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Influence of Fiber Surface Treatment on Mechanical Performance of *Xanthoceras sorbifolia* Bunge Husk Fibers/PP Composites

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ABSTRACT: The PP Composites containing *Xanthoceras sorbifolia* Bunge husks fibers with different surface treatments were prepared. The mechanical properties such as tensile properties and impact properties of the composites were investigated. It is revealed that the composites with fibers treated by alkali and the following treatments of silane coupling agents KH570, titanate coupling agent JN-9A, acetic anhydride, MAPP, or bleach, all performed higher in tensile properties than that with untreated fibers, while lower in impact properties. Meanwhile, all treated fibers performed better thermal stability than untreated fibers. The fibers treated by alkali followed by KH570 treatment were added into PP with different contents. It is found that as the fiber content increases, the elastic modulus and impact strength of the composites increase sharply at first followed by a decrease, while the tensile strength decrease initially and increase with a peak at 10%, then decrease continuously. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41217.

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INTRODUCTION

As a kind of endemic oil tree in China, *Xanthoceras sorbifolia* Bunge has high oil content and can be used as bio-diesel. However, the yield ratio of its seed and husk is about 18 : 8 to 10 : 9, so the husk should be utilized to make full use of the resources and decrease the cost to make the bio-diesel. As the husk of *X. sorbifolia* Bunge has rich celluloses, it is a possible solution to add the husks into some thermoplastic resins like polyethylene, polypropylene, polyvinyl chloride, and so on to develop natural fiber polymer composites.

Natural fibers have been researched widely in recent years as they are renewable resources, biodegradable, and have marketing appeal,[1] such as pine cone,[2] coconut husks\coir,[3,4] flax,[5–9] sisal,[10–12] hemp,[13] jute,[14] betel,[15] wood,[16] etc.[17] They are increasingly used in automotive, construction, and packaging materials,[1] properties of mechanical, thermal, interfacial, wettability are all investigated. The most common issue between the natural fibers and polymers is the interfacial problem. As known, natural fibers consist of cellulose, lignin, hemicellulose and water soluble substances, etc. All of these components contain hydroxyl group which represent hydrophilic and polar properties, whereas polymers of hydrocarbon are inclined to be nonpolar and hydrophobic. In order to improve the properties of the composites, the key is to ameliorate the interface between the fibers and matrices. By now, many methods have been developed like alkali treatment,[4,17,18] silane[10] and titanate coupling agents treatment, maleic anhydride grafted treatment,[19–21] bleach treatment, etc.

In this article, we have tried different fiber surface treatments to improve the interactions between the fibers and PP. As a new natural fiber the fiber of *X. sorbifolia* Bunge husks was added into PP by a twin screw extruder. Two coupling agents of silane and titanate as well as maleic anhydride grafted polypropylene, namely KH570, JN-9A and MAPP, were used to improve compatibility. Composites with different fiber contents from 5 to 35 wt % were tested. All the tensile and impact samples of these composites were produced using an injection molding machine.

EXPERIMENTAL

Materials

Polypropylene (PP, Panjin Ethylene) was used as the matrix in all tests. The fibers of XSB husk were used as the filling phase for the sake of taking advantage of the local resources. The picture of the XSB husk is shown in Figure 1. The raw fibers of XSB husk were obtained through three steps: at first, the husks were grinded by a grinder (ML-SC10III), then sieved them to choose the size between 0.6 and 1.18 mm, washed and dried (80°C,48 h) them afterwards. The chemicals used in this work, such as sodium hydroxide (NaOH), acetic acid (CH_3COOH), hydrogen peroxide (H_2O_2), acetic anhydride ($(CH_3CO)_2O$), and KH570 ($CH_2{=}C(CH_3)COOC_3H_6Si(OCH_3)_3$) were all purchased from Sinopharm Chemical Reagent. The titanate coupling agent JN-9A (Titanium tris(dodecylbenzenesulfonate)isopropoxide)

