Grafting of Casein onto Polyacrylonitrile Fiber for Surface Modification

Zhao Jia[1,2]* and Shanyi Du[1]

[1]*College of Materials Science and Engineering, Harbin Institute of Technology, Haerbin 150001, People's Republic of China*
[2]*College of Materials Science and Engineering, Shandong University of Technology, Zibo 255049, People's Republic of China*

Abstract: Polyacrylonitrile (PAN) fiber was grafted with casein after alkaline hydrolysis and chlorination reactions of the original fiber. The structures and morphologies of the casein grafted fiber were characterized by Fourier transform infrared spectroscopy (FTIR), X-Ray diffraction (XRD), and scanning electron microscope (SEM). Moisture absorption, specific electric resistance, water retention value, and mechanical properties were also investigated. The results showed that casein was grafted onto the surface of the PAN fiber and the grafted PAN fiber presented better hygroscopicity compared with the untreated fiber. With proper tensile strength, the modified fiber could still meet the requirement for wearing. A mechanism was proposed to explain the deposit of casein on the synthetic acrylic fiber.

Keywords: Polyacrylonitrile fiber, Casein, Grafting modification, Hygroscopicity

Introduction

Casein makes up approximately 80 % of the protein in milk with the rest being whey proteins [1]. Besides its relevance as a nutritional product, casein has been used as the raw material for application in many fields such as man-made fibers, adhesives, glues, and paint binders [2,3]. Though casein fiber is praised as the healthy and comfortable fiber, it still has some major drawbacks such as poor wet-rub resistance and susceptibility to microbial attack [4].

In recent years, there is a growing interest in the attempts to combine the natural polymer with a synthetic polymer through graft copolymerization, since such treatments, in general, improve some of the disadvantages associated with these fibers with only negligible bulk changes of properties. Many works have been carried out during past years on grafting of casein with vinyl monomers such as acrylonitrile [4-7], styrene [8], methyl methacrylate [9], acrylamide [10,11], butyl acrylate [12,13], and n-butyl methacrylate [14], etc onto casein using different initiator. Although a lot of studies concerning grafting of vinyl monomers onto casein can be found in the literatures, it is surprising to note that, to our knowledge, there is little information about the grafting modification of casein onto synthetic polymers. Furthermore, the main purpose of these studies are concentrated on the improvement of some physical properties of casein fiber and the samples studied were usually graft copolymers.

As a widely employed polymer, PAN is used in the textile industry in quantities and has a prominent place among the synthetic fibers. However, in spite of many superior properties of PAN fibers, some of their poor features such as low moisture absorption and poor antistatic properties limit their further usage. So, surface modification is particularly important with PAN fiber.

Our interest here is to graft casein onto PAN fiber directly to get the surface modified fibers. The chemical structure of the PAN-g-casein fiber was characterized by FTIR and XRD. The surface morphology of the grafted fiber was studied by SEM. Some physical properties such as mechanical properties, moisture absorption, water retention, and antistatic property were also investigated.

Experiment

Materials

Polyacrylonitrile (PAN) fiber, a commercial product, was kindly provided by Zibo Polyacrylonitrile Corp., PR China. The dried casein was obtained from Shanghai Maisha Biological Technology Co., China. The other chemicals used in the study were of reagent grade and used without further purification.

Graft Modification

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

First, 30 g of PAN fiber was added to a 500-m*l* flask with 300 m*l* of 8 % (w/w) NaOH aqueous solution and stirred at 80 °C for 10 min to get the hydrolyzed fiber (HPAN). Then the HPAN fiber was collected, rinsed with deionized water until it became neutral, and then dried in an oven at 50 °C to constant weight. Then, HPAN fiber was put into a hermetically sealed vessel which was filled with SOCl$_2$ at 100 °C for 20-30 min to make the chlorinated fiber.

