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Processing–Formulation–Performance Relationships of Polypropylene/Short Flax Fiber Composites

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ABSTRACT: This work is a comprehensive study of the effect of extrusion process parameters and formulation on the properties of polypropylene (PP)/short flax fiber composites. The parameters that were varied during the twin-screw extrusion process were screw configuration, revolutions per minute (rpm), extrusion temperature, and flow rate. The effect of the feeding zone location of cellulosic fiber was also considered. This study investigates the effect of the formulation, cellulosic fiber content, the presence of a coupling agent, and of a reactive additive on composite performance. The composites were characterized in terms of morphology and microstructure, fiber length, rheological, thermal, and mechanical properties. Sensibility to humidity and recyclability were also considered. When compared with as-received PP, the tensile strength of injection-molded parts increased with cellulosic content by up to 40 vol %, and the tensile modulus increased 3.5 times when a combination of coupling and reactive agents was used. Exposed to controlled humidity of 50% during 1 year, these composites exhibited a very low level of humidity uptake around 0.85 wt %. The processability of these materials using a cast film line and the mechanical properties of extruded sheets are also presented. Furthermore, these materials demonstrate a good recyclability using injection molding by keeping the integrality of their mechanical properties after five reprocessing cycles. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41528.

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INTRODUCTION

Thermoplastic polymer/cellulosic fiber composites have attracted the attention of researchers and manufacturers because of the renewable nature of fibers, good mechanical properties, lack of abrasion during compounding, little environmental impact, low weight, and cost savings when compared with the glass, Kevlar, or carbon fiber counterparts. On the other hand, cellulosic fibers present some drawbacks such as low thermal stability, high humidity sensitivity, limited fiber length, hydrophilic nature, and intrinsic variability. The variability originates from harvest conditions, quality of the soil and climate, geographic location, and preconditioning. This variability can also be observed within the same plant as the fibers obtained from the bottom of the stem have different mechanical and physical properties when compared with those obtained from the top of the stem. Composite mechanical properties and, therefore, their final applications will depend on fiber source,[1–4] on fiber treatment,[5–10] on fiber/polymer affinity,[1,11–16] and on the compounding conditions.[17]

Among the drawbacks of the cellulosic fibers, one of the most significant one is the incompatibility with the majority of polymeric matrices that are known to be hydrophobic. The innate lack of affinity between the hydrophilic cellulosic fibers and hydrophobic matrices results in low polymer/fiber interfacial adhesion. Increased affinity between the two components can be achieved by chemical treatment in solution of the fiber surface, by adding small amounts of a grafted matrix during the melt compounding, or by applying both strategies simultaneously. The chemical treatment of fiber surfaces consists of various precompounding strategies to treat reactive solutions of the cellulosic fibers with the purpose to bond chemical groups on their external surfaces that could reduce the hydrophilicity and could further react with the chains of the polymer matrix. For the polypropylene (PP)/flax system, it was shown that fiber treatment with silane,[16,18–21] acetylation,[12,18–23] esterification fiber treatment in a solution of maleic anhydride (MA),[16,18–20] and treatment with PP-*g*-MA in a boiling xylene solution[16–20,24,25] could effectively contribute to an increased affinity between the flax fibers and PP, and therefore help their interfacial adhesion. A second strategy is the incorporation of small quantities of PP-*g*-MA in the melt during the composites compounding, which increases the polarity of the matrix because of

the presence of the anhydride groups. The formation of covalent bonds between the hydroxyl (OH) groups of cellulose and these anhydride groups is one of the reasons for composite strength improvement. In addition, entanglements between PP-*g*-MA and PP chains can be created depending on the PP chain length segment of the PP-*g*-MA macromolecule, therefore creating physical links.[12,21–24,26–30] From an industrial viewpoint and when compared with the chemical treatment in solution of the fiber surface, the use of PP-*g*-MA is less time consuming, involves no solvent disposals, and is a more economical strategy to increase the affinity between the cellulosic fibers and the polymer.

Although many studies have been done regarding the cellulosic fiber surface treatment and the coupling agent addition to increase PP/cellulosic fiber adhesion, the role of the variation of the melt compounding parameters on the composite properties has been less studied. In the case of PP/short cellulosic fiber composites, compounding in a twin-screw extruder is usually done before the injection molding of finished products. It was demonstrated that the reduction in fiber length associated to the injection-molding step does not significantly affect the tensile properties of PP/cellulosic fiber/PP-*g*-MA composites because of fiber orientation along the polymer flow direction.[31] Some studies exist concerning the effect of cellulosic fiber content and type on the fiber damage during composites extrusion.[31–34] However, these studies do not consider the effect of extrusion parameters such as screw configuration, fiber feeding zone, temperature, flow rate, and revolutions per minute (rpm) on composite final performance.

This article discusses the effect of the formulation and extrusion parameters such as screw configuration, screw speed, fiber feeding zone, compounding temperature, and flow rate on the properties of PP/flax fiber composites processed by injection molding. The first efforts were concentrated on the feeding method of the cellulosic fibers in a continuous manner. This operation is often problematic because of the low bulk density of the cellulosic fibers, which cannot freely flow through the volumetric feeder resulting in an inconsistent feeding rate. As a precompounding step, an increase of the bulk density of short flax fibers is thus necessary to make them easier to manipulate and to make the composite manufacturing possible. For this purpose, the flax and hemp fibers were pelletized by passing them through a pellet mill.

The composite compounding study was divided into two parts. For the first part, the composite formulation was kept constant, whereas the extrusion parameters were varied. The compounding of the composites was done in successive steps, where each step corresponded to the variation of one extrusion parameter. The obtained composites were characterized for each set of parameters. For the second part of this study, the best combination of screw configuration, fiber feeding zone position, extrusion temperature, flow rate, and screw speed was kept constant for the remaining of the trials, whereas the composite formulation was varied. The effect of flax and hemp fiber concentrations and the incorporation of additives on the composite properties were investigated. Finally, the composites processability and recyclability using injection molding and cast sheet extrusion are also discussed.

EXPERIMENTAL

Materials

Isotactic polypropylene Pro-fax 1274 from Basell BV (Hoofddorp, The Netherlands) with an average molecular weight of 300,000 and a melt flow index of 12 g/10 min was used as matrix. Flax and hemp fibers with a content of 10 wt % impurities, mainly shives, were provided by Schweitzer Mauduit (Canada). The concentration of fibers in PP was varied from 10 to 40 vol %. The PP-*g*-MA used as a coupling agent was Eastman Epolene-43 (E43; AN = 45, M_w = 9100, with 4.81 wt % of MA). Its concentration, after variation in composites between 0 and 5 vol % to evaluate the optimal one, was set to 3.75 vol %. Calcium oxide (CaO), obtained from Laboratoire MAT (98 wt % purity), was used as a reactive filler. Previous work done in our laboratory[35] showed that this basic reactive filler plays a role in absorbing moisture in fibers, neutralizes acidity of fiber impurities, and therefore minimizes the oxidation and degradation of cellulosic fibers during melt processing. Consequently, CaO also helps to increase strength and modulus of the final composites. The recommended concentration of CaO in PP-based composites with natural fibers is 3.5 vol % (10 wt %). Glass fibers of 6.5 mm in length were also used to produce equivalent composites with the purpose to evaluate the potential of the flax and hemp fibers as reinforcement replacement in PP composites.

Processing

Extrusion Process. To feed the cellulosic fibers during the extrusion process, a mechanical treatment step is necessary because the cellulosic fibers are fluffy and difficult to feed in this shape without compromising the consistency of fiber flow rate. A proprietary technology was used to produce cellulosic fiber pellets with minimum fiber length degradation. Prior to extrusion, the cellulosic fiber pellets were dried at 80°C for a minimum of 24 h.

The extruder used to process the composites was a Leistritz 34 mm corotating twin-screw extruder having 12 mixing zones and an *L*/*D* ratio of 40. This extruder has two feeding locations, and the capillary die at its exit had a diameter of 2 mm.

The composite melt extrusion study was divided into two essential parts. For the first part, the composite formulation was kept constant (20 vol % of flax and 2.5 vol % of E43), whereas the extrusion parameters were varied one by one. The compounding of the composites was done in successive steps, where each step corresponded to the variation of one extrusion variable. As presented in Figure 1, a severe, a medium, and a soft screw configuration were initially tested. The degree of screw severity was differentiated by the ratio of shear disks situated in the fourth and eighth zones, that is, 10/10 [Figure 1(a)], 5/5 [Figure 1(b)], and 5/0 [Figure 1(c)]. For each configuration, the flax pellets were fed in two manners: first, at the same time as PP into zone 0, and second, into the fifth zone. The obtained composites were characterized, and the best combination of screw configuration/fiber feeding zone position was determined and used for the second part of this study. Then, different extrusion

