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Research Article

PREPARATION AND CHARACTERIZATION OF POLYPROPYLENE/ PLASTICIZED CORN STARCH BLENDS: EFFECT OF ORGANO-MAGHNITE CLAY AND COMPATIBILIZER ON THE MORPHOLOGICAL, MECHANICAL AND THERMAL PROPERTIES

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ABSTRACT

A biobased nanocomposite was prepared from polypropylene (PP) and thermoplastic starch (TPS). Different percentages of polypropylene-grafted-maleic anhydride are added to the two phases to improve their compatibility. This system was reinforced with organoclay, modified by alkylammonium. The compatibilizer effect and TPS on morphology and properties of PP/organoclay nanocomposites obtained by melt compounding are studied. A good dispersion of filler into polymer matrix is demonstrated by X-ray diffraction. Exfoliated structure with improved compatibility between PP and TPS are obtained using MA-g-PP compatibilizer. Scanning electron microscopy proved strong interfacial adhesion between the components. 7% wt of MA-g-PP compatibilizer and 30% wt of TPS without compatibilizer induce an increase in modulus. Tensile strength and elongation decreased in all materials. TGA-DTA showed an increase in decomposition temperature of compatibilized materials.

Keywords: Polypropylene (PP), Thermoplastic starch (TPS), Organo-Maghnite, MA-g-PP, melt intercalation, Nanocomposites.

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1. INTRODUCTION

Limited resources of fossil fuels require finding new alternatives for the non-degradable petroleum-based plastics by biodegradable polymer materials obtained from renewable sources. Synthetic polymers usually originated from petroleum have been widely used in many fields of human activities like surgery, pharmacology, agriculture, automobile, cable, packaging industries and environment [1]. However, the environmental impact towards the use of plastics induced a search for sustainable solutions [2]. In the last decades, a great interest for using biodegradable polymers in packaging industries to reduce significantly environmental pollution essentially caused from diverse plastic wastes [3].

Among biodegradable polymers, starch was considered as a promising candidate for its availability, its low cost associated to its high performances efficiently activating the degradation process of these new materials. So, the starch is a polysaccharide, composed from linear amylase with amylopectin which commonly known as highly branched. Starches, in their native forms, are organized into semi-crystalline granules [4-7]. In general, starch is a non-expensive, renewable polymer that could be considered as a potential raw material for manufacturing plastic-like materials. Moreover, starch-based materials present some drawbacks. For instance, starch has poor water resistance and relatively poor mechanical properties with difficulties of processability [8]. In its naturally granular form, starch cannot be processed in the same manner as traditional thermoplastics. Therefore, the crystallinity of granular starch can be disrupt by plasticization, creating a material called thermoplastic starch (TPS) [9,10]. The most commonly used plasticizers for starch are water and polyols such as glycerol [11-14]. Plasticizers are commonly added into native starch in order to transform the semi–crystalline granules into a homogeneous material by destructing hydrogen bonds between the starch granules under shear, leading to the synchronous formation of new hydrogen bonds between plasticizer and starch. Nevertheless, the products made from TPS continue to present low mechanical properties due to its high sensitivity towards water for its absorption character. An alternative approach improving the mechanical properties is to blend TPS with layered silicates in order to create TPS-clay nanocomposites [15-18]. This subject is well documented in the literature, since it showed that if the clay is well dispersed, its platelets act as reinforcing agent strengthening its stiffness [19-21]. So, the TPS-clay nanocomposites have been reviewed by Zhao et al. [22] and as expected these authors have been concluded that the clay increases the tensile strength and the modulus of TPS.

Maleated polypropylene (MA-g-PP) has been extensively used as compatibilizer in various PP/TPS blends. Most studies have been initially focused their ideas on the composite systems.

