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Improving the Processing Ability and Mechanical Strength of Starch/Poly(vinyl alcohol) Blends through Plasma and Acid Modification

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Summary: In this study, maleic anhydride (MA), and citric acid (CA) used as the processing additive and plasma treatment to improve the processing ability and mechanical strength of biodegradable starch/poly (vinyl alcohol) (PVA) blends were studied. The melt flow index (MFI) of starch/ glycerol/PVA (300g/60g/80g) blend was increased from 2.3g/10min to 32.7g/10min by adding 3g of MA and to 130 g/10min by adding MA and plasma treatment. The tensile strength of starch/glycerol/PVA blend increased from 3.48 to 6.21 MPa by adding 1.5g of MA and 1.5g of CA, while it increased to 6.26 MPa by plasma treatment. Esterification reaction which was evidenced by FTIR has been showed to improve the compatibility between starch and PVA when MA was dissolved into glycerol and glycerol grafted onto plasma pretreatment PVA. Thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) imaging were used to study the morphology of extruded blends.

Keywords: biodegradable; citric acid; maleic anhydride; starch; thermogravimetric analysis (TGA)

Introduction

Synthetic polymers, made from petrochemical industry and used in many technological applications, have given a serious impact for waste disposal. The main path to solve this problem is the use of biodegradable plastics. These plastics from renewable resources can be able to oxidize to transform into carbon dioxide, water, and biomass by certain bacteria or fungi. Generally, biodegradable polymers from renewable resources can be classified into three groups[1]: (1) nature polymers, such as starch,[2–4] and cellulose[5]; (2) biodegradable synthetic polymers, such as PVA,[6–8] and polylactic acid (PLA)[9]; (3) polymers from microbial fermentation, such as polyhydroxybutyrate (PHB).[10]

Starch is a widely useful material for making biodegradable plastics, but pure starch lacks the tensile strength, processability and dimensional stability. To improve some of these drawbacks, blending of starch or its derivatives with various thermoplastic polymers[11–12] and adding plasticizers have been investigated enormously. Many studies involving blends of starch and PVA have shown that PVA imparted significant strength to starch melts allowing for easier processing and improved product stability.[13–14] Increasing the content of plasticizer, such as glycerol and water,[14–15] causes a decrease of glass-rubber transition temperature (Tg), can advance the processing property of starch and its blends. Besides, some modification or techniques, i.e. plasma, irradiation or acid treatment,[16–18] can also enrich the mechanical property of starch and its blends.

In this work, various blends of PVA and starch were prepared by single-screw extruder to demonstrate the promotion of processing and mechanical properties of starch/PVA biodegradable materials. Glycerol and water were used as plasticizers. Chemical reaction of PVA and glycerol was

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evidenced by FTIR measurement after plasma treatment. Acid modification by maleic anhydride and citric acid could enhance the compatibility of PVA and starch. The results corresponded well with the processing and mechanical properties.

Experimental Part

Materials

Commercial PVA (BC-05, Chang-Chun Petrochemical Co., Ltd, ROC) was produced at polymerization degree of average 300 and hydrolysis degree of 74%. Native tapioca starch, unmodified of food grade, was dried at 100 °C for three hours before processing. Glycerol, MA and CA were obtained from Wako Pure Chemical Industries, Ltd. and deionized water was used for the solvent of PVA.

Blends

After studying several blends of different composition, the chosen detail compositions of abbreviations of blends were shown in Table 1.

PVA grains were dissolved in boiling water, and stirred continuously for 15 minutes. Added glycerol into the PVA solution and kept stirring to form homogeneous mixture at 100 °C for 20 minutes. Then the mixture was poured into the dried starch and beaten up by mixer about 20 minutes and extruded by single screw extruder ($\psi = 25$mm, L/D = 32) through four-step temperatures (80, 95, 105 and 100 °C) controlled and rotating speed of 20 rpm. The extruded blend was A sample. The same process was used for B to F samples except the acid and plasma modification. The glycerol used in B sample was adding MA and preheated at 90 °C for 30 minutes. The CA used in C sample was added in boiling water and then mixed with PVA. In D sample, CA was added in boiling water and MA was treated like in B sample. In E sample, PVA grains were pretreated by argon plasma equipment operating at 40 watts for 3 minutes. The self-made rotary argon plasma equipment and its conditions used for polymer substrates are similar to those reported in our earlier work.[19] In F sample, PVA grains were pretreated by argon plasma and MA was treated like in B sample.

