Available online at www.sciencedirect.com
SCIENCE DIRECT
Carbohydrate Polymers 65 (2006) 139–143
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Mechanical and thermal properties of thermoplastic acetylated starch/poly(ethylene-*co*-vinyl alcohol) blends

Wenbo Jiang, Xiuying Qiao, Kang Sun *

State Key Laboratory of Metal Matrix Composites, College of Material Science and Engineer, Shanghai Jiao Tong University, 1954 Hua Shan Road, Shanghai 200030, People's Republic of China

Received 21 July 2005; received in revised form 16 November 2005; accepted 28 December 2005
Available online 20 March 2006

Abstract

Blends of thermoplastic acetylated starch (TPAS) and poly(ethylene-*co*-vinyl alcohol) (EVOH) were prepared with different components by melt blending method and the mechanical and thermal properties of these blends were investigated. Tensile testing shows that with the increasing of EVOH content, the mechanical properties of TPAS/EVOH blends are improved significantly. Dynamic mechanical analysis (DMA) indicates that there is a good miscibility between TPAS and EVOH, and the molecular interactions of TPAS/EVOH blends become stronger with the increasing of EVOH content. Differential scanning calorimetry (DSC) results also reveal that there are some interactions between TPAS and EVOH that can interrupt the crystallization of EVOH. It can be inferred from thermogravimetry analysis (TGA) that EVOH can increase the thermal stability of TPAS.

Keywords: Acetylated starch; EVOH; DMA; DSC; TGA

1. Introduction

In recent years, increasing concern about environmental issues has renewed great interest in the development of the biodegradable materials.

Among these materials, starch-based plastics have drawn more attention because of its availability, low price and good performance. In fact, the melting temperature (T_m) of native starch lies above its decomposition temperature, so starch itself cannot be considered as a typical thermoplastic polymer. Previous research has focused on the plasticization of the native starch to make starch to be processed like common plastics under the action of adequate temperature and mechanical shear force. Various plasticizers (glycerol, water, urea and formamide, etc.) have been added in starch to decrease molecular chain interactions and to improve its mechanical properties. Yet, these native starch-based plastics still have poor mechanical properties and remarkable sensitivity to moisture content that limit the wide application of starch-based plastics (Liu, Yi, & Feng, 2001; Lorcks, 1998; Ma, Yu, & Jin, 2004).

In order to broaden application, chemical modification has been performed to improve the starch plastic product quality. It has been reported that acetylation of starch hydroxyl groups may reduce the tendency of starch to form strongly hydrogen-bonded networks and decrease the T_g and gelatinization temperature, and acetylated starch should have better thermo plasticity and processibility than native starch (Fringant, Rinaudo, Foray, & Bardet, 1998; Gonzalez & Perez, 2002; Shogren, 1996).

Acetylation is also one approach to increase the water resistance of starch, since the hydrophilic hydroxyl groups are substituted with hydrophobic acetyl groups that prevent the formation of hydrogen bonding between the hydroxyl groups and water molecules (Fringant, Desbrieres, & Rinaudo, 1996; Lawal & Adebowale, 2005; Miladinov & Hanna, 1999). Moreover, acetylation can increase the transparency of starch films too, by preventing or minimizing the associations of amylopectin outer branches which can cause cloudiness and syneresis in aqueous dispersions of starches (Lawal & Adebowale, 2005).

Blending with some other degradable synthetic polymers is another way to improve the mechanical properties of starch-based plastics, such as poly(lactic acid), PLA, poly(vinlyl alcohol), PVA, and poly(caprolactone), PCL (Lee et al., 2004;

* Corresponding author. Tel.: +86 21 62932555; fax: +86 21 62830735.
E-mail address: ksun@sjtu.edu.cn (K. Sun).

0144-8617/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2005.12.038

Wu, 2003; Zeng, Liu, & Li, 1999). In this study, thermoplastic acetylated starch/poly(ethylene-*co*-vinyl alcohol) (TPAS/EVOH) blends were prepared with glycerol as a plasticizer; a blend which, in consideration of the acetylation has hardly been reported before. EVOH has high crystallinity and fine mechanical properties, and is usually used for packaging because of its excellent gas barrier properties. During our research work, EVOH with an ethylene content of 38 mol%, which exhibits good mechanical property and oxygen barrier properties (Stenhouse & Ratto, 1997), was chosen to modify the TPAS material. Mechanical and thermal properties of TPAS/EVOH blends were investigated.

