

Effects of L-aspartic acid and poly(butylene succinate) on thermal stability and mechanical properties of poly(propylene carbonate)

Xueyan Yun, Jiaxin Wu, Yu Wang, Zilong Zhao, Ye Jin, Tungalag Dong

College of Food Science and Engineering, Inner Mongolia Agricultural University, 306 Zhaowuda Road. Hohhot, Inner Mongolia 010018, China

Correspondence to: T. Dong (E-mail: dongtlg@163.com)

ABSTRACT: Poly(propylene carbonate) (PPC) was modified by L-aspartic acid (Asp) and poly(butylene succinate) (PBS). To assess the effects of Asp and PBS on the thermal stability, mechanical properties of PPC, different PPC/Asp, PPC/PBS, and PPC/PBS/Asp blends were prepared by twin-screw extruder. The results indicated that the thermal stability improved with the Asp content increasing from 0.5 to 5%. With trace presence of 2% Asp, the degradation temperature of PPC was greatly increased upon extruding and the Yield strength and Young's modulus increased 62 and 849 times, respectively, at 20°C. The flexibility of PPC was effectively improved by blending with PBS, the PBS has no significant effect on the thermal stability of PPC until PBS up to enough amount. Besides the Asp additive in PPC/PBS blends not only improved the thermal stability PPC, but improved the interfacial compatibility of the blend.

© 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42970.

KEYWORDS: composites; films; graphene and fullerenes; nanotubes; properties and characterization; sensors and actuators

Received 24 July 2015; accepted 22 September 2015

DOI: 10.1002/app.42970

INTRODUCTION

In 1969, Inoue *et al.* used diethyl zinc as a catalyst for the copolymerization of carbon dioxide and propylene oxide, and poly(propylene carbonate) (PPC) was prepared successfully for the first time.¹ PPC is an important member of aliphatic polycarbonate family,² and it can be used as adhesive, barrier material, flexibilizer, solid electrolyte, photoresist, and plasticizer, microelectronics product.^{3,4} It attracts great attention because it is biodegradable and its carbon dioxide can be effectively utilize during manufacture. PPC also has many other attractive features, such as transparency, high elongation at break, and excellent gas barrier property.⁵⁻⁷

Despite these attractive features, PPC has a relatively low decomposition temperature and a glass transition temperature (T_g) close to room temperature, which limited its commercial applications as a replacement for conventional plastics.⁸ PPC with polymeric reinforcement has been used to improve its properties.⁹⁻¹⁴ To enhance mechanical performance of PPC, Qin *et al.* blended PPC with *o*-lauroyl chitosan (OCS) by solution casting. A two to three degree celsius increase in glass transition temperature and a 5% improvement (46–53°C) in weight loss temperature ($T_{5\%}$) were observed in the PPC/OCS blend with 10–20 wt % OCS. Compared with neat PPC, the maximum elongation at break of the blend with 10 wt % OCS increased twofold to 8.1% and Young's modulus increased nearly three-

fold to 1014 MPa.¹⁵ Also Ma *et al.* studied the mechanical properties and thermal stability of poly(L-lactic acid)/PPC (PLLA/PPC) blends and found that PLLA and PPC are partially miscible, which lead to increases of T_g and degradation temperature of PPC in blends.¹³ In a word, improving the thermal and mechanical properties of PPC and make it more suitable for industry production is the key for the wider application of this environmental friendly plastic.

PBS, another one of aliphatic polyester, is a semicrystalline polymer. It possesses good biodegradability, superior mechanical properties, and excellent thermal stability, which are due to its crystalline structure.^{16,17} However, it should be noticed that PBS also has excellent processability, as it can be processed in the field of textiles into melt blow, monofilament, multifilament, flat, nonwoven, and in the field of plastics into injection-molded products.¹⁸ Thus, PBS is a promising polymer for various potential applications. However, other properties of PBS, such as poor gas barrier properties and melt viscosity for further processing, often hinder its use for various applications.¹⁹ Pang *et al.* added different contents of PBS to PPC to make the composite membrane through melt blending. They found that comparing to pure PPC, the thermal degradable temperature of the composites raised by 30–60°C. However, the poor compatibility between PPC and PBS resulted in poor thermal stability of the composites.²⁰ Zhang *et al.* also used PBS as a filler in

PPC and studied the miscibility, crystallization, and mechanical properties of PPC/PBS blends. The results indicated that the glass transition temperature of PPC/PBS blends can be improved about 13°C, with a 40% PBS composition. PPC/10%PBS is miscible, its tensile strength and impact strength are improved.²¹ Thus, PBS is an excellent material for PPC to improve its physical properties.

One method that Yao *et al.* proposed to improve the thermal stability and mechanical properties of PPC is by preparing PPC/maleic anhydride (PPC/MA) mixture through melt blending extrusion. The results showed that the thermal degradation temperature at 5% weight loss ($T_{5\%}$) has improved 140°C by adding 1 wt % MA in to neat PPC. The tensile strength of PPC/MA blends with 0.5 wt % MA is nine times higher than neat PPC has approached to the strength of bulk polymers. That is because the chemistry of MA is very rich, reflecting its ready availability, and bifunctional reactivity. In PPC/MA composite, MA acted as end capping agent because the produce of maleic acid upon the co-extrusion.⁵ However, MA is a skin and respiratory sensitizer and may cause respiratory tract, eye irritation, skin irritation, and respiratory irritation. Thus, MA cannot be used for packaging materials of many products contacting the human body, such as food packs. L-Aspartic acid (Asp), which has similar double carboxyl structure to maleic acid, is one of the 20 amino acids commonly found in proteins and one of the most essential amino acids for human.²² It is a small molecule and its melting temperature is above 230°C with no exact melting point.^{23,24} Thus, Asp is a safe additive for modification of materials.

In this article, we report on PPC/Asp, PPC/PBS and PPC/PBS/Asp blends prepared via melt blending with the Asp acting as thermal stabilizer and the PBS as a polymeric reinforcement. The thermal stability, molecular weight, mechanical properties, and morphology of the blends are characterized by thermogravimetric analysis, differential scanning calorimetry, gel permeation chromatography, tensile test, and scanning electron microscopy.