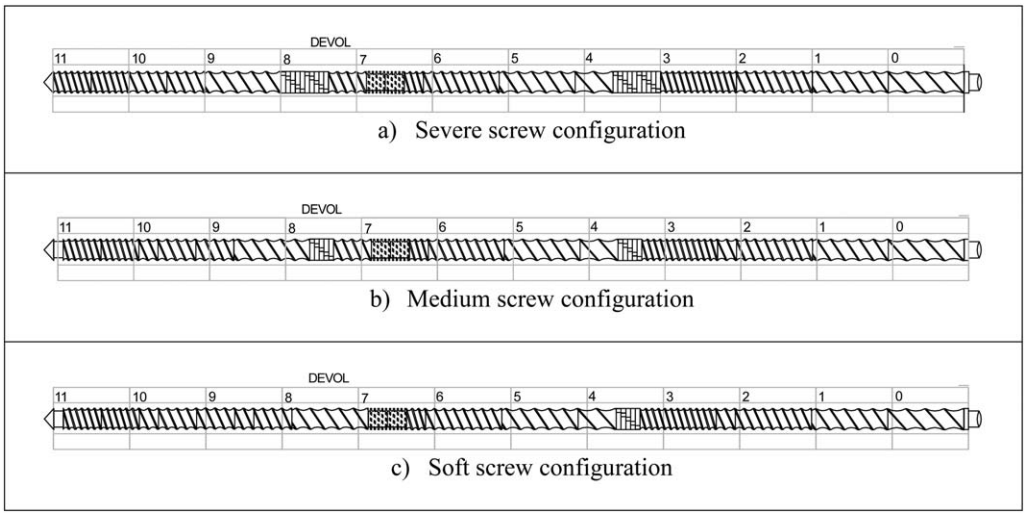

Figure 1. Screw configurations used in extrusion process of composites.

temperatures were tested by using three flat profiles (200°C, 185°C, and 170°C), and a fourth one in which the temperature was decreased constantly from 200°C to 170°C toward the die exit. After the sample characterization, the best temperature profile was set for the continuation of the work. Finally, the flow rate and revolutions per minute variations were considered. Three total flow rates were used: 5, 7.5, and 10 kg/h. The screw speeds were set at 100, 150, and 200 rpm. Once again, the obtained composites were characterized, and the best combination of flow rate/screw speed was determined and used further. After each of these trial stages, the flax fibers were separated from the composites by PP solubilization in xylene. The average length of the fibers and the mechanical and rheological properties of the composites were evaluated.

For the second part of this study, the optimal extrusion parameters resulting from the first series of experiments were kept constant, whereas the composite formulations were varied, and PP composites with flax, hemp, and glass fiber contents from 10 to 40 vol % were compounded. The PP-*g*-MA coupling agent was used at a concentration of 3.75 vol % (3.5 wt %) and the CaO reactive agent at a concentration of 3.5 vol % (10 wt %).

Injection Molding. Samples selected for mechanical testing were first dried at 80°C for 24 h and then injection molded using a 34-ton BOY injection-molding press with a melt temperature of 190°C and a mold temperature of 30°C. Standard specimens were molded according to ASTM D-638 and D-259 for tensile and Izod impact properties evaluation, respectively. The recyclability of flax composites was evaluated for composites made of 10 and 30 vol % flax. The composite pellets were reprocessed by repeating the injection/grinding/drying cycle for five times.

Sheet Extrusion. The composite pellets prepared as described above were first dried and then extruded into sheets using a cast film line, that is, a Davis-Standard single-screw extruder equipped with a 20-cm-wide flat die. The melt temperature was 180°C, and 1-mm-thick sheets were inserted between water-cooled rolls maintained at 40°C. Only selected compounds were extruded into sheets, that is, the ones containing 10 and 30 vol % flax. Blends containing 10 and 30 vol % glass fibers were also extruded into sheets for comparison purposes.

Characterization

Morphology. Scanning electron microscopy (SEM) was carried out on polished and impact-fractured composite surfaces. A coating of gold/palladium alloy was applied on the specimens prior to the observation. A JEOL JSM-6100 SEM at a voltage of 10 kV was used to analyze the dispersion of the fibers into the matrix and the interface between fibers and PP matrix.

Fiber Qualitative Analysis. Fiber damage during extrusion was assessed using a fiber extraction method followed by an average fiber length measurement. A jacketed Soxhlet extractor was used, allowing the continuous extraction of the matrix with clean hot solvent. Extruded biocomposite strands weighing ~ 2.5 g were dried first for 24 h. The weight was recorded, and the pieces were introduced into a double-wall cellulose thimble. The thimble was introduced into the extraction cup of the jacketed Soxhlet extractor connected to a distilling pot and a condenser. Xylene (450 mL) was introduced into the distilling pot and heated to reflux at 145°C during 24 h. Fibers were recovered, dried, and weighed. Average flax fiber lengths and diameters were determined using a High-Resolution Fiber Qualitative Analyzer (HiRes FQA) from Optest Equipment.

Rheology. The rheological properties of the composites were evaluated at 185°C using a rotational Advanced Rheometric Expansion System rheometer, with a plate–plate geometry in dynamic mode. The plate diameter was 25 mm and the gap was around 1.7 mm. Frequency sweeps were carried out to determine the complex viscosity over a frequency ranging from 0.1 to 100 rad/s. The tests were conducted using a deformation of 15%. The samples were dried at 80°C for 48 h before testing. The samples were kept under a nitrogen blanket during the rheological testing to minimize oxidation and to maintain a dry environment.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) was used to determine the melting temperature, the crystallization temperature, and the crystallinity content of the composite materials. The tests were done using a TA

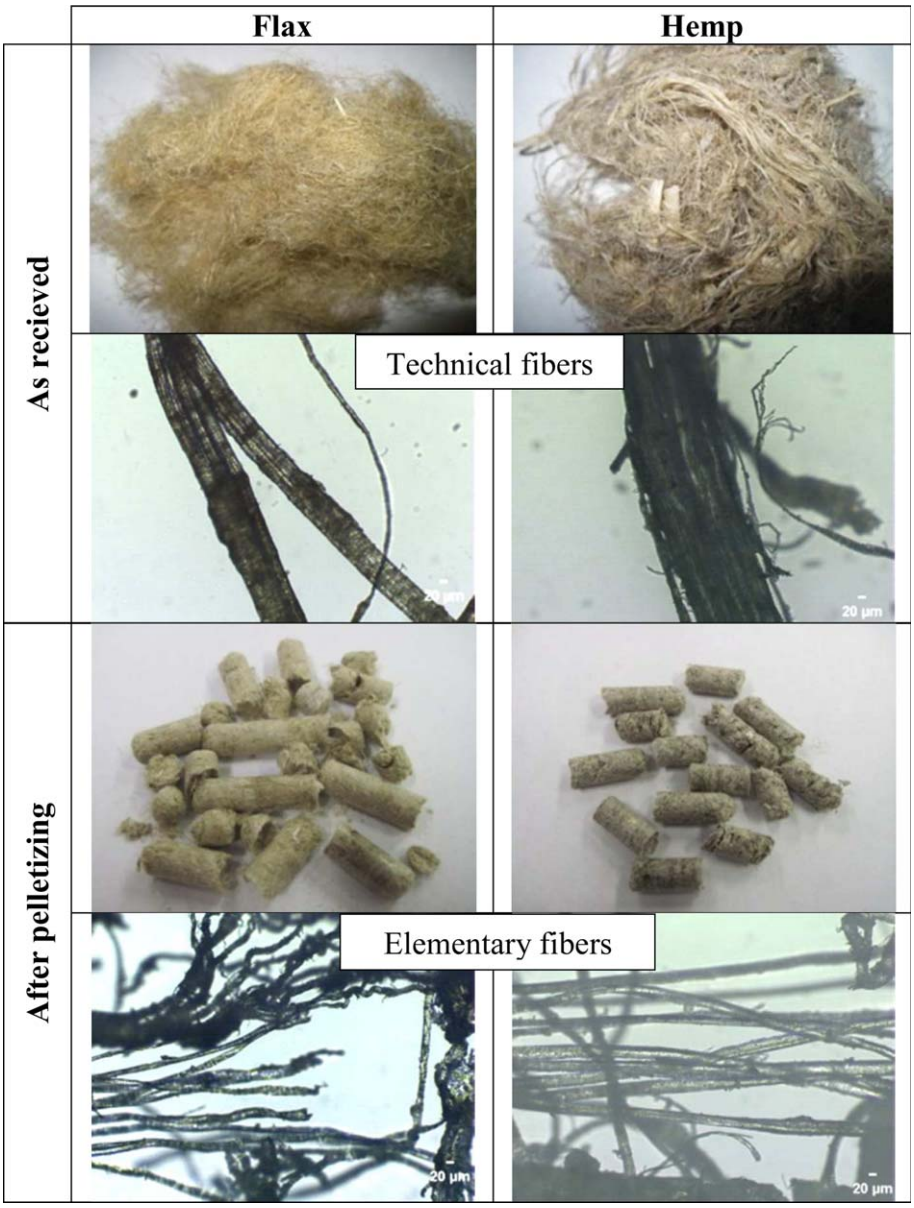

Figure 2. Physical aspect of flax and hemp fibers before the extrusion step: original and pelletized. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Instruments Q2000 calibrated using an indium standard. The samples, with a weight around 10 mg, were heated from 30 to 200°C at 20°C/min, kept at 200°C for 5 min to erase the thermal history and cooled back down to 30°C at 20°C/min. For the calculation of the crystallinity level, the heat of fusion of PP (100% crystalline) was taken as 207.1 J/g.[36]

Mechanical Properties. The tensile testing was carried out according to ASTM D-638 at a velocity of 5 mm/min on standard Type I dog-bone shaped samples. The tensile properties of the cast sheets were measured in both machine (MD) and transverse (TD) directions. The tensile modulus (TM) and the tensile strength (TS) were evaluated. A video extensometer was used to determine the elastic modulus. The Izod impact strength (IS) was evaluated according to ASTM D-259 using notched specimens and 2 kg hummer. All reported values are the average of five tests. Before testing, the specimens were dried in an oven for 24 h at 50°C ± 3°C, cooled in a desiccator, and immediately weighed to the nearest 0.001 g before testing.

