

Physical Properties and Morphology of Polycaprolactone/Starch/Pine-Leaf Composites

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ABSTRACT: Polycaprolactone (PCL)/starch and PCL/starch/pine-leaf composites, which can be possibly applied as biodegradable food packaging materials with natural pine flavor, were prepared and characterized in this study. The effect of incorporating a silane coupling agent at different content levels on the physical properties and morphology of the composites was studied. To investigate the melting behavior of the composites, a differential scanning calorimetry was employed. A universal testing machine was used to investigate the tensile properties of the composites and the water absorption properties of the composites were also investigated. Scanning electron microscope was used to investigate the morphology of the composites. The physical

properties and morphology of the PCL/starch and PCL/starch/pine-leaf composites were largely affected by the composition, especially the content of the silane coupling agent. The silane coupling agent led to a much better interfacial compatibility between the PCL matrix and the fillers and resulted in better physical properties of the composites. The PCL/starch/pine-leaf composite with the silane coupling agent showed a morphology, indicating a good interfacial adhesion between the PCL matrix and the fillers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 928–934, 2007

Key words: biodegradable; composites; polycaprolactone; starch; pine-leaf

INTRODUCTION

The volume of plastic wastes has continually increased and resulted in many serious environmental problems. Landfill has been a widely used method to dispose domestic and industrial plastic wastes, but the number of available landfill sites has been decreasing and most plastic wastes are not biodegradable. Plastic wastes can be reutilized by recycling to useful products rather than burying them, but it is not economically feasible and technically difficult, especially in the case of plastics packaging and other disposable products such as plastics plates and cutlery from domestic wastes.^{1–5} Therefore, the concept of reabsorbing plastics into the biological cycle has been an attractive ecological alternative to lock away plastic wastes in landfill.

The use of biodegradable polymers as replacement of commodities for large scale applications is quite small because not only their performance is poor but also their cost is still not competitive. One economically and ecologically attractive approach to overcome these limitations is to incorporate natural organic fillers into biodegradable polymers such as polycaprolactone (PCL), poly(lactic acid) (PLA), and poly-

hydroxybutyrate (PHB) to obtain environmentally compatible composite materials, which combine biodegradability, compostability, and compatibility with different forms of waste disposal and remarkable physical performances. The composites of starch and aliphatic polyester, especially PCL, have been considered as completely biodegradable plastics because both components are biodegradable.^{6–9} Biodegradable polymers are generally degraded by microorganisms and chemical reactions in aquatic and terrestrial environments. The rate of degradation is sensitive to microorganism population, moisture, temperature, and oxygen in the environments.^{10–14} PCL was chosen because of its good mechanical properties such as tensile strength and elongation and also its good compatibility with many types of polymers. Starch helps to lower the cost of the final products as well as improves the physical properties of the composites. However, the poor miscibility between PCL and starch has been a problem to be overcome for enhancement of the properties of the composites.

Therefore, in this work, to compatibilize the composites of PCL and starch, a silane coupling agent was used. Furthermore, pine-leaf powder was incorporated into the PCL/starch composites to explore the possibility of developing new functional plastic materials with natural pine flavor for special packaging applications. The PCL/starch and PCL/starch/pine-leaf composites were prepared at different composi-

