

Studies on the Properties of Poly(vinyl alcohol) Film Plasticized by Urea/Ethanolamine Mixture

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ABSTRACT: This study investigated the effects of urea/ethanolamine mixture (UE) on the crystallinity, thermal, and mechanical properties of poly(vinyl alcohol) (PVA) films. PVA films were prepared from solutions containing PVA, urea, ethanolamine, and water by casting and evaporating at 50°C for 12 h. The plasticization efficiency of UE was compared with that of glycerol (GL), the conventional plasticizer for PVA. The properties of PVA films plasticized by UE and GL, abbreviated to UE-plasticized PVA film and GL-plasticized PVA film, respectively, were investigated by Fourier-transform infrared spectroscopy, X-ray diffraction, differential scanning calorimetry, thermogravimetric analysis, and mechanical testing. It was proved that UE could form more stable hydrogen bonding with the hydroxyl group of PVA molecule and was more effective in breaking the hydrogen bonds between the hydroxyl groups. Thus, the crystallinity of UE-plasticized PVA films was lower than that of GL-plasticized PVA

films. The melting temperatures of UE-plasticized PVA films were lower than those of GL-plasticized PVA films. It was found that UE-plasticized PVA film showed a higher degradation temperature compared with GL-plasticized PVA film. The degree of swelling of UE-plasticized PVA film was higher than that of GL-plasticized PVA film but solubility (S) of UE-plasticized PVA film was lower in aqueous solution. Furthermore, UE-plasticized PVA films show lower tensile strength and higher elongation at break (E) than those of GL-plasticized PVA films. The tensile strength, E, and Young's modulus of PVA film containing 30% UE mixture reached 50.78 MPa, 591.19% and 76.9 MPa, respectively. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 697–703, 2012

Key words: poly(vinyl alcohol); films; urea; additives; modification

INTRODUCTION

Poly(vinyl alcohol) (PVA) is one of the most popular water-soluble polymers produced on a large scale commercially. PVA has found a great potential in various industrial applications, such as emulsifier, a stabilizer for colloid suspensions, adhesive. Because of its excellent properties, such as good barrier property, high strength, good film-forming property and highly hydrophilic property, PVA has been used in the shape of fibers, films, hydrogels, and glues.^{1–4} Because the melting point (T_m , typically 226°C) and the decomposition temperature of PVA are closed to each other, the thermal degradation also undergoes simultaneously during melting.⁵ Thus, PVA has been processed mainly from an aqueous solution even though the melt processing is more economically favored. The realization of thermal processing

of PVA would surely be a great progress in PVA industry.

PVA is a semicrystalline polymer in which high physical interactions between polymer chains exist, due to the hydrogen bonding between hydroxyl groups. It is this hydrogen bonding which also controls the thermal properties of PVA, making T_m of PVA much higher in comparison with polyethylene ($T_m = 117–135^\circ\text{C}$).⁶ The thermal properties of PVA film can be tailored by changing the intensity of the hydrogen bonding. For example, by blending a small amount of poly(GEMA) with PVA, the thermal stability of PVA was significantly improved. This was considered to be due to the strong intermolecular hydrogen bonds between hydroxyl and carbonyl groups, which suppressed the oxidative decomposition of PVA.⁵ Another widely used way to modify the thermal property of PVA is by adding the plasticizer. The basic rationale of the plasticization of PVA film is that the plasticizer can form stable hydrogen bonds with PVA chain and therefore reduce the inter- or intramolecular interactions between PVA chains. The widely used plasticizers for PVA are high boiling water soluble organic compounds containing hydroxyl groups, such as ethylene glycol,⁷

