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Preparation and properties of novel fishnet fibers with inhibitory effects on the adhesion of seaweeds

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Abstract A novel Nylon-6 fiber with the anti-adhesion of seaweeds was prepared for the use of fishnet by the technique of graft modification. The modification was performed by UV radiation-induced graft polymerization of Poly(acrylic acid) (PAA) onto Nylon-6 fibers, and to form crosslinked PAA hydrogels on the surface of them. The structure of the anti-adhesion fibers was investigated by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). The mechanical properties and water retention capacity were measured, respectively. Three kinds of seaweeds (Chlorella, Dunaliella and Chrysophyte) were employed to evaluate the inhibitory effects on the adhesion. The results showed that Nylon-6 fibers modified by PAA hydrogels had a strong effect on the adhesion of the three kinds of seaweeds. The effects were improved with the increase of the grafting amount. Results from the mechanical analysis revealed that the tensile strength of the modified fibers decreased, however, the ratio of elongation increased with the increase of the grafting amount. The novel fibers also showed a good water retention capacity.

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Introduction

With the marine pollution becoming more and more serious, the adhesion of marine organisms, such as seaweed, shellfish, and other invertebrates, to the ship hulls, fishnets and some other marine facilities has been one of the most serious environmental problems in the world. Fishnet is one of very practical tools in the fisheries industry, and most of fishnets are made of Nylon-6, which can be easily adhered by the seawater microbes, especially seaweed. The adhesion of the seaweed can do much harm to the mariculture and bring about much trouble to the fishers. Therefore, anti-adhesion has recently received considerable attention all around the world. Many conventional methods, such as surface-coating chemicals, can only make the marine pollution from bad to worse [1]. So the development of a new method to replace the conventional ones is of considerable interest.

At present, hydrogel materials with no harmful chemicals appear to be very useful for an adhesive inhibitor of marine organisms [1]. As hydrogels have crosslinked hydrophilic polymeric networks, they show many fascinating properties. Some hydrogels exhibit swelling behaviors in response to changes in environment, such as pH, temperature, ionic strength, electrical field, solvent, stress, light and so on. They have been extensively applied to drug delivery, switch control, mass separation, molecular recovery, etc. [2–5]. Crosslinked PAA hydrogels, as a well-studied stimuli-responsive hydrogels, has the novel nature against the adhesion of seaweed. In our earlier studies, we have reported that PAA hydrogel was fit to be used as inhibitory attachment materials since the germination ratio of attached spore on the surface of these hydrogels is nearly zero [6]. During the polymerization of acrylic acid (AA) to PAA, PAA hydrogel was formed at the

same time. Therefore, a method of surface-coating PAA hydrogels by graft-modification of the fibers maybe get unthinkable inhibitory effects on the adhesion of seaweed.

The present work focuses on the development of a convenient technique for preparation of the modified Nylon-6 fishnet materials for the anti-adhesion of marine organisms. Nylon-6 substrate of the fishnets fibers was used for UV-induced grafting. The monomers used were AA, forming surface-coating PAA and its crosslinked hydrogels with different degree of grafting and hydrophilicity [7–13]. The structure and surface characterization of the modified fibers were studied, and the inhibitory effect of the modified fibers on the adhesion was tested for the presence of different kinds of seaweeds, such as Chlorella, Dunaliella and Chrysophyte.

Experimental section

Materials

Nylon-6, in the form of fibers, was used as substrates for modification. The fibers with a diameter of about 0.7 mm cut from a new fishnet supplied by Tianjin Fishnet Group Co. (China). AA monomer was obtained from Tianjin Chemical Reagents Co. (China) and distilled at 50 °C under a reduced pressure of 5 mmHg to remove hydroquinone mono-methyl ether inhibitor and stored at –20 °C. Ammonium iron (II) sulfate hexahydrate as inhibitor was supplied by Chemical Plant of Tianjin University (China). Seaweeds used in this work are Chlorella, Dunaliella and Chrysophyte, which were cultured by School of Marine Science & Engineering of Tianjin Science & Technology University (China).

Preparation of modified Nylon-6 fibers

The samples of the fibers were prepared with two different lengths in terms of the experimental use. Some ones were cut into pieces about 2 cm in length, and the others about 15 cm. All the fibers were kept in a beaker filled with benzene for about 24 h to remove the grease adhered on the surface of them, then took the fibers out of the benzene and dipped in absolute alcohol for 20 min to wash the benzene out of them. At last, those fibers were washed with deionized water, dried and weighed.

The surface modification was performed by UV irradiation of the Nylon-6 fibers in the atmosphere at room temperature with a 100 W low-pressure mercury lamp. The main wavelength of the UV radiation from the lamp was approximate 254 nm, and the radiation distance was about 30 cm, irradiation time was controlled from 6 to 24 h, according to the experiment demands.