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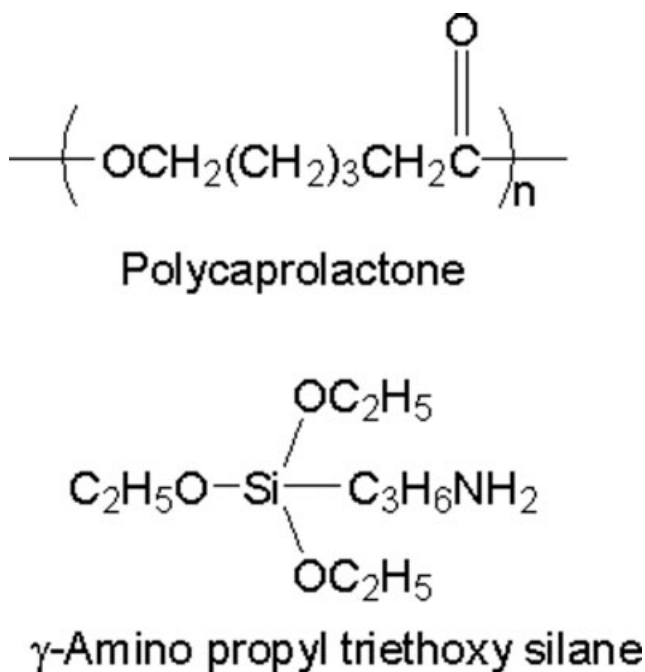


Figure 1 The chemical structure of the materials used in this study.

tion levels together with the silane coupling agent and their physical properties and morphology were investigated.

EXPERIMENTAL

Materials

The polycaprolactone (PCL; CAPA6800 from Solvay, UK) used in this study has a molecular weight of 80,000 g/mol. The starch (Hitex from Daesang, Korea) used in this study was a modified starch having sodium octenyl succinate groups. γ -Amino propyl triethoxy silane (Shin Etsu Silicone, Korea) was used as a coupling agent for the composites. To prepare pine-leaf powder (passed through a 400-mesh sieve with nominal sieve openings of 37 μ m), pine leaves of the most common pine trees (*forma multicaulis*) in Korea were collected, dried, and then ground. Figure 1 shows the chemical structures of the PCL and the silane coupling agent.

Preparation of composites

PCL/starch and PCL/starch/pine-leaf composites were prepared by melt-mixing using an internal mixer (Haake Rheomix 600, Germany). As shown in Figure 2, the thermal degradation of the pine-leaf powder started at about 200°C. Therefore, to protect the filler from thermal degradation, the mixing temperature was maintained at 160°C. The mixing was carried out for 10 min at a rotor speed of 60 rpm. Before melt-mix-

ing, all the materials were dried in a vacuum oven at 50°C for 48 h. The mass ratio of the PCL/starch composites prepared in this study was changed from 10/0 to 3/7. We tried to incorporate the starch into the PCL matrix as much as we can with the consideration of both commercial applicability and biodegradability of the composites as packaging materials. But, making the PCL/starch composite with the ratio of 2/8 was difficult because the amount of PCL in the composite was not enough. Therefore, the PCL/starch ratio for the PCL/starch/pine-leaf composites was fixed to 3/7 and pine-leaf powder loading for the composites was changed up to its maximum of 20 phr (parts per hundreds of PCL/starch content in the composites).

Thermal analysis

To investigate the thermal transitions of the composites, a differential scanning calorimetry (DSC 2910, TA Instruments, New Castle, DE) was used. About 10 mg of each composite was sampled and placed in a hermetic aluminum sample pan and tested immediately after sealing. Each scan was carried out under nitrogen gas atmosphere from 10 to 200°C at a heating rate of 10°C/min.

To investigate the thermal degradation behavior of the materials used in this study, a thermogravimetric analyzer (SDT 2960, TA Instruments, New Castle, DE) was used. Each scan was carried out under nitrogen gas atmosphere from room temperature to 600°C at a heating rate of 10°C/min.

