

Preparation and Properties of Molded Blends of Wheat Gluten and Cationic Water-Borne Polyurethanes

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ABSTRACT: Cationic water-borne polyurethanes (CWPU) were prepared and blended with wheat gluten (WG) in aqueous dispersion. The freeze-dried blend powders of WG/CWPU were thermally compression-molded into sheets. The tensile strength of the WG/CWPU blends decreased with increasing CWPU content, showing a relationship between the composition of the sheets and their mechanical properties. FTIR spectra reveal that the free carbonyl in the blend results in a decrease in the hydrogen-bonding interaction of the WG. SEM images show that the morphology of the cross-sections of the blends is homogenous. The dynamic thermal behavior of the blends illustrates that the WG is plasticized by CWPU, with the result that the relaxation transition of the WG becomes broader and the temperature transition of WG changes slightly. The water resistance of the WG was also improved by blending it with the CWPU. Biodegradation of the blends in soil resulted in a loss in mass of the samples of more than 60% w/w after burial for 15 days. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: cationic water-borne polyurethane; wheat gluten; blend; physical properties; biodegradability

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INTRODUCTION

There has for some time been a need to develop environmentally benign plastics using renewable resources, to provide alternative materials to petroleum-based polymers. One such renewable and biodegradable material that is used as an agropolymer in films and coatings is wheat gluten.^{1–4} That is the protein byproduct of the fabrication of wheat starch by wet process, and is readily and cheaply available in large quantities. Wheat gluten is nontoxic and degrades fully within 50 days in farmland soils⁵; furthermore, its unique viscoelastic properties have attracted a great deal of research interest.

The proteins contained in wheat gluten exhibits brittle behavior that results from strong inter- and intramolecular interactions, such as hydrogen bonding, hydrophobic interaction and disulphide bonds.⁶ Small polar plasticizers such as water, glycerol, ethylene glycol, and propylene glycol, have been used to reduce intermolecular forces and increase the mobility of the polymeric chains in order to modify the three-dimensional structure of the proteins. The plasticized proteins can then be used as structural polymers. However, the addition of glycerol dramatically

increases the permeability to water vapor, and lowers the transition temperature.^{7,8} The properties of polymers may be improved by blending them with other materials. It is well known for example that aliphatic polyesters such as poly (ϵ -caprolactone) (PCL) are readily biodegradable. PCL has previously been blended with starch to produce an inexpensive biodegradable polysaccharide.⁹ Furthermore, commercial aliphatic polyesters have previously been blended with wheat gluten to form inexpensive biodegradable gluten-based plastics that have good physical and thermal properties.¹⁰ Some adhesion between wheat gluten and PCL occurs in the green composite, and FT-IR analysis confirmed the existence of a physical rather than a chemical interaction between the PCL and wheat gluten.^{11,12} The PCL was modified by a small amount of maleic anhydride to incorporate a functional group that could interact with the functional groups on the protein. The resulting blend of wheat gluten and modified PCL showed improved physical properties compared with simple mixtures of wheat gluten and PCL.¹³ Furthermore, compression-molded blends of wheat gluten and thiolated poly (vinyl alcohol) had improved fracture strength, elongation, and modulus compared with molded wheat gluten.¹⁴ Poly (hydroxyl ester ether) (PHEE), was blended with

Table I. Tensile Properties of CWPU Films

Diol/di-isocyanate	Molar ratio of diisocyanate/diol/N-MDEA	Hard segment/wt %	Tensile strength/MPa	Tensile modulus/MPa
PCL-1/MDI	4 : 0.8 : 3.2	46	19.21	149.80
PCL-1/MDI	4 : 1:3	40	18.60	155.40
PCL-2/MDI	4 : 0.8 : 3.2	46	7.67	0.19
PCL-2 /MDI	4 : 1:3	40	9.00	0.31
PC/MDI	4 : 0.8 : 3.2	46	18.28	40.22
PC /MDI	4 : 1:3	40	13.37	8.80
PCL-1/IPDI	4 : 0.8 : 3.2	46	4.45	20.34
PCL-2/IPDI	4 : 0.8 : 3.2	46	0.53	0.66

selected cereal proteins to produce thermoplastics using commercial extrusion and molding equipment, and, did not require the addition of plasticizers to yield materials with acceptable mechanical properties.¹⁵

Research on biodegradable polyurethane (BPU) has recently seen a surge of interest due to the excellent physical properties of this material, its relatively good biocompatibility and biodegradability, and the improvements it affords to the properties of natural polymers. It has been applied extensively to problems in medical and environmental fields in particular.¹⁶ Blends of water-borne polyurethane (WPU) and starch (ST) displayed better tensile strength and elongation at break, and showed a degree of miscibility between the two substances in terms of the whole composition ratio.¹⁷ A water-borne polyurethane prepared using plant oil-based polyol was used to improve the mechanical properties and water sensitivity of the starch materials. The blend films were successfully prepared and showed improved mechanical properties and a better water resistance.^{18,19} Corn starch modified using poly(ϵ -caprolactone)-based polyurethane may be used as a filler in biodegradable starch and in the preparation of new hydrophobic copolymers.²⁰ A blend of polymerized whey proteins and oil-modified polyurethane was used as an environmentally friendly wood-finish product which was compatible with blending and resistant to mold.²¹ Chitosan was successfully blended with water-borne polyurethane and exhibited superior elongation. The resulting blends were partially compatible, had better biocompatibility and thermal stability, and had reasonable mechanical strengths.²²

In view of their biodegradable characteristics, other workers prepared polyurethanes (PUs) based on poly (ϵ -caprolactone) (PCL) as a soft segment.^{23–25} Polyurethane has many functional groups that can interact with the functional groups on wheat protein. The effect of hydrogen bonding caused by carbamates and peptides on the interaction between PUs and gluten proteins can affect the properties of wheat gluten materials. Polyurethane has been successfully used to toughen epoxy resin without affecting the hardness of the resin.²⁶ In general, in the production of wheat gluten films it is desirable to improve the brittleness of the wheat gluten. We herein attempt to prepare molded blends of wheat gluten and cationic water-borne polyurethanes (CWPU). We

investigated the morphology and physical properties of the blends in some detail, and also assessed the biodegradability of the blend.

