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INTERRELATION BETWEEN MELT PROCESSING CONDITIONS, FORMULATION AND PROPERTIES OF POLYPROPYLENE / SHORT FLAX AND HEMP FIBER COMPOSITES

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Abstract

This work investigates the effect of extrusion parameters and formulation on the properties of polypropylene / short flax fiber composites. The parameters that were varied during the twin-screw extrusion process were screw configuration, screw rate, extrusion temperature and flow rate. The effect of the location of the feeding zone of flax fibers is also considered. Concerning the composite formulation, the effect of flax content, presence of coupling agent and of a reactive additive on composite properties are analyzed. Composites obtained with hemp fibers in the same extrusion process are also considered for comparison purposes. The materials were characterized in terms of morphological characteristics, rheological, thermal and mechanical properties. The variation of extrusion parameters shows that polypropylene / flax fibers composites have a large process window that can be considered as an advantage of PP/flax compounding. Tensile strength increased up to 50% with flax fibers content when coupling agent and reactive agent are used. Due to its high flexibility, flax fibers are less oriented in the flow direction and the part performance will be more homogeneous. Furthermore, these composites show a good recyclability by keeping the integrality of their mechanical properties after five reprocessing cycles.

Introduction

Polypropylene / natural fibers composites have attracted attention of researchers and manufacturers because of renewable nature of fibers, good mechanical properties, lack of abrasion during the compounding, low environmental impact, weight and cost savings comparing to polypropylene - glass fibers, Kevlar or carbon fibers counterparts. On the other hand, natural fibers have as drawbacks low thermal stability, high humidity sensitivity, limited fiber length and, the most important, the intrinsic variability. This variability consists in harvest conditions, quality of the soil and climate, geographic location, and the preconditioning. This variability can be observed also when considering the same plant because the fibers obtained from stem have different mechanical and physical properties comparing with fibers obtained from leaves. Composites mechanical properties and, therefore, their final applications, depend on fiber source [1-4], fiber treatment [5-9], the presence of coupling agents [1, 10-12], and compounding parameters.

If a lot of work is done with regards on natural fiber surface treatment and polypropylene/fiber adhesion, the pre-compounding and the melt compounding aspects have less attracted the attention. Concerning the compounding of polypropylene / short cellulosic fibers composites, usually a co-rotating twin screw extruder is used before injection molding in different object shapes. On the other hand, little work exists concerning the effect of natural fibers content on the fiber damage during composites extrusion [13, 14] but without considering a discussion on the effect of extrusion parameters.

This paper discusses the effect of extrusion parameters, i.e. screw configuration, screw rate, fiber feeding zone, temperature, and flow rate on the properties of polypropylene/flax fiber composites for a given composite formulation. Feeding the natural fibers in continuous extrusion process is often problematic due to its low bulk density that will be reflected into an inconsistent feeding rate [15]. The increase of the bulk density of natural short fibers is thus necessary to make the composite manufacture possible at small and medium scale. Hence, the flax and hemp fibers were fed in a pelletized shape obtained by passing the fibers trough a pellets mill. After the setting optimal extrusion parameters, the effect of flax and hemp fiber concentrations and additives on composite properties was examined.

Experimental Part

Materials

Isotactic polypropylene (iPP) Pro-fax 1274 from Basell BV (Hoofddorp, Netherlands) with weight average molecular weight of 300,000 was used as the composite matrix. Flax and hemp fibers with a content of 10% of impurities, mainly shives, were provided by Schweitzer Mauduit, Canada. The concentration of fibers in polypropylene was varied between 10 and 40 vol%. The maleic anhydride grafted polypropylene used as coupling agent was Eastman Epolene-43 (E-43) (AN = 45, M_w = 9,100, with around 4.81 wt% of MA). Its concentration was varied between 2.5 and 5 vol%. The CaO 98% purity from Laboratoire MAT Inc was used as reactive filler. It is a basic reactive filler that has the role to absorb moisture in fibers, neutralize acidity of fiber impurities and therefore minimize the oxidation and degradation of fibers during melt processing. Consequently, the CaO helps also to increase strength and modulus of final composites. The recommended concentration of CaO in PP composites with natural fibers is 3.5 vol% (10 w%) [16].

