Effect of Interactions Between Poly(vinyl alcohol) and Urea on the Water Solubility of Poly(vinyl alcohol)

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ABSTRACT: Poly(vinyl alcohol) (PVA) is an important water-soluble polymer. Its many applications (e.g., textile sizing, dispersants, and adhesives) greatly depend on its water solubility and particularly on its dissolution rate in water. In this study, urea, combined with methanol, was adopted to improve the water solubility of PVA. The structures, properties, and dissolving mechanism of the modified PVA were studied with Fourier transform infrared spectroscopy, NMR, laser light scattering, differential scanning calorimetry, and wide-angle X-ray diffraction. The results showed that through specific chemical reactions between PVA and urea in methanol, isocyanate and methyl carbamate groups were generated on the lateral chains of PVA. These large side groups could effectively expand PVA macromolecular chains and hence increase their intermolecular distance, weaken the intramolecular and intermolecular hydrogen bonds of PVA, change the aggregation structure of PVA, and decrease its lattice energy and crystallinity. In addition, the isocyanate groups on the PVA macromolecular chains strongly interacted with water. All these effects benefited the water solubility of PVA. Therefore, the dissolution rate of the modified PVA increased by 50% versus that of the neat PVA, and the quality of the modified PVA aqueous solution was improved quite a bit. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 517–523, 2009

Key words: modification; water-soluble polymers

INTRODUCTION

Poly(vinyl alcohol) (PVA), having many multihydroxyl groups and strong hydrogen bonds in its system, is an important water-soluble polymer and has been widely used in many applications, such as coatings, adhesives, paper and textile sizing, dispersant agents, fibers, and films.[1–4] Many of these applications are based on its good water solubility and particularly on its dissolution rate in water.

The water solubility of PVA usually depends on its polymerization degree and especially its hydrolysis degree. For example, at the same polymerization degree of, for example, 1700, PVA with a hydrolysis degree of 88% can dissolve in water at 40°C; however, PVA with a hydrolysis degree of 99% cannot dissolve in water if the temperature is lower than 80°C. This big difference is due to the different intramolecular and intermolecular hydrogen bonds in 99% hydrolyzed PVA and 88% hydrolyzed PVA. For the former, the large number of hydrogen bonds that form in the almost completely hydrolyzed system restricts the dissolution of many PVA macromolecules in water. However, for the latter, the number of formed hydrogen bonds is much less, and there are still many residual acetate groups on the PVA macromolecular chains; these can decrease the number of hydrogen bonds and hence contribute to an increase in the water solubility of PVA.[5]

To modify the water solubility of PVA, a chemical method such as copolymerization is often adopted by many scientists.[6–12] For example, Manuel et al.[13] obtained PVA products with good water solubility through the copolymerization of vinyl acetate with a small amount of acrylamide and then the partial hydrolyzation of the prepared copolymers. Moritani and Okaya[14] prepared modified PVA via the copolymerization of a vinyl acetate matrix with a small amount of N-methoxyl methyl group acrylamide or N-methylol methyl group acrylamide and then the hydrolyzation of the prepared copolymers. Kazushi and Takaaki[15] prepared modified PVA with different solubility via the open loop polymerization of a lactone compound with hydroxyl groups of PVA and the subsequent adjustment of the polymerization degree of the modified lactone. Wen and Zhang[16] obtained water-soluble PVA through the Michael addition reaction of PVA with acrylamide and subsequent hydrolyzation with an alkali as the catalyst. Although these chemical methods improve the water solubility of PVA, the related preparation process is quite complex and difficult to industrialize.

Developing a simple, efficient, and environmentally friendly technique for modifying the water solubility of highly hydrolyzed PVA is still a challenge.

In this study, urea combined with methanol was adopted to modify the water solubility of PVA with a 99% hydrolyzation degree, and the related structures, water solubility, and properties of the modified PVA were investigated.

EXPERIMENTAL

Materials

PVA with a polymerization degree of 1700 and a hydrolyzation degree of 99 mol % was commercially obtained from Sinopec Sichuan Vinylon Works (Chongqing, China). Urea and methanol, analytically pure, were purchased from Kelong Chemical Reagent Plant (Chengdu, China).

