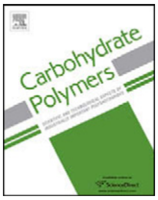
Carbohydrate Polymers 86 (2011) 1260–1265

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Preparation and properties of biodegradable blend containing poly (propylene carbonate) and starch acetate with different degrees of substitution

Songshan Zeng, Shuanjin Wang*, Min Xiao, Dongmei Han, Yuezhong Meng*

The Key Laboratory of Low-carbon Chemistry & Energy Conservation of Guangdong Province/State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-Sen University, Guangzhou 510275, PR China

ARTICLE INFO

Article history:
Received 21 February 2011
Received in revised form 1 June 2011
Accepted 9 June 2011
Available online 16 June 2011

Keywords:
Poly (propylene carbonate)
Starch acetate
Biodegradable blend
Reinforcement

ABSTRACT

A series of starch acetates (SAs) with different degrees of substitution (DS) were prepared by chemically converting the hydroxyl group of natural cornstarch (NS) into an acetyl group. Biodegradable poly (propylene carbonate) (PPC) was melt blended with these SAs in a Haake mixer. The morphologies, mechanical and thermal properties of PPC/SA and PPC/NS blends were investigated. PPC/SA ($DS < 0.88$) showed better tensile property and impact strength than those of PPC/NS. Scanning electron microscopy (SEM) and Fourier transform infrared spectra (FTIR) revealed strong interfacial adhesion between the SA fillers and PPC matrix. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) demonstrated the addition of SA led to improved thermal stability of the blend. Among all the samples prepared, the PPC/SA ($DS = 0.51$) has the optimal mechanical and thermal properties. The methodology described here represents a promising approach for the production of cost competitive biodegradable polymer blends.

1. Introduction

The green house effect has resulted in dramatic climate change and is a serious environmental issue (Meehl & Washington, 1996), which can be attributed to the massive production of carbon dioxide (CO_2) by human activities (Broecker, 1997; Kacholia & Reck, 1997). Much action has been taken to reduce the excessive emission of CO_2 (Tollefson, 2010). An alternative approach is to make use of CO_2 as feedstock for chemical transformations. The materials for packaging are often made from synthetic polymers, and they are non-biodegradable and unrecyclable, and inappropriate disposal of these plastics resulted in pollution and posed severe environmental problem. Apparently, synthesis of biodegradable polymers useful as packing materials is highly desirable, and has been intensively studied. The copolymerization of carbon dioxide with propylene oxide (PO) could be catalyzed by various catalysts, such as metallic complexes, organometallic compounds and their complexes, as well as polymer supporting bimetallic catalysts (Chen, Shen, & Zhang, 1991; Gorecki & Koran, 1985; Nishimura, Kasai, & Tsuchida, 1978; Rokicki & Kuran, 1981; Tsuchida & Kasai, 1980).

Recently, poly (propylene carbonate) (PPC) with a very high molecular weight has been successfully synthesized from CO_2 and PO by using supported catalysts in our laboratory (Wang, Tjong, Du, Zhao, & Meng, 2002; Zhu, Meng, Tjong, Zhao, & Chen, 2002). The resulting PPC exhibited an alternating molecular structure as illustrated in Fig. 1, and it also showed excellent mechanical properties and considerable degradability in both soil and buffer (Song et al., 2008; Wu, He, Xiao, Wang, & Meng, 2009). Further, more than 40 wt% of CO_2 could be fixed into PPC (Meng, Du, Tiong, Zhu, & Hay, 2002).

As an inexpensive, biodegradable and renewable resource, starch has attracted much interest since its blending with biodegradable polymers can reduce production costs and improve the mechanical properties of the blend. As a filler, starch tends to reduce the toughness of the blend and to enhance the modulus (Averous, 2004). In our previous work, we reported natural cornstarch (NS) could be melt blended with biodegradable PPC to produce biodegradable and economical blends (Ge, Li, Zhu, Li, & Meng, 2004). The modulus of the resulting blends increased when the content of starch increased. However, the SEM image indicated that the compatibility between hydrophobic PPC and hydrophilic starch was weak. Hence, these blends were brittle and had low impact strength. Moreover, the PPC could get hydrolyzed when the moisture absorbed by the hydrophilic starch fillers reached a certain level (Gaspar, Benko, Dogossy, Reczey, & Czigany, 2005; Shogren, 1992).

To successfully blend these two components without significant alteration of the mechanical properties, physical or chemical modification of natural starch may be necessary to improve its compatibility with PPC. Modifications of starch via esterification and grafting have been extensively studied (Fanta & Shogren,

---

* Corresponding authors. Tel.: +86 020 84115506; fax: +86 020 84114113.
E-mail addresses: wangshj@mail.sysu.edu.cn (S. Wang), mengyzh@mail.sysu.edu.cn (Y. Meng).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.06.023

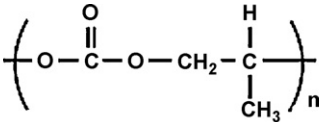


Fig. 1. Structure of poly (propylene carbonate) (PPC).