Extrusion Process

Regarding the appropriate way to feed natural fibers into the extrusion process, a pre-treatment step is necessary because natural fibers are fluffy and hard to feed in this shape without compromise the consistency of fiber flow rate. A proprietary technology was used to produce natural fiber pellets with minimum fiber length degradation.

The extruder used to process the composites was a Leistritz 34 mm co-rotating twin-screw having 12 mixing zones and a L/D ratio of 40. Two feeding location are available in this extruder and the capillary die at the exit of the extruder had a diameter of 2 mm.

For the first part of this study the composite formulation was kept constant, (20 vol% of flax and 2.5 vol% of E43), while the extrusion parameters were varied. Three screw configurations, (a severe, a medium and a soft one) were tested. The degree of screw severity was differentiated by the ratio of shear disks situated in the zones $4^{th}/8^{th}$, i.e. 10/10, 5/5 and 5/0. For each configuration, the flax pellets were fed in two manners: in the same time as PP into the zone 0, and secondly into the 5^{th} zone. Concerning the extrusion temperature, 3 flat profiles (200, 185 and 170^{o}C) were selected and one in which the temperature was decreased constantly from 200^{o}C down to 170^{o}C. The total flow rate was varied from 5 to 10 kg/h and the screw rate from 100 to 200 rpm.

In the second part of this study, the optimal extrusion parameters resulted from the first step were kept constant while the composite formulation was varied and PP composites with flax and hemp fiber contents from 10 to 40 %vol were produced.

Morphology

Scanning electron microscopy (SEM) was carried out on polished composites surfaces, coated or fractured. A coating of gold/palladium alloy was applied on the specimens prior to the observation. 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.

Rheology

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

Differential Scanning Calorimetry

The DSC method was used to determine the melting and the crystallization temperature of the PP matrix. The tests were done using a TA Instrument's Q2000 calibrated using an indium standard. The samples were heated from 30 to 200^{o}C at 20^{o}C/min, kept at 200^{o}C for 5 minutes to erase the thermal history and cooled again down to 30^{o}C at 20^{o}C/min. The PP heat of fusion was considered 207.1 J/g [17].

Mechanical Properties

The samples designated for mechanical testing were first dried and then injection molded using a Boy injection molding press with a screw temperature of 190^{o}C and a mold temperature of 30^{o}C. The tensile testing was carried out according to ASTM D638 on standard type I dog-bone shaped samples with a thickness of 3 mm. The impact testing was carried out according to ASTM D259.

Recyclability

The recyclability of flax composites was evaluated using tensile mechanical testing for formulation with 10 and 30 vol% flax. The composite pellets were reprocessed by injection molding 5 times.

Results and Discussion

Trials to feed the flax fibers into the extruder in their natural shape failed because it low bulk density that gave an important variation of fiber flow rate or blocked into the feeder. An increase in the bulk density was obtained using a proprietary pellet technology. To facilitate the pelletizing, the flax fibers were first cut at 6.5 mm and then uniformly wetted using equivalent water content. In pelletizing process, the wetted flax fibers were pressed trough a die plate using two rotating roll mills. The first row in the Figure 1 presents the physical aspect of flax fibers in their original/as received state and after the pelletizing step. There was no thermal degradation or important fiber shortening observed after the pelletizing step. The temperature during the process was kept constant at around 70^{o}C. As measured using a HiRes FQA device, the length average fiber length was around

3.3 mm before and after pelletizing. The second row shows optical micrographs of initial fibers and the ones extracted from the flax pellets. An important advantage of this pelletizing step is the separation of the technical fibers (diameter around 100 µm) into elementary fibers (diameter around 20 µm). Prior to extrusion the natural fiber pellets were dried at 80°C for a minimum 48 hours.