Preparation of the modified PVA

PVA pellets, distilled water, methanol, and urea in certain proportions were mixed at room temperature for 10 min and then dried in a modified rotary evaporator under vacuum conditions at a certain temperature. Different modified PVA products were obtained through changes in the drying temperature and the degree of vacuum.

Dissolution of the PVA samples

Modified PVA samples (4 g) were added to 96 g of water with continual stirring for 10 min at room temperature and then heated at a certain temperature until they were completely dissolved.

Purification of the modified PVA

Before the measurements [including Fourier transform infrared (FTIR) spectroscopy, NMR, laser light scattering (LLS), differential scanning calorimetry (DSC), and X-ray diffraction (XRD)], the modified PVA was Soxhlet-extracted with methanol and then dried for characterization.

Characterization

The FTIR analysis was carried out on a Nicolet 20SXB FTIR spectrophotometer (Madison, WI) in the transmission mode with KBr disks or pellets at room temperature.

^{13}C-NMR (400 MHz) spectra were recorded on an Inova Varian spectrometer (Zug, Switzerland) in deuterated dimethyl sulfoxide.

The light scattering measurements were taken with a Malvern series 9000 apparatus (Holtsville, New York). The light source was a 1-W argon-ion

laser operated at a power of 100 mW and a wavelength of 532 nm; it was focused on the sample cell through a temperature-controlled chamber (the temperature was controlled within $\pm 0.01°C$) filled with distilled water. PVA solutions with concentrations of 0.001–1 g/L were prepared in a precleaned wide-mouth bottle with stirring at 80°C for 2 h until homogeneous solutions were formed, and then they were filtered with Millipore (Chengdu, China) 0.45-μm filters directly into sealed test tubes. The sample solutions were kept in a thermostat oven at a constant temperature of 25°C for 1 day for stabilization before dynamic light scattering and static light scattering measurements.

The DSC analysis was conducted on a Netzsch DSC-204 thermal analyzer (Selb, Germany) at a heating rate of 10°C/min from 30 to 250°C under a nitrogen flow with a sample weight of approximately 6 mg. The melting and crystallization behaviors of the samples were recorded. The crystallinity (X) of PVA and modified PVA was calculated according to the following formula:

$$X(\%) = \frac{\Delta H_f}{\Delta H_f^0} \times 100\%$$

where ΔH_f is the fusion enthalpy of the modified PVA and ΔH_f^0 is the fusion enthalpy of the 100% crystalline PVA (i.e., 168 J/g).[17]

The XRD patterns of PVA and modified PVA were measured with graphite monochromatized Cu Kα radiation generated at 40 kV and 35 mA in a X'Pert Pro MPD X-ray diffractometer (Almelo, The Netherlands) at a scanning speed of 0.08°/s from 2θ = 10° to 2θ = 50°. The scan mode was continuous, and the step size was 0.02°.

RESULTS AND DISCUSSION

Improvement of the water solubility of PVA

The dissolution results for PVA samples treated with different urea contents are shown in Table I. With an increase in the urea content, the dissolving

TABLE I
Dissolving Temperature and Dissolving Time for Modified PVA Treated with Different Amounts of Urea

Amount of urea (%)	Dissolving temperature (°C)	Dissolving time (min)	State of the solution
0	80	>120	Presence of many undissolved particles
1	80	95	Clear and transparent
2	80	89	Clear and transparent
3	80	83	Clear and transparent
4	80	78	Clear and transparent
5	80	70	Clear and transparent

time of the modified PVA rapidly decreased and the limpidity property of the solution became better in comparison with pure PVA; this indicated that urea could obviously enhance the dissolution rate of PVA in water and improve the quality of an aqueous PVA solution.

PVA is a multihydroxyl polymer. The hydroxyl groups endow PVA with good water solubility. However, excessive hydroxyl groups would produce many very strong hydrogen bonds between both intra-PVA and inter-PVA macromolecular chains and, on the contrary, would prevent PVA from dissolving in water. PVA is also a semicrystallinity polymer, and its dissolution process includes two stages: swelling and dissolution. During the dissolution process, water enters first the loose, amorphous region of PVA and then the crystalline region until PVA particles are completely dissolved. The improvement in the solubility of PVA with the incorporation of urea may be attributed to the interaction between urea and PVA, which weakens the intrahydrogen and interhydrogen bonds of PVA, reduces the intramolecular or intermolecular interactions in PVA, depresses the melting point and crystallinity of PVA, and thus accelerates the dissolution of PVA.

