Novel Fishnet Fibers with Anti-adhesion of Seaweeds Obtained by UV-Irradiation Technique

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ABSTRACT: A novel Nylon-6 fishnet fiber with the anti-adhesion of seaweeds was prepared by UV radiation-initiated grafting of acrylic acid (AA) onto Nylon-6 fibers, and its structure was characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The influences of grafting conditions, such as irradiation dose, temperature, concentration of monomer, inorganic acid, and inhibitor etc., on grafting rate were studied, and the antiadhesion of seaweeds was evaluated with Dunaliella. The results showed that the grafting amount of Nylon-*g*-AA was increased with the increase of irradiation time. With the increase of concentration of AA, temperature, reaction time, inorganic acid, and inhibitor, the grafting amount increased firstly and then decreased, respectively. Nylon-6 fibers modified by Poly(acrylic acid) (PAA) had a strong effect on the adhesion of Dunaliella, and the antiadhesion was improved with the increase of the grafting amount. Results from the mechanical analysis revealed that the tensile strength of the UV-irradiation fibers decreased. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1252–1256, 2007

Key words: fibers; radiation; graft copolymers; hydrogels; adhesion

INTRODUCTION

In recent years, the adhesion of marine organisms, such as seaweeds, 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.[1] Many conventional methods, such as surface-coating chemicals, can only make the marine pollution from bad to worse.[2] So there has been a resurgence of increasingly difficult problems passed by our growing need to recover valuable materials to prevent or correct damage to the sea environment.

In our earlier studies, we have reported that Poly (acrylic acid) (PAA) hydrogels, as a well-studied stimuli-responsive hydrogels, had the novel nature against the adhesion of seaweeds and 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.[3] So the development of a new method to attach PAA hydrogels onto Nylon-6 fishnet fibers is of considerable importance.

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Radiation-initiated grafting covers a very broad field of polymer chemistry with numerous potential applications of industrial uses over the last 30 years.[4–10] Functionalized graft copolymers prepared by radiation grafting method may be of great interests in antiadhesion technology and as one of the tools to overcome such problems.

In the present work, the modified Nylon-6 fishnet materials for the antiadhesion of marine organisms were prepared by UV-initiated grafting. The monomers used were AA, forming surface-coating PAA and its crosslinked hydrogels with different degree of grafting and hydrophilicity. The grafting conditions and properties of the novel fibers were studied.

The mechanism of UV radiation-initiated grafting of AA onto Nylon-6 fibers can be explained with two reasons. On the one hand, the nitrogen atom in the amido bond of Nylon-6 macromolecule can be the grafting site, and can react with AA.[11] On the other hand, 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 suitable monomer like AA.

Through the interaction of free radicals and these active groups that existed in the Nylon-6 main chain with the AA monomer, the AA could be initiated and polymerized at these grafting sites to form graft copoly-

mer, the reaction of graft copolymerization was realized. The reaction can be represented as eq. (1).
During the graft copolymerization, crosslinked PAA hydrogels was obtained synchronously, for PAA is very active to self-crosslinking to form its hydrogels.

EXPERIMENTAL METHODS

Materials

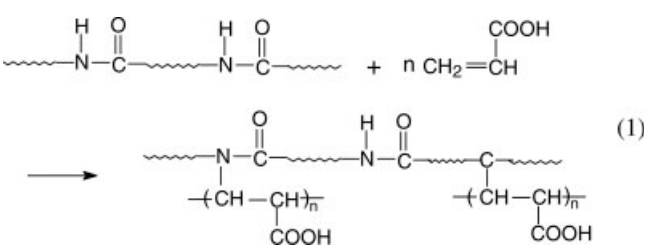
Nylon-6, in the form of fibers, was used as substrates for modification. The fibers with a diameter of about 0.7 mm were cut from a new fishnet supplied by Tianjin Fishnet Group Co. (China). AA monomer was obtained from Tianjin Chemical Reagents Co. (China) and distilled at 50°C under a reduced pressure 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). Seaweed used in this work is Dunaliella, cultured by the School of Marine Science and Engineering of Tianjin Science and Technology University.

Preparation of nylon-6-*g*-AA fibers by UV-irradiation

Nylon-6 fiber samples with the lengths of about 2 cm and 15 cm were prepared respectively. All the fibers were kept in a beaker filled with benzene 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 UV irradiation of the Nylon-6 fibers was carried out in nitrogen atmosphere at room temperature with a 100 W low-pressure mercury lamp. The main wavelength of the UV eradiated from the lamp was approximately 254 nm, and the radiation distance was about 30 cm, irradiation time was controlled according to the experiment demands.