These systems like polypropylene acts as a matrix where the non-plasticized starch is only dispersed in its powder form. Bagheri [23] has varied the concentration of starch from 2 to 6 wt %, and observed uniform particles dispersion in the matrix after five minutes of mixing. Hamdan *et al*. [24] investigated the compatibility studies of PP Sago-Starch blends using dynamic mechanical thermal analysis (DMTA). Sago starch was melt-blended with PP using various concentrations of sago-starch in the blends between 10% and 50% by weight. The E′ and tan δ remain unchanged for sago-starch concentration between 10% and 33% but, these parameters continue its increasing until the content reached 50%. The blend containing 50% as sago-starch was superior when it compared to the other blends in the DMTA measurements. Through the use of a Differential Scanning Calorimeter (DSC), the melting endothermic of the miscible blends was found to be constantly increased with increasing sago-starch content, while the tensile properties of the blends decreased with sago-starch content. The exploration of the surface blends with a Scanning Electron Microscope (SEM) showed that the sago-starch granules were well dispersed in the PP matrix. Liu *et al*. [25] studied the crystallization of polypropylene filled with starch grains at different sizes. A homogeneous dispersion was also observed even if polypropylene and starch are not compatible. Starch acts by reducing the rate and temperature of the crystallization of the polymeric matrix. Rosa *et al*. [26] attempted to evaluate mixtures of high-density polyethylene (HDPE) and polypropylene (PP) with thermoplastic starch (TPS). So, in this case, it was verified that the incorporation of TPS reduces the melting flow index (MFI) of PP and increases of HDPE and HDPE/PP blends. A decrease of the mechanical properties was observed for all formulations studied. This could be attributed to the phase separation between the polyolefins and TPS. The same authors [27] also studied the mechanical and thermal properties of PP/TP (20 wt% glycerol). It has been shown that the incorporation of plasticized starch without using coupling agent significantly reduces the mechanical properties accompanied by a decrease in thermal stability of the resulting materials. Deleo *et al*. [28,29] have evaluated the possibility of developing renewable elastomers containing amounts of starch. Potato starch plasticized with glycerol was melt-blended with small quantities (5 wt% or 15 wt%) of MA-g-PP. These authors indicate that the blends are constituted by two-phase materials, in which the continuous phase TPS is cross-linked by PP domains. These materials showed rubbery properties, due to a low glass transition temperature which was estimated to ~ -50 °C. Inherika [31] concluded that the presence of starch in PP induces changes in its biodegradability depending on the quantity of starch introduced into polypropylene matrices.

The higher amount of starch as loading above 30 wt% induced more degradation but, this process was accompanied with low mechanical properties while with lower starch loadings below 30%, the mechanical properties were found to be reinforced and not be sufficient to cause biodegradation. Thus, below 30 wt% starch content, mechanical properties of the polymer will still be favorable and the degradation can also occurred.

Recently, a new class of polymer/clay nanocomposites has been emerged. This class of materials has assumed to exhibit improved barrier, thermal stability and mechanical properties due to the high aspect ratio and easy phase-to-phase energy transfer, even at very small amounts. Montmorillonite (MMT) is the most commonly used natural clay and has been successfully applied in numerous nanocomposites systems due to its availability, low cost and significant properties enhancement [32-34]. However, most of the prepared PP/TPS/MMT nanocomposites suffer from poor dispersion, which is required for obtaining high performance materials. As a consequence, MMT is often modified by alkylammonium cations such as octadecylammonium chloride, stearyl dihydroxyethylammonium chloride, cetyltrimethylammonium bromide and hexadecyltrimethylammonium chloride [35]. According to the literature [36], the structure and properties of the resulting materials is dependent on the state of the clay in the nanocomposite.

The Algerian clay is considered among the clays which possessing a high Si/Al ratio. It has been studied and characterized for the first time by Belbachir *et al.* [37] and it is now known by the word (Maghnite) which was given by the same research group. The Maghnite has 11.9 % more SiO_2 than the clay from Wyoming (Texas, USA). Maghnite clay has been extensively used in a wide range of scientific fields including in heterogeneous catalysis in order to initiate the polymerization reactions. Recently, Maghnite clay reinforced polymer nanocomposites have received substantial recognition in the field of composites due to their potential to exhibits great improvements in the mechanical, thermal, dimensional stability, UV stability, gas barrier properties and flammability of the matrix polymer [38-40].

Recent studies were based on the effect of organoclay on blends of plasticized thermoplastic starch and polypropylene. The both components were plasticized individually, for instance, glycerol and acetyltributylcitrate (ATBC) were used as plasticizers for starch and PP, respectively. A commercial MA-g-PP was added to the mixtures as a compatibilizing agent. A commercial organoclay was also incorporated in various contents (1.0, 2.5 and 5.0 wt% over the total weight of the blends). X-ray diffraction results indicated that the addition of ATBC contribute to the increase of PP crystallinity from 62 to 72%. XRD, SEM and DMA data revealed that the improvements in the compatibility between the immiscible components were achieved by a simple incorporation of the organoclay [10].