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GL^{8,9} and low molecular weight poly(ethylene glycol).¹⁰ But the plasticizing effects of these plasticizers are limited due to the partial evaporation and thermal decomposition of the plasticizer. The research of new and high efficiency plasticizer for PVA is meaningful. According to the results before, the functional part of these plasticizers is hydroxyl group. The "C=O" and "–NH₂" groups could form more stable hydrogen bonding with the hydroxyl groups¹¹ and were more effective in breaking the hydrogen bonding between the PVA hydroxyl groups. Therefore theoretically urea could be a better plasticizer for PVA. In addition, previous studies have shown that urea can destroy the hydrogen bonding of PVA molecules in the thermal processing.¹² The studies of Ma and Yu¹³ show that the introduction of ethanolamine, which is a good solvent for urea, could prevent urea from separating out from starch and the mixture of urea and ethanolamine was a better plasticizer for starch compared with glycerol (GL). But no research about the urea/ethanolamine mixture (UE) as a complex plasticizer for PVA was reported. In this study, we employed ethanolamine as a solvent for urea and found ethanolamine could prevent urea from separating out from PVA. The mixture of UE could effectively modify the thermal and mechanical properties of PVA.

EXPERIMENTAL

Materials

PVA (DP = 1750, degree of hydrolysis 99%) was provided by Sichuan Vinylon Factory, SINOPEC (China). The commercial PVA products were used after washing several times with distilled water until a pH of 7 was attained and were dried at 60°C to a constant weight. Urea was purchased from Shenyang chemical Co. (Shenyang, China). Ethanolamine and GL were purchased from Kelong chemical Co. (Chengdu, China). Distilled water was used throughout the experiments. Analytically pure grade urea, ethanolamine, and GL were used as received.

Preparation of PVA films

PVA films were prepared by the casting method. First, a calculated amount of PVA, urea, ethanolamine or GL were dissolved in distilled water by heating in an oil bath at 95°C for 2 h, and a 5 wt % PVA aqueous solution was prepared, which was called the film-forming solution. The film-forming solutions were casted onto the petridish and dried at 50°C for 12 h to completely eliminate water. Dried films were put in polyethylene bags and stored at room temperature for 1 week before testing. The plasticized films were named with the first letter P

for PVA and UE, GL for UE, GL, respectively. The suffixes 10, 20, 30, 40 represent the concentration of the plasticizer added. For example, PUE30 presents the PVA film plasticized by 30 wt % (weight base of dry PVA) UE. In this article, all UE were blended by the weight ratio of 1 : 1.

Fourier-transform infrared (FT-IR) spectroscopy

The infrared spectra were measured with a FT-IR spectrophotometer (Nicolet 560). The film-forming solutions were casted to the transparent slices. The measurement was carried out at 4 cm⁻¹ and 32 scans.

X-ray diffraction measurements

X-ray diffraction (XRD) patterns were recorded in the reflection mode in the angular range 5–40° (2θ) at ambient temperature by an X' Pert Pro MPD diffractometer. The radiation from the anode, operating at 50 KV and 35 mA, monochromized with a nickel foil. The measurement was performed at a scanning speed of 2θ = 0.08° s⁻¹.

Differential scanning calorimetry

The melting point (*T_m*) was measured by a differential scanning calorimeter (NETZSCH DSC 204). Slices of the plasticized PVA films with total weight of 5–7 mg were weighted and sealed in an aluminum pan. The pans were heated from 30 to 250°C at a rate of 10°C/min under a flow of Nitrogen. *T_m* was determined as the peak temperature of the melting endotherm.

Thermogravimetric analysis

PVA films were cut into small pieces, which were tested by TA 2950 TGA thermal analysis instrument (DuPont). The samples were about 5–10 mg in a sealed aluminum pan. The scope of the testing temperature was from 30 to 600°C at a heating rate of 10°C/min.

Degree of swelling and solubility of PVA films

Dried films were immersed in distilled water at the temperature of 30°C. After the equilibrium (24 h), the moisture on the surface of the film was removed by filter paper, and the weight of the film was measured. The degree of swelling (DS) in film was calculated as (1):

$$DS = (W_e - W_o)/W_o \quad (1)$$

where, *W_e* is the weight of PVA film at the adsorbing equilibrium, and *W_o* is the weight of the first dry PVA film.