Sensitivity to Ambient Humidity. Moisture absorption tests (ASTM D-5229/D-5229M-92) were done on injected dog bones containing 20 vol % flax fibers exposed in a controlled humidity chamber at 50% ambient humidity for a duration of 1 year. For each formulation, five exposed dog bones were tested.

RESULTS AND DISCUSSION

Fiber Pelletizing

The feeding trials of the flax or hemp fibers in their original bulk form using a volumetric feeder failed because of their low

Table I. Mechanical Properties of Composites: Variation of Extrusion Parameters

Sample	TS (MPa)	TM (GPa)	IS (MPa)
Reference polypropylene			
As-received	31.9 (1)	1.5 (0.1)	1.85 (0.5)
Extruded	31.1 (0.1)	1.6 (0.1)	1.57 (0.4)
Variation of screw configuration and feed zone			
Severe, 0	39.0 (0.3)	3.2 (0.4)	2.5 (0.3)
Severe, fifth zone	38.5 (0.3)	3.2 (0.2)	3.0 (0.0)
Medium, 0	37.0 (0.3)	3.0 (0.1)	2.7 (0.4)
Medium, fifth zone	37.7 (0.2)	3.0 (0.1)	2.9 (0.5)
Soft, 0	38.0 (0.5)	3.2 (0.2)	2.0 (0.0)
Soft, fifth zone	38.4 (0.3)	3.4 (0.2)	2.3 (0.4)
Variation of extrusion temperature (°C)			
200	40.2 (0.6)	3.5 (0.1)	2.7 (0.4)
185	37.7 (0.2)	3.1 (0.1)	2.9 (0.5)
170	39.2 (0.3)	3.4 (0.2)	3.0 (0.8)
200–170	38.4 (0.2)	3.3 (0.1)	3.0 (0.0)
Variation of the total flow rate (kg/h) and revolutions per minute			
5, 100	39.0 (0.3)	3.4 (0.2)	2.9 (0.3)
5, 150	37.7 (0.2)	3.1 (0.1)	2.9 (0.5)
5, 200	37.8 (0.2)	3.2 (0.1)	2.4 (0.2)
7.5, 100	38.2 (0.4)	3.3 (0.1)	3.0 (0.0)
7.5, 150	38.3 (0.2)	3.4 (0.1)	2.9 (0.4)
7.5, 200	37.2 (0.8)	3.2 (0.1)	2.5 (0.3)
10, 100	37.0 (0.7)	3.2 (0.2)	2.8 (0.3)
10, 150	37.8 (0.6)	3.3 (0.1)	3.0 (0.0)
10, 200	37.9 (1.1)	3.3 (0.2)	2.8 (0.3)

Standard deviation is given in parenthesis.

bulk density. Important variation of the fiber flow rate and bridges into the feeder were observed. An increase in the bulk density was hence obtained by performing the pelletizing step before compounding. To facilitate this pelletizing, the bulk cellulosic fibers were first unpacked by cutting them to a length of 6.5 mm and then uniformly wetted with water. During the pelletizing process, the wetted cellulosic fibers were pressed through a die plate using two rotating roll mills.

Figure 2 presents the physical aspect of flax and hemp fibers in their original/as-received shapes and after the pelletizing step. In addition, optical microscopy images show details of the flax and hemp fibers before and after pelletizing. The temperature during the pelletizing process was kept constant at around 70°C. As measured using a HiRes FQA device, the average length of the flax fibers was 3.310 mm before and 2.954 mm after the pelletizing step. Therefore, this indicates that there was no thermal degradation or important fiber shortening (mechanical degradation) after the pelletizing step. The optical micrographs of Figure 2 show details on the initial fibers and the ones extracted from the flax pellets. An important advantage of this pelletizing step is the separation of the technical fibers with an initial diameter of around 100 μm, into elementary fibers with diameters about 20 μm. It should be stressed that this pelletizing step released the elementary fibers from bundles and separated them from each other with less nonfiber tissue attached on their surface. In such a case, the aspect ratio (length/diameter) was increased. This indicates that the cellulosic fibers were introduced into the PP melt as elementary fibers that probably eased the fiber wetting during the melt blending.

Variation of Processing Parameters

In the first part of this work, the biocomposite composition was maintained constant (77.5 vol % of PP, 20 vol % of flax fibers, and 2.5 vol % of PP-*g*-MA), whereas the screw configuration, the feeding zone of flax pellets, and the extrusion parameters were varied. The resulting composites after each step of parameter variation were characterized using mechanical testing, shear viscosity measurements, and fiber length analysis to select the best extrusion conditions.

For mechanical characterization, the composites were injection molded into standard shape specimens for tensile and impact tests, and the results are presented in Table I. For comparison purposes, as-received PP and extruded PP were also evaluated. As-received PP had a TS of 32 MPa and a TM of 1.5 GPa. After

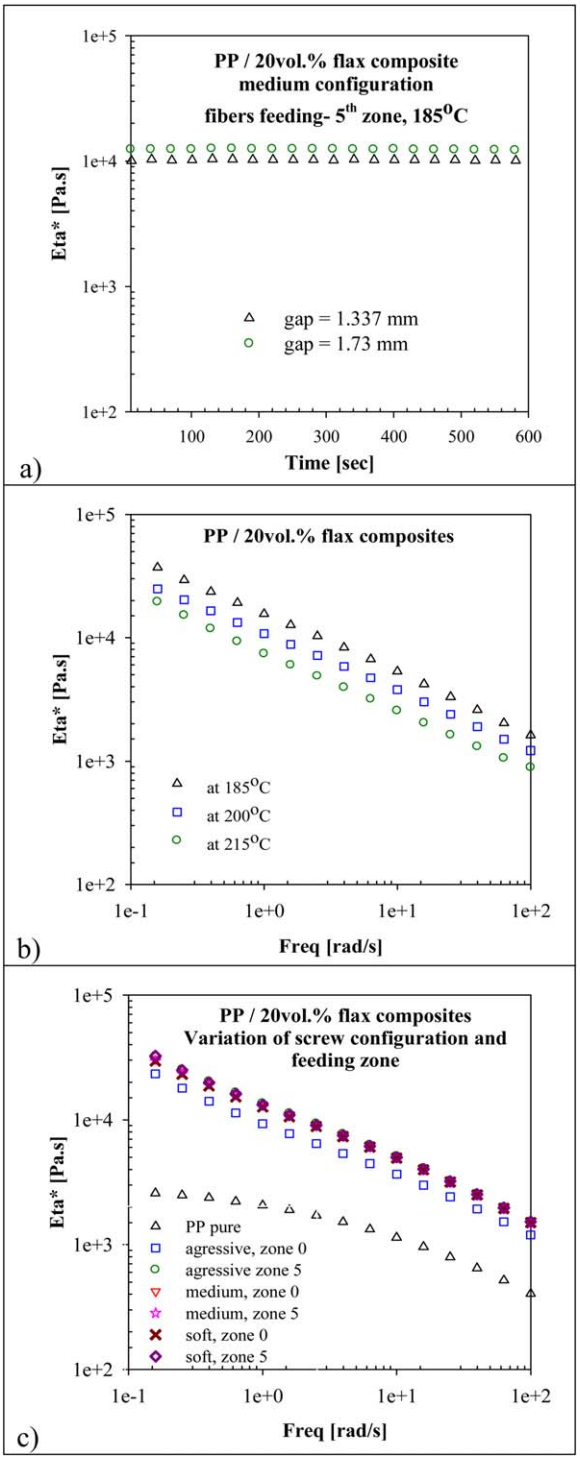

Figure 3. Complex viscosity of PP/20 vol % flax fibers/2.5 vol % E43 as (a) a function of testing time and gap, (b) temperature, and (c) screw configuration and feeding zone. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

extrusion, it was found that PP preserved its mechanical properties and that even the most severe screw configuration did not seem to damage the macromolecular chain integrity. The addition of fibers in PP led to an increase of TS and TM to about 37–40 MPa and 3.00–3.50 GPa, respectively, whatever the extrusion parameters. As discussed before, the flax technical fibers were separated into elementary fibers during the fiber-pelletizing step that helped the dispersion and distribution of the fibers in the PP melt. Usually, this split out of the technical fibers into elementary ones has to take place in the extruder. However, it was not the case as the flax fibers were already fed as elementary fibers.

