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Preparation and properties of biodegradable poly(propylene carbonate)/thermoplastic dried starch composites

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Abstract

The biodegradable poly(propylene carbonate) (PPC)/glycerol-plasticized thermoplastic dried starch (GPTPS) composites are prepared in a screw extruder. The dried starch is used, because the moisture in native starch easily induces the degradation of PPC during the processing. The effects of succinic anhydride (SA) on the morphology, thermal properties, dynamic mechanical thermal analysis, as well as mechanical properties of PPC/GPTPS composites, are investigated. Scanning Electron Microscope (SEM) shows that SA improves interfacial adhesion between PPC and GPTPS. Fourier Transform Infrared (FTIR) Spectroscopy reveals that SA can improve the interaction between PPC and GPTPS. Thermogravimetric Analysis (TGA) results show that SA leads a significant improvement of thermal stability for PPC/GPTPS composites. Mechanical testing illustrates that SA can increase mechanical properties of PPC/GPTPS composites. The tensile strength and elongation at break of PPC/GPTPS/SA(75/25/1) composite can reach 19.4 MPa and 88.5%, respectively.

Keywords: Poly(propylene carbonate); Thermoplastic starch; Succinic anhydride

1. Introduction

Many renewable resource-based biopolymers such as starch plastics, cellulose plastics, polylactides (Kulinski & Piorkowska, 2005), polyhydroxyalkanoates (bacterial polyesters) (Pantazaki, Tambaka, & Langlois, 2003), and soy-based plastics (Swain, Biswal, & Nanda, 2004) have been investigated to alternate conventional non-degradable or incompletely degrading synthetic polymers (e.g. polyolefin) in the application scopes of one-off materials (Mohanty, Misra, & Drzal, 2002). Poly(propylene carbonate) (PPC) is a biodegradable aliphatic polyester. At the existence of heterogeneous catalyst system, propylene oxide and carbon dioxide produce a regular alternating copolymer PPC (Chisholm, Navarro-Llobet, & Zhou, 2002; Chisholm & Zhou, 2004), which shows reasonable melt processing, high transparency, and good biodegradability in surroundings of both soil and buffer solution. Moreover, a large amount of CO_2 (more than 40 wt% within the copolymer) can be fixed into the PPC with its cost competitiveness and environment friendly advantage (Ge, Xu, & Meng, 2005).

Starch is one of the promising materials for the production of biodegradable plastics. Starch is renewable and biodegradable from a great variety of crops. Since 1970s starch has been incorporated into polyethylene in order to increase the biodegradability. Biodegradable composites of poly(propylene carbonate) (PPC) reinforced with unmodified granular cornstarch have been studied by Peng, Wang, and Dong (2005) Ge, Li, and Zhu (2004). Succinic anhydride (SA) as an active agent is introduced to PPC/granular starch composites. SA is prone to react with hydroxyl groups in starch, which introduce ester groups into starch and improve the compatibility between PPC matrix and starch (Ma, Yu, & Zhao, 2006). Ge et al. (2005) blend starch-g-poly(methyl acrylate) (S-g-PMA)

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copolymer containing 28.6 wt% PMA with PPC to improve phase adhesion between granular reinforcement and PPC matrix. Gelatinization (or plasticization) of starch is also a good method to enhance the interfacial affinity (Coffin, Fishman, & Cooke, 1995; Kim & Kim, 2000; Martin & Averous, 2001). In the presence of water and other plasticizers, thermoplastic starch (TPS) is processed in order to disintegrate granules and overcome the strong interaction of starch molecules, which improves the dispersion in other polymers (Coffin et al., 1995; Martin & Averous, 2001). However, water would result in the serious degradation of biodegradable polyesters such as polycaprolactone (PCL), polylactides (PLA) and PPC during the processing. In this paper, dried starch granules substitute native starch containing moisture to avoid the serious degradation of PPC, when PPC/glycerol-plasticized TPS (GPTPS) composites are processed. SA is also added to improve the interaction between PPC and GPTPS. The morphology, Fourier Transform Infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), dynamic mechanical thermal analysis (DMTA) and mechanical properties of PPC/GPTPS composites are investigated.

