Effect of different compatibilizers on the mechanical and thermal properties of starch/polypropylene blends

Xianhong Chen,*[1] Leiyong Zhou,[1] Xiaomei Pan,[2] Jinhui Hu,*[3] Yixing Hu,[1] Shanshan Wei[1]

[1]College of Packaging and Materials Engineering, Hunan University of Technology, Zhuzhou 412007, People's Republic of China
[2]Hunan Province Plastics Research Institute, Changsha 410001, People's Republic of China
[3]People's Hospital of Hunan Province, Changsha 410005, People's Republic of China
Correspondence to: X.-H. Chen (E-mail: xianhongchen@hnu.edu.cn) and J.-H. Hu (E-mail: 798076678@qq.com)

ABSTRACT: Starch was treated with three kinds of compatibilizers (coupling agents or modifying agents), KH-550, KH-570, and glycerin monostearate. Blends of polypropylene (PP) and treated starch were prepared by a twin-screw extruder. The effects of the starch before and after treatments and the kinds and contents of the compatibilizers on the mechanical and thermal properties of the PP/starch blends were investigated in this study. We found that the mechanical properties (tensile strength, impact strength, and elongation at break) of the blends were obviously improved with increasing content of different kinds of compatibilizers. Meanwhile, the most significant improvement in the mechanical properties was obtained in the samples containing just a 1 wt % loading of compatibilizers, and KH-570 had the best improved effects among the different kinds of compatibilizers. The results of thermogravimetric analysis demonstrate that to some extent, the thermal stability of the PP/starch blends was improved after the addition of compatibilizers. Scanning electron microscopy showed that the dispersion of starch in the PP matrix and adhesion between the starch and PP matrix were obviously improved after the addition of compatibilizers. KH-570 not only had the best improved effects among the coupling agents but also still acted as a similar plasticizer. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43332.

INTRODUCTION

It is well known that plastic materials are indispensable in our lives, as they are used extensively in diverse fields, such as agriculture, the automobile industry, and packaging. In general, these materials have a short useful life (in many cases, <2 years) and withstand environmental degradation.[1] These factors have led to an obvious increase in the amount of polypropylene (PP) and high-density polyethylene (PE) waste because they account for a significant percentage of waste materials in recent years. Some scientific and technological efforts have been directed toward minimizing the environmental impacts derived from the use of polymer materials. Therefore, steady growth will occur in the use of biodegradable plastics with the increasing availability of suitable materials due to societal and legislative pressure. One possible solution to this problem, at least partly, would be to induce a certain level of biodegradability by the addition of biodegradable additives in the form of master batches and/or pro-oxidants.[2–7] Among natural biopolymers, starch is a carbohydrate storage material accumulated by green plants in the form of granules; it has been considered as one of the most promising candidates because of its low specific gravity,

low-cost, biodegradable nature, and renewability. Starch can promote the biodegradability of a nonbiodegradable plastic when blended.[8] Recent studies have focused on starch-based biodegradable blends for reducing environmental pollution[9–19]; these blends get consumed by microorganisms and leave behind a matrix with higher surface area. This accelerates the degradation process.[2,20,21] Meanwhile, it has also been found that only a high enough content of starch (>30 wt %) guarantees the satisfactory degradability of the system.[10,11] However, some researchers have found that an increase in the starch content in the composition results, as a rule, in drastic decreases in the mechanical and thermal stability, rheological properties, and processability of the system.[15,18,22–27] In addition, some research findings have further demonstrated that the main disadvantage of starch-based polyolefin blends/composites seems to be the incompatibility between the hydrophilic starch and the hydrophobic polyolefin matrix; this leads to poor interfacial adhesion.[5,9,11,23] On the other hand, Hamdan et al.[14] reported that the tensile properties of PP/sago starch blends decreased with increasing sago starch content in the blend even when the sago starch granules were well dispersed in the PP matrix. This

further indicated that interfacial interactions between the constituent polyolefin and starch strongly influence the mechanical properties of the blends. This results in poor adhesion and prevents the reinforcing filler from acting effectively within the composite. This inconsistency generates poor stress transfer between the matrix and the filler and limited starch dispersion in the polyolefin melt; this leads to unsatisfactory final properties in the materials produced.