2.0 g casein was dispersed in 50 m*l* distilled water and pH was adjusted to 10-11 with 10 wt.% NaOH aqueous solution at room temperature under constant stirring for 10 min. The chlorinated HPAN fiber was put into the above made mixture directly. The grafting reaction was carried out at 80 °C for 10 min. Then the grafted PAN Fiber was separated and washed thoroughly with deionized water and then dried under vacuum at 50 °C to a constant weight.

*Corresponding author: hgdcara@126.com

Grafting Efficiency Calculation

Grafting efficiency can be calculated as follows:

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

where m_1 and m_2 are the mass of PAN fiber before and after casein grafting, respectively.

Measurements

SEM Analysis

A scanning electron microscope (SEM, Sirion 200, FEI, Holland) at 10 kV was used to examine the surface morphologies of PAN fiber before and after grafting modification.

FTIR Analysis

Infrared spectra of fiber samples with KBr pellets were obtained from FT-IR spectrometer (Nicolet 5700 spectrometer).

X-ray Diffraction Studies

A D8 ADVANCE power X-Ray Diffractometer (Bruker AXS, Germany) was used to study the wide angle XRD patterns. Ni-filtered CuK$_\alpha$ radiation ($\lambda = 1.54$ Å) was used with a generator voltage of 40 kV and a current of 30 mA. The scanning speed was 4 °/ min, scanning step was 0.02 °.

Mechanical Properties Determination

Fiber mechanical properties were obtained using YG-003 fiber tensile tester. All tests were performed on single filaments using a gauge length of 10 mm and crosshead speed of 20 mm/min at room temperature. The average of 50 fibers was presented for each sample.

Determination of Moisture Content

The moisture absorptions of the samples were calculated from increase in the weight of dried original fibers (dried at 60 °C in a vacuum for 72 h) after being conditioned at 25 °C and 65 % RH for 48 h as follows:

$$\text{Moisture absorption (\%)} = (W_2 - W_1)/ W_1 \times 100$$

where W_1 and W_2 denote the weights of the original and the conditioned fibers, respectively.

Antistatic Property

Specific electric resistance of the blend fiber was determined by using YG321 Specific Resistance Indicator.

Water Retention Capacity

Sample of fiber was soaked into distilled water for 24 h at ambient temperature. After centrifugation at 2000 rpm for 20 min, the weight of the fiber was measured (W_w) The sample was dried at 110 °C for 4 h and the sample was reweighed (W_d). The water retention value (*WRV*) was
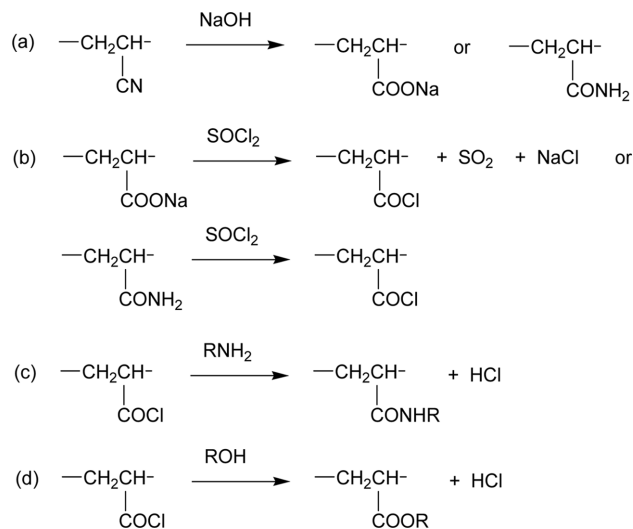

Figure 1. Graft modification of PAN fiber with amines and alcohols.

calculated as follows:

$$\text{WRV(\%)} = (W_w - W_d)/W_d \times 100$$

Results and Discussion

Mechanism of Grafting Modification

The graft modification is illustrated in the chemical scheme in Figure 1. Generally, the whole procedure involves three parts: hydrolysis, chlorination, and grafting reactions. First, the -C≡N groups in PAN fiber are converted to -COONa and -CONH$_2$ in NaOH aqueous solution. Then, the HPAN reacts with SOCl$_2$ to give -COCl groups. Finally, the introduction of casein was achieved when nitrogen acylation and esterification are carried out after -COCl group reacts with amino group -NH$_2$ and hydroxyl group -OH.