FTIR analysis

To identify the formation of the special interactions between PVA and urea, the FTIR spectra of PVA and modified PVA were tested, as shown in Figure 1. A new absorption peak at about 2160 cm^{-1} appeared in the infrared spectrum of the modified PVA, and its intensity increased with an increase in the urea content. As is well known,[18] the absorption peaks at 2160 cm^{-1} are properly attributed to the stretching
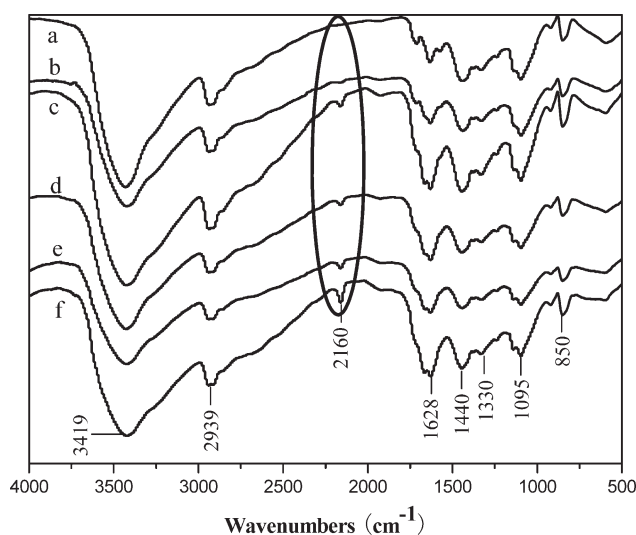

Figure 1 FTIR spectra of (a) PVA and (b–f) modified PVA with a urea content of 1, 2, 3, 4, or 5 wt %, respectively.
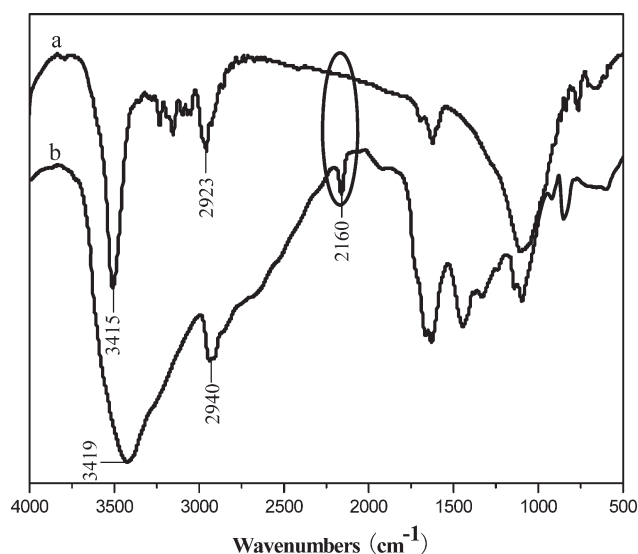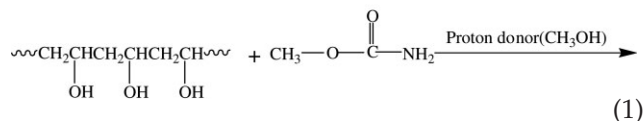

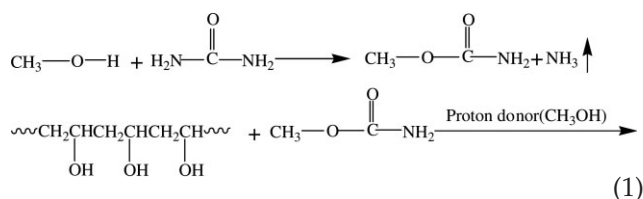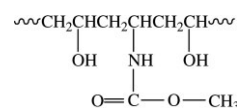**Figure 2** FTIR spectra of modified PVA (a) without methanol and (b) with methanol.

vibration of —C=C=C—, —C≡C—, —C≡N—, and —N=C=O groups. However, in our modified PVA, it was very difficult for the —C=C=C—, —C≡C—, and —C≡N— groups to form. Therefore, the absorption band at 2160 cm^{-1} could be attributed to the stretching vibration of —N=C=O. To describe the formation of —N=C=O, the FTIR spectra of modified PVA with and without methanol, samples with and without PVA, and water-washed and unwashed modified PVA were recorded, as shown in Figures 2–4.