After the UV radiation-induced treatment, the fibers were immediately transferred into 200 cm^3 graft aqueous solution in a three-necked flask with churn-dasher. The graft aqueous solution consists of 0.46 mol/dm^3 sulfuric acid and 0.002 mol/dm^3 ammonium ferrous sulfate hexahydrate salt. At the same time, the AA monomers was weighed according to the experiment demands and trickled into the flask via a tundish. The grafting process was performed in a nitrogen atmosphere at 70 °C.

After grafted for some time, the grafted fibers were extracted in deionized water overnight to remove monomer residuals and homopolymer, and were dried and measured subsequently. Then the extraction process of the grafted fibers was repeated again till the weight of the fibers was invariable [14, 15]. The grafting amount was calculated according to Eq. 1:

$$\text{Grafting amount } (\%) = 100(W_2 - W_1)/W_1 \quad (1)$$

where W_1 and W_2 were the weight of the substrates of dry fibers before and after grafting, respectively.

Characterization

The FT-IR spectra were recorded on a Bruker spectrophotometer. The samples of the fibers before and after modification were powdered and mixed with KBr, and pressed to produce films. To determine the surface coverage of fibers grafted with PAA and its hydrogels, SEM was used. The surface and cross section of the substrates before and after modification were coated with gold before the analysis, which were performed with a Quanta-200 scanning electron microscopy.

Mechanical properties of the fibers (about 15 cm in length) before and after modification were measured with tensile test machine (PC/LLY-06, Lanzhou Electron Instrument, China) at drawing speed of 20 mm/min. All measurements were performed with five samples for an average.

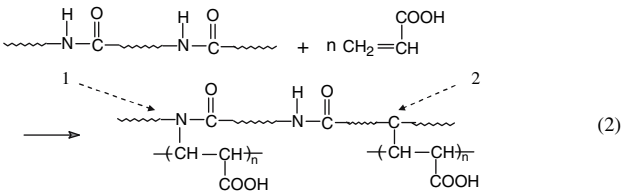
The fibers before and after modification were put into two same culture dishes, filled with 10 cm^3 autoclaved seawater respectively, which contains culture medium and some kinds of seaweeds easily adhered to the fishnet, from Chlorella, Dunaliella to Chrysophyte in turn. The culture experiment were carried out at 20 °C for 2 weeks under a cool white fluorescent lamp, then took out the fibers and washed with deionized water for 10 s. The adhesion and development of the seaweed on the fibers were observed under an optical microscope (JVC Color Video Camera, Japan). Ten fields of vision were selected at random, and took count of the number of seaweeds accreted in every field of vision for average.

Results and discussion

Characterization of the graft copolymer

The mechanism of UV radiation-induced grafting AA onto Nylon-6 fibers can be explained with two reasons. At first, the nitrogen atom in the amido bond of Nylon-6 macromolecule can be the grafting site, and can react with AA [16] (arrowhead 1 in the Eq. 2). Second, UV irradiation of the surface of Nylon-6 fiber results in the formation of instable peroxide species and different kinds of stable oxidized groups. The instable peroxide species can be decomposed by the heat to produce free radicals as peroxide groups at the surface of the fibers, which also can be the grafting site to be used for the graft coupling of monomer AA (arrowhead 2 in the Eq. 2).

In conclusion, through the interaction of free radicals and these active groups present in the Nylon-6 main chain with the acrylic acid monomer, the AA could be initiated and polymerized at these grafting sites to form graft copolymer, the reaction of graft copolymerization was realized. The reaction can be represented as follows.



(2)

To characterize the structure of the modified fibers, SEM and FT-IR spectra were investigated. Figure 1 shows that compared with the curve of unmodified fibers (a), there is a band around 1709.80 cm^{-1} in the curve of modified ones (b), which is from the carboxyl of PAA molecules.

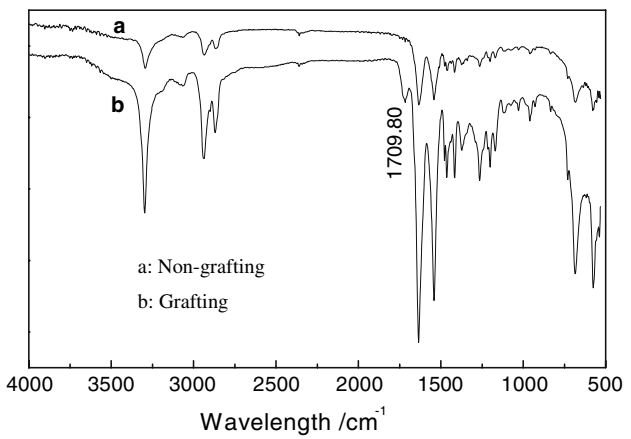


Fig. 1 FT-IR spectra of Nylon-6 (a) and modified Nylon-6 (b)

Figure 2 shows that in the cross section micrographs, the unmodified fiber has a perfectly smooth surface, whereas a thin, evenly distributed coating can be observed on the Nylon-6-g-AA fiber. The SEM micrographs in combination with the FT-IR spectra results suggest that homogeneous coating of PAA and its hydrogels on the Nylon-6 fiber taken place.