2. Experimental

2.1. Materials

PPC was obtained from State Key Polymer Physics and Chemistry Laboratory, Changchun Institute of Applied Chemistry, China. Its molecular weight measured by GPC was 130,000 and $M_w/M_n = 4.3$. Cornstarch (12% moisture) obtained from Langfang Starch Company (Langfang, Heibei, China). Succinic anhydride (SA) and glycerol were analytical reagents, purchased from Tianjin Chemical Reagent Factory (Tianjin, China).

2.2. Preparation of the composites

Cornstarch was dried at 120 °C for 4 h to eliminate the moisture. Glycerol was mixed with dried starch (3000 rpm, 2 min) by using of High Speed Mixer GH-100Y (made in China), and stored overnight. The ratio of glycerol and dried starch (wt/wt) was 40:100. PPC and/or SA were added to prepare PPC/GPTPS and PPC/GPTPS/SA composites. 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, China). The screw speed was 20 rpm. The temperature profile along the extruder barrel was 125, 130, 135, 115 °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 cryo-fractured surfaces of extruded composites were performed with Scanning Electron Microscope Philips XL-3 (FEI Company, Hillsboro, OR, USA), operating at an acceleration voltage of 20 kV. The composites were cooled in liquid nitrogen, and then broken. The fracture surfaces were vacuum coated with gold for SEM.

2.4. Fourier transform infrared (FTIR)

FTIR spectra were obtained at 2 cm^{-1} resolution with BIO-RAD FTS3000 IR Spectrum Scanner. Typically, 64 scans were signal-averaged to reduce spectral noise. The extruded strips were compressed to the transparent slices with the thickness of around 0.2 mm in the Flat Sulfuration Machine, and tested by the transmission method.

2.5. Dynamic mechanical thermal analysis (DMTA)

The DMTA using a Mark Netzsch DMA242 analyzer was performed on hot-pressed (5 MPa, 100 °C) thick specimens ($40 \times 7 \times 2$ mm), in a single cantilever bending mode at a frequency of 3.33 Hz and a strain × 2N, corresponding to a maximum displacement amplitude of 30 μm. The range of temperature was from −120 to 120 °C. The standard heating rate used was 3.0 °C/min.

2.6. Thermogravimetric analysis (TGA)

The thermal properties of the blends were measured with a ZTY-ZP type thermal analyzer. The sample weight varied from 10 to 15 mg. Samples were heated from the room temperature to 500 °C at a heating rate of 15 °C/min.

2.7. Mechanical testing

The Testometric AX M350-10KN Materials Testing Machine was operated and a crosshead speed of 50 mm/min was used for tensile testing (ISO 1184-1983 standard). The data was averages of 5–8 specimens.

3. Results and discussion

3.1. Microscopy

The morphology structure of polymer composites was a very important characteristic because it ultimately determined many properties of polymer composites, such as thermal stability and mechanical properties. The morphology of GPTPS, PPC and PPC/GPTPS composites were shown in Fig. 1a–h, respectively.

During the usual thermoplastic processing of TPS, water contained in starch played an indispensable role (Ma & Yu, 2004). In processing, glycerol and water molecules entered into starch granules, and replaced starch intermolecular and intramolecular hydrogen bonds and destructed starch granules. However, when water was removed in native starch, starch could not be completely plasticized. As shown in Fig. 1a, the fracture surface of GPTPS was combined with great deals of residual starch granules even at a high glycerol content (40 wt% based on dry starch). As pre-