After the UV-radiation initiated treatment, the fibers were immediately transferred to the graft solution, which was prepared by diluting concentrated sulfuric acid and dissolving ammonium ferrous sulfate hexahydrate salt in equal amounts (200 mL) of deionized water in a three-necked flask with churn-dasher according to the percentage. At the same time, different amount of AA monomers (weight percentage from 10 to 30%) were weighed and trickled into the flask via a tundish. The grafting process was performed in a nitrogen atmosphere, and the temperature of the graft copolymerization was conducted at different temperatures from 50°C to 90°C.



Scheme 1

After grafted for some time, the fibers were then extracted and dried, and the grafting amount was calculated according to eq. (2):

$$\text{Grafting amount } (\%) = 100\ (W_2 - W_1)/W_1 \quad (2)$$

where W_1 and W_2 were the weights of the dry fiber substrates before and after grafting modification with UV-radiation, respectively.

Characterization

The FTIR spectra were recorded on a Bruker spectrophotometer from 4000 to 500 cm^{-1}, and SEM (Quanta-200 scanning electron microscopy) was used to determine the surface coverage of fibers grafted with PAA.

Mechanical properties of 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 mL autoclaved seawater respectively, which contained some culture medium and some Dunaliella. Culture experiments were carried out at 20°C for two weeks under a cool white fluorescent lamp, then the fibers were taken out and washed with deionized water for 10 s. The adhesion of the development of the Dunaliella was observed under an optical microscope (JVC Color Video Camera, Japan). Ten fields of vision were selected at random, and the amount of seaweeds in every field of vision was taken count of for average.

RESULTS AND DISCUSSION

Characterization of the graft copolymer

FTIR spectra shows that compared with the curve of unmodified fiber substrates, there is a band around 1709.80 cm^{-1} in the curve of UV-initiated grafting ones, which is from the carboxyl of PAA molecules. For the SEM measurement of the broken-out section of the fibers, it can be seen that the unmodified fiber has a perfectly smooth surface, whereas a thin, evenly distributed coating can be observed on the Nylon-6-*g*-AA fiber. These results suggest that homogeneous coating of PAA on the Nylon-6 fiber has taken place.

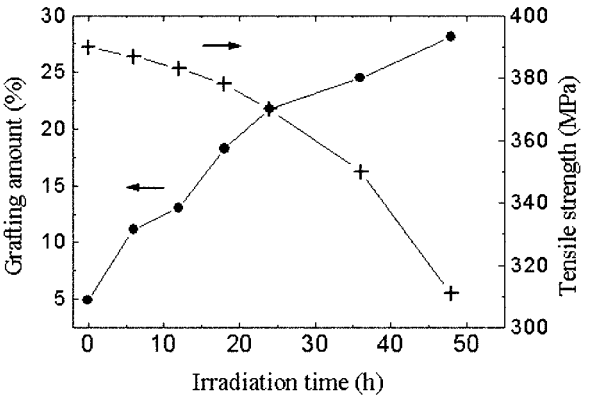


Figure 1 Effects of the irradiation time on the grafting amount and tensile strength of the fibers. Reaction conditions: 70°C, reaction time is 4 h, the concentration of AA is 20%, inhibitor is 0.05% and H_2SO_4 is 0.10 mol/L.

