

Improvement in Impact-, Tensile-, and Dynamic Properties of Injection Molded Wheat-Pulp-Polypropylene Composites Through Fiber Finishing

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ABSTRACT: This study was focused on the improvement of mechanical properties of injection molded wheat-pulp polypropylene (PP) composites through fiber surface modifications. Ten different sizing and finishing agents, including fats, starch derivatives, and polysiloxanes were used as surfactants for the cellulosic pulp. As a result of polydimethylsiloxane treatment (0.3 wt %), impact strength was increased by 85%, tensile strength by 23%, and an augmentation in tensile modulus of 12% was also achieved. In consideration of the dynamic mechanical properties, the stronger effects of the modifiers on the

storage-modulus were observed with increasing temperature. A new approach quantifying the extent of the dispersion of the pulp fibers using image analysis through transmission light micrographs was tested. The enhancement of tensile strength, tensile modulus, and impact strength could be attributed to the improved dispersion of the cellulosic fibers. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2697–2707, 2011

Key words: biofibers; poly(propylene); surfactants; compatibility; imaging

INTRODUCTION

The use of natural fibers as reinforcements in polymers offers many advantages over conventional reinforcements like glass- or carbon-fibers. These include renewable resource origins, low densities, high specific properties, and less machine wear during thermal processing.^{1–3} Cellulosic reinforcements which are originated from agricultural residues provide improved cost effectiveness. Wheat straw exists in the waste streams of commercial crop processing plants and has little inherent value.⁴ Moreover, the unique physical structure of wheat straw makes it an excellent candidate for fibers and fillers in structural composites.⁴ Many studies on the preparation and evaluation of thermoplastic composites filled with lignocellulosic materials from wheat straw have been carried out.^{5–11} Most of these studies used lignocellulosic material or partially purified and fibrillated cellulose from wheat straw as reinforcement in composites. To the best of the author's knowledge, no literature exists related to composites reinforced with commercially available Kraft pulp extracted from wheat straw.

Cellulosic fibers, however, are distinguished by hygroscopicity, because they contain polar hydroxyl groups. Thus, incorporation of cellulose into hydrophobic-nonpolar polyolefins results in poor interfacial fiber–matrix adhesion. A very simple and effective way to solve this contradiction is the addition of suitable polyolefins, which are grafted with maleic anhydride.^{12,13} Further methods, which are used to improve the performance of composites, are based on surface treatments of the fibers. These include isocyanates, silanes, fatty acids, and silicone oils.^{1,3,14–16}

Although the adhesion between hydrophobic matrices and hydrophilic fibers can be easily improved by the use of coupling agents, there are still some additional drawbacks associated with the use of cellulosic fibers as reinforcements. Due to their low thermal resistance, the choice of suitable matrices is limited. In addition, limitations for the use of cellulose-fibers as reinforcements in composites for structural applications may arise from their tendencies to agglomerate and adhere. This is especially true for pulp fibers. They are designed to develop strong adhesive forces between each other to achieve high-paper strengths. The occurrence of fiber agglomerations in a composite impedes the ability of the matrix to wet and enclose the fibers. In consequence, the stress transfer from the matrix to the stronger fibers is restricted. An even distribution of single fibers could reduce the formation of stress concentrations¹⁷ and hence, the occurrence of

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predetermined breaking points. High shear processing, which enhances dispersion, may damage cellulosic reinforcements by reducing their lengths and thereby reducing the advantage of fiber reinforcement.^{18,19}

Additives, which are traditionally used by the textile industries to facilitate manufacturing and improve the performance of natural fiber based products, are agents for fiber sizing and finishing.²⁰ Before processing, sizing agents are applied to impart strength and smoothness to the textile fibers. These aids are removed after manufacturing. Fiber finishes are used to increase the final performance. They are tailor made for antipilling, crease-proofing, shrink-proofing, anti-swelling, soil releasing and softening. Numerous chemicals such as silicone oils, polyamides, polyurethanes, phyllosilicates, and quaternary ammonium-bases, among others²⁰ are used for these purposes.

This study focused on the improvement of the mechanical, thermal, and physical properties of wheat-pulp polypropylene (PP) composites through the enhancements of fiber dispersion and fiber strength as a result of the application of different chemically surfactants. Pulp fibers were chosen as thermoplastic reinforcements because of their greater thermal stability compared with lignocellulosic fibers.¹⁰ This was attributed to the higher onset of degradation temperature of cellulose compared with lignin and hemicellulose.¹⁰ In addition, the total removal of volatiles as waxes or extractives might contribute to a reduced formation of voids during thermal processing.²¹

The theories and hypotheses forming the basis of these experiments were H1: The shear forces which are generated in the extruder during processing are supposed to be insufficient in achieving a homogeneous dispersion of the pulp fibers. This assumption is based on the fact that pulp fibers are strongly compacted through press operations and develop strong adhesive forces between each other. Proper selection of surfactants could smooth the fiber surfaces and thus reduce their ability to mechanically interlock. In consequence, the separation and disentanglement of cellulose fibers from the pressed pulp flashes should be alleviated and a homogenous dispersion of the cellulose fibers achieved.

H2: The treatment of cellulose fibers with hydrophobizing agents should minimize repulsions between hydrophilic fibers and hydrophobic matrices during melt processing. This could contribute to an upgrade of strong fiber–matrix interfaces.

H3: An upgraded fiber dispersion could enhance stress transfer mechanism due to better encapsulations of the fibers by the matrix and an increase in fiber surface area. In addition, stress concentrations could be minimized by homogenous fiber dispersion. In consequence, tensile and impact strengths should be increased.

H4: An improved fiber dispersion can in principle increase the thermal protection of the fibers provided by the more heat resistant matrix. Thus, the mechanical performance at higher temperatures could be improved.

For this study, the compatibility of the finishing agents to the wheat pulp was evaluated through impact, tensile and dynamical testing of each of the resulting composites. An approach to quantify the degree of fiber dispersion through image analysis of optical micrographs was performed. The relationships between the dispersion of fibers and the improvement in mechanical properties were determined through Pearson correlations.

