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

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ABSTRACT

Flax is a kind 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 affect negatively the mechanical property of composites. In this work, the shive was manually removed from the commercial flax fibers by screening and combing to obtain different shive contents from 0 to 30wt%. On the other hand, 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 improve further the composites properties. The possible reason was that the proper mechanical treatment (screening and combing) prior alkaline treatment has effectively loosed the fiber bundles for better single fiber separation in matrix and removed significantly the impurities, thus the effect of alkaline treatment became not obvious.

INTRODUCTION

Flax is a kind of widely applied natural fiber 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 affect negatively the mechanical properties of composites. On the other hand, flax also presents important shortcomings, such as hydrophilic nature, high moisture absorption and low thermal resistance which restrict its application like 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 work, 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.

EXPERIMENTS

The dew-retted Canadian linseed flax fibers with 30% and 10% of shive (F30 and F10, respectively) were kindly provided by Schweitzer-Mauduit Company. Homopolypropylene Pro-fax PDC 1274 (PP) ($\bar{M}_w$) = 250 Kg / mol) obtained from Basell was used as the matrix for the composites. Coupling agent polybond 3200 (PB) ($\bar{M}w$ = 84 Kg / mol, MA content: 1.0 wt %) was kindly supplied by Chemtura Inc.. Calcium oxide (CaO) was purchased from Aldrich.

Mechanical Treatment

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

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 1h at 80 ºC 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 in order to prevent fiber agglomeration. The whole system was further dried at 105 ºC for 1 day prior compounding. The fiber yield was about 74% as the non-cellulose portions were well removed from F0 by the alkali.

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 105ºC for 1 day, and then compounded with PP, PB and CaO according to the formulation shown in Table 1 using a Brabender. All the components were mixed totally for 10 min at a screw speed of 60 rpm and temperature of 190ºC. The obtained composites were kept in a vacuum oven at 100ºC for 24h before moulding. Composite testing samples were prepared by compression moulding at 190 ºC.

Table 1 - Formulation of Flax / PP Composite

	F1-30 (g)	F1-10 (g)	F1-0 (g)	F1-0-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							

Characterization

<u>SEM Observation</u>

A JEOL JSM-6100 SEM at a voltage of 10kV 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.

<u>SFTT</u>

The tensile properties of flax fibers were evaluated according to the procedure described in [12].

FTIR Characterization

FTIR spectra of the flax were obtained from a Nicolet Magna-IR 860 spectrometer of the Spectra-thermo electron Company. 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.

Thermal analysis

DSC-7 Perkin-Elmer calorimeter was used to study the melting and crystallization behaviour of PP and flax / PP composites at a heating and cooling rate of 10 ºC / min during all the process. The sample was first heated to 200 ºC and kept for 5 min. And then the sample was cooled down to room temperature and performed the second heat scan thereafter. The crystallinity of the PP matrix in the composites was determined using the following equation:

$$X_c = \Delta H_m / (f_P \times \Delta H_f^0) \times 100 \%$$ (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 SETRAM TGA. The measurements were carried out from 25 to 700ºC at a heating rate of 20ºC/min in inert nitrogen gas. All samples were kept in the air without further drying before the measurement.

Mechanical Characterization

Flexural and impact properties of composites were measured according to ASTM test methods D790 on Instron 5500R machine, and D256 on TMI Impact Testing machine, respectively.

