

Effect of Fiber/Matrix Chemical Modification on the Mechanical Properties and Water Absorption of Extruded Flax/Polypropylene Composite

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ABSTRACT: Compound of flax/polypropylene (PP) is characterized concerning the mechanical properties of stiffness, strength, and impact in addition to the water absorption behavior. Manufacturing takes place by twin-screw extruder. The extruder screw layout is modified through different kneading elements to get high fiber aspect ratio. Sodium hydroxide solution was used as a washing solution for the flax fibers' surfaces. Both fiber and matrix are chemically modified. Selected groups of the fibers were further treated using trimethoxyvinylsilan TMVS and acrylic acid AA. The PP matrix is also treated with different coupling agents; namely, maleated PP MAPP, TMVS-MAPP, and acrylic acid-functionalized PP AAPP. The combinations of different fiber/matrix are extruder compounded, injection molded, and finally tested. Fiber modification

seems to be positive with AA-modified surface. AAPP matrix modification improves the stiffness four times that of the untreated flax/PP. Till 30 and 40 wt %, the more the fiber is the more the strength and stiffness, respectively. MAPP-modified matrix improves the mechanical properties and keeps low water absorption values. AAPP-modified matrix shows the best stiffness values. TMVS-MAPP does not seem to have distinguished improvement compared with MAPP. NaOH-TMVS/MAPP and NaOH-TMVS/AAPP systems can serve as alternatives to the normal NaOH/MAPP treatment. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2279–2289, 2009

Key words: natural fibers; composites; extrusion; copolymerization; mechanical properties

INTRODUCTION

Increasing need to a higher environmental friendly component in the polymer applications draws the research potential toward the using of natural fiber as reinforcement in thermoplastic composites on an industrial scale.^{1–4} Production of composites competent to glass and carbon fibers polymeric composites is the current challenge facing the researchers. These composites should also be characterized as reproducible with higher specific mechanical properties and acceptable physical properties such as water absorption resistance and thermal degradation. It is worthily noted that the mixing process of fibers and the polymer matrix should ensure keeping high aspect ratio of fibers (length/diameter > critical ratio of fiber strength to interfacial shear strength) to share good load bearing.^{5,6} This work focuses on the flax/polypropylene (PP) composite and aims to improve its properties through different modifications either mechanically or chemically. Different

extruder layouts are carried out for getting high aspect ratio, better distribution of fibers, and apparent adhesion with the matrix. Different chemical modifications were tried for either fiber or matrix to improve the adhesion of matrix to fiber overcoming the hydrophobic nature of the fiber.^{7–9} Increase of fiber matrix adhesion leads to the rise of the interfacial shear strength and the decrease of the critical aspect ratio. This aim can be achieved by modifying the hydroxyl groups present mainly in fibers' cellulose with reactions such as alkalization, acetylation, isocyanation, coupling agent treatment, and grafting. Alkalization promotes fibrillation and rough surfaces formation, which in turn increases the mechanical efficiency.^{1,2} Acetylation is useful for the sake of dimensional stability of the end-product.⁸ Isocyanation induces better interaction with thermoplastics.¹⁰ Coupling agents such as silane or maleated anhydride-grafted PP improve the fibers' wettability because of the agent's long chain, and thus improves the affinity to the thermoplastic matrix as PP.¹ Silanation restrains fiber swelling.¹¹ Both fiber pull-out and fiber-matrix debonding are reduced.¹² Finally, grafting of either vinyl groups or thermoplastics induced with peroxides onto the surfaces of fibers enhanced the fiber-matrix adhesion.^{1,13}

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It is planned to investigate the possible methods to enhance the natural fiber-reinforced polymers NFRP properties. One way is to isolate the load-bearing cellulose.⁴ Another way is to investigate the different modifications methods to exploit this hydroxyl group replacement and in turn to enhance the fiber matrix adhesion. In this work; flax fibers are first alkalinized, then modified either by silanation with TMVS or acrylation using AA. These treatments help primarily in forming strong covalent bonding, and thus raise the mechanical strength and stiffness.¹¹ Also, water absorption is expected to decrease because of the reduced hydrophilicity of fibers resulting from the hydroxyl groups' reaction. Fibers are treated with solutions of the coupling agents. Polypropylene matrix PP is functionalized with maleic anhydride (MA), liquid TMVS, and AA. Thereby, coupling agents of MAPP, TMVS, and AAPP are formed.

In this work, fiber is treated by TMVS and AA, while the matrix is treated with MAPP, AAPP, and finally a mixture of TMVS with MA is tried in PP grafting.

EXPERIMENTAL

Material

Flax fibers were supplied by Sachsenleinen-Germany in bundle form. The constituents are cellulose 63%, hemicelluloses 16%, pectin/lignin 4%, fats and waxes 1%, proteins/ash/minerals 4%, and water content 12%. Homopolymer PP developed for thin-wall high-speed injection molding is used as the host matrix and is supplied by DOW GmbH (MFR = 52 at 230°C/2.16 kg and specific density of 0.9). MA (M625 powder) and peroxide 90% "Luperox 101 in. are supplied by Sigma-Aldrich. TMVS (molecular wt. = 148.23 g/mol) and AA (molecular wt. = 72.06 g/mol) are both supplied by Merck Schuchardt.

Fiber treatment

Fiber bundles are washed with 2% sodium hydroxide solution for 1 h to remove possible impurities. Treatment is pursued as by Sreekala et al.^{14,15} The fibers are washed with water, then with acetone. Fibers are then left to dry at 80°C for 48 h. Treatment of fibers by TMVS and AA takes place before the drying step using 10% solution for almost 5 min prior to washing. Scanning electron microscopic (SEM) tests are also applied to investigate the fiber adhesion to matrix. Infra red analysis FTIR is carried out on the treated fibers using Bio-Rad-7000 FTIR spectrophotometer with photoacoustic detectors over a wave number range of 4000–400 cm⁻¹.

