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Pelletized cellulose fibres used in twin-screw extrusion for biocomposite manufacturing: Fibre breakage and dispersion

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ABSTRACT

Pelletizing is effective in compacting cellulose fibres, but it also causes fibre breakage and poor dispersion due to increased hydrogen bonding. This study investigated whether fibre dispersion and length could be improved by the addition of a lubricant, a commonly used composite processing aid, into cellulose pellets, or by using pelletized fibres that have not been completely dried to reduce hydrogen bonding. Cellulose pellets with different lubricant and moisture contents were prepared and compounded using twin-screw extrusion with polypropylene with 5 wt% fibre and 50 wt% fibre contents. The fibre dispersion, morphology and mechanical properties of the prepared composites were analysed. Dispersion and composite strength were improved with the addition of 4–6 wt% of lubricant while moisture had a negative effect on both properties. This study demonstrated that pelletization in the presence of a lubricant is a promising way to compact cellulose fibres and enable their continuous processing into biocomposites with improved mechanical properties.

1. Introduction

The use of lignocellulose fibres, such as wood and other natural fibres, as reinforcement in thermoplastic composites has become increasingly popular due to the growing need for more environmentally friendly, sustainable and recyclable materials. In comparison to inorganic or synthetic fillers, lignocellulose fibres are biodegradable, renewable and widely available; moreover, they have low density, competitive specific mechanical properties and a relatively low cost [1,2]. Currently in Europe approximately 400,000 tons of biocomposites are produced each year, and the market for them is expected to grow in the future [3]. Biocomposites are used mainly to manufacture interior parts for the automotive industry, outdoor decking materials and other consumer goods [4,5]. However, in order to use thermoplastic biocomposites in more demanding applications, it is necessary to improve their mechanical properties.

The lignocellulosic materials used to reinforce thermoplastics are often ground into smaller particles before melt compounding to obtain material that is easier to continuously feed into the processing equipment. Typically, these particles consist of bundles of fibres instead of individual fibres, and they have aspect ratios (l/d) ranging between 1 and 5 [6]. Previous studies have reported that higher strength biocomposites can be obtained when cellulose fibres (CF) with a higher aspect ratio, such as pulp fibres (l/d > 50), are used as composite reinforcement materials due to improved stress transfer from the matrix to the fibres [7,8]. However, because dry fibres have low bulk density and a non-free flowing nature, their handling and constant feeding in melt compounding is problematic [9,10]. One of the most suitable methods used to overcome this problem is to compact the low bulk density fibres into pellets via a pelletizing machine [7,10–12].

Even though pelletizing has been shown to be a very useful method for steady feeding of CF in melt compounding, poor dispersion of pelletized fibres in composites and fibre shortening, originating from the pelletizing process, have been reported [10,12–14]. Mechanical entanglements, strong hydrogen bonding between fibres and the hornification phenomenon causing irreversible bonding and stiffening of CF during drying and rewetting are some of the causes of poor dispersion of pelletized CF [13,15]. The shear forces applied to fibres when they are being pressed through the die plate in the pelletizing machine are considered as the cause of fibre shortening in pelletizing [12].

To reduce the fibre breakage and/or to improve the fibre dispersion of pelletized fibres, previous studies have investigated the effect of the extrusion parameters [12] and pelletizing moisture content [13], and the addition of carboxymethyl cellulose (CMC) [13]. Le Baillif and Oksman [12] found that the length of the original CF was reduced by 52% in pelletization. Higher extrusion speed (300 rpm) and a second extrusion step were found to improve the dispersion of pelletized CF in polypropylene (PP), but as the dispersion improved, the fibre length

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decreased because the fibres were subjected to additional shear energy [12]. Le Baillif and Echtermeyer [13] found that variations of the CF dry content in pelletization did not reduce the fibre length, but the addition of 3 wt% CMC had a small impact on reducing fibre breakage. However, the addition of CMC had a negative impact on the dispersion of the cellulose pellets in composites because the number of inter-fibre bonds increased [13].

Moisture is commonly thought to be a problem in the manufacture of thermoplastic biocomposites because it causes swelling of the fibres thereby enabling the formation of voids at the fibre-matrix interface [16,17]. However, Virtanen et al. [17] found that fibre shortening of non-pelletized softwood pulp in twin-screw extrusion with polylactic acid was reduced when moist pulp fibres were used. Using fibres with 25% moisture content reduced the fibre breakage by 39% in comparison to dried fibres [17]. Lubricants are typically used to modify the rheology of molten thermoplastic, with or without reinforcing fibres, although their effect is more pronounced in highly-filled thermoplastics [18]. Lubricants are used to increase the material output, widen the processing window, lower the processing temperature and reduce the melt viscosity [19]. In a study by Li and Wolcott it was found that an ester-type lubricant was highly effective in dispersing maple filler particles in polyethylene without interfering with the coupling agent's role as a compatibiliser [20].

In order to reduce fibre shortening and improve fibre dispersion, the present study examined the influence of using a lubricant as a pelletizing additive, as well as the impact of the moisture content of the pellet on the fibre length and dispersion and mechanical properties of the final composite. It was hypothesised that fibre dispersion could be improved by reducing hydrogen bonding and hornification via the use of lubricated or moist cellulose pellets. The twin-screw extrusion process was used to manufacture composites with pelletized CF using PP as the matrix polymer, and the fibre dimensions, fibre dispersion and mechanical performance and microstructure of the composites was studied.

