

Processing and Final Properties Improvement of Polyolefin-Sepiolite and Carbon Nanofibre Nanocomposites

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Summary: In this work polypropylene (PP) nanocomposites with different nanofillers (sepiolites and carbon nanofibres) have been produced, processed by injection moulding and fibre spinning and analyzed in terms of mechanical properties improvements. Different concentrations of both fillers were used in nanocomposites preparation. The influence of nanofiller type and amount on mechanical properties were analyzed and discussed for each process studied. This study was completed with a basic morphological characterization in order to analyze the nanofiller dispersion, distribution and orientation in the nanocomposites. The results achieved show that it is possible to obtain a good dispersion and distribution of each kind of nanofillers with conventional processing methodologies when the nanofiller concentration is small. Moreover the nanocomposites obtained had better properties than the starting polymers, showing that sepiolite and carbon nanofiller are able to provide an important contribution to the improvement of mechanical properties of the materials analyzed, enlarging the final application possibilities of PP based products.

Keywords: polypropylene nanocomposites; sepiolite and carbon nanofibre

Introduction

Polypropylene (PP) nanocomposites are very interesting materials because they combine the properties of matrix and nanofillers in a synergetic manner. In this sense, the use of sepiolite fillers improve processing, dimensional stability, mechanical strength and thermal resistance of PP as well as, they allow controlling the rheological behaviour of the polymer enhancing their stability under a wide temperature range.^[1–4] Conversely, Carbon Nanofibres (CNF) reinforced nanocomposites have been widely studied due to their potential high-technological applications. Important results in the electrical and physical fields have been achieved and the potential of

structural enhancements is still considered a major technological challenge very interesting also for industrial applications.^[5–8]

The goal of the present work is to analyze final properties of the nanocomposites prepared with acicular nanofillers in two different processing operations, injection moulding and fibre spinning. Different concentrations of each nanofibre were used and the influence of the kind and filler amount were analyzed and discussed for each process studied. Also a morphological characterization was performed in order to analyze the dispersion, distribution and orientation of nanofillers in the nanocomposites.

Experimental Part

Materials

Polypropylene homopolymer Moplen HP 501L, with a Melt Flow Rate

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(MFR) (230 °C/2.16 Kg) of 6 g/10 min, kindly supplied by Basell, has been used as matrix. Two different kinds of filler were used: commercial sepiolite, purchased to TOLSA Group (Spain) and a commercial grade CNFs from Antolin GANF 3.

Nanocomposites Preparation

The nanocomposites were prepared in a twin screw micro-extruder *DSM Micro-5&15-Compounder (TSE)*, at 150 rpm, with a temperature profile of 170, 190 and 200 °C, from feed to die. The micro-extruder allows a recirculation of the material to improve the quality in terms of dispersion and homogeneity; therefore all nanocomposites formulations have been processed with re recirculation time of 1 min inside the extruder. This time was selected as better compromise in terms of maximization of dispersion and homogeneity and minimization of material degradation. The nanocomposites were prepared with different content of sepiolites (1, 3, 5 wt%) and CNFs (0.1, 0.5, 1 and 5 wt%).

Dog-bone shape specimens were obtained by injection moulding in a *DSM Micro 10 cc Injection Moulding Machine*, with the mould at 30 °C. Molten nanocomposite suspension flows from the *DSM Micro-5&15-Compounder* directly into the injection moulding machine.

Regarding the fibres production, the following procedure was adopted. The nanocomposite was compounded in the *DSM Micro-5&15-Compounder*, then it was pelletized and subsequently melt spun in a *DSM Micro Fibre Spinning Device* equipped with *winding-unit* to collect fibres and a *stretching-unit* to perform thermal stabilization and stretching. The fibres collected on the take up roll have been subjected to “*single-stage drawing process*” performed at 80 °C with a draw ratio of 3, according to literature,^[9] the drawing process parameters have been determined in order to obtain the best combination between thermal stabilization and increase in mechanical properties of fibres.

Characterization Techniques

Scanning Electron Microscopy (SEM)

Pure components and nanocomposites, were analyzed in ZEISS SUPRA 25 electron microscope equipped with secondary electron detection. Pure materials were analyzed as it is. Nanocomposites were fractured under liquid nitrogen and these surfaces were observed. The samples were previously coated with Au in a sputter coater.

