Macromol. Symp. **2008**, 262, 170–181

DOI: 10.1002/masy.200850217

Improvement of Fibre-Matrix-Adhesion of Natural Fibres by Chemical Treatment

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Summary: Plastics, also called synthetic polymers, are playing an important role in daily living. To raise more applications it is necessary to modify known polymeric systems to reach improved materials/material systems.

A possibility to create new optimised materials out of neat polymers is offered by compounding them with different filling material. Besides chemical modification of polymers, mixing, combining or use of different fillers, one possibility is given by the composite technique, whereas the combination of the polymeric matrix and the embedded reinforcement (e.g. fibre) are yielding in optimised materials adjusted to the required properties. Concerning the polymeric matrix, either thermoplastic or thermoset material can be used. In case of the reinforcement, either synthetic (carbon-, glass- or polymeric fibres) or natural fibres are introduced to composites. To obtain an appropriate adhesion of the matrix to the reinforcement system, synthetic fibres are equipped with an avivage. For natural fibres, there are no such materials available and the hydrophilic property of this system surface prevents an adhesion to hydrophobic polymers, as well as to sizings.

In this paper, ways are shown to modify the natural fibres via chemical treatment to yield higher physical properties at better adhesion. Also we will explain activities on the use of natural fibres as reaction systems and processing tools as well as the attempt to isolate the different compounds of the neat fibre via selective work-up.

Keywords: cellulose; modification; natural fibre; reinforcement; thermoplastic

Introduction

Recently, the reinforcement of plastics is practised by use of carbon-, glass or polymer fibres. Besides these fibres, natural fibres can also be used to get composite materials, even though they yield less reinforcement capacities compared to the other fibre types due to their structure and stability. Moreover, natural fibres are not equipped with further treatment (e.g. an avivage) to get better adhesion between fibre and matrix.

To solve this problem and additionally increase the value of these natural fibres, several attempts were pursued to modify the fibre *via* chemical treatment.

All modifications are followed by embedding the modified fibres into thermoplastics and, later on, thermosets to determine the thermal, mechanical and physical properties of the resulting composite material.

This paper gives an overview of different topics in improvement of fibre properties done by selective purification and chemical treatment of both components of the composite, fibre and polymeric matrix.

Selective Purification

As to be seen in Table 1, vegetable fibres are composed of mainly cellulose and further polysaccharides like pectin and hemicelluloses, wax and lignin.

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Table 1.
Composition of natural fibres (percent by weight).

Fibre	Cellulose	Lignin	Hemicellulose	Others	Humidity
Palm	46	20	18	5	11
Cotton	82.7	0	5.7	1.6	10
Hemp	67	3.3	16.1	3.6	10
Flax	56–65	2.5–5	16	4	10
Sisal	65.8	9.9	12	2.3	10
Jute	61–72.4	11.8–14.2	12–13.3	1.8	10
Ramie	68.6–83	0.6–0.7	13.1–14.5	8.4	10
Coconut	43	45	<1	4	7

In the entire fibre construction each of them accounts for diverse physical and mechanical properties. Several chemical treatments were performed to investigate the impact of each fibre component on the natural fibre bonding in the fibre-reinforced composite. Figure 1 shows the schematic representation of purifying the flax fibres from chemical components. The results were compared to the outcome of the analysis method of van Soest.[1]

Methods

Each treatment except the investigation of Kappa number was performed by using flax tow (Sachsen Leinen, Germany) due to the further continuous processing steps. The flax fibres were chopped with a laboratory mill for investigation of the Kappa number.

The method of van Soest comprises the analysis of the fibre constituents soluble in neutral-detergent solution (pectin, wax and hemicelluloses located in the primary cell wall), acid-detergent solution (hemicelluloses), sulphuric acid (cellulose) and the insoluble lignin as well as inorganic compounds.[1]

As visualized in Figure 1, the extraction of wax was carried out by a Soxhlet apparatus by the use of hexane treatment for 8 h. The recovered extract was concentrated by rotary evaporator. After the treatment, the flax fibres were dried at 100 °C over night, and the weight loss had been measured.

