Environmental durability of flax fibres and their composites based on polypropylene matrix

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Environmental Durability of Flax Fibres and their Composites based on Polypropylene Matrix

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Abstract. The environmental degradation behaviour of flax fibres and their polymer composites are explored. New upgraded Duralin flax fibres, which have been treated by a novel treatment process for improved moisture and rot sensitivity were studied. Environmental studies showed that these upgraded Duralin flax fibres absorb less moisture than untreated Green flax fibres, whereas the mechanical properties of the treated fibres were retained, if not improved. The effect of this novel flax fibre treatment on the environmental behaviour of natural-fibre-mat-reinforced thermoplastics (NMTs) is investigated by monitoring the moisture absorption and swelling, and measuring the residual mechanical properties of the flax/polypropylene composites at different moisture levels. The moisture absorption and swelling of the upgraded flax fibre composites is approximately 30% lower than that of composites based on Green flax fibres.

Key words: natural fibres, flax fibres, Duralin, polypropylene, thermoplastic composites, NMT, moisture absorption, environmental properties.

1. Introduction

E-glass fibres are one of the most important reinforcing fibres for polymer composites. However, glass fibres have some disadvantages. They are non-renewable and give problems with respect to ultimate disposal at the end of a materials lifetime since they cannot be thermally recycled by incineration. They are also very abrasive, which leads to increased wear of processing equipment such as extruders and moulds. Glass fibres can also cause problems with respect to health and safety, for example, they give skin irritations during handling of fibre products, and processing and cutting of fibre-reinforced parts.

Ecological concern has resulted in a renewed interest in natural materials. An interesting environmentally friendly alternative for the use of glass fibres as reinforcement in engineering composites are ligno-cellulosic natural fibres such as flax,

hemp, sisal and jute [1]. These fibres are renewable, nonabrasive, can be incinerated for energy recovery since they possess a good calorific value and they give less concern with health and safety during handling of fibre products. In addition, they exhibit excellent mechanical properties, low density and low price. This excellent price-performance ratio at low weight in combination with the environmental friendly character is very important for the acceptance of natural fibres in large volume engineering markets such as the automotive and construction industry.

The microstructure of natural fibres is extremely complicated, in that it comprises different hierarchical microstructures [2]. The single fibre, or better elongated cell, has a diameter of around 10–20 μm and consists of a microfibrillar cellulose phase and a matrix phase, which is mainly composed of hemicellulose (branched cellulose of low molecular weight) and lignin (phenolic-like aromatic compound). The microfibrils have a diameter of about 10 nm and are made up of 30 to 100 cellulose molecules in extended chain conformation and provide mechanical strength to the fibre. A good orientation of the microfibrils and high cellulose content are essential for obtaining a fibre with good mechanical properties. The non-crystalline matrix phase of the cell wall is very complex and consists of various compounds, including hemicellulose, lignin and some pectin, which all form complicated macromolecular networks. The hemicelluloses hydrogen bond to cellulose and act as cross-linking molecules between the cellulose microfibrils, forming the cellulose-hemicellulose network, which is thought to be the main structural component of the fibre cell. The hydrophobic lignin network affects the properties of the other network in a way, that it acts as a coupling agent and increases the strength of the cellulose-hemicellulose network. The outer cell wall is porous and consists also of pectin and other non-structural carbohydrates. The pores of the outer skin are the prime diffusion paths of water through the material. Each fibre cell consists of a primary cell wall and three secondary cell walls. Each cell wall contains a lignin-hemicellulose matrix surrounded by cellulose microfibrils, which are oriented in different directions in the different wall layers. The bulk of the fibre is made of secondary cell wall. The lumen in the centre of the fibre contributes to the water uptake properties of these fibres [3]. In most of today's applications fibre bundles or strands are used rather than individual fibres. Within a fibre bundle, fibre cells overlap and are bond together by pectin to give strength to the bundle as a whole. However, the strength of this composite-like bundle structure is significantly lower than that of the individual fibre cell.

A major restriction in the successful use of natural fibres in durable composite applications is their high moisture absorption and poor dimensional stability (swelling), as well as their susceptibility to rotting. Swelling of fibres can lead to micro-cracking of the composite and degradation of mechanical properties. Different models have been developed in order to describe the moisture absorption of materials [4]. A problem, in which the temperature and the moisture distribution inside the material are to be determined, is often referred to as the 'moisture prob-

lem'. Such problems can be solved analytically and the moisture absorption can be called 'Fickian' when the following assumptions can be made:

1. Heat transfer is by conduction only and can be described by Fourier's law.
2. A concentration dependent form of Fick's law can describe moisture diffusion.
3. The temperature inside the material approaches the equilibrium much faster than the concentration gradient, hence the energy (Fourier) and the mass transfer (Fick) equations are decoupled.
4. The thermal conductivity and the mass diffusivity depend only on the temperature and are independent of moisture concentration or of the stress levels inside the material.

Calculations can be made requiring knowledge of the following parameters:

1. Geometry (material thickness h in case of a one-dimensional problem).
2. Boundary conditions: ambient temperature and relative humidity (100% in case of immersion).
3. Initial conditions: temperature and moisture concentration M_i inside the material.
4. Material properties: density ρ, specific heat C, thermal conductivity K, mass diffusivity D, maximum moisture content M_m and a relationship between the maximum moisture content and the ambient conditions.

The moisture content M_t as a function of the square root of time for a typical Fickian process is schematically given in Figure 1. The relative moisture absorption can be described by the following equation:

$$\frac{M_t}{M_\mathrm{m}} = 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \mathrm{e}^{D(2j+1)^2\pi^2 t/h^2}. \tag{1}$$

This equation is used to calculate the diffusivity D and the maximum moisture content M_m of the materials.

Recently a novel upgrading process for ligno-cellulosic materials has been developed to improve the poor environmental- and dimensional-stability of these materials [5]. This upgrading process, which was initially developed for wood, has also proven its applicability to natural fibres and has let to the development of upgraded flax, the so-called Duralin flax [6]. The process is currently commercialised by CERES B.V. (Wageningen, The Netherlands) and the availability of an upgrading process for natural fibres could remove one of the main restrictions for the successful application of natural fibres in high-quality engineering composites.