Mechanical tests

To measure the tensile properties of the PCL/starch and PCL/starch/pine-leaf composites, sheet-shape molded products with 0.5 mm thick were prepared by hot-pressing each composite at 120°C. The tensile

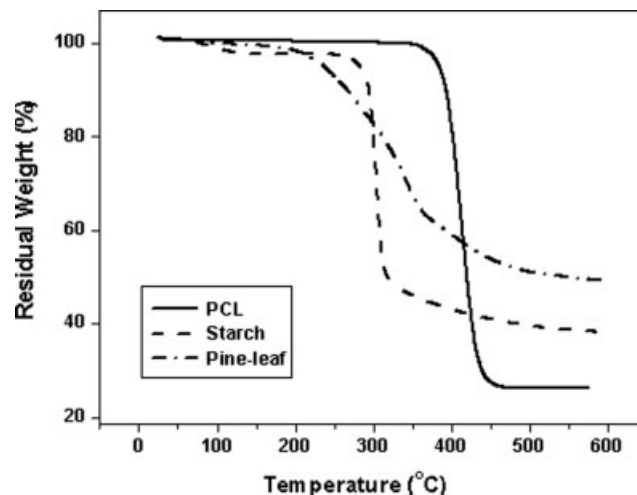


Figure 2 Thermal degradation behavior of the PCL, starch, and pine-leaf powder.

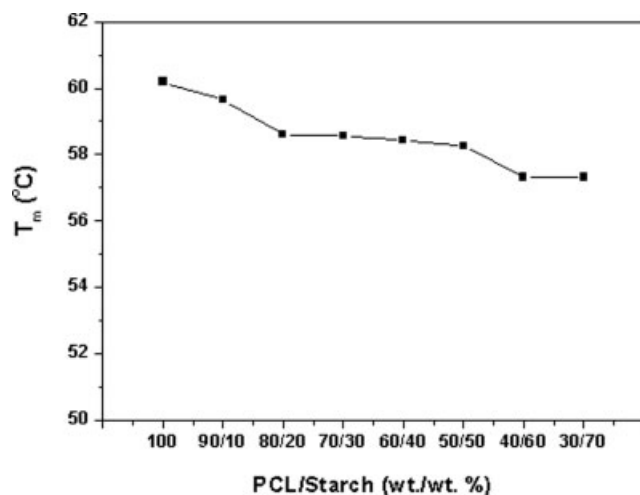


Figure 3 Melting temperatures of the PCL/starch composites as a function of starch content.

tests specimens with the dimension of 25 mm × 6 mm × 0.5 mm were prepared by cutting the sheets. Tensile tests were performed using a universal testing machine (LR-30K, Lloyd Instruments, Hampshire, UK) at room temperature according to ASTM D638. The gauge length was 13 mm, and each test was performed at a constant crosshead speed of 10 mm/min. At least five sample specimens were tested for each composite to obtain an average tensile test data to report.

Water absorption

To measure the water absorption characteristics of the PCL/starch and PCL/starch/pine-leaf composites, sample specimens with the dimension of 25 mm × 40 mm × 0.5 mm were prepared by cutting the sheets prepared for the tensile tests. Samples were dried in a vacuum oven at 50°C for 48 h and immediately weighed to the nearest 0.001 g (this weight designated as W_{dry}). Thereafter, the conditioned samples were immersed in distilled water, maintained at (23 ± 0.5)°C, for 4 days. During this 4-day period, they were removed from the water at 1-day interval, excess water on the surface was gently wiped out with tissue paper, and then immediately weighed to the nearest 0.001 g (this weight designated as W_{wet}). For each sample, an average value was obtained from three measurements. The percentage increase of water by weight (% W_f) was calculated to the nearest 0.01% using the following equation¹⁵

$$\%W_f = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \times 100$$

Morphology

The morphology of the composites was investigated using a scanning electron microscope (Hitachi S-2500C,

Japan). All specimens for SEM analysis were prepared by freezing them in liquid nitrogen, followed by fracturing them. Fractured surfaces of samples were coated with gold to avoid charging under the electron beam during SEM operation.