Figure 2 shows that without methanol, no characteristic absorption peak appeared at 2160 cm^{-1} (the featured absorption of —N=C=O), whereas this absorption peak appeared in the presence of methanol, showing that methanol plays a very important role in the formation of —N=C=O. However, even in the presence of methanol, no absorption at 2160 cm^{-1} appeared in the range of 2100–2500 cm^{-1} in the FTIR spectra of the sample without PVA [Fig. 3(a)]. Therefore, we can deduce eqs. (1) and (2); that is, urea first reacts with the hydroxyl group of methanol, and then the reactant methyl carbamate further reacts with the hydroxyl groups of PVA under protonic conditions:
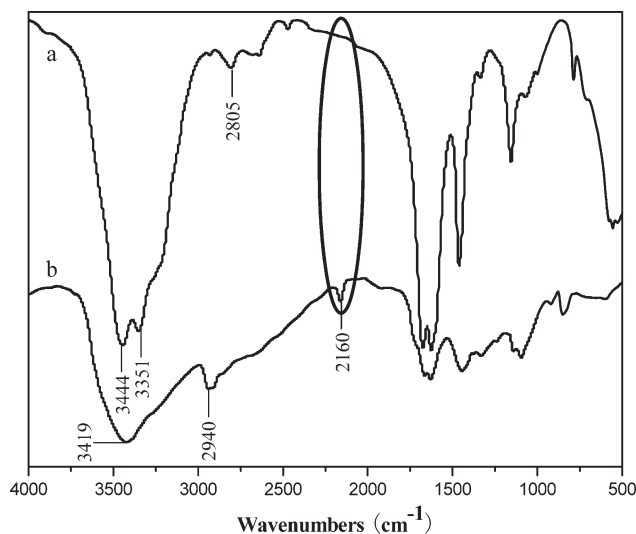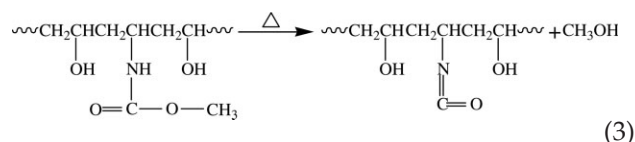

(1)

(2)

Figure 3 FTIR spectra of (a) urea/methanol/water and (b) PVA/urea/methanol/water.

Figure 4 FTIR spectra of (a) water-washed and (b) unwashed modified PVA.

When the reactant in eq. (2) is dried, a kind of modified PVA containing α-isocyanate groups can be produced, as presented in eq. (3):

$$\tag{3}$$

As mentioned previously, the absorption bands between 2100 and 2500 cm^{-1} in the spectra may be the stretching vibration characteristic absorptions of —C=C=C—, —C≡C—, —C≡N—, and —N=C=O groups. Among these groups, only the isocyanate group can react with water and form carbamide; the characteristic absorption peak at 2160 cm^{-1} thus disappeared. It can be seen from the FTIR spectra of the water-washed and unwashed modified PVA (Fig. 4) that no peak appeared at 2160 cm^{-1} when modified PVA was washed with water; this verified the formation of the modified PVA with α-isocyanate.

It can also noticed in Figure 1 that the characteristic absorption peak of the isocyanate group in our modified systems shifted to a lower frequency in comparison with their normal location,[18] that is, 2255–2275 cm^{-1}. This was due to the presence of strong interactions between the oxygen in the isocyanate group and the hydroxyl group of PVA.