2. Experimental

2.1. Materials

Acetylated starch (PURITY 77), a modified food starch derived from tapioca with an amylose/amylopectin ratio of 21:79, was supplied by National Starch and Chemical Ltd EVOH (38 mol% ethylene) was purchased from JiangSu HuaYi Plastic Limited Company. Glycerol was produced by China National Pharmaceutical Group, with a boiling point of 290 °C (101.3 KPa). During preparation, acetylated starch and glycerol were premixed by hand and sealed for 24 h. Glycerol was added as a plasticizer at 50% of the acetylated starch weight. After that, EVOH was blended with the premixtures using a Thermo Haake Rheomix 900 for 10 min in varying proportions as shown in Table 1. The screw speed was 100 rpm and the blend temperature was 150 °C. Then, the TPAS/EVOH blends were hot pressed and cut into standard shapes for testing. To investigate the difference between acetylated starch and native starch, some thermoplastic native starch/EVOH (TPS/EVOH) blends were also prepared in the same way for testing.

2.2. Analytical methods

Tensile properties were measured on an Instron 4465 Universal Tensile Tester with 2 Kg load cell and a 10 mm/min tensile speed at room temperature.

Dumbbell samples (1 mm thick) were tested with a gauge length of 20 mm.

Values of elongation at break and tensile strength of TPAS/EVOH blends were determined from the average of five samples.

Differential scanning calorimetry (DSC) measurements were done on a Q10 system (TA Instruments, Wilmington, DE, USA) under nitrogen atmosphere. About 5–10 mg samples, weighed accurately and encapsulated in aluminum crucibles, were first heated to 250 °C quickly to eliminate previous thermal history of melt characterization. Samples were cooled and reheated in the temperature range of 25–250 °C with a scan rate of 20 °C/min, resulting in endothermic curves. The values of melting temperatures (T_m), and heat (enthalpy) of melting (ΔH) were obtained by the use of Thermal Analysis Instruments Universal Analysis 2000 program, version 3.8B.

Table 1
Compositions of thermoplastic acetylated starch/EVOH blends ($W/W\_starch \times 100$)

Component	TPAS	TPAS-E15	TPAS-E30	TPAS-E45	TPAS-E60	TPAS-E75
Acetylated starch	100	100	100	100	100	100
Glycerol	50	50	50	50	50	50
EVOH	0	15	30	45	60	75

Dynamic mechanical analysis (DMA) was carried out on a DMTA IV instrument (TA Instruments, Wilmington, DE, USA) in a single cantilever mode from −100 to 120 °C with a frequency of 1 Hz and a heating rate of 5 °C/min. During testing, the dynamic mechanical property parameters of storage modulus (E'), loss modulus (E'') and loss factor ($\tan\delta = E''/E'$) were recorded as a function of temperature.

Thermogravimetric analysis (TGA) was operated on TGA2050 system (TA Instruments, Wilmington, DE, USA) under nitrogen atmosphere. The samples were heated from room temperature to about 750 °C at a heating rate of 20 °C/min and a nitrogen gas flow rate of 60 ml/min. The derivative of TGA was obtained using TA analysis software.

3. Results and discussion

3.1. Mechanical properties

The tensile strength and elongation at break of TPAS/EVOH and TPS/EVOH blends are shown in Fig. 1. As the content of EVOH in TPAS/EVOH blends is increased, the tensile strength increases significantly. When the EVOH content is increased to 75/100 (EVOH/acetylated starch), the tensile strength is about five times compared with TPAS. The increased tensile strength of TPAS/EVOH blends could be due to the high mechanical strength of EVOH originating from high crystallinity of EVOH and the interactions between EVOH and acetylated starch. Perhaps, interactions are through hydrogen bonds, which will be explored by DMTA and DSC below. It is noticed that when EVOH content is increased to high level, TPS/EVOH blends will become very brittle, but the elongation at break of TPAS/EVOH blends decreases slightly, because acetylated starch has better thermoplasticity than native starch and acetylated groups can be considered as an internal plasticizer.