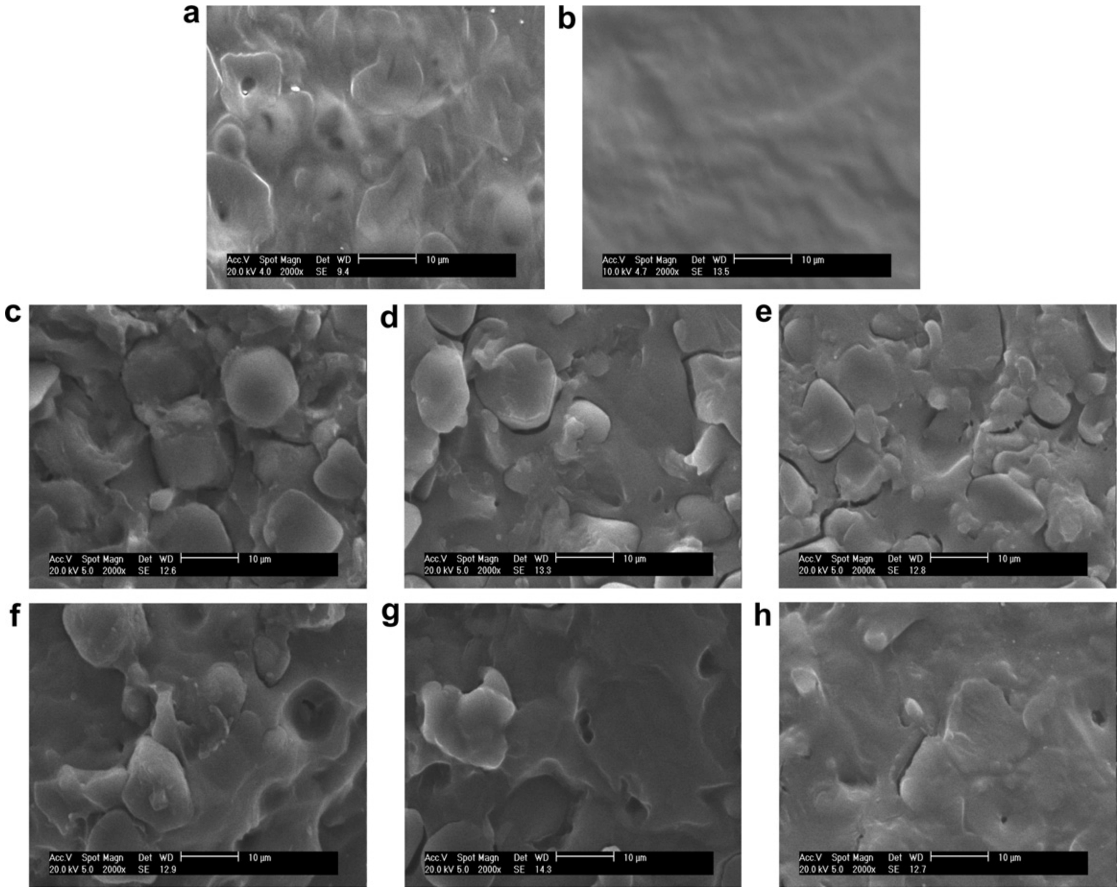

Fig. 1. SEM micrographs (2000×) of cryo-fractured GPTPS, PPC and PPC/GPTPS composites. (a) GPTPS; (b) PPC; (c) PPC/GPTPS(75/25); (d) PPC/GPTPS(50/50); (e) PPC/GPTPS(25/75); (f) PPC/GPTPS/SA(75/25/1); (g) PPC/GPTPS/SA(50/50/1); (h) PPC/GPTPS/SA(25/75/1).

vious reports (Forssell, Millila, & Moates, 1997; Smits, Kruiskamp, & van Soest, 2003), glycerol was recognized as a less effective plasticizer than water, and its poor permeation effect into dry starch granules limited the mobility and orientation of starch molecules. And the morphology of PPC/GPTPS composites without SA was so different from pure PPC (Fig. 1b). Many starch granules were obviously not disrupted in Fig. 1c–e. The interface and the gap were very clear, which ascribed to the high interfacial tension between hydrophilic starch and hydrophobic PPC. It was obvious that the addition of PPC deteriorated the plasticization of starch further in PPC/GPTPS composites.

When SA was added (Fig. 1f–h), the interface and the gap were not clear between PPC and starch. The improved interfacial adhesion could be attributed to the chemical and physical interaction. Besides the end-capped reaction between PPC and SA (Ma et al., 2006), the chemical interaction presumably resulted from reaction of hydroxyl groups in starch with anhydride groups in SA (Bhandari & Singhal, 2002) under the extrusion conditions of high temperature and high shear. At the same time, accompanying with the increasing of starch contents, the number of residual starch granules decreased, and the dispersion between PPC and GPTPS was improved in the PPC/GPTPS/SA composites. When the contents of GPTPS increased from 25 to 75 wt%, GPTPS varied from dispersed phase to continuous phase. The negative effect of PPC on starch plasticization was weakened.

