Preparation and Characterization of Konjac Glucomannan and Sodium Carboxymethylcellulose Blend Films

CHAOBO XIAO, YONGSHANG LU, HONGJUAN LIU, LINA ZHANG

Department of Chemistry, Wuhan University, Wuhan 430072, People's Republic of China

ABSTRACT: The novel blend films of konjac glucomannan (KGM) and sodium carboxymethylcellulose (NaCMC) were prepared by casting the mixed polymer aqueous solutions. The physical properties of the blend films from konjac glucomannan and sodium carboxymethylcellulose were investigated by using FT-infrared (FTIR), wide-angle X-ray diffraction (WAXD), differential thermal analysis (DTA), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and measurements of mechanical properties. The experimental results showed that the occurrence of the interactions between KGM and NaCMC molecular chains through hydrogen bond formation, and the physical properties of the films largely depend on the blending ratio. The thermal stability, mechanical properties of both tensile strength, and elongation at break of the blend films were improved by blending KGM with NaCMC. The surface morphology of the films observed by SEM was consistent with the results mentioned above. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 26–31, 2001

Key words: konjac glucomannan; sodium carboxymethylcellulose; blend films; hydrogen bond; physical properties; miscibility

INTRODUCTION

Recent research and development of biomaterials have been directed to blending different polymers to obtain new products having some of the desired properties of each component. Moreover, blending different existing polymers is of considerable importance as an alternative to graft copolymerization and the very high cost to develop new homopolymers.[1] Among the various new biomaterials that have been introduced, natural polymers become more and more important because of their low cost, rich resource, nontoxicity, degradability, and biocompatibility.

Konjac glucomannan is a natural water-soluble polysaccharide similar to cellulose. It is composed of a backbone chain of β-1,4 linked D-mannoses and D-glucose,[2] and there are some branching points at the C-3 of the mannoses.[3] The applied research on KGM has made a great progress in pharmaceutical, food, chemical engineering, and fabric aspects.[4–7] Some blend films of KGM with other natural or synthetic polymers have been reported. Component of the blends include pullulan,[8] cellulose,[9,10] and hydroxypropylcellulose.[11] In our previous work,[12] blend films of KGM and chitosan were prepared and characterized by FTIR, WAXD, SEM, DTA, and TGA. The results indicated the occurrence of hydrogen bonds between two polymers, and improvement of mechanical strength, thermal stability, and swelling properties with the increase of KGM in the blend films.

Due to the presence of hydrogen bonding between COO⁻ groups in sodium alginate and OH groups in KGM, the blend films of sodium algi-

nate and KGM having improved mechanical properties and thermal stability have been successfully obtained in our laboratory.[13] This prompted us to study the blend films of KGM and NaCMC. The sodium salt of carboxymethylcellulose is a highly water-soluble anionic polysaccharide.[14] Its mucous-like consistency, as well as the ability of COO^- and unsubstituted OH groups in NaCMC to interact with OH and $COCH_3$ groups in KGM through hydrogen formation may produce new materials that possess essentially superior properties compromise between the pure components. Such materials may be biodegradable and recyclable. Thus, they are suitable materials for environmental conservation. In this article, the blend films of KGM and NaCMC were prepared using the solvent-casting technique. The physical properties and morphology of the films were studied by using FTIR, WAXD, TDA, TGA, SEM, and by measurements of mechanical properties. The properties of the resulting blend films will be studied in detail in relation to the blending ratios. The results reported in this article may be of help in finding further applications of this blended material in biomedical and pharmaceutical fields.

EXPERIMENTAL

Materials

NaCMC was purchased from the Chemical Agents Factory of Shanghai. Konjac glucomannan was extracted and purified from the tuber of *Amorphophallus konjac* (supplied by the Zhuxi Konjac Institute, Hubei) according to our previous work.[12] The viscosity average molecular weight of KGM was calculated to be 2.5×10^5 by using viscometry according to the Mark-Houwink equation[15]: $[\eta] = 3.8 \times 10^{-2} M^{0.723}$. Other chemical agents used were analytically pure.

