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Urea and formamide as a mixed plasticizer for thermoplastic wheat flour

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Abstract

Urea and formamide were used as a mixed plasticizer for preparing the thermoplastic wheat Flour (TPF) by a single screw extruder. Wheat flour granules were proved to transfer to a continuous phase by Scanning Electron Microscope (SEM). Rheology analysis illustrated that during the thermoplastic processing both the extruder screw speed and the processing temperature could effectively adjust the flow behavior of TPF. TG curves revealed that when the plasticizer weight content (PC) was under 40%, the whole of the plasticizer could be effectively bounded to wheat flour. TPF with 30% PC had the relatively good mechanical properties: The tensile strength, elongation at break, energy break and Young's modulus were 2.07 MPa, 44%, 0.35 N m and 20.1 MPa, respectively. X-ray analysis showed that the mixed plasticizer could effectively restrain the starch retrogradation of TPF. And water absorption testing showed that the lower PC was the better water resistance of TPF was.

Keywords: Wheat flour; Formamide; Urea; Thermoplastic

1. Introduction

Much effort has recently been made to develop biodegradable materials because of the worldwide environment and resources problems resulted from petroleum-derived plastics. (Fishman, Coffin, & Konstance, 2000; Formes, Hunter, & Paul, 2004; Park, Lee, & Cho, 2003) One of the emerging major themes in polymer science for the 21st century is the preparation of sustainable materials from the renewable resources, as distinct from petrochemicals (Stepto, 2003). Starch, a natural renewable polysaccharide obtained from a great variety of crops, is one of the promising raw materials for the production of biodegradable plastics (Copinet, Bliard, & Onteniente, 2001; Petersen, Væggemose, & Bertelsen, 1999). The thermo-plastics processing of nature starch is a recent development with wide possible applications (Averous, Fauconnier, & Moro, 2000; Fang & Hanna, 2001). During the thermoplastic process, water contained in starch and added plasticizers play an indispensable role (Hulleman, Janssen, & Feil, 1998; Wang, Shogren, & Carriere, 2000), because the plasticizers can form the hydrogen bonds with starch, take the place of the strong action between hydroxyl groups of starch molecules, and make starch thermoplastic. However, starch-based materials are susceptible to aging and starch re-crystallization (retrogradation). TPS plasticized with glycerol, a conventional TPS, was thought to tend to retrogradation after being stored for a period of time, and this retrogradation embrittled TPS (Van Soest & Knooren, 1997). Urea was proven to prevent retrogradation. It is, however, a solid with little internal flexibility and hence urea-plasticized TPS becomes rigid and brittle (Stein & Greene, 1997). Formamide could availably suppress the retrogradation of thermoplastic cornstarch and make thermoplastic starch more flexible, but the tensile failure stress was weak (Ma & Yu, 2004a). Since formamide is a good solvent for urea, a combination of urea and formamide could effectively restrain TPS retrogradation and improve mechanical properties of TPS (Ma & Yu, 2004b).

Wheat flour, a starch-rich material, was mainly composed of starch and protein, however wheat flour was rarely made use of for thermoplastic materials. In this paper, urea and formamide as a mixed plasticizer were used to prepare the thermoplastic wheat flour (TPF). Compared to

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conventional glycerol as the plasticizer of thermoplastic starch, urea and formamide could interact with not only starch component but also protein component in wheat flour. The properties of the TPF, such as the microcosmic morphology, rheology, thermal stability, mechanical properties, retrogradation and water absorption, were studied.

2. Experimental

2.1. Materials

Wheat flour (11% moisture, 10% protein, above 76% starch) was purchased from Harbin HI-Tech Group Company Ltd. (Harbin, Heilongjiang, China). The plasticizers, urea and formamide, were purchased from Tianjin Chemical Reagent Factory (Tianjin, China).

2.2. Plasticization

Urea and formamide were mixed and the ratio of urea and formamide (wt/wt) was 1:2. The mixed plasticizers were blended (300 rpm, 2 min) with wheat flour by use of High Speed Mixer GH-100Y (Beijing Plastic Machinery Factory, Beijing, China), then stored overnight. The mixtures were manually fed in to the single screw Plastic extruder SJ-25(s) (Screw Ratio L/D = 25:1, Beijing Plastic Machinery Factory, Beijing, China). The screw speed was 20 rpm. The temperature profile along the extruder barrel was 120, 130, 130, 120 °C (from feed zone to die). The die was a round sheet with the 3 mm-diameter holes. Here the mixed plasticizer weight contents (PC), defined as the plasticizer weight/the wheat flour weight, were 25, 30, 40 and 50%.