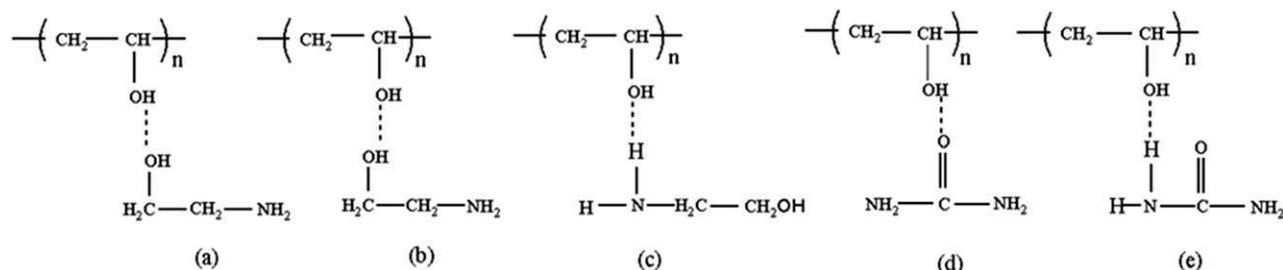


Figure 1 Possible hydrogen bonds between PVA and UE.

The swelled PVA films were dried again for 24 h at 60°C. And its solubility (S) was calculated by the following eq. (2):

$$S = (W_o - W_d) / W_o \quad (2)$$

where, W_d is the dry weight of the swelled PVA film.

Mechanical measurements

The tensile strength (TS), Young’s modulus, and elongation at break of PVA films were tested by extension measurements at room temperature using a tensile tester (Instron 5567). The crosshead speed was 50 mm/min. The initial gauge length of the specimen was 20 mm. The width of each tensile sample is 4 mm. Thickness of the film was measured with a micrometer in triplicate. Samples were equilibrated in vacuum desiccators over the saturated solution of $Mg(NO_3)_2$ giving RH of 54% for 72 h before mechanical testing. The date was average of 5–7 specimens.

RESULTS AND DISCUSSION

Most films prepared were transparent and showed good mechanical cohesion. However, after casting, PUE50 were brittle, opaque, nonhomogeneous dry product, which could not be considered as suitable materials. After for a storage time, the phase separation could also occur for PUE40 samples. Phase separation of PVA plasticized by beyond 40% GL has been indentified before.⁸ So the threshold amount of the plasticizer used in this article is 40%.

The hydrogen bonding interaction between plasticizers and PVA

The basic rationale of the plasticization of PVA film is that the plasticizer can form stable hydrogen bonding with PVA molecules. The intensity of the hydrogen bonding between the plasticizer and PVA is crucial for the plasticization efficiency. Both UE and GL can form hydrogen bonding with PVA molecule. The possible hydrogen bonds between UE

and PVA molecules are shown in Figure 1. The most obvious investigation of hydrogen bonding is in the infrared region, where the vibrations of molecules can be studied. The spectra of PVA, PG30, and PUE30 are shown in Figure 2. The appearance of a double absorption peak at 1660 and 1630 cm^{-1} in the PUE30 spectrum is the $-NH_2$ absorption peak of urea and ethanolamine molecules.

PVA molecule is generally associated with the inter- and intramolecular hydrogen bonding and there is no absorption band of free “-OH” at 3600 cm^{-1} .¹⁴ The absorption band of “-OH” engaged in the hydrogen bonding at 3330 cm^{-1} is obvious. The plasticizer can form hydrogen bonds with PVA molecules and the addition of plasticizer will result in the decreasing in the inter- and intramolecular hydrogen bonds of PVA molecules. The change of the wavenumber of hydroxyl groups with the concentration of UE was shown in Figure 3. It can be seen that the wavenumber of “-OH” shifted to a higher value with the increment of UE concentration. This indicates that the addition of UE can weaken the inter- and intramolecular hydrogen bonding between PVA molecules. Furthermore, the magnitude of band shift for PUE30 was larger than that of PG30, indicating that UE could form more stable hydrogen bonding with PVA chains than GL.

