

# MicroInjection of Polipropylene with Nanoclays

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**ABSTRACT:** Polypropylene (PP)/montmorillonite (MMT) nanocomposites micro samples was produced by micro injection molding at concentrations 2, 6 and 10% of Nanomax. The dispersion of the nanoclay particles in polypropylene was characterized using optical microscopy in polarized light, X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) and the mechanical characterisation was performed using the tensile test.

The results of x-ray diffraction indicated the formation of nanocomposites with partially exfoliated or intercalated structures, depending on the concentration of clay, with a maximum basal spacing of 6.217 nm. The micrographs obtained by scanning electron microscopy of fractured nanocomposite showed good dispersion of clay in polymer matrix without the presence of clusters. The tensile strength of PP/MMT is not much improved compared with pure PP but deformation increased significantly.

## 1 INTRODUCTION

The miniaturization of components and systems has clearly become a global trend of the most advanced technological sectors with the rapid development of micro-engineering technologies. The development of new micro devices is highly dependent on manufacturing systems that can reliably and economically produce micro parts in large quantities. [1, 2]

In this context, micro-injection molding of polymer materials is one of the most common manufacturing processes of micro in microsystems' technology, mainly for thermoplastic materials, because of the short cycle time, the high degree of automation, the high accuracy and consistency, low production cost, mass production capability, applicability for many materials and good tolerance, etc. [3- 5]

The injection molding is one of the most economically relevant methods of processing plastics seeing as almost all thermoplastic materials can be injected, with or without charges and / or reinforcements. Of all the different polymeric materials, nanocomposites have been deemed very interesting for applications that require high performance. This is due to the good properties that these materials present, such as mechanical properties (strength and stiffness), decreased permeability to water and gas, thermal stability, chemical resistance, surface appearance and

reduced gas emissions. For this reason, nanocomposites are ideally suited for the microinjection molding process, mainly for applications where the micro-components are required to provide high module and high impact resistance. An example of this are the micro-components used in the electronics and automobile [6].

The development of new nanostructured materials has been a very hot and stimulating topic in the sphere of Science and Engineering of Materials in the past few decades. Within the area of nanomaterials, the nanocomposites stand out to be among the most promising of this emerging "nanoEra". The nanocomposites go far beyond the performance of the conventional composites, clearing the way into into new applications and improving the mechanical and physical properties of the polymer. These properties result from the individual contributions of each component as well as from the synergistic interactions between the components that happen almost at the molecular level. [7]

In recent years polymer/layered silicate (PLS) nanocomposites have attracted great interest, both in industry and in academia, because they often exhibit remarkable improvement in materials properties when compared with virgin polymer or conventional microand macro-composites. These improvements can include high moduli, increased strength and heat

resistance, decreased gas permeability and flammability, and increased biodegradability of biodegradable polymers. [8-10]

The main reason for these marked improvements stem from the large aspect ratio of layered silicate, for example, montmorillonite (MMT). Each individual layer of MMT has a thickness on the order of 1 nm with lengths ranging from 100 to 300 nm. [9, 10]

The properties of the nanocomposites are strongly influenced by how the clay is dispersed in the polymer. Polymer-clay nanocomposites can be classified morphologically into (a) separated, (b) intercalated, and (c) exfoliated (delaminated) states, as shown in Figure 1.

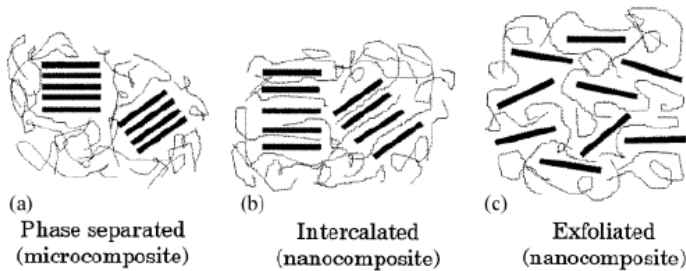


Figure 1 - Schematic showing polymer-clay nanocomposite classifications.

The most desirable morphological state for the polymer-clay nanocomposites is exfoliation, followed by intercalation. [10-12]

## 2 EXPERIMENTAL

### 2.1 Micro parts

The micro parts produced for this work are two (Figure 22), and their dimensions have been adapted to the process of microinjection.