To solve these problems, studies have been performed on surface modification and treatment with a compatibilizer. The strong interfacial bonding strength obtained through improvements in the compatibility between the hydrophilic filler and hydrophobic matrix polymer can improve the physical, mechanical, and thermal properties of the composite system.[28–30] To improve the compatibility between starch and polyolefin, many researchers have done studies, such as on the modification of starch,[31–34] PE, or PP[7,17,18,35–38] and/or the introduction of compatibilizer into blends of starch and PE or PP.[10,19,28–30] For example, Bikiaris et al.[17] reported that blends prepared with a poly(ethylene-g-maleic anhydride) copolymer as a reactive compatibilizer showed a better dispersion within the low-density PE matrix, and the mechanical properties of the blends were significantly improved in comparison to those of the uncompatibilized blends. Until now, the main drawback of the application of the compatibilizer has been the cost of the production, so it is very important to find a simple technology to reduce the cost. The most important chemical modification involves coupling methods. The coupling agent used contains chemical groups, which can react with starch and the polymer. The bonds formed are covalent and hydrogen bonds, which improve the interfacial adhesion. Thus, only favorable molecular interactions can improve the load transfer via bonded or nonbonded means.[15]

To date, little reported work has been done on the effects of modified starch with different compatibilizers (coupling agents or modifying agents) on the mechanical properties of polyolefin/starch composites. The aim of this study was to search for a simple and effective approach for modifying starch and to further demonstrate the industrial potential of the use of low-cost corn starch (CST) for the development of biocomposites with better mechanical properties. This would provide a theoretical foundation and practical reference and would also be highly beneficial from the point of view of applications and environmental protection. We investigated the effect of three sorts of compatibilizers (coupling agents or modifying agents), glycerin monostearate (GMS), (3-aminopropyl) triethoxysilane (KH-550), and methacryloxypropyl trimethoxyl silane (KH-570), on the thermal behaviors, mechanical properties, and morphological structures of the PP/starch composites.

EXPERIMENTAL

Materials

Commercial PP (XD-045, melt flow index = 2.0–5.5) was obtained from Yue Yang Xing Chang Petro-Chemical Co., Ltd. (China) and was dried at 80°C for 8 h before use. The native CST (11% moisture) was purchased from Shijiazhuang, Hebei Province Lisheng Starch Sugar Co., Ltd. (China), and was dried

in a vacuum oven at 80°C for 72 h before use. GMS was provided from Jiangxi Hongyuan Chemical Co., Ltd. (China). (3-Aminopropyl) triethoxysilane (KH-550) and methacryloxy propyl trimethoxyl silane (KH-570) were manufactured by Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd. (China). Other chemicals were obtained from commercial sources and were used as received.

Sample Preparation

Hydrolysis of KH-550 (or KH-570). The procedure of the hydrolysis of KH-550 (or KH-570) was as follows. The solvent was made up of distilled water and alcohol. The solution contained 20 wt % KH-550, 72 wt % absolute ethyl alcohol, and 8 wt % distilled water. In detail, a quantity of 20 g of KH-550 was first dissolved in 72 g of absolute ethanol at room temperature for 10 min under stirring. Then, 8 g of distilled water was dropped into the mixture at a feed rate of 0.2 mL/min until the process was completed. The final mixture was KH-550 (or KH-570) used in our experiments. The weight percentage of KH-570 (or KH-550) indicates the mean weight percentage of pure KH-570 (or KH-550).

Surface Modification and Blending. The blending of PP with CST was carried out in a high-speed mixer (GH2100Y, Beijing Plastic Machinery Factory, China) at room temperature and at a rotary speed of 200 rpm for 6 min. A fixed amount (30 wt %) of CST (because it was the best recommended amount according to the research results of our group) and six levels of the three different types of compatibilizers (KH-570, KH-550, and GMS) at loadings of 0.3, 0.5, 0.7, 1.0, 1.2, and 1.5 wt % were used in the sample preparation. In detail, a certain amount of PP was placed into a high-speed mixer, and a certain amount of CST was added to the mixer under a rotary speed of 60 rpm while a certain amount of the dilute solution of KH-570 or KH-550 was added to the mixer by means of spraying for 15 min. Subsequently, the blend was mixed under a rotary speed of 500 rpm. Finally, the modified blend was obtained after drying. The modified blend with GMS, which was directly added to the mixer, was obtained according to the aforementioned procedures.

Preparation of the PP/Starch Composites

The obtained blends were melt-blended in a twin-screw extruder (TE-35, Nanjing Keya Corp., China). The conditions of temperature used during blending in the barrel from the feed zone (zone 1) to zones 2, 3, and 4 to the nozzle were 160, 185, 190, 200, and 195°C, with a screw speed of 60 rpm. The blends were extruded through a multihole die (3.5 mm), and the extrudates were then fed into a granulator, which converted them into granules. The obtained granules were dried at 80°C for 6 h before we studied them.

Characterization

Thermogravimetry–differential scanning calorimetry measurements were conducted on a STA 449C instrument (Germany) under nitrogen at a heating rate of 10°C/min from room temperature to 600°C. The sample weight varied from 10 to 15 mg.