1997). It was reported that poly (methyl acrylate) had been grafted to starch, and the resulting starch-g-poly (methyl acrylate) (S-g-PMA) was then utilized for blending with PPC. The PPC/S-g-PMA blends showed slightly improved thermal stability and mechanical properties, compared with the PPC/NS blends. Nevertheless, the preparation was rather complicated, and the grafting ratio of S-g-PMA was very low, making the potential industrial applications less feasible (Ge, Xu, Meng, & Li, 2005). By converting part or all of the hydroxyl groups into ester groups, acetylation is a simple and economic way to modify natural starch. High degrees of substitution (DS) around 0.2–3 with starch acetate have been extensively investigated in recent years, and the hydrophobicity, melting processability and mechanical properties of the modified starch were shown to be very different from the native starch (Gonzalez & Perez, 2002). It is believed that the hydrophobic nature of starch acetate should improve its compatibility with PPC. In this work, a series of PPC/SA blended with different DS and varied SA contents were prepared, and the correlation between the morphology of the blends and their properties was studied.

2. Experimental

2.1. Materials

The PPC used in this work with a number-average molecular weight of more than 250,000, and polydispersity of 1.91 was provided by Henan Tianguan Enterprise Group Co. Ltd., China. Natural cornstarch (NS, content of amylose: 25%) was purchased from Shenyang Jilong Corn Co. Ltd., China. The physical and chemical properties of NS were determined by the standard of GB/T8885-2008. Starch was dried at 80 °C in the convection oven for 24 h prior to acetylation and blending. Acetic acid anhydride (AR) was purchased from Guangzhou Chemical Reagent Factory.

2.2. Preparation of SA

A series of SA with different DS were prepared by reacting with acetic anhydride in the presence of sodium hydroxide (Mark & Mehltretter, 1972). For example, starch (95 g) was placed into a 500 mL three-neck flask with a mechanical stirrer and a condenser, followed by the addition of acetic acid anhydride (307 mL). After stirring the mixture for 5 min, 50 wt% aqueous sodium hydroxide solution (18 g) was added dropwise. The reaction temperature was kept at 123 °C, and the reactions were performed for different reaction times to gain SA with different DS. The mixture was washed with excess distilled water, and dried at 80 °C in a convection oven.

2.3. Preparation of PPC/SA blend

Both PPC and SA were dried at 80 °C in the convection oven for 24 h prior to use. The PPC/SA blends with weight ratios of 90/10, 80/20 and 70/30 as well as neat PPC and PPC/NS blend were prepared in a Haake Rheomix-600 mixer (50 cm^3 chamber volume). The mixing was set at 170 °C with a rotary speed of 50 rpm for 8 min. All the specimens were placed in a tightly sealed desiccator to prevent moisture absorption.

The prepared blended samples were melt pressed at 170 °C into standard tensile bars (according to ASTM D638) and standard v-shaped notched impact bars (according to ASTM D256-05).

2.4. Measurements

2.4.1. Titration for determining the degrees of substitution (DS)

DS levels for SA were determined by titration (Chi et al., 2008). SA (0.5 g) and distilled water (50 mL) were placed in a 250 mL conical flask, and the pH was then adjusted to 7.0 with the addition of 0.01 mol/L NaOH. After that, 25 mL of 0.5 mol/L NaOH was added to the flask. The mixture was stirred at room temperature for 24 h before being titrated with 0.5 mol/L hydrochloric acid.

Acetyl content (ω) and DS were calculated as:

$$\omega = \frac{(\nu_1 - \nu_2) \times c_{\mathrm{HCl}} \times 0.043 \times 100\%}{m_{\mathrm{SA}}} \quad (1)$$

$$\mathrm{DS} = \frac{162\omega}{43 - 42\omega} \quad (2)$$

where ν_1, blank value (mL) (consumption of HCl for blank values); ν_2, volume of hydrochloric acid for titration (mL); c_{HCl}, molarity of hydrochloric acid (mol/L); m_{SA}, weight of SA (mg).

2.4.2. Static tensile properties

The static tensile properties were measured at 25 °C and relative humidity (RH) of 50% using a SANS CMT tensile tester, according to the standard of ASTM D638. The crosshead speed was set at 50 mm/min. Six specimens of each sample were measured and the average results were reported. All the Samples were aged for 24 h at 25 °C and 50% RH before testing.