The main objective of this paper is to examine the effect of MA-g-PP and TPS concentrations on the morphological and properties of PP/organo-Maghnite clay nanocomposites prepared by melt compounding mixing process using an internal mixer. The Maghnite clay particles were intercalated with hexadecyltrimethylammonium chloride cations and then incorporated into the polymer matrix at mass rates of 5 wt%. The tensile tests were performed to investigate the mechanical performance, and thermogravimetric analysis (TG-DTA) was carried out to evaluate the thermal properties. Additionally, the morphological characteristics were evidenced by X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

2. EXPERIMENTAL

Materials

- Commercial grade of polypropylene is used in this study as matrix polymer. It was supplied by SABIC PP504P (Saudi Basic), with a melt flow index of 3.2 g/10 min at 190°C/2.16 Kg and a density of 0.905 g/cm^3.
- The compatibilizer selected was MA-g-PP, obtained from Sigma-Aldrich. The grafting level of maleic anhydride is about 8 - 10 wt %, with molecular weight M_w = 9100, M_n = 3900, purified by gel permeation chromatography (GPC) corresponding to a density of 0.934 g/cm^3 and acid number of 45-47.
- Regular corn starch composed of 23% amylose and 77% amylopectin was also obtained from Sigma –Aldrich.
- The non-volatil plasticizer was analytical glycerol with reagent grade. This compound was also purchased from Sigma-Aldrich and was used as received without any further purification.
- The clay used in this study is an untreated montmorillonite, called Maghnite. This raw material was obtained from Maghnia in North-West Algeria region, supplied by company “ENOF” (an Algerian manufacture specialized in the production of nonferric products and useful substances). The chemical composition of the native Maghnite is given in Table 1.
- The alkylammonium used as surfactant was hexadecyltrimethylammonium chloride (abbreviated as C16); supplied by Aldrich with a molecular mass of 364.46 g/mol.

Table 1. Chemical composition of the native Maghnite

Formula	L.O.I*	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
wt%	8.21	51.52	19.03	1.98	3.08	0.16	1.17	0.36

*L.O.I: Loss on ignition

Preparation and processing of materials

This study is divided in three steps, preparation of organoclay, preparation of thermoplastic starch and preparation of nanocomposite.

Preparation of organoclay

Firstly, the clay is saturated with 1M NaCl solution to obtain homoionic clay (Na-Mag). Then, organically modified Maghnite was prepared by cationic exchange between Na^+ finding in the galleries of clay with hexadecyltrimethylammonium chloride cations in aqueous solution. A total of 5 g of Na-Mag was suspended and stirred for several hours in 250 ml of distilled water. An aqueous solution of 5 mmol of the organoammonium salts was added gradually under stirring. The mixture of aqueous suspension of Na-Mag and organic salts was stirred for about 3h at 80°C. The exchanged clay was filtered and washed with distilled water until no chloride ions were detected with using 0.1N $AgNO_3$ solution. After that, the mixture was washed by solutions of water and ethanol (1:1, volume ratio) for three times. It was then dried in vacuum oven for 48h at 60°C. The organophilic clay noted C16-Mag was ground using a mortar and pestle.

Preparation of thermoplastic starch (TPS)

The starch was premixed with glycerol and water to add the thermoplasticity in following compositions, starch, glycerol, water: 54: 23: 23. First, starch was introduced in a turbo mixer, and then water was added slowly with stirring. Second, glycerol was also slowly added with stirring. After that, the mixture was mixed at high speed to obtain a homogeneous dispersion and then conserved 48 h for swelling at ambient temperature.

Samples preparation

The samples were obtained by intercalation from melt-processing preparation methods. The various mixtures have been prepared by a melt-compounding process in an internal mixer, Brabender Gm Bh & Co. KG. The operating conditions are: Rotor speed of 50 rpm, mixing temperature of 190°C and a residence time was fixed for 10 min. The composition of the samples discussed in the present study is summarized in Table 2.

In the adopted notation, the following initials letters MA-g-PP, C16-Mag and TPS correspond to the mass weights of compatibilizer, modified Maghnite and thermoplastic starch respectively. Thin films of dried samples were prepared by compression using a heated hydraulic press at 190°C for 5 min.

Characterization

X-ray diffraction patterns were obtained with a D8 ADVANCE BRUKER AXS diffractometer. The used wavelength was $K\alpha_1$ copper radiation (λ= 0.154 nm). Scans were made in the range of 2θ = 2-40° and 2θ = 2-10° by steps of 0.02° of 6s for each one of them. The d spacing was determined by substituting the 2θ scattering peak into the Bragg's law:

$$n\,\lambda = 2d\,\sin\theta$$

where n is an integer, λ is the wavelength of incident wave, d is the spacing between any two atomic planes in the crystal lattice, and θ is the angle of reflection.

