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Surface Modification of Acrylic Fiber by Grafting of Casein

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A novel chemical modification method of acrylic fiber was employed by grafting of casein—a natural polymer, onto the surface of acrylic fiber. The effects of reaction conditions, such as chlorination time, chlorination temperature, grafting time and temperature, and pH value on grafting efficiency were investigated systematically. The structure and morphology of the casein grafted fiber were characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The results showed that casein had been grafted onto the acrylic fiber. Moisture absorption, water retention and specific electric resistance were found to be improved compared with the untreated fiber. Mechanical properties of the grated fiber could still meet the requirement for wearing fiber. The possible mechanism is proposed to explain the grafting of casein onto the synthetic acrylic fiber.

Keywords: acrylic fiber; casein; graft; surface modification

1 Introduction

Acrylic fiber, due to its relatively cheap price and many superior characteristics such as soft, wool-like hand, machine washable and dryable and excellent color retention, is widely used in the textile industry. But acrylic fiber also exhibits some obvious disadvantages, such as low moisture-absorbency and electrostatic tendency, which greatly limits its further applications. Chemical grafting has proved to be a successful technique to provide the synthetic fiber with desirable properties without deterioration in the bulk properties of the fiber (1–3). The presence of polar groups in natural polymers, such as hydroxyl -OH and amine -NH_2 has made them a highly promising substance for modifying the acrylic fiber. A large amount of research published has been focused on the graft copolymerization of acrylonitrile (AN) and natural polymers, such as wool (4–6), silk (7–9) starch (10–13), cellulose (14–16), and chitosan (17–19), etc.

Casein makes up approximately 80% of the protein in milk with molecular weight ranging from 19,007 to 25,230 daltons (20). Casein contains many polar groups, such as -COOH, -NH_2, and -OH etc., which contribute to the hydrophilicity, as well as the reactivity of the casein molecules. Casein abounds in the world as a natural polymer and thus made it an attractive natural resource for improving the characteristic of synthetic fibers (21, 22). In recent years, more and more attention has been paid on the graft copolymerization of AN and casein. Dong Q. et al. have studied the grafting of casein with AN in aqueous solution of sodium thiocyanate (23, 24). N. Somanathan, et al. have made a study on grafting of casein with AN in a water medium using potassium persulphate at 60°C (25, 26). However, to our knowledge, little research has been done on the direct grafting modification of the acrylic fibers themselves.

In this article, the results of the direct surface modification of acrylic fiber via grafting of casein were presented. The effects of varying chlorination and grafting conditions on the grafting efficiency were reported. The structure, morphology, moisture absorption, water retention, specific electric resistance and tensile properties of the grafted acrylic fiber were investigated. The results showed that casein had been grafted onto the acrylic fiber and the casein-grafted fiber exhibited improved hygroscopicity and proper mechanical properties.

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2 Experimental

2.1 Materials

Acrylic fiber was kindly supplied by the Sinopec Qilu Company Ltd. The dried casein was obtained from Beijing Abxing Biological Technology Co, China. The other chemicals were all of analytical reagent and used without further purification.

2.2 Grafting Modification

The grafting modification involves three steps: (a) hydrolysis of acrylic fiber; (b) chlorination of the hydrolyzed fiber; (c) grafting of casein onto the above made chlorinated fiber.

First, the hydrolyzed acrylic fiber was prepared according to the reported procedure (27, 28). Then, the hydrolyzed acrylic fiber was put into a hermetically sealed vessel, which was filled with $SOCl_2$ to make the chlorinated fiber. 2.0 g casein was dispersed in 50 mL distilled water and pH was adjusted to 10–11 with 10% (w/w) NaOH aqueous solution at room temperature under constant stirring for 10 min. The chlorinated acrylic fiber was put into the above made mixture directly for some time. After completion of the grafting reaction, casein grafted acrylic fiber was separated and washed thoroughly with both water and ethanol and then dried under vacuum at 50°C to get the modified acrylic fiber.

2.3 Definition of the Grafting Efficiency

Grafting efficiency can be calculated as follows:

$$\text{Grafting efficiency (\%)} = \frac{m_2 - m_1}{m_1} \times 100$$

where m_1 and m_2 are the mass of original and casein grafted acrylic fiber, respectively.