EXPERIMENTAL

Material

The PPC ($M_n = 1.17 \times 10^5$; $M_w/M_n = 4.2$) used in this study was provided by Mengxi Hi-Tech Group (Inner Mongolia, China). PBS ($M_n = 5.8 \times 10^4$; $M_w/M_n = 1.7$) was provided by Cohen Corporation (Wuhan, China). Asp was obtained from ZiYi Pharmaceutical Group (Shanghai, China). PPC, PBS, and Asp were dried in a vacuum oven for 24 h at 25°C.

The neat PPC, PPC with 0.5, 2, 5 wt % Asp (PPC/0.5Asp, PPC/2Asp, PPC/5Asp) were mixed for 10 min and extruded by a twin-screw extruder (Ruiming Machinery Manufacture, Wuhan, China) at 120, 130, 140, and 150°C. The neat PBS and PPC with 10, 20, 30, 40, 50, 60, 70, 80, and 90 wt % PBS with 2 wt % Asp additives were mixed for 10 min and extruded at 120°C by the twin-screw extruder. All PPC/PBS and PPC/PBS/2Asp samples in the tests of the decomposition, tensile test, DSC and SEM were extruded at 120°C.

The samples were molded into the rectangular film with a dimension of $100 \times 100 \times 0.3 \text{ mm}^3$ by pressing with a constant pressure of 20 MPa at 110°C for 3 min. To remove the effect of thermal stress relaxation, they were stored at room temperature for 2 weeks. For the PPC/PBS and PPC/PBS/Asp blends, all the number before PBS and Asp indicated their percentage in blends, respectively.

Thermogravimetric Analysis (TGA)

TGA values of the blends were measured with a Thermogravimetric analyzer (Q50, TA Instruments, USA) under a N_2 protective atmosphere. The samples were heated from room temperature to 400°C at a heating rate of 5°C/min. The temperature at maximum weight loss was determined based on the derivation of the TGA results.

Gel Permeation Chromatography (GPC)

The molecular weight of samples was measured on a GPC system (Waters-2414, Waters). Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1 mL/min. The number-average (M_n) and weight-average molecular weights (M_w), as well as the polydispersity index (PDI; M_w/M_n), were calculated through a data acquisition system.

Differential Scanning Calorimetry (DSC)

The samples were scanned with differential scanning calorimetry (DSC Q20, TA Instruments, USA). The samples (5–10 mg) were initially scanned from -50 to 150°C with a heating rate of $10^\circ\text{C}/\text{min}$. All the scanning processes were under a protective atmosphere of N_2 . The midpoint of the transitions in the traces recorded in the heating scan were taken as the values of glass transition temperatures.

Tensile Test

The tensile tests were performed at 20 and 40°C on a texture analyzer (QTS-250, Stable Micro System, UK) with an air conditioning and an electric heating appliance to control the temperature. The tensile speed was set at 5 mm/min. Eight specimens of each sample were tested, and the average results were recorded.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy of tensile fracture surface of blends were performed with a field emission scanning electron microscope (HITACHI UHR FE-SEM SU8000 Series, SU8010) operating at 1 kV accelerating voltage.

RESULTS AND DISCUSSION

Thermal Stability

TGA is used to investigate the effects of Asp and PBS on the thermal stability of PPC. TGA curves of PPC, PPC/Asp blends are shown in Figure 1. The extrusion photograph of PPC and PPC/2Asp at 120 and 150°C are shown in Figure 2. The changes of molecular weight related with extrusion temperatures are summarized in Table I.

Figure 1 suggests that the degradation of neat PPC can be divided into three stages. The weight loss began slowly around 100°C. There was then an increase by 150°C and the degradation speed achieved its maximum around 200°C. It has been reported that thermal decomposition of high molecular weight

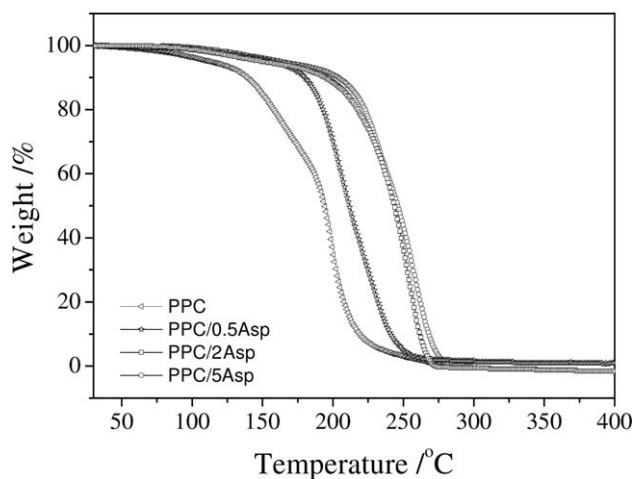


Figure 1. TGA curves for PPC, PPC/Asp blends.

PPC proceeds in two steps: (1) “Unzipping” occurred in the presence of residual polymerization catalysts at or above room temperature; (2) random chain-breaking at high temperatures.^{25–27} Luinstra *et al.* reported that backbiting occurs at temperatures as low as 150°C in the presence of catalyst residues and thus this gives cyclic propylene carbonate and chain scission at temperatures over 200°C with possible involvement of initial hydrolysis.²⁸ Liu *et al.* found that at low temperature the dominant mechanism of degradation was unzipping and the degradation process at higher temperature was a mixture of the two mechanisms: “Unzipping” and “Random chain-breaking”.²⁹ Peng *et al.* suggested that the degradation of uncapped PPC can be divided into three stages. In the first stage, corresponding to relatively lower temperature range, the chain unzipping

dominates the degradative process. With the increase in temperature, competing multistep reactions occur. In the last stage, corresponding to relatively higher temperature range, random chain scission plays an important role on the degradation.²⁶

From the experimental results of TGA, as a whole, “unzipping” degradation of neat PPC occurred as low as 100 °C. With increasing temperature, “random chain-breaking” appeared around 150°C, which increased the number of chain-end. In turn, more chain-ends further promoted “unzipping” degradation process. By 200°C, PPC degraded rapidly with “random chain-breaking” becoming the dominant mechanism of degradation. Accordingly, it can be seen from the Table I, the number average molecular weight (M_n) of original PPC (without extrusion) was 1.17×10^5 , but upon extruding M_n sharply decreased to 0.27×10^5 at 120°C. With increasing extrusion temperature, the M_n further decreased and the polymer exhibits a fluid state when the extrusion temperature higher than 140°C.

