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Electromechanical deformation sensors based on polyurethane/polyaniline electrospinning nanofibrous mats

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ABSTRACT

Conducting electrospun nanofibrous mats elicit great interest in a wide range of applications. In this paper, polyurethane/polyaniline (PU/PANi) mats were prepared via the elecrospinning route with a polyurethane/dimethyl formamide spinning solution, and then in situ chemical polymerization of aniline monomers on the surface of PU nanofibers to deposit conductive PANi layer. In details, the morphology and structure of the PU/PANi mats were characterized by SEM, FTIR and the results indicated that the polyaniline stably deposited on the surface of polyurethane nanofiber. The electrical conductivity measurements indicated PU/PANi mats expressed good electrical conductivity (0.43 S/cm) at the optimal polymerization time as 120 min. As expected, PU/PANi mats showed strain sensitivity of $(R\text{-}R_0)/R_0 = 0.75$ (curvature = 0.4 cm^{-1}) and the average strain gauge factor could reach 17.15 with applied stretching deformation (0 ~ 110%). Therefore it could be deemed as the recommended nano-materials for flexible wearable device.

1. Introduction

Conductive polymers such as polyaniline, polypyrrle and polythiophene attracted tremendous attention due to a wide variety of applications, including anti-static coating [1–3], batteries [4–7], sensors [8–11], electrodes [12,13] and so on. Among these conductive polymers, polyaniline (PANi) might be the most promising because of its good environmental stability, ease of synthesis, thermal stability and an inexpensive synthetic route. However, as an intrinsically conducting polymer (ICP), the widely practical application of PANi is restricted by its limited processability, insolubility, infusibility and poor mechanical properties [8]. In order to overcome these drawbacks, many researchers attempted to introduce PANi with an insulating polymer matrix with high mechanical strength, e.g. rubber [14], textiles [15,16], plastic [17]. Especially, Polyurethane (PU) elastomer was receiving considerable attention for a large range of transducer and actuator applications. Furthermore, PU exhibited excellent flexibility, good film/fiber forming property and resistance to solvent and it could carry out the energy conversion between mechanical energy and electrical energy [18].

The remarkable composites with PU as elastomer substrate and PANi as electrical filler have attracted considerable attention during the last decade. The PU/PANi composites can be commonly classified into two categories based on the preparing procedure, the first type is surface-modified PU/PANi whose structure is composed by the inner substrate PU substrate and the outside deposited PANi layer, the other type is volume-modified PU/PANi which is blended with PU and PANi under certain weight ratios. Hrehorova et al. [19] pointed out that surface-modified PU/PANi film possessed lower percolation threshold level than volume-modified PU/PANi ones, therefore, surface-modified PU/PANi composite materials can be recommended as an ideal candidate for electromechanical strain sensors. Prabhakar et al. [20] modified PU films with PANi and PANi-AgNp and could render the surface conductive, suggesting potential application in electrochemical

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biosensors. Gu et al. [21] prepared biomimetic artificial nanofibrous bundle using electrospun PU nanofibers deposited with PANi nanoparticles. In smart strain sensor application, Qin et al. [22] prepared elastic, conductive PU/PANi fiber by in-situ chemical oxidative polymerization of PANi on PU fiber surfaces. And the average strain gauge factor of resultant functional fiber could reach to 3 which is 1.5 times higher than normal case. As we all know, nanofiber with high specific surface area, ultrathin and flexible properties could show some advantage performances in strain sensor area. Nanofiber sensor could contact with human skin in a more compact interface owing to its ultrathin and flexible structure. It could also perform isotropic strain response owing to its random nonwoven structure. In addition, more PANi nanoparticles could deposited on the substrate nanofiber owing to its higher specific surface area character.

Therefore, depositing PANi nanomaterials onto flexible PU materials was seemed as a reasonable route to produce a novel strain sensors for monitoring minute structural deformations or damage detection. Compared with the structure of conventional macro-conductive PU fiber, electrospun flexible PU nanofibers could provide extraordinarily high surface area/volume ratios, lightweight, flexible and designable multifunctionalities. These outstanding structure properties might be helpful for the performance of PU/PANi strain sensor and the detailed results will be investigated in this paper. Moreover, after deposited with PANi layer, electrospun PU/PANi nancomposite fiber mats had no specific direction sensing and provided multidirectional and multipoint strain sensing, similar to carbon-nanofilm strain sensors [23].

In this paper, PU nanofiber mats were prepared through the elecrospinning process and used as substrate for the preparation of conducting nanocomposites. It was reported that in situ polymerization was a reasonable method for preparing PANi-coated materials because it did not result in the damage of the substrate and enhanced conductive properties [24]. So we prepared PU/PANi fiberous nanocomposite through in situ chemical polymerization of aniline monomers on the surface of the PU nanofibers. And then its electrical properties were measured and the strain sensitivity was discussed.

