EFFECTS OF CHEMICAL TREATMENTS ON THE STRUCTURAL, MECHANICAL AND MORPHOLOGICAL PROPERTIES OF POLY(VINYL CHLORIDE)/*Spartium junceum* FIBER COMPOSITES

BOUHANK SALIM and NEKKAA SORYA

Laboratory of Physical-Chemistry of High Polymers, Department of Process Engineering,
Faculty of Technology, University Setif 1, Algeria
✉ *Corresponding author: Nekkaa Sorya, s_nekkaa@yahoo.fr*

This study investigates the effects of surface treatments by sodium hydroxide (NaOH) and vinyltrimethoxysilane (VTMS) of *Spartium junceum* (SJ) fibers on the structural and physical properties of *Spartium junceum* fibers. SJ fibers were characterized by Fourier Transform Infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and optical microscopy. FTIR was performed to see the extent of chemical modification of the fibers, the results obtained from XRD indicated an improvement in the crystallinity index of the SJ fibers by treatments. The effects of the treatments on the properties of the prepared SJ fiber reinforced poly(vinyl chloride) (PVC) composites were investigated. Also, the treatments improved notably the mechanical properties of the composites. The observations by scanning electron microscopy (SEM) of fracture surfaces of PVC/SJ composites showed more intimate contact between fibers and PVC matrix after surface modification.

Keywords: poly(vinyl chloride), *Spartium junceum*, treatment, crystallinity

INTRODUCTION

Natural fiber composites are one of the outstanding topics nowadays to make reconciliation between industry and environment. Many efforts have been done to investigate the suitability of natural fiber as a reinforcing component of poly(vinyl chloride) (PVC) polymers during the last few years.[1] Because of its high level of combustion resistance, as well as its low cost, demands for natural fiber/PVC composites are increasing dramatically.[2] They are typically used in building construction applications, such as window/door profiles, decking, railing and siding.[2-4] In addition, natural fiber reinforced composites have many advantages, such as light weight, reasonable strength and stiffness, renewability and biodegradability.[5-7] The composites therefore provide economical and ecological properties.[5] However, the main disadvantage of these natural fiber/polymer composites seems to be the incompatibility between the hydrophilic natural fiber and the hydrophobic thermoplastic matrix.[8-9] In other words, there are significant problems of compatibility between the fiber and the matrix due to the weak interface.[10]

Therefore, surface modification of natural fiber by means of treatment is one of the largest areas of recent research to improve compatibility and interfacial bond strength.[10-11] Various options, including chemical treatments of lignocellulosic fibers and the use of compatibilizers, have been suggested in order to achieve the necessary compatibility of surface energies between the fibers and matrix.[12] Approaches, such as alkali, silane, acetylation, benzoylation, use of maleated coupling agents, peroxide, permanganate, and isocyanate treatment, were considered. Amongst the various methods presented, alkaline and silane treatments have been widely reported.[12-13] The chemical process of alkaline treatment is widely used to modify many types of cellulosic fibers. It is a well-known surface treatment for fibers using alkaline solution, prior to composite formation. Most of non-cellulosic components and part of the amorphous cellulose can be removed by the alkali treatment.

The surface treatment not only changes the chemical composition of fibers, but also can rearrange or transform the crystalline structure of cellulose. Silane coupling agents present major advantages: at one end, they contain alkoxy silane groups capable of reacting with -OH rich surface, whereas at another end they have a large number of functional groups, which can be tailored as a function of the matrix to be used. It ensures a good compatibility between the reinforcing element and the polymer matrix or even covalent bonds between them.[14] In addition, some research work has shown that the silane coupling agent is effective in improving the interfacial adhesion between *Spartium junceum* fibers and polypropylene. Nekkaa *et al.*[15] found that the addition of 30 wt% of *Spartium junceum* fibers treated with 1.5 wt% of silane N[-3 Trimethoxysilyl propyl] ethylene diamine to polypropylene results in an increase of storage modulus. Also, the calorimetric investigations showed that the incorporation of *Spartium junceum* fibers in polypropylene caused an apparent increase in crystallinity.[8] Nekkaa *et al.*[16] also observed that the incorporation of *Spartium junceum* flour modified the lattice parameters of the monoclinic α phase of the polypropylene matrix.

The objective of this study was to investigate the influence of treatments by 5wt% of sodium hydroxide (NaOH) and 5wt% of vinyltrimethoxysilane (VTMS) on the structural and physical properties of *Spartium junceum* fibers. In addition, the effects of chemical treatments and fiber content on the properties of the PVC/SJ fiber composites were investigated. The properties of PVC/SJ composites were examined by using X-ray diffraction, tensile testing and scanning electron microscopy.

EXPERIMENTAL
Materials
The polymer matrix used in this study was poly(vinyl chloride) PVC (SE 1200, with K value ranging between 71-73), and a bulk density between 0.42-0.47 g/cm^3. The PVC was compounded with several additives namely: calcium-zinc stabilizer (Ca/Zn) is a white powder, non-toxic complex with good thermal stability, marketed under the name NEWSTAB_26; DOP (di-octyl phthalate) is a plasticizer marketed under the brand PLASTIMED 2001 by the company SGP (Tunisia); methyl methacrylate/butadiene/styrene (MB870) is an impact modifier for PVC sold as white powder by the company LG Chemical Ltd. (Korea), and stearic acid as lubricant. The *Spartium junceum* fibers were obtained from local sources (the shurb can be cultivated manually), and the fibers were cleaned and chopped. The fiber size ranged from 200 to 400 μm. The chemical composition of *Spartium junceum* fibers is listed in Table 1.[17]

Pretreatment of *Spartium junceum* fibers
As pretreatment, *Spartium junceum* fibers were dewaxed by stirring in water (1% detergent solution) to remove the contaminants and adhering dirt for 24 hours (h) at 50 °C. Thereafter, they were washed with distilled water several times. After filtration, the fibers were dried at 60 °C for 24 h.