Figure 2 shows the flow state of PPC extruded at 120 and 150°C. As seen in Figure 2(A), the extruded PPC become thinner from the extruded exit to the end of strip extrudate, indicating the poor mechanical property and processability of neat PPC during extrusion at 120°C. As seen in Figure 2(B), with addition of 2% Asp, the extruded PPC shows an extrusion swell phenomena and that is a Barus effect. With further increasing extrusion temperature, it can be seen from Figure 2(C), the extruded PPC exhibits the fluid state as lower viscosity because of severe degradation at 150°C. However, as shown in Figure 2(D), by adding 2%Asp, the extruded PPC melt shows smooth surface and uniform shape, indicating that the PPC still has high molecular weight level.

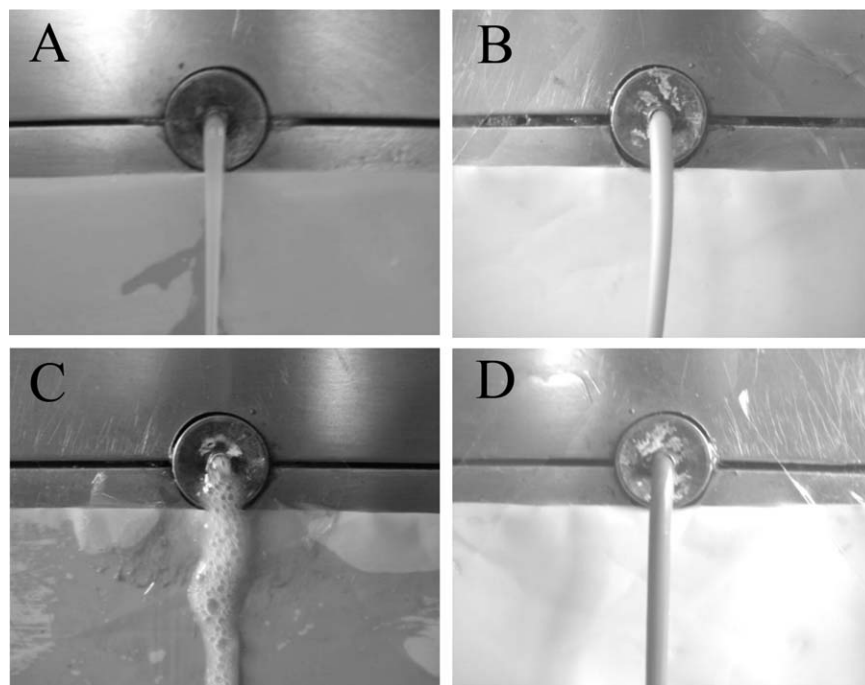


Figure 2. The extrusion photographs of (A) extruded neat PPC at 120°C, (B) extruded PPC/2Asp at 120°C, and (C) extruded neat PPC at 150°C, (D) extruded PPC/2Asp at 150°C.

Table I. Molecular Weight of PPC and PPC/Asp Blends at Different Extrusion Temperatures

Extrusion Temp.	PPC		PPC/0.5Asp		PPC/2Asp		PPC/5Asp	
	$M_n/\times 10^5$	M_w/M_n	$M_n/\times 10^5$	M_w/M_n	$M_n/\times 10^5$	M_w/M_n	$M_n/\times 10^5$	M_w/M_n
120°C	0.27	4.0	0.81	3.5	1.01	3.9	1.19	3.5
130°C	0.17	4.3	0.75	3.3	0.93	3.8	1.05	3.8
140°C	-	-	0.34	3.9	0.82	3.6	0.95	3.4
150°C	-	-	-	-	0.74	3.7	0.83	3.2
Original PPC	1.17	4.2	-	-	-	-	-	-

As shown in Table I, regarding the change of molecular weight, the molecular weight of PPC/0.5Asp was 0.81×10^5 , far higher than neat PPC extruded at 120°C, but slightly decreased compared with original PPC. That indicating the degradation of PPC was greatly relieved by adding a small quantity of Asp. With further increasing Asp content to 2%, the molecular weight of PPC more close to original PPC and the M_n of PPC/5Asp even equal to that of original.

With increasing extrusion temperature, the molecular weight of pure PPC decreases sharply, by adding a small amount of Asp, PPC still maintaining high molecular weight, suggesting that the Asp slow down the thermal degradation of PPC.

Since so little difference of the M_n and the TGA curves between PPC/2Asp and PPC/5Asp, from a logistics and cost perspective, we choose 2% addition level to prepared PPC/PBS/Asp blends. Figure 3 presents the TGA curves of PPC, PBS, PPC/2Asp, and PPC/20PBS/2Asp, and the temperature at maximum weight loss (T_d) was summarized in Table II, which was calculated from derivation of TGA result. It can be clearly observed from Figure 3 and Table II that the thermal degradation temperature was significantly improved with the addition of Asp. For PPC/Asp blend, the weight loss of PPC was not obvious between 100 and 150°C and the T_d reached 254°C, indicating that the trace presence of Asp (2 wt %) inhibited and delayed the “unzipping” degradation of PPC. It has been proven previously that

unzipping degradation of PPC could be depressed by end capping significantly.³⁰ Therefore, the Asp may act as a kind of end capping agent in this study.

Thermal stability of PBS is much better than that of PPC, and the T_d of PBS reaches 371°C.²⁰ In this case, the TGA curves of PPC/20PBS blends are higher than PPC/2Asp, between 100 and 180°C, and a sharp steep appeared around 186°C. This results implied that the addition of PBS increased the appearance of chain-breaking to a higher temperature. But this can barely function to prevent the start of random chain scission under high temperature. That may be because the PBS chain scattered in PPC phase absorbed a lot of heat during the process of heating up and prevented the degradation under a certain temperature range. But under higher temperature, made bit significant on further degradation.