The morphology of the samples was assessed by using a JEOL 6700F scanning electron microscope (SEM), equipped with a field emission gun (FEG). The microscope was operating at an acceleration voltage of 10.00 KV. The atomic force microscopy (AFM) was also used to explore the surface state of the resulting samples by imaging describing their morphologies. This characterization was carried out using a pacific Nanotechnology type atomic force microscope in non-contact mode.

Tensile measurements were performed using ZWICK ROELL testing machine. The measurements were carried out at room temperature with using a cross-head speed of 10 mm/min. The Young's modulus, yield stress (elastic limit), yield strain, yield stress and elongation at break of the nanocomposites were determined. The E modulus is defined as the tangent of the slope angle of a stress – strain curve in the linear relation. The results are based on data collected from 5 specimens for each sample and the mean values and standard deviations were then calculated.

Thermal degradation of nanocomposites and pure components were analyzed with a TG-DTA 92-16.18 Setaram in the range from 20 to 600 °C at a heating rate of 10 °C/min under air flow. Measurements were performed in accordance to the standard PN-EN ISO 11358:2004.

Table 2. Composition and designation of PP/TPS/C16-Mag nanocomposites

Sample	PP (wt%)	C16-Mag (wt%)	TPS (wt%)	MA-g-PP (wt%)	Code
PP	100	0	0	0	F0
PP/C16-Mag	95	5	0	0	F1
PP/TPS/C16-Mag	85	5	10	0	F2
PP/TPS/C16-Mag	75	5	20	0	F3
PP/TPS/C16-Mag	65	5	30	0	F4
PP/C16-Mag/MA-g-PP	92.5	5	0	2.5	F5
PP/C16-Mag/MA-g-PP	95	5	0	5	F6
PP/C16-Mag/MA-g-PP	88	5	0	7	F7
PP/C16-Mag/MA-g-PP	85	5	0	10	F8
PP/TPS/C16-Mag/MA-g-PP	72.5	5	20	2.5	F9
PP/TPS/C16-Mag/MA-g-PP	70	5	20	5	F10
PP/TPS/C16-Mag/MA-g-PP	68	5	20	7	F11
PP/TPS/C16-Mag/MA-g-PP	65	5	20	10	F12
PP/TPS/C16-Mag/MA-g-PP	80	5	10	5	F13
PP/TPS/C16-Mag/MA-g-PP	70	5	20	5	F14
PP/TPS/C16-Mag/MA-g-PP	60	5	30	5	F15

3. RESULTS AND DISCUSSION

Structural characteristics

The XRD patterns of sodium Maghnite (Na-Mag) and modified Maghnite (C16-Mag) have been illustrated in Figure 1. The characteristic diffraction peaks appearing, at the 2θ values ranging from 7.75° to 4.19° were commonly assigned to Na-Mag and C16-Mag, respectively. These results indicate that the gallery spacing d_{001} of these both materials are 1.26 and 2.31nm, respectively. The results obtained are consistent with those described in the literature [41-45] for similar materials. In the case of C16-Mag, the organic cations (ammonium ions) penetrate into the interlayer space of clay and replacing the sodium cations.

This fact should lead to an enlarging of the gallery spacing and hence the shift of the peak position to the lower angles for the XRD patterns. So, it can be noted here that the gallery spacing distance is proportional to the cation size. As example, the atomic radius of sodium cation is currently known as 0.102 nm [46].