Preparation of the Films

Desired quantities of NaCMC and KGM were dissolved in water to obtain the solution of 3 wt %, respectively. The pure and mixture solution of NaCMC and KGM with different weight ratios (100/0, 90/10, 70/30, 50/50, 30/70, 10/90, 0/100, KGM/NaCMC) were cast on a Teflon gasket. The water was allowed to evaporate at the room temperature. The films of pure and blend were dislodged carefully, and then subjected to further drying under vacuum for 48 h to obtain the dried films. The films of the different ratios above were coded as KGM, KC-1, KC-2, KC-3, KC-4, KC-5, and CM, respectively. The films thickness was ranged 80 ± 5 μm.

Measurements

Infrared spectra (IR) of the films were measured by using a Nicolet (U.S.A.) 170SX FTIR spectrometer and used as KBr pellets. The X-ray diffraction patterns of the films about 80-μm thickness with a Rigaku (Japan) Dmax-II X-ray diffractometer and used CuK_α target at 40 kV and 50 mA, the diffraction angle ranged from $40-4°$, and the crystallinities (X_c) of the films were calculated by[16]

$$X_c = F_c/(F_c + F_a) \times 100\%$$

where F_c and F_a are the area of crystal and noncrystal regions, respectively. The TGA and DTA of powered samples of the films were performed by a PRT-2 TGA-DTA thermobalance (Beijing Optical Instruments Factory, China) under nitrogen atmosphere with a flow capacity of 30 mL/min. The starting decomposition temperature was evaluated by considering the intersection point of tangents of TGA curves. The stress–strain measurements were performed by an AG-A electron tensile tester (Shimadzu Co.) at the environment of 24°C and 60% relative humidity using a crosshead speed of 5 mm/min, the specimens (80 ± 5 μm thickness and 4 mm width) used were 30 mm long. The morphology of film surfaces was observed and photographed by using a Hitachi SX-650 scanning electron microscopy (Japan) after gold coating.

RESULTS AND DISCUSSION

General Properties of the Films

Pure and blend films in all blending ratio were transparent and optically clear to the naked eye. The films of pure and blend were so easily dissolved in the distilled water that we could not obtain their water absorbability.

FT-infrared is of importance to the study of the molecular structure. The width and intensity of spectral bands as well as position of the peaks are all sensitive to environmental changes and to conformations of macromolecules on the molecular level. Intermolecular interactions occur when dif-
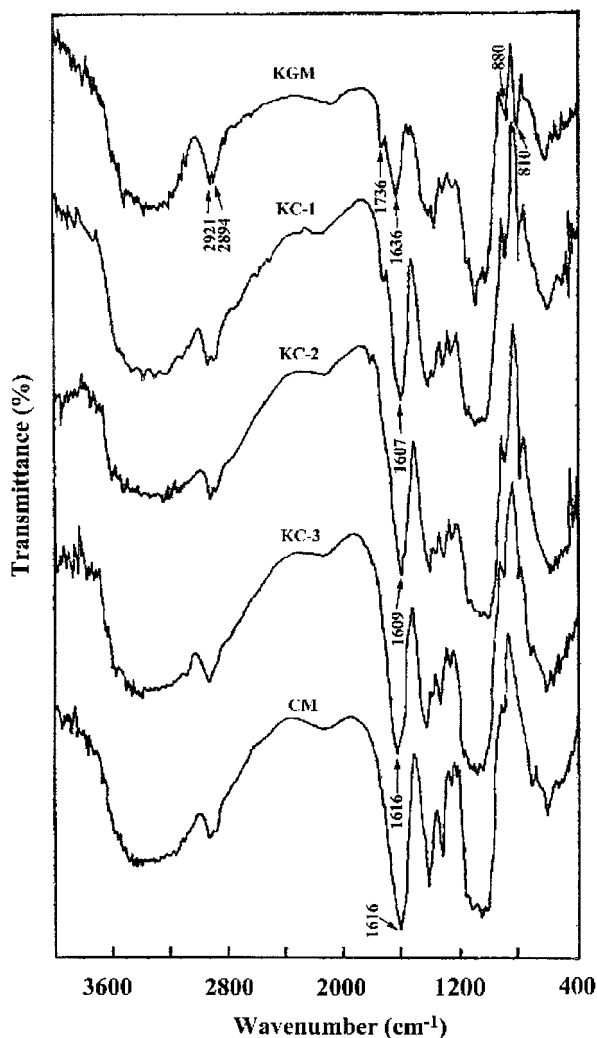
Figure 1 FTIR spectra of the pure and blend films.