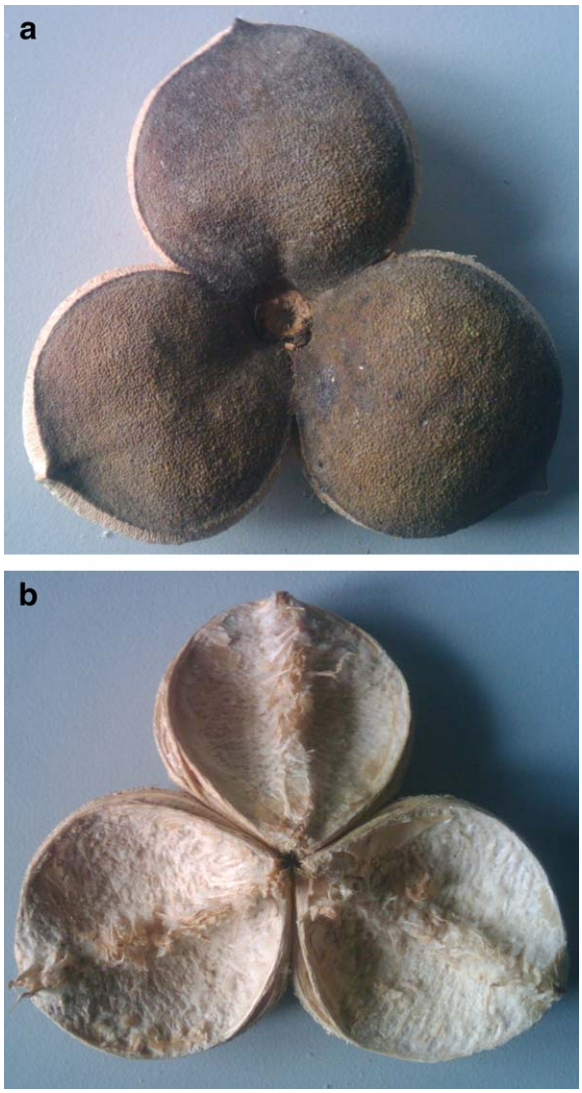

Figure 1. Photograph of the XSB husk (a) outside and (b) inside. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was obtained from Changzhou Jinai Chemical. The MAPP (PP-G-4) was purchased from Nanjing Deba Polymer Materials.

Fiber Treatments

As to the alkali treatment, the raw fibers were put into the 5 wt % sodium hydroxide solution and then stirred the solution with fibers constantly for 1 h to make the fibers react with the solution evenly and adequately. After that, the fibers were washed fully by water with acetic acid to neutralize the solution, and dried by the oven at 80°C for 48 hours. Fibers treated by different coupling agents KH570 or JN-9A were obtained by being soaked in the 3 wt % agent solution for 3 h. The KH570 solution were prepared by put 3 wt % KH570 with respect to the fiber weight into the 1 : 1 distilled water and ethyl alcohol solution, then added some acetic acid to adjust the pH between 3.5 to 4.5. On the other hand, the JN-9A solution were obtained by putting the same amount of JN-9A into the pure ethyl alcohol as it is insoluble in water, and it did not need the pH adjustment. As to the acetylation treatment, fibers were soaked in the acetic anhydride for 2 h, then washed by water and adjusted the pH to 7 by Na_2CO_3 solution. With regard to the MAPP treatment, 5 wt % with respect to the fiber weight MAPP was dissolved in boiling xylene, and the fiber was immersed in the solution for 6 min, then washed and dried the fiber thoroughly.[19] Regarding alkali and bleach treatment, alkali-treated fibers were immersed in a solution that was composed of H_2O_2 and the same volume of CH_3COOH, then heated the solution by oil bath at 60°C for 6 h two times with an interval of 6 h out of the oil bath pan and standing. Different treatments and their acronyms have been listed in Table I.

The treated fibers were tested by a FTIR spectrophotometer to compare their ATR spectra, as well as by TGA analyzer to evaluate their thermal properties.

Specimen Preparation

Test specimens with 20 wt % XSB husk fiber have been prepared by extrusion compounding and injection molding. The extrusion compounding was done using a co-rotating twin screw extruder TSE-20 (Nanjing Ruiya Extrusion Systems Limited) with the main rotor speed of 240 rpm and the side-feeding screw speed at 120 rpm. The processing temperature varied between 155°C and 170°C. After the extrusion, the composites were cooled by water, and pelletized into granules ready for molding the test samples. The injection molding was carried out using a vertical injection molding machine FT-200 (FOMTEC MACHINERY) with the press barrel temperature of 180°C, nozzle and mold temperatures of 170°C and 50°C, respectively.