The changes of the rheological properties of PP/flax fiber composites obtained for different extrusion parameters were investigated under dynamic oscillatory conditions. In principle, polymer/fiber composite viscosity should be a function of fiber length, fiber content, matrix properties, extrusion parameters, and formulation. In this first series of experiments, the extrusion parameters are the only variables with a potential consequence on fiber length. The complex viscosity dependency of the PP/20 vol % flax fibers/2.5 vol % E43 composite on the test time, test temperature, and on screw configuration/fiber feeding zone is presented in Figure 3(a–c), respectively. Composites stability at high temperature is important during the time of testing to guarantee that the materials were not chemically altered and did not degrade. As presented in Figure 3(a), the materials are very stable for at least 10 min at 185°C and PP, and moreover, flax fibers did not undergo thermal degradation during the rheological test. It can be assumed that this is also the case during the compounding step, for which the extrusion residence time is estimated to be around 2 min. In addition, the results of oscillatory tests done at two different gaps proved that composite viscosity depends slightly on this testing parameter. For the rest of the rheological testing done for this study, a constant gap of 1.7 mm was selected for all tested samples. It is well known that the gap has to be three times larger or more than the fiber length to avoid the occurrence of wall-slip phenomena.[37] Figure 3(b) presents the complex viscosity of the composite as a function of frequency at three different testing temperatures. A simple shear thinning behavior without Newtonian plateau is observed for the entire frequency range. This is in contrast with the behavior of the PP that exhibits a clear Newtonian plateau and shear thinning only at high frequencies. However, as expected, the composite viscosity decreases with increasing temperature, which is similar to the behavior of PP. Figure 3(c) reveals the complex viscosity of composites obtained when varying the screw configuration and the feeding zone location of the flax pellets. The viscosity of pristine PP is also presented for comparison purposes. All curves corresponding to the composites are almost overlaid with the exception of the composite obtained with the severe screw configuration, which is slightly lower. The same overlaying of the viscosity curves was observed for the composites obtained when varying the extrusion temperature. These rheological results confirm the ones obtained from mechanical testing. Because changes in screw configuration and in fiber feeding zone location gave the same composite viscosities and same mechanical properties, it can be therefore postulated that all flax fibers in the composites have similar lengths.

Figure 4 presents the complex viscosity as a function of frequency for composites obtained by varying the extruder total flow rate and screw speed (revolutions per minute), whereas all

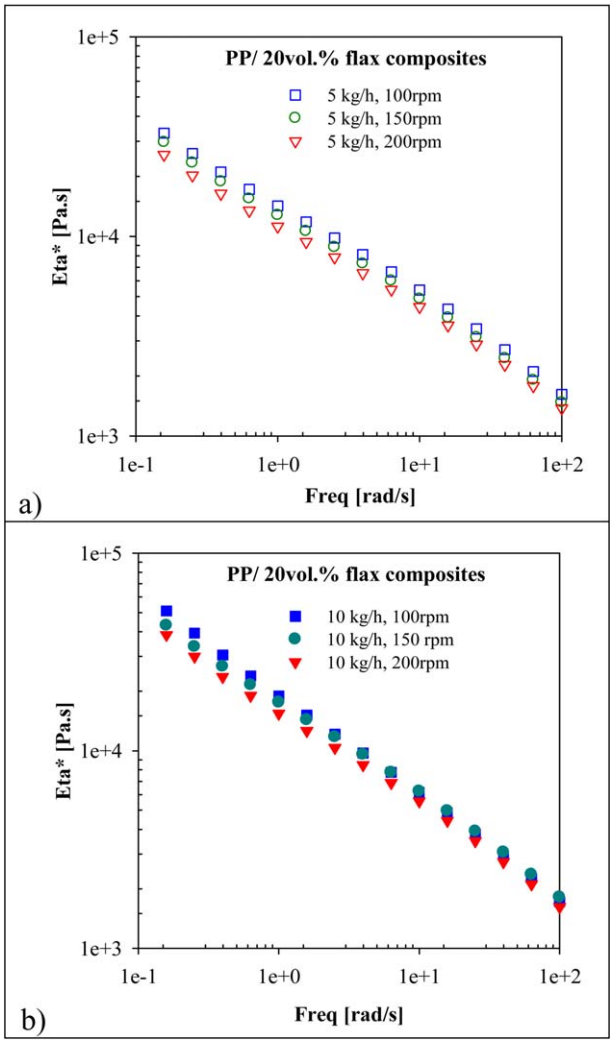

Figure 4. Complex viscosity as a function of revolutions per minute of PP/20 vol % flax fiber composites at different total flow rates of the extruder: (a) 5 kg/h and (b) 10 kg/h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the other processing parameters were kept constant. Figure 4(a) shows the composite viscosities obtained at a flow rate of 5 kg/h, and Figure 4(b) shows the composite viscosities obtained at 10 kg/h. The composite viscosities obtained at the intermediate total flow rate of 7.5 kg/h exhibited a similar behavior (data not shown). The viscosity values are very similar no matter what the flow rate and screw speed were, with a slight decreasing trend when increasing the screw speed. It is believed that higher revolutions per minute increased the fiber–fiber and polymer–fiber interactions, which further slightly affected the fiber attrition. This very slight viscosity decrease with revolutions per minute was detected during rheological evaluation because of the rheometer's higher sensibility to material composition when compared with macroscopic mechanical testing. Overall, these results confirmed once again the TSs presented in Table I. The viscosity results obtained when varying revolutions per minute and flow rates are also very similar with the ones obtained when varying the screw configuration, feeding zone, and extrusion temperature (the results are not presented here because of their similarity). Therefore, in all these cases, the flax fibers were subjected to similar attrition dynamics. This seems to indicate that all the flax fibers in composites obtained for different extrusion parameters gave similar reinforcement effect.

The extraction of the flax fibers from the composites was done to evaluate the fiber attrition during compounding as a function of the extrusion parameters. Only the results for the variation of screw configuration and fiber feeding zone, along with the initial flax fiber lengths, are presented in Table II, in terms of average length-weighted length. The flax fibers extracted from the composites exhibited very similar lengths. These fiber lengths are six to seven times lower than the initial flax fibers, that is, around 3 mm. Similar results were reported in the literature for PP/flax fiber composites.[24,25,27,34,38] The extrusion process affects the final fiber length of the composites due to the fiber–fiber interactions and due to the strong shear stresses acting in the viscous molten PP. During extrusion, the flax fibers are mechanically degraded into thinner and smaller fibers when the hydrodynamic forces exceed the fiber strength and the cohesive forces between the individual fibers. In addition, the cellulosic fibers have natural and artificial imperfections as well as kink bands. These weak areas are the most probable rupture points along the fiber length when the fiber is mechanically stressed. This uniformity of flax fiber length confirms our results obtained from mechanical and rheological testing, and our assumption that all flax fibers undertook similar attrition during compounding no matter what the extrusion parameters were.

To confirm this important finding, a supplementary extrusion trial was done by changing the extrusion parameters with the intention to minimize fiber attrition. As illustrated in Figure 5, the screw configuration was further softened by eliminating the shear disks from the second half, the feeding zone of the flax fibers was moved from the fifth zone toward the extruder end at the seventh zone, and the composite strands were cut at maximum length during the granulation step before feeding the injection-molding machine. The flax fibers were fed by hand in their original bulk shape (no cutting or pelletizing prior to the extrusion). The same composite formulation was used as previously. The mechanical results disclosed a TS of around 39 MPa and a TM of 3.3 GPa, which are very similar as for the first trials. The length-weighted length of flax fibers extracted from the composites had this time a value of 0.8 mm. This slightly higher value of the fiber length in comparison with 0.5 mm obtained from the first tests demonstrates that this attempt to diminish the fiber attrition during the extrusion was successful. On the other hand, the tensile results were not affected by this slightly higher flax fiber length. All these results obtained for different extrusion parameters demonstrate once again that the mechanical properties of the studied composite are not affected by the screw configuration, revolutions per minute, flax feeding zone, flow rate, and extrusion temperature. This provides evidence of a very large extrusion window of PP/flax short fiber composites, and it can be considered as an advantage of short flax fibers/PP composite compounding. This large processing window was induced by two important factors: the shape of the flax fibers

Table II. Length of As-Received Flax Fibers and of Flax Fibers Isolated from Compressed Pellets and from the Composites Obtained for Different Extrusion Parameters

Reference flax samples	L_w (mm), SD = 0.005
As-received	3.310
From compressed pellets	2.954
Variation of screw configuration and feed zone	
Severe, 0	0.422
Severe, fifth zone	0.619
Medium, 0	0.682
Medium, fifth zone	0.459
Soft, 0	0.419
Soft, fifth zone	0.398

that were introduced into the melt in elementary form because of the pelletizing step, and the original length of about 3 mm of the original flax fibers. The flax fibers used were of Canadian industrial grade, and their original length is believed to be under the critical fiber length value.

Variation of Biocomposite Composition

For the second part of this study aiming at determining the importance of formulation on the composite performance, the extrusion operating conditions were set at 185°C, 100 rpm, and 10 kg/h. The flax and hemp pellets were fed using a gravimetrical feeder normally used for polymer pellets. The screw configuration and fiber feeding zone corresponded to the one represented in Figure 1(b). The flax, hemp, and glass fiber content was varied from 0 to 40 vol %. Composites were obtained without additives and by adding a combination of coupling and reactive agents. Figures 6 and 7 present the 2D morphological features of longitudinal polished surfaces of PP/flax, PP/hemp, and PP/glass fiber extruded strands.

It should be first noted that the selected extrusion parameters and screw configuration gave a very good split out of flax pellets and very good fiber dispersion no matter what the fiber type and fiber concentrations were. Some shives could be seen in the natural fiber composites; this was expected as the industrial flax and hemp used in this work contained 10 wt % impurities, mainly shives. The cellulosic fibers, because of their flexibility, are less oriented in the flow direction than the glass fibers, which are rigid. The length of the fibers extracted from the composites obtained when varying the cellulosic content and measured using FQA analyzer (Table III) varied between 0.487 and 0.669 mm. These values are very similar to the ones observed in the first part of this study (variation of extrusion parameters), that is, around 0.500 mm. Therefore, the final mechanical properties of the composites will be affected only by the fiber concentration and additive content.