MATERIALS AND METHODS

Materials

The wheat-pulp was provided as flash [Fig. 1(a)] by the Delfort group AG, Traun, Austria. The basic recipe of the composite was composed of 30 wt % pulp, 67 wt % of the high-flow PP 222CC50 (Ineos Polyolefins, Brussels, Belgium), and 3 wt % of the coupling agent Scona TPPP 8112 FA (Kometra GmbH, Neugattersleben, Germany).

Ten different chemicals composed of carbohydrates, fats, and silicones were selected for fiber finishing (Table I).

The agents were applied to the fibers in concentrations of 0.3 and 0.15 wt % based on the dry substance of the composite. Modified and untreated fibers were mixed at an adjusted moisture content of 60 wt % in the laboratory kneader IKA-Duplex HKD-T0.6D for half an hour [Fig. 1(b)]. Fiber preparation with the water-insoluble diisotridecyl adipate (G) was performed by addition of ethanol (Roth; 60%) as a solvent. Due to a new supply of raw material, a modification using the lower concentrations (0.15 wt %) of the modifiers H to J had to be processed in a second run. All of these samples, including the new reference, were marked with an asterisk. After chemical treatments, the cellulose fibers were dried in a Heraeus UT 6120 circulating air oven at 80°C for approximately 24 h.

To advance mixing, the PP granules were milled with a Dreher S26/41GFS cutting mill to pass through a 3 mm screen. Mixing of all components was performed in the laboratory kneader for 10 min.

Processing

Compounding of the cellulose-PP composites was carried out on a Collin ZK 25 counter rotating twin screw extruder. The screw had a length to diameter ratio of 18 and was equipped with two shear generating elements. The barrel temperatures of the extruder

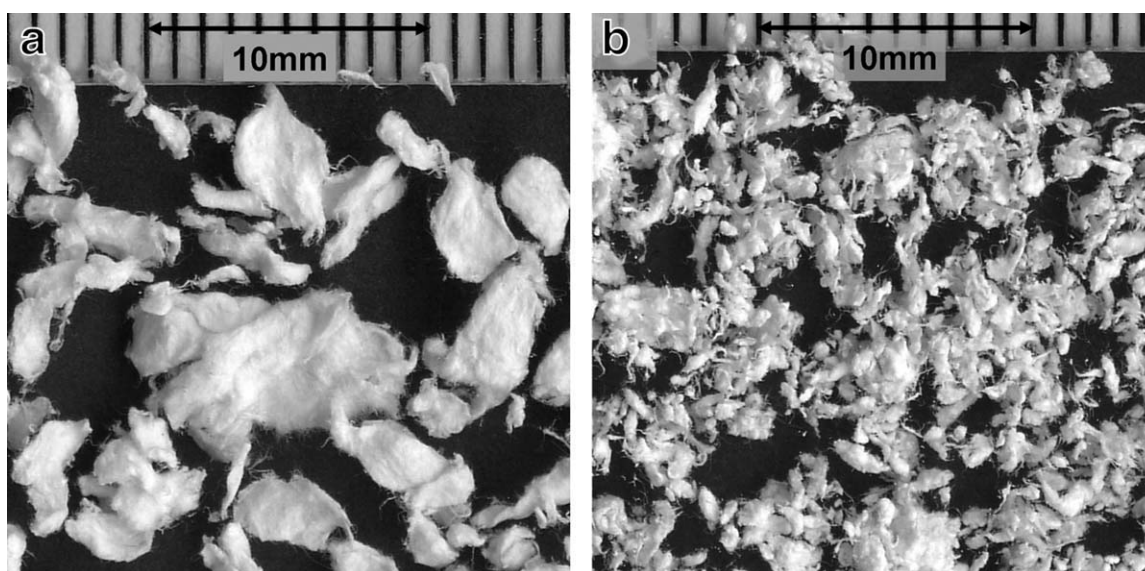


Figure 1 Wheat pulp as delivered (a) and slightly opened fiber bundles after treatment (b).

were set to 80°C in the feeding section, to 180°C in the succeeding two heating zones and to 160°C in the die. The rotation speed of the screw was adjusted for all recipes to 160 rpm, to enhance feeding of the bulky, cellulosic flakes. The resulting strands had diameters of 4 mm and were cut by use of a Rieter Primo 100 granulator to a length of approximately 5 mm.

Before injection molding, the granules were dried at 70°C for a total of 14 h. Manufacturing of the tensile test bars (ISO 527; model 1A) was performed by a Battenfeld HM 60/210 injection molding machine which was equipped with a test bar tool according to ISO 3167. The standard screw had a diameter of 30 mm and a length to diameter ratio of 22. The barrel temperatures were adjusted to 185°C in the metering section and to 190°C in the consecutive

three heating zones. The mold was tempered at 30°C. A dwell pressure of 70 MPa was used during a pressure holding time of 6 s. The back pressure was adjusted at 5 MPa, the change over point was settled to 7 cm³ and an injection speed of 30 mm/s was used for all recipes.

Microscopy

Transmission light microscopy and image analysis

Optical microscopy was used to investigate the aspect ratio of the cellulosic fibers and to quantify the degree of fiber dispersion in each of the wheat-pulp composites. The images were taken with an Olympus CKX41 microscope which was equipped with a mmi-DX a204cF-K07 cell camera. Measurements of

TABLE I
Chemical Composition and Recommended Applications of the Selected Modifiers

Finish	Company	Description ^a	Applications ^a
A	Wacker Chemie ^b	Nonionic/anionic silicone resin oil in water emulsion	Care products, release agents
B	Wacker Chemie ^b	Waterthinable emulsion of polysiloxane-functional silicone resin	Masonry water repellents, anti-blocking agent
C	Agrana ^c	Esterificated polysaccharides	Sizing agent for textiles
D	Wacker Chemie ^b	Alkyl-modified polysiloxan	Care products (polishes)
E	Wacker Chemie ^b	Silicone wax	Skin protection, skin care
F	Wacker Chemie ^b	Silane/siloxane microemulsion	Masonry water repellents
G	Peter Greven ^d	Diisotridecyl adipate	Lubricant for high temperature applications
H	Wacker Chemie ^b	Nonionic, aqueous emulsion of a silicone wax	Polishes sector
I	Wacker Chemie ^b	Polydimethylsiloxane dispersed in water	Release agent for ironing aids
J	Clariant ^e	Cationic distearyl dimethyl ammonium chloride	For softener formulations

^a According to the companies.