Tensile Properties Measurement

Dog-bone shape specimens were tested for all nanocomposites in a Lloyd Instruments mod. LR 30 K universal dynamometer equipped with a 30 KN load-cell, at room temperature with cross speed of 1 mm/min according to the UNI EN ISO 527-1/2 standards. Particularly, elongation at break was measured using 50 mm/min of cross speed, in order to obtain the breakage of specimens in reasonable time, but still remaining in the range of plastic response for nanocomposites. Furthermore, the mechanical characterization of nanocomposite fibres was performed according to ASTM D3379-75: single filaments were mounted in a sample holder and the speed of testing was set to 50 mm/minute, in such a way to obtain tensile rupture in less than one minute of testing (as required by the norm).

Results and Discussions

The needle-like morphology of both nanofillers, sepiolite and CNFs, is presented in Figure 1. Sepiolite is a hydrated magnesium silicate with needle-like morphology. Their particles have a three-dimensional arrangement of atoms and planes (Figure 1a). For this reason sepiolite has the greatest surface area of all the clay minerals: about 300 m²/g with a high density of silanol groups (-SiOH) which explain the high hydrophilicity of this filler. The silicate lattice has not a significant negative charge and so the cation exchange capacity of this clay is very

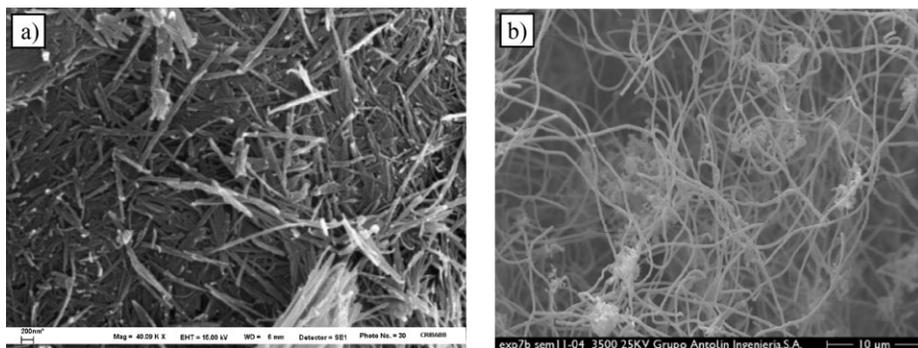


Figure 1. SEM micrograph of nanofillers (a) Sepiolites, (b) CNF.

low. The tiny elongated particles have an average length of 1–2 μm , a width of 0.01 μm and contain open channels with dimensions of 3.6 $\text{\AA} \times 10.6 \text{\AA}$ running along the axis of the particle. These particles are arranged forming loosely packed and porous aggregates with an extensive capillary network which causes the high porosity and light weight because of the high amount void space. The high surface area and porosity is responsible of the remarkable adsorptive and absorptive properties of this clay: it adsorbs vapour and odours and can absorb approximately its own weight of water and other liquids. The high hydrophilicity of sepiolite may represent a problem during the processing of nanocomposites, since the release of the water may cause formation of bubbles and other defects.^[10,11]

Carbon Nanofibres (Figure 1b) are sub-micron Vapor Grown Carbon Fibres (s-VGCF) with very small diameter (20–80 nm), excellent aspect ratio (>100), and highly graphitic structure ($>60\%$). It seems to be flexible and entangled each other. It is a very important factor to take into account during compounding.^[12]

The nanofillers dispersion, distribution and orientation during injection were analyzed by SEM in dog-bone specimen nanocomposites. The specimens were cryogenically fractured perpendicularly to the injection direction (see scheme in Figure 2). The samples were analyzed in the entire

surface and the micrographs are a representative sample of the general observations. The nanofillers are generally well dispersed at all sepiolite concentrations studied, in fact only small fillers agglomerations were observed (Figure 3). However, as expected, the frequency of agglomeration increases as the sepiolite concentration increases (see Figure 3c). The samples also showed well distribution of nanoparticles in PP matrix; in particular not differential sepiolite concentrations were observed. In this sense, it is possible to assert that the selected compounding conditions were good enough to optimize either the distributive and dispersive mixing in the TSE with recycle.

The major amount of nanoparticles is aligned toward the direction of the injection flow, as expected. Taking into account that the mould fill is mainly due to shear flow (Hele-Shaw) and the sepiolite particles have one dimension higher than the other two, the alignment mechanism in the flow direction is expected to be similar to short fibre orientation in reinforced PP.^[13] Another important observation is that

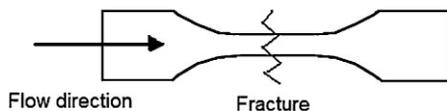


Figure 2. Dog-bone injection and fracture scheme.