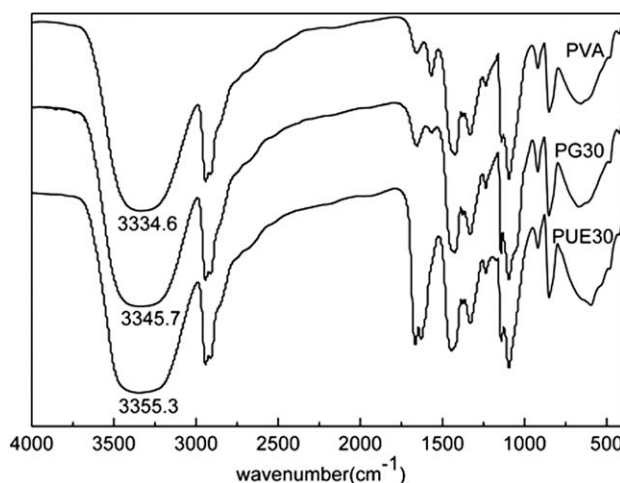


Figure 2 The FT-IR spectra of PVA, PG30, and PUE30.

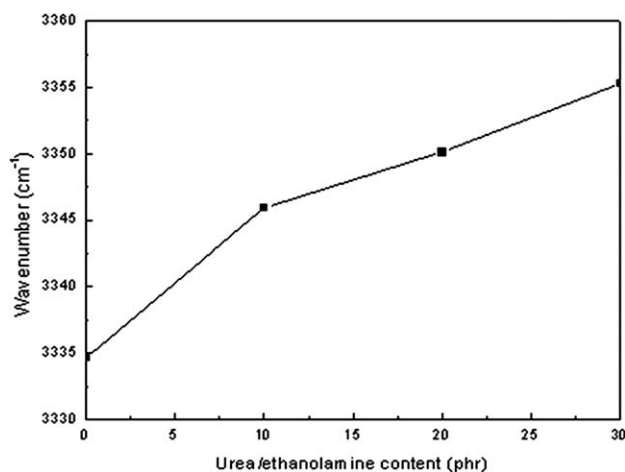


Figure 3 The change of wavenumbers of the infrared absorption band with the concentration of UE.

XRD analysis

The XRD patterns of PVA, plasticized by different concentration of UE, are shown in Figure 4. The diffraction traces are displaced from one another vertically for PVA films containing different concentration of UE. Within this angular range there are four crystalline maxima which may be indexed as 001 at $2\theta = 16.1^\circ$, $10\bar{1}$ at $2\theta = 19.4^\circ$, 101 at $2\theta = 20.0^\circ$ and 200 at $2\theta = 22.7^\circ$ for PVA.^{6,15} The crystal peak at around 22.5° in Figure 4 could be ascribed to urea crystallinity. With the increment of the concentration of UE, the diffraction peaks decreased rapidly in intensity. It is clear that the introduction of UE into PVA can destroy the crystal structure of PVA and reduce the degree of the crystallinity of PVA films. The Bragg peak of urea at $2\theta = 22.5^\circ$ only appeared in PUE40 sample. This is in accordance with our previous results. Urea and ethanolamine molecules can form stable hydrogen bonds with PVA chains

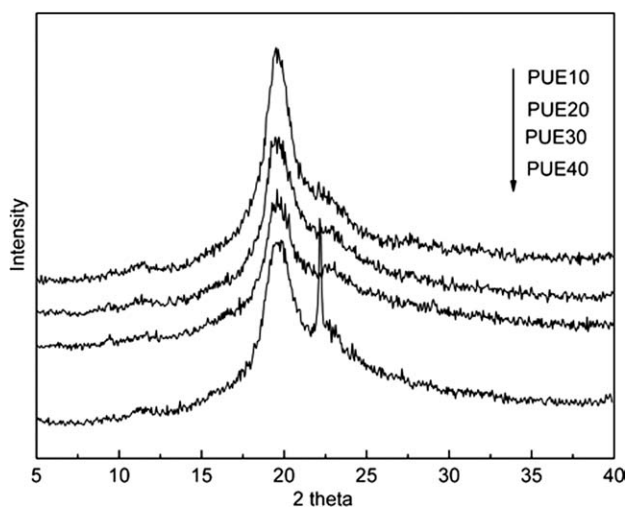


Figure 4 X-ray diffraction patterns from PVA films with different concentration of UE.

and thus break the intermolecular hydrogen bonds of PVA chains. In other words, the interaction between PVA and urea, ethanolamine reduces the crystallinity of PVA, resulting in an amorphous structure. This destruction also caused the decrease in the melting temperature (T_m) as discussed later.