^b Wacker Chemie AG, München, Germany.

^c Agrana Beteiligungs-AG Holding, Vienna, Austria.

^d Peter Greven Fett-Chemie GmbH & Co.KG, Bad Münstereifel, Germany.

^e Clariant AG, Muttenz, Schweiz.

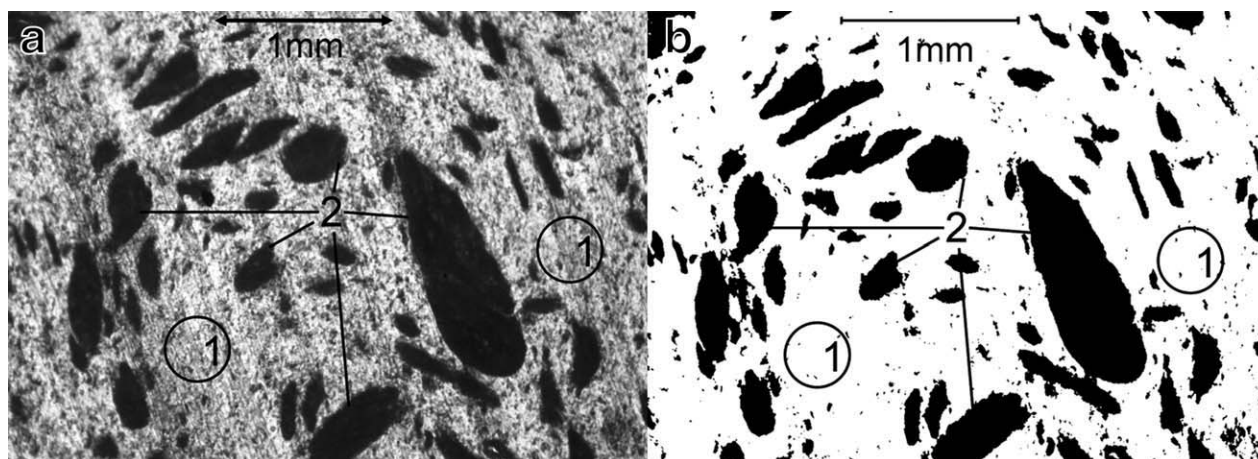


Figure 2 Image analysis of fiber dispersion through converting of transmission light micrographs (a) to monographs (b); 1: Polypropylene- matrix with dispersed fibers. 2: Agglomerations of cellulosic pulp which appear as black particles.

lengths, diameters, and sizes of the fiber agglomerations were performed with the image-analysis software Scion Image Alpha (version 1.3). This was carried out before compounding. The fiber lengths of 300 fibers were measured on micrographs with a magnification of $4\times$. A magnification of $20\times$ was used to determine the diameters of the fibers.

Cross-sectional micro-slices of $40\text{-}\mu\text{m}$ thickness were cut from the test bars with a Reichert 15182 sliding microtome. Subsequently, the slices were dyed with ink and finally washed in distilled water. Micrographs were taken at a magnification of $4\times$. The optical micrographs [Fig. 2(a)] were converted to monographs [Fig. 2(b)]. All areas of fiber agglomerations which exceeded $3000\ \mu\text{m}^2$ were measured and the agglomerations per % unit area were isolated for analyses. Six pictures or $65\ \text{mm}^2$ of cross-sectional area were analyzed by automatic image analysis for each specimen.

Scanning electron microscopy

Scanning electron microscopy was used to investigate fracture mechanism. The fracture surfaces of certain composites were sputter coated with gold by use of an Edwards Scancoat Six Sputter Coater. These surfaces were observed with a Phillips XL 30 environmental scanning electron microscope (ESEM) in the high vacuum mode with an acceleration voltage of 10 and 5 kV.

Tests and analyses

After 2 weeks storage at a standard climate (23°C , $50\%\text{r.H.}$), tensile properties (ISO 527) were determined by use of a UPM Frank 81816 universal testing machine. The Charpy impact strength of the samples was tested using a Frank 53303 impact testing machine (7.5J-pendular) according to ISO 179/1fU.

The dynamic mechanical properties of the untreated references and of all composites, modified with concentrations of 0.3 wt % surfactants, were analyzed by use of a Netzsch DMA 242 C. The specimens were subjected to a heating process at an increasing temperature rate of $3^\circ\text{C}/\text{min}$ from -50 to 150°C . The dynamic flexure was determined at a frequency of 1Hz. The values at 25°C and 100°C of the storage modulus (E') were selected as results.

Data were analyzed with the program SPSS 11.5 and tested for normality, using Kolmogorov-Smirnov tests. The relationships between fiber dispersion and mechanical properties were determined using Pearson-correlations. The averaged values were calculated for all correlations.

RESULTS AND DISCUSSION

Morphological characterization

The dimensions of reinforcement determine its capability of contributing its properties to the composite.²² A reinforcement exhibiting a long dimension discourages the growth of incipient cracks normal to the reinforcement that might otherwise lead to failure.²² On the basis of this concept, the wheat pulp used in this study was distinguished by an average fiber diameter of $8\ \mu\text{m}$ and an average aspect ratio around 48. The aspect ratios obtained by Panthapulakkal et al.¹⁰ through mechanical and chemical processing of wheat straw were around 20 and 35. The high aspect ratio of the commercial wheat-pulp fibers suggested a high reinforcing and strengthening potential for these pulp fibers.

Beside the geometry of the reinforcement, the mechanical performance is also strongly influenced by the dispersion and uniformity of a composite. Stress is assumed to be transferred from the matrix to the fiber by a shear transfer mechanism.²³ It can be

concluded that achieving high mechanical strength in a composite requires a strongly formed interface. Clustering of fibers impedes the ability of the matrix to wet and infiltrate the fibers. This results in poorly bonded fibers and voids in the composite and the reinforcing potential of long fibers cannot be resourced.

