# Preparation and Properties of Biodegradable Thermoplastic Starch/Poly(hydroxy butyrate) Blends

**S.-M. Lai,[1] T.-M. Don,[2] Y.-C. Huang[3]**

[1]*Department of Chemical and Materials Engineering, National I-Lan University, I-Lan 260, Taiwan, Republic of China*
[2]*Department of Chemical and Materials Engineering, Tamkang University, Tamsui 25137, Taipei, Taiwan, Republic of China*
[3]*Institute of Materials Engineering, Chinese Culture University, Taipei 111, Taiwan, Republic of China*

Received 5 May 2005; accepted 2 September 2005
DOI 10.1002/app.23085
Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The vital differences using three types of thermoplastic starches (TPS), including potato starch, corn starch, and soluble potato starch, with two different gelatinization degrees to blend with poly(hydroxy butyrate) (PHB) are thoroughly discussed in this study. For blends containing a certain amount of PHB, thermal stability remains in a certain degree. In all cases of this study, mechanical properties of TPS blended with PHB confer higher performance than those of pristine TPS. In particular, a significant increase on tensile strength and tear strength is observed for TPS (potato starch) blended with PHB at low gelatinization degree. A suitable degree of gelatinization of starch is critical to achieve optimum performance. The investigation on the morphological observation partly features the supporting evidence of the above findings. The assessment of biodegradability indicates that the values of water absorption and weight loss increase with increasing treatment period and glycerol content, but decrease with increasing amount of PHB content. Among three types of starches investigated, the TPS (soluble starch)/PHB blend gives the highest level of water absorption and weight loss. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2371–2379, 2006

**Key words:** thermoplastic starch; potato starch; corn starch; poly(hydroxy butyrate); biodegradability

## INTRODUCTION

Biodegradable polymers featuring ecological advantage toward sustainable development have been of great commercial interest due to a growing environmental concern.[1] Biodegradable polymers such as poly(lactic acid) (PLA), poly(hydroxyalkanoate) (PHA), poly(vinyl alcohol) (PVOH), poly(butylene succinate) (PBSU), and so on are available commercial products. In addition, biopolymer derived from annually renewable resources, such as starch, is also rather attractive material due to its low price. However, poor mechanical properties of starch have caused a limitation in practice. Thus, biodegradable blends based on those aforementioned biodegradable polymers and starch have received much attention recently.

Starch, one of most abundant natural food sources from most of plants, has been considered as an attractive biopolymer due to its low cost, low density, nonabrasive nature, biodegradability, and so forth. Starch is primarily composed of amylose and amylopectin. Amylose is a linear polymer of $\alpha$-1,4-linked glucose units, while amylopectin is a highly branched polymer of $\alpha$-1,4-linked chains connected by 1,6-linkages.[2] Griffin in 1975 pioneered to blend granular starch with plastics materials.[3] Unfortunately, native starch generally exists in a granular state because of the inherent hydrogen bonding between adjacent molecules. This in turn fails to disperse starch in an extremely fine scale of size into the plastic matrix. Efforts to face this problem have led to the recent development of thermoplastic starch (TPS) prepared by incorporating suitable amounts of water and/or plasticizers, a process termed "gelatinization."[4] Properties have been considerably improved for synthetic plastics to blend with gelatinized or TPS since then.[5] Unfortunately, a completely degradable blend was often questioned. Thus, numerous works have been investigated regarding the blending of biodegradable polymer with starch,[6–21] including ethylene-*co*-vinyl alcohol (EVOH),[6] thermoplastic polyurethane,[7] PLA,[8] polycaprolactone,[10,11] PBSU,[12,13] and PHB.[14–21]

Among those biodegradable polymers, poly(hydroxy butyrate) (PHB) is one of the bacterially produced PHAs with high molecular weight under a commercial scale. PHB is produced as accumulated intracellular carbon source and energy reservoir, while a variety of bacteria are under a condition of nutrient deficiencies and an excess of carbon source. General structures of PHAs were described in the

*Correspondence to:* S.-M. Lai (smlai@niu.edu.tw).
Contract grant sponsor: ROC Government; contract grant number: NSC 92–2621-Z-197–001.

literature.[22] Because of its extremely high cost, the blends of PHA with starch have been carried out in several studies. Binary blends of PHB were prepared with natural starch, starch–adipate, and grafted starch–urethane derivatives by Innocentini-Mei et al.[14] Godbole et al. have discussed the mechanical properties, thermal stability, glass transition temperature, and melting temperature for the different proportions of PHB and starch.[15] The results revealed that blend films had a single glass transition temperature for all the proportions of PHB and starch tested. Tensile strength was optimum for the PHB: starch ratio of 7:3 (wt/wt). Furthermore, the maximum amount of destructured starch that could be added to the PHB matrix was much higher, at about 40%.[16] Imam et al.[17] pointed out that poly(ethylene oxide) (PEO) could enhance the adherence of starch granules to poly(hydroxy butyrate-*co*-valerate) (PHBV) blends.

Though PHB has been reported to blend with starch in several studies, there were no literatures available in discussing TPS as a matrix reinforced with PHB. This work was undertaken to in depth discuss the effect of PHB content on the physical and mechanical properties of TPS/PHB blends. Three types of starches including potato starch, corn starch, and soluble potato starch (denoted as soluble starch) were gelatinized at different degrees as TPSs. The thermal stability of blends was characterized with thermogravimetric analyzer. Tensile strength and tear strength were evaluated and elucidated by morphology study, through a scanning electron microscope. Biodegradability was also assessed in a soil environment.