RESULTS AND DISCUSSION

Thermal properties

Figure 3 shows the melting temperatures of the PCL/starch composites determined by DSC as a function of the composition. The melting temperature of the PCL/starch composites decreased slightly with increasing starch content. This decrease in melting temperature with increasing starch content indicates that the crystalline structure of PCL was affected by starch, which could inhibit crystallization of PCL during cooling after melt-mixing. Incomplete crystalline structure or defects in the crystalline region of PCL would be induced by the inhibition by starch. The formation of hydrogen bonds between the hydroxyl groups of starch and carbonyl groups of PCL would be a main factor inhibiting the crystallization of PCL by making the chain mobility of PCL decrease. This inhibition effect on PCL crystallization can explain the slight decrease in the melting temperature of the composites with increasing starch content. Similar results were also observed by other researchers.¹⁶

Figure 4 shows the melting transitions of the PCL/starch (3/7) composites with different loadings of the silane coupling agent. Compared to the PCL/starch (3/7) composite showing its melting temperature at about 58°C, the PCL/starch composites with the silane coupling agent exhibited their melting temperatures at about 54°C for 1 phr silane loading and 53°C

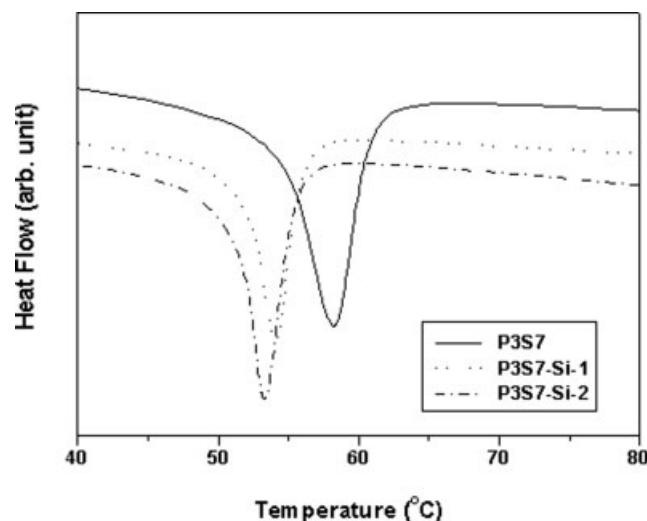


Figure 4 Effect of silane content on the melting transitions of the PCL/starch (3/7) composites.

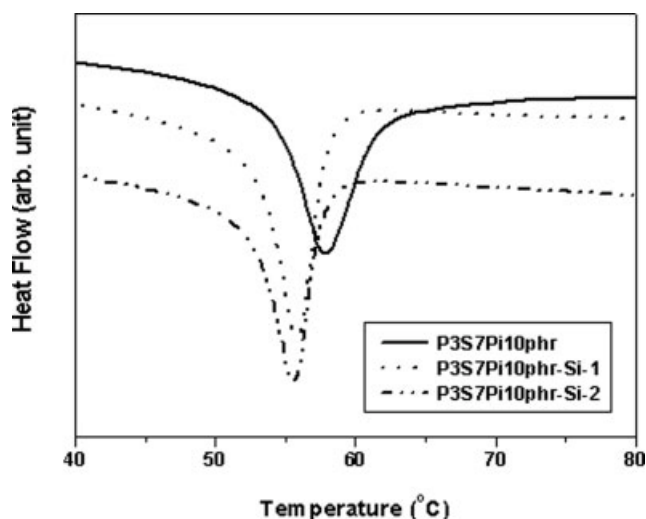


Figure 5 Effect of silane content on the melting transitions of the PCL/starch (3/7)/pine-leaf (10 phr) composites.

for 2 phr silane loading, respectively. The melting temperature shifts to the lower temperatures for the PCL/starch composites with the silane coupling agent seemed to be caused by the enhanced coupling effect of the silane between PCL and starch at the interfaces. The coupling effect would inhibit free molecular motion of PCL chains for crystallization. As a result, incomplete crystalline structure or defects would be produced in the PCL matrix during crystallization process.

Figure 5 shows the melting transitions of the PCL/starch (3/7)/pine-leaf composites with different loadings of the silane coupling agent. Compared to the results shown in Figure 4, the melting temperature decrease by the silane coupling agent was not so severe. The pine-leaf powder in the composites seemed to result in less inhibited molecular mobility of PCL for crystallization.

