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Characterization of polypropylene composites reinforced with flax fibers treated by mechanical and alkali methods

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Abstract

Flax is a type of natural fiber widely used as reinforcing materials for polymer composites. The commercially available flax fibers in Canada consist of a significant amount of shive and other impurities, which could act as stress concentration regions to negatively affect the mechanical property of composites. In this study, the shive was manually removed from the commercial flax fibers by screening and combing to obtain different shive contents from 0 to 30 wt%. By contrast, the obtained flax fibers were further treated with alkaline solution. The fibers obtained from mechanical and alkali treatment were compared on their thermal and mechanical properties. As expected, it was found that the thermal stability and mechanical properties of the flax reinforced polypropylene composites increased significantly with the removal of the shive content. However, the alkali treatment on flax fiber did not further improve the composites properties. The possible reason was that the proper mechanical treatment (screening and combing) prior to alkaline treatment effectively loosened the fiber bundles for better single fiber separation in matrix and significantly removed the impurities, thus the effect of alkaline treatment did not become obvious.

Keywords: alkaline treatment; flax; mechanical treatment; polypropylene composites; shive.

1. Introduction

Flax is a type of widely applied natural fiber used as reinforcing materials for composites [1–3]. The commercially available flax fibers in Canada consist of a significant amount of shive and other impurities, which could act as stress concentration regions to negatively affect the mechanical properties of composites. By contrast, flax also presents important shortcomings, such as hydrophilic nature, high moisture absorption and low thermal resistance which restrict its application similar to other natural fibers. Its hydrophilic nature results in its incompatibility with the polymer matrix and bad interfacial fiber/matrix adhesion, which causes a decrease of the mechanical properties of composites.

Various chemical treatments, such as alkali, acetic anhydride, silane, etc., have been used to treat the fiber surface to improve the adhesion between the natural fiber and matrix [4–6]. Alkalization is a relatively simple and cheap method [7–11]. Various concentrations of alkali and pretreatment time and temperature conditions have been applied on flax, hemp, wheat straw and other natural products. Alkalization could remove the lignin, wax and oils covering the external surface of fiber. It was reported that alkaline treatment can increase the amount of cellulose exposed on the fiber surface to increase the reaction sites amount. Therefore, alkaline treatment can improve the mechanical properties of fiber and also fiber-reinforced composites.

In this study, mechanical and alkali treatments were applied on the Canadian linseed flax. Scanning electron microscopy (SEM), Fourier transform infrared (FTIR), thermal gravimetric analysis (TGA) and an improved single fiber tensile test (SFTT) were applied to characterize the treated fibers. Flax fiber obtained from mechanical treatment and further with alkali treatment was compounded with polypropylene (PP) to compare with mechanically treated flax/PP composites. The shive ratio and alkali treatment effect on composite properties were examined.

2. Materials and methods

The dew-retted Canadian linseed flax fibers with 30% and 10% of shive (F30 and F10, respectively) were kindly provided by Schweitzer-Mauduit Company (Winkler, MB, Canada). Homopolypropylene Pro-fax PDC 1274 (PP) (M_w=250 kg/mol) obtained from LyondellBasell Industries N.V. (Rotterdam, Netherlands) was used as the matrix for the composites. Coupling agent polybond 3200 (PB) (M_w=84 kg/mol, MA content: 1.0 wt%) was kindly supplied by Chemtura Corporation (Philadelphia, PA, USA). Sodium hydroxide (NaOH) and calcium oxide (CaO) were purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA).

2.1. Mechanical treatment

The shives were first removed from F10 by screening, then further combing to obtain the fiber with 0% of shive (F0). The yield was approximately 83%, because the shives and other impurities were removed from flax.

2.2. Alkali treatment

F0 fibers were aligned into bundle and cut into 5 mm in length. These short fibers were treated in 2% NaOH solution for 1 h at 80°C while stirring. After the treatment, the fibers were rinsed several times by deionized water, and then neutralized by 1% acetic acid to remove the NaOH. After that, fibers were further washed by excess of deionized water until pH became neutral. Finally, the obtained flax fiber (F0-NaOH) was mixed with PP powder according to the weight ratio in Table 1 by stirring, and then dried at room temperature overnight to prevent fiber agglomeration. The whole system was further dried at 105°C for 1 day prior compounding. The fiber yield was approximately 74% as the non-cellulose portions were well removed from F0 by the alkali.