ferent polymers are compatible. Therefore, the FTIR spectra of the blends are different from those of pure polymers, which is advantageous to the study of compatibility between two polymers. Figure 1 shows the infrared spectra for the films of KGM, the blends and NaCMC in the wavelength range of 4000–400 cm^{-1}. The characteristic absorption bands of mannose in KGM appeared at 810 and 880 cm^{-1}.[17] The stretching vibration peaks of C—H of methyl at 2921 and 2894 cm^{-1} and of the carbonyl at 1736 cm^{-1} were assigned to the aceto groups in KGM.[18] The bands at 1616 cm^{-1} was attributed to the characteristic absorptions of asymmetrical stretching vibration of COO^- in NaCMC.[19] For the blend films, the stretching peak of carbonyl group at 1736 cm^{-1} appeared for pure KGM disappeared gradually. Furthermore, the strong absorption band at 1616

cm^{-1} for NaCMC film shifted to 1607 cm^{-1} and the bands at around 3400 cm^{-1} broaden and shifted to a higher wavelength with the increase of the NaCMC content. Based upon these results, it seems that the COO^- and OH groups in NaCMC should participate in intermolecular hydrogen bonds with the OH and $COCH_3$ groups in KGM, respectively.

Crystallinities of the Films

X-ray diffraction patterns of pure and the blend films are shown in Figure 2. If the KGM and NaCMC have low compatibility, each polymer would have its own crystal region in the blend films; thus, the X-ray diffraction patterns are expressed as simply mixed patterns of KGM and NaCMC with the same ratio as those for blending. However, the patterns of the blend films in Figure 2 show that the diffraction peaks of NaCMC at $2\theta = 6°$ disappeared, and the intensity of the diffraction peaks at about $2\theta = 10°$ increased with the increase of the KGM content. The crystallinities of KGM, KC-2, KC-3, KC-4, and CM were calculated, and were in the order of CM > KC-2 > KC-3 > KC-4 > KGM. The crystallinities of the blend films decreased, compared with the pure NaCMC, indicating that some intermolecular in-

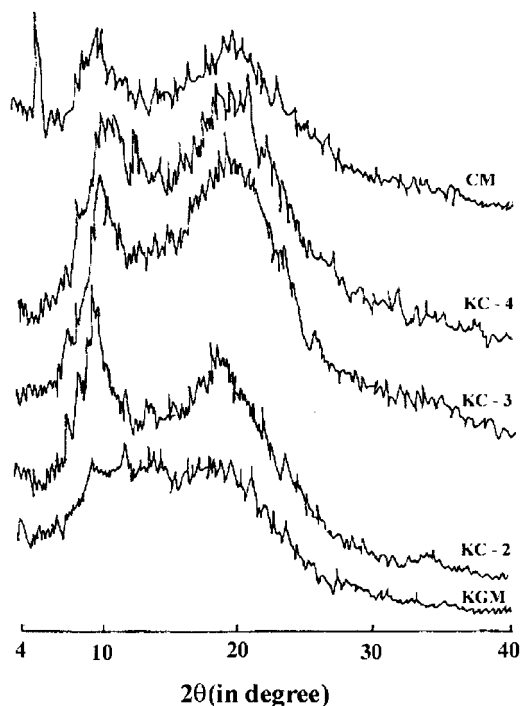**Figure 2** Wide-angle X-ray diffraction of the pure and blend films.