Scanning Electron Microscopy

SEM micrographs of ungrafted and grafted PAN fibers were taken and the results are presented in Figure 2 and 3. Figure 2(a) and (b) show the external surface of ungrafted and grafted PAN fiber samples, respectively. It can be seen that the surface of ungrafted fiber is quite smooth and there are a number of longitudinal cracks caused by high-ratio stretching in spinning, whereas the surface of the grafted fiber becomes more rugged and there is obvious deposition after grafting, which indicated that a casein film was formed on the surface. Figure 3(a) and (b) show the cross section of the grafted and ungrafted PAN fiber, respectively. As can be seen, the pore size of the grafted fiber increases when compared with those of the ungrafted fiber. Besides, the ungrafted fiber presents a relatively compact internal structure, whereas the internal structure of the grafted fiber is quite loosened.
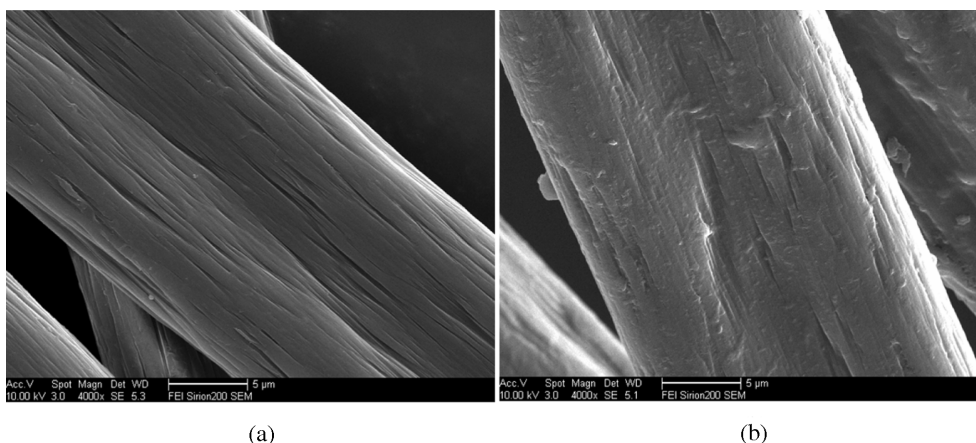
Figure 2. SEM micrographs of external surface of (a) original PAN fiber and (b) grafted PAN fiber.
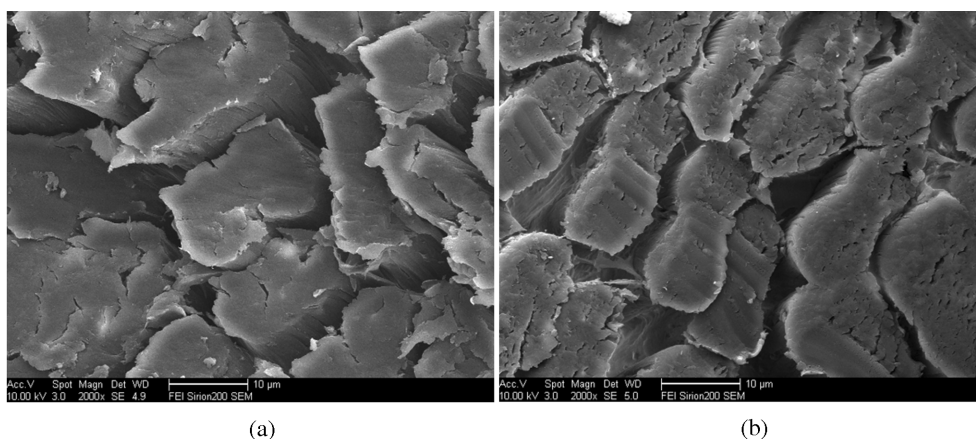