2.3. Compounding with PP

F30, F10 and F0 were stranded into rope for better and easier chopping into 5 mm length. The obtained short fibers were dried at 105°C for 1 day, and then compounded with PP, PB and CaO according to the formulation shown in Table 1 using a Plasti-Corder of the C.W. Brabender Instrument Inc. (So. Hackensack, NJ, USA). All the components were mixed totally for 10 min at a screw speed of 60 rpm and temperature of 190°C. The obtained composites were kept in a vacuum oven at 100°C for 24 h before molding. Composite testing samples were prepared by compression molding at 190°C.

2.4. Characterization

2.4.1. SEM observation A JEOL JSM-6100 SEM from the JEOL Ltd. (Tokyo, Japan) at a voltage of 10 kV was utilized to observe the fiber surface and also the composite interface. Before SEM observation, the samples were coated with Au/Pd to ensure good conductivity. For SFTT, the tensile properties of flax fibers were evaluated according to the procedure described in [12].

2.4.2. FTIR characterization FTIR spectra of the flax were obtained from a Nicolet Magna-IR 860 spectrometer of the Thermo Fisher Scientific (Waltham, MA, USA). An ATR Thunderdome accessory with non-concave tip was used for sampling. Sample preparation consisted of placing the sample on a germanium crystal and pressing the material against the crystal using a plunger. Each spectrum represents 128 co-added scans collected at a spectral resolution of 4 cm^{-1}. An air background data set was acquired and subtracted by the obtained spectra.

2.4.3. Thermal analysis A DSC-7 Perkin-Elmer calorimeter from the PerkinElmer Inc. (Waltham, MA, USA) was used to study the melting and crystallization behavior of PP and flax/PP composites at a heating and cooling rate of 10°C/min during the process. The sample was first heated to 200°C and kept for 5 min. Then the sample was cooled down to room temperature and the second heat scan was performed thereafter. The crystallinity of the PP matrix in the composites was determined using the following equation:

$$X_c=\Delta H_m/(f_P\times\Delta H_f^0)\times 100\% \tag{1}$$

where ΔH_m (J/g) is the enthalpy of melting of composites, f_P is the PP weight fraction in composites, and ΔH_f^0 is the enthalpy of melting of pure crystalline PP (207.1 J/g, [13]).

The thermal stability of treated flax fiber and flax/PP composite was measured on a TG 96 SETARAM TGA from the Setaram Inc. (Mt. Laurel, NJ, USA). The measurements were carried out from 25°C to 700°C at a heating rate of 20°C/min in inert nitrogen gas. All samples were kept in the air without further drying before the measurement.

2.4.4. Mechanical characterization Flexural and impact properties of composites were measured according to ASTM test methods D790 on an Instron 5500R machine of the Instron Inc. (Norwood, MA, USA), and D256 on a TMI Impact Testing machine from the Testing Machines Inc. (New Castle, PA, USA), respectively.

Table 1 Formulation of flax/PP composite.

	F30 (g)	F10 (g)	F0 (g)	F0-NaOH (g)	PB 3200 (g)	CaO (g)	PP1274 (g)
PPF30	15				1	5	29
PPF10		15			1	5	29
PPF0			15		1	5	29
PPF0-NaOH				15	1	5	29
PP							

3. Results and discussion

3.1. Characterization of flax fibers

3.1.1. SEM observation Figure 1A shows the SEM image of F10 without any treatment. It is obvious that technical fiber is in fact a bundle of elementary fibers which are bundled together by pectin, lignin and other non-fibrous cementing substances. Figure 1B presents the flax fiber F0 obtained after the mechanical treatment. The elementary fiber could be observed to be more separated from fiber bundles with fewer cuticles attached on the fiber surface. It seemed the mechanical treatments not only removed the shives but also loosened the fiber bundle and removed the impurities on fiber surface to some extent. Figure 1C shows the SEM photo of flax fiber F0 treated with 2% NaOH at 80°C for 1 h. The F0 fibers were fully separated into single fibers. The fiber surface was very clean, as the hemicelluloses, pectin and lignin were removed through the alkali treatment.