EXPERIMENTAL

Materials

Vital wheat gluten (WG, 86.20% protein, 5.40% residual moisture) was purchased from Henan TianGuan Group, China. Poly(ϵ -caprolactone) glycol (PCL) of molecular weight 2000 (PCL-1, $T_m = 57^\circ\text{C}$; PCL-2, $T_m = 17^\circ\text{C}$) were obtained from Daicel Chemical, Japan. Polycarbonate glycol (PC) of molecular weight 2000 was supplied from the Asahi Kasei Corporation, Japan. 4, 4'-Diphenylene methane diisocyanate (MDI) and isophorone diisocyanate (IPDI), and *N*-methyl-diethanolamine (N-MDEA), were obtained from commercial sources and used as received. Methyl ethyl ketone (MEK), glacial acetic acid, and dibutyl tin dilaurate (DBTDL) were purchased from Shanghai Chemical Reagents Plants, China, and treated with 4 Å molecular sieves before use.

Preparation of Cationic Water-Borne Polyurethane

Polyester glycol was added to a 500-mL round-bottom, four-necked flask equipped with mechanical stirrer, condenser, inert gas inlet, and thermometer, and then heated to and maintained at 110°C under vacuum for 1 h and then cooled. Thereafter, N-MDEA (as a hydrophilic chain extender), diisocyanate, and DBTDL were introduced successively. The reaction was purged by dry argon gas and carried out at 80°C until the content of isocyanate group (-NCO) reached a given value in terms of a dibutylamine back titration. The polyurethane prepolymer was cooled to 50°C , and glacial acetic acid and MEK were added dropwise for neutralization and dilution. After neutralization (for 60 min), deionized water was added dropwise to the prepolymer at 35°C , and then the CWPU was prepared by phase-inversion with vigorous stirring for 20 min followed by normal stirring for 60 min. The NCO/OH molar ratios and hard segment contents of the eight resulting products are listed in Table I. The aqueous dispersions of CWPU were cast in a Teflon plate mold and dried at room temperature for a week to form films. The normal dumbbell-shaped films were then cut and their tensile properties were tested.

Blends of Wheat Gluten and CWPU

The CWPUs were diluted with known quantities of deionized water in a 500-mL three-necked flask with mechanical stirring. Thereafter, the WG powders were slowly added to the flask with stirring for 1 h. The dispersions were then poured to culture dishes and, freeze-dried for 48 h, and ground in a miller to form the powdered blend of WG/CWPU.

Known quantities of WG/CWPU powders were added to a multicavity mold and molded at 140°C for 5 min under a pressure of 6.5 MPa and 15 min under 10 MPa, then molded by cold compression for 10 min under 10 MPa to form brown homogeneous dog bone and bar specimens of thickness of approximately 2 mm according to the standard test specimens for tension and bending, i.e., ASTM D638 TYPE V and D790, respectively. By varying the CWPU content (10, 20, 30, 40, and 50 per one hundred of WG by weight), we obtained a series of molded blends coded as WP-10, WP-20, WP-30, WP-40 and WP-50, respectively. All molded blend specimens were stored in a desiccator for 48 h at a humidity of 52.9% in accordance with ASTM E104-85 2002 standard prior to testing.

Testing and Characterization

The tensile properties of the CWPU films and WG/CWPU blend sheets were evaluated using a universal testing machine (CMT2203, Shenzhen SANS Test Machine Co. Ltd., China). The extensometer grips were set to a standard length of 10 mm, and the cross-head speed was set at 250 mm/min for the film samples and 1 mm/min for the sheet specimens. The bend properties of the WG/CWPU blend samples were tested for a span of 25.4 mm at a rate of cross-head motion of 0.7 mm/min. Force and deformation were measured electronically, and the resulting stress–strain curves were obtained. An average of at least five replicates of each material was obtained.

Fourier transform infrared spectra of CWPU, WG, and WG/CWPU blend powders were recorded using a Nicolet 5700 FT-IR spectrometer with KBr pellets. Each spectrum was the result of 32 scans with a resolution of 4 cm⁻¹.

Differential scanning calorimetry (Modulated DSC 2910, TA instrument, USA) was used to measure the thermal behavior of the CWPU films at a heat rate of 10 °C min⁻¹.

The dynamic mechanical behavior of the CWPU films and WG/CWPU blend sheets were determined using dynamic mechanical thermal analyzer (Rheogel-E4000, UBM, Japan) with a bending mode of 1 Hz and a heating rate of 5 °C min⁻¹.

Morphologies of the bend-fractured cross-sections of the blends were investigated by scanning electron microscopy (JEOL JSM-6360LV). The cross-sections of the blend sheets were coated with gold for observation purposes.