3.2. FTIR

The interaction of polymer composites could be identified by FTIR spectra. It was known that, if two polymers were compatible, a distinct interaction (hydrogen-bonding or dipolar interaction) existed between the chains of one polymer and those of the other, causing the infrared spectra of the composites to change (e.g. band shifts, broadening) (Peng et al., 2005). As a result, FTIR could identify segment interactions and obtained information about the phase behavior of polymer composites.

Fig. 2 shows FTIR spectra of GPTPS/PPC composites at room temperature in several specific stretching regions. PPC had a strong carbonyl stretching absorption at A region. With the addition of GPTPS, the C=O peak of PPC at 1738 cm^{-1} shifted to a higher wave number by 4 $\text{cm}^{-1}$when the PPC content increased from 0 to 50 wt%. The interaction formation would change the stretching vibration frequency of the carbonyl bound and give rise to a shift, as extensively studied in poly(hydroxy ether of bisphenol A)/polycaprolactone composites (Coleman & Moskala, 1983). It meant that carbonyl groups of PPC could form the hydrogen-bonding interaction with

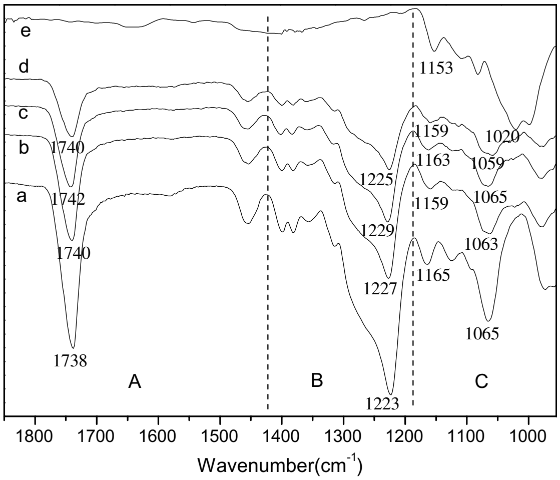

Fig. 2. The FTIR spectra of PPC/GPTPS composites. (a) PPC; (b) PPC/GPTPS(75/25); (c) PPC/GPTPS(50/50); (d) PPC/GPTPS/SA(50/50/1); (e) GPTPS.

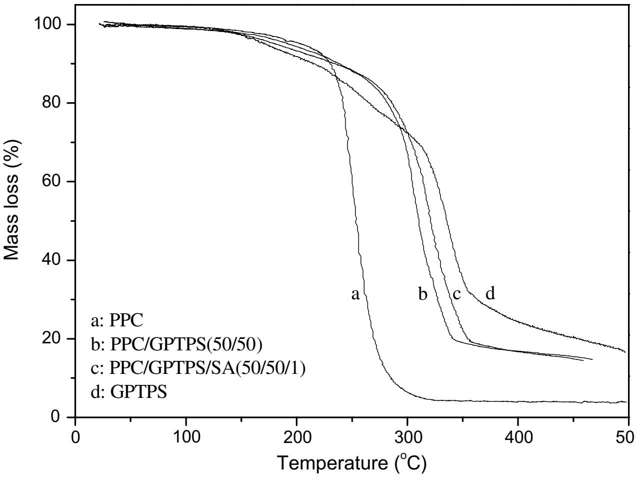

Fig. 3. Thermogravimetric curves for PPC, GPTPS and PPC/GPTPS composites at a heating rate of 15 °C/min in air.

hydroxyl groups of GPTPS. According to Fei, Chen, and Peng (2004), the —O—C—O— stretching modes gave rise to intense and complex multiple peaks in B region. The —O—C—O— stretching vibration appeared at 1223 cm^{-1}, which deviated more with the decreasing of PPC contents. As shown in C region of Fig. 2, the peaks of PPC separately related to —C—O— stretching vibration in —CH—O— group (1165 cm^{-1}) and —O—C=O group (1124 and 1065 cm^{-1}), while the characteristic peak at 1153 cm^{-1} was ascribed to C—O bond stretching of C—O—H group in GPTPS and two peaks at 1084 and 1020 cm^{-1} were attributed to C—O bond stretching of C—O—C group in the anhydroglucose ring of starch. In C region, all of —C—O— stretching vibration varied with the contents of PPC. In FTIR spectra of PPC/GPTPS composites, the shifting and broadening of some bands for PPC and GPTPS indicated that there were several specific interactions between the chains of PPC and GPTPS.

