Unidirectional Hemp and Flax EP- and PP-Composites: Influence of Defined Fiber Treatments

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Received 24 July 2003; accepted 18 February 2004
DOI 10.1002/app.20712
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In some technical areas, mainly in the automotive industry, glass fiber reinforced polymers are intended to be replaced by natural fiber reinforced polymer systems. Therefore, higher requirements will be imposed to the physical fiber properties, fiber-matrix adhesion, and the quality assurance. To improve the properties of epoxy resins (EP) and polypropylene (PP) composites, flax and hemp fibers were modified by mercerization and MAH-PP coupling agent was used for preparing the PP composites. The effects of different mercerization parameters such as concentration of alkali (NaOH), temperature, and duration time along with tensile stress applied to the fibers on the structure and properties of hemp fibers were studied and judged via the cellulose I–II lattice conversion. It was observed that the mechanical properties of the fibers can be controlled in a broad range by using appropriate mercerization parameters. Unidirectional EP composites were manufactured by the filament winding technique; at the PP matrix material, a combination with a film-stacking technique was used. The influence of mercerization parameters on the properties of EP composites was studied with hemp yarn as an example. Different macromechanical effects are shown at hemp- and flax-PP model composites with mercerized, MAH-PP-treated, or MAH-PP-treated mercerized yarns. The composites' properties were verified by tensile and flexural tests.
 J Appl Polym Sci 93: 2150–2156, 2004

Key words: natural fibers; composites; mercerization; polypropylene (PP); structure–property relations

INTRODUCTION

The optimization of the fiber-matrix adhesion is essential for improved physical, particularly mechanical properties of natural fiber reinforced polymer composites. Therefore, a physical or chemical modification of natural fibers or the use of coupling agent or that of a combination of both is possible to reach the required properties.[1–3] Because of their suitability for injection molding or extrusion processing, thermoplastic matrix materials are very important for greater design freedom. Polypropylene (PP) is the most commonly used thermoplastic matrix material (likewise in hybrid fiber compounds) in automotive applications. Epoxy resins (EP), on the other hand, are frequently used thermosets to be reinforced as well with natural fibers. As the polar natural fiber and the nonpolar matrix material as PP have different and incompatible surface polarities, maleic-anhydride-polypropylene copolymer (MAH-PP) is commonly used for upgrading the interphase compatibility.[1–6] The alkali treatment (mercerization) of natural fibers can change the fiber structure like type of crystalline lattice, crystallinity, fiber orientation, and also the properties such as strength, elasticity, luster, and handle.[7] Recently, it was shown as well that the properties of polymer composites can be improved by using premercerized bast fibers.[8,9]

In the present article, the changes of the mechanical and structural properties of fibers generated by mercerization were investigated by tensile tests and by wide-angle X-ray scattering. Mercerization procedures were performed with a home-built laboratory device making possible experiments with varying NaOH concentrations, steeping bath temperatures, and tension modes of the yarns. To study the efficiency of natural fiber modifications for polymer reinforcements, unidirectional (UD) laminates were prepared, representing a well-defined state of a composite. The UD laminates were processed by a filament winding technique (EP composites) and by a combination of winding and film-stacking techniques for PP composites. Epoxy resin was used as the matrix material with hemp yarn as an example only. UD-reinforced PP composites were employed to study extensively the strengthening effect of appropriately mercerized hemp and flax fibers in the composites, including the role of MAH-PP coupling agents. The degree of lattice conversion from cellulose I (native fiber) to cellulose II (fully mercerized fiber) as a mea-

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Contract grant sponsor: Agency of Renewable Resources.
Contract grant sponsor: Federal Ministry of Consumer Protection

sure of the mercerization effect on the crystalline structure was measured by X-ray scattering. The physical properties of the composites were investigated by tensile and flexural tests.

The present article was part of the outcome of a research project[9–12] dealing with the development of higher performance natural fiber composites for technical applications with higher loading demands.