2.4.3. Charpy impact strength

The Charpy impact strength of notched specimens was measured at 25 °C and 50% RH. The experiment was carried out in a SANS ZBC-4B Charpy impact tester, according to the standard of ASTM D256-05. The Charpy pendulum with a mass of 2.02 kg was dropped from a height of 23 cm, generating a velocity of 2.9 m/s. Six specimens of each sample were measured and the average results were reported. All the samples were aged for 24 h at 25 °C and 50% RH prior to test.

2.4.4. Fourier transform infrared (FTIR) spectra

FTIR spectra were recorded on a Perkin-Elmer FTIR-100 spectrometer. The frequency range of FTIR was 1900–800 cm^{-1} with a resolution of 4.0 cm^{-1}. Typically, 12 scans are signal-averaged to reduce spectral noise. Samples were compressed to give transparent thin film around 50 μm thick and tested by the transmission method.

2.4.5. Differential scanning calorimetry (DSC)

The DSC was determined in a Netzsch 204 (Burlington, Germany) instrument under a nitrogen flow of 20 mL/min. The samples were initially heated from 30 °C to 150 °C at 10 °C/min and then scanned back to −15 °C to eliminate previous thermal history. They were subsequently rescanned from −15 °C to 150 °C with a heating rate of 10 °C/min nitrogen atmosphere. The glass transition temperatures were evaluated from the second heating run.

2.4.6. Thermogravimetric analysis (TGA)

Thermal degradation performances of the samples were tested on a Perkin-Elmer TGA-6 instrument under nitrogen atmosphere. The temperature is ranged from 30 to 550 °C with a heating rate of 10 °C/min. All the samples were dried at 80 °C for 24 h before test.

2.4.7. Scanning electron microscope (SEM) morphology observation

The tensile bars were fractured by tweezers in liquid nitrogen. The morphology of the fractured surfaces was observed by scanning electron microscopy (JEOL JSM-6380). Before the observation, the fractured surfaces were coated with a thin layer of gold.

3. Results and discussion

3.1. DS levels of SA

The DS levels of a series of SA determined by titration turned out to be 0.25, 0.51, 0.88, 1.44, and 2.52. Theoretically, the highest DS is 3.0, corresponding to the complete conversion of the 3 hydroxyl groups in one glucose unit to the acetate groups. The SA prepared in this work has a DS level varied from 0.25 to 2.52. Therefore, correlation of the properties of the blend and interfacial chemistry with the DS levels could be comprehensively studied. The objective of this work is to find the exact level of DS which can provide PPC/SA blend with optimal mechanical and thermal properties.

3.2. FTIR investigation

The interaction of the two components in the blend can be studied by FTIR spectra. It is known that a distinct interaction exists between polymer chains when they are miscible or compatible, which would result in the absorption band shifts and broadening in the FTIR spectrum. The lower the shift with respect to the absorption peak, the stronger the hydrogen bond interaction that would exist between the polymer blends. Thus, FTIR is a useful tool for the study of compatibility or miscibility and phase behaviors of a polymer blend (Peng, Wang, & Dong, 2005). FTIR spectra of neat PPC, PPC/NS and PPC/SA blends with different DS levels in the 1900–450 cm^{-1} regions are shown in Fig. 2. In the presence of SA, the C=O absorption peak at 1749 cm^{-1} and the –O–C–O– absorption peak at 1236 cm^{-1} of PPC shifted towards a lower wave number and became broader due to the hydrogen-bonding interaction between the hydroxyl groups of starch and PPC. The above shifts are more obvious than those of PPC/NS blend, indicating that the interaction of PPC/SA was stronger than PPC/NS blend, because the two absorption peaks showed enhanced position-shifting and band-broadening tendency with increasing DS of SA in the blends. Compared with NS, SA has better compatibility or miscibility with PPC. Furthermore, the compatibility could be improved when DS of SA was increased. The FTIR results were consistent with the SEM observation which can be described in following section.

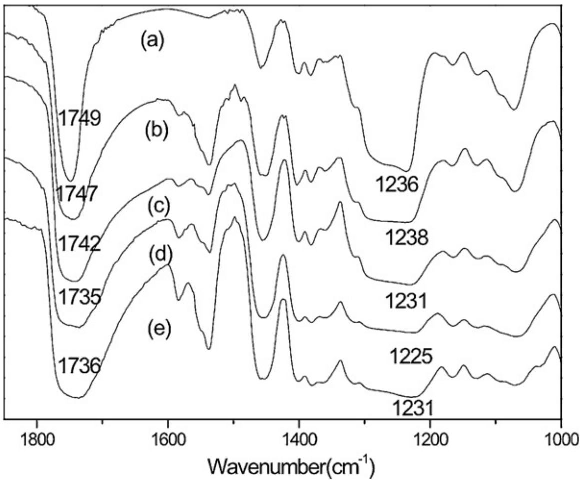


Fig. 2. FTIR spectrum of PPC/SA blends. (a) Neat PPC; (b) PPC/NS (70/30); (c) PPC/0.51SA (70/30); (d) PPC/0.88SA (70/30); (e) PPC/2.52 SA (70/30).