The results obtained from viscosity measurements performed on different PP/flax, PP/hemp, and PP/glass fiber composite systems and the PP reference are presented in Figure 8. A comparison between flax and hemp fiber composite viscosities with increasing fiber content is presented in Figure 8(a), and between flax and glass fiber composites in Figure 8(b). The viscosity of PP containing E43 and CaO slightly increased when compared with pristine PP (3030 Pa s when compared with 3568 Pa s, evaluated at a frequency of 0.1 s^{-1}). Increasing the flax fiber content from 10 to 30 vol % highly increased the composite viscosity from 16,962 up to 130,617 Pa s. The viscosities of hemp fiber composites are slightly higher than that for flax fiber composites, increasing from 20,955 up to 177,113 Pa s with increasing hemp fiber content. This rise in PP/flax or hemp composites viscosity with fiber concentration is due to the increase of fiber–fiber interactions. Moreover, higher fiber content leads to a more pronounced shear thinning behavior. It should be noted that the increase of the viscosity with fiber content is more noticeable at low frequencies. At high frequencies, the effect is weakened probably due to the fact that fibers coalesce together during the rheological testing, yielding a more dominant effect of the matrix.

Figure 8(b) shows the complex viscosity as a function of frequency of PP/flax fibers biocomposites and PP/glass fiber composites. When increasing the flax content up to 40 vol %, the zero-shear viscosity of the PP matrix increased from 3030 Pa s to 226,562 Pa s, which is much higher when compared with the addition of 40 vol % glass fibers (zero-shear viscosity of 26,993 Pa s). For a content of 40 vol % glass fibers, the zero-shear viscosity of the composites is comparable with the viscosity of PP reinforced with only 10 vol % flax fibers. For equivalent volumes occupied in the PP matrix, the number of flax fibers will be higher when compared with the number of glass fibers, and, hence, there will be more matrix–fiber and fiber–fiber interactions. Moreover, the cellulosic fibers had a more significant effect on the viscosity than the glass fibers at the same volumetric content because of the higher fiber–fiber entanglements.

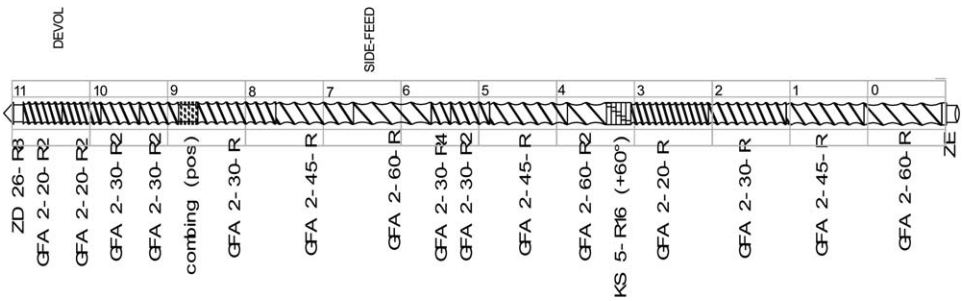

Figure 5. Softer screw configuration used in extrusion process of composites.

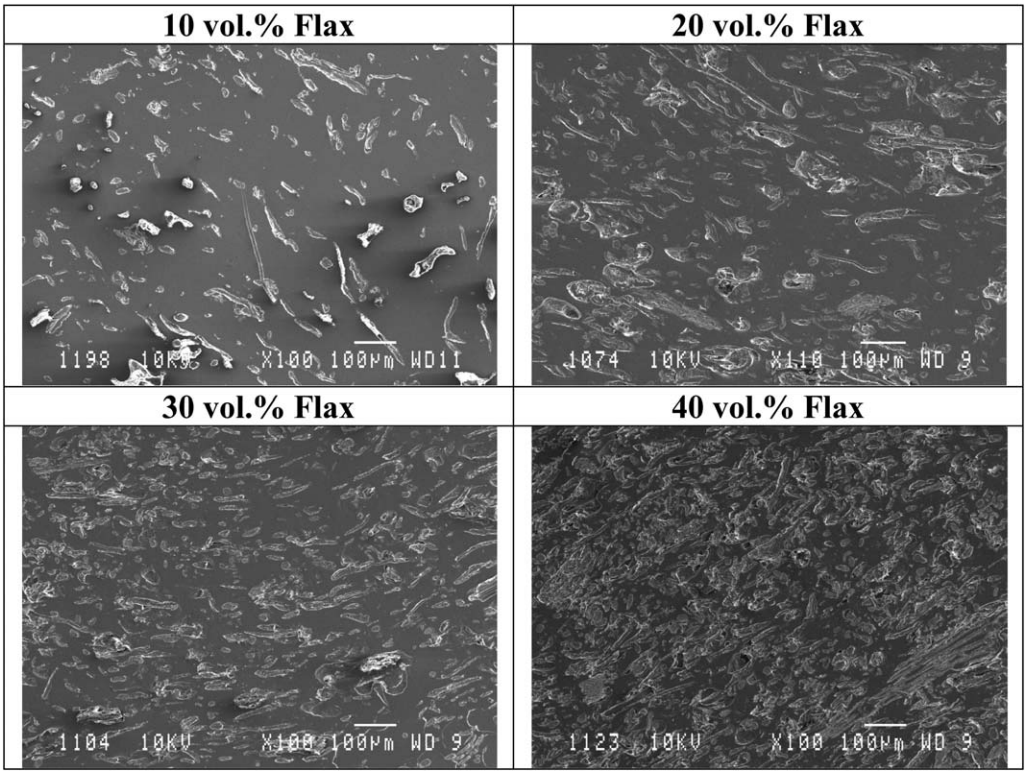

Figure 6. SEM micrographs of longitudinal polished surfaces of flax composites obtained at 10, 20, 30, and 40 vol % fibers.

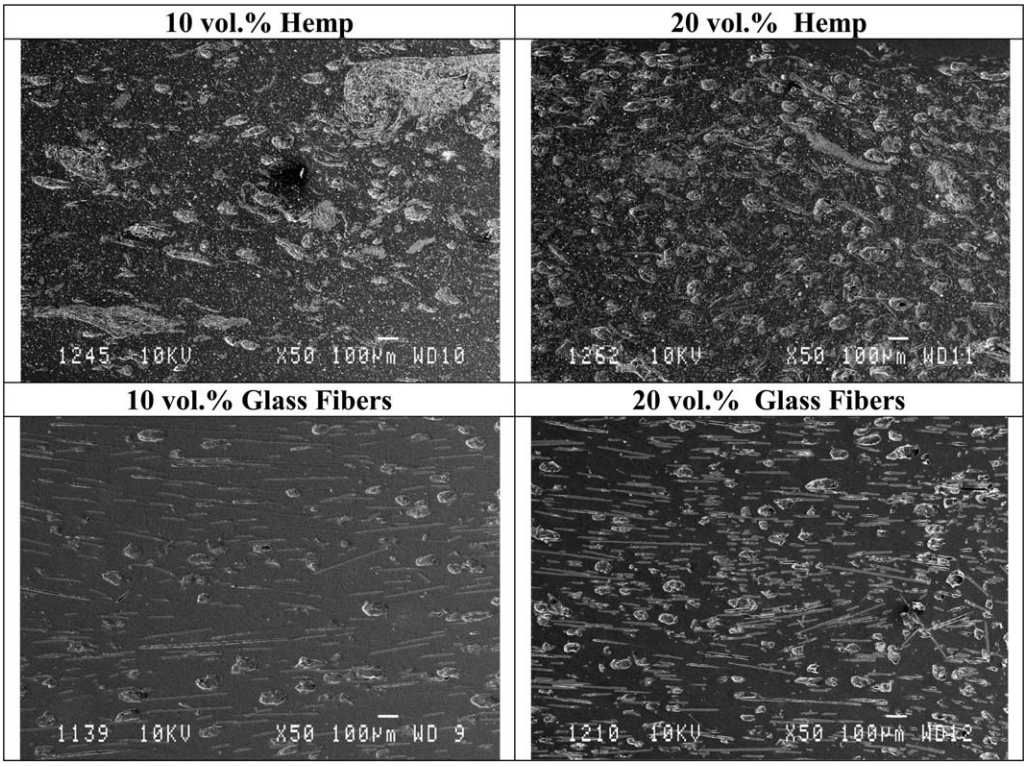

Figure 7. SEM micrographs of longitudinal polished surfaces of 10 and 20 vol % hemp composites and 10 and 20 vol % glass fiber composites.