2. Materials and methods

2.1. Materials

The present study used never-dried bleached softwood sulphate pulp CF (Stora Enso, Oulu, Finland). The chemical composition of the softwood pulp was determined using standard methods: TAPPI T280 (acetone extractives), T222 (Klason lignin), T212 (NaOH solubility) and ISO 1762 (ash content). The pulp contained 4.2 wt% hemicellulose, 0.3 wt% lignin and 0.5 wt% inorganics. All the chemicals used in the study (acetone, sodium hydroxide, sulfuric acid and xylene) were of reagent grade and purchased from VWR International Oy (Helsinki, Finland). The PP used in the composites was PP homopolymer 194-NA25 (INEOS Olefins and Polymers Europe) with a melt flow index of 25 g/10 min (230 °C/2.16 kg).

The coupling agent used in the composites was maleic anhydride grafted polypropylene (MAPP) Exxelor PO1020 (Exxon Mobil, USA). TPW 113 lubricant (Struktol, USA), which is a modified fatty acid ester blend used as a processing additive for manufacturing filled polymer compounds, was used as the additive in the CF pellets and the composites with 50 wt% fibre content, unless the pellets already contained a lubricant. For use as a CF pellet additive, the lubricant beads were pulverised using a Waring blender and 5 × 5 s pulses.

2.2. Pelletizing of cellulose fibres

The CF pellets were produced using a KAHL pelleting press (Amandus Kahl, Reinbek, Germany) and a die plate with 3 mm diameter channels. The dry matter content of the pulp during pelletization, 40 wt%, was based on previous studies on cellulose fibre pelletization [7,12,13]. After pelletizing, the pellets were either dried at room temperature to reach the desired moisture content: 5 wt% (5M), 10 wt% (10 M) or 27 wt% (27 M), or dried in an oven at 60 °C until the moisture content was below 2 wt% (Dry).

To prepare the CF pellets with lubricant, the never-dried cellulose pulp was diluted into slurry containing 3 wt% dry matter using deionised water. The pulverised lubricant was added to the pulp slurry and mixed using a laboratory overhead stirrer (RW20, IKA, Staufen, Germany) for 15 min at 500 rpm. The amount of added lubricant varied based on the dry weight of the CF, as follows: 4 wt% (4L), 6 wt% (6L) or 12 wt% (12L). After stirring, the slurry was concentrated by filtration using filter paper with 12–15 μm pore size, after which the pulp mixture was dried at room temperature to ~40 wt% dry matter content for pelletization.

2.3. Extrusion

Cellulose fibre-polypropylene (CF-PP) composites with 5 wt% and 50 wt% pelletized CF contents were melt compounded using a ZSK-18 MEGALab co-rotating twin-screw extruder (Coperion W&P, Stuttgart, Germany) equipped with two K-Tron gravimetric feeders (K-Tron, Niederlenz, Switzerland) and a twin–screw side feeder, two atmospheric vents and a vacuum vent. Composites with 50 wt% CF content were extruded into strands using a die with two ø 3 mm openings. After exiting the die, the strands were cooled in a water bath and cut into pellets with a strand pelletizer mill. The composites with 5 wt% CF content were extruded into samples using a rectangular die with a 3 mm × 18 mm opening. The extruder barrel consisted of nine (9) temperature zones, and the processing temperatures varied from 170 to 190 °C. The screw configuration used is shown in Fig. 1. The screw speed used in the compounding was 250 rpm, and the material throughput varied from 2.6 kg/h to 3.1 kg/h due to the variability of the lubricant and moisture content in the pellets.

2.4. Specimen preparation

The extruded composites were used to prepare the specimens for further testing. The specimens used for flexural testing were moulded using a LabEcon 300 hydraulic press (Fontijne Presses, Vlaardingen, The Netherlands). The composite pellets with 50 wt% CF content were placed between aluminium plates and Teflon-coated fabric sheets on top of the metal frame with three (3) openings (100 mm × 10 mm × 4 mm); the pellets were then placed between the

	SC	C	C	C	C	2KE	3KE	3KE	3KE	C	C	C	C	C	C	C	C	C	2KE	2KE	2KE	2KE	C	C	2KE	C	MIX	MIX	MIX	C	C	C	C	C	SC	END
L, mm	8	24	24	24	24	24	16	16	16	24	24	24	24	24	24	24	24	24	24	16	8	8	24	24	24	24	12	12	12	24	24	24	24	24	12	END

SC = short conveying, right-handed; C = regular conveying, right-handed; 2KE= double-flighted kneading, 45°, right-handed; 3KE = triple-flighted kneading, right-handed; MIX = tooth mixing element.

Fig. 1. The screw design used in twin-screw extrusion to manufacture CF-PP composites.

press platens. The material was first preheated for 3 min at 195 °C without pressure and then pressed for 3 min using 3.3 MPa pressure at 195 °C, after which the pressure was increased to 16.7 MPa for 5 min. The material was then cooled under the same pressure to 25 °C for 5 min. For tensile testing, dog-bone shaped specimens, 90 mm (length) × 5 mm (width) × 1.5 mm (height), were made using a Haake Minijet (Thermo Scientific, Karlsruhe, Germany) laboratory scale injection moulding machine. A cylinder temperature of 230 °C and an injection pressure of 60–65 MPa were used in the injection moulding. For dispersion analysis, thin films were made using composites with 5 wt% CF content. The samples were prepared by placing a 2.6 g piece of composite between the aluminium plates and the Teflon-coated fabric, preheating the material in press for 3 min without pressure at 195 °C and then pressing using 1.6 MPa pressure for 1 min (195 °C), after which the pressure was increased to 3.2 MPa for 2 min.