Coupling agents preparation

Three coupling agents are prepared, namely MAPP, TMVS, and AAPP according to the way mentioned by Karnani et al.⁷

- The compatibilizer MAPP is prepared by mixing PP with MA in a weight ratio of 98 : 2, and then 1% of the peroxide catalyst is added. The mixture is dry blended and fed through the hopper at 5 kg/h. The mixture is extruded at 180°C and 200 rpm. Length of the extruder is 40 D. The output material is water cooled and pelletized.
- TMVS-MAPP: TMVS is mixed with MA, peroxide, and PP with the ratio of 4.5 : 4.5 : 1 : 90. The mixture is then extruded at 180°C and 200 rpm. Finally, the mixture is cooled and pelletized.
- AAPP: Acrylic acid is mixed with PP in ratio of 3 : 97 and then extruded together at 180°C and 200 rpm. And then, the mixture is cooled and pelletized.

Matrix preparation and composite production

The prepared pellets of any of the three previous coupling agents are mixed mechanically in a rotating vessel with PP in a weight ratio of 5 : 95. The compounding process takes place in Berstorff ZE25 twin corotating extruder. Fibers are drawn as a continuous bundle not chopped fibers as reported by Bos et al.¹⁶ The flax bundle weighs 20 g/m in average. The modified matrix is fed in such a way to get the required weight fraction, which ranges between 10 and 50% in steps of 10%. At higher fiber contents such as 50%, it is preferred to increase the extruder speed rather to decrease the feeding rate of PP. This is to ensure the accuracy of feeding rate, and thus lessens the dwell time of the fiber in the extruder chamber. However, the speed increase at 50% composite and higher leads to fibers burning. This is detected visually or by fiber odor. To lessen these negative effects on the fibers at high percent composites, temperature pattern in the extruder is chosen to keep 200°C at the feed port of the fibers and ends with 180° at the outlet. The output material does not flow continuously in a strand form, so it is air cooled and then chopped using a shredder.

Nomenclature of the composite blends is as shown in Table I. Nonmodified Flax and PP is also extruded at different fiber loading of 0–50% to represent reference material for comparison. Four systems of modifications namely NaOH/MAPP, NaOH-TMVS/MAPP, and NaOH-TMVS/TMVS-MAPP are tested also for the whole range of 0–50%. Other systems are compounded only at the 30% fiber weight.

TABLE I
Nomenclature of the Fiber/Matrix Chemical Modification

Matrix treatment	Fiber treatment		
	NaOH	NaOH-TMVS	NaOH-AA
MAPP	NaOH/MAPP*	NaOH-TMVS/ MAPP*	NaOH-AA/ MAPP
TMVS-MAPP	NaOH/TMVS-MAPP*	NaOH-TMVS/TMVS-MAPP*	NaOH-AA/TMVS-MAPP
AAPP	NaOH/AAPP	NaOH-TMVS/AAPP	NaOH-AA/AAPP

* These systems in addition to -- (nonmodified fiber/matrix composite) are tested at different fiber contents [0–50%]. The other systems are tested at 30% fiber content.

Extruder configuration is selected according to some preliminary experiments. These experiments are carried out to determine the number of kneading elements required for more fibrillation, and hence high fiber aspect ratio. Therefore, a group of samples underwent different extruder configurations with different number of kneading elements. Fiber kneading is known to have the effect of good mixing, high applied pressure, and technical fibers decomposition to elementary ones. This enhances the fiber load bearing efficiency. On the other side, it could cause fiber damages along its length because of the stress at fiber dislocation areas and kink bands.¹⁷ Three screw configurations were examined by extruding fibers, namely without kneading elements, with two kneading elements, and excessive kneading using four elements. The two-kneading elements system gives the highest fiber aspect ratio of 18. Therefore, this system is chosen to follow the work. After cooling and shredding, the resulting pellets are injection molded at a temperature pattern of 185–190–195–200°C using Allrounder 220C 600–250, Arburg, Lossburg, Germany, while the conditioning is applied for all specimens at 23°C/50% relative humidity for 24 h.

Testing

Tension tests were made with at least five samples using Zwick 0.25 ton tensile machine according to DIN EN ISO 527-1 at 2 mm/min testing rate. Test sample is injection molded to the 1BB form (Width × thickness × gauge length = 2 × 2 × 10 mm³) according to ISO 527-2. Test is conducted and evaluated according to ISO 527-1. Tensile strain rate is 2 mm/min strain rate for 10 specimens. Modulus of elasticity is calculated as the slope of the stress–strain curve at the recommended strains (0.0005 and 0.0025) in ISO 527-1. Water absorption tests according to DIN 53495 were made with five samples at 100°C for 30 min followed by water bath at 23°C for 15 min. Specimens are then dried and weighed to be compared with the original weight. SEM tests are also applied to investigate the failure mode corresponding to the different chemical modifications.

Thermal gravimetric analysis (TGA) conducted on portions cut from the injection molded samples using TGA 2950, TA Instruments, Alzenau, Germany in air at 10°C/min.

RESULTS AND DISCUSSION

Fiber modification

Photographs of flax fibers before and after treatment obtained by SEM are shown in Figure 1. Impurities are easily observed on the surfaces of the raw flax fibers in Figure 1(a). Alkalization process helped in removing these impurities as in Figure 1(b). Fibers treated with TMVS exhibit slightly a polymer-like surface as shown in Figure 1(c). AA treatment has also gained the same surface feature with a greater scale as shown in Figure 1(d). Even at higher magnification in the zoomed area of Figure 1(d), the surface seems to be etched and fibrillated as there are continuous parallel lines along the technical fiber direction. This remark is also supported by Baltazar et al.¹⁸ Figure 2 shows the FTIR analysis of the four fibers. Table II presents the main changes in peak positions corresponding to the vibration groups. The peak at 3350 cm⁻¹ corresponds to the free hydroxyl group.¹⁹ Increased intensity of this peak is observed through sodium hydroxide washing. This is attributed to the cleavage of the alkali-sensitive bonds²⁰ and the breaking of the hydrogen bonding in cellulose O–H groups.^{21,22} This result also can be observed at the peak of 1740 cm⁻¹, which corresponds to C=O stretching vibration suggests the existence of carboxylic/ester groups. The disappearance of the 1740 cm⁻¹ peak is attributed to the removal of pectin and fatty substances on the fibers.²³ This peak is lessened partially with sodium hydroxide and thereby implies the exposure of new hydroxyl groups. But after treatment with TMVS, the peak intensity of 1740 cm⁻¹ shows a remarkable decrease. This peak is almost disappearing in case of reaction with AA in spite what is reported by Li and Matuana²⁴ that AA is likely to homopolymerize rather than to react with fiber. This indicates that the cellulosic fibers undergo chemical reaction. Lignin