## EXPERIMENTAL

### Materials

The materials used were PHB and three types of starches. PHB with the melting temperature of 172°C was supplied from Aldrich Chemical Corn starch (Amyral®) was purchased from African Products Ltd. Potato starch (Rose®) was provided from KMC (Germany). Soluble potato starch (soluble starch) is the product of Nacalai Tesque (Japan). Glycerol obtained from Acros Organics was of reagent grade for gelatinization.

### Sample preparations

All pristine resins were predried for 24 h at 50°C in a dehumidified air-circulated oven prior to further treatment. Gelatinized starch was prepared by adding various amounts of water and glycerol according to Table I. Gelatinization was completed in an internal mixer (Brabender, Plastograph) at a rotor speed of 50 rpm for 30 min at 90°C for corn starch, and 70°C for both potato starch and soluble starch. Gelatinized starch was then stored in a vacuum drier. The mixing of gelatinized corn starch or potato starch and PHB (1, 3, 5, 7 wt %) was carried out using an internal mixer at a rotor speed of 50 rpm for 10 min at 180°C. Similar mixing condition of gelatinized soluble starch/PHB blends was performed but with a lower processing temperature close to the melting temperature of PHB. The prepared batch was then hot pressed to obtain 1-mm thin sheet. Tensile test specimens complied with ISO-37 Type III standard were then prepared through a die cut. Tensile measurements based on an ASTM standard D 638 were conducted. Trousers tear test specimens with a thickness of ~1 mm were prepared with backing cloth at one side and with a center groove of 0.2-mm deep on both sides of specimen to guide crack propagation. Thus, the thickness remained to be torn through is about 0.6 mm. At least 1 day of storage in a vacuum drier after sample preparation was kept before any measurements were taken.

**TABLE I**
**Formulations for Gelatinized Starch**

| Sample Code | Starch content (wt %) | Water content (wt %) | Glycerol content (wt %) |
|---|---|---|---|
| Glycerol 25% | 50 | 25 | 25 |
| Glycerol 33% | 50 | 17 | 33 |

As for the biodegradability test, tensile test specimens were soil buried about 10 cm below the surface of soil contained in a soil chamber with the dimension of 45 × 30 × 25 $cm^3$. The test condition was maintained under 80% relative humidity at 22.5°C, recorded with an immersed thermometer in the soil. The soil was sampled from the campus within Chinese Culture University. A total of 100 min observation time with each 20 min period of sampling time was implemented for TPS. In the case of TPS/PHB blend, 5 h of observation time with each 30 min period were employed.

### Measurements

#### Structure and thermal characterizations

All test specimens were preconditioned in a vacuum drier at least for 24 h before tests. The infrared spectra for starch/PHB blends were recorded on a Fourier Transform Infrared Spectrophotometer (JASCO, 460 PLUS) at a resolution of 4 $cm^{-1}$ for 64 scans from 4000–700 $cm^{-1}$. Thermogravimetric analysis (PerkinElmer, TGA6) was used to evaluate the thermal stability of the blends with a heating rate of 20°C/min from 25 to 800°C.

#### Mechanical properties

Tensile measurements were conducted based on ASTM D 638 at a crosshead speed of 10 cm/min using

a Universal Tensile Testing Machine model GY6040A4. Tensile strength was recorded. Trousers tear test was carried out in a similar condition to determine fracture energy ($G_c$) for this type of blend, using eq. (1)

$$G_c = 2F/t \quad (1)$$

where $F$ is the minimum force required to propagate a crack and $t$ is the torn thickness.

### Morphological observations

The morphology of fractured sample under cryogenic condition was elucidated using a scanning electron microscope (JEOL, JSM-6335F). TPS/PHB blends were subjected to chloroform treatment to remove PHB domains. All samples were sputtered with gold before further characterization.

### Biodegradability

The weight loss as an indication of biodegradability has been calculated as follows:

$$\text{Weight loss (\%)} = (W_o - W_f)/W_o \quad (2)$$

where $W_0$ is the original sample weight and $W_f$ is the final sample weight after soil burial.

All test samples were dried at 50°C for 24 h before recording. The water absorption of blends was also evaluated. Morphologies of blends after a soil test to evaluate biodegradability have been observed using an optical microscope (Carl Zeiss, Axiotech).

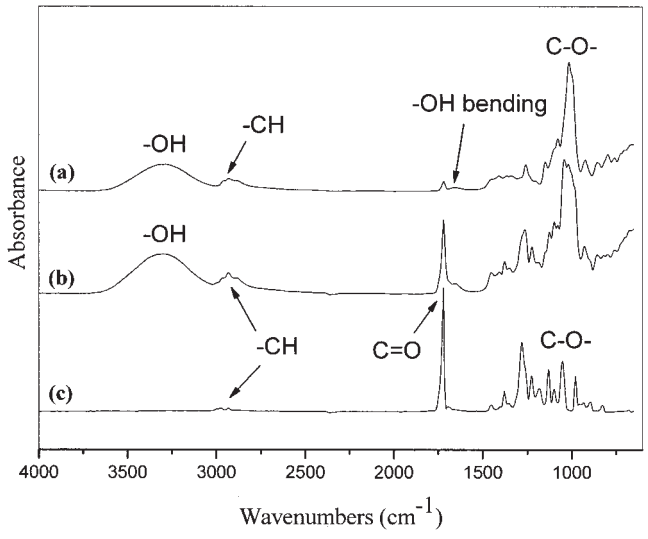



**Figure 1** FTIR curves of various samples: (a) TPS (potato starch, 25% glycerol), (b) TPS (potato starch, 25% glycerol)/PHB blend containing 7% PHB, (c) pristine PHB.