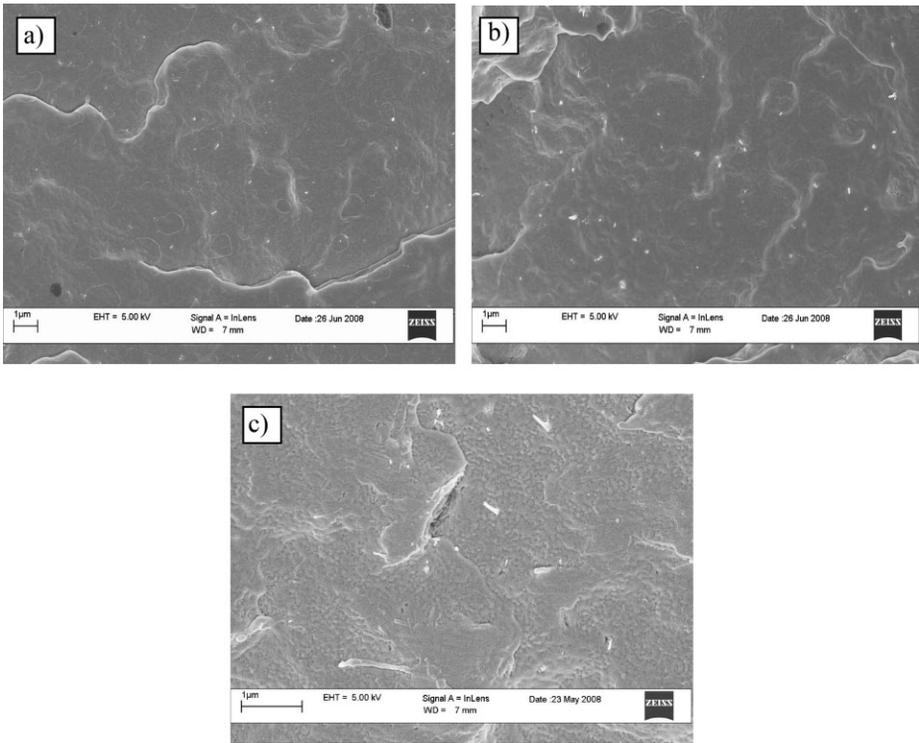


Figure 3. SEM micrograph of fracture surface of sepiolite reinforced nanocomposites with: a) 1 wt%, b) 3 wt%, c) 5 wt%.

sepiolite nanoparticles are generally fractured in the same plane of PP, evidencing a good adhesion between them, only a short amount of them shows pull out behaviour. The above observations are directly applicable to CNF nanocomposites morphological analysis (Figure 4). However, the

dispersion of CNF seems to be finer than in the sepiolite/PP nanocomposites also in samples loaded with high percentages of carbon nanofibres (i.e. 5 wt%).

The main mechanical properties, Young modulus, strength and elongation at break, measured for injected pure PP and

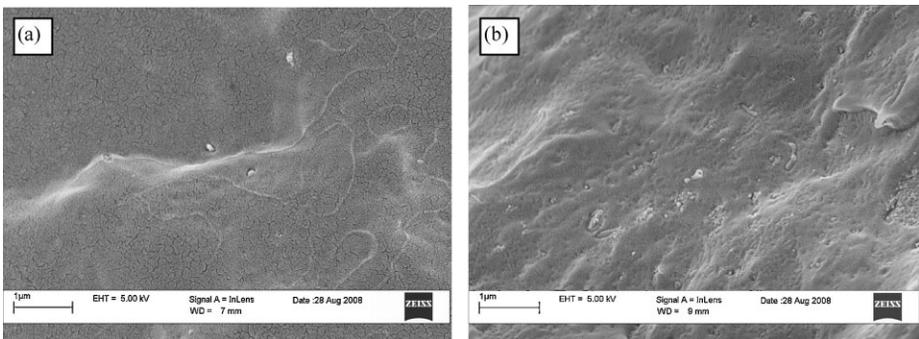


Figure 4. SEM micrograph of fracture surface of CNF reinforced nanocomposites with: a) 0.1 wt%, b) 5 wt%.

Table 1.

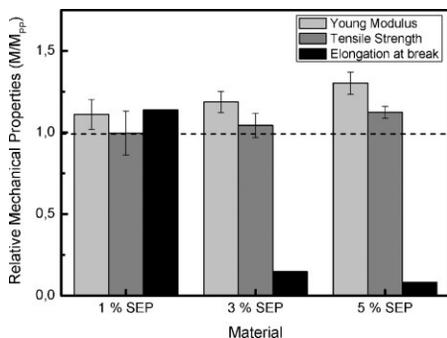
Mechanical properties of PP/sepiolite and PP/CNF nanocomposites measured on dog bone shape specimens.

