

Physical properties of polypropylene composites with hydrophobized cellulose powder by soybean oil

Song Yi Jang, Dae Su Kim

Department of Chemical Engineering, Chungbuk National University, 1 Chungdaero, Seowongu, Cheongju, Chungbuk 362-763, Korea

Correspondence to: D. S. Kim (E-mail: dskim@cbnu.ac.kr)

ABSTRACT: Cellulose materials have attracted lots of interest as potential natural fillers in the production of green polymer composites because they are ecofriendly and economic. In this study, to improve the interfacial bonding strength between cellulose powder and a hydrophobic polypropylene (PP) matrix, the surface hydrophobization of cellulose powder by soybean oil was carried out via a simple transesterification reaction procedure. Weight change measurements, Fourier transform infrared spectroscopy, and compatibility testing were used to quantitatively and qualitatively analyze the hydrophobization of the cellulose powder. By changing the hydrophobization conditions, the soybean oil content attached to the cellulose powder changed from 8.0 to 57.8%. PP composites with 20% of each hydrophobized cellulose powder were prepared by melt blending followed by compression molding. The mechanical properties of the PP composites were investigated with a universal testing machine and an Izod impact tester. Compared to the composite with pristine cellulose powder, the PP composite with the hydrophobized cellulose powder and an attached soybean oil content of 29.6% showed largely increased impact strength (46.3%), tensile strength (47.5%), and elongation at break (27.3%) values. The scanning electron microscopy images for the fracture surfaces of the composites showed that the hydrophobization induced much stronger interfacial bonding between the PP matrix and cellulose powder. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42929.

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INTRODUCTION

Cellulose is one of the most abundant natural, ecofriendly, and biodegradable materials in the world. It can be obtained easily from many natural sources. For the last few decades, interest in producing polymer composites with cellulose materials has received considerable attention.^{1–5} Polymer composites with cellulose fillers have many advantages compared to typical polymer composites with inorganic fillers. The main advantages of cellulose fillers include the possibility of easy recycling, biodegradability, high specific strength and modulus, low density, and low thermal conductivity. Recently, many studies have focused on the mechanical properties and environmental features of polymer composites with cellulose fillers.^{1,5–9}

The thermomechanical properties of commodity thermoplastics such as polypropylene (PP), polyethylene, and poly(vinyl chloride) decrease with increasing temperature.^{10–14} However, the addition of fillers such as wood flour or cellulose powder to thermoplastics can effectively improve their thermomechanical properties. PP, which is generally used to make household appliances, medical supplies, and automotive and other industrial

products, has been widely used as a polymer matrix to make such thermoplastic composites with biomass fillers. However, the effective addition of cellulose fillers to a typical polymer matrix such as PP has been not so easy because of the fillers' high polarity and hydrophilicity; this makes dispersion in the matrix and interfacial adhesion to the nonpolar hydrophobic polymer matrix poor.^{15–17} The poor compatibility of cellulose fillers to a nonpolar hydrophobic polymer results in their agglomeration and weak interfacial interaction with the polymer matrix. This leads to poor mechanical properties. Therefore, many studies to enhance the hydrophobicity of cellulose fillers by reactive modification have been reported.^{18–20}

Cellulose fillers have lots of hydroxyl groups that can easily react with the corresponding functional groups, such as carboxyl groups, of reactive modifiers. Linolenic acid, linoleic acid, and oleic acid can be used as reactive modifiers to give cellulose fillers hydrophobicity. Cellulose materials can be hydrophobized in an ecofriendly manner by vegetable oils composed of many fatty acids via an acid-catalyzed or base-catalyzed transesterification reaction.^{21,22}

In this study, the surface hydrophobization of cellulose powder by soybean oil was carried out in an ecofriendly manner via a simple transesterification reaction procedure at a relatively high temperature without the use of any acid or base catalyst. Weight change measurements, Fourier transform infrared (FTIR) spectroscopy, and compatibility testing were performed to quantitatively and qualitatively analyze the hydrophobization of cellulose powder. PP composites with 20% hydrophobized cellulose powder were prepared by melt blending followed by compression molding, and then, the effects of the hydrophobization of the cellulose powder on the physical properties of the PP–cellulose composites were investigated extensively.

EXPERIMENTAL

Materials

PP [B-310, melt flow index = 0.5 g/10 min, density = 0.90 g/cm³, and heat distortion temperature (HDT) (at 4.6 Kgf/cm²) = 100°C] was supplied by Lotte Chemical Co. (Korea). The PP was a type of impact block PP copolymer with ethylene–propylene rubber inside homopolypropylene. Cellulose powder, manufactured by the crushing of the waste scraps of paper cup sheets, was supplied by ERI Co. (Japan). The average particle size of the cellulose powder was 41 μm, and its specific surface area was 0.174 m²/cm³. The soybean oil (CJ Cheiljedang Co., Korea) that was used for the surface hydrophobization of the cellulose powder had a density of 0.917 g/cm³. A lubricant (TPX-1300), a modified fatty acid ester blend, was supplied from Dongwon Co. (Korea). The lubricant had a density of 1.05 g/cm³, a molecular weight of 170 g/mol, and a melting temperature of 71–86°C. Ethanol (SK Chem., Korea) was used to make soybean oil–ethanol solutions for the hydrophobization of the cellulose powder and to wash unreacted residual soybean oil after the hydrophobization reaction. Dichloromethane (Junsei Chem., Japan, $d = 1.335$ g/cm³, where d is density) was used as an organic solvent in the compatibility test.