Similar sized (~ 10 mm × 10 mm) fractured bending samples were used for water absorption testing (ISO62-1980(E)). First, the original weight of the molded blending specimens was recorded (W_0), and the blend sheets were then immersed in water at room temperature. The samples were removed at intervals, blotted with tissue paper to remove the excess water on the surface of the samples, then weighed (W_t). Two samples were

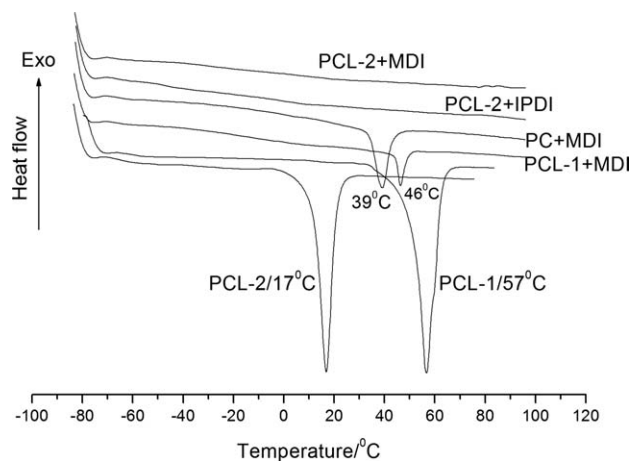


Figure 1. DSC curves of PCL-1, PCL-2 and the various CWPU films.

required for each condition to check the reproducibility of the results. The water absorption of the sample was calculated as:

$$\text{Water absorption (wt\%)} = [(W_t - W_0)/W_0] \times 100\% \quad (1)$$

Biodegradability was determined using a simple soil burial test. The molded bending specimens of the blends were buried in the university campus (Shanghai, China). The pH of the soil was 7.65, and the organic content as determined by loss on ignition was 1.78%. All samples were buried at a depth of 10–15 cm. At various time intervals the degraded samples were retrieved, assessed in terms of their external appearance, cleaned and dried under vacuum at 50°C for 24 h. In order to prevent the deformation of the each samples during the desorption of water from the soil, the samples were clamped between two stainless steel plates with the size of 200 mm × 200 mm. The performance under bending, and the weight loss of the samples, were then measured. Three replicates of each sample were tested.

RESULTS AND DISCUSSION

Tensile and Thermal Properties of CWPU Films

Polyester-polyurethane is highly susceptible to degradation in soil, losing up to 95% of its tensile strength.²⁷ A biodegradable poly (ϵ -caprolactone) glycol was previously used to prepare polyurethane elastomers^{23,28} and aqueous polyurethane dispersions^{24,29} as a soft segment. These PCL-based polyurethanes showed hydrolytic degradability and biodegradability. Here, PCL diol was used to prepare CWPU as a soft segment. For comparison, PC diol and two diisocyanates were also used to synthesize CWPUs. The tensile properties of all our CWPU films are listed in Table I. The results show that the tensile strength of the CWPU films that have PCL-1 as a soft segment is much greater than those that use PCL-2, and also greater than those with PC diol and the same diisocyanate. The CWPU with a symmetric aromatic diisocyanate is superior to that with an asymmetric aliphatic ring diisocyanate in terms of the strength of the resulting films. In microphase-separated polyurethane, urethane, and ionic chain-extenders belong to hard segments that are provided with ordered microstructure, and polyester diols are soft

Table II. Mechanical Properties of Molded WG/CWPU Blend Sheets

Diol/di-isocyanate ¹	Samples	Tensile strength/MPa	Elongation at break/%	Tensile modulus/MPa	Bend strength/MPa	Bend modulus/MPa
PCL-1/MDI	WG	47.71	6.60	736.70	80.58	5748.10
	WP-10-1	37.95	9.17	736.54	48.73	3101.83
	WP-20-1	39.46	11.04	722.57	52.00	2859.57
	WP-30-1	36.18	11.93	689.95	35.04	2396.70
	WP-40-1	34.23	12.80	594.09	28.08	2011.31
	WP-50-1	30.71	14.78	453.95	21.42	1559.97
PCL-2/MDI	WP-10-2	26.89	9.53	541.20	44.62	3452.15
	WP-20-2	33.65	13.39	467.80	47.18	2735.56
	WP-30-2	30.17	14.89	450.50	36.08	2282.30
	WP-40-2	30.12	15.66	386.02	28.96	1915.44
	WP-50-2	27.08	15.88	313.10	25.04	1523.63

¹Molar ratio of diisocyanate to diol is 1.

segments. As a dispersed phase, the hard domains act as a reinforcing filler and as a thermally reversible cross-link.³⁰

The thermal behavior of CWPU films with 46% hard segments by weight are shown in Figure 1. The melting temperatures in the soft segments of the CWPU films reflect the presence of PCL-1, PC, and MDI, and the melting temperature of the film that has PCL-1 as a soft segment is higher than that which has PC diol. However, no melting peaks occur in the CWPU films that contain PCL-2, MDI, and IPDI. The changes arise from the destruction of the ordered structures in PCL-1 and PCL-2 after polymerization with MDI and N-MDEA. In addition to the physical interactions of the CWPU films that result from the hard segments, the crystallization of the continuous phase also improves the interaction of the CWPU segments at ambient temperature. The different microstructures of the CWPU films reflect the effects of diols in CWPUs on the tensile strengths of the CWPU films. The increase in the number of interactions in the CWPU film causes an increase in the tensile strength of the film.

The Mechanical Properties of WG/CWPU Blend Sheets

The cationic water-borne polyurethanes prepared using PCL-1 and PCL-2 as a soft segment and MDI as a hard segment were used to plasticize wheat gluten. The mechanical properties of the molded WG/CWPU blend sheets are listed in Table II. The results show that the tensile strength, tensile moduli, and bending properties of the molded blends all decreased with the addition of CWPU to WG. The tensile strength and modulus decreased from 47.7 to 27.1 MPa and 736.7 to 313.1 MPa, respectively, and the bending strength and modulus from 80.58 to 25.04 MPa and 5748.1 to 1523.6 MPa, respectively. However, the elongation at break of the molded blends increased with addition of CWPU. The incremental elongation reached more than 120% on the addition of 50 parts of CWPU. It should be noted that the optimal mechanical properties of WG/CWPU blend sheet are occurred when 20 parts of CWPU were blended with WG. The mechanical behavior of the WG/CWPU blends differed from that of the blends of the waterborne polyurethane

and thermoplastic starch,¹⁹ whose mechanical properties exhibited maximum values in comparison with thermoplastic starch.