Literature indicates that pectic polysaccharides can be sequentially extracted by the use of water based solutions. McColloch and Rouse *et al.* classify the extraction of pectin in three main groups:[2,3]

- High value of methoxyl groups (soluble in water)

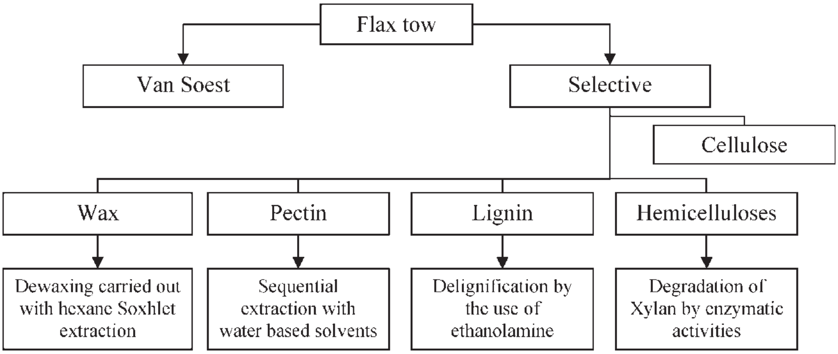

Figure 1.
Schematic representation of purifying flax tow from chemical cell constituents.

Table 2.
Reaction conditions for determination of Kappa number of treated flax fibre tow.

T[°C]/t[h]	neat	120/3	140/3	160/3	170/3	160/1	160/3 pre-treated
Kappa [–]	17.6	8.46	8.52	7.79	9.14	8.69	5.81
Lignin [%]	2.64	1.27	1.28	1.17	1.37	1.30	0.87

- Low value of methoxyl groups and pectinic acids (soluble in water based complexing agents bonding calcium)
- Protopectin (extractable with sodium hydroxide or boiled acid)

The latter group causes an undesired modification of cellulose due to the use of alkali and acid.[4]

According to Davis *et al.* pectic substances were isolated from flax fibres by sequential extraction with water and aqueous 5% ammonium oxalate.[5] Flax fibres were stirred three times with distilled water for 1 h at room temperature, the slurry was concentrated and the residue collected. Subsequently, the pre-treated fibres were stirred two times with aqueous 5% ammonium oxalate for 1 h at room temperature. Afterwards, the fibres were washed with distilled water for 1 h, and dried overnight at 100 °C. During the sequential extraction the weight loss was determined.

According to I. Claus, a sulphuric free method for delignification was used.[6] The treatment of flax fibres was performed using ethanolamine as reagent for cleaving ether bonding in the 3-dimensional macromolecular structure of lignin. Ethanolamine as selective solvent for lignin can be recycled as a particular benefit. Delignification was carried out in a round bottom flask equipped with a reflux. Flax fibres had been placed when ethanolamine was poured in the flask and stirred at certain temperatures for a range of times; these were 1 and 3 hours. Temperature was chosen from 120 °C, 140 °C, and 160 °C to 170 °C, respectively. Fibres were washed with hot water till colourless solution appeared immediately after removing from round bottom flask, followed by washing once with methanol and drying for 24 hours at 100 °C.

To characterize the degree of delignification the Kappa number was determined *via* TAPPI method T236-o-76 and DIN 54357.[7,8] This method is an established determination of the degree of delignification in the pulp and paper industry and represents the residual lignin in wood or vegetable fibre. The residual lignin content can be estimated by multiplying Kappa by 0.15 (Table 2).

In laboratory work the use of sodium hydroxide and potassium hydroxide is reported to reach hemicelluloses.[9,10] As mentioned before, an undesirable modification of cellulose is published in literature.[4] An enzymatic degradation to purify the flax fibre of hemicelluloses was performed as alternative approach. Xylan is the main polysaccharide of hemicelluloses and was degraded with a specific Xylanase from *Trichoderma viride*.[11] Enzymatic activities are dependent on temperature and pH-value. The applied type of Xylanase has a temperature optimum at 40 °C and a pH-value optimum of 6.[11] The degradation was carried out in a glass beaker and the magnetic stirrer separated from flax fibres with a wire mesh cage. The fibre-enzyme-buffer-system was stirred for 24 h at 40 °C, followed by heating up to 80 °C for 30 min to deactivate enzymes. Fibres were then washed several times with distilled water and dried over night at 100 °C.

Results

As previously stated, the above determined results were compared to the analysis method of van Soest. A representation of the results of van Soest compared to purifying methods will be shown in Figure 3. The author recommends the examination of the purifying methods before comparing to the outcome of van Soest.

Dewaxing flax fibre tows was performed by using hexane extraction. The extraction was repeated eight times. An average yield of wax of 1.0% was determined.