Figure 3. SEM micrographs of cross section of (a) original PAN fiber and (b) grafted PAN fiber.
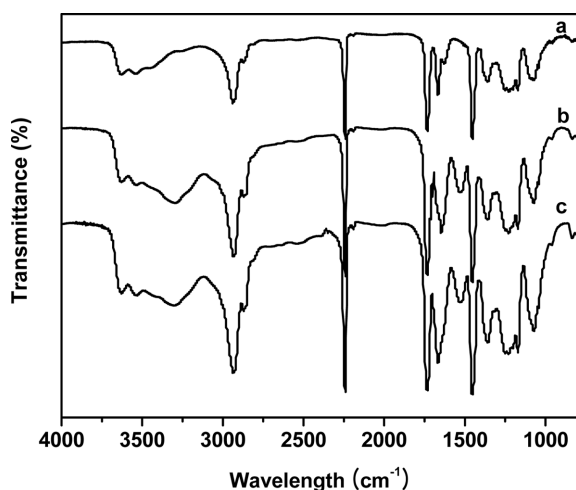

Figure 4. FTIR spectra of (a) original PAN fiber, (b) grafted PAN fiber (GE = 3.31 %) and (c) grafted PAN fiber (GE = 6.38 %).

FT-IR Spectroscopy

The chemical structure of the original and casein grafted PAN fiber was studied by FT-IR spectroscopy. The FT-IR absorbance spectra of all the samples are shown in Figure 4. The spectrum of the unmodified PAN fiber (Figure 4(a)) agrees with the literature [15] and shows the characteristic absorption peaks at 2244 ($\nu_{C\equiv N}$), 1732 ($\nu_{C=O}$), and 1454 (δ_{CH2}) cm^{-1}. Significant changes were observed for the PAN fiber grafted with casein protein (Figure 4(b) and (c)): a pronounced band at 1645 cm^{-1} ($\nu_{C=O}$, amide I), along with 1531 cm^{-1} (δ_{N-H}, amide II) of the CONH groups and around 3300 cm^{-1} ν_{OH}) of the casein are present in all the PAN-g-casein samples [16]. On the other hand, with the increase in the grafting efficiency, the intensities of the absorption bands at 1645 cm^{-1} and 1531 cm^{-1} are enhanced, suggesting an increase deposition of the casein grafted onto the PAN fiber.

X-ray Diffraction

The wide-angle XRD patterns of the original and grafted PAN fiber are shown in Figure 5(a) and Figure 5(b), respectively. The XRD pattern of original PAN fiber illustrated a sharp diffraction at $2\theta = 16.8$ °, a relatively weak diffraction at $2\theta = 29.6$ ° and amorphous between $2\theta = 20$ ° and 30°. This
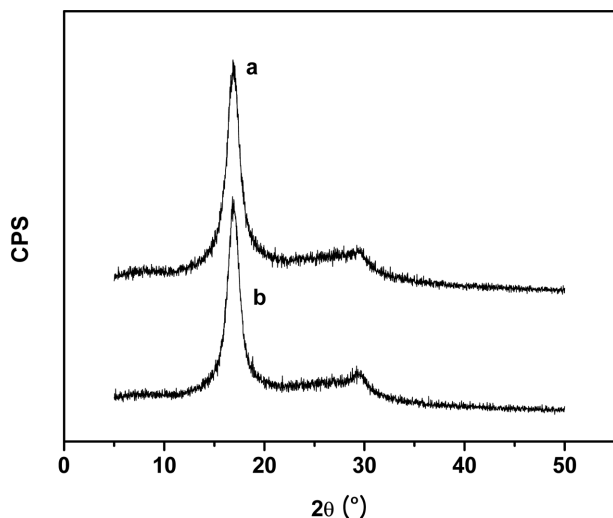
Figure 5. X-ray diffraction of (a) original PAN fiber, (b) grafted PAN fiber.