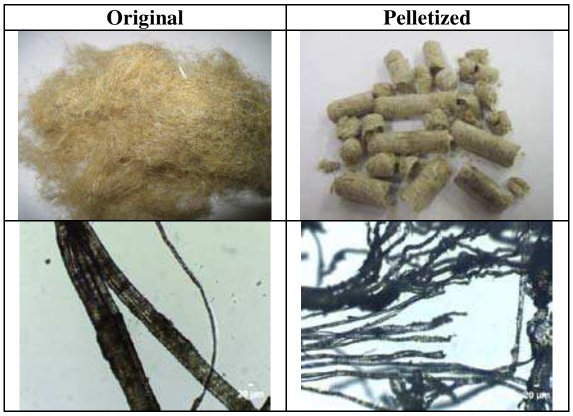

Figure 1. Physical aspect of flax fibers: original and pelletized

For the first extrusion part of this work, the composite formulation was maintained constant, (77.5 vol% PP, 20 vol% flax and 2.5 vol% E43), while screw configuration, feeding zone of fiber pellets and extrusion parameters were varied. The composites were injection molded into samples for tensile and impact tests and the results are presented in Table 1.

Table 1. Mechanical properties of composites: variation of extrusion parameters.

Sample	TS (MPa)	TM (MPa)	IS (MPa)
Reference Polypropylene			
As received	31.9 (0.97)	1543 (64)	1.85 (0.54)
Extruded	31.1 (0.14)	1560 (78)	1.57 (0.37)
Variation of screw configuration and feed zone			
Severe, 0	39.0 (0.29)	3230 (361)	2.5 (0.29)
Severe, 5th	38.5 (0.31)	3232 (208)	3.0 (0.00)
Medium, 0	37.0 (0.28)	2980 (97)	2.7 (0.39)
Medium, 5th	37.7 (0.15)	3050 (107)	2.9 (0.52)
Soft, 0	38.0 (0.45)	3177 (172)	2.0 (0.00)
Soft 5th	38.4 (0.29)	3358 (196)	2.3 (0.37)
Extrusion temperature (°C)			
200	40.2 (0.55)	3465 (137)	2.7 (0.37)
185	37.7 (0.15)	3050 (107)	2.9 (0.52)
170	39.2 (0.32)	3374 (151)	3.0 (0.75)
200 to 170	38.4 (0.22)	3282 (82)	3.0 (0.00)
Total flow rate (kg/h) and rpm			
5, 100	39.0 (0.29)	3356 (177)	2.9 (0.25)
5, 150	37.7 (0.15)	3050 (107)	2.9 (0.52)
5, 200	37.8 (0.19)	3215 (117)	2.4 (0.20)
7.5, 100	38.2 (0.35)	3273 (131)	3.0 (0.00)
7.5, 150	38.3 (0.19)	3379 (133)	2.9 (0.36)
7.5, 200	37.2 (0.76)	3200 (94)	2.5 (0.25)
10, 100	37.0 (0.72)	3182 (153)	2.8 (0.25)
10, 150	37.8 (0.64)	3268 (87)	3.0 (0.00)
10, 200	37.9 (1.08)	3245 (236)	2.8 (0.26)

Injection molding sample of as-received polypropylene pellets has a tensile strength (TS) of 31.9 MPa and a tensile modulus (TM) of 1543 MPa. After extrusion, it was found that PP preserved its mechanical properties and this means that the screw configuration did not damage the matrix integrity. The addition of fibers led to an increase of TS and TM around 37-39 MPa and 3000-3300 MPa respectively, no matter the extrusion parameters were. This demonstrates that the extrusion window of PP/flax composites is very large and it can be considered as an advantage for flax composite compounding. As explained before, the flax technical fibers were separated in elementary fibers during fiber pelletizing step that helped further the internal extruder work for fiber dispersion and distribution. Usually, this split out of technical fibers in elementary ones have to take place into the extruder. It was not the case, and as the flax was already fed in elementary fiber shape we probably enlarged the extrusion window. Moreover, SEM morphological observations of composite polished surfaces and length average length of fibers extracted from composites (results not shown here) further helped us to tune out the optimal alternative for composites extrusion: medium screw configuration and fibers feeding in the middle of the extruder. Final extrusion operation conditions were set at 185°C, 100 rpm and 10 kg/h.