NMR analysis

To obtain basic information about the structures of the modified PVA and the conversion rate of PVA and urea, ^{13}C-NMR spectra of PVA and modified PVA at room temperature were analyzed (Fig. 5). In comparison with Figure 5(a,b), a weak characteristic

peak appeared in the 170 ppm region, but a strong characteristic peak appeared in the 160 ppm region. The characteristic peak shifted to the low region with the treatment of urea, thus showing that a new compound formed in our modified systems. As is
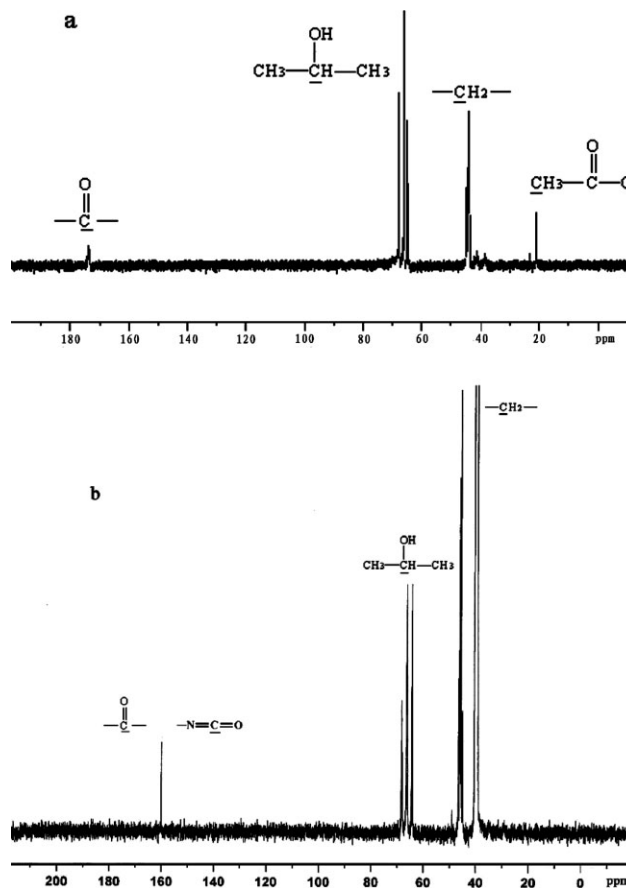

Figure 5 ^{13}C-NMR spectra of (a) PVA and (b) modified PVA treated with 5 wt % urea.

known, the displacement from 160 to 180 ppm is the characteristic peak of the double bond of carbon to oxygen.[19] In the analysis of the FTIR spectrum, the corresponding chemical reaction between PVA and urea in the modified systems was confirmed, and this indicated some α-isocyanate and methyl carbamate groups in the lateral chains of PVA. With the ratios of the integration intensity of the proton resonance of pure PVA and modified PVA in the 160–180 ppm region, the conversion of the reaction between PVA and urea was calculated. The results showed that about 58% of the urea was converted into α-isocyanate and methyl carbamate.