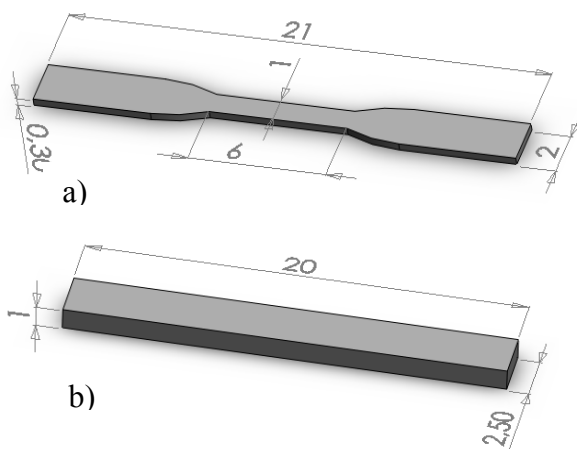


Figure 2 - Micro samples a) Traction b) Impact

### 2.2 Material

The polypropylene (PP) Domolen 1100N was used as the matrix and the nano clay montmorillonite as the reinforcement; this is presented in the form of masterbatch (Nanomax), provided by the company Nanocor. The nanocomposites contained 2, 6 and 10% of masterbatch.

### 2.3 MicoInjection Moulding

The microinjection machine used to produce nanocomposites was BOY 12A, equipped with a plasticization screw of 14mm diameter. The conditions were set in the typical values used in this type of processing for these materials and in the technical specifications.

In order to achieve the best processing conditions for this material we began to inject some parts until we had stabilized the process and in this way obtaining the ideal conditions for the production of the samples, which resulted in the following conditions:

Table 1 - Processing Conditions for micro samples with PP

Processing Conditions	PP + Nanoclay				
Barrel Temperature (°C)	140	160	185	215	230
Injection pressure (bar)	120				
Mold temperature (°C)	80				
Injection Speed (mm/s)	240				
Cushion (mm)	2				

### 2.4 Characterization

#### 2.4.1 Optical microscopy of polarized light

The optical microscopy analyses was been used in some studies as a preliminary method of observation of the microstructure to observe the existence of clusters.

In this work, we used an optical microscope, polarized light, Olympus model B; the observations were performed using a 3.3 x ocular and an objective magnification of 4, 10 and 20 x.

#### 2.4.2 Scanning electron microscopy

The technique of the scanning electron microscopy is used to analyze the microstructure of the samples, it allows to characterize the morphology of the particles of clay. The samples were fractured and coated with gold-palladium alloy and later observed in a scanning electron microscope of ultra high resolution (New Nanos 200) in the Materials Characteri-

zation's Services' Laboratory at the University of Minho (SEMAT / A)

#### 2.4.3 X-ray diffraction

The materials were characterized according to type of structure obtained by the diffraction of the X-rays, the equipment used was the Bruker AXS NanoStar, from the Materials Characterization's Services' Laboratory, University of Minho (SEMAT / A). This equipment used a potential difference in the tube 40KV, an electrical current of 35mA and CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The scan was used in the range of  $2\theta$  from 1 to 24 degrees.

#### 2.4.4 Tensile Test

The tensile tests were performed in Microtester, a homemade machine, specially designed to characterize the mechanical behavior of micro-components. The tests were performed at room temperature and at a constant speed of 1 mm / minute with a load cell of 500N.

### 3 RESULTS AND DISCUSSION

#### 3.1 Morphology of nanocomposites Optical microscopy of polarized light

Through the optical microscope, in bright field, we could verify the existence of clusters in some of the samples. In the impact and tensile samples, with 2% of nanoclays, there wasn't any cluster visible this is due to the reduced amounts of nanoclays and to the high shear rate. The same happened with the 6 and 10% nanoclays tensile samples, where there wasn't any visible agglomerate due to the samples' geometry being thin when compared to the impact samples', so promoting higher shear rate and, thus, better dispersion. Moreover, the impact samples with 6 and 10% of nanoclays present, in certain areas of the sample, the existence of agglomerate. This is due to the thickness of the sample, which being higher than the tensile's test-piece results in that the material isn't subject to higher shear rate, and this in turn results in the presence of agglomerates.