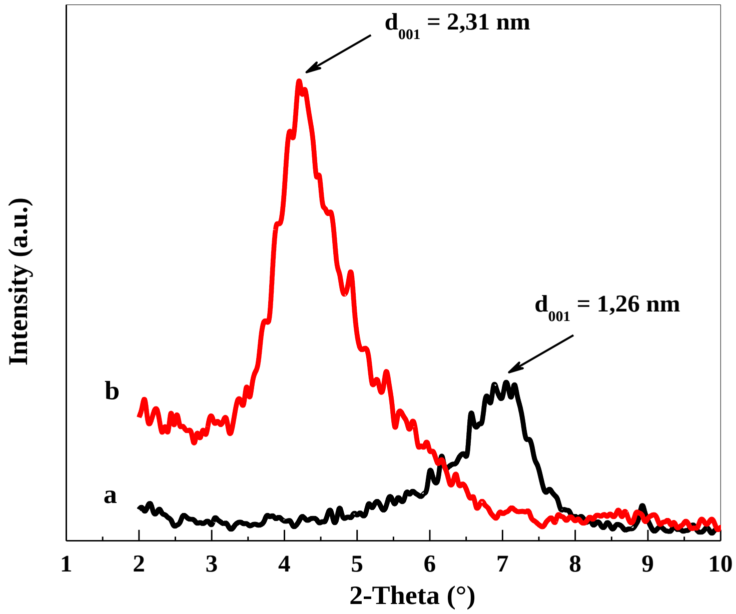


Fig.1. XRD patterns recorded of: (a) Na-Mag and (b) C16-Mag

Figure 2 displays the typical XRD curves, recorded for starch and TPS, respectively. Generally, the native starches show three crystalline types, namely A-type for cereal starches, B-type for tuber and amylose rich starch and C-type which has a hybrid structure, formed from those of A- and B-types [47-49]. During the transformation of native starch into thermoplastic starch (TPS), the granular structure is partially or completely destroyed giving an amorphous polymeric matrix. According to Van Soest and Vliegenthart [50], two types of crystallinity can be distinguished after processing of the thermoplastic starch: residual crystallinity and process-induced crystallinity. The residual crystallinity is often caused by an incomplete melting of starch during its processing leading probably to A-, B- or C-type as currently occurred in the native starches. The induced crystallinity is rather associated to the crystallization of amylose appearing as V_H-, V_A- or E_H-types.

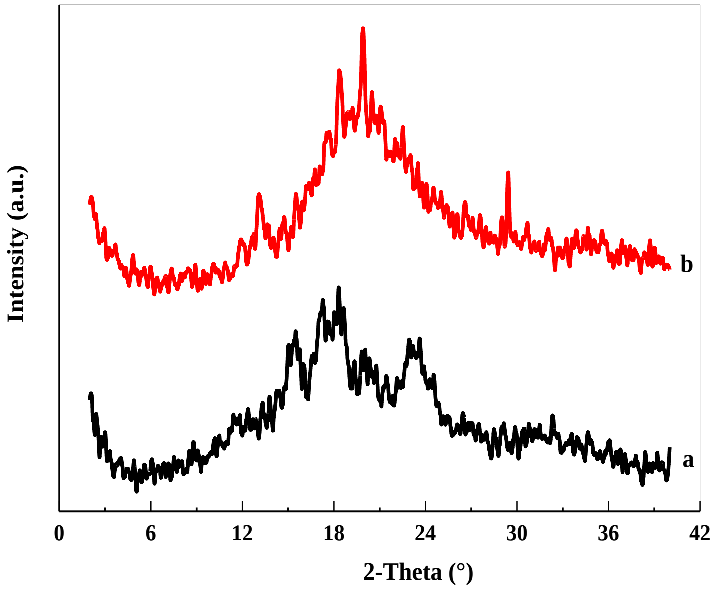


Fig.2. XRD patterns of: (a) native and (b) thermoplastic starch (TPS)

For TPS alone, different crystalline structures were observed. The reflection angles (2θ), observed at 13° and 22°, were assigned to the V_A-Type crystallinity. Van Soest *et al.* [47] found that V_{A-} and V_H of amylose structures for corn starch and rice starch, highly extruded, contains less than 10% of water after extrusion. The reflection at ~ 20° was assigned to the V_H-type crystallinity which may be induced from processing. The reflection seen at 17° (2θ) was rather attributed to the β-type crystallinity.

Figure 3a and 3b illustrate the diffractograms of the neat polypropylene matrix and polypropylene with 5 wt% of organoclay (C16-Mag), respectively. The X-rays diffraction patterns of PP, four peaks were observed between 14 and 20°. These peaks explain the crystalline structure of PP chains [10,51]. As for the peaks, observed at 14.32°, 17.11°, 18.77°, 21.27°, 22.12° and 29.53°, they correspond to the hkl reflections (110), (040), (130), (111) (131) and (041), respectively. These data represent the main characteristics of lattice planes of monoclinic system of α-phase of PP. The peak at 16.14° is due to the (300) reflection plane of the β-type hexagonal crystal structure of the PP chain. The X-rays diffraction patterns of PP containing 5 wt% of organoclay (Mag-C16), two other additional peaks are as well seen at 4.85° and 26.67°. The first one is characteristic of the clay while the second is ascribed to the quartz that usually accompanies the clay. For this reason, we have seen that the crystallinity of polypropylene is increased.