3.2. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out to get more information about molecular motion and structure, with a focus on miscibility and interactions between the components. It can reveal the glass transition of materials and the change of dynamic mechanical modulus sensitively. Fig. 2 shows the variation in loss factor ($\tan\delta$) and dynamic storage modulus (E') of TPAS, EVOH and the TPAS/EVOH blends measured over the temperature range from −100 to 120 °C. For TPAS, the dynamic storage modulus falls in two steps, the first between −60 and −20 °C where the modulus decreases slightly and the second between 0 and 70 °C where the modulus

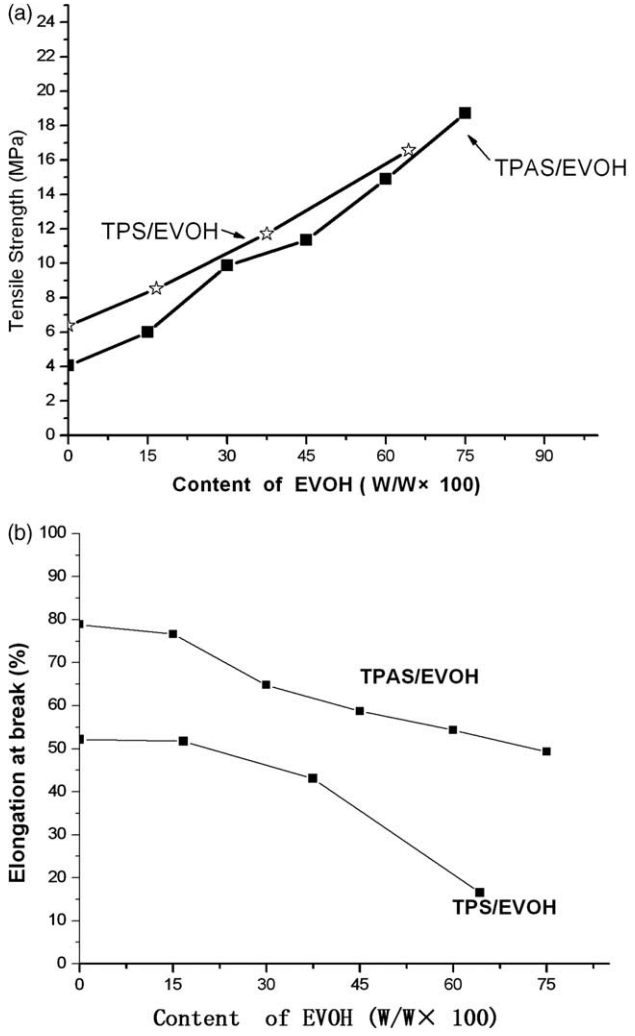

Fig. 1. Variation of mechanical properties of TPAS/EVOH and TPS/EVOH blends: (a) tensile strength, (b) elongation at break.

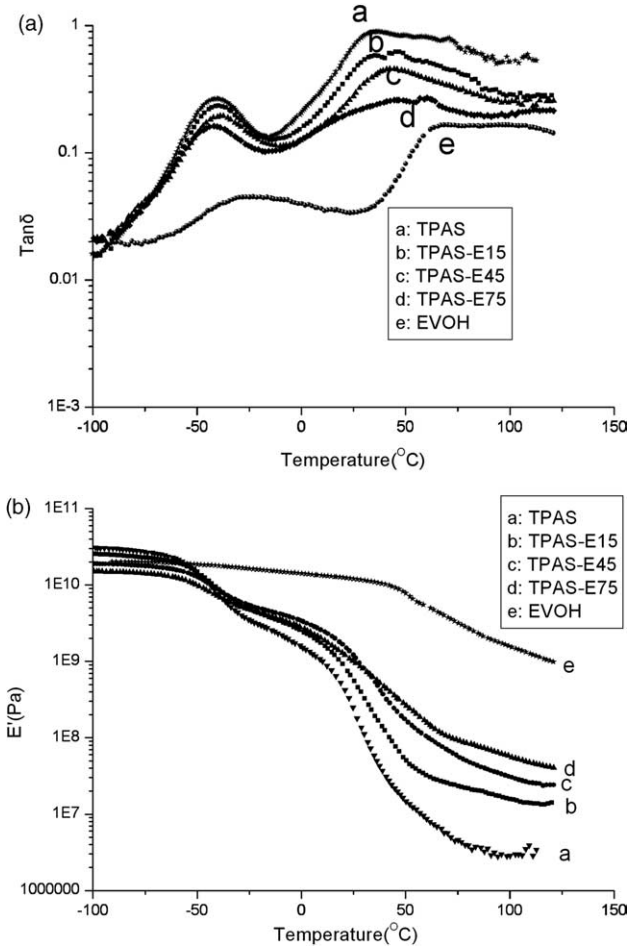

Fig. 2. Effect of EVOH content on DMA properties of TPAS/EVOH blends: (a) loss factor (tan δ) versus temperature, (b) dynamic storage modulus (E') versus temperature.