The changes in the mechanical properties of the WG improved by CWPU reflect the improved flexural properties of the WG blend sheets. The effect of the elastic CWPU on the mechanical properties of WG blends results from the improvement of the inter- and intramolecular interactions of the WG protein molecules. The interaction between CWPU and WG reduces the noncovalent interactions (hydrogen bonding, van der Waals', electrostatic and hydrophobic interactions), and even the inter- and intramolecular disulphide bonds in the WG. These noncovalent interactions, and inter- and intramolecular disulphide bonds, cause the brittle behavior of WG materials. At the same time, the tensile strength and moduli, and the bending properties of WG sheets plasticized by CWPU with PCL-1 as a soft segment are greater than those of sheets plasticized by CWPU with the same content of PCL-2, since the mechanical properties of the CWPU with PCL-1 are superior to those with PCL-2. However, the elongation at break of the molded blends with PCL-1 is less than that with PCL-2.

The mechanical properties of blends of WG and CWPU prepared using different diisocyanates and polyester diols are shown in Table III. For comparison, PC diol was used as a soft segment instead of biodegradable PCLs in CWPU, but the mechanical properties of blend of WG and CWPU with PC diol are also inferior. The mechanical properties of blends of WG and CWPU with aliphatic IPDI as a hard segment are less good than those with aromatic MDI. The variation of the mechanical properties of the WG/CWPU blend sheets is similar to that of the CWPU film.

Miscibility and Morphology of WG/CWPU Blend Sheet

Figure 2 shows the FTIR spectra of vital WG and molded WG. The spectra of the two wheat glutes with polypeptide chains exhibit the same strong amide I (C=O) peak at 1650 cm⁻¹ and medium amide II (NH) peak at 1540 cm⁻¹, as well as the broad hydroxyl (OH) bands centred at 3320 cm⁻¹ that are typical of proteins.³¹ Indeed, the bands of free N—H stretching and

Table III. Mechanical Properties of Molded WG and CWPU Blend Sheets^a

Diol/di-Isocyanate ^b	Tensile strength/MPa	Tensile modulus/MPa	Elongation at break/%	Bend strength/MPa	Bend modulus/MPa	Storage modulus at 33 °C/MPa
PCL-1/MDI	39.46	722.57	11.04	52.00	2859.57	2393.00
PCL-2/MDI	33.65	467.80	13.39	47.18	2735.56	2158.64
PC/MDI	35.38	430.15	13.49	43.81	2925.36	2107.47
PCL-1/IPDI	30.61	409.89	12.38	36.18	2729.19	2087.11
PCL-2/IPDI	26.64	355.37	13.71	29.91	2515.88	1974.37

^aWeight ratio of CWPU to WG is 20 : 100.

^bMolar ratio of diisocyanate to diol is 1.

H-bonded N—H stretching also appear in the broad spectral region between 3100 and 3500 cm⁻¹. The results show that there are no major chemical differences between unprocessed and molded WG, implying that the chemical composition of molded WG is not noticeably degraded by heating during the molding process.

The FTIR spectrum of synthetic CWPU is shown in Figure 3. Which shows the absorption peaks of free NH, OC=O, and O=CNH at 3450, 1650, and 1530 cm⁻¹, respectively. The formation of the -NHCO- (urethane) group in the chemical structure of CWPU is confirmed by these three groups. It may also seen that the characteristic absorption peak of N=C=O at 2270 cm⁻¹ disappears, indicating that the isocyanate group at the end of CWPU was completely reacted.

Figure 3 shows that the spectra of the two molded blends of WG and CWPU with different contents are similar. Comparison of the FTIR spectra of the molded WG and WG/CWPU blends reveals that the occurrence of an appreciable absorption peak at 1730 cm⁻¹ may be attributed to the formation of free carbonyl (see Figures 2 and 3). This implies that the H-bonded molecular interaction of WG decreased after blending with CWPU, and the hydrogen bonding interactions between the urethanes of CWPU and the polypeptides in WG occurred during blending and molding. These interactions led to an increased compatibil-

ity of WG and CWPU during blending. As previously mentioned, the deterioration in the tensile and bending properties of molded WG/CWPU blends resulted from a decrease in the H-bonded interaction of the WG.

SEM was performed to observe the morphology of the transverse sections of bend-fractured WG and WG/CWPU blend sheets. Images of the cross-sections of various blends are shown in Figure 4. The cross-section of the WG sheet shows a rough microstructure, with pores and some residual starch granules [Figure 4(a)]. The morphology of the WG sheet is similar to those reported for a thermo-pressed wheat gluten film.³² The microstructures of WG/CWPU blend sheets [Figure 4(b–d)] are similar to that of the WG sheet, but become rougher with increasing CWPU content in WG blends. The coarse fracture surfaces of the WG/CWPU blend sheets indicate that the rupture of the blend sheets is not brittle. The brittleness of WG sheets can be improved by CWPU dispersed into the WG matrix. More pores are present when CWPU with PCL-1 and MDI as diol and diisocyanate is blended at 50 parts by weight. This results from the further addition of CWPU to the more hydrophilic groups in the WG continuous phase. The sizes of starch granules in the blends are somewhat smaller, probably reflecting their destruction during compression-molding. Moreover, the cross-sections of the WG/CWPU blends show that the surface

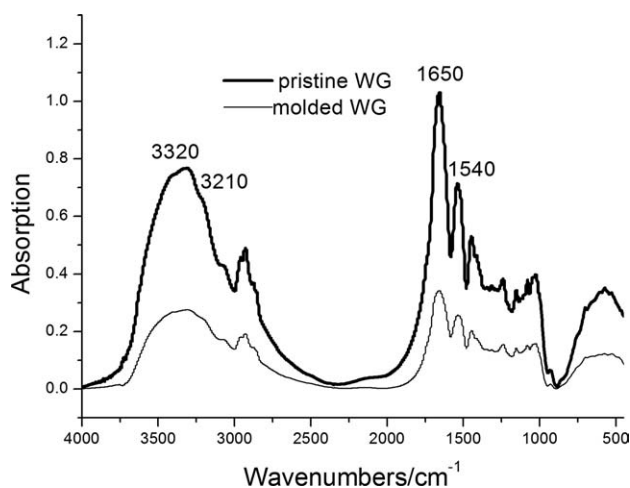


Figure 2. FTIR spectra of pristine and molded WG.