Water retention capacity of the modified fibers

As has been mentioned, PAA hydrogel has the swelling capacity in water due to its hydrophilic groups and cross-linking structure. Accordingly, it is expected that the water uptake of Nylon-6 fibers should be increased after modification with AA. This increase can be taken as evidence of grafting. Thus, the measurement of swelling in water is a simple and useful technique to characterize the fibers modified with hydrophilic monomers. The variation of the swelling ratio was illustrated in Fig. 3. It shows that the swelling ratio in water increased with increasing the immersing time and then the curve tended to level off. It suggests that the interaction through bonding of the carboxylic groups on the modified fibers with water molecules occurs. At the same time, with the increase of grafting amount, the equilibrium-swelling ratio of the fibers increased too.

The anti-adhesion of modified fibers

To confirm the viability of different kinds of marine seaweeds on untreated Nylon-6 fibers, adhesion of three kinds of seaweeds were investigated at first. Figure 4 summarizes the temporal variations of the adhesion for Chlorella, Dunaliella and Chrysophyte. It can be observed that various kinds of the seaweeds had different abilities in adhesion on the fibers under the same circumstances. Chlorella as a kind of green alga attached on the fiber more easily, compared with Dunaliella and Chrysophyte. With extending the culture time, the average adhesive number in one visual field increased rapidly. Therefore Chlorella was selected to evaluate the anti-adhesion of the modified fibers.

The germination of Chlorella on the modified Nylon-6 fibers with different grafting amount was investigated and shown in Fig. 5. It suggests that compared with the untreated ones, the average adhesive number in one field of vision on the modified fibers showed a drastic decrease with the same culture time. This indicated that the development and growth of Chlorella were greatly restrained by the surface-coating PAA hydrogels, and with the culture time increasing, the adhesion amount tends to level off. Furthermore, with the increase in the degree of grafting

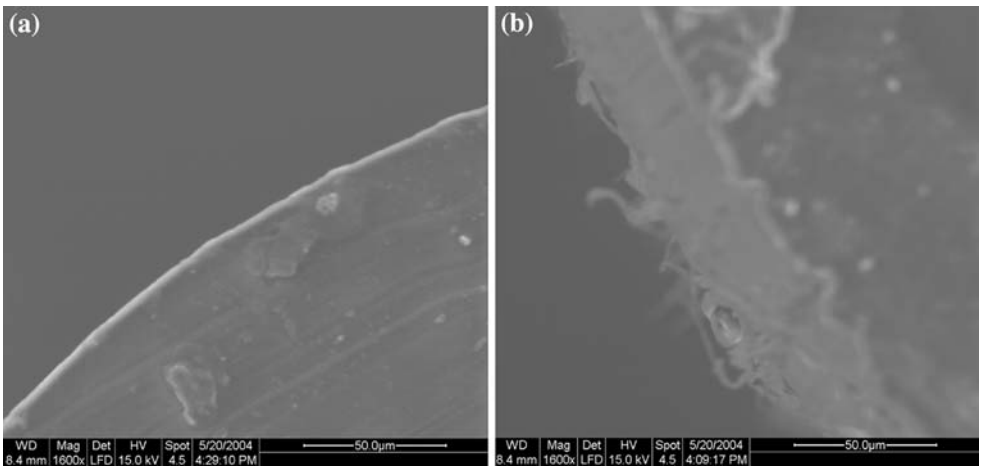


Fig. 2 SEM photographs of the sections of Nylon-6 and modified Nylon-6 fibers: (**a**) Nylon-6; (**b**) modified Nylon-6

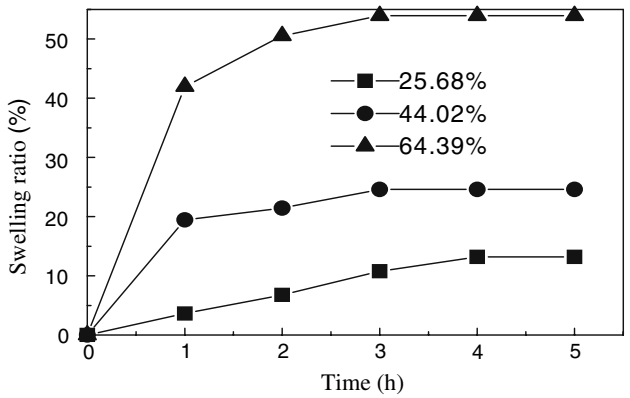


Fig. 3 Influence of the grafting amount on the equilibrium swelling ratio of the fibers (25 °C)