3.1.2. FTIR characterization The FTIR spectrum of F0 is shown in Figure 2. The characteristic peak of -OH is between 1000 and 1500 cm^{-1}, and the peak at 1726 cm^{-1} presents the refraction of carboxylic group on hemicellulose. Peak at 2915 cm^{-1} presents the C-H stretching vibration in cellulose and hemicelluloses. The peak at approximately 1250 cm^{-1} belongs to a C-O stretching vibration of the acetyl group in hemicelluloses and lignin. The observed peak at 898 cm^{-1} indicates the presence of the β-glycosidic linkages between the monosaccharides. All these characteristic absorbance peaks were similar with other natural fibers, such as hemp, sisal, jute and kapok [8–10]. The FTIR spectra of F0 treated with alkali is also shown in Figure 2. Alkaline treatment

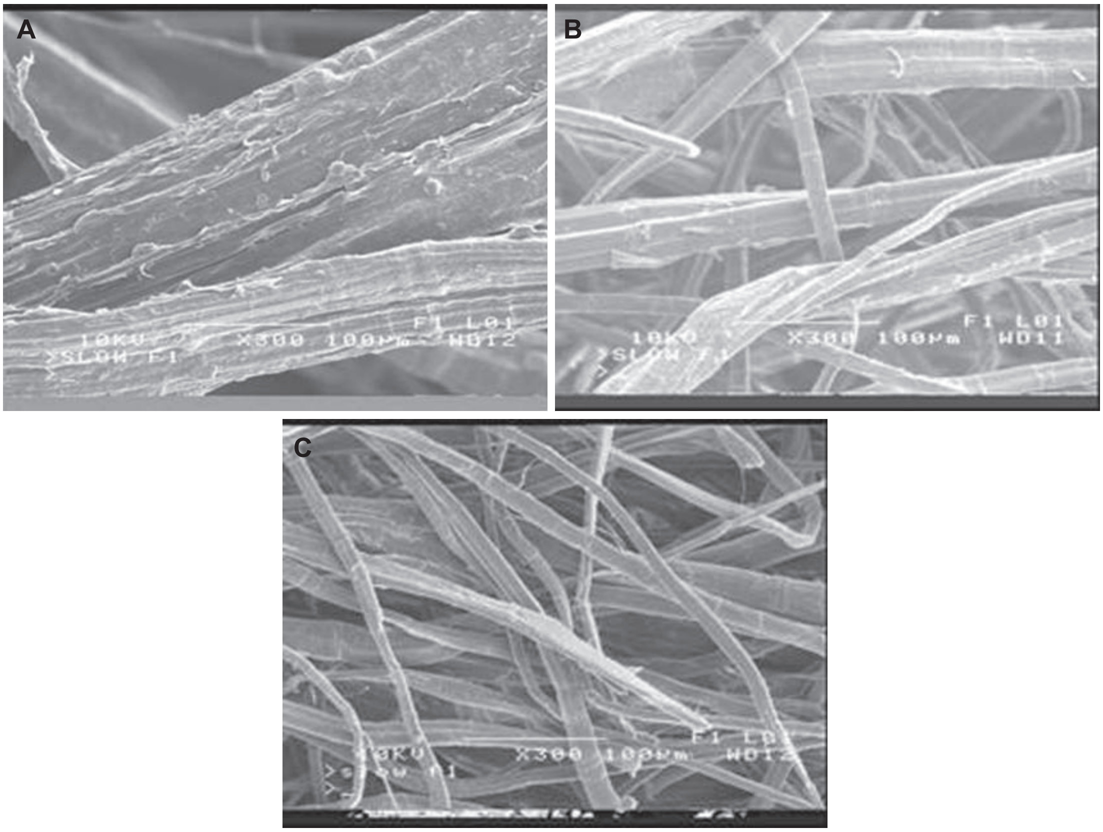

Figure 1 (A) Flax fiber from F10 without any treatment; (B) F0; (C) F0-NaOH.

could reduce hydrogen bonding by removing the hydroxyl groups via the reaction with the sodium hydroxide. The free -OH concentration of the treated F0 therefore increased, as demonstrated by the increased intensity of peak between 1000 and 1500 cm^{-1} bands compared to F0. The disappearance of the peak at 1726 cm^{-1} after the alkali treatment was due to the removal of the carboxylic group on hemicelluloses by alkali treatment via a desertification process. The disappearance of the peak at 2915 cm^{-1} also indicates the removal of hemicellulose [8–10]. The reduction of the peak at approximately 1250 cm^{-1} demonstrates that the alkali treatment removed the hemicelluloses and lignin partially. All these changes demonstrated that the alkalization effectively removed a large amount of non-cellulose portions.