decreases significantly with corresponding relaxation peaks of tan δ at about −42 and 37 °C. This can be attributed to the existence of two phases that originated from the partial miscibility of glycerol and acetylated starch (Forssell, Mikkila, Moates, & Parker, 1998). The relaxation at the upper temperature, which is the main relaxation, results from the glass transition of starch-rich phase, whereas, the lower relaxation likely results from the glass transition of glycerol-rich phase (pure glycerol has a glass transition of −78 °C (Standing, Rindlav-Westling, & Gatenholm, 2001)).

The tan δ curve of EVOH also shows two relaxation peaks. The main relaxation is due to the glass transition of EVOH at about 70 °C, which is consistent with the result of DSC, where the dynamic storage modulus decreases significantly. The lower relaxation at about −26 °C is a second relaxation attributed to short pendant branches originating from the olefinic portion of the modified ethylene copolymer, which is also reported by others (Samios & Kalfoglou, 1998).

Similar to TPAS and EVOH, TPAS/EVOH blends still show two relaxation peaks. The lower relaxations could be attributed to the glass transition of glycerol-rich phase, because the shape of relaxation peaks is more similar to that of TPAS than to that of EVOH. It should be noticed that the secondary relaxation of EVOH is not shown in TPAS/EVOH blends, perhaps because of the small amount of EVOH content in the TPAS/EVOH blends. Or the peak might be overlaid by the relaxation peak originating from the glycerol-rich phase. At the temperature range from 0 to 120 °C, the relaxation peaks originating from the glass transition of starch-rich phase and EVOH have overlapped to one relaxation peak. This relaxation can be ascribed to the cooperant motion of acetylated starch and EVOH which implies that acetylated starch and EVOH have a good miscibility through hydrogen bonds. As the EVOH content increases, the upper relaxation peaks of TPAS/EVOH blends become broader and the peak temperatures shift to higher temperature indicating that the interactions between EVOH and acetylated starch become stronger. Above 0 °C, the dynamic storage modulus (E') increases with the increasing of EVOH content in the TPAS/EVOH blends, which is consistent with the result of tensile strength.

3.3. Differential scanning calorimetry

DSC second-heating results of TPAS, EVOH and TPAS /EVOH blends are shown in Fig. 3. No transition arising from

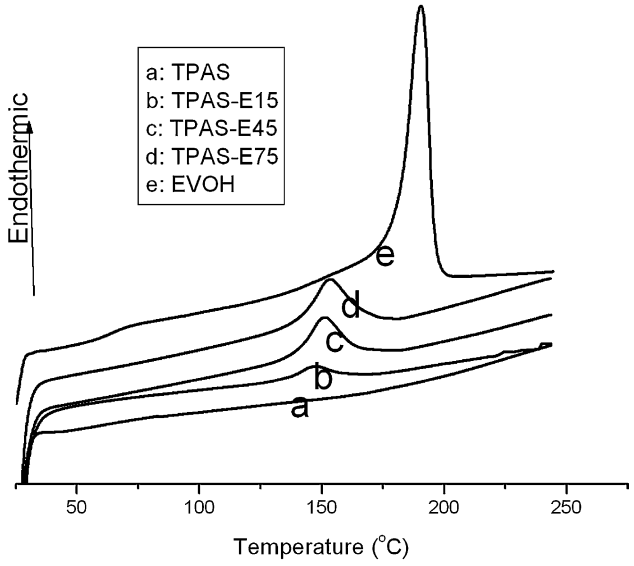

Fig. 3. The heating flow cures obtained by DSC second heating scans.

Table 2
The melting temperature and enthalpy of melting for the samples

Component	TPAS	TPAS-E15	TPAS-E45	TPAS-E75	EVOH
T_m (°C)	None	146.33	150.82	153.04	190.42
ΔH (J/g)	None	35.06	41.01	43.41	84.27

TPAS can be seen from the heat-flow curves because of the low sensitivity of DSC measurement so all transitions (melting, glass transition) observed by DSC should be assigned to EVOH. A clear EVOH glass transition (about 69 °C) is observed in the EVOH DSC curve but not in the TPAS/EVOH blends. These results are consistent with the study of native starch/EVOH blend by Stenhouse and Ratto (1997). It could be due both to the lower concentration of EVOH and to the interactions between the acetylated starch and EVOH, which appears to broaden the glass transition observed by DMTA. More information about the glass transitions of the TPAS, EVOH and TPAS/EVOH blends has been discussed above through the analysis of DMA results. Table 2 shows the EVOH melting temperature (T_m) and melting enthalpy (ΔH) normalized to the EVOH content for TPAS, EVOH and the TPAS/EVOH blends. The T_m and ΔH of the melting peak are significantly higher in the pure EVOH than in the TPAS/EVOH blends, which also indicate that there are interactions between TPAS and EVOH which interrupt the crystallization of EVOH.