EXPERIMENTAL

Materials

Matrix materials

PP (STAMYLAN P 17M10; Stamylan Deutschland GmbH, Düsseldorf, Germany) and EP (LY 5082 and HY 5083; 100 : 23, Ciba Spezialitätenchemie Pfersee GmbH, Langweid a. Lech, Germany) were used as matrix materials for the preparation of the UD composites.

Natural fibers

The following natural fiber yarns were used for the model composites: hemp 10/1, fineness 99.5 tex (Rohemp, Fürstenfeld, Austria) and flax F4/1, fineness 262.2 tex (J. Schilgen GmbH & Co., Emsdetten, Germany).

Coupling agent

The MAH-PP Licomont AR 504 as a coupling agent was obtained from Clariant GmbH (Gersthofen, Germany).

Processing

Fiber mercerization

A laboratory mercerization device was constructed at the Fraunhofer Institute for Applied Polymer Research for performing systematic investigations of the alkaline treatment (mercerization) of fibers. The equipment enables mercerization procedures with defined length or loading of the fibers including the isometric mode (constant fiber length), a treatment with constant strain of the yarn, and the mode with free fiber shrinkage (slack mercerization) at different fixed temperatures and treatment times.

Figure 1 shows a schematic drawing of the device making possible the mercerization of cellulosic yarns with the length of 1 m up to 400 m wound around a frame. The fiber tension can be measured continuously and can be kept constant by a defined force transmission by using a clamped weight. The mercerization occurs by (1) steeping the frame with the yarn into the NaOH solution, (2) dipping into water, (3) then neutralizing in a weak acetic acid, and (4) washing of the yarn in running cold water.

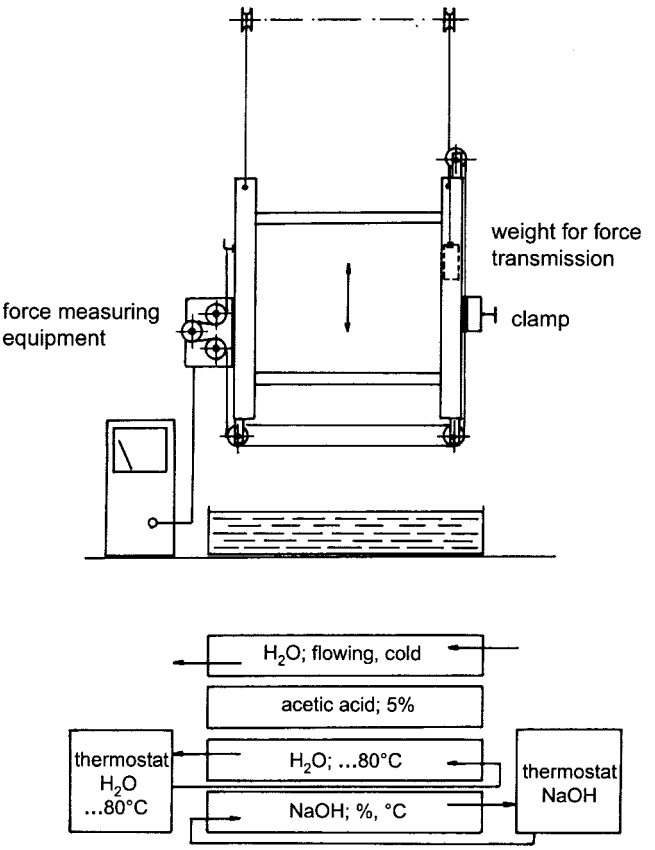

Figure 1 Schematic drawing of the laboratory mercerization equipment.

Composites manufacturing

Figure 2 shows a scheme of the filament winding equipment used at the University of Kassel for preparing the EP and PP laminates. Premodified hemp yarns were impregnated with epoxy resin and wound to unidirectional laminates before curing.