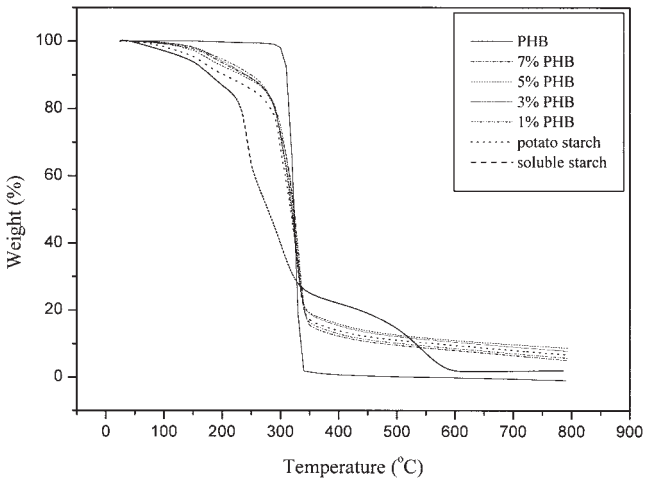



**Figure 2** TGA curves of TPS (potato starch, 25% glycerol), TPS (soluble starch, 25% glycerol), and TPS (potato starch, 25% glycerol)/PHB blends at various PHB contents.

## RESULTS AND DISCUSSION

For ease of comparison, a typical blend of TPS (potato starch)/PHB is presented here, since the results for mechanical properties show the highest reinforcement, unless otherwise stated.

### Structure and thermal characterizations

Major regions of the FTIR spectra of a TPS (potato starch, 25% glycerol)/PHB blend are depicted in Figure 1 for a comparison. Characteristic absorption ranges of TPS include absorption bands of O—H (3900–3300 $cm^{-1}$), C—H (2920 $cm^{-1}$), O—H bending of absorbed water (1640 $cm^{-1}$), and C—O— stretching (1250–900 $cm^{-1}$).[23] In addition, those of PHB absorption bands are $CH_3$ (2968, 1453, 1380 $cm^{-1}$), $CH_2$ (2923 $cm^{-1}$), C═O ester bonding (1720 $cm^{-1}$), and C—O— (1186, 1123 $cm^{-1}$).[24] In general, as PHB was incorporated into starch, most of typical absorption bands remained unchanged. The appearance of strong absorption bands of ester bonding is observed. The possible interaction between O—H groups on TPS and C═O groups on PHB due to hydrogen bonding is not discernible on the TPS/PHB blend, because of the overlapping. Additionally, no clear effect of PHB dosage is seen on the difference in the infrared spectra. Similar findings were seen for TPS (corn starch)/PHB and TPS (soluble starch)/PHB blends, not shown here.

The thermal stability of blends containing various amounts of PHB is illustrated in Figure 2. A representative blend of TPS (potato starch, glycerol 25%)/PHB, pristine PHB, TPS (soluble starch, glycerol 25%) were evaluated for comparison. Comparing PHB and TPS(soluble starch, glycerol 25%), the last one showed stability up to ~200°C at 10% of weight loss, while PHB exhibited the same weight loss only at 310°C. For

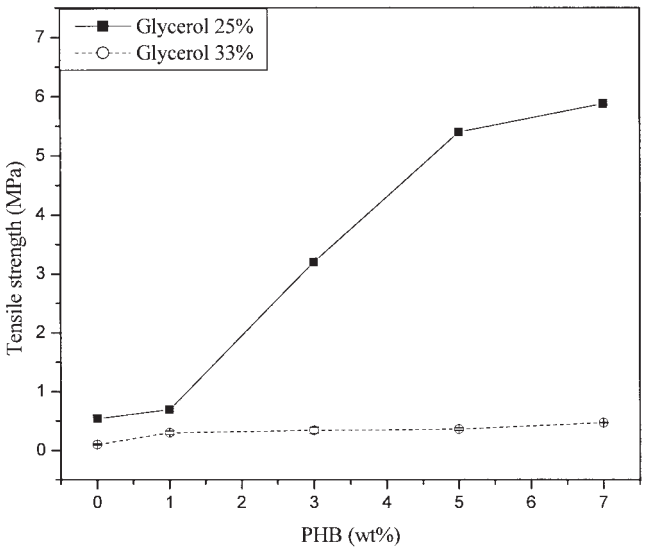



**Figure 3** The effect of PHB content on tensile strength of TPS (potato starch)/PHB blends at two gelatinization degrees.

blends containing a certain amount of PHB, the thermal stability remains in a certain degree within an experimental error. The initial loss of gelatinized starch indicates that a small portion of water remains after the gelatinization process. Interestingly, ash contents for gelatinized starch and its blends are kept at about 7–9% up to 800°C. This might be associated with its chemical structure prone to form a thermal resistance layer to give a high degree of residual carbon. Similar results are found for other TPS (corn starch)/PHB blends at different degrees of gelatinization.