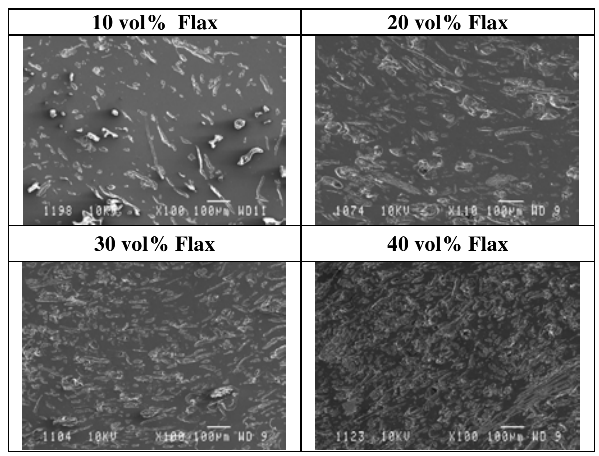

Figure 2. SEM micrographs of longitudinal polished surfaces of flax-composites obtained at 10, 20, 30 and 40% fibers.

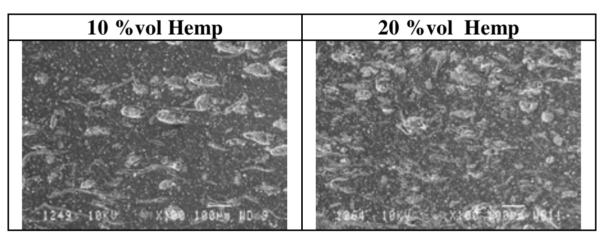

Figure 3. SEM micrographs of longitudinal polished surfaces of hemp-composites obtained at 10 and 20 %vol fibers in the presence of E43 and CaO.

PP/flax and PP/hemp composites were obtained using the same optimal extrusion parameters. Figure 2 and Figure 3 present the morphological features of longitudinal polished surfaces of PP/flax and PP/hemp extruded composites. The selected extrusion parameters gave a very good dispersion of fibers, no matter the fiber type and fiber concentrations were.

The rheological properties of neat PP and the effect of different additives on PP viscosity were investigated under dynamic oscillatory conditions. The complex viscosity dependency on time is presented first in Figure 4 for the neat PP/20 vol% flax fibers. Composites stability in time is important during oscillatory tests to guarantee that materials don't change their internal composition at the testing temperature. In our case it seems that the materials are very stable for at least 10 min at 185°C and, therefore PP and flax fibers didn't undergo thermal degradation during testing. Oscillatory tests done at two different gaps proved that composites viscosity depends on this testing parameter. For the continuation of rheological testing a gap of 1.7 mm was selected. It is well known that the gap have to be three times and higher than the fiber length to avoid the interference of wall-slip phenomena [18].

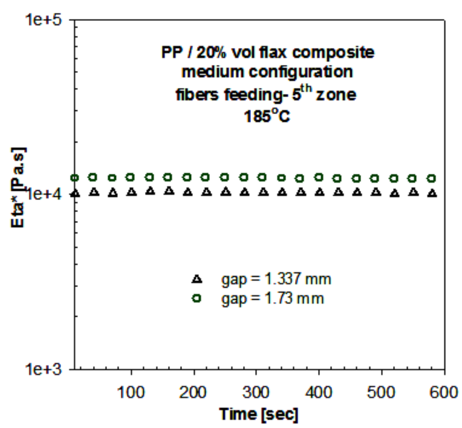

Figure 4. Complex viscosity as a function of time for neat PP/20 vol% flax fibers.