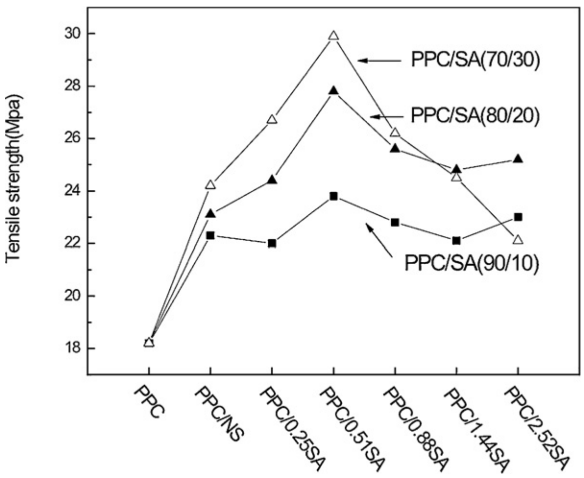


Fig. 3. Tensile properties for neat PPC, PPC/NS and PPC/SA (different DS) blends in (a) tensile strength; (b) elongation at break.

3.3. Mechanical properties

The mechanical properties of polymer/filler blend system dependent on the particle size of the filler, the content of the filler, the interfacial adhesion between the fillers and the polymer matrix, as well as the dispersion of the fillers within the matrix (Willett, 1994). For the PPC/NS blends, the weak affinity of the NS granules for PPC resulted in poor toughness and impact strength. To improve the compatibility of this system, PPC was blended with chemically modified NS, i.e., SA which contains hydrophobic acetate groups. In the presence of SA, a stronger linkage at the PPC/SA interface was identified by FTIR. Consequently, the PPC/SA blends are expected to exhibit improved mechanical properties and thermal stability.

The mechanical properties of neat PPC, PPC/NS and PPC/SA are shown in Figs. 3 and 4, respectively. Neat PPC is a ductile polymer with elongation of about 120% and a tensile strength of around 18.2 MPa under ambient conditions. As expected, for the PPC/NS, the NS granules in the PPC matrix acted as stress transfer centers, frequently inducing crack and being responsible for the low toughness. With the addition of 10% NS to PPC, the elongation at break dropped to 8.1% and the impact strength decreased to 2.92 kJ/m^2.

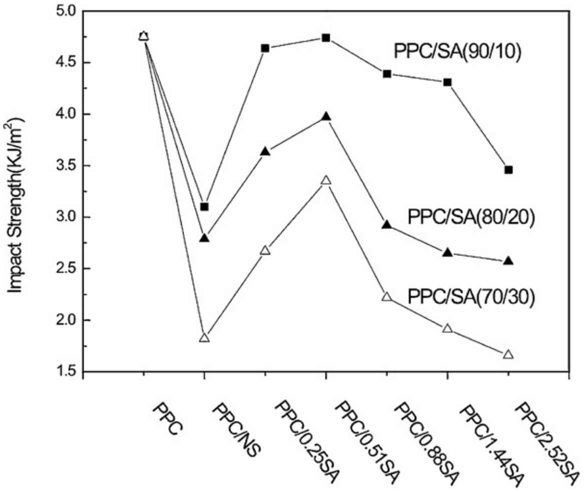


Fig. 4. Impact strength for neat PPC, PPC/NS and PPC/SA (different DS) blends.

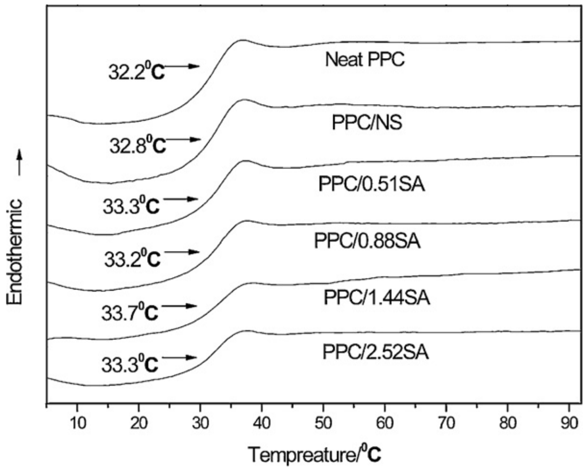


Fig. 5. DSC curves for neat PPC, PPC/NS (80/20), and PPC/SA (80/20) with different DS.