The aim of this paper is to study the environmental behaviour of flax fibres and natural-fibre-mat-reinforced thermoplastics (NMTs), being glass-mat-reinforced thermoplastic (GMT)-like materials [7] based on flax fibres and a polypropylene (PP) matrix [8–12]. The effect of the upgrading treatment is evaluated by comparing the moisture absorption and residual mechanical properties of treated Duralin- and Green-flax fibres as well as the moisture absorption, swelling and residual

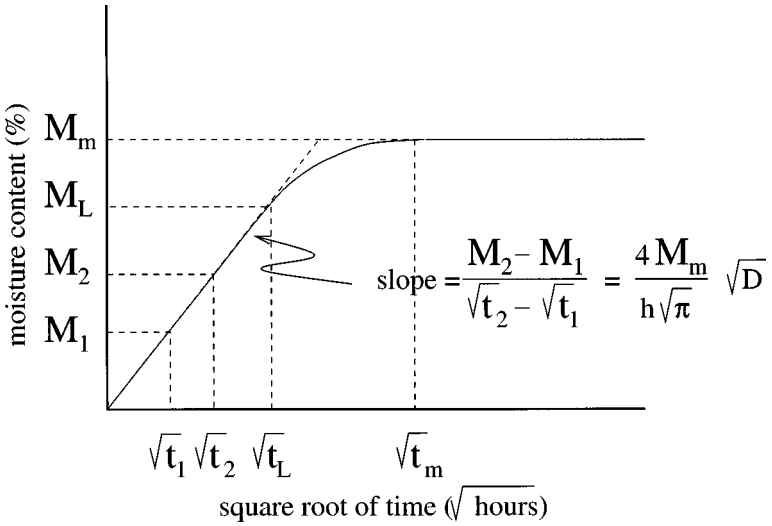

Figure 1. Moisture content as a function of time for a typical Fickian process [4].

mechanical properties of NMTs based on Duralin- and Green-flax-fibre mats. Furthermore, the influence of the fibre/matrix interface on these properties is investigated by using both isotactic-PP and maleic-anhydride grafted PP (MA-PP) as an adhesion promotor [9, 10, 13–15].

2. Experimental

2.1. FLAX FIBRE TREATMENT

The upgrading process for flax as developed by CERES B.V. uses full rippled (deseeded) straw-flax. The use of straw-flax turned out to be beneficial for both strength and reproducibility (no dew-retting required) of the treated fibres. In addition, a valuable by-product, the treated flax-shives, is produced from which, e.g., water-resistant chipboards could be made. The Duralin treatment consists of a steam or water-heating step of the rippled straw-flax at temperatures above 160°C during approximately 30 minutes in an autoclave. A drying step and a heating (curing) step above 150°C during approximately two hours follows the first step. During this treatment, the hemi-cellulose and lignin are depolymerized into lower molecular aldehyde- and phenolic functionalities, which are combined by the subsequent curing reaction into a water resistant resin, which cements the cellulose microfibrils together. After the treatment the fibres can easily be separated from the stem by a simple breaking and scutching operation. The fibres obtained by these procedures are fibre bundles rather than individual fibres. These treated flax fibre bundles were subsequently converted into a non-woven mat by Eco Fibre Products B.V. (The Netherlands) via a conventional punch-needling process.

2.2. MOISTURE ABSORPTION OF FIBRES AND COMPOSITES

The moisture absorption of two types of flax fibres (Green and Duralin) was studied in accordance with the German specifications DIN 53495. Prior to testing the fibres were dried in an oven at 60°C for 24 h. Bundles of fibres were kept together and suspended in dessicators. The dessicators contained solutions of potassium acetate, sodium nitrate, ammonium monophosphate and distilled water and their environment had a relative humidity of 20, 66, 93 and 100%, respectively. The weight of fibres was measured at different time intervals and the moisture absorption was calculated by the weight difference.

In order to measure the water absorption of the composites, all samples were immersed in water for about 60 days at room temperature. The weight and the thickness of the NMT plates were measured at different time intervals and the moisture content versus time was plotted. The maximum moisture content $M_{m,c}$ was found from the intercept at the saturation point and the diffusivity D_c was calculated from the slope (see Figure 1) by fitting Equation (1) to the experimental data.

2.3. SINGLE FIBRE TENSILE TESTING

Individual Green- and Duralin-flax fibres were carefully separated out by hand from the bundles. Samples were then prepared by fixing the fibres on special cardboard frames of gauge lengths 3.5 and 8 mm. Prior to testing the samples were conditioned in different relative humidities for at least 5 min. The samples (15 samples of each 3.5 and 8 mm length for each fibre) were tested with the help of a specially designed microtensometer based in Silsoe Research Institute (Silsoe, UK), with a maximum load cell of 1.0 N. The microtensometer was placed in a humidity chamber, which could create a constant environment of 30, 66 and 90% humidity at a constant temperature of 35°C. The fibre diameter was measured prior to testing with the help of an optical microscope.

2.4. COMPOSITE MANUFACTURING AND TESTING

In this study random non-woven needled flax fibre mats in combination with an isotactic-polypropylene (PP) matrix of Montell (XS6500S) with a melt flow index of 38 were used. As an adhesion promoter maleic-anhydride modified polypropylene (MA-PP) was used [13, 14]. The blending of PP with a commercially available MA-PP (Polybond 3002, BP Chemical Ltd.) was performed on a Werner and Pfleiderer ZSK 25 co-rotating twin-screw extruder. In this study 5 wt.% of MA-PP is added to the i-PP. For convenience, this blend will simply be designated as MA-PP. Next, the PP and MA-PP pellets were compression moulded into 0.1 mm thick sheets using a hot-press. NMT composites were made using the film stacking method. First, flax fibre mats (250×250 mm) were cut and dried in an oven at 60°C for 2 hours. Alternating layers of non-woven flax mats and PP-sheets were stacked

Table I. Average maximum moisture content of flax fibres at different levels of Relative Humidity (RH).

Flax fibre	Maximum moisture content $M_{m,f}$ (%)			
	20% RH	66% RH	93% RH	100% RH
Green	3.61	15.03	24.0	42.58
Duralin	2.70	10.76	9.0	14.33

and impregnation was achieved by applying heat (200°C) and pressure for about 15 minutes. The composites obtained after cooling had a thickness of approximately 3 mm and a fibre volume fraction of about 38%. As a reference, similar composite plates based on non-woven Green flax mats were made. The obtained composite plates were pre-dried in an oven at 60°C for one day to reach the initial moisture level. Next, these plates were cut into specimens of 200 × 200 mm, which were immersed into a tank filled with tap water. Weight and thickness were measured as a function of time in order to study swelling of the composites. At certain moisture levels tensile tests were performed on test specimens cut from these plates to investigate the effect of moisture on residual strength and stiffness. Three different types of NMTs were evaluated: (i) treated Duralin flax/PP, (ii) treated Duralin flax/MA-PP and (iii) untreated Green flax/PP as a reference.

3. Results and Discussion

3.1. ENVIRONMENTAL BEHAVIOUR OF FLAX FIBRES

Table I shows the average maximum moisture, which was absorbed by the fibres at different relative humidities. It is obvious (Figure 2) that generally, the moisture content of both Green and Duralin flax fibres increases with increasing the relative humidity. The moisture content of Green flax is, however, higher than the moisture content of Duralin flax fibres for all the relative humidities.