When succinic anhydride (SA) was added into PPC/GPTPS composites, as shown by line c and d in Fig. 2, the characteristic peaks of C=O, —O—C—O— and C—O stretching vibration at A, B and C regions all shifted to the lower wave number. The lower the wave number corresponding to absorption peak, the stronger was the hydrogen bond interaction between polymer composites (Ma et al., 2006). It meant that SA enhanced the interaction between PPC and GPTPS, which was related to C=O, —O—C—O— and C—O groups. This was consistent with the SEM results.

3.3. TGA

Thermogravimetric analysis (TGA) was performed for the composites, where the mass loss due to the volatilization of the degradation products was monitored as a function of temperature. The thermogravimetric (TG) and Derivative thermogravimetric (DTG) curves of pure PPC, GPTPS, PPC/GPTPS and PPC/GPTPS/SA composites in air at a heating rate of 15 ° C/min were shown in Figs. 3 and 4, respectively.

The mass loss before the onset temperature was related to the volatilization of glycerol. So the difference of mass loss at onset temperature was mainly due to the different contents of GPTPS in Fig. 3. The more GPTPS content was, the more the mass loss at onset temperature was. And SA had little effect on mass loss at onset temperature of PPC/GPTPS composites.

The decomposed temperature, $T_{\max}$ was the temperature at maximum rate of mass loss, i.e., the peak temperature shown in Fig. 4. The degradation of GPTPS took place at higher temperature than that of PPC, although glycerol resulted in more mass loss of GPTPS. PPC was easily decom-

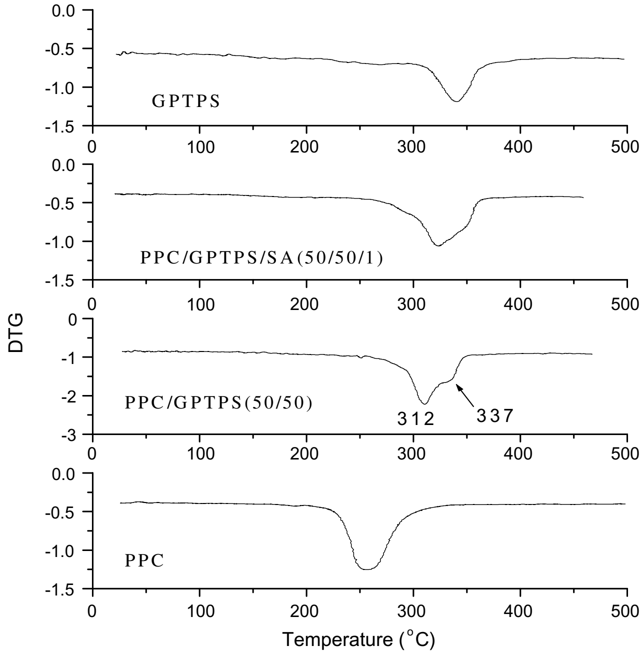

Fig. 4. Derivative thermogravimetric curves for PPC, GPTPS and PPC/GPTPS composites at a heating rate of 15 °C/min in air.

posed under the influence of heat in two-step pyrolysis mechanism: main chain random scission and unzipping (Peng, An, & Chen, 2003). In PPC/GPTPS(50/50) composite, the addition of GPTPS increased $T_{\max}$ of PPC from 255 to 312 °C, but decreased $T_{\max}$ of GPTPS from 341 to 337 °C. SA almost amalgamated $T_{\max}$ of PPC and GPTPS, and improved the decomposed temperature of PPC further. This improvement ascribed to the interfacial interaction between PPC and GPTPS in PPC/GPTPS/SA(50/50/1) composite, as revealed by FTIR. SA could also end-cap PPC to improve thermal stability of PPC (Peng et al., 2003).

3.4. DMTA

DMTA was a very useful technique to study the viscoelastic response of the polymers as well as their composites in a wide range of temperatures. The behavior of storage modulus for PPC, GPTPS and PPC/GPTPS composites was shown in Fig. 5. The storage modulus for PPC/GPTPS composites was significantly higher than that for PPC, but lower than that for GPTPS. It was known that storage modulus detected by DMTA was related to the stiffness. The stiffness of composites was increased with the increasing of GPTPS contents. SA could obviously improve the storage modulus of PPC/GPTPS composite. This improvement was possibly associated with the interaction between PPC and GPTPS.