However, the PPC/SA blends with the DS of the SA lower than 0.88 exhibited the ductile properties as well as enhanced tensile strength, compared with PPC/NS with the same filler content. For example, the tensile strength of PPC/0.51SA (80/20) increased by about 24.5% and 50.5%, respectively, compared with PPC/NS (80/20) and neat PPC. PPC/0.51SA (80/20) has an impact strength of 24.5%, higher than that of PPC/NS (80/20). The remarkable enhancement of PPC/SA suggested a significantly improved compatibility between SA and the PPC matrix. These results are consistent with FTIR spectra and SEM measurements.

It should be noted that the DS level of SA significantly affects the mechanical properties of the PPC/SA blends. At the levels of DS within 0.25–0.51, the tensile strength of the PPC/SA blends increased with the DS of SA and reached optimal with PPC/0.51SA blend. When the levels of DS exceeded 0.88, there was a marked decrease in the tensile strength further increasing the DS of SA. The same trend was observed for impact strength. The distinct decrease in strengths is ascribed to the phase transition of the blend from a two-phase microstructure to a single-phase as identified by SEM observation in following section. For the DS level around 0.25–0.51, the SA acts as rigid fillers for PPC matrix in two-phase microstructure, the strength enhances significantly with stronger interfacial adhesion. Also, such adhesion might not severely restrict the mobility of PPC matrix which is capable of preserving the ductile properties. As a result, SA exhibited positive effects both on strength and toughness. For the DS level exceeding 0.88, the SA particles were well dispersed within PPC matrix in a single phase structure. However, this might break down the continuity of ductile PPC matrix, resulting in the formation of blend without the toughness feature, which may explain the deterioration in mechanical properties. In conclusion, the PPC/SA (DS = 0.51) (80/20) blend had the optimal performance in terms of tensile properties and impact strength.

3.4. Thermal behaviors

The DSC thermograms of neat PPC, PPC/NS (80/20) and PPC/SA (80/20) blends with different DS are presented in Fig. 5. All the blends had higher T_g values than neat PPC. When the DS level of SA increased, T_g remained almost constant at around 33 °C, presumably due to the stronger interfacial adhesion between SA and PPC. The rigid SA filler might constrain the molecular movement of PPC matrix via hydrogen bonding as indicated by FTIR investigation. This result also implied the improved compatibility between PPC and SA fillers compared with that of PPC and NS.

Table 1
Thermal properties of neat PPC, PPC/NS (80/20), and PPC/SA (80/20) blends with different DS.

Sample	$T_{-5\%}$ (°C)	$T_{-10\%}$ (°C)	$T_{\max}$ (°C)
PPC	261.7	274.6	297.9
PPC/NS	279.1	290.8	310.6
PPC/0.52SA	279.4	290.5	308.1
PPC/0.88SA	269.4	276.4	304.1
PPC/1.44SA	268.5	276.5	297.9
PPC/2.52SA	264.9	276.4	293.8

The thermogravimetric curves for neat PPC, PPC/NS (80/20), and PPC/SA (80/20) blends with different DS levels are shown in Fig. 6, where the weight loss of the degradation products was plotted as a function of temperature. The 5% weight loss temperature ($T_{-5\%}$), 10% weight loss temperature ($T_{-10\%}$) and maximum weight loss temperatures ($T_{\max}$) are summarized in Table 1. All $T_{-5\%}$, $T_{-10\%}$ and $T_{\max}$ of PPC/SA blend were higher than those of neat PPC. For example, the $T_{-5\%}$, $T_{-10\%}$ and $T_{\max}$ of PPC matrix in PPC/SA (DS = 0.51) increased by 18 °C, 17 °C and 13 °C, respectively, compared with neat PPC, which demonstrated that the SA can improve the thermal stability of PPC matrix. It was reported (Li, Meng, Zhu, & Tjong, 2003) that the pyrolysis of PPC follows two-step mechanism: main chain random scission and unzipping. The OH group of PPC is responsible for initiating the unzipping of polymer chain. Presumably, in the presence of strong hydrogen-bonding of the OH groups on starch and PPC, it might be able to retard the end-initiated unzipping depolymerization. It should be noted that a second stage of thermal degradation can been seen in PPC/SA with DS exceeding 1.44. Xu, Miladinov, and Hanna (2004) reported that the decomposition temperatures of SA increased with increasing DS level. They found the major thermal degradations of SA with DS levels of 0.57 and 1.68 took place at 297 °C and 347 °C, respectively. Thus, the second stage weigh loss might be associated with the degradation of SA within PPC matrix. However, no obvious second stage decomposition was observed in PPC/SA with DS lower than 0.88, and this phenomenon can be explained by the closer decomposition temperatures between SA with low DS and PPC matrix. As shown in Table 1, the $T_{\max}$ of neat PPC is 297.9 °C, it is close to the onset decomposition temperature of SA with DS of 0.57 reported by Xu.

