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Post-Print Modification of Polyacrylonitrile by Krill Protein

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Abstract

Using water as the reaction medium, krill protein was activated with maleic anhydride and subsequently copolymerized with acrylonitrile to obtain krill protein maleic anhydride ester grafted polyacrylonitrile copolymer (AKPM-g-PAN). Wet spinning was then employed to prepare AKPM-g-PAN fibers, and their mechanical and thermal properties were investigated. The results indicate that the optimal formulation and conditions for preparing AKPM-g-PAN are: a mass ratio of AKP, maleic anhydride, and PAN of 2:2:12.5, initiator mass of 10% of the PAN mass, and a reaction temperature of 60°C. Under these optimal process conditions, the graft polymerization reaction yielded a polymer with a molecular weight of 1.58$×$10^5. The breaking strength of AKPM-g-PAN fibers increases with increasing spinning solution concentration, while it first increases and then decreases with increasing coagulation bath concentration and temperature. The incorporation of AKP enhances the water retention rate of the composite fibers but disrupts the original molecular chain regularity of polyacrylonitrile and diminishes part of its crystallization ability.

Full Text

Preamble

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Modification and Performance of Polyacrylonitrile with Maleic Anhydride Grafted Krill Protein

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Abstract

Using water as the reaction medium, krill protein was activated with maleic anhydride and then copolymerized with acrylonitrile to obtain a krill protein maleic anhydride ester grafted polyacrylonitrile copolymer (AKPM-g-PAN). AKPM-g-PAN fibers were subsequently prepared via wet spinning, and their mechanical and thermal properties were investigated. The results demonstrate that the optimal formulation and conditions for preparing AKPM-g-PAN are: a mass ratio of krill protein (AKP), maleic anhydride, and PAN of 2:2:12.5, initiator amount of 10% (mass fraction) relative to PAN, and a reaction temperature of 60°C. Under these optimal conditions, the graft polymerization yielded a polymer with a molecular weight of 158,000. The fracture strength of AKPM-g-PAN fibers increased with rising spinning solution concentration, while it initially increased and then decreased with increasing coagulation bath concentration and temperature. The incorporation of AKP enhanced the water retention rate of the composite fibers, but disrupted the regularity of the original PAN molecular chains and diminished their crystallization ability.

KEY WORDS organic polymer materials, polyacrylonitrile, krill protein, modification, wet spinning

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Introduction

With improving living standards, conventional synthetic fibers can no longer meet people' s demands, necessitating modification of existing synthetic fibers to achieve superior comprehensive performance. Polyacrylonitrile (PAN) fiber exhibits good bulkiness, elasticity, and thermal insulation, making it an ideal substitute for wool. However, due to its poor moisture absorption and tendency to generate static electricity, the modification of PAN has remained a research focus.

Antarctic krill is a marine organism with high protein content, regarded as a future protein resource reservoir for humanity. The amino acid composition of Antarctic krill protein shares structural similarities with human skin, which can impart good skin affinity when incorporated into fibers. Many countries are researching renewable protein fibers. In this study, refined Antarctic krill protein (AKP) was used as raw material. The protein was activated with maleic

anhydride to prepare a protein maleic anhydride ester, which was then copolymerized with acrylonitrile monomer to synthesize a protein maleic anhydride ester grafted polyacrylonitrile molecule (AKPM-g-PAN). Finally, AKPM-g-PAN fibers were prepared via wet spinning. The thermal properties, crystallinity, moisture absorption, and surface morphology of AKPM-g-PAN fibers were investigated to achieve comprehensive modification of polyacrylonitrile fibers.

Experimental

Materials

The raw materials used included krill powder, sodium hydroxide, acrylonitrile, potassium persulfate, hydrochloric acid, maleic anhydride, N,N-dimethylformamide, and dimethyl sulfoxide.

Preparation of AKPM-g-PAN

AKPM-g-PAN was prepared via aqueous solution precipitation polymerization. First, a certain amount of maleic anhydride aqueous solution was added to a three-neck flask, heated, and stirred until completely dissolved. Krill protein aqueous solution was then added dropwise via a separatory funnel over 1 hour. After continuing the reaction for 30 minutes, krill protein maleic anhydride ester (AKPM) was obtained. A predetermined amount of acrylonitrile monomer and potassium persulfate aqueous solution was subsequently added dropwise to this solution, and the reaction continued for 3-5 hours to yield AKPM-g-PAN. Orthogonal design was employed to optimize the formulation and process parameters, with the selected factors and levels listed in Table 1 .

Preparation of AKPM-g-PAN Fibers

A specified amount of AKPM-g-PAN (#9) was dissolved in dimethylformamide (DMF) to prepare the spinning solution. After standing to remove air bubbles, the solution was coagulated and shaped in a DMF-H_2O bath, then washed with water, stretched in hot water, and dried and set to obtain AKPM-g-PAN fibers.