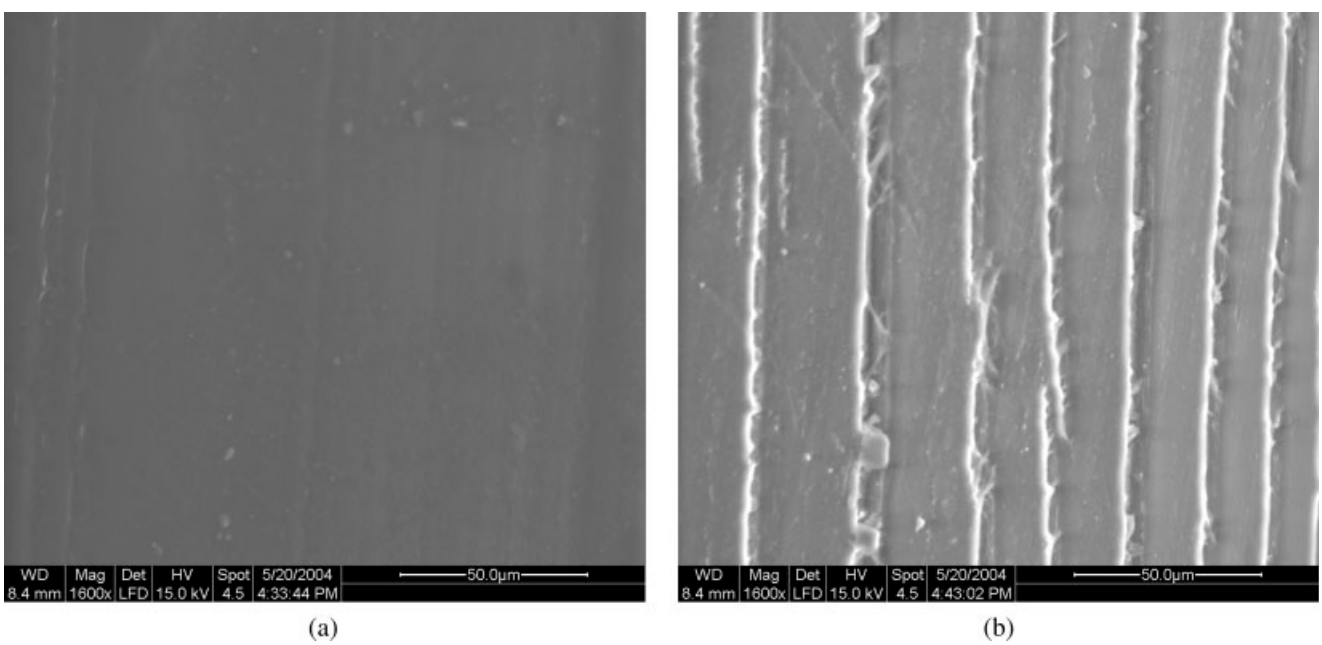
Effect of grafting conditions on grafting amount

As the radiation dose is one of the most important parameters determining the grafting amount,[8–9] the grafting amount of AA onto Nylon-6 depending on the irradiation was studied. The irradiation time had great effect on the graft copolymerization and the strength of the fibers. Figure 1 shows clearly that the grafting amount increased with increasing the time of UV-irradiation, which can be attributed to the increase of free radicals initiated by UV. Generally speaking, UV-radiation can only activate the surface macromolecules of the polymer. But enhancing the radiant intensity can make the interior macromolecules be activated to produce free radicals. Lengthening the irradiation time was equivalent to enhance the radiant intensity, so the longer UV irradiated, the more free radicals produced.

As one of the most important characteristics, the changes of mechanical properties of the modified fibers were studied. Figure 1 shows that the tensile strength of the modified fibers dramatically decreased with the increase of the irradiation time. This is owing to the macromolecular degradation occurred during the irradiation, which destroyed the surface of the fibers. The SEM photographs in Figure 2 shows that compared with the unmodified one, a number of longitudinal cracks or grooves on the surface of the copolymer fiber irradiated by UV and grafted by AA can be seen clearly. Therefore it should not just to increase the grafting amount by prolonging the time of irradiation for the fishnets fibers.

The influence of the concentration of AA monomer on the grafting amount was investigated by varying the concentration. Figure 3 indicated that the influence of AA concentration on the graft copolymerization could be divided into two stages: when the concentration of AA is under 20%, the grafting amount was increased with the increase of the concentration. However, when the concentration of AA is higher than 20%, the grafting amount was relatively decreased with the increase of the concentration.

Increasing concentration of AA may increase the concentration of PAA, both grafted for copolymerization and ungrafted for homopolymerization consequently, which will result in increased viscosity of the solution. In a general way, the grafting is known to occur by the front mechanism where the grafting



(a) (b)

Figure 2 SEM photographs of the surface of Nylon-6 (a) and Nylon-6-*g*-AA fibers (b). Reaction conditions: 70°C, reaction time is 4 h, the concentration of AA is 20%, inhibitor is 0.05% and H_2SO_4 is 0.10 mol/L.