Figure 3 shows the average moisture content of Duralin and Green fibres as a function of time for 66% of relative humidity. At this relative humidity level the upgraded Duralin fibre absorbs about 30% less moisture than the Green flax fibre. The rate that moisture diffuses into or out any solid is governed by Fick's First Law, which says that the mass of moisture that passes through a cross-section, called the flux, is proportional to the concentration gradient of moisture dc/dx. The proportionality constant is the diffusion coefficient or diffusivity D (cm^2/sec). In the case of the membrane problem the First Fick's Law is useful because the concentration gradient is constant and at steady state D is constant as well. Most problems in diffusion such as the fibre problem have a region where the concentra-

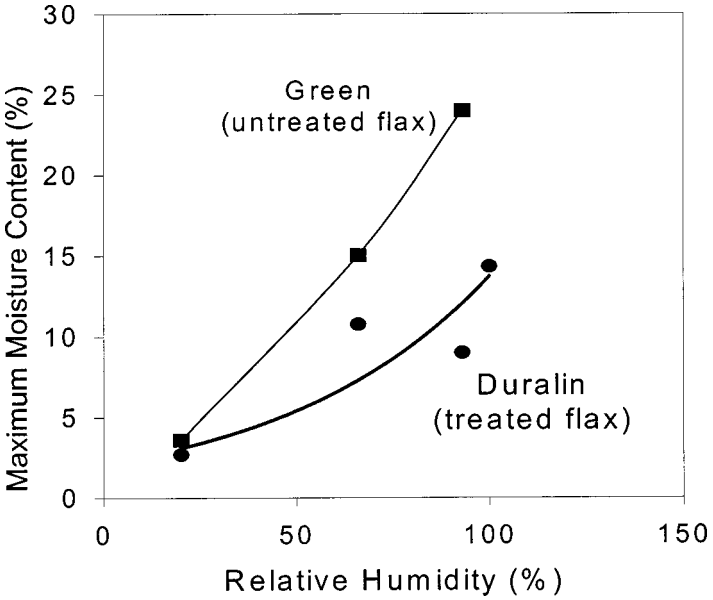

Figure 2. Effect of the relative humidity on the moisture absorption of Green and Duralin flax fibres.

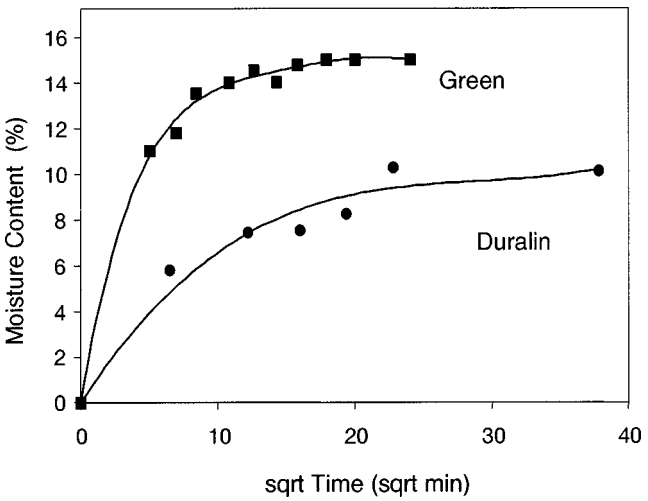

Figure 3. Average moisture content for Green- and Duralin-flax fibres at 66% of relative humidity.

tion of moisture changes with time. Fick's First Law is not useful in this case but another expression that describes the flux, which corresponds to the experimental conditions, is needed. Fick's Second Law may describe the moisture absorption in fibres and it is useful to determine concentration as a function of time. The analysis of the problem with Fick's Second Law allows us to determine the approximate time for a fibre to reach equilibrium that is the time required to satisfy: $x^2/4D_f$,

where x is the radius of the fibre and D_f the diffusivity of the fibre [1]. From studies on the diffusivity within a hygroscopic fibre at medium humidities a value of 10^{-7} cm^2/s may be taken. The diffusivity increases rapidly with increasing concentration of water in fibres. At the dry state, diffusion is very slow but it becomes more rapid at moderate and high regains. The variation in moisture content through a fibre that absorbs water shows a sharp boundary. The observation of the rate of advance of this boundary is another method to determine the diffusion coefficient in a fibre [16]. Another effect that may slow down the approach to the final equilibrium (as it is observed for Green fibres) is the presence of swelling stresses. When water is absorbed in the fibre swelling stresses are set up. It has been observed [1] that after the initial diffusion process there is a second stage where these stresses relax. Consequently, the equilibrium moisture condition towards the diffusion proceeding is changed. Therefore the attainment of the final steady state can be delayed. During the conditioning of a bundle of fibres, diffusion takes place in three stages: During the first stage there is diffusion in the air from the water vapour to the fibre surface, the second stage involves diffusion in the air in spaces between fibres from the surface of the bundle to the surface of a single fibre and the third stage involves diffusion from the surface of a fibre to its interior. The time needed for diffusion in the air (inside or outside the specimen) depends on the size, shape and density of the specimen. On the other hand the time needed for the diffusion in the air within the specimen is difficult to be determined. However, it is expected that both effects will take place concurrently and at times of the same order of magnitude. It should be noted that the time for diffusion in air is greater than the time of diffusion within the fibre. Diffusion within the fibre occurs very fast. Consequently, in calculations involving fibre bundles or a mass of fibres, the fibres should be considered as being in equilibrium with the air at their surfaces. In our case, the fibre samples used for the moisture absorption analysis were bundles of fibres bound together. If we consider this as a single fibre with a radius of approximately 1.5 mm the diffusivity of Green- and Duralin-flax fibres at 66% of relative humidity can be calculated using Equation (1). The diffusivity D_f for Green- and Duralin-flax fibres at 66% is 4.04×10^{-6} and 7.8×10^{-7} cm^2/sec, respectively. It is obvious that the diffusivity for Green fibres is higher compared to Duralin and this has been observed for all the examined relative humidities. Taking into consideration that the time needed to reach the equilibrium is proportional to $x^2/4D_f$, the conditioning time for single flax fibres can be approximated. For Green and Duralin fibres at 66% of relative humidity the equilibrium time is 0.25 and 1.28 sec, respectively. However, in real experiments this time will be greater. The equilibrium time has been estimated for other fibres such as cotton and wool as well and has always been found to be greater than the values estimated theoretically. The reason is that other factors besides the diffusion of moisture are involved. Such factors can be the heat evolved when the fibres absorb water or the structural relaxation and changes during water absorption.

