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**NANOCOMPOSITES OF PET GLASS FIBER
REINFORCE (ARNITE AV2 340.) AND
NANOPARTICLES OF CLOISITE: PROCESS
CONDITIONS AND CHARACTERIZATION**



INSTITUTO TECNOLÓGICO DE ARAGÓN

**Area of Research,
Development and
Technological Services**



INDEX

1	SCOPE	3
2	CHARACTERIZATION.....	4
2.1	<i>TENSILE TESTS</i>	<i>4</i>
2.2	<i>TGA</i>	<i>4</i>
2.3	<i>TEM.....</i>	<i>4</i>
2.4	<i>DSC</i>	<i>4</i>
3	SAMPLES DESCRIPTION	5
4	RESULTS	5
4.1	<i>Study of process conditions.....</i>	<i>5</i>
4.2	<i>Study of the influence of nanoclay concentration</i>	<i>12</i>
4.3	<i>Study of the matrix morphology</i>	<i>15</i>
4.4	<i>Study of influence of Cloisite 15A in the polymer matrix without fiber.....</i>	<i>18</i>
4.5	<i>Summary of mechanical results</i>	<i>21</i>
5	STUDY OF THE DISPERSION OF SILICATE LAYERS IN PET.....	22
6	CONCLUSIONS	26

1 SCOPE

The objective of this work was to evaluate the influence of the nanoclay Cloisite 15A in the mechanical properties of Arnite AV2 340 (PET with 20% of glass fiber). It is well known that a nanocomposite is reached when exits a good dispersion of nanoparticles and when the nanoclays are good exfoliated. Different ways of preparing the nanocomposites are possible, but in this case melt mixing was the one selected. As it is indicated in Ref¹f. and Ref² one of the ways of getting good dispersion and good exfoliation was to use great shear forces in the melt mixing process. To get that it was analysed the influence of several extrusion conditions in the final exfoliation and dispersion of the particles and therefore in the mechanical properties. Another factor analysed was the percentage of nanoparticle added in the matrix.

The degree of crystallinity influences on the mechanical properties of a thermoplastic polymer like PET. The presence of nanoclay increases the onset of crystallization, although this addition has a limited effect depending of the crystalline state and the clay exfoliation³.

Figure 1 sums up the studies carried out in the Arnite AV2 340 in order to analyse the nanoparticles addition and the melt-mixing conditions:

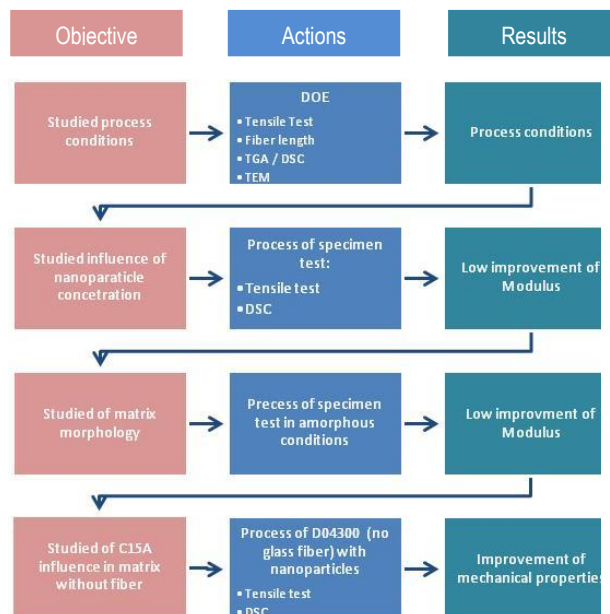


Figure 1. Diagram of the tests performed with the Arnite AV2 340.

¹ Polymer nanotechnology: Nanocomposites; D.R. Paul; L.M. Robeson; Polymer 49 (2008) 3187-3204.

² Structure and properties of Poly(ethylene terephthalate)/Na+-Montmorillonite nanocomposites prepared by solid state shear milling (S3M) Method; G.Wang, Y.Chen et al; Polymer Science: Part B: Polymer Physics

³ The role of nanoclay in the generation of poly(ethylene terephthalate) fibers with improved modulus and tenacity ; D.W. Litchfield, D.G. Baird ; Polymer 49 (2008) 5027-5036.

2 CHARACTERIZATION

Arnite AV2 340 processed in different conditions and the samples obtained had been characterize by means of mechanical and thermal analysis. The conditions of those analyses are described in next points.

2.1 TENSILE TESTS

The tensile test conditions were:

<i>Speed test:</i>	1 mm/min
<i>Preload:</i>	5 N
<i>Test temperature:</i>	Ambient ($20 \pm 1^\circ\text{C}$)
<i>Load Cell:</i>	5 KN
<i>Test equipment:</i>	Zwick (code 2PG43052-100-01) Videoextensometer (code 2PG43052-100-05)

2.2 TGA

Thermogravimetric Analyser (code 2PG30052-871) was used to calculate the degradation temperature in the material.

<i>Test equipment:</i>	TGA Pyris One (code 2PG30052-871)
<i>Test atmosphere:</i>	Nitrogen
<i>Temperature program:</i>	1.-Hold for 1.0 min at 50°C 2.-Heat from 50°C to 800°C at $10^\circ\text{C}/\text{min}$

2.3 TEM

Transmission Electron Microscopy was necessary to analyse the nanoparticles (Cloisite 15A) dispersion in the polymer matrix. Samples were cut with cryo-ultramicrotome. Structural analysis was done with a Transmission Electron Microscopy (TEM) JEOL-2000 FXII from the Universtiy of Zaragoza.

2.4 DSC

Differential Scanning Calorimetry (code: 2PG30052-710) was used to determine the glass transition temperature (T_g) and the crystallinity percentage.

The test conditions were the following:

1. Hold for 1 min at 30°C
2. Heat from 30°C to 285°C at $30^\circ\text{C}/\text{min}$ (First heating)
3. Cool from 285°C to 30°C at $30^\circ\text{C}/\text{min}$
4. Heat from 30°C to 285°C at $30^\circ\text{C}/\text{min}$ (Second heating)

3 SAMPLES DESCRIPTION

The Arnite AV2 340, montmorillonite Cloisite 15A, and Arnite D04 300 were dried at 100°C at least during 7 hours, before melt extrusion, according to the technical recommendations. Table 1 shows the different specimens and the melt processing conditions to perform all the activities mentioned before.

Table 1. Samples identification.

ITA code	% of nanoparticle in the total polymer	Extruder conditions	Injection molding machine conditions
GF20_ITA_12	0	T _{melt} : 280°C; Motor: 200 rpm; Time: 10min; Screw 1	T _{mold} : 130°C T _{injection} : 285°C
GF20_0,5C15A_ITA_13	0,625	T _{melt} : 280°C; Motor: 150 rpm; Time: 10min; Screw 1	
GF20_3C15A_ITA_14	3,75	T _{melt} : 280°C; Motor: 250 rpm; Time: 10min; Screw 1	
GF20_0,5C15A_ITA_15	0,625	T _{melt} : 280°C; Motor: 150 rpm; Time: 10min; Screw 2	
GF20_3C15A_ITA_16	3,75	T _{melt} : 280°C; Motor: 250 rpm; Time: 10min; Screw 2	
GF0_ITA_10	0	T _{melt} : 280°C; Motor: 200 rpm; Time: 10min; Screw 1	T _{mold} : 30°C T _{injection} : 285°C
GF0_2C15A_ITA_17	2,5		
GF0_4C15A_ITA_18	5		
GF0_6C15A_ITA_19	7,5		
GF20_0.5C15A_ITA_20	0,625	T _{melt} : 280°C; Motor: 150 rpm; Time: 10min; Screw 1	T _{mold} : 130°C T _{injection} : 285°C
GF20_0C15A_ITA_21	0		
GF20_2C15A_ITA_22	2,5		
GF20_4C15A_ITA_23	5		
GF20_6C15A_ITA_24	7,5		
GF20_0C15A_ITA_25	0	T _{melt} : 280°C; Motor: 150 rpm; Time: 10min; Screw 1	T _{mold} : 30°C T _{injection} : 285°C
GF20_2C15A_ITA_26	2,5		
GF20_4C15A_ITA_27	5		
GF20_6C15A_ITA_28	7,5		

4 RESULTS

4.1 Study of process conditions

Design of experiments was done to analyse the influence of the process conditions (motor speed and screw type) and the influence of percentage of nanoclay add to the polymer matrix. It was used an orthogonal array, with two-level design and three factors (percentage of nanoparticles, screw type and motor speed) (see Figure 2).

Control factors			
↓	C1	C2	C3
	% C15A	screw	rpm
1	0,5	1	150
2	0,5	2	150
3	3,0	1	250
4	3,0	2	250

Level values

Figure 2. Taguchi design.

This design allowed, in one hand to reduce the number of experiments and on the other hand to evaluate the influence of the selected factors. Mechanical properties by means of Tensile Strength, Elongation at Tensile Strength and Tensile Modulus were analysed, five specimens of each process condition were obtained and tested.

Next figure shows the screw types. Screw type 2 includes a modification in the geometry to improve the shear in the mixing.

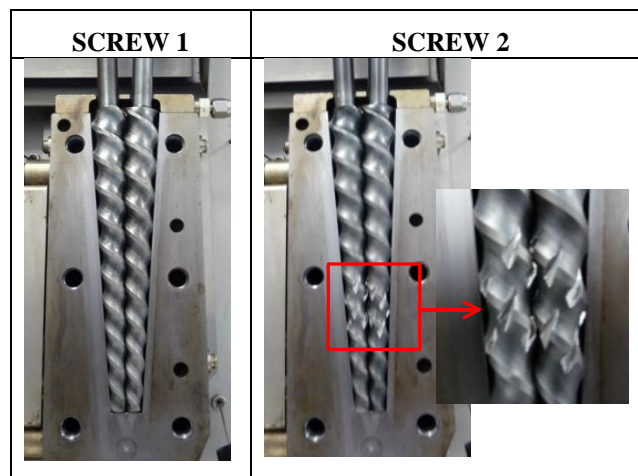


Figure 3. Extruder modification: Screw types.