The effects of the concentrations and type of modifier on the dispersion of the pulp fibers were determined by use of transmission light micrographs. This method was chosen because it enabled a rapid and cost-effective evaluation over large areas. Nearly all of the surfactants used enhanced the separation and dispersion of cellulose fibers (Table II). With few exceptions, the higher concentration of the surfactants appeared to be more effective in homogenizing the composites. Figure 3(a–d) display optical micrographs of the untreated as well as of some of the modified pulp-composites. Numerous large fiber agglomerations, which appear as dark particles, are seen on the micrograph of the untreated pulp fiber composite [Fig. 3(a)]. The best uniformity of the wheat cellulose pulp was achieved using polydimethylsiloxane-treatment (I) in a concentration of 0.3 wt % [Fig. 3(d)].

Impact properties

The impact resistance is the sum of the energies required to produce fracture initiation, fracture propagation, bending of the sample, production of vibration, friction loss in the arm bearing and on the surface of the sample after failure.²⁴ Debonding, pull-out, and fracture of the fibers are the three mechanisms of energy absorption during impact.²⁵ This energy depends on various factors like toughness of the matrix and the fiber itself, defects in the packing of fiber/matrix and crystalline morphology, among others.²⁶ The effect of the fiber–matrix interface on the impact strength seems to depend strongly on the fibers and matrices used. In some cases, an optimized interface between the fibers and the matrix through the use of compatibilizers or coupling agents can improve the toughness of natural fiber composites.^{13,27,28} Other studies suggest that a higher level of fiber–matrix adhesion generally lead to a lower level of impact strength.^{25,29}

The effects of the surfactants on the impact strength of the cellulose-PP composites were summarized in Table III. With exception of the silicone resin oil in water emulsion (A), considerable increases in impact performance could be achieved by use of all of the surfactants. This was primarily attributed to the enhanced dispersion of the fibers. A significant correlation ($r_p = -0.71$, $P = 0.00$) was determined between the agglomerations per unit

TABLE II
Agglomerations Per Unit Area as Results of the Image Analysis of Treated and Untreated Wheat Cellulose Polypropylene Composites, Including the Percentage Change ($\Delta\%$) Related to the Unmodified References

	Agglomerations per unit area in % ^a			
	Untreated	Untreated*	Untreated	Untreated*
			33,34	34,05
Agent	0.15 wt % % ^a	Finish $\Delta\%$ ^b	0.30 wt % % ^a	Finish $\Delta\%$ ^b
A	22.2	–33	26.9	–19
B	9.0	–73	6.9	–79
C	19.3	–42	22.9	–31
D	14.9	–55	13.2	–61
E	17.9	–46	15.8	–53
F	22.9	–31	11.3	–66
G	27.0	–19	20.3	–39
H	16.6*	–51*	13.7	–59
I	8.6*	–75*	5.7	–83
J	14.5*	–57*	10.0	–70

^a Values, obtained in the second run, are marked with an asterisk.

area and the improvement in impact strength [Fig. 4]. The highest impact value was achieved by use of the polydimethylsiloxane surfactant (I) in a concentration of 0.3 wt %. The fracture surface of this composite as compared with that of the unmodified reference is seen in Figure 5.

Lower magnification of the fracture surface of the reference-compounds [Fig. (5a)] revealed the presence of large areas of fiber agglomerations [Fig. 5(a-2)]. The higher magnification micrograph displayed insufficient wetting of the fibers due to the presence of agglomerations [Fig. 5(c-2)]. Scattered fibers [Fig. 5(c-1)] indicate acceptable compatibility between the PP matrix and the wheat-pulp fibers. Broken fibers and well formed interfaces were seen on both images [Fig. 5(a,c)]. These prove the efficiency of the selected coupling agent. The overview micrograph of the composite treated with 0.3 wt % dimethylsiloxane clearly demonstrates the predominance of single distributed fibers [Fig. 5(b-1)]. Higher magnification of this fracture surface reveals also sufficient bonding between the fibers and the PP-matrix. Most of the fibers are broken in one plane with the matrix or strongly enclosed by the matrix [Fig. 5(d-3)]. Only a few, slightly longer fibers with smooth fiber surfaces were seen on this picture [Fig. 5(d-4)].

The concentration required to achieve the highest increase in impact strength depended strongly on the type of modifier. In some cases, the lower concentrations of surfactants were found to be barely adequate for smoothing and separating the cellulosic fibers (see Table II). Examples include those modified with silicone wax (E), silane/siloxane microemulsion (F), and