For the PPC/20PBS/2Asp, the weight loss did not occurred until around 200°C and increased slightly between 200 and 250°C. A sharp steep appeared only about 250°C. The results indicated that both “unzipping” and “random chain-breaking” of PPC/20PBS/2Asp are relieved with the presence of both PBS and Asp. The PPC/20PBS/2Asp has a much better thermal stability than PPC blends with either Asp or PBS alone.

As can be seen in Table II, the degradation temperature (T_{d-PPC}) of neat PPC is 199°C. The T_{d-PPC} of PPC/2Asp is 254°C, an improvement of 55°C after blending with trace Asp. The T_{d-PPC} of PPC/PBS blends increased with increasing PBS content. But the PPC/PBS/2Asp blends kept a stable higher T_{d-PPC} about 260°C, with the PBS percentage range from 20 to 80%. This improved about 60°C compared with neat PPC. The T_{d-PBS} kept values between 355 and 371°C, which indicated the thermal stability of PBS phase in blends is not affected by the presence of PPC and Asp during degradation.

DSC Analysis

Figure 4(A,B) depict the DSC trace of samples. The variation trends of related parameters including the glass-transition temperature (T_g) of the PPC phase and crystallinity (X_c) of the PBS phase were presented in Figure 4(C,D), respectively. X_c was calculated from $\Delta H_{m-PBS}/\Delta H_{m-PBS}^0$, where ΔH_m^0 is the melting enthalpy of the PBS when its crystallinity is 100%. The ΔH_{m-PBS}^0 of PBS has been reported to be 200 J/g.^{30,31} $\Delta H_{m-PBS} = \Delta H_m/\text{PBS fraction}$, where ΔH_m is the melting enthalpy of composites calculated from DSC curves.

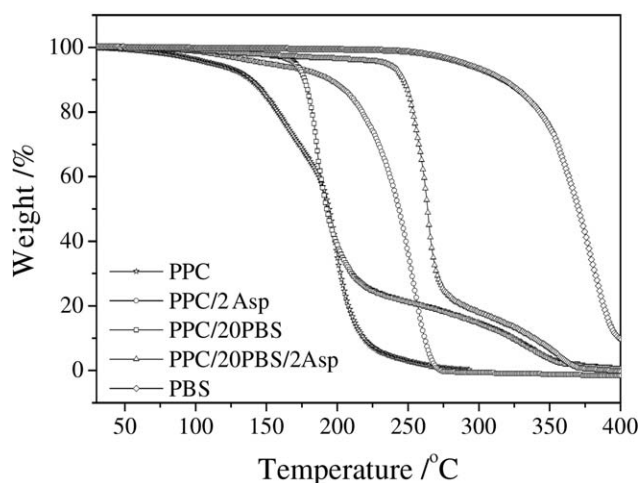
**Figure 3.** TGA curves for PPC, PBS, PPC/2Asp, PPC/20PBS, and PPC/20PBS/2Asp blends.

Table II. Degradation Temperatures of PPC, PBS, PPC/2Asp, PPC/PBS, and PPC/PBS/2Asp Blends

PPC/PBS	T_{d-PPC} °C	T_{d-PBS} °C	PPC/PBS/2Asp	T_{d-PPC} °C	T_{d-PBS} °C
PPC	199	–	PPC/Asp	254	–
PPC/20PBS	186	368	PPC/20PBS/Asp	263	355
PPC/50PBS	220	366	PPC/50PBS/Asp	260	362
PPC/80PBS	253	368	PPC/80PBS/Asp	265	370
PBS	–	371	PBS	–	371

The T_g of PBS is about -34°C ^{32,33} and cannot be observed in the curves since the fully crystallization of PBS phase. Generally, the T_g of PPC without extrusion is about 27°C ,³⁴ but as shown in Figure 4(A), the T_g of extruded PPC was only 7.4°C because the molecular weight of PPC greatly decreased after extruding. While for the PPC with 2 wt % Asp addition, the molecular weight remain almost unchanged at 1.01×10^5 , so the PPC/2Asp has a high T_g about 29.7°C . After blending with PBS, the T_g of PPC was raised to $27.8\text{--}35.3^\circ\text{C}$ with PBS content ranging from 10 to 70%. It can be seen from Figure 4(B), the T_g improved from 30.8 to 41.0°C compared with neat PPC with the PBS percentage increased from 10 to 80% in the case of PPC/PBS/2Asp blends.

Figure 4(C) summarized the variation of T_g of PPC with different PBS content in the PPC/PBS and PPC/PBS/2Asp composites. In the case of the PPC/PBS/2Asp blends, the T_g s were a little bit higher than PPC/PBS blends. Considering both T_g and TGA results, the presence of PBS with a trace of Asp decreased the degradation of PPC, especially the Asp additive.

It can be seen from Figure 4(A,D) that T_m of neat PBS was about 100°C , the T_m and X_c of PBS component in both systems remained almost unchanged over the whole range of weight fraction of the PBS component. But the PPC/PBS/2Asp blends showed slightly lower X_c than PPC/PBS blends. This imply that

