Processing and Properties of Mineral-Interfaced Cellulose Fibre Composites

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ABSTRACT: Polypropylene (PP) or, in some cases, poly (lactic acid) (PLA) were compounded with cellulosic fibres. The amount of fibres used was in the range 10–30 vol % and, in case of PP, a series of compounds was prepared with a minor amount of maleated PP as a compatibiliser. This matrix was denoted MAPP. Before compounding the polymers and the fibres, undelaminated bentonite (industrial scale) or delaminated clay (nanoclay) was deposited on the fibres in different amounts to improve the dispersion of the fibres in the polymer matrix, i. e., to avoid detrimental fibre bundles. The PP-based compounds were either extruded or injection moulded, whereas the PLA-compounds were only injection moulded. The mechanical properties were primarily evaluated for the injection moulded specimens. In general, the fibres had a strong effect on the mechanical behaviour of the materials, especially in the case of PLA and MAPP. Treating the fibres with undelaminated clay or nanoclay improved to some extent the dispersion of the fibres and the mechanical performance of the composites, but further optimization of the function of the mineral in this respect is probably required. The combination of the mineral treatment with a debonding agent appeared to be an interesting route here. With such a combination, a visually very good dispersion of the fibres in the PP-based matrix could be obtained, partly at the expense of the mechanical performance. The compounding of the cellulosic fibres with PP led in this case to a marked decrease in the fibre length. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 918–929, 2008

Key words: biofibres; clay; composites; mechanical properties; processing

INTRODUCTION

As soon as synthetic polymers were introduced into society, combinations with cellulosic materials became available, cf.[1] In some cases, this has been motivated by economic benefits. However, during the last decades or so, there have been numerous studies on how to combine synthetic polymers with cellulosic fibres to take advantage of the inherent properties of the fibres, i. e. to use them as reinforcing elements.[2–7]. There are several reasons for this interest; the fibres are renewable, are available in large quantities, have reasonably good mechanical properties, are not abrasive with regard to the manufacturing tools and so on. Some applications have been successful; an obvious example is laminated structures consisting of paperboard and synthetic polymeric films. The more wide-spread use of cellulosic fibres as reinforcing elements in a thermoplastic matrix has however been hampered by processing problems and the less favourable physical performance of the composites.

Somewhat simplified, there are four problems associated with the incorporation of cellulosic fibres into a thermoplastic material; (a) degradation of the cellulosic material at high temperatures, (b) insufficient adhesion between the fibre and the polymer, (c) the moisture sensitivity of the fibres and d) flocculation of the fibres into bundles or fibre-rich areas. With regard to (a), most thermoplastic processing methods involve shaping the polymer melt at a rather high temperature, often higher than 200–250°C, at which the thermal degradation rate of cellulose can be significant. This limits the possible selection of polymeric matrices and restricts the processing cycle time. The insufficient adhesion between the fibres and the matrix (b) is not easily solved, but improvements can be achieved by surface treatment of the fibres or by modifying the polymer matrix (incorporation of functional groups).[5–8] The moisture sensitivity (c) is generally difficult to deal with, although modification of the fibre or cross-linking of cellulosic fibres,[9] may be possible routes.

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The present work focuses mainly on problem (d), but the others are considered to some extent. When cellulosic fibres in the form of untreated fluff pulp are dry defibered, there are always a small amount of ''knots'' or fibre bundles due to the development of hydrogen bonds between the fibres. This aggregation may be further enhanced during the compounding with the polymer matrix material; it is normally quite difficult to disperse the fibres uniformly in the matrix. Furthermore, fibre bundles in the solid polymer matrix inherently lead to a deterioration in the mechanical performance of the composites or, expressed in another way, the potential advantages of the fibres cannot be fully utilised. In the present work, a potential route involving to some extent nanotechnology to reduce the tendency of the cellulosic fibres to aggregate is evaluated.

There has been a tremendous development in the field of polymer nanocomposites since the pioneering work of Toyota.[10,11] In many cases, layered silicates were employed as the nanoparticles in these composites. To obtain a significant improvement in the mechanical properties of the composites, the silicate layers should be intercalated or, preferable, delaminated, so that individual silicate layers are homogeneously distributed throughout the polymer matrix. Composites containing nanoclay structures of this type may exhibit rather good barrier properties, since the delaminated planar particles reduce the permeability (increases the length of the diffusion path) of the composite.[12]

In the present case, the layered silicates are used in a different way from the polymer nanocomposites. The cellulosic fibres were covered with either nondelaminated or delaminated bentonite (nanoclay in the latter case) by making the cellulosic surfaces cationic followed by deposition of the negatively charged bentonite particles.[13,14] This treatment is expected to block the hydrogen bonds between the fibres to a significant extent, and thus reduce the tendency to form fibre bundles. It is also expected to facilitate the dispersion of the fibres in the polymer matrix without excessive fibre aggregation. Since it has been reported that the thermal stability of polymer composites is improved by using layered nanoclays,[15] it may also be that the covered cellulosic fibres exhibit a better resistance against thermal oxidation, which would be beneficial with regard to the thermoplastic processing at high temperatures. This is not however investigated here.

The polymer used as matrix material in this study was in most cases polypropylene (PP), motivated by its widespread use for technical applications, e. g. in the automotive industry. Some experiments using a biobased polymer, poly(lactic acid) (PLA), were also performed, to produce a composite based on nonfossil materials and biodegradable. The techniques used to produce the mineral-reinforced composites were extrusion and injection moulding, which are the major thermoplastic processing methods in current use.

EXPERIMENTAL

Materials

The reference pulp, obtained in a defibrillated dry form, was Vigorfluff A. This sulphate pulp (from softwood) contained no layered silicates. The pulp treated with sodium bentonite was Vigorfluff S, on which the deposition of the clay particles was facilitated by the use of a retention aid (Alcofix 110, AB CDM, Sweden). Both types of pulp were produced on an industrial scale by Korsnäs AB, Gävle Sweden. When the fibres are treated on the industrial scale, it is not expected that the silicate particles are deposited on the fibres in the delaminated state. The sodium bentonite grade used for the treatment of the pulp was Hydrocol MD (AB CDM, Sweden), and it was used at two different levels. The pulp with the lower amount of clay (0.4 wt %) is denoted CF1 and the other (containing 0.7 wt % relative to the pulp) is denoted CF2.

Delaminated montmorillonite particles (nanoclay) were obtained from the above-mentioned sodium bentonite grade and deposited on the cellulosic fibres in the laboratory as described by Lindström et al.[14] The pulp used in these experiments was Vigorfluff A. This pulp was extracted with acetone to remove extractives, after which the pulp was washed with 0.01*M* HCl in 30 min followed by deionized water, 0.001*M* $NaHCO_3$, and deionized water again. The bentonite was swollen for 24 h in deionised water, disintegrated at a concentration of 4 g/L and finally homogenized in a high-pressure homogenizer, Mini-lab type 8.30H (APV Homogeniser group). The clay was then allowed to settle and a clear aqueous phase (clay concentration 3.8 g/L) was collected and used in the subsequent experiments. The adsorption of the clay particles is described and discussed in detail by Lindström et al.[14] Here it may suffice to state that pulp fibres with different amounts of clay deposited on them were used (0.1, 0.2, 0.5, 1, and 2 wt % relative to weight of the fibres). Using electron spectroscopy for chemical analysis, the corresponding degrees of surface coverage (by the clay) of the cellulosic fibres were estimated, amounting to 4, 7, 18, 36, and 72 %, respectively. These fibres were denoted CF3–CF7.