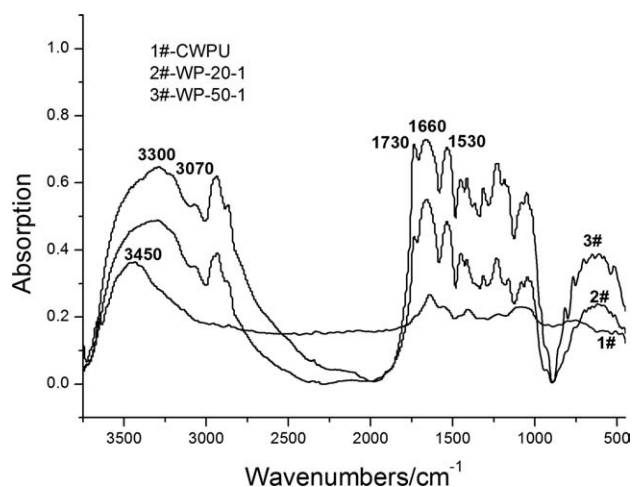


Figure 3. FTIR spectra of powders of CWPU and two molded WG/CWPU blends with PCL-1 diol and MDI (hard segment: 46%).

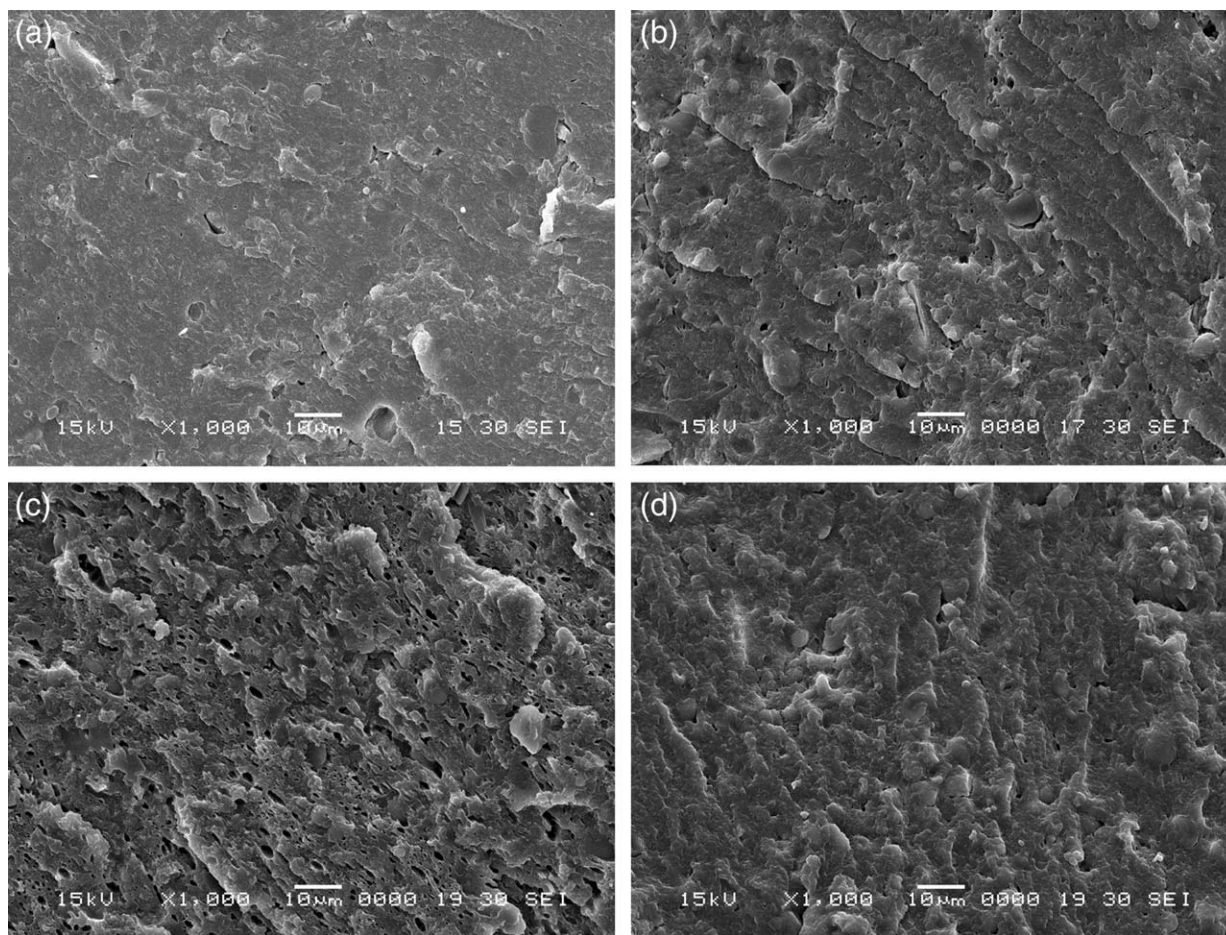


Figure 4. SEM images of fractured WG/CWPU blend sheets with different types and contents of CWPU (a) Pristine WG (b) WP-20-1 (c) WP-50-1 (d) WP-20-2.

of the sections is homogeneous, without any obvious phase separations. There is good interfacial adhesion between the WG and CWPU components because of the hydrogen bonding interactions between the urethane groups of the PU and the amide groups on the WG. The hydrogen bonding interactions reduce the interfacial tension between the anionic PU and the thermoplastic starch, causing compatibility.¹⁹ These interactions also improve the miscibility of the blends of WG and CWPU. The homogenous morphology and good interfacial adhesion are beneficial and increase the impact strength of the materials. The micrographs of the blend sheets show that the 20 parts by weight of the CWPU in the WG blend is optimal, in view of the morphological characteristics that result.