2.4 Measurements

The FT-IR spectra of original and casein-grafted acrylic fibers were recorded on a Nicolet 5700 spectrometer using the potassium bromide pellets technique and the scanning was carried out from 400 cm^{-1} to 4000 cm^{-1}. The surface morphology of both samples coated with gold was carried out on a Sirion 200. The moisture absorption experiments were performed as follows: Fibers were balanced for 48 h at 25°C, 65% RH, and then weighed (m_1/g). After balancing for 60 h at 60°C in vacuum baking oven, it was weighed (m_2/g). The moisture absorption (%) of the fibers was calculated by the following formula:

$$\text{Moisture absorption (\%)} = \frac{m_1 - m_2}{m_1} \times 100$$

Water retention capability was studied as follows: Samples of both the ungrafted and grafted PAC fibers were dried for 1 h at 110°C and weighed as DRY. Subsequently, the fibers were emerged in distilled water for 20 min. After that, the fibers were taken out and placed in a glass tube, centrifuged for 15 min at 1500 rpm to remove the excess water, and then weighed. This weight of the samples was recorded as WET. Water absorption was expressed as the water retention and was calculated as follows:

$$\text{Water retention (\%)} = \frac{\text{WET} - \text{DRY}}{\text{DRY}} \times 100$$

Specific electric resistance of the blend fiber was determined by using YG321 Specific Resistance Indicator. Mechanical properties of fibers were determined by using YG-003 fiber tensile machine, length between two holding jigs was 10 mm, and drop rate was 20 mm/min at room temperature.

3 Results and Discussion

3.1 Mechanism of Grafting Modification

The graft modification is illustrated in the chemical scheme in Figure 1. The nitrile group -C≡N in acrylic fiber is converted to carboxyl group -COOH and amide group -$CONH_2$ after acrylic fiber is hydrolyzed in NaOH aqueous solution. Afterwards, chloroformyl group -COCl is obtained by treating with $SOCl_2$. Finally, nitrogen acylation and esterification are carried out when -COCl group reacts with amino group-NH_2 and hydroxyl group -OH of casein under the conditions of room temperature and constant pressure.

3.2 Effect of Chlorination Time on Grafting Efficiency

As shown in Figure 2, when the chlorination temperature, grafting time, grafting temperature as well as pH value are kept invariably, the chlorination of hydrolyzed acrylic fiber was carried out for different periods. Results show that the grafting efficiency increased steadily with the increasing reaction time at first. Beyond 40 min, the chlorination time had a small effect on the grafting reaction. With increasing time, the chlorinating extent is rapidly increased due to more availability of $SOCl_2$ reacting with -COOH or -$CONH_2$, which enhances the grafting sites for casein to be grafted onto the fiber and so increases the grafting efficiency. However, the number of active sites remains almost stable with a longer chlorination time. So, after 40 min, the tendency of increase leveled off.

3.3 Effect of Chlorination Temperature on Grafting Efficiency

When the other reaction conditions are invariable, the grafting efficiency at various chlorination temperatures is shown in Figure 3. The grafting efficiency showed an increasing trend up to 100°C and maintained a plateau. The improvement in grafting efficiency can be explained as follows: The dynamic energy of both $SOCl_2$ and acrylic fiber are enhanced with the increasing reaction temperature, and the number of grafting sites is increased too, which ultimately leads to the increasing grafting efficiency. At higher temperature, the extent of increase was not much and the maximum grafting efficiency of 4.34% (w/w) was obtained, which may be due to the almost completion of chlorination reaction.

3.4 Effect of Grafting Time on Grafting Efficiency

The effect of grafting time on the grafting efficiency was studied for different reaction time while other effective