An average weight loss of 5% pectic substances was measured by sequential extraction with water based solvents. Wax and pectin are located in the primary cell wall as well as small amounts of hemicelluloses. This has to be considered when comparing to results of neutral-detergent solvents according to van Soest.

Flax fibres were partially delignified by the use of ethanolamine. The Kappa number was determined and is displayed in Table 2.

As to be seen in Table 2, the sequential extraction by distilled water and aqueous 5% ammonium oxalate followed by delignification with ethanolamine lowered the amount of rest lignin in the fibre with a degree of 67%. Generally, the lowest value of rest lignin in flax fibre without pretreatment was observed at treatment parameters of temperature at 160 °C for 3 hours.

In case of degradation of xylan by *endo*-1,4-β-xylanase, the buffer system based on sodium citrate/sodium hydroxide dissolved in distilled water has, most likely, influence on undesired extraction of pectic substances. However, the experimental series includes three times treatment at same conditions but without addition of enzymes. Weight loss of 6.06% was measured without adding enzymes and was subtracted from the yield. Figure 2 displays the observations of degradation induced by Xylanase. In this diagram, the results of flax fibres, pre-treated by sequential extraction to dissolve pectin followed by degradation, have been included.

As to be seen in Figure 2, the flax fibres purified of pectin and subsequently degraded by Xylanase integrate in the experimental series and lead to the assumption that pectic substances were extracted by the buffer system.

In summary, the determinations of the analysis method of van Soest in comparison to selective purification are shown in Figure 3. Again it has to be considered that cell-wall components dissolve by the use of neutral-detergent solvents according to van Soest; this includes wax, pectin and partly hemicelluloses.

Chemical Modification of Natural Fibres

Application of natural fibre thermoplastic composites on industrial scale receives increasing attention from researchers.[12–15] Production of composites with reproduci-

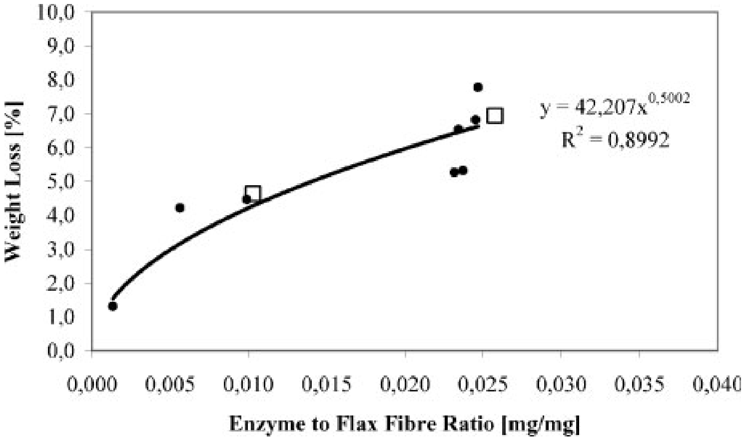

Figure 2.

Weight loss [%] by enzymatic degradation of flax tow by using *endo*-1,4-β-xylanase plotted against the enzyme to flax fibre ratio [mg/mg], Degradation conditions: T = 40 , t = 24 h, pH = 6; ● = Degraded flax fibres, ☐ Pre-treated with water based solvents.

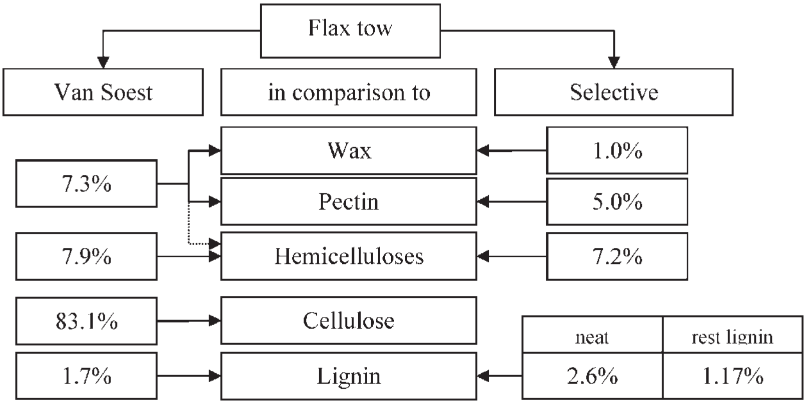

Figure 3.
Results of experimental series in comparison to the analysis method of van Soest.

ble, higher specific mechanical properties and acceptable physical properties such as water absorption resistance and thermal degradation is the current challenge facing the researchers. This part aims to improve the properties associated with polypropylene/Sisal fibres composite through different modifications to fibre. Modification aims to improve the adhesion of matrix to fibre overcoming the hydrophilic nature of the fibre. This can be attained by removing the hydroxyl group present mainly in the cellulose component in the fibres, Figure 4.