The diffraction trace of PUE30 is compared with that of PG30 in Figure 5. As shown in Figure 5, the diffraction peak of PG30 is sharper and stronger than that of PUE30, indicating that the crystallinity of PG30 is higher than that of PUE30. This is in accordance with the later result that T_m value of PG30 is higher than that of PUE30.

DSC measurements

Most of the plasticizers used in PVA can reduce the glass transition temperature (T_g) and T_m of PVA. This is one of the most used technical solutions to achieve thermoplastic PVA. The relationship between T_g of PVA and the plasticizer has been estimated by Kelly-Bueche equation.^{16,17} In this article, DSC method is used to determine T_m of PVA. The peak temperature of the melting endotherm is taken as T_m .

Figure 6 shows the DSC heating thermograms of PVA with different content of UE. PVA shows a melting endotherm at 229.5°C followed by another endotherm peak at a higher temperature. The latter endotherm corresponds to the thermal degradation of PVA,¹⁶ which brings a difficulty in the thermal processing of PVA. With the addition of UE, the melting endotherm takes place at a lower temperature. PUE30 shows a straight base line after the melting endotherm and no further endotherm can be observed at the higher temperature. This implies that the UE complex plasticizer can not only reduce T_m of PVA but also suppress the thermal degradation of PVA.

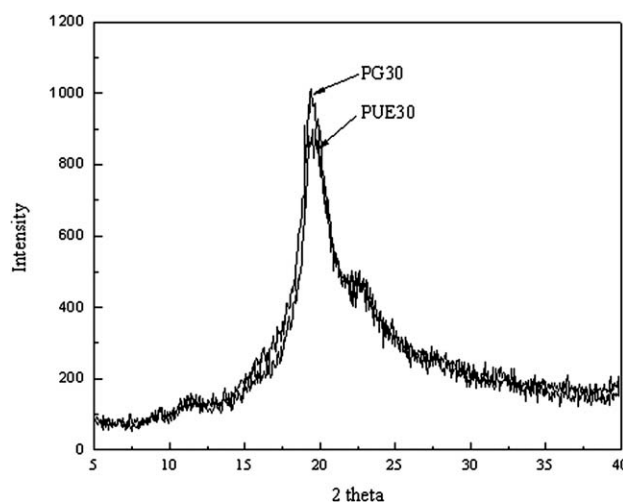


Figure 5 X-ray diffraction patterns of PG30 and PUE30.

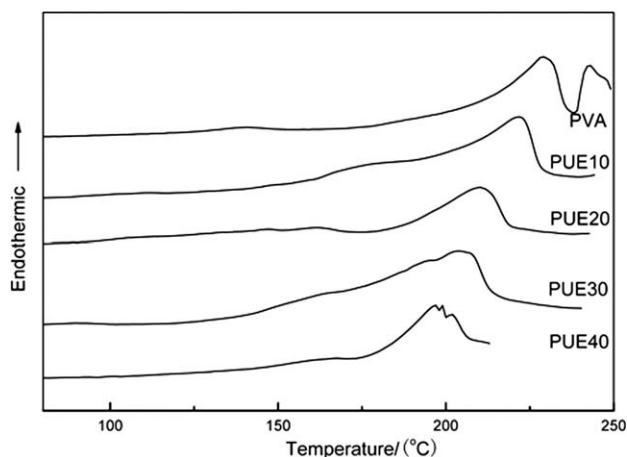


Figure 6 DSC heating thermograms of PVA with different concentration of UE.