Hydrophobization of the Cellulose Powder

To remove impurities, a cellulose–water suspension with 6% cellulose powder was stirred with a homogenizer at 6500 rpm for 1 h; then, after we removed water by centrifugation, the sediment was dried in an oven at 105°C for 2 h. An amount of 400 g of the soybean oil–ethanol solution with 5 g (or 10, 15, or 20 g) of soybean oil was prepared first, and then, after 20 g of the pretreated cellulose powder was added to the solution, the suspension was stirred for 5 min. The suspension was partially dried until the mixture weight became 100 g, and it was then reacted in an oven at 110°C for 1 h to hydrophobize the cellulose powder. The reacted mixture was washed with ethanol, filtered three times, and then dried in an oven at 105°C for 2 h.

Preparation of the PP–Cellulose Composites

Platy PP–cellulose composites were prepared by the melt blending of all of the components in a Haake Rheomix 600 mixer equipped with a rolling blade rotor at 170°C for 15 min at 60 rpm and then the compression molding of the melt mixture in a Carver hydraulic hot press at 180°C for 6 min under 1000 psi. We optimized the processing conditions adopted in this study in our previous study for PP–cellulose composites with maleic anhydride grafted polypropylene (MAPP) by checking the colors of the composites

prepared at different processing conditions to prevent or minimize any possible degradation of the cellulose powder.²³ Specimens for mechanical tests were prepared by cutting the platy composites out into desired sizes. To mainly determine the effects of the hydrophobization of the cellulose powder on the physical properties, the compositions of all of the components in the composites were fixed to 80 parts PP, 20 parts pristine or hydrophobized cellulose powder, and 2 parts lubricant.

Measurements

Compatibility Testing. Compatibility testing was performed to qualitatively analyze the hydrophobicity of the pristine and hydrophobized cellulose powders.¹⁸ An amount of 5 mg of each cellulose powder was mixed with a heterogeneous solution composed of two immiscible solvents, water and dichloromethane, with different polarities and densities in a vial, and then, the solution in the vial was shaken vigorously by hand and left alone for a while to observe the compatibility of the cellulose powder with the solvents.

Spectroscopy. To investigate the hydrophobization of the cellulose powder, FTIR spectroscopy (Nicolet IR200, Thermo Scientific Co.) was used. The FTIR spectra of the pristine and hydrophobized cellulose powders were obtained in the wave-number range 4000–600 cm⁻¹.

Thermal Analysis. To analyze the hygroscopicity of the hydrophobized cellulose powders, a thermogravimetric analyzer (SDT 2960, TA Instruments, New Castle, DE) was used. Each measurement was carried out under a nitrogen atmosphere (100 mL/min) from room temperature to 200°C at 10°C/min.

Impact Testing. The notched Izod impact testing of the PP–cellulose composites was performed at room temperature with an impact tester (SJI-103, Sung Jin Co., Korea) according to ASTM D 256. The dimensions of specimens were 50 × 11 × 4 mm³. The average value of at least 10 specimens' impact strength data is reported for each composite.

Tensile Testing. The tensile properties of the PP–cellulose composites were measured with a universal testing machine (LR-30K, Lloyd, Hampshire, United Kingdom) with a load cell of 1 kN at a crosshead speed of 5 mm/min according to ASTM 638. The dimensions of the specimen were 64 × 9.53 × 0.5 mm³. The average value of at least six specimens' tensile property data is reported for each composite.

Water-Absorption Test. The water absorption and thickness swelling properties of the PP–cellulose composites were measured in accordance with ASTM D 570. The composites samples were immersed in a distilled-water bath maintained at 23 ± 1°C for 1 day and taken out from the bath for weighing after they were gently blotted with tissue paper to remove excess water from their surfaces. They were then immediately returned to the bath for the next measurements for longer times of 2–5 days).

The percentage weight increase due to water absorption at time t (W_t) was calculated by eq. (1):

$$W_t = \frac{(W - W_0)}{W_0} \times 100\% \quad (1)$$

where W_0 and W are the weights of the dry and immersed wet samples, respectively.

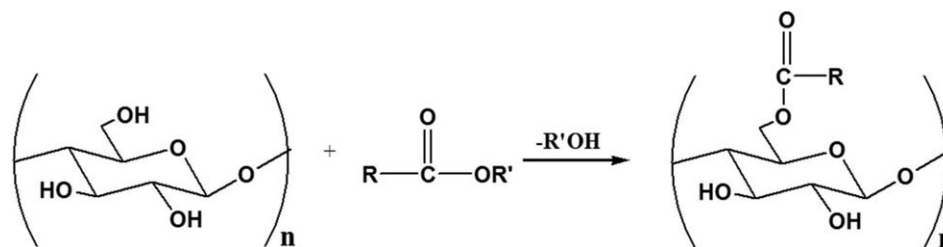


Figure 1. Simple transesterification reaction procedure for hydrophobizing cellulose powder by soybean oil.