Note that TPS (soluble starch, 25% glycerol) shows the peculiar behavior of two decomposition stages due to a relatively low heat stability of soluble starch. The maximum-rate degradation temperature at the first stage is ~250°C, which is lower than that of corn starch and potato starch. Yet, the weight continues to decrease and second-stage degradation is observed for soluble starch. For corn starch and potato starch, only one stage degradation behavior is observed, where the maximum-rate degradation temperature is close to 310°C. This is due to the selective dehydration and transglucosidation.[25]

## Mechanical properties

Figure 3 shows the effect of PHB content on tensile strength of typical TPS (potato starch)/PHB blends at two gelatinization degrees. As PHB content increases, tensile strength of blends generally increases, which is ascribed to the high strength of PHB and a reasonable compatibility between TPS and PHB. For TPS (potato starch) blended with PHB at a lower gelatinization degree (25% glycerol), a significant increase, up to 11-fold, on tensile strength is observed. The maximum value reaches 5.9 ± 0.1 MPa for the TPS/PHB blend containing 7% of PHB, but is still far from tensile strength of pristine PHB, 30.5 ± 1.8 MPa. Furthermore, at higher dosage of glycerol amount (33%), tensile strength marginally increases with increasing PHB content due to some plasticizing effect. Apparently, a suitable gelatinization of potato starch should be achieved to promote its compatibility with PHB. Similar findings on the effect of gelatinization degree on tensile strength of TPS (corn starch)/PHB and TPS (soluble starch)/PHB blends were also observed.

To further compare the effect of three types of starches on tensile strength of TPS/PHB blends, the results for gelatinized potato, corn, and soluble starch with 25% glycerol, respectively, are shown in Figure 4. Among the three types of starches investigated, tensile strength all increases with the addition of PHB. In particular, TPS (potato starch) and TPS (soluble starch) exhibit the highest improvement and the lowest increment in tensile strength, respectively. This is ascribed to the higher molecular weight of potato starch than that of soluble potato starch. The difference between TPS (corn starch) and TPS (potato starch) is associated to a highly bonded superhelical compact structure of potato starch, which renders TPS (potato starch) a more cohesive nature (see Ref. 2, p. 294). This is also manifested in the less water absorption of TPS (potato starch) that will be discussed in the Biodegradability section.

To put in evidence the importance of gelatinization and the PHB amount on the mechanical properties of TPS/starch blends, the tear test to measure fracture energy (tear strength) was carried out. Figure 5 depicts the effect of PHB content on tear strength of the blends for two different gelatinization degrees. As seen in

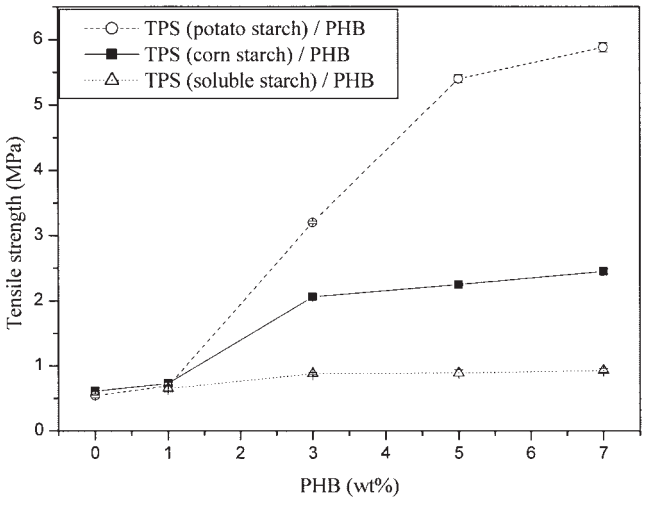



**Figure 4** The effect of PHB content on tensile strength of TPS/PHB blends for different types of starch gelatinized with 25% glycerol.

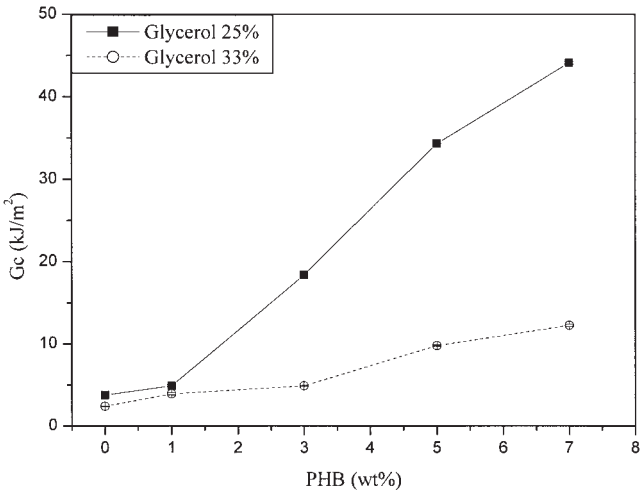



**Figure 5** The effect of PHB content on tear strength of TPS (potato starch)/PHB blends at various gelatinization degrees.

tensile properties, tear strength progressively increases with increasing PHB content. For TPS (potato starch) blended with 7% PHB, tear strength reaches 44.1 ± 0.2 kJ/m$^2$, a 12-fold increase compared with unfilled TPS at 25% glycerol content. Apparently, PHB is of benefit to improve the strength of the blend, which is attributed to the energy dissipated in crystalline deformation of PHB domains along with high interaction within the blend. However, one also has to notice that higher glycerol content do not increase significantly the tear strength of the blends due to the plasticizing effect mentioned earlier. This is manifested in TPS at 33% glycerol content with a less increment in tear strength. The effect of gelatinization degree on tear strength also shows similar trends for TPS (corn starch)/PHB and TPS (soluble starch)/PHB blends.

To further elucidate the tear strength for all three investigated starches, Figure 6 illustrates the detail comparisons with various PHB content at 25% glycerol dosage. TPS (potato starch)/PHB show a pronounced effect in tear strength with the addition of PHB, compared to the other blends. This is again attributed to aforementioned subtle difference in structure. TPS (soluble starch)/PHB blends gives the lowest enhancement. This is due to a low molecular weight of soluble starch which is detrimental to the strength of materials.