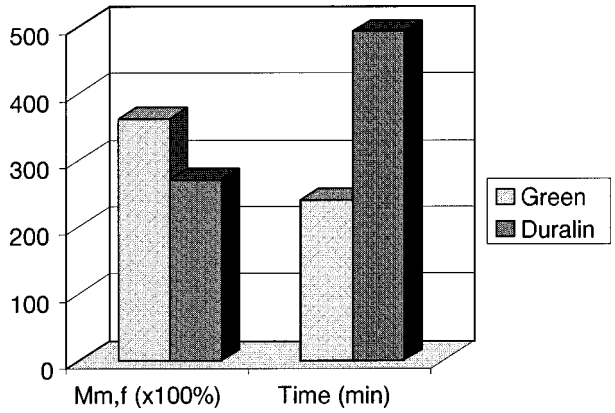

Figure 4. Time dependence of moisture absorption of Green- and Duralin-flax fibres at 20% of relative humidity.

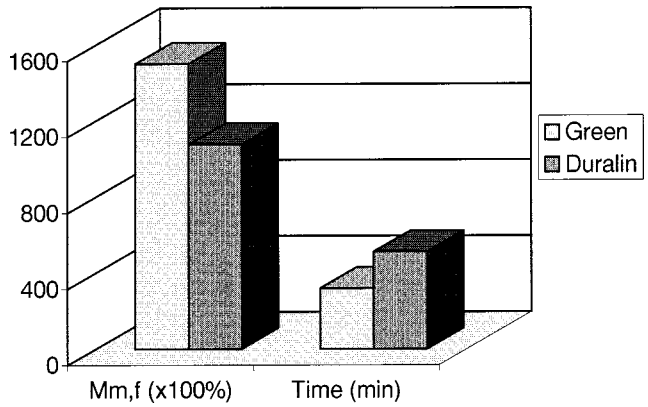

Figure 5. Time dependence of moisture absorption of Green- and Duralin-flax fibres at 66% of relative humidity.

Figures 4–6 represent the relationship between the equilibrium time and the maximum moisture content in the fibre ($M_{\mathrm{m,f}}$). It can be observed that the treated Duralin fibres need more time to reach their saturation point compared to the untreated Green flax fibres with the exception of 93% of relative humidity, where Duralin fibres need less time to reach their saturation point (Figure 6). In this case, as it has been mentioned before, it is possible that at high relative humidities when the Green fibres reach a high level of moisture uptake close to their saturation point, they need more time to stabilise as the water already absorbed inhibits the process. In all cases the Green flax fibres absorb more moisture than the treated Duralin flax fibres, whereas the treatment becomes more effective at high relative humidities.

Figure 7 shows a SEM micrograph of a dry Duralin fibre. The structure of flax is being made up of cellulose microfibrils bound together by a matrix of lignin and hemicellulose, which are then subsequently bond together to form larger fibre bundles. Kinks or nodes can be clearly seen (Figure 8) at regular intervals along the

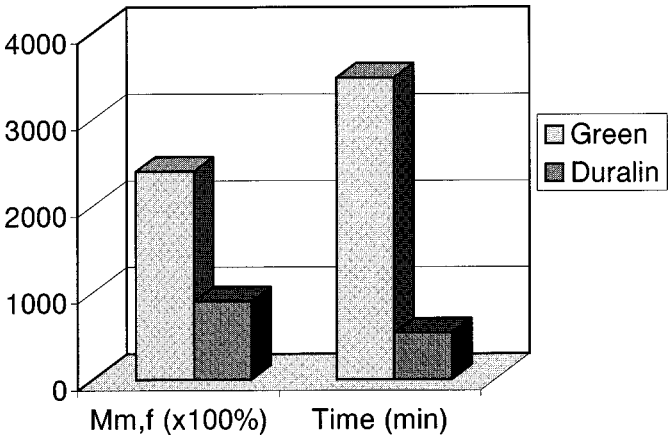

Figure 6. Time dependence of moisture absorption of Green- and Duralin-flax fibres at 93% of relative humidity.

Figure 7. Dry Duralin single flax fibre.

fibre surface, which may be attributed to fibre cell tip overlap within the bundles or defects on the fibres surface due compression. The individual fibres are well connected by the pectin matrix. Figure 9 shows a SEM micrograph of Duralin flax fibres after conditioning at 100% of relative humidity. Even after water absorption the fibre surface remains smooth and unchanged from its dry state. Although the individual fibres are still intact the fibre bundle is well separated and the matrix

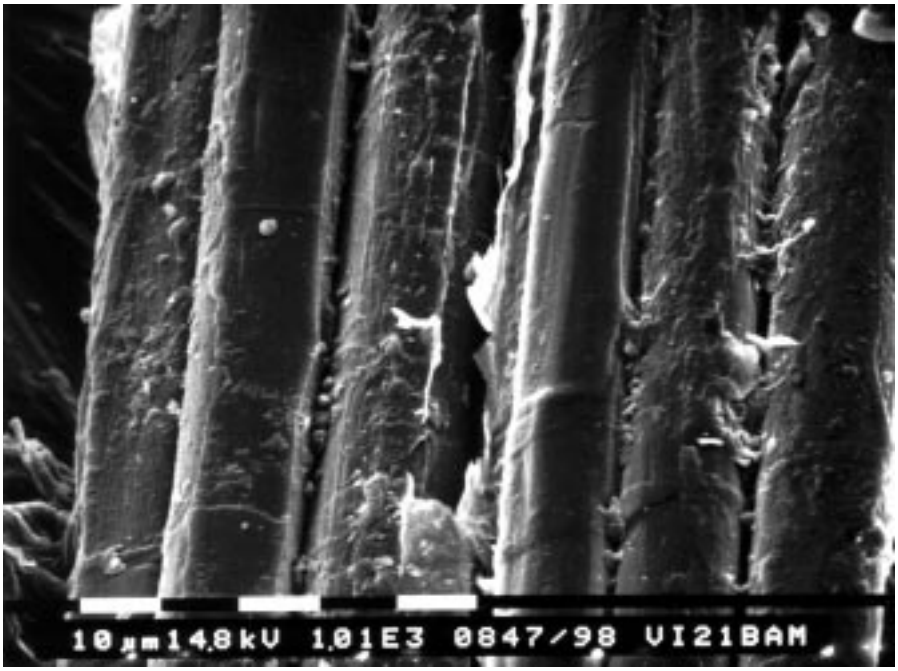

Figure 8. Dry Duralin flax fibres.