In general, the storage modulus decreased as temperature increased. However, in the region corresponding to the maximum in loss factor (tan delta) plots, the decrease of storage modulus was usually rapid. Fig. 6 shows the curves of loss factor (tan delta) as a function of temperature for PPC, GPTPS and PPC/GPTPS composites. The loss factor was sensitive to the molecular motions and its peak was related to the glass transition temperature. The curve of GPTPS revealed two thermal transitions. There were several different viewpoints for two thermal transitions of TPS. Here an explanation was favored in terms of the transitions corresponding to the glass transitions of two separate phases in GPTPS. The upper transition (58 °C) was clearly due to a starch-rich phase, whereas the lower transition (−47 °C) was due to a starch-poor phase (Forssell et al., 1997). As shown in Fig. 1a, the residual granular starch was starch-rich phase, while the continuous region was starch-poor phase. PPC had only one glass transition at 45 °C between the lower transition and the upper transition of GPTPS. In PPC/GPTPS composites, both starch-rich phase and starch-poor phase could form composites with PPC, respectively, which represented the upper transition (50 °C) and the lower transition (−34 °C). The addition of SA improved the interaction between PPC and GPTPS, which brought adjacent chains of PPC and starch close, and hence reduced the free volume and raised the glass transitions of composites.

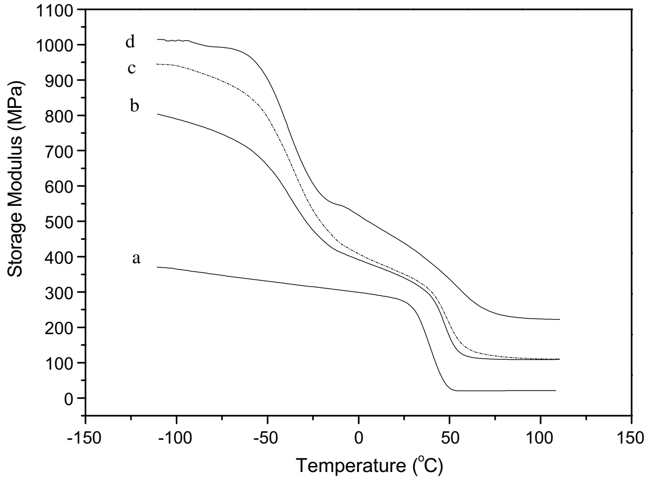

Fig. 5. DMTA (storage modulus) of PPC (a), GPTPS (b), PPC/GPTPS(50/50) (c) and PPC/GPTPS /SA(50/50/1) (d) composites.

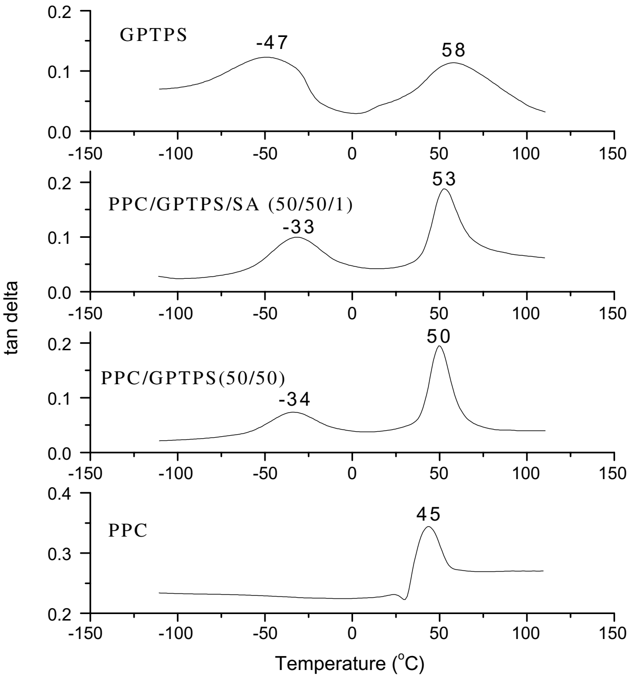

Fig. 6. DMTA (tan delta) of PPC, GPTPS, PPC/GPTPS(50/50) and PPC/GPTPS/SA (50/50/1) composites.