In one series of experiments, the fibres with 2 wt % delaminated nanoclay were also treated with a debonding agent to further promote the dispersion of the fibres in the polymer matrix. It is known that debonding agents or surface active agents can

change the fibre-to-fibre friction, and thus also promote the disentanglement of the fibre network.[16] In the present case, 5 wt % (relative to the pulp) of a tertiary amine was used.

The PP-grade used as the main matrix material was BC250MO (Borealis A/S, Denmark) with a melt index of 4 g/10 min (MI 230/2) and a density of 904 kg/m^3. In some cases, a maleic-anhydride-grafted PP (Epolene G-3015, Eastman Chemicals BV, Netherlands), density 913 kg/m^3, $\overline{M}_n$ = 24,800 g/mole, $\overline{M}_w$ = 47,000 g/mole and acid number (mg KOH/g) 15, was added as a compatibiliser. In those cases, 5 wt % of the maleated PP was added to the unmodified PP-grade and this modified PP-material is hereafter denoted MAPP. The PLA used was Hycail HM 1010 from Hycail BV, Netherlands with a melt index of 3–8 g/10 min and a density of 1240 kg/m^3. As reference material, a PP-grade containing 20 wt % glass fibres (GB205U, Borealis A/S, Denmark) and with a melt index of 2 g/10 min (MI 230/2) and a density of 1040 kg/m^3 was used (denoted PP-GF).

Compounding of fibres and thermoplastics

The defibrillated pulp was dried at 80°C for 2 h prior to the subsequent processing. After drying, the cellulosic fibres and the polymer (in the form of pellets) were first together blown through a tube loop for 5 min and then manually fed into a Buss co-kneading extruder, PR 46 (screw diameter D = 46 mm and length L = 11D), Switzerland. The barrel temperature was 180°C and the screw speed 24 rpm for both PP and PLA compounds. A cylindrical die was used and the resulting extrudate was cut into pellets. To reduce deviations in fibre concentration due to a possible uneven feeding of the fibres, the pellets where run once more through the cokneader.

Injection moulding

Prior to injection moulding, the compounded pellets were dried at 80°C in an oven. An Arburg Allrounder, 221E/170R, Austria, was used to produce test bars of a dog-bone-shape (DIN 53455) with a gauge length of 70 mm. The barrel temperature was 210–220°C and the mould temperature was 30°C for both PP- and PLA-based materials.

Extrusion

Dried pellets from the compounding were extruded with a Brabender compact extruder; Brabender OHG, Duisburg, Germany, screw diameter D = 19 mm and screw length 25D. The extruder was designed with three individually controlled temperature zones and equipped with a temperature-controlled slit die with variable slit height and a fixed slit width of 100 mm. The temperature of the zone close to the hopper was 195°C and, in the other zones and the die, the temperature was kept at 210°C. The screw speed was 40 rpm. PLA was not used as the matrix material in the extrusion trials.

Prior to any measurement, the specimens were conditioned at room temperature [(23 ± 1)°C] and at a relative humidity of (50 ± 5)% for at least 24 h.

Capillary viscometry

The melt viscosity of the compounded material was measured as a function of the shear rate with a Ceast Rheoscope 1000 6742/00 (Ceast SpA, Pianezza, Italy) capillary viscometer. Three different capillaries with the same diameter (1 mm) but with different length-to-diameter ratios (5, 10, and 40) were used. The measurements were performed at 200°C for both PP- and PLA-based materials and corrections according to Rabinowitsch and Bagley were applied. The results were fitted to a power law equation and the corresponding material parameters K (consistency) and n (flow exponent) were evaluated:

$$\eta = K\dot{\gamma}^{n-1} \tag{1}$$

where η denotes the melt viscosity and $\dot{\gamma}$ the shear rate.

Tensile tests including impact resistance

The tensile mechanical properties, [i. e., tensile modulus, tensile strength—maximum stress of the stress(strain)-curve] and elongation at rupture, were measured according to ISO 527-1 with a Zwick 1455 tensile testing machine, Germany, equipped with free-standing clip-on extensometer with adjustable gauge length. A cross-head speed of 10 mm/min, corresponding to a strain rate of about 2.4 × 10^{-3} s^{-1}, was used for all measurements and the gauge length of the extensometer was 40 mm. The tensile modulus was calculated from data points between 0.05 and 0.25% strain. The measurements were performed at room temperature [(23 ± 1)°C] and at a relative humidity of (50 ± 5)%.

The Charpy impact strength of the tensile test specimens was measured perpendicular to the flow direction under the same conditions as above with a Frank Impact Meter according to ISO 179 with single-notched samples. The specimens were notched edgewise (2-mm deep) in a Ceast 6525 notching machine. Typically, about 10 specimens of the same type were used for evaluating the tensile properties and impact resistance.

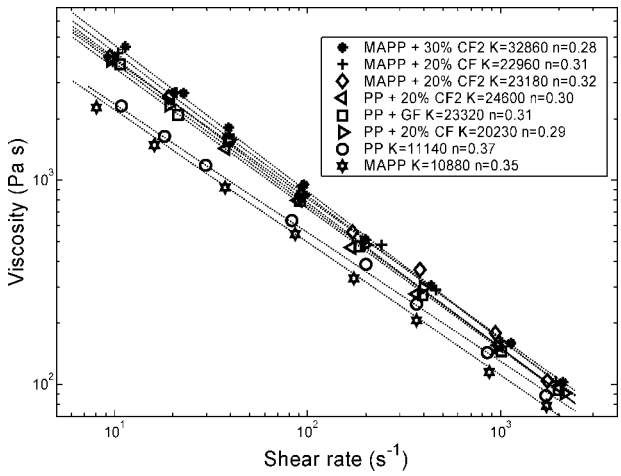

Figure 1 The melt viscosity as a function of the shear rate at 200°C for neat PP, MAPP, PP-GF, and PP containing 20 or 30 vol % treated or untreated cellulosic fibres, with and without compatibiliser.

Fibre length distribution

The fibre length distribution of the virgin pulp as well as of the fibres after processing was determined using a FiberMaster-equipment (Lorentzen and Wettre, Sweden). In the case of the processed material, the PP-matrix was first dissolved in 1,2-dichlorobenzene at 150°C. After washing in acetone and water, the isolated fibres were collected and analysed.

Scanning electron microscopy

Scanning electron micrographs of fracture surfaces of the produced specimens were obtained with a Digital Scanning Electron microscope Zeiss DSM 940, Carl Zeiss, Germany. Prior to the SEM investigations, the surfaces were coated with an ~ 50 Å thick gold layer using a Sputter Coater s150B, BOC Edwards, UK. The fracture surfaces were obtained from the tensile test performed at room temperature.

