

Plasma Treatment for Enhancing Mechanical and Thermal Properties of Biodegradable PVA/Starch Blends

Sung-Yeng Yang, Chi-Yuan Huang

Department of Materials Engineering, Tatung University, Taipei 104, Taiwan

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ABSTRACT: Two series of biodegradable polyvinyl alcohol (PVA)/starch blends, i.e., PVA with/without plasma treatment (PP/P series), were produced by single-screw extruder. The influences of plasma pretreatment and PVA content on the tensile properties, thermal behaviors, melt flow index, and biodegradability of blends were investigated. PVA pretreated by plasma (PPVA) reacted with glycerol was found not only to mechanically strengthen the PPVA/starch blend but also to improve the compatibility of PPVA and starch. Compared with PVA/starch blends, the melt flow indices of PPVA/starch blends were improved significantly by 200–300% and their tensile strength also increased two-to-three-fold. Thermogravimetry analysis (TGA) showed that the thermal stability of PPVA/starch (85/300g) blend

was better than PVA/starch blend at processing temperature and outperformed than PVA and starch at high temperature. Both the PPVA/starch and PVA/starch blends finished biodegradation within 9–10 weeks in soil burial tests. The esterification reaction of PPVA and glycerol was characterized by FTIR spectroscopic measurement and TGA test. The morphologic evolutions of the blend during biodegradation were investigated carefully by scanning electron microscope (SEM) imaging. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2452–2459, 2008

Key words: polyvinyl alcohol (PVA); polysaccharides; thermogravimetric analysis (TGA); blends; biodegradable; plasma

INTRODUCTION

Plastics made from petrochemical industry have been widely used throughout the world, and its waste increases significantly since many years. Nowadays the disposal of waste plastics has become a serious environmental problem. Therefore, the development of novel plastics that can be degraded by microorganisms in soil/compost has been endeavored recently. The current research about biodegradable materials has been focused on four directions: namely, synthetic polymer/starch blends such as PE/starch,^{1–5} degradable polymers such as PVA, PCL, and PLA,^{6–10} degradable polymer/starch blends e.g., PCL/starch, PLA/starch and PVA/starch^{11–16} and pure starch-based materials.^{17–20} It seems that the latter two directions are more feasible because of the biodegradability and cheapness of starch.

Polyvinyl alcohol is a kind of water-soluble synthetic polymer with a broad range of applications. Because of solubility by water, no toxicity, and biodegradation by bacteria and fungi,^{8,21–24} PVA which is an excellent biodegradable polymer has been increasingly used as hydrogels, adhesives, and pack-

ing materials. Starch is one of the most abundant polysaccharides but packaging films composed entirely of starch lack the tensile strength and rigidity to withstand the stresses to which many packaging materials are subjected necessarily. PVA/starch blends can offer a good alternative for developing degradable materials, which often consist of glycerol and water as plasticizer. Also, they have been widely used to fabrication hydrogels,^{25,26} sheets, and films.^{13,14,24}

“Mater-bi”, i.e., biodegradable plastics produced through physically blending PVA with starch has been commercialized and used successfully for several years. However, plasma and irradiation treatment can improve the mechanical properties of PVA/starch blends, since they can cause a chemical reaction or graft functional group on to PVA backbone without adding initiator or chemical substances.^{13,19,25–27} In the past decade, our research group has extensively studied the mechanism of modifying the polymer surface by plasma.^{2,28–31} In this work, two series of PVA/starch and PPVA/starch blends were prepared by single-screw extruder to produce PVA/starch biodegradable materials. The chemical reaction of plasma pretreated PVA and glycerol was evidenced by FTIR measurement and thermogravimetry analysis (TGA). The optimal blending ratio for the mechanical properties, morphology of and biodegradability of the PVA/starch blends were also studied in detail.

Correspondence to: C.-Y. Huang (cyhuang@ttu.edu.tw).

EXPERIMENTAL

Materials

Commercial PVA (BC-05, Chang-Chun Petrochemical Co., Ltd, ROC) was produced at polymerization degree of average 300 and hydrolysis degree of 74%. The starch used in this study was unmodified native tapioca starch of food grade. It was dried at 100°C for 3 h before processing. Glycerol was obtained from Wako Pure Chemical Industries and deionized water was used for the solvent of PVA.