In all cases of this study, mechanical properties of TPS blended with PHB confer higher performance than those of unfilled TPS. Yet, it is interesting to see how the detail molecular structure affects the mechanical properties. Further study is needed to elucidate this effect in detail.

## Morphological observations

The SEM micrographs of TPS (25% glycerol)/PHB blends containing 7 wt % of PHB are shown in Figure 7. In all cases, the dimension of starch granules is in the order of 1 $\mu$m. Figure 7(A), TPS (potato starch) blended with 7% PHB gives a similar dimension of dispersed cavity of etched PHB as in Figure 7(B). By the results obtained, it is difficult to explain the higher mechanical strength of TPS (potato starch)/PHB blends than that of TPS (corn starch)/PHB and TPS (soluble starch)/PHB blends. According to the theory, the finer the dispersion of PHB gives the higher mechanical properties for the same matrix. One should not judge the mechanical strength based on the observed cavities, since different starch matrix has been employed for a comparison. Here, this morphological features should only serve as one possible rational for the observed mechanical properties earlier. TPS gelatinized with 33% glycerol gives similar findings.

## Biodegradability

Higher water absorption indicates that the materials are prone to organisms' attack. Since PHB is hydrophobic, the degree of water absorption is rather limited. On the other hand, TPS is hydrophilic; a significant increase in water absorption is seen for three types of TPSs (not shown here for brevity). This increase is generally associated with the hydrogen bonding of TPS and water. In particular, TPS (soluble starch) gives the highest level of water absorption, reaching up to 70.9%, while TPS (potato starch) exhibits the least increment, only 52.1%, for only 100 min of treatment. This difference in water absorption is related to each characteristics of neat starch investigated

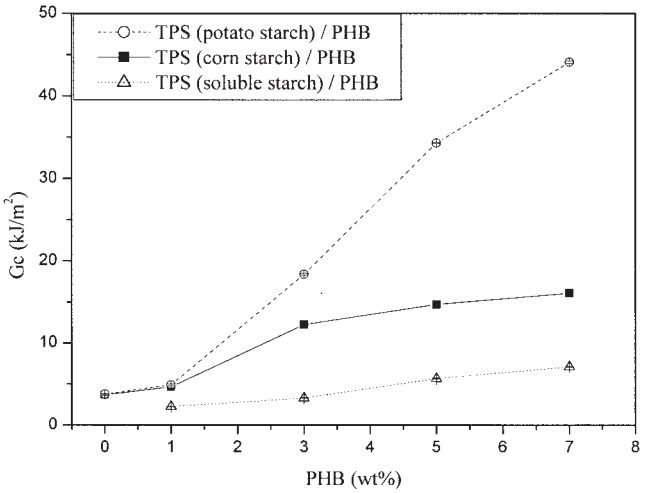
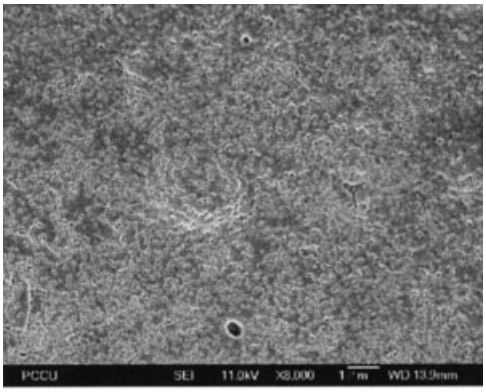
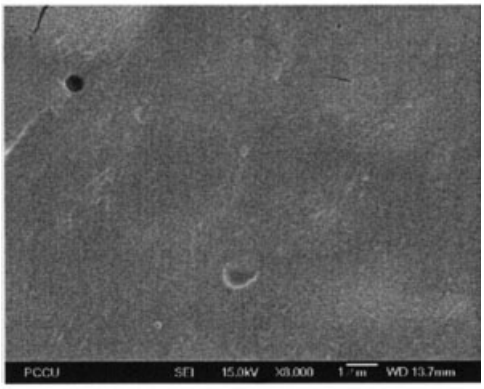


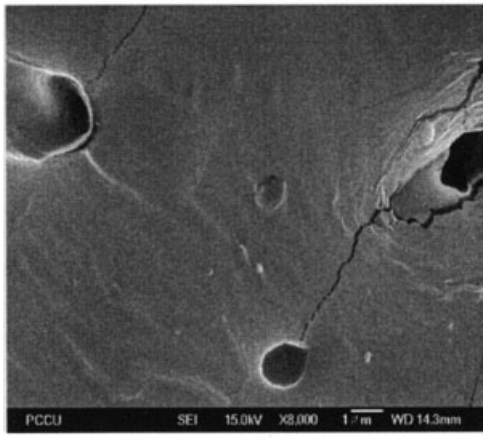

**Figure 6** The effect of PHB content on tear strength of TPS/PHB blends for different types of starch gelatinized with 25% glycerol.