The model composites consisting of flax or hemp fiber–PP were processed by the film-stacking technique in combination with the filament winding system (30–35 vol % fiber content). Here, mercerized fibers (29%, 20°C, 20 min, isometric) and/or fibers treated with MAH-PP in toluene at 95°C were employed.

Test methods

Fiber characterization

The mercerization of natural fibers gives rise to a lattice conversion of the cellulose I modification into the cellulose II modification, which can be studied by

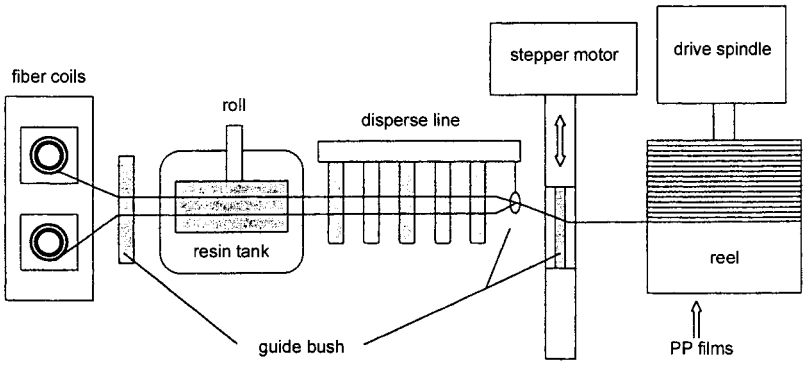

Figure 2 Schematic illustration of the filament winding system.

X-ray scattering to characterize the progress or completeness of the specific mercerization procedure. To this end, wide-angle X-ray scattering patterns of the fibers were taken with a universal X-ray planar film camera by using Ni-filtered CuK_α radiation (40 kV, 35 mA). The degree of lattice conversion was determined by comparing the X-ray patterns of the mercerized sample with a series of X-ray diagrams made from defined mixtures of cellulose I (untreated fiber) and cellulose II (fully converted fiber) samples.[14] By this method, a maximum deviation in the range of $\pm 10\%$ was anticipated.

The mechanical properties of the fibers were investigated by a Zwick universal testing machine 1446 with a test speed of 250 mm/min and a distance of clamped support of 500 mm at normal climate. The shown parameters are always mean values of 10 to 20 measurements.

Composites testing

The physical tests of the composites were carried out according to current standards.

RESULTS AND DISCUSSION

Fiber mercerization

The mercerization of natural fibers generates changes of the surface energy (in all probability to a more polar behavior) and surface topography (rougher surface with excavated fibrils). The more polar fiber surface improves the connection to the coupling agent's polar part and the rougher surface topography furthers the wettability and form fit of the matrix material and thus causes a better fiber–matrix adhesion. Extensive structural changes can be caused by the mercerization of natural fibers, which in turn depend strongly on the parameters of the alkaline treatment (e.g., caustic solution concentration, treatment temperature, duration of treatment, and fiber tension).[13,14] The following characteristic structural changes were observed: (1) lattice conversion of the cellulose (modification I in modification II) with the appropriate conditions of a mercerization (18–24% NaOH); (2) a compaction of the cross-section morphology; and (3) the modification of the surface texture of the fibers, which is significant for the positive effect of the mercerization reinforcing

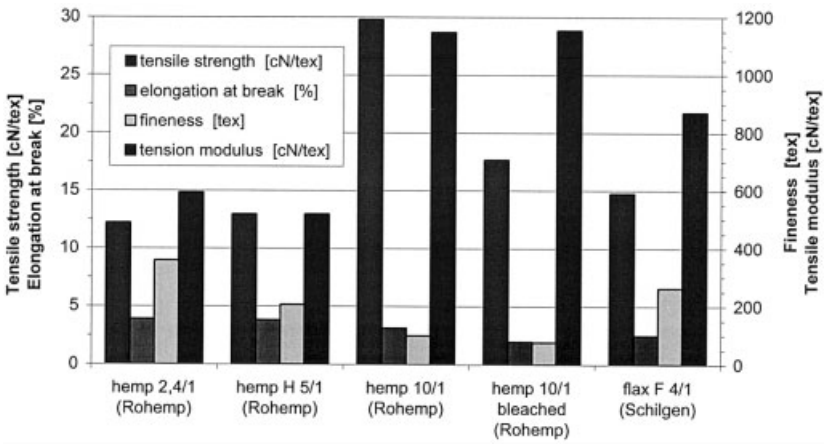

Figure 3 Physical properties of hemp yarns (fiber bundles) (distance of clamped support = 500 mm, test speed = 250 mm/min).