2.3. Scanning electron microscope (SEM)

The native wheat flour and the fracture surfaces of extruded TPS strips were performed with Scanning Electron Microscope Philips XL-3 (FEI Company, Hillsboro, Oregon, USA), operating at an acceleration voltage of 20 kV.

Native wheat flour powders were suspended in acetone. The suspension drops were drawn on the glass flake, dried for removing the acetone, and then vacuum coated with gold for SEM. TPS strip samples were cooled in liquid nitrogen, and then broken. The fracture faces were vacuum coated with gold for SEM.

2.4. Rheology

TPF was cut into small pieces, which were tested by XLY-IIrheometer (Jilin University Instrument Factory, Jilin, China).

2.5. Thermal analysis (TG)

TPF was cut into small pieces, which were tested by ZRY-ZP thermal analysis instrument (Beijing Plastic Machinery Factory, Beijing, China). The samples were about 5–10 mg, the scope of testing temperature was from the room temperature to 450 °C and the heated rate was 15 °C/min.

2.6. Mechanical testing

Samples 8 cm × Φ 3 mm in Size were cut from the extruded strips. The Testometric AX M350-10 KN Materials Testing Machines (The Testometric Company Ltd, Rochdale Lancashire, United Kingdom) operated and a crosshead speed of 10 mm/min was used for tensile testing.

2.7. X-ray diffractometry

The extruded TPS strips were pressed at 10 MPa with the Flat Sulfuration Machine (Beijing Plastic Machinery Factory, Beijing, China) and the slices were placed in a sample holder for X-ray diffractometry (Beijing University Instrument Factory, Beijing, China). The native wheat flour powders were packed tightly in the sample holder. X-ray diffraction patterns were recorded in the reflection mode in angular range 10–30°(2θ) at the ambient temperature by a BDX3300 diffractometer, operated at the Cu Kαwavelength of 1.542 Å. The radiation from the anode, operating at 36 kV and 20 mA, monochromized with a 15 μm nickel foil. The diffractometer was equipped with 1° divergence slit, a 16 mm beam bask, a 0.2 mm receiving slit and a 1° scatter slit. Radiation was detected with a proportional detector.

2.8. Water contents

The original water contents (dry basis) of TPS were determined gravimetrically by drying small pieces of TPS at 105 °C overnight. At this condition, evaporation of the plasticizers was negligible (Curvelo, de Carvalho, & Agnelli, 2001). When TPS was stored for a period of time, its water content was calculated on the base of its original weight, its current weight and its original water content.

3. Results and discussion

3.1. SEM analysis

Compared with native wheat flour granules (Fig. 1a), the microcosmic morphology of the extruded TPF was shown in Fig. 1a few percent of residual granular structure was present in the continuous phase for TPF containing 30% weight content of plasticizer (Fig. 1c), while a quantity of

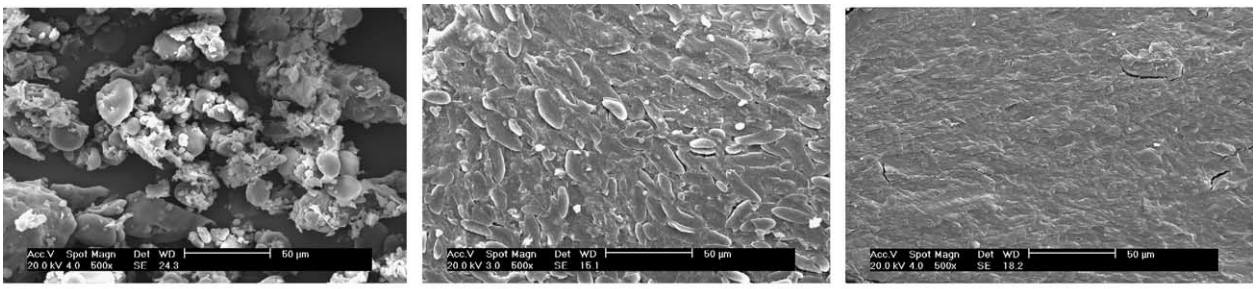

Fig. 1. SEM micrograph of native wheat flour granules (a) and the fracture face of TPF containing 25% (b) and 30% (c) weight content of plasticizer.