Dynamic behavior of Molded WG/CWPU Blend Sheets

Wheat gluten is an amorphous and multicomponent agropolymer, in which polyurethane can be used as an elastomer. Dynamic mechanical thermal analysis is an effective technique for investigating the viscoelastic behavior of materials in order to obtain information about the relaxation mechanism that may be correlated with the dynamics and microstructure of the material, and the compatibility of the blend. The temperature sweeps in the dynamic mechanical analysis of the molded WG and various WG/CWPU blends are shown in Figures 5–8. The

results show that the rigidity of the WG sheets reduce markedly with the addition of CWPU, and decrease with increasing CWPU content at ambient temperature. The decrease in the storage modulus of the WG sheet is more than 1000 MPa when 10 parts by weight of CWPU are blended with WG. At the same

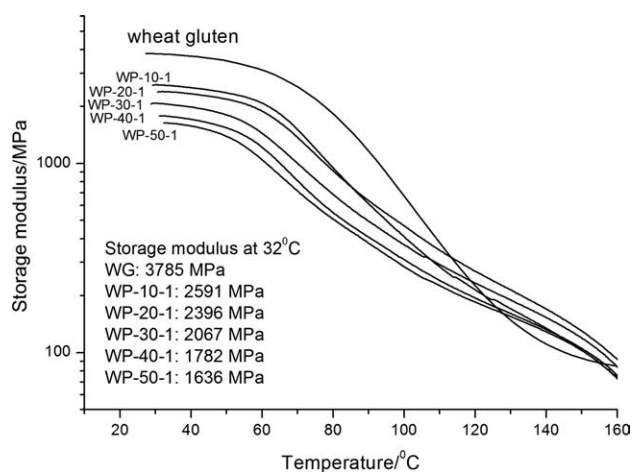


Figure 5. Temperature dependence of storage modulus for molded WG and blends of WG and CWPU consisting of PCL-1 as diol.

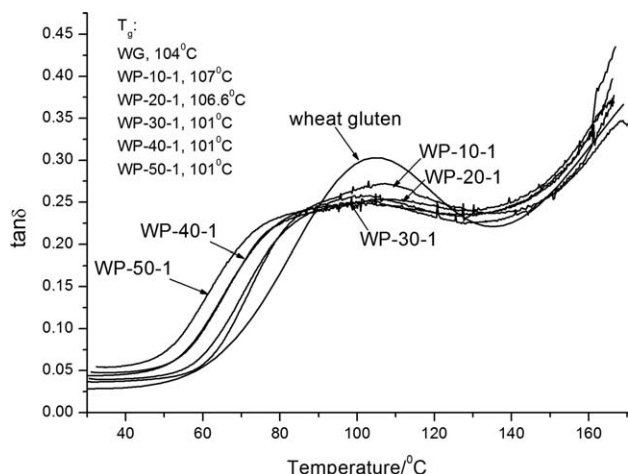


Figure 6. Temperature dependence of mechanical loss factor ($\tan \delta$) for molded WG and blends of WG and CWPU consisting of PCL-1 as diol.

weight ratio of CWPU in blended sheets, the stiffness of the molded blend of WG and CWPU with PCL-1 as diol is higher than that with PCL-2, because the soft segment in the former has a crystalline structure, and the soft segment in the latter is amorphous at 32°C (see Figure 1). The storage moduli of the various blends of WG and CWPU consisting of MDI, IPDI, and three polyester diols are listed in Table III. The variation in the elasticity of the WG/CWPU blend sheets at 33°C accords with the changes in the bending strength of the blend sheets.

The damp properties of the WG sheets declined when blended with CWPU, and the relaxation transition of the WG/CWPU sheets became broader. This is an indication that some specific interactions took place between the polar groups of the WG and CWPU. The plasticization of the CWPU facilitated the local motions of the WG molecules, so that the relaxation transitions of the WG occurred at a low temperature in the WG/CWPU blends, and gradually lower temperatures for increasing weight ratios of CWPU using PCL-1 as diol in the blends. In

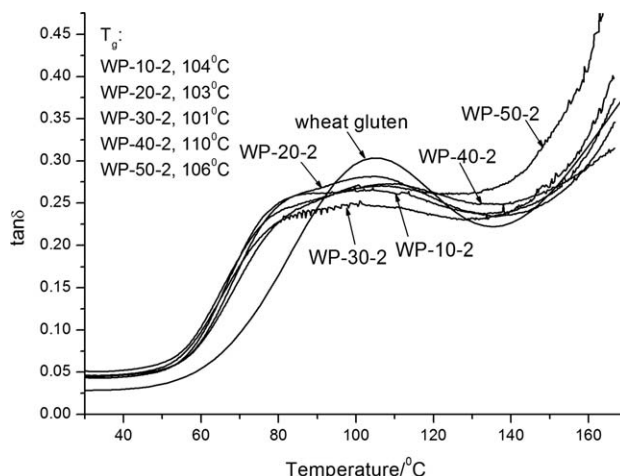


Figure 8. Temperature dependence of mechanical loss factor ($\tan \delta$) for molded WG and blends of WG and CWPU consisting of PCL-2 as diol.

contrast, the effect of CWPU content based on PCL-2 as a soft segment on the relaxation transition of WG is not clear. The amorphous CWPU based on PCL-2 as diol mixes easily with WG such that a small amount of CWPU can enhance the movement of the WG segments. The broadening of the $\tan \delta$ peaks for glycerol-plasticized wheat gluten films was previously described by Gontard and Ring.³³ This effect is due to the wide distribution of molecular weights of the proteins ($\sim 30,000$ to millions). On the other hand, the effect of the plasticization of the poly(ϵ -caprolactone)-based CWPU on the glass transition of WG is not obvious. The small shift in glass transition temperature for blending with various weight ratio of WG/CWPU indicates that the molded blends of WG/CWPU have some degree of compatibility with the heterogeneous morphology and multicomponent system. The reduction in the dynamic mechanical thermal properties of the molded WG/CWPU sheets implies that CWPU is an effective plasticizer for WG, just as anionic water-borne polyurethanes (AWPU) have been used to plasticize starches.^{17–19}

