The effect of thermoplastic starch on the properties of polypropylene/ high density polyethylene blend reinforced by nano-clay

The Effect of Thermoplastic Starch on the Properties of Polypropylene/High Density Polyethylene Blend reinforced by Nano-Clay

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Abstract

Polypropylene (PP) and high density polyethylene (HDPE) was melt-blended in pairs at a constant of 80:20 (m/m) compositions; this blend is prepared by one-step reactive extrusion in a single-screw extruder. The present study aims to investigate the effect of thermoplastic starch (TPS) on the properties of PP and HDPE blend. This later has been investigated in the absence and presence of maleic anhydride grafted polyethylene (PE-g-MA), and reinforced by nano-clay. All the blends/nano-bio-composites were prepared in an internal mixer. The results indicates changes in the blends in terms of morphological, Mechanical, Thermal, structural and rheological properties. However, the different blends and nano-bio-composites were studied by means of Thermogravimetry (TG), Differential scanning calorimeter (DSC), Melt flow index (MFI), Izod impact (unnotched) tests, Scanning Electron Microscopy (SEM) and X- ray diffraction (XRD).

1. Introduction

The development of TPS blends and polyolefins has gained considerable attention of many researchers in recent times .The aim is to obtain low-cost materials with high quality mechanical properties. In addition, they are easily dismantled by microorganisms at the end of use (Ferreira, Khalili et al. 2014).Thermoplastic starch is a very hydrophilic material with limited performance (Taguet, Huneault et al. 2009) , it has disadvantages such as poor mechanical properties and high water solubility. In order to decrease the weaknesses of thermoplastic starch, the researchers mix it with other syntactic polymers that have advantages .Such as, high mechanical properties, high temperature resistance, high flow properties, cheap and hydrophobic (Waryat, Suryani et al. 2013; Waryat, Romli et al. 2013).Several studies have been conducted on starch/polymer blends like polyester/starch (Ratto, Stenhouse et al. 1999), starch-chitosan (Shukur and Kadir 2015), linear low-density polyethylene /starch (Chandra and Rustgi 1997), (Shujun, Jiugao et al. 2005), (Rodriguez-Gonzalez, Ramsay et al. 2003), (St-Pierre, Favis et al. 1997), starch/polycaprolactone (Ortega-Toro, Muñoz et al. 2016) and starch/polypropylene (Ferreira, Khalili et al. 2014); this can be used in many fields including, agriculture, industry, medicine and canning, etc. After our theoretical study, we find that the majority of studies focused on mixing starch with polyolefins but, biodegradable plastic from synthetic polymer/TPS material blend has a problem, this problem is an incompatibility between hydrophilic starch and hydrophobic synthetic (Waryat, Suryani et al. 2013; Waryat, Romli et al. 2013). Recently, many researchers have done much work to improve the compatibility of the blend including, the modification of starch, the modification of polyolefin's and/or the introduction of compatibilizer (Shujun, Jiugao et al. 2005) . However, others try to improve its properties by adding nanofillers to obtain an intercalated structure or/and exfoliated. The good dispersion of nanofillers in the matrix, unlike the formation of agglomerates which caused directly the decline of proprieties. Combining TPS with nanofillers to produce nanocomposites aim to enhance the mechanical, thermal and barrier properties of the polymeric matrix, this is currently the focus of numerous studies(McGlashan and Halley 2003), (Ray and Okamoto 2003), (Bordes, Pollet et al. 2009), (Avérous and Pollet 2012). The properties of the corresponding multiphase systems (so-called nano-bio-composites) are strongly dependent on the amount of nanofiller and its dispersion state. The improvement in the mechanical properties

with the inclusion of nanofillers is primarily a result of good dispersion and strong polymer-filler interactions (Bourbigot, Duquesne et al. 2006). Later, they have a mixed thermoplastic starch with two polymers, in a ternary system, Teyssandier (2011) suggested to mix and compatibilize polyamide/ polypropylene and plasticized starch ternary polymer blend using reactive extrusion process. whileSabetzadeh (2015) studied the ternary low density polyethylene and linear low density polyethylene in addition to thermoplastic starch blend films.

According to researches, polypropylene and polyethylene are immiscible and incompatible; this will lead to decline in the properties of the blend specially the mechanical one. In this study, we mix polypropylene and polyethylene, this blend called reference blend.Then when we added 5% of PE-g-MA into reference blends PP/PE named as a compatible reference blend. Many samples of blends of PP/PE and PP/PE-g-MA/PE were prepared with different TPS rates that are: 10%, 20%, and 30%. The main objective of this study is to investigate the effect of blending TPS and PP/PE using and without using Compatibilizer. The nano-clay is added to the mixtures to improve the thermal and mechanical properties of bio-nano-composites.

2. Experimental

2.1. Material used

Table 1: summarizes the materials used in this work as well as the specific characteristics.

2.2. Sample preparation

The preparation of blends/nano-bio-Composite is composed of three steps: first, preparation PP/PE and PP/PE-g-MA/PE. Secondly, preparation of thermoplastic starch and finally ,production of blends/nano-bio-composite.

2.2.1. Preparation of PP/PE and PP/PE-g-MA/PE

PP/PE and PP/PE-g-MA/PE are prepared in the same way, The difference is in adding 5 % of PE-g-MA to PP/PE, The formulation uses to prepare the blend containing 80 wt% of polypropylene and 20 wt% of high density polyethylene; it is prepared through melt-mixing procedure, which uses an intermeshing single-screw extruder, the four heating zones of the extruder are maintained at 170, 180, 190, 190 °C, and The screw speed was 60 rpm.

2.2.2. Preparation of thermoplastic starch (TPS)

TPS is prepared using two procedures: first, the starch was premixed with glycerol and water , The formulation used is containing 54 wt% of native corn starch, in addition to 23 wt% of glycerol and 23 wt% of water (Chivrac, Pollet et al. 2010). The starch powder is introduced into a turbo-mixer.after that, the water is slowly added under stirring. After finishing from adding water, then, the glycerol is added slowly with agitation; the mixture is then placed in a ventilated oven at 150 ◦C for 20 min. To allow the evaporation of water, then the dry blend obtained is melted by mixing it in Mixer interns Haake Rheomix 600 at 90 °C. The rotor speed was 30 rpm and mixing time was 5 min, in order to obtain a homogeneous dispersion.

2.2.3. Preparation of blends/nano-bio-composites

All the blends/nano-bio-composites are prepared through a melt-mixing procedure, using Mixer interns Haake Rheomix 600 with Contra rotating blades. The volume of the mixture room is 60 cm^3, which corresponds to a mass about 44g, while The temperature used is 180°C and the residence time is 10 minutes with 50 rpm speed. For all the formulations, The detailed formulation of samples is listed in Table **2**.

Table 2: summerizes the designation and composition.

3. Characterization

3.1 Differential scanning calorimeter (DSC)

The thermal behaviors of samples are measured on a DSC TA Instrument Q200 in a nitrogen atmosphere. The samples are scanned at a heating rate of 10 °C min^{-1}. Two heating cycles are used for each sample. The samples are first heated from room temperature to 200◦C for eliminating their thermal history. After that, they were cooled as to the room temperature and immediately reheated from −60◦C to 200◦C.