The results of sample without nanoparticles (GF20_ITA_12) are included as a reference. In the following table can be observed all experimental values and in Figure 4 it can be shown the comparison between the stress-strain curves for the DOE samples:

Table 2. Comparative tensile test results: DOE SAMPLES.

CODE	Tensile Strength (MPa)	Elongation at Tensile Strength (%)	Tensile Modulus (MPa)
GF20_ITA_12	99,34	3,52	6490,42
GF20_0.5C15A_ITA_13	98,34	2,44	6861,21
GF20_3C15A_ITA_14	67,60	1,13	7223,48
GF20_0.5C15A_ITA_15	93,41	2,71	6099,38
GF20_3C15A_ITA_16	74,26	1,48	6265,59

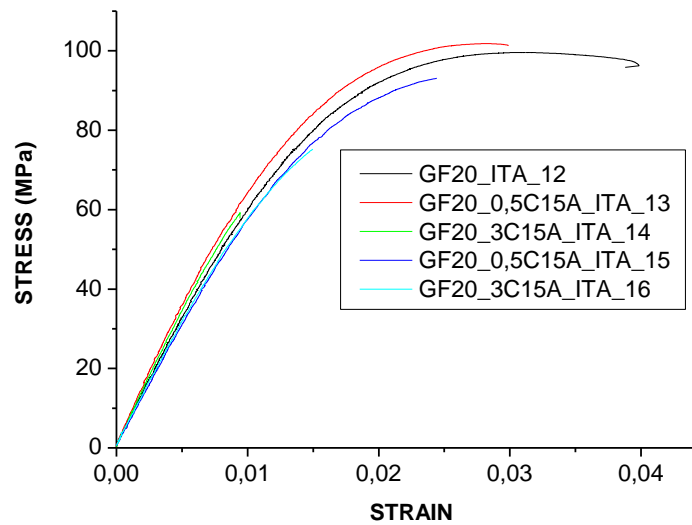


Figure 4. Stress-Strain curve: DOE results.

Figure 5 shows the improvement of about 10% in Tensile Modulus when screw type 1 was used.

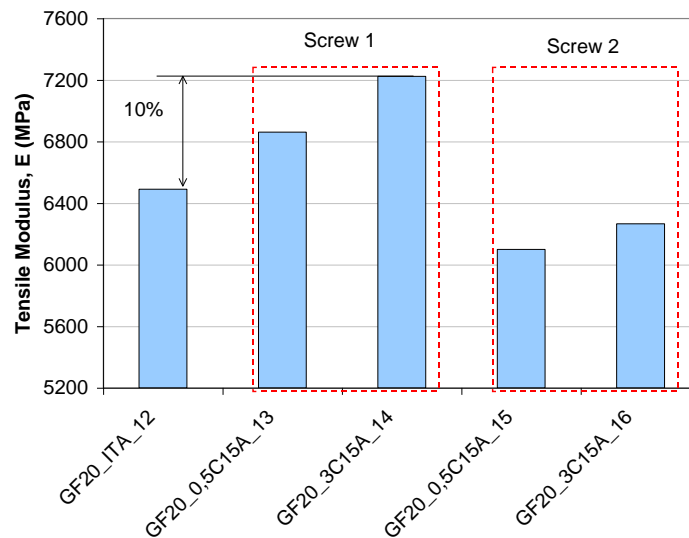


Figure 5. Experimental values: Tensile Modulus (MPa).

Mechanical properties have not been improved as expected, what could be caused by other factors like not exfoliation of nanoparticles, glass fiber degradation... structural analysis were carried out to study the possible causes.

Glass fiber can be broken during process; with the objective of evaluate the degradation after processed, samples were burnt in oxygen atmosphere during one hour at 500°C and 15 minutes at 700 °C; after cooling, the fiber length was measured with an optical microscope. Figure 6 shows the results of length fiber. There is a difference between the raw and the processed material; that could be attributed to the compounding process, since the material passed through kneading

blocks into the extruder, causing the milling of the fiber. It can be said that during the process conditions of ITA, fibers suffers a degradation of about 35% in relation with the original length.

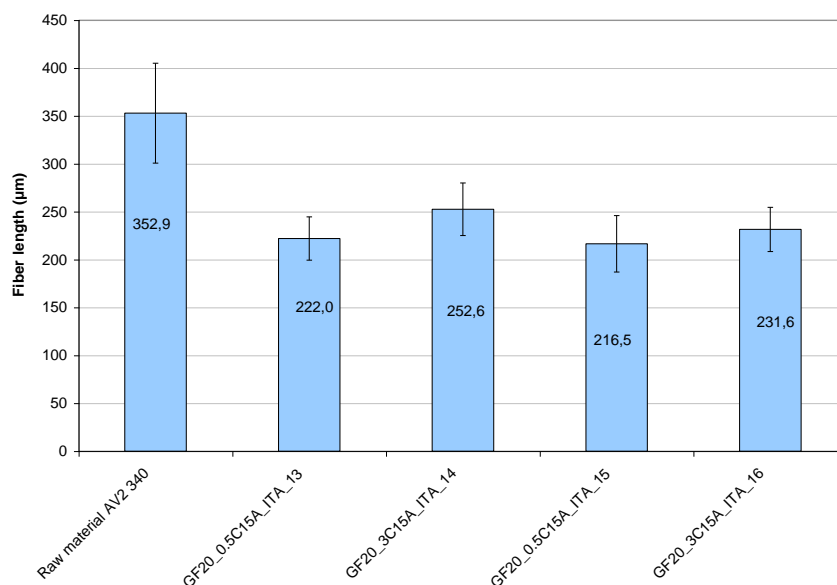


Figure 6. Fiber length average for the samples analysed.

TEM images were used to evaluate the distribution and exfoliation of nanoclays in the polymer matrix reinforced by glass fiber (ARNITE AV2 340). Samples GF20_0.5C15A_ITA_13 and GF20_3C15A_ITA_14 was selected to do the TEM analysis because those samples were the ones with higher tensile modulus.

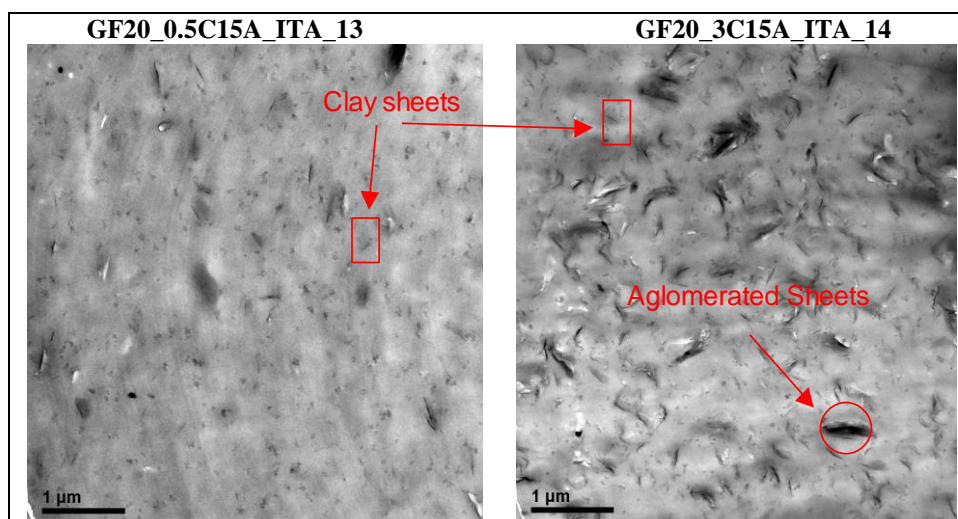


Figure 7. TEM analysis.

In Figure 7 it can be observed that the nanoclays were good dispersed in the matrix. The use of 0.5 or 3 % wt (total weight polymer plus fiber) of Cloisite 15A show the same distribution of particle, it can be observed clay sheets and some agglomerated sheets (nanoclays that have no

been exfoliated). There is no influence of percentage of nanoparticle on the grade of dispersion. There is no an orientation of the sheets of nanoclays in the PET matrix that can also influence in the final mechanical properties⁴.

To analyse the fibers orientation the sample GF20_0.5C15A_ITA_13 have been observed with the optical microscope (x500). The central part of the halterio sample was cut and mounted in an epoxi resin and then polished. Most of the fibers are oriented in flow direction showing a circular section about 10µm of diameter (see figure 8). As it was expected there is no difference in the orientation of the fibers in samples tested or not tested.

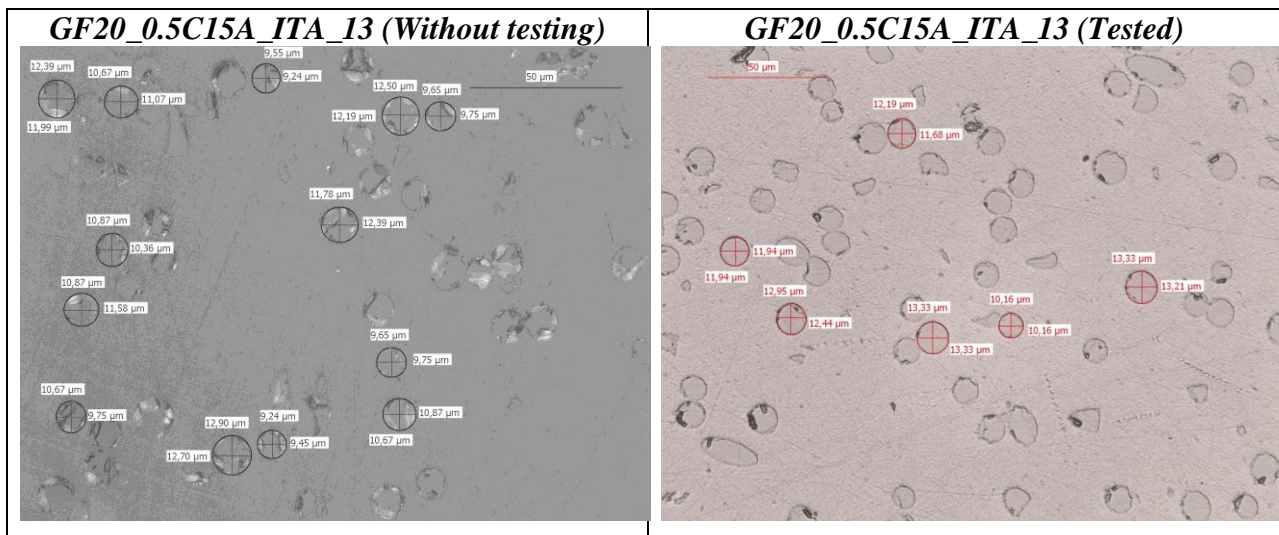


Figure 8. Fibers orientation in the sample: GF20_0.5C15A_ITA_13.