Argon plasma treatment

In this investigation, we used rotary argon plasma equipment to modify the surface of PVA grains. The self-made equipment and its conditions used for polymer substrates are similar to those reported in our earlier works.^{2,28,29} PVA grains were placed into the rotating inner cylinder and then subjected to a plasma treatment. Prior to the plasma treatment, the pressure in the chamber was reduced to 150 mTorr by vacuum pump. The pure argon (99.999%) gas was then introduced into the chamber and maintained at a pressure of approximately 250 ± 2 mTorr. After the pressure became stable, the plasma treatment was carried out by RF power generator operating at 40 W for 3 min. PVA grains were denoted as PPVA grains after this argon plasma treatment.

Blends

At first, PVA grains were dissolved in boiling water, and stirred continuously for 10 min. The mass ratio of the water to the PVA is 1.5. Secondly, added glycerol into the PVA solution and kept stirring to form homogeneous mixture at 100°C for 20 min. Finally, the mixture was poured into the dried tapioca starch and beaten up by mechanical mixer about 20 min to form a lamellar PVA/starch mixture. The mixture was extruded by single screw extruder ($\psi = 25$ mm, $L/D = 32$). The extrusion process was controlled at four-step temperatures: 80, 95, 105, and 100°C. The rotating speed of screw was maintained at 20 rpm. The extruded PVA/starch blends were P series blends. In PP series blends, the same process was used except PVA grains were replaced by PPVA grains. The detail compositions of abbreviations of blends were shown in Table I.

FTIR spectroscopic analysis

The pure PVA film was PVA grains dissolved in little hot deionized water and coated on the aluminum foil as thin as possible, then dried at $45 \pm 5^\circ\text{C}$ in a vacuum oven for 24 h. PPVA film was dried PVA film after plasma treatment operating at 40 W for

TABLE I
The Detail Compositions of Abbreviations of Blends

Composition	P series				PP ^a series			
	P65	P75	P85	P95	PP65	PP75	PP85	PP95
PVA	65	75	85	95	65	75	85	95
DI water ^b	97.5	112.5	127.5	142.5	97.5	112.5	127.5	142.5
Glycerol			60				60	
Starch			300				300	

Unit: g.

^a PVA was treated by plasma with 40 W; 3 min.

^b Deionized water.

3 min. PPVA film reacted with glycerol was performed by the PPVA film steeping in hot glycerol for 20 min in the air, then washed with alcohol to remove surplus glycerol sufficiently. All the films were recorded at ambient temperature using a Micro-IR spectrometer (MFT-2000, JASCO, Japan) at a resolution of 4 cm^{-1} in the range $650\text{--}4000\text{ cm}^{-1}$.

Thermogravimetric measurements

TGA was carried out with a thermal analyzer (model 2050, TA, Germany). The samples, size/weight varied from 10 to 12 mg, were maintained at 100°C for 3 min and then heated from 100 to 600°C at a heating rate of 10°C/min and an air gas flow rate of $90\text{ cm}^3/\text{min}$.

Tensile test

An Instron Universal Test Machine Model 4400 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 500 kg 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.

Scanning electron microscope imaging

To observe the morphology of specimens, the specimens were coated with a thin layer of gold (coating 3 min) and then monitored by scanning electron microscope (SEM) (JSM-6300, JEQL).

Soil burial test

Specimens molded in form of square plates with dimensions of $3 \times 3\text{ cm}^2$ and thickness of 1 mm were buried perpendicularly in the compost. The soil burial test included the sample conditioning at ambient temperature and 30% water content in the preparation box ($60 \times 40 \times 20\text{ cm}^3$). Specimens were