The percentage thickness increase due to water absorption at time t (TS_t) was calculated by eq. (2):

$$TS_t = \frac{(T_t - T_0)}{T_0} \times 100\% \quad (2)$$

where T_0 and T_t are the thicknesses of the dry and immersed wet samples, respectively.

Morphology. To determine the structure of the interface between the PP matrix and the cellulose powder, the fracture surfaces of the composites were observed with a scanning electron microscope (JEM-840A, JEOL Co., Japan) at an acceleration voltage of 20 kV. The fracture surfaces of the composites were coated with Pt before scanning electron microscopy (SEM) observation.

RESULTS AND DISCUSSION

Hydrophobization of the Cellulose Powder

Figure 1 shows a simple transesterification reaction procedure for hydrophobizing the cellulose powder by soybean oil without any acid or base catalyst. Table I shows the attached soybean oil content to the cellulose powder loaded after the hydrophobization reaction under various conditions. By changing hydrophobization condition, we changed the attached soybean oil content to the cellulose powder from 8.0% to 57.8%. With increasing soybean oil content in the solution, the amount of soybean oil covalently bonded to the surfaces of the cellulose powder increased; this was also as expected.

The amount of soybean oil covalently bonded to the surfaces of the cellulose powder was almost the same regardless of the increasing reaction temperature from 110 to 130°C; this meant that the hydrophobization reaction finished in 1 h at 110°C.

However, the amount of soybean oil covalently bonded to the surfaces of the cellulose powder decreased from 5.92 to 4.54 g when the hydrophobization reaction time was shortened from 1 to 0.5 h at 110°C; this meant that there was an incomplete reaction under these conditions. Therefore, the hydrophobization reaction conditions of 1 h at 110°C were applied to all of the other solutions with different soybean oil contents.

Figure 2 shows the dispersion images of the pristine cellulose powder (labeled C) and the hydrophobized cellulose powders (each labeled H-C with the soybean oil content in the parenthesis) suspended in the water–dichloromethane solution. Compared to the inherently hydrophilic pristine cellulose powder, which resided in the top water layer, all of the hydrophobized cellulose powders resided in the bottom dichloromethane layer. This proved proving that the hydrophobization of the cellulose powder was successful.^{24–27}

Figure 3 shows the FTIR spectra of the soybean oil (top) and the pristine and hydrophobized cellulose powders (bottom). The FTIR spectra of the soybean oil showed two distinct strong absorption peaks, one at 2900–3000 cm^{-1} caused by many C–H bonds in alkyl chains and the other at 1745 cm^{-1} caused by C=O bonds in carboxylic acid ester linkages. As shown in Figure 3 (bottom), a new absorption peak appeared at 1745 cm^{-1} in each spectra of each hydrophobized cellulose powder (named H-cellulose), and its absorption intensity increased with increasing soybean oil content covalently attached to the surfaces of the cellulose powder. This also proved that the hydrophobization reaction, which provided ester groups on the surfaces of the cellulose powder, occurred successfully.

Table I. Soybean Oil Content Attached to the Cellulose Powder Loaded after the Hydrophobization Reaction under Various Reaction Conditions

Cellulose powder loaded (g)	Soybean oil content in solution [g (wt %)]	Reaction temperature (°C)	Reaction time (h)	Soybean oil content attached to cellulose powder loaded after reaction [g (wt %)]
20	5 (1.25)	110	1	1.60 (8.0)
		110	0.5	4.54 (22.7)
	110	1	5.92 (29.6)	
	120	1	6.00 (30.0)	
	130	1	6.06 (30.3)	
20	15 (3.75)	110	1	8.80 (44.0)
	20 (5)	110	1	11.56 (57.8)

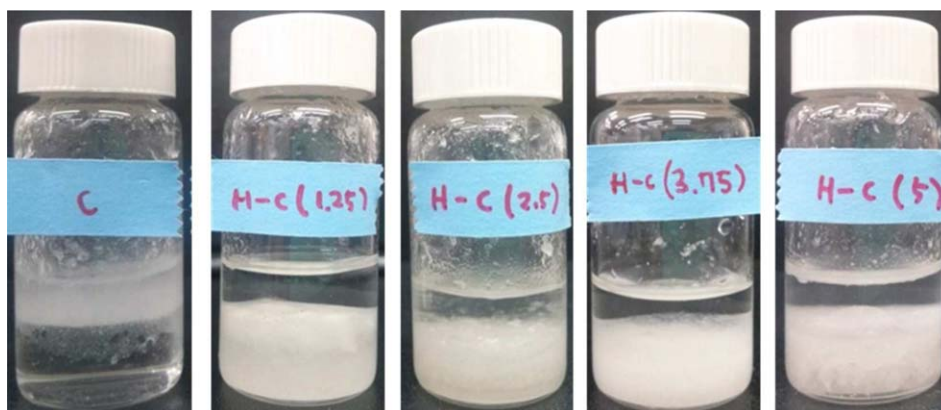


Figure 2. Dispersion images of the pristine cellulose powder (labeled C) and the hydrophobized cellulose powders (each labeled H-C with the soybean oil weight percentage in the solution in parentheses) suspended in a water–dichloromethane solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To investigate the hygroscopicity of the pristine and hydrophobized cellulose powders, 1 g of each cellulose powder was dried in an oven at 105°C for 2 h and exposed to air (at 65% relative humidity) for 1 day at room temperature. Figure 4 shows the TGA curves for the pristine and two hydrophobized cellulose