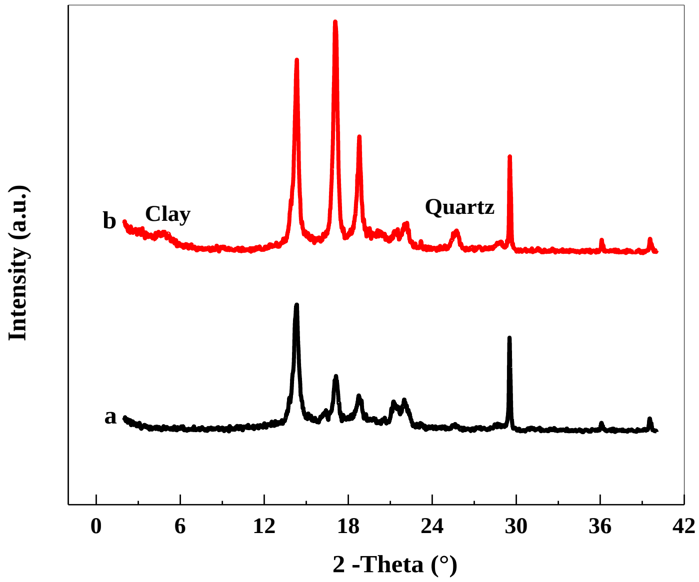


Fig. 3. XRD patterns of: (a) PP and (b) PP/C16-Mag

Figure 4 shows the XRD patterns for PP/10TSP/C16-Mag, PP/20TPS/C16-Mag and PP/30TPS/C16-Mag. It was observed that the appearance of the new peak at 2θ = 2.77° (d_{001} = 3.18 nm) for 30 wt % of TPS (PP/30TPS/C16-Mag), which indicates the intercalated species like TPS and PP in the gallery of the montmorillonite containing silicate layer. However, under these experimental conditions, the exfoliation degree seems to be not very efficient.

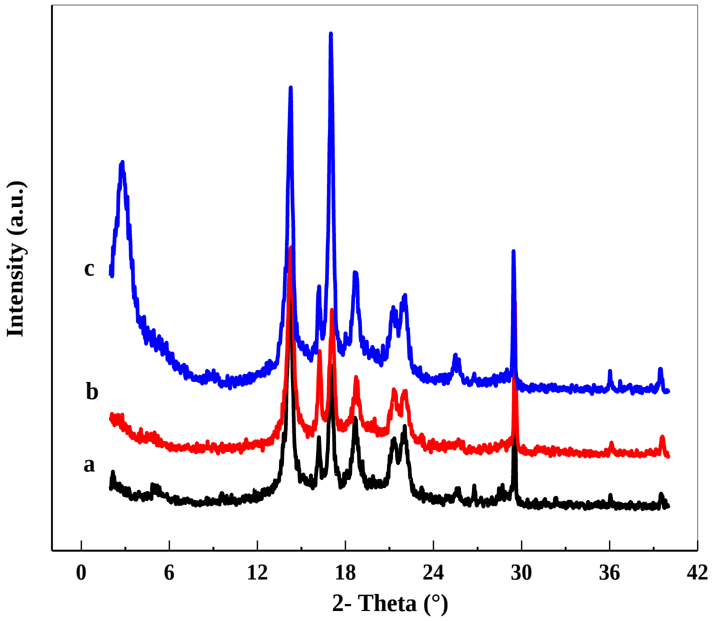


Fig.4. XRD patterns of: (a) PP/10TPS/C16-Mag, (b) PP/20TPS/C16-Mag and (c) PP/30TPS/C16-Mag

The XRD patterns for the PP/C16-Mag/2.5MA-g-PP, PP/C16-Mag/5MA-g-PP, PP/C16-Mag/7MA-g-PP and PP/C16-Mag/10MA-g-PP are given in Figure 5. A noticeable displacement was obviously observed at weaker angles (<2°) for the formulation PP/C16-Mag/2.5MA-g-PP with its characteristic peak of clay (001) whereas the appearance of this characteristic peak was not seen for PP/C16-Mag/5MA-g-PP, PP/C16-Mag/7MA-g-PP and PP/C16-Mag/10MA-g-PP. This observation suggests that this material is exfoliated owing to the presence of MA-g-PP as compatibilizer.