2.5. Fibre characteristics

The fibre dimensions, namely the average width and length-weighted average length, of the original pulp fibre, pelletized fibres and fibres in the composites were analysed using tube flow fractionation (Valmet Automation Oy, Kajaani, Finland). The tube flow fractionation method is described in more detail by Laitinen et al. [21]. During the fractionation analysis, a high-speed camera records approximately 600 images of the diluted fibre sample. After fractionation, the recorded images are analysed using kajaani IMG image analysis software (Valmet Automation Oy, Kajaani, Finland). Two replicates were analysed for each fibre sample using fractionation. The aspect ratio (l/d) was determined from the image analysis results by dividing the length weighted fibre length by the width of the fibre after which the average aspect ratio was calculated from the l/d values for each sample. All the fibre samples were diluted with deionised water into a suspension of 0.3 wt%, then soaked overnight, or longer, and dispersed manually before tube flow fractionation. For the analysis, fibres from the composite pellets were obtained using boiling xylene (5 g of pellets, 24 h in boiling xylene) to dissolve the PP matrix. The fibres were separated from the hot xylene by filtration, rinsed once with hot xylene and dried before dilution with deionised water.

2.6. Fibre dispersion

The fibre dispersion was quantified using the composite films with 5 wt% pelletized CF content as the composite films with 50 wt% fibre content were not suitable for the analysis. With lower fibre content, it was possible to obtain films in which fibre aggregates are easy to distinguish without overlapping and thus get an indication of how the dispersion behaviour of pelletized fibres could be in the composite with the higher fibre content. Three (3) films of each formulation were first scanned into 600 ppi (pixels per inch) resolution images using an EPSON 1680Pro scanner; then, Fiji ImageJ image analysis software (National Institutes of Health, Bethesda, Maryland, USA) was used to threshold and analyse the number and size of the aggregates in the scanned images. The software was used to measure aggregates larger than 0.25 mm^2, and both the number of aggregates and the percentage of aggregates per film (total aggregate area/film area × 100%) for each formulation were calculated. The parameters used in the thresholding and image analysis were the same for all specimens.

2.7. Melt rheology

The melt rheological properties of the composites with 5 wt% CF were measured using a Discovery HR-1 rheometer (TA Instruments, New Castle, DE, USA) equipped with parallel-plate geometry, 25 mm diameter plates and 2 mm distance. Discs, 25 mm in diameter and 3 mm in thickness, were prepared using a LabEcon 300 hydraulic press at a temperature of 195° and pressure of 15 MPa. Before testing, the sample was equilibrated for 5 min at 195 °C. Dynamic frequency sweeps (100–0.1 rad^{-1}, 195 °C) were run using a strain amplitude of 2%. Strain sweep tests were conducted in advance to ensure that the rheological properties were measured at the linear viscoelastic region. At least two replicates for each formulation were analysed.

2.8. Mechanical properties

The mechanical properties of the composites were measured using flexural and tensile testing according to EN 790 (three-point bending) and ISO 527 (tensile testing) standards. A Zwick Z010 TH Allround Line universal testing machine (Zwick GmbH & Co.KG, Ulm, Germany) equipped with a 10 kN load cell was used for flexural testing. A test speed of 5 mm/min was used for all the samples. Tensile testing was conducted using a Zwicki Z2.5 TN (Zwick GmbH & Co.KG, Ulm, Germany) testing machine and 1 kN load cell. Modulus of elasticity was determined using 1%/min speed, after which the test was continued using a speed of 5 mm/min. The gauge length was 30 mm. A minimum of five (5) replicates of each material formulation were tested in both tests, and one-way analysis of variance (ANOVA) followed by the Tukey–Kramer multiple comparison test with a 0.05 significance level was used to analyse the results.

2.9. Microstructure

A field emission scanning electron microscope, FESEM Zeiss Sigma (Carl Zeiss, Jena, Germany), was used to study the fracture surfaces of the composites with 50 wt% cellulose content. Fracture surfaces were created by breaking the samples that were frozen in liquid nitrogen. The samples were mounted on sample holders and sputter-coated with a layer (~6 nm) of platinum before observation with FESEM using 5 kV acceleration voltage.

3. Results and discussion

3.1. Pelletization and fibre length

The pelletized CF formulations are listed in Table 1. Pelletizing is a very effective way to compact pulp fibres. When the pulp fibres were mixed with 6 wt% or 12 wt% lubricant, the pelletizing process was somewhat slower because the lubricant made the fibres more slippery. After pelletizing, the materials were either dried in an oven (Dry, 4L, 6L and 12L pellets) or at room temperature to reach the desired moisture content (5M, 10M, 27M pellets) prior to compounding with PP.

All the prepared pellets were easy to feed into the twin-screw extruder using gravimetric feeding. The pellets with higher moisture content, 10 wt% and 27 wt%, started to disintegrate after exiting the feeding screw, but this did not affect the feeding rate of the fibres. The prepared composites and their formulations are listed in Table 2.

Analysis of the fibres showed that the pelletizing process caused CF breakage because the fibre length was reduced by 30–43% (Table 3). These results are similar to the findings reported in previous studies in which the fibre breakage for pelletized CF was 39–53% [10,12,13]. The addition of the lubricant had a positive effect on the fibre length; it

Table 1
CF pellets prepared with different moisture and lubricant contents.

Pellet	CF (wt%)	Moisture (wt%)	Lubricant (wt%)
Dry	100	–	–
5M	95	5	–
10M	90	10	–
27M	73	27	–
4L	96	–	4
6L	94	–	6
12L	88	–	12

Table 2
Compositions of the composites with 5 wt% and 50 wt% pelletized CF.

Composite	CF (wt%)	PP (wt%)	Lubricant (wt%)	MAPP (wt%)
Dry-PP_5	5.0	95.0	–	–
5M-PP_5	5.0	95.0	–	–
10M-PP_5	5.0	95.0	–	–
27M-PP_5	5.0	95.0	–	–
4L-PP_5	5.0	94.8	0.2	–
6L-PP_5	5.0	94.7	0.3	–
12L-PP_5	5.0	94.3	0.7	–
Dry-PP_50	50.0	45.0	2.0	3.0
5M-PP_50	50.0	45.0	2.0	3.0
10M-PP_50	50.0	45.0	2.0	3.0
27M-PP_50	50.0	45.0	2.0	3.0
4L-PP_50	50.0	45.0	2.0	3.0
6L-PP_50	50.0	44.0	3.0	3.0
12L-PP_50	50.0	41.0	6.0	3.0

Table 3
Dimensions and aspect ratios of the original CF, pelletized CF and fibres separated from the 50 wt% CF-PP composites. The standard deviations given are the deviations in average values of two replicated measurements.