Scanning electron microscopy (SEM) images were obtained on a JEOL JSM-6700F (Tokyo, Japan) scanning electron microscope
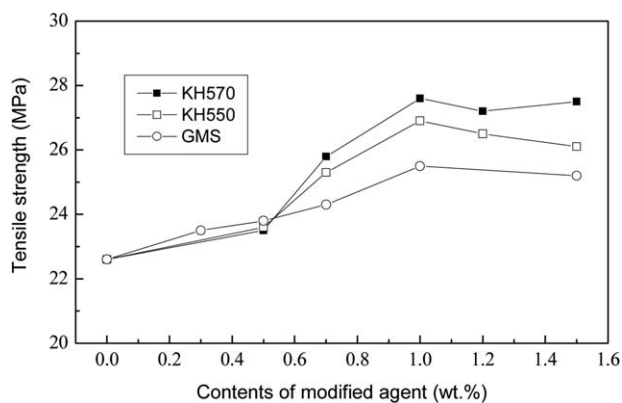
Figure 1. Effects of the kinds and contents of different compatibilizers on the tensile strength.

Figure 3. Effects of the kinds and contents of different compatibilizers on the elongation at break.

at an accelerating voltage of 15 kV. The fracture surfaces were sputter-coated with gold before examination.

Determination of the Mechanical Properties

After extrusion, the materials were injection-molded in the shape of standard specimens according to GB/T1040-1992 and GB/T1043-1993 standard methods (China's national standard), respectively. Tensile tests were carried out with a universal testing machine (model LWK-250, Guangzhou Experimental Instrument Factory, China) according to GB/T1040-1992 at a stretching speed of 50 mm/min. The impact strength was measured by an impact tester (model CBL-11, Changchun Second Testing Machine Co., Ltd., China) according to GB/T1040-1993, notched mode. The test samples were conditioned at 25°C and 50% relative humidity for several days before testing, and all of the tests were performed under the same conditions. All of the results were taken as the average values of seven samples.

RESULTS AND DISCUSSION

Effects of the Kinds and Contents of Different Modifying Agents on the Mechanical Properties of the Composites

In this study, the weight percentages of CST and PP were fixed at 30 and 70%, respectively. In general, the properties of the PE or PP/starch blends decreased significantly because of their poor interfacial adhesion strength.[15,17,25] The effects of different compatibilizers and different added amounts on the blends were
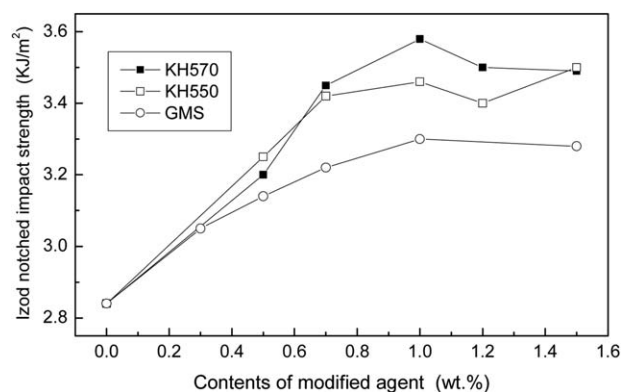