Figure 3 DTA curves of the pure and blend films.
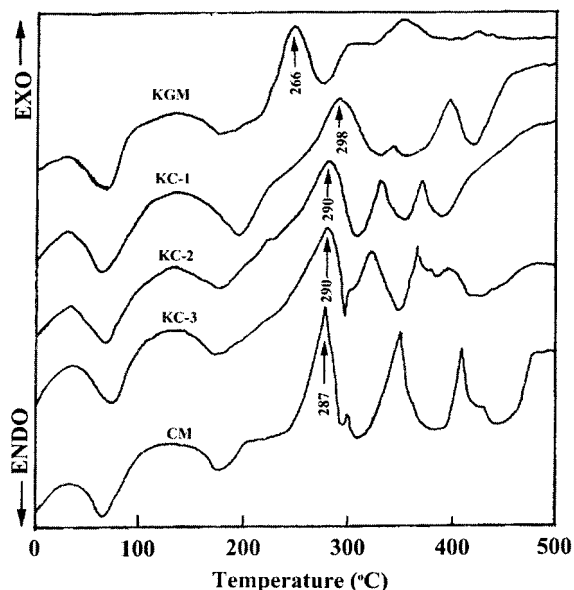

Figure 4 TGA curves of the pure and blend films.

teractions between KGM and NaCMC occurred, which destroyed the original crystalline domains of NaCMC, resulting in the changes of WAXD patterns of the blends. This is in good agreement with the latter results obtained from SEM.

Thermal Properties of the Films

The thermal behaviors of the pure and blend films obtained by means of DTA are shown in Figure 3. The DTA curve of the pure KGM film shows an endothermic shift at about 66°C was due to loss of moisture. An exothermic peak at about 266°C was attributed to the thermal degradation of KGM. The DTA curve of the NaCMC shows exothermic peaks at about 287°C, which was attributed to the greatest thermal disintegration peak. However, all DTA curves of the blend films show that the exothermic peaks at about 290°C, which were believed to be the greatest thermal disintegration peaks (see TGA results), shifted to the higher temperature, compared with the pure components.

The results of TG measurements of the pure and blend films are shown in Figure 4. The three active weight-loss steps of the blend films were found at about 60–80, 250–320, and 350–500°C. The first step was due to the loss of moisture. The second step was attributed to the disintegration of intermolecular side chains.[20] The third weight loss was believed to be caused by a chemical reaction, such as main-chain disintegration or rear-
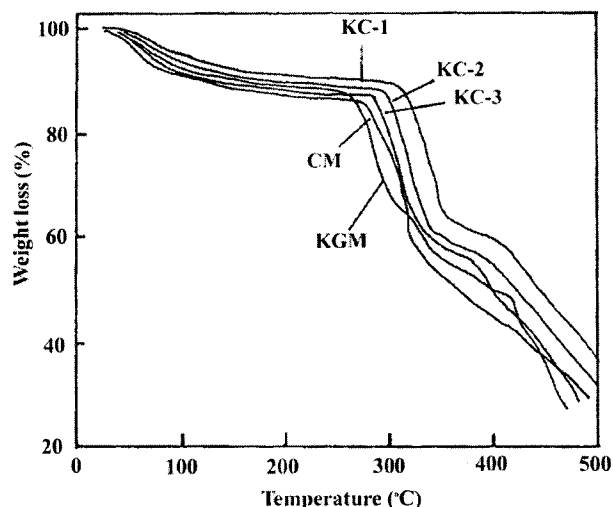
rangement.[21] The starting temperature of the greatest decomposition for the blend films was in the order of KC-1 (291°C) > KC-2 (285°C) > KC-3 (272°C) > NaCMC (260°C) > KGM (250°C).