Glass transition temperature and percentage of crystallinity of the different samples have been determined by Differential Scanning Calorimetry. The results of the samples analysed are tabulated in the Table 3:

Table 3. DSC Results: DOE samples.

ITA CODE	FIRST HEATING		SECOND HEATING	
	Tg Onset (°C)	Peak area Onset (°C)	Tg Onset (°C)	Peak area Onset (°C)
GF20_ITA_12	62,23	240,18	76,11	252,33
GF20_0,5C15A_ITA_13	70,22	241,02	91,33	254,82
GF20_3C15A_ITA_14	66,36	242,01	68,70	234,39
GF20_0,5C15A_ITA_15	71,11	240,94	75,44	254,27
GF20_3C15A_ITA_16	65,53	241,11	71,81	237,83

⁴ Optimization of the mechanical properties of polypropylene-based nanocomposite via the addition of a combination of organoclays. K. S. Santos et al Composites: Part A 40 (2009) 1199-1209.

The presence of nanoclay increases the onset of crystallization and the peak crystallization temperature relative to pure PET.

The crystallinity percentage was calculated over the first heating and the results were showed in Table 4 (and in the **¡Error! No se encuentra el origen de la referencia.** of the “Total Results”). In Figure 9, can be observed the crystallinity effect on the mechanical properties.

Table 4. Crystallinity results ofDOE samples.

ITA CODE	% of nanoparticle in relation to total polymer	Crystallinity (%)	T _{recrystallization Onset} (°C)
GF20_ITA_12	0	18	208,849
GF20_0,5C15A_ITA_13	0,625	15	209,217
GF20_3C15A_ITA_14	3,75	21	206,750
GF20_0,5C15A_ITA_15	0,625	16	208,086
GF20_3C15A_ITA_16	3,75	20	205,222

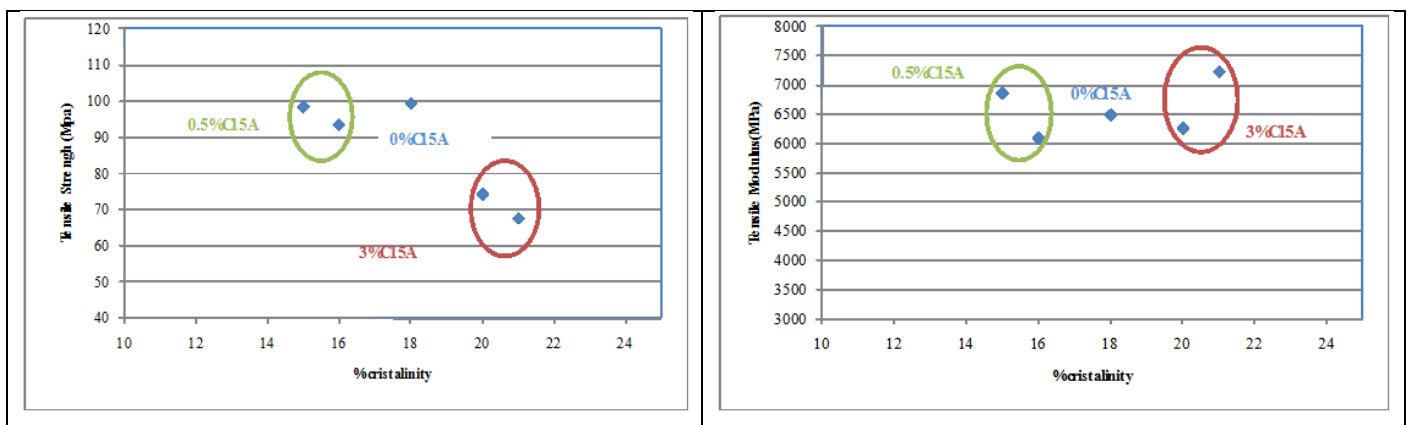


Figure 9. DOE Analysis: Crystallinity effect on the mechanical properties.

Table 4 shows the onset temperature of cool crystallization and the percentage of crystallinity. It can be observed a little difference between percentage of 0,5 and 3% of C15A. With 3% of nanoclays the crystallinity degree is a little bit higher and the temperature of crystallization is lower, so it can be said that with higher quantities of nanoclays, the crystallization process occurs at lower temperatures and the amorphous phase is lower.

Thermogravimetric analysis was done in order to know the influence of nanoclays in degradation temperature. It can be observed two different steps at approximately 415°C and at 580°C (see Figure 11). The first one could be related with the degradation of polymer matrix and it is possible to see that for sample without nanoparticles the temperature is higher, what means that in this case nanocomposites degradation occurs about 3°C earlier. Second step could be

related with some kind of degradation of fiber glass. In these nanocomposites there is not a tendency of the degradation temperature.

Figure 10 shows the TGA analysis for the following samples:

- GF20_ITA_12
- GF20_0.5C15A_ITA_13
- GF20_3C15A_ITA_14
- GF20_0.5C15A_ITA_15
- GF20_3C15A_ITA_16

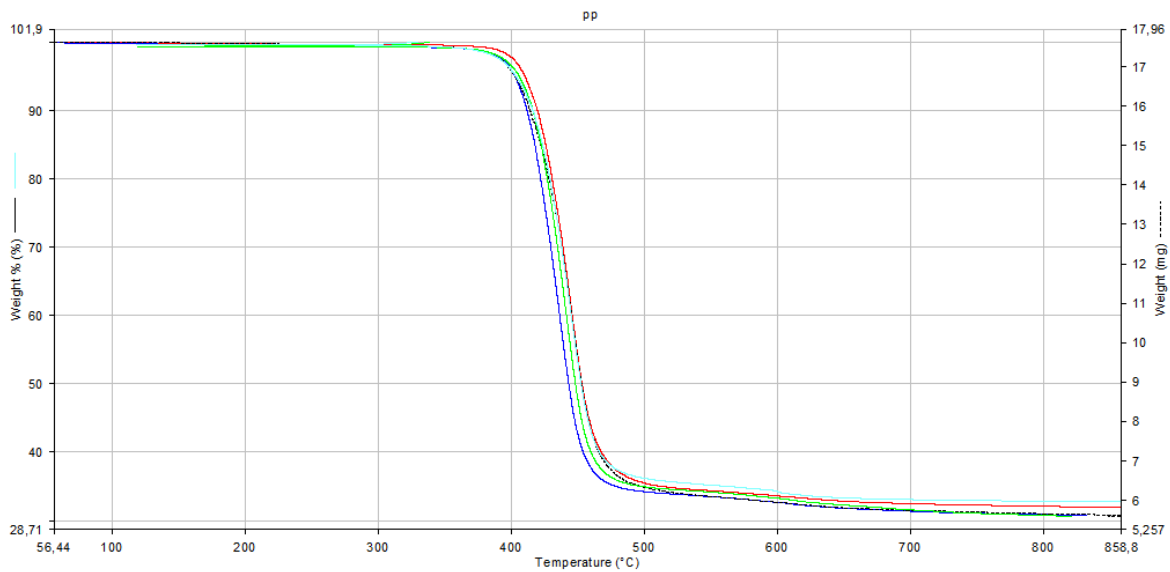


Figure 10. TGA analysis.

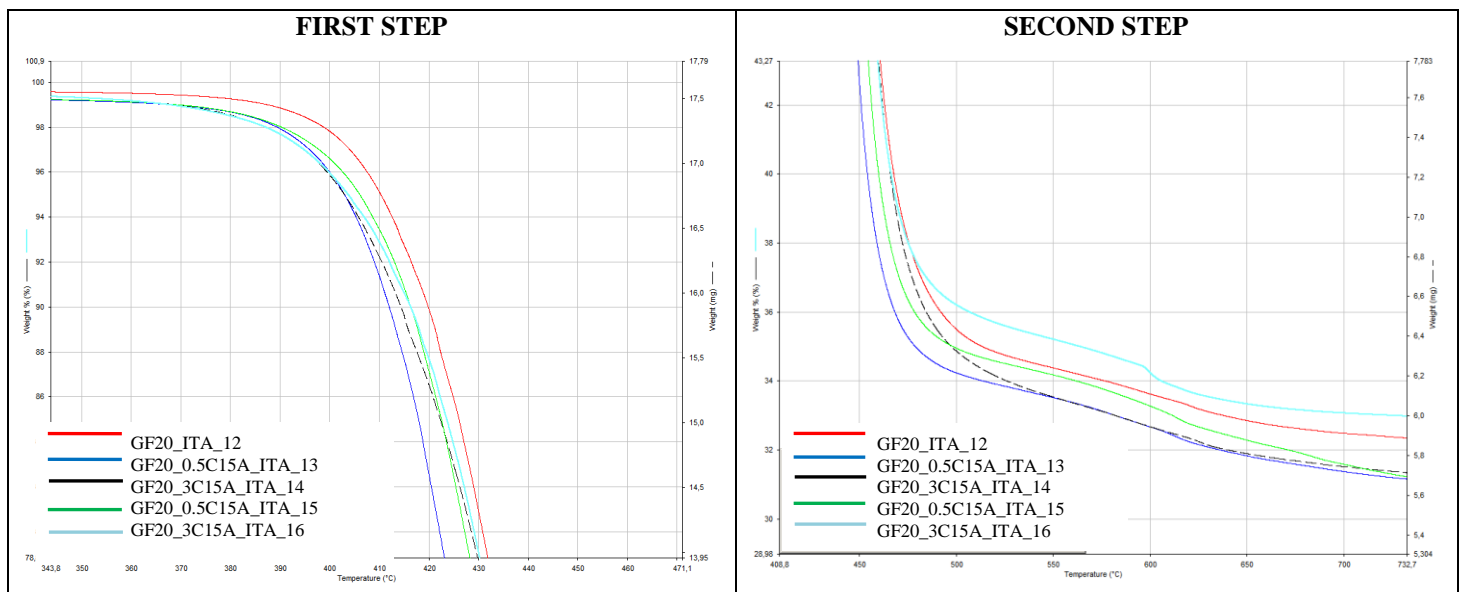


Figure 11. First and second step in the TGA analysis.