(A)




(B)




(C)

**Figure 7** The SEM micrographs of TPS(25% glycerol)/PHB blends containing 7 wt % of PHB (A) potato starch, (B) corn starch, and (C) soluble starch.

and is reflected in the rate of weight loss as an indication of biodegradability that will be discussed later. For instance, the granular size of corn starch, before gelatinization, is quite small compared with that of

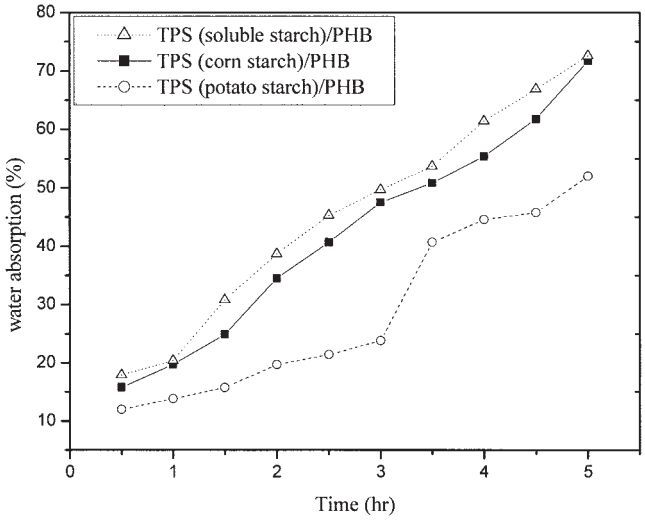



**Figure 8** The water absorption curves of TPS (25% glycerol)/PHB blends containing 7% PHB.

potato starch. The structure within corn starch granules is open lattice structure for available water. In contrast, the structure of potato starch is a highly bonded superhelical structure. This situation also holds for the gelatinization of starch (see Ref. 2, p. 294). The water absorption curves of TPS (25% glycerol)/PHB blends containing 7% PHB are shown in Figure 8. The extension of water absorption time of 5 h was fixed to attain a similar order of water absorption time as adopted for TPS/PHB blends.

In addition, the water absorption (%) was investigated for different gelatinization degrees and PHB contents, whose results are illustrated in Figure 9. The water absorption capacity generally decreases with increasing PHB content. Note that, the water absorp-

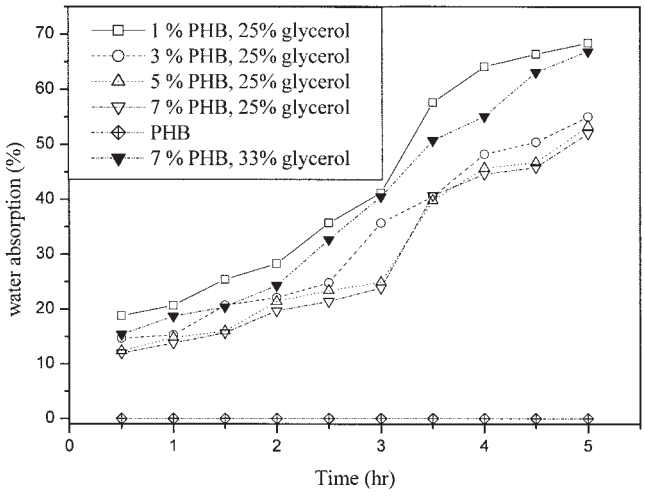



**Figure 9** The water absorption curves of TPS (potato starch)/PHB blends at various PHB contents and gelatinization degrees.

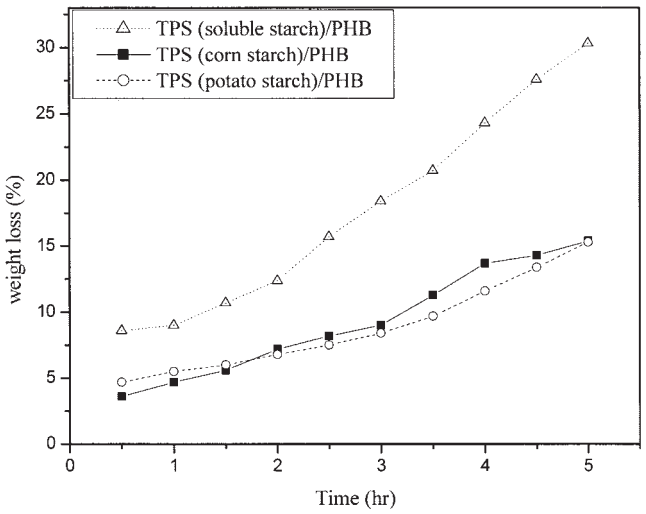



**Figure 10** The weight loss of TPS (25% glycerol)/PHB blends containing 7% PHB.

tion is higher for TPS gelatinized at higher amount of glycerol, taking 7% PHB as a typical example. This is attributed to a large gelatinization degree of starch that causes the disruption of hydrogen bonding between crystalline galleries, resulting in a more opened structure for water to diffuse. However, the glycerol excess must be considered in the water absorption, since it contributes to enhance the hydrophilicity of the system. These findings are also held for other blends as well.

To further assess the biodegradability of TPS/PHB blends, the samples were soil buried about 10 cm below the surface of soil contained in a conditioned soil chamber with the dimension of $45 \times 30 \times 25$ cm$^3$. A similar procedure can be found in the literature.[26] The weight loss due to the decomposition of organisms' attack was recorded according to eq. (2). The results for TPS (25% glycerol)/PHB blends containing 7% PHB are depicted in Figure 10. PHB is quite stable in this short term of investigation. On the other hand, the intensive biodegradation is found for TPS, a profound increase in weight loss is seen for three types of TPSs (not shown here for brevity). Starch, a natural polymer, could be readily used as a carbon source by the organisms. In particular, TPS (soluble starch) gives the highest level of weight loss, reaching up to 20.2%, but TPS (potato starch) exhibits the least increment, only 11.5%, at 100 min of treatment. This difference in weight loss is related to each characteristics of neat starch and is originated from the water absorption capacity discussed earlier. As for TPS/PHB blends, the weight loss decreases due to the addition of PHB, the treatments were then carried out for 5 h for a reasonable comparison. When the treatment period increased, the values of weight loss increase. TPS (soluble starch)/PHB gives the highest level of weight loss, reaching up to 30.3%, but TPS (potato starch)/PHB and TPS (corn starch) exhibit the similar increment, only 15.4%, for up to 5 h of treatment.