powders with attached soybean oil contents of 5.92 and 11.56 g, respectively. The greater the amount of soybean oil covalently attached to the cellulose powder was, the lower the hygroscopicity of the cellulose powder was. Compared to the pristine cellulose powder, the hydrophobized cellulose powders absorbed less moisture in the air.

Mechanical Properties of the PP–Cellulose Composites

The impact strengths of the PP–cellulose composites are shown in Figure 5 as a function of the soybean oil content attached to the cellulose powder. The impact strength of the composite increased monotonically with the attached soybean oil content because the interfacial adhesion strength between the PP matrix and the cellulose powder could also be increased with the attached soybean oil content.^{28–31} Furthermore, the alkyl chains attached to the cellulose powder could behave as a plasticizer, and this effect also increased with the attached soybean oil content. All of the mechanical properties of the PP–cellulose composites are listed in Table II for accuracy.

The tensile properties of the composites are shown in Figure 6 as a function of the soybean oil content attached to the cellulose

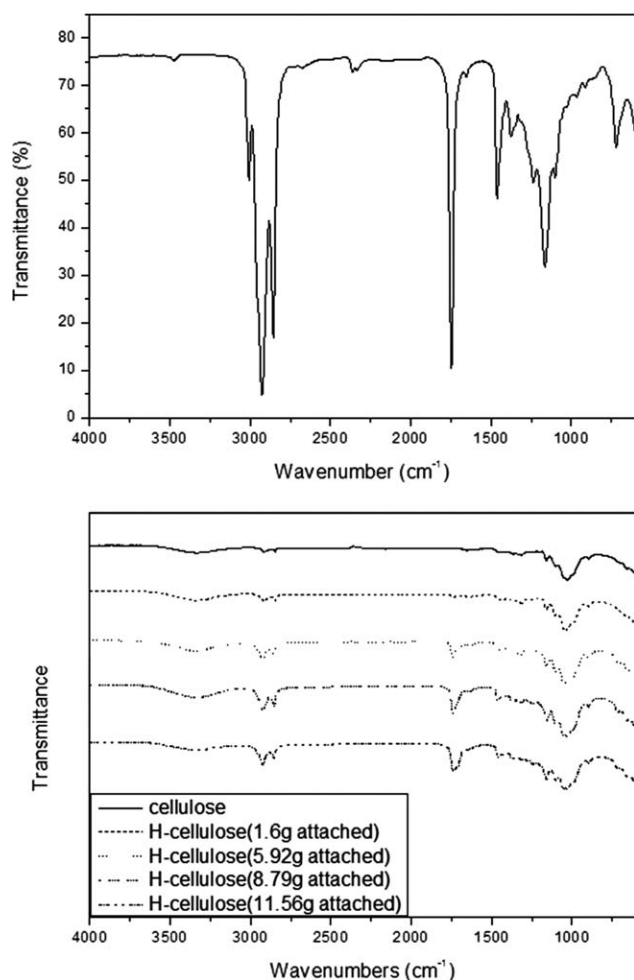


Figure 3. FTIR spectra of the soybean oil (top) and the pristine and hydrophobized cellulose powders (bottom).

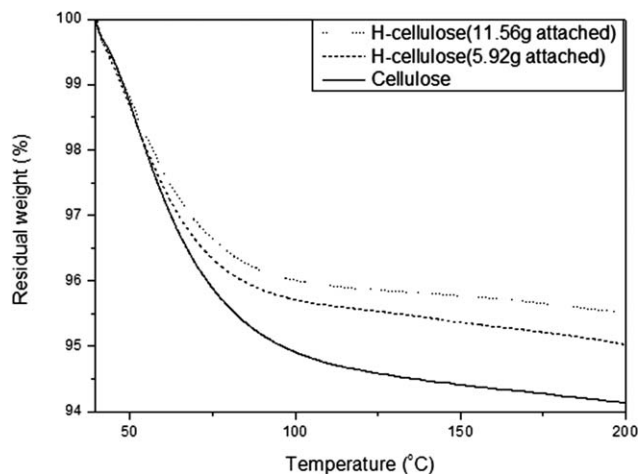


Figure 4. TGA curves for the pristine cellulose powder and two hydrophobized cellulose powders with attached soybean oil contents of 5.92 and 11.56 g, respectively.