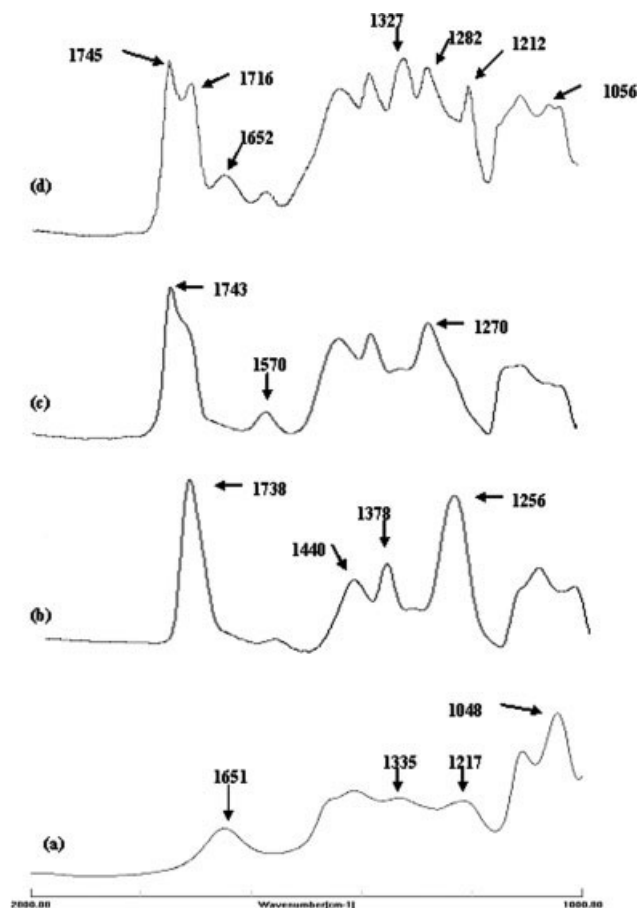


Figure 1 The FTIR spectrum of (a) glycerol, (b) pure PVA, and (c) PVA after plasma treatment, (d) PVA after plasma treatment and reacted with glycerol.

placed at 3 cm beneath the surface and separated from each other in a distance of 3 cm. After removal from the compost, samples were cleaned carefully and dried at $45 \pm 5^\circ\text{C}$ in a vacuum oven for 24 h. Samples were then allowed to equilibrate in a desiccator before weighting. The weight of each sample was routinely measured before and after degradation.

RESULTS AND DISCUSSION

In this study, the weight of starch and glycerol are fixed at 300 and 60 g. Table I shows the detailed compositions of abbreviations of blends. The effects of PVA and PPVA content were investigated.

FTIR analysis

The spectra of glycerol, pure PVA film, and PPVA film were studied and compared with PPVA film reacted with glycerol. All the spectra are presented in Figure 1.

Figure 1(a) is the FTIR spectrum of glycerol. The peaks of the spectrum at 1217 and 1335 cm^{-1} are attributed to C—H deformation vibration of secondary alcohol and 1048 cm^{-1} is attributed to the strong C—O stretching vibration of primary alcohol. Figure 1(b) is the spectrum of pure PVA film. It shows C—H deformation vibration of secondary alcohol peaks at 1256, 1378, and 1440 cm^{-1} . The peak at 1738 cm^{-1} is corresponding to the carbonyl of vinyl acetate groups in partially hydrolyzed BC-05.^{6,14} Figure 1(c) is the FTIR spectrum of PPVA film. The peaks are similar to pure PVA film, but the absorption band at 1743 cm^{-1} becomes wider and the peak at 1570 cm^{-1} is stronger. This can be interpreted that the plasma reaction is concentrated in carbonyl groups.⁶ As the spectra of PPVA film reacted with glycerol [see. Fig. 1(d)], 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 attributed to the esterification reaction of PPVA and glycerol. The peaks at 1056, 1212, 1327, and 1652 cm^{-1} shown in Figure 1(d) 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 PPVA producing carbonyl groups after plasma treatment.

TGA

Figure 2 shows TGA of P85, PP85, pure PVA, Starch, and glycerol. P85 shows three decomposition stages from 100 to 600 $^\circ\text{C}$. According to the TGA curves, approximately between 130 and 280 $^\circ\text{C}$ is related to the first stage of degradation and glycerol is mainly volatile material of elimination. The second and the third thermal decomposition stage of P85 are 280–370 $^\circ\text{C}$ and 460–540 $^\circ\text{C}$. However, PP85 shows only two decomposition stages in terms of the TGA

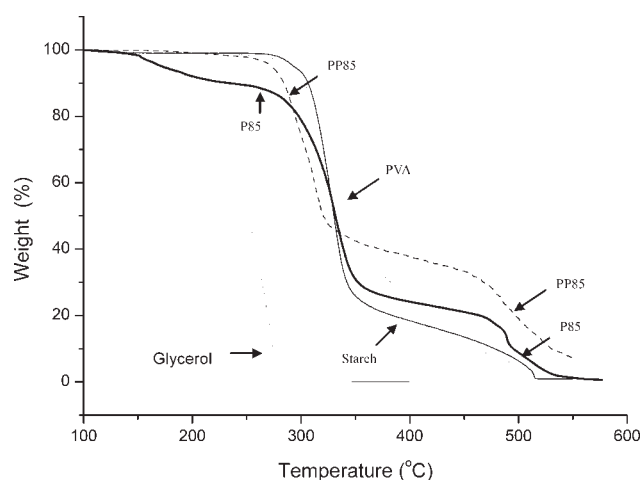


Figure 2 TGA curves of P85, PP85, PVA, Starch, and glycerol.