In addition, the weight loss (%) was investigated for different gelatinization degrees and PHB contents, whose results are illustrated in Figure 11. The weight loss generally decreases with increasing PHB content. Note that, if one takes blends containing 7% PHB as a typical example, the weight loss is at least 50% higher for TPS gelatinized at higher amount of glycerol than that for lower amount of glycerol. This is attributed to aforementioned discussion on the easy diffusion of water molecule. Further, a possible loss of glycerol being carbon source for microorganisms is also responsible for this observation. Similar results are also found for other types of blends in this study.

Typical photographs of TPS (potato starch, 25% glycerol)/PHB blends containing 7% PHB at various periods in a soil test are shown in Figure 12. The original sample without soil burial is also shown for a comparison [Fig. 12(A)]. Other photographs indicate a significant growth of organisms [Fig. 12(B–F)]. It is difficult to tell the growth rate of organisms from different treatment periods. Sample surfaces show some variations in height. Once some position has been in focus, and the other positions with different depth are out of focus resulting from a basic limitation of optical microscope. Similar situations are found for all other investigated blends.

## CONCLUSIONS

The vital differences using three types of gelatinized starches with two different gelatinization degrees to blend with PHB are thoroughly discussed in this study. For blends containing a certain amount of PHB,

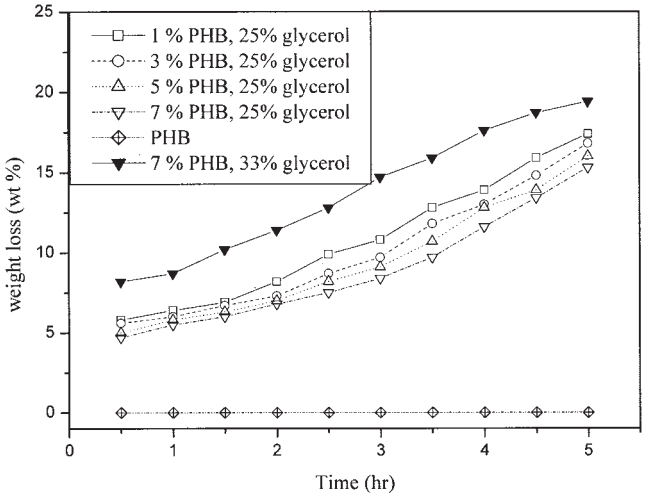



**Figure 11** The weight loss of TPS (potato starch)/PHB blends at various PHB contents and gelatinization degrees.

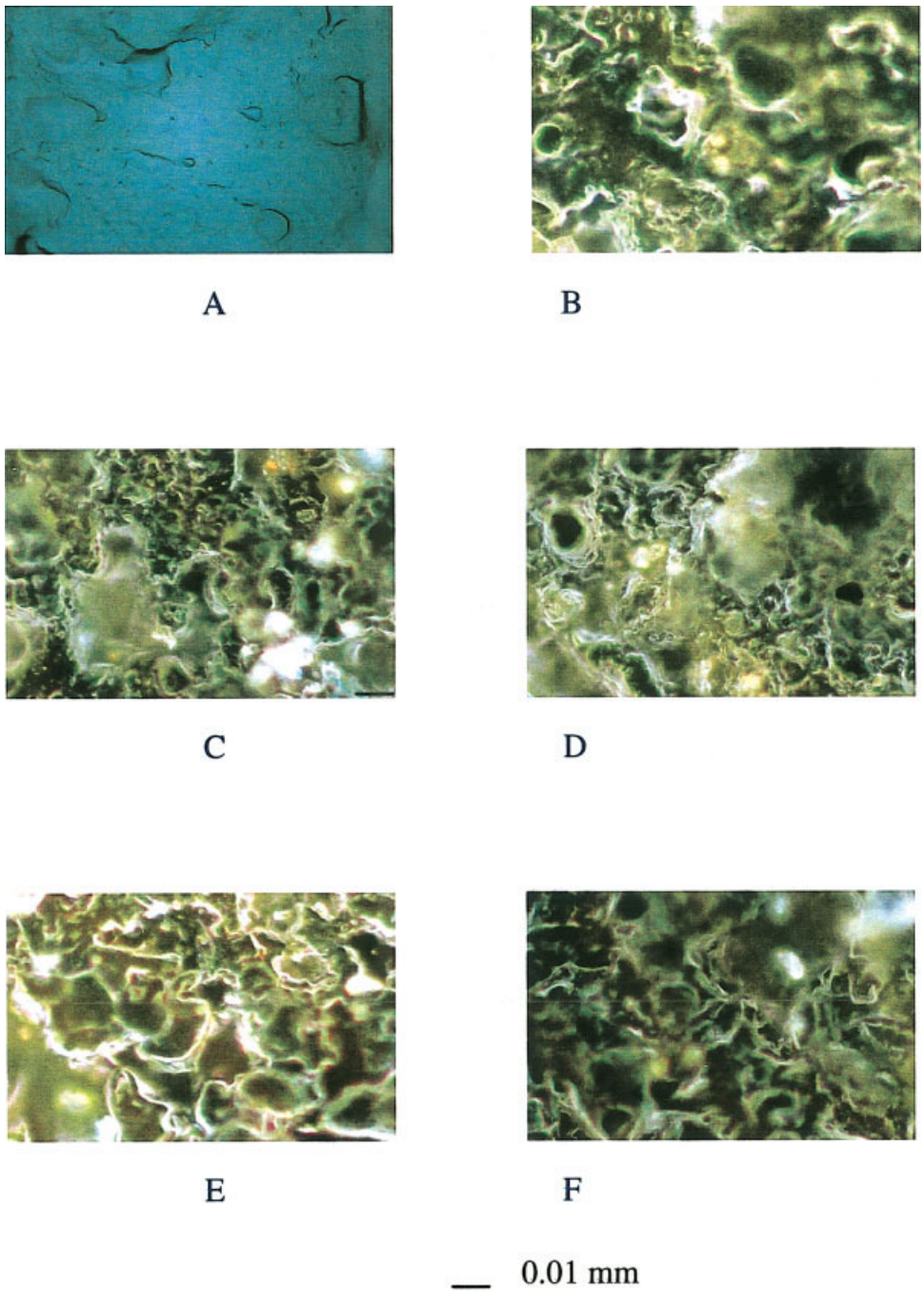



**Figure 12** Optical photographs of TPS (potato starch, 25% glycerol)/PHB blends containing 7% PHB at various periods in a soil test: (A) 0 h, (B) 1 h, (C) 2 h, (D) 3 h, (E) 4 h, and (F) 5 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

thermal stability remains in a certain degree. As for mechanical properties, a significant increase, up to 11-fold, on tensile strength is observed for TPS (potato starch) blended with PHB at low gelatinization degree. Apparently, a suitable degree of gelatinization of starch is critical to achieve optimum performance. Similarly, tear strength increases up to 12-fold for the above blends. In all cases of this study, mechanical properties of TPS blended with PHB confer higher performance than those of pristine TPS. The investigation on the morphological observation partly features the supporting evidence of the above findings. The assessment of biodegradability indicates that the values of water absorption and weight loss increase with increasing treatment period and glycerol content, but decrease with increasing amount of PHB content. Among three types of starches investigated, the TPS (soluble starch)/PHB blend gives the highest level of