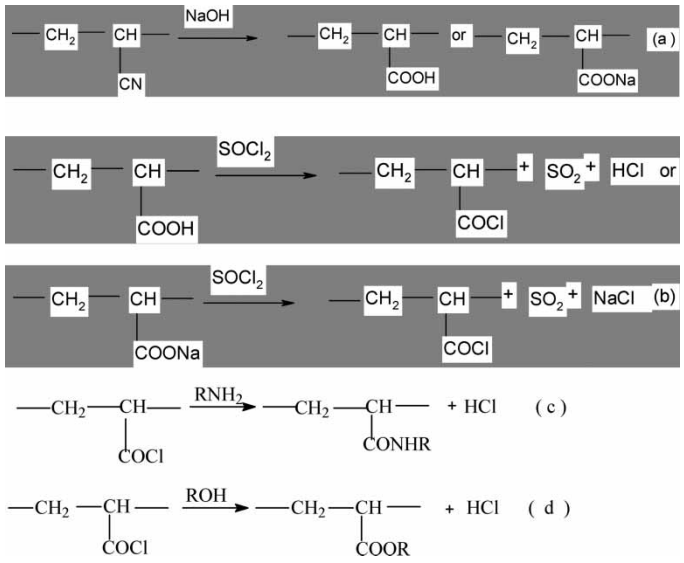

Fig. 1. Graft modification of acrylic fiber.

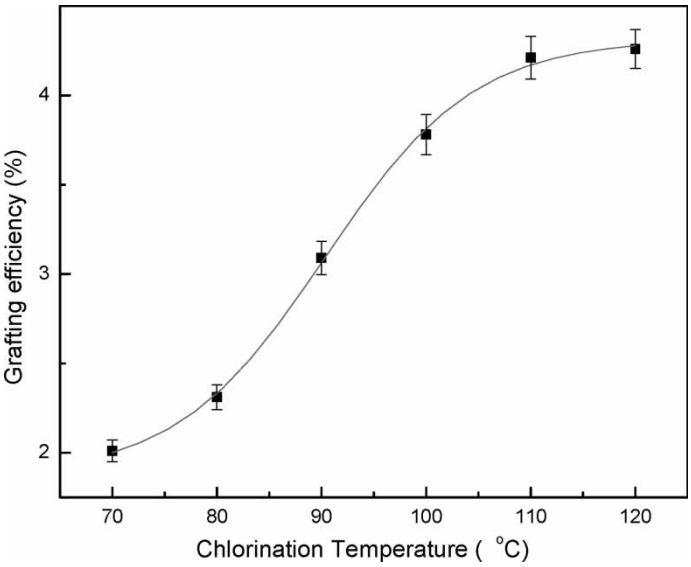

Fig. 3. Effect of chlorination temperature on grafting efficiency: chlorination time: 40 min grafting time, 20 min; grafting temperature, 70°C and pH = 11.

factors were unchanged. As shown in Figure 4, the grafting efficiency increased significantly first, reaching a maximum value with the increasing grafting time and then declined with further grafting time. As the -COCl group has a high activity, the grafting sites are increased with rising grafting time. As a result, the grafting efficiency increases at first. However, the denaturation of casein in the alkaline aqueous solution is exacerbated with longer time (29). Meanwhile, the hydrolysis of acrylic fiber is intensified too with a prolonged reaction time. Therefore, the grafting efficiency decreases with a further increasing grafting time.

3.5 Effect of Grafting Temperature on Grafting Efficiency

Keeping the other variables constant, the grafting reactions were carried out at different temperatures between 40°C and 90°C. In Figure 5, grafting efficiency increased in the beginning up to 70°C, and then decreased with further increasing of temperature. The increase of grafting efficiency initially can be ascribed to the high reaction activity of casein and acrylic fiber, which provides more grafting sites for the reaction with the increase of temperature. However, beyond 70°C, the grafting efficiency declined dramatically, which

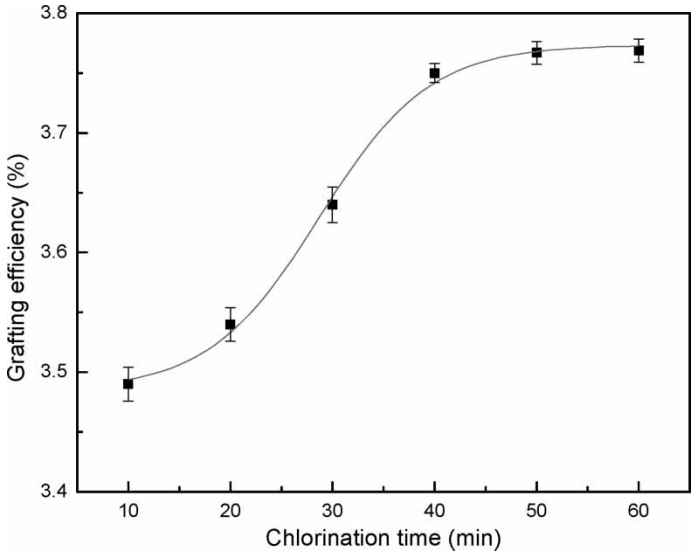

Fig. 2. Effect of chlorination time on grafting efficiency: chlorination temperature, 100°C; grafting time, 20 min; grafting temperature, 70°C and pH = 11.