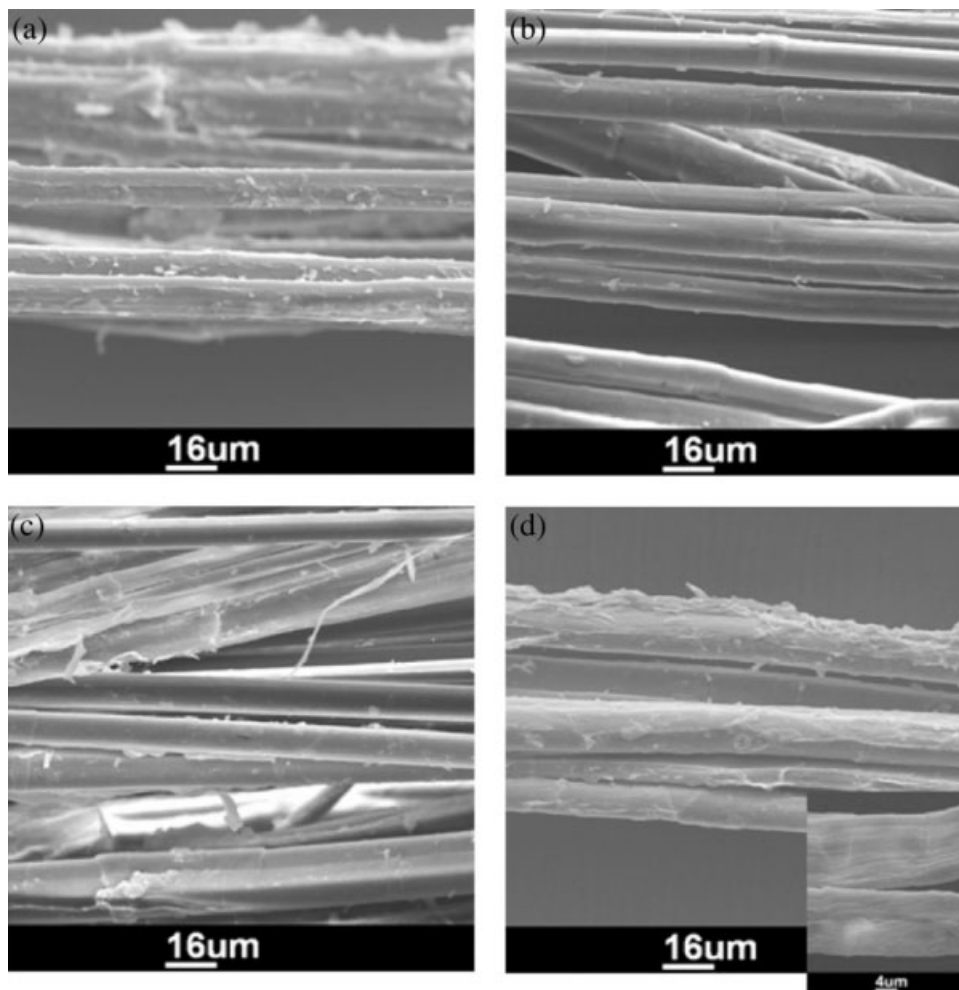


Figure 1 Effect of treatment on flax fiber surface: (a) not treated, (b) NaOH, (c) NaOH-TMVS, and (d) NaOH-AA.

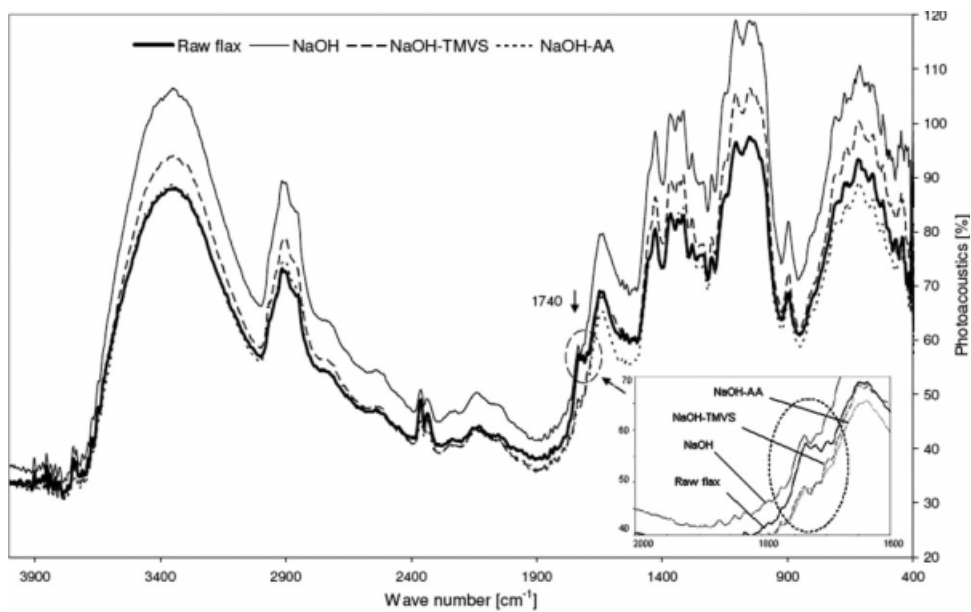


Figure 2 FTIR of the flax treated fibers.

TABLE II
FTIR Spectral Data of Raw and Treated Flax

Photoacoustic absorption band [cm^{-1}] of flax with the following treatment				Notes
-/-	NaOH/-	NaOH-TMVS	NaOH-AA	
3349	3349	3349	3350	O-H stretching present in cellulose and hemicelluloses
2920	2916	2912	2916	CH ₂ and CH vibration groups in cellulose and hemicelluloses
2847	2866	2873	2870	CH ₂ and CH vibration groups in waxes and fats
1732	1736	1736	1732	C=O stretching of COOH groups present in pectin
1636	1637	1636	1637	Asymmetrical oscillation of ionized carboxyl groups in pectin
1508	1516	1516	1516	C=C stretching vibration
1450	1454	1458	1454	Lignin component
1429	1428	1428	1428	Symmetrical oscillation of ionized carboxyl groups in pectin
1373	1373	1373	1373	C-H bending
1342	1338	1338	1338	O-H bending
1053-1110	1060-1110	1056-1110	1056-1110	C-O stretching of acetyl in lignin
887-817	902-813	989-813	894-810	C=C-H alkenes stretching in lignin

presence is detected by the shoulder at 1450 cm^{-1} band, peak at 1050, 887, and 817 cm^{-1} .