Table 1.
The detail compositions of abbreviations of blends.

Name	PVA	DI water[b)]	Glycerol	MA	CA	Starch
A	80	20	60	0	0	300
B				3	0	
C				0	3	
D				1.5	1.5	
E[a)]				0	0	
F[a)]				3	0	

unit: gram

[a)]: PVA was treated by plasma treatment with 40W; 3 mins.

[b)]: deionized water.

Characterization

The plasma PVA film was molded PVA film dried at 45 ± 5 °C in a vacuum oven for 24 hours and then treated by argon plasma equipment operating at 40 watts for 3 minutes. Plasma PVA film reacted with glycerol was performed by the plasma PVA film steeping in hot glycerol for twenty minutes in the air, then washed with alcohol in order to remove surplus glycerol sufficiently. These two films were recorded at ambient temperature using a Micro-FTIR spectrometer (MFT-2000, JASCO, Japan) at a resolution of 4 cm^{-1} in the range 650–4000 cm^{-1}.

Thermogravimetry analysis (TGA) was carried out with a thermal analyzer (model 2050, TA, America). The samples, size/weight varied from 10 to 12 mg, were maintained at 35 °C for three minutes and then heated from 35 to 600 °C at a heating rate of 10 °C /min and an air gas flow rate of 90 cm^3/min.

An Universal Test (Model 4400, Instron, UK) was used to measure the tensile strength and elongation of the composites according to the standard procedure described by ASTM D638-99. The cross-head load was 500Kg and the extending speed was 10 mm/min. Six specimens were tested for each PVA/starch blend. The tensile strength and elongation values of the PVA/starch blends were determined by the average of six values.

Morphologies of the blends were studied by Scanning electron microscope (SEM) scanning cryo surfaces. Cryo fracture surfaces were prepared by immersing the specimens in liquid nitrogen till breaking spontaneously. The broken surfaces were coated with a thin layer of gold (coating 3 min) and then monitored by SEM (JSM-6300, JEQL).

Results and Discussion

Acid Modification

Melt Flow Index (MFI) is the output rate (flow) in grams that occurs in 10 minutes through a standard die. It is well known that the MFI of a polymer or blends is critical to anticipating and controlling its processing ability. The MFI of A to F samples, determined by the average of the five measurements, is shown in Figure 1. The MFI of the samples exhibits in the order: F > B > C > E > D > A. A sample shows the MFI of unmodified starch/PVA blend is poor. It can be improved significantly by acid modification and plasma treatment. The effect of plasma treatment will be discussed later.

Figure 2 shows thermogravimetry analysis of samples shows three decomposition stages at various temperatures ranging from 35 to 600 °C. Water and glycerol are mainly volatile materials of elimination within the first stage. High molecule weight starch and the crystalline of PVA and starch are decomposed within the third stage. The additive of MA and CA significantly reduce the degradation temperature of starch/PVA blends means MA and CA can decompose the macromolecular starch to enhance the plasticity of blend successfully. It is possible that the degradation temperature of B sample is lower than that of C within the third stage because MA is more acid than CA. The MFI of sample B is much better than C not only because MA is more acid than CA but also MA can react with glycerol.[20] The esterification reaction of glycerol with MA enhanced the plasticization ability of glycerol. As a result, the MFI of starch/PVA blend is increased from 2.3g/10min to 32.7 g/10min. Figure 3 shows the SEM micrographs of liquid nitrogen fracture surface of A-D samples, in which the granular phase belongs to the starch. The smaller or less granular phase implies the more compatibility of the system. The compatibility of the starch/PVA blends exhibits in the order as B > C > D > A is accordant with the result of MFI test.

