Synthesis and spinning of A Novel Poly (acrylonitrile-co-silk fibroin peptide)

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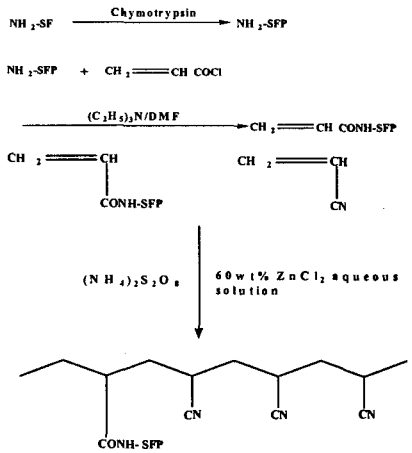
Abstract

A series of novel spinning acrylic polymer containing silk protein were synthesized by copolymerization of acrylonitrile (AN) and silk fibroin peptide (SFP) modified by acryloyl chloride (AC) with vinyl groups. The viscosity values of these copolymers showed that the copolymers have good spinnability, which are synthesized under the condition of putting a micro amount of metal ions into synthesizing solvent. The fiber based on the poly (AN-co-SFP) was prepared and characterized by SEM, FTIR measurement of its shell and core flakes, and moisture absorption. The fiber appeared a smooth surface and could be assumed to have excellent adhesive between SFP and PAN. Furthermore, these fibers showed a shell-core structure and excellent moisture absorption.

Introduction

As an important fiber material, polyacrylonitrile (PAN) are used for the textile industry in quantities not only as due to its relatively cheap price and good mechanical properties, but also because acrylonitrile can be easily copolymerized with one or two comonomers by vinyl copolymerization and then obtain various novel fiber material. In recent years there has been increasing interest in the combination of PAN and silk protein. The conventional methods have (1) blending of PAN and SF and (2) grafting of AN onto SF fiber. These polymers show very poor adhesive properties, and the mechanical properties are inferior to those of polyacrylonitrile homopolymer [1][2][3]. For this reason, we synthesized a new acrylic polymer containing silk protein by vinyl copolymerization of AN and modified silk fibroin peptide (SFP). In this paper, we report the synthesis of a series of poly (acrylonitrile-co-silk fibroin peptide)s from SFP monomer and AN in various compositions that can be used as spinning polymer intermediate. The chemical composition, viscosity, thermal properties are characterized, furthermore, the characterizations of the fibers prepared by Poly (acrylonitrile-co-silk fibroin peptide)s are examined.



Experimental

As the scheme above, the SF powder was decomposed with enzyme to form silk fibroin peptide (SFP). And then SFP macromonomer was prepared by acylation of the SFP with acryloyl chloride. The copolymerization of SFP macromonomer and AN was performed in 60wt% $ZnCl_2$ aqueous solution. Particularly, a little amount of Fe, Cu ion was added in synthesizing solvent during copolymerization procedure.

Results and Discussion

Spectroscopic analysis showed that Poly (acrylonitrile-co-silk fibroin peptide)s are a copolymer consisting of SFP and AN, and the conformation of SF changed inducing by copolymerization.

The compositions of the copolymers were

determined from the elementary analysis. In the copolymerization, the SFP macromonomer was found to be more reactive than AN monomer, thus it was considered that only a little amount of SFP is loaded in the copolymerization, the copolymer would be given the merits similar as silk protein. And the intrinsic viscosity of the copolymers synthesized after putting a micro amount of Fe, Cu ions into synthesizing solvent is about 1.64, 1.70, 2.20dl/g in DMF at 25℃, respectively, is concluded to have good spinnability. By using a simple wet-spinning method, a continuous fiber based on copolymers was obtained. It was confirmed that the fiber has shell-core structure by spectroscopic analysis of the shell and core flakes of the fiber with FTIR using Infrared microscope detector. From SEM photographs of the fiber, we could see the fiber has smooth surface with a little microstripes and no fractured structure. Because of no fractured structure, it was assumed that the poly (acrylonitrile-co-silk fibroin peptide)s have good adhesion between SF and PAN.

We have investigated thermal property of the spinning copolymers. The Tg values of the copolymers varied from 39 to 77℃, and the melting temperature is from 196 to 176℃, depending on the composition. From TG curves, we found that the copolymers underwent a three-step degradation, and the degradation behavior of these copolymer backbones occur at about 285 to 290℃. These degradation temperatures are lower than that of PAN homopolymer, but always higher than that of SFP. At about 400℃, cyclization between AN segments occurred. And the TG curves suggest that the copolymers are high weight residue. From these results, it was thought that these copolymers have good thermal stability.

As is shown in the fig., the result of the moisture absorption showed the moisture absorption of the fibers based on the copolymers is much higher than that of powders of the copolymers, and depended on the molar ratio of SFP in the copolymers, attributed that the fiber has a large surface area, and presence of SFP covered on the surface of fiber. Consequently, we knew that these fibers are excellent moisture absorption nearing the silk protein.

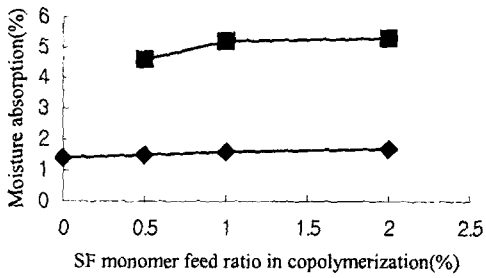


Fig. Moisture absorption dependence of SF monomer feed ratio in copolymerization. (◆) copolymer powders and (■) those fibers.

Acknowledgments

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