Table III. Average Length of Flax Fibers Extracted from Composites Containing Different Levels of Cellulosic Fibers

Sample	L_w (mm), SD = 0.005
Flax composites	
10 vol %	0.487
20 vol %	0.604
40 vol %	0.573
Hemp composites	
10 vol %	0.660
30 vol %	0.669

Nonisothermal crystallization behavior of PP/flax fiber composites without and with additives is presented in Figure 9. Similar results were obtained for PP/hemp fiber composites (results not shown). The first graph shows the melting curves and the second one the cooling curves obtained by DSC. The curves corresponding to the pristine PP, extruded PP, and PP formulated with different additives are presented. The melt temperatures (T_m), crystallization temperatures (T_{cc}), fusion and crystallization enthalpies (ΔH_m and ΔH_{cc}), and crystallinity values (X_{ch} and X_{cc}) are presented in Table IV. During the first heat cycle,

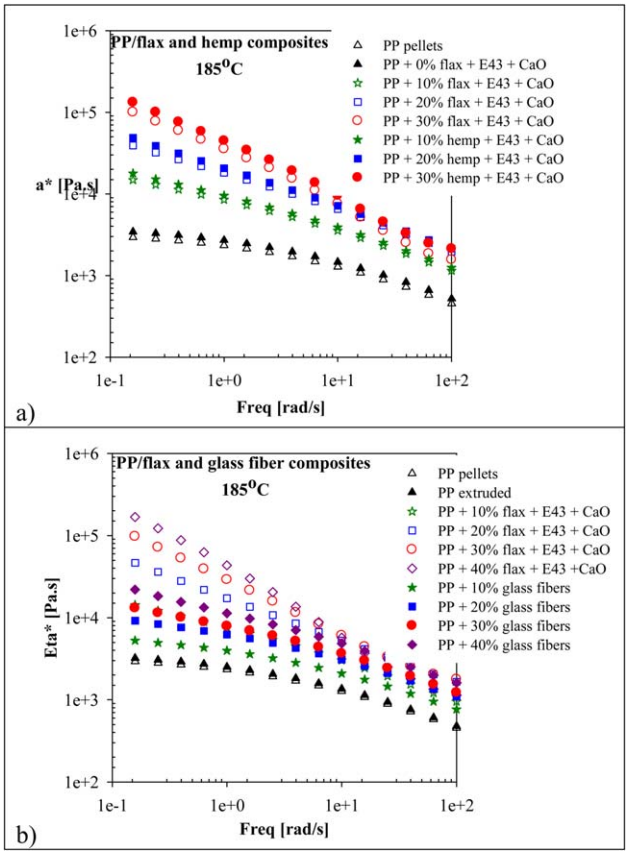

Figure 8. Complex viscosity as a function of frequency: (a) PP/flax vs. PP/hemp fiber composites and (b) pure PP/flax vs. PP/glass fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

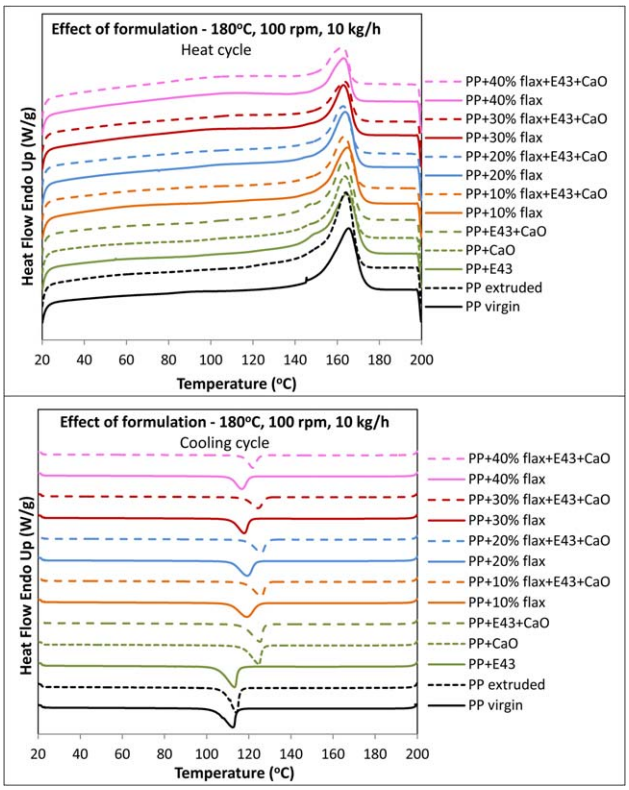

Figure 9. Heating and cooling thermograms obtained from DSC for PP/flax composites of different compositions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the curves show that the PP and its composites do not crystallize because they are already fully crystallized after the compounding. The fiber addition did not change the T_m that remained at around 163°C; however, the PP matrix crystallinity increased slightly from 46 to 51% with increasing flax fiber content and the addition of CaO. The E43 coupling agent had no obvious effect. Considering the curves obtained during the cooling cycle, it should be observed that the crystallization temperature, T_{cc}, was highly affected by the presence of the fibers and of CaO. This crystallization temperature was shifted to higher temperatures by about 5°C because of the presence of flax fibers and by 12°C when CaO was present. Both accelerated the crystallization phenomena. The crystallinity reached during the DSC cooling increased with flax fiber and CaO content from 53% up to 60%. In consequence, the flax fibers and CaO act, as expected, as nucleating agents in the crystallization process of the composites by inducing crystallization and by increasing the crystallinity.

The TS and TM of PP/flax composites with increasing flax fiber content without and with E43 + CaO as additives are presented in Figure 10(a,b), respectively. The composites obtained with hemp fibers presented similar tensile properties, and the corresponding results are therefore not presented here. The values of TS and modulus for pristine PP and PP with different additives are also shown. As observed in Figure 10(a), there are negligible differences in TS between pristine PP and PP + E43, PP + CaO, and PP + E43 + CaO formulations. The TS of composites

Table IV. Nonisothermal Data Obtained During the Heating and Cooling Cycles of Extruded PP/Flax Composites Without and with E43 and CaO

	Heating			Cooling		
	T_m (°C)	ΔH_m (J/g)	X_{ch} (%)	T_{cc} (°C)	ΔH_{cc} (J/g)	X_{cc} (%)
PP pristine	165	84	41	112	103	50
PP extruded	164	85	42	114	110	53
PP + E43	165	89	43	113	109	53
PP + CaO	164	79	42	125	95	51
PP + E43 + CaO	163	78	42	125	93	50
PP + 10% flax	165	69	39	119	90	51
PP + 10% flax + E43 + CaO	163	60	38	126	76	48
PP + 20% flax	164	63	42	119	83	55
PP + 20% flax + E43 + CaO	163	57	44	126	68	52
PP + 30% flax	163	55	44	118	68	54
PP + 30% flax + E43 + CaO	164	47	44	124	59	55
PP + 40% flax	163	45	44	117	59	57
PP + 40% flax + E43 + CaO	162	43	51	122	50	60

obtained without any additive decreased to some extent with flax fiber content when compared with pristine PP. On the contrary, in the presence of both E43 and CaO, the TS increased from 31 for pristine PP up to 43 MPa for composites containing 30 vol % of flax fibers. A slight decrease to 40 MPa is observed when increasing the fiber content from 30 to 40 vol %. However, the addition of E43 as a coupling agent simultaneously with CaO as a reactive agent promoted very efficiently the flax fiber/PP matrix adhesion and had an important effect on the TS of the composites. In terms of TM, a regular increase was observed as a function of fiber loading. Pristine PP did not present any change in modulus with the addition of E43. Nevertheless, the addition of 10 wt % of CaO increased the PP modulus from 1.55 up to 2.1 GPa. When the flax fibers were used as reinforcements without any additive, the TM increased continuously up to 5 GPa at a loading of 40 vol % flax fibers. The use of E43 and CaO as coadditives helped to increase additionally the TM of the PP/40 vol % flax fiber composite up to 5.45 GPa.

The results for Izod impact testing of pristine PP, of formulated PP without fibers, and of the composites obtained with flax and glass fibers are presented in Figure 11. Composites reinforced with hemp fibers exhibited similar ISs as the composites containing flax fibers (data not shown). Pristine PP and PP formulated only with the additives (E43 and CaO) had similar values of Izod IS. The increase of the flax fiber content in PP resulted in materials having ISs higher than PP alone, and the IS value increased with flax fiber content. It should be stressed that the composites containing glass fibers present ISs more than twofold higher than the composites reinforced with flax fibers. This is expected because of the inherent higher rigidity and higher impact resistance of the glass fibers. To improve the toughness of the composites obtained with cellulosic fibers, a further improvement in fiber/matrix adhesion should be achieved and/or several elastomers/impact additives should be used as impact modifiers in these fiber-reinforced PP composites.

Scanning electron micrographs of fractured surfaces after Izod impact tests are presented in Figure 12. The upper and lower rows represent the composites containing 10 and 30 vol % flax

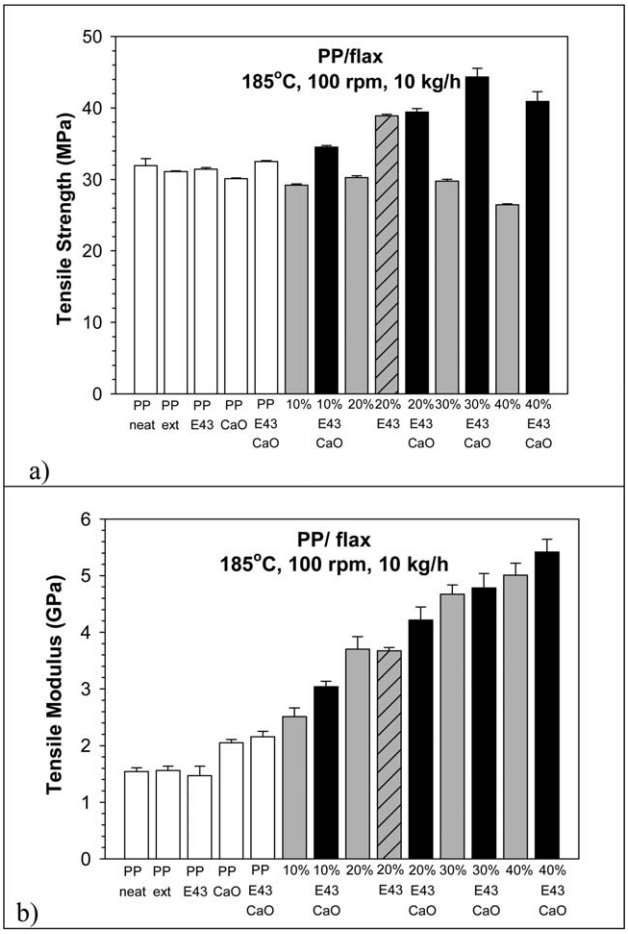

Figure 10. Tensile properties of PP/flax composites: (a) tensile strength and (b) tensile modulus.