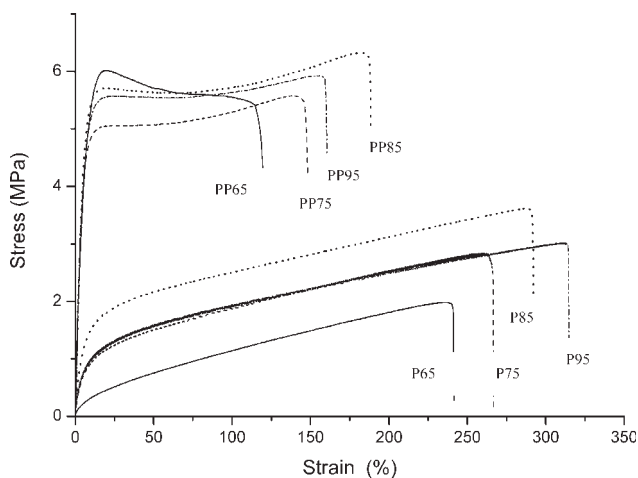


Figure 3 Stress-strain curves of P and PP series blends.

curves within 100–600°C. It is interesting to note that glycerol is not eliminated under 280°C so there is no obvious weight loss in PP85 during 130 to 280°C. This phenomenon proves again glycerol reacted with PPVA in PP series blends, while glycerol and PVA in P series are simply mixed by physics. The temperature range required for processing or blow extrusion of PVA/starch blends falls within 130–230°C depending on the type of polymer used and the extruders.⁶ Therefore, this part of the TGA curve is very important for the evaluation of blends thermal stability. Since glycerol reacted with PVA, the thermal stability during the temperature range for processing of PP series blends will be much better than P series blends. In this study, the thermal stability of blends could be increased by using plasma to treat PVA before compound.

T95 and T30 are defined as the temperature of 5 and 70% weight loss in TG analysis in this study. T95 of P85, PP85, PVA, and starch are situated in 172.5, 273.3, 290.2, and 293.5°C. T30 of P85, PP85, PVA, and starch are situated in 352.3, 468.2, 382.4, and 342.1°C. It can be confirmed by TG analysis that the thermal stability of PP85 is much better than that of P85 during processing temperature and even better than that of PVA and starch respectively, during high temperature exceeds 400°C.

Mechanical properties measurement

The stress-strain curves of blends chosen by approaching the average value of tensile test are shown in Figure 3. These curves show that the visco-elastic behavior of PP series blends is quite different from that of P series blends. PVA/starch blends are soft and weak materials with high elongation and low tensile strength. However, as PVA was pretreated by plasma (glycerol reacted with PPVA), the PPVA/starch blends are formed into hard,

tough, and strong materials. PP series blends have significant yield point and necking during stretching as shown in Figure 3. In materials or mechanical engineering, 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.³² In other words, though the elongation of PP series blends decreased slightly, the yield strength, tensile strength, and toughness increased greatly. Improving of a wide margin mechanical properties will contribute the practicability of PVA/starch blends modified by plasma treatment. The comparatively lower elongation to break may be because of higher molecular weight and forming branch of glycerol and PPVA.³²

Mechanical properties of the compression-molded blends (P and PP series) show a dependency on PVA content. Figure 4(a) shows the tensile strength of P series blends increases with increasing PVA content till 85 g and slightly dropped in 95 g. The