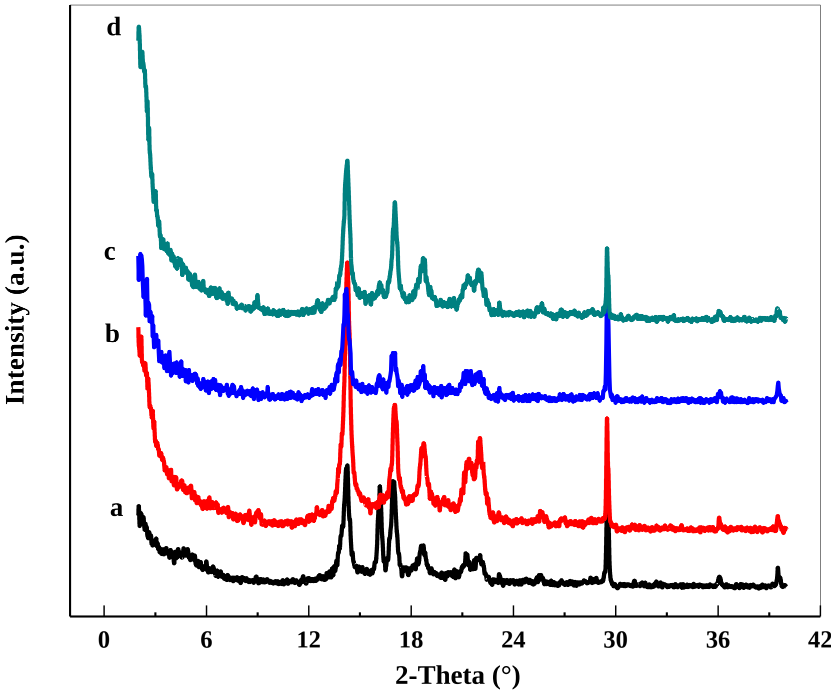


Fig.5. XRD patterns of: (a) PP/10TPS/C16-Mag), (b) PP/20TPS/C16-Mag and (c) PP/30TPS/C16-Mag

Figures 6 and 7 show also the XRD patterns for PP/20TPS/C16-Mag/2.5MA-g-PP; PP/20TPS/C16-Mag/5MA-g-PP; PP/20TPS/C16-Mag/7MA-g-PP; PP/20TPS/C16-Mag/10MA-g-PP; PP/10TPS/C16-Mag/5MA-g-PP; PP/20TPS/C16-Mag/5MA-g-PP and PP/30TPS/C16-Mag/5MA-g-PP samples for which no diffraction peaks were observed in the 2θ values ranging from 1.5 to 10°. This observation seems to be reproducible for all prepared film samples. The characteristic peak corresponding to the clay material is as well not observed. The loss of the d_{001} peak of the clay was attributed to uniform clay dispersion leading to the formation of disordered clay platelets, and low concentration of the clay agglomerates. This result should also be considered as a significant indication for an exfoliation process. The addition of MA-g-PP as compatibilizer can, therefore, develop the interactions between the PP, TPS and organoclay.

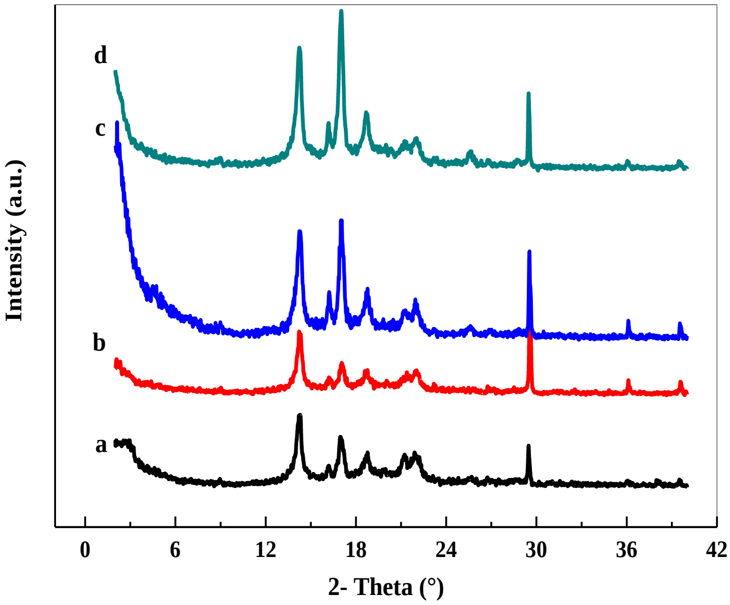


Fig. 6. XRD patterns of: (a) PP/20TPS/C16-Mag/2.5MA-g-PP, (b) PP/20TPS/C16-Mag/5MA-g-PP, (c) PP/20TPS/C16-Mag/7MA-g-PP) and (d) PP/20TPS/C16-Mag/10MA-g-PP