Surface modification of *Spartium junceum* fibers
Alkali treatment of *Spartium junceum* fibers
The fibers were treated with sodium hydroxide (NaOH) aqueous solution (5 wt%) for 24 h at ambient temperature, then neutralized with a solution of distilled water containing 2% acetic acid for 30 min at room temperature. The fibers were rinsed several times with distilled water. Subsequently, the fibers were dried for 24 h at 60 °C.

Silane treatment of *Spartium junceum* fibers
Vinyltrimethoxysilane (VTMS) was dissolved in a 50/50 v/v solution of water and ethanol, 5 wt% VTMS (weight percentage compared to the fibers) was used. The pH of the solution was adjusted to 4 with acetic acid and stirred continuously during 1 h. Next, the fibers were soaked in the solution for 24 h at ambient temperature. The fibers were rinsed several times with distilled water. Lastly, the fibers were oven dried at 60 °C for 24 h.

Alkali and silane treatment of *Spartium junceum* fibers
First, *Spartium junceum* fibers were treated by a sodium hydroxide solution, as described in the alkali treatment step. Next, the fibers were treated by VTMS as described in the silane treatment step.

Table 1
Chemical composition of *Spartium junceum*

Composition	Cellulose	Lignin	Hemicelluloses	Pectins	Ash
%	44.5 ± 0.2	18.5 ± 0.3	16.3 ± 0.1	13.3 ± 0.1	4.0 ± 0.2

Compounding and processing

The mixtures of poly(vinyl chloride) and other additives were prepared in a two-roll mixer (Busto Arsizio) at a temperature of 170 °C and a mixing rate of 30 rpm/min for 3 min, then SJ fibers were added, followed by mixing for 4 min. The resulting sheets were cut into small pieces, then were subjected to mechanical grinding using a grinder-type Brabender Breher. Different PVC/SJ fiber composites were prepared; the *Spartium junceum* fiber amounts employed were 10, 20, 30 and 40 phr. Pressed specimens of the composites were obtained by compression molding at 175 °C under a pressure of 150 kg/cm^2, followed by air cooling.

FTIR spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectra were obtained with a Perkin Elmer spectrophotometer with a resolution of 32 cm^{-1} using KBr disks. Fibers of *Spartium junceum* were dispersed in a KBr matrix, followed by compression to disks. All spectra were registered from 4000 to 400 cm^{-1}.

X-ray diffraction

X-ray diffraction analysis of the materials was performed at room temperature by using a Bruker D8 Advance diffractometer, using copper radiation K α1 ($\lambda = 1.54184$ A°). All tests were performed with $2\theta = 6°$ and $2\theta = 70°$.

Density

The density measurement of a sample was carried out using a pycnometer for solids with water as the immersion liquid, according to EN ISO 1675. The density was calculated using the following formula:

$$d = \frac{m_2}{m_1 + m_2 - m_3} \qquad (1)$$

where m_1 is the mass of the pycnometer filled with water,

$$m_1 = m_{pyc} + m_{liq} \qquad (2)$$

m_2 is the single sample mass,
m_3 is the mass of the pycnometer full of water with the sample immersed in it.

$$m_3 = m_{pyc} + m_{liq} + m_2 \qquad (3)$$

Mechanical testing
Impact test

Impact testing was performed according to ASTM D256. Izod impact measurements were carried out with a CEAST RESIL Impact instrument in accordance with EN ISO 180 standard. The capacity of the pendulum is 7.5 kg. The impact strength of unnotched specimens was calculated.

Tensile test

The tensile strength properties were measured according to DIN EN ISO 527-1, using a universal tensile machine ZWICK/Roell Z1.0. The tests were carried out at room temperature with a strain rate of 5 mm/min.

Microscopy observations

The morphology of the untreated and treated SJ fibers was observed using KARLZCISS AXIOVERT 40 MAT optical microscopy. Scanning electron microscopy (SEM) JEOL-JSM-7001F was used to investigate the surface morphology of the fractured PVC/SJ samples.

RESULTS AND DISCUSSION
Characterizations of *Spartium junceum* fibers
FTIR spectroscopy

Fig. 1 shows the FTIR spectra of untreated, alkaline, silane and alkaline-silane treated *Spartium junceum* fibers. For untreated fibers (Fig. 1 a), it can be seen that the band at 3423 cm^{-1} was assigned to the stretching vibration of the hydroxyl group O-H. The peak observed at 2913 cm^{-1} reflects C–H asymmetric deformation. However, the vibration peak at 1732 cm^{-1} was attributed to the stretching vibrations of the C=O carbonyl groups of acetyl groups in hemicellulose or pectin.[18-19] The peak at 1644 cm^{-1} in the untreated SJ fibers is associated with the adsorbed water, due to the hydrophilic character of the cellulosic fibers. The peaks around 1509 cm^{-1} and 1450 cm^{-1} are assigned to aromatic C=C groups in lignin, while the absorbance peak at 1241 cm^{-1} corresponds to the C-O-C stretching vibration of the ether group in lignin. Also, a peak appeared at 1035 cm^{-1} is assigned to C-O stretching.[20-21] After alkaline treatment (Fig. 1 b), the peaks around 1732 cm^{-1} and 1241 cm^{-1} disappeared. This change in the spectra indicates extraction of hemicellulose and lignin from the fiber surface by the aqueous alkaline solution.[13,21-24]