LLS analysis

The $\langle R_g \rangle / \langle R_h \rangle$ ratios and A_2, where $\langle R_g \rangle / \langle R_h \rangle$ is the ratio of the average radius of gyration to the average hydrodynamic radius and A_2 is the second viral coefficient, 1values of PVA and modified PVA, which were obtained from the LLS analysis, are shown in Table II. It is well known that the $\langle R_g \rangle / \langle R_h \rangle$ ratio can reflect the structure of a polymer chain or a particle, and A_2 is a measurement of the interactions between the solute and solvent. For uniform nondraining spheres, hyperbranched clusters, and random coils, $\langle R_g \rangle / \langle R_h \rangle$ is approximately 0.774, 1.0–1.2, and 1.5–1.8, respectively. Obviously, with an increase in the urea content, $\langle R_g \rangle / \langle R_h \rangle$ increased from 1.5 to 1.75, and this indicated the collapse of PVA chains on the periphery. As confirmed by FTIR and NMR analyses, α-isocyanate and methyl carbamate groups formed in the side chains of PVA after the urea treatment. The α-isocyanate and methyl carbamate groups had larger volumes than the hydroxyl group and could destroy the closely packed arrays of PVA chains and cause PVA chains to become looser, thus increasing the $\langle R_g \rangle / \langle R_h \rangle$ ratio. A_2 also increased from 6×10^{-4} to 2.4×10^{-3} cm³ñmol/g² with an increase in the urea content, and this showed that the interactions between PVA and water were strengthened. The newly formed α-isocyanate group very easily reacted with water, and with an increase in the urea content, more α-isocyanate groups were generated, leading to stronger interactions between the α-isocyanate groups and
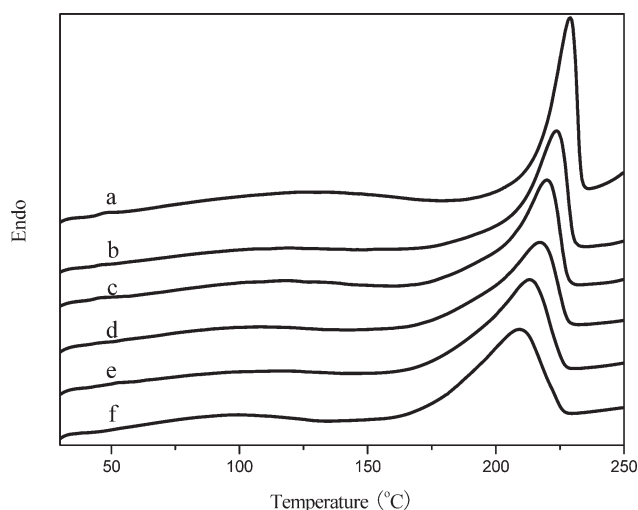

Figure 6 DSC curves of (a) PVA and (b–f) modified PVA with a urea content of 1, 2, 3, 4, or 5 wt %, respectively.

water and therefore increases in A_2. This is one of the reasons that the modified PVA could dissolve in water faster than the pure PVA with the treatment of urea.

DSC analysis

The DSC heating curves of PVA and modified PVA are shown in Figure 6, and the corresponding thermal parameters are listed in Table III. Obviously, the melting point and crystallinity of PVA decreased after modification with urea and methanol, and the decreasing trend became more apparent with an increase in the urea content.

As mentioned previously, the α-isocyanate groups, which had a bigger spatial volume than the hydroxyl groups, formed in the side chains of PVA, therefore increasing the intermolecular distance of the PVA macromolecules. As a result, a looser aggregation structure of PVA formed. In addition, the newly formed isocyanate groups in PVA also weakened the original intramolecular and intermolecular hydrogen bonds between the hydroxyl groups of PVA. It can also be seen that with increasing urea content, the breadth of the corresponding melting peak increased and the crystallinity decreased (Table III); this indicated that the urea

TABLE II
$\langle R_g \rangle / \langle R_h \rangle$ and A_2 of PVA and Modified PVA with Urea

	$\langle R_g \rangle / \langle R_h \rangle$	A_2 (cm³·mol/g²)
PVA	1.50	6.0×10^{-4}
PVA/1% urea	1.55	1.25×10^{-3}
PVA/2% urea	1.59	1.55×10^{-3}
PVA/3% urea	1.65	1.8×10^{-3}
PVA/4% urea	1.69	2.0×10^{-3}
PVA/5% urea	1.75	2.4×10^{-3}

TABLE III
Crystallinity of PVA and Modified PVA with Urea

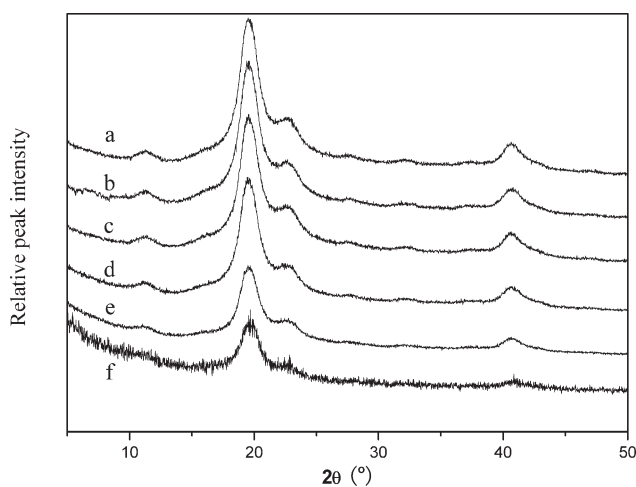|	Melting temperature (°C)	Crystallinity (%)
PVA	228.9	51.2
PVA/1% urea	223.8	50.3
PVA/2% urea	220.1	49.9
PVA/3% urea	217.1	49.4
PVA/4% urea	213.2	48.6
PVA/5% urea	209.6	47.5