3.2 Thermogravimetric analysis (TGA)

Thermal stability of blends/nano-bio-composites investigated using TGA analysis. The measurements are performed on a Q500 analyzer, TA instruments, at a heating rate of 10°C. min^{-1}, under nitrogen atmosphere from 30 to 600 °C.

3.3. Melt flow index (MFI)

Melt flow index is measured by using Melt Flow Indexer (at 180°C, load 2.16 kg); The former is a simple parameter to obtain, and very useful which gives us indications on the viscosity of a polymer, the rate of branching, in addition to the free volume between the chains and the degree of crystallinity.

3.4. Mechanical properties

Measurements of the mechanical properties, such as tensile strength, The specimens are prepared according to ASTM D4812. ISO 180 standard, Izod impact (unnotched) tests are performed on a Zwick instrument, For each sample five measurements are made and the results with their average value.

3.5. Phase morphology studies of PP/HDPE/TPS blends

Scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The microscope used is (phillips X L20) operating 10-15 KV, SEM is used to study phase morphology of the PP/PE-g-MAPE/PE/TPS blends. The samples are sheets of 2 mm in thickness; the scanning is at the fracture surfaces of the samples.

3.6. X- ray diffraction (XRD)

For this analysis, we uses Diffractomètre PANalytical: XPERT-PRO, Where the thicknesses of the samples are about 2 mm. To be diffracted by the lattice planes of the crystalline phases present, they have exposed to an X-ray beam; Indeed, There is a relationship between the angle of the diffracted beam And the reticular distance separating the planes of atoms within a crystal lattice .Therefore,this is governed by: The Bragg's law **n λ = 2dsinθ** (Where λ = wave length in angstroms, d = cross-sectional distance in angstroms and θ = diffraction or reflection angle in degrees).However,the Condition of analysis are Wave length, CuKα [Å]: 1,5418 Starting angle [°2Th.]: 2,0000 and Final angle [°2Th.]: 70,0000.

4. Results and discussion

4.1. Thermal stability

The results of the blends/nano-bio-Composites are shown in Figure1. For the blend PP/PE, the initial thermal decomposition temperature (T_{onest}) has observed

around 285 °C, and the temperature of maximum rate of masse loss is detected at 390 °C. The addition of PE-g-MA does not indicate any change in the thermal stability of blend. However, The TPS increases the thermal stability of the reference blend PP/PE and the compatible reference blend PP/PE-g-MA/PE, as shown in the table **3**, the blends that contain TPS gradually decomposed; they were started by the first shift at around 100∘C, and produced by water evaporation. The second shift Starts at 180 °C, and it is produced due to the evaporation of glycerol. At 300∘C, the thermal decomposition of starch occurs according to(Shujun, Jiugao et al. 2005) . The last shift increases for the reference blend and compatible reference blend, corresponds to the heat degradation of blend PP/PE. The thermoplastic starch decomposition products protect the blend PP/PE and PP/PE-g-MA/PE from heat degradation According to (Nguyen, Vu et al. 2016).As can be seen from Figures 1,and 2 and table 3, with the increase in starch content, the residue increased according to (Roy, Ramaraj et al. 2011).

(a)

(b)

Figure 1: Thermal Stability of blends according to rate of TPS:

a) PP/PE, b)   PP/PE-g-MA/PE.

Thermal properties of polypropylene/clay nanocomposites are influenced by several characteristic parameters such as the clay content, the type of surfactant and the elaboration process according to (Zdiri, Elamri et al. 2017). In almost time , nano-clay increases the thermal stability of the polymers, it is observed that the initial decomposition temperature (T_{onest}) of PP/PE-g-MA/PE was 291 ∘C, the addition of 10 wt% of TPS with 2.5, 3.5 and 4.5 wt% MMT increase the T_{onest} decomposition of the PP/PE-g-MA/PE blend to 390, 395, and 397∘C ,that indicate an improvement in the stability. A similar trend was observed by (Zdiri, Elamri et al. 2017) . The enhanced thermal stability of the polymer-Clay nanocomposites is attributed to the lower permeability of oxygen , and the lower diffusibility of the degradation products, from the polymer bulk due To the exfoliated clay in the composites according to

(Chiu, Yen et al. 2010) . The thermograms ATG of the PP/PE-g-MA/PE/TPS/MMT nano-bio-materials are illustrated in Figure 2.

Figure 2: TGA of composites PP/PE-g-MA/PE/TPS/MMT.

The thermograms show increasing in the temperature at the beginning of the degradation (T_{onest}) of PP/PE-g-MA/PE in the nano-bio-composite by comparison with that of the PP/PE-g-MA/PE/TPS blend. After evaporation of water and degradation of starch and glycerol, the improvement in the thermal resistance is due to the barrier effects of the nano-clay layers, the best stability with (T_{onest}) is at 397 ° C that is observed at 3.5% in MMT. The formation of the residue is well observed with the increase of clay content; On the other hand, the maximum degradation temperatures (T_{max}) decrease significantly. Each thermal transition of ATG and DSC of blends/nano-bio-composites stripped in Table **3.**

Table 3: The values of the ATG and DSC.

The effect of blending TPS, PE-g-MA and organoclay on the thermal parameters, like melting temperatures and crystallinity of the PP/PE blends is shown in Figures 3 and 4 respectively, it is illustrated two melting endotherms corresponding to PP and HDPE phases (Jose, Aprem et al. 2004). The melting temperatures of the PP and PE on the blend of PP/PE are 166 and 133 °C respectively. And on the blend compatibilized are 164 and 130 °C respectively, the presence of TPS have decreased slightly the melting temperatures (T_{ms}) of components in the reference blend (PP/PE) and compatible reference blend (PP/PE-g-MA/PE). This effect is may be due to the melting lower temperature of TPS; this is because TPS contains water and glycerol that have low solubility.

Figure 3: DSC heating thermo grams of the samples.

The crystallization behavior of the samples under cooling rate of 10 °C/min is shown in Figure (4), the blends show only one crystallization temperature (T_c) according to (Chiu, Yen et al. 2010). Which are in most cases intermediate to those of PP and PE. According to Table **3**, it is seen that the addition of PE-g-MA into reference blend PP/PE increases crystallization temperature , the influence of adding

TPS on the crystallizations of PP/HDPE and PP/PE-g-MA/PE blends increases. With the presence of organo-clay, the composite has similar crystallization behavior.

Figure 4: DSC cooling thermo grams of the samples.

4.2. Melt flow rate

The Melt flow rate is a measure of the viscosity of the plastic material when exposed to heat above the melting temperature (Waryat, Suryani et al. 2013; Waryat, Romli et al. 2013). The addition of PE-g-MA to the PP/PE blend reduced the value of the MFI, as noted in Figure (5). And therefore an increase in viscosity was obtained, consequently the amount of extrusion decreased, this may be an indication of a physical interaction between the PP/PE blends produced by the addition of PE-g-MA.