Characterization

Thermo gravimetric analysis (TGA, SETSYS Evolution18 integrative analyzer, SETARAM) was employed to both raw fibers and treated fibers to compare the thermal stability and observe their thermal properties from room temperature to 500°C at a heating rate of 5°C/min. Fourier transform infrared spectroscopy (FTIR, BRUKER TENSOR 27) was used to evaluate whether the fibers were treated successfully, so both original fibers and different treated fibers were tested in the range of 4000–600 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans were collected, meanwhile, attenuated total reflection (ATR) was chosen as the size of fibers is large enough.

The mechanical properties like tensile properties and impact properties were tested by the universal testing machine of

Table I. Acronyms of the Different Surface Treatments

Acronym of treatments	Full name of treatments
U	Untreated
A	Alkali treatment
A+M	Alkali followed by MAPP treatment
A+A	Alkali followed by acetylation treatment
U+KH570	Untreated followed by KH570 treatment
A+KH570	Alkali followed by KH570 treatment
U+JN-9A	Untreated followed by JN-9A treatment
A+JN-9A	Alkali followed by JN-9A treatment
A+B	Alkali followed by bleach treatment

mechanics (WSM-20KN, Changchun Intelligent Instrument Equipment) and impact testing machine (JJ-20, Changchun Intelligent Instrument Equipment) respectively. After the tests, the fracture samples of impact test were treated by cleanout, desiccation, fixing, and gold spraying; and the Scanning electron microscopy (SEM, JSM-6301F, JEOL) was employed to observe the morphology and microstructure of the composites fracture surfaces.

RESULTS AND DISCUSSION

Infrared Spectroscopy Analysis

Figure 2 shows the FTIR-ATR spectra of the husk fibers before and after treatments, including untreated (U), alkali treatment (A), silane, or titanate coupling agent treatment with or without alkali-treated (U+KH570, A+KH570, U+JN-9A, A+JN-9A), bleach or acetylation after alkali-treated (A+B, A+A), MAPP treatment after alkali-treated (A+M).

Peaks close to 3340, 2920, 1420, and 1323 cm^{-1} were considered associated with the —OH bond stretching, C—H stretching vibration, CH_2 symmetric bending, and O—H bending, respectively. The peak at around 1650 cm^{-1} can be observed in all the spectra, which would be related to the existence of absorbed water.[13] Fibers after alkali treatment have weaker peaks in the frequency range 600–800 cm^{-1}, which may be caused by the noncellulosic components disappeared.[17] Meanwhile, the region between 1600 and 1800 cm^{-1} is related to the formation of the new ester groups between the hydroxyl groups from cellulose of fibers and the applied agents.[22] It can be observed that the husk fibers are characterized by the peak at about 1750 cm^{-1} connected with the carbonyl (C═O) stretching, possibly because of the hemicellulose and lignin of the fibers, as well as the reactions like esterification between fibers and applied agents.[19,22] At the same time, the stretching changes of ether (C—O—C) and alcohol (C—OH) of cellulose in the spectra supporting the formation of the stable ester bond at the interface between the applied agents and the husk fibers, at 1157, 1103, and 1034 cm^{-1}, respectively,[23] as shown in Figure 2(b).

The peaks 772 and 706 cm^{-1} of fibers treated by KH570 with or without alkali-treated were associated with the —Si—C— and Si—O—Si symmetric stretching, respectively; from here we can see that fibers were treated successfully. The peak appearing at 1240 cm^{-1} was corresponding to C—O stretching of acetyl in lignin,[13] the peaks here were weaker at alkali-treated and alkali with bleach-treated fibers as after these two treatments lignin were removed partially. Peaks at around 3000 cm^{-1} represent C—H of benzene ring stretching vibration, while peaks emerging close to 1600 and 1500 cm^{-1} were because of the benzene skeleton vibration. The benzene rings existed in the hemicelluloses and lignin of fibers, as well as the titanium coupling agent JN-9A when it comes into the treated fibers. Meanwhile, fibers treated by the silane coupling agent KH570 may also have peaks at 1600 cm^{-1}, as a result of the conjugated effect of C═C and C═O of the agent.

