Fly ash-reinforced thermoplastic starch composites

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Abstract

As a by-product from the combustion of pulverized coal, fly ash was, respectively, used as the reinforcement for formamide and urea-plasticized thermoplastic starch (FUPTPS) and glycerol-plasticized thermoplastic starch (GPTPS). The introduction of fly ash improved tensile stress from 4.56 MPa to 7.78 MPa and Youngs modulus increased trebly from 26.8 MPa to 84.6 MPa for fly ash-reinforced FUPTPS (A-FUPTPS), while tensile stress increased from 4.55 MPa to 12.86 MPa and Youngs modulus increased six times from 76.4 MPa to 545 MPa for fly ash-reinforced GPTPS (A-GPTPS). X-ray diffractograms illustrated that fly ash destroyed the formation of starch ordered crystal structure, so both A-GPTPS and FUPTPS could resist the starch re-crystallization (retrogradation). Also fly ash improved water resistance of TPS. As shown by rheology, during the thermoplastic processing, the extruder screw speed effectively adjusted the flow behavior of A-FUPTPS, while the increasing of the processing temperature effectively ameliorated the flow behavior of A-GPTPS. However, superfluous ash contents (e.g., 20 wt%) worsened processing fluidity and resulted in the congregation of fly ash in FUPTPS matrix (tested by SEM) rather than in GPTPS matrix. This congregation decreased the mechanical properties and water resistance of the materials.
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1. Introduction

In the last decades, environmental protection had become a global concern providing much impetus for the development of alternative utilization of the non-biodegradable plastics (e.g., polyolefin) in the application of one-off materials. Many efforts were underway world-wide to utilize renewable feedstock as raw materials for the production of plastics. Starch, a natural renewable polysaccharide obtained from a great variety of crops, was one of the promising raw materials for the production of biodegradable plastics (Petersen, Væggemose, & Bertelsen, 1999). Starch was a multi-hydroxyl polymer. There were so vast intermolecular and intramolecular hydrogen bonds in starch that native starch was not a true thermoplastic. But in the presence of plasticizers (e.g., water, glycerin, sorbitol, etc.) at high temperatures (90–180 °C) and under shear, it readily melted and flowed, allowing for its use as an injection, extrusion or blow molding material, similar to most conventional synthetic thermoplastic polymers (Curvelo, De Carvalho, & Agnelli, 2001).

Natural starch was usually about 15–45% crystalline. During the thermoplastic process, water contained in starch and other plasticizers would destroy starch crystallinity. In most literatures for thermoplastic starch, polyols as plasticizers were usually used such as glycerol (Fishman, Coffin, Konstance, & Onwulata, 2000), glycol (Yu, Gao, & Lin, 1996), sorbitol (Wang, Shogren, & Carriere, 2000) and sugars (Barret, Kaletunc, Rosenburg, & Breslauer, 1995). This kind of TPS was thought to tend to re-crystallization (retrogradation) after being stored for a period of time and retrogradation embrittled TPS. To prepare TPS with retrogradation resistance and good mechanical properties, some plasticizers containing amide groups, such as formamide (Ma & Yu, 2004a, 2004b), acetamide (Ma, Yu, & Feng,

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2004) and urea (Ma & Yu, 2004a) were used. Formamide and urea were proved to be a fine mixed plasticizer to prepare formamide and urea-plasticized TPS (FUPTPS) (Ma et al., 2004). Unfortunately, the properties (e.g., mechanical properties) of thermoplastic starch (TPS) were not satisfied with some applications such as packaging. One significant approach was the use of reinforced materials such as fibers (Wollerdorfer & Bader, 1998) or silicate–aluminate (i.e., montmorillonite) as reinforcement for TPS matrix (Huang, Yu, & Ma, 2004).

Fly ash was a by-product from the combustion of pulverized coal in the power plants and it was known as one of the major problems of all coal combustion power plants, because they had effects on environment such as air pollution and groundwater quality problem due to leaching of metals from the ashes, especially unused fly ash which had very small particle size (Iyer, 2002; Janos, Wildnerova, & Loucka, 2002; Duchesne & Reardon, 1999; Cheerarot & Jaturapitakkul, 2004; Simsiman, Chesters, & Andren, 1987). Composites involving low cost fillers of fly ash were among the newer entrants to the family of particulate filled polymer composites, which found many applications in civil engineering (Kishore, Sunil, & Sharathchandra, 2002).

The objectives of this primary research were to study the properties of fly ash-reinforced FUPTPS (A-FUPTPS) and fly ash-reinforced GPTPS (A-GPTPS) in order to improve the properties of TPS and reduce the landfill area. The fractured surface micrograph, rheology, mechanical properties, starch retrogradation and water resistance were studied with fly ash contents.