Differential scanning calorimetry

A power-compensated DSC7 from PerkinElmer, USA, was used to determine the melting points (T_m) of PP and PLA and the glass transition temperature (T_g) of PLA. The temperature was increased from 0 to 200°C at a heating rate of 10°C/min, cooled to 0°C at a rate of 60°C/min, held at this temperature for 2 min, and then increased again at 10°C/min. The transition temperatures were evaluated from the second run. Two samples were evaluated and the average value was reported. The instrument was calibrated against indium before the measurements.

The T_g of PLA, determined as above, was 57°C and the T_m-values were 169 and 148°C for PP and PLA, respectively.

RESULTS

Capillary viscometry

Figure 1 shows the melt viscosity as a function of the shear rate at a temperature of 200°C for some of the different types of reinforced PP used. Only the fibres treated on the industrial scale were employed here and the amount of fibres used was 20 or 30 vol %. All the melts were clearly shear-thinning in the shear rate region covered by the experiments and the corresponding material parameters K and n are given in Table I. The addition of the cellulosic fibres obviously increased the viscosity of the PP-based melts at a given shear rate appreciably and the degree of shear-thinning also became more pronounced, i.e. the flow exponent n decreased. The fibre content, the clay treatment, the use of the compatibiliser and the amount of clay deposited on the fibres obviously had only a small effect on the viscosity curves for the reinforced systems, although there was a tendency for the untreated fibres (at a given volume content) to give the highest viscosity. This may be attributed to a greater tendency for the fibres to flocculate or aggregate.

The addition of the maleated PP to the neat PP did not have any great effect on the dependence of the viscosity on the shear rate, Figure 1. The flow behaviour of the glass-fibre-containing PP was similar to that of the other systems. Addition of the debonder to the treated fibres resulted in a somewhat lower viscosity level at a given fibre content, probably due to a disruption of the fibre flocs, i.e. an improved dispersion, but the effect was not very pronounced.

The neat PLA-melts and the PLA-melts containing 20 vol % CF exhibited viscosity levels similar to those of the neat PP-melt. The addition of the cellu-

TABLE I
The Material Parameters K and n for Some of the PP-Based Melts at 200°C

Material	K (Pa s^n)	n
PP	11140	0.37
PP + 20% CF	20230	0.29
PP + 20% CF2	18520	0.30
MAPP	10880	0.35
MAPP + 20% CF	28640	0.30
MAPP + 20% CF2	23180	0.32
MAPP + 30% CF2	32860	0.28
MAPP + 20% CF, with nanoclay and debonder	22960	0.31
PP + 20 wt % GF	23320	0.31

Fibres treated on the industrial scale.

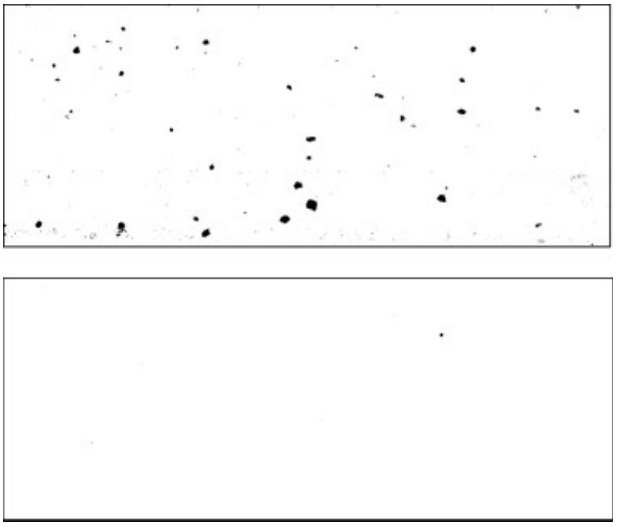

Figure 2 Image-processed illustration of the fibre bundles in extruded PP-sheets containing untreated fibres (upper) and laboratory-treated fibres, with a deposited amount of 20 mg clay/g fibres (lower).

losic fibres thus did not increase the viscosity; in fact it became somewhat lower, which may appear surprising. It could be that the matrix material underwent some changes due to the rather harsh compounding phase. A more detailed study is however required to substantiate this.

Distribution of the fibres in the extruded PP-sheets

The extruded PP-sheets were cut to convenient dimensions, placed on a light table and photographed. Using image processing, the presence of fibre bundles or flocs in the extruded sheets then could be visualised, as illustrated in Figure 2. In this case, the fibre content was 10 vol %. The fibres were treated in the laboratory and the amount of deposited nanoclay was 20 mg/g fibres (2 wt %). Images of the corresponding composite containing the untreated fibres are also included in the figure. The deposition of the clay obviously reduced the amount of fibre bundles in the composite, which is the desired result. Reducing the amount of deposited clay led to a progressive increase in formation of fibre flocs.

Figure 2 represents the best situation achieved with the present experimental set-up. In some cases, pronounced flocculation also occurred with the clay-treated fibres. To some extent, this can be attributed to the manual handling of the fibres during the compounding phase, but it also seemed that the relative humidity of the ambient air during the compounding played an important role. A lower humidity led to a better dispersion of the fibres (in the present case).

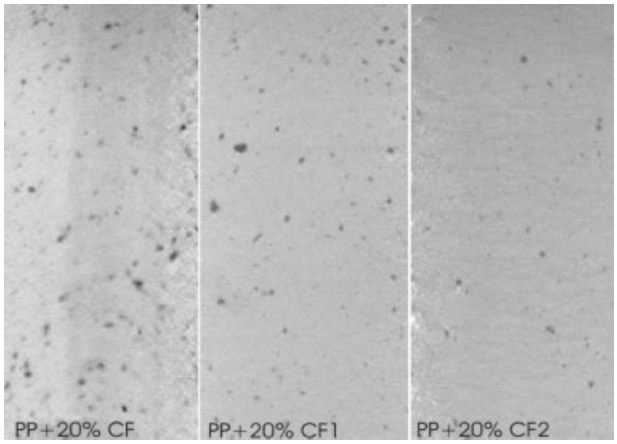

Figure 3 Photograph of the fibre dispersion in the extruded PP-sheets containing untreated fibres (CF) as well as CF1 and CF2. The fibre content was 20 vol % and the width of the extruded sheets was ~ 100 mm.

A similar result was also achieved when the fibres were treated with the nondelaminated bentonite (industrial scale), although the improvement in dispersion was not as pronounced, as shown in Figure 2. To some extent, this can be associated with the lower amount of clay used. Figure 3 is a photograph of the extruded sheets under transmitted light. The fibre content was 20 vol % and untreated fibres as well as CF1 and CF2 were used in the PP-matrix.