Viscosity measurements performed for different PP-flax and hemp composite systems are presented in Figure 5. The extrusion process did not modify PP viscosity which is a second evidence that the selected screw configuration and extrusion parameters did not damage the length of PP molecular chains. The viscosity of extruded PP/E43+CaO is slightly higher than for pure PP. Their values are 3030 and 3568 Pa.s for a frequency of 0.1 s^{-1}. Increasing the flax fibers content from 10 to 30 vol % highly increases the composite viscosity from 16962 up to 130617 Pa.s respectively. The rheological behavior of composites with 40 vol% were impossible to be evaluated because high fiber content, i.e. around 50 w%. The viscosities of hemp fiber composites are slightly higher than for flax fiber composites. This increment in PP/flax or hemp composites viscosity with fiber concentration is due to the fiber flexibility and to the increase of fiber-fiber interactions reflected in fiber-fiber entanglements. 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 for low frequencies. At high frequencies the effect weakened probably due to the fact that fibers coagulate together and the effect of the matrix becomes dominant.

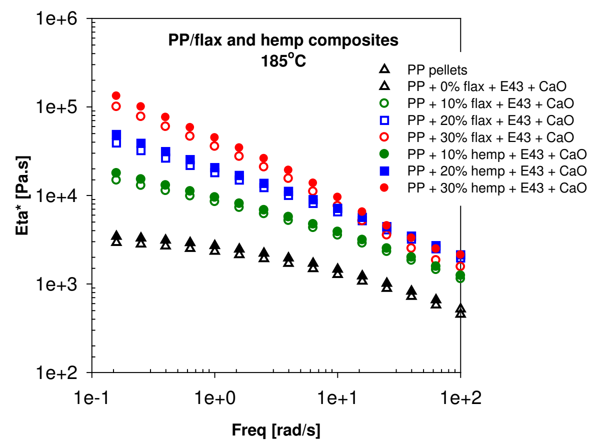

Figure 5. Complex viscosity as a function of frequency for pure PP/flax and PP/hemp composites respectively.

Non-isothermal crystallization behavior of PP/flax composites is presented in Figure 6. The first graphic discloses the melting curves and the second one the crystallization cooling curves obtained in DSC testing. The corresponding melt temperatures (T_m), crystallinity values (X_{ch}, X_{cc}) and crystallization temperatures (T_{cc}) data are additionally presented in Table 3 only for complete formulations. The heating curves show that the PP and its composites do not crystallize during the heating cycle because they are already fully crystallized. The fiber addition didn't change the T_m that is kept around 163°C. In opposition, the initial crystallinity was highly increased at fiber addition, i.e. from 48% for PP matrix up to 70% for the formulation with 40 vol% flax fibers and CaO. In consequence, the fibers could act as expected as nucleating agents in the crystallization process of composites. The crystallization temperature during the cooling, T_{cc}, was highly affected by CaO presence. It accelerates the crystallization that started 5-11°C earlier than for composites without CaO. The crystallinity reached during the DSC cooling was kept around 44%. This crystallinity level of composites was moderated by the imposed cooling flow rate of 20°C/min, and therefore by the limited time allowed for matrix crystallization.