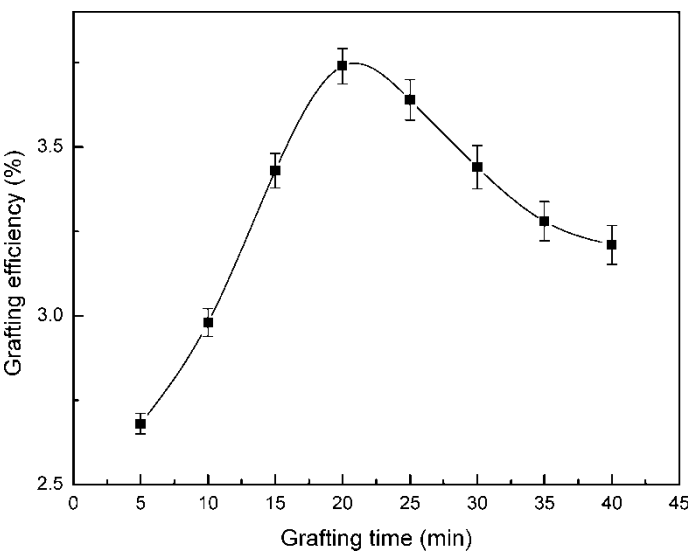

Fig. 4. Effect of grafting time on grafting efficiency: chlorination time, 40 min; chlorination temperature, 100°C; grafting temperature: 70°C and pH = 11.

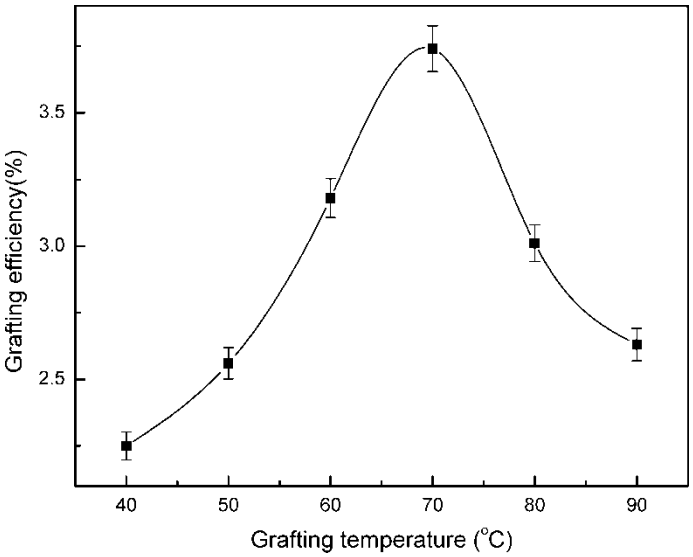

Fig. 5. Effect of grafting temperature on grafting efficiency: chlorination time, 40 min; chlorination temperature, 100°C; grafting time: 20 min and pH = 11.

could be partly due to both the over-hydrolysis of acrylic fiber and denaturation of casein with increasing reaction temperature (30).

3.6 Effect of pH on Grafting Efficiency

The effect of pH on the grafting efficiency, while keeping all other conditions constant is presented in Figure 6. It can be seen that the grafting efficiency increased at first and then decreased obviously with increasing pH value. The maximum grafting efficiency of 2.38 wt% was achieved at