The over-all best dispersion according to the visual evaluation was achieved when the fibres were treated with both delaminated clay and debonder, which may not be surprising. Figure 4 shows photo-

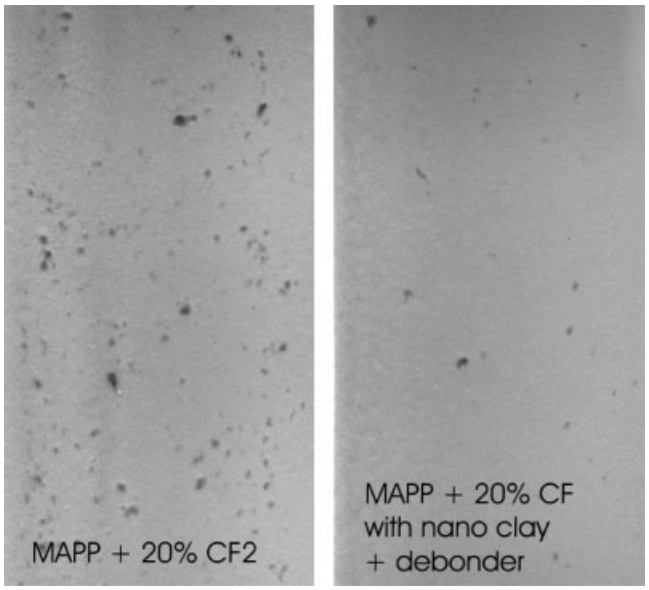

Figure 4 Photograph of extruded MAPP-sheets containing 20 vol % CF2 (left) and 20 vol % cellulosic fibres treated with both delaminated clay (2 wt %) and debonder (right). The width of the sheets was ~ 100 mm.

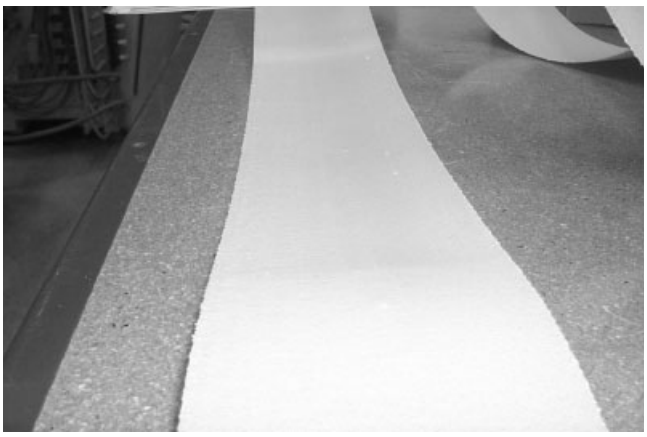

Figure 5 Photograph of a MAPP-sheet leaving the extruder. The fibres were treated with both delaminated clay (2 wt %) and debonder.

graphs of an extruded MAPP-sheet (placed on a light board) containing 20 vol % of fibres treated in this manner as well as a corresponding MAPP-sheet containing 20 vol % CF2. It should be pointed out that, in the latter case there was still a considerable amount of fibre bundles. With this matrix, there were no great differences in the degree of dispersion between untreated (CF) and treated fibres (CF2); there were only indications of fewer and smaller bundles in the latter case.

Figure 5 shows the extruded MAPP-sheet containing the fibres treated with the delaminated clay and the debonder leaving the extruder, after passing through a calender nip. The uniform appearance of the sheet is evident.

Mechanical properties of the composites without any added compatibiliser

Figure 6 presents data for the tensile modulus and tensile strength (the maximum nominal stress that the material can withstand, approximately corresponding to the yield strength). The results shown relate to injection-moulded specimens, but the same general pattern of behaviour was also obtained with the extruded sheets. The matrix used was PP without any added compatibiliser and the specimens were injection moulded into test bars and tested in the flow direction. The modulus of PP increased markedly as expected with increasing fibre content, whereas the effect of the fibre addition on the maximum stress was less pronounced.

Somewhat surprisingly, the clay deposition on the fibres had only marginal effects on the modulus and the maximum stress despite the positive influence on the dispersion of the fibres in the polymeric matrix, cf Figures 2 and 3. One reason may be that, although the fibre distribution was more homogeneous, the stress transfer from the matrix to the fibre elements became less efficient, thus counteracting the benefits of the improved dispersion. This will be commented on more later.

In more or less all cases, the tensile elongation at rupture suffered significantly from the addition of fibres. The unfilled injection-moulded PP had an elongation at rupture greater than 50% whereas, after the fibre addition, it decreased typically to 10% or lower. The composites containing the fibres treated on the laboratory scale exhibited somewhat higher values of the ultimate elongation than those containing CF1 or CF2. The detrimental effect of the fibre addition on the ductility is also illustrated by the impact strength data (notched samples) shown in Figure 7.

The influence of the fibre addition on the mechanical behaviour of the injection-moulded specimens is also illustrated by the stress-strain curves shown in Figure 8. The tensile modulus was clearly improved by the fibre addition; there was also some improvement in the strength, but the elongation at rupture was substantially reduced by the presence of the fibres.

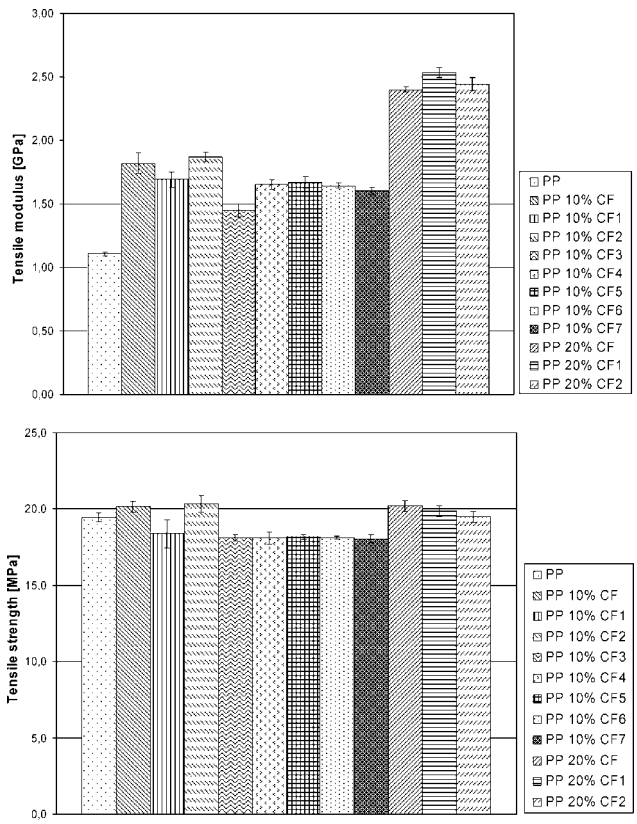

Figure 6 The tensile modulus and the tensile strength of the injection-moulded PP-composites. The properties were measured in the flow direction and the matrix material did not contain any compatibiliser.