Figure 7. Comparison of specific electric resistance of original and grafted PAN fiber; chlorination temperature: 100 °C, chlorination time: 30 min, grafting temperature: 80 °C, grafting time: 10 min.

pattern is identical to the data-base known in the literature for PAN [17,18]. According to these literatures, these two peaks are related to Bragg planes [010] and [300], with distances of 5.29 and 3.04 Å between the planes, respectively. This crystalline structure can be expected from the special spatial helical conformation of PAN chains due to the strong dipole of the nitrile groups [19]. As can be seen from the Figure 5(b), the XRD pattern of the grafted PAN fiber was almost unchanged, which indicated that crystalline structures of the treated fiber has not been affected by the grafting modification of casein.

Moisture Absorption

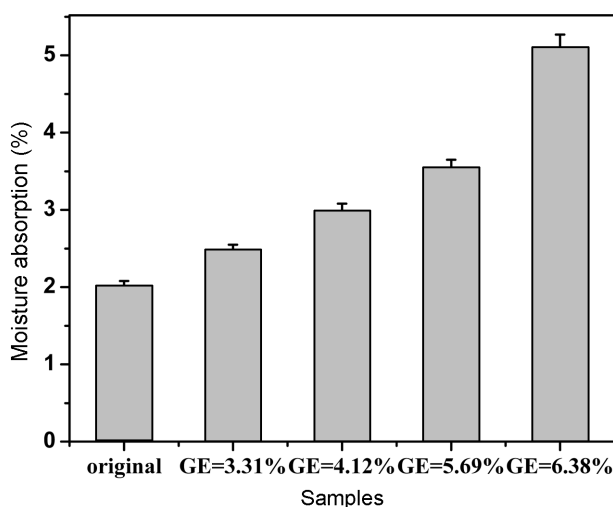After grafting of casein, some polar groups such as amine

Figure 6. Comparison of moisture absorption of original and grafted PAN fiber; chlorination temperature: 100 °C, chlorination time: 30 min, grafting temperature: 80 °C, grafting time: 10 min.
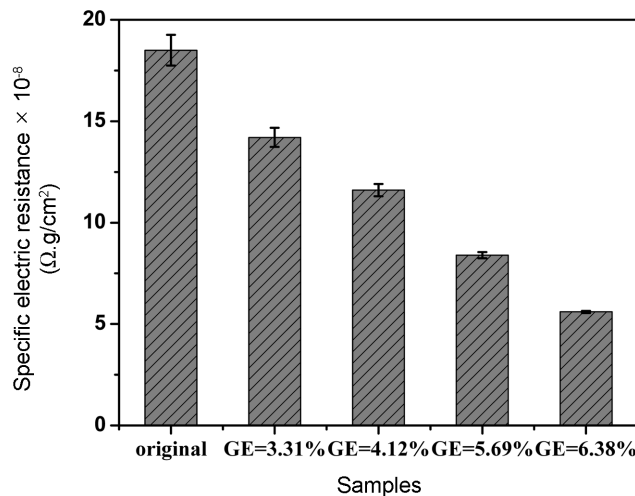
groups ($-NH_2$, $-NH-$), $-OH$, $-COOH$, and so on were introduced onto the PAN fiber. As shown in Figure 6, moisture absorption of the grafted PAN fiber was improved to some extent when compared with the original fiber. It should be pointed out that there is no reason to believe that the grafting conditions selected here are the optimum conditions. Therefore, moisture absorption of the grafted fiber, obtained in the present study, may be improved by choosing more suitable hydrolysis, chlorination, and grafting conditions, which will be the main subject of our further study. However, it can be seen that grafting of casein has already improved the wearing comfort of the fiber.