3.4. Thermogravimetry analysis

Fig. 4 presents the TGA experimental results of TPAS/EVOH blends. As for TPAS, considering that the boiling point of glycerol is above 100 °C, mass loss below 100 °C should be ascribed to water loss. The mass loss from 100 °C to the onset decomposition temperature is related to the volatilization of both water and glycerol. A significant mass loss occurs within the temperature range of 280–350 °C due to the pyrolytic

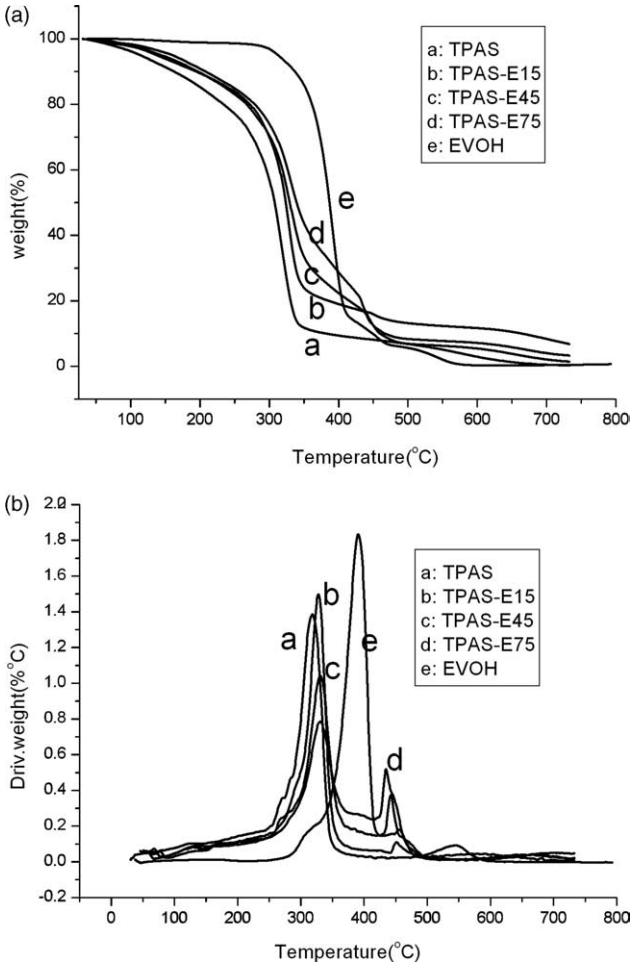

Fig. 4. Thermogravimetric curves of TPAS, EVOH and TPAS/EVOH blends: (a) weight versus temperature, (b) deriv. weight versus temperature.

volatilization of acetylated starch. According to some opinions about native starch (Chandra & Rustgi, 1997), the weight loss observed in this temperature range deals with the 1,6 bond formation between two chains of glucose units or with intermolecular dehydration to form leavoglucosan, and some volatile products, such as carbon dioxide, other lower aldehydes, methylfuranes and ketones among this temperature range. A gradual mass loss above this temperature to 800 °C can be assumed as char. The thermal decomposition of TPAS/EVOH blends is similar to TPAS except for adding the thermal decomposition of EVOH above about 400 °C.

Pure EVOH has the best thermal stability and its initial decomposition temperature (IDT) is about 360 °C. The IDT of the TPAS/EVOH blends is also higher than TPAS, indicating that EVOH can increase the thermal stability of acetylated starch. Fig. 4(b) shows the derivative weight of TPAS/EVOH blends with respect to temperature. Both TPAS and EVOH have one main peak, and the peak temperature is about 320 °C for acetylated starch and 390 °C for pure EVOH. However, all the TPAS/EVOH blends have two peaks, one for the acetylated starch in the TPAS/EVOH blends and the other for the EVOH.