Characterization

To determine the intrinsic viscosity of AKPM-g-PAN, 0.1 g, 0.2 g, and 0.3 g samples were dissolved in dimethyl sulfoxide in 25 ml volumetric flasks to prepare polymer solutions of different concentrations. The intrinsic viscosity was measured using an Ubbelohde viscometer at 25°C and atmospheric pressure, and the viscosity-average molecular weight was calculated using the Mark-Houwink equation where K and α are characteristic constants for the polymer-solvent system at a given temperature.

Fourier transform infrared (FTIR) spectra were recorded on a Spectrum One-B spectrometer using the KBr pellet method over the range of 4000-400 cm^{-1}. Thermogravimetric analysis (TGA) of the polymerized AKPM-g-PAN samples was performed on a TGA-Q50 analyzer under nitrogen atmosphere at a flow rate of 40 ml/min, heating rate of 20°C/min, and temperature range of 0-700°C. X-ray diffraction (XRD) analysis was conducted using a D/max3B diffractometer. The polymerized AKPM-g-PAN samples were ground into powder, spread on a glass slide, pressed into tablets with a spatula, and moistened with a few drops of ethanol. Test conditions were: tube voltage 20-60 kV, tube current 2.5-80 mA, Cu target, 2 range 0-60°, scanning speed 4°/min.

Differential scanning calorimetry (DSC) was performed on a Mettler DSC-2 instrument at a heating rate of 10°C/min over a temperature range of 0-400°C. The physical and mechanical properties of the fibers were tested using an LLY-06 electronic single-fiber strength tester. Each group was tested 10 times with a gauge length of 10 mm, stretching speed of 20 mm/min, at 20°C and 65% relative humidity. The microstructure of AKPM-g-PAN fibers was observed using a JSM-6360LV scanning electron microscope (SEM) after gold sputtering.

Results and Discussion

Reaction Mechanism Analysis

Since direct reaction between krill protein and acrylonitrile is difficult, maleic anhydride was introduced as an intermediate to connect the protein molecular chains with the polyacrylonitrile molecular chains. First, a small amount of water was used to dissolve the maleic anhydride, which hydrolyzed to generate -COOH groups before adding the protein to ensure sufficient reaction. Acrylonitrile monomer was then added under the action of the initiator $K_2S_2O_8$ to obtain AKPM-g-PAN. The reaction scheme is shown in Figure 1 [Figure 1: see original paper].

Analysis of AKPM-g-PAN Process Conditions and Molecular Weight

An orthogonal experimental design was employed with protein/maleic anhydride mass ratio (Factor A), acrylonitrile amount (Factor B), initiator amount (Factor C), and temperature (Factor D) as influencing factors to analyze their effects on polymer molecular weight. The molecular weight results are presented in Table 2 . The variation of polymer molecular weight with each factor was analyzed to determine the optimal graft polymerization conditions based on mean values and ranges.

The range values in Table 2 indicate that the order of factors affecting graft polymer molecular weight is: acrylonitrile amount > initiator amount > reaction temperature > protein/maleic anhydride mass ratio. By comparing the mean values of the four factors, the optimal graft polymerization conditions were

determined to be $A_3B_3C_2D_1$. The optimized polymerization scheme is: protein and maleic anhydride each 2 g, acrylonitrile 12.5 g, initiator 1.5 g, and reaction temperature 60°C. Under these optimal conditions, the graft polymerization yielded a polymer with a molecular weight of 158,000.

The mean value trend for Factor A shows that polymer molecular weight increases with increasing protein/maleic anhydride dosage. This indicates that higher reactant concentrations provide more activated molecules for the reaction, resulting in higher molecular weight polymers. For Factor B, molecular weight increases with acrylonitrile dosage because higher monomer concentrations create more active centers, increasing the probability of copolymerization and thus polymer molecular weight. For Factor C, molecular weight initially increases with initiator amount but decreases when the initiator exceeds a certain level. This occurs because while increased initiator raises the concentration of primary active species and degree of polymerization, excessive free radicals create too many active centers, which is detrimental to achieving high molecular weight during monomer polymerization. Therefore, an initiator amount of 12% of the total mass is appropriate. For Factor D, molecular weight decreases with increasing polymerization temperature because temperatures above 70°C cause krill protein denaturation. Although higher temperatures accelerate the reaction, they also accelerate polymer decomposition. Since polymerization is exothermic, excessively high temperatures are unfavorable for the reaction.