Mechanical properties

Figure 6 shows the tensile strength of the PCL/starch (3/7) and PCL/starch (3/7)/pine-leaf (10 and 20 phr) composites as a function of the silane coupling agent content. The PCL/starch composite without the silane coupling agent showed the lowest tensile strength among the composites tested in this study, indicating very weak interfacial adhesion and poor compatibility between PCL and starch.¹⁷ Some previous works have also reported that starch and PCL were thermodynamically immiscible with each other.^{6,7,9,18} They showed that there was a significant decrease in tensile strength at a higher percentage of starch granules because the starch coalesces into larger aggregates and is not uniformly distributed within the PCL matrix. So, it is essential to obtain small and well-dis-

persed starch domains within the PCL matrix for good mechanical properties of the PCL/starch composites even though they are immiscible. Instead of using a silane coupling agent to improve compatibility at the interfaces, some researchers used modified PCL or starch such as PCL copolymer grafted by acrylic acid¹⁹ or esterified starch.²⁰ They observed considerable increase in the performance of the PCL/starch composites they prepared. A PCL-based compatibilizer was also used to compatibilize PCL/starch composites, and the composites showed better performance compared to the ones without the compatibilizer.²¹

The PCL/starch/pine-leaf composites without the silane coupling agent showed slightly higher tensile strength than the PCL/starch composite without the silane coupling agent, but the difference was not so significant. By introducing the silane coupling agent to the composites, the tensile strength was increased considerably, but the effect of increasing silane content was relatively small, especially for the PCL/starch composite. Just 0.5 phr of the silane seemed to be almost enough to compatibilize PCL and starch in the PCL/starch composite, and the tensile strength of the composite did not increase very much with increasing the silane content over 0.5 phr.

However, the tensile strength of the PCL/starch/pine-leaf composites was more dependent on the silane content compared to the PCL/starch composites. The tensile strength of the PCL/starch/pine-leaf composites increased considerably with increasing the silane content within the range we studied in this work. For the composites with the silane coupling agent, the tensile strength of PCL/starch/pine-leaf composites was lower than that of the PCL/starch composites, because as more pine-leaf powder was added to the composites, the fraction of PCL would decrease

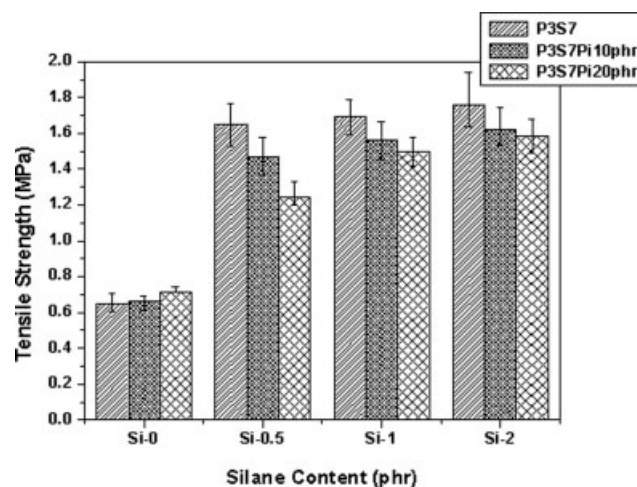


Figure 6 Tensile strength of the PCL/starch (3/7) and PCL/starch (3/7)/pine-leaf composites as a function of silane content.