granule did not fuse into one continuous phase for TPF containing 25% weight content of plasticizer (Fig. 1b). It meant that enough plasticizer was necessary to from the homogeneous TPF. Due to the high shear and temperature conditions with the action of formamide and urea, native wheat flour granules were molten or physically broken up into small fragments. The mixed plasticizers of formamide and urea above 30% weight content were known to disrupt intermolecular and intramolecular hydrogen bonds and made the native wheat flour plastic.

3.2. Rheology

The capillary viscometer used to determine the viscosity of the blends was XYL-II capillary rheometer. The capillary viscometer consists of a barrel into which material was loaded before being pushed by a plunger through a capillary was controlled by a surrounding heating unit. The radius of capillary is 1 mm and L/D is 40. The small pieces were placed into the barrel through a funnel and then packed down with the plunger until the first extrudate appeared at the capillary exit. The sample was allowed to come to temperature (10–15 min), and was then forced through the capillary by the plunger at pre-selected velocities. The load on the plunger and plunger speed provide the total pressure drop through the barrel and capillary and the volume flow rate. Shear rate (γ) and shear stress (τ) were calculated by stand methods. In order to understand the TPF processing properties, the rheology experiments were carried at 120 and 130 °C, which covered the processing temperature range.

The melting volumetric flow rate through the capillary was given

$$Q = \frac{\pi R^3}{4}\gamma\frac{4n}{3n+1} \tag{1}$$

where R, capillary radius, γ, shear rate at the capillary wall, n, flow index depending on the temperature. The term $4n/3n+1$ was the Rabinowitsch correction factor.

According to Onteniente, Abbès, and Safa (2000), Thermoplastic starch exhibited power-law behavior:

$$\tau = K\gamma^n \tag{2}$$

The apparent viscosity η was defined by Eq. (3):

$$\eta = \tau/\gamma \tag{3}$$

where τ, shear stress, γ, shear rate at the capillary wall, K, consistency of the materials depending on the temperature, the structure and the formulation of the polymer.

Substituting Eq. (3) for τ in the relationship (2) between τ and γ yielded:

$$\eta = K\gamma^{n-1} \tag{4}$$

Pressures were monitored, and shear stress values were calculated using the following equation:

$$\tau = \frac{\Delta P\cdot R}{2L} \tag{5}$$

where ΔP, pressure at the capillary entrance, L, capillary length, R, capillary radius.

According to Arrehnius equation:

$$\eta = A\cdot e^{\Delta E_\eta/RT} \tag{6}$$

$$\log\eta = \log A + \Delta E_\eta/(RT\ln 10) \tag{7}$$

where ΔE_η, the vicious flow activation energy, A, the consistency related to structure and formulation, R, Gas constant 8.314 J mol^{-1} K^{-1}.

The $\eta\sim\gamma$ curves were plotted using a double logarithmic (in Fig. 2). With increasing shear stress the viscosity of each TPF decreased. Such flow behavior was called shear thinning, which was mainly ascribed to the gradual demolishment of starch intermolecular action. As shown in Fig. 2, the effect of both plasticizer weight content (PC) and the temperature on TPF rheological behavior was much. According to the listed linear fit equations in Fig. 2, TPF was prone to the flow along with the increasing temperature at the same PC, and the apparent viscosity η was decreasing with the increasing of PC at the same temperature.