Sample	Fibre length L (l) (mm)[a]	Fibre width (μm)	Aspect ratio (l/d)[b]	Decrease in length (%)
CF	1.69 ± 0.05	23.08 ± 0.25	61	–
Pelletized CF				–
Dry	0.97 ± 0.05	26.13 ± 1.14	37	43
4L	1.03 ± 0.01	25.54 ± 1.85	40	39
12L	1.18 ± 0.05	26.55 ± 3.13	47	30
Composites				
Dry-PP_50	0.83 ± 0.01	18.63 ± 0.38	51	51
5M-PP_50	0.85 ± 0.01	27.00 ± 1.39	50	50
10M-PP_50	0.87 ± 0.02	31.72 ± 1.85	50	49
27M-PP_50	0.88 ± 0.02	24.38 ± 4.71	50	48
4L-PP_50	0.85 ± 0.02	18.85 ± 0.18	52	50
6L-PP_50	0.95 ± 0.04	21.95 ± 6.19	47	44
12L-PP_50	0.98 ± 0.03	26.05 ± 5.93	50	42

[a] ISO fibre length, 0.2–7 mm.
[b] Aspect ratios are calculated using ISO fibre lengths.

slightly reduced the breakage. The composites with a lubricant content of 12 wt% had ~20% higher fibre length than the composites that were pelletized without a lubricant. In an earlier study by Le Baillif and Echtermeyer [13], 3 wt% CMC was also found to reduce the fibre breakage in pelletizing, but addition of CMC had a negative effect on the fibre dispersion in the composites due to the increased amount of inter-fibre bonding in the pellets.

It is well-known that extrusion compounding causes fibre breakage [22,23], and the results presented in Table 3 also show that the length of the pelletized fibres was further shortened after the composites underwent the extrusion process. In the lubricated CF pellets, the fibre breakage was reduced in the melt compounding, to some extent, because the composites with 6L and 12L CF pellets had the greatest fibre lengths (Table 3). Higher moisture content in the CF pellets did not reduce the fibre breakage in melt compounding to the same degree as the use of a lubricant. Virtanen et al. [17] showed that using kraft pulp fibres with a moisture content of 25 wt% reduced the fibre breakage by 39% in melt compounding with polylactic acid in comparison to dry pulp fibres. However, [17] did not pelletize the cellulose prior to the melt compounding, which probably explains the different result; in our study, pelletizing resulted in the greatest decrease in fibre length.

Although the aspect ratios were reduced from 61 for the original CF to 47–52 for the pelletized CF after compounding (Table 3), the aspect ratios of the pelletized cellulose after compounding were still much higher than those reported for wood flour (~1–5). It is well known that a higher aspect ratio is associated with improved composite strength properties [24]. Aspect ratios are greatly dependent on the fibre width value, which showed greater variability in the results in comparison to the fibre length measurements due to swelling of the fibres in water before the fibre analysis.

3.2. Fibre dispersion and image analysis

The film samples with 5 wt% pelletized fibres were used to analyse the dispersion of the fibres in PP. Fig. 2 shows the percentage and number of aggregates/film analysed using image analysis. The lubricant in the CF pellets reduced the number of aggregates, and higher moisture content clearly increased the number of aggregates in comparison to the composite made with dried pellets. Visual observation of the films revealed that the composite with 12L pellets had very good fibre dispersion, whereas the higher moisture content in the CF pellets led to larger amount of fibre aggregates (Fig. 2). Moisture is known to act as a plasticiser for cellulose fibres [25]; thus, it is possible that the shear forces of the twin-screw extruder were not sufficient to disintegrate and disperse the moist CF pellets or the dry CF pellets. Peltola et al. [14] also noted that when a polymer with lower melt viscosity was used, poorer dispersion of pelletized CF fibres in matrix was achieved due to the decreased amount of shear forces. The formation of a water vapour layer (the so-called Leidenfrost effect) may have protected the moist pellets from the shear forces in the extrusion process [17,26]. The amount of aggregates for the dry pellets and the pellets with lubricant were the same, less than 1%, except for the composite with 6L pellets, which had a somewhat greater amount of aggregates (1.1%, Fig. 2). The higher moisture content in the CF pellets clearly increased the number of aggregates in the samples.

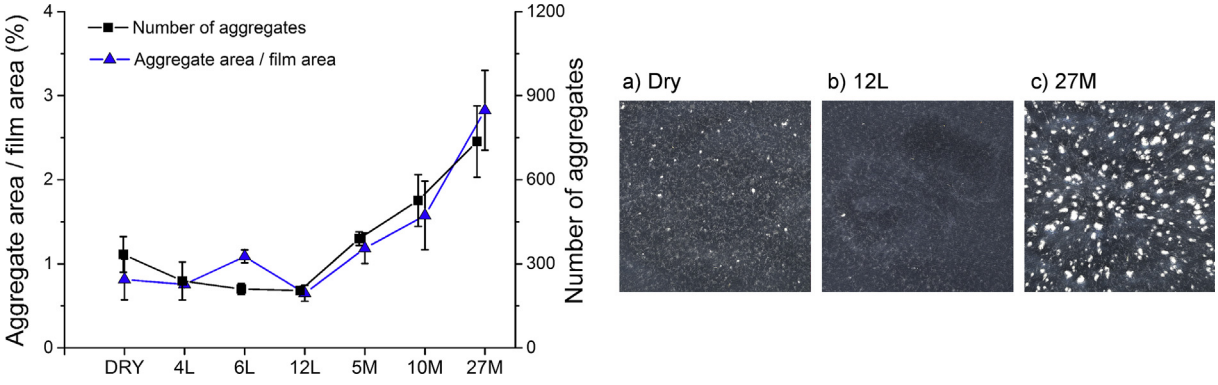

Fig. 2. The number of aggregates and the percentage of fibre aggregates in the 5%CF-PP films measured using image analysis. Example images of the films include: (a) Dry-PP_5, (b) 12L-PP_5, (c) 27M-PP_5. The images depict the middle section of each film.