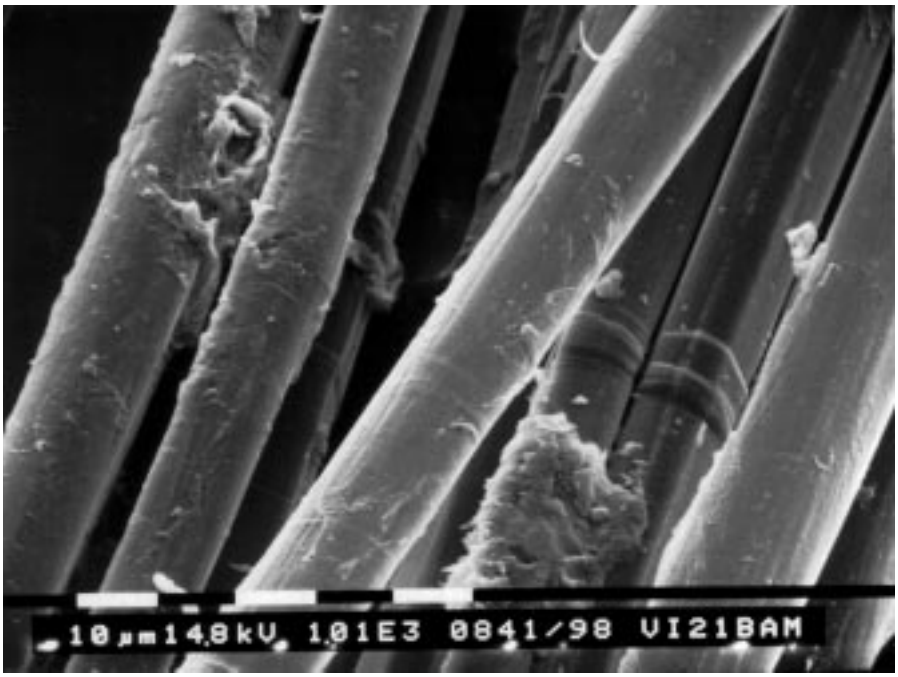

Figure 9. Duralin flax fibres after conditioning at 100% of relative humidity.

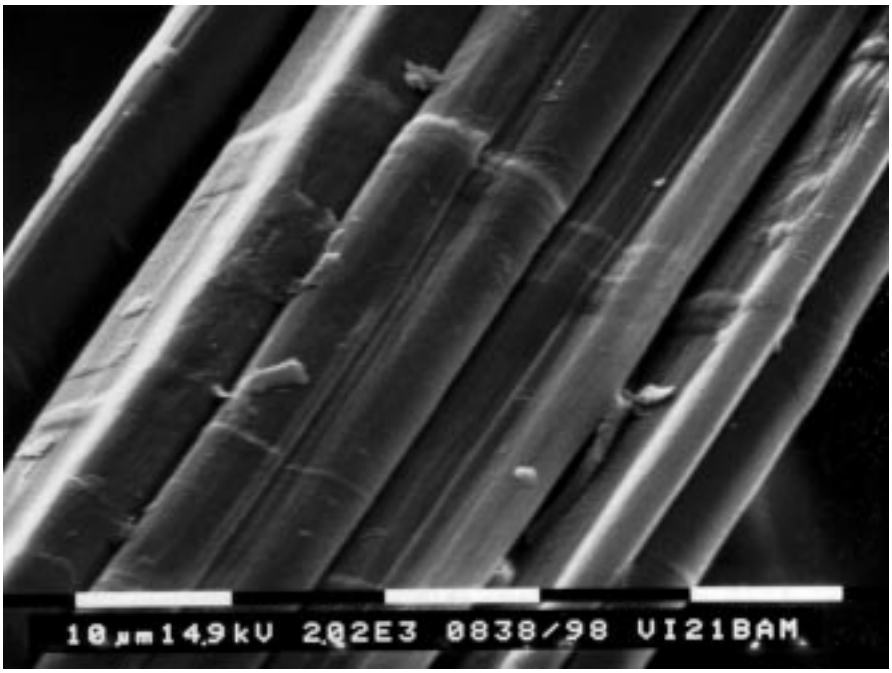

Figure 10. Dry Green flax fibres.

in between the individual fibres is dissolved. Dry untreated Green flax fibres are shown in Figure 10. The surface of the fibres is smooth and kink bands are visible along the fibre axis. The fibres are well connected by the organic matrix and form a fibre bundle. Figure 11 shows conditioned Green fibres at 100% of relative humidity. Unlike the Duralin fibres they are swollen and their surface appears to be rougher than the dry Green fibres. Also here the individual fibres are well separated and damage is observed in the form of kink bands. The organic matrix between the fibres is very poor and almost non-existent. After being subjected to moisture, the effects on both types of fibres are different. The surface of Duralin did not appear to be damaged, whereas the surface of Green flax fibres became rougher. The matrix, which connects the fibres, was in both cases almost non-existent.

The load-displacement curves of the fibres were typical of materials fracturing by brittle failure. Table II represents the results of tensile tests of humidified flax fibres. The average ultimate tensile strength of flax fibres changes as the relative humidity increases. The average tensile strength of both types of fibres at 3.5 mm gauge length is somewhat higher than those at 8 mm gauge length with the exception of Duralin, which at 90% of relative humidity exhibits a lower tensile strength. The increase in strength at decreasing fibre length is expected since the longer the fibre the larger the probability of defects. In general, compared to the Green flax fibres, the Duralin fibres exhibited a somewhat higher and more uniform strength with less scatter. Clearly, the improvement in moisture resistance obtained was not

Figure 11. Green flax fibres after conditioning at 100% of relative humidity.

Table II. Average tensile strength of humidified flax fibres.

Relative humidity (%)	Flax fibre	Fibre length (mm)	Average tensile strength (MPa)	Standard deviation (MPa)
30	Green	3.5	677	425
	Duralin		809	134
66	Green	3.5	799	398
	Duralin		1080	368
90	Green	3.5	818	318
	Duralin		642	344
30	Green	8	619	461
	Duralin		651	176
66	Green	8	760	390
	Duralin		913	250
90	Green	8	761	369
	Duralin		884	180

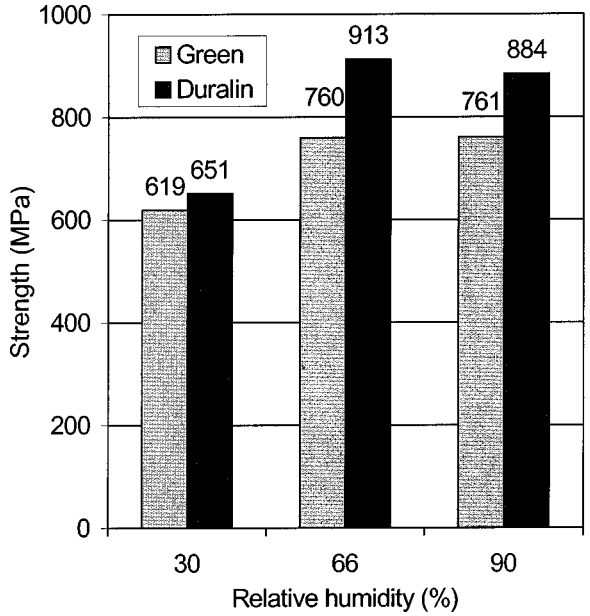

Figure 12. Effect of relative humidity on the average tensile strength of Green- and Duralin-flax fibres (8 mm gauge length).

at the expense of the mechanical properties of the fibre. Figures 12 and 13 show the effect of the relative humidity on the average tensile strength of both fibres for 3.5 and 8 mm of gauge length. Surprisingly, Duralin fibres go through a maximum at a relative humidity of 66% for both gauge lengths. There seems to be two opposing effects of humidity on the fibre tensile strength. Up to a maximum of ca. 66% of relative humidity, water uptake is advantageous for Duralin fibres possibly due to a fibre plasticising effect as a result of the presence of 'free' water. Excess of humidity however, leads to an increase of the absorbed bound water and decrease of 'free water'. Therefore, in high relative humidities where the largest amount of absorbed water is bound the plasticisation effect [17] becomes less, resulting in reduced fibre strength.