Specific Electric Resistance

The specific electric resistance of the original and grafted PAN is depicted in Figure 7. The specific electric resistance of the original fiber was $1.84 \times 10^9 \, \Omega \cdot g/cm^2$, and the results of the grafted fiber were obviously lower than that of ungrafted fibers. The decreased specific electric resistance indicated that the antistatic property of the grafted fibers was improved. The improved hydrophilicity of the fibers contributed to the enhancing antistatic property, which was due to the combination of natural protein and synthetic PAN fiber.

Water Retention Value

The different WRVs of grafted and original PAN fibers are recorded in Figure 8. The WRV of ungrafted PAN fiber was the lowest among all the tested samples. The enhanced WRV of the modified fiber indicated that casein grafted PAN fiber has quantitatively higher water accessibility than the untreated fiber. With increase in grafting efficiency, more casein had been introduced onto PAN fiber with more hydrophilic groups, which helped to improve the water retention of the resulting fiber.
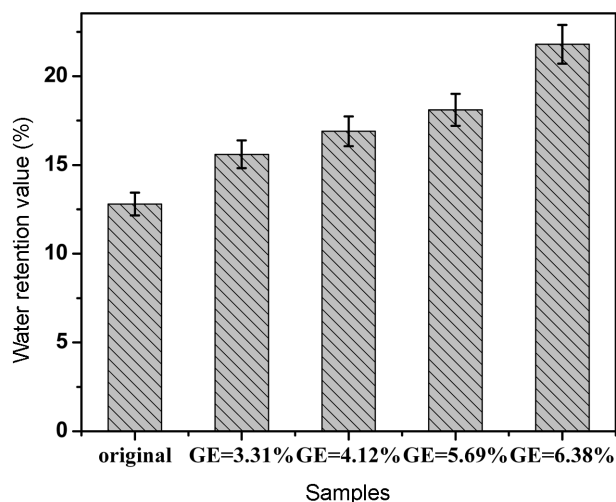
Figure 8. Comparison of water retention value of original and grafted PAN fiber; chlorination temperature: 100 °C, chlorination time: 30 min, grafting temperature: 80 °C; grafting time: 10 min.

Table 1. Comparison of mechanical properties of both original and grafted PAN fibers

Sample	Grafting efficiency (%)	Breaking strength (CN/dtex)	Breaking elongation (%)
Original	0	2.51 ± 0.15	26.7 ± 1.97
Grafted	3.31 ± 0.26	2.38 ± 0.21	26.5 ± 2.07
Grafted	4.12 ± 0.31	2.17 ± 0.23	25.4 ± 2.23
Grafted	5.69 ± 0.53	2.14 ± 0.29	27.7 ± 2.14
Grafted	6.38 ± 0.74	2.11 ± 0.28	27.6 ± 2.11

Conditions: chlorination temperature: 100 °C, chlorination time: 30 min, grafting temperature: 80 °C, grafting time: 10 min.

Mechanical Properties

The tensile strength and elongation at break of the grafted and ungrafted PAN fiber with different grafting efficiency are given in Table 1. It can be observed that the tensile strength of the casein grafted fiber decreased as compared with that of the original fiber. Several researchers have studied the alkaline hydrolysis of PAN fiber for super absorbents [20,21]. They found that as the hydrolysis progresses, alkali travels gradually from the fiber surface to its core and a gradual loss in the weight of the fiber occurs. Such structure changes caused certain negative impacts on mechanical properties such as the loss of tensile strength. In our present study, alkali hydrolysis leaded to surface erosion of the fiber and the pore size became relatively larger. This loosening of the structure decreased the intermolecular interaction between the PAN macromolecular chains. In our separate studies on the hydrolysis of PAN fiber [22,23], we found the similar observations. In spite of all these factors, the grafted PAN fiber still meets the requirement for wearing fiber.

Conclusions

The results of the present study can be summarized as follows:

1. Casein grafted PAN fiber is employed after a series of hydrolysis, chlorination, and grafting reactions to combine the merits of natural polymer and synthetic fiber.

2. SEM micrographs show that the surface of the grafted fiber is covered with casein which is confirmed by FTIR spectroscopic analysis. The crystal structure of modified PAN fiber is relatively unchanged upon grafting with casein.