RESULTS AND DISCUSSIONS

Characterization of Flax Fibers

SEM Observation

Fig. 1(a) shows the SEM images 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. Fig. 1 (b) presented 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 fiber surface. It seemed the mechanical treatments not only removed the shives, but also loosed the fiber bundle and removed the impurities on fiber surface to some extent. Fig.1(c) shows the SEM photo of flax fiber F0 treated with 2% NaOH at 80°C for 1h. The F0 fibers were fully separated into single fibers. The fiber surface was very clean, as the hemicelluloses, pectin and lignin have been removed through the alkali treatment.
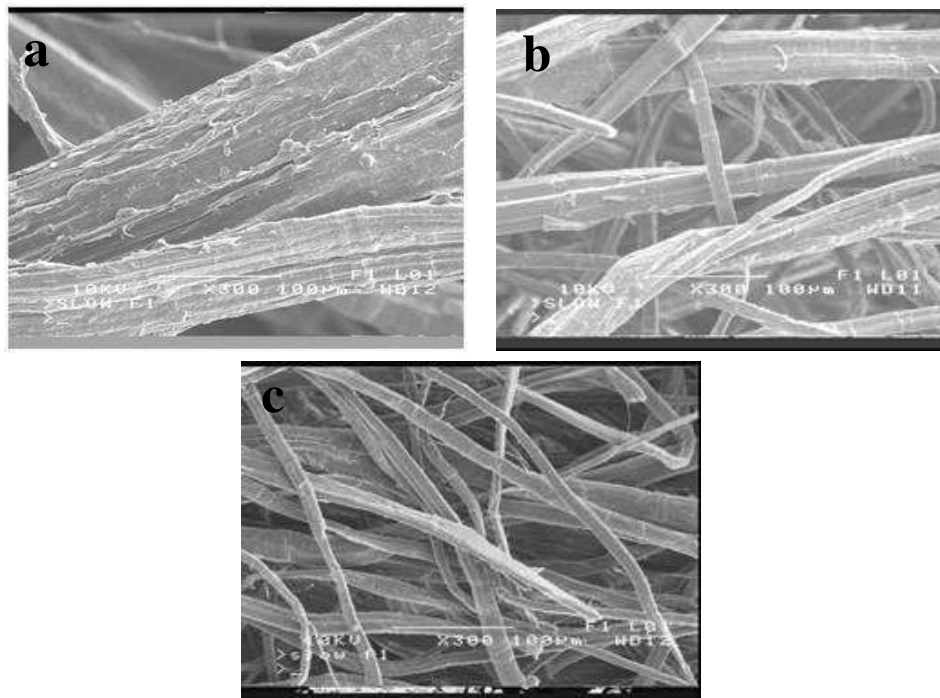

Figure 1. (a) Flax fiber from F10 without any treatment; (b) F0; (c) F0-NaOH.

FTIR Characterization

The FTIR spectrum of F0 was shown in Fig. 2. The characteristic peak of –OH is between 1000-1500cm^{-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 about 1250 cm^{-1} belongs to a C-O stretching vibration of the acetyl group in hemicelluloses and lignin. The observed peak at 898cm^{-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 was also shown in Fig. 2. Alkaline treatment 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 proved by the increased intensity of peak between 1000-1500cm^{-1} bands compared to F0. The vanish 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 desertification process. The disappearance of the peak at 2915 cm^{-1}

5

also indicates the removal of hemicellulose [8-10]. The reduction of the peak at about 1250 cm^{-1} demonstrates that the alkali treatment removed the hemicelluloses and lignin partially. All these changes proved the alkalization removed effectively a large amount of non-cellulose portions.
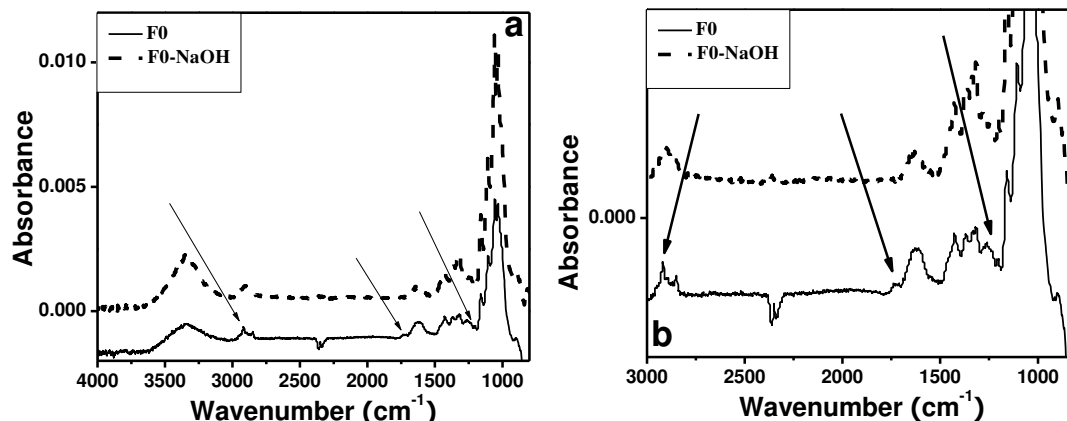
Figure 2. FTIR spectra of F0 and F0-NaOH, (b) is the enlarged spectra of part of (a).