Water is able to penetrate the cullulose network of the fibre into the capillaries and spaces between the fibrils and into less bound areas of the fibrils and it may attach itself by chemical links to groups in the cellulose molecules. The water molecules force the cellulose molecules apart destroying some of the rigidity of the cellulose structure. In this way the water acts as a plasticiser. It permits the cellulose molecules to move more free. Consequently the mass of cellulose is softened and can change shape more easily with an application of force [3]. It has been suggested [18, 19] that the failure of cellulosic fibres under axial application of tensile stresses is subjected to control by the cellulose content and the micro-fibril angle ϑ. Proportionality between mechanical and physical properties to the content of cellulose, micro-fibrils angle and size of cells has been shown by Murkherjee

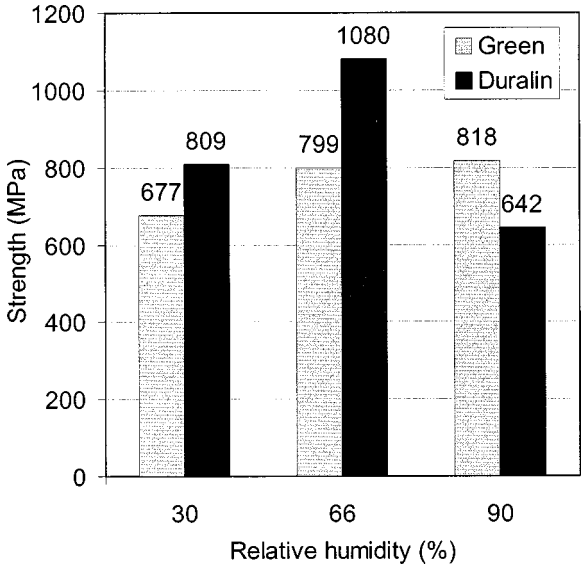

Figure 13. Effect of relative humidity on the average tensile strength of Green- and Duralin-flax fibres (3.5 mm gauge length).

et al. [20]. The spiral angle in the case of flax fibres has been calculated to be 10%. There is a clearly defined correlation between the anisotropy of swelling and tensile properties with the wall structure of fibres. The microscopic structure of cellulose shows a significant anisotropy in that the swelling is larger in a direction perpendicular to the chains than in a direction parallel to the fibre-axis. Mainly the orientation and the angular dispersion affect this anisotropy. In simple words, the anisotropy can be reduced both as angular dispersion increases and as the spiral becomes flatter. The study of strength properties in natural fibres showed that flatter spirals have higher extensibility, lower Young's modulus and lower tensile strength compared to the fibres with steeper spirals. In the case that the fibres are stretched wet, the angle ϑ changes in such a way that the spiral becomes steeper [18].

Green fibres seem to be less affected by the two opposing influences, as referred to above, and maintain a more or less constant tensile strength with humidity with a small increase at 66 and 93% of relative humidity. It is important to note that the effect of humidity on the mechanical properties of the fibres depends also on the time of exposure in certain humidity conditions. For example, it has been observed that moisture causes fungus development on the fibre surface often after 3 days of exposure, resulting in degradation of the fibres and the decrease of their mechanical properties.

Table III. Maximum moisture content and diffusivity of flax/polypropylene composites.

Composite	Max. moisture content $M_{m,c}$ (%)	Diffusivity D_c (cm^2/s)
Green flax/PP	18.0	1.3×10^{-2}
Duralin flax/PP	12.8	7.8×10^{-3}
Duralin flax/MA-PP	13.5	5.0×10^{-3}

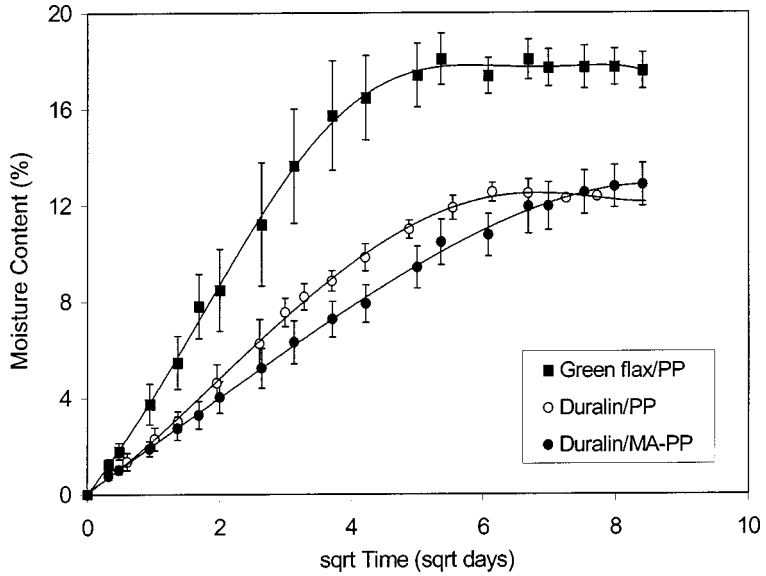

Figure 14. Moisture content as a function of time for Green flax/PP, Duralin/PP and Duralin/MA-PP composites.

3.2. ENVIRONMENTAL BEHAVIOUR OF FLAX/POLYPROPYLENE COMPOSITES

Figure 14 shows the moisture absorption of flax/PP NMT plates as a function of time. By fitting Equation (1) to the experimental data, the maximum moisture content in the composite ($M_{m,c}$) and the diffusivity (D_c) of the different types of composites were determined (Table III). Green flax fibre based composites are clearly more sensitive to moisture than the other two types of composites based on upgraded Duralin flax. The maximum moisture content in Duralin flax fibre composites is reduced by some 30% compared to Green flax fibre composites. Also, the diffusivity of Duralin flax fibre composites (Table III), as calculated from the initial slope of the moisture uptake curves, is much lower than that for NMTs based on Green flax fibre mats.