3.1.3. TGA characterization The thermal property of F0 and F0-NaOH was characterized by TGA. Figure 3 shows their TGA and DTGA curves. Their main characterized degradation

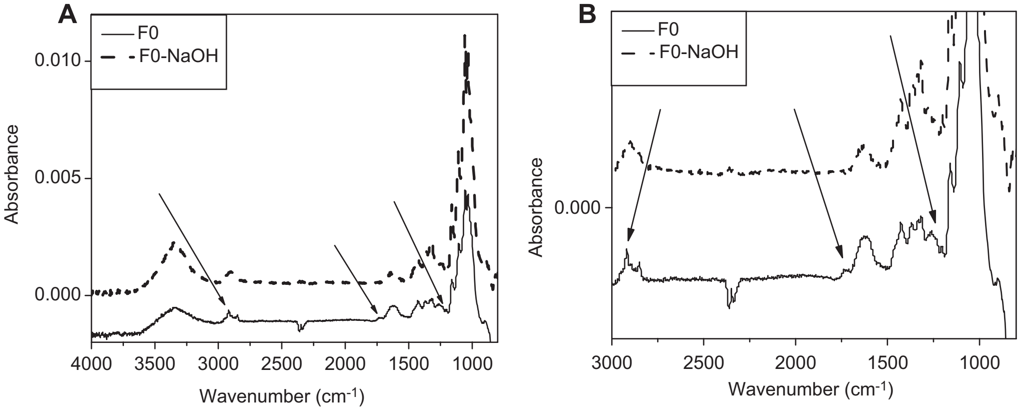

Figure 2 FTIR spectra of F0 and F0-NaOH, (B) is the enlarged spectra of part of (A).

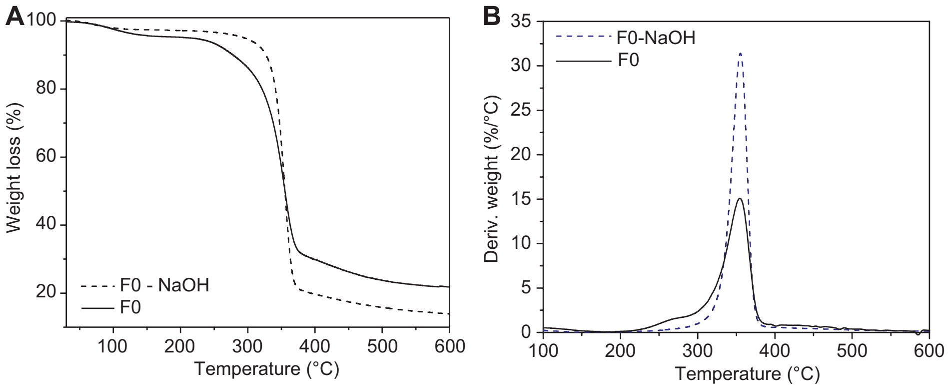

Figure 3 TGA (A) and DTGA (B) of F0 and F0-NaOH.

temperatures, such as 5% and 10% of weight loss temperature (T_5, T_{10}) are shown in Table 2. T_5 and T_{10} increased after the alkali treatment due to elimination of pectin, lignin and other non-cellulose portions by the alkaline treatment. No sudden weight loss began at approximately 250°C for F0-NaOH in thermogravimetric curves (Figure 3A), which was due to hemicellulose portions in F0 [10]. Correspondingly, it could be clearly observed in Figure 3B that the small shoulder-like peak on the DTGA spectra of F0 at approximately 250°C also completely disappeared after the alkali treatment. The peak temperature on the DTGA curve (T_{max}) of F0 was 355°C, which was related to the degradation of cellulose. The same peak at the same temperature could be observed on the DTGA curve for F0-NaOH. This denotes that the alkalization did not damage the cellulose structure.

Table 2 Thermal properties of alkali treated flax.