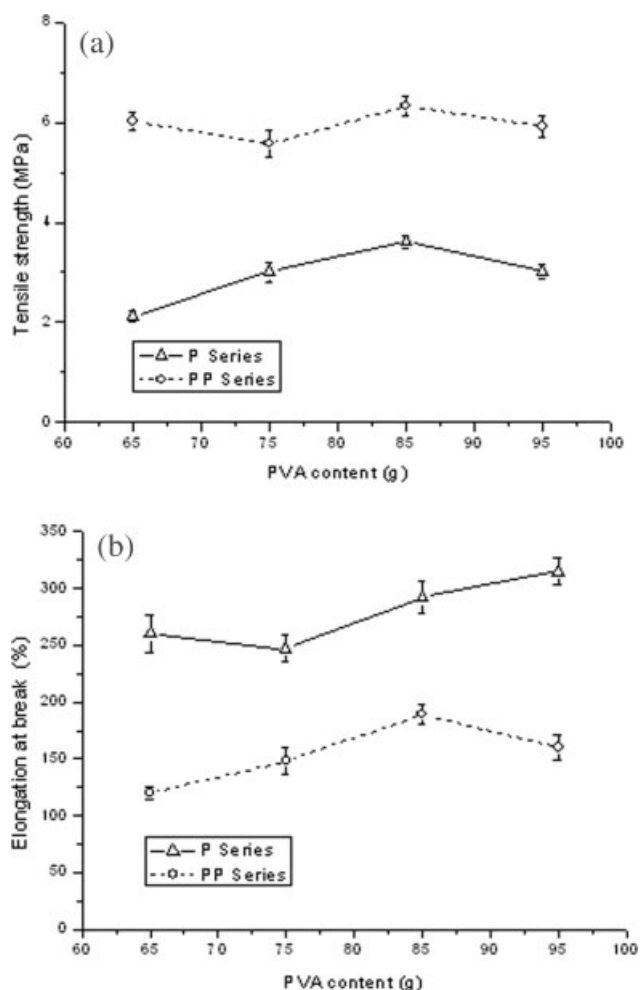


Figure 4 (a) Tensile strength (b) elongation at break of P and PP series blends.

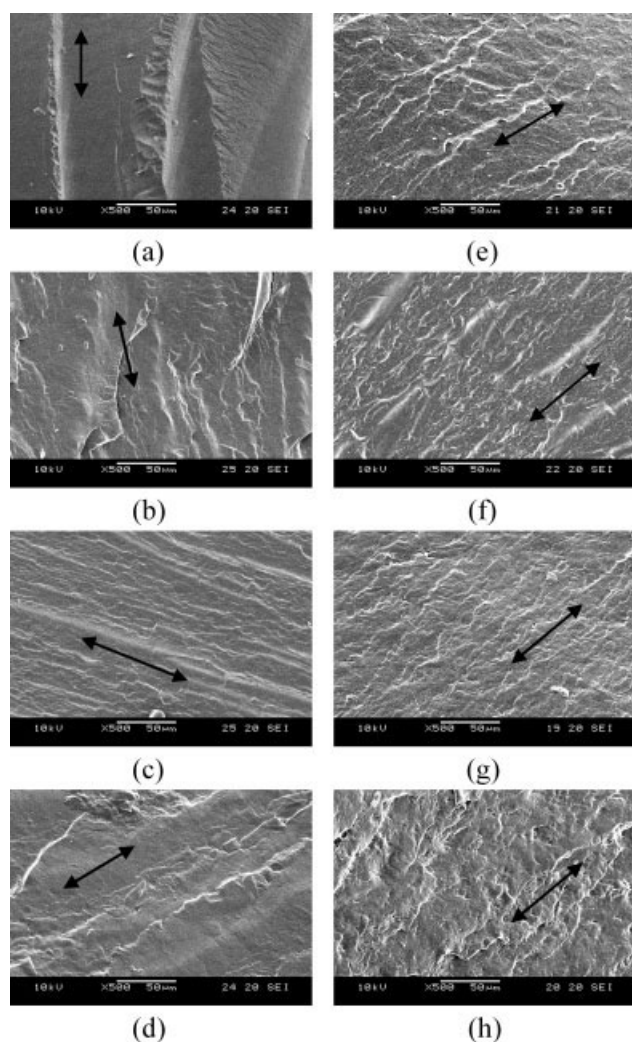


Figure 5 SEM micrographs of the liquid nitrogen fracture perpendicular to the tensile fracture surface: (a) P65; (b) P75; (c) P85; (d) P95; (e) PP65; (f) PP75; (g) PP85; (h) PP95. The direction of tensile stress is signed as the black arrow.