2. Experimental

2.1. Materials

Cornstarch (11% moisture) was obtained from Langfang Starch Company (Langfang, Heibei, China). Coal fly ash with 1–5 μm granularity was obtained from Tianjin Steel Company. The plasticizers, glycerol, formamide and urea were purchased from Tianjin Chemical Reagent Factory (Tianjin, China).

2.2. Plasticization

The plasticizers were blended (3000 rpm, 2 min) with cornstarch and fly ash by use of High Speed Mixer GH-100Y (made in China), and then stored overnight. The ratio of plasticizers and cornstarch (wt/wt) was 30:100. When formamide and urea (weight ratio 1/2) were used together, the pre-mixture of them was required. The mixtures were manually fed in to the single screw Plastic Extruder SJ-25(s) (screw ratio L/D = 25:1, made in China). The screw speed was 20 rpm. The temperature profile along the extruder barrel was 120 °C, 130 °C, 130 °C, 110 °C (from feed zone to die). The die was metal plate of 10 mm thick with eight holes of 3 mm diameter.

2.3. Scanning electron microscope (SEM)

The fracture surfaces of extruded TPS strips were performed with Scanning Electron Microscope Philips XL-3, operating at an acceleration voltage of 20 kV. TPS strip samples were cooled in liquid nitrogen, and then broken. The fracture surfaces were vacuum coated with gold for SEM.

2.4. Rheology

TPS was cut into small pieces, which were tested by XLY-IIrheometer (Jilin University Instrument Factory, Jilin, China). The capillary viscometer used to determine the viscosity of the blends was XYL-IIcapillary rheometer. The capillary viscometer consisted of a barrel into which material was pushed by a plunger through a capillary was controlled by a surrounding heating unit. The radius of capillary was 1 mm and L/D was 40. The small pieces were placed into the barrel through a funnel and then pushed through a capillary die 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 method. In order to understand the TPS processing properties, the rheology experiments were carried out at 110 °C, 120 °C and 130 °C, which covered the processing temperature range.

2.5. Mechanical testing

Samples of 8 cm × ⌀3 mm in size were cut from the extruded strips, pressed with vulcanizing hot press. The Testometric AX M350-10KN Materials Testing Machine was operated and a crosshead speed of 10 mm/min was used for tensile testing (ISO 1184-1983 standard). The data was averages of 5–8 specimens.

2.6. X-ray diffractometry

The extruded TPS strips were pressed at 10 MPa with the Flat Sulfuration Machine. The slices were placed in a sample holder for X-ray diffractometry, while the 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 CuKα wavelength of 1.542 Å. The radiation from the anode, operating at 36 kV and 20 mA, monochromatized 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.

2.7. Water contents

Water contents (dry basis) were determined gravimetrically by drying small pieces of TPS at 105 °C overnight. At this condition, evaporation of the plasticizers was negligible.

3. Results and discussion

3.1. Microscopy

SEM micrograph at 500× magnification of fractured surface of GPTPS filled with different fly ash contents and native starch granules were shown in Fig. 1. The good dispersion of fly ash was shown in GPTPS matrix. There

was no obvious congregation of fly ash even at 20 wt% fly ash contents. However, the residual starch granular structure increased with the increasing of fly ash contents. At the high shear and temperature conditions with the action of plasticizers, native cornstarch granules (as shown in Fig. 1e) were molten or physically broken up into small fragments, and the continuous GPTPS matrix formed. The introduction of superfluous fly ash would definitely block TPS fluid and affect starch thermoplastic processing.