Previous work reported that this aim is achieved by linear anhydrides.[16,17] But the formation of carboxylic acid as a by-product represents a drawback, as the acidic compounds reacts with the fibre itself.[18]

In this case, the chemical treatment taking place is either by cyclic anhydrides or lactones. It is expected to have the same reaction without aggression to the fibre or the formation of by-products. In these experiments using cyclic anhydrides, the length of the substituent and the role of the double bond were investigated. Furthermore, in a second experiment, the role of lactones as reactive systems was investigated.

Methods

Polypropylene (PP) is used as the host matrix, and is supplied by DOW GmbH (MFR = 52 at 230 °C/2.16kg and specific density of 0.9). Sisal fibres were supplied in bundle form by Caruso Vliesstoff-Werk GmbH. The chemical reagents, such as succinic anhydride, maleic anhydride,

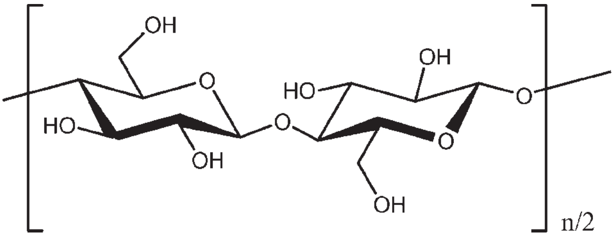

Figure 4.
Chemical structure of cellulose.

2- octenyl succinic anhydride and dodecenyl succinic anhydride and γ-butyro-, γ-valero-, δ-valero- and ε-caprolactone were received from Sigma-Aldrich.

To modify the fibres, they are chopped to an approximately 1 cm length and put into the oven at 100 °C overnight. The chemical modification using anhydrides proceeds by placing 10 g of sisal fibre in a beaker at 100 °C. Acetone is then used as a solvent for the anhydride reagent. Sulphuric acid is taken as a catalyst. Reaction prolongs for 2 hours. The reaction is then stopped with an ice water bath.[19] Fibres are cleaned with acetone then by distilled water and diethylether for 10 minutes.

On the other hand, reactions with lactones have different conditions. Solvent is chosen to be THF. The temperature is set at 80 °C and hold for only 30 minutes. The appropriate catalyst is Tin(II)-octoate (0.0926 mol for each conditions). The catalyst is dropped in the beaker first before introducing the lactone reagent.[20] The reaction is stopped by water bath and the same cleaning procedure as for the anhydrides is followed. After the chemical modification of the fibres by either anhydrides or lactones, the fibres are left at 100 °C overnight.

After the chemical modification, compounds of 20% of fibres were made with the Haake Rheomix 3000 kneader using 10 g of fibres and 40 g of polypropylene. First, the rotating of polypropylene continues for about 5 minutes until torque equilibrium is reached. Then sisal fibres were added and kneading process continues also until the torque stabilizes to guarantee well compounding. After cooling and removing of the compound, the resulting mixture was cut into small pieces using mechanical shearer. Finally, the chopped particles are injected using injection moulding process at 500 and 400 bars of injection and post injection pressures respectively. The mould temperature was set to 40 °C. Temperature pattern of the injection moulding machine is set at 30–170–175–180–190 °C and finally the injection speed was set to be 22cm^3/s to yield testing samples.

Using these samples, tension tests were made with at least 5 samples using Zwick 0.25 ton tensile machine according to DIN EN ISO 527-1. Water absorption tests according to DIN 53495 were made with 3 samples at 100 °C for 30 minutes followed by water bath at 23 °C for 15 minutes. Specimens are then dried and weighed to be compared with the original weight.

Results

Results of tension tests are shown in Figure 5. Improvement with lactones treatment is observed in comparison with that of any used anhydrides or even the neat polypropylene. For instance, δ-valerolactone shows the best improvement compared to the other modifications whereas it has to be stated that none of the modifications is able to reach the value of the polypropylene/neat sisal fibre-composite.