Table 5. TGA results.

ITA CODE	ONSET (°C) First step	ONSET (°C) Second step
GF20_ITA_12	419,73	575,58
GF20_0.5C15A_ITA_13	411,90	571,24
GF20_3C15A_ITA_14	417,88	573,41
GF20_0.5C15A_ITA_15	416,87	600,96
GF20_3C15A_ITA_16	418,21	593,29

According to the tensile test results obtained in the design of experiments (DOE), the sample with the best mechanical properties is the code GF20_0.5C15A_ITA_13, and the extruder conditions to process this sample was: Screw type 1 and 150 rpm.

4.2 Study of the influence of nanoclay concentration

The best conditions obtained in the study of process conditions were selected to process the samples to evaluate the effect of the concentration of the cloisite 15A (percentages: 2, 4, 6 % wt) in the polymer matrix.

Tensile tests have been performed to characterize the samples mechanically, and the results are shown in the following table:

Table 6. Tensile tests results: ARNITE AV2 340+ %C15A.

CODE	% of nanoparticle in relation to total polymer	Tensile Strength (MPa)	Strain at Tensile Strength (%)	Tensile Modulus (MPa)
GF20_0C15A_ITA_21	0	105,434	3,440	6510,335
GF20_0.5C15A_ITA_13	0,625	99,99	2,54	6894,02
GF20_2C15A_ITA_22	2,5	97,038	1,982	6823,061
GF20_4C15A_ITA_23	5	84,487	1,804	6911,677
GF20_6C15A_ITA_24	7,5	74,777	1,225	7549,603

Figure 12 shows the results obtained. The best sample compared with the reference GF20_0C15A_ITA_21 is the GF20_0.5C15A_ITA_13. Talking about tensile strength and strain, there are no improvements when the cloisite is add to the polymer-fiber matrix, on the other hand in reference to tensile modulus, it is possible to see an increment of 16%.

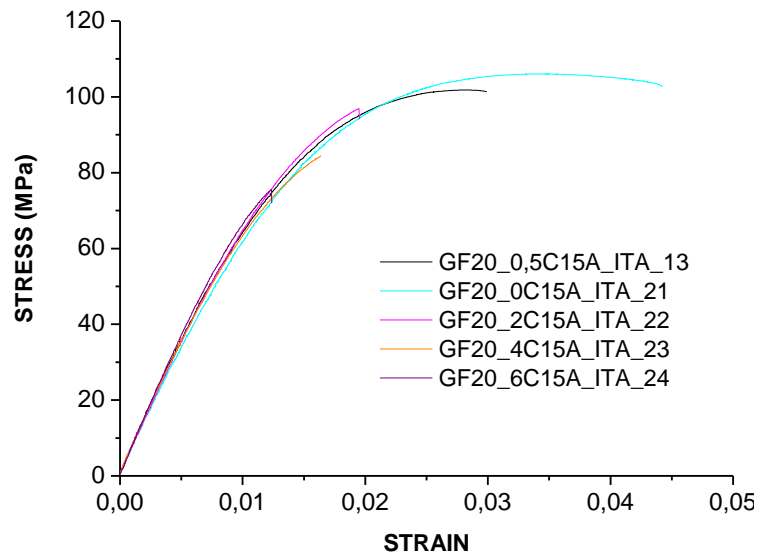


Figure 12. Stress-Strain curve: comparison between the samples processed in the same conditions (Screw type 1, 150 rpm).

To evaluate the different parameters: tensile strength, tensile modulus, elongation at tensile strength can be observed the next figure:

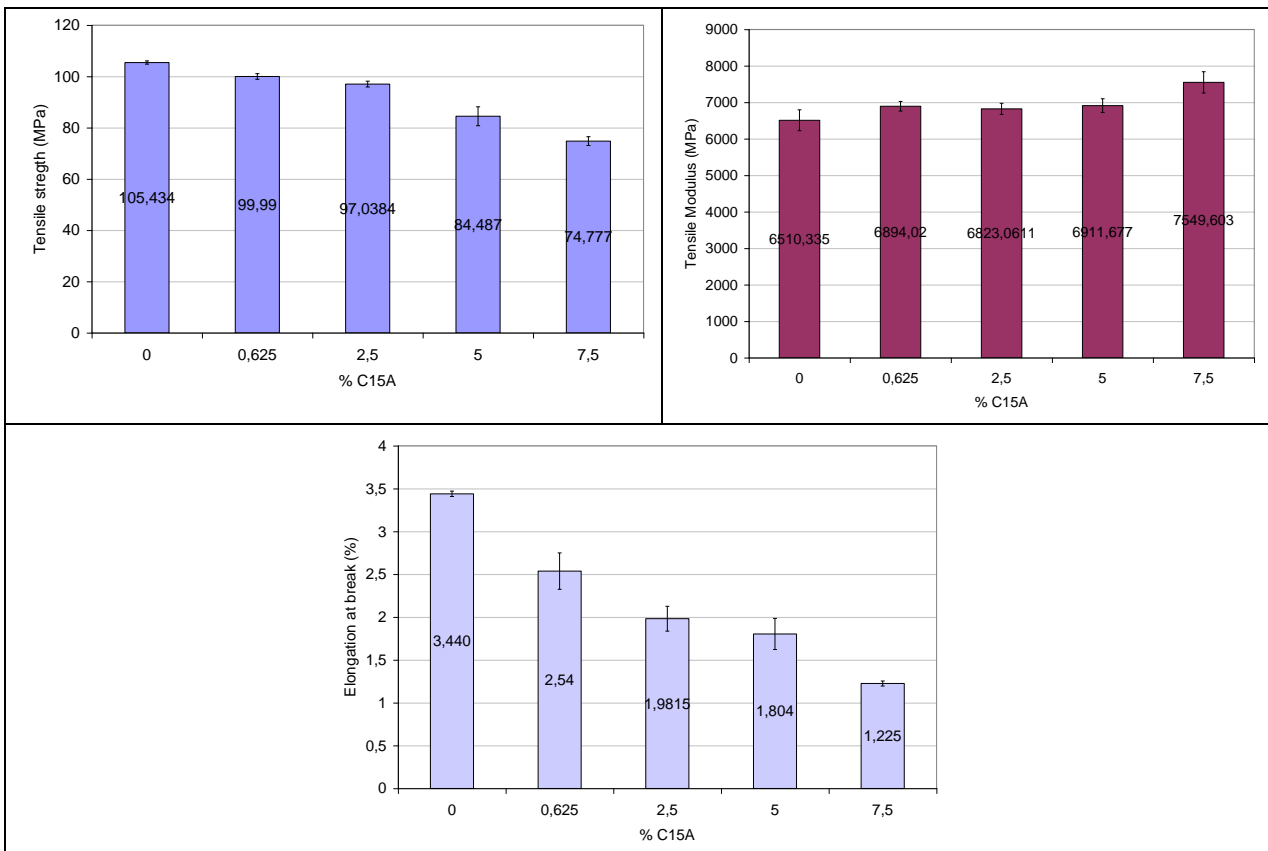


Figure 13. Influence on the different parameters with the cloisite percentage in the ARNITE AV2 340.

When 7.5% of Cloisite in the polymer matrix is added:

- tensile strength decreased 29%,
- tensile modulus increased 14%, and
- elongation at tensile strength decreased 64%.

Scanning calorimeter was done to analyse the percentage of crystallinity in the material developed (see Table 7 and Table 8)

Table 7. DSC Results: ARNITE AV2340 + %C15A.

ITA CODE	FIRST HEATING		SECOND HEATING	
	Tg Onset (°C)	Peak area Onset (°C)	Tg Onset (°C)	Peak area Onset (°C)
GF20_0C15A_ITA_21	80,975	239,498	77,753	236,367
GF20_0,5C15A_ITA_13	70,22	241,02	91,33	254,82
GF20_2C15A_ITA_22	75,965	257,813	73,076	232,548
GF20_4C15A_ITA_23	75,076	259,419	73,661	238,850
GF20_6C15A_ITA_24	68,532	259,379	70,667	240,189

Table 8. Crystallinity results: ARNITE AV2340 + %C15A.

ITA CODE	% of nanoparticle in relation to total polymer	Crystallinity (%)
GF20_0C15A_ITA_21	0	16
GF20_0,5C15A_ITA_13	0,625	15
GF20_2C15A_ITA_22	2,5	22
GF20_4C15A_ITA_23	5	23
GF20_6C15A_ITA_24	7,5	18

There is an improvement of the degree of crystallinity when the percentage of nanoclay increases.

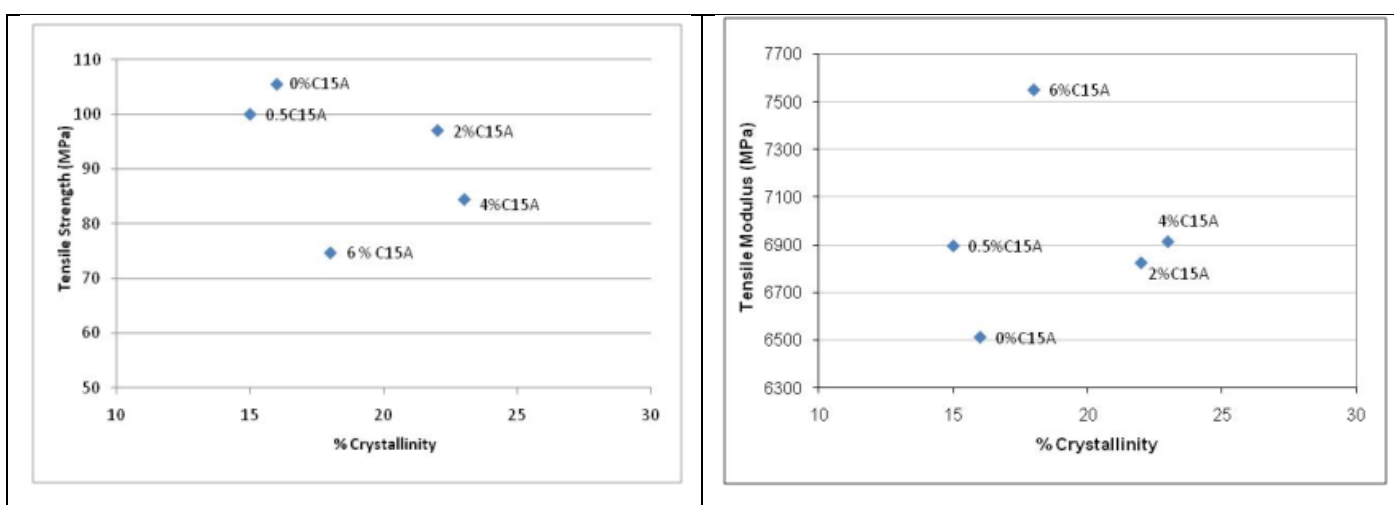


Figure 14. Influence of nanoclay concentration: Crystallinity effect on the mechanical properties.