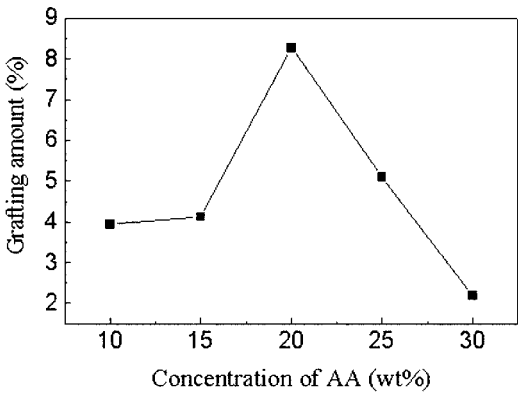


Figure 3 Influence of the concentration of AA on grafting amount. Reaction conditions: 70°C, irradiation time is 8 h, reaction time is 4 h, the concentration of AA is 20%, inhibitor is 0.05% and H_2SO_4 is 0.10 mol/L.

starts at the surface and slowly proceeds inwards by the diffusion process. The grafted chains on the surface swell in the grafting medium, so allowing the diffusion of the monomer into the core of the fibers too. In the first stage, the increasing trend in grafting amount might be ascribed to the effect of the lower viscosity of the system to the diffusion of AA monomer, thereby more amount of monomer is available for grafting in the vicinity of the grafting sites, which resulted in higher degree of grafting. But in the second stage, high viscosity of the solution caused the hindrance in diffusion of the AA, and destroyed the competition between graft copolymerization and homo-polymerization, the efficiency of grafting decreased. To restrain the homopolymerization, the method of trickle of AA monomer was adopted.

The effect of the reaction temperature is illustrated in Figure 4. It shows that the grafting amount increased initially and then decreased after an optimum value of 70°C with the increase of temperature. As has been mentioned, there is the concurrence of copolymerization and homopolymerization in the system of graft solution containing polymer monomer and solvent. The efficiency of grafting

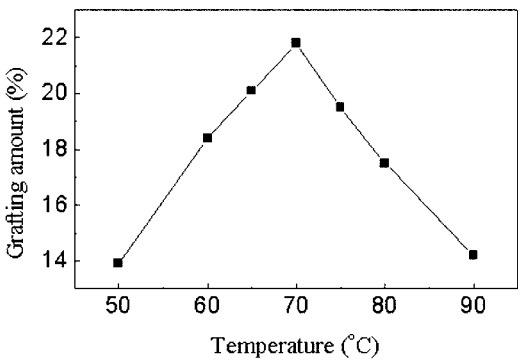


Figure 4 Influence of the reaction temperature on grafting amount. Reaction conditions: irradiation time is 24 h, reaction time is 4 h, the concentration of AA is 20%, inhibitor is 0.05% and H_2SO_4 is 0.1 mol/L.

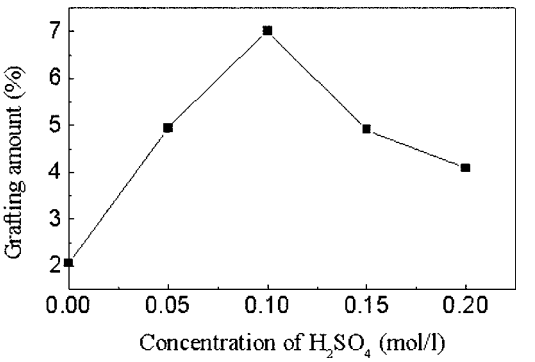


Figure 5 The influence of the concentration of H_2SO_4 on grafting amount. Reaction conditions: 70°C, irradiation time is 2 h, reaction time is 4 h, the concentration of AA is 20% and inhibitor is 0.05 %.

depends greatly upon the concentration of monomer and free radicals created on the fibers. In the reaction system, temperature played an important and complicated role in the graft polymerization. As shown in the eq. (3) of Arrhenius, temperature is one of the most important parameters in graft copolymerization kinetics.

$$k = Ae^{-E/RT} \tag{3}$$

where k represented the reaction velocity constant of the graft copolymerization, E was the activation energy, and T was the temperature of the reaction system, respectively.

It can be seen obviously that k is increased with the rising of the T. Heat can increase the yields of free radicals and strengthen their activities, and accelerate the movement of the chain segment of the macromolecular chain too. Heat also can speed up the diffusion of AA monomers. All those were highly advantageous to the grafting. So more graft copolymer could be obtained, and the grafting amount was increased too. On the other hand, the acceleration of the movement of the chain segment

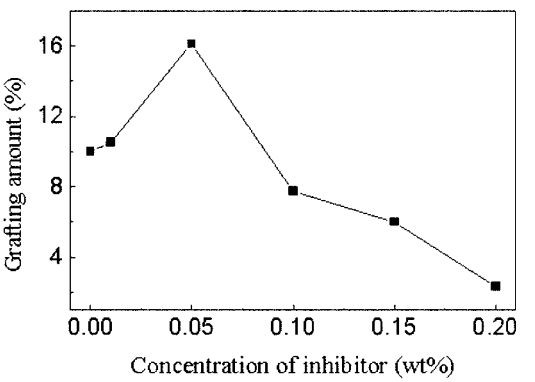


Figure 6 The influence of the concentration of inhibitor on grafting amount. Reaction conditions: 70°C, irradiation time is 15 h, reaction time is 4 h, the concentration of AA is 20%, H_2SO_4 is 0.10 mol/L.