Thermal Properties and Physical Structure

The DTG analysis curves of the XSB husk fibers are shown in Figure 3. It can be evidenced that the treated fibers have higher thermal stabilities than the untreated fibers through the results of DTG analysis. Specifically, the modified fibers have higher initial decomposition temperatures (T_i) as A (196°C), A+M (196°C), A+A (189°C), KH570 (184°C), A+KH570 (199°C),

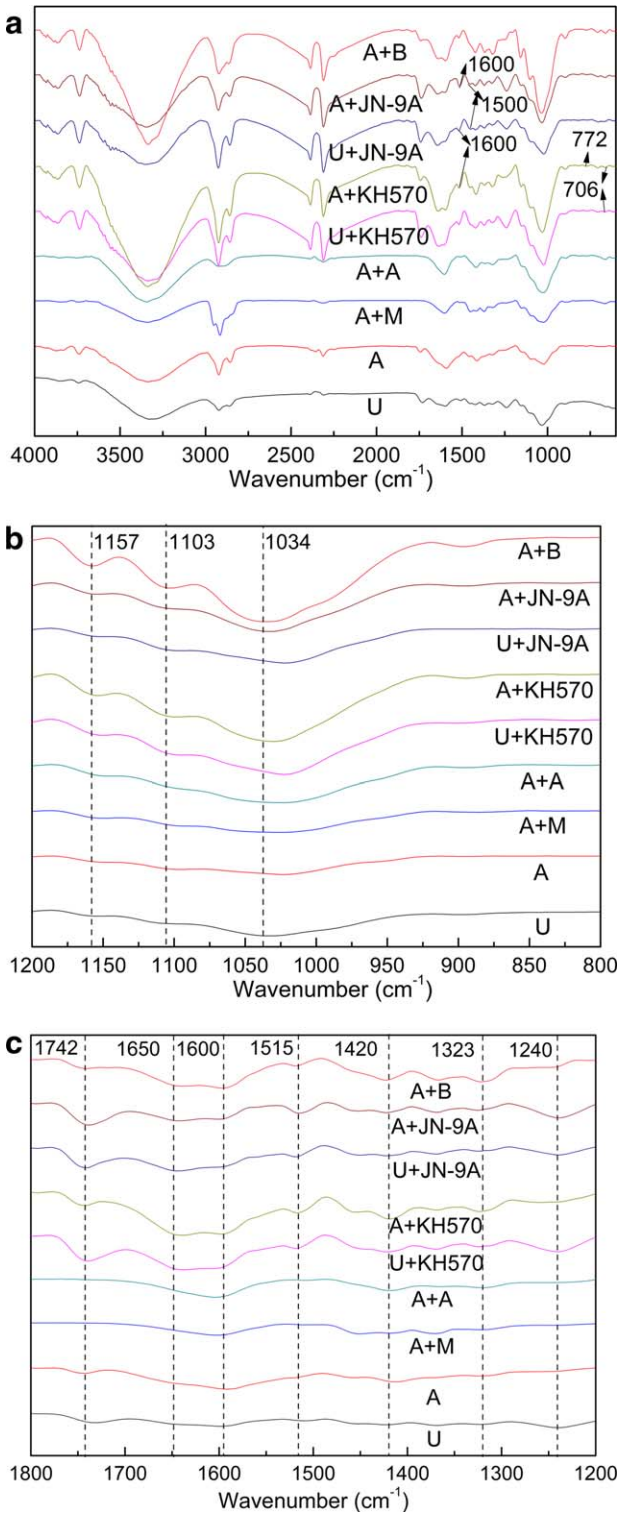

Figure 2. FTIR spectra of treated XSB husk fibers in the region (a) 4000–600 cm^{-1}, (b) 1200–800 cm^{-1}, and (c) 1200–1800 cm^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