water absorption and weight loss. To summarize, the compromise of mechanical properties and biodegradability through different gelatinization degrees is rather imperative for designing this type of blend. This study would be of benefit to a better understanding of the blend performance and to predict the best way to produce new generation of biodegradable plastics for our environment.

Equipments supported from Dr. W.-C. Chen at the Department of Chemical Engineering, Chinese Culture University, TAIWAN, are appreciated.

## References

1. Kweon, D. K.; Cha, D. S.; Park, H. J.; Lim, S. T. J Appl Polym Sci 2000, 78, 986.
2. Whistler, R. L.; Bemiller, J. N.; Paschall, E. F. Eds. Starch: Chemistry and Technology, 2nd ed.; Academic Press: San Diego, 1984; p 294.
3. Griffin, G. J. L. Biodegradable Fillers in Thermoplastics, ACS Advances in Chemistry, Series No. 134, 1975.
4. Wittwer, F.; Tomka, I. US Pat No. 4,673,438 (1987).
5. Bikiaris, D.; Panayiotou, C. J Appl Polym Sci 1998, 70, 1503.
6. George, E. R.; Sullivan, T. M.; Park, E. H. Polym Eng Sci 1994, 34, 17.
7. Seidenstücker, T.; Fritz, H. G. Polym Degrad Stab 1998, 59, 279.
8. Park, J. W.; Im, S. S.; Kim, S. H.; Kim, Y. H. Polym Eng Sci 2000, 40, 2539.
9. Dubois, P.; Narayan, R. Macromol Symp 2003, 197, 233.
10. John, J.; Tang, J.; Yang, Z.; Bhattacharya, M. J Polym Sci Part B: Polym Phys 1997, 35, 1139.
11. Wu, C. S. J Appl Polym Sci 2003, 89, 2888.
12. Mani, R.; Bhattacharya, M. Eur Polym J 2001, 37, 515.
13. Lai, S.-M.; Huang, C.-K.; Shen, H.-F. J Appl Polym Sci 2005, 97, 257.
14. Innocentini-Mei, L. H.; Bartoli, J. R.; Baltieri, R. C. Macromol Symp 2003, 197, 77.
15. Godbole, S.; Gote, S.; Latkar, M.; Chakrabarti, T. Bioresour Technol 2003, 86, 33.
16. Koller, I.; Owen, A. J. Polym Int 1996, 39, 175.
17. Imam, S. H.; Chen, L.; Gordon, S. H.; Shogren, R. L.; Weisleder, D.; Greene, R. V. J Environ Polym Degrad 1998, 6, 91.
18. Yasin, M.; Holland, S. J.; Jolly, A. M.; Tighe, B. J. Biomaterials 1989, 10, 400.
19. Rosa, D. S.; Rodrigues, T. C.; Guedes, C. G. F.; Calil, M. R. J Appl Polym Sci 2003, 89, 3539.
20. Petersen, K.; Nielsen, P. V.; Olsen, M. B. Starch/Staerke 2001, 53, 356.
21. Zhang, L.; Deng, X.; Zhao, S.; Huang, Z. Polym Int 1997, 44, 104.
22. Lee, S. Y. Biotechnol Bioeng 1996, 49, 1.
23. Mano, J. F.; Koniarova, D.; Reis, R. L. J Mater Sci 2003, 14, 127.
24. Nurbas, M.; Kutsal, T. Presented at the 9th Asia Pacific Confederation of Chem Engineering Congress and CHEMECA, Christchurch, NZ, Sept. 2002. Paper 132.
25. Greenwood, C. T. Adv Carbohydr Chem 1967, 22, 486.
26. Huang, C.Y.; Lu, W. L. Mater Sci Forum 2003, 426–432, 3279.