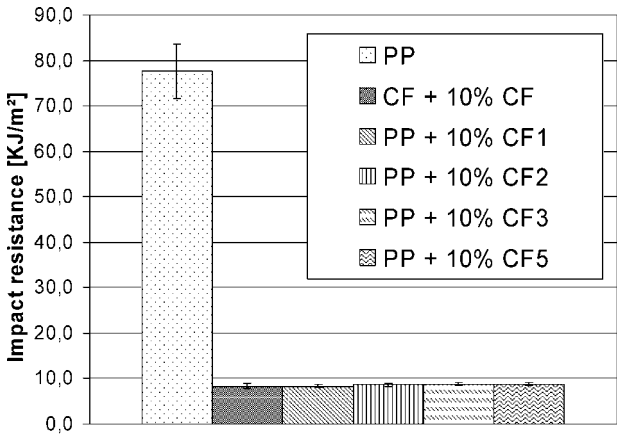

Figure 7 The impact strength of notched injection-moulded PP-composites containing 10 vol % cellulosic fibres. The impact resistance was measured perpendicular to the flow direction and the matrix material did not contain any compatibiliser.

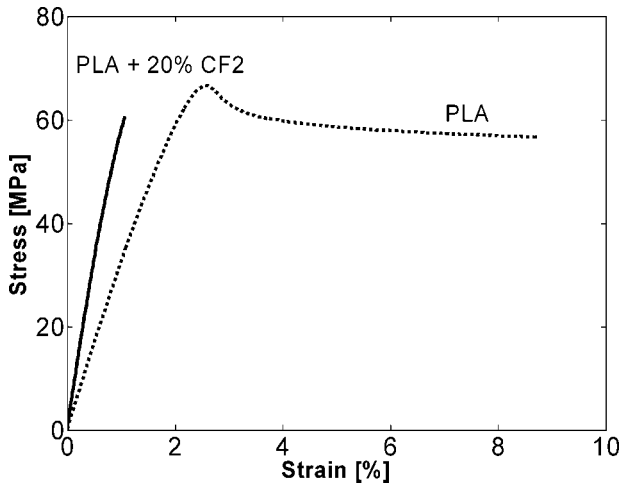

Figure 9 Stress-strain behaviour of unreinforced PLA and PLA containing 20 vol % CF2 (cellulosic fibres treated on the industrial scale). The specimens were injection moulded and tested in the flow direction.

Figure 9 shows the stress-strain curves for unfilled PLA and PLA reinforced with 20 vol % CF2. The test specimens were obtained from injection moulding. Obviously the cellulosic fibres had a dramatic influence on the stiffness, the tensile modulus being almost doubled from 3.4 to 6.7 GPa. The tensile strength (maximum stress) was not however markedly affected by the fibres and there was a corresponding substantial decrease in the elongation at rupture. The tensile properties of PLA reinforced with untreated fibres were also determined. The treatment of the fibres with bentonite did not improve the properties of the composites; on the contrary, it led to an increase in the brittleness of the reinforced PLA (and a corresponding slight reduction in the tensile strength). The cellulosic fibres appeared in general to be very well dispersed in the PLA-matrix.

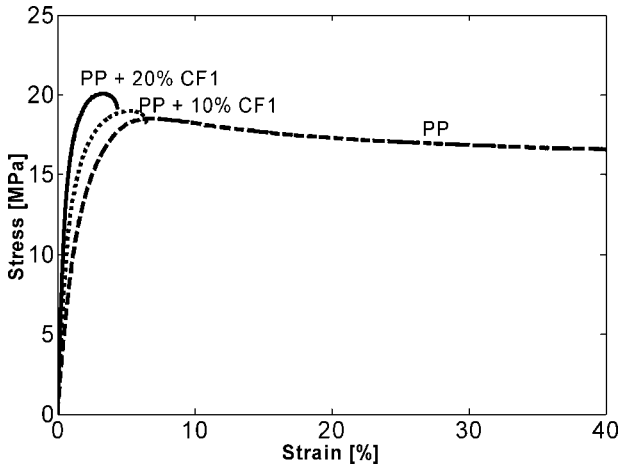

Figure 8 Stress-strain behaviour of unreinforced PP and PP containing 10 and 20 vol % CF1 (cellulosic fibres treated on the industrial scale). The specimens were injection moulded and tested in the flow direction.

Effect of the compatibiliser on the mechanical properties of the composites

Here 5 wt % of the maleated PP was used as a compatibiliser to improve the properties of the reinforced materials. The low amount of the combatibiliser did not affect the mechanical properties of the PP-matrix appreciably. It can however be argued that maleated PP increase the adhesion between the PP-matrix and the cellulosic material and thus improve the mechanical performance of the composite. It has been suggested that the maleic anhydride groups of the copolymer can react with the available hydroxyl groups of the cellulose fibres through a transesterification reaction,[17] thus providing chemical bonding and consequently improved mechanical properties, cf. also.[18,19] It is also known that maleated PP interacts with a number of filler surfaces and it has been shown to improve the mechanical performance of PP containing certain organically modified nanoclays.[20,21]

The results shown in Figure 10 and Table II confirm that the maleic anhydride-grafted PP has a positive effect on the mechanical properties of the injection-moulded reinforced polymer, not only on the tensile strength but also on the elongation at rupture. At a fibre content of 20 vol %, the treatment of the cellulosic fibres with bentonite (CF2) increased the tensile strength and the elongation at rupture, although the improvements were quite modest. The better mechanical performance is presumably associated with the more homogeneous dispersion of the fibres in the matrix (although this was not very pro-

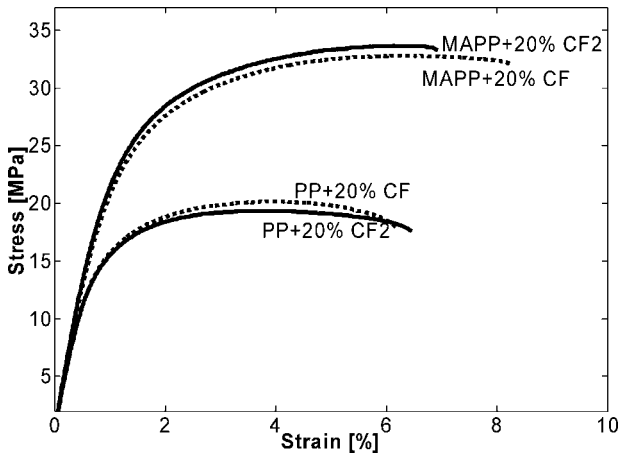

Figure 10 Stress-strain behaviour of compatibilised PP containing 20 vol % CF or CF2 (cellulosic fibres treated on the industrial scale). The specimens were injection moulded and tested in the flow direction.

nounced according to the visual inspection). Increasing the fibre content up to 30 vol % raised the tensile modulus to ~ 3.7 GPa and the tensile strength to 37 MPa, without too severe a decrease in the elongation at failure (5.2%), see Figure 11. This refers to MAPP reinforced with the treated fibres (CF2). Although these results are quite encouraging, the tensile modulus and tensile strength values were appreciably lower than those of the PP-composite containing 20 wt % glass fibres (corresponding to 8 vol %). On the other hand, the ductility, expressed in terms of the elongation at rupture, was better in the case of the natural-fibre-reinforced materials.

Treatment of the cellulosic fibres with the debonding agent improved their dispersion in the MAPP-matrix, but it had a less favourable influence on the mechanical properties of the injection-moulded composites. The tensile modulus of the material containing 20 vol % fibres decreased slightly, from 2.7 to 2.3 GPa. The effect on the tensile strength was even more pronounced, as can be seen in the stress-strain curves in Figure 12. On the other hand, the elongation at failure was not appreciably affected (or even improved). The deterioration in the mechanical performance is here probably associated with a lower degree of adhesion between the matrix and the reinforcing elements due to the fibre treatment.