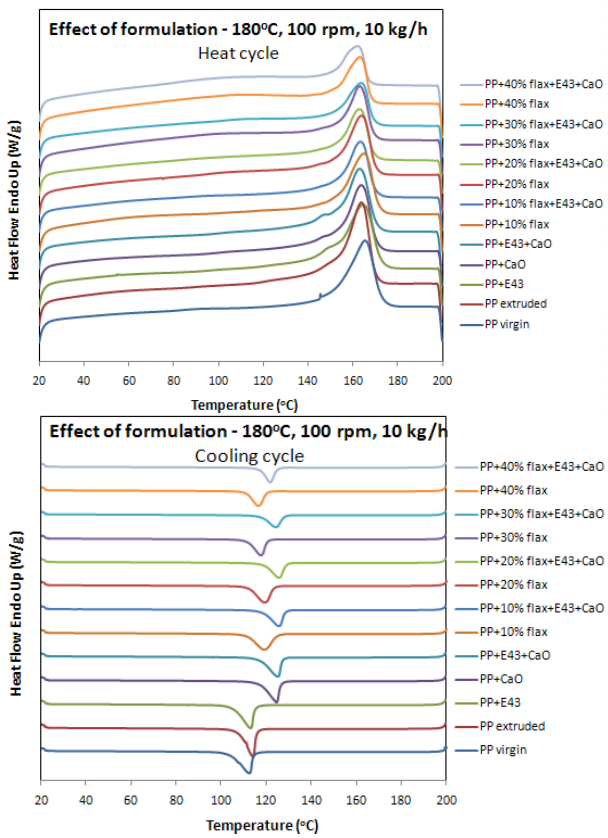

Figure 6. Heating and cooling curves obtained in DSC for PP/flax composites at different formulations

Table 3. Non-isothermal data obtained during the heating and cooling cycles for extruded PP/flax composites that contain E43 and CaO

	EXTRUSION					
	Heating			**Cooling**		
	Tm (°C)	**ΔHm (J/g)**	**Xch (%)**	**Tcc (°C)**	**ΔHcc (J/g)**	**Xcc (%)**
PP	165	85.97	42	112	104.30	50
PP extruded	164	100.00	48	114	109.90	53
PP+E43+CaO	163	87.26	42	125	94.43	47
PP+10%flax	163	72.25	40	126	75.63	42
PP+20%flax	163	75.04	50	126	67.71	45
PP+30%flax	164	74.33	56	124	57.68	44
PP+40%flax	162	77.77	70	122	50.14	45

Tensile properties of PP/flax composites are presented in Figure 7. As expected, the tensile strength of composites obtained without compatibilization additives decreased to some extent with the increase of fiber content. However, the addition of E43 coupling agent and CaO reactive agent promoting fiber/matrix adhesion has an important effect on tensile strength of the composites. The tensile strength increased from 31 for pure PP up to 43 MPa for composite containing 30 vol% of flax fibers, and a slight decrease to 40 MPa is observed for the composites made of 40 vol% of flax fibers. Speaking in terms of tensile modulus, a regular increase is observed as a function fiber loading.

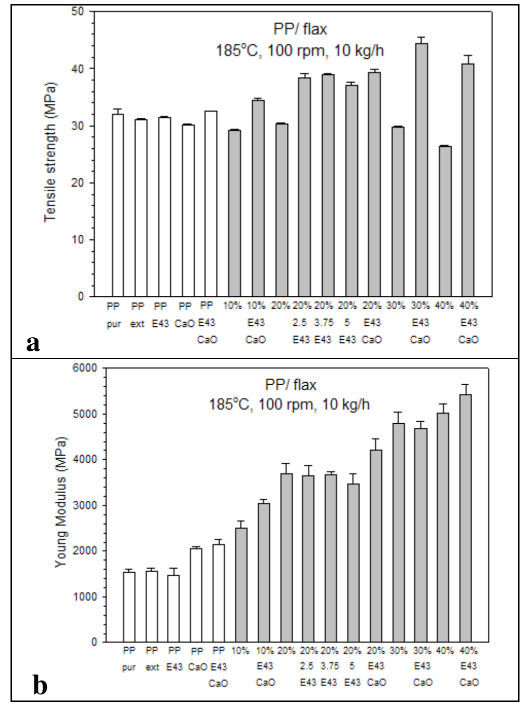

Figure 7. Tensile properties of PP/flax composites: a) tensile strength and b) tensile modulus.