The micrograph of A-FUPTPS was different from A-GPTPS. At low fly ash contents (e.g., 10 wt%), there was no obvious congregation of fly ash in A-FUPTPS. But at high fly ash contents (e.g., 20 wt%), as the arrows showed in Fig. 2, there were obvious evidence of fly ash congregation in FUPTPS matrix. Compared to GPTPS, poor
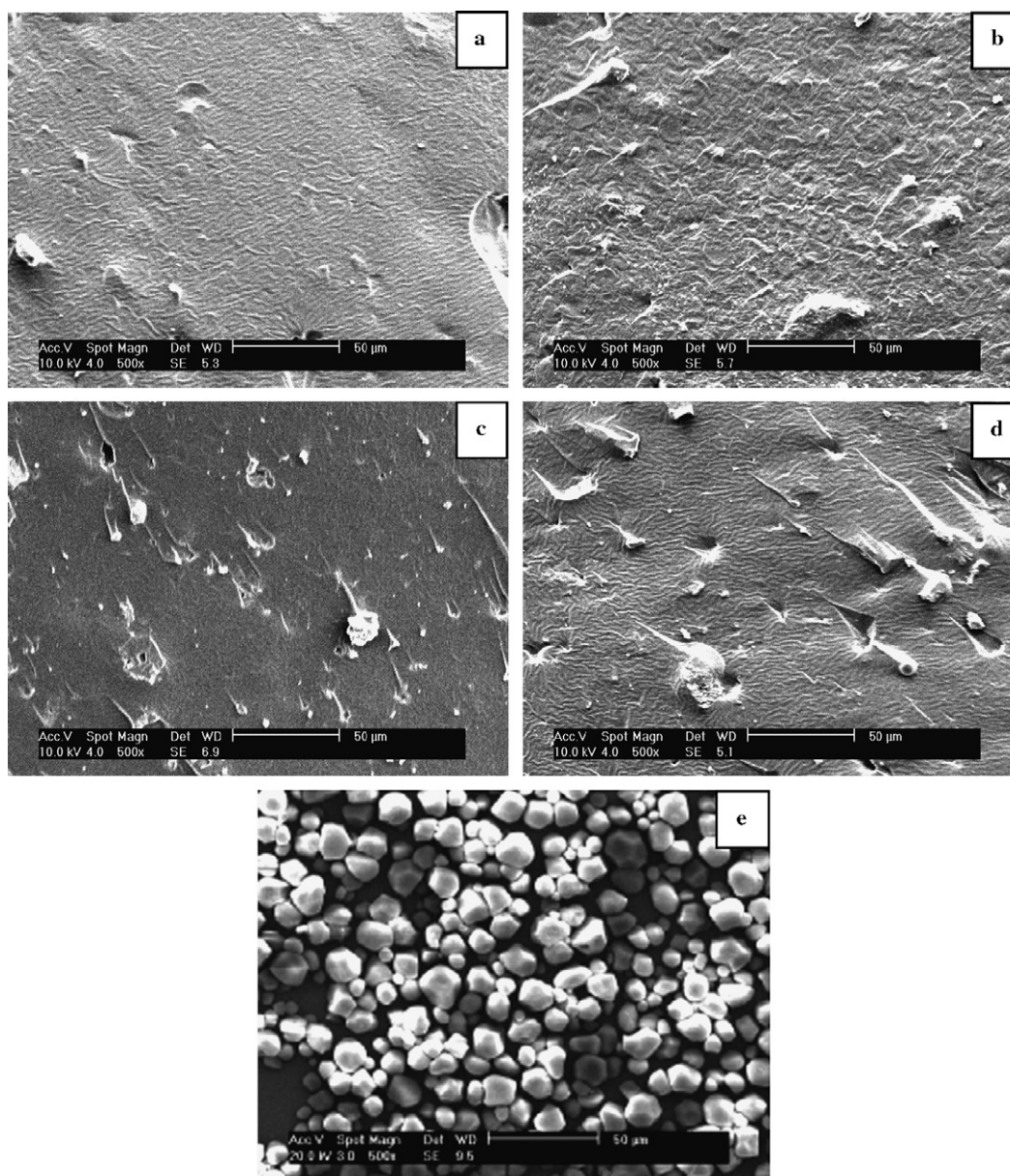

Fig. 1. SEM micrograph at 500× magnification of fragile fractured surface of GPTPS filled with different fly ash weight contents (a, 5%; b, 10%; c, 15%; d, 20%) and native starch (e).
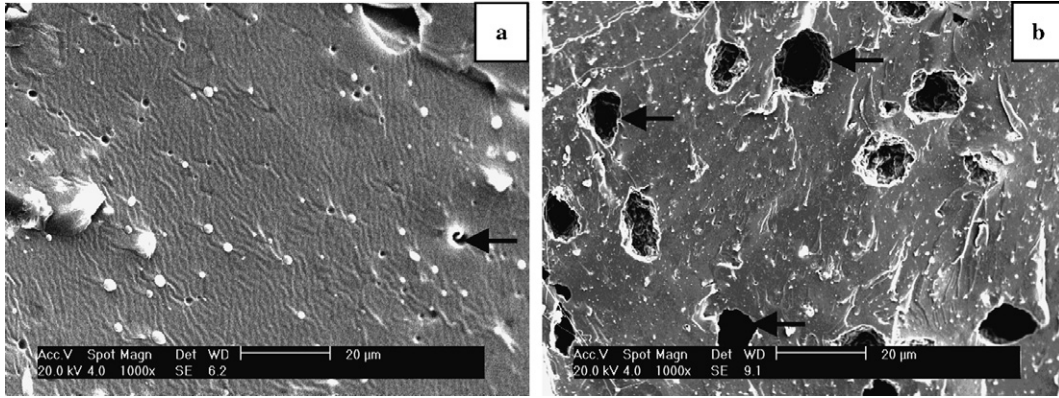
Fig. 2. SEM micrograph at 1000× magnification of fragile fractured surface of FUPTPS filled with wt 10% and 20% fly ash contents.