The tensile mechanical properties of the PP- and the PLA-based composites are summarised in Table II.

It is known that the compounding and processing of polymer melts containing cellulosic fibres can lead to a significant reduction in fibre length.[22] This was also observed in this study, and a typical example is shown in Figure 13. Because of the processing, the fibres are shortened significantly and they were also damaged to some extent. Before processing together with the PP-matrix, the average fibre length was about 2.3 mm, whereas the processing reduced it to ~ 0.4 mm. This shortening of the fibres will, as is well known, reduce their reinforcing ability in the polymer matrix.

TABLE II
The Tensile Mechanical Properties of the PP- and the PLA-Based Composites, Means, and Standard Deviations

Material	Tensile modulus (GPa)	Tensile strength (max; MPa)	Elongation at failure (%)
PP	1.11 ± 0.01	19.4 ± 0.3	> 50
MAPP	1.12 ± 0.03	19.5 ± 0.4	> 50
PP + 10CF	1.82 ± 0.08	20.1 ± 0.4	9.1 ± 2.9
PP + 10CF1	1.69 ± 0.06	18.4 ± 0.9	6.8 ± 2.2
PP + 10CF2	1.87 ± 0.04	20.3 ± 0.6	6.5 ± 1.0
PP + 10CF3 (delam)	1.45 ± 0.05	18.1 ± 0.2	27.6 ± 12.6
PP + 10CF4 (delam)	1.65 ± 0.04	18.1 ± 0.4	14.4 ± 4.4
PP + 10CF5 (delam)	1.67 ± 0.05	18.2 ± 0.2	11.9 ± 4.3
PP + 10CF6 (delam)	1.64 ± 0.02	18.1 ± 0.1	11.5 ± 3.5
PP + 10CF7 (delam)	1.60 ± 0.03	18.1 ± 0.3	17.0 ± 8.6
PP + 20CF	2.40 ± 0.02	20.2 ± 0.4	5.0 ± 1.6
PP + 20CF1	2.53 ± 0.04	19.9 ± 0.3	5.1 ± 1.1
PP + 20CF2	2.44 ± 0.05	19.5 ± 0.4	6.2 ± 1.2
PP + 20 wt % GF	4.55 ± 0.03	68.6 ± 0.8	3.7 ± 0.2
MAPP + 20 CF	2.65 ± 0.03	32.5 ± 0.6	7.2 ± 1.7
MAPP + 20 CF2	2.72 ± 0.06	33.6 ± 0.6	6.9 ± 1.4
MAPP + 20 CF with nanoclay and debonder	2.26 ± 0.04	28.7 ± 0.3	8.4 ± 1.4
MAPP + 30 CF2	3.73 ± 0.07	37.5 ± 0.3	5.2 ± 0.9
PLA	3.36 ± 0.04	66.4 ± 0.6	7.2 ± 3.7
PLA + 20 CF	6.58 ± 0.83	71.8 ± 5.2	1.5 ± 0.1
PLA + 20 CF2	6.68 ± 0.18	57.8 ± 3.5	1.0 ± 0.1

Tensile strength (max) refers to the maximum in the stress–strain curve. Unless otherwise stated, the fibre content is given in vol %.

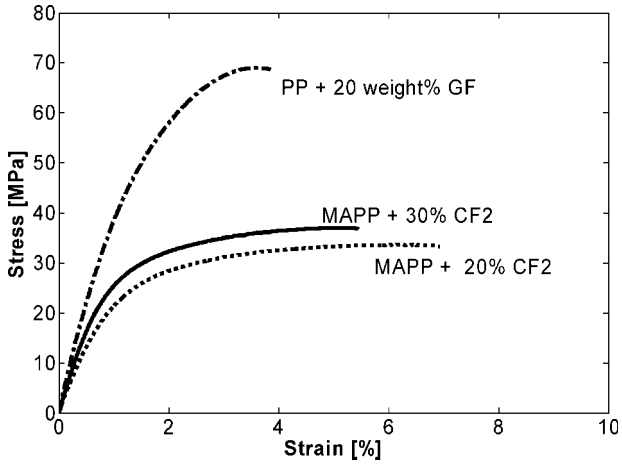

Figure 11 Stress-strain behaviour of compatibilised PP containing 20 and 30 vol % CF2 (cellulosic fibres treated on the industrial scale) and PP-GF. The specimens were injection moulded and tested in the flow direction.

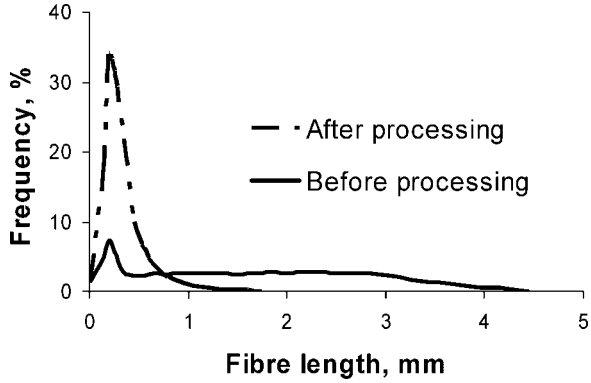

Figure 13 Fibre length distribution of the virgin fibres and an example of the corresponding distribution after processing together with the PP-matrix. In the latter case, the PP-matrix was dissolved in 1,2-dichlorobenzene.

Scanning electron microscopy

Scanning electron micrographs of fracture surfaces of the reinforced PP (no compatibiliser used) are shown in Figure 14. The injection-moulded specimens were fractured at room temperature during the tensile testing, and they contained 20 vol % untreated cellulosic fibres or the same amount of CF1. In the composite containing the untreated fibres, areas with a rather significant degree of fibre pull-out could be noted. This was less pronounced when the mineral-treated fibres were used for the reinforcement, indicating a somewhat improved adhesion between the fires and the PP-matrix and thus a change in the fracture mechanism. However, as already pointed out, the change in tensile properties of these composites due to the bentonite treatment was modest or even nonexistent.

With compatibilised MAPP as the matrix material, the appearance of the fracture surfaces was different, as illustrated by the left micrograph in Figure 15, which refers to MAPP containing 30 vol % CF2. Hardly any fibres can be seen, which can be attributed to a low degree of fibre pull-out and an improved adhesion between the fibres and the polymeric matrix. This is also reflected in the improved mechanical property profile of these reinforced materials. Comparing fracture surfaces of the MAPP-composites containing untreated and bentonite-treated fibres did not however reveal any clear differences.

When the debonder was used as an additional fibre treatment, there were again indications of fibre pull-out, as shown in the right hand micrograph in Figure 15. This is in agreement with the mechanical behaviour discussed earlier.