According to Figure 3 and Figure 4, it is understood that the thermal stability of the blend films was improved by blending NaCMC with KGM due to hydrogen bonding interactions between two kinds of polymer molecules.

Mechanical Properties of the Films

With polymer blends exhibiting two behaviors, definite advantages can be derived if mechanical compatibility can be achieved. With miscible polymer mixtures, the mechanical compatibility is assured, and a property compromise between the constituents is therefore achieved. Thus, with a
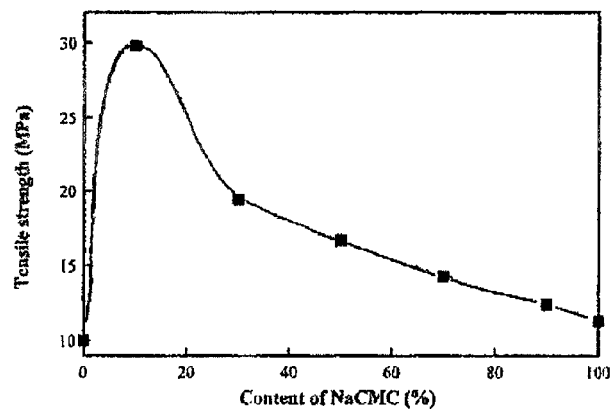

Figure 5 Dependence of tensile strength on the content of NaCMC for the pure and blend films.
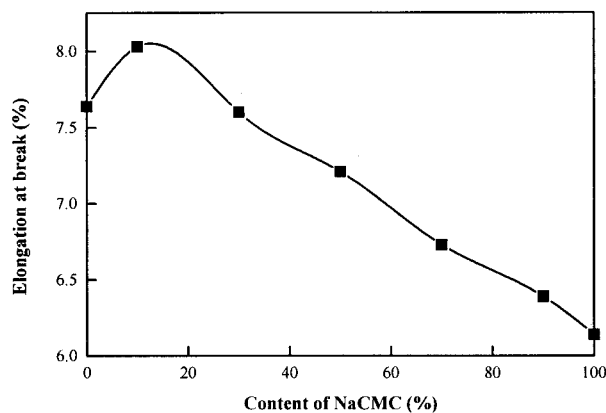
Figure 6 Dependence of the elongation at break on the content of NaCMC for the pure and blend films.

miscible polymer blend, a range of performance characteristics between the component polymers can lead to a large number of potentially useful