FUPTPS fluidity restrained the dispersion of fly ash in the matrix at the thermoplastic processing. The rheology study would make it clear in Section 3.2. The congregation of fly ash in FUPTPS would worsen the mechanical properties of the materials, which would be discussed in Section 3.3.

3.2. Rheology

The melting volumetric flow rate through the capillary was given as

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

where R = capillary radius, γ = shear rate at the capillary wall, n = flow index depending on the temperature. The term $\frac{4n}{3n+1}$ 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):

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

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:

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

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 Arrhenius equation:

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

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

where ΔE_η = the viscous flow activation energy, A = the consistency related to structure and formulation, T = the temperature, R = gas constant 8.314 J mol^{-1} K^{-1}.

The η–γ_w curves were plotted using a double logarithmic (in Fig. 3). With increasing shear rate the viscosity of each TPS decreased. Such flow behavior was called shear thin-
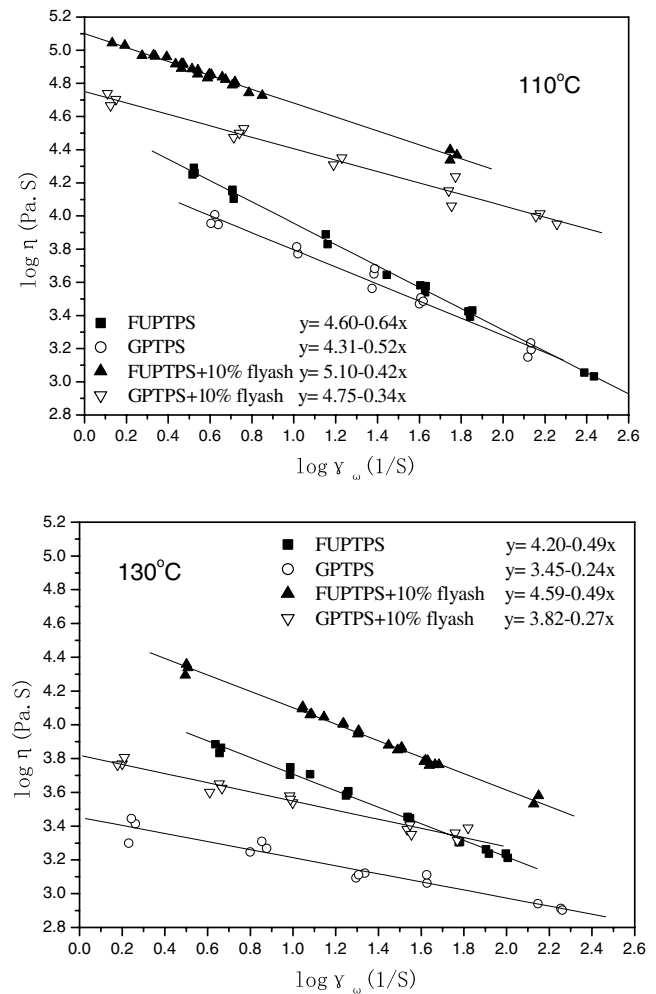

Fig. 3. The rheology curves of GPTPS and FUPTPS with wt 0% and 20% fly ash contents at 110 °C and 130 °C.

Table 1
The effect of plasticizer weight contents on the viscous flow activation energy $\Delta E_\eta(X=0)$ and flow index n of TPF at 130 °C

TPS	ΔE_η (kJ/mol) ($X=0$)	Flow index n at 130 °C
GPTPS	346.7	0.76
GPTPS + 5% fly ash	364.5	0.71
GPTPS + 10% fly ash	375.3	0.73
GPTPS + 15% fly ash	380.8	0.67
GPTPS + 20% fly ash	385.7	0.75
FUPTPS	161.3	0.51
FUPTPS + 5% fly ash	184.3	0.52
FUPTPS + 10% fly ash	205.6	0.51
FUPTPS + 15% fly ash	207.9	0.49
FUPTPS + 20% fly ash	210.3	0.54

ning, which was mainly ascribed to the gradual demolishment of starch intermolecular action. As shown in Fig. 3, the effect of plasticizer, fly ash weight content and the temperature on TPS rheological behavior was obvious.