Figure 4 shows the relationship between mechanical properties and percentage of crystallinity.

4.3 Study of the matrix morphology

To distinguish the reinforcement effect of the clay from the crystallinity on modulus, the matrix state was changed into amorphous, decreasing the mould temperature until 30 °C. The other conditions to process these samples were: 200 rpm and Screw type 1.

Next table and figure show the results of the tensile test of the samples processed with the amorphous conditions.

Table 9. Tensile tests results: ARNITE AV2 340+ %C15A.

CODE	% of nanoparticle in relation to total polymer	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Modulus (MPa)
GF20_0C15A_ITA_25	0	77,14	2,56	5406,63
GF20_2C15A_ITA_26	2,5	79,83	2,40	5428,90
GF20_4C15A_ITA_27	5	76,22	2,15	5576,40
GF20_6C15A_ITA_28	7,5	71,66	1,58	6536,89

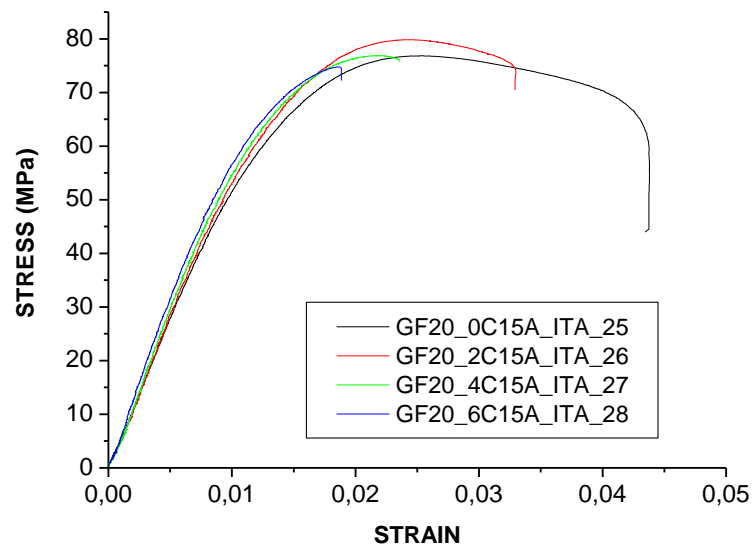


Figure 15. Stress-Strain curve: influence %C15A in the Arnite AV2 340.

The addition of the 2% wt of the Cloisite 15A (what means a total of 2.5% in relationship of polymer content) improve the mechanical properties of the nanocomposite. If this percentage increases the mechanical properties decrease and it could be because the cloisite was

agglomerated and acted as a tensile concentrator; what needs to be confirmed by structural analysis like TEM.

Next figure shows the results obtained for the studied of the cloisite effect on the Arnite AV2 340 in the amorphous state can. There is a little increment (3.5%) of the tensile strength property with a 2.5% of nanoclay in reference to the polymer weight, and a decrease of 7.1 % when 7.5% C15A is added. Talking about modulus, a increase of 21% with 7.5% of loading is observed while the elongation decreased 38 % with this concentration.

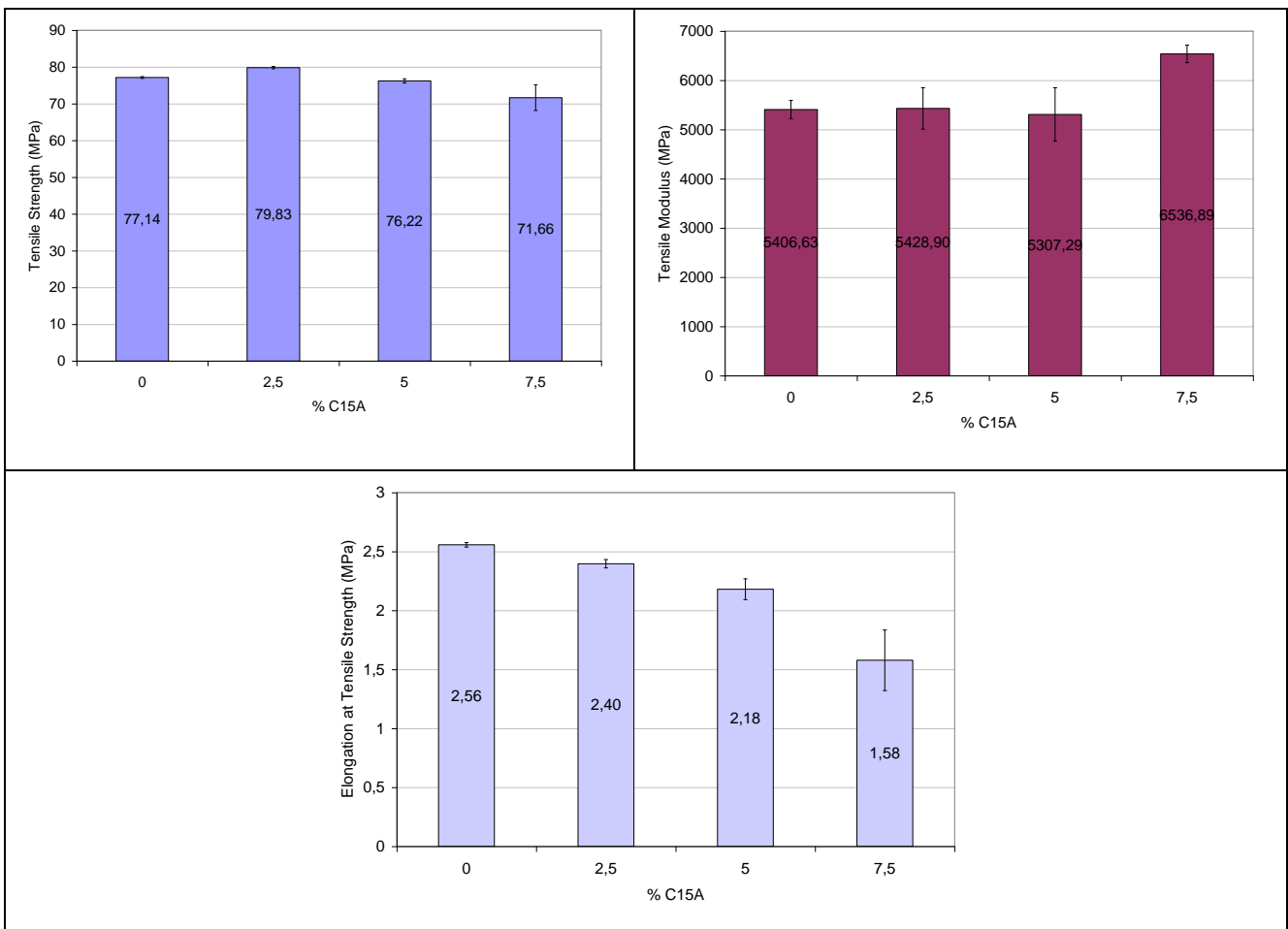


Figure 16. Influence on the different parameters with the cloisite percentage in the ARNITE AV2 340 (amorphous state).

As the addition of the 2.5% of Cloisite 15A in the total polymer increases the mechanical properties (tensile strength and modulus), the sample GF20_2C15A_ITA_26 was characterized by TEM. Next picture shows how the cloisite is good dispersed in the matrix and also there are some nanoparticles not good exfoliated forming agglomerates.