TGA Characterization

The thermal property of F0 and F0-NaOH was characterized by TGA. Fig. 3 shows their TGA and DTGA curves. Their main characterized degradation 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. There was no sudden weight loss began at about 250°C for F0-NaOH in thermogravimetric curves (Fig. 3 (a)), which was due to hemicellulose portions in F0. [10] Correspondingly, it could be observed clearly in Fig. 3(b) that the small shoulder-like peak on the DTGA spectra of F0 at about 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. Same peak at the same temperature could be observed on the DTGA curve for F0-NaOH. This meant the alkalization did not hurt the cellulose structure.

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 damage the fiber structure. Single fiber tensile test was then performed on the alkali treated fiber to compare with 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 meant the mechanical treatment did not affect the fiber

6

quality. On the other hand, F0 also presented similar mechanical properties compared with F0-NaOH if standard deviation is taken into account, which meant 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.
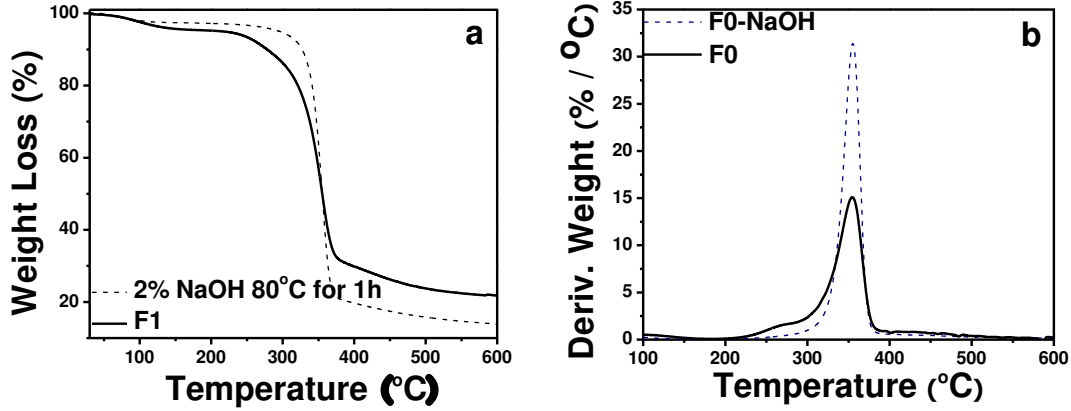
Figure 3. TGA (a) and DTGA (b) of F0 and F0-NaOH.

Table 2 - Thermal Properties of Alkali Treated Flax

	T_5 (^{o}C)	T_{10} (^{o}C)	T_{max} (^{o}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

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

Characterization of Flax / PP Composites

Crystallization Behavior

The melting and crystallization behaviour of composites were studied using DSC. The crystallization curves of flax / PP composites (not shown here) presented similar crystallization behaviours 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 ºC to 120 ºC 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 literatures [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.

Table 4 - Crystallization Properties and Thermal Stability of PP and Flax / PP Composites

|	T_c (ºC)	T_m (ºC)	X_c (%)	T_5 (ºC)	T_{10} (±1ºC)	T_{max1} (±1ºC)	T_{max2} (±1ºC)
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

Thermal Stability

The main thermal stability parameters of composites, such as temperature of 5% weight loss (T_5) and 10% (T_{10}) of all the samples were shown in Table 4. For PP, there was only one peak in its DTG curve at 461ºC which corresponded to the degradation of PP chain. There were two main peaks observed on the DTGA spectra (not shown here) of the composites. T_{max1} at about 355 ºC was corresponding to the degradation of cellulose, and the higher peak T_{max2} at about 468 ºC may 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. On the other hand, it is also shown T_5 and T_{10} of PPF0 were lower than those of PPF0-NaOH, especially the T_5 of PPF0 was about 20ºC lower than that of PPF0-NaOH. This was related to the more non-cellulose portion in the F0, such as hemicelluloses, lignin, etc. It proved that alkaline treatment could improve further the composite thermal stability.