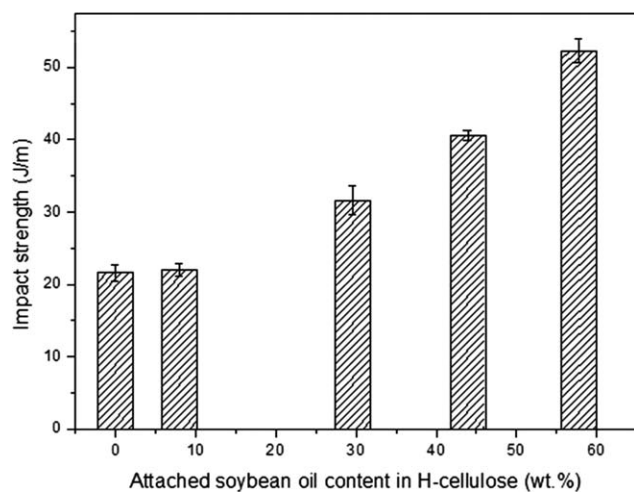


Figure 5. Impact strength of the PP–cellulose composites as a function of the soybean oil content attached to the cellulose powder.

powder. The tensile properties of the thermoplastic composites with biomass fillers such as wood and cellulose are one of the most important mechanical properties from the viewpoint of commercial applications, such as packaging, of the composites.²⁶ The tensile strength and modulus of the composite were at maximum values at an attached soybean oil content of 29.6%, which was optimum for the tensile properties, as shown in Figure 6(a). Above the attached soybean oil content of 29.6%, the tensile properties of the composite decreased with increasing attached soybean oil content because of increased flexibility and softness. The factors improving the impact strength also made the elongation at break of the composite increase largely with increasing attached soybean oil content, as shown in Figure 6(b).

As described previously, the impact strength of the composite increased monotonically with the attached soybean oil content because of an improved interfacial adhesion strength and the plasticizing effect of the attached soybean oil with long alkyl chains. The hydrophobization level increase up to 29.6% gradually improved the interfacial bonding strength between the PP matrix and the cellulose powder, but hydrophobization levels over 29.6% did not change the interfacial bonding strength considerably, although plasticizing effect of the excess soybean oil increased continually with increasing hydrophobization level. This was the reason why the tensile strength and modulus of the composites were at a maxima at an attached soybean oil

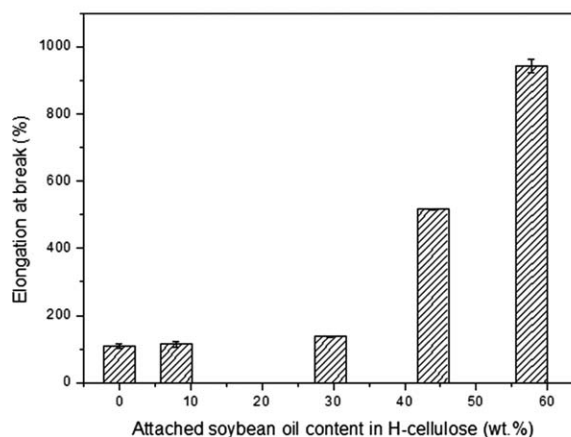
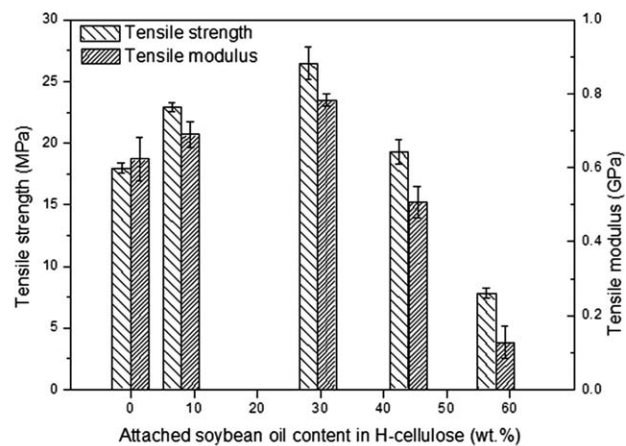


Figure 6. Tensile strength and modulus (top) and elongation at break (bottom) of the PP–cellulose composites as a function of the soybean oil content attached to the cellulose powder.

content of 29.6% and why the composites with the hydrophobized cellulose powder showed a very high elongation at break, especially at high hydrophobization levels over 29.6%.

In our previous study, we reported the impact strength and the tensile properties of PP–cellulose composites with a maleic anhydride grafted PP copolymer as a compatibilizer.²³ The impact strength and tensile properties of the PP–pristine cellulose composite with the MAPP and the PP–hydrophobized cellulose composite of this study were compared with each other, together with the PP–pristine cellulose composite without the MAPP, as shown in Figures 7 and 8, respectively. The impact strength (31.6 J/m) of the composite with the hydrophobized

Table II. Mechanical Properties of the PP–Cellulose (80:20) Composites

Soybean oil content attached to cellulose powder (%)	Impact strength (J/m)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
0	21.6 ± 1.1	17.9 ± 0.4	0.62 ± 0.058	108.9 ± 8.2
8.0	22.0 ± 0.8	22.8 ± 0.4	0.69 ± 0.034	114.9 ± 8.3
29.6	31.6 ± 2.0	26.4 ± 1.3	0.78 ± 0.017	138.6 ± 2.0
44.0	40.6 ± 0.7	19.2 ± 1.0	0.50 ± 0.042	516.7 ± 1.8
57.8	52.3 ± 1.7	7.8 ± 0.4	0.13 ± 0.044	941.5 ± 20
0 (MAPP 3%)	25.5 ± 1.6	30.5 ± 1.8	0.96 ± 0.040	23.1 ± 2.9