The addition of thermoplastic starch tends to decrease the value of MFI. TPS serves as a filler material which tends to increase the viscosity of the blend according to (Waryat, Suryani et al. 2013; Waryat, Romli et al. 2013), Figure (5) also Shows that the MFI values of PP/PE/TPS composites decreased, as the thermoplastic starch content increased from 0 to 20 wt %, this indicates that the viscosity of composite increased. This is similar to the results obtained for most filled thermoplastic and in agreement with that reported by researchers before, stating that the MFI of starch composite decreased as the filler loading increased (Thakore, Iyer et al. 1999) . This can be due to certain compatibility between the PP/PE and the thermoplastic starch. But the Adding of 30 % of TPS to PP/PE raises the value of MFI; consequently a decrease in viscosity is obtained, this may be due to the increase in the free volume which is created by glycerol in the TPS.

Figure 5: Melt flow rate value of blends.

Figure (6) clearly illustrates that the presence of nano charge MMT causes a decrease in the values of the melt flow index in all nano-bio-composites, this result can be explained by the effect of the good dispersion of the organo-clay layers during mixing them, which develops interactions at the interface with the PP/HDPE/TPS in the presence of PE-g-MA.

Figure 6: Melt flow rate value of nano-bio-composites.

4.3. Mechanical properties of blends/nano-bio-composites

The tensile modulus and strength of the blends are significantly decreased by adding the TPS to the high-density polyethylene (PE), polypropylene (PP), polystyrene (PS), polylactic acid (PLA), and polycaprolactone (PCL) according to (Huneault and Li 2012). The tensile strength of the blends/nano-bio-composites are shown in Figures (7) and(8) . We try to study the influence of TPS on the tensile strength of PP/PE with and without compatibilizer and in the presence of organo-Clay, the results clearly show that the incorporation of PE-g-MA into PP/PE blend affected the mechanical properties as the Impact strength, the increase in mechanical properties may be due to the physical interaction with PE and PP. as it is observed in the Figure 7, the impact strength decreased by adding TPS according to (Ray and Okamoto 2003). The incorporation of TPS into reference blend and compatible reference blend has reduced the tensile strength, But with less extent in the compatible refrence blend, This is due to the presence of PE-g-MA. Figure 8, represents the impact strength of nano-bio-comoposite versus nanoclays content. About 3% increases in impact strength, this can be reached by incorporation of 2,5 wt.% of nano-clays. A 7 % and 17 % decreased; this is observed when 3,5 and 4,5 wt.% of nanoclay is added respectevly.

Figure 7: Impact strength versus TPS content.

Figure 8: Impact strength versus nanoclay content.

4.5. Morphology

By their immiscibility, the blends have different microstructures depending on the composition. There are two major classes: firstly, a discrete structure of droplet type in a matrix. Secondly, a co-continuous morphology with inter penetration of the isentropic networks in three dimensions. Of course, there are several other types of morphologies such as, laminar structures, where the phases are oriented by forming fibers if the flow allows. Composite drops are observed in some cases, close to phase inversion compositions or droplets of one phase, which are encapsulated in an oriented or co-continuous geometry of the other phase (Favis and Chalifoux 1988).

The morphological phase of PP/PE blend and their composites was investigated by SEM. Figure (9 a) shows the PP/HDPE blend, the HDPE phase dispersed in the PP

matrix in the form of spherical particles (in the case of small nodules), or ellipsoid (in the case of large nodules). The HDPE network is still built by the well-known shaded structure. In comparison, the PP lamellae seems to be more disordered and shows a more pronounced curvature. The addition of 5% of PE-g-MA resulted a good dispersion of HDPE in the PP matrix compared without compatibilizer, as shown in Figure (9 b), the objective of adding PE-g-MA is to reduce the interfacial tension to facilitate the dispersion of the HDPE particles in the PP matrix. This reflected positively on the mechanical properties of the PP/HDPE blend, as noted in Figure (7),

The addition of thermoplastic starch tends to cover the PP/HDPE blend, as we observed in the figure (9 c).The presence of starch between the molecules of the PP/HDPE blend in a homogeneous manner and many studies have shown that. The presence of a large amount of starch in plastic blends weakens the mechanical properties due to the presence of solid granules as shown in figures (7) and (8).

Figure 9: SEM images of (a) PP/HDPE; (b) PP/PE-g-MA/PE; (c) PP/HDPE/TPS.

4.4. Structural analysis

Figure 10, shows the XRD Patterns of nano_clay and the nano_bio_composite, the primary (001) diffraction of nano_clay is evident, indicating a D-spacing of 18,29 nm (pos $2\theta = 4,83°$) for the nano_bio_composites PP/PE/TPS/PE-g-MA, the (001) diffraction position of nano-clay changed completely, Where it is noted the disappearance of the position for nano-bio-composite. This observation implies the exfoliation of nano-clay, the absence of the characteristic clay intense peak in the nanocomposites indicates the exfoliation of the clay platelets in the matrix. (Tang, Hu et al. 2003) attributed the absence of diffraction peaks to the delaminating of the clay. It has been also reported elsewhere that the disappearance or decrease of intensity of diffraction peaks could be attributed to the fact that the silicates are partially or completely exfoliated (Nam, Maiti et al. 2001), the good dispersion of the clay feuiellets can be during the mixing process.

Figure 10: XRD spectra for the nano-clay and their bio-nano-composites

The figure (11) Presents the diffractograms of PP/PE-g-MA/PE/TPS and their nanocomposites at Large angles, an increase is observed in the intensity of clean peaks to the crystalline phases of the PP/PE/PE-g-MA/TPS/MMT, This can be

Indicated that the presence of nanoclay and TPS increases the crystallinity rate of our systems.

Figure 11: Diffractograms RX of PP/PE nano-bio-composites whose ratio TPS/MMT/PP-g-MA.

Conclusion

The present study aims to investigate the effect of Thermoplastic starch on the properties of PP/PE and PP/PE-g-MA/PE blends and the use of nano-clay as a reinforcing filler.

According to the tests and the expirments done, the results obtained can be summerized in the following:

From the thermal analyses, the decomposition products of the thermoplastic starch protect the PP / PE and PP/PE-g-MA/PE from thermal degradation. Concerning nano-bio-composites. However, the increase in the starting temperature of degradation is due to the dispersion of the clay layers; which interfere the diffusion of oxygen in our system.

For rheological properties, the addition of TPS causes a decrease in the melt flow index by increasing the level of the thermoplastic starch to 20%, this may be due to certain compatibility between PP / PE and thermoplastic starch. But, the addition of 30% has an antagonistic effect, As well as when adding the TPS to the PP/PE-g-MA/PE because of the large number of polar function presence in the TPS and the PE-g-MA. The addition of nano-clay to the system decreased the Melt flow index, this may be due to the reaction between The modifying agent of the clay and Maleic anhydride being presented in PE-g-MA or/and the hydroxide in the glycerol.