Mechanical Properties

The flexural strength, modulus and notched Izod impact strength of the composites formulated with PB and CaO are shown in Fig. 4. CaO is very good additive for natural fiber reinforced composites according to our previous work. [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 coupling agent. Therefore, it acts as reinforcement in the composites and lead 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 of PP; and its flexural strength and impact strength increased 20% and 40% compared with pure PP, respectively. The reason should be due to the higher strength and modulus of flax fiber (~ 411.2 ± 35.0 MPa and 27.0 ± 3.2GPa, respectively) than PP, and the good interface resulting from the presence of PB and CaO. Fig. 5 shows the SEM images of the fractured composites. Large size of shive can be observed in the PPF30 and PPF10 composite, though the fiber-matrix interface was good for the short fiber pull-out and few cracks could be observed. No shive can be found in PPF0 composite, which also show very good interface. It proves that the shive and other impurities could act as stress concentration regions to affect negatively the mechanical property of composites.
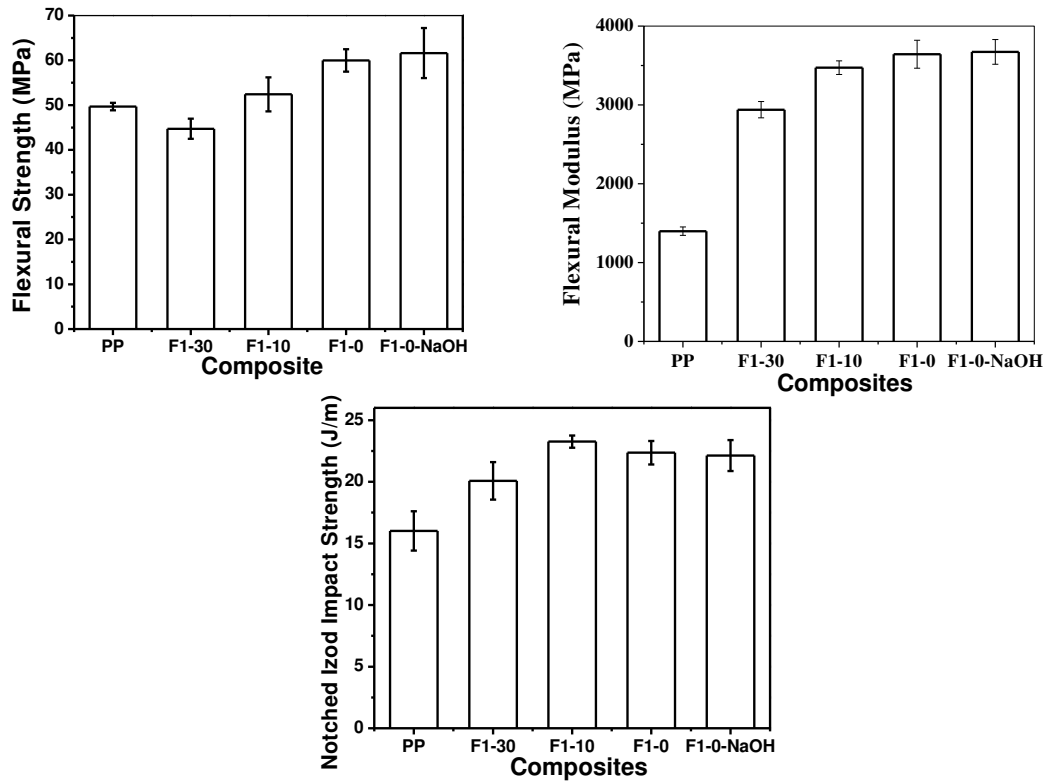
Figure 4. Flexural strength (a); flexural modulus (b) and notched izod impact strength (c) of flax / PP composites as a function of formulation.