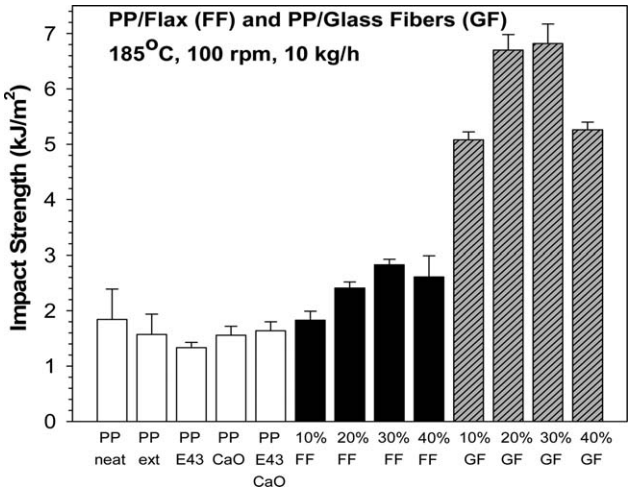

Figure 11. Izod impact strength of PP formulations, PP/flax, and PP/glass fiber composites. The flax fiber composites contain both 3.75 vol % E43 and 3.5 vol % CaO. The values for glass fiber composites are for comparison purposes.

fibers, respectively. All micrographs were taken at the same magnification for comparison purposes. The fractured surfaces of composites obtained with 20 and 40 vol % flax fibers or hemp fibers exhibited similar morphological features and are therefore not presented here. The fractured surfaces of the composites without additives (left column) displayed poor interfacial adhesion as observed from important fiber pullout and holes in the matrix. This is consistent with the tensile properties that showed a decline with the increase of the fiber content in the absence of additives. When E43 and CaO are incorporated into the composites, the fractured surface exhibited less fiber pullout. It is believed that the cracks were propagated predominantly through the PP matrix because the fiber-matrix strength was higher than the flax fiber strength. In addition, mechanical measurements were in agreement with these observations, showing a considerable increase in the composite tensile properties when the coupling agent and reactive agent were added to the composites. All these observations confirmed the enhancement of polymer/fiber adhesion in the compatibilized system and the higher mechanical strength values with the addition of E43 and CaO.

The mechanical performance of the cast sheets was also evaluated. The TM and the TS were evaluated in both MD and TD. Figure 13 reports the data for the cast sheets containing 10 vol % flax and glass fibers (left column) and of the composites containing 30 vol % flax and glass fibers (right column). The compatibilized flax fiber composites contain both 3.75 vol % E43 and 3.5 vol % CaO. The values for glass fiber composites are for comparison purposes. The values of the elastic modulus for pristine PP were similar in both MD and TD. As expected, the composites were less isotropic, and the values in TD were considerably lower. This is even more pronounced for the composites containing glass fibers, which, because of their higher

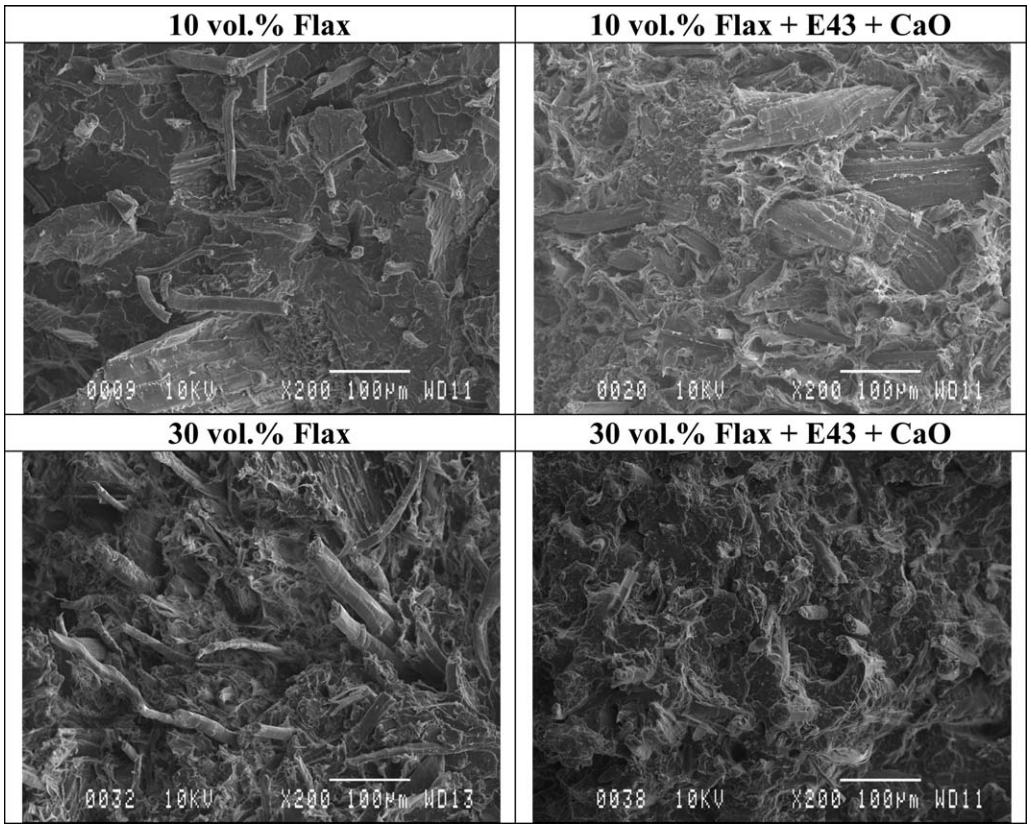

Figure 12. SEM microstructural details of fractured surface of injected samples of PP/10 vol % flax and PP/30 vol % flax, without (left column) and with additives (right column).

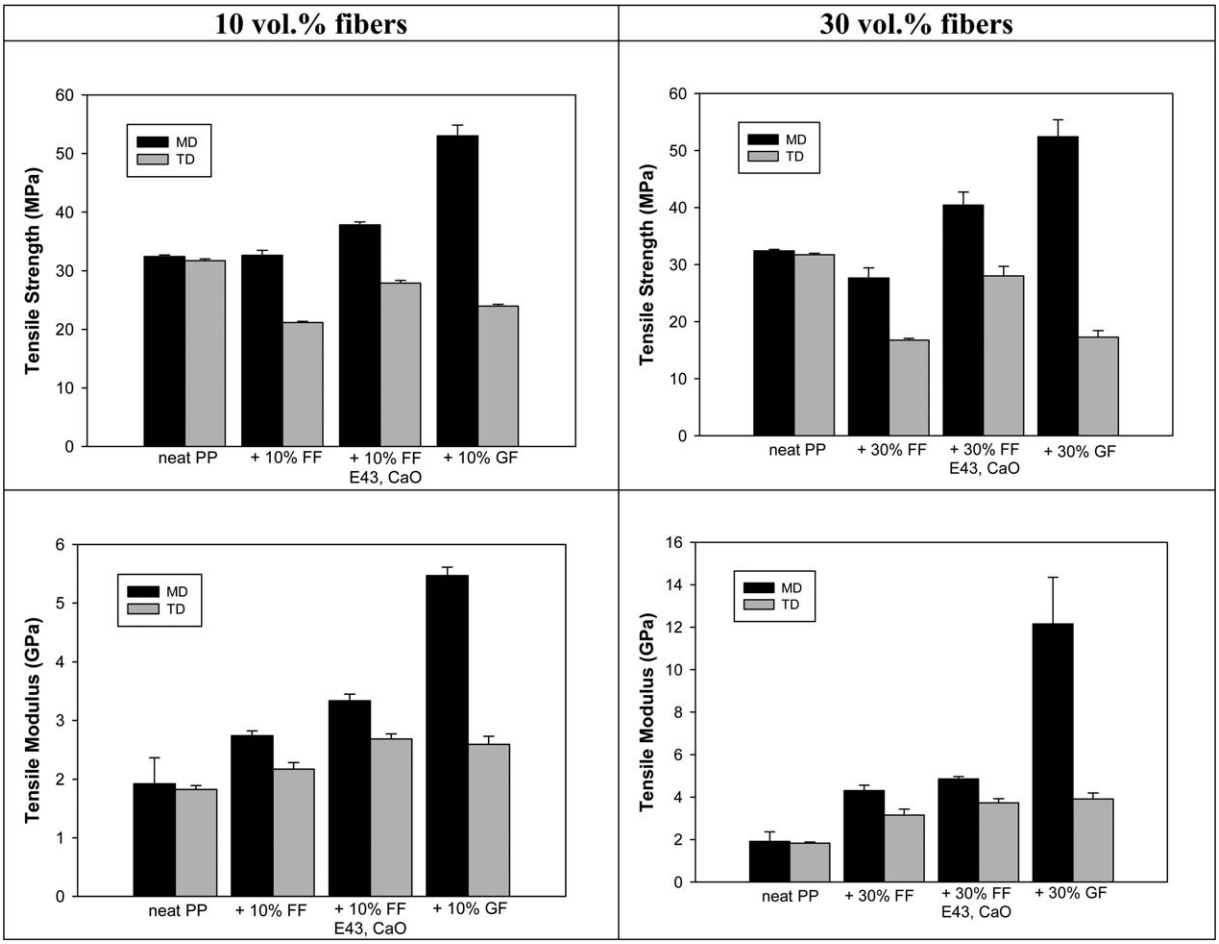

Figure 13. Tensile properties of cast sheets containing flax (FF) and glass fibers (GF) at 10 vol % (left column) and at 30 vol % (right column). MD, machine direction; TD, transverse direction. The values for glass fiber composites are for comparison purposes.

rigidity, can be more easily oriented in the MD during melt extrusion and sheet manufacturing. The modulus increased with the addition of flax fibers, with or without additives. The best results were obtained for the compatibilized composites (containing both CaO and E43). These trends were also observed for the TS. The elongation at break of neat PP was very high (900%) in the MD but quite low in the TD (20%). All composites, including the PP/glass fibers formulations, exhibited very low elongation at break (below 10%), in both MD and TD (data not shown). The sheets obtained from the composites with flax fibers are also more isotropic than in the case of the composites containing glass fibers.