3. The moisture absorption, specific electric resistance and water retention value are all improved to some extent, which is attributed to the presence of some hydrophilic groups of the natural protein grafted onto PAN fiber.

4. Though the tensile strength of the grafted PAN fiber decreases to some degree as compared with that of the original fiber, it still meets the requirement for wearing.

References

1. A. Aschi, A. Gharbi, L. Bitri, P. Calmettes, M. Daoud, V. A. Beghin, and R. Douillard, *Langmuir*, **17**, 1896 (2001).
2. B. Purevsuren and Y. Davaajav, *Journal of Thermal Analysis and Calorimetry*, **65**, 147 (2001).
3. N. G. Wang, L. N. Zhang, Y. S. Lu, and Y. M. Du, *J. Appl. Polym. Sci.*, **91**, 332 (2005).
4. Q. Z. Dong and Y. L. Hsieh, *J. Appl. Polym. Sci.*, **77**, 2543 (2000).
5. N. Somanathan, R. G. Jeevan, and R. Sanjeevi, *Polym. J.*, **25**, 937 (1993).
6. N. Somanathan, *J. Appl. Polym. Sci.*, **62**, 1407 (1996).
7. Q. Z. Dong, L. Gu, and Y. Hsieh, *Journal of China Textile University, English Edition*, **17**, 31 (2000).
8. Y. H. Liu, W. Q. Zhou, L. B. Bai, N. Zhao, and Y. W. Liu, *J. Appl. Polym. Sci.*, **100**, 4247 (2006).
9. Y. H. Liu, J. B. Li, L. Y. Yang, and Z. Q. Shi, *J. Macromol. Sci.-Pure and Applied Chemistry*, **41A**, 305 (2004).
10. K. A. Rasheed, K. Ahmed, and A. H. K. Yousufzai, *Pakistan Journal of Scientific and Industrial Research*, **37**, 92 (1994).
11. D. Mohan, G. Radhakrishnan, S. Rajadurai, R. K. Venkata, and G. G. Cameron, *J. Polym. Sci., Part A: Polym. Chem.*, **27**, 2123 (1989).
12. D. Mohan, G. Radhakrishnan, S. Rajadurai, T. Nagabhushanam, and K. T. Joseph, *J. Appl. Polym. Sci.*, **29**, 329 (1984).
13. Y. H. Liu, Y. Z. Zhang, Z. H. Liu, and K. L. Deng, *Euro. Polym. J.*, **38**, 1619 (2002).
14. N. Somanathan, V. Arumugam, and R. Sanjeevi, *Euro. Polym. J.*, **23**, 803 (1987).
15. S. B. Deng, R. B. Bai, and J. P. Chen, *J. Colloid Interf. Sci.*, **260**, 265 (2003).
16. D. Raval, B. Narola, and A. Patel, *Int. J. Polymeric*

Materials, **54**, 731 (2005).

17. L. Boguslavsky, S. Baruch, and S. Margel, *J. Colloid Interf. Sci.*, **289**, 71 (2005).

18. B. Jung, J. K. Yoon, B. Kim, and H. W. Rhee, *J. Memb. Sci.*, **246**, 67 (2005).

19. G. H. Olive and S. Olive, *Adv. Polym. Sci.*, **32**, 123 (1979).

20. M. L. Gupta, B. Gupta, W. Oppermann, and G. Hardtmann, *J.*

Appl. Polym. Sci., **91**, 3127 (2004).

21. Z. S. Cai and G. Sun, *J. Appl. Polym. Sci.,* **97**, 1227 (2005).

22. Z. Jia, Y. G. Yang, H. D. Wang, and R. Ding, *Hecheng Xianwei Gongye*, **27**, 27 (2004).

23. H. D. Wang, Y. G. Yang, R. Ding, and Z. Jia, *Shandong Ligong Daxue Xuebao (Sci & Tech)*, **17**, 94 (2003).