P85 has the strongest tensile strength (3.56 MPa) among the P series. Figure 4(b) shows the break elongation increase with increasing PVA content and the maximum break elongation achieves up to 320%. The tendency of PP series blends is similar to P series, but the tensile strength increase doubly or triply; however, the break elongation decreases slightly. The tensile strength of PP85 is 6.24 MPa; the highest in the pp series. The elongation at break reaches 188%. Our results show the plasma-pre-treated PVA/starch sheet can sustain under higher elongation but it has less tensile strength, compared with the EB-irradiated counterpart reported in previous literature.¹³ In practice, elongation is also one of the most important effects which should be considered in the blow extrusion technology for PVA blends. It is worthwhile to be pointed out that irradiating or plasma treating with the whole PVA/starch

film induce crosslinking reaction will sacrifice the characteristic of elongation.

The obvious increase in the tensile strength of PPVA/starch blends can also be explained by the SEM micrographs at the cross section perpendicular to the fracture surface after tensile test, shown as Figure 5. The density and width of the crack lines could express the magnitude of the tensile strength. Among Figure 5(a-d), P85 is the largest one of tensile strength in P series blends, so the crack lines are thinner and denser. In Figure 5(e-h), the SEM micrographs of PP series blends, many crazes grow up beside the thin cracks shows the greater resistance of PP series blends in the tensile tests. Figure 5(g) demonstrates that the finest resisting pattern of PP85 make the tensile strength up to 6.24 MPa.

Melt flow index

Melt Flow Index (MFI) is the output rate (flow) in grams that occurs in 10 min through a standard die. It is well known that the MFI of a polymer or blends is vital to anticipating and controlling its processing ability. The MFI of P and PP series, determined by the average of five times measured, is shown in Figure 6. The MFI of PVA/starch blends (P series) is lower than 1.14 g/10 min. However, the MFI of PPVA/starch blends (PP series) are obviously higher than those of PVA/starch blends (P series). Figure 6 shows that the MFI of PP85 (4.42 g/10 min) is four times higher than that of P85 (1.14 g/10 min). Since glycerol reacted with PPVA shown as Figure 2(d), the reacted glycerol does not evaporate during compounding and can be dispersed homogeneously in blends. Furthermore, the reacted glycerol induces the plasticization effect during compounding and improves the processability of blends.

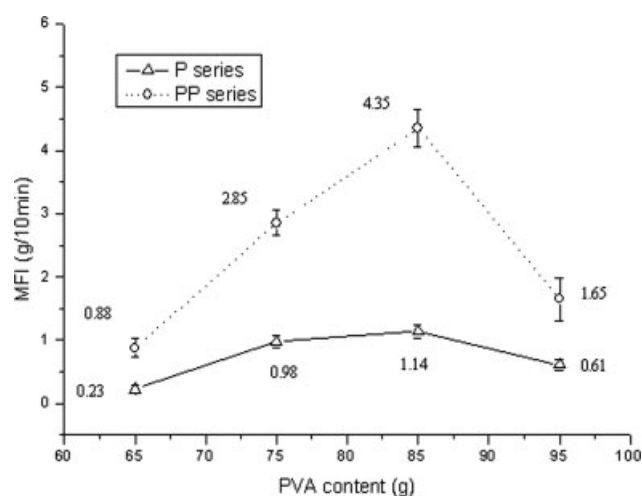


Figure 6 The melt flow indices of P and PP series blends.