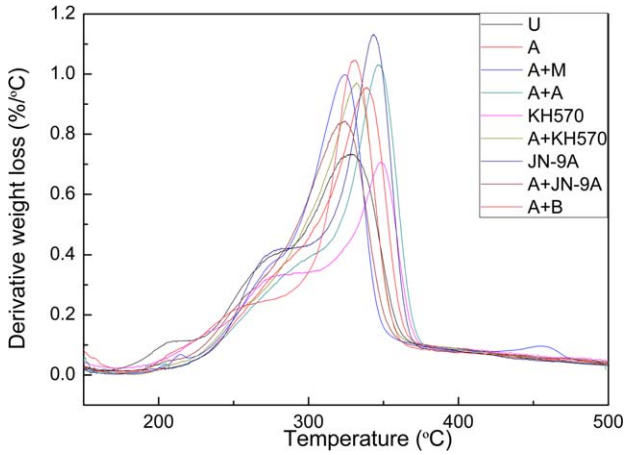

Figure 3. DTG curves of treated XSB husk fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

JN-9A (179°C), A+JN-9A (183°C), A+B (188°C), respectively, while the untreated fibers (U) with 163°C. This may be caused by the elimination of the noncellulose components through alkali and bleach treatments, as well as coupled action between coupling agents and fibers.

Meanwhile, when it comes to the temperatures of maximum rate of degradation (T_p), it can be observed in Figure 3 that they differ from the untreated one ($T_p = 326$°C) with different degrees, namely A (339°C), A+M (323°C), A+A (348°C), KH570 (348°C), A+KH570 (332°C), JN-9A (343°C), A+JN-9A (324°C), and A+B (331°C). As the decomposition procedure includes mainly four steps: the first started is the elimination of the structural water molecules in the range of 150–240°C, followed by the hemicellulose decomposition from 200°C to 260°C, then it came to the cellulose decomposition in the region of 240–350°C, finally the lignin decomposition happened between 280°C and 500°C.[24] From this we can see that the maximum degradation rate occurred at the decomposition of cellulose and lignin, and the different temperatures T_p may be caused by the changes of these two components ratio[25] or the cellulose structure,[17,26] which occurred during the process of treatments.

The surface morphologies of the XSB husk fibers are shown in Figure 4, it can be observed that untreated fibers [Figure 4(a)] have a relatively smooth surface with a covering layer like waxes, lignin, and pectin. The whole structure is compact comparatively. Meanwhile, with the waxes and other noncellulosic components removed, the alkali-treated husk fibers [Figure 4(b)] have a more course surface and loose structure, which may improve its adhesive characteristics.[15] With the further treatment of bleach, structures of fibers [Figure 4(c)] are looser and more rough, as well as the sizes of fibers become smaller. The diameters of the untreated and A+B-treated fibers are around 112.62 and 8.85 μm, respectively, which have been analyzed by a software called Nano Measurer. As for fibers without coupling agent treatments, any improvement is owing to the physical anchoring between polymer chains and fibers,[2] fibers after alkali and bleach treatments may have more firm combination with polypropylene. However, some reports indicated that the existence of some noncellulose components like lignin may improve the compatibility of the fiber and matrix.[27]