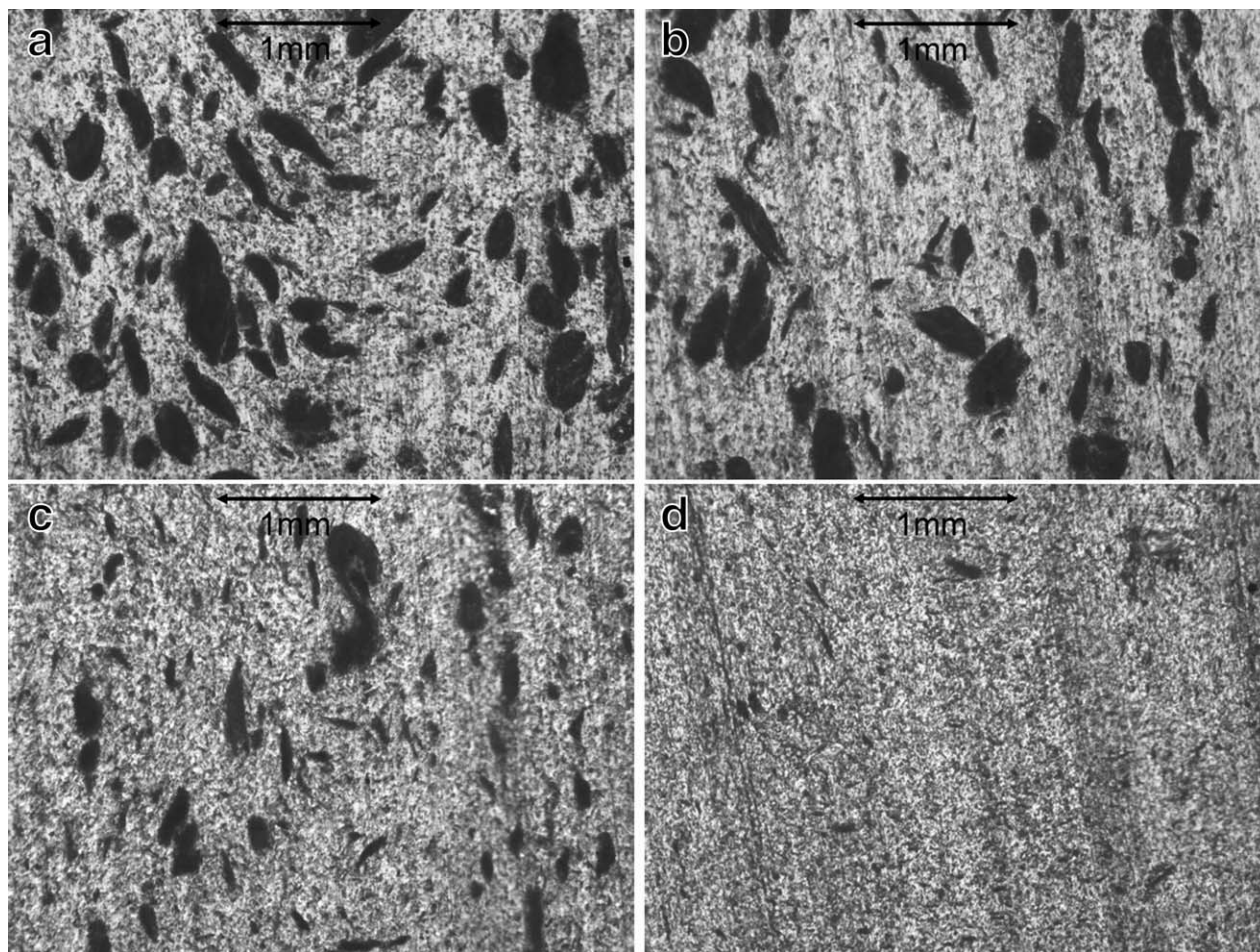


Figure 3 Cross-sectional, transmission light micrographs of some pulp fiber composites. (a) Untreated reference with numerous fiber agglomerations (34% agglomerations per unit area). (b) Treatment with esterificated starch (Table I-C) in a concentration of 0.3 wt % (23% agglomerations per unit area). (c) Treatment with silicone wax (Table I-E) in a concentration of 0.3 wt % (16% agglomerations per unit area). (d) Treatment with polydimethylsiloxane (Table II) in a concentration of 0.3 wt %.

TABLE III
Charpy—Impact Strength of the Modified and Untreated Cellulose Composites, Including the Percentage Change ($\Delta\%$) Related to the Unmodified References

	Unnotched Charpy impact strength in kJ/m^2 ^{a,b}			
	0.15 wt % Finish		0.30 wt % Finish	
Agent	kJ/m^2 ^{a,b}	$\Delta\%$	kJ/m^2 ^{a,b}	$\Delta\%$
Untreated	12.9 (1.41)			
Untreated*	20.8 (4.10)*			
A	12.3 (1.18)	-5	13.2 (0.89)	3
B	19.6 (2.26)	52	15.1 (1.31)	17
C	17.1 (2.30)	33	14.5 (2.26)	12
D	17.6 (2.76)	37	17.5 (2.13)	36
E	16.4 (1.88)	27	18.0 (2.56)	40
F	15.4 (1.38)	19	17.8 (2.15)	38
G	14.6 (1.80)	14	15.3 (1.82)	19
H	25.8 (1.54)*	19*	19.0 (2.03)	48
I	26.6 (2.66)*	28*	23.9 (3.48)	85
J	24.5 (2.80)*	18*	18.9 (2.45)	47

^a Standard deviation of the measurements is shown in parentheses.

^b Values, obtained in the second run, are marked with an asterisk.

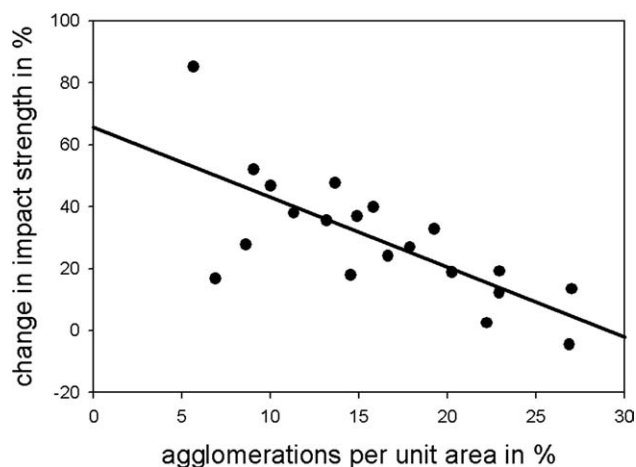


Figure 4 Relationship between improvement of impact strength and fiber dispersion, expressed by means of the agglomerates/unit area.

diisotridecyl adipate (G). The results of the impact tests which were obtained with the samples modified with the polysiloxan/functional silicone resin-emul-

sion (B) were unexpected. Higher impact strength was determined for the samples modified in the lower concentration, although the dispersion of the fibers was found to be more uniform in the case of the applied higher concentration.