According to the listed linear fit equations in Fig. 3, both FUPTPS and GPTPS were prone to the flow along with the increasing temperature (from 110 °C to 130 °C), and the apparent viscosity η of FUPTPS and GPTPS com-

posites increased with the increasing of fly ash content at the same temperature.

As shown in Fig. 3, the logη–logγ_w curves of FUPTPS were above ones of GPTPS at the temperature of both 110 °C and 130 °C, which meant that as the matrix of fly ash, GPTPS had better fluidity than FUPTPS. And compared to A-FUPTPS, A-GPTPS also was prone to fluidity at the same fly ash contents (e.g., 10 wt%, shown in Fig. 3). The congregation of fly ash appeared in SEM photography of FUPTPS matrix filled with 20 wt% fly ash contents (shown in Fig. 2), while there was no congregation in GPTPS matrix. Poor FUPTPS fluidity restrained the dispersion of fly ash in the matrix at the thermoplastic processing.

The viscous flow activation energy ΔE_η and flow index n of TPS at 130 °C were listed in Table 1. The viscous flow activation energy ΔE_η represented the effect of the temperature on the behavior of TPS. The more ΔE_η was the more sensitive the behavior of TPS was to the temperature. According to the values of ΔE_η in Table 1, with the increasing of fly ash the effect of the temperature on the behavior of both A-GPTPS and A-FUPTPS was increasing. It
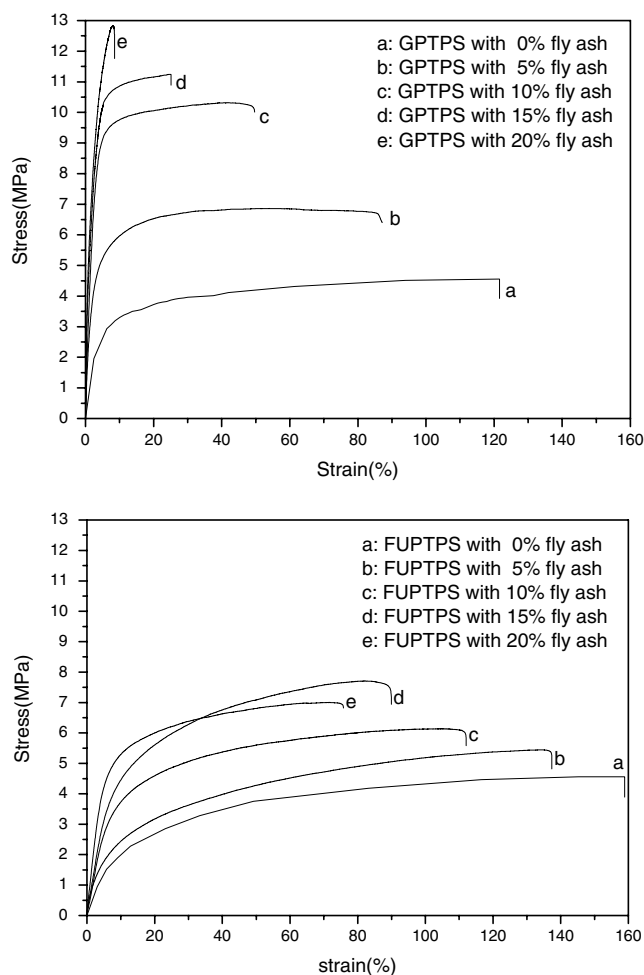