It seems that the fibre build-up is destroyed throughout the reaction so that the resulting fibre-matrix adhesion is lowered. Further investigations in improving the present results by changing of reaction parameters are still going on.

The results of the water absorption behaviour of the composites are illustrated in Figure 6.

Even in this case it is obvious that the reference (PP/neat sisal composite) shows the best water absorption behaviour compared to the cases of composites with modified fibres. Nevertheless, the water absorption of the cyclic anhydrides-modified composites is less than those of the lactone-modified ones. This behaviour can be explained by the resulting groups that occur from the reaction between hydroxyl groups of the fibre compounds with the reagent. In case of lactones new hydroxyl groups can be obtained resulting in a constant number of those functional groups in the fibre. In the case of anhydrides, carboxyl groups are occurring at the end of the spacer, resulting in a different interaction between fibre and water compared to a hydroxyl group. In

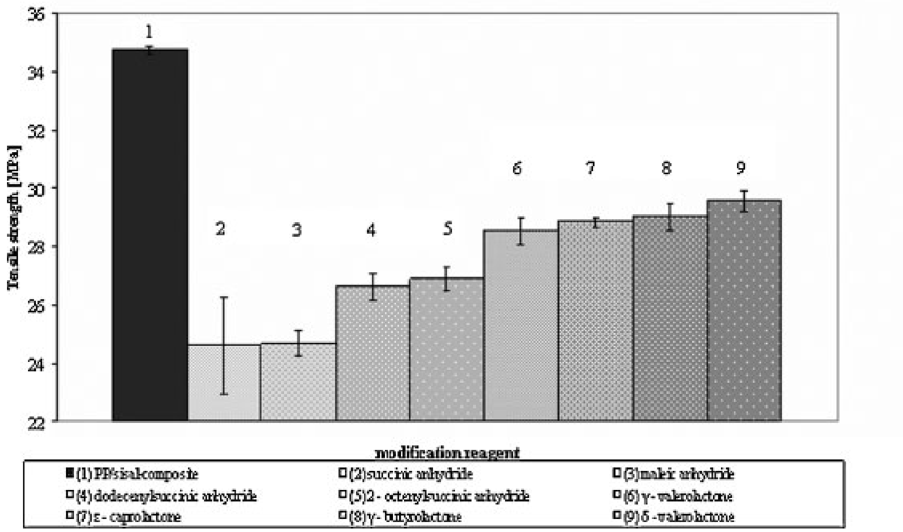

Figure 5.
Tensile strength of PP/sisal-composites with and without fibre treatment.

these investigations, this may lead to the decrease in water uptake.

Until now, the influence of the chain length, either in the case of lactones or anhydrides, is not finally interpreted due to the great standard deviations in these experiments. But it seems that side chains influence the water absorption behaviour to smaller values and therefore to better mechanical behaviour whereas swelling fibre will reduce the properties of the resulting composites.

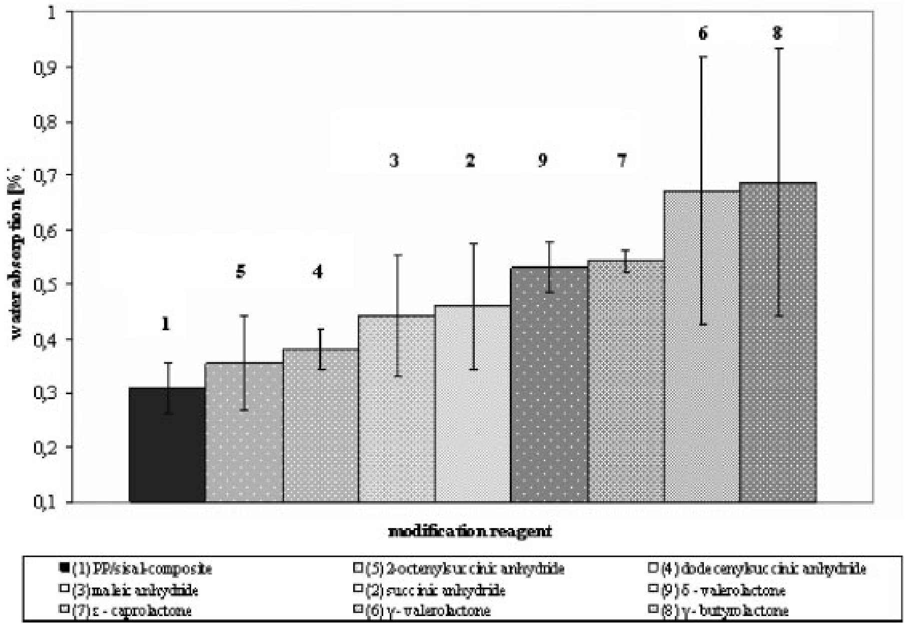

Figure 6.
Water absorption behaviour of composites with and without fibre treatment.

