solution casting method only produces the α-phase PVDF structure without other processes, and its crystal structure has zero dipole moment and zero polarization, so there is no piezoelectric property [5]. In order to change the dipole distribution of PVDF polymers, generate piezoelectric effects in the crystal structure of PVDF polymers, one tends to apply mechanical stretching and high-voltage polarization to PVDF polymers. The all-trans TTT conformation is directional and can be used to prepare PVDF with high β-phase by stretching [6], spin-coating [7], solution casting [8] and traditional electrospinning method [9]. In order to further improve the electrical properties of PVDF fibres or films, it is common practice to add additives, such as clay, salt, nanoparticles, ionic liquids, etc [10]. For example, Lopes et al. [11] prepared PVDF films with 0, 5 and 10wt.% [Emim] BF4 by solvent casting method, and the content of β-phase was significantly improved. When the added amount was 10wt.%, the content of β-phase exceeded 60%. Thakur et al. [12] confirmed the formation of an electroactive β-phase in the PVDF matrix after the addition of clay minerals. Damaraju et al. [13] prepared PVDF fibres by electrospinning method and the presence of β-phase was 25% at 72kV.

However, the methods of preparing PVDF fibres or films with high β-phase, such as casting, stretching and electrostatic filament imitation, are still not suitable for the complex shapes of wearable products, and the special shape of PVDF still require subsequent cutting and other processes. In order to solve the above problems, some scholars use a new near electric field 3D printing method to prepare PVDF fibres or films [14]. The near electric field 3D printing method can prepare PVDF fibres at lower voltages and closer distances and can make fibres or films with specific shapes according to predefined trajectories, and parameters such as size and thickness can be controlled [4,15]. In the preparation process, the traction of the PVDF dipole by the electric field and the mechanical traction force generated by the mutual motion between the needle and the collector make the prepared PVDF contain a high β-phase without post-processing such as stretching and polarization [16-20]. Therefore, the PVDF with high β-phase prepared by near-electric field 3D printing method not only has excellent electrical properties but also can be customized in shape. It greatly reduces the steps and production costs of device preparation and provides a new idea for the preparation of PVDF intelligent fabrics and devices [20]. However, there are still some technical problems to be solved in this kind of manufacturing method, such as insufficient manufacturing accuracy, inability to produce in large quantities and many influencing factors.

Conclusion

PVDF has the characteristics of high flexibility, good piezoelectric performance, and chemical stability, which have broad application prospects in the field of intelligent fabric applications. The piezoelectric properties of PVDF depend on its β-phase content and orientation. Solution casting method, electrospinning method, stretching and adding nano-additives can obtain PVDF with high β-phase content, but they cannot meet the complex shape requirements of wearable products at one step. Near-electric field 3D printing method is a new type of auxiliary printing technology. Due to the addition of electric field and mechanical stretching in the printing process, the prepared PVDF fiber and film have excellent piezoelectric characteristics without post-polarization treatment, and the near-electric field 3D printing method can customize the shape of PVDF film. There is no need for tailoring and other processing when preparing intelligent fabrics and other devices, which greatly reduces the steps of preparation and reduces the production cost and provides a new idea for the preparation of intelligent fabrics and PVDF devices.

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