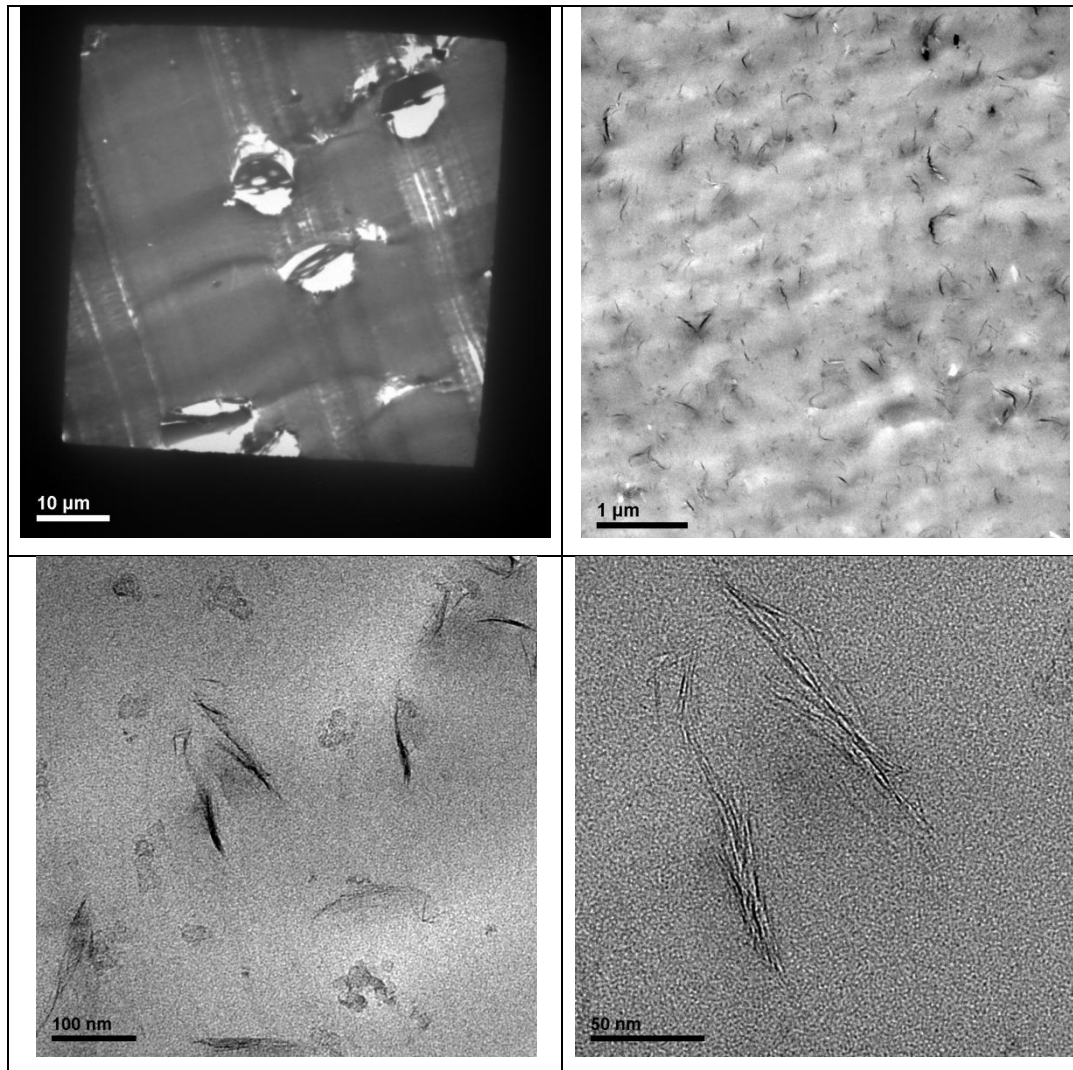


Figure 17. TEM images: GF20_2C15A_ITA_26.

Samples were analysed by DSC in order to confirm the amorphous morphology of the matrix and to study the influence of nanoparticle cloisite 15A in the crystallinity and glass transition temperature. Table 10 and 12 shows the results obtained.

Table 10. DSC Results: ARNITE AV2 340 + %C15A (amorphous state).

ITA CODE	% of nanoparticle in relation to total polymer	FIRST HEATING		SECOND HEATING	
		Tg Onset (°C)	Peak area Onset (°C)	Tg Onset (°C)	Peak area Onset (°C)
GF20_0C15A_ITA_25	0	79.514	240.710	73.486	235.095
GF20_2C15A_ITA_26	2,5	79.858	241.988	70.878	234.037
GF20_4C15A_ITA_27	5	78.261	241.124	68.603	239.557
GF20_6C15A_ITA_28	7,5	76.755	241.385	68.093	240.416

Table 11. Crystallinity results: ARNITE AV2 340 + %C15A (amorphous state).

ITA CODE	% of nanoparticle in relation to total polymer	Crystallinity (%)
GF20_0C15A_ITA_25	0	10
GF20_2C15A_ITA_26	2,5	2
GF20_4C15A_ITA_27	5	5
GF20_6C15A_ITA_28	7,5	4

Comparing the mechanical results of point 4.2 and 4.3 it can be concluded that the matrix morphology has more influence in the mechanical properties than the addition of nanoparticles. In case of amorphous state, as it was expected the material is more ductile and the tensile strength is lower than in the semicrystalline one. At this point where we have found not a big influence of the nanoparticle addition, it is necessary to study the possible influence of the glass fiber in the nanocomposite.

4.4 Study of influence of Cloisite 15A in the polymer matrix without fiber

To analyse the reinforcement effect of nanoclay in the polymer matrix without taking into account the fiber glass influence, there were developed nanocomposites using as matrix the material Arnite D04 300. In this case, the processing conditions were modified (according to material specifications, the molding temperature were decreased until 30°C) what made the matrix to change to amorphous state.

Following the studied planed, tensile tests were performed on nanocomposietes of Arnite D04 300 (0% GF) and different percentage of the cloisite (see Table 12, and Figure 18).

Table 12. Tensile tests results: ARNITE D04 300+ %C15A.

CODE	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Modulus (MPa)
GF0_ITA_10	46,190	3,340	2445,46
GF0_2C15A_ITA_17	51,834	3,162	2664,50
GF0_4C15A_ITA_18	52,484	3,120	2772,43
GF0_6C15A_ITA_19	52,711	3,056	2812,53

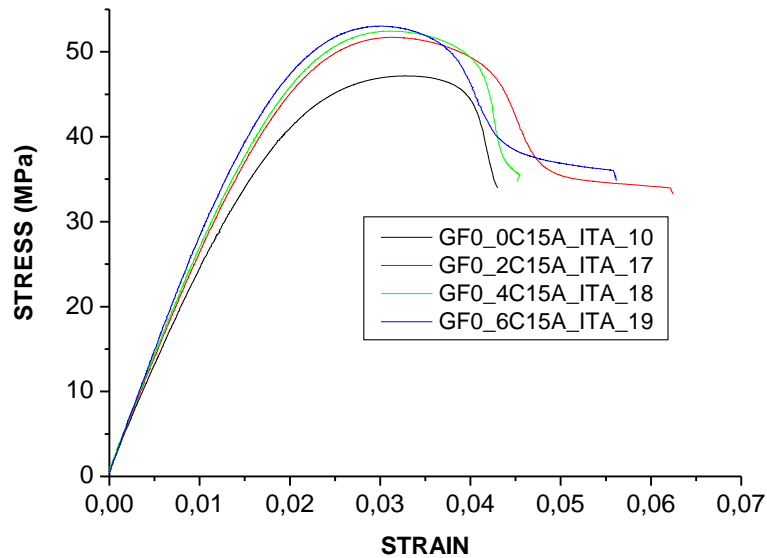
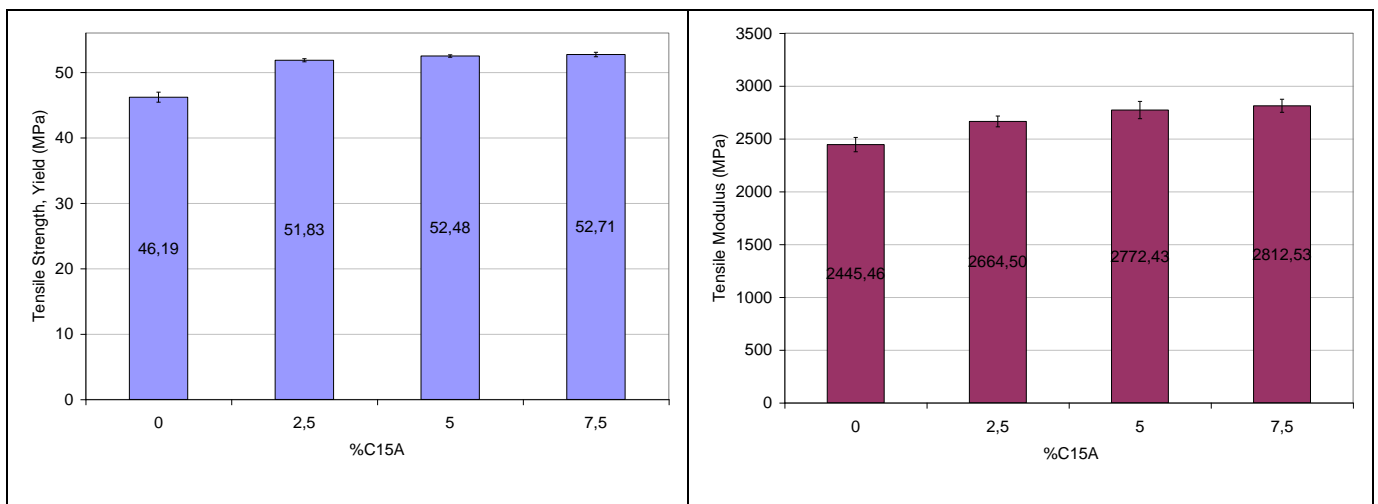


Figure 18. Stress-Strain curve: influence %C15A in the Arnite D04 300.

When the Arnite material does not have glass fiber in their matrix, it can be observed that the addition of 7.5% of Cloisite 15A in the total of the polymer improved the mechanical properties about 14% in tensile strength and in tensile modulus but no in elongation at tensile strength at yield (8% decreased).

To summarize the cloisite effect on the Arnite D04 300 the different parameters were analysed:



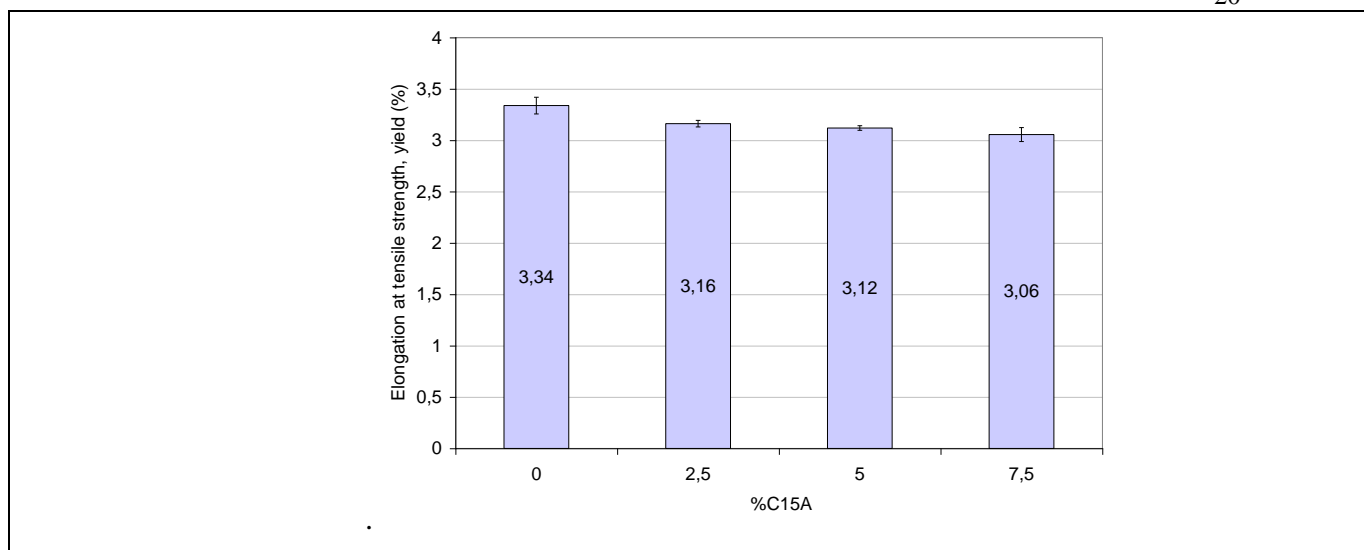


Figure 19. Influence on the different parameters with the cloisite percentage in the ARNITE D04 300.