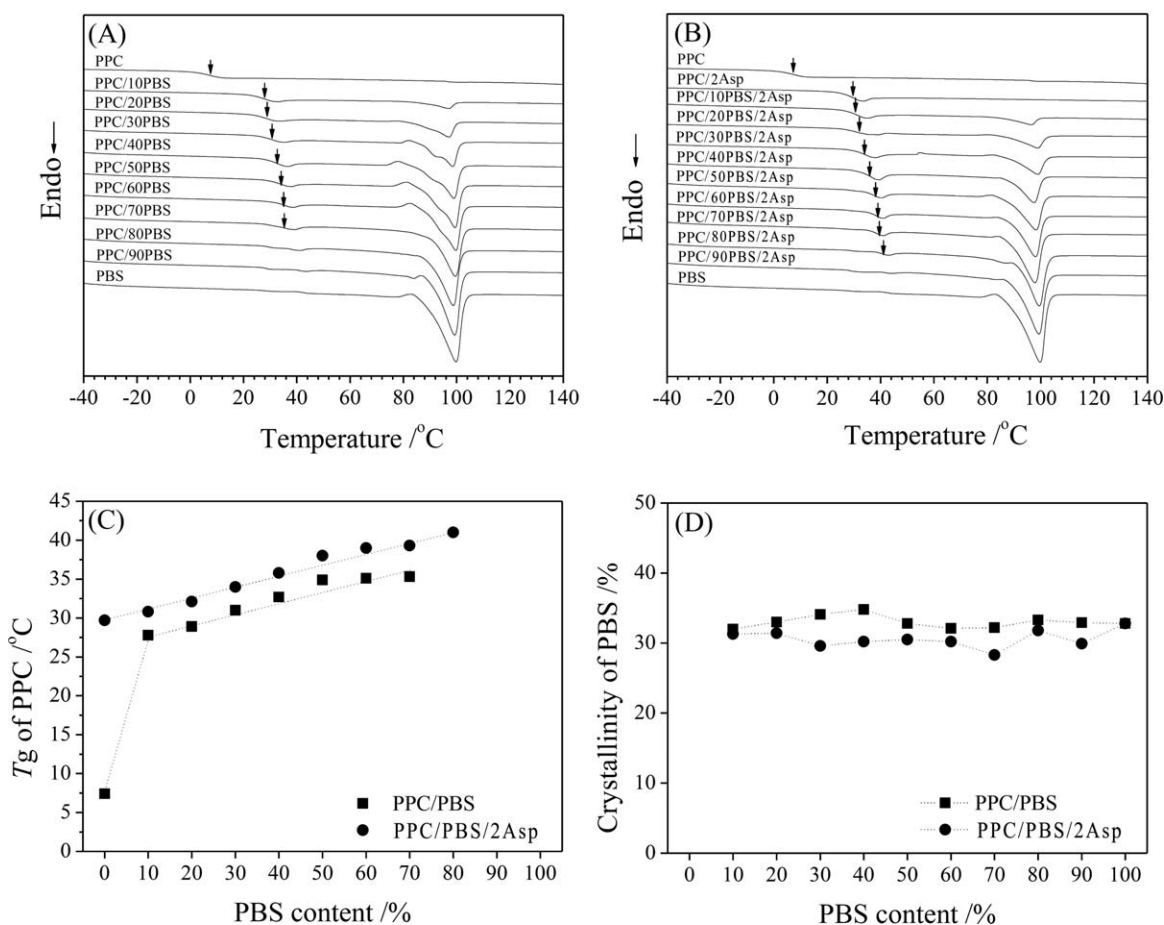


Figure 4. DSC curves of samples of (A) PPC/PBS blends, (B) PPC/PBS/Asp blends, and (C) T_g of neat PPC and PPC phase in blends, (D) the crystallinity of neat PBS and PBS phase in blends.

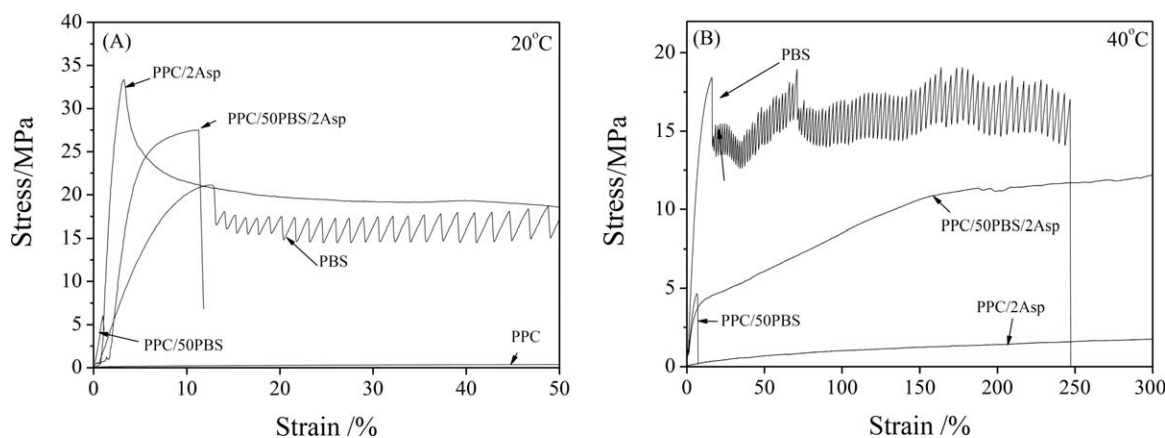


Figure 5. Stress–strain curves of neat PBS, PPC, PPC/2Asp, PPC/50PBS, and PPC/50PBS/2Asp blends at 20 and 40°C.

the presence of Asp affects the crystallization of PBS phase and the miscibility of the two components.

Mechanical Properties

The stress–strain curves of neat PBS, PPC, PPC/2Asp, PPC/50PBS, and PPC/50PBS/2Asp blends at 20 and 40°C are shown in Figure 5. It can be seen from Figure 5(A), the extruded neat PPC has quite low strength at 20°C that far high than its tested glass transition temperature. For PPC/2Asp, the curves indicating that its much better strength than neat PPC. In the cause of PPC/50PBS blend, broken occurred before the Yield and the elongation at break is only 1.4%. That is the blend showed a brittle fracture due to the incompatibility of PBS and PPC. Upon Asp adding, the PPC/50PBS/2Asp showed much better flexibility and the elongation reached 11% and improved about 10 times due to the improvement of their interface compatibility.

As seen in Figure 5(B), all blends showed relative lower strength than at 20°C. The strength of PPC/2Asp is lower than other samples and elongation at break exceed 300%. It was because the test temperature was higher than the T_g of PPC/2Asp, the PPC was in its high elastic and resulted in poor strength. But the strength of neat PBS and the PPC/50PBS blends only slightly decreased. That can be considered that the temperature has little impact on the mechanical property of PBS in fully crystalline state and the PBS acts as a physical reinforcement. The elongation at break of PPC/50/PBS is about 8%, with 2% Asp, the elongation of PPC/50PBS/2Asp is improved to more than 300% due to better interface compatibility.