Electron micrographs of the fracture surfaces of these composites were presented in Figure 6. The lower resolution micrograph of the composite modified with the lower concentration of polysiloxan/functional silicone resin displayed many fiber agglomerations [Fig. 6(a-2)]. Some singly dispersed fibers [Fig. 6(a-1)] were broken without jutting out of the matrix, indicating well formed interfaces. The modification in the higher concentration resulted in a more uniform fiber dispersion [Fig. 6(b)]. Unfortunately, a great number of smooth fiber surfaces [Fig. 6(b-4)] and fiber pull-outs [Fig. 6(b-5)] were found in this image as well. Higher resolution images of this composite confirm the formation of mainly weak interfaces [Fig. 6(d)]. In contrast, the high resolution micrograph of the composite, modified in lower concentration, exhibited fibers strongly enclosed and

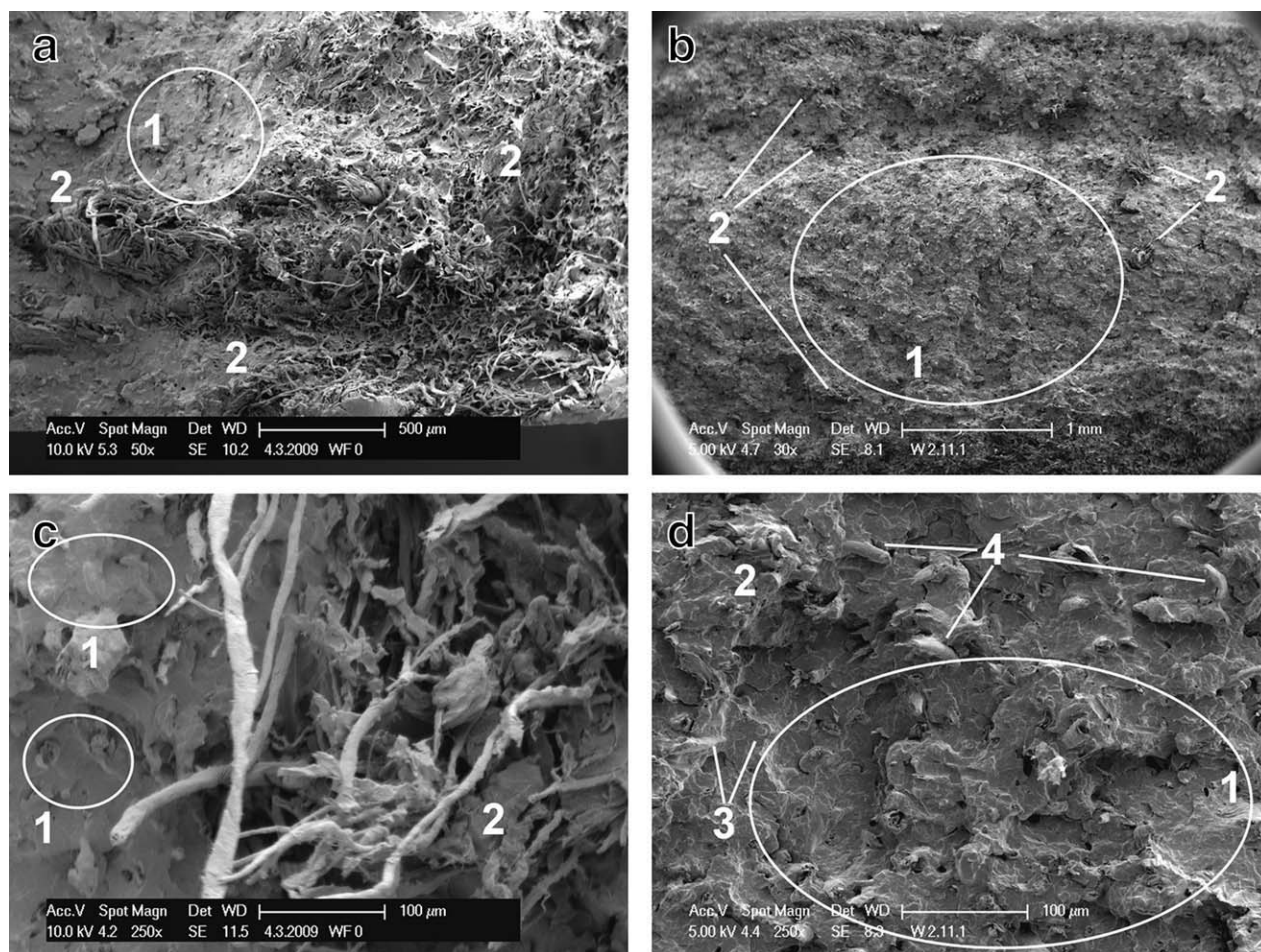


Figure 5 ESEM micrographs of the fracture surfaces of the reference composite (a, c) and the compound modified with 0.3 wt % dimethylsiloxane (b, d); 1: single distributed fibers, 2: fiber agglomerations, 3: strong formed interface, 4: smooth fiber surface.