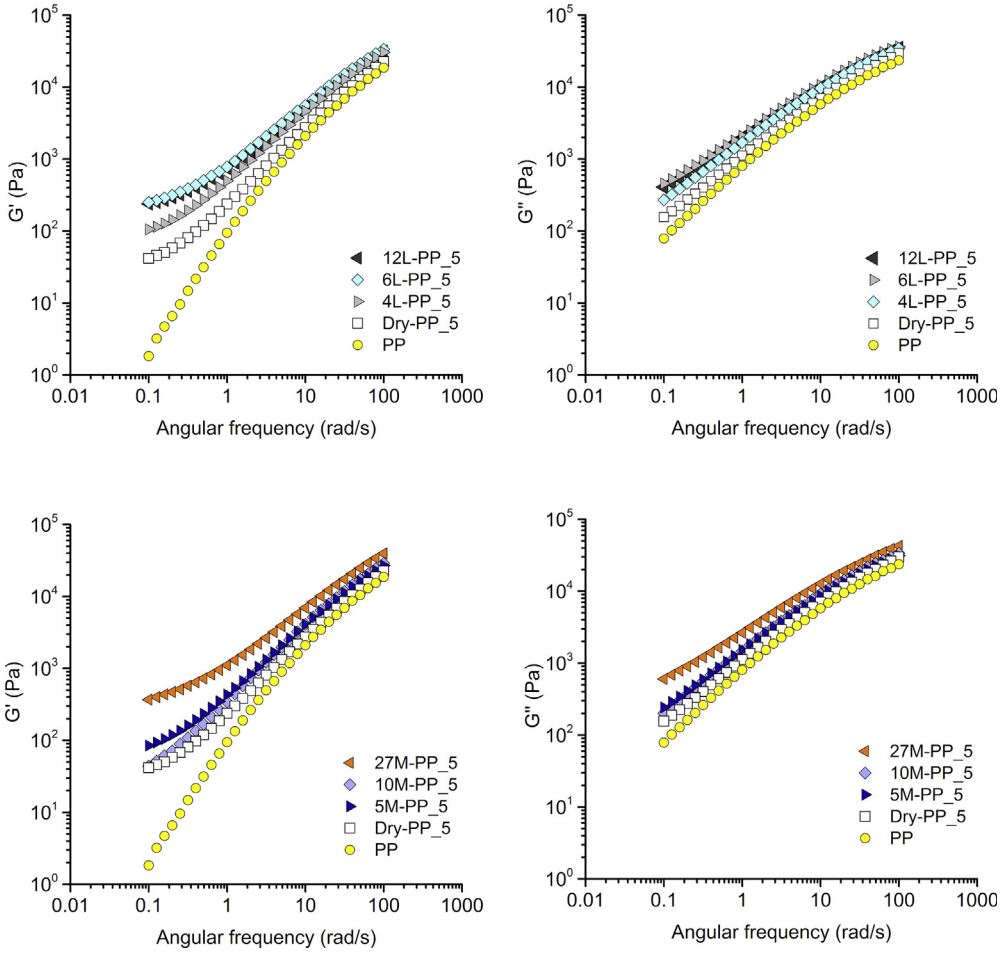

Fig. 3. Storage (G′) and loss modulus (G″) as a function of the angular frequency of the 5% CF-PP composites and the neat PP. Top images: composites made with CF pellets with a lubricant, bottom images: composites made with CF pellets with different moisture contents.

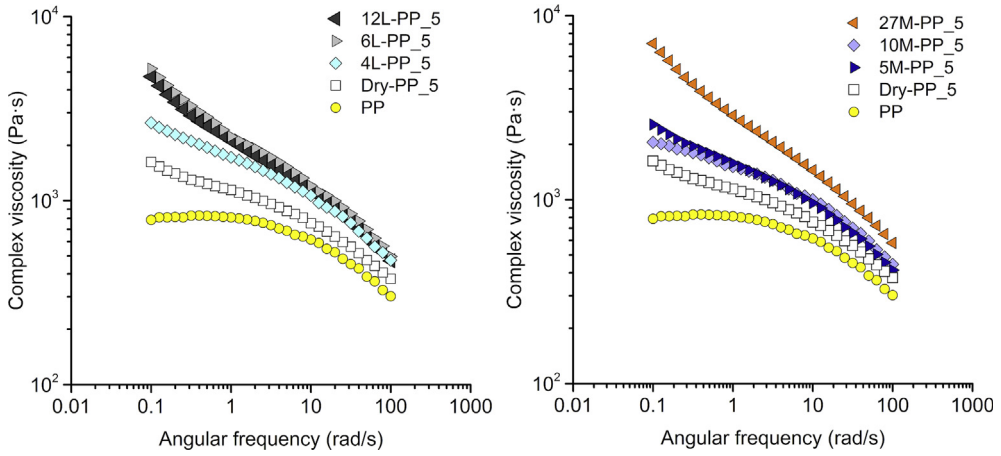

Fig. 4. Complex viscosities as a function of the angular frequency of the neat PP and the PP with 5 wt% pelletized fibres. Left side image: composites made with CF pellets with a lubricant. Right side image: composites made with CF pellets with different moisture contents.