Figure 7 XRD patterns of (a) PVA and (b–f) modified PVA with a urea content of 1, 2, 3, 4, or 5 wt %, respectively.

treatment could decrease the perfection degree of the PVA crystal. As mentioned previously, this benefited the penetration of water into PVA aggregates and hence greatly enhanced the water dissolution of PVA.

XRD analysis

According to DSC analysis, urea has a great influence on the crystallization structure of PVA. To further prove this, an XRD analysis was carried out. The XRD patterns of PVA and modified PVA are shown in Figure 7. The corresponding parameters are listed in Table IV. Six featured diffraction peaks of PVA appeared in the 2θ range of 10–50°, that is, peak 100 at $2\theta \approx 11.5°$, peak 001 at $2\theta \approx 16.1°$, peak $10\bar{1}$ at $2\theta \approx 19.5°$, peak 101 at $2\theta \approx 20.1°$, peak 200 at $2\theta \approx 22.7°$, and a compound peak of $1\bar{1}1$, 111, $2\bar{1}0$, and 210 at $2\theta \approx 40.5°$.[20] The 101 diffraction peak of PVA is due to the intermolecular interface between PVA molecular chains in the direction of intermolecular hydrogen bonding.[21] The decrease in the intensity of the 101 diffraction peak after modification, as shown in Figure 7, corresponds to the decrease in the number of PVA chains packing together and

hence results in a smaller crystallite size in the modified PVA, as shown in Table IV.

The crystallinities of PVA and modified PVA were obtained with the area integral method, and the results are shown in Table IV. With increasing urea content, the diffraction peaks broadened gradually, especially for the sample with 5 wt % urea, and the intensity of the crystalline peaks decreased and shifted to a lower diffraction angle. The weakening and broadening of the diffraction peaks of modified PVA showed that the number of PVA macromolecular chains heaped together decreased, the crystalline structures of modified PVA became more blurred, and the crystallite size of modified PVA decreased. All of this was mainly due to the reaction between urea and PVA.

CONCLUSIONS

The water solubility of PVA was successfully improved by a urea treatment combined with methanol in a specially modified rotary dryer. FTIR, NMR, LLS, DSC, and wide-angle XRD were adopted to study the dissolving mechanism of the modified PVA. FTIR and NMR investigations proved that modified PVA with few isocyanate groups and methyl carbamate groups could be obtained through a special chemical reaction between PVA and urea in methanol. LLS, DSC, and XRD results indicated that the isocyanate groups in the modified PVA increased the intermolecular distance of PVA. As a result, modified PVA particles with a looser structure were obtained because of the formation of a long chain with isocyanate and methyl carbamate groups, which could reduce the lattice energy and also reduce the crystallinity of PVA. Therefore, the water could easily enter PVA macromolecules through the loosened PVA structure. The water penetrating the PVA macromolecules could dissolve the amorphous fraction and simultaneously corrode the crystallization fraction of PVA more effectively with further depression of the crystallinity of PVA. As a result, PVA particles were dissolved more quickly.

TABLE IV
Interplanar Spacing, Crystallinity, Half-Peak Breadth, and Crystallite Size of PVA and Modified PVA with Urea

	Interplanar spacing (Å)		Crystallinity (%)	Half-peak width	Crystallite size (Å)
	($10\bar{1}$)	(101)			
PVA	4.51	4.44	51.6	1.320	66
PVA/1% urea	4.52	4.46	50.1	1.326	60
PVA/2% urea	4.55	4.47	49.8	1.330	58
PVA/3% urea	4.57	4.50	49.4	1.333	57
PVA/4% urea	4.61	4.51	48.8	1.351	56
PVA/5% urea	4.63	4.51	47.6	1.422	55

After treatment with urea, the dissolving time of PVA could be shortened by approximately 50%.

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