3.5. Mechanical properties

Mechanical properties of PPC/GPTPS composites were shown in Fig. 7. Pure GPTPS was rigid and fragile with high tensile strength and poor elongation at break, while PPC had low tensile strength and favorable elongation at break. Compared with GPTPS (PPC 0 wt%), PPC/GPTPS(25/75) composites (PPC 25 wt%) decreased tensile strength, but increased the elongation at break. Compared with pure PPC (PPC %), PPC/GPTPS(75/25) composites (PPC 75 wt%) with PPC as continuous phase had higher tensile strength and lower the elongation at break. Mechanical properties of PPC/GPTPS(50/50) composites (PPC 50 wt%) were lower than both PPC/GPTPS(75/25) and PPC/GPTPS(25/75) composites. The introduction of SA could clearly enhance mechanical properties of PPC/

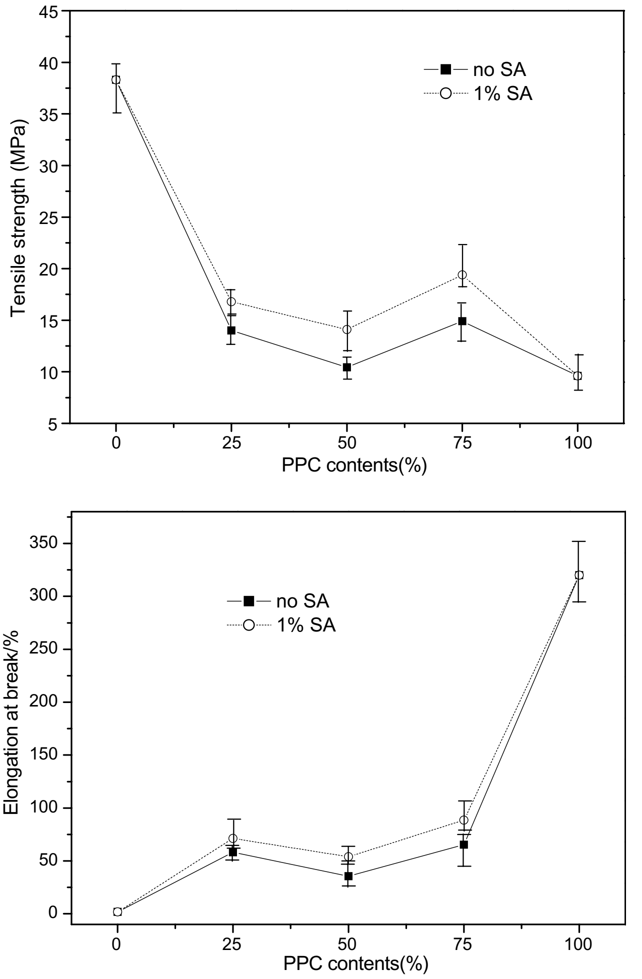

Fig. 7. The effect of PPC contents and SA on mechanical properties of composites.

GPTPS composites on account of the improvement of interfacial interaction between PPC and GPTPS. PPC/GPTPS/SA(75/25/1) composites had good mechanical properties with 19.4 MPa tensile strength and 88.5% elongation at break.

4. Conclusions

In this study, dried starch was used instead of native starch with moisture to avoid the serious degradation of PPC, and biodegradable PPC/GPTPS composites were prepared as potential one-off materials. SEM revealed that PPC had the negative effect on the plasticization of dried granular starch, however the addition of SA could reduce the interface between PPC and starch. As shown by FTIR, SA could enhance the interaction between PPC and GPTPS, which was related to C=O, —O—C—O— and C—O groups. This interaction improved thermal stability, storage modulus, glass transition temperature and mechanical properties of PPC/GPTPS composites. The tensile strength and elongation at break of PPC/GPTPS/SA(75/25/1) composite were 19.4 MPa and 88.5%, respectively.

References

Bhandari, P. N., & Singhal, R. S. (2002). Studies on the optimisation of preparation of succinate derivatives from corn and amaranth starches. *Carbohydrate Polymers, 47*, 277–283.