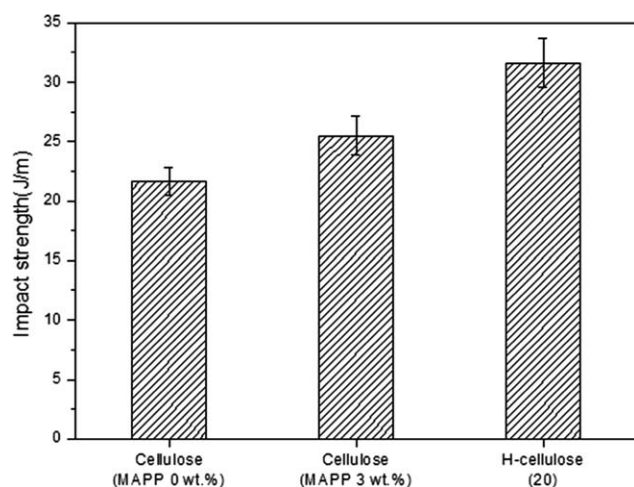


Figure 7. Impact strength of the PP–pristine cellulose composite without MAPP, PP–pristine cellulose composite with MAPP, and PP–hydrophobized cellulose composite.

cellulose powder was considerably higher (23.9% increase) than that (25.5 J/m) of the composite with the MAPP, as shown in Figure 7. Although the tensile strength (26.4 MPa) of the composite with the hydrophobized cellulose powder was slightly lower (13.1% decrease) than that (30.4 MPa) of the composite with the MAPP, the elongation at break (138.6%) of the composite with the hydrophobized cellulose powder was significantly higher (500% higher) than that (23.1%) of the composite with the MAPP, as shown in Figure 8. It was also noteworthy that compared to the composite with pristine cellulose powder, the PP composite with the hydrophobized cellulose powder of the attached soybean oil content of 29.6% showed a largely increased impact strength (46.3%), tensile strength (47.5%), and elongation at break (27.3%). As shown in Figures 7 and 8, the mechanical performance of the composite with the hydrophobized cellulose powder was superior to that of the composite with the MAPP. We considered that the composite with the MAPP had PP–cellulose interfaces with the MAPP molecules bonding the PP matrix and the cellulose powder through

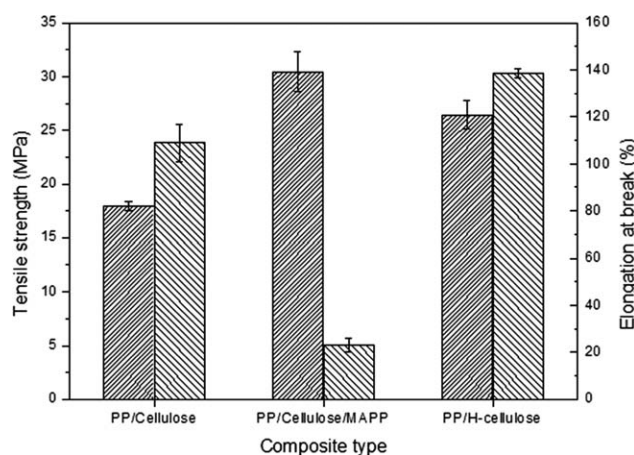


Figure 8. Tensile properties of the PP–pristine cellulose composite without MAPP, PP–pristine cellulose composite with MAPP, and PP–hydrophobized cellulose composite.

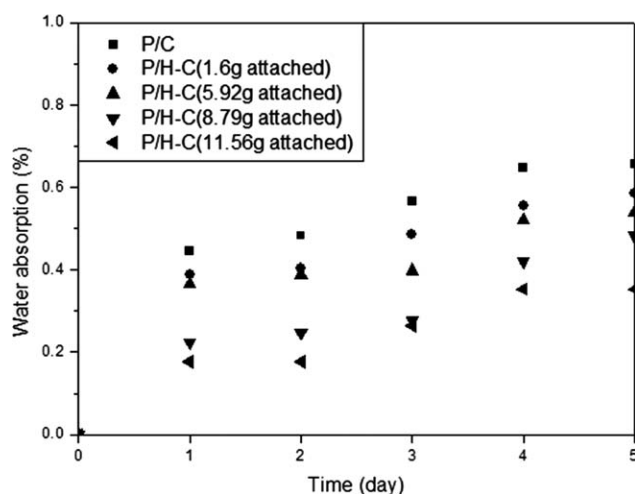


Figure 9. Water absorption of the PP–cellulose composites as a function of the soybean oil content attached to the cellulose powder.

noncovalent nonpolar intermolecular interactions with the PP matrix side and noncovalent polar intermolecular interactions with the cellulose powder side. However, the PP composite with the hydrophobized cellulose powder had PP–cellulose interfaces with long alkyl chains bonded covalently to the cellulose powder; this made interfacial bonding stronger, and the long alkyl chains of the cellulose powder had noncovalent nonpolar intermolecular interactions with the PP matrix side. In particular, the composite with the hydrophobized cellulose powder showing a very high elongation at break could be much more easily adaptable to packaging applications that mostly need a thermoforming process of sheets. Packaging applications would be one of the major application areas of these ecofriendly PP–cellulose composites.

