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Endurable conductivity of nylon fibers by interfacial grafting and aniline polymerization

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ABSTRACT

Interfacial grafting was combined with aniline polymerization to modify nylon fibers for high and endurable conductivity. A large amount of acrylic acid grafted to the surfaces of nylon66 fibers. The grafted polyacrylic acid further promoted in situ polymerization of aniline within the interfacial layer of nylon fibers. The electric conductivity of the final nylon fibers reached an unprecedentedly value of 1.1 S/cm. The presence of strong adhesion between polyaniline layer and nylon fibers further significantly promoted the rub resistance and water resistance of conductive fibers.

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1. Introduction

Design of conductive synthetic fibers and fabrics had long been recognized as the key technical hindrance to develop wearable electronics for health sensing, energy harvesting and storing *etc.* [1–3]. Nylon fibers (PA) were identified as one of the most widely used synthetic fibers due to their exceptional combination of tensile strength, solvent resistance and self-lubricating properties [4]. However, their high electric insulation frequently resulted in accumulation of static charge which might be very harmful. PANI was used to improve the conductivity of PA fibers through in-situ polymerization [5–8]. However, achievement of high and endurable conductivity still kept challenging for PA due to poor interfacial adhesion between PANI and nylon [5,9–11]. *Prior*-processed by surface treatments such as plasma [12], supercritical processing [13] and chemical etching [14] etc. had been investigate to improve the interfacial adhesion. Nevertheless, these fibers had their conductivity either far below the requirements of wearable devices or highly sensitive to water due to de-doping of PANI.

Herein we proposed a facial and scalable method to modify PA fibers with high conductivity, rub resistance and water resistance by combining grafting acrylic acid and aniline polymerization. Abundant carboxyl groups were homogeneously distributed on the surfaces of PA fibers, which strengthened the interactions with amino groups of PANI. The conductivity of the final fibers (PA-A-AN) reached to as high as 1.1 S/cm, which was one order of magnitude higher than other conductive nylon fibers in the literature [10]. Moreover, their conductivity had super water resistance and rub resistance, which promised potential applications in wearable electric devices.

2. Experimental section

Nylon66 fibers (0.5 g) were immersed in three-necked flask with 30% HCOOH for 20 min. 100 ml $KMnO_4$ solution and a certain volume of H_2SO_4, acrylic monomers (AA) were added under the protection of nitrogen to achieve the acrylic grated fiber (PA-A). After the reaction, the fibers PA-A were immersed in boiling water for 1 h, and then extracted by Soxhlet extractor for 12 h to remove the homopolymer on the fiber surface to calculate the grafting yield. Then PA-A were soaked in the solution (aniline 0.8 M, ammonium persulfate1 M, HCl 0.8 M) to complete the in-situ polymerization of the aniline monomer on the fiber surface at ice-water bath for 4 h. The final fiber (PA-A-AN) were repeatedly washed with deionized water to remove the residue and dried in an oven at 50 °C.

The resistance was tested by surface resistance tester (SL-030). Five different locations were measured randomly and averaged.

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FTIR-ATR spectra were taken on TGA-IR Vertex spectrometer (TGA-IR Vertex70). The fiber morphologies were examined by laser scanning confocal microscope (LSCM, LEXT OLS4100).

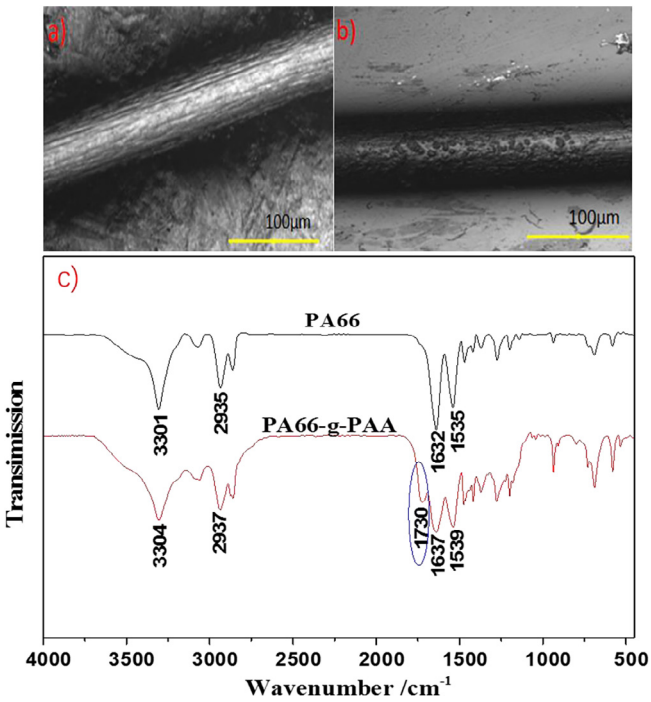

Fig. 1. Optical micrographs of (a) PA fiber, (b) PA-A fiber, (c) FTIR spectra of PA and PA-A fibers.