3.5. Morphology observation

The morphological structure of a polymer blend is a very important factor for the properties of polymer blends, such as thermal stability and mechanical properties. The morphologies of PPC/NS (70/30) and PPC/SA (70/30) blends were investigated by scanning

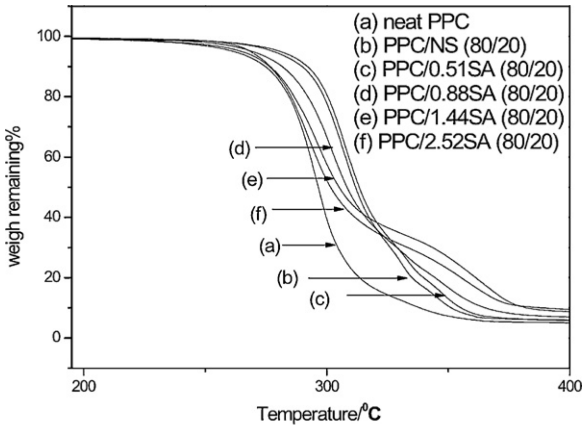


Fig. 6. TGA curves for neat PPC, PPC/NS (80/20), and PPC/SA (80/20) blends with different DS.

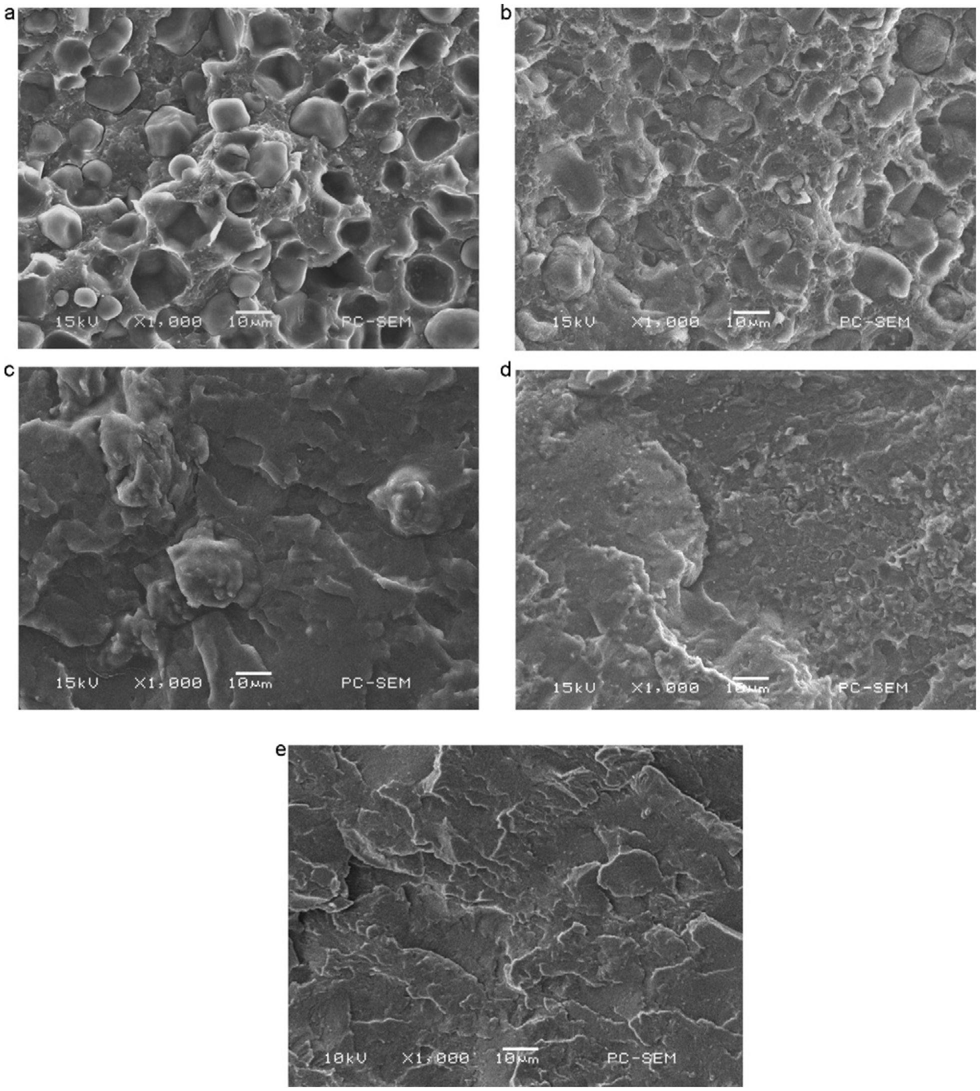


Fig. 7. SEM micrographs of PPC/SA blends. (a) PPC/NS (70/30); (b) PPC/0.51SA (70/30); (c) PPC/0.88SA (70/30); (d) PPC/1.44SA (70/30); (e) PPC/2.52SA (70/30).