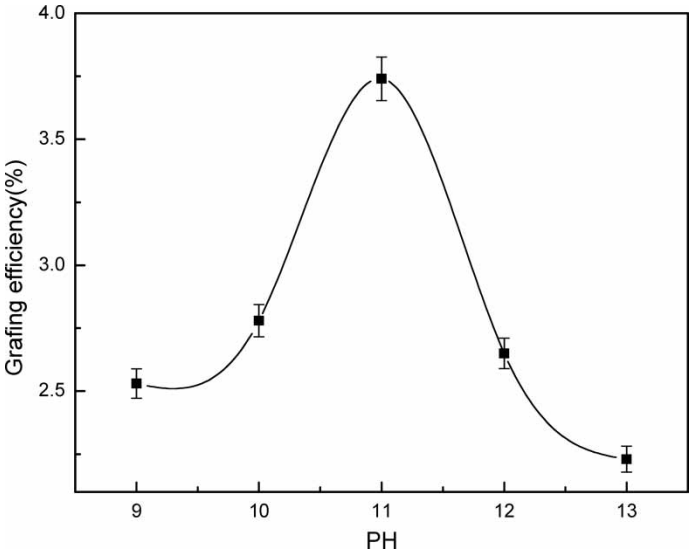

Fig. 6. Effect of pH on grafting efficiency: chlorination time, 40 min; chlorination temperature, 100°C; grafting time, 20 min; grafting temperature, 70°C.

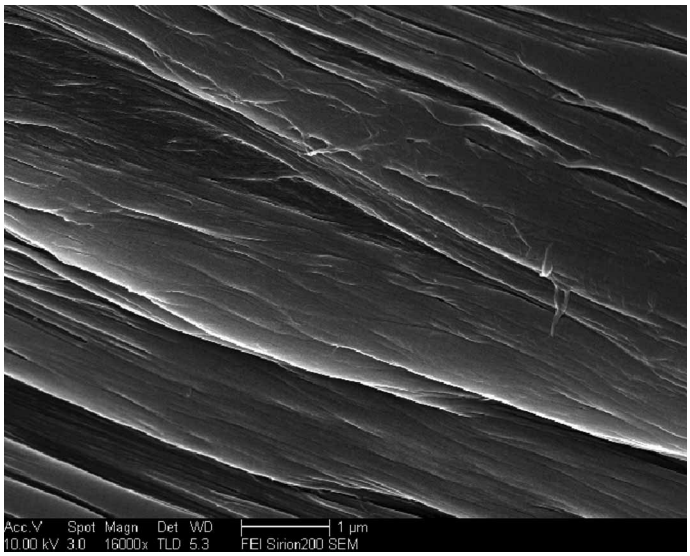

Fig. 7. SEM photographs of original acrylic fiber.

pH = 11. In the grafting of casein onto acrylic fiber, NaOH is employed to neutralize the hydrochloric acid HCl which is produced in the nitrogen acylation and esterification reactions as depicted in Figure 1 (c) and (d). PH also affects the hydrolysis of the acrylic fiber and the denaturation of the casein. With increasing the addition of NaOH, the hydrolysis of acrylic fiber will be performed excessively which may result in the decrease of the weight of the fiber itself. Besides, the denaturation of casein intensifies at high pH value (31). Therefore, the grafting efficiency decreases rapidly.

3.7 Scanning Electron Microscopy

The surface morphology of the original and casein-grafted acrylic fiber is presented in Figures 7 and 8, respectively.

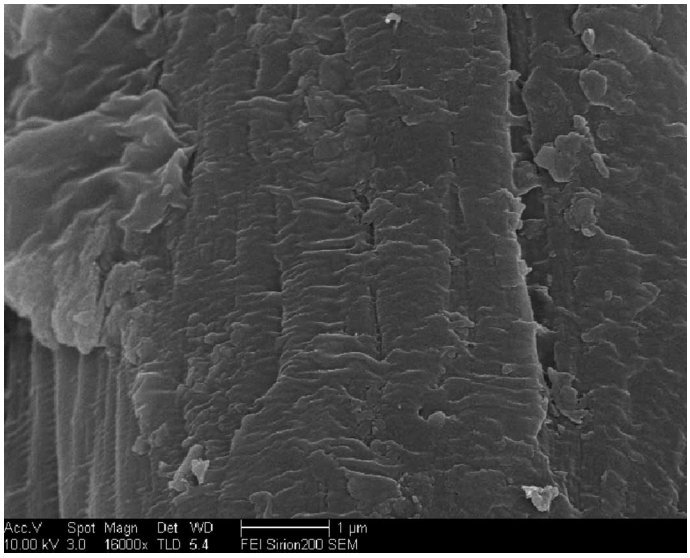

Fig. 8. SEM photographs of grafted acrylic fiber.