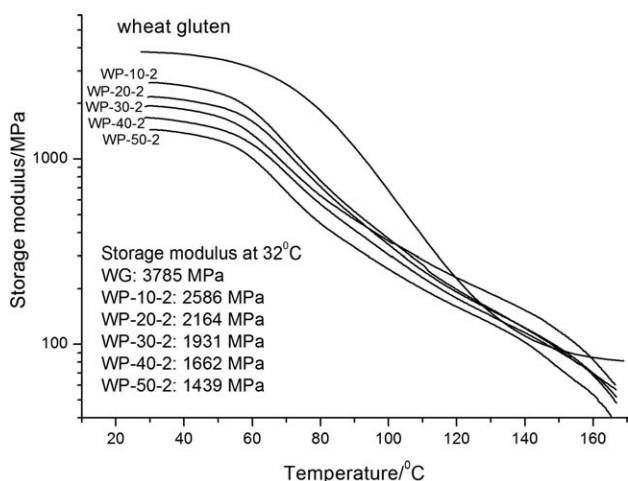


Figure 7. Temperature dependence of storage modulus for molded WG and blends of WG and CWPU consisting of PCL-2 as diol.

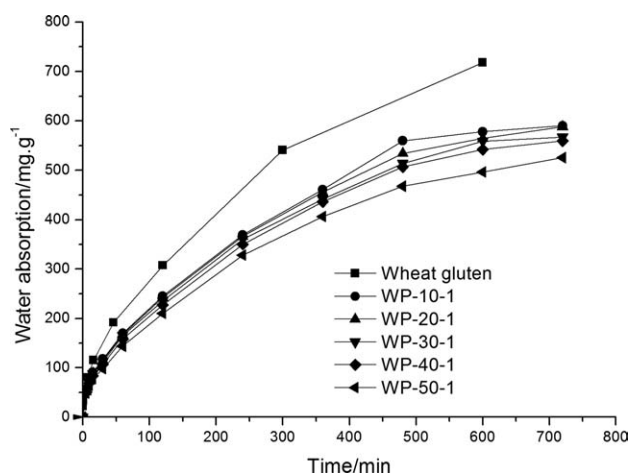


Figure 9. Water absorption curves of the molded WG and WG/CWPU blend sheets.