electron microscopy (SEM). Fig. 7(a) shows the micrographs of the fractured surfaces of PPC/NS (70/30). The morphology of PPC/NS (70/30) was a typical two-phase microstructure. The NS particles in granular form were homogeneously dispersed in PPC matrix. However, there were numerous clear gaps at the interface of NS particles and PPC phase. In addition, numerous voids could be seen which resulted from pulling out of natural starch particle when being fractured. These abundant interface cracks were ascribed to their large interfacial tension and low interfacial adhesion which was consistent with the results reported in recent studies (Liu, Wang, & Sun, 2003).

The morphology of PPC/0.51SA fractured surface is shown in Fig. 7(b). The SA granules were well dispersed in PPC matrix with a two-phase microstructure similar to PPC/NS. However, these two-phase domains were tightly adhered to each other, and SA granules were well embedded into PPC matrix without noticeable gaps. These observations suggested that both SA (DS = 0.51) and PPC matrices have strong interfacial adhesion, agreeing well with other experimental results. The improved interfacial compatibility in turn resulted in the optimal performance in mechanical and thermal properties.

The fractured surface morphology of PPC/0.88SA is shown in Fig. 7(c). When the interfacial adhesion increased, the PPC matrices tended to swallow up the SA particles, causing the destruction of granule structures. The exposures of SA granules thus became invisible in SEM image, demonstrating the two-phase microstructure of the blend starting to convert into a single-phase microstructure when the DS of SA was above 0.88. This single-phase structure can be further confirmed by the observed morphologies of PPC/1.44SA and PPC/2.52SA as shown in Fig. 7(d) and (e), respectively. For the filler reinforced polymer blend, it is well known that the best improvement on the properties of the blend lies in the existence of two-phase structure in the blend with filler granules (generally with a particular size of about several microns) firmly adhered to polymer matrix in the boundaries. The single-phase structure shows less or no reinforcement on the mechanical properties of the blend. It was also believed that the transition from the two-phase structure to the single-phase resulted in the inferior performance on impact strength for the PPC/SA blends with DS further greater than 0.88.

4. Conclusions

Starch acetate (SA) with different DS (degrees of substitution) levels can be simply melt-blended with biodegradable poly (propylene carbonate) (PPC) to obtain biodegradable and cost-competitive blends. An improved thermal stability was obtained in PPC/SA, compared with PPC/NS and neat PPC. The stronger intermolecular interaction between PPC matrix and SA was confirmed by FTIR technique. SEM results demonstrated the stronger interfacial adhesion and compatibility between SA and PPC matrix than those of PPC/NS blends, thus the PPC/SA (DS < 0.88) exhibited superior reinforcement in tensile properties and impact strength, compared with those of PPC/NS blends. The optimal mechanical and thermal properties of PPC/SA (DS ranging from 0 to 2.52) could be realized in the samples containing SA with a DS = 0.51, due to the two-phase microstructure of the blend starting to convert into single-phase microstructure with DS level greater than 0.88.

Acknowledgments

The authors would like to thank the China High-Tech Development 863 Program (2009AA034900 and 2009AA03Z340), Guangdong Province Universities and Colleges Pearl River Scholar Funded Scheme (2010), Guangdong Province Sci & Tech Bureau (Key Strategic Project Grant No. 2008A080800024 and 10151027501000096), and Guangdong Education Bureau (Key Project. cxzd1004); Chinese Universities Basic Research Funding for financial support of this work.

References

Averous, L. (2004). Biodegradable multiphase systems based on plasticized starch: A review. *Journal of Macromolecular Science Part C: Polymer Reviews*, *44*, 231–274.

Broecker, W. S. (1997). Thermohaline circulation, the Achilles heel of our climate system: Will man-made CO_2 upset the current balance. *Science*, *278*, 1582.

Chen, X., Shen, Z., & Zhang, Y. (1991). New catalytic systems for the fixation of carbon dioxide. Copolymerization of carbon dioxide and propylene oxide with new rare-earth catalysts-RE(P2O4)3-Al(i-Bu)3-R(OH)*n*. *Macromolecules*, *24*, 5305.

Chi, H., Xu, K., Wu, X., Chen, Q., Xue, D., & Song, C. (2008). Effect of acetylation on the properties of cornstarch. *Food Chemistry*, *106*, 923–928.

Fanta, G. F., & Shogren, R. L. (1997). Modification of starch–poly(methyl acrylate) graft copolymers by steam jet cooking. *Journal of Applied Polymer Science*, *65*, 1021.