TABLE I
Variation of the Structure and Properties of Hemp Yarn (hemp 10/1, Rohemp) Due to Mercerization (22% NaOH)

Mercerization temperature (°C)	Mercerization time (min)	Stress at the mercerization	Degree of conversion cell I in cell II (%)	Tensile strength (cN/tex)	Elongation at break (%)	Tension modulus (cN/tex)
Untreated		—	0	29.8	3.15	1148
4	60	Isometric	≈50	28.5	2.34	1617
10	60	Isometric	≈50	24.9	2.45	1214
20	60	Isometric	≈50	28.2	2.27	1701
10	40	Free shrinkage	≈70	17.6	6.86	357
10	60	Constant load (100 g)	≈40	29.2	2.60	1499

Note. Distance of clamped support = 500 mm, test speed = 250 mm/min.

fibers (improvement of the fiber-matrix adhesion). Depending on the applied fiber tension, a changing fibril orientation has to be anticipated as well. However, a substantial increase of the already highly oriented bast fibers[14] seems hardly to be attainable in comparison with fibers with a lower orientation, as, for example, cotton fibers.

Figure 3 depicts characteristic properties of various untreated fiber yarns. Obviously, in the case of the hemp yarns (as with flax fibers from different sources), we have to accept strongly varying properties of the raw materials.

The variation of mechanical and structural properties of hemp yarn upon mercerization in dissimilar conditions is shown in Table I. The mercerization with the rather high alkali concentration (22%) never leads to a complete lattice conversion of cellulose I in cellulose II. As expected, the highest degree of conversion (70%) is reached by a freely shrinking yarn. Further, it turns out that the mercerization of hemp yarn under isometric conditions or with constant fiber load (100 p) at a NaOH concentration of 22% results in a crystalline lattice conversion of ≈40–50% only, however, combined with the highest strengths and moduli of the fiber bundles. It is also observed that only the tensile modulus of elasticity exceeds the value of the original unmodified material. On the other hand, the reduction of the modulus and strength by the slack mercerization is related to an increase of the elongation at break, which could be useful for increasing the impact strength of a composite for regenerated cellulose fibers for PP reinforcement.[15]

The resulting tensile properties of the yarns are rather low because of the test conditions chosen (e.g., free gauge length of 500 mm), which are not directly applicable and transferable to the actual composite properties.

In addition to the bulk fiber structure and the mechanical yarn properties, for reinforcing fibers, the surface structure is supposed to play an important part as well. It was shown[14] that alkalization procedures as scouring and mercerization affect the surface morphology of bast fibers remarkably, resulting in a more distinct exposition of the surface fibrils and a more pronounced surface relief.

Model EP composites

To assess the influence of mercerization on the composites' properties, model composites with EP matrices were produced. Selected mechanical properties of mercerized hemp fibers and their composites are listed in Table II.

Table II demonstrates that the composites' flexural strength can be increased from 148 MPa up to ≈ 230 MPa and the flexural modulus of elasticity can be increased from 5900 MPa up to ≈ 12000 MPa by the use of optimal mercerized hemp fibers. In contrast to this, the differences between the composites' properties by variation mercerization temperature of the fibers were rather marginal.