The vicious flow activation energy ΔE_η and flow index n of TPF at 130 °C were listed in Table 1. The vicious flow activation energy ΔE_η represented the effect of the temperature on the behavior of TPF. The more ΔE_η was, the more sensitive the behavior of TPF was to the temperature. According to the values of ΔE_η in Table 1, with the increasing of PC the effect of the temperature on

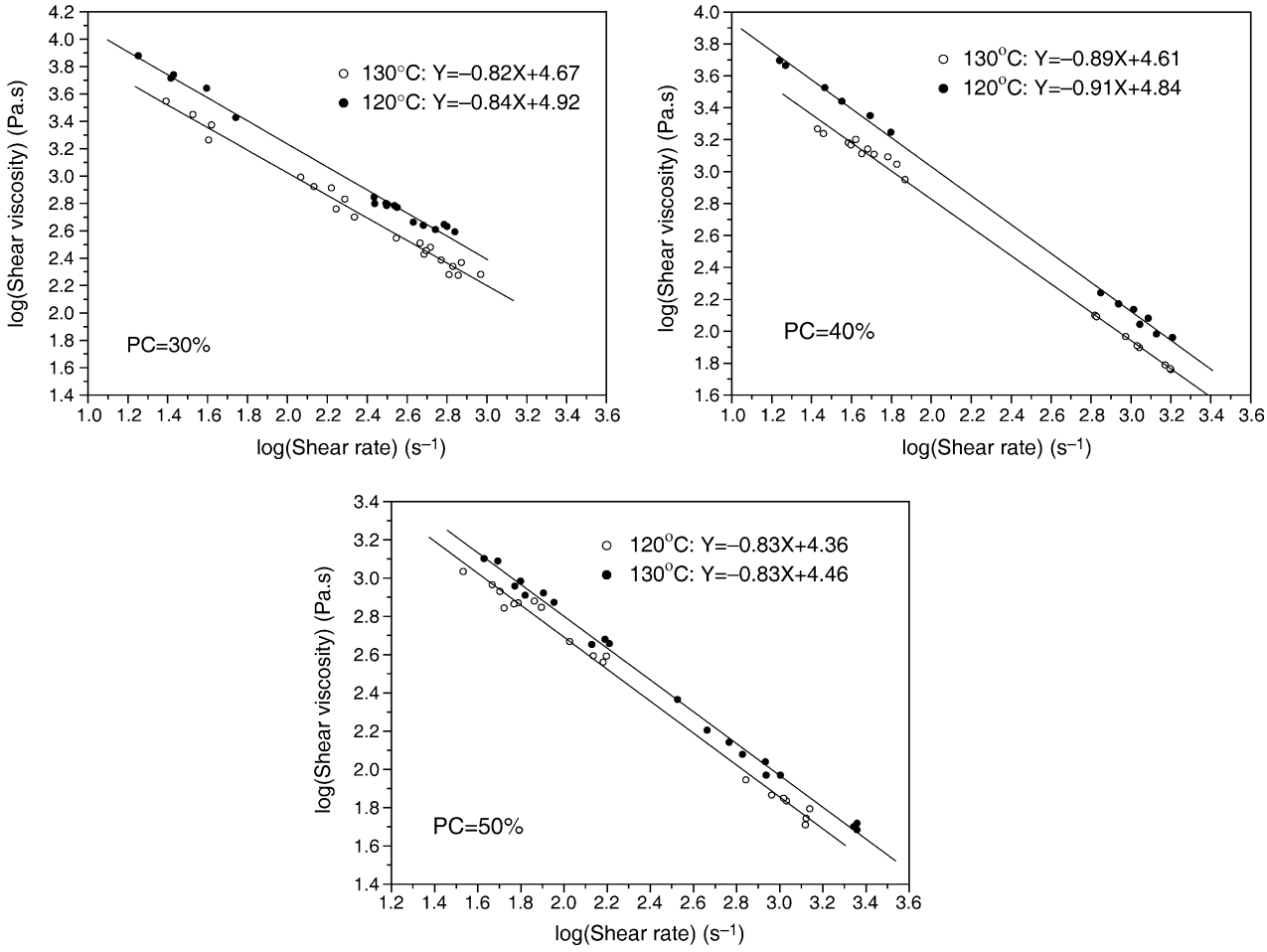

Fig. 2. Shear viscosity related to shear stress in the linear fit for TPF with different PC (30, 40 and 50%) at 120 and 130 °C.

the behavior of TPF was decreasing. It meant that during the processing of TPF, it was available for ameliorating the flow behavior of TPF (PC = 30 and 40%) to improve the processing temperature rather than TPF (PC = 50%). On the other hand, the flow index n between 0.11 and 0.18 meant that they were the non-Newtonian fluid. The slope of the $\log\eta \sim \log\gamma$ curves were above 0.8. It meant that TPF was sensitive to the shear rate. Therefore, during the thermoplastic processing the extruder screw speed could effectively adjust the flow behavior of TPF with different PC.