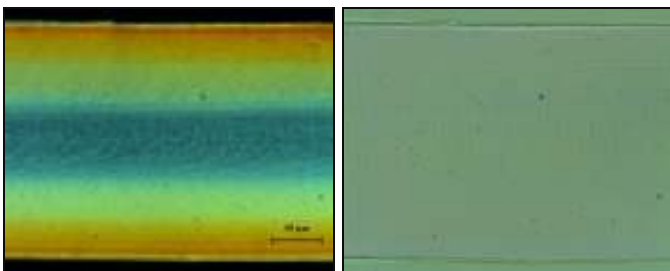


Figure 3 - Longitudinal section of tensile samples with 6% nanoclays a)polarized light b)bright field (magnification 20x3.3)

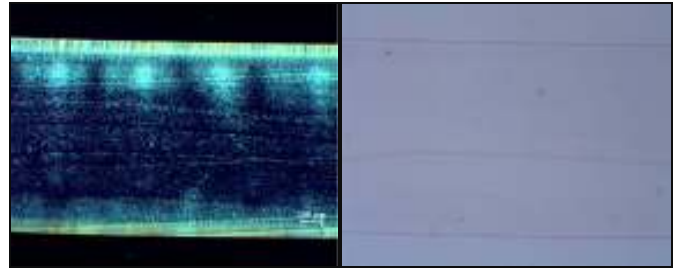


Figure 4 - Longitudinal section of impact samples with 10% of nanoclays a)polarized light b)bright field (Magnification 4x3.3)

#### 3.2 Scanning Electron Microscopy

The images of the fracture surfaces of the nanocomposites with different compositions, obtained by SEM, showed that there is a good distribution and dispersion of reinforcement in the matrix.

When analyzing the tensile and impact samples with lower magnification it is noticeable that these present a good distribution/dispersion of nanoclays, however, when the magnification is increased it appears that the distribution is not 100% homogeneous, only this is due to the fact that it is a very small sample area that is being analyzed. This observation is well illustrated by the cross sections micrographs of the nanocomposites prepared with different compositions (2, 6 and 10% masterbatch), obtained by SEM and represented in Figure 5.

Figure 6 a) shows that the layers of nanoclays have lengths and thickness in the range of nanometers. In Figure 6 b) can be verified that nanoclays' layers seems to have a good adhesion between the polymer and the nanofiller, which will be of significant importance to improve the mechanical properties. Good adhesion, good distribution and a dispersion of the layers of nanoclays contributes to a significant increase in properties in relation to the pure polymer.

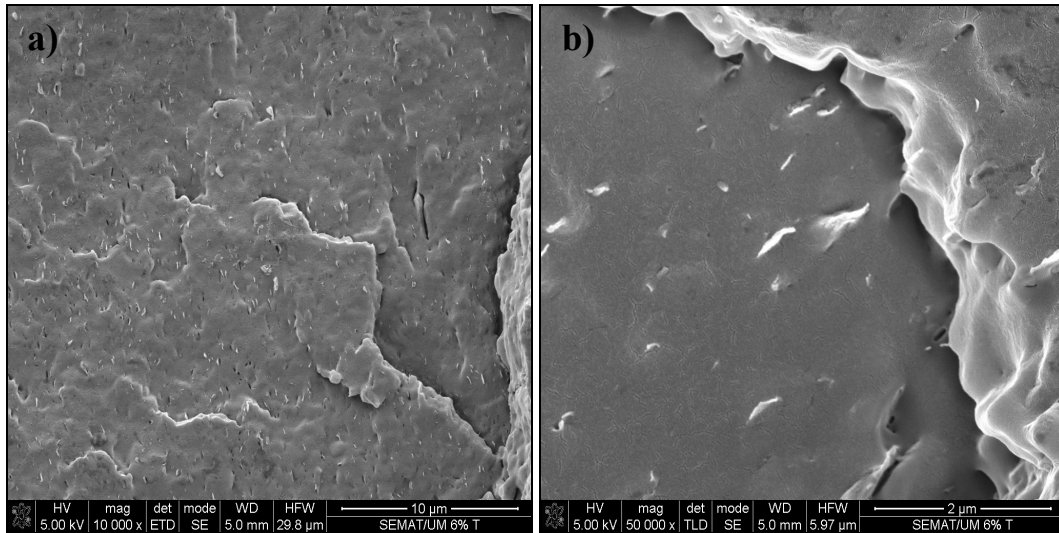


Figure 5 - Fracture surface of tensile samples containing 6% nanoclays with a magnification of a) 10 000x b) 50 000x