Chisholm, M. H., Navarro-Llobet, D., & Zhou, Z. P. (2002). Poly(propylene carbonate). 1. More about poly(propylene carbonate) formed from the copolymerization of propylene oxide and carbon dioxide employing a zinc glutarate catalyst. *Macromolecules, 35*, 6494–6504.

Chisholm, M. H., & Zhou, Z. P. (2004). Concerning the mechanism of the ring opening of propylene oxide in the copolymerization of propylene oxide and carbon dioxide to give poly(propylene carbonate). *Journal of the American Chemical Society, 126*, 11030–11039.

Coffin, D. R., Fishman, M. L., & Cooke, P. H. (1995). Mechanical and microstructural properties of pectin/starch films. *Journal of Applied Polymer Science, 57*, 663–670.

Coleman, M. M., & Moskala, E. J. (1983). FTIR studies of polymer blends containing the poly(hydroxy ether of bisphenol A) and poly(ε-caprolactone). *Polymer, 24*, 251–257.

Fei, B., Chen, C., & Peng, S. W. (2004). FTIR study of poly(propylene carbonate)/bisphenol A blends. *Polymer International, 53*, 2092–2098.

Forssell, P. M., Millila, J. M., & Moates, G. K. (1997). Phase and glass transition behaviour of concentrated barley starch–glycerol–water mixtures, a model for thermoplastic starch. *Carbohydrate Polymers, 34*, 275–282.

Ge, X. C., Xu, Y., & Meng, Y. Z. (2005). Thermal and mechanical properties of biodegradable composites of poly(propylene carbonate) and starch-poly(methyl acrylate) graft copolymer. *Composites Science and Technology, 65*, 2219–2225.

Ge, X. C., Li, X. H., & Zhu, Q. (2004). Preparation and properties of biodegradable poly(propylene carbonate)/starch composites. *Polymer Engineering and Science, 44*, 2134–2140.

Kim, S. H., & Kim, Y. H. (2000). Biodegradable polymer blends of poly(L-lactic acid) and gelatinized starch. *Polymer Engineering and Science, 40*, 2539–2550.

Kulinski, Z., & Piorkowska, E. (2005). Crystallization, structure and properties of plasticized poly(L-lactide). *Polymer, 46*, 10290–10300.

Ma, X. F., Yu, J. G., & Zhao, A. (2006). Properties of biodegradable poly(propylene carbonate)/starch composites with succinic anhydride. *Composites Science and Technology, 66*, 2360–2366.

Ma, X. F., & Yu, J. G. (2004). The plastcizers containing amide groups for thermoplastic starch. *Carbohydrate Polymers, 57*, 197–203.

Martin, O., & Averous, L. (2001). Poly(lactic acid): plasticization and properties of biodegradable multiphase systems. *Polymer, 14*, 6209–6219.

Mohanty, A. K., Misra, M., & Drzal, L. T. (2002). Sustainable biocomposites from renewable resources: Opportunities and challenges in the green materials world. *Journal of Polymers and the Environment, 10*, 19–26.

Pantazaki, A. A., Tambaka, M. G., & Langlois, V. (2003). Polyhydroxyalkanoate (PHA) biosynthesis in thermus thermophilus: Purification and biochemical properties of PHA synthase. *Molecular and Cellular Biochemistry, 254*, 173–183.

Peng, S. W., An, Y. X., & Chen, C. (2003). Thermal degradation kinetics of uncapped and end-capped poly(propylene carbonate). *Polymer Degradation and Stability, 80*, 141–147.

Peng, S. W., Wang, X. Y., & Dong, L. S. (2005). Special Interaction between Poly (Propylene Carbonate) and Corn Starch. *Polymer Composites, 26*, 37–41.

Smits, A. L. M., Kruiskamp, P. H., & van Soest, J. J. G. (2003). Interaction between dry starch and plasticisers glycerol or ethylene glycol, measured by differential scanning calorimetry and solid state NMR spectroscopy. *Carbohydrate Polymers, 53*, 409–416.

Swain, S. N., Biswal, S. M., & Nanda, P. K. (2004). Biodegradable soy-based plastics: Opportunities and challenges. *Journal of Polymers and the Environment, 12*, 35–42.