GL can reduce the T_m of PVA and the plasticization effect of GL for PVA has been studied by Jyongsik Jang.⁸ In this article, we compare UE with GL in reducing the T_m of PVA. The DSC heating thermograms of PVA with different concentration of GL are shown in Figure 7. T_m values of PVA with different content of UE and GL are shown in Figure 8. At the same concentration, T_m of UE-plasticized PVA films are lower than those of GL-plasticized PVA films. As we have discussed earlier, this is because UE could form more stable hydrogen bonds with PVA and is more effective in reducing the degree of crystallinity of PVA than GL.

Thermogravimetric analysis

DSC measurements indicate that the addition of plasticizers can suppress the thermal degradation of PVA and enhance the thermal stability of PVA. In this part, the thermal stability of PVA was measured

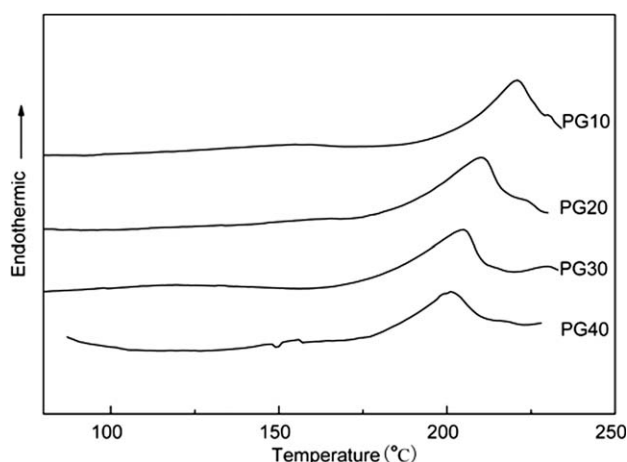


Figure 7 DSC heating thermograms of PVA with different concentration of GL.

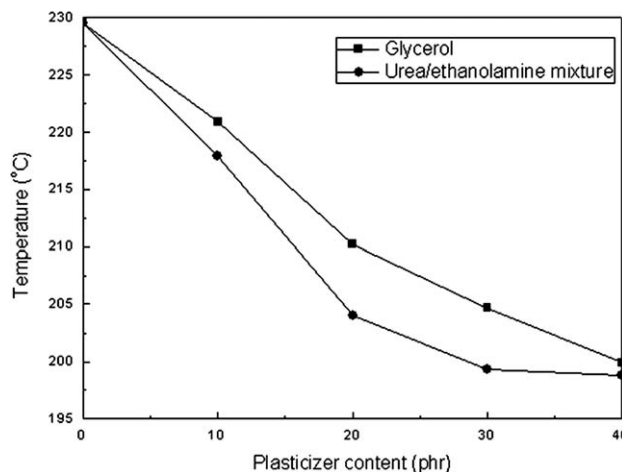


Figure 8 The change of T_m values of PVA with the concentration of UE and GL.

by a thermogravimeter. The measurement was carried out from room temperature to 600°C at a heating rate of 10°C/min. The thermogravimetric curves of PG30 and PUE30 samples are shown in Figure 9. The DTG curves of PG30 and PUE30 are shown in Figure 10. Previous studies prove that the thermal degradation of PVA is initiated by the elimination of side groups from the main chain and follows a two-step mechanism.¹⁸ The first degradation step of PVA is the elimination of the hydroxyl and acetate side groups.¹⁹ For fully hydrolysis PVA, the ratio of acetate side groups is very small. These indicate that at least hydroxyl groups take part in the thermal degradation of PVA, and the stability of hydroxyl groups is crucial for the stabilization of PVA. Thus, the addition of the plasticizers can suppress the thermal degradation of PVA and enhance the thermal stability of PVA.