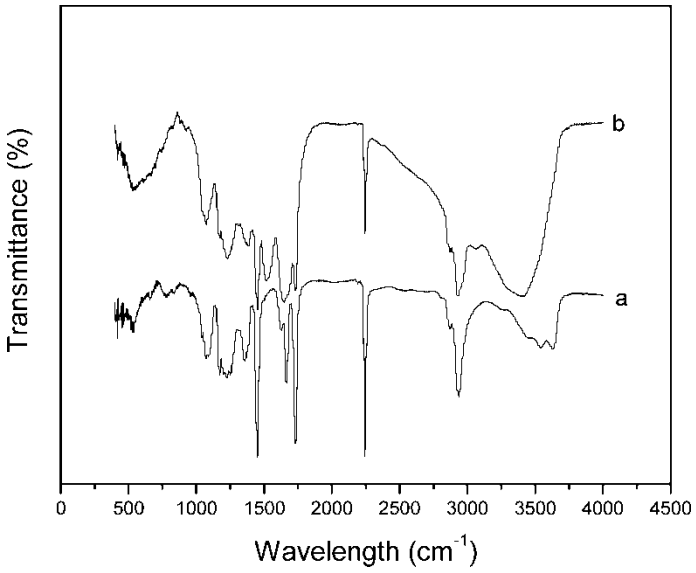

Fig. 9. FTIR spectra of (a) original acrylic fiber; (b) casein grafted acrylic fiber.

As shown in Figure 7, the surface of ungrafted fiber is quite smooth and there are a number of longitudinal cracks during the high-ratio stretching in spinning. After grafting, the surface of the modified fiber (Figure 8) became much rougher and both the surface and the original cracks were covered with some deposition, which indicated that the casein has been grafted onto the acrylic fiber.

3.8 FT-IR Spectroscopy

The structure of the original and grafted acrylic fiber was characterized by FT-IR, respectively. As shown in Figure 9(a), the FTIR spectra of untreated acrylic fiber shows characteristic absorption peaks at 2244 (γ C≡≡N), 1732 (γ C═O), and 1454 (δ CH_2) cm^{-1}, where γ represents a stretching vibration and δ a blending vibration. The FT-IR spectra of the casein grafted fiber (Figure 9(b)) exhibits a characteristic absorption band at 1650 cm^{-1}, amide I band, resulting from the amide C═O vibration. A strong amide II band, which arises from the coupling of N-H bending of C-N-H group, is observed at 1517 cm^{-1}. Strong absorption band at 3400 cm^{-1} is due to N-H stretching of casein (32). The presence of these intense absorption bands indicates the successful grafting of casein onto acrylic fiber.

3.9 Moisture Absorption, Water Retention and Specific Electric Resistance

Moisture absorption and water retention reflect hydrophilic properties of fibers, and they have a great effect on the applications of fibers. Specific electric resistance is an index of antistatic property and spinnability for fibers. Fibers with high value of the specific resistance are easy to accumulate static charge, inhibiting spinning of fiber.

The comparison of moisture absorption, water retention and specific electric resistance of original and grafted acrylic fiber is shown in Table 1. Moisture absorption, water retention capability and specific resistance of untreated fiber are 2.07%, 14.51%, and $1.94 \times 10^9 \Omega \cdot g/cm^2$, respectively. However, on the case of grafted fibers they were all improved. The percentage of moisture absorption and water retention was found to increase with the increasing of grafting efficiency and their maximum value were 5.39% and 25.32%, respectively. At the same time, the specific electric resistance was found to decrease as the grafting efficiency increased. Generally, the antistatic property depends on the moisture content of fiber materials. Grafting with casein increases hydrophilicity of the fiber as a result of the introduction of the polar groups. This change in the hydrophilic nature is responsible for the enhancement of the moisture absorption and water retention with increasing the percentage of grafting efficiency and thus consequently reduces specific electric resistance of the fiber. So, the antistatic properties of the grafted fibers are improved, too.