Figure 2. Effects of the kinds and contents of different compatibilizers on the Izod notched impact strength.
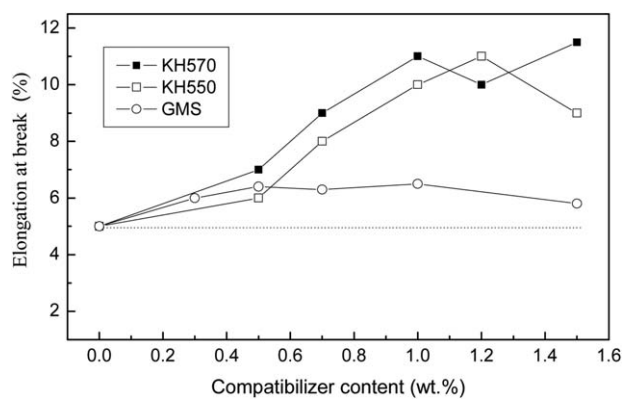
investigated, and the results are shown in Figures 1–3. As shown in Figure 1, the tensile strength of all of the samples increased obviously with increasing amount of modifying agent (KH-570, KH-550, and GMS) compared to the sample without the addition of compatibilizers (the same as discussed later), respectively, and this was followed by a slight decrease. This implied that these compatibilizers had a positive effect on the tensile properties. The tensile strength reached a maximum when the modifying agent content was 1 wt %, and the tensile strengths were 22, 19, and 13% higher, respectively, than the blends without compatibilizers. The Izod impact tests were conducted at room temperature on notched specimens. Figure 2 shows the Izod impact strengths of the CST filler–PP composites made with the different compatibilizers. The effects of the different compatibilizers in the blends on the Izod impact strengths were similar to those of the tensile strength. We found that the blend samples containing just a 1 wt % loading of compatibilizers exhibited an increase in their ultimate strengths. The Izod notched impact values increased about 26, 22, and 16% at a 1 wt % loading of KH-570, KH-550, and GMS, respectively, compared to that of the blend without compatibilizers. The elongation at break also presented the same trend as that of the tensile strength (see Figure 3). The elongation at break values obviously improved about 120, 100, and 30% at 1 wt % of KH-570, KH-550, and GMS, respectively, compared to that of the blend without compatibilizers. These results illustrate that it was advantageous to the improvement of the mechanical properties of blends when compatibilizers were added to the blends. A similar trend in the results was obtained by Sailaja and Chanda[18] and Willett[22] when they used ethylene-co-acrylic acid copolymer (EAA) as a compatibilizer for blends of low-density PE–CST and low-density PE–potato starch and maleic anhydride-grafted PP as a compatibilizer for high-density PE–tapioca starch blends, respectively. In general, the mechanical properties of the composites strongly depended on the extent of load transfer between matrices and modified components. For our research system, the good dispersion and better interfacial adhesion were the key factors under the same PP and CST and the same content conditions. We found that tensile strength, Izod notched impact strength, and elongation at break increased with increasing compatibilizer loading (KH-570, KH-550, and GMS). This

was attributed to the improvement in the dispersion of the starch and the adhesion between PP and starch in the blend. On the one hand, the modifying agents anchored its nonpolar part to the PP matrix in the blend, whereas there were also hydrogen-bonding interactions between the hydroxyl groups of the hydrolyzed KH-570, KH-550, or GMS with that of the starch in the blends.[18,19,29] Also, perhaps there were also etherification reactions of hydroxyl groups of hydrolyzed KH-570, KH-550, or GMS with that of the starch because of dehydration under the processing conditions.[37,38] Therefore, the interfacial adhesion strength between PP and starch was obviously enhanced after the addition of modifying agents into the blend system. On the other hand, the starch was distributed more evenly in PP matrix because the surface of the starch particles was treated/modified with modifying agents. Additionally, the ester of the KH-570, KH-550, or GMS/starch compound was a good plasticizer for the CST/PP blends and also contributed to the dispersion of CST in the PP matrix.[19] Consequently, the good dispersion of CST in the PP matrix and the better bonding between CST and PP benefitted the stress propagation and caused the comprehensive mechanical properties to increase as the compatibilizers loading increased.[37] Meanwhile, we found that the tensile strength, Izod notched impact strength, and elongation at break of the CST/PP blends with the different modifying agents (KH-570, KH-550, or GMS) all reached a maximum when the modifying agent content was 1 wt %; this indicated that the optimal amount of different modifying agents in the blend system was 1 wt %. However, further increases in the various modifying agent contents (>1 wt %) led to gradual decreases in the tensile strength, Izod notched impact strength, and elongation at break. The reason for these results might have been that the modifying agents already covered CST very well. When the amount of the different modifying agent was 1 wt %, CST was covered by KH-570, KH-550, or GMS, according to the model of the monomolecular layer. When the amount of the modifying agent was over 1 wt %, the modifying agent covers CST according to the model of the polymolecular layer instead of the monomolecular layer. Hence, the molecular layer of the modifying agent became the weakest ingredient of the absorbing patch. Breakage first occurred in the polymolecular layer because when the fracture occurred, the first broken place was at the weakest location of the absorbing patch. In addition, the coupling agent used in the blend system belonged to a micromolecular compound. One part of the excessive modifying agents could act as the impurity,[39] and another part could work as a plasticizer to a certain extent[40]; this made the consistency bad and decreased the tensile strength and elongation at break in the blend system. So, the optimal amount of KH-570, KH-550, or GMS is 1 wt %.