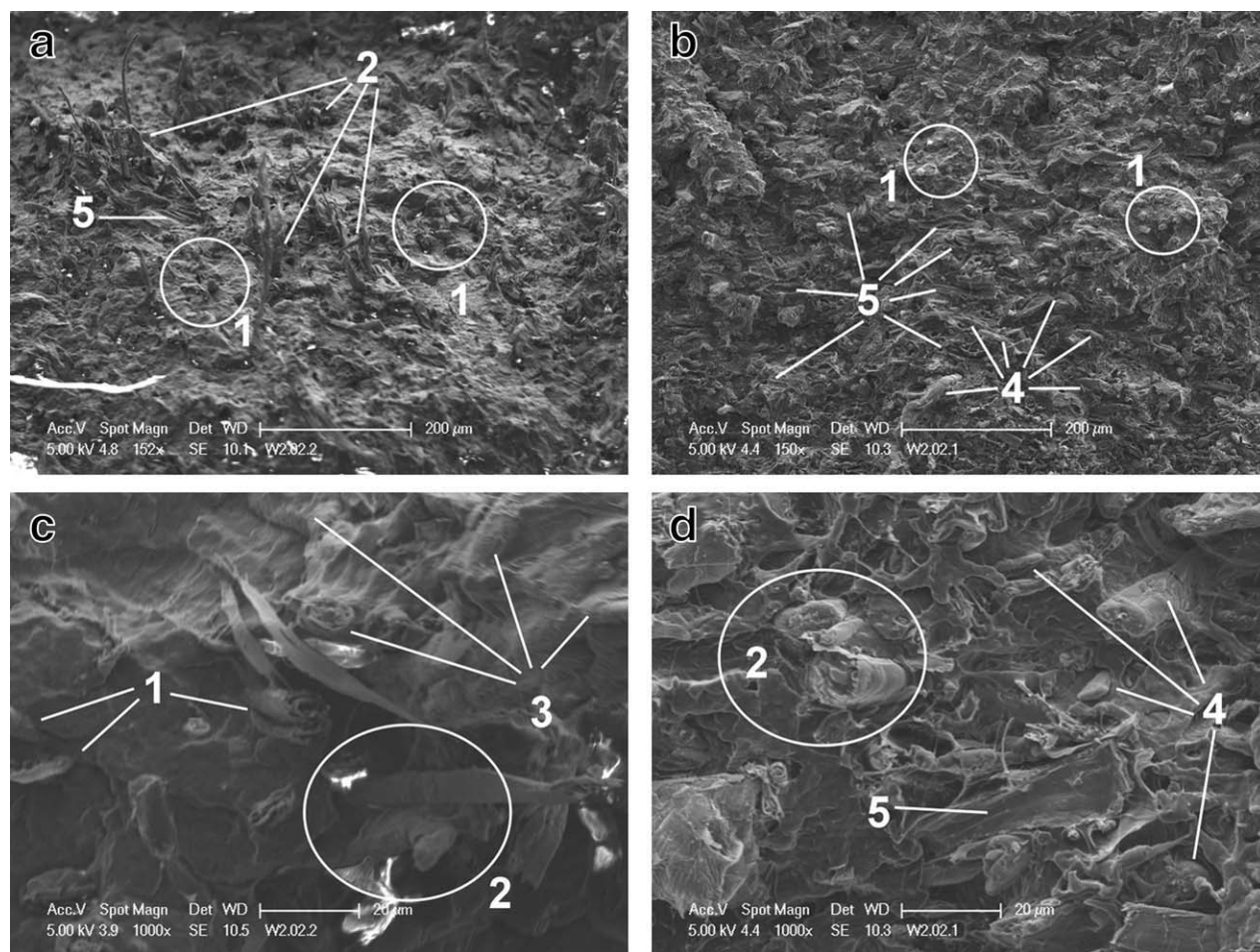


Figure 6 Fracture surfaces of composites, modified with 0.15 wt % (a, c) and 0.3 wt % (b, d) polysiloxan/functional silicone resin-emulsion (Table I-B); 1: single distributed fibers, 2: fiber agglomerations, 3: strong formed interface, 4: smooth fiber surface, 5: fiber pull-outs.

covered by the matrix [Fig. 6(c-3)]. The comparison of the ESEM micrographs clearly demonstrated an impediment of the effectiveness of the coupling agent by using the higher concentration of the polysiloxan/functional silicone resin-emulsion (B). Hence, it can be concluded that an increased improvement in impact strength of these pulp composites required also strongly formed interfaces in addition to the uniform dispersion of the cellulosic fibers.

Tensile Properties

The results of the tensile tests were stated in Table IV. With the exception of the silicone-resin oil-in-water emulsion (A), again, tensile strengths could be increased by use of all other modifiers (B–J). ESEM micrographs (Fig. 7) were used to investigate the failure-mode of the cellulose composite modified with 0.15 wt % silicone-resin oil-in-water emulsion (A). The low resolution micrograph revealed the presence of small, but indeed a large number of fiber agglomerations [Fig. 7(a-2)]. The interface appears to be par-

tially strong [Fig. 7(b)]. Some of the dispersed and broken fibers were closely surrounded by the matrix [Fig. 7(b-1)]. However, there were also many fibers with smooth and clean surfaces [Fig. 7(b-4)] which indicate only poor adhesion between the components.

The improvement in tensile strength through fiber finishing was lower than the achieved augmentation of impact strength. Nevertheless, an improvement of about 25% was achieved by polydimethylsiloxane (I)-treatment and modification with the cationic di-*tert*-butyl-dimethyl-ammonium chloride (J). Highly significant correlations were determined between the change in tensile strength and the agglomerations per unit area ($r_p = 0.80$, $P = 0.00$). This coherence was attributed to the fact that better wetting of fibers occurred in the composites which had a reduced number of agglomerations. This enabled the formation of a stronger fiber–matrix interface. Consequently, the applied load could easily be transmitted to the stronger fibers and strength was then increased. Although, further effects provided by surfactants such as enhanced shear resistance of the

TABLE IV
Tensile Properties of the Modified and Untreated Cellulose Composites, Including the Percentage Change ($\Delta\%$) Related to the Unmodified References

Agent	Tensile strength in MPa ^{a,b}				Tensile modulus in MPa ^{a,b}			
	0.15 wt % MPa ^{a,b}	Finish $\Delta\%$	0.30 wt % MPa ^{a,b}	Finish $\Delta\%$	0.15 wt %	Finish $\Delta\%$	0.30 wt % MPa ^{a,b}	Finish $\Delta\%$
Untreated	33.8 (0.25)				1945 (27)			
Untreated*	31.0 (0.25)*				2010 (31)*			
A	33.3 (0.15)	-2	34.3 (0.13)	1	2039 (22)	5	2071 (25)	7
B	41.0 (0.14)	21	36.9 (0.22)	9	2226 (34)	14	2168 (42)	12
C	37.6 (0.32)	11	34.9 (0.17)	3	2007 (43)	3	1975 (51)	2
D	38.9 (0.16)	15	38.9 (0.20)	15	2151 (31)	11	2137 (50)	10
E	38.0 (0.26)	12	39.4 (0.22)	17	2098 (37)	8	2118 (39)	9
F	37.1 (0.38)	10	40.1 (0.22)	19	1976 (40)	2	1988 (21)	2
G	35.9 (0.24)	6	36.7 (0.18)	9	1892 (38)	-3	1955 (36)	1
H	35.0 (0.29)*	13*	39.2 (0.29)	16	2240 (21)*	11	2096 (85)	8
I	38.7 (0.37)*	25*	41.5 (0.44)	23	2370 (34)*	18*	2175 (47)	12
J	37.6 (0.34)*	21*	42.3 (0.38)	25	2310 (40)*	15*	2228 (255)	15

^a Standard deviation of the measurements is shown in parentheses.

^b Values, obtained in the second run, are marked with an asterisk.

fibers during processing, further improvement of the fiber-matrix interfaces or strengthening of the fibers were not ruled out.