Mechanical parameters get from the stress–strain curves of neat PBS, PPC, PPC/PBS, and PPC/PBS/2Asp blends at 20 and 40°C are shown in Figure 6. As shown in Figure 6(A), for neat extruded PPC, the Yield strength was only 0.55 MPa at 20°C. After blending with Asp, the Yield strength of PPC improved to 34 MPa. This is mainly because of the markedly molecular weight decrease of extruded PPC, the T_g of PPC is lower the room temperature and leads to PPC in a high elastic state. With the addition of Asp, the PPC has a relative high T_g due to the degradation being restrained by Asp additive, thus PPC was in glassy state under that testing temperature. For PPC/PBS blends, the Yield strength of PPC/10PBS increased to 32.8 MPa.

As reported in TGA results, the presence of PBS can reduce the “chain-breaking” degradation of PPC. Therefore, the extruded PPC phase has kept a relative high T_g because the PBS has restrained the degradation of PPC. But with further increase of the PBS content, the Yield strength showed a sharp decrease. The Yield strength recovered to normal high value with the PBS content increasing to 80%. The main reason for this phenomenon is the incompatibility of PPC and PBS.²⁰ With further increase of PBS content over 80%, the PBS becomes the major component and the tensile property of PPC/PBS blends mainly decided by PBS. PBS acts as physical reinforcement and the blends exhibiting higher Yield strength. However, after adding 2%Asp to PPC/PBS blends, the tensile property of PPC/PBS/2Asp significantly differed to the PPC/PBS blends. It also can be seen from Figure 6(A), the Yield strength of PPC/PBS/2Asp blends slowly decreases with increasing PBS content. Finally, the tensile property of PPC/PBS/2Asp is almost the same to neat PBS. This phenomenon indicates that the presence of trace Asp improve the interfacial compatibility of PPC and PBS and further lead to higher Yield strength.

Figure 6(C) shows the Young’s modulus of blends. Due to the degradation in banburying process of extrusion, the molecular weight of PPC sharply decreases and leads to low T_g . The neat PPC shows a relative low Young’s modulus value, since the polymer was in high elastic state at 20°C. With 2%Asp addition, the PPC has a relative high rigidity and the Young’s modulus reach 1800 MPa. The Young’s modulus of PPC/PBS and PPC/Asp/PBS blends decrease with increasing PBS content, but the PPC/Asp/PBS blends still kept a higher the Young’s modulus value than PPC/PBS. When the PBS contents increased to above 70%, the modulus tends to be the same value.

As shown in Figure 6(E), the elongation at break of extruded neat PPC up to about 900% since it is in high elastic state. After adding 2%Asp, the PPC/Asp is in glassy state at 20°C. Its elongation at break reach about 600% and the film shows good toughness property. But the elongations at break of blends with higher PBS content are small. That may because the incompatibility of the two components leading to the brittleness in the films. The films cannot reach its Yield point in tensile test. The elongations at break of blends remains low and almost

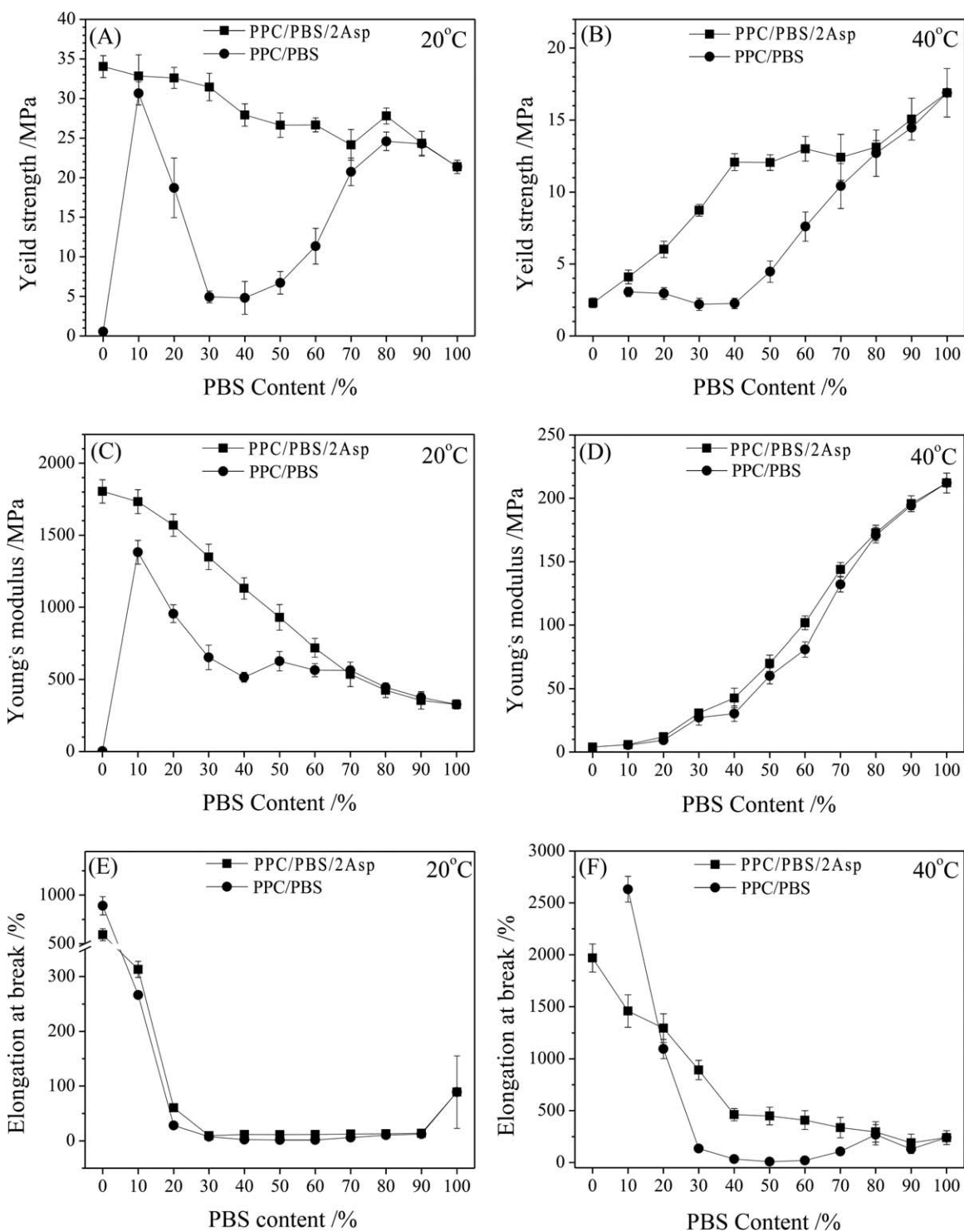


Figure 6. Tensile properties of PPC/PBS and PPC/PBS/Asp blends at 20 and 40°C.

unchanged within PBS ranged from 30 to 90%. But the elongation of PPC/PBS/2Asp blends slightly higher than PPC/PBS blends since the Asp additive improved the compatibility of PPC/PBS.