	T_5 (°C)	T_{10} (°C)	T_{max} (°C)
F0	216.0±0.5	278.2±0.7	354.5±0.6
F0-NaOH	296.3±0.6	327.1±0.6	355.0±0.5

3.1.4. SFTT According to the SEM, FTIR and TGA characterization, the non-cellulose portion on fiber surface was removed by the alkali treatment. Therefore, the thermal stability was improved after the alkalization. However, it is not easy to determine if this treatment damaged the fiber structure. Single fiber tensile testing was then performed on the alkali treated fiber to compare with the non-alkali treated fiber. Table 3 shows the strength and modulus of different fibers. It is shown that the fiber mechanical properties of F10 and F0 were similar, which denotes that the mechanical treatment did not affect the fiber quality. By contrast, F0 also presented similar mechanical properties compared with F0-NaOH if standard deviation is taken into account, which suggests that alkali treatment condition neither improved the mechanical property nor damaged the fiber structure. This obtained fiber was compounded with PP to compare with the F0 reinforced PP composite for the inspection of alkalization effect.

3.2. Characterization of flax/PP composites

3.2.1. Crystallization behavior The melting and crystallization behaviors of composites were studied using DSC.

Table 3 Mechanical data of different flax fibers.

	Diameter (µm)	SD (µm)	Strength (MPa)	SD (MPa)	Modulus (GPa)	SD (GPa)	Strain (%)	SD (%)
F10	42.6	6.7	421.3	38.6	28.1	3.7	2.03	0.84
F0	66.3	11.2	411.2	35.0	27.0	3.2	3.48	0.42
F0-NaOH	41.5	10.7	453.0	53.8	31.5	5.3	3.03	1.19

Table 4 Crystallization properties and thermal stability of PP and flax/PP composites.

	T_c (°C)	T_m (°C)	X_c (%)	T_5 (°C)	T_{10} (°C)	T_{max1} (°C)	T_{max2} (°C)
PP	105±0.5	162±0.5	45.2±0.3	423±0.5	435±0.5		461±0.5
PPF30	122±1	163±1	49.5±0.7	283±0.5	324±0.6	338±0.5	468±0.6
PPF10	121±1	163±1	49.2±0.8	311±0.6	342±0.5	357±0.6	469±0.5
PPF0	120±1	163±1	49.9±0.7	318±0.5	345±0.8	359±0.5	470±0.7
PPF0-NaOH	120±2	160±2	49.1±0.5	337±0.8	348±0.5	354±0.7	468±0.5

The crystallization curves of flax/PP composites (not shown here) presented similar crystallization behaviors with PP. The crystallization temperature (T_c), melting temperature (T_m) and crystallinity (X_c) are summarized in Table 4. It is shown that T_c increased from 105°C to 120°C after the fiber was inserted into pure PP. And X_c of the composites also increased in comparison with PP. This can be explained by the fact that the flax fibers acted as nucleating agent for PP which is in agreement with the literature [14, 15]. It should be noted here that shive ratios and alkaline treatment did not make much difference on the crystallization behavior of the composites.

3.2.2. Thermal stability The main thermal stability parameters of composites, such as temperature of 5% weight loss (T_5) and 10% weight loss (T_{10}) of all the samples are shown in Table 4. For PP, there was only one peak in its DTGA curve at 461°C which corresponded to the degradation of the PP chain. There were two main peaks (T_{max1} and T_{max2}) observed on the DTGA spectra (not shown here) of the composites. T_{max1} at approximately 355°C corresponded to the degradation of cellulose, and the higher peak T_{max2} at approximately 468°C could be related to the decomposition of PP [10, 15]. According to Table 4, T_5, T_{10}, T_{max1} of composites decreased with the shive ratio indicating the poor thermal stability of shive and its impact on the thermal stability of the composites as a whole. However, their T_{max2} did not show much difference. By contrast, it is also shown that T_5 and T_{10} of PPF0 were lower than those of PPF0-NaOH, especially the T_5 of PPF0 which was approximately 20°C lower than that of PPF0-NaOH. This was related to the more non-cellulose portion in the F0, such as hemicelluloses, lignin, etc. It demonstrated that alkaline treatment could further improve the composite thermal stability.