Effect of fiber content

Figure 3 shows the effect of the fiber content on the stiffness. Results of MAPP and TMVS modified matrices are given in comparison with the results of the nonmodified fiber-matrix composites. All of the non-reinforced matrices show an increase in stiffness as an evidence of the increase of the polymer crystallinity. With the increase of fiber content, all treatments are manifesting an improvement in stiffness compared with the untreated composite. For instance, the improvement at 40 wt % is almost 181–300% for the different modifications. This is more than that reported by Taha et al.²¹ through the alkalization process, which was about 150% improvement in mechanical properties. The improvement trends seem to be linear until 40 wt %. Stiffness values are positively affected with the increase of fiber content. This is reported and modeled previously.⁵ Stiffness of 8–9 GPa is reached at the 40 wt %, which is con-

sidered NaOH/MAPP and NaOH-TMVS/TMVS-MAPP treatments exhibit slightly better stiffness results than those of NaOH/TMVS-MAPP and NaOH-TMVS/MAPP. A drop in stiffness is observed at 50 wt %. This is attributed to the extrusion mixing method. Poor fiber distribution and some burned fibers are observed during the extrusion of high fiber content. The reason is believed to be the high speed required to get high fiber wt %. Bos et al.¹⁶ reported that the extruder speed is kept at a speed of maximum 200 rpm for high fiber content.

In contrary to stiffness, strength does not show the linear improvement with the increase of fiber content as shown in Figure 4. Maximum strengths are attained at 30 wt % with 176–210% improvement for the different modifications, and then more fiber content causes a drop of the recorded results. This is also attributed to the nonideal mixing conditions in the extrusion. In general, MA matrix treatment exhibits best tensile strength results while TMVS appears to give some softening for the matrix, which

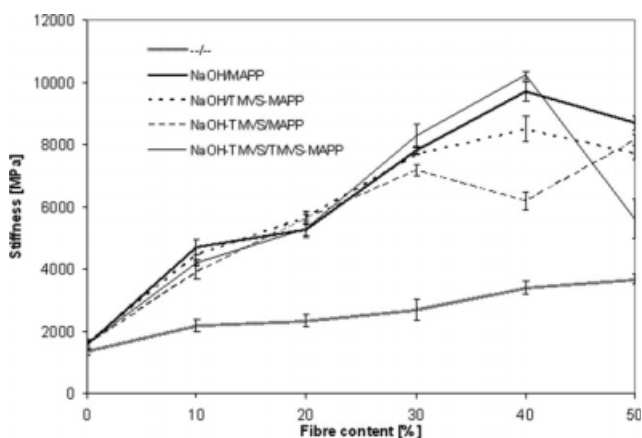


Figure 3 Stiffness of the composite at different fiber wt %.

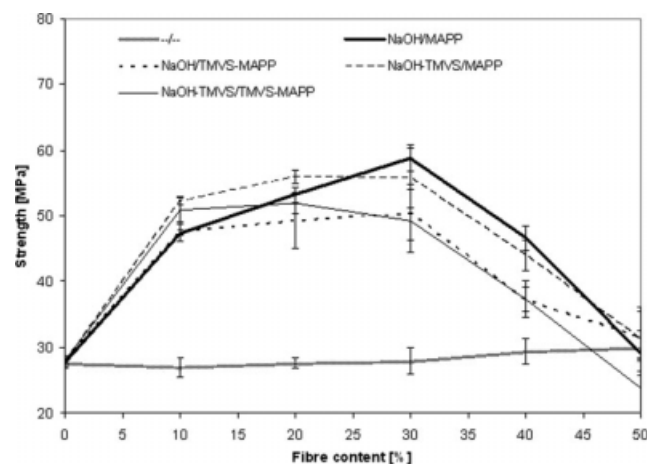


Figure 4 Strength of the composite at different fiber wt %.

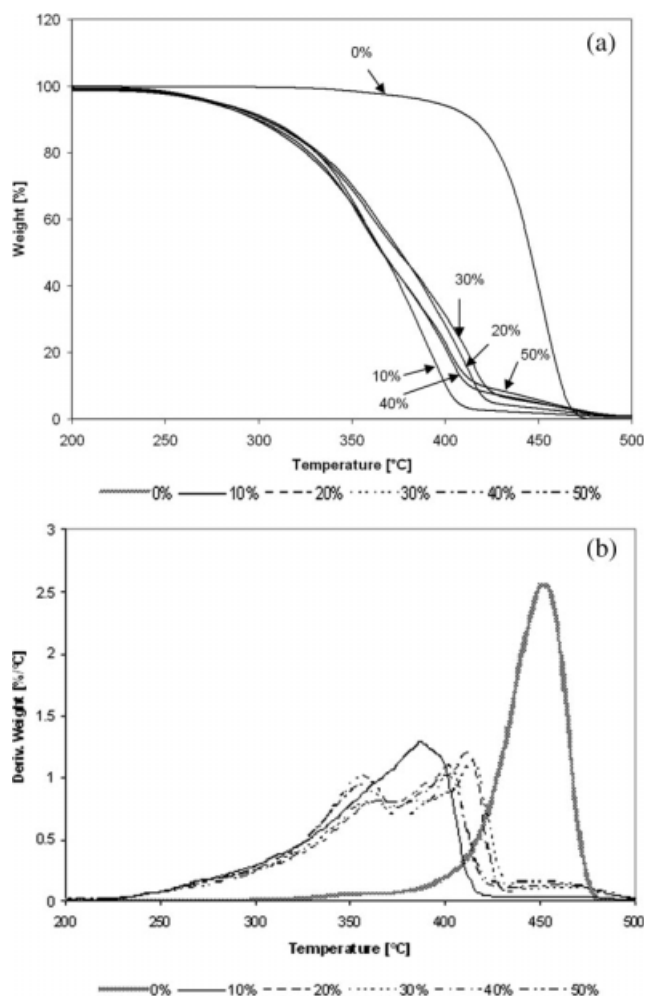


Figure 5 TGA of the NaOH/MAPP composites at different fiber wt % (a, TGA and b, DTG).