Gaspar, M., Benko, Z., Dogossy, G., Reczey, K., & Czigany, T. (2005). Reducing water absorption in compostable starch-based plastics. *Polymer Degradation and Stability*, *90*, 563–569.

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

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

Gonzalez, Z., & Perez, E. (2002). Effect of acetylation on some properties of rice starch. *Starch/Stärke*, *54*, 148–154.

Gorecki, P., & Koran, W. (1985). Diethylzinc–trihydric phenol catalysts for copolymerization of carbon dioxide and propylene oxide: Activity in copolymerization and copolymer destruction processes. *Journal of Polymer Science Part C: Polymer Letters*, *23*, 299.

Kacholia, K., & Reck, R. A. (1997). Comparison of global climate change simulations for $2 \times CO_2$-induced warming. *Climate Change*, *35*, 53.

Li, X. H., Meng, Y. Z., Zhu, Q., & Tjong, S. C. (2003). Thermal decomposition characteristics of poly (propylene carbonate) using TG/IR and Py-GC/MS techniques. *Polymer Degradation and Stability*, *81*, 157–165.

Liu, W., Wang, Y. J., & Sun, Z. (2003). Effects of polyethylene-grafted maleic anhydride (PE-g-MA) on thermal properties, morphology, and tensile properties of low-density polyethylene (LDPE) and cornstarch blends. *Journal of Applied Polymer Science*, *88*(13), 2904–2911.

Mark, A. M., & Mehltretter, C. L. (1972). Facile preparation of starch triacetates. *Starch/Stärke*, *24*, 73–76.

Meehl, G. A., & Washington, W. M. (1996). El Niño-like climate change in a model with increased atmospheric CO_2 concentrations. *Nature*, *382*, 56.

Meng, Y. Z., Du, L. C., Tiong, S. C., Zhu, Q., & Hay, A. S. (2002). Effects of the structure and morphology of zinc glutarate on the fixation of carbon dioxide into polymer. *Journal of Polymer Science Part A: Polymer Chemistry*, *40*, 3579.

Nishimura, M., Kasai, M., & Tsuchida, E. (1978). Copolymerization of carbon dioxide with propylene oxide catalyzed by poly (p-hydroxystyrene)/diethylzinc system. *Die Makromolekulare Chemie*, *179*, 1913.

Peng, S. W., Wang, X. Y., & Dong, L. S. (2005). *Polymer Composites*, *26*, 37.

Rokicki, A., & Kuran, W. (1981). The application of carbon dioxide as a direct material for polymer syntheses in polymerization and polycondensation reactions. *Journal of Macromolecular Science: Reviews in Macromolecular Chemistry*, *21*, 135.

Shogren, R. (1992). Polymer compatibility and biodegradation of starch–poly (ethylene-co-acrylic acid)–polyethylene blends. *Polymer*, *19*, 83–90.

Song, P. F., Xiao, M., Du, F. G., Wang, S. J., Gan, L. Q., Liu, G. Q., et al. (2008). Synthesis and properties of aliphatic polycarbonates derived from carbon dioxide, propylene oxide and maleic anhydride. *Journal of Apply Polymer Science*, *109*, 4121.

Tollefson, J. (2010). Climate talks focus on lesser goals. *Nature*, *468*, 488.

Tsuchida, E., & Kasai, M. (1980). Copolymerization of carbon dioxide with propylene oxide catalyzed by O-methylated or crosslinked poly (p-hydroxystyrene)/diethylzinc system. *Macromolecular Chemistry and Physics*, *181*, 1612.

Wang, S. J., Tjong, S. C., Du, L. C., Zhao, X. S., & Meng, Y. Z. (2002). Synthesis and characterization of alternating copolymer from carbon dioxide and propylene oxide. *Journal of Apply Polymer Science*, *85*, 2327.

Willett, J. L. (1994). Mechanical properties of LDPE/granular starch composites. *Journal of Applied Polymer Science*, *54*, 1685.

Wu, J., He, H., Xiao, M., Wang, S., & Meng, Y. (2009). Terpolymerization of carbon dioxide, propylene oxide and cyclohexene oxide by supported zinc glutarate. *Acta Scientiarum Naturalium Universitatis Sunyatseni*, *48*(z2).

Xu, Y., Miladinov, V., & Hanna, M. A. (2004). Synthesis and characterization of starch acetates with high substitution. *Cereal Chemistry*, *81*(6), 735–740.

Zhu, Q., Meng, Y. Z., Tjong, S. C., Zhao, X. S., & Chen, Y. L. (2002). Effects of the structure and morphology of zinc glutarate on the fixation of carbon dioxide into polymer. *Polymer International*, *51*, 1079.