Water-Absorption Properties of the PP–Cellulose Composites

Figures 9 and 10 show the water absorption and thickness swelling of the PP–cellulose composites as a function of the soybean oil content attached to the cellulose powder. With increasing

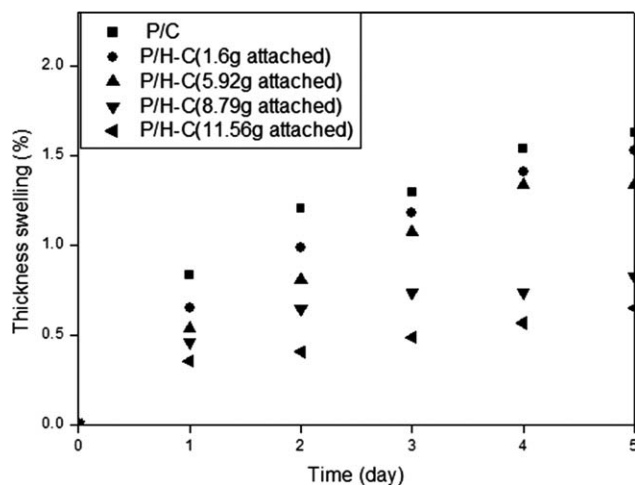


Figure 10. Thickness swelling of the PP–cellulose composites as a function of the soybean oil content attached to the cellulose powder.

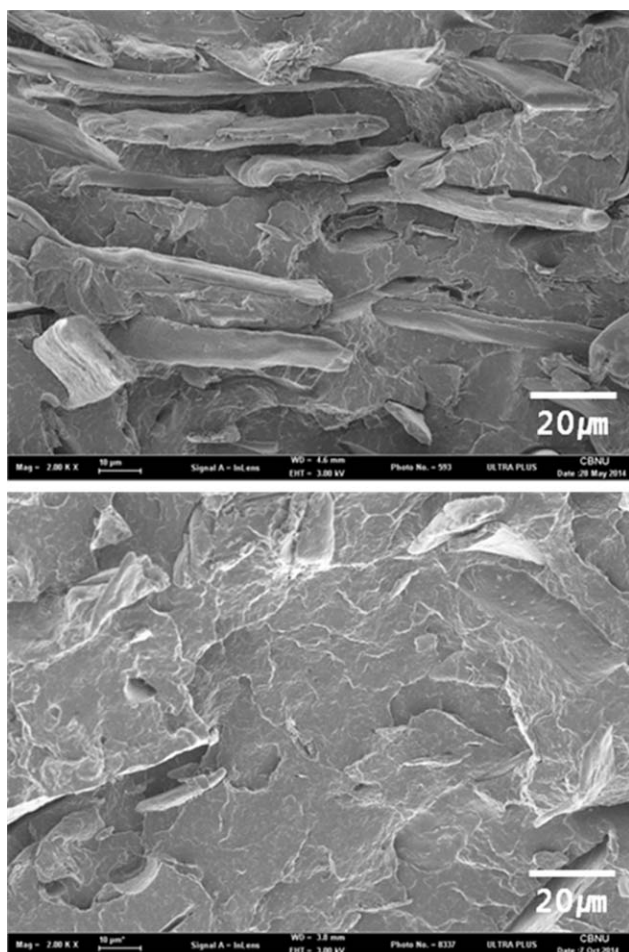


Figure 11. SEM images for the fracture surfaces of the PP–cellulose composites with the pristine cellulose powder (top) or the hydrophobized cellulose powder (bottom). The attached soybean oil content was 5.92 g.

attached soybean oil content, the water absorption and thickness swelling of the composite decreased considerably because the hydrophobization reaction with the soybean oil increased the hydrophobicity of the cellulose powder. Compared to the composite with the pristine cellulose powder, the water absorption and thickness swelling of the composite with the hydrophobized cellulose powder (attached soybean oil content = 11.56 g) decreased drastically to 1:3.

Morphology of the PP–Cellulose Composites

The SEM images of the fracture surfaces of the PP–cellulose composites with the pristine cellulose powder or the hydrophobized cellulose powder (attached soybean oil content = 5.92 g) are shown in Figure 11(a,b), respectively. The fracture surface of the PP–cellulose composite with the pristine cellulose powder looked very rough and showed the detachment or even pullout of cellulose fibers and particles from the PP matrix. However, the fracture surface of the PP–cellulose composite with the hydrophobized cellulose powder looked very smooth without any detachment or pullout of cellulose fibers and particles because the soybean oil attached to the cellulose powder improved the interfacial interaction between the PP matrix and the cellulose powder significantly.