As was already shown with regard to the jute and flax fibers,[8] these property enhancements might result from the changes of the strength and stiffness of the

TABLE II
Influence of the Mercerization of Hemp Yarns on the Mechanical Properties of the Fibers and of the EP Composites

Fiber treatment (22% NaOH, 60 min) treatment temperature	Fiber properties		Composite properties	
	Tensile stress at break (cN/tex)	Modulus of elasticity in tension (cN/tex)	Flexural strength (MPa)	Flexural modulus of elasticity (MPa)
Untreated	29.8	1148	148	5919
4°C	28.5	1617	226	11995
10°C	24.9	1214	228	11726
20°C	28.2	1701	219	12351

TABLE III
Influence of Different Fiber Treatments to the Flexural Strength of Unidirectional Flax-PP-Composites

Fiber treatment	Flexural strength [N/mm^2]
Untreated	77
Mercerized[a]	115
MAH-PP[b]	127
Mercerized +MAH-PP	149

Note. lengthwise, fiber content: 35 vol %.
[a] 29% NaOH at 20°C, 20 min, isometric.
[b] 1% Licomont AR 504 in toluene, 10 min.

fibers, but indeed mercerization also changes the surface properties of the fibers (roughness, polarity). For this reason, the fiber-matrix adhesion with polar matrices such as epoxy resin can be increased.[1,16]

First of all, the enhancements of the yarns' modulus of elasticity caused by mercerization can be observed as an increase of the stiffness of the composites, which normally hardly depends on the fiber-matrix adhesion. However, no enhancement of the fiber fracture strength was determined, whereas the breaking strength of the composite increased remarkably.

Model PP composites

The natural fiber-matrix adhesion was studied by using differently modified flax and hemp fibers in UD-PP laminates prepared by the film stacking technique. The resulting composites were investigated with regard to the mechanical properties mainly by flexural tests.

Table III shows explicitly that besides the significant effects of single mercerization and MAH-PP treatments, a combination of the isometric mercerization procedure (e.g., increasing fiber strength) and the coupling agent results in the highest increase of the composite property of ≈ 90% in comparison to a composite with untreated flax fibers for reinforcement.

The concentration of the applied MAH-PP coupling agent significantly influences the macromechanical properties of flax-PP composites, as can be seen from Figure 4 for the flexural strength. Obviously, a maximum of strength improvement appears at ≈ 1% (by weight) of the agent in the applied solution. With nonmercerized fibers, the flexural strength of the composites can be enhanced by ≈ 40% by a pretreatment of the fibers with the optimum coupling agent concentration of 1%. However, a two-step pretreatment of mercerization and coupling agent application can increase the flexural strength even more, up to 50% as compared to the composites with untreated fibers for reinforcement. In the latter case of the composites with the two-step pretreatment, results were obtained even with a 5% (volume) lower fiber content as compared with the composites of the dewaxed fibers finished with the coupling agent only. So, with regard to the natural fiber-PP interface adhesion, a synergistic effect of mercerization and coupling agent application can be stated. Assuming a higher polarity and lower wettability of the mercerized fibers, the coupling agent with its polar coupling site can be bound more efficiently as compared to an untreated or dewaxed fiber. Additionally, the higher roughness of the fiber surface after mercerization and the resulting better anchorage of the matrix within the fibers become more meaningful after the preparation of the fibers with the MAH-PP coupling agent and the resultant match of the surface tension with that of PP. On the other hand, an improvement of the mechanical properties of the fibers by the mercerization should be considered as well, which has not been taken into account for fibers treated with coupling agents solely (see Table V). Ac-