3.3. Thermal stability

Fig. 3 presented the TG experimental results. If PC were excessive, the redundant plasticizer would not be bounded to wheat flour. For example, about 0.25 g of urea bounded to per g of starch in TPS composed of urea and starch (Shogren, Swanson, & Thompson, 1992). So the unbound plasticizer was prone to volatilization when TPF was heated. At the same time, with the increasing of the temperature, Brownian motion would weak the interaction

Table 1
The effect of plasticizer weight contents on the vicious flow activation energy ΔE_η ($X = 0$) and flow index n of TPF at 130 °C

Plasticizer weight contents	30%	40%	50%
The flow index n	0.18	0.11	0.17
ΔE_η (kJ/mol) ($X = 0$)	79.78	69.74	30.32

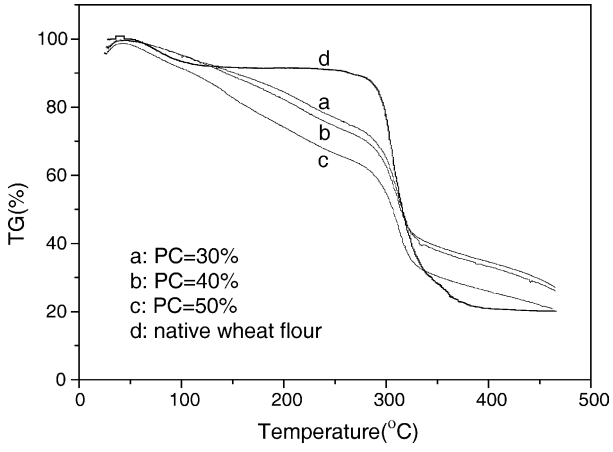

Fig. 3. The TG curves of several TPFs with different PC.

between wheat flour and plasticizer, so the plasticizer mass bounded to per g of starch would decrease.

As shown in Fig. 3, Curve c was different from Curve a and b. The mass loss below 100 °C was mainly ascribed to water loss for Curve a, b and d, while one for Curve c additionally included a small quantity of the unbound plasticizer. Compared with native wheat flour (a in Fig. 3), the proper PC (a and b in Fig. 3) could restrain the water loss below 100 °C because of the interaction between water and TPF. The mass loss from 100 °C to the onset temperature was related to the volatilization of both water and plasticizers. So the difference in the decomposition onset and mass loss at onset temperature was mainly due to the volatility of the plasticizer in TPF with different PC.

The difference of mass loss between TPF with 40% PC (b in Fig. 3) and TPF with 50% PC (c in Fig. 3) was much more than the one between TPF with 30% PC (a in Fig. 3) and TPF with 40% PC (b in Fig. 3). These illustrated that when PC was under 40%, the plasticizer could be bounded well to wheat flour.

3.4. Mechanical testing

The mechanical properties of TPF with different PC were shown in Table 2. After TPF ribbons were extruded from the single screw plastic extruder and stored at the room temperature for one week, mechanical properties of TPF materials were tested. Plasticizer could form the hydrogen bond interaction with starch and weaken the interaction of starch molecules, and the slippage movement among starch molecules was facile, when TPF materials experienced the tensile testing. Therefore, with the increasing of PC in TPF, the tensile strength, Young's modulus and energy break of TPF decreased, while the elongation at break improved. TPF with 30% PC had the relatively good mechanical properties: The tensile strength, elongation at break, energy break and Youngs modulus were 2.07 MPa, 44%, 0.35 N m and 20.1 MPa, respectively.