In the case of VTMS treated SJ fibers (Fig. 1 c), the peak intensity at 1732 cm^{-1} reduced, which can be ascribed to the partial dissolution of hemicellulose. In addition, the intensity of the peaks at 1035 cm^{-1}, 1641 cm^{-1} and 3423 cm^{-1} decreased. These results can be due to partial dissolution of the lignin, waxes and pectins. The broad and intense bands around 1260 cm^{-1} and 1100 cm^{-1} are assigned to the stretching of the Si–O–Cellulose and Si–O–Si bonds, respectively. These bands suggest that both the grafting of silane onto cellulose and the intermolecular condensation between adjacent adsorbed Si–OH groups have been substantially enhanced.[25-26]
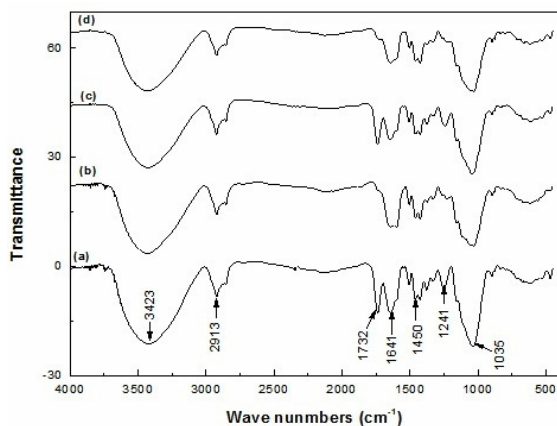
Figure 1: FTIR spectra of *Spartium junceum* fibers, (a) untreated, and treated with (b) NaOH, (c) VTMS and (d) NaOH+VTMS
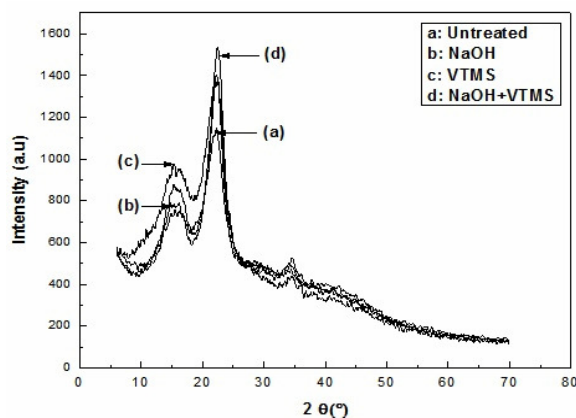

Figure 2: X-ray diffraction of untreated and treated *Spartium junceum* fibers

Table 2
Crystallinity index and crystallite size of untreated and treated *Spartium junceum* fibers

Treatments	I_{002} (2θ = 22°)	I_{am} (2θ = 18°)	β	Crystallinity index CrI(%)	L (nm)
Untreated SJ fiber	1147.71	646.57	2.83	43.66	2.88
NaOH	1348.42	600.14	2.28	55.49	3.53
VTMS	1404.40	808.00	3.04	42.46	2.66
NaOH+VTMS	1490.14	669.71	2.56	55.05	3.14

X-ray diffraction

Fig. 2 displays the X-ray spectra for the untreated and treated *Spartium junceum* fibers. From this figure, it is observed that all of the spectra contained two peaks that are particularly well defined for natural fiber. The presence of these diffraction peaks indicates that the untreated and treated cellulose fibers are semi-crystalline. According to several authors,[6] these two peaks situated at 2θ = 15.7° and 2θ = 22.2° can be attributed to cellulose I. Also, it is observed that the peaks of the fibers treated with NaOH, VTMS and NaOH+VTMS are more intense than those of untreated fibers, which means that the chemical treatment removed part of the amorphous material covering the fibers, thus exposing the cellulose. These results are in accordance with the FTIR analysis, and in good agreement with those presented by Fernandes *et al.*,[7] Sreenivasa *et al.*[27] and by Beckermann *et al.*[28]

The crystallinity index (Ic) of the treated and untreated SJ fibers was calculated using Eq. (4)[29-30] and the results are summarised in Table 2.

$$CrI(\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \qquad (4)$$

where I_{002} is the maximum intensity of the 002 lattice reflection of the cellulose crystallographic form (I) at 2θ=22° and I_{am} is the intensity of diffraction of the amorphous material at 2θ=18°.[28,31]

It can be seen in Table 2 that the crystallinity index of SJ fibers was increased by NaOH and NaOH+VTMS treatments. This is attributed to the removal of amorphous components, like lignin and hemicelluloses.[20,32] Also, we note that the fibers treated with NaOH have a slightly higher crystallinity index compared to the fibers treated with VTMS and NaOH+VTMS. These results are in agreement with those presented by Sreenivasan *et al.*[31] and Troedec *et al.*[33] An estimate of

crystallite size (L) was made using Scherrer's formula:[27]

$$L = \frac{K.\lambda}{\beta.\cos\theta} \qquad (5)$$

where K=0.9 is Scherrer's constant, β is the full-width at half maximum of the peak and λ=1.54 A° is the wavelength of the radiation, 2θ=22.2°.[27,31] The crystallite size (L) of the untreated and treated SJ fibers computed using Eq. (5) is reported in Table 2. It is also clear that NaOH treated fibers possessed the highest crystallite size (L).

Density

The effect of treatment on the density of SJ fibers is presented in Fig. 3. We can say that the treatment with NaOH or NaOH+VTMS improves the density of *Spartium junceum* fibers. This is explained by the weight loss, which eliminates the cell wall components, such as lignin, pectin, and the waxy substance that covers the outer surface of the cell wall of the fiber. This allows an approximation of cellulose microfibrils, leading to a more compact and higher density.