can be assured by the corresponding stiffness values in Figure 3. The strength results for extruded NaOH/MAPP system reached 58.7 MPa. It is reported in Ref. 16 that extruded compound of MAPP-modified PP matrix at 50 wt % reached almost similar values. In other words, the results of this work show faster improvement till 30 wt % compared with Ref. 16. At higher wt %, the literature results continue its improvement in contrary to the work results, which dropped to lower strengths. This remark can be attributed to two factors. First is the nonideal mixing conditions at higher wt % as mentioned previously in paragraph ("Matrix preparation and composite production"), and second is the implemented constant amount of copolymer, which is not sufficient to perform complete modification of the fibers' surfaces. Later reason is supported by TGA analysis shown in Figure 5. Figure 5(a) shows that the composites' thermal degradation starts earlier than that of PP. However, the increase of fiber content from 10% to higher value enhances relatively the thermal stability. Fig-

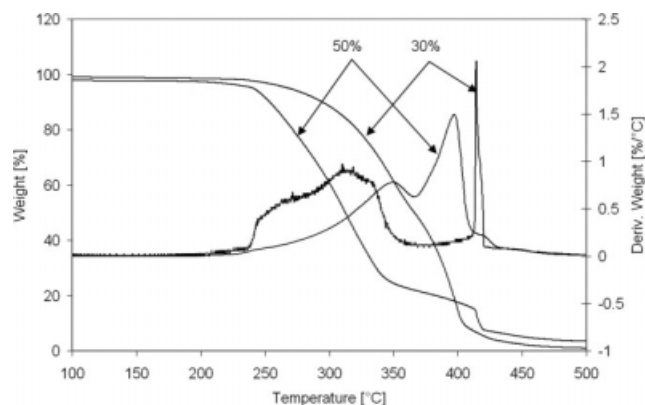


Figure 6 TGA of the NaOH/TMVS-MAPP composites at 30 and 50 wt %.

ure 5(b) proves the insufficiency of the coupling agent for composites with more than 30% as their weight derivative curves have two clear peaks corresponding to the fiber and the matrix. Similar behavior is recorded with other systems, for example, TMVS-MAPP matrix treatment as in Figure 6. As the 30% sample shows better thermal stability compared with the 50%, the sample of 50% shows two separate peaks in the weight derivative curve of Figure 6 as an evidence of inappropriate coupling. Figure 7 represents the elongation results. Breaking elongation drops from 567% as in PP to low values around 12% for the untreated fiber-matrix composite and 6% for the treated ones. Figure 8 represents the impact toughness results. Drop in toughness is remarkable type from 35–42 to 8–10 kJ/m² according to the treatment type. After that a persistent decreasing trend is followed. From Figures 3, 4, 7, and 8, it can be deduced that the increase of flax fiber content to 30–40 wt % leads to corresponding improved stiffness and strength properties. On the other hand, a drop in the unnotched impact values is clear

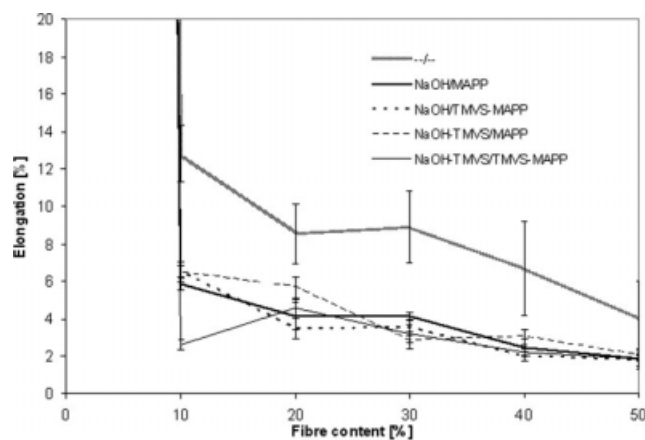


Figure 7 Elongation of the composites at different fiber wt %.

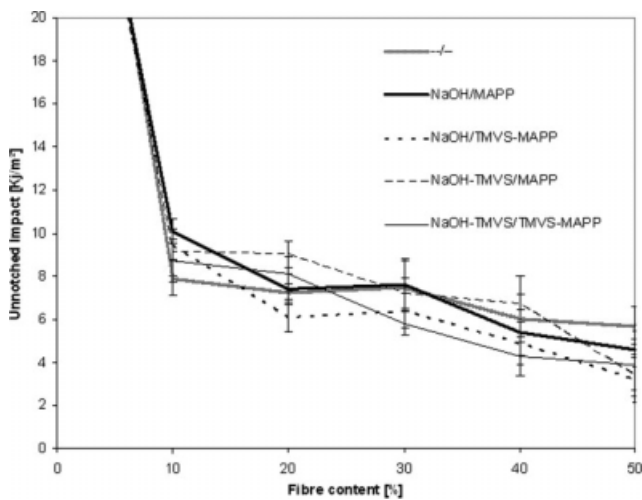


Figure 8 Impact of the composites at different fiber wt %.

regardless the treatment type in comparison with the original PP specimen.

According to Ref. 5, pull-out failure mechanism dominates the fracture area when the fiber content is

less than a critical value. Otherwise features of fiber or matrix fracture characterize the sample fracture. Figure 9 shows SEM photographs of the fracture surface areas for samples of different fiber content. It should be noted for all samples that the fibers' lateral surfaces are coated with polymer surface due to the success of MAPP as a coupling agent. The fibers are more or less difficult to be differentiated regardless the fiber content. This indicates that the fibers are not pulled out alone but they are well adhered with the host matrix. Also, it is inferred from Figure 9(a) where fiber content is 10% that the pulled out fibers' terminals are also coated with polymer. This is an evidence of fiber pull out without fiber fracture. In contrary; Figure 9(b) shows clear fiber fracture at 20 wt % in many fibers. Figure 9(c) shows the more fiber fracture features at 40 wt %. Figure 9(d) shows a zoom-in for one of these fibers. Debonding between fiber and matrix where the force direction is in orthogonal direction to the fiber length is illustrated in the zoomed area of Figure 9(d). Finally, another observation is highlighted that even with high fiber content the fibers seem to be