Additionally, we found that there were distinct differences in the improvement degree of the mechanical properties of blends. The order of improving effects from good to poor was KH-570, KH-550, and GMS in turn; this implied that KH-570 was the best compatibilizer among three compatibilizers. This could have been due to the result of different structures of the modifying agents. The order of the number of active groups from more to less and of the polarity from strong to weak was hydro-
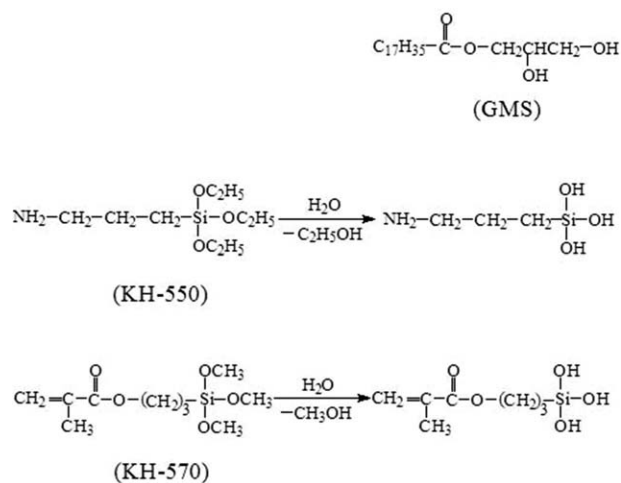

Figure 4. Molecular structural characteristics of GMS, KH-550 (after hydrolysis), and KH-570 (after hydrolysis).

lyzed KH-550 [—OH (three), —NH$_2$ (one)], hydrolyzed KH-570 [—OH (three), —COO— (one)], and GMS [—OH (two), —COO— (one)] in turn, (see Figure 4). In addition, there were C=C bonds on the molecular structure of KH-570; this was similar to the residual C=C bonds of PP. According to the principle of dissolution in the similar material structure, the compatibility between PP and CST could be further improved. In fact, not all active groups were involved in the reaction to form chemical bonds. A large number of facts show that the chain length was neither too long nor too short from the coupling/modifying agent perspective. The order was GMS, KH-570, and KH-550 in descending order of the chain length of molecules. Merely from this point of view, KH-570 was the most appropriate compatibilize (or coupling agent) among the three compatibilizers in a comparison of the chain length. In other words, KH-570 had the best improved effects, and the comprehensive mechanical properties of the sample with KH-570 was best. This behavior was also reflected in the morphologies of the blend (see the discussion on the morphology of the blends later).

Thermogravimetric Analysis (TGA)

The thermal stability of a polymeric material depends on the inherent characteristics of the samples and on the molecular interactions between the different macromolecules. Here, we only report the results of PP/CST (70:30) blends with different KH-570 contents, because it is the best recommended modifying agent in the aforementioned research, because of the same tendency for other two modifying agents. Figure 5 shows the TGA curves of PP, starch and PP/starch blends with different KH-570 contents. The typical features of PP degradation were observed. The decomposition of PP started above 345°C. There were two weight loss stages for the pure/original starch. The first weight loss in the temperature range below 145°C reflected the evaporation of water, and the weight loss rate was about 10%. Then, the weight loss rate remained almost the same in temperature range from 145 to about 266°C; this indicated that the starch structure was unchanged. The second mass loss started around 266°C, at which temperature the starch started
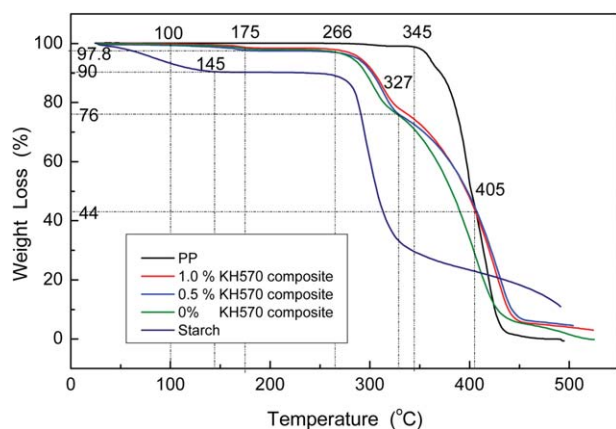
Figure 5. TGA curves of PP, starch, and PP/CST (70:30) composite (or blends) with different KH-570 contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

oxidizing or degrading/decomposing. By contrast, there were three weight loss stages for the blends. The first mass loss in the temperature range from 100 to 175°C displayed the deprotonation of humidity. The weight loss rate was about 2.2% and was obviously lower than that of the original starch. The second mass loss in the temperature range from 266 to 327°C was attributed to the degradation/decomposition of the original starch.[30] At around 327°C, the total weight loss of samples was 24 wt %. The third mass loss started at 327°C and was caused by the thermal decomposition of PP and the thermal degradation/decomposition of the residual starch. Moreover, we

observed that the thermal weight loss of the PP/CST blends was between that of pure starch and the pure PP, far lower than that of the pure CST, and slightly higher than that of the pure PP; this indicated that PP played a leading role in the thermal stability of the PP/starch blends. However, there were some differences in the degree of thermal weight loss that we found through a more careful examination of the TGA curves of the different PP/starch blends. We found that the weight loss of blend with treated starch slightly increased with increasing content of KH-570 in the temperature range from 100°C to approximately 266°C, and this tendency was especially obvious above 266°C as compared to that without compatibilizer (0 wt % KH-570 blends or composite); this suggested that the addition of KH-570 was in favor of improving the thermal stability of the PP/starch composites. This was due to the induction of the improvement of the dispersion and interfacial adhesion between PP and starch.[28]