Morphology

The observation of untreated and treated fibers by optical microscopy allows visualizing the morphology of these fibers. Images of the outer surface are presented in Fig. 4. There is a layer of wax and dust adsorbed on the outside of the crude fibers (Fig. 4 a), which disappeared after the treatments (Fig. 4 b, c and d). This means that the treatments clean the fibers and dissolve the lignin and hemicellulose compounds, as well as other organic substances, such as pectin and waxes.
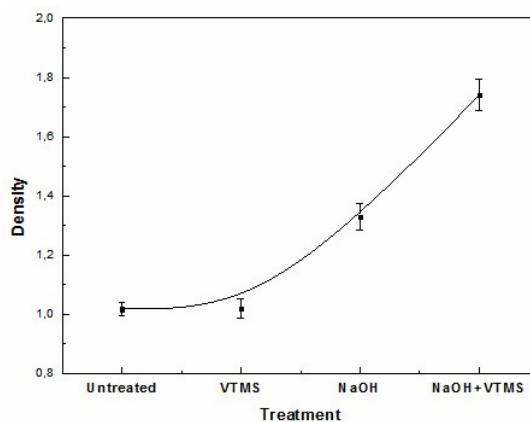

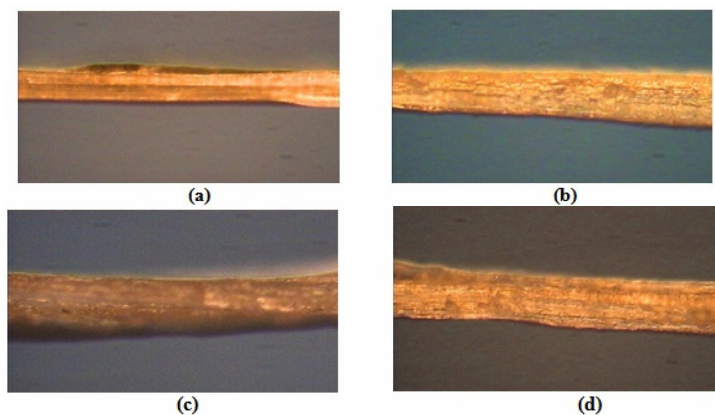Figure 3: Effect of treatment on the density of *Spartium junceum* fibers

Figure 4: Optical microscopy images of *Spartium junceum* fibers: (a) untreated, and treated with (b) NaOH, (c) VTMS and (d) NaOH+VTMS

Properties of PVC/SJ composites
X-ray diffraction

The crystallinity degree of PVC matrix and PVC/SJ composites was determined using the equation:

$$CrI(\%) = \frac{Ac}{At} = \frac{Ac}{Ac + Aa} \times 100 \qquad (6)$$

where Ac is the crystalline area, Aa is the amorphous area and At is the total area.[34]

Fig. 5 shows the XRD patterns of PVC matrix and PVC/SJ composites. It may be observed that all of the spectra contain two large peaks in the directions of 15° and 17°. The presence of these large diffraction peaks indicates that the PVC matrix and PVC/untreated SJ fiber composites are amorphous. Fig. 6 presents the crystallinity degree obtained. It can be seen that the crystallinity degree of the PVC matrix increased when adding SJ fibers to the PVC matrix. This can be explained by the fact that the surface of cellulosic fibers acts as a nucleation site for the crystallization of the polymer, promoting the growth and the formation of transcrystalline regions around the fibers.[8]

The X-ray spectra of the PVC filled with 30 (phr) SJ fibers submitted to different treatments and the influence of the surface treatment on the crystallinity degree of the composites are presented in Fig. 7 and Fig. 8, respectively. From Fig. 8, it is noted that all the chemical treatments used in this research increased the crystallinity degree of the composites. The crystallinity degree of PVC/SJ fibers was increased by the alkali treatment, and was due to the removal of pectins and other amorphous constituents from the fibers after alkali treatment.[28] It can also be seen that the crystallinity degree of the PVC composites containing SJ fibers treated with silane slightly increased, due to the partial elimination of the amorphous components.
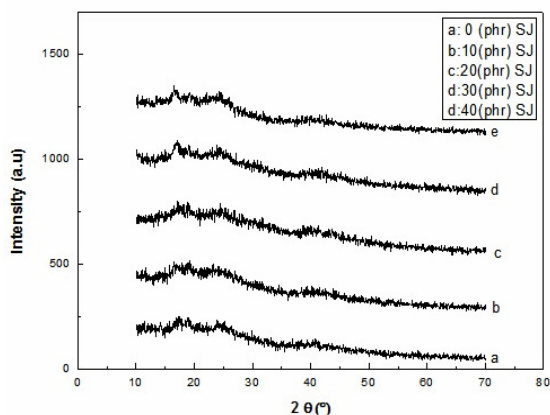

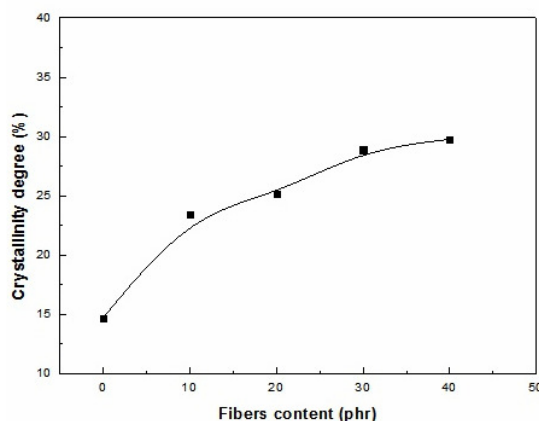Figure 5: X-ray diffraction spectra of PVC and PVC/SJ fiber composites