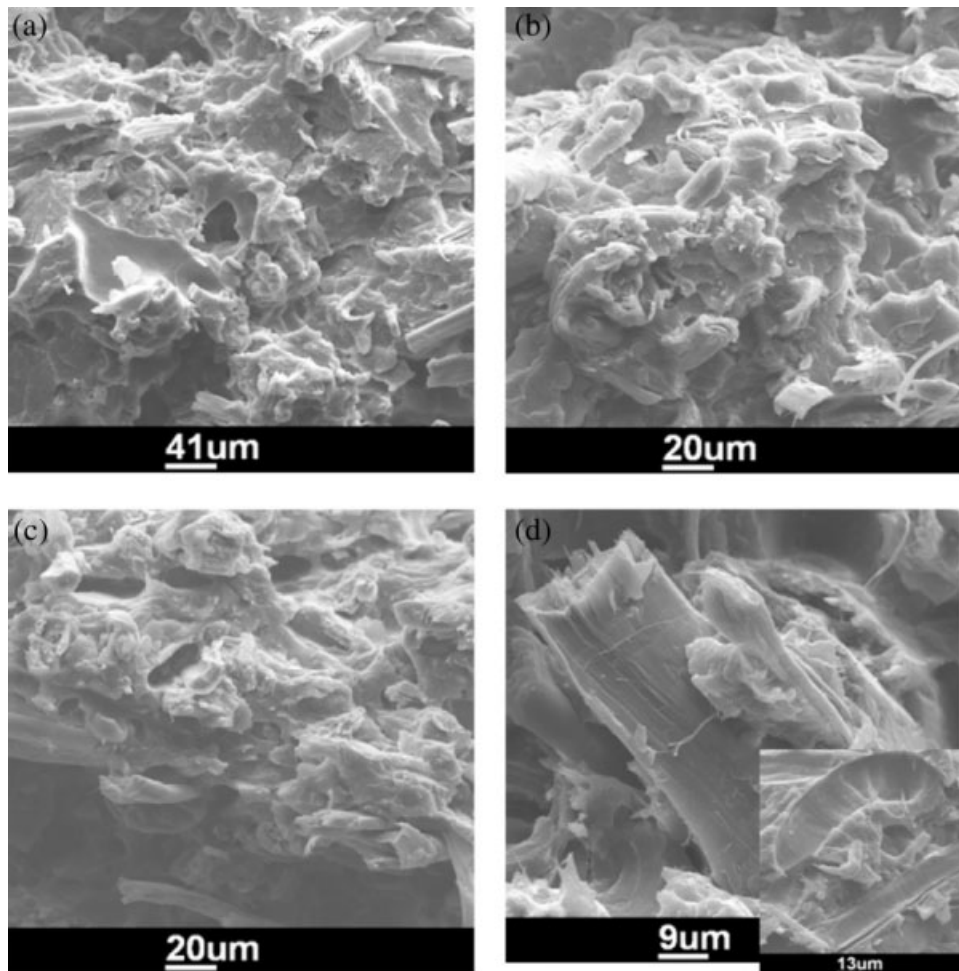


Figure 9 SEM of impact specimens of NaOH/MAPP system a, 10; b, 20; and c, d, 40%.

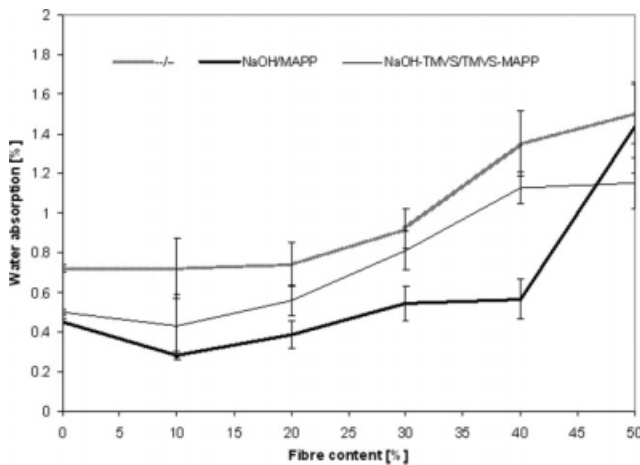


Figure 10 Water absorption at different fiber wt %.

well distributed without agglomeration features. This is also reported previously by Arbelaz et al.²⁵ about the role of MAPP as dispersing agent between polar fibers and nonpolar matrix. This is attributed to the lowering of the surface energy of the flax fibers to be close to that of the matrix. Thus results in the good wettability of PP onto the surfaces of the flax fibers' surfaces.

Figure 10 shows the results of water absorption test at different fiber load. Only NaOH/MAPP and

NaOH-TMVS/TMVS-MAPP systems are chosen for illustration. As expected, the increase of fiber content leads to an increase in water absorption. This is activated by diffusion exploiting the microgaps, compounding microcracks in matrix, or the incomplete wettability positions between fibers and matrix.²⁶ Both silanated and MAPP samples exhibit an improvement in resisting water absorption. MAPP samples show better behavior till 40%. Treated systems present less water absorption in comparison with the nontreated system. This is attributed to the reaction with the free hydroxyl group and to the lessening of the voids between the fiber and the matrix as an indication of better adhesion.²⁷ This may explain the better behavior of MAPP samples shown in Figure 10.

Effect of fiber and matrix modification

Figure 11 shows both the mechanical and water absorption results attained with different modifications of the fiber/matrix system at flax load of 30 wt %. For comparison, reference lines of the nonmodified system -/- is always attached with each sub figure in Figure 11. Figure 11(a) shows that the stiffness is almost four times positively affected with AAPP matrix treatment regardless of the fiber treatment. On the other side, fiber treatment with AA