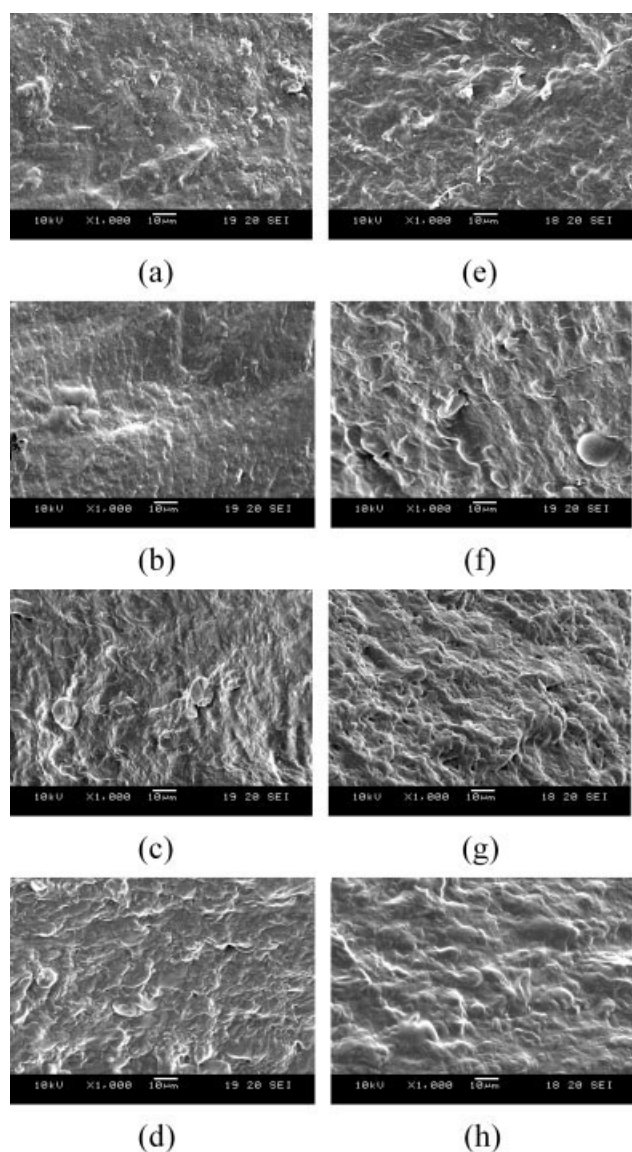


Figure 7 SEM micrographs of the liquid nitrogen fracture surface of P and PP series blends: (a) P65; (b) P75; (c) P85; (d) P95; (e) PP65; (f) PP75; (g) PP85; (h) PP95.

Figure 7 shows the SEM micrographs of liquid nitrogen fracture surface of P and PP series blends. Compared with the loose structure of P series blends, the structure of PP series blends are three-dimensional and entangled. Such morphological changes of PP series should be caused by glycerol and PPVA reaction. The chemical bonding of glycerol and PPVA have not reduced the molecular mobility but enhanced the compatibility of PVA and starch instead. As a result, the glycerol-PPVA can be acted as a good plasticizer and compatibilizer for PVA/starch blends to increase the MFI as well as compatibility.

According to the fracture pattern shown in Figure 5 and entanglement phase in Figure 7, the chemical bonding of glycerol and PPVA have strengthened

the PPVA/starch blends and enhanced the compatibility of PVA and starch as well.

Soil test analysis

In this study, the method of soil burial was used. PVA, starch, and its blend could be exhausted by fungus and bacteria,^{21–24,33–35} but water diffused and swelled would accelerate the weight loss ratio in soil burial tests.³⁶ To prevent tiny water droplet staying on the test samples to dissolve PVA and starch, lower water content was in compost. More importantly, the samples were buried perpendicularly on the ground for acquiring more accurate images from the test, especially for SEM scanning. According to Figure 8, the biodegradation rate of the samples exhibits in the order: P65 > P75 > P85 > P95 > PP series. It can be explained that (1) because the biodegradability of PVA is lower than starch, the biodegradation rate decreases with increasing PVA content; (2) glycerol consumed fast during biodegradation, the initial biodegradation rate of PP series is less than P series because of esterification of glycerol and PPVA. Since all the samples of P series and PP series were biodegraded in compost within 10 weeks, PVA/starch blend is absolutely an excellent biodegradation material.

To gain more information regarding the biodegradability of PVA/starch blends, the change of morphology of the film surface during biodegradation was carried out by SEM microscopy and visual observation. Figure 9(a) shows the homogeneous dispersion of PP85, in which the granular phase belongs to the starch. Water and glycerol which are consumed firstly formed many cracks in the sample and the surface of blends begins to biodegrade during the first week,³⁵ shown in Figure 9(b). The hypha