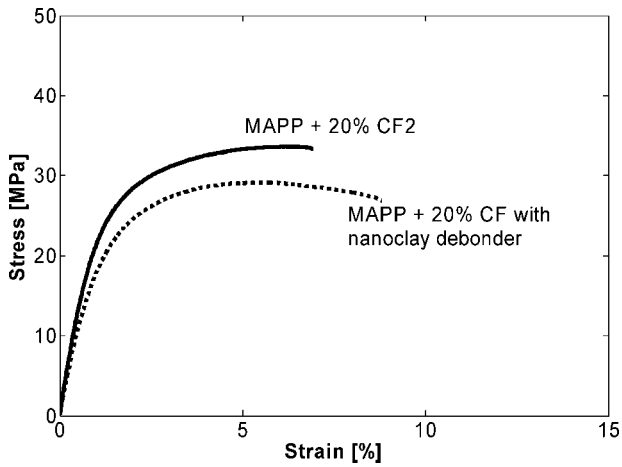

Figure 12 The effect of the debonding agent on the stress-strain behaviour of compatibilised PP containing 20 vol % CF2 or the same amount of fibres treated with delaminated nanoclay and debonder. The specimens were injection moulded and tested in the flow direction.

DISCUSSION

The results obtained certainly indicate that the mechanical properties of the PP and PLA are markedly improved or affected by the incorporation of cellulosic fibres, as expected, and furthermore that a treatment of the fibres with mineral particles and/or debonding agents can lead to an additional change in the mechanical behaviour of such composites.

One of the main objectives of this work was to improve the uniformity of the fibre dispersion in the final composite material. Breaking up the fibre bundles would make the fibre surfaces more available for the polymer melt and thus increase the interfacial area between the polymer and the fibres, which in turn could improve the adhesion between the constituents and affect the mechanical performance of the composites. To some extent this was achieved by the deposition of mineral particles, although, admit-

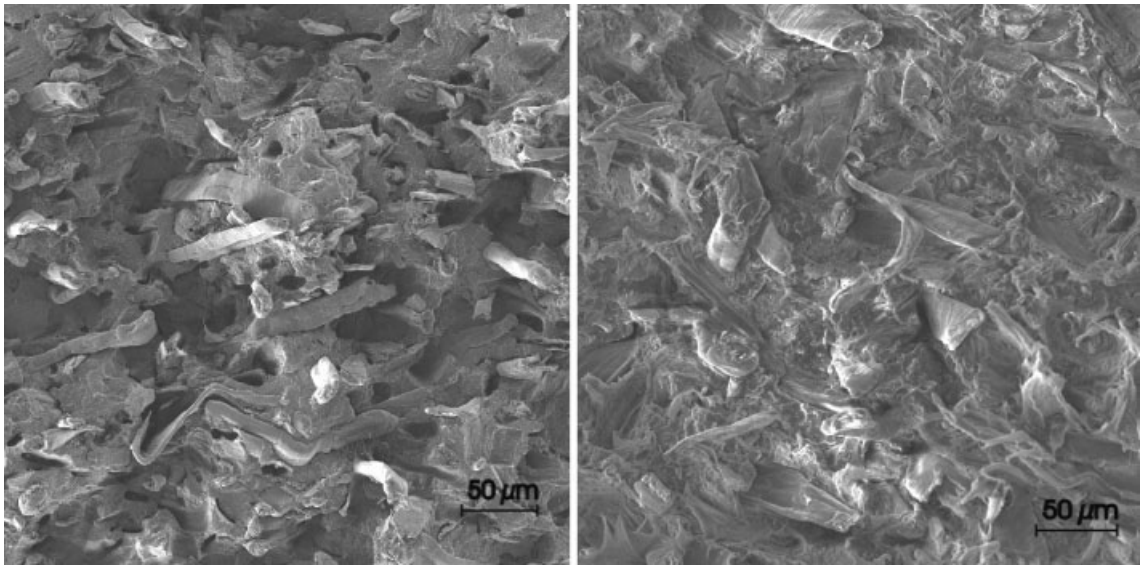

Figure 14 Fracture surfaces of injection-moulded PP containing 20 vol % untreated fibres (left) or the same amount of CF1 (right). The fracture surfaces were obtained from the tensile testing of the composites.

tedly, significant amounts of fibre bundles were still present in many of the specimens. The use of delaminated nanoparticles in relatively large amounts gave a more dispersed structure as desired. The use of smaller amounts of the undelaminated bentonite clay gave also the same result, but this treatment was less effective (with regard to the dispersion), which can partly be attributed to the lower clay content and the lower degree of surface coverage of the cellulosic fibres. On the other hand, avoiding the delamination operation would clearly be beneficial with regard to the production efficiency and here there is room for optimization of the fibre treatment. An additional issue is the influence of the humidity. There were indications that the fibre dispersion was improved when PP and the fibres were compounded at a low relative humidity. The role of the relative humidity requires further attention.

Treatment of the fibres with the undelaminated bentonite gave no clear improvement in the fibre dispersion in the MAPP-matrix. Fibre bundles or flocs were still clearly distinguishable in the extruded sheets, although there was a tendency for the flocs to be somewhat fewer and smaller compared with the corresponding sheets containing untreated fibres. Combining the mineral particles

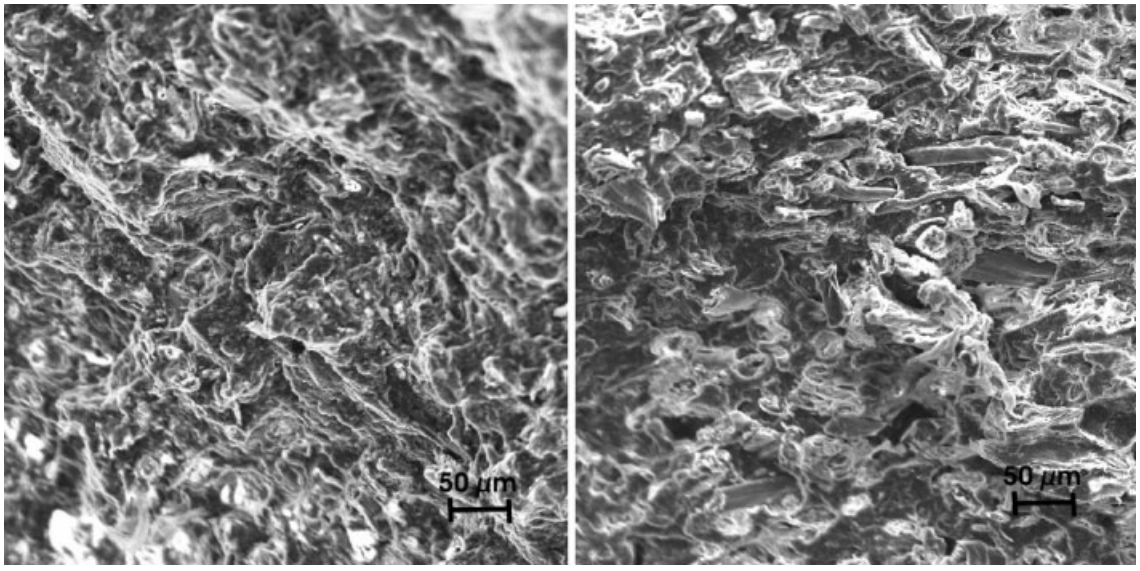

Figure 15 Fracture surfaces of injection-moulded MAPP containing 30 vol % CF2 (left) and 20 vol % fibres treated with nanoclay and debonder (right). The fracture surfaces were obtained from the tensile testing of the composites.

with a debonding agent led to the best dispersion of the fibres in the MAPP-matrix with only a few visible fibre bundles. A combination of this type might be the most viable route to be studied in future work.