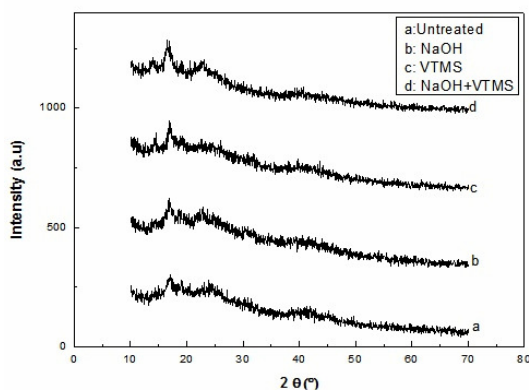Figure 6: Crystallinity degree of PVC and PVC/SJ fiber composites

Figure 7: X-ray diffraction spectra of PVC composites filled with 30 (phr) SJ fibers submitted to different treatments
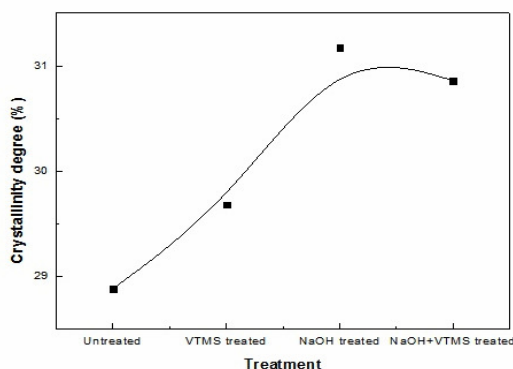

Figure 8: Crystallinity degree of PVC composites filled with 30 (phr) SJ fibers submitted to different treatments

Density

The influence of the content of SJ fibers and their surface treatments on the variation in the density of the PVC/SJ composites is shown in Fig. 9. We notice a weak reduction in the density with the increase of fiber content. This decrease is due to the difference between the density of the fibers and the matrix ($d_{matrix} = 1.2571$, $d_{fiber} = 1.0175$). However, it can be observed from Fig. 10 that the effect of surface treatments on the density of the PVC/SJ composites was not considerable. We notice a weak improvement in the density of PVC/SJ composites when the fibers were treated with NaOH and NaOH+VTMS. These results can be explained by the effect of the alkali treatment, which eliminates the cell wall components.

Impact strength

Fig. 10 shows the variation of the impact strength as a function of fiber content of PVC/SJ composites. It appears that the incorporation of *Spartium junceum* fibers into the PVC matrix causes a marked decrease of its impact strength. The Izod impact strength of the unfilled PVC was found to be 41.726 KJ/m^2. Overall, the impact strength of the composites decreases as *Spartium junceum* fiber loading increases. This is due to the incompatibility between the polymer matrix (PVC) and vegetable fibers (SJ). In addition, SJ fibers have a stiffness value greater than that of the PVC matrix, which significantly increases the stiffness of the composite material, and also

causes a decrease in impact strength. These results are in agreement with those presented by Petchwattana *et al.*[35] and Zheng *et al.*[36]

The impact strength of the fiber reinforced polymeric composites depends on the nature of the fiber, the polymer, and the fiber–matrix interfacial bonding.[37] Fig. 11 shows the impact strength of PVC filled with untreated and treated SJ fibers. The treatment of the fiber surface leads to an improvement of the impact strength of the composites with treated fibers, compared to those with untreated fibers. The alkali treatment caused the cellulosic fibers to swell and removed the hemicellulose and other impurities from the fiber surface. The removal of the impurities led to better mechanical properties, fiber wetting characteristics and fiber–matrix adhesiveness in composite applications.[18] The treatment permits to separate the lignin of the SJ fibers, decreasing the number of agglomerates and thus contributing to a better scattering of the particles in the polymeric matrix. In the case of the silane coupling agent treated SJ fibers, one can say that the positive contribution of the coupling agent lies in the efficiency of the stress transfer at the fiber-matrix interface.[19] It was found that the alkali-followed by silane treatment on the fibers improved their mechanical properties. This might be explained by the removal of waxes, hemicelluloses, and partially, of the lignin from the fiber surface enhances the availability of sites for cellulose-silane interactions.[22]
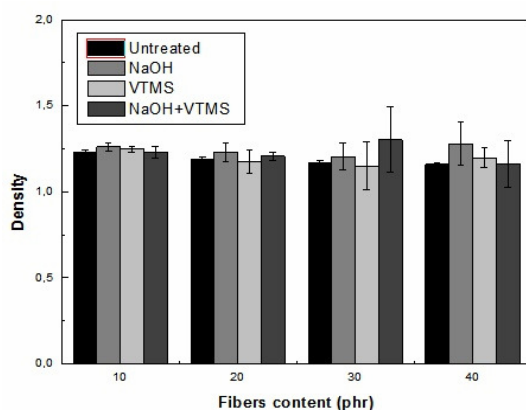

Figure 9: Effects of fiber content and surface treatment on the density of PVC/SJ fiber composites
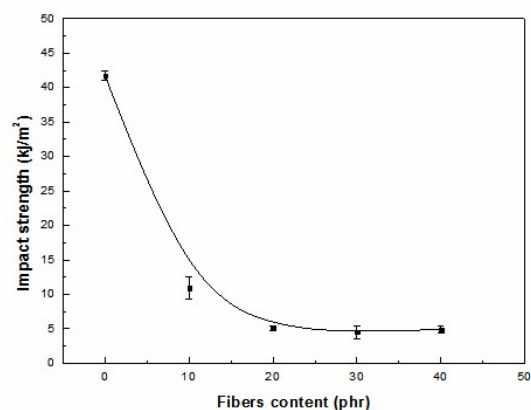