Conclusion

Chemical modification of sisal fibres with cyclic anhydrides is beneficial compared to the treatment with lactones regarding water absorption especially with longer side chains, even though the lactone-systems have higher mechanical properties. So optimization study is recommended to decide which chain length is convenient.

In case of strength properties, the chemical treatment with lactone results in significant better properties compared to the anhydride-treatment even though the properties don't reach the value of the composite with untreated fibres.

Chemical Modification of Flax Fibres and Matrix

To investigate the effects the chemical modification has on the improvement of properties associated with flax/polypropylene composite, the matrix as well as the fibres themselves are treated by reagents to overcoming the gap between the hydrophilic nature of the fibre and the hydrophobic property of the polypropylene (PP) matrix.

For modification of the fibres, the surface of flax bundles is prior washed with sodium hydroxide solution. The chemical modifications are carried out using either trimethoxyvinylsilan or acrylic acid. To modify the Matrix, maleated polypropylene (modified by 2% w/w maleic anhydride), trimethoxyvinylsilan as well as acrylic acid is used.

The combinations of different fibre/matrix are extruder compounded, injected moulded and finally tested.

Methods

Polypropylene, which is supplied by DOW GmbH (MFR = 52 at 230 °C/2.16 kg and specific density of 0.9), is a homopolymer developed for thin wall, high speed injection moulding. Maleic anhydride (MA) is supplied by Sigma-Aldrich. Trimethoxyvinylsilan and Acrylic acid (AA) are both supplied by Merck Schuchardt. Flax fibres in bundle were supplied by Sachsenleinen, Germany. The lengths of fibres vary from 100 to 500 mm and diameter of 68 μm in average. The constituents of the flax fibres are cellulose 63%, hemicelluloses 16%, pectin/lignin 4%, fats and waxes 1%, proteins/ash/minerals 4% and water content 12% with overall specific gravity of 1.4. Tensile test is carried out according to DIN 53816 for 50 single fibres and the tensile strength found to be 1350 MPa as well as the elastic modulus of 49.6 GPa.

The matrix system MAPP is prepared by mixing PP with maleic anhydride in a weight ratio of 98:2, prior to the addition of 1% of the peroxide catalyst. This mixture is extruded at 180 °C and 200 rpm. Then, the resultant is mixed mechanically with PP at 5% weight fraction.

In case of vinylsilan modification, vinylsilan is mixed with MA, dissolved in acetone, peroxide and PP the ratio 4.5:4.5:1:90. This mixture is extruded and blended with PP in 5:95. Finally AAPP prepared by mixing acrylic acid with PP in 3:97 PP, then extruded together at 180 °C and 260 rpm. Afterwards, the mixture is mixed mechanically with PP in ratio of 5:95.

The fibre bundle is washed with sodium hydroxide solution to remove possible impurities and greases for 1 hour. Then it is neutralized by acetic acid and finally washed with acetone. The fibre is then left to dry at 80 °C for 48 hours. Other fibre bundles are also washed with sodium hydroxide solution and cleaned prior to modification with trimethoxyvinylsilan or acrylic acid before the drying step.

The compounding process takes place in Berstorff ZE25 twin co-rotating extruder. Fibres are drawn as a bundle and the modified matrix is fed in such a way to get the required weight fraction which ranges between 10 to 50% in step of 10%. Temperature pattern is chosen to keep 200 °C at the entrance of the fibres and ends with 180° at the outlet. Two Kneader steps are induced to get the maximum homogeneous distribution and the possible finest size of the fibres. After cooling, the resulting compound was cut using mechanical