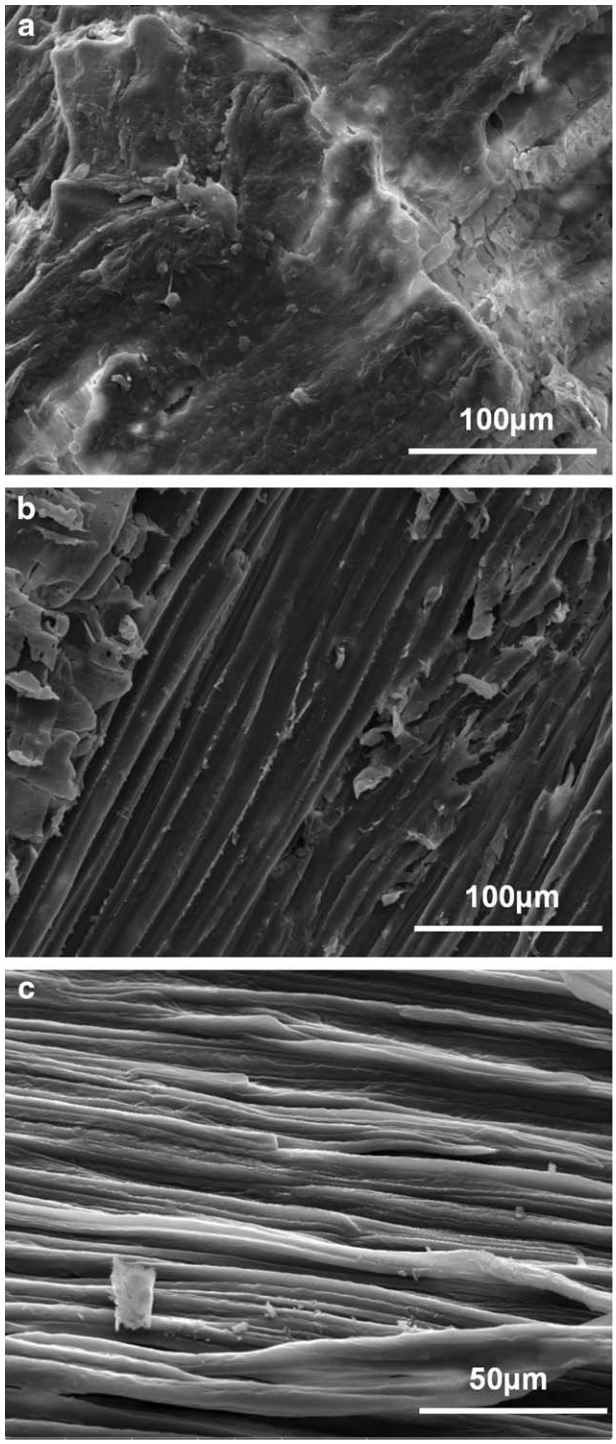

Figure 4. SEM images of XSB husk fibers of (a) as received, (b) alkali-treated, and (c) alkali- and bleach-treated.

Effect of Fiber Treatment on Mechanical Properties of Composites

The tensile and impact strengths as well as tensile modulus for polypropylene composites with 20 wt % fibers of different treatments are summarized in Table II. It can be seen that the

Table II. Mechanical Properties of the Composites with Untreated and Treated Fibers

Fiber treatments	Tensile strength (MPa)	Impact strength (kJ/m^2)	Tensile modulus (MPa)
U	28.4±0.3	6.2±0.3	1785±53
A	27.4±0.4	5.9±0.3	1701±46
A+M	29.8±0.6	5.7±0.3	2029±39
A+A	30.0±0.9	6.0±0.5	2129±23
U+KH570	27.7±0.5	5.9±0.5	1777±43
A+KH570	32.0±0.5	5.9±0.3	2000±45
U+JN-9A	28.2±0.3	5.5±0.3	2007±40
A+JN-9A	31.4±0.5	5.9±0.3	1982±39
A+B	31.1±0.4	5.1±0.3	2070±37

composite with fibers treated only by coupling agents has no obvious improvement or even worse compared with that with untreated fibers in mechanical properties. The main reason may be that the fibers were not treated adequately because of the existence of waxes and pectin on the fiber surface, as shown in Figure 4(a). And the coupling agents not having reacted with the fibers were left free standing on the fiber/matrix interphases in a form of small molecule, which do deteriorate the mechanical properties of the composites. Meanwhile, composites with alkali-treated fibers have less tensile and impact strength, and less tensile modulus than the untreated one. On one hand, the alkali-treated fibers have loose structure as some noncellulose components have been removed which may cause loss in the mechanical properties of the fibers. On the other hand, the removed components like waxy layer with polymeric nature can provide a better interface for accelerating stress transfer from polypropylene to the fibers.[3]

However, when the fibers were treated by alkali and agents, the composites showed obvious improvement in tensile strength and modulus, while not apparent improvement in impact strength. This was mainly because of the loose structure and rough surface of the alkali-treated fibers that made the coupling agents, maleic anhydride grafted polypropylene or acetic anhydride work thoroughly with the treated fibers, namely, chemical bonding mechanism was built up as identified in Figure 2. The fiber polarity decreased after reacted with the agents fully, and thus more compatible interfaces as well as strengthened composites were acquired.