Material	Young Modulus	St.	Tensile Strength	St.	Elongation at break	St.
	(MPa)	Dev.	(MPa)	Dev.	[%]	Dev.
PP	1596	157	29.7	1.2	428	22
1 wt% SEP	1773	145	29.6	4.0	487	6
3 wt% SEP	1895	103	31.0	2.2	63	16
5 wt% SEP	2079	110	33.4	1.1	35	9
0.1 wt% CNF	1690	39	30.8	1.5	521	9
0.5 wt% CNF	1727	160	29.9	0.2	513	12
1 wt% CNF	1582	45	31.4	0.4	500	17
5 wt% CNF	1616	108	30.0	1.3	152	2

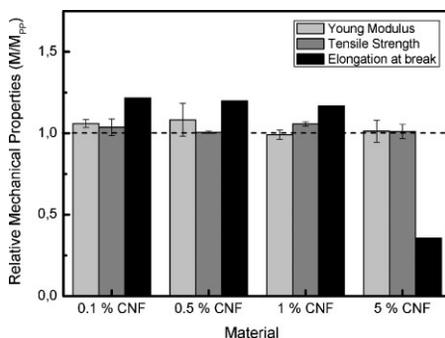
PP/sepiolite nanocomposites are summarized in Table 1. The values of relative mechanical property (M/M_{PP}) as a function of the sepiolite content (Figure 5) are reported in order to perform a comparative analysis of the influence of the sepiolite on the matrix mechanical properties. By the analysis of this figure it can be seen that Young modulus of nanocomposites is higher than pure PP (signed as straight line at 1) and, as expected, increases with the nanofiller content due to nanofillers rigidity and to the effect of nanofillers on PP crystallization.^[14] The tensile strength of nanocomposites with 1 wt% of sepiolite is similar to that of the pure matrix one, and increases with the filler content.

However, the most interesting results are evidenced by the analysis of the elongation at break. From such analysis the maximum value is obtained for samples containing 1 wt% of nanofiller, it is also

evidenced the steep decrease when the filler concentration approaches 3 wt% and over. Such behaviour is also reported in literature,^[15] and can be explained considering that elongation at break is influenced by different factors: stress concentration factor associated with nanofillers, free volume, matrix-filler interactions and filler-matrix interface properties. The improvement observed in samples with 1 wt% evidences a good adhesion between sepiolite and PP. Moreover with this level of nanofiller content, the dispersion is good and not massive agglomerations were observed. In these conditions, the fracture mechanism of nanocomposites implies the failure of the matrix-nanofiller interphase. However, although the overall sepiolite dispersion is good, the higher presence of agglomerates in high concentration nanocomposites involves the failure in the sepiolite-sepiolite interparticle union, which is weaker than

**Figure 5.**

Relative mechanical properties of PP/sepiolite nanocomposites.

**Figure 6.**

Relative mechanical properties of PP/CNF nanocomposites.

Table 2.

Mechanical properties of PP/sepiolite and PP/CNF nanocomposites fibres.

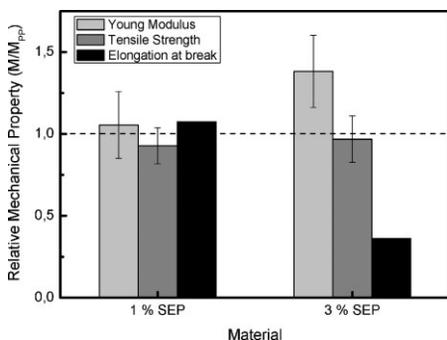
	Young Modulus	St.	Tensile Strength	St.	Elongation at break	St.
	(MPa)	Dev.	(MPa)	Dev.	(%)	Dev.
PP	3111	844	373	30	174	15
1 wt% SEP	3281	636	346	41	187	21
3 wt% SEP	4303	686	361	53	63	16
0.1 wt% CNF	3502	723	372	37	203	23
1 wt% CNF	3488	729	366	50	140	22
5 wt% CNF	3875	635	368	41	157	19

matrix-nanofiller interphase. Therefore, the presence of bigger agglomerates inside the matrix, can be considered as defects promoting crack nucleation and propagation.

The mechanical properties results for PP/CNF are also listed in Table 1. In the same way, relative properties of these nanocomposites are shown in Figure 6. From relative Young modulus values, it seems that the best performances are achieved with an amount of carbon nanofibres of 0.5 wt%. However, the changes measured in these properties are not very important and the variations are inside the error range. The more interesting results are presented for relative elongation at break. The ductility of CNF nanocomposites with a nanofiller content lower than 5 wt% are around of 30% higher than for pure PP, on the other hand it is evident the steep decrease in elongation at break for samples containing 5 wt% of carbon nanofibres. This behaviour can be explained considering that when the filler content is

low the dispersion and homogeneity is high with consequent good adhesion between PP-CNF, instead when the CNF content increases they are entangled each other promoting the break due to mechanisms similar to those observed in sepiolite nanocomposites.