Fig. 4. The effect of fly ash contents on the stress–strain curves of GPTPS and FUPTPS.
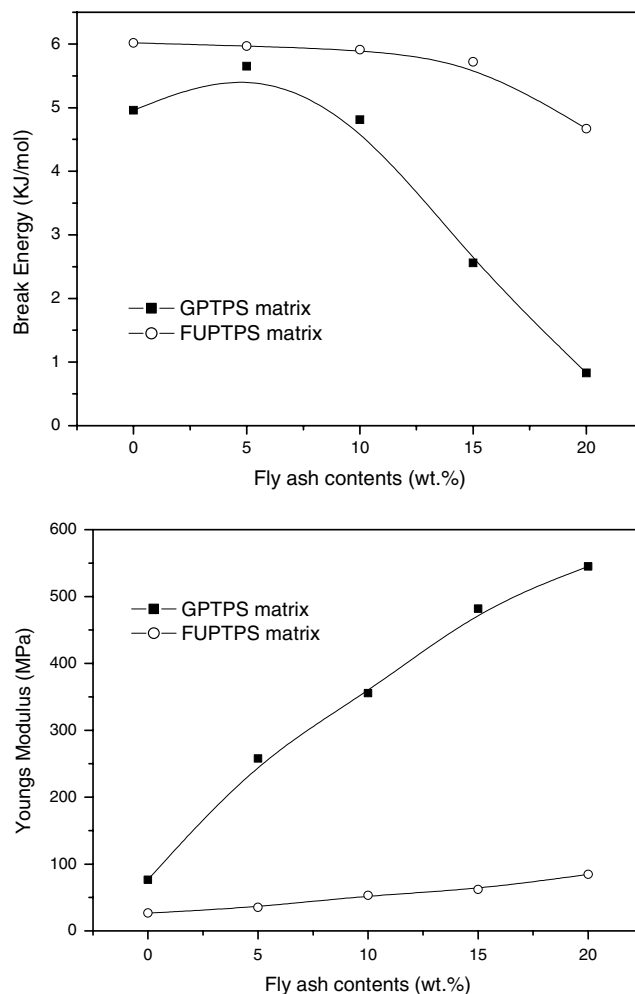

Fig. 5. The effect of fly ash contents on the break energy and Youngs modulus of composites.

meant that the improvement of the temperature, which made TPS flow easily, was propitious to the dispersion of fly ash during the processing of TPS containing higher flay ash contents.

Moreover, A-GPTPS were more sensitive to the temperature change. It meant that during the processing, the flow behavior of A-GPTPS could be more easily changed than that of A-FUPTPS by changing the processing temperature. On the other hand, the viscosity of A-FUPTPS was more sensitive to the change of shear rate than that of A-GPTPS because of its lower flow index. Therefore, during the thermoplastic processing the extruder screw speed could effectively adjust the flow behavior of A-FUPTPS.

3.3. Mechanical properties

Fig. 4 showed the stress–strain curves of TPS, which were immediately enveloped after thermoplastic processing and stored for one week in the plastic bags before the testing. The stress–strain diagrams of GPTPS with low fly ash contents (0 wt%, 5 wt% and 10 wt%) represented the typical pattern of rubbery starch plastic materials reported previously (Van Soest & Knooren, 1997). The plots were essentially linear at low strain and curved towards the strain axis at higher strains. With the increasing of fly ash contents, the height of the rubber plateau was increased although the length was shortened. When the content of fly ash increased from 0% to 20%, the maximum stress of GPTPS matrix materials was trebled up to 12.86 MPa, while the break strain decreased from 122% to 9%.