Figure 10: Effect of fiber content on the impact strength of PVC and PVC/SJ fiber composites
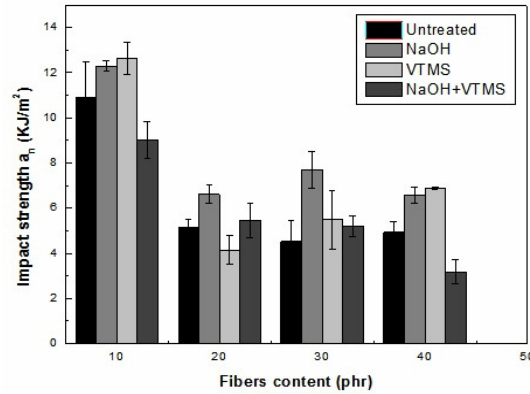
Figure 11: Effect of fiber surface treatment on the impact strength of PVC/SJ fiber composites
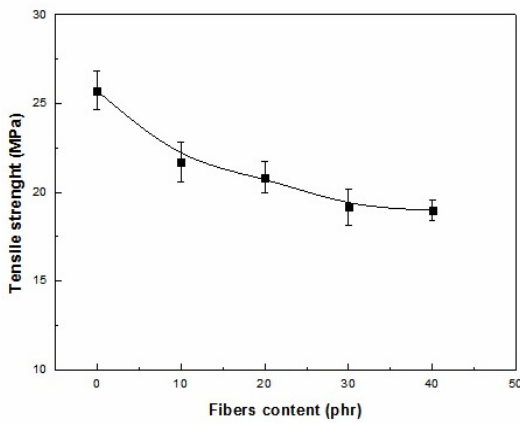

Figure 12: Effect of fiber content on the tensile strength of PVC/SJ fiber composites
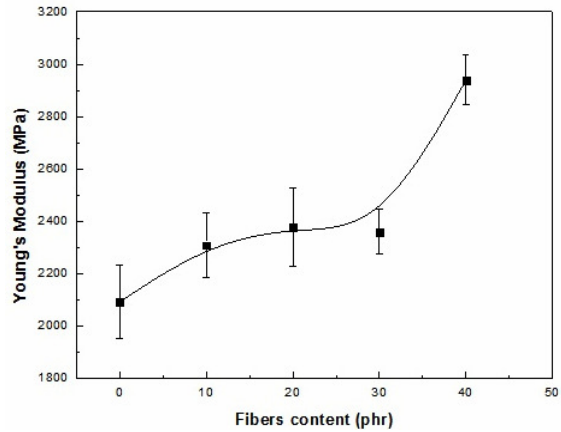

Figure 13: Effect of fiber content on Young's modulus of PVC/SJ fiber composites
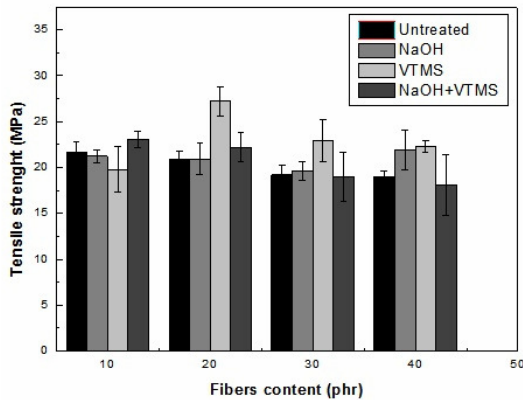

Figure 14: Effect of fiber surface treatment on the tensile strength of PVC/SJ fiber composites
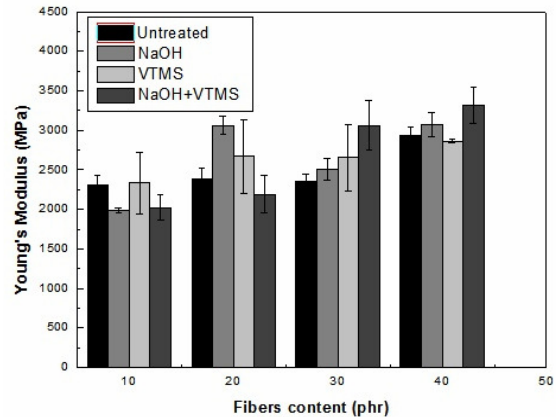

Figure 15: Effect of fiber surface treatment on Young's modulus of PVC/SJ fiber composites

Tensile properties

Fig. 12 illustrates the influence of fiber content on the tensile strength of the PVC/SJ composites. As can be seen in this figure, the tensile strength of the composites decreased with increased fiber content. This is mainly related to poor entanglement, causing a low degree of adhesion between the SJ fibers and the PVC matrix.[38] Secondly, most polymers, especially thermoplastics, are non-polar (hydrophobic)

substances, which are not compatible with polar (hydrophilic) fibers.[19] The effect of the fiber content on Young's modulus is shown in Fig. 13. It can be seen that Young's modulus increases in proportion to SJ fibers. It is consistent with the results of other studies.[23,38-39]