3.3. Rheological properties

Melt rheology was used to study the fibre dispersion and the interaction between the fibres and the matrix of the composites with 5 wt % CF content. Previously, melt rheology has been especially used to study fibre or particle dispersion in biocomposites when the reinforcement has been nanoscale cellulose [27–29]. Figs. 3 and 4 show the dynamic rheological properties of the 5% CF-PP composite melts, including the storage and loss modulus and the complex viscosities. All the composites with 5 wt% CF had higher storage moduli (G′) than the neat PP, thus indicating that the fibres restrict the deformation of PP (Fig. 3). At low frequency, the G′ of the composite melts showed an indication of a plateau formation, which is related to the presence of apparent yield stress due to the interactions between the particles dispersed in the melt [20,30,31]. The complex viscosity (η^*) of all the samples decreased with increasing angular frequency (Fig. 4),

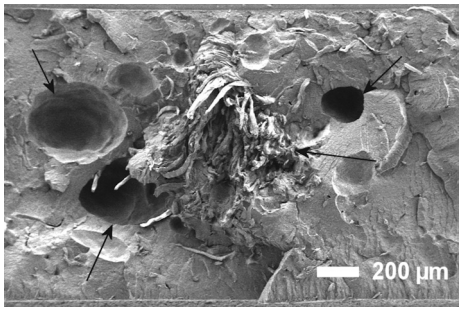

Fig. 5. Fracture surface of the PP composite sample used in the melt rheology with 5 wt% pelletized CF containing 27 wt% moisture. Arrows point to the aggregated CF and the voids caused by the moisture.

indicating the pseudoplastic characteristics of the PP matrix in all cases [32]. Fig. 4 also shows that all the CF fibre-filled PP systems had higher viscosities than the neat PP. Fibres are known to disturb the normal flow of molten polymer, thus hindering the movement of polymer chain segments in the flow [32,33].

Although all the composites had the same amount of pelletized CF, some differences in the G′ of the composite melts were observed. A higher amount of lubricant (6L-PP_5, 12L-PP_5) in the pellets resulted in higher storage moduli than when no lubricant was added to the pellets (Dry-PP_5) (Fig. 3). Because the presence of a lubricant in wood-polymer composites is known to reduce the G′ and viscosity of a polymer melt [19,20], the higher G′ is most likely due to better dispersion of the pelletized CF containing a lubricant. This observation is also supported by the results from the image analysis (Fig. 2). However, of the composites containing pellets with different amounts of moisture (Fig. 3), the 27M-PP_5 composite had the highest G′ despite the high amount of fibre aggregates (Fig. 2). Possible reason for this behaviour is that larger size fibre aggregates can also interact with each other resulting in melt behaviour similar to a highly filled polymer system, resulting in a higher G′. Similar behaviour was observed by Song and Youn [34] in their study of poorly dispersed carbon nanotubes in a liquid epoxy matrix.

The lubricated CF pellets increased the viscosity more than the non-lubricated pellets (Fig. 4). Higher viscosity can be related to better dispersion of pelletized fibres that contain lubricant because better dispersion is expected to result in greater interactions between the fibres and the PP matrix, resulting in higher viscosity [35]. Moreover, the greater average fibre length of the pellets with a higher amount of lubricant may increase the viscosity of the polymer melt [36]. However, the 5%CF-PP composite with CF pellets with 27% moisture content had the highest complex viscosity among all the studied materials (Fig. 4). As previously mentioned, this result was unexpected because the image analysis showed (Fig. 2) that the CF pellets with the highest moisture content also had the largest number of aggregates in PP. To clarify the reasons for the higher storage modulus and melt viscosity values, the fracture surface of the 27M-PP_5 sample used in the melt rheology was studied by FESEM (Fig. 5).

As seen in Fig. 5, large voids are clearly visible in the specimen fracture surface surrounding the large fibre aggregate. It also appears that the moisture in the cellulose pellets has vaporised causing the voids in the PP matrix. Thus, the higher storage modulus and complex viscosity of the 27M-PP_5 sample can be explained by the interactions between the large fibre aggregates, which resulted in the system behaving similar to a highly filled composite. Based on the results, melt rheology cannot be solely used as the measure of cellulose fibre dispersion in PP, though in the case of lubricated CF pellets the results were in accordance with the image analysis. Therefore, other methods, such as image analysis and microscopy, are still needed to verify the obtained results.

3.4. Mechanical properties

The mechanical properties of the composites with 50 wt% CF are presented in Table 4 and in Fig. 6. The tensile strength of the PP matrix was improved by 10% when dried CF pellets were added and by 26% when 4 wt% lubricant was added to the pellets. Overall, the composite made with pellets containing 4 wt% lubricant (4L-PP_50) had the highest tensile and flexural properties among all the studied materials.

The typical tensile stress-strain curves for each material presented in Fig. 6(a) also show, that 4 wt% and 6 wt% lubricated CF pellets had positive impact on the composite toughness. The effect of 4 wt% lubricant in the CF pellet on the composite strength is very interesting because the composite made with pellets without lubricant (Dry-PP_50) has an identical composition (except 4 wt% lubricant was added to the composite in compounding step). Yet, the tensile and flexural properties are significantly better in the composite with lubricated pellets than the composite with unlubricated pellets. Thus, the lubricant in the CF pellets presumably improves the CF dispersion similarly as with the composites with lower fibre content (Fig. 2) because better fibre dispersion is expected to lead to higher composite strength. However, with high amount of lubricant in the CF pellets (12 wt%), the strength properties of the composites decreased (Fig. 6b). Another reason for the strength improvement could be the higher degree of fibre orientation when lubricated CF pellets are used, as it is known that processing induced fibre orientation affects the modulus and strength properties of biocomposites [37]. It is possible, that the injection moulded tensile strength specimens had more orientated fibres in flow direction. In flexural specimen, fibre orientation is assumed as random due to sample preparation procedure.