In terms of structural analyses, the results of DRX shows a good dispersion of the nano-clay layers, That is to say obtaining an exfoliated structure and/or partially exfoliated, it is also shown that the addition of a small amount of TPS and organo clay to PP / PE improved PP / PE crystaliness.

For morphological properties, the addition of thermoplastic starch tends to cover the PP/HDPE blend.

Concerning mechanical properties, We conclude that the addition of 5 % of PE-g-MA to refrence blend improved the impact strength of this latter, When adding the TPS to the refrence blend and the compatible refrence blend , a decrease in impact strength increases the rate of TPS. Incorporation of 2.5% of the nano-clay slightly increases the impact strength of our system.

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(a)

(b)
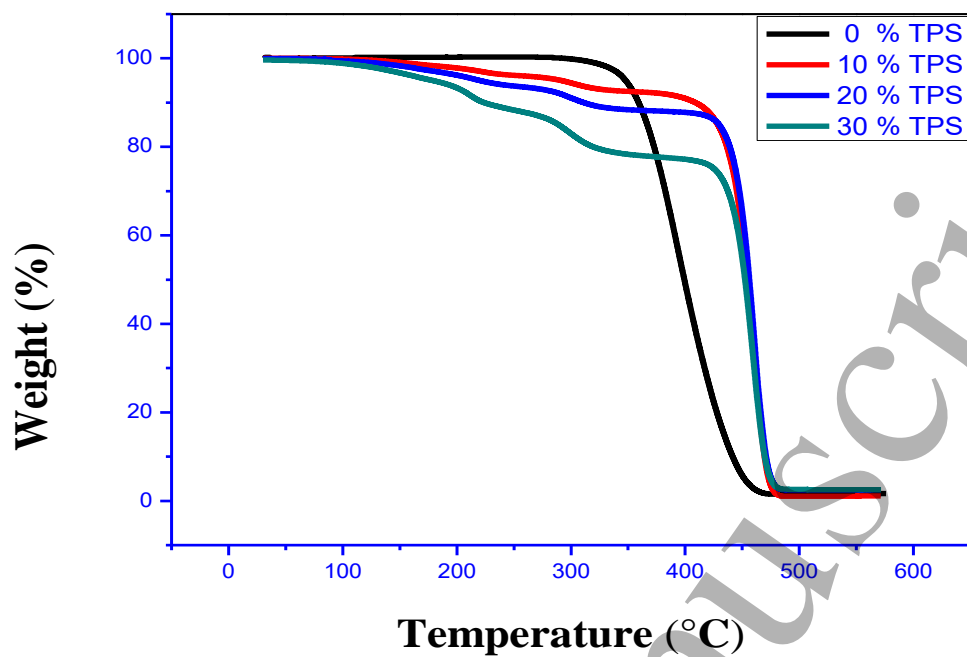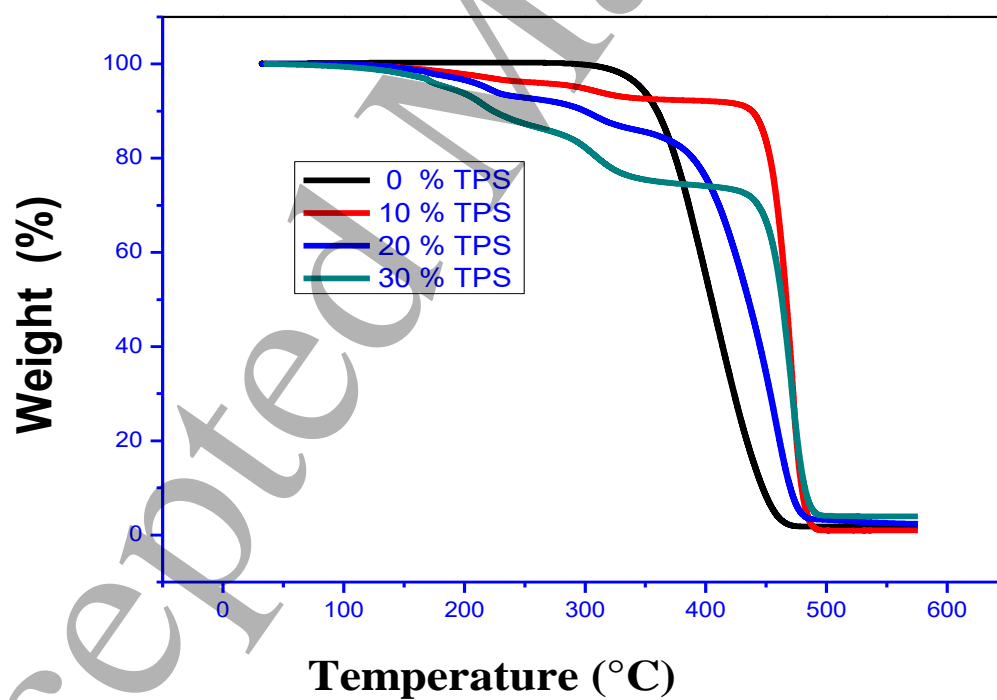
Figure 1: Thermal Stability of blends according to rate of TPS: a) PP/PE,
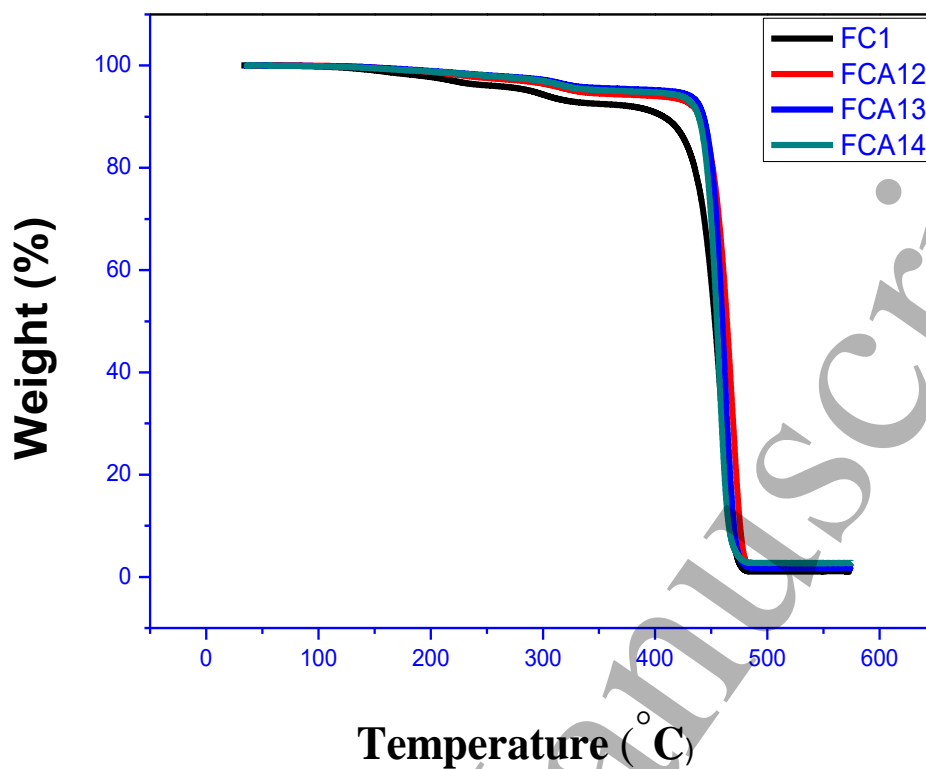
b) PP/PE-g-MA/PE.
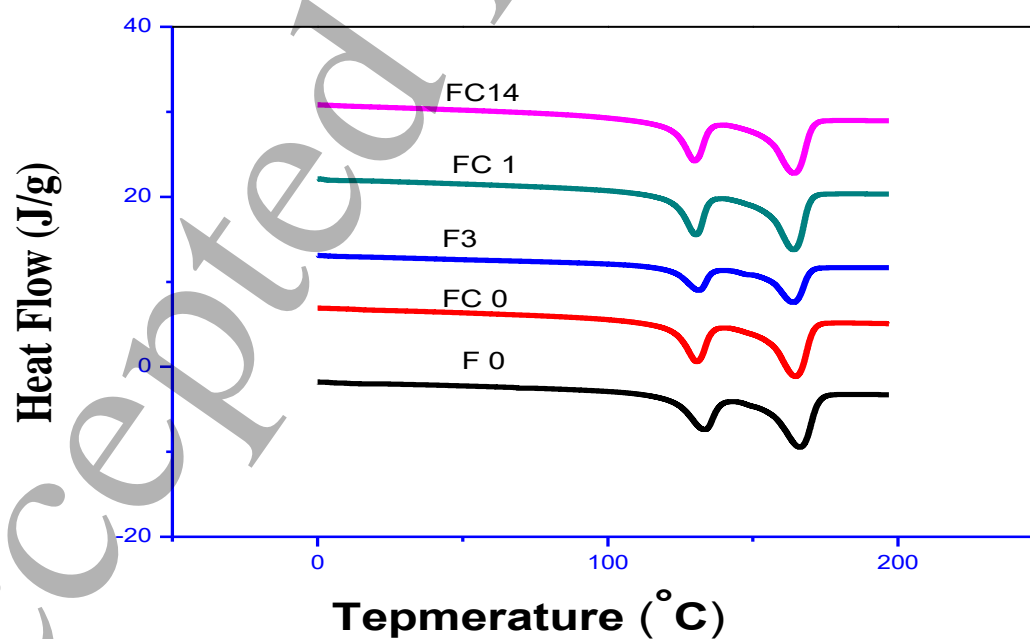
Figure 2: TGA of composites PP/PE-g-MA/PE/TPS/MMT.