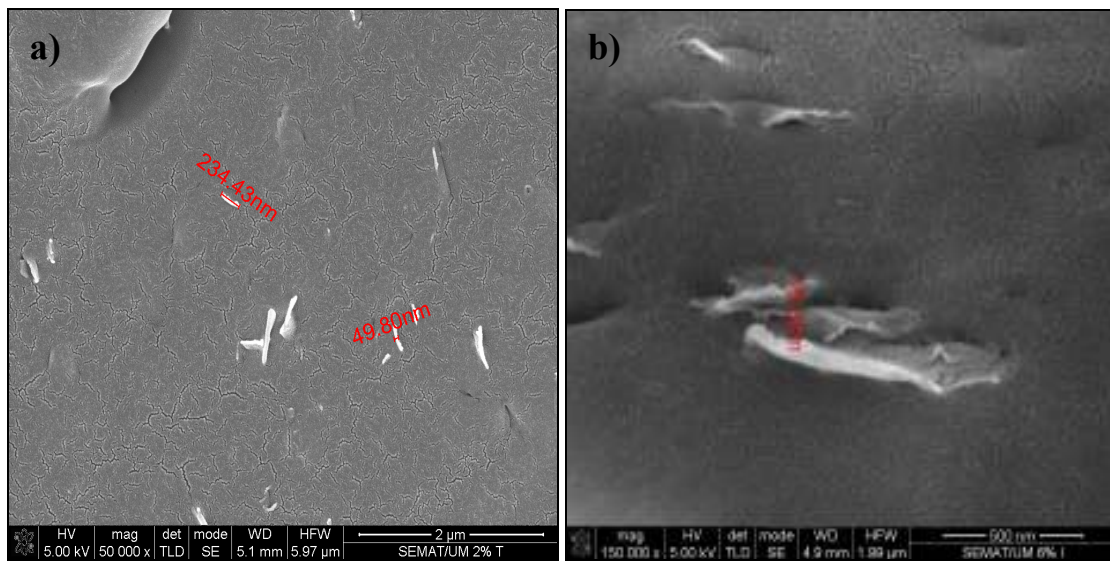


Figure 6 - Detail of the size of the layers of nanoclays. a)magnification 5000x b)magnification 150000x

### 3.3 X-rays Diffraction

The Figure 7 shows the XRD results obtained for the masterbatch and nanocomposites. The diffraction peaks of interest in the characterization of the nanocomposites are those that appear in the regions between the  $1^\circ$  and  $3^\circ$ ; these peaks are related to the basal spacing of clay. To complete this analysis, the ideal would be to analyze the XRD also for nanoclay natural (montmorillonite), but due to the absence of this material it wasn't possible to make the diffraction of X-rays. However, according to the literature [11, 13, 14, 15, 16], the montmorillonite has diffraction peaks between 3 ( $d = 2.8$  nm) and 5 ( $d = 1.7$  nm), and its peak appears primarily at  $2\theta = 4$  ( $d = 2.1$  nm).

After analyzing the results obtained, it can be said that the masterbatch already has an interleaved structure, because the montmorillonite presents a peak at the  $4^\circ$  with a basal spacing of 2.1 nm, while the masterbatch's peak of clay has a displacement of

1.57 and the basal's spacing was increased to 5.623 nm, showing that there is an intercalation of the PP between the layers of clay. Thus, as the masterbatch

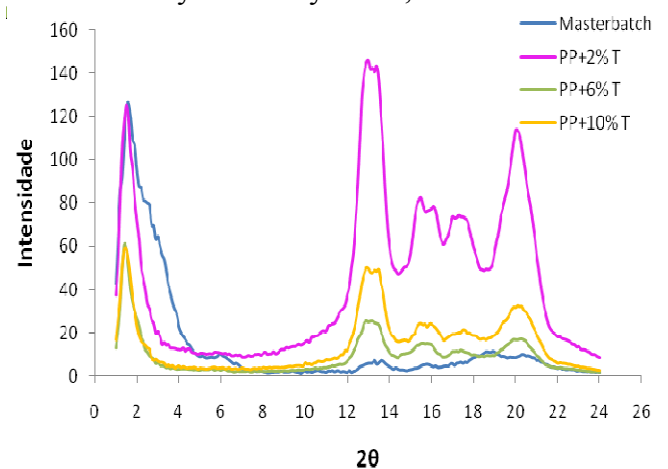


Figure 7 – XRD graphics of masterbatch and PP nanocomposites (samples Traction)

already has a structure intercalated, the nanocomposites will possibly also present an exfoliated or intercalated structure. This is something that was predict-



ed by the analysis in the SEM, which shows a structure with good distribution / dispersion.