3.10 Mechanical Properties

The mechanical properties of both ungrafted and grafted acrylic fibers are recorded in Table 2. The breaking strength and breaking elongation were 2.41 CN/dtex and 25.4% for the untreated acrylic fiber, respectively. However, compared with the untreated acrylic fiber, the breaking strength of the grafted acrylic fiber was lower while the breaking elongation did not changed much. Similar observations have also been reported by a number of authors, and it is believed (33–34)

Table 1. Moisture absorption, water retention and specific electric resistance of acrylic fiber before and after grafting

Sample	Grafting efficiency (%)	Moisture absorption (%)	Water retention (%)	Specific electric resistance ($\Omega \cdot g/cm^2$)
Ungrafted	0	2.1 ± 0.1	14.5 ± 0.6	$(1.9 \pm 0.1) \times 10^9$
Grafted	1.2 ± 0.1	3.1 ± 0.1	17.9 ± 0.5	$(3.2 \pm 0.1) \times 10^8$
Grafted	2.3 ± 0.2	4.0 ± 0.2	19.2 ± 1.0	$(1.3 \pm 0.2) \times 10^8$
Grafted	3.5 ± 0.2	4.6 ± 0.3	21.8 ± 1.4	$(9.9 \pm 0.4) \times 10^7$
Grafted	4.3 ± 0.3	5.4 ± 0.3	25.3 ± 1.5	$(5.4 \pm 0.3) \times 10^7$

Table 2. Mechanical properties of acrylic fiber before and after grafting

Sample	Grafting efficiency (%)	Breaking strength (CN/dtex)	Breaking elongation (%)
Ungrafted	0	2.4 ± 0.1	25.4 ± 1.7
Grafted	1.2 ± 0.1	2.1 ± 0.2	25.5 ± 1.3
Grafted	2.3 ± 0.2	2.1 ± 0.2	27.6 ± 1.6
Grafted	3.5 ± 0.2	2.0 ± 0.1	27.9 ± 1.7
Grafted	4.3 ± 0.3	1.9 ± 0.2	26.6 ± 2.0

that the alkaline treatment leads to the surface erosion of the acrylic fiber and loosening of the structure. So the intermolecular interaction between the polymeric chains decreases, which results in the decline of the tensile strength. In spite of all these factors, the grafted polymer still meets the requirement for wearing fiber.

4 Conclusions

As a combination of natural polymer and synthetic fiber, casein grafted acrylic fiber was prepared after a series of hydrolysis and chlorination reactions. The individual factors of the reaction, such as chlorination time and temperature, grafting time and temperature and pH value of the solution affected the grafting efficiency obviously. FTIR spectroscopic analysis and SEM micrographs of the original and grafted fiber were used to confirm the grafting of casein onto the acrylic fiber. This morphology has important implications for moisture absorption, water retention, antistatic properties and mechanical properties of the fiber. Casein-grafted acrylic fiber exhibits better hygroscopicity, anti-static property and spinnablity, which gives the proof that the surface properties of the original acrylic fiber have been improved. Therefore, it is necessary and significant to investigate other properties of casein-grafted acrylic fiber in future work.