Figure 6(B,D,F) show the Yield strength, Young's modulus and elongation at break of PPC/PBS and PPC/PBS/2Asp blends under 40°C, respectively. As shown in Figure 6(B,D), the

varying tendency of the Yield strength and Young's modulus at 40°C is very different with those at 20°C. The neat PPC was unable to be tested under 40°C. The PPC/Asp showed low Yield strength and Young's modulus about 2.2 and 4.4 MPa. That due to the test temperature are far higher than the T_g of PPC, the amorphous state of PPC has poor physical properties. However, the Yield strength and the Young's modulus of PPC/PBS and

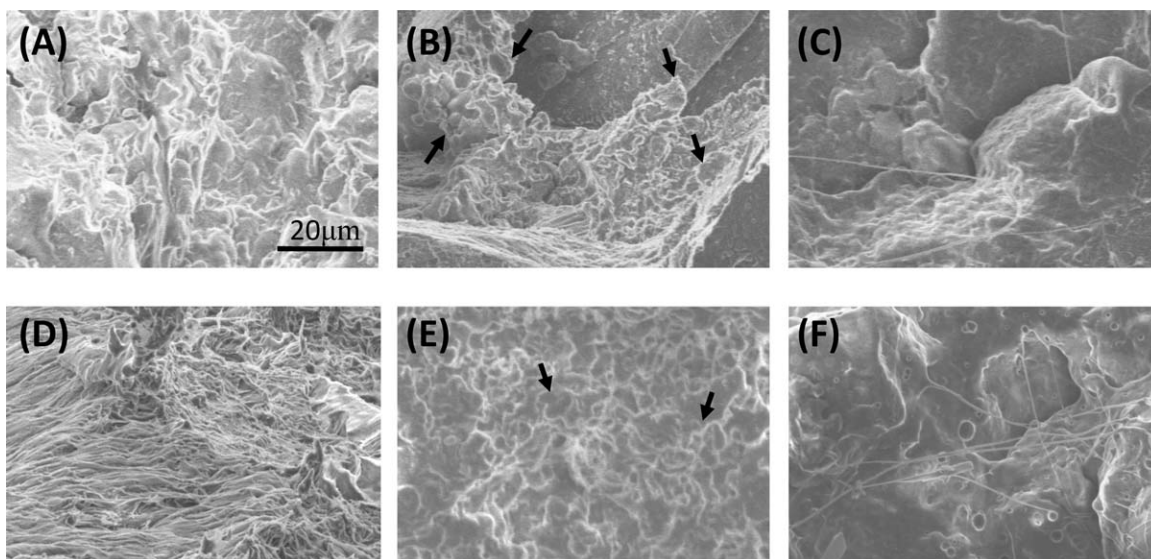


Figure 7. SEM micrographs of PPC/PBS and PPC/PBS/2Asp blends: (A) PPC/20PBS, (B) PPC/50PBS, (C) PPC/80PBS, (D) PPC/20PBS/2Asp, (E) PPC/50PBS/2Asp, and (F) PPC/80PBS/2Asp.

PPC/PBS/2Asp blends increased with the increase of weight fraction of the PBS component and when the films with high PBS content, they had mechanical property close to PBS. This is the PBS phase still has good mechanical property due to its crystallization at 40°C. The temperature ranged from 20 to 40°C has almost no impact on the physical property of PBS and it still acts as a physical reinforcement in system. But with the Asp additive, the physical property of PPC was improved. Thus, the PPC/PBS/2Asp blends have relative high Yield strength and Young's modulus than PPC/PBS blends due to the improvement of interface compatibility of two phases.

In Figure 6(F), the elongation of PPC/Asp exceed 2000% under 40°C. The elongation at break of PPC/PBS blends is still lower than the value of PPC/PBS/2Asp blend film when the PBS content is within 30–70%, which indicates that the presence of Asp may improve the interfacial compatibility of PPC and PBS and may enhance the toughness of blend film. Meanwhile, the Yield strength and Young's modulus of blends with Asp addition are higher than PPC/PBS blends.

Fractured Surfaces

The morphology of PPC/PBS and PPC/PBS/2Asp samples at the failure point was investigated by SEM and the micrographs of fractured surfaces obtained after tensile tests and are shown in Figure 5. As shown in Figure 7(A,C), the fracture surface of PPC/20PBS and PPC/80PBS were relative homogeneous continuous phase, which indicated that the two phase are somewhat compatible with a small amount presence of one component. As shown in Figure 7(B), for PPC/50PBS, the micrograph shows an obvious phase separation, and the fractured surface presents a relatively smooth topography, indicating a brittle fracture. On the whole, the blends tend to have a brittleness character with the increasing PBS content.

On the contrary, the rough topography and the presence of deformed structure are an indicative that PPC/PBS/2Asp films

present more ductile behavior during tensile deformation, and the fracture surface presented more homogeneous continuous phase compared with PPC/PBS blends. As shown in Figure 7(D,F), the size of dispersed phase for PPC/20PBS/2Asp and PPC/80PBS/2Asp decreased and the surface showed more homogeneous. Meanwhile, obvious phase separation was not observed for PPC/50PBS/2Asp and the micrographs showed a relative homogeneous continuous phase. This indicated that adding trace Asp into PPC/PBS blends can modify the interface between PPC and PBS phase and decreased the interfacial tension.