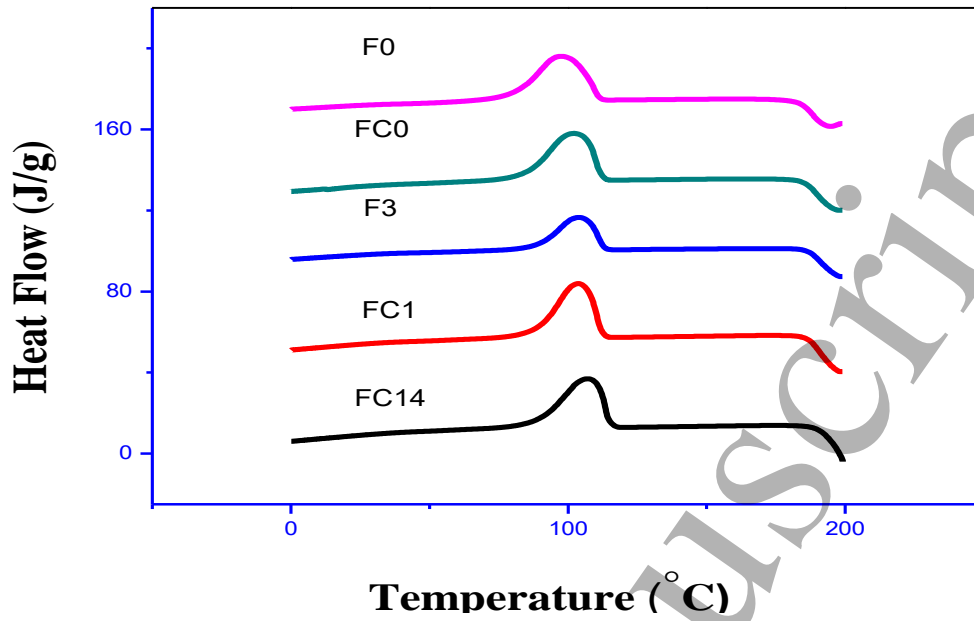**Figure 3:** DSC heating thermo grams of the samples.

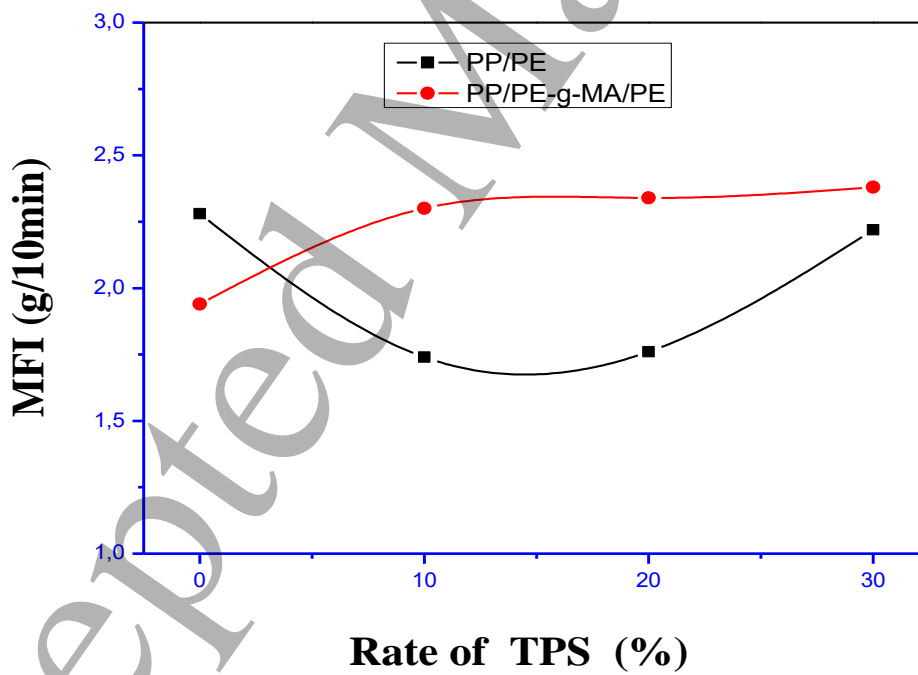**Figure 4:** DSC cooling thermo grams of the samples.