5 References

1. Konkin, A.A. (1969) *Fibre Chem.*, n1, 8–12.
2. Perepelkin, K.E. (2005) *Khimicheskie Volokna*, **2**, 37–51.
3. Lokhande, H.T. and Teli, M.D. (1985) *CEW Chem. Eng. World*, **20(3)**, 71–75.
4. Breusova, I.P., Morin, B.P., Rogovin, Z.A.M. and Berlin, A.A. (1979) *Polymer Science USSR*, **21**, 217.
5. Batty, N.S., Gradwell, A.J. and Guthrie, J.T. (1976) *Polymer*, **17(8)**, 705–709.
6. Li, C., Zhao, X., Zhou, Z., Wang, T.D. and Chen, S.M. (1993) *Nucl. Sci. Tech.*, **4(3)**, 168–170.
7. Chen, Z.M., Suzuki, M., Kimura, M., Kondo, Y., Hanabusa, K. and Shirai, H. (2004) *J. Appl. Polym. Sci.*, **92(3)**, 1540–1547.
8. Sen Gupta, S.K., Sinha, R.K. and Chaudhary, N.N. (1996) *J. Polym. Mater.*, **13(4)**, 351.
9. Sun, Y., Shao, Z.H., Zhou, J. and Yu, T. (1998) *J. Appl. Polym. Sci.*, **69(6)**, 1089–1097.
10. Sugahara, Y. and Ohta, T. (2001) *J. Appl. Polym. Sci.*, **82(6)**, 1437–1443.
11. Pourjavadi, A., Zohuriaan, M. and Mohammad, J. (2002) *Starch*, **54(3–4)**, 140–147.
12. Lutfor, M.R., Rahman, M.Z.A., Sidik, S., Mansor, A., Haron, J. and Wan Yunus, W.M.Z. (2001) *Des. Monomers Polym.*, **4(3)**, 253–260.
13. Lim, D.W., Whangq, H.S., Yoon, K.J. and Ko, S.W. (2001) *J. Appl. Polym. Sci.*, **79(8)**, 1423–1430.
14. Farag, S. and Al-Afaleq, E.I. (2002) *Carbohydr. Polym.*, **48(1)**, 1–5.
15. Mohammad, J.Z., Ali, P. and Mohammad, S. (2005) *Iran. Polym. J. Eng. Ed.*, **14(2)**, 131–138.
16. Gupta, K.C. and Sahoo, S. (2001) *J. Appl. Polym. Sci.*, **79(5)**, 767–778.
17. Pourjavadi, A., Mahdavinia, G.R., Zohuriaan-Mehr, M.J. and Omidian, H. (2003) *J. Appl. Polym. Sci.*, **88(3)**, 2048–2054.
18. Sjngh, V.T., Devendra, N., Tiwari, A. and Sanghi, R. (2005) *J. Appl. Polym. Sci.*, **95(4)**, 820–825.
19. Harish Prashanth, K.V. and Tharanathan, R.N. (2003) *Carbohydr. Polym.*, **54(3)**, 343–351.
20. Thorn, D.C., Meehan, S., Sunde, M., Rekas, A., Gras, S.L., MacPhee, C.E., Dobson, C.M., Wilson, M.R. and Carver, J.A. (2005) *Biochemistr.*, **44(51)**, 17027–17036.
21. Liu, Y.H., Zhang, Y.Z., Liu, Z.Z. and Deng, K.L. (2002) *Eur. Polym. J*, **38**, 1619–1625.
22. Liu, Y.H., Zhou, W.Q., Bai, L.B., Zhao, N. and Liu, Y.W. (2006) *J. Appl. Polym. Sci.*, **100**, 4247–4251.
23. Dong, Q. and Gu, L. (2002) *Eur. Polym. J*, **38(3)**, 511–519.
24. Dong, Q. and Gu, L. (2002) *J. Appl. Polym. Sci.*, **84(9)**, 1721–1728.
25. Somanathan, N., Jeevan, R.G. and Sanjeevi, R. (1993) *Polym. J*, **25(9)**, 937–946.
26. Somanathan, N. and Sanjeevi, R. (1994) *Eur. Polym. J*, **30(12)**, 1425–1430.
27. Jia, Z., Yang, Y.G., Wang, H.D. and Ding, R. (2004) *China Synthetic Fiber Industry*, **27**, 27–28.
28. Yang, M.C. and Tong, J.H. (1997) *J. Membr. Sci.*, **132(1)**, 63–71.
29. Rawal, S.R., Zaidi, A.H. and Aneja, V.P. (1986) *J. Inst. Eng. India, Part AG.*, 63–64.
30. Vasbinder, A.J., Van Mil, P.J.J.M., Bot, A. and De Kruif, K.G. (2001) *Colloids Surf. B Biointerfaces*, **21(1–3)**, 245–250.
31. Alexander, M. and Dalgleish, D.G. (2005) *Langmuir*, **21(24)**, 11380–11386.
32. Zuev, Y., Faizullin, D., Idiyatullin, B., Mukhitova, F., Chobert, J.M., Fedotov, V. and Haertle, T. (2004) *Colloid Polym. Sci.*, **282(3)**, 264–269.
33. Gupta, M.L., Gupta, B., Oppermann, W. and Hardtmann, G. (2004) *J. Appl. Polym. Sci.*, **91(5)**, 3127–3133.
34. Deng, S.B., Bai, R.B. and Chen, J.P. (2003) *J. Colloid Interface Sci.*, **260**, 265–272.