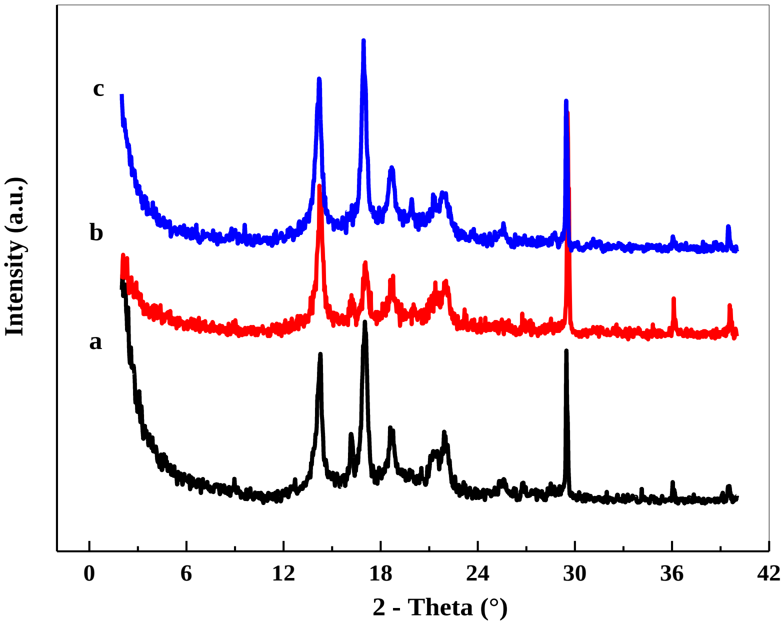


Fig.7. XRD patterns of: (a) PP/10TPS/C16-Mag/5MA-g-PP, (b) PP/20TPS/C16-Mag/5MA-g-PP and (c) PP/30TPS/C16-Mag/5MA-g-PP

Morphological characteristics

Morphology of the elaborated materials was explored by the SEM. This technique is used to examine the effect of TPS, C16-Mag and MA-g-PP compatibilizer on the textural surface of the materials. The results obtained are illustrated as images in Figure 8. For TPS micrograph, Figure 8(a) displays a continuous phase with only few residual granules is observed for a neat TPS plasticized with 23% of glycerol and 23% of water. In this case, it appears that the incorporation of glycerol as plasticizer agent have effectively eliminated the inter- and intra-molecular hydrogen bonds in the native starch under high mixing rate and temperature conditions of the internal mixer [52] . Micrographs of Figure 8(b) and Figure 8(d) show as well a good dispersion of TPS on the sample surfaces (continuous phase). The good compatibilization and miscibility of PP/TPS blends is finally achieved by combining the matrix with organoclay C16-Mag and MA-g-PP as compatibilizer. Dispersed domains in a continuous matrix can be seen in Figure 8(c). However, some domains of higher brightness can be observed (Figure 8(e)) which indicating that the PP component crystallizes in the TPS matrix.

In order to observe clearly the morphology of these materials at various scales, an additional study using the AFM was carried out. AFM was also included to study the morphological surface of the samples. As it can be seen in Figure 9 showing images, obtained in non-contact mode for PP; TPS; PP/C16-Mag; PP/C16-Mag/30TPS; PP/C16-Mag/20TPS/10MA-g-PP; PP/C16-Mag/10TPS/5MA-g-PP; PP/C16-Mag/20TPS/5MA-g-PP; and PP/C16-Mag/30TPS/5MA-g-PP; respectively. For the PP and TPS, a roughness has been obviously seen. It is worthy to notice the presence of clay causing a decrease of the roughness of the PP matrix. For PP/C16-Mag/30TPS, a neat change in the roughness has been seen. The AFM image of PP/C16-Mag/20TPS/5MA-g-PP shows that contains fragments witch display slender rods and has a broad distribution in size. In the case PP/C16-Mag/20TPS/10MA-g-PP, PP/C16-Mag/30TPS/5MA-g-PP and PP/C16-Mag/10TPS/5MA-g-PP, the refinement of the morphology can also be observed.