and different products.[22] The dependence of tensile strength on the content of KGM for the pure and blend films are shown in Figure 5. The tensile strength seems to vary according to the NaCMC content in two steps. In the first step, the tensile strength increased linearly with the content of NaCMC, achieved a maximum value 29.8 MPa at about 10 wt % of the NaCMC content. In the second step, the tensile strength decreased with the increase of NaCMC. Figure 6 shows the dependence of the elongation at break on the content of NaCMC for the pure and blend films, the curve of the breaking elongation expresses a tendency similar to that of tensile strength, and reaches to a maximum value when the NaCMC content in the blend film was 10 wt %. The conclusion can be drawn that blending NaCMC with KGM is effective in inducing significant changes to the mechanical properties of the blending films. The improved mechanical properties of the blend
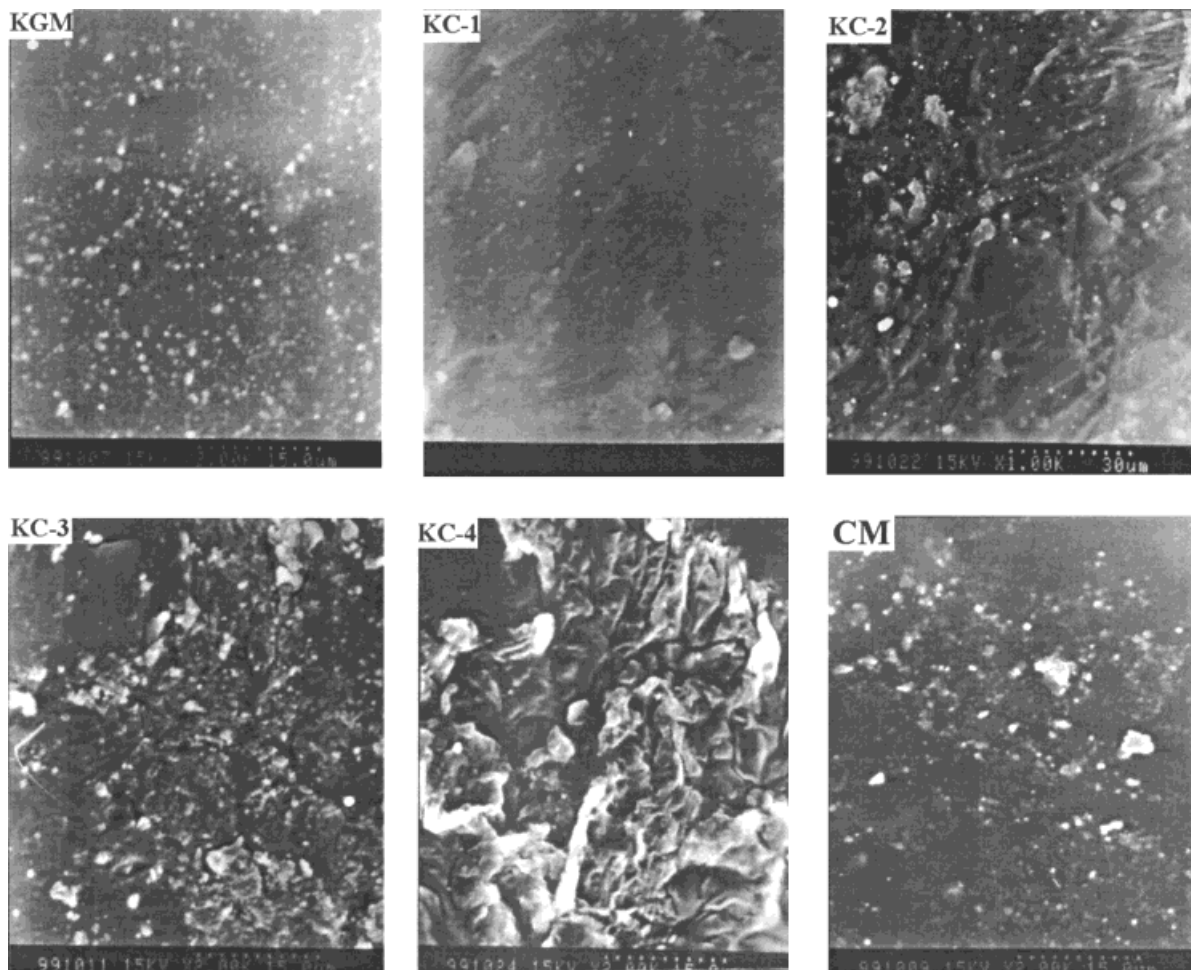

Figure 7 SEMs of the pure and blend films.

films were believed to the intermolecular interactions through hydrogen bond formation.

Morphological Characteristics of the Films

The surface exposure to air of the pure and blend films were examined by SEM. The morphology of the pure and blend films are shown in Figure 7. The films of pure KGM and NaCMC exhibit a uniform microstructure, which leads to the formation of homogenous films having densely packed molecules of KGM or NaCMC. The blend films of KC-1 and KG-2 show smooth morphology, suggesting that high miscibility occurred when the content of the NaCMC in the blend films was low. As the NaCMC content increased, the morphology of the blend film surfaces changed from being smooth to becoming rough resulted from phase separation, which may lead to the decrease of crystallinities of the blend films.