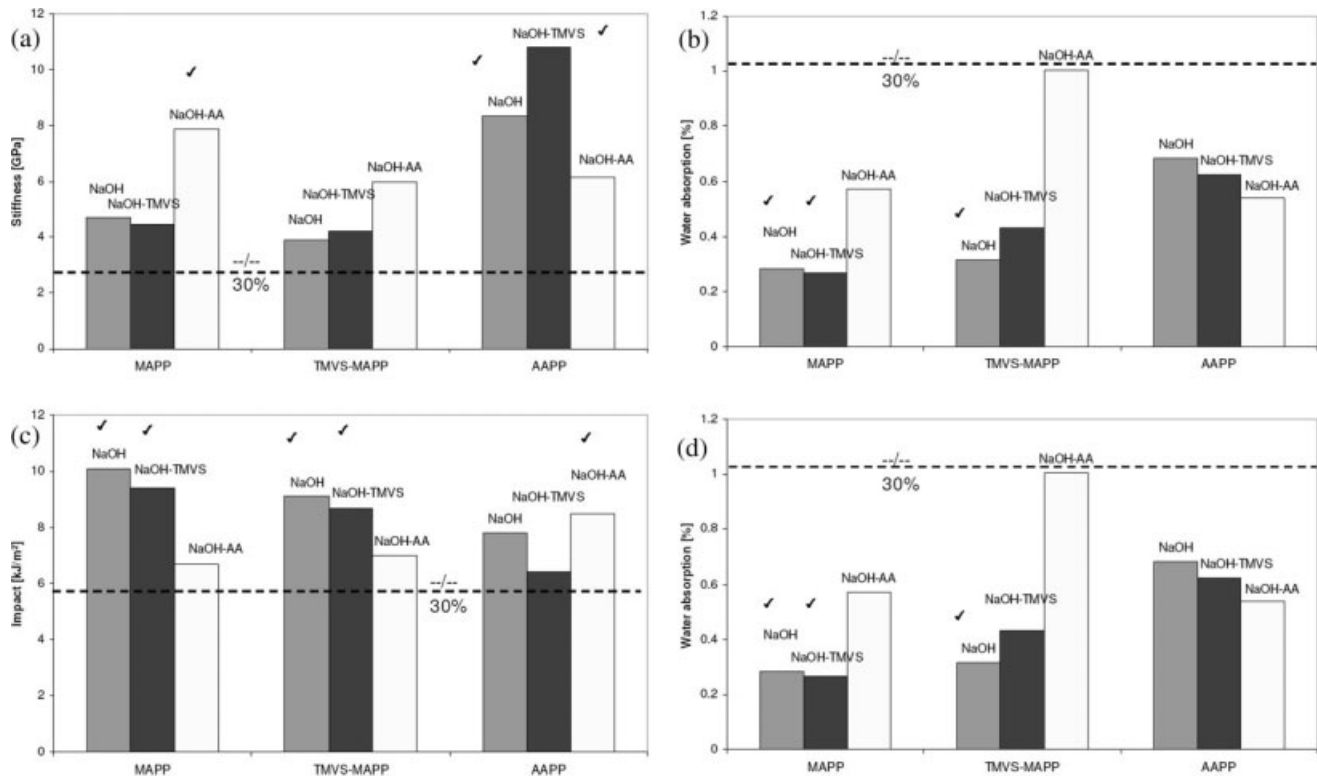


Figure 11 Effect of different fiber/matrix treatment on the mechanical properties and water absorption for 30 wt %. a, Stiffness; b, strength; c, impact; and d, water absorption.

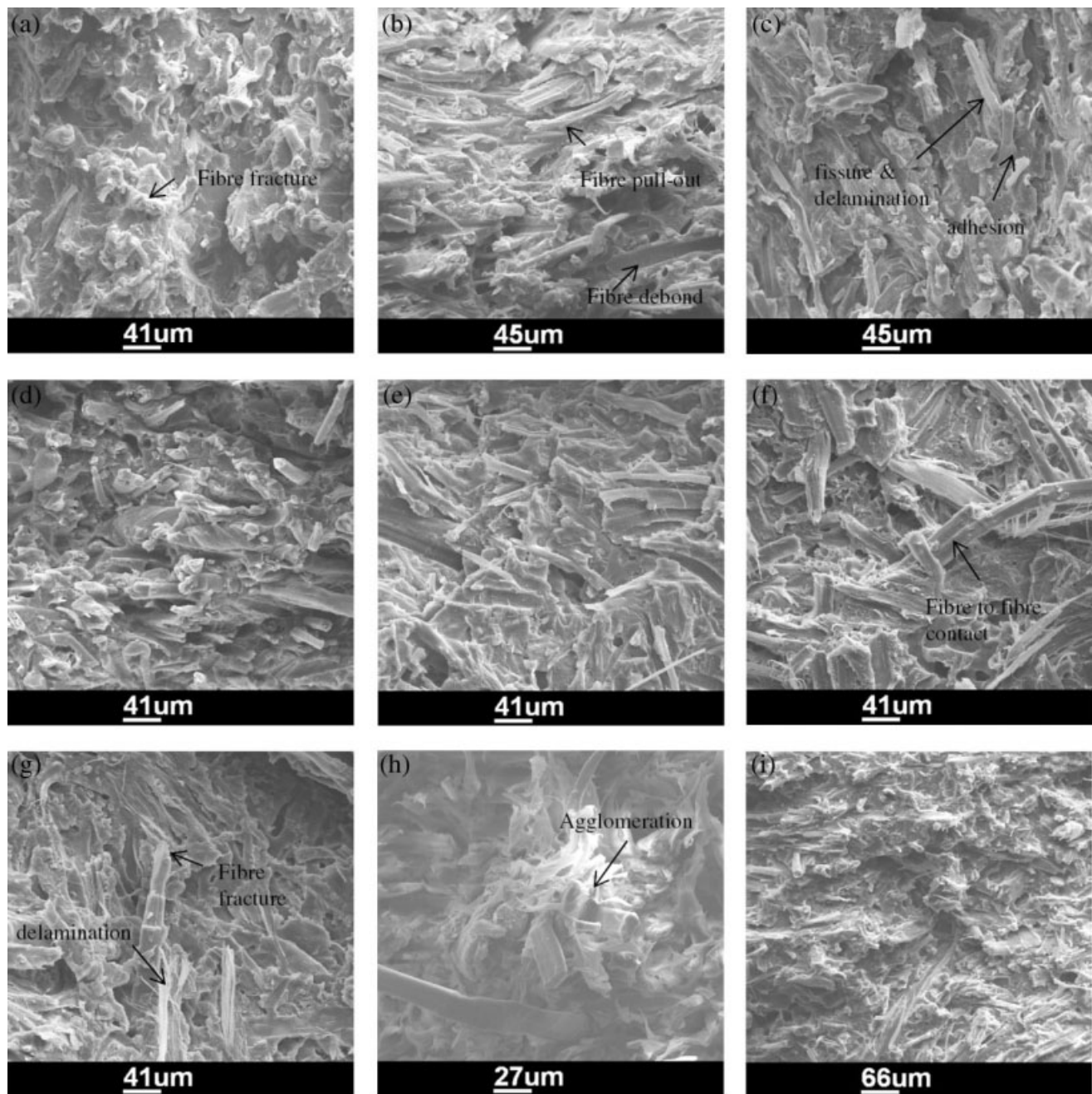


Figure 12 SEM photographs of fracture impact specimens with fiber/matrix treatment of: a, NaOH/MAPP; b, NaOH/TMVS-MAPP; c, NaOH/AAPP; d, NaOH-TMVS/MAPP; e, NaOH-TMVS/TMVS-MAPP; f, NaOH-TMVS/AAPP; g, NaOH-AA/MAPP; h, NaOH-AA/TMVS-MAPP; and i, NaOH-AA/AAPP.