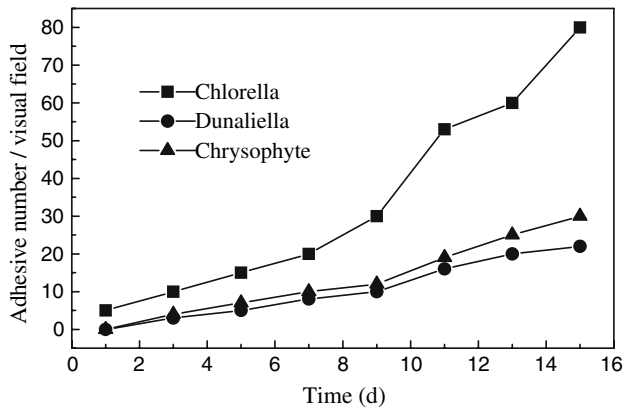


Fig. 4 Behaviors of the three kinds of seaweeds adhered on untreated Nylon-6 fibers

from 4.5 to 18.35%, the average adhesive number reduced. These results show that degree of the modification had a strong effect on the germination of Chlorella. The higher of the grafting amount, the lower of the adhesion of the Chlorella. These results may be due to the reason that fibers

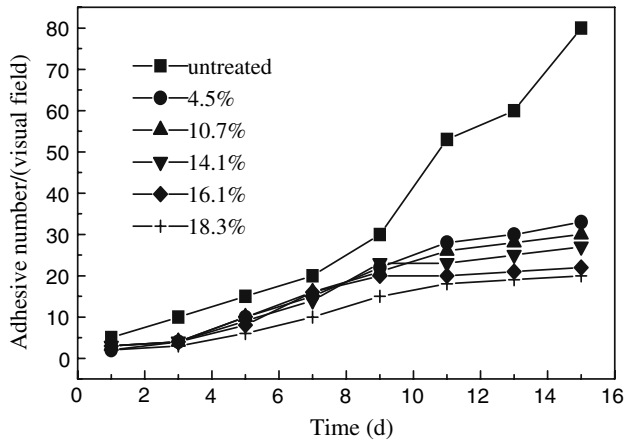


Fig. 5 Behaviors of the Chlorella adhered on Nylon-6 fibers before and after modification

modified with PAA and its hydrogels had anionic surfaces, which disturbed the development and propagation of the seaweeds.

It is also found that the adhesion of Dunaliella and Chrysophyte on the novel Nylon-6 fibers obtained by the same methods above also show similar behavior of anti-adhesion. Therefore the modified Nylon-6 fibers have the inhibitory effect on the adhesion of seaweeds.

Mechanical properties of the modified fibers

The modification had great effect on the mechanical properties of the fibers especially the tensile strength and ratio of elongation. As shown in Fig. 6, the tensile strength dramatically decreased and yet the ratio of elongation gradually increased, with the increase of grafting amount, as a result of the treatment of UV radiation and grafting. UV radiation destroyed the surface of the fibers for the macromolecule degradation occurred during the irradia-

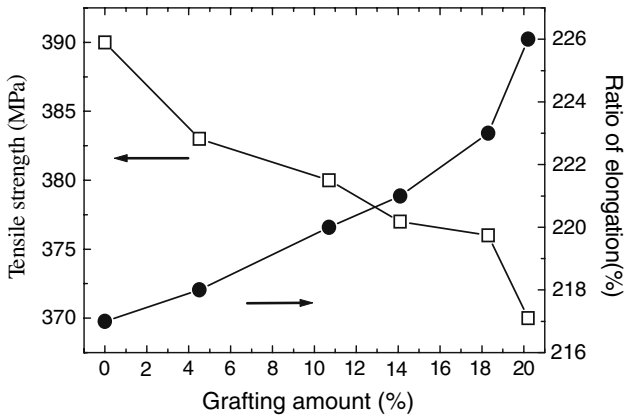


Fig. 6 Influence of modification on tensile strength and ratio of elongation of the fibers

tion, but the grafting of PAA increased the flexibility of the whole fiber for the crosslinked structure of the hydrogels. Therefore it should not obtain good inhibitory effects just by increasing the grafting yield with overlooking the mechanical properties.

Conclusions

A novel fishnet fiber was obtained by UV radiation-induced graft polymerization of PAA onto the substrate of Nylon-6 fibers to form surface-coating hydrogels. The novel fibers show strong anti-adhesion of the three kinds of seaweeds. The anti-adhesion was enhanced with the increase of the grafting amount. Modification brought about some change to the water retention capacity and mechanical properties of the fibers. The tensile strength of the modified fibers decreased with the increase of the grafting amount, however, the ratio of elongation and equilibrium swelling increased. The novel fiber can be used as fishnet materials for anti-adhesion in marine applications.

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