3.2.3. Mechanical properties The flexural strength, modulus and notched izod impact strength of the composites formulated with PB and CaO are shown in Figure 4. CaO is a very good additive for natural fiber reinforced composites according to our previous research [16]. The addition of CaO in the formulation can neutralize the acidity of the compound during processing, thus reducing oxidation and degradation of the composites. In addition, CaO can chemically react with the coupling agent. Therefore, it acts as reinforcement in the composites and leads to improvement in the overall mechanical performance. It was shown that the composites mechanical properties decreased with the shive ratio. Shives are porous and large in size, they should be considered as defects in the composites which generate stress concentration during testing. Thus, it is not surprising to see a great deterioration in mechanical properties with the increasing amount of shive in the composite. The flexural modulus of PPF0 was 2.6 times that of PP; and its flexural strength and impact strength

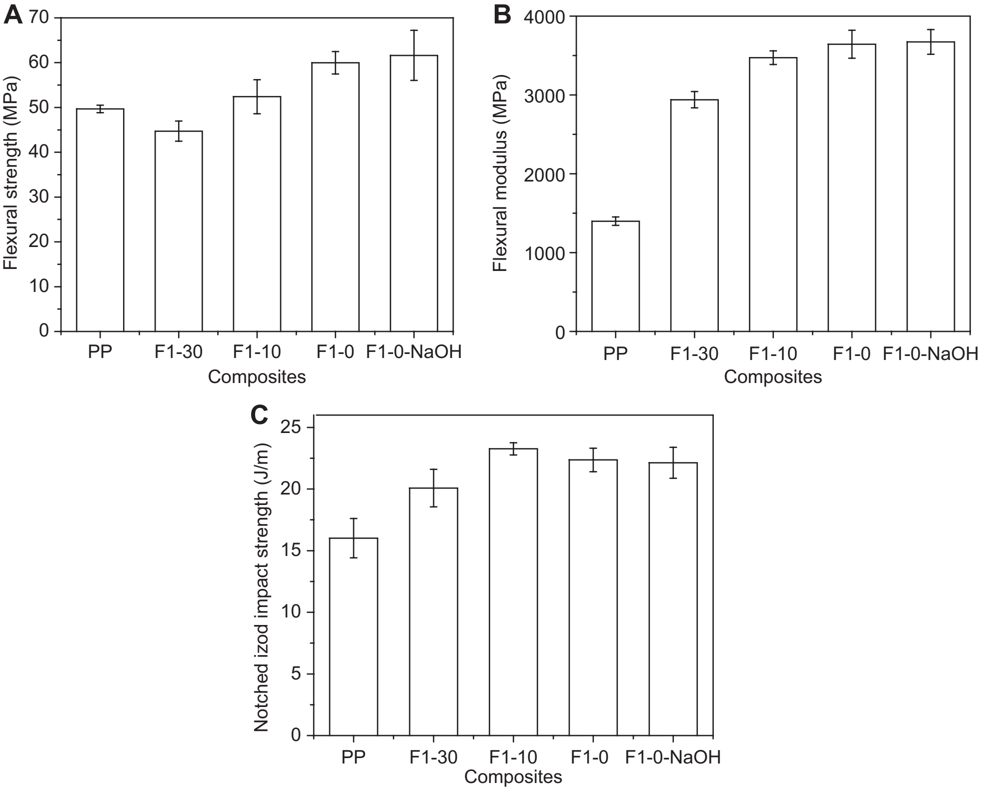

Figure 4 Flexural strength (A), flexural modulus (B) and notched izod impact strength (C) of flax/PP composites as a function of formulation.

increased 20% and 40% compared with pure PP, respectively. The reason could be due to the higher strength and modulus of flax fiber (~411.2±35.0 MPa and 27.0±3.2 GPa, respectively) than PP, and the good interface resulting from the presence of PB and CaO. Figure 5 shows the SEM images of the fractured composites. Large size of shive can be observed in the PPF30 and PPF10 composite, although the fiber-matrix interface was good for the short fiber pull-out and few cracks were observed. No shive can be found in the PPF0 composite, which also shows very good interface. It proves that the shive and other impurities could act as stress concentration regions to negatively affect the mechanical property of composites.

By contrast, PPF0-NaOH did not present obvious improvement on mechanical properties compared with PPF0 if standard deviation is taken into account as shown in Figure 4. In Figure 5D, good interface could be observed in PPF0-NaOH composite in which very rare pull-out fibers and cracks between fibers and matrix could be observed. Such good interface is similar with that of other composites. Thus, the possible reason for this result could be that the mechanical treatment presented a similar effect on fiber aspect ratio after compounding as the alkali treatment. The fiber bundles after the mechanical treatment were already loosened to be ready for the separation into single fibers during the compounding process. In Figure 1B, the cuticles that bundled the elementary fibers were broken and should be easily removed. Some elementary fibers were even already isolated from the technical fiber bundles. Therefore, the further alkali treatment did not make a very obvious difference from the mechanical treatment on the fiber separation, i.e., aspect ratio. In addition, during the screening and combing process, most of the impurities, loosened cuticles and other non-cellulose portions, which could act as the stress concentration regions, were also possibly removed from the flax fibers. Thus, the alkalization effect on mechanical properties of composites became minor.