Morphologies of the Blends

The blend morphologies of the impact-fractured specimens loaded with 30 wt % starch are shown in Figure 6. Figure 6(A) shows the SEM photograph of PP blended with 30 wt % CST. We observed that there were a lot of different granular particles of CST or left voids (or cavities) of CST on the fractured surface. Most of them exhibited irregular and discrete globular particles, and the diameter of the granules or voids was between 7 and 12 μm; this implied that CST was not fully destroyed even after the extrusion was done. Meanwhile, granular deposits (see square) and some ditches (see arrows) were also found; this indicated that the dispersion of starch in PP is poor. On the
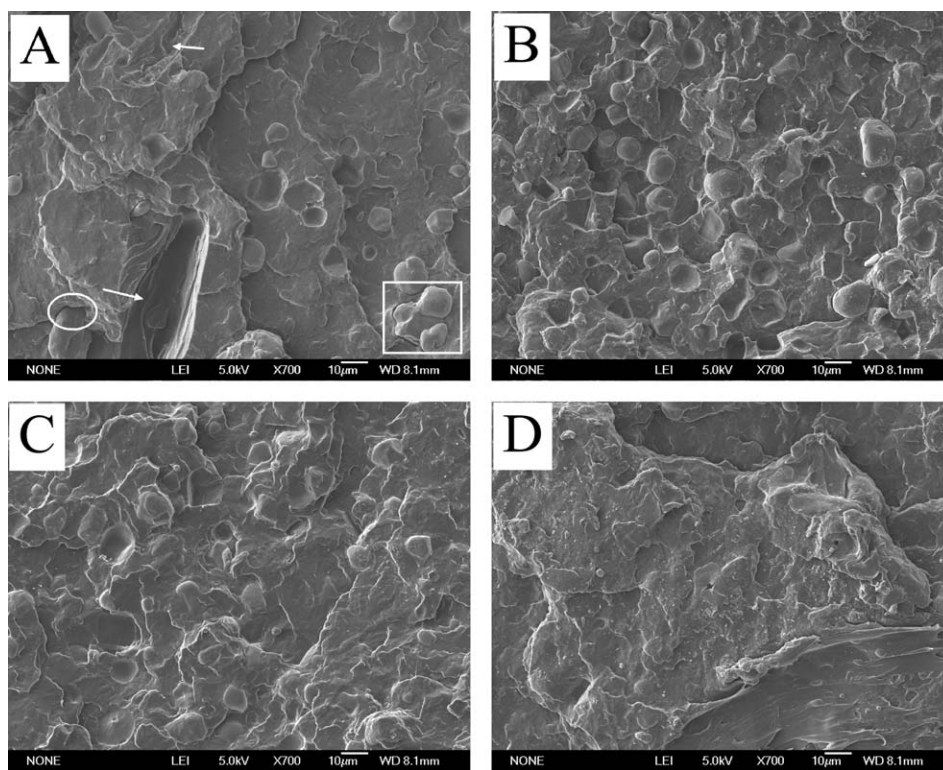

Figure 6. SEM images of the fractured surfaces of (A) 70:30 PP/CST, (B) 70:30:1 PP/CST/GMS, (C) 70:30:1 PP/CST/KH-550, and (D) 70:30:1 PP/CST/KH-570.