Compared to GPTPS matrix materials, FUPTPS matrix materials had better break strain but poor stress, which was related to the effects of plasticizers on mechanical properties of TPS (Ma et al., 2004). With the increasing of fly ash content from 0 wt% to 20 wt%, the break strain of FUPTPS matrix materials decreased from 159% to 76%, while the maximum stress of FUPTPS matrix materials increased from 4.56 MPa to 7.78 MPa except FUPTPS with 20 wt% fly ash. As it was known, fine fly ash had the large specific surface, which would physically adsorb
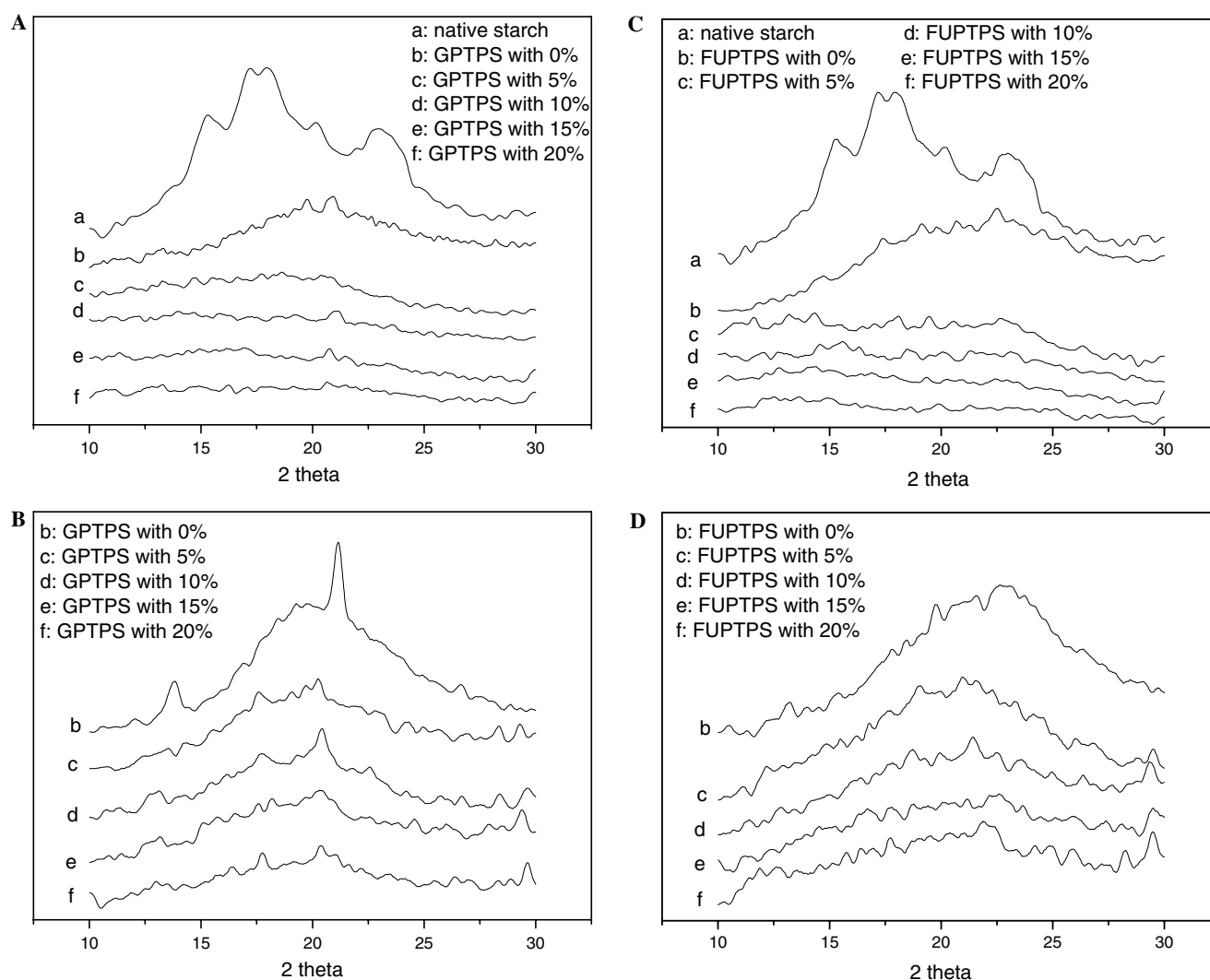

Fig. 6. The X-ray diffractograms of GPTPS and FUPTPS with different fly ash contents. (A and C) 0-day storage time. (B and D) 60-day storage time.

starch molecules, take effects of physical crosslinking and reinforce the TPS matrix materials. However, if fly ash granule conglomerated with the increasing of fly ash content, shrunken specific surface would decrease the stress. As shown in Fig. 2, the conglomeration appeared in FUPTPS matrix materials with 20 wt% fly ash rather than in GPTPS matrix materials, because fly ash dispersed better in runny GPTPS matrix materials at the processing temperature, as shown in Fig. 3.

Fig. 5 showed that the effect of fly ash contents on break energy and Youngs modulus of composites. With the increasing of fly ash contents from 0 wt% to 20 wt%, break energy of FUPTPS matrix materials varied little from 6.02 kJ/mol to 4.67 kJ/mol, while the dependence of break energy for GPTPS matrix materials on fly ash contents had the maximal value 5.65 kJ/mol at 5 wt% fly ash content. With the increasing of fly ash contents, Youngs modulus of both FUPTPS matrix and GPTPS matrix materials increased. However, Youngs modulus of FUPTPS matrix increased trebly from 26.8 MPa to 84.6 MPa, while Youngs modulus of GPTPS matrix increased six times from 76.4 MPa to 545 MPa.

3.4. X-ray diffractometry

The X-ray diffraction patterns of native cornstarch and newly prepared GPTPS materials were shown in Figs. 6A and B. Native cornstarch was the A-style crystallinity, while there were no obvious crystals in newly prepared GPTPS or A-GPTPS. Compared with native cornstarch (a in Fig. 6A), the crystal behavior of GPTPS changed significantly whether fly ash was introduced or not. In the processing, plasticizer molecules entered into starch particles, replaced starch intermolecular and intramolecular hydrogen bonds and destructed the crystallinity of starch (Ma & Yu, 2004a). As shown in Figs. 6A and B, the crystallization of GPTPS was clear after 60-day storage time, which attributed to the starch re-crystallization (retrogradation). However, the addition of fly ash restrained starch retrogradation. It meant that the granular fly ash destroyed the formation of ordered crystal structure in GPTPS matrix.