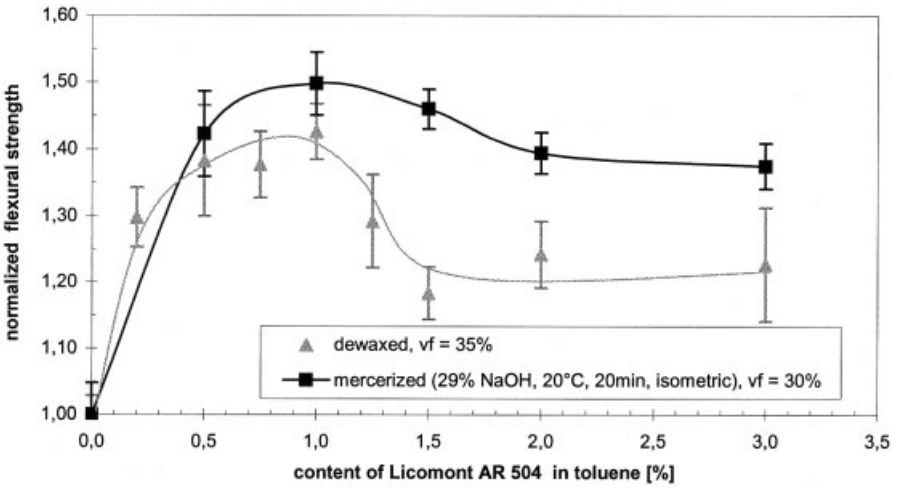

Figure 4 MAH-PP content versus normalized flexural strength of unidirectional flax-PP-composites with and without fiber mercerization. vf = fiber volume content.

TABLE IV
Influence of Different Fiber Treatments to the Transverse Tensile Strength (across the fiber grain) σ_2 of Unidirectional Flax-PP-Composites

fiber treatment		σ_2 (N/mm^2)
Untreated	$v_f = 0.35$[c]	7.6
Mercerized[a]	$v_f = 0.30$	7.9
MAH-PP[b]	$v_f = 0.30$	12.6
Mercerized + MAH-PP	$v_f = 0.35$	11.5

[a] 29% NaOH at 20°C, 20 min, isometric.
[b] 1% Licomont AR 504 in toluene, 10 min.
[c] v_f = fiber content (vol %)/100%.

cordingly, the improved fiber properties were mainly transferred into the composites behavior by an advanced fiber-matrix adhesion caused by the application of MAH-PP coupling agents. At the combination of fiber mercerization with coupling agent application, the critical fiber length would be decreased, particularly. This is very important for use of natural fibers because of the existing high number of fiber failures.

For studying the fiber-matrix adhesion separately, we investigated the transverse tensile strength of the UD laminates (matrix dominant property of the composite). Results of these measurements are given in Table IV. It was shown that the transverse tensile strength is hardly influenced by a single NaOH treatment of the fibers (i.e., that the mercerization treatment does not lead to a change of the fiber-matrix adhesion within a PP matrix). Moreover, it can be concluded from the results of tensile tests across the fiber grain that the maximum efficiency of the MAH-PP coupling agent depends little on the preceding NaOH treatment.

Measurements of the longitudinal and transverse strength were performed also with UD hemp-PP composites prepared with untreated fibers and with fibers finished with coupling agents solely (Table V). The tensile strength values of the composites are increased remarkably in the transverse direction as expected from the results of flax-PP composites (Table IV). However, with the hemp-PP compounds, we did not find any improvement of the lengthwise strength [σ_1] by the application of coupling agents, which does not correspond to the results of the flax-PP composites and earlier results of jute-PP composites.[8]

Nevertheless, the investigation of the tensile strength lengthwise and across the fiber grain clearly shows that, by the use of hemp fibers treated with MAH-PP copolymers, the fiber-matrix adhesion within these composites results in similar effects as with the flax-PP composites.[1]

The increase of the transverse tensile strength (across the fiber grain) is clearly more pronounced than with the flax-PP composites. The lengthwise tensile strength of the hemp-PP composites, however, remained constant.

The significantly different results of the effects of the MAH-PP coupling agents on the flexural strength and transverse tensile tests (across the fiber grain) between the flax and hemp-PP composites must be explained, among other factors, by the different failure mechanisms for the tensile, compression, and shear stresses of the two types of fibers with different finenesses and fiber processing.