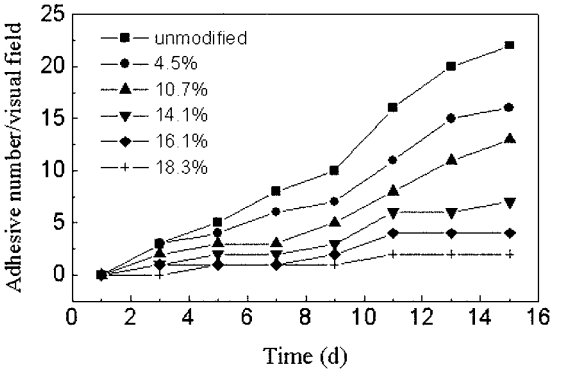


Figure 7 Behaviors of Dunaliella adhered on the Nylon-6 fibers before and after modification.

could increase the terminating of activated chains and free radicals simultaneously. Therefore the efficiency of grafting decreased accordingly.

Mineral acid added in the grafting system could be favorable for the graft copolymerization. In our work, sulfuric acid (H_2SO_4) was used to improve the grafting. The influence of H_2SO_4 on grafting system was studied as shown in Figure 5. The same trend was observed as AA on the graft copolymerization, it suggests that the percentage of grafting increased remarkably with an increase in the concentration of H_2SO_4, but it decreased slightly beyond the concentration of about 0.10 mol/L. In recent years, many in-depth studies have been in progress to demonstrate the mechanism of the effect of mineral acid on the graft copolymerization. Most people insisted that the function of the acid could increase the solubility of monomers in the systems to a certain extent, and also could increase the viscosity of the solution. Therefore after an optimum concentration of value of 0.10 mol/L, the grafting amount decreased.

During graft copolymerization, inhibitors are usually added to minimize the homopolymer formation.[9] Figure 6 shows that the effect of the concentration of ammonium ferrous sulfate hexahydrate salt on the grafting. It suggests that the grafting amount reached a maximum value when the concentration of inhibitor up to 0.05%, then declined. The result might be due to following reasons: (1) The homopolymerization of AA could be effectively restrained by ammonium ferrous sulfate hexahydrate salt acted as inhibitor, which improved the concentration of AA monomers to a greater extent. (2) Copolymerization of Nylon-*g*-AA could also be restrained by the inhibitor, and the influence became more and more bigger with the increase of the inhibitor concentration. So the grafting amount decreased in accordance.

The antiadhesion of modified fibers

To evaluate the viability of seaweeds on the modified Nylon-6 fibers, we investigated the germination and adhesion of Dunaliella on the fibers before and after modification. As a kind of green alga, Dunaliella attaches on the fiber more easily in the salt water. Figure 7 summarizes the temporal variations of the adhesion for the Dunaliella. It can be seen that the adhesive number in one field of vision on the modified fibers showed a drastic decrease with the same culture time, compared with the unmodified ones. And with the culture time increasing, the adhesion amount tends to level off. Furthermore, with the increase in the degree of grafting from 4.5% to 18.3%, the adhesive number reduced remarkably. This indicated that the development and growth of the Dunaliella were inhibited, and the degree of the modification had a strong effect on the germination of Dunaliella. The higher the degree of the modification, the lower the adhesion of Dunaliella. These results may be due to the reason that fibers modified with PAA and its hydrogels had anionic surfaces, which disturbed the development and propagation of the seaweeds.

CONCLUSIONS

The technique of UV-initiated grafting can be used to prepare a novel fishnet fiber with the antiadhesion of seaweeds. The antiadhesion of Dunaliella was improved with the increase of the grafting. The grafting amount increased with the increase of irradiation time, and increased firstly then decreased with the increase of concentration of AA, temperature, inorganic acid and inhibitor, respectively. Results from the mechanical analysis revealed that the tensile strength of the UV-irradiation fibers decreased.

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