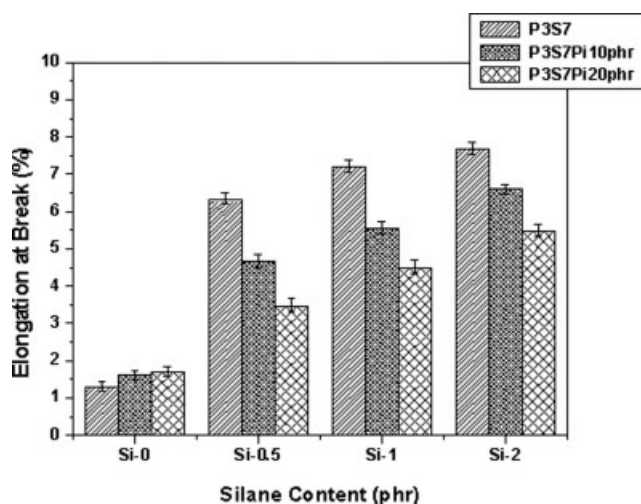


Figure 7 Elongation at break of the PCL/starch (3/7) and PCL/starch (3/7)/pine-leaf composites as a function of silane content.

and this would result in poor tensile properties of them.

Figure 7 shows the elongation at break of the PCL/starch and PCL/starch/pine-leaf composites with or without the silane coupling agent. The trend was almost same compared to the tensile strength results. With increasing the silane coupling agent, the elongation at break of all the composites increased considerably. It was clear that the mechanical properties of the composites were strongly dependent on the coupling agent, the amount, and dispersion of the fillers.

Water resistance

Bikiaris and Panayiotou reported that the percentage water absorption increased with starch content in the

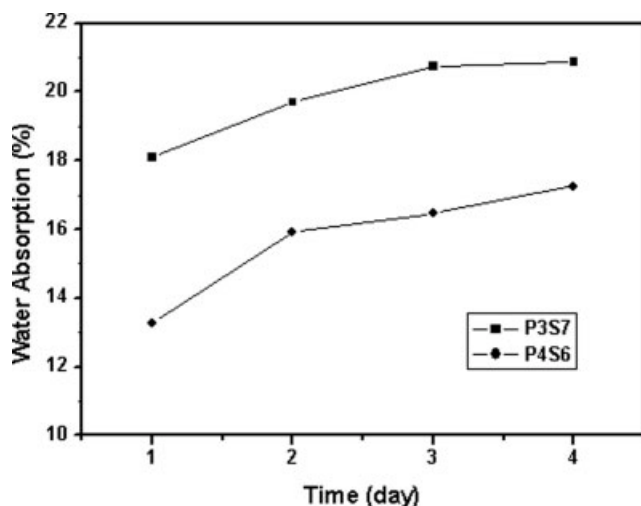


Figure 8 Effect of the composition on the water absorption characteristics of the PCL/starch composites.

case of polyethylene/starch composites.²² They deduced that the marked increase in water absorption was probably caused by the increased difficulty in forming polymer chain arrangements as the starch inhibited the movements of the polymer chains, and also that the hydrophilic character of starch led to poor interfacial adhesion with the hydrophobic polyethylene. This phenomenon was also observed for the PCL/starch composites of this work as shown in Figure 8, indicating more water absorption in the case of the PCL/starch (3/7) composite compared to the PCL/starch (4/6) composite. This result is natural because starch is more hydrophilic than PCL and with increasing starch content in the composite, more starch granules would be placed at the surface of the composite, allowing easy access of water into the composites through the interfaces.

The PCL/starch (3/7) composite with 1 phr silane loading exhibited moderately good water resistance, showing quite lower water absorption than the PCL/starch (3/7) composite without the silane coupling agent as shown in Figure 9. Compared to the PCL/starch composite with the silane coupling agent, the amount of water absorption for the PCL/starch composite without the silane coupling agent was about 5–7% higher. This means that the silane coupling agent compatibilized PCL and starch at the interfaces and increased interfacial adhesion strength between them, which did not allow easy access of water into the composite.