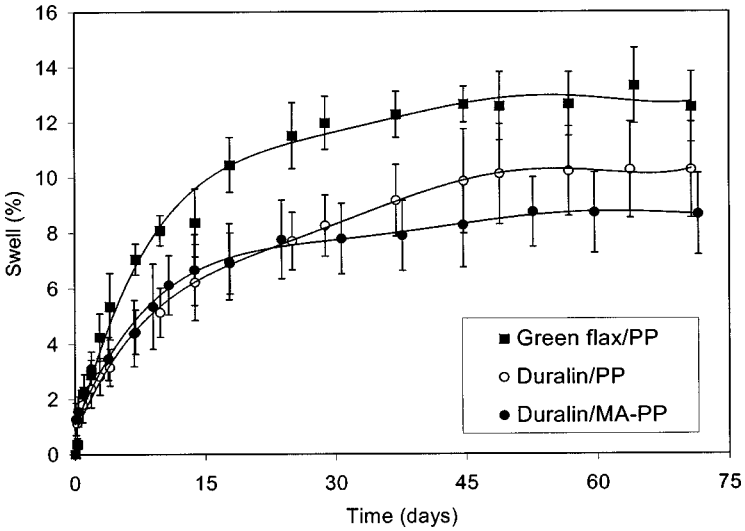

Figure 15. Thickness of composite plates as a function of time for Green flax/PP, Duralin/PP and Duralin/MA-PP composites.

It is interesting to note that the use of MA-PP as a compatibiliser lowers the diffusivity even further. Clearly, the initial moisture uptake in this composite system is taking place at a lower rate than for the PP system without compatibiliser. The maximum moisture content level is, however, similar for both PP and MA-PP based treated flax systems. The higher diffusivity for the PP system without compatibiliser, indicates that initially a fair amount of moisture uptake takes place along the fibre/matrix interface. For Duralin flax/PP, as well as for Green flax/PP, a plateau value for moisture uptake is reached after about one month immersion in water. Compared to the moisture absorption data of single fibres given in Figure 2 and Table I, the moisture absorption of the composites is quite high. Based on a fibre volume fraction of 0.38 and assuming that only the fibre is responsible for moisture uptake in the composites the moisture absorption should be much lower and in the order of 6% for Duralin based composites and 12% for Green flax fibre composites. However, in reality these composites absorp up to 12% and 18%. The difference in moisture content between a fibre in air and a fibre in a composite is similar for both Duralin- and Green-flax and around 6% and probably the result of voids which are often present in natural fibre composites.

It can be expected that the absorption of moisture affects the dimensional stability of the composite plates. Figure 15 shows the thickness-swell of the samples immersed in water for 60 days at room temperature. The performance of the Duralin composites is much better than that of the Green flax based composites. The thickness of the Green flax composite increases by about 13%, whereas the Duralin flax composite swells about 9%.

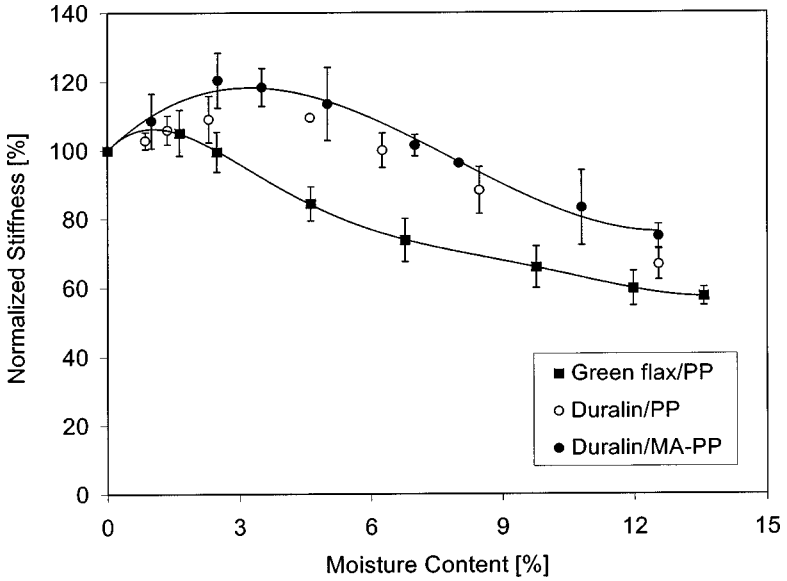

Figure 16. Effect of moisture content on the modulus of Green flax/PP, Duralin/PP and Duralin/MA-PP composites.

With respect to the durability of natural fibre composites, the most serious effect of moisture absorption is the degradation of mechanical properties. Therefore, the residual stiffness and strength of NMTs based on Green- and Duralin-flax was measured as a function of moisture content. The initial stiffness and strength values for these type of natural-fibre-reinforced composites is about 8 GPa and 50 MPa, respectively. In Figure 16 the normalised stiffness is plotted as a function of moisture content. In the case of Duralin composites an initial increase in stiffness is followed by a drop in composite stiffness, whereas for Green flax fibre based composites no initial increase in stiffness is observed and the drop in stiffness is more obvious. For Green flax composites the modulus of the saturated samples is quite significant and is about 40% lower than that of dry samples. Similar to the fibre strength data as mentioned in the previous section, also the fibre stiffness and hence composite stiffness in the case of Duralin fibres seems to improve at mild levels of moisture uptake. Figure 17 shows the normalised tensile strength as a function of moisture content. Compared to the drop in composite stiffness, the tensile strength of flax-fibre-reinforced composites is not so much affected by the water uptake. Similar effects of water absorption on composite mechanical properties where reported earlier for thermoplastic composite systems based on jute fibre [21]. Although the overall drop in composite strength is not as significant as the drop in stiffness, it is clear that, again, the Green fibre composites are more affected by the water uptake compared to the Duralin composites. At high moisture content, the strength of Green flax/PP is about 25% lower than that of the dry reference sample. Similar to the trend in composite stiffness, also here an initial