PUE30 had the first degradation peak at 271.19°C, whereas PG30 had the first degradation peak at

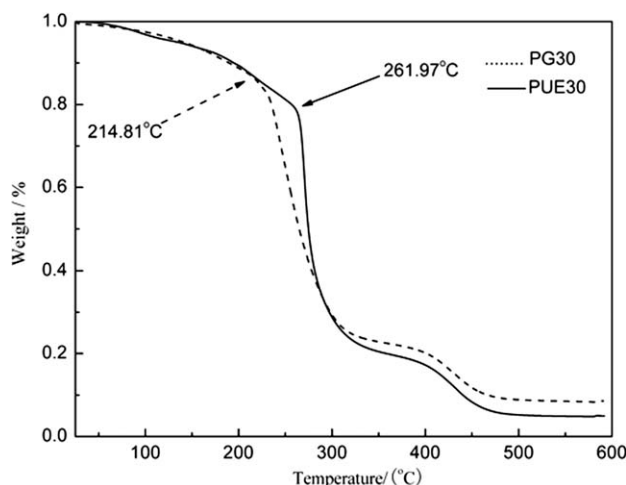


Figure 9 Thermogravimetric analysis traces of PG30 and PUE30.

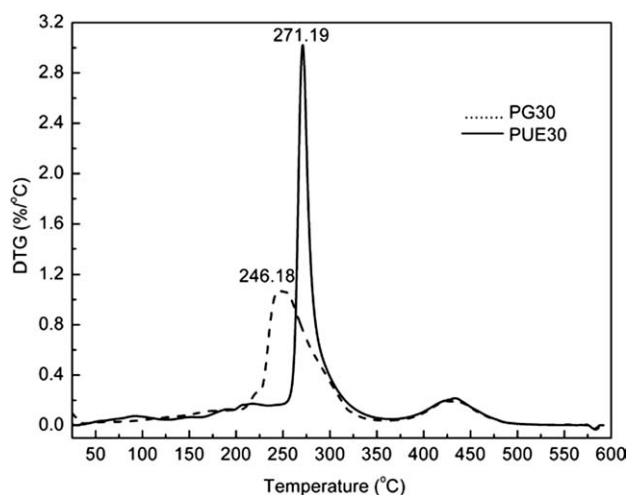


Figure 10 DTG curves of PG30 and PUE30.

246.18°C. It indicates that PUE30 was more stable than PG30 in the first degradation step.

It can be interpreted that UE can form stronger hydrogen bonds with hydroxyl groups of PVA and thus the hydroxyl groups of PUE30 is more stable than those of PG30. Volatilization or degradation of plasticizers also occurs in this step. The crystallinity of PUE30 is lower than that of PG30 and the degradation is initiated in the amorphous region. So PUE30 shows a larger degradation rate than PG30 as shown in Figure 10.

Degree of swelling and solubility of PVA films

DS and S values of different PVA films are shown in Table I. With the increment of the concentration of UE or GL, DS values of PVA films decrease and S values increase. DS decreased mainly because free volume decreases for the addition of UE or GL. S values increased mainly because the plasticizer would dissolve out at the attack of water molecules. It has been claimed that the crystallites are more resistant to attack from water molecules because of the higher packing efficiency.²⁰ DS of UE-plasticized

TABLE I
DS and S of Different PVA Films Having Various Concentrations of Urea/Ethanolamine and Glycerol

	Degree of swelling (DS)	Solubility (S)
PVA	1.650	0.06
PG10	0.865	0.0909
PG20	0.820	0.12
PG30	0.735	0.224
PG40	0.568	0.294
PU E10	1.200	0.089
PUE20	1.020	0.098
PUE30	0.820	0.196
PUE40	0.720	0.240

TABLE II
Mechanical Parameters of PVA Samples Having Various Concentration of Urea/Ethanolamine and Glycerol

	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
PVA	88.21	139.78	3743.44
PG10	72.13	227.09	2243.96
PG20	71.27	331.09	535.75
PG30	57.67	468.14	113.76
PG40	38.21	454.39	61.55
PUE10	80.19	224.10	2046.98
PUE20	70.61	347.73	384.4
PUE30	50.78	591.19	76.9
PUE40	45.57	694.25	59.2

PVA film is slightly higher than that of GL-plasticized PVA film. It can be interpreted that the degree of crystallinity of UE-plasticized PVA film is lower. The same phenomenon has been observed for Starch/PVA film containing citric acid by Hye-Ryoung Park.²¹ Meanwhile, UE-plasticized PVA films show lower S values than that of GL-plasticized PVA films. This indicates that UE was attached to PVA more tightly and was more resistant to the attack from water molecules than GL.