CONCLUSIONS

The hydrophobization of cellulose powder by soybean oil to improve the interfacial bonding strength between the cellulose powder and the PP matrix was carried out via a simple transesterification reaction procedure. The FTIR spectra and compatibility test results confirmed that the hydrophobization of the cellulose powder was successful. By changing the hydrophobization conditions, the attached soybean oil content to the cellulose powder changed from 8.0 to 57.8%. With increasing attached soybean oil content, the hygroscopicity of the cellulose powder decreased. The impact strength and elongation at break of the composite increased with increasing attached soybean oil content. The PP composite with hydrophobized cellulose powder with an attached soybean oil content of 29.6% showed considerably improved impact strength (46.3%), tensile strength (47.5%), and elongation at break (27.3%) values in comparison to the composite with pristine cellulose powder. The SEM images for the fracture surfaces of the composites showed that the hydrophobization induced much stronger interfacial bonding between the PP matrix and the cellulose powder.

REFERENCES

- An, S. H.; Kim, D. S. *Polym. (Korea)* **2014**, *38*, 129.
- Tanem, B. S.; Kvien, I.; Helvoort, A. V.; Oksman, K. *ACS Symp. Ser.* **2006**, *938*, 48.
- Petersson, L.; Kvien, I.; Oksman, K. *Compos. Sci. Technol.* **2007**, *67*, 2535.
- Panaitecu, D. M.; Notingher, P. V.; Ghiurea, M.; Paven, H.; Iorga, M.; Florea, D. *J. Optoelectron. Adv. Mater.* **2007**, *9*, 2524.
- An, S. H.; Kim, D. S. *Polym. (Korea)* **2013**, *37*, 204.
- Panaitecu, D. M.; Donescu, D.; Bercu, C.; Vuluga, D. M.; Iorga, M.; Ghiurea, M. *Polym. Eng. Sci.* **2007**, *47*, 1228.
- Mathew, A. P.; Oksman, K.; Sain, M. *J. Appl. Polym. Sci.* **2005**, *97*, 2014.
- Wittaya, T. *Int. Food Res. J.* **2009**, *16*, 493.
- Wu, Q.; Henriksson, M.; Liu, X.; Berglund, L. A. *Biomacromolecules* **2007**, *8*, 3687.
- Felix, J. M.; Gatenholm, P. *J. Appl. Polym. Sci.* **1991**, *42*, 609.
- Li, X.; He, L.; Zhou, H.; Li, W.; Zha, W. *Carbohydr. Polym.* **2012**, *87*, 2000.
- Qiu, W.; Endo, T.; Hirotsu, T. *J. Appl. Polym. Sci.* **2004**, *94*, 1326.
- Hristov, V.; Vasileva, S.; Krumova, M.; Lach, R.; Michler, G. *Polym. Compos.* **2004**, *25*, 521.
- Seo, Y. W.; Kim, D. S. *Polym. (Korea)* **2014**, *38*, 327.
- Spoljaric, S.; Genovese, A.; Shanks, R. A. *Compos. A* **2009**, *40*, 791.
- Wang, Y.; Weng, Y.; Wang, L. *Polym. Test.* **2014**, *36*, 119.
- Zampano, G.; Bertoldo, M.; Bronco, S. *Carbohydr. Polym.* **2009**, *75*, 22.

18. Tang, X. G.; Hou, M.; Zou, J.; Truss, R. *Key Eng. Mater.* **2011**, 471, 355.
19. Özge Erdohan, Z.; Çam, B.; Turhan, K. N. *J. Food. Eng.* **2013**, 119, 308.
20. Qiu, W.; Zhang, F.; Endo, T.; Hirotsu, T. *J. Appl. Polym. Sci.* **2003**, 87, 337.
21. Peydecastaing, J.; Girardeau, S.; Vaca-Garcia, C.; Borredon, M. *Cellulose* **2006**, 13, 95.
22. Freire, C.; Silvestre, A.; Neto, C. P.; Belgacem, M. N.; Gandini, A. *J. Appl. Polym. Sci.* **2006**, 100, 1093.
23. Jang, S. Y.; Kim, D. S. *Polym. (Korea)* **2015**, 39, 130.
24. Dong, X.; Dong, Y.; Jiang, M.; Wang, L.; Tong, J.; Zhou, J. *Ind. Crops Prod.* **2013**, 46, 301.
25. Jiang, X.; Gu, J.; Tian, X.; Li, Y.; Huang, D. *Bioresour. Technol.* **2012**, 104, 473.
26. Karmarkar, A.; Chauhan, S. S.; Modak, J. M.; Chanda, M. *Compos. A* **2007**, 38, 227.
27. Lee, J. H.; Park, S. H.; Kim, S. H. *Macromol. Res.* **2014**, 22, 424.
28. Kiziltas, A.; Gardner, D. J.; Han, Y.; Yang, H. *Thermochim. Acta* **2011**, 519, 38.
29. Nakatani, H.; Hashimoto, K.; Miyazaki, K.; Terano, M. *J. Appl. Polym. Sci.* **2009**, 113, 2022.
30. Oksman, K.; Mathew, A. P.; Bondeson, D.; Kvien, I. *Compos. Sci. Technol.* **2006**, 66, 2776.
31. Purohit, P. S.; Somasundaran, P. *J. Colloid Interface Sci.* **2014**, 426, 235.