The mechanical properties of fibres produced with both kinds of nanocomposites were also listed in Table 2. Figure 7 reports the relative properties of PP/sepiolite nanocomposites fibres. In this figure, the relative Young Modulus increase with the sepiolite content is evident and can be attributed to the morphological rearrangement of polymeric chains during the drawing process. On the other hand, the tensile strength suffers a little decrease respect to pure PP; but it seems that the amount of sepiolite does not affect it. This tendency makes in evidence that the strength behaviour of nanocomposites fibres is more influenced by the PP molecules orientation than by the presence of sepiolite. The increases in Young modulus with a decrement in tensile strength with respect pure PP fibres were also reported by other authors.^[16,17] The analysis of elongation at break shows interesting results because it evidences that in this case better results are achieved with lower percentage of sepiolite and it could be related to sepiolite orientation during the fibres stretching. The results achieved for fibres with 3 wt% of sepiolite are good both in terms Young modulus and tensile strength, instead elongation at break steep decrease due to the higher agglomerates content with consequent nanofillers slipping one over other as main cause of failure.

**Figure 7.**

Relative mechanical properties of PP/sepiolite nanocomposites fibres.

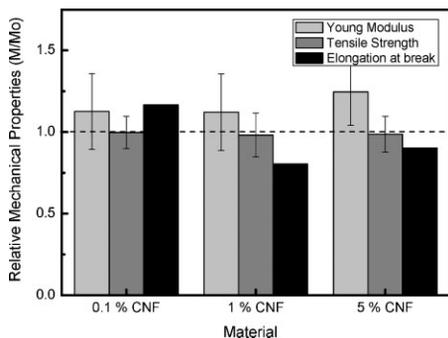


Figure 8.

Relative mechanical properties of PP/CNF nanocomposites fibres.

In Figure 8 relative mechanical properties of PP/CNF fibres are shown. It is possible to observe that Young modulus increases with CNF content. The higher improvement is observed for nanocomposites with 5 wt% of CNF due to the nanofillers content, as expected. On the other hand, it seems that tensile strength is not particularly affected by the presence of CNF; in fact, as in the case of sepiolite, this behaviour is more influenced by the PP molecules orientation than by the nanofiller presence. Elongation at break also presents interesting results; for 0.1 wt% CNF nanocomposite fibres it is clearly higher than pure PP, whereas at higher concentration it decreases under the pure PP fibres value. This behaviour could be explained in terms of CNF alignment and entanglements. At low concentration they behave as single nanofibres aligned in the fibre stretching direction; but as the concentration increases the resistance is mainly dominated by the CNF entanglements that increase as the concentration of CNF increase. From these results one can assert that the presence of CNF improves mechanical properties.

Conclusion

In this work the influence of the kind and amount of needle-like nanofillers on PP properties was analyzed. PP/sepiolite and PP/CNF nanocomposites have been pro-

duced with different concentrations and processed by injection moulding and fibre spinning. The morphological analysis showed that a good dispersion and distribution of both kinds of fillers in the matrix, mainly for low nanofillers contents, was achieved.

Tensile test on PP/sepiolite nanocomposites have confirmed a general improvement of the mechanical properties of samples, in particular the modulus and the tensile strength increased as the percentage of nanofillers increased. The elongation at break was reduced at sepiolite concentration higher than 1 wt%.

The mechanical characterization of nanocomposites based on PP and carbon nanofibres showed very interesting features: all the main properties such as Young modulus, tensile strength and elongation at break were increased; indicating that, an optimal dispersion of nanofibres inside the polypropylene matrix was achieved. An effective and complete reinforcement was observed up to 3 wt% concentration. At higher CNF concentrations a decrease of the elongation at break was measured.

Furthermore, it was showed that these kinds of nanocomposites can be processed by fibre spinning. Nanocomposite fibres were obtained, and their mechanical properties were measured. In this case, the Young modulus of nanocomposites fibres was enhanced; however the tensile strength does not show an important variation. The elongation at break was higher than pure PP for both kinds of nanocomposite fibres when the minimum amount of filler was used. (1 wt% for sepiolite and 0.1 wt% for CNF) and then decreased when the amount of filler increased.

The results obtained for both kind of reinforcement have shown that is possible to improve the PP fibre properties without compromising the processing characteristics.

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