Fig. 14 and Fig. 15 depict the influence of surface treatment on the tensile strengths and Young's modulus of the PVC/SJ composites,

respectively. The modification of the fibers increased the tensile properties of these composites, relative to the untreated ones. This result suggests that the stress is expected to transfer from the matrix to the fibers, indicating better interfacial bonding with a consequent improvement in the mechanical properties.[19,40]
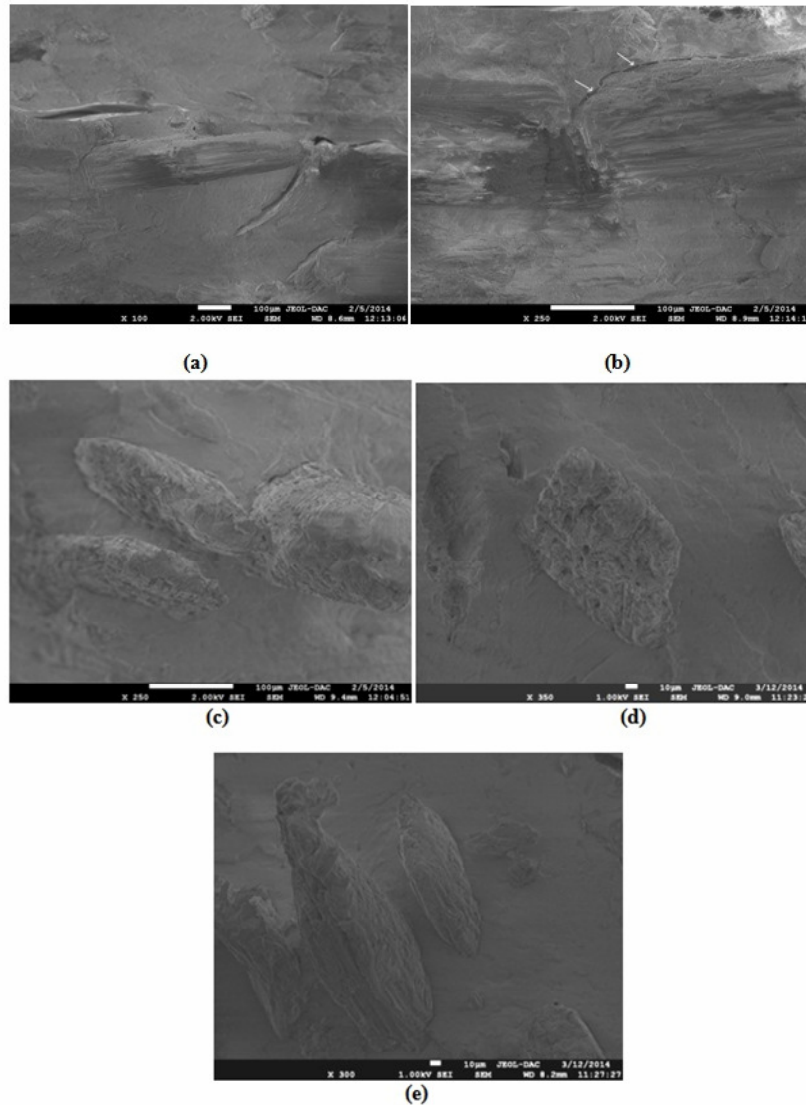

Figure 16: SEM micrographs of PVC/SJ composites with untreated fibers (a and b); and with fibers treated with (c) NaOH, (d) VTMS and (e) NaOH+VTMS

Morphology

The effect of the surface treatment on the interface between the PVC and SJ fibers was studied by examining the fracture surfaces of the impact tested composites with SEM. SEM

micrographs of the fracture surface of the untreated and treated composites containing 30 phr of SJ fibers can be seen in Fig. 16 a, b, c, d and e. The examination of the fracture surface of untreated SJ composites (Fig. 16 a and b)

indicates that there are voids between the fibers and the matrix, which is an evidence of poor adhesion. Poor adhesion seems to facilitate debonding of the fibers. To the contrary, it could be seen from Fig. 16 c, d and e that the composites with treated fibers present a more intimate contact the between fibers and the matrix. All these observations are consistent with the mechanical test results.[1,5]

CONCLUSION

1. The FTIR results indicated the disappearance of the peaks around 1732 cm^{-1} and 1241 cm^{-1}. This is due to the removal of hemicelluloses and lignin from the fiber surface by the alkali treatment. Also, the appearance of the bands around 1260 cm^{-1} and 1100 cm^{-1} is attributed to the asymmetric stretching of Si-O-Si linkage and Si-O-Cellulose for the VTMS treated SJ fibers.

2. The crystallinity index and the density of SJ fibers were increased by the treatments. This is due to the removal of the amorphous components, like lignin and hemicelluloses from the fiber surface, as confirmed by optical microscopy. Also, NaOH treated SJ fibers demonstrated superior density and crystallinity index, in comparison with the fibers treated with VTMS and NaOH+VTMS.

3. The impact strength and tensile strength of the composites decreased with an increase in SJ fiber content. Young's modulus of the composites increased in proportion to SJ fiber addition. However, the surface treatment resulted in improved mechanical properties of the composites. This can be attributed to the increase in interfacial adhesion after the surface treatment, as confirmed by the morphological study by SEM.

REFERENCES

[1] H. Wang, K. C. Sheng, T. Lan, M. Adl, X. Q. Qian *et al.*, *Compos. Sci. Technol.*, **70**, 847 (2010).

[2] Y. Fang, Q. Wang, C. Guo, Y. Song and P. A. Cooper, *J. Anal. Appl. Pyrol.*, **100**, 230 (2013).

[3] M. Müller, H. Militz and A. Krause, *Polym. Degrad. Stabil.*, **97**, 166 (2012).

[4] X. Bai, Q. Wang, S. Sui and C. Zhang, *J. Anal. Appl. Pyrol.*, **91**, 34 (2011).