Moisture in the CF pellets did not have a positive effect on the strength properties of the composites (Fig. 6c). Overall, all the strength properties of the composites made with the CF pellets containing moisture were inferior to those of the composite with dried CF pellets (Dry-PP-50). The composites with moist pellets also had the poorest

Table 4
Tensile and flexural properties of the composites with 50 wt% pelletized CF. The given values are average values of five replicates with standard deviations.

	Tensile properties			*Flexural properties*		
Material	$E_{tensile}$ (GPa)	σ_{Max} (MPa)	ε at break (%)	$E_{flexural}$ (GPa)	σ_{Max} (MPa)	ε at break (%)
PP	1.07 ± 0.01	36.1 ± 1.5^{a}	23.5 ± 4.8	–	–	–
Dry-PP_50	2.08 ± 0.03	39.8 ± 1.2	3.7 ± 0.3^{a}	3.17 ± 0.25	47.5 ± 1.6	2.2 ± 0.4^{a}
5M-PP_50	2.09 ± 0.09	37.1 ± 1.5^{b}	3.2 ± 0.4^{a}	3.24 ± 0.14	40.9 ± 1.3	1.9 ± 0.1
10M-PP_50	1.98 ± 0.03	35.9 ± 0.9^{ac}	3.5 ± 0.3^{a}	2.65 ± 0.32	43.5 ± 2.1^{a}	2.6 ± 0.4^{a}
27M-PP_50	1.97 ± 0.04	36.4 ± 1.2^{abc}	3.6 ± 0.1^{a}	2.81 ± 0.24	43.3 ± 1.2^{a}	2.4 ± 0.3^{a}
4L-PP_50	2.13 ± 0.03	45.5 ± 1.9	4.4 ± 0.3^{a}	3.53 ± 0.22	52.8 ± 3.3^{b}	2.1 ± 0.2^{a}
6L-PP_50	1.82 ± 0.02	43.3 ± 1.1	5.4 ± 0.3^{a}	2.72 ± 0.14	52.0 ± 1.2^{b}	3.1 ± 0.4^{a}
12L-PP_50	2.07 ± 0.05	38.5 ± 1.9	3.9 ± 0.2^{a}	2.67 ± 0.25	37.4 ± 0.8	2.2 ± 0.4^{a}

The mean values which are marked with the same superscript letter within the same column are not statistically significantly different based on the ANOVA and the Tukey–Kramer pairwise comparison test results (alpha = 0.05).

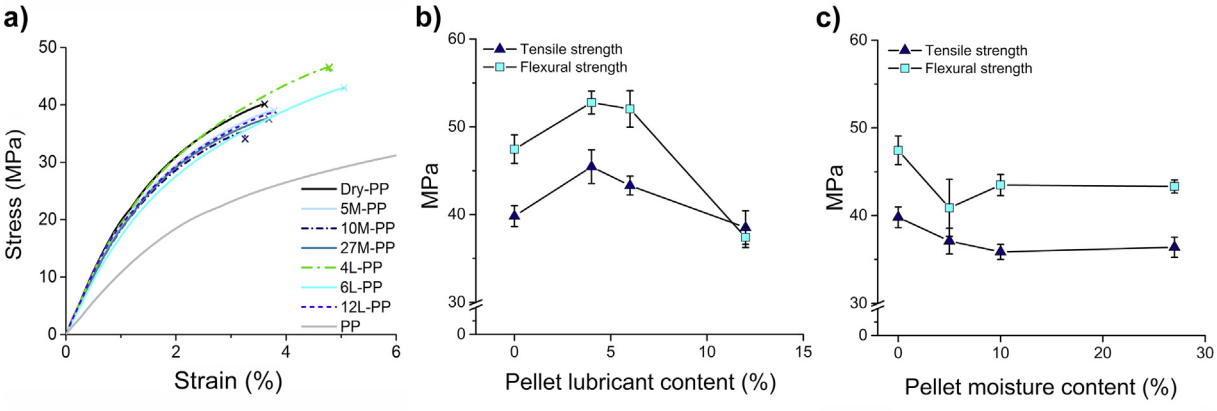

Fig. 6. (a) Typical tensile stress – strain curves of PP in comparison with composites with different types of CF pellets. Tensile and flexural strength of the composites with 50 wt% CF as a function of the: (b) lubricant content and (c) moisture content of the CF pellets.