Moreover, composite with alkali- and bleach-treated fibers shows rather high tensile strength. After the alkali-bleach treatment, the fibers became purer and finer. On one hand, because of the changes of component like the elimination of hydrotrope, the hydrophily of the fibers decreased, and the compatibility between the polymer and fibers was improved. On the other hand, with the size decreasing, more small fibers were obtained and they could distribute widely in the matrix as shown in Figure 5(a). This will strengthen the physical anchoring between polymer chains and fibers, the main schedule of reinforcement in physical.[2] In addition, from the SEM images, we can see that

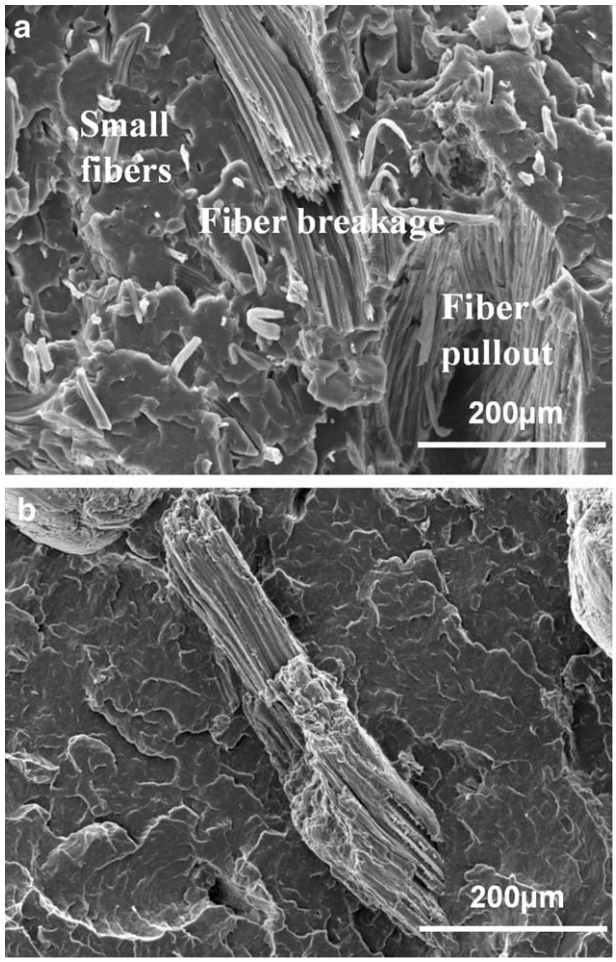

Figure 5. SEM images of fracture surfaces of composites with (a) A+B-treated husk fiber and (b) A+JN-9A-treated husk fiber.

there are fiber breakage and fiber pullout which are the main functions of the fibers during the fracture of the composites. As to the composites with A+JN-9A-treated fibers [Figure 5(b)], although there are not small fibers, the interface of the fibers and matrix is really compact which will be beneficial to the mechanical properties as well.

In general, composite with alkali- and KH570-treated fibers shows the best mechanical properties, especially in tensile strength which increased 12.7% compared with the untreated one. Then this treatment was applied to different fiber contents to study its influence.

Effect of Fiber Content on Mechanical Properties of Composites

In consideration of the above results, the alkali followed by KH570 treatment was chosen as the fibers surface treatment to investigate the effect of fiber content. About 0% to 35% was chosen as the range of the content and mechanical properties of the composites were studied.

As shown in Figure 6, generally, with the fiber content increasing, the composites show increasing followed by decreasing trends in Young's modulus and impact strength, with the summits at 30% (2095.4 MPa) and 5% (5.8 kJ/m*m), respectively.