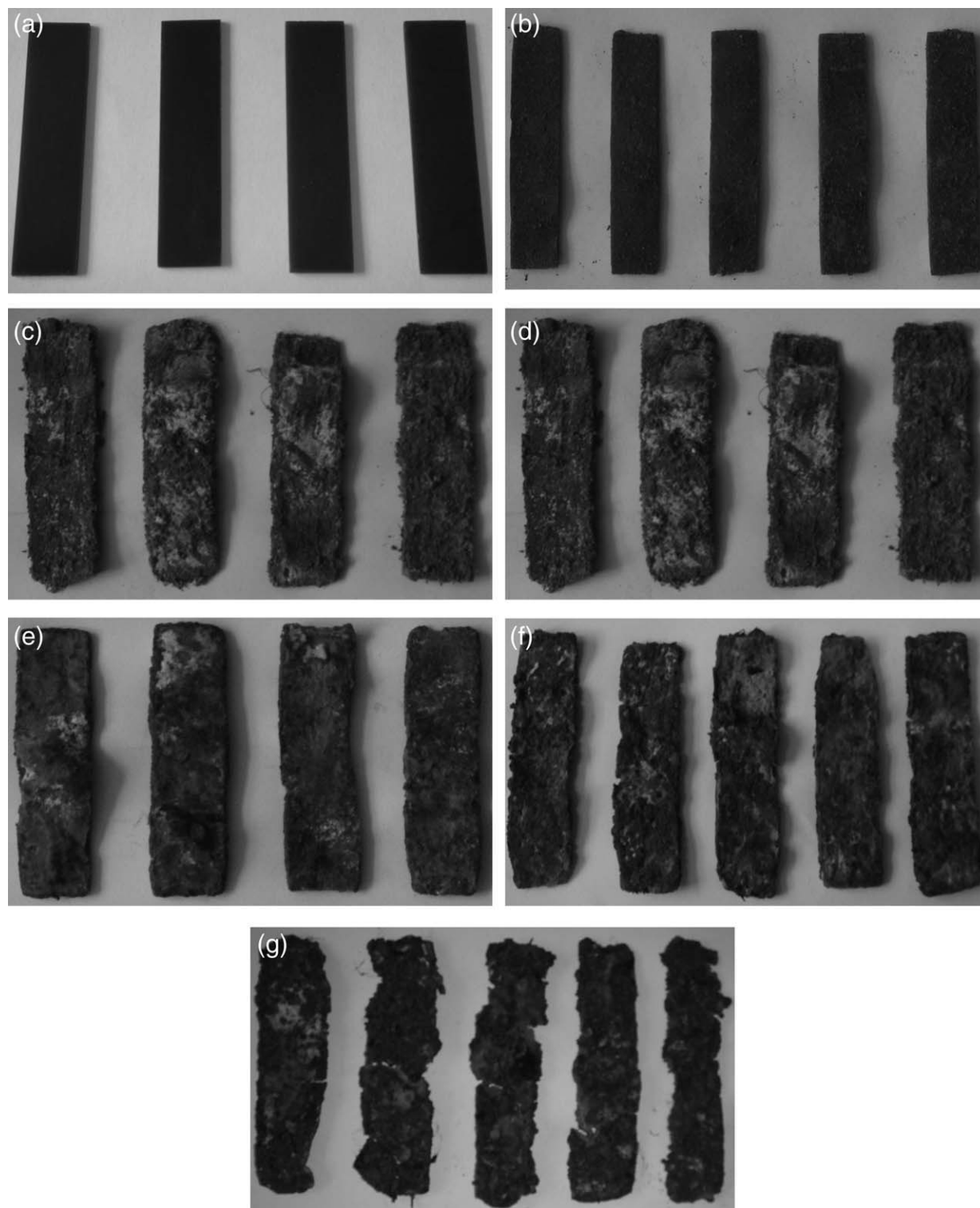


Figure 10. Appearance of WP-20-1 blend sheet before burial (a), after 1 day (b), 3 days (c), 5 days (d), 7 days (e), 10 days (f), and 15 days (g).

Water Absorption of Molded WG/CWPU Blend Sheets

The dependence of the water absorption of the molded blends of WG and WG/CWPU with time are shown in Figure 9. The results indicate that the water uptake of the molded sheets increase with immersion time, and decrease with the addition of CWPU. The water absorption of the molded WG/CWPU

blends reaches a saturation plateau after immersion for 6 h, and declines with increasing CWPU content in blends. As an agro-polymer, wheat gluten not only contains amino-groups and the carboxyl-group, but also has nonpolar and ionic properties to interact with water. The morphology and molecular structure formed after processing also affect the hydration of wheat

Table IV. Changes in Weight Loss and Bending Properties of WP-20-1 During Biodegradation

Run	Degradation time/day	Temperature and weather	Moisture/%	Weight before degradation/g	Weight after degradation/g	Weight-loss/%	Bending strength/MPa	Bending modulus/MPa
1	0	/	/	/	/	/	52.00	2859.57
2	1	37°C /fine	50	5.9428	5.8762	1.12	33.56	1443.03
3	3	38°C /fine	50	4.2971	3.9901	7.14	13.11	423.14
4	5	38°C/rainstorm	50	5.5794	4.4111	20.94	7.21	231.39
5	7	38°C /shower	56	4.8473	3.6999	32.67	/	/
6	10	37°C /shower	56	5.9138	3.0084	49.13	/	/
7	15	35°C /cloudy	55	5.979	2.2768	61.92	/	/

gluten. The number of sorption sites exposed to the surface of the molded sheet decreased with the addition of polyurethane, i.e., of less hydrophilic groups. On the other hand, the polyurethane-plasticized wheat gluten contains protein molecules that are easy to fold, such that some of the sites can be segregated from the surface. Blending thus allows less water absorption. The molded blend of WP-50-1 exhibits a relatively high degree of water resistance, although there is a greater degree of porosity in the cross-section of the blend [see Figure 4(c)]. CWPU can greatly improve the water uptake of WG sheets. AWPU also played a crucial role in improving the surface- and bulk-hydrophobicity and water resistance of the blends of starch thermoplastics (TPS).^{18,19} The decrease in the water uptake of the blends with increasing AWPU content suggests the occurrence of strong hydrogen bonding interaction between AWPU and TPS. The effect of the various CWPUs listed in Table III on the water absorption of WG sheet shows that CWPU based on different diisocyanates and diols can improve the water resistance of WG materials. The water uptake of the blend sheet of WG and CWPU composed of MDI as diisocyanate and PCL-1 as diol is lower than that of the blend of WG and other types of CWPU, and the hydrophobic effect of the MDI on the CWPU is more distinct. Indeed, the hydrogen bonding interaction between WG and CWPU can improve the moisture sensitivity of WG by blending polyurethane that is environmentally-friendly.

Biodegradation of Molded WG/CWPU Blend Sheets

Polyurethanes based on poly (ϵ -caprolactone) diol as a soft segment are biodegradable in soil.²³ To observe this, the molded WP-20-1 sheets listed in Table II were buried in soil. Figure 10 shows the changes in the appearance of the samples after different periods of time. The weight loss and bending properties of the corresponding samples are listed in Table IV. The results show that there is no difference in appearance after one day [Figure 10(a,b)], but the bending properties of the specimen do change, reducing by 35% in bending strength and by 49% in bending modulus. The considerable loss of bending capacity implies that the primary mechanism at work in the biodegradation of the blend sheets is random chain scission. Some white molds appeared on the surface of the specimens after 3 days [Figure 10(c)]. The shapes of the specimens varied unpredictably, the weight loss of the samples reached 20.94%, and the flexural strength and bending modulus decreased respectively by 85.56 and 80.91% after 5 days [Figure 10(d)]. The bending

properties of the specimens could not be tested because of the formation of large cracks after 7 [Figure 10(e)] and 10 days [Figure 10(f)]. After 15 days, more than half the weight loss had occurred [Figure 10(g)], as a result of microbial degradation in the soil.

CONCLUSIONS

We successfully prepared cationic waterborne polyurethanes using polyester glycols as a soft segment and diisocyanate MDI, IPDI, and N-MDEA as a hard segment. The CWPUs were blended with wheat gluten in aqueous dispersions, and the freeze-dried blend powders were then successfully thermally compression-molded to form blend sheets. The mechanical and dynamic mechanical thermal properties of the blend sheets indicate that CWPU can improve the brittleness of WG materials. Blend sheets with 20 parts of CWPU have reasonably good mechanical properties. We observed compatible and homogenous morphology, and good interfacial adhesion of the blends by SEM. The water absorption of WG sheets decreased with the addition of CWPU. Optimal water resistance was found for molded sheets blended with WG and CWPU based on PCL with a higher melting point as a soft segment, and MDI as a hard segment. Experiments on the biodegradation of the blend in soil showed that the bending strength and modulus of blend sheets reduced by 35 and 49% after one day. After 15 days, the mass loss of the sample reached 61.9% by weight.

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