The PCL/starch/pine-leaf composite with the silane coupling agent showed lower water absorption than the PCL/starch composite with the silane coupling agent. This means that pine-leaf powder could inhibit somewhat the access of water into the compos-

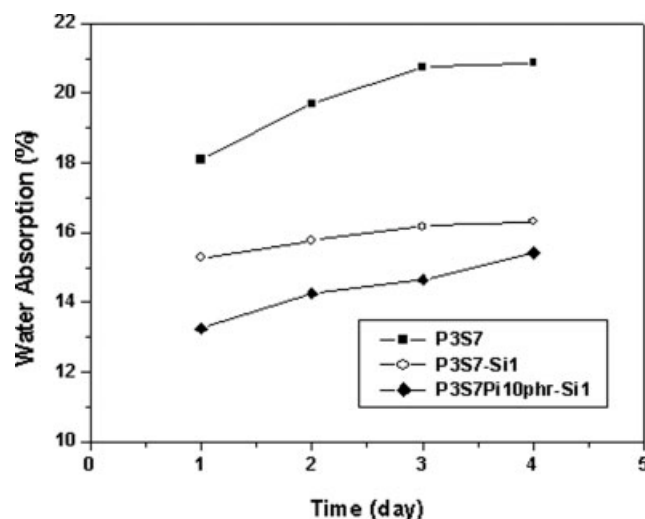


Figure 9 Effect of the pine-leaf powder and the silane on the water absorption characteristics of the PCL/starch (3/7) composites.

ite, and pine-leaf powder is less hydrophilic compared to starch. The comparatively lower water absorption of the PCL/starch and PCL/starch/pine-leaf composites both with the silane coupling agent was caused by the fact that starch and pine-leaf powder are well distributed in the PCL matrix and compatibilized successfully with PCL at the interfaces to

form good interfacial adhesion in the presence of the silane coupling agent.

Morphology

For polymer composites, it is essential to study the morphology of them, since most of their properties