3.5. X-ray diffraction analysis

The X-ray diffraction patterns of native wheat flour and the TPF with different PC stored at RH = 50% for one month were shown in Fig. 4. Compared with native wheat flour (a in Fig. 4), the crystal behavior of TPF with different PC changed much. The crystal of native wheat flour was the A-style crystallinity (Van Soest & Vliegenthart, 1997), ascribed to starch component in the wheat flour, while there were no obvious crystals in TPF. In the thermoplastic processing, plasticizer molecules entered into starch particles, and should replace starch intermolecular and intramolecular hydrogen bonds and destruct the crystallinity of starch. There was no obvious starch molecular crystal peak (b–d in Fig. 4) when TPFs were stored at RH = 50% for 1 month. It meant that the mixed plasticizers of urea and formamide could effectively suppress the re-crystallization of starch component at RH = 50%. The hydrogen bond between starch and the mixed plasticizers was so strong that it could prevent starch molecules from interacting and crystallizing again during the storage time.

Table 2
The mechanical properties of TPF with different PC

PC	30%	40%	50%
Tensile strength (MPa)	2.07	1.19	0.82
Elongation at break (%)	44	65	74
Energy break (N m)	0.35	0.29	0.26
Young's modulus (MPa)	20.1	10.6	7.8

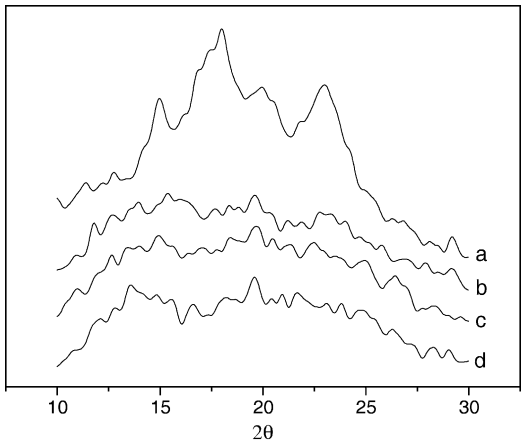

Fig. 4. The diffractograms of native wheat flour and the TPF with different PC stored at RH = 50% for 1 month. (a) Native wheat flour, (b) TPF (PC = 30%), (c) TPF (PC = 40%), (d) TPF (PC = 50%).

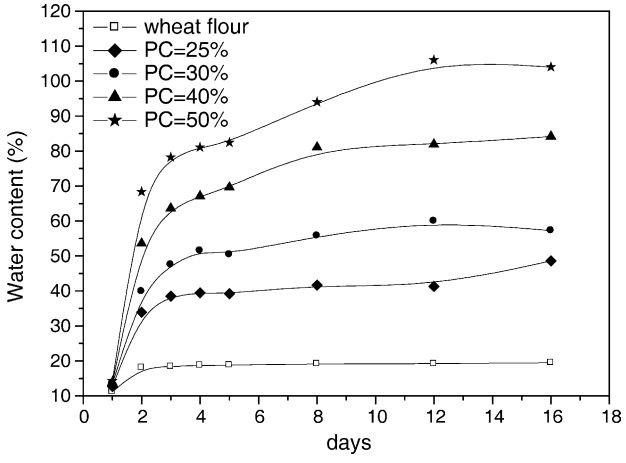

Fig. 5. Water contents of TPF with different PC at the different storage time at RH = 100%.

3.6. Water absorption

As shown in Fig. 5, water absorption of TPF was increasing with the increasing PC. TPF reached the balance of water absorption after they were stored at the environment of relative humidity 100% for 16 days. The balance water contents were respectively 19.6, 48.6, 57.3, 84.2 and 104% for native wheat flour and TPF with PC = 25, 30, 40 and 50%. Those indicated that water resistance of TPF could be improved by decreasing PC, because formamide had a poor water resistance.

4. Conclusion

We reported here the mixed plasticizer of urea and formamide was a favorable plasticizer for TPF, proved by SEM and X-ray methods, and it could also suppress the starch retrogradation in TPF. According to rheology study, TG analysis and mechanical testing, the optimum processing conditions were as following: PC was between 30 and 40%, and both the extruder screw speed and the processing temperature could effectively adjust the flow behavior of TPF. And water absorption testing showed that TPF with low PC had the relatively good water resistance. Long term leaching of formamide should be investigated, since it is well known that even large molecular sized additives are prone to leaching out with time. As a novel thermoplastic material, TPF is worth researching in detail, and will be helpful for ameliorating the properties of TPF and extending TPF application scopes.

Acknowledgements

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