Thermal analysis was performed in order to complete the characterization. Table 13 and Table 14 shows the results obtained. Because the material was molded at 30°C it was obtained as an amorphous phase and no degree of crystallinity can be observed.

Table 13. DSC Results: ARNITE D04 300 + %C15A.

ITA CODE	FIRST HEATING		SECOND HEATING	
	Tg Onset (°C)	Peak area Onset (°C)	Tg Onset (°C)	Peak area Onset (°C)
GF0_ITA_10	80,927	239,908	81,346	233,207
GF0_2C15A_ITA_17	82,031	236,515	79,610	236,197
GF0_4C15A_ITA_18	79,906	237,678	70,475	238,282
GF0_6C15A_ITA_19	80,594	238,587	77,362	238,465

Table 14. Crystallinity results: ARNITE D04 300 + %C15A.

ITA CODE	Crystallinity (%)
GF0_ITA_10	1
GF0_2C15A_ITA_17	5
GF0_4C15A_ITA_18	2
GF0_6C15A_ITA_19	5

Table 15. Cooling onset in the Arnite D04 300 (amorphous state).

ITA CODE	T _{recrystallization} Onset (°C)
GF0_ITA_10	192,067
GF0_2C15A_ITA_17	189,649
GF0_4C15A_ITA_18	189,169
GF0_6C15A_ITA_19	192,209

There is no influence on the degree of crystallinity by the nanoclay addition in the Arnite D04 300, only there is an influence by the mould temperature (30°C).

4.5 Summary of mechanical results

As was reported before, nanocomposites in amorphous and crystalline state was processed in order to study the possible influence of the matrix morphology in the mechanical properties. As it was hoped, the presence of crystalline state increases the modulus of the nanocomposites but decrease the elongation that is higher in the amorphous state because of the ductility of this phase.

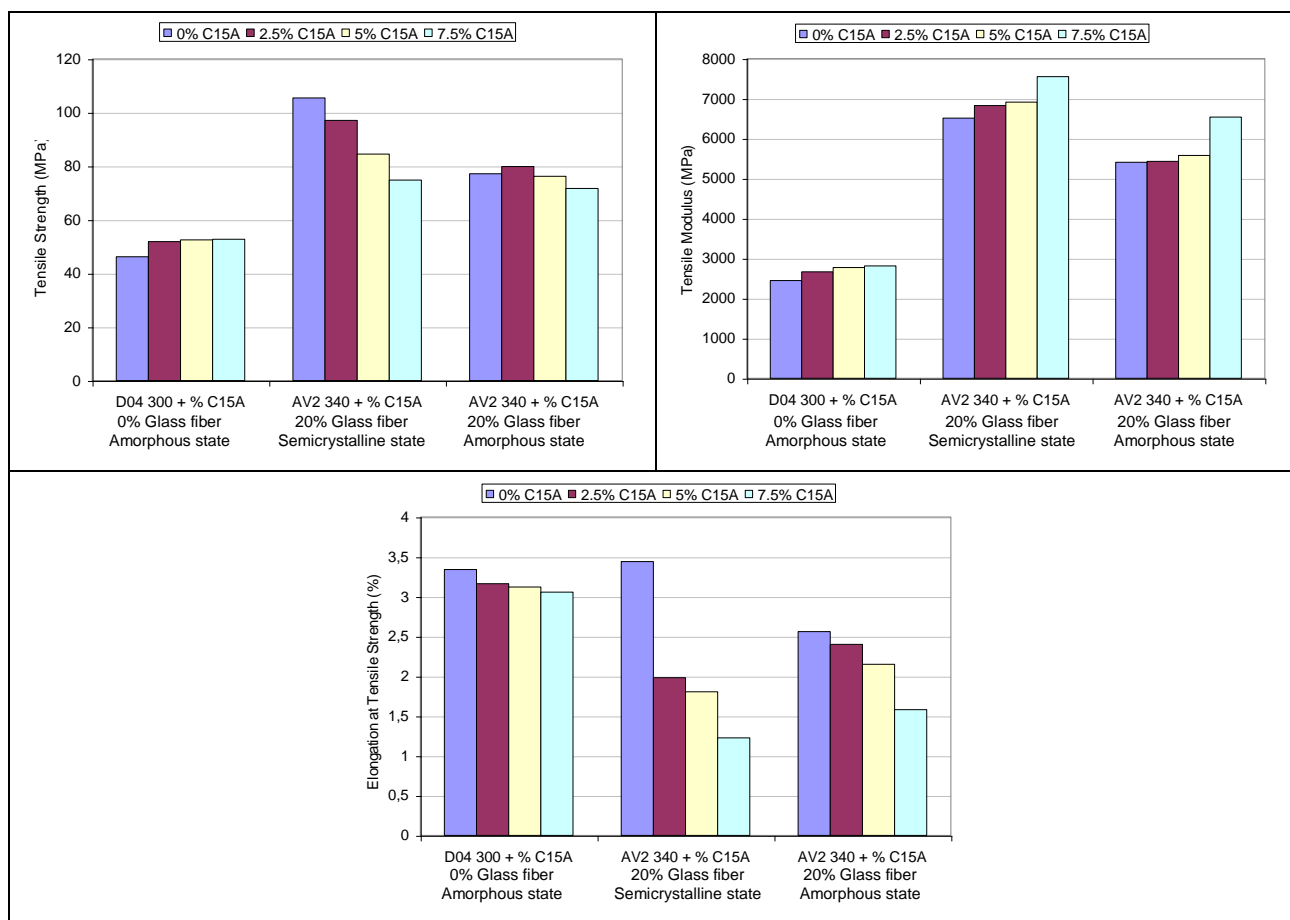


Figure 20. Influence on the different parameters with the cloisite percentage in the ARNITE AV2 340 (amorphous and semicrystalline state) and comparison between the material ARNITE D04 300.

It can be observed that there is big influence of glass fiber in the final mechanical properties of nanoclays. Only in the case of matrix with no glass fiber it is possible to see the influence of nanoparticles in the tensile strength, in the cases of polymer with glass fiber, the properties have not been improved.



Figure 21. Stress-Strain curve comparisson in the Arnite AV2 340.

5 STUDY OF THE DISPERSION OF SILICATE LAYERS IN PET

As additional study of the Cloisite 15A dispersion in the polymer matrix, the following samples were analysed by the rheometer:

- GF0_0C15A_ITA_10 (PET)
- GF0_4C15A_ITA_18 (PET/4C15A)
- GF20_0C15A_ITA_21 (PET/20GF)
- GF20_4C15A_ITA_23 (PET/20GF/4C15A)

These samples were measured by the rheometer “Nano-Geminin” in an oscillatory mode with parallel plate geometry using 25 mm diameter plates at 265 °C. The strain region in which the material can be regarded as linear viscoelastic was determined by amplitude sweep experiments, it is in the order of 8 %. Samples (for the rheological testing) with a plate geometry of 25 mm diameter and 1 mm thickness were prepared by compression moulding at 265 °C.

In the Figure 22 and Figure 23 storage modulus and dynamic viscosity versus frequencies are shown for various PET composites and nanocomposites.

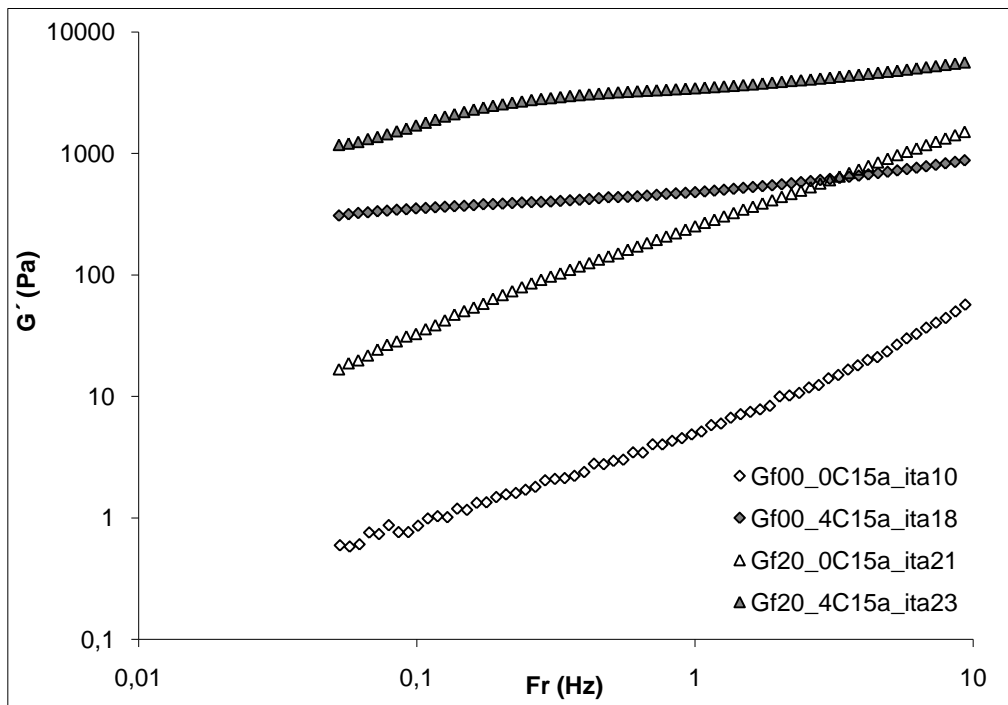


Figure 22. Storage modulus versus frequencies for various PET composites and nanocomposites containing 4wt% of silicate layers at 265 °C.