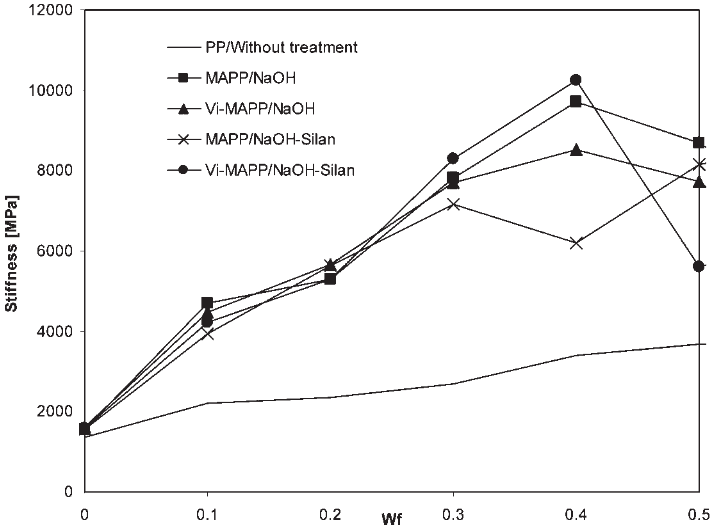

Figure 7.
Stiffness of the composite at different weight fractions.

shearer. Injection moulding is conducted at a temperature pattern of 185–190–195–200 °C, while the conditioning is applied for all specimens at 23 °C/50% humidity for 24 hours.

Tension tests were made with at least 5 samples using Zwick 0.25 ton tensile machine according to DIN EN ISO 527-1 at 2 mm/min testing rate. Water absorption tests according to DIN 53495 were made with 3 samples at 100 °C for 30 minutes followed by water bath at 23 °C for 15 minutes. Specimens are then dried and weighed to be compared with the original weight. Scanning electron microscopic tests are also applied to investigate the fibre

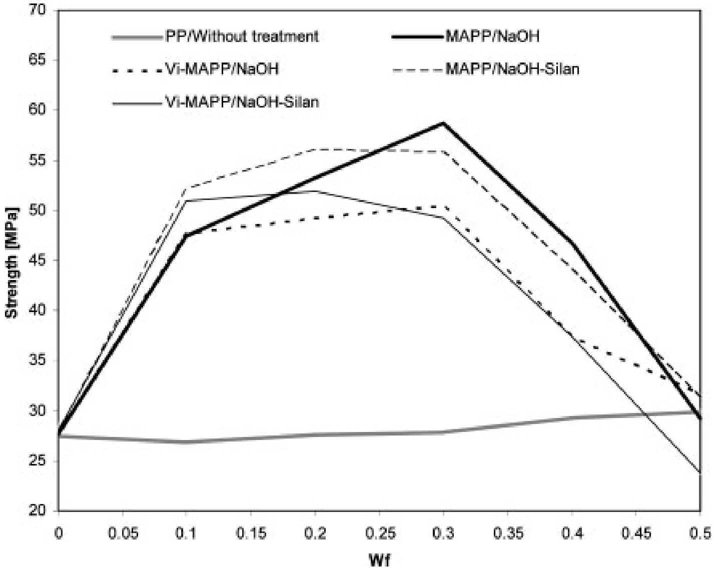

Figure 8.
Strength of the composite at different weight fractions.

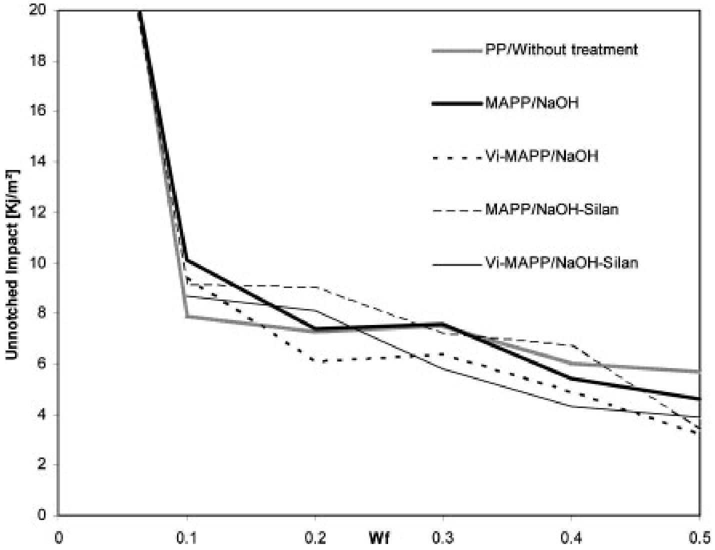

Figure 9.
Impact of the composite at different weight fractions.

adhesion to matrix and the failure mode corresponding to the different chemical modifications.