[5] H. Demir, U. Atikler, D. Balkose and F. Tıhmınlıoglua, *Compos.: Part A*, **37**, 447 (2006).

[6] V. S. Sreenivasan, D. Ravindran, V. Manikandan and R. Narayanasamy, *Mater. Design.*, **37**, 111 (2012).

[7] E. M. Fernandes, J. F. Mano and R. L. Reis, *Compos. Struct.*, **105**, 153 (2013).

[8] S. Nekkaa, M. Guessoum, F. Chebira and N. Haddaoui, *Int. J. Polym. Mater.*, **57**, 771 (2008).

[9] O. Nozari, M. Madanipour, M. Farsi and A. Tabei, *Cellulose Chem. Technol.*, **47**, 295 (2013).

[10] T. Alsaeed, B. F. Yousif and H. Ku, *Mater. Design.*, **43**, 177 (2013).

[11] B. F. Yousif, A. Shalwan, C. W. Chin and K. C. Ming, *Mater. Design.*, **40**, 378 (2012).

[12] O. M. L. Asumani, R. G. Reid and R. Paskaramoorthy, *Compos.: Part A*, **43**, 1431 (2012).

[13] K. B. Goriparthi, K. N. S. Suman and N. M. Rao, *Compos.: Part A*, **43**, 1800 (2012).

[14] J. M. Park, P. G. Kim, J. H. Jang, Z. Wang, B. S. Hwang *et al.*, *Compos.: Part B*, **39**, 1042 (2008).

[15] S. Nekkaa, N. Haddaoui, A. C. Grillet, and G. Merle, *Int. J. Polym. Mater.*, **55**, 837 (2006).

[16] S. Nekkaa, M. Guessoum, R. Benamara and N. Haddaoui, *Polym. Plast. Technol. Eng.*, **52**, 175 (2013).

[17] B. Gabriele, T. Cerchiara, G. Salerno, G. Chidichimo, M. V. Vetere *et al.*, *Bioresour. Technol.*, **101**, 724 (2010).

[18] L. Boopathi, P. S. Sampath and K. Mylsamy, *Compos.: Part B*, **43**, 3044 (2012).

[19] S. Nekkaa, M. Guessoum, A. C. Grillet and N. Haddaoui, *Int. J. Polym. Mater.*, **61**, 1021 (2012).

[20] N. Cordeiro, C. Gouveia and M. J. John, *Ind. Crop. Prod.*, **33**, 108 (2011).

[21] Y. Wang, B. Tong, S. Hou, M. Li and C. Shen, *Compos.: Part A*, **42**, 66 (2011).

[22] S. Hemsri, K. Grieco, A. D. Asandei, and R. S. Parnas, *Compos.: Part A*, **43**, 1160 (2012).

[23] F. Z. Arrakhiz, M. El Achaby, A. C. Kakou, S. Vaudreuil, K. Benmoussa, *et al.*, *Mater. Design.*, **37**, 379 (2012).

[24] M. M. Kabir, H. Wang, K. T. Lau, F. Cardona and T. Aravinthan, *Compos.: Part A*, **43**, 159 (2012).

[25] M. Abdelmouleh, S. Bouffi, M. N. Belgacem, A. P. Durate, A. Ben Saleh *et al.*, *Int. J. Adhes. Adhes.*, **24**, 43 (2004).

[26] S. M. Luz, J. D. Tio, G. J. M. Rocha, A. R. Gonçalves and Jr. A. P. Del'Arco, *Compos.: Part A*, **39**, 1362 (2008).

[27] V. S. Sreenivasan, D. Ravindran, V. Manikandan and R. Narayanasamy, *Mater. Design.*, **32**, 2444 (2011).

[28] G. W. Beckermann, and K. L. Pickering, *Compos.: Part A*, **39**, 979 (2008).

[29] X. J. Jin and D. P. Kadem, *Cellulose Chem. Technol.*, **43**, 229 (2009).

[30] V. Tserki, N. E. Zafeiropoulos, F. Simon and C. Panayiotou, *Compos.: Part A*, **36**, 1110 (2005).

[31] V. S. Sreenivasan, S. Somasundaram, D. Ravindran, V. Manikandan and R. Narayanasamy, *Mater. Design.*, **32**, 453 (2011).

[32] A. C. H. Barreto, D. S. Rosa, P. B. A. Fechine, and S. E. Mazzett, *Compos.: Part A*, **42**, 492 (2011).

[33] M. L. Troedec, D. Sedan, C. Peyratout, J. P. Bonnet, A. Smith *et al.*, *Compos.: Part A*, **39**, 514 (2008).

[34] C. M. O. Müller, J. B. Laurindo and F. Yamashita, *Carbohyd. Polym.*, **77**, 293 (2009).

[35] N. Petchwattana and S. Covavisaruch, *J. Bionic Eng.*, **10**, 110 (2013).

[36] Y. T. Zheng, D. R. Cao, D. S. Wang and J. J. Chen, *Compos.: Part A*, **38**, 20 (2007).

[37] K. Mylsamy and I. Rajendran, *Mater. Design.*, **32**, 4629 (2011).

[38] N. Rocha, A. Kazlauciunas, M. H. Gil, P. M. Gonçalves and J. T. Guthrie, *Compos.: Part A*, **40**, 653 (2009).

[39] R. Bodîrlău, I. Spiridon and C. A. Teacă, *Cellulose Chem. Technol.*, **43**, 205 (2009).

[40] Md. R. Rahman, Md. M. Huque, Md. N. Islam and M. Hassan, *Compos.: Part A*, **40**, 511 (2009).