proves to be effective for all matrix treatments except with AAPP. Figure 11(b) presents insignificant effects of both fiber and matrix treatments. Nevertheless, AAPP matrix treatment with AA fiber treatment gives the highest strength result. Impact toughness results are presented in Figure 11(c). MAPP matrix treatment with NaOH-washed fibers gives the highest result. Also but with a little bit less, good results are attained with the TMVS-treated fibers. MAPP-treated matrix dominates the other matrix treatments and NaOH-washed fibers appear

to be the best among all other treatments. Finally, Figure 11(d) presents the water absorption results. MAPP presence seems to be very effective in resisting water absorption regardless the presence of TMVS as it reaches one-third of the $-/-$ water absorption value. While AA presence or its functionalized groups shows the worst influence on the composite water absorption. From Figure 11, it can be inferred that the NaOH fiber washing is enough as further treatment such as AA acts negatively except for the stiffness case. On the other side,

matrix modification plays more important role than fiber modification. Arbelaz et al.²⁵ also reported a similar observation that matrix is more influenced than fibers by TMVS treatment. Best systems are denoted with the symbol \checkmark . They are named as NaOH/MAPP, NaOH-TMVS/MAPP, and NaOH-TMVS/AAPP.

Regardless of the low impact values for the treated fiber/matrix systems at 30 wt % but SEM photographs illustrate some interesting observations. The highest impact toughness value achieved by NaOH/MAPP is justified by the fiber with an adhering matrix as shown in Figure 12(a). Good adhesion and dispersion, fiber fracture- fiber pull-out length is short, fiber fracture is clear- matrix shows crystalline fracture. Figure 12(b) shows the effect of different fiber modification with the same MAPP matrix modification. More fiber pull-out leads to lower stiffness compared with NaOH/MAPP in Figure 12(a). Defibrillation is also less than that observed in Figure 12(a). Fiber debonding is noted. Figure 12(c) shows the fracture behavior of NaOH/AAPP system. Fibers are well adhered to the matrix but the fibers' surfaces are attacked by the AAPP. In some places, fiber delamination takes place instead of pull-out or even fiber fracture, and thus explains the high stiffness and moderate strength resulting in less impact. Figure 12(d) shows more void content with NaOH-TMVS/MAPP modification. These voids are attributed to incompatibility between the coupling agents and the less adhesion. Thus causes less stiffness compared with the NaOH/MAPP specimen. However, the dispersion of fibers is still acceptable. Figure 12(e) shows the suffering from fiber matrix debonding is obvious but its effect is slight on the mechanical properties compared with the case of NaOH-TMVS/MAPP in Figure 12(d). Figure 12(f) illustrates the effect of NaOH-TMVS/AAPP on the fracture behavior. Copolymer does not succeed in fiber well dispersion as there is some fiber to fiber contact. Stiffness is lessened in comparison to NaOH/AAPP because of the TMVS incompatibility but it is still better than that of NaOH-TMVS/MAPP-TMVS. Figure 12(g) expresses the impact failure surface of NaOH-AA/MAPP. Good adhesion and dispersion are noted. Fiber are fractured or delaminated as the case with AAPP matrix modification. Thus assures the positive effect of AA modification on the adhesion and hence the stiffness. However, slight improvement in strength. This leads to lower impact value. It is obvious that the fibers are coated with a layer indicating successful function of the copolymer agent. Figure 12(h) is for NaOH-AA/TMVS-MAPP. Figure 12(d) highlights the effect induced by the TMVS. Stiffness is less than that of NaOH-AA/MAPP; however, the strength and impact are not affected. This shows that TMVS gives

some softness. The fibers are not homogeneously distributed in the matrix modified. Some fibers are good immersed in the matrix and others are agglomerating. So, fibers are pulled out easily. Although these observations of bad dispersion, the fibers retain their integrity and no signs of fibrillation are exhibited. Finally, Figure 12(i) shows the NaOH-AA/AAPP effect. Evidence of fiber delaminating is clear. Stiffness is reduced but strength is the highest and the impact is also considered high. This is attributed to the AA treatment compatibility for both matrix and fiber.

Some notes are noticed. Fiber modification has not the same potential as the matrix modification. Another observation is that the dispersion of fibers in MAPP-modified matrix is always better than that of AAPP matrix. This may be attributed to the tendency of homopolymerization of AA, which lessen its coupling effect.²⁴ However, the spectrum of the attained results either for both fiber and matrix treatments gives us new possible alternatives of the classical MAPP treatment.

CONCLUSIONS

Good mechanical properties can be achieved using moderate kneading of flax fibers with the PP matrix. MAPP proves its ability to disperse the fibers and thereby better homogeneous material is attained. Increase of fiber content improves the stiffness linearly until 40 wt %. NaOH/MAPP and NaOH-TMVS/TMVS-MAPP show 285 and 300% increase in stiffness at 40 wt %, respectively. Strength increased with the addition of fibers till 30%. NaOH/MAPP system improved the strength by 210%. Drop of the strength at higher percent is related to inadequate extrusion conditions and inappropriate coupling agents.

Matrix modification with AAPP shows better results for stiffness as it increased four times. Although the MAPP modification is superior considering impact and water absorption, it is difficult to detect significant difference between matrix treatments on the tensile strength. Considering fiber surface modification, TMVS was distinguished for stiffness and strength, whereas the sodium hydroxide washing was enough considering impact and water absorption. Washing of fibers with sodium hydroxide 2% was able to get rid of the impurities from the fibers' surfaces. Except AA, chemical treatment of fibers does not show a big significance considering the mechanical properties in comparison with the matrix treatment. Finally, NaOH-TMVS/MAPP and NaOH-TMVS/AAPP systems prove their applicability in comparison with the classical NaOH/MAPP.

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