2. Experimental

2.1. Materials

Polyurethane (PU) was purchased from Huakai resin Co., Ltd., China. Aniline monomer (ANI) was commercially available from Tianjin Guangfu technology Co., Ltd., China. Ammonium persulfate (APS) (≥99.5%), hydrochloric acid (HCl) (37%) was supplied by Tianjin Guangfu technology Co., Ltd., China. Dimethyl formamide (DMF) (≥99.5%) and alcohol (≥99.7%) were purchased from Tianjin Fuyu chemical Co., Ltd., China. All the chemicals used were of analytical grade and were used as received.

2.2. Preparation of polyurethane/polyaniline fiberous nanocomposites

The prepared process of polyurethane/polyaniline fiberous nanocompsites was shown in Fig. 1. Suitable amount of polyurethane was dissolved in *N*,*N*-dimethylformamide (DMF) with a concentration 20 wt.%. The mixture was continuously stirred until a homogeneous solution formed. This solution was fed into a 5 mL syringe with a stainless steel needle and the syringe attached to an electrospinning apparatus. The flow rate of the solution kept constant at 0.1 mL/h. A voltage of 20 kV was applied directly to the spinneret. And the distance between the needle tip and the collector was maintained at 12.5 cm.

Polyurethane/polyaniline (PU/PANi) nanofibrous mats were prepared through in situ chemical polymerization of aniline monomers on the surface of the as-obtained PU nanofibers. In the typical procedure, aniline monomers were dissolved in ethanol solution (the volume ratio of aniline to ethanol at 1:4) and PU nanofibrious mats were first immersed in the solution for 2 h. And then PU nanofibers were removed and placed into APS/HCl reactive solution and the concentration of APS and HCl was 30 g/L and 0.5 mol/L respectively. Under this condition, the polymerization

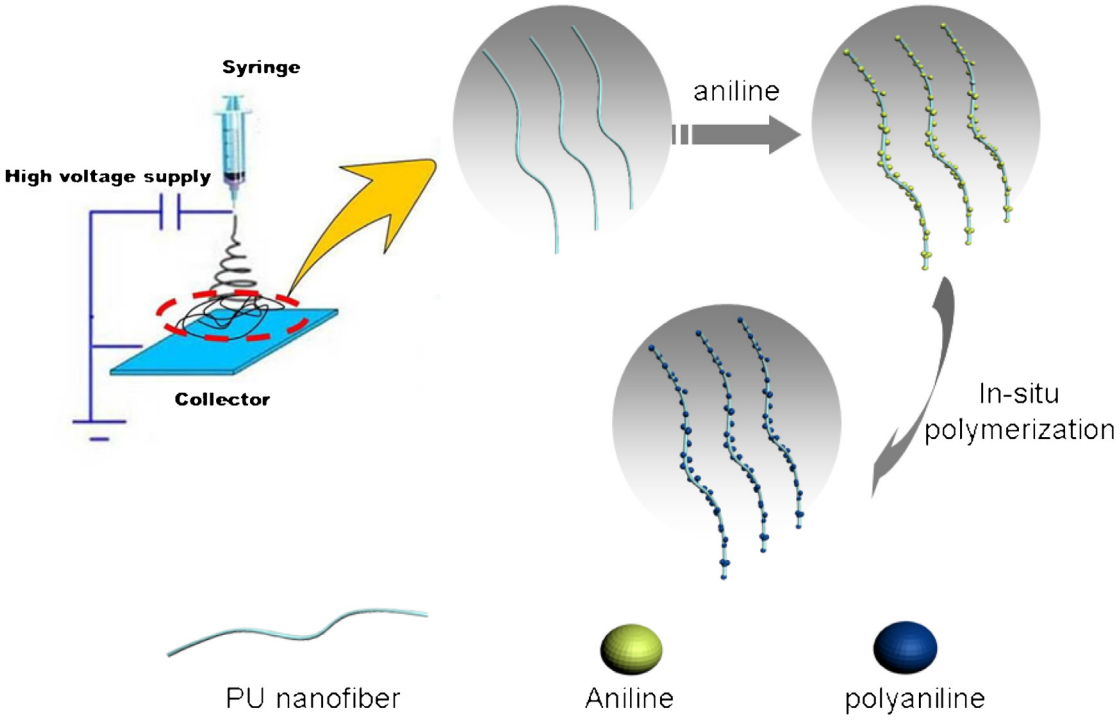

Fig. 1. The schematic process of polyurethane/polyaniline nanofibrous mats.