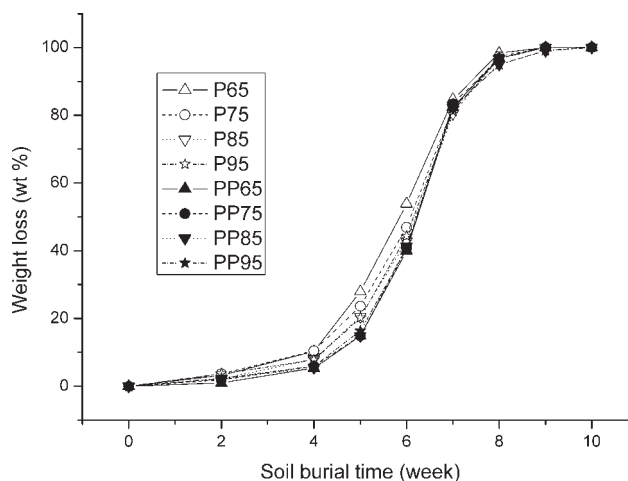


Figure 8 Biodegradation curves of P and PP series samples in soil burial tests.

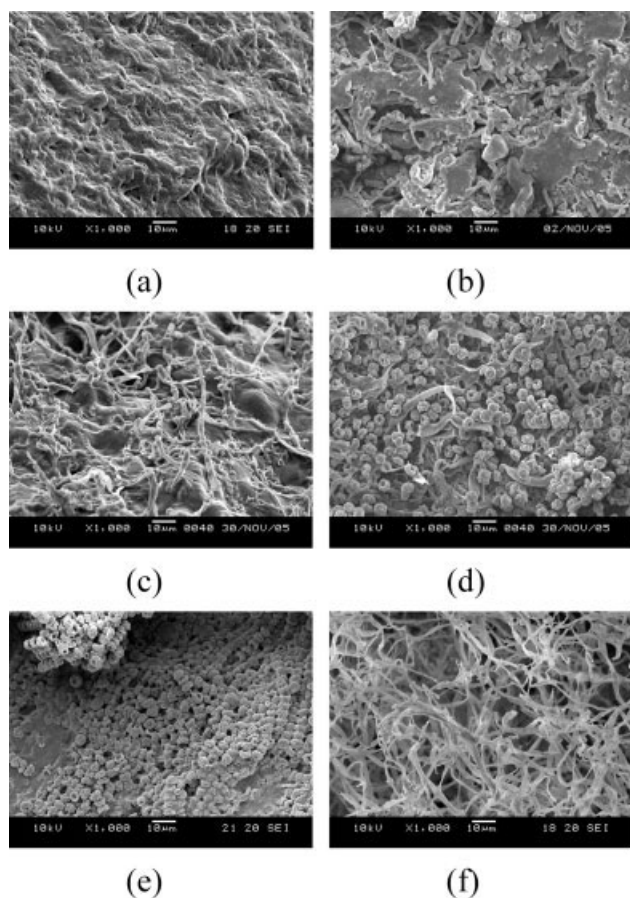


Figure 9 SEM micrographs of PP85 before and after biodegradation: (a) PP85 (b) biodegradation during the first week (c) PP85 biodegraded in the presence of hypha of fungi (d) PP85 biodegraded in the presence of hypha of fungi and bacteria (e) a large amount of bacteria in PP85 (f) mycelium left in PP85 after biodegradation.

of fungi is present in PP85 film isolated from compost after two weeks biodegradation as shown in Figure 9(c). Figure 9(d) shows that the bacteria are present in PP85 film isolated from compost grows together with fungi. After biodegradation for four to five weeks, a large amount of bacteria is present in the PP85 film as shown in Figure 9(e). The diameter of sphere bacterium is about 5 μm . Figure 9(f) shows the mycelium is present in the PP85 film after complete biodegradation.

CONCLUSIONS

We have demonstrated that high density polyethylene treated by plasma can possess large amount of free radicals on the polymer surface.²⁷ In this study, the plasma-pretreated PVA (PPVA) reacted with glycerol, acts as plasticizer and compatibilizer in (PP series) blends to form biodegradable material and therefore exhibits better thermal, processing, and

mechanical (tensile) properties than P series blends of physical mixing. Compared with P85, the MFI of PP85 is improved significantly by more than 300% and its tensile strength also increases twofold. Also, necking after high yield point of PP series blends which were examined by the tensile test have shown that their Young's modulus and toughness increase significantly. Furthermore, the thermal stability of PP85 is much better than that of P85 because glycerol reacts with PPVA and not eliminates during 130–280°C. Soil burial test investigation indicates that all the samples of P series and PP series are biodegraded in compost within ten weeks. Overall, fine biodegradable PPVA/starch blends have good processing ability, thermal stability, and higher tensile strength.

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