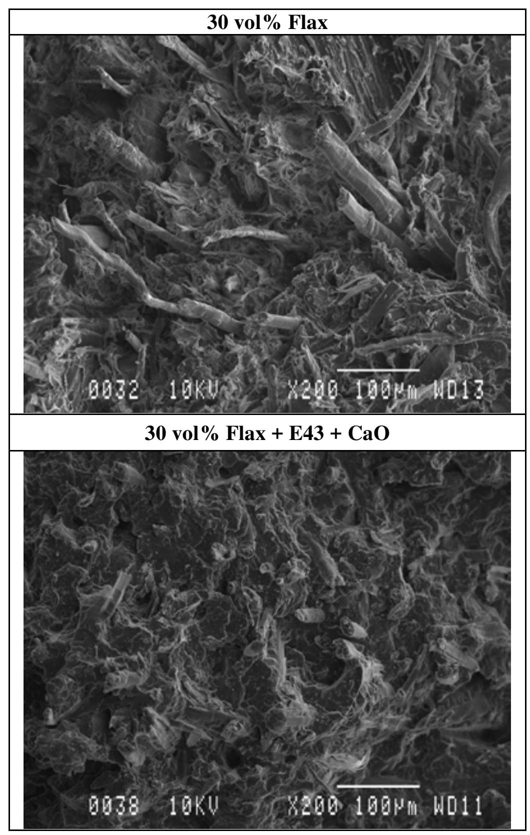

Figure 8. SEM microstructural details of fracture surface of injected samples PP/30 vol% flax.

Micrographs corresponding to fractured surface of 30 vol% flax composites with and without compatibilization are presented in Figure 8 and unveil the effect of coupling agent addition in PP/fiber adhesion. The excellent lessening of fiber pull out is an important sign of the increment of polymer/fiber adhesion in the compatibilized system and it confirms the tensile strength higher values at the addition of E43.

Results on recycling experiments done on composites made of 30 vol % flax fibers formulated with E43 and CaO are presented in Figure 9. It can be easly observed that after five injection cylces the composites almost didn't show any change in tensile strength and tensile modulus.

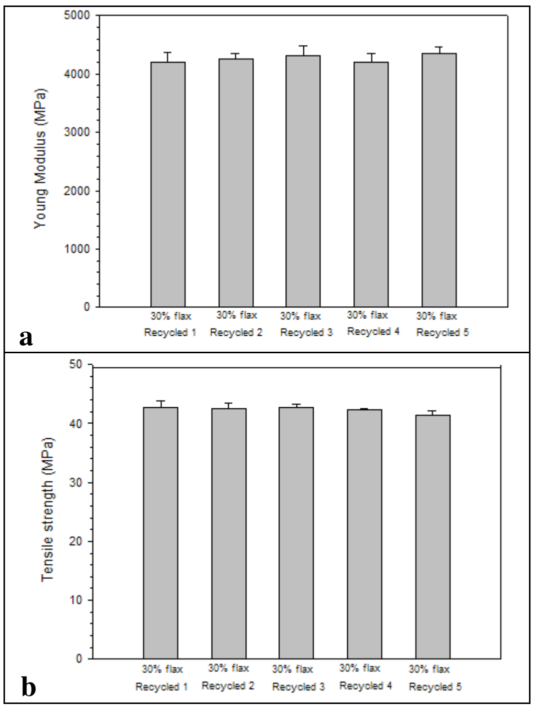

Figure 9. Tensile properties of recycled PP composites with 30% flax fiber content: a) tensile modulus and b) tensile strength

Conclusions

Polypropylene/flax and hemp fiber composites were compounded using a twin screw extruder and specimens were obtained by injection molding. A pre-treatment step of fibers was found to be necessary to correctly feed them into the extruder in order to conserve consistent flow rate and, therefore, a consistent fiber concentration in the composite. The pelletizing step of flax fibers was proven to be very beneficial. In addition, during this pelletizing step, the flax technical fibers were split down in elementary fibers without compromising the fiber length. Rheological, thermal and mechanical behavior increased significantly with fiber content. Tensile strength increased up to 40% with the addition of 30 vol% of flax fibers content when coupling agent and reactive agent are used. Using the correct additives in flax or hemp/polypropylene formulation, the obtained composites can easily be used in construction field, for interior or exterior applications.

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