other hand, it could be observed that these surfaces or boundaries of the granular deposits, voids (or cavities) and ditches are clear and smooth. Additionally, by carefully observing Figure 6(A), we found gaps (see circle) between the granular CST and PP. These facts indicate that the interfacial adhesion between the starch and matrix PP was weak. The poor dispersion of CST in PP and the weak interfacial adhesion between the starch and PP led to brittle fracture.[19] Figure 6(B) displays the micrograph of the impact-fractured sample with the addition of 1 wt % GMS compatibilizer to this blend. We observed that the CST morphology in the PP blend had the tendency to become circular or more regular globular particles and leave voids (or cavities) of CST. The size of the granules or voids (or cavities) was between about 4–11 μm. Also, the granular deposits and gaps between the granules and the matrix could be hardly observed. These facts indicated that the dispersion of CST in PP and the interfacial adhesion between CST and PP, to a certain extent, were improved. The fractured surface of this blend with an interfacial modifier revealed a slight deformation before fracture compared to that without GMS [Figure 6(A)], although the fracture was still predominantly brittle. Figure 6(C) displays the morphology of the impact-fractured PP/CST/KH-550 composite (70:30:1). The addition of KH-550 in the composites produced a more uniform surface with fewer voids and cavities. At the same time, a much more homogenized morphology was evident. On the other hand, the gaps between the granules and the matrix could not be found on the surface of the impact-fractured specimen. This illustrated that KH-550 brought a further positive effect to the interface and the adhesion between the starch and PP. For the PP/CST/KH-570 composite (70:30:1) specimen, the impact-fractured micrograph is shown in Figure 6(D). We observed that the obvious globular particles and voids (or cavities) and granular deposits of starch almost disappeared; this indicated that with KH-570, there was better dispersion than with KH-550, as shown in Figure 6(C). Meanwhile, the surface of the impact-fractured specimen showed a change from a brittle fracture pattern to a typical ductile fracture pattern. This may have been due to KH-570, which acted as not only a coupling agent but also as a similar plasticizer.[19] The fact could also explain why the comprehensive properties of the composite with the incorporation of KH-570 were the best. This result coincided with that of the mechanical properties of composites described previously.

CONCLUSIONS

CST was treated with three different compatibilizers, KH-550, KH-570, and GMS, and then, PP/CST blends were prepared by a twin-screw extruder. The effects of different compatibilizers and their contents on the mechanical and thermal properties of the PP/CST blends were examined in this study. We found that the mechanical properties (tensile strength, impact strength, and elongation at break) of the blends were obviously improved with the addition of and increasing amounts of the compatibilizers, respectively, because they strengthened the interfacial bonding between the filler and the matrix polymer, resulted in good stress propagation, and improved the tensile strength. The most significant improvement in the mechanical properties of

the samples containing just a 1 wt % loading of compatibilizers was obtained. The order of improving effects from good to poor was KH-570, KH-550, and GMS in turn. The TGA measurements showed that the thermal stability of the PP/CST blends improved somewhat after the addition of compatibilizers in comparison to that of the uncompatibilized blend. The thermal weight loss of the PP/CST blends was between those of the pure CST and the pure PP, higher than that of the pure CST, and lower than that of the pure PP. The SEM results show that there were better dispersion and better interfacial adhesion between CST and PP when the compatibilizers were added to the blend system. KH-570 not only had the best improved effects among coupling agents but also still acted as a similar plasticizer. We believe that the result will guide biodegradable plastics development.

REFERENCES

1. Ramis, X.; Cadenatoa, A.; Sallaa, J. M.; Moranchoa, J. M.; Valles, A.; Contat, L.; Ribes, A. *Polym. Degrad. Stab.* **2004**, *86*, 483.

2. Erlandsson, B.; Karlsson, S.; Albertsson, A.-C. *Polym. Degrad. Stab.* **1997**, *55*, 237.

3. Morancho, J. M.; Ramis, X.; Fernandez, X.; Cadenato, A.; Salla, J. M.; Valles, A.; Contat, L.; Ribes, A. *Polym. Degrad. Stab.* **2006**, *91*, 44.

4. Roy, P. K.; Surekha, P.; Rajagopal, C.; Choudhary, V. *Express Polym. Lett.* **2007**, *1*, 208.

5. Roy, P. K.; Surekha, P.; Rajagopal, C.; Choudhary, V. *J. Appl. Polym. Sci.* **2007**, *103*, 3758.

6. Roy, P. K.; Surekha, P.; Rajagopal, C.; Chatterjee, S. N.; Choudhary, V. *Polym. Degrad. Stab.* **2006**, *91*, 1791.

7. Roy, P. K.; Swami, V.; Kumar, D.; Rajagopal, C. *Int. J. Polym. Mater.* **2012**, *64*, 241.

8. Hanifi, S.; Oromiehie, A.; Ahmadi, S.; Farhadnejad, H. *J. Vinyl Additive Technol.* **2014**, *20*, 16.

9. Zaman, H. U.; Khan, M. A.; Khan, R. A.; Mollah, M. Z. I.; Pervin, S.; Al-Mamun, M. D. *J. Reinf. Plast. Compos.* **2010**, *29*, 1930.