Mechanical measurements

The mechanical properties of PVA with different concentration of plasticizers were evaluated from stress-strain curves. They were tested for TS, elongation at break (E), and Young's modulus. The trends in tensile property change with respect to the amount of plasticizers are shown in Table Table II. PVA film without plasticizer is brittle, showing high TS and low E. No matter which types of plasticizers were added, TS decreased and E increased with increasing the amount of plasticizer. This arises from the fact that that both UE and GL can decrease the crystallite region of PVA and increase the segmental mobility of PVA.

Furthermore, it can be observed that UE-plasticized PVA films show lower TS and higher E than those of GL-plasticized PVA film. It can be interpreted that UE can form stronger hydrogen bonds with PVA and the crystallinity of UE-plasticized PVA film was lower.

CONCLUSIONS

In this article, we have studied the properties of UE-plasticized PVA film and GL-plasticized PVA film to compare the plasticization effect of UE with GL. UE was more effective in modifying the thermal and mechanical properties of PVA. It was proved that UE could form stronger hydrogen bonds with PVA chains than GL. This was the origin of the difference

between the plasticizing effect of UE and GL. In conclusion, the high-efficiency plasticizer for PVA should be polyfunctional organic compounds, which can form stable hydrogen bonding with the hydroxyl groups of PVA chains.

References

1. Yan, L. X. Water-soluble polymers. Beijing: Chemical Industry Press 1998, 42.
2. Chiellini, E.; Corti, A.; Salvatore, D.; Solaro, R. Prog Polym Sci 2003, 28, 963.
3. Chen, N.; Li, L.; Wang, Q. Plast Rubber Compos 2007, 36, 284.
4. Bolto, B.; Tran, T.; Hoang, M.; Xie Z. L. Prog Polym Sci 2009, 34, 969.
5. Nishino, T.; Kani, S.; Gotoh, K.; Nakamae, K. Polymer 2002, 43, 2869.
6. Assendert, H. E.; Windle, A. H. Polymer 1998, 39, 4295.
7. Fujio, M.; Kenichi, Y.; Hiroshi, K. Jpn. Pat. 37009768; 1962.
8. Jang, J.; Lee, D. K. Polymer 2003, 44, 8139.
9. Ku, T.; Lin, C. Text Res J 2005, 75, 681.
10. Wysong, R. D. US, Pat, 4 206 101; 1980.
11. Hong, P. D.; Chou, C. M.; He, C. H. Polymer 2001, 42, 6105.
12. Novara, C. B.; Frontaneto, D.; Agogna, B. V.; Sesto Calende, G. D. T.; Oleggio, R. P. US, Pat, 5462981; 1995.
13. Ma, X. F.; Yu, J. G. Wan J. J Carbohyd Polym 2006, 64, 267.
14. Dai, L. X.; Ying, L. N. Macromol Mater Eng 2002, 287, 509.
15. Assendert, H. E.; Windle, A. H. Polymer 1998, 39, 4303.
16. Sakellariou, P.; Hassan, A.; Rowe, R. C. Eur Polym Mater 1993, 29, 937.
17. Sakellariou, P.; Hassan, A.; Rowe, R.C. Int J Pharm 1994, 102, 207.
18. Thomas, P. S.; Guerbois, J.-P.; Russell, G. F.; Briscoe, B. J. J Therm Anal Calorim 2001, 64, 501.
19. Alexy, P.; Lacik, I.; Simkova, B.; Bakos, D.; Pronayova, N.; Liptaj, T.; Hanzelova, S.; Varosova, M. Polym Degrad Stab 2004, 85, 823.
20. Hodge, R. M.; Edward, Gr. H.; Simon, G. P. Polymer 1996, 37, 1371.
21. Yoon, S. D.; Chough, S. Y.; Park, H. R. J Appl Polym Sci 2006, 100, 2554.