3. Results and discussion

3.1. The grafting reaction condition of PA-A fiber

Fig. 1(a and b) showed the optical micrographs of nylon fibers before and after acrylic acid grafting by LSCM. The successful grafting reaction was confirmed by the increasing roughness and appearance of micrometric dots on the smooth surfaces of nylon fibers. Fig. 1(c) showed the infrared spectra of PA and PA-A fibers. After the grafting reaction, a new FTIR absorption peak at 1730 cm^{-1} appeared, which was assigned to the specific absorbing peak of carboxyl groups. Blue shifts occurred also for C=O stretching in amide and N—H bending in secondary amide.

As shown in Fig. 2(a), a highest grafting rate up to 35% was achieved with the concentration of H_2SO_4 of 0.25 M. The decreasing grafting rate at higher concentrations of H_2SO_4 was resulted from the termination possibility of living chains because more Mn^{4+} reacted with macromolecular radicals.

Fig. 2(b) diescribed the influence of AA concentration on the grafting ratio. The initially increasing AA concentration promoted the grafting ratio till the AA concentration was 14% when the grafting rate of a maximum of 36%. Because the gel effect at higher monomer concentrations might retard the free radical polymerization [15].

Fig. 2(c) showed that the grafting ratio had a maximum value of 34% at 65 °C. This could be explained by the competition between chain growth and termination. The rate of chain initiation and growth were greater than the rate of termination below 65 °C because of the rapid diffusion of free radicals. Above 65 °C, the chain termination rate was greater than the chain growth rate, the monomer free radicals and macromolecular free radicals collided with each other which increased the probability of chain termination. The radical active points located in the nylon

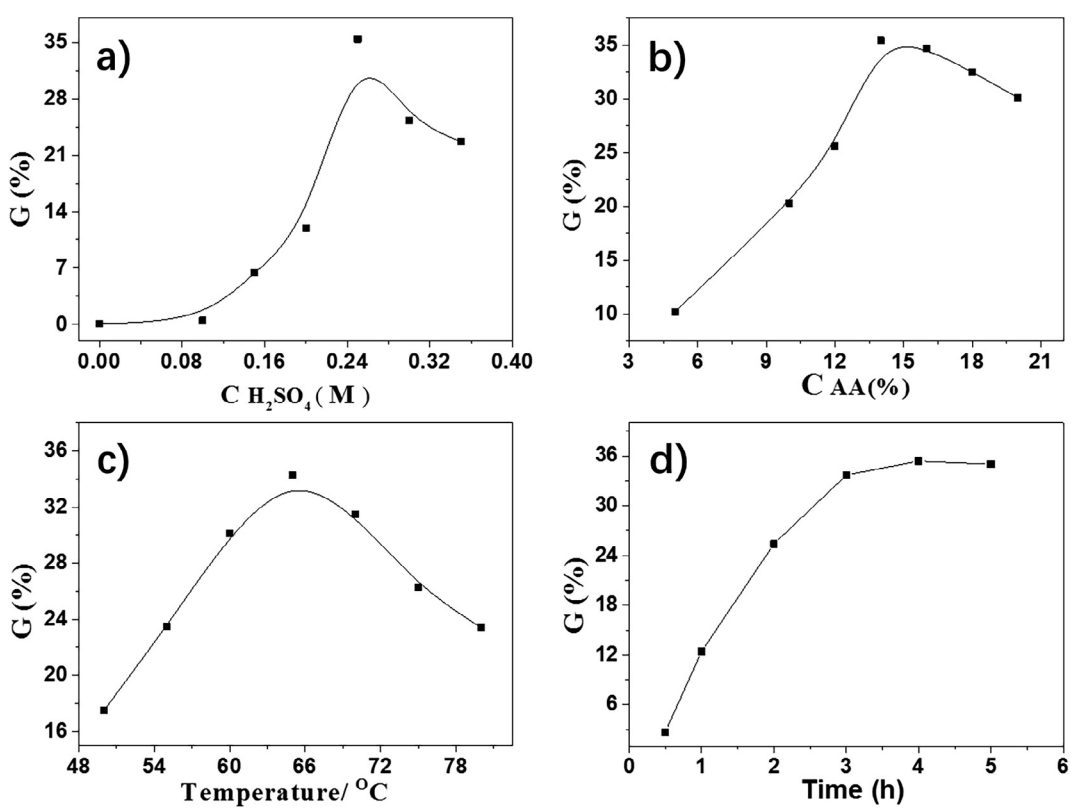

Fig. 2. Effect of experimental conditions on grafting reaction of PAA: (a) concentration of H_2SO_4, (b) concentration of acrylic acid, (c) temperature, (d) time.

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