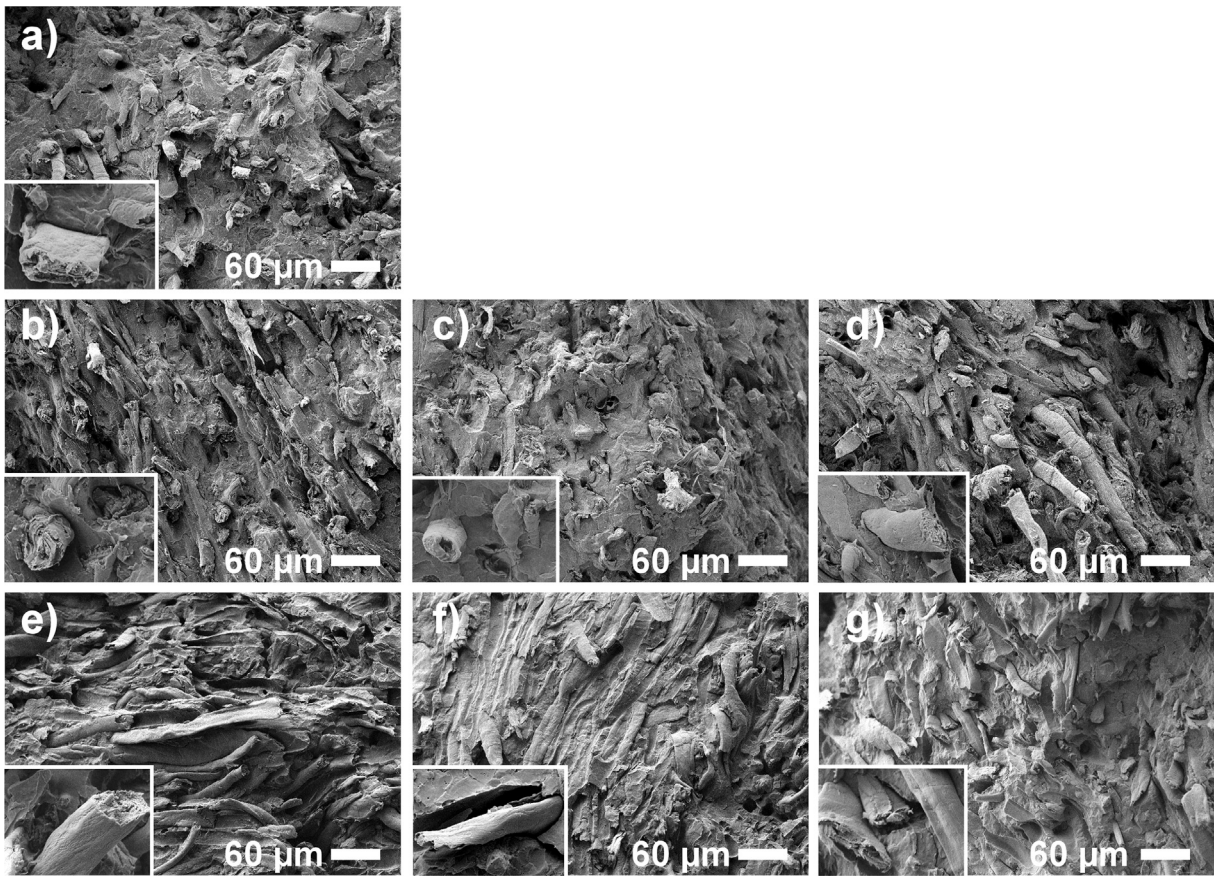

Fig. 7. Fracture surfaces of the PP composites made with 50 wt% pelletized CF: (a) Dry-PP_50, (b) 4L-PP_50, (c) 6L-PP_50, (d) 12L-PP, (e) 5M-PP_50, (f) 10M-PP_50, (g) 27M-PP_50. Details of each fracture surface taken with higher magnification are shown in the smaller corner image.

fibre dispersion and highest number of aggregates with lower fibre content (Fig. 2), thus poor fibre dispersion may explain their inferior mechanical properties with 50 wt% fibre content.

The stiffness of the PP polymer was increased 70% to 98% by the addition of 50 wt% CF, and all the CF-PP composites had tensile modulus of approximately 2 GPa (Table 4), except the composite with pellets containing 6 wt% lubricant (6L-PP_50), which had a somewhat lower tensile modulus but a higher elongation at break (Table 4). The 4L-PP_50 composite having the highest strength properties and expectedly the best fibre dispersion, had also the highest tensile and flexural moduli among the composites.

3.5. Composite microstructure

FESEM images of the fracture surfaces of the composites with 50 wt % fibre content are shown in Fig. 7. For all the studied composites, the adhesion between the fibres and the PP matrix could have been better because the fibre pull-outs and the clean fibre surfaces were visible in all the samples. Thus, more coupling agent, MAPP, could have been used to improve the mechanical properties of the composites.

However, somewhat fewer fibre pull-outs and clean fibre surfaces were observed in the fracture surfaces of the composites made with CF pellets with lubricant (Fig. 7b–d) indicating better adhesion, especially when the amount of lubricant was 4 wt% and 6 wt%. With 12 wt%

lubricant the adhesion clearly became worse. Presence of moisture in the CF pellets had a negative impact on adhesion, as greater amounts of clean fibre surfaces and fibre pull-outs were observed in the fracture surfaces of the composites made with moist CF pellets (Fig. 7e–g). The poorer adhesion between the moist CF and the PP matrix explains the inferior strength properties of the composites presented in Table 4. A difference in the fibre morphology was also observed, as the fibres in the composites made with moist pellets were more flattened and twisted than in the other composites. Due to the high cellulose content in the composites with 50 wt% CF content, fibre dispersion or the presence of aggregates could not be estimated from the FESEM images.

4. Conclusions

This study investigated the effect of lubricant and moisture on the performance of pelletized CF as reinforcement in PP in order to overcome the dispersion and fibre breakage problems related to the use of pelletized CF in thermoplastic biocomposites. The results from dispersion study with 5 wt% fibre content show that the addition of a lubricant (TPW 113) to the cellulose pellets instead of the composite compounding aided the dispersion of the fibres in the matrix, while the moisture content had a negative effect on the dispersion. The strength properties of composites with 50 wt% fibre content improved when the amount of lubricant remained moderate (4–6 wt%). The tensile strength of PP was improved by 26% and the stiffness by 98% when adding 50 wt% CF pellets with 4 wt% lubricant. Thus, it can be assumed that improved fibre dispersion led to improved mechanical properties of the composites. Although the problem of fibre breakage was not completely overcome in this study, the fibre breakage was reduced by the addition of a lubricant to CF.

Overall, pelletization of CF in the presence of a lubricant is a very promising method because it enables the use of low bulk density CF with a higher aspect ratio in continuous melt processing of biocomposites. When a lubricant is added directly to the CF pellet, composite strength is improved in comparison to composites in which a lubricant is added during melt compounding.

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