On the other hand, PPF0-NaOH did not present obvious improvement on mechanical properties compared with PPF0 if standard deviation taken into account as shown in Fig. 4. In Fig. 5 (d), good interface could be observed in PPF0-NaOH composite with very rare pull-out fibers and cracks just similar with other composites. So the possible reason for this result was the mechanical treatment presented the similar effect on fiber aspect ratio after compounding as the alkali treatment. The fiber bundles after the mechanical treatment were already loosed to be ready for the separation into

single fibers during the compounding process. In Fig. 1(b), the cuticles bundled the elementary fibers was broken and should be easily to be removed. Some elementary fibers were even already isolated from the technical fiber bundles. Therefore, the further alkali treatment could not make 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, loosed cuticles and other non-cellulose portions, which could act as the stress concentration regions, were also possibly to be removed from the flax fibers. Thus, the alkalization effect on mechanical properties of composites became minor.
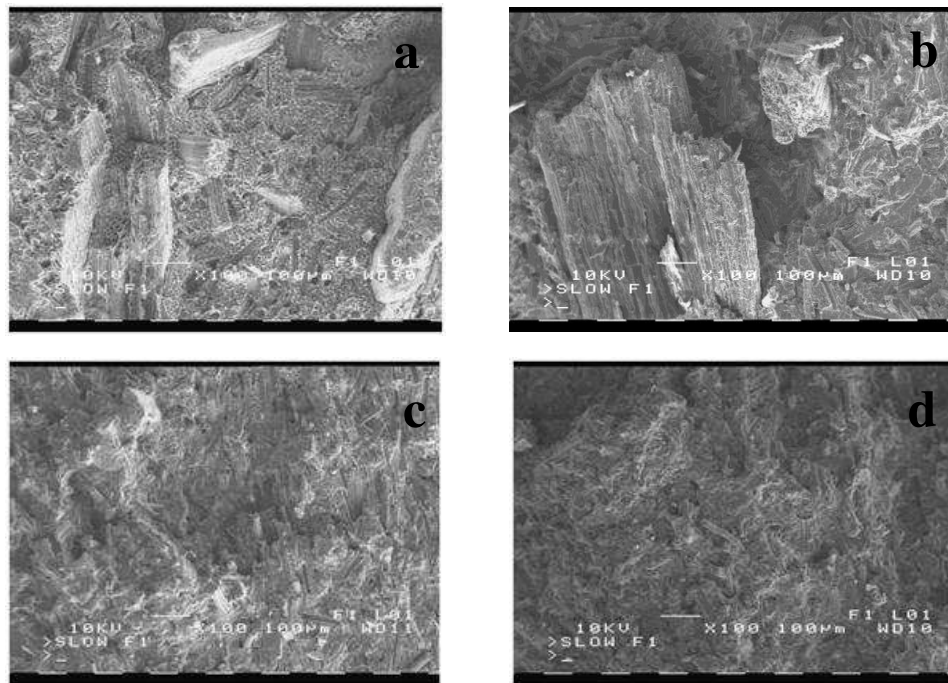
Figure 5. SEM photos of fractured flax/PP composites reinforced with (a) F30; (b) F10; (c) F0 (d) F0-NaOH

CONCLUSIONS

In this work, the shives were manually removed from the commercial flax fibers by screening and combing to obtain different shive contents from 0 to 30wt%. On the other hand, the obtained flax fibers from mechanical treatment were further treated with alkaline solution. The flax / PP composites were fabricated by melt compounding using the Brabender Plasticoder. 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 improve further the composites properties obviously. It indicated that the appropriate mechanical treatment (screening and combing) could significantly remove the impurities, and facilitate fiber separation and dispersion in the composite. Hence further chemical treatment became less important.

10

ACKNOWLEGEMENT

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