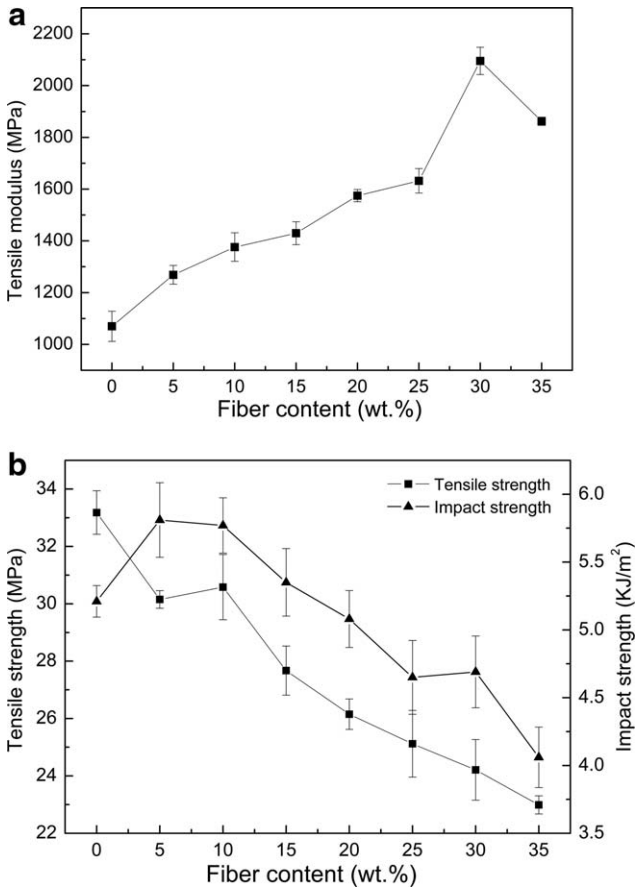

Figure 6. Effect of fiber contents on (a) tensile modulus and (b) tensile and impact strength of PP/XSB husk fibers (A+KH570-treated) composites.

As to the tensile strength, it shows a trend decreasing followed by increasing slightly then decreasing continuously, with a peak at 10% (30.6 MPa). In particular, it can be observed a marked increase in Young's modulus of composites when compared to the neat PP (1069.8 MPa), with 18.6%, 28.6%, 33.6%, 47.2%, 52.6%, 95.9%, and 74.1% improvements corresponding to the fiber contents at 5%, 10%, 15%, 20%, 25%, 30%, and 35%, respectively. This increase in Young's modulus was owing to the good interfacial adhesion between the fibers and polypropylene the matrix, and it can be found the similar trend in PP composites with pine cone or jute fibers.[2,28] These trends could be explained by reasons as follows. At low fiber content, poor fiber population causes low load transfer capacity among the fibers, which would produce stress concentration at certain points of the composites and lead to poor mechanical properties; at high fiber content, fibers may get agglomerated in the matrix which would produce uneven stress transfer capacity and contribute to microcrack formations on the interface, which will cause the decrease of strength and modulus of the composites.[28]

CONCLUSIONS

To further the use of the composite, the properties of it need to be improved. As the interface between the fibers and polypropylene is the key, eight treatments were employed, including alkali, alkali and MAPP, alkali and acetylation, untreated or alkali-treated and coupling agents KH570 or JN-9A, alkali and bleach. All the dual processing methods obtained good results, while there is not much improvement as to each single process. In fact, the tensile strength of composites with fibers after treated by alkali only decreased 3.5% compared with the untreated one, as the waxy layer which would be advantageous to the interface strength was removed. However, composites with fibers after A+M, A+A, A+KH570, A+JN-9A and A+B all performed better, namely 5.0%, 5.6%, 12.7%, 10.8%, and 9.7% improvement in tensile strength respectively, in comparison with the untreated one. Especially through alkali and bleach treatment, fibers have been fined and micron dimension even nanometer scale fibers have been obtained, and composites with these fibers showed preferable properties. Besides, fibers after treated all have better performances than the untreated one in thermal properties.

A+KH570-treated fibers with different contents were added into the matrix, and Young's modulus soared from 1069.8 MPa, modulus of pure polypropylene, to 2095.4 MPa, nearly doubled it. Meanwhile, the tensile strength performs a trend decreasing followed by slightly increasing then continuously decreasing with a peak at 10%, while impact strength shows an increasing followed by decreasing trend with the fiber content increasing.

STATEMENT: The authors designed the research together. Miss Yao carried out, analyzed and drafted it with the guidance and revise of Prof. Sui and A/Prof. Liu.

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