CONCLUSION

The influence of a mercerization treatment on the structure and properties of bast fibers was studied systematically with hemp yarn. By using flax and hemp fibers, the effect of fiber pretreatments (mercerization, application of MAH-PP coupling agents) on the properties of unidirectional EP and PP model composites was investigated.

The structural conversion of the fibers (lattice transition from cellulose I to cellulose II) and the mechanical properties (tensile strength, tension modulus, elongation at break) can be affected in a broad range by using appropriate mercerization parameters (shrinkage, fiber stress, NaOH concentration, temperature, and duration of the treatment). The fiber stress generated by shrinkage turns out to be most important for controlling the fiber properties. For example, by an isometric mercerization procedure, the tensile modulus was increased by about 45% with a slightly reduction of the elongation at break. Moreover, the mercerization procedure affects the fibers' surface structure, thus contributing to an improved fiber-matrix adhesion.

The application of mercerized hemp fibers in unidirectional EP composites shows that the mercerization parameters influence the properties of the composites significantly. By using suitable mercerization parameters, the flexural modulus of the composites can be increased to $\approx$ 100% and the flexural strength can be increased to $\approx$ 45%, which is superior to the increase of the fiber properties by the mercerization. The stronger effect of the mercerization found in the composites as compared to the fibers may be explained by different gauge lengths of the mechanical measurement of the yarn according to the standards and the composite

TABLE V
Influence of Different Fiber Treatments to the Lengthwise σ_1 and Transverse Tensile Strength σ_2 of Unidirectional Hemp-PP-Composites

Fiber treatment	σ_1 (N/mm^2)	σ_2 (N/mm^2)
Untreated	125	8.2
MAH-PP[a]	122	14.6

Note. Fiber content: 35 vol %.
[a] 0.5% Licomont AR 504 in toluene, 10 min.

with a gauge length near to the critical fiber length on the one hand, and by the affected surface structure and thus changed interface adhesion on the other hand.

The use of mercerized and MAH-PP-treated flax in PP composites leads to a significant increase of the flexural strength up to 90% at the lengthwise tested unidirectional specimens. Tensile tests across the fiber grain demonstrated the influence of the MAH-PP-coupling agents with a tensile strength enhancement of about 50% by the application of coupling agents as compared with the untreated and mercerized fiber composites, which did not differ remarkably. As compared with the flax-PP composites, with hemp-PP composites, remarkable differences with regard to the reinforcing effects were found. Across the fiber grain of the composite with MAH-PP-treated hemp yarn, the transverse tensile strength shows an increase of about 75%; however, the lengthwise tensile strength is similar to composites with untreated fibers.

In addition, the testing length of the specimens used in flexural tests is also shown to be significant. This leads to the conclusion that the determination of the effective properties of natural fibers with regard to the reinforcement of composites must be considered as an open problem. To standardize the testing of fibers and make assessments more objective, the use of unidirectional natural fiber epoxy resin composites that have to be prepared according to an appropriate method may be suggested as a first step.

In summary, the tests demonstrated that by optimizing the fiber structure as well as its surface the already known disadvantages of natural fibers and natural fiber composites such as an insufficient fiber-matrix adhesion or a sometimes insufficient tensile or flexural strength could be debugged in most cases. By using the technique of mercerization, the fiber properties can be homogenized and controlled in a broad range. However, not only the improvement of the fiber modulus and strength is important, but also a decrease of the fiber stiffness and thus a higher elongation at break to achieve advanced composites' impact properties (crucial for automotive), should be considered for technical applications.

The authors acknowledge the support provided by the Agency of Renewable Resources (FNR), Gülzow, Germany and the Federal Ministry of Consumer Protection, Food, and Agriculture (BMVEL), Berlin, Germany. We thank the following companies for the generous supply of the materials: Ciba Spezialitätenchemie Pfersee GmbH, Langweid a. Lech, Germany, Clariant GmbH, Gersthofen, Germany, Stamylan Deutschland GmbH, Düsseldorf, Germany, J. Schilgen GmbH & Co., Emsdetten, Germany.

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