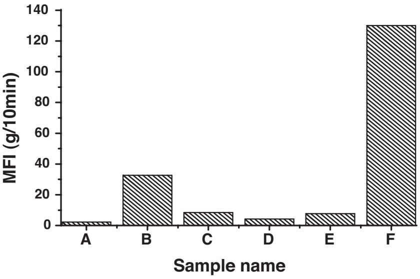

Figure 1.
The melt flow indices of different Starch/PVA blends.

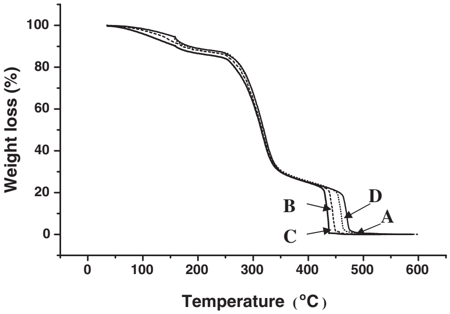

Figure 2.
TGA curves of A, B, C, D blends.

The stress-strain curves of blends chosen by approaching the average value of tensile test are shown in Figure 4. Compared to A sample, the tensile elongation of C is increased because citric acid can form strong interactions (hydrogen bonds) with starch and weaken the interaction among starch molecules.[18] For B sample, the esterification of MA and glycerol can lubricate the blend to increase the elongation but loss the stress. Figure 5 shows the

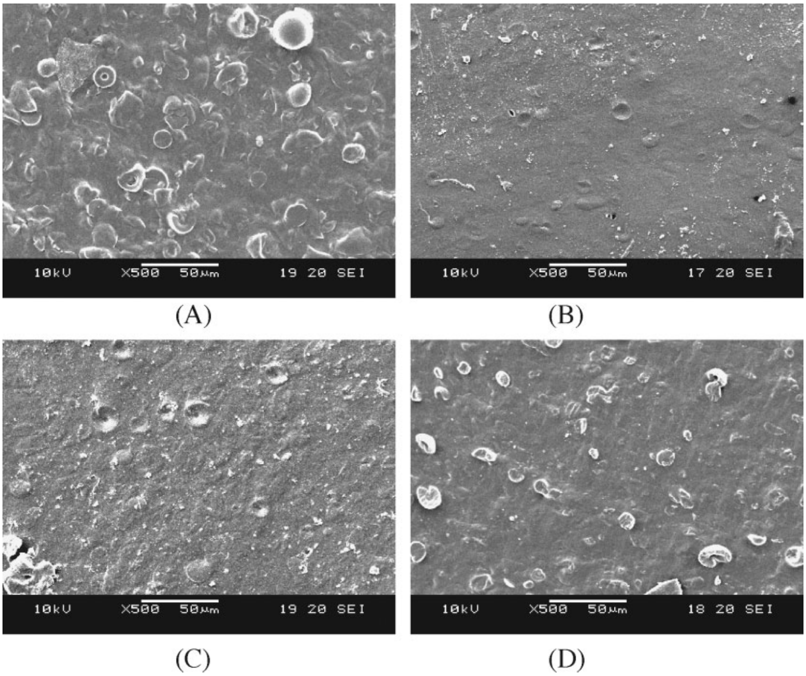

Figure 3.
SEM micrographs of the liquid nitrogen fracture of A, B, C and D blends.

tensile strength of six different starch/PVA blends. It is interesting that the stress of D sample is much higher than A, B and C. It is possible that citric acid construct stronger hydrogen bonds interacting with the esterification of MA and glycerol to improve the tensile stress.

Plasma Treatment

PVA after plasma treatment can react with glycerol to improve the processing and mechanical properties of starch/PVA blends. Figure 6(A) is the FTIR spectrum of PVA film treated by argon plasma. The peak at 1743 cm^{-1} is corresponding to the carbonyl of vinyl acetate groups in partially hydrolyzed BC-05. As the spectra of plasma PVA film reacted with glycerol shown in Figure 6(B), the original characteristic peak of residual acetate groups shifts to 1745 cm^{-1} and a new strong peak at 1716 cm^{-1} shows various carbonyl groups

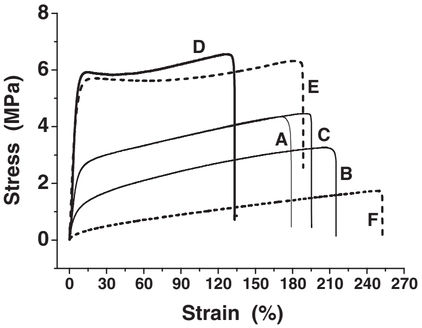

Figure 4.
The S-S curves of different Starch/PVA blends.