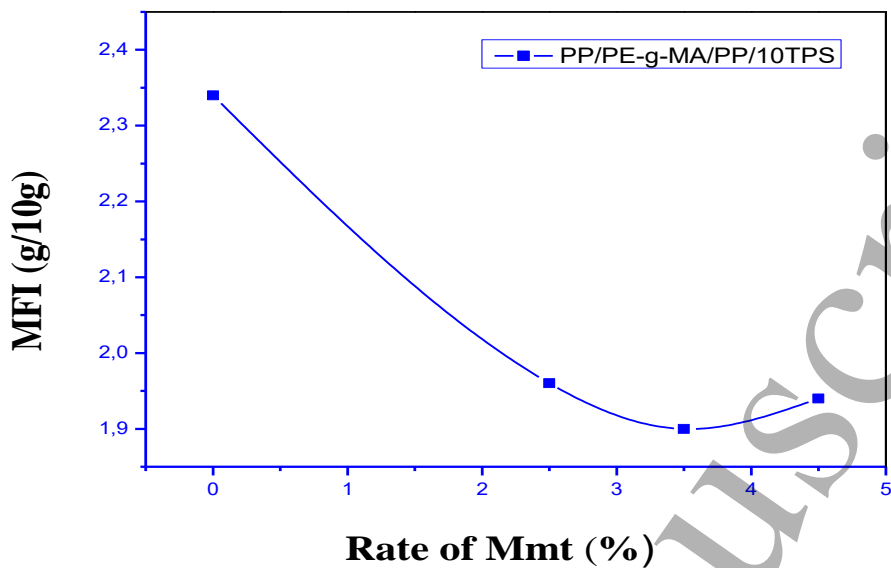**Figure 5:** Melt flow rate value of blends.

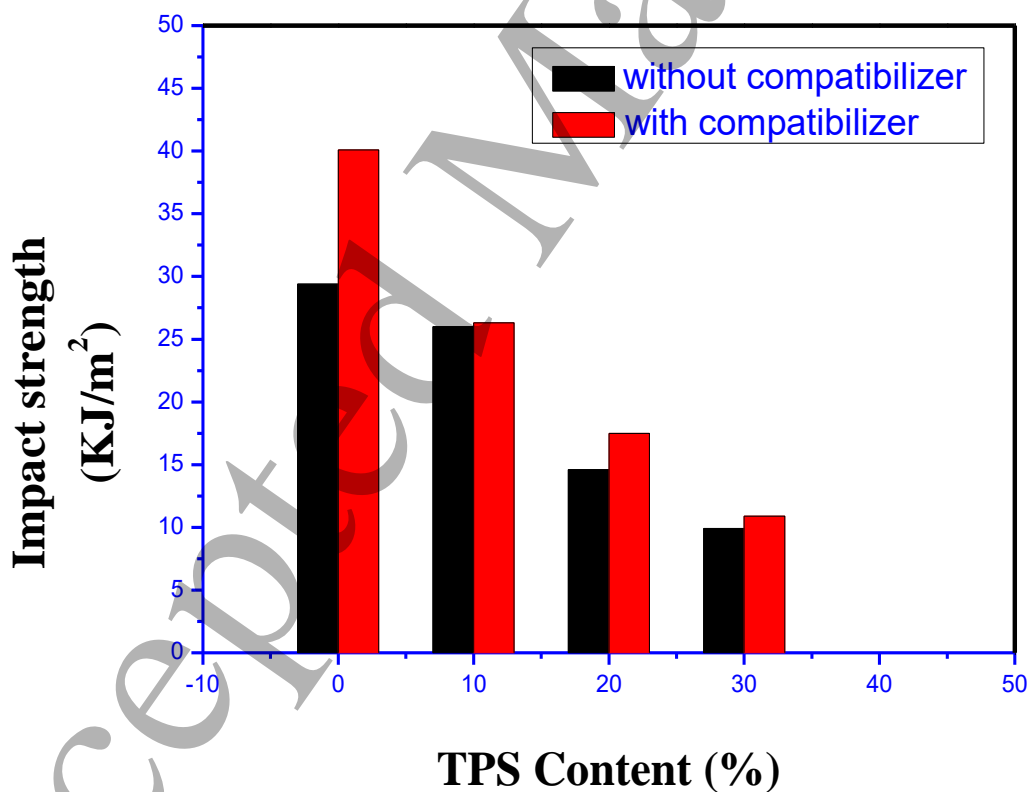**Figure 6:** Melt flow rate value of nano-bio-composites.
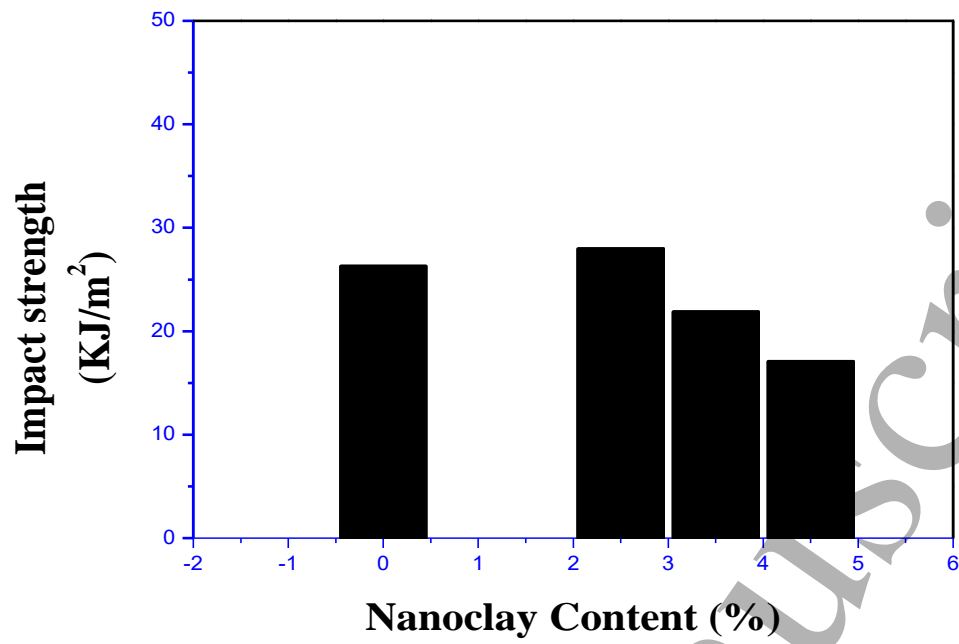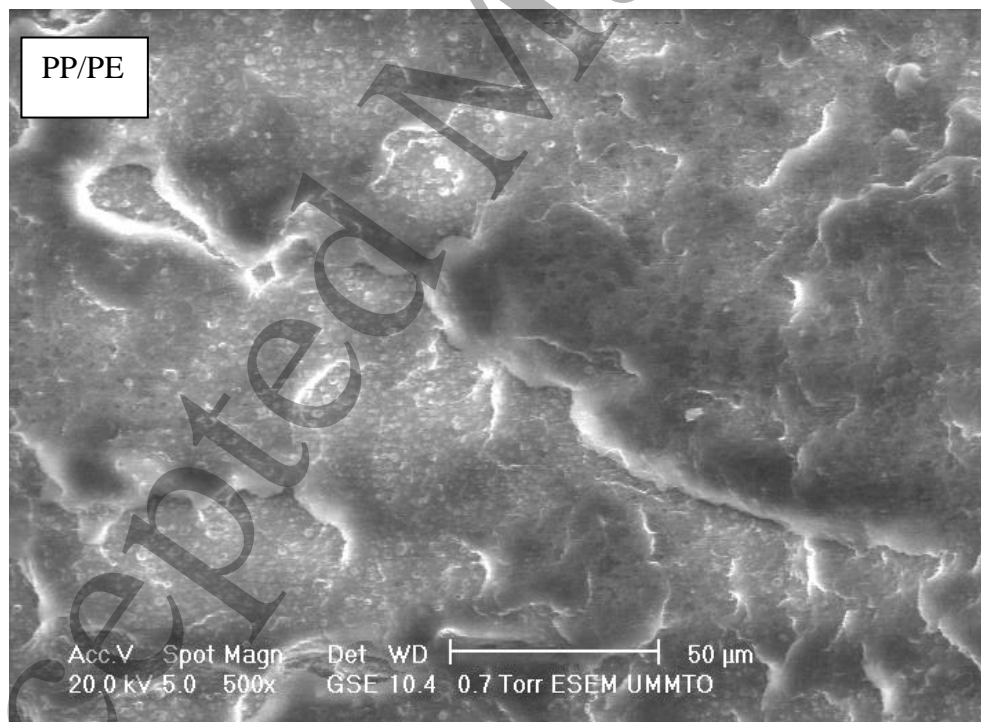