Both the homogeneity of the fibre dispersion and the adhesion between the fibres and the polymeric matrix are expected to affect the mechanical performance of the reinforced material. The wetting and penetration of the melt into any existing fibre flocs may also be important. The adhesion between the untreated fibres and the PP-matrix appeared to be less than perfect since fibre pull-out from the matrix could be observed in the SEM-micrographs (Fig. 14). Treating the fibres with nanoclay or undelaminated clay had no major effect on the mechanical properties of the PP-based composites, although the fibres were then better dispersed. This may indicate that the adhesion between the polymer and the mineral particles did not exceed that of the adhesion between the fibre material and PP. The improved dispersion did not in itself lead to better mechanical properties, e. g. higher modulus or tensile strength. There were indications that the degree of fibre pull-out was lower in the case of the treated fibres, cf. Figure 14, but this was evidently not sufficient to be reflected in the mechanical performance. The lower degree of fibre pull-out may simply be a visual impression due to the improved dispersion of the individual fibres. Note that there were no greater differences in modulus and strength between the PP-composites containing the fibres treated with undelaminated bentonite and those containing fibres with the nanoclay, but the elongation at rupture was significantly greater in case of the latter materials.

Replacing PP by MAPP led to marked improvement in the mechanical properties of the composites, especially the tensile strength, which is probably associated with an increased adhesion between the matrix and the cellulosic fibres. This is also supported by the SEM-study where almost no fibre pull-out could be detected, Figure 15. In the case of the MAPP-based composites, fibre bundles were still quite frequent even with the bentonite-treated fibres. At a given fibre content, the composites containing the CF2-fibres exhibited somewhat improved mechanical properties compared to those of MAPP reinforced with untreated fibres. This may be because the slightly improved fibre dispersion due to the mineral treatment (pointed to earlier) rendered the fibres more accessible to the polymer melt. Another possibility is that the adhesion between the MAPP and the clay is higher than that between the polymer and the fibres. A combination of these factors is also possible. Treating the fibres with the debonder clearly improved the dispersion of the fibres, but it also reduced their adhesion to the MAPP-matrix. This is reflected in the mechanical properties and supported by an increased amount of fibre pull-out, see Figure 15.

In this context, it is appropriate to point out that the effect of the mineral particles on the degree of dispersion as well as on the adhesion naturally depends on whether or not the mineral particles are partly detached from the fibre surface during the compounding and processing steps. On the other hand, if the mineral particles were removed from the fibre surface they would probably be incorporated in the polymer matrix and then contribute to the mechanical properties. Further study is required to clarify the situation.

In general, the fibre-reinforced materials exhibited relatively good mechanical properties with a tensile modulus exceeding 3.5 GPa (in the case of MAPP with 30 vol % CF2) while still maintaining a reasonable ductility, as reflected in the elongation at failure. It is here of interest to obtain an indication of how well the cellulosic fibres are utilised as reinforcing elements in this case and, for that purpose, the tensile modulus of the fibres was estimated. Such an estimation involves a number of simplifications and approximations. For instance, it was assumed that the fibres were straight and cylindrical in shape, which is clearly not the case for cellulosic fibres, and that the adhesion between the fibre material and the matrix was sufficiently good. To simplify the analysis, it was furthermore assumed that all the fibres were aligned in the flow direction (the direction in which the modulus was measured), which is not too unrealistic in case of injection-moulded test bars. In terms of the shear-lag theory,[23] the modulus of the composite (E_c) then can be evaluated as

$$E_c = \eta_f \phi E_f + (1 - \phi) E_m \tag{2}$$

where ϕ is the volume fraction of the fibres, E_f the tensile modulus of the fibres in the longitudinal direction and E_m the modulus of the unreinforced polymer (here taken to be 1.1 GPa for the PP-based matrix, cf. Table II). The factor η_f corrects the fibre modulus for the shortness of the fibres and is given by

$$\eta_f = 1 - \frac{\tanh(na)}{na} \tag{3}$$

where a is the aspect ratio of the fibres, i.e. the ratio of the fibre length (l) to the fibre diameter (d), and n is obtained from

$$n = \sqrt{\frac{2G_m}{E_f \ln\left(\frac{2R}{d}\right)}} \tag{4}$$

where G_m is the shear modulus of the matrix material and $2R$ is the distance from a fibre to its nearest neighbour.

When estimating the fibre modulus, the tensile modulus of MAPP containing 20 vol % CF2 (2.7 GPa, Table II) was used, partly because the adhesion between the matrix and the fibres appeared to be good, cf e. g. Figure 15. Assuming that the fibres are arranged in a square array, *R/d* can be evaluated from the volume content of the fibres ($\phi = 0.2$ in this case). The aspect ratio *a* of the fibres after processing (assuming a fibre diameter of 20 μm) can be estimated to be of the order of 30. With these values, the fibre modulus can be estimated to be $\sim$ 12 GPa. This value is quite realistic,[24,25] considering that the fibres were probably quite damaged during the compounding and processing. In turn, this indicates that the fibres were rather efficient in reinforcing the material. In passing, it can be mentioned that a similar analysis as the above but using the modified Halpin–Tsai equation[26] instead of the shear-lag theory gives about the same value for the fibre modulus.

A similar type of analysis for the PLA-based composites yielded a calculated fibre modulus somewhat higher than 20 GPa, i.e. significantly higher than the value evaluated for the PP-composites. One reason for this may be that the fibres were less damaged and not shortened to the same extent during the processing of the material as when PP was the matrix material. From the experimental stress-strain behaviour, Figure 9, it is obvious that incorporation of the cellulosic fibres into the PLA-matrix was very effective in raising the modulus, especially when the fibres were mineral-treated. On the other hand, the composites were rather brittle (Table II). It may be that the interactions between the PLA and the fibres were too strong to give a good balance between the different mechanical properties, cf. also.[27,28]

FINAL REMARKS

The stiffness and tensile strength of PP can be significantly enhanced by incorporating cellulosic fibres, especially if the matrix contains a compatibiliser in the form of maleated PP. Treating the fibres with a undelaminated clay or nanoclay improves, to some extent, the dispersion of the fibres and the mechanical performance of the composites, but further optimization of the function of the mineral in this respect is required. Combination of the mineral treatment with a debonding agent appears to be an interesting route. In the case of PLA, cellulose fibre reinforcement appears to be an effective way to increase the stiffness of the material.

It is obvious that the processing techniques used in conventional thermoplastic manufacture can have a detrimental effect on the fibre length. The development of processing techniques that better preserve the aspect ratio of the fibre component is probably an important way to improve the mechanical performance of this kind of composite.

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