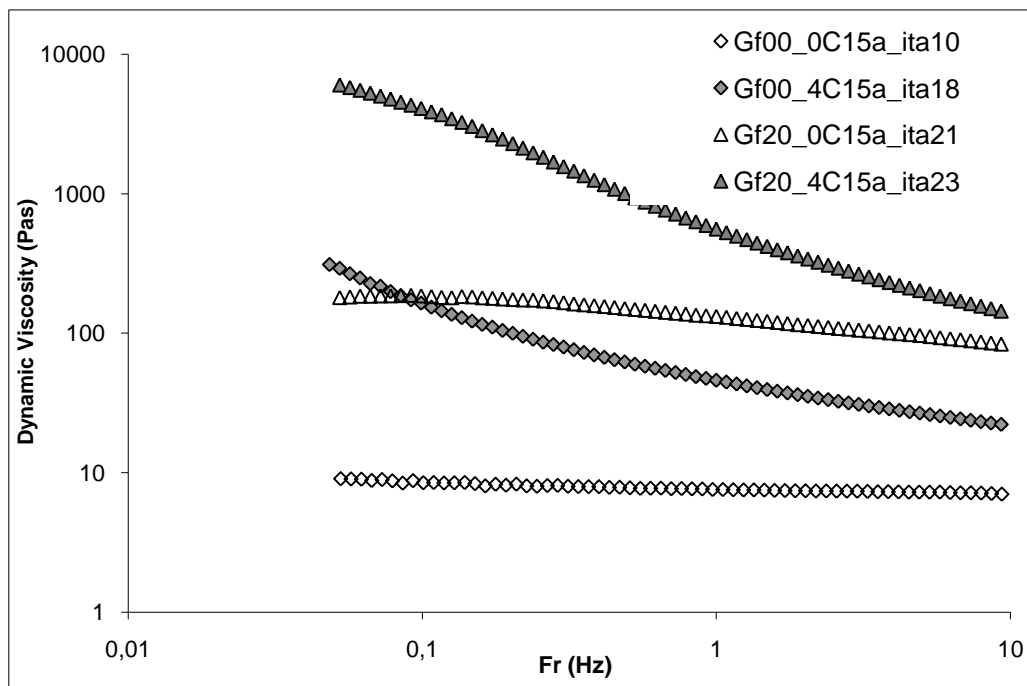


Figure 23. Dynamic viscosity versus frequencies for various PET composites and nanocomposites containing 4wt% of silicate layers at 265 °C.

The investigation of the rheological properties is an interesting tool to examine the nano-dispersion of the silicate layers in the PET/GF matrix. The melt-state rheological experiments are used to assess the relative dispersion of the silicate layers in these nanocomposite materials. The

frequency dependence of the storage modulus G' and the dynamic viscosity measured at 265 °C for both PET and PET/4C15, PET/20GF and PET/20GF/4C15 are shown in Figure 22 and Figure 23, respectively. Figure 22 shows that in the whole frequency range, PET is much less elastic than PET/20GF at 265 °C. The frequency dependence of G' for the glass fibre composites PET/20GF (open symbols) exhibits the normal response of a conventional filled thermoplastic polymer, with a liquid-like behavior at the lowest frequencies (below 0.1 Hz). In sharp contrast, the storage modulus for the nanocomposites PET/4 C15 and PET/20GF/4C15 containing 4 wt% of silicate layers (filled symbols) increases strongly in the frequency range of 0.05 to 1 Hz. Furthermore at low frequencies (corresponding to a regime where the unfilled polymer exhibits liquid-like behavior), the storage modulus for these nanocomposites shows a diminished frequency dependence, where PET/20GF/4C15 and PET/4C15 nanocomposites behave solid-like. The storage modulus becomes nearly independent on the frequency for PET/4 C15 nanocomposites. At high frequencies (5– 10 Hz), where the polymer chains are no fully relaxed, the viscoelastic behavior of the nanocomposites remains almost unaffected by the addition of silicate layers, with the exception of a monotonic increase in the modulus value. Based on the dynamic oscillatory shear experiments, it is clear that the addition of the silicate layers to PET has a profound influence on the long-time relaxation of the nanocomposites (at low frequencies). With adding the silicate layers to PET and to PET/20GF, the liquid-like relaxation observed for the pure matrix and for the conventional filled composites (PET/20GF) changes to a solid-like behavior for PET/4C15 and PET/20GF/4C15 nanocomposites (containing the silicate layers). This behavior can be attributed to the retardation of molecular relaxation processes induced by the confined geometric effect⁵. Solid-like behavior at low frequencies has been observed in both polycaprolactone and polyamide exfoliated nanocomposites with low silicate contents (3–5 wt%); it was attributed to the percolation of a three-dimensional filler network structure comprising a random orientation of exfoliated layers. The exfoliation of the silicate layers in PET matrix results mainly the formation of a percolated network structure of the silicate layers, which is in a good agreement with the morphological investigations. It should be mentioned and as it is shown in Figure 22, that the storage modulus for PET/20Gf/4C15 nanocomposites shows a less diminished frequency dependence that that of PET/4C15 at low frequencies, suggesting may be a less dispersion of the silicate layers in the PET/20GF/4C15 than in PET/4C15 due to the presence of the glass fibres. The dynamic viscosity as a function of the frequency for PET and PET/4C15, PET/20GF and PET/20GF/4C15 is shown in Figure 23. Over the whole frequency range (0.1–10

⁵ Krishnamoorti R, Silva AS. *Rheological properties of polymerlayered- silicate nanocomposites*. In: Pinnavaia TJ, Beall G, editors. *Polymer-clay nanocomposites*. New York: Wiley; 2000. p. 315.

Hz), the viscosity of the PET/20GF and PET nanocomposites is much higher than that of the corresponding matrix, respectively. At high frequencies (10 Hz), which correspond to high shear rates, the silicate content affects only slightly the melt viscosity. However, at low frequencies (less than 1Hz), the influence of the silicate content on the viscosity becomes significant. At this low frequencies range, the nanocomposites exhibit a solid-like behavior, while the polymer matrix shows a liquid-like relaxation (Figure 22). A similar trend has been observed by Krishnamoorti et al. ⁶. They observed that the shear viscosity of the nanocomposites increased monotonically with clay loading and the nanocomposites display a shear thinning behavior at low shear rates. The presence of the silicate layers and the lack of complete relaxation of the chains contribute to the solid-like response at low frequencies. On the basis of mesoscopic structure at low clay concentrations, it is suggested that, beyond a critical volume fraction, the tactoids (clay crystallites) consisting of intercalated silicate platelets as well as individual layers are incapable of freely rotating and are prevented from complete relaxation when subjected to shear. This incomplete relaxation due to the percolation leads to the solid-like behavior observed in the exfoliated nanocomposites ⁷. Thus, it appears that intimate contact between the polymer and the silicate layers alters the relaxation processes of the polymer, leading to the low frequency plateau in the storage modulus with increasing silicate layers loading ⁸.

⁶ Krishnamoorti R, Giannelis EP. *Macromolecules* 1997;30:4097.

⁷ Ren J, Silvia AS, Krishnamoorti R. *Macromolecules* 2000;33:3739.

⁸ Krishnamoorti R, Giannelis EP. *Macromolecules* 1997;30:4097.

6 CONCLUSIONS

- Design of experiments (DOE) was performed to analyse the extruder conditions on the mechanical properties by the addition of nanoclay. Sample GF20_0.5C15A_ITA13 (with 0.625% of C15A) shows the better results in terms of tensile strength. The process conditions of this sample were selected to process the rest of the samples. These conditions are:
 - $T^{\text{a}}_{\text{melt}}$: 280°C
 - Motor: 200 rpm
 - Time: 10min
 - Screw 1
 - $T^{\text{a}}_{\text{mold}}$: 130°C
 - $T^{\text{a}}_{\text{injection}}$: 285°C
- Microstructural analysis of samples was done by TEM. It is possible to see that when adding a 0.625% of nanoparticle of Cloisite 15A in relation to the total polymer weight (what means a 0.5% of total weight), and the nanoclays are good dispersed and exfoliated. When the percentage increases some agglomerations of the nanoclays appear.
- There is no an orientation of nanoclays, while fibers are oriented in injection process.
- Fiber length was analysed in order to know the influence of process conditions. Even thought the measurements have great deviation, it is possible to see that all the process conditions decrease the fiber length in approximately 35%.
- In thermogravimetric analysis it is possible to see that the addition of nanoclays decrease the degradation temperature about 3°C.
- Different percentage of nanoclay (2.5, 5 and 7.5% in relation to polymer weight) was added to the PET matrix in order to study their influence. Samples were processed in conditions selected. Talking about tensile strength and strain, there are no improvements with the addition of Cloisite 15A in the polymer-fiber matrix. On the other hand, in reference to tensile modulus, it is possible to see an increment of 16% with the addition of 7.5%.
- DSC analysis shows that there is a rise in degree of crystallinity when the amount of nanoclays increases, for the material processed in semicrystallintiy conditions.
- Mould conditions where changed in order to study the influence of matrix morphology. Samples were mould at 30°C instead of 130°C. There is an increment of 3.5% of the tensile strength when a 2.5% of nanoclay (in reference to the polymer weight) is added. Talking about modulus that increases a 21% when a 7.5% of nanoparticle is added. What means that when the matrix is amorphous the influence of nanoclay in mechanical properties (modulus) is

bigger than in the crystalline state. Even though the semicrystalline material has higher values of modulus than the amorphous.

- PET matrix without glass fiber (Arnite D04 300) was processed with nanoclay to study the nanoparticle influence in the pure matrix. In this case not only the tensile modulus but also the tensile strength increases about a 14% with the amount of nanoclay. This improvement did not occur with the glass fiber matrix, what could indicate that in presence of macro reinforcement as fiber glass, the influence on nanoclays is masked.
- The storage modulus for PET/20Gf/4C15 nanocomposites shows a less diminished frequency dependence than that of PET/4C15 at low frequencies, suggesting may be a less dispersion of the silicate layers in the PET/20GF/4C15 than in PET/4C15 due to the presence of the glass fibres