Figs. 6C and D illustrated that FUPTPS matrix restrained the retrogradation of starch before fly ash was added into the matrix. Urea and formamide could resist the retrogradation, because they could form more strong and stable hydrogen bonds with starch than glycerol, and then prevent starch molecules from interacting and crystallizing again during the storage time (Ma et al., 2004).

3.5. Water absorption

Water sensitivity is another important criterion for many practical applications of starch products. Fig. 7 showed the relation of water contents in GPTPS and FUPTPS with different fly ash content and storage time at RH = 100%. The equilibrium water content for pure GPTPS and FUPTPS were respectively about 46% and
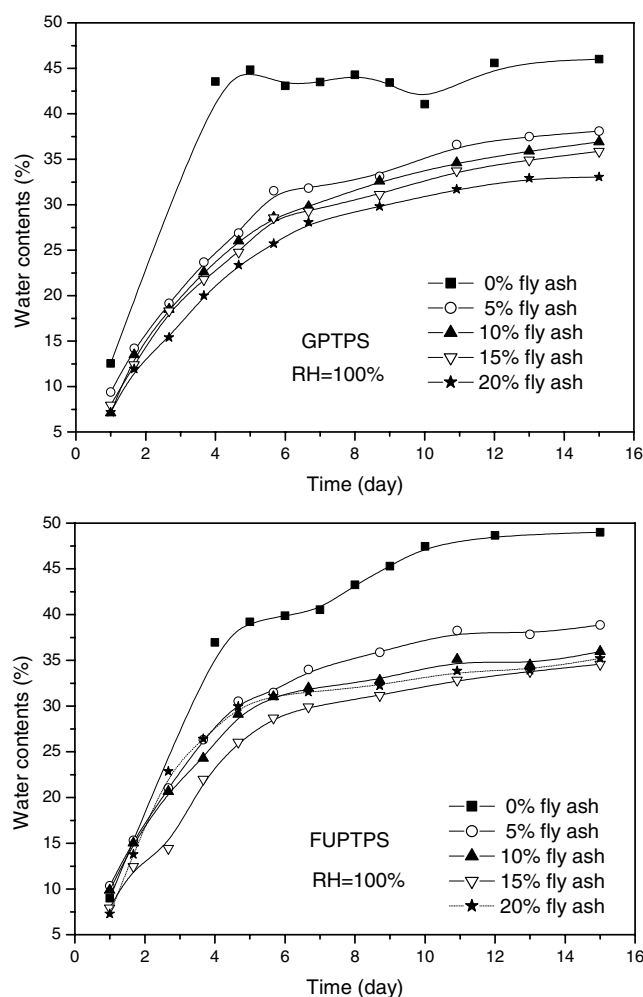

Fig. 7. The relation of water contents in GPTPS and FUPTPS with different fly ash content and storage time at RH = 100%.

49%, while equilibrium water content for A-GPTPS and A-FUPTPS were, respectively, from 33% to 38% and from 34.5% to 38.9%. As a whole, at high humidities the fly ash component could effectively restrain the water absorption of TPS matrix, and reduced water sensitivity of TPS. This behavior was related to the hydrophobic character of fly ash in comparison to starch hydrophilic property. Basically, the more the fly ash were, the less the water absorption of fly ash-reinforced TPS was. However, FUPTPS containing 20 wt% fly ash was exceptional. This attributed to the congregation of fly ash in FUPTPS (shown in Fig. 2), which actually decreased effectual content of fly ash.

4. Conclusions

In this study, coal fly ash-reinforced GPTPS and FUPTPS was researched. At the high shear and temperature conditions with the action of plasticizers, native cornstarch granules were molten or physically broken up into small fragments, and the continuous TPS matrix formed. Poor FUPTPS fluidity restrained the dispersion of fly ash in the matrix at the thermoplastic processing. At high fly

ash contents (e.g., 20 wt%), there were obvious congregation of fly ash in FUPTPS matrix rather than in GPTPS matrix. This congregation worsened the mechanical properties of the materials. In view of tensile stress and Youngs modulus, GPTPS matrix materials enhanced much more than FUPTPS matrix. The introduction of fly ash improved water resistance of TPS and destroyed the formation of ordered crystal structure in GPTPS matrix. Both A-GPTPS and FUPTPS could resist the starch retrogradation. During the thermoplastic processing, the extruder screw speed would effectively adjust the flow behavior of A-FUPTPS, while the increasing of the processing temperature would effectively ameliorate the flow behavior of A-GPTPS.

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