Figure 7: Impact strength versus TPS content.

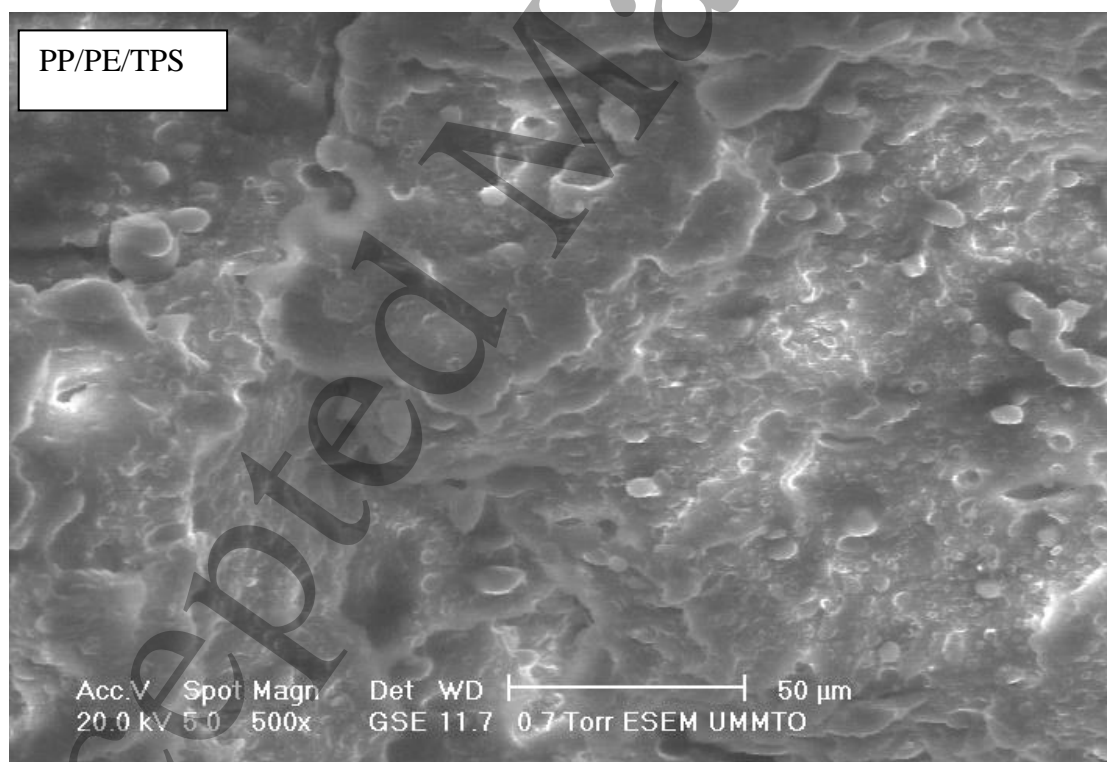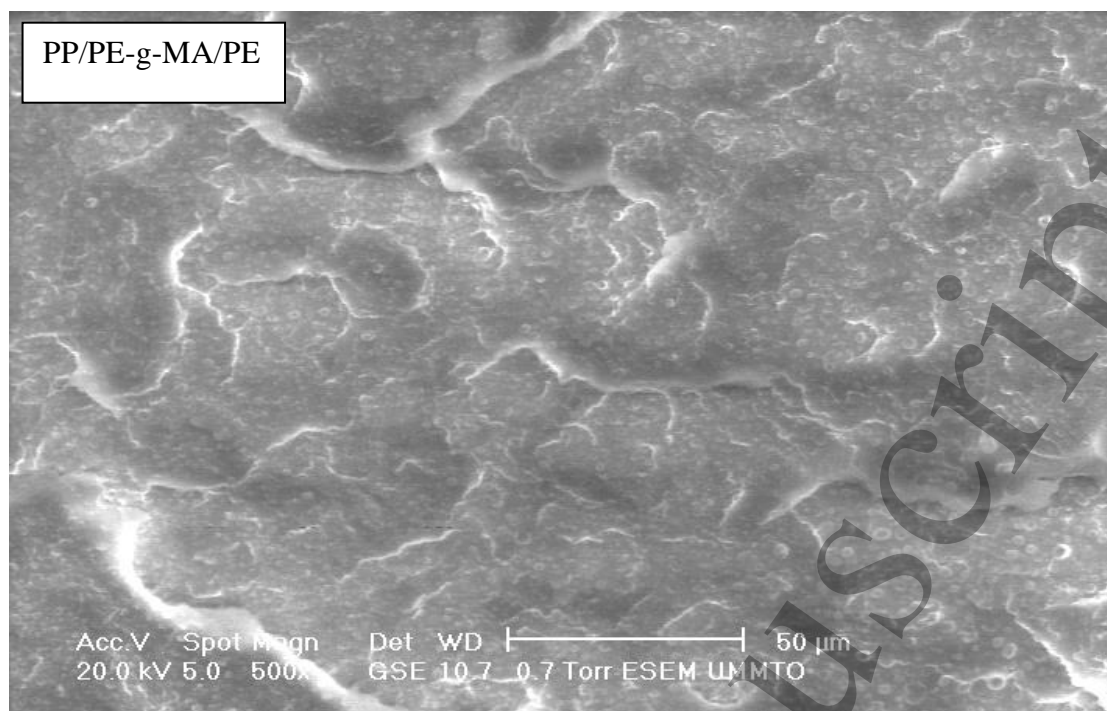**Figure 8:** Impact strength versus nanoclay content.