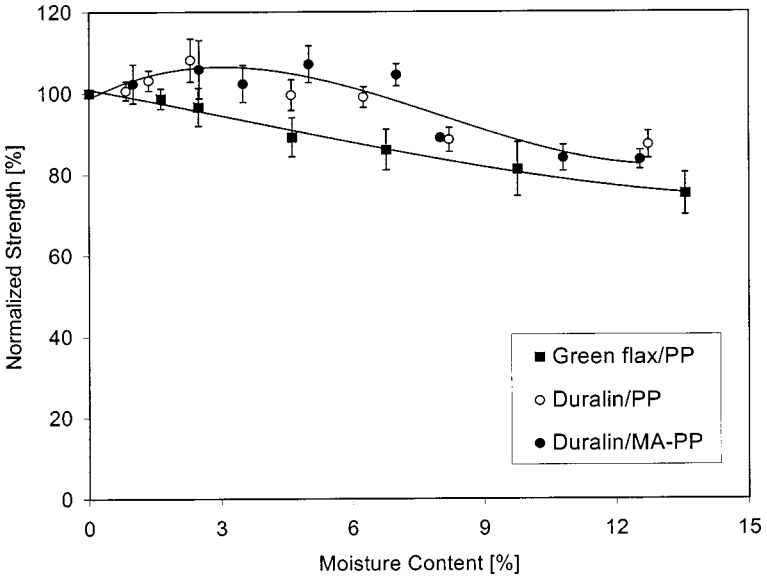

Figure 17. Effect of moisture content on the tensile strength of Green flax/PP, Duralin/PP and Duralin/MA-PP composites.

increase in composite performance with moisture content is observed for Duralin composites, whereas the Green flax fibre composites show a more gradual decrease in composite strength with water uptake. This behaviour seems to be in agreement with the environmental behaviour of the single Duralin fibres, where a maximum in fibre strength was observed at intermediate levels of relative humidity (see Figures 12 and 13). However, the drop seen in composite strength at high moisture is not observed for single fibres. It should be noted, however, that in contrast to the short environmental conditioning times in the case of fibres, the composites were immersed in water for several days or even weeks, which could lead to strength degradation mechanisms other than the ones responsible for the effects shown in Figures 12 and 13. For example, during the environmental behaviour studies on flax fibres it has been observed that moisture causes fungus development on the fibre surface after a couple of days of exposure, resulting in degradation of the fibres and the decrease of their mechanical properties. This could be the reason for the drop in strength for Duralin fibre composites at moisture content levels above 7%. Since the diffusivity of Duralin-flax-fibre-reinforced composites is much lower than that of Green flax/PP composites, these composites are immersed much longer in water than Green flax fibre composites with similar moisture contents. For example, in the case of a Duralin flax/MA-PP composite a moisture content of 12% is reached after an immersion time of about two months, whereas in the Green flax/PP composite this moisture content level is already reached after 8 days. Clearly, this may have an effect on the mechanical behaviour of the fibres and composites. Still, this relatively small drop in composite strength even after such a long exposure

time is a clear indication for the good environmental durability of Duralin flax based composites. No effect of maleic-anhydride modified PP on residual stiffness and strength of Duralin composites was observed. Although the maleic-anhydride interface modification slowed down the water uptake (see Figure 14), it does not seem to affect the (residual) mechanical properties of the interface and hence the composites. Studies by Karmaker et al. [22, 23] even suggest that the interfacial shear strength in natural fibre thermoplastic composite systems may increase with moisture absorption. They studied the effect of thickness swelling of fibres on the interfacial gap and on the mechanical and physical properties of ligno-cellulosic fibre reinforced polypropylene and showed that the gap between natural fibre and polypropylene can be filled by the dimensional increase of fibres when they are swollen by water, leading to higher interfacial shear strengths between fibre and polymer matrix. Unlike composite systems based on brittle thermosetting resins like unsaturated polyester, microcracking of the matrix as a result of fibre swelling is not likely to occur in the case of a ductile matrix like PP. Hence, rather than the result of interface failure or matrix cracking, the mechanical degradation of the composites at relatively long immersion times is most likely the result of fibre degradation. It could be argued that the initial increase in composite properties with moisture absorption is the result of fibre swelling and its positive effect on the interfacial shear strength. However, since an increase in composite properties is only observed in the case of Duralin flax/PP it is very unlikely that the initial increase in stiffness and strength as shown in Figures 16 and 17 is actually the result of a better stress transfer mechanism through fibre swelling. In that case a similar or even stronger effect should have been observed for Green flax fibres since these swell even more than Duralin flax.

4. Conclusions

Upgraded Duralin fibres absorb less water than the untreated Green flax fibres. SEM micrographs show that Duralin fibres, even after conditioning in 100% of relative humidity, retain a smooth fibre surface, whereas the individual fibres are well separated. Conditioned Green fibres appeared swollen at 100% of relative humidity, and their surface shows to be rough with the individual fibres well separated and damage observed in the form of kink bands. The organic matrix which acts as a glue between the fibres to make them form a fibre bundle is very poor and almost non-existent.

During the separation of a single fibre from a bundle of fibres, damage of the fibre may occur, which may lead to a consequent decrease of the tensile strength. As the mechanical properties can be strongly affected by handling this may well be, together with the problem of defining the exact cross-sectional area, responsible for the relatively large scatter found in the strength values of natural fibres. The load-displacement curves of the fibres were typical of materials fracturing by brittle failure.

Generally, the Duralin fibres exhibit a somewhat higher and more uniform strength with less scatter, meaning that the applied upgrading process not only improves the moisture resistance of these fibres but that the fibre properties are at least retained, if not improved. The average tensile strength of flax fibres changes with relative humidity as well as test length. In almost all cases the highest strengths were observed for the shortest gauge length (3.5 mm compared to 8 mm), with the exception of one Duralin sample, which at 90% of relative humidity exhibited a lower strength at the shorter length. With increasing relative humidity, the Duralin fibres seem to go through a maximum in strength at a relative humidity of 66% due to a water plasticisation effect. At high relative humidities where the largest amount of absorbed water is bound the plasticisation effect becomes less, resulting in reduced strength of the Duralin fibre. Green fibres maintain an almost constant tensile strength with humidity with a small increase at 66 and 93% of relative humidity.

The absorption of moisture by flax-fibre-reinforced polypropylene (PP) composites can adequately be described by Fick's law. The moisture content is linear to the square root of time until about two weeks of immersion in water. After that, the moisture content levels off to a maximum moisture content. The moisture resistance of natural-fibre-mat-reinforced thermoplastics (NMTs) based on flax fibres and a PP matrix can be improved by the use of upgraded Duralin flax fibres. The moisture absorption of upgraded flax/PP composites is about 30% lower than that of Green flax composites and the dimensional stability (swelling) is also significantly improved. The use of maleic-anhydride modified PP as a compatibiliser for improved interfacial bonding lowers the diffusivity, being the water uptake rate, significantly. The maximum moisture content is however not affected by the interfacial properties. The stiffness of Duralin flax/PP composites shows an initial increase with moisture content, followed by a small drop in stiffness at high levels of moisture content. The stiffness reduction of Green flax/PP composites is more pronounced and can be as high as 40% at moisture content levels of 12% and an immersion time of around 8 days. The tensile strength is not as much affected by the water uptake as the stiffness, which is in agreement with the fibre results where no drop in strength was observed with increasing relative humidity. Again also here the Duralin fibre composites show a better environmental durability compared to Green flax/PP composites.

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