The tensile modulus revealed only marginal increases through fiber modification (Table IV). It is well known, that the incorporation of a second, stiffer component increases the stiffness of the composite above the modulus of the neat matrix.³⁰ The influence of fiber surface modifications on the tensile modulus was investigated at constant fiber contents in this study. In nearly all cases, the modulus was increased. The best results were achieved by using the polydimethylsiloxane-water dispersion (I) and the distearyl-dimethyl-ammonium chloride (J). The

improvement in stiffness was unexpected. These results did not follow a frequent trend where any factor, which enhances stiffness, is harmful to toughness and *vice versa*. Examples include results obtained by a variation in natural filler content,¹⁹ addition of impact modifier,³¹ and use of certain coupling agents.³²

In this study, impact strength, tensile strength, as well as stiffness of the composites were improved through the application of certain surfactants. The enhanced stiffness of the modified composites might originate from improved fiber dispersion. Significant increases in the improvement of the tensile modulus with decreasing agglomerations/unit area were

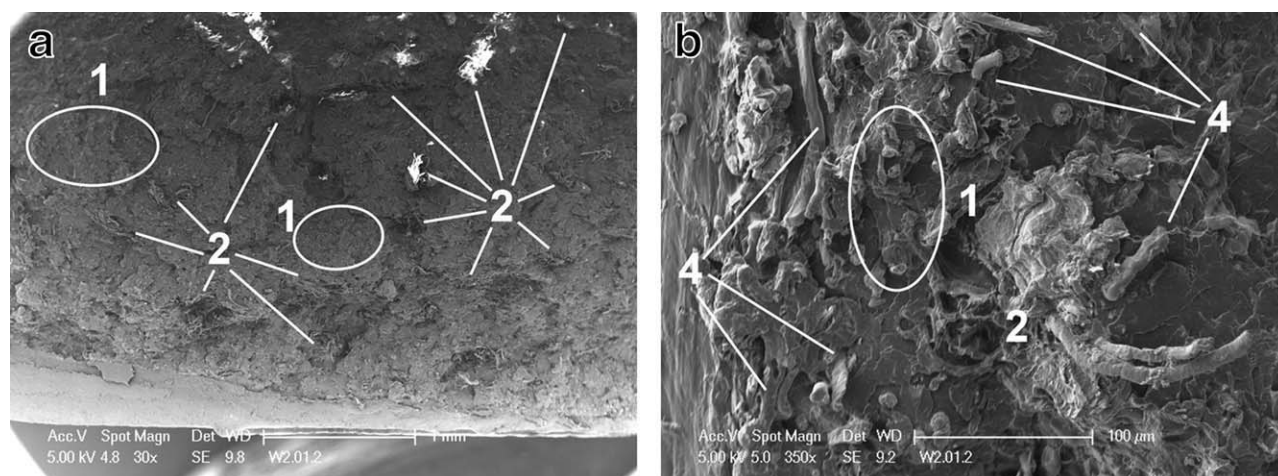


Figure 7 ESEM micrographs of the fracture surface of the fiber composite modified with 0.15 wt % silicone resin oil-in-water emulsion (Table I-A) at low (a) and at high (b) magnification; 1: single distributed fibers, 2: fiber agglomerations, 4: smooth fiber surface.

TABLE V
Storage Modulus at 25°C and 100°C of Untreated and Modified Cellulose Composites, Including the Percentage Change ($\Delta\%$) Related to the Unmodified References

Reference	Storage modulus in MPa			
	At 25°C		At 100°C	
	MPa	$\Delta\%$	MPa	$\Delta\%$
	4601		1099	
A	4818	5	1222	11
B	4927	7	1073	-2
C	4432	-4	1117	2
D	4913	7	1318	20
E	4862	6	1391	27
F	4796	4	1365	24
G	4812	5	1325	21
H	5286	15	1481	35
I	5132	12	1306	19
J	4830	5	1319	20

determined ($r_P = -0.73$, $P = 0.00$). These were attributed to the reduction of voids and air pores which lead to improved stiffness of the composite.¹⁵

Storage modulus

The effects of the surfactants on the dynamic-mechanical properties of the cellulose composites were studied by considering the storage modulus (E'') at 25°C and at 100°C (Table V). The dynamic mechanical analyses (DMA) were performed on the references, as well as on the composites modified with the higher concentrations of the modifiers.

The best improvement in storage modulus at 25°C of around 15% occurred by use of the silicone wax emulsion (H). The enhancements in the dynamic mechanical properties became even more distinct at higher temperatures. At 100°C, the storage modulus increased by 35% through application of the same surfactant. According to Ljungberg et al.,¹⁵ the improvement in storage modulus can be explained by better dispersion, leading to a material with reduced formation of fiber aggregates and thus air pore. Since the increase became more distinct at higher temperatures an increased thermal resistance of the fibers, provided by the surfactants cannot be ruled out either. The results further suggest a more sufficient coating of the sensitive natural fibers by the thermal more resistant matrix.

CONCLUSIONS

Applying different surfactants, particularly polysiloxane-compounds, to cellulose fibers was a simple and cost effective way to enhance impact strength, dynamic strength under flexural load, tensile strength, and stiff-

ness of wheat cellulose composites. In comparison with the enhancement of tensile properties, higher improvements were observed in impact strengths through fiber modifications. The effectiveness in improving the mechanical properties depended strongly on the applied concentration and type of modifier. Impact strength was improved by 85%, tensile strength is increased by 23%, and an augmentation in tensile modulus of 12% was achieved through surface modification with 0.3 wt % polydimethylsiloxane. The strong improvement in several mechanical properties was attributed to an upgraded, uniform dispersion of the cellulose fibers through surface modification. No improvement in the mechanical properties was achieved through fiber modification with the silicone resin oil in water emulsion. In these composites many, albeit small fiber agglomerations were still present and the interfaces appeared to be partially weak.

Further investigations should be carried out to optimize concentrations of the surfactants and coupling agents. The high improvements in the mechanical properties of these wheat-pulp PP composites through surface modification should be verified with the use of different types of fibers and matrices. The transfer of these fiber treatments to use in industrial manufacturing should be initiated.

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