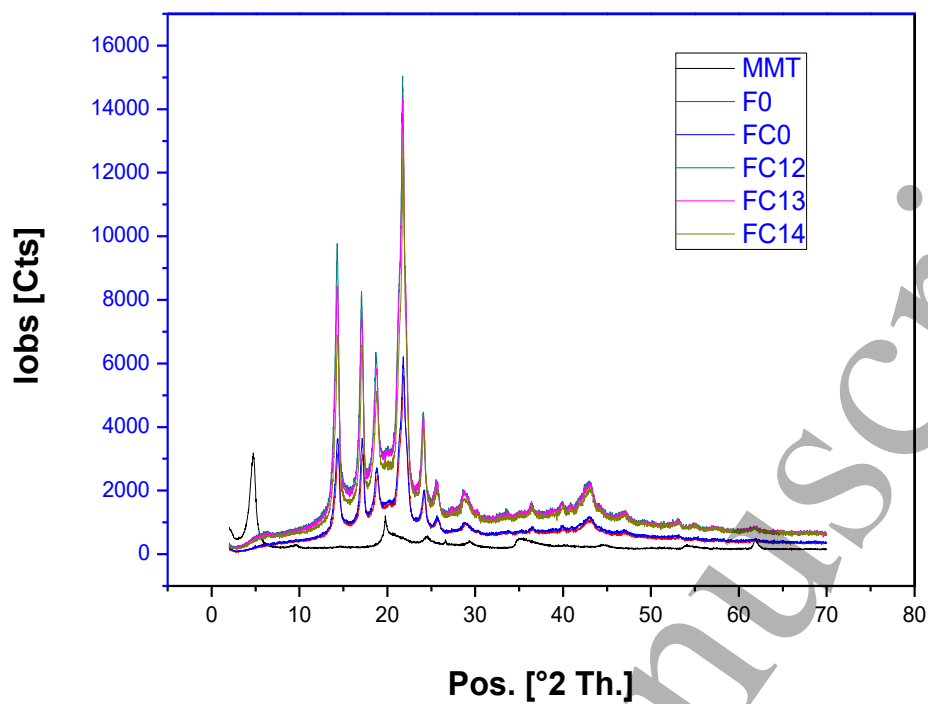**Figure 9:** SEM images of (a) PP/HDPE; (b) PP/PE-g-MA/PE; (c) PP/HDPE/TPS.

Figure 10: XRD spectra for the nano-clay and their bio-nano-composites.
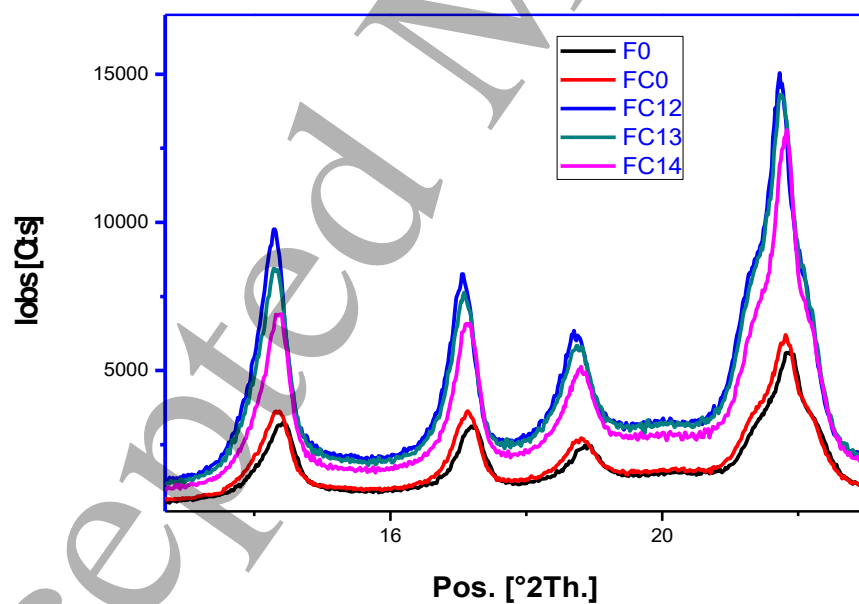

Figure 11: Diffractograms RX of PP/PE nano-bio-composites whose ratio TPS/MMT/PP-g-MA.

Table 1: summarizes the materials used in this work as well as the specific characteristics.

Materials	Characteristics	Suppliers
PP	– Isotactic polypropylene, semi-crystalline – MFI = 3,4 (g/10 min), (2,16 g at 230 °C)	Basell
PEHD	–MFI = (2, 5- 4,5) g/10 min (190°C/2,16 kg) – Density of (0.90 -0,95) g/cm^3	Complexe CP2 k
PE-g-MA	– MFI =(2, 5- 4,5) g/10 min (190°/2,16 kg) – Density of (0.90 -0,95) g/cm^3	Arkema
Corn Starch	– Containing 30 wt% amylose and 70 wt% amylopectin	Sigma-Aldrich
Nano- clay	– clay surface modified with 25-35 wt.% methyl dihydroxyethyl hydrogenated tallow ammonium	Sigma-Aldrich
Glycerol	– Density of 1,25g/cm^3	Bbiochem

Table 2: summerizes the designation and composition

Samples	PP/PE 80/20	TPS	Organo_clay
F0	100	0	0
F1	90	10	0
F2	80	20	0
F3	70	30	0
	PP/PE/PE-g-MA (80/20/5)	TPS	Organo_clay
FC0	100	0	0
FC1	90	10	0
FC2	80	20	0
FC3	70	30	0
FC12	87,5	10	2,5
FC13	86,5	10	3,5
FC14	85,5	10	4,5

Table 3: The values of the ATG and DSC

Samples	melting temperatures of the PP	$\Delta H(m)$ PP	melting temperatures of the PE	ΔH (m) PE	T(C)	ΔH (C)	(T_{onest}) of Decop-ostion	(T final) of decopo-sition	M(R)
F0	166.36	57.52	133.25	29.71	102.01	123,1	291	473	1,55
F1	165.03	53.25	132.01	27.73	105,10	109,9	363	485	1,06
F2	162.41	55.08	130.57	34.47	112, 39	105	384	486	2,49
F3	162.41	48,84	130.57	25,28	107,43	95	390	490	2,06
FC0	164.92	56.85	130.45	35.87	106,44	118,22	291	479	1,81
FC1	164.06	56.18	130.27	30.00	108,06	110,5	390	496	0,98
FC2	162.41	55.08	130.57	34.47	112, 39	102,4	398	491	0,9
FC3	163,77	40,54	129,96	20,89	108,06	97,25	398	489	3,95
FC12	164.68	58.72	130.47	34.48	107,29	113	391	489	1,05
FC13	165.24	55.22	130.37	33.63	105,37	111,5	397	487	1,75
FC14	164.25	51.90	129.85	29.12	107,07	104,05	395	483	2,69