To investigate the recyclability of these composites, the mechanical performance of samples with different thermomechanical histories was evaluated. Samples were collected after several passes through an injection-molding machine, and then the TS and modulus were measured. The results are shown in Figure 14 for the composites made of 10 vol % (left column) and 30 vol % flax fibers (right column) formulated with E43 and CaO. It can be observed that after five injection cycles, both composites did not exhibit any significant change in TS and TM when compared with those of nonrecycled materials. The cellulosic fiber content seems to have no effect in the composites recyclability. Therefore, mechanical recycling of PP/flax fiber composites is possible, as mechanical properties remain similar even after several reprocessing cycles.

Figure 15 presents the humidity uptake as a function of time for the composites containing 20 vol % flax fibers. The sample was exposed for 1 year at 50% humidity and at 21°C in a controlled humidity laboratory. The weight change of pristine PP is presented as a reference. When compared with hydrophobic PP, for which the weight increase was only 0.02 wt % after 1 year, the composites exhibited a 0.8 wt % humidity uptake. This is an extremely low value taking into account that the flax fibers are highly hydrophilic. Moisture can be absorbed into the composite material due to water vapor diffusion, which could take place through the interstitial spaces at fiber/polymer interface and through the flax fibers. When the adhesion between the fibers and the matrix is high, the interstitial spaces at the fiber/polymer interphase should be very low or even absent. The very low humidity absorption in flax fiber composites at 10 and 30 vol % flax content demonstrates again that the adhesion between flax fibers and PP, in the presence of E43 and CaO additives, is superior and confirms the mechanical results. Besides, tensile tests done on samples exposed for 1 year to humidity showed no changes in mechanical properties (results

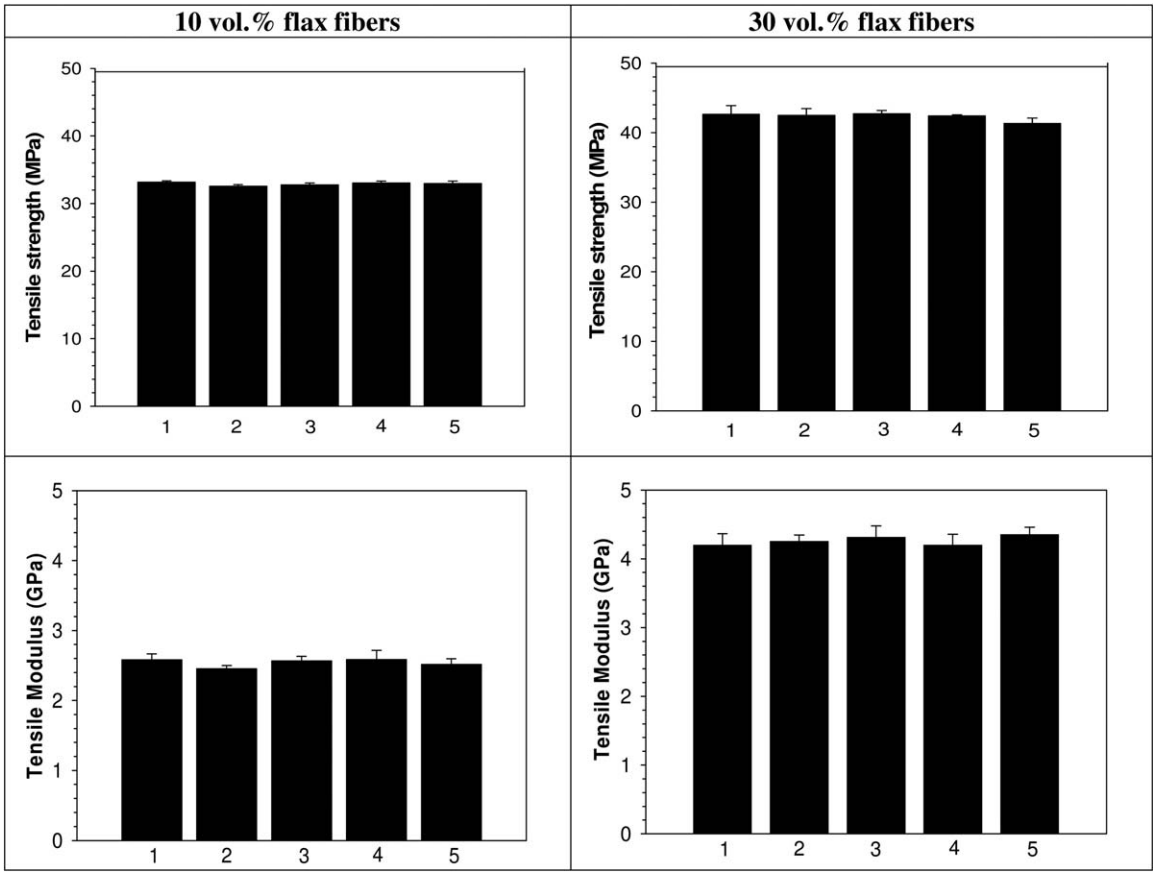

Figure 14. Tensile properties of recycled PP composites with 10 and 30 vol % flax fiber content: tensile strength (upper row) and tensile modulus (lower row).

not shown here). These composites not only can have multiple utilization cycles but can also be used in a humid environment without losing their mechanical performance.

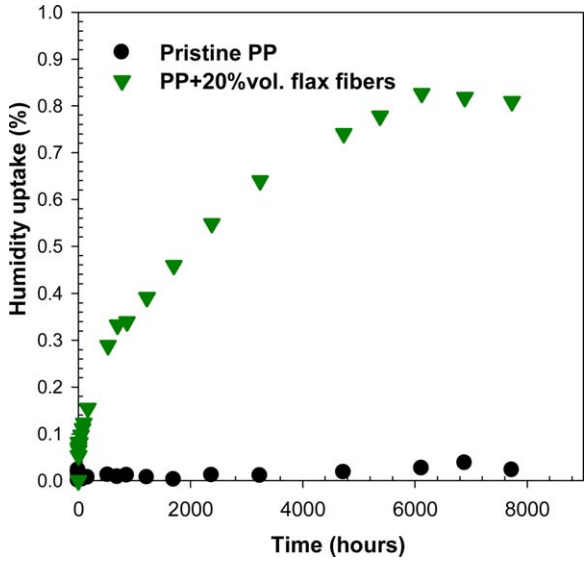

Figure 15. Humidity uptake of PP/20 vol % flax fiber composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

PP/flax and PP/hemp fiber composites were compounded using a twin-screw extruder. PP-*g*-MA was used as a coupling agent and CaO as reactive filler. Composites containing glass fibers were also produced for comparison purposes. A pretreatment step (pelletizing) of the fibers was found to be necessary to uniformly feed them into the extruder and to insure consistent flow rate and, therefore, a uniform fiber concentration in the composite. During this pelletizing step, the flax technical fibers were split down into elementary fibers without compromising the fiber length. The first part of this study consisted of optimizing the processing parameters for enhanced composites performance. The obtained composites were characterized in terms of morphology, fiber length, rheological, thermal, and mechanical properties, sensibility to humidity, and recyclability.

The study of the variation of extrusion parameters such as fiber feeding zone position, extrusion temperature, flow rate, and screw speed revealed that these composites have a large processing window that can be considered as an advantage of PP/short flax or hemp fiber compounds. The uniformity of flax fiber length confirmed the results obtained from mechanical and rheological testing and the assumption that all flax fibers undertook similar attrition during compounding no matter what the extrusion parameters were. In the second part of this study, the optimal extrusion parameters determined during the first trials

were kept constant, whereas the composite formulation was varied. The effect of flax and hemp fiber and additives content on the composite properties was examined. Rheological, thermal, and mechanical behavior varied significantly with fiber content. In addition, increases of the TS (up to 40%) were observed, indicating that good fiber/matrix adhesion was achieved by the addition of PP-*g*-MA and CaO.

To investigate the recyclability of these composites, the mechanical performance of samples with different thermomechanical histories was evaluated. It was shown that even after five injection cycles, flax-based composites did not exhibit any significant change in TS and TM when compared with those of nonrecycled materials. Therefore, these composites can have multiple utilization cycles. In addition, the humidity absorption in flax fiber composites was shown to be extremely low.

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