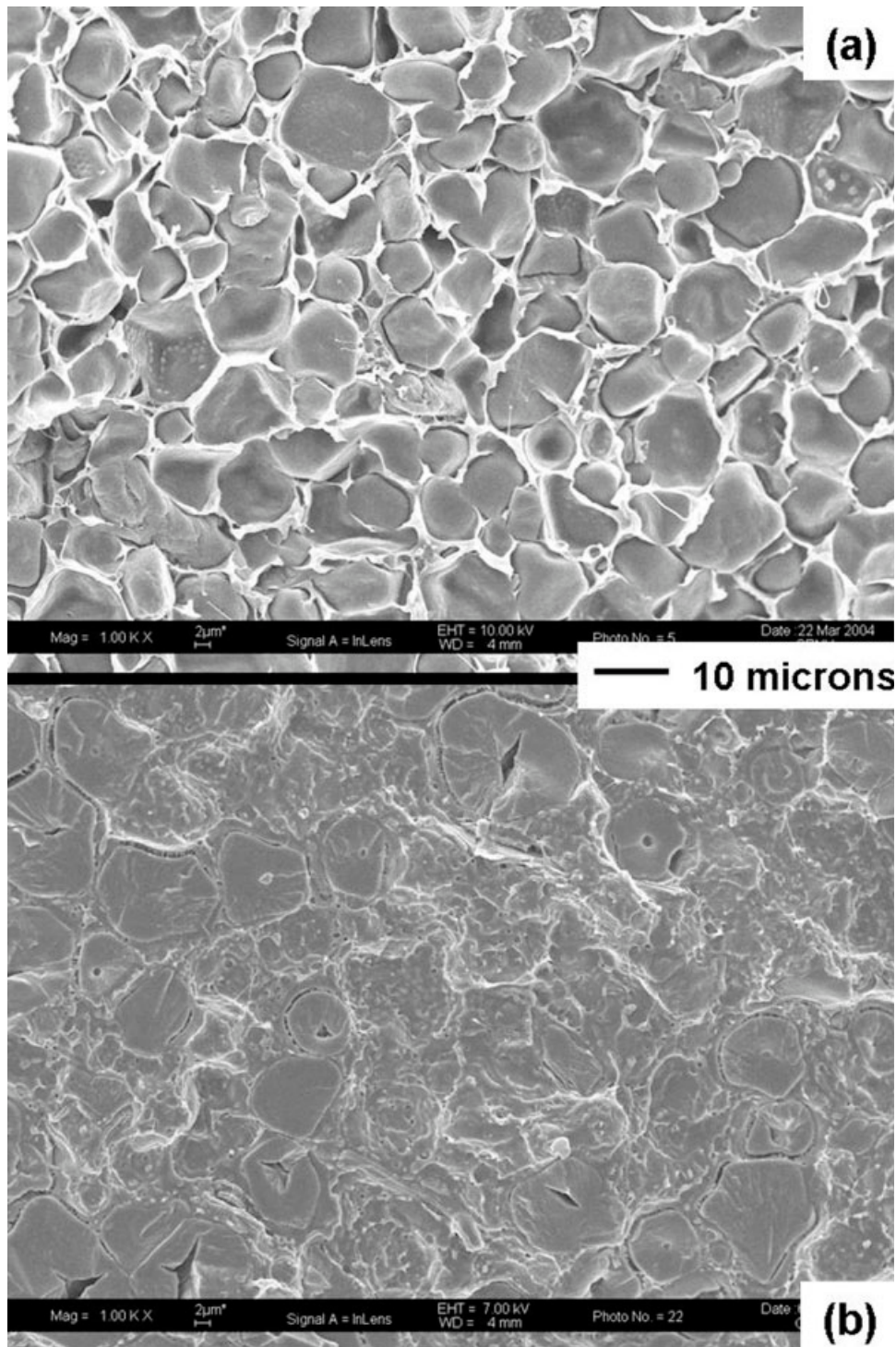


Figure 10 SEM images ($\times 1000$) for the fracture surfaces of (a) the PCL/starch (3/7)/pine-leaf (10 phr) composite without the silane, and (b) the PCL/starch (3/7)/pine-leaf (10 phr) composite with the silane loading of 2 phr.

are very dependent on their morphology, especially morphology at the interfaces.

Figure 10 shows the SEM images of the fractured surfaces of the PCL/starch (3/7)/pine-leaf (10 phr) composites without (a) and with (b) the silane coupling agent. Both SEM images show that the filler particles were well-distributed and dispersed in the PCL matrix. The composite without the silane coupling agent showed a morphology, indicating a poor interfacial adhesion between PCL and the fillers. Many empty cavities were observed on the fracture surface and they were produced by pulling out of many filler particles from the PCL matrix as the composite was being fractured. On the contrary, the composite with the silane coupling agent showed a morphology indicating a good interfacial adhesion between the PCL matrix and the fillers. No cavities were observed on the fracture surface and it was even not easy to discern the interfaces between PCL and the fillers. Furthermore, the fracture surface of the composite with the silane coupling agent showed the fact that the filler particles were also fractured by inherent failure when the composite was being fractured. Only adhesion failures at the interfaces were observed for the composite without the silane coupling agent as shown in Figure 10(a).

CONCLUSIONS

The physical properties and morphology of the PCL/starch and PCL/starch/pine-leaf composites were largely affected by the composition, especially the content of the silane coupling agent. The melting temperature of the PCL/starch composite decreased with increasing starch content, but this decrease was relatively small in the case of the composite containing pine-leaf powder. This melting temperature decrease of the composites was considered to be due to the formation of hydrogen bonds between the hydroxyl groups of starch and the carbonyl groups of PCL, which inhibits the movements of PCL chains for crystallization. Tensile properties and water resistance of the composites were improved considerably by the silane coupling agent. The silane coupling agent could compatibilize PCL and the fillers at the interfaces and this resulted in the improvement of the physical properties. SEM images showed that the PCL/starch/

pine-leaf composite with the silane coupling agent had a morphology, indicating a good interfacial adhesion between PCL and the fillers.

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