Furthermore, with increasing EVOH content in TPAS/EVOH blends, the peak of derivative weight for acetylated starch

moves to higher temperature. The peak temperatures for EVOH decomposition in blends are higher than that for pure EVOH too. This result also indicates that there are molecular interactions between EVOH and acetylated starch in TPAS EVOH blends.

4. Conclusions

In this study, acetylated starch was used to prepare thermoplastic materials that are expected to be degradable in the environment. Degradable synthetic polymer-EVOH was blended with TPAS to improve the mechanical properties. The results show that with the increasing of EVOH content, the mechanical properties of TPAS/EVOH blends are enhanced significantly compared with TPAS. DMA and DSC results indicate that molecular interactions exist between TPAS and EVOH, which can increase the miscibility of TPAS and EVOH and interrupt the crystallization of EVOH. TGA results show that EVOH can improve the thermal stability of TPAS too.

References

Chandra, R., & Rustgi, R. (1997). Biodegradation of maleated linear low-density polyethylene and starch blends. *Polymer Degradation and Stability*, *56*(2), 185–202.

Forssell, P. M., Mikkila, J. M., Moates, G. K., & Parker, R. (1998). Phase and glass transition behaviour of concentrated barley starch–glycerol–water mixtures, a model for thermoplastic starch. *Carbohydrate Polymers*, *34*(4), 275–282.

Fringant, C., Desbrieres, J., & Rinaudo, M. (1996). Physical properties of acetylated starch-based materials: Relation with their molecular characteristics. *Polymer*, *37*(13), 2663–2673.

Fringant, C., Rinaudo, M., Foray, M. F., & Bardet, M. (1998). Preparation of mixed esters of starch or use of an external plasticizer: Two different ways to change the properties of starch acetate films. *Carbohydrate Polymers*, *35*(1–2), 97–106.

Gonzalez, Z., & Perez, E. (2002). Effect of acetylation on some properties of rice starch. *Starch-Starke*, *54*(3–4), 148–154.

Lawal, O. S., & Adebowale, K. O. (2005). Physicochemical characteristics and thermal properties of chemically modified jack bean (*Canavalia ensiformis*) starch. *Carbohydrate Polymers*, *60*(3), 331–341.

Lee, S. H., Kim, D. J., Kim, J. H., Lee, D. H., Sim, S. J., Nam, J. D., et al. (2004). Compatibilization and properties of modified starch–poly(lactic acid) blend. *Polymer-Korea*, *28*(6), 519–523.

Liu, Z. Q., Yi, X. S., & Feng, Y. (2001). Effects of glycerin and glycerol monostearate on performance of thermoplastic starch. *Journal of Materials Science*, *36*(7), 1809–1815.

Lorcks, J. (1998). Properties and applications of compostable starch-based plastic material. *Polymer Degradation and Stability*, *59*(1–3), 245–249.

Ma, X. F., Yu, J. G., & Jin, F. (2004). Urea and formamide as a mixed plasticizer for thermoplastic starch. *Polymer International*, *53*(11), 1780–1785.

Miladinov, V. D., & Hanna, M. A. (1999). Physical and molecular properties of starch acetates extruded with water and ethanol. *Industrial and Engineering Chemistry Research*, *38*(10), 3892–3897.

Samios, Costas. K., & Kalfoglou, Nios. K. (1998). Compatibilization of poly(ethylene-co-vinyl alcohol)(EVOH) and EVOH/HDPE blends with ionomers. Structure and properties. *Polymer Journal*, *39*(16), 3863–3870.

Shogren, R. L. (1996). Preparation, thermal properties and extrusion of high-amylose starch acetates. *Carbohydrate Polymers*, *29*(1), 57–62.

Standing, M., Rindlav-Westling, A., & Gatenholm, P. (2001). Humidity-induced structural transitions in amylose and amylopectin films. *Carbohydrate Polymers*, *45*(3), 209–217.

Stenhouse, P. J., & Ratto, J. A. (1997). Structure and properties of starch/poly(ethylene-co-vinyl alcohol) blow films. *Journal of Applied Polymer Science*, *64*(13), 2613–2622.

Wu, C. S. (2003). Physical properties and biodegradability of maleated-polycaprolactone/starch composite. *Polymer Degradation and Stability*, *80*(1), 127–134.

Zeng X. C., Liu B. L., & Li K. F. (1999). Effect of high speed stirring on the properties of starch/PVA blend solution. *Acta Polymerica Sinica*, (1), 68–73.