Results

Figures 7, 8 and 9 show the results of mechanical testing considering stiffness, tensile and impact, respectively. Mechanical properties are obviously improved with the implementation of MAPP modification to matrix. This improvement is slight regarding stiffness and remarkable regarding strength. Fibre washing with sodium hydroxide seems to be enough for fibre surface modification. Tensile results reach its maximum in 30–40% range but then drop in tensile results are clearly obvious indicating worse load transfer between the fibre and the matrix.

In contrary, stiffness exploits the increase of fibre content in an increasing

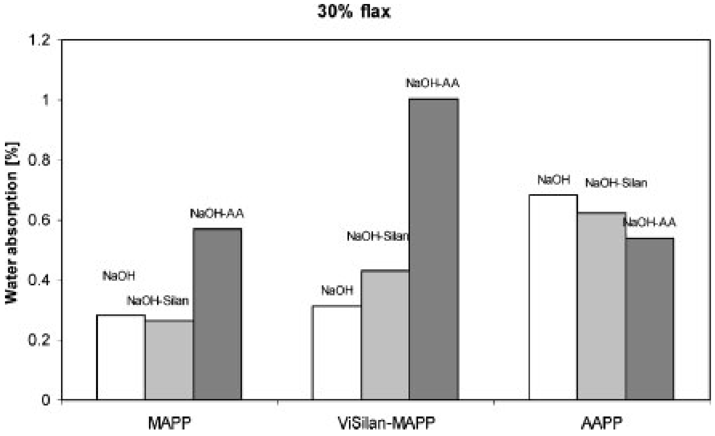

Figure 10.
Water absorption of the composite at different matrix modification (X-axis) and different fibre modifications (Y-axis).

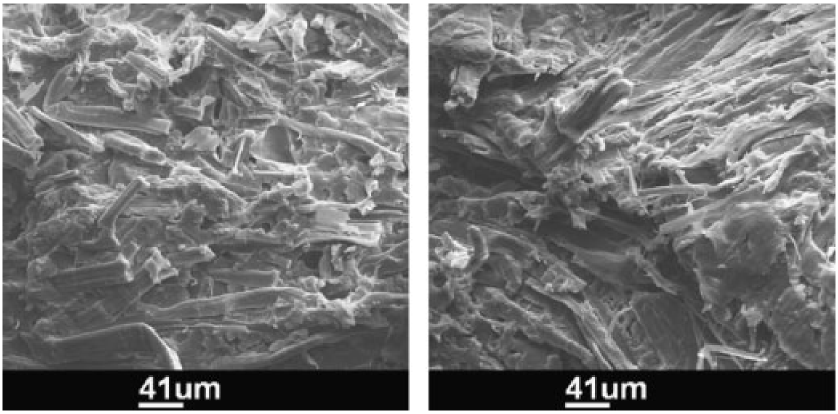

Figure 11.
SEM photographs of PP/Flax (left) and MAPP/Flax (right).

trend of improvement. This is reported and modelled previously.[21]

The water absorption in Figure 10 is shown to be improved by MAPP modification whatever the fibre modification is, except with acrylic acid. Figure 4 results are taken at equal fibre content of 30% for the sake of comparison. Acrylic acid matrix modification shows the highest level water absorption indicating the bad effect arisen by this acid.

Scanning electron microscopy indicates the better interfacial bonding between the fibre and the matrix with the matrix modification especially with MAPP. Figure 11 illustrate different failure modes at PP and MAPP matrices. Figure 11 (left) shows that the fibres are easily pulled out of the matrix in contrary to the case of fibres covered with matrix at the right side of Figure 11. Fibre length at the right side is also obviously to be shorter indicating that the fibre affinity to be pulled out is so low due to the good adhesion with the matrix.

Conclusion

Stiffness is slightly sensitive to these chemical modifications. Flax surface washing with sodium hydroxide is sufficient without further modifications. Strength improvement of almost 200% is reached by the matrix modification with the maleic anhydride copolymer. Vinylsilan modification exhibits about 170% of improvement, but with better toughness resistance. Also better water absorption resistance is shown by the anhydride modifications and an unacceptable one in case of acrylic acid modification either with matrix or fibre.

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