4. Conclusion

In this study, the shives were mechanically removed from the commercial flax by screening and combing to obtain different shive contents from 0 wt% to 30 wt%. By contrast, the obtained flax fibers without shive (0% shive) from mechanical treatment were further treated with alkaline solution. The flax/PP composites were fabricated by melt compounding using the Plasti-Corder. It is interesting to find that the thermal stability and mechanical properties of the composites increased significantly with the removal of the shive content. However, the alkali treatment on flax fiber did not obviously further improve the composites properties. It indicated that the appropriate mechanical treatment (screening and combing) could significantly remove the impurities and facilitate fiber separation and dispersion in

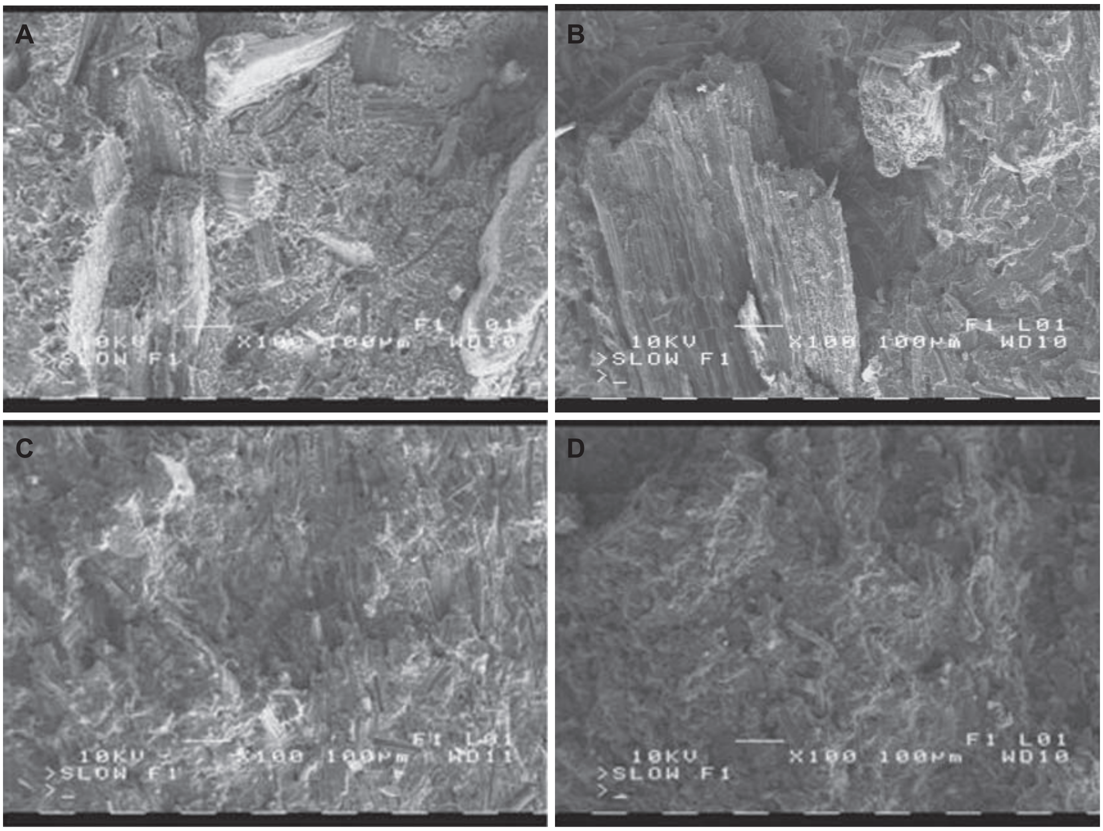

Figure 5 SEM photos of fractured flax/PP composites reinforced with (A) F30, (B) F10, (C) F0 and (D) F0-NaOH.

the composite. Hence, further chemical treatment became less important.

Acknowledgments

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