Infrared Spectroscopy Analysis

Figure 2 [Figure 2: see original paper] presents the FTIR spectra of polyacrylonitrile, the grafted product AKPM-g-PAN, and the protein. In the PAN spectrum, the characteristic peak at 2243 cm^{-1} corresponds to the -C N stretching vibration. In the protein spectrum, the bands at 1654 cm^{-1} (amide I, C=O stretching), 1541 cm^{-1} (amide II, N-H bending), and 1242 cm^{-1} (amide III, C-N stretching) are observed. The AKPM-g-PAN spectrum exhibits both the protein characteristic amide I band and the PAN characteristic -C N peak, indicating successful grafting of protein onto polyacrylonitrile macromolecules. The weakened intensity of the amide II N-H vibration band and disappearance of the amide III C-N band suggest that C-N bonds were broken during grafting, partially destroying the peptide bond structure. Additionally, the reduced absorption intensity of the PAN characteristic peak in AKPM-g-PAN indicates decreased -C N group content, likely due to oxidation of some -C N groups to ester groups during grafting, further confirming the grafting reaction.

Thermogravimetric Analysis of AKPM-g-PAN

The TG curves in Figure 3 [Figure 3: see original paper] show similar trends for different AKPM-g-PAN compositions. However, compared with PAN and protein curves, the protein exhibits significantly greater weight loss than AKPM-g-PAN, which in turn shows greater weight loss than pure PAN. These results indicate that krill protein has poorer thermal stability than AKPM-g-PAN, while

AKPM-g-PAN is less thermally stable than pure PAN. The TG curves reveal that from 25°C to 200°C, both protein and AKPM-g-PAN (#9) show noticeable weight loss. This occurs because, on one hand, protein has a low decomposition temperature and undergoes initial degradation involving peptide bond cleavage with CO_2 release and breakdown of macromolecules into smaller molecules. On the other hand, the hydrophilic groups in AKPM-g-PAN polymer and protein absorb moisture from air, which evaporates as temperature increases. Comparing the curves for samples #3, #6, and #9 clearly shows that #9 exhibits greater weight loss than the other two samples, indicating higher protein group content in the #9 AKPM-g-PAN polymer. The second stage (200°C-400°C) involves degradation of protein in the AKPM-g-PAN macromolecular chains and weight loss from cyclization and dehydrogenation of PAN molecular chain nitrile groups. Analysis of weight loss percentages (#9: 31%, #6: 41%, #3: 37%) reveals that the #9 polymer has better thermal stability than the other samples. The third stage occurs after 400°C. During PAN cyclization and dehydrogenation, ladder structures form, and further heating of these thermally stable structures reduces weight loss, with almost no weight loss observed after 500°C. This demonstrates that #9 also has higher thermal stability than the other samples.

XRD Analysis of AKPM-g-PAN

Peak deconvolution software analysis of XRD curves (Figure 4 [Figure 4: see original paper]) reveals that PAN has two main crystalline peaks at 2 values of 16.70° and 28.42°, while krill protein has three main crystalline peaks at 20.98°, 31.68°, and 45.38°. Both materials demonstrate good crystallinity. In contrast, AKPM-g-PAN shows major crystalline peaks near 16.7°, 28.4°, 45°, and 65°, where the 16.70° and 28.42° peaks primarily originate from acrylonitrile self-polymerization crystallization. Notably, as protein content increases, the characteristic PAN crystalline peaks become more pronounced, indicating that sample #9 has better crystallinity than samples #6 and #3. This phenomenon can be explained by the strong polarity of nitrile groups within and between PAN molecules, which hinders regular chain arrangement, resulting in a quasi-crystalline structure. AKPM addition reduces this strong polarity, disrupts PAN structural regularity, enhances chain mobility, allows more AN sequences to enter crystalline regions, increases crystallite size, and improves crystallization ability. Additionally, protein molecules facilitate nucleation formation, further enhancing crystallization. The absence of protein absorption peaks in AKPM-g-PAN indicates that protein crystallinity is lost due to restriction by the PAN main chain. The crystalline peaks appearing near 45° and 65° in AKPM-g-PAN may be related to thermal denaturation.

DSC Analysis of AKPM-g-PAN

The DSC curves (Figure 5 [Figure 5: see original paper]) show no significant difference in decomposition temperatures among different AKPM-g-PAN com-

positions, all concentrated around 260°C. However, the decomposition heat varies, with sample #9 exhibiting higher decomposition enthalpy than the other samples. During thermal degradation of AKPM-g-PAN, intermolecular and intramolecular chemical reactions (cyclization and oxidation) occur simultaneously, gradually transforming long-chain macromolecules into more stable ladder-like structures through an exothermic process. Consequently, sample #9 shows higher exothermic enthalpy than the other samples.