CONCLUSIONS

The results reported confirm that NaCMC can be usefully added to KGM for preparation of the blends by blending the natural polymers solution. The blend films are transparent and optical to the naked eye. The physical properties of the blend films largely depend on the blending ratio. Changes in shape and intensity of infrared spectral absorption frequencies characteristic of either KGM or NaCMC have been attributed to the presence of interactions between KGM and NaCMC chains. The crystallinities of the blend films decreased with the increase of NaCMC content in blend films. The thermal stability and mechanical properties of the blend films were improved. This point was confirmed by the results from SEM. It is worth noting that blending KGM with NaCMC permits the preparation of films having excellent mechanical properties, particularly when the NaCMC content in blend films was about 10 wt %. The interchain hydrogen bonding of COO^- and OH groups in NaCMC with OH and $COCH_3$ groups in KGM exist in the blend films, resulting in the improvement of the properties. These materials having a highly functional performance, acquired by blending KGM with NaCMC, may become attractive in the application of biomedical and pharmaceutical devices.

REFERENCES

1. El-Salmavi, K.; Abu-Zeid, M. M.; El-Nagger, A. M.; Mamdouh, M. J Appl Polym Sci 1999, 72, 509.
2. Katoo, K.; Matsuda, K. Agic Biol Chem 1969, 42, 1446.
3. Maeda, M.; Shimahara, H.; Sngiyama, N. Agic Biol Chem 1980, 44, 245.
4. Brannon, P. L.; Reilly Williams, J. J. Proc Int Symp Controlled Release Biact Biomater 1996, 23, 497.
5. Tian, B.; Dong, C.; Chen, L. J Appl Polym Sci 1998, 67, 1035.
6. Kohyama, K.; Nishinari, K. JARQ 1997, 31, 301.
7. Shen, Y.; Yang, X. Food Sci (Chin) 1995, 16, 14.
8. Yue, C. L.; Dave, V.; Kaplan, D. L.; McCarthy, S. P. Polym Prepr 1995, 36, 416.
9. Yang, G.; Zhang, L.; Yamane, C.; Miyamoto, I.; Inamoto, M.; Okajima, K. J Membr Sci 1998, 139, 47.
10. Zhang, L.; Yang, G.; Yamane, C.; Miyamoto, I.; Inamoto, M.; Okajima, K. Polym Mater Sci Eng 1997, 77, 636.
11. Shimichi, S.; Keiji, S.; Kazuhiro, A.; Hitoshi, N. Sen-i Gakkashi 1992, 48, 437.
12. Xiao, C.; Gao, S.; Wang, H.; Zhang, L. J Appl Polym Sci 2000, 75, 509.
13. Xiao, C.; Gao, S.; Zhang, L. J Appl Polym Sci 2000, 77, 617.
14. Chatterji, P. R.; Kaur, H. Polymer 1992, 33, 2388.
15. Kishira, N. Agric Biol Chem 1979, 43, 2391.
15. Rabek, J. F. Experimental Methods in Polymer Chemistry: Applications of Wide-Angle X-ray Diffraction (WAXD) to the Study of the Structure of Polymers; Wiley Interscience: Chichester, 1980; p 505.
16. Jia, C.; Chen, S.; Mo, W. Chin Biochem J 1988, 4, 407.
17. Maeda, M.; Shimahara, H.; Sugiyamsa, N. Agric Biol Chem 1980, 44, 245.
18. Williams, D. H.; Fleming, I. Spectroscopic Methods on Organic Chemistry; McGraw-Hill Book Company: London, 1980; 3rd ed.
19. Hirabayashi, K.; Suzuki, T.; Nagura, M.; Ishikawa, H. Bunseki Kiki 1974, 12, 437.
20. Liang, C.; Hirabayashi, K. J Appl Polym Sci 1992, 45, 1937.
21. Olabisi, O.; Robinson, L. M.; Show, M. T. Polymer-Polymer Miscibility; Academic Press: New York, 1979.