10. Zuchowska, D.; Steller, R.; Meissner, W. *Polym. Degrad. Stab.* **1998**, *60*, 471.

11. Schlemmer, D.; Sales, M. J. A.; Resck, I. S. *Carbohydr. Polym.* **2009**, *75*, 58.

12. Rosa, D. S.; Bardi, M. A. G.; Machado, L. D. B.; Dias, D. B.; Silva, L. G. A.; Kodama, Y. *J. Therm. Anal. Calorim.* **2010**, *102*, 181.

13. Tran, T.; Lee, B.-H.; Yang, H.-S.; Chotineeranat, S.; Sriroth, K.; Kim, H.-J. *Starch* **2011**, *63*, 637.

14. Hamdan, S.; Hashim, D. M. A.; Ahmad, M.; Embong, S. *J. Polym. Res.* **2000**, *7*, 237.

15. Tran, T.; Lee, B.-H.; Yang, H.-S.; Chotineeranat, S.; Sriroth, K.; Kim, H.-J. *Starch* **2011**, *63*, 649.

16. Joshi, S. S.; Mebel, A. M. *Polymer* **2007**, *48*, 3893.

17. Bikiaris, D.; Prinos, J.; Koutsopoulos, K.; Vouroutzis, N.; Pavlidou, E.; Frangis, N.; Panayiotou, C. *Polym. Degrad. Stab.* **1998**, *59*, 287.

18. Sailaja, R.; Chanda, M. *J. Appl. Polym. Sci.* **2001**, *80*, 863.

19. Huang, V.-Y.; Roan, M.-L.; Kuo, M.-C.; Lu, W.-L. *Polym. Degrad. Stab.* **2005**, *90*, 95.

20. Roy, P. K.; Surekha, P.; Rajagopal, C. *J. Appl. Polym. Sci.* **2011**, *122*, 2765.

21. Chiellini, E.; Corti, A.; Swift, G. *Polym. Degrad. Stab.* **2003**, *81*, 341.

22. Willett, J. L. *J. Appl. Polym. Sci.* **1994**, *54*, 1685.

23. Dintzis, F. R.; Bagley, E. B. *J. Appl. Polym. Sci.* **1995**, *56*, 637.

24. Ndiaye, D.; Gueye, M.; Diop, B. *Arab. J. Sci. Eng.* **2013**, *38*, 59.

25. Kaseem, M.; Hamad, K.; Deri, F. *Polym. Bull.* **2012**, *68*, 1079.

26. Rosa, D. S.; Guedes, C. G. F.; Carvalho, C. L. *J. Mater. Sci.* **2007**, *42*, 551.

27. Bagheri, R.; Naimian, F. *J. Appl. Polym. Sci.* **2007**, *104*, 178.

28. Wang, S.; Yu, J.; Yu, J. *J. Appl. Polym. Sci.* **2004**, *93*, 686.

29. Bikiaris, D.; Panayiotou, C. *J. Appl. Polym. Sci.* **1998**, *70*, 1503.

30. Shujun, W.; Jiugao, Y.; Jinglin, Y. *Polym. Degrad. Stab.* **2005**, *87*, 395.

31. Thakore, I. M.; Desai, S.; Sarawade, B. D.; Devi, S. *Eur. Polym. J.* **2001**, *37*, 151.

32. Khalil, H. P. S. A.; Chow, W. C.; Rozman, H. D.; Ismail, H.; Ahmad, M. N.; Kumar, R. N. *Polym. Plast. Technol. Eng.* **2001**, *40*, 249.

33. Kiatkamjornwonga, S.; Thakeowb, P.; Sonsukc, M. *Polym. Degrad. Stab.* **2001**, *73*, 363.

34. Aburto, J.; Thiebaud, S.; Alric, I.; Borredon, E.; Bikiaris, D.; Prinos, J.; Panayiotou, C. *Carbohydr. Polym.* **1997**, *34*, 101.

35. Mortazavi, S.; Ghasemi, I.; Oromiehie, A. *Polym. Test.* **2013**, *32*, 482.

36. Liu, L.; Yu, Y.; Song, P. *Ind. Eng. Chem. Res.* **2013**, *52*, 16232.

37. Yang, H.-S.; Wolcott, M. P.; Kim, H.-S.; Kim, S.; Kim, H.-J. *Compos. Struct.* **2007**, *79*, 369.

38. Jesionowski, T.; Krysztafkiewicz, A. *Appl. Surf. Sci.* **2001**, *172*, 18.

39. Liu, L. Z.; Weng, L.; Song, Y. X.; Gao, L.; Zhao, H.; Lei, Q. Q. *Pigment Resin Technol.* **2011**, *40*, 222.

40. Yongbao, F.; Tai, Q.; Jun, Z.; Chunying, S. *J. Wuhan Univ. Technol. Mater. Sci. Ed.* **2006**, *21*, 78.