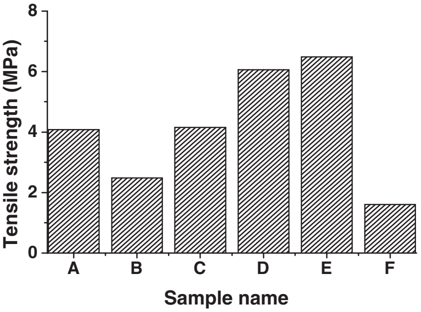

Figure 5.
The tensile strength of different Starch/PVA blends.

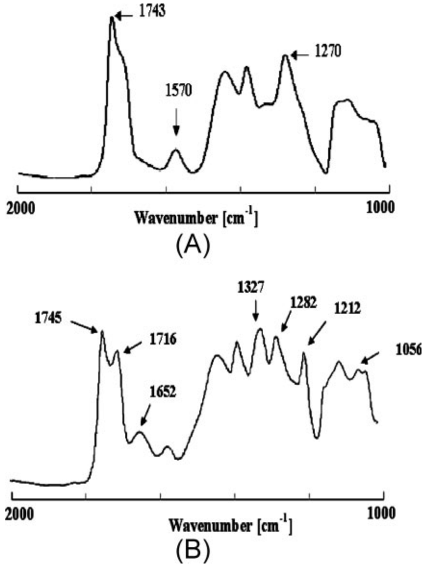

Figure 6.
FTIR spectrum of (A) plasma PVA film and (B) plasma PVA film reacted with glycerol.

attributed to the esterification reaction of plasma PVA and glycerol. The peaks at 1056, 1212, 1327, and 1652 cm^{-1} shown in Figure 6(B) are attributed to the characteristic peaks of glycerol. As a result, the chemical reaction side at 1716 cm^{-1} shows glycerol can be grafted onto plasma PVA producing carbonyl groups. Due to the esterification reaction of plasma PVA and glycerol, the PVA/starch blend is formed into hard, tough and strong materials. The tensile strength of blend increases from 3.48 (sample A) to 6.26 MPa (sample E). The sample E also has significant yield point and necking during stretching as shown in Figure 4. For the application in mechanics of materials, high yield point represents an upper limit to the load applied to a structure and necking is a mode of ductile flow of a material in tension. Necking after the yield point means that there must be a strain hardening process increasing the modulus and tensile strength.[21] In other words, though the elongation of sample E decreased slightly compared to sample A, the yield strength, tensile strength and toughness increased greatly.

Figure 1 shows the highest MFI is sample F (130 g/10 min). It can be explained that (1) MA react with glycerol to lubricate the slippage among starch molecules. (2) the esterification reaction of plasma PVA and glycerol facilitate the compatibility of PVA and starch molecules. (3) MA decomposes the macromolecular starch to enhance the plasticity of starch/PVA blend. These factors improving the blend increase not only the MFI but also the tensile elongation (see Figure 4). If MFI is as high as sample F, the starch/PVA blend can be applied to the field of injection molding in the future.

Conclusion

In this study, two methods, acid modification and plasma treatment, are used to improve the processing ability and mechanical properties of starch/PVA blends. The melt flow index of starch/PVA blend is increased from 2.3g/10min to 8.5 g/10min by adding citric acid, to 32.7 g/10min by adding MA and to 130 g/10min by adding MA and plasma treatment. Glycerol esterifies with MA and plasma PVA greatly modify the compatibility of PVA and starch molecules to enhance the processing ability of starch/PVA blends. The tensile strength of starch/PVA blend increases from 3.48 to 6.21 MPa by adding MA and CA, while it increases to 6.26 MPa by plasma treatment. The yield strength and modulus also increases significantly but elongation decreases.

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