CONCLUSION

PPC can be simply melt-blended with PBS and Asp to prepare completely biodegradable PPC/PBS, PPC/PBS/Asp blends. For PPC, severe degradation occurred and the molecular weight sharply decreased in the extrusion process. The lower molecular weight leads to lower Yield strength and Young's modulus, and thus the film completely loses its functional value. The trace Asp additive greatly decreased the thermal degradation of PPC. Furthermore, the Asp additive in PPC/PBS blends improved the interfacial compatibility between PPC and PBS, thus flexibility and the Yield strength and Young's modulus were increased remarkably. Besides, the flexibility and thermal stability of PPC was also effectively improved by blending with enough amount of PBS upon extruding.

ACKNOWLEDGMENTS

This work was supported by Dr. Startup funds of Inner Mongolia Agricultural University (209-206035), "Project of Prairie Excellence" Inner Mongolia Autonomous Region (2011, 108-108037) and National Natural Science Foundation of China (No. 51163010).

REFERENCES

1. Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci. B: Polym. Lett. Ed.* **1969**, *7*, 287.
2. Wang, J. T.; Shu, D.; Xiao, M.; Meng, Y. Z. *J. Appl. Polym. Sci.* **2006**, *99*, 200.
3. Lu, X. L.; Zhu, Q.; Meng, Y. Z. *Polym. Degrad. Stab.* **2005**, *89*, 282.
4. Spencer Todd, J.; Kohl, P. A. *Polym. Degrad. Stab.* **2011**, *96*, 686.
5. Yao, M.; Mai, F.; Deng, H.; Ning, N.; Wang, K.; Fu, Q. *J. Appl. Polym. Sci.* **2011**, *120*, 3565.
6. Sugimoto, H.; Inoue, S. *Pure Appl. Chem.* **2006**, *78*, 1823.
7. Pang, S.; Xu, N.; Xu, G.; Pan, L.; Lin, Q.; Wang, X. *J. Appl. Polym. Sci.* **2013**, *128*, 2020.
8. Jiao, J.; Wang, S. J.; Xiao, M.; Xu, Y.; Meng, Y. Z. *Polym. Eng. Sci.* **2007**, *47*, 174.
9. Ma, X. F.; Chang, P. R.; Yu, J. G.; Wang, N. *Carbohydr. Polym.* **2008**, *71*, 229.
10. Wang, N.; Zhang, X. X.; Yu, J. G.; Fang, J. M. *Polym. Int.* **2008**, *57*, 1027.
11. Zhang, Z. H.; Lee, J. H.; Lee, S. H.; Heo, S. B.; Pittman, J. *Polymer* **2008**, *49*, 2947.
12. Xu, J.; Li, R. K. Y.; Meng, Y. Z.; Mai, Y. W. *Mater. Res. Bull.* **2006**, *41*, 244.
13. Ma, X. F.; Yu, J. G.; Wang, N. *J. Polym. Sci. B: Polym. Phys.* **2006**, *44*, 94.
14. Chiellini, E.; Cinelli, P.; Solaro, R.; Laus, M. *J. Appl. Polym. Sci.* **2004**, *92*, 426.
15. Qin, Y. S.; Chen, L. J.; Wang, X. H.; Zhao, X. J.; Wang, F. S. *Carbohydr. Polym.* **2011**, *84*, 329.
16. Park, J. W.; Im, S. S. *J. Appl. Polym. Sci.* **2002**, *86*, 647.
17. Ohkita, T.; Lee, S. *J. Appl. Polym. Sci.* **2005**, *97*, 1107.
18. Fujimaki, T. *Polym. Degrad. Stab.* **1998**, *59*, 209.
19. Ray, S. S.; Okamoto, K.; Okamoto, M. *Macromolecules* **2003**, *36*, 2355.
20. Pang, M. Z.; Qiao, J. J.; Jiao, J.; Wang, S. J.; Xiao, M.; Meng, Y. Z. *J. Appl. Polym. Sci.* **2007**, *107*, 2854.
21. Zhang, H. L.; Sun, X. H.; Chen, Q. Y.; Ren, M. Q.; Zhang, Z. H.; Zhang, H. F.; Mo, Z. S. *Chin. J. Polym. Sci.* **2007**, *25*, 589.
22. Lee, T.; Lin, Y. K. *Crystallogr. Growth Des.* **2010**, *10*, 1652.
23. Nomenclature Symbolism, *Eur. J. Biochem.* **1984**, *138*, 9.
24. Shinoda, H.; Asou, Y.; Suetsugu, A.; Tanaka, K. *Macromol. Biosci.* **2003**, *3*, 34.
25. Lai, M. F.; Li, J.; Liu, J. J. *J. Therm. Anal. Calorim.* **2005**, *82*, 293.
26. Peng, S. W.; An, Y. X.; Chen, C.; Fei, B.; Zhuang, Y. G.; Dong, L. S. *Polym. Degrad. Stab.* **2003**, *80*, 141.
27. Lia, X. H.; Meng, Y. Z.; Zhu, Q.; Tjong, S. C. *Polym. Degrad. Stab.* **2003**, *81*, 157.
28. Luinstra, G.; Endres, B. *Synthetic Biodegradable Polymers. Springer, Berlin* **2012**, p 29.
29. Liu, B.; Chen, L.; Zhang, M.; Yu, A. *Macromol. Rapid Commun.* **2002**, *23*, 881.
30. Dixon, D. D.; Ford, M. E.; Montell, G. J. *J. Polym. Sci. C* **1980**, *18*, 131.
31. Miyata, T.; Masuko, T. *Polymer* **1998**, *39*, 1399.
32. Snowdon, M.; Mohanty, A. K.; Misra, M. *Macromol. Mater. Eng.* **2015**, *300*, 118.
33. Dong, T.; Yun, X. Y.; Shi, C. C.; Sun, W. X.; Fan, G. S.; Jin, Y. *Polym. Sci. A* **2014**, *56*, 830.
34. Yun, X. Y.; Zhang, X. Y.; Jin, Y.; Yang, J. J.; Zhang, G. J.; Dong, T. *J. Macromol. Sci. B* **2015**, *54*, 275.