For the tensile nanocomposites, all the compositions show an intercalated structure. Not only the masterbatch has a basal spacing greater than the montmorillonite, but also the compositions with 2, 6 and 10% of masterbatch have a slightly higher basal spacing than the masterbatch as can be seen from the Table 2.

Table 2 – basal spacing of the nanocomposites

Sample	2θ	Basal spacing (nm)
Masterbatch	1,57	5,623
PP + 2% Tensile	1,50	5,885
PP + 6% Tensile	1,42	6,217
PP + 10% Tensile	1,45	6,088
PP + 2% Impact	1,51	5,846
PP + 6% Impact	1,52	5,808
PP + 10% Impact	1,60	5,518

The structure presented in the impact samples is also interspersed, while, for tensile samples, the values for the diffraction peaks are very similar to the masterbatch. As shown in the Table 2, the basal spacing for these nanocomposites did not vary much and are slightly lower than the tensile test-piece. However, excluding the sample with 10%, these spacings are greater than in the masterbatch.

Some studies [17] showed that from a certain percentage of nanoclay up the basal spacing of the nanoclay in the PP and in other polymers decreased with the increase of the percentage of the nanoclay. This is because high amounts of clay can lead to a non-uniform dispersion, hindering the penetration of the polymer into the layers of the nanoclay.

### 3.4 Tensile test

The results of the tensile tests for the PP nanocomposites are summarized in Table 3.

Table 3 - Summary of mechanical properties of nanocomposites

Properties	PP 0%	PP 2%	PP 6%	PP 10%
Maximum Stress (MPa)	38,67 ±4,533	39,11 ±2,636	37,616 ±1,571	37,265 ±0,786
Stress at rupture (MPa)	29,882 ±5,56	22,411 ±11,244	1,757 ±0	1,757 ±0
Deformation at rupture (%)	155,803 ±43,011	164,7 ±56,798	286,958 ±80,9	367,146 ±87,890

The values of maximum stress were very similar for both the pure PP and nanocomposites. However, the nanocomposites with only 2% of masterbatch (49.11 MPa) have a higher maximum stress than the pure PP (38.67 MPa) and the other compositions.

As the concentration of nanoclays increases, the Stress at rupture decreases, and there is a greater decrease in the compositions of 6 and 10% compared to the pure PP and the PP with 2% masterbatch; the stress in the compositions of 2 and 6% of masterbatch reduces from 22.4 MPa to 1.75 MPa.

The fact that the stress at rupture is less in the compositions with a higher quantity of nanoclays is due to the greater quantity of nanoclays layers dispersed in the matrix. The good adhesion between the nanoclays and the polypropylene, promotes the sliding of the nanoclays when subjected to the tensile forces. Contrary to what is presented in the literature [9, 11, 18], where the results show that the deformation at rupture decreases with increase of the percentage of nanoclays in the matrix, the results obtained in this study show the opposite, ie, the deformation at the rupture increases with the increase of nanoclays. This observation is due to the fact that we have used a lower test speed (1mm/min) and masterbatch. When is used a masterbatch that already contains the clay modified to be compatible with the polymer, promotes good adhesion and interaction between the matrix and nanoclay, creating strong links between them, and consequently an increase in deformation [19].

A good distribution and dispersion of clay layers in the matrix leads to the improvement tensile strength, which can be attributed to the tenacity of the layers of nanoclay that contribute to the formation of immobilized or partially immobilized polymeric phases. It is also possible that the orientation of the layers of clay as well as the molecular orientation contribute to the observed reinforcement effects [11].

## 4 CONCLUSIONS

The methodology used in the preparation of the nanocomposites resulted in materials with interspersed structures in all the compositions. The largest basal spacing (6.217 nm) was observed in the tensile samples, in the composition with 6% of nanoclays.

The images of the microstructure of the nanocomposites revealed homogeneity, which indicates that there was a good dispersion of the clay layers in the matrix of polypropylene.

The mechanical properties of these nanocomposites have improved with the addition of nanoclays and contrary to what appears in the literature, the incorporation of nanoclays in the matrix of the PP provided a very significant increase of the deformation.

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