Fiber Mechanical Properties

Effect of Coagulation Bath Temperature on Fiber Strength The relationship curve between coagulation bath temperature and fiber fracture strength (Figure 6 [Figure 6: see original paper]) shows that fiber strength initially increases with temperature, then decreases. As coagulation temperature rises, the double diffusion between solvent in the spinning solution and coagulant accelerates, macromolecular chain segments become more mobile, and PAN molecules more readily form ordered structures with improved crystalline perfection, thereby increasing fiber fracture strength. However, excessively high coagulation bath temperature causes rapid surface solidification, quickly forming a skin layer on the fiber surface. When this skin layer develops sufficient strength to counteract applied tension, the fiber interior remains in a semi-solid graft polymer gel state. Without adequate stretching, polymer molecular chain orientation decreases, preventing formation of highly ordered, uniformly compact structures. Additionally, the intense coagulation process at high temperatures easily creates physical defects within the fiber. Conversely, if the coagulation bath temperature is too low, solidification becomes too slow and insufficient. The frozen graft polymer macromolecular chains have reduced mobility, which is also unfavorable for molecular chain orientation during stretching. Therefore, both excessively high and low coagulation bath temperatures reduce fiber orientation.

Effect of Coagulation Bath Concentration on Fiber Strength The relationship curve between coagulation bath concentration and fiber fracture strength (Figure 7 [Figure 7: see original paper]) demonstrates that fiber strength initially increases then decreases with rising coagulation bath concentration. Both excessively high and low concentrations are detrimental to fiber coagulation and formation. At high coagulation bath concentrations, the small concentration difference between the filament interior and exterior slows diffusion, reduces solidification rate, causes severe filament swelling, and results in insufficient coagulation. During stretching and orientation, this leads to over-stretching that damages the aggregated structure and compromises mechanical properties. At low coagulation bath concentrations, the diffusion process accelerates, and the filament outer surface easily forms a brittle, hard skin layer that hinders diffusion between the inner layer and coagulation bath, creating a skin-core structure. During stretching and orientation, this causes non-uniform stress distribution, generates voids in the fiber, and reduces

mechanical performance.

Effect of Spinning Solution Concentration on Fiber Strength As shown in Figure 8 [Figure 8: see original paper], fiber strength increases with spinning solution concentration. When spinning solution concentration varies between 6%-12%, higher concentrations result in denser grafted molecular chains in the fiber that can withstand greater tension, macroscopically manifested as increased fiber strength.

Fiber Microstructure Analysis

Different spinning conditions create various microstructures on fiber surfaces, such as skin-core structures, striations, grooves, and pits, which can be used to evaluate fiber performance.

Figure 9a [Figure 9: see original paper] reveals an irregular kidney-shaped cross-section. This structure primarily results from large differences between spinning solution concentration and coagulation bath concentration, or excessively high/low coagulation bath temperatures, which hinder diffusion in the coagulation bath. The fiber core solidifies more slowly and remains insufficiently coagulated, while the thin surface layer has low hardness, causing the cross-section to collapse into an irregular kidney shape. As coagulation bath concentration or temperature changes to increase solidification rate, the core becomes more fully solidified, skin layer thickness and hardness gradually increase, and the difference between internal and external solidification decreases. When the core contracts, the skin layer contracts accordingly, eventually forming a circular cross-section.

Figure 9b shows an uneven fiber surface with bright spots visible under electron microscopy and non-uniform brightness across the fiber body. The fiber surface exhibits grooves and striations, with surface roughness arising from two main factors. First, spinning coagulation involves double diffusion of water in the coagulation bath and solvent in the fiber. As spinning dope solvent exudes and water molecules enter, the fiber gradually solidifies. However, solute contraction during this process is somewhat non-uniform, creating groove structures. Second, the dispersed distribution of grafted protein within the fiber leads to varying water absorption in different parts. During drying and densification, substantial water evaporation creates significant negative pressure in microvoids formed by non-uniform contraction of the spinning dope, generating grooves on the fiber surface.

Conclusions

This study investigated the modification of polyacrylonitrile through grafting with krill protein. The results demonstrate that the amount of acrylonitrile is

the most significant factor affecting graft polymer molecular weight, followed by initiator amount, reaction temperature, and protein/maleic anhydride ratio. The optimal graft polymerization conditions were determined to be: protein and maleic anhydride each 2 g, acrylonitrile 12.5 g, initiator 1.5 g, and reaction temperature 60°C, yielding a polymer with molecular weight of 158,000. The grafted product contained both the characteristic amide groups of protein macromolecules and the nitrile functional groups of PAN, confirming successful grafting. While protein incorporation affected the thermal stability and crystallization ability of PAN molecules, it significantly improved the water retention rate of PAN composite fibers. Wet spinning of the protein/acrylonitrile composite fibers showed that fracture strength initially increased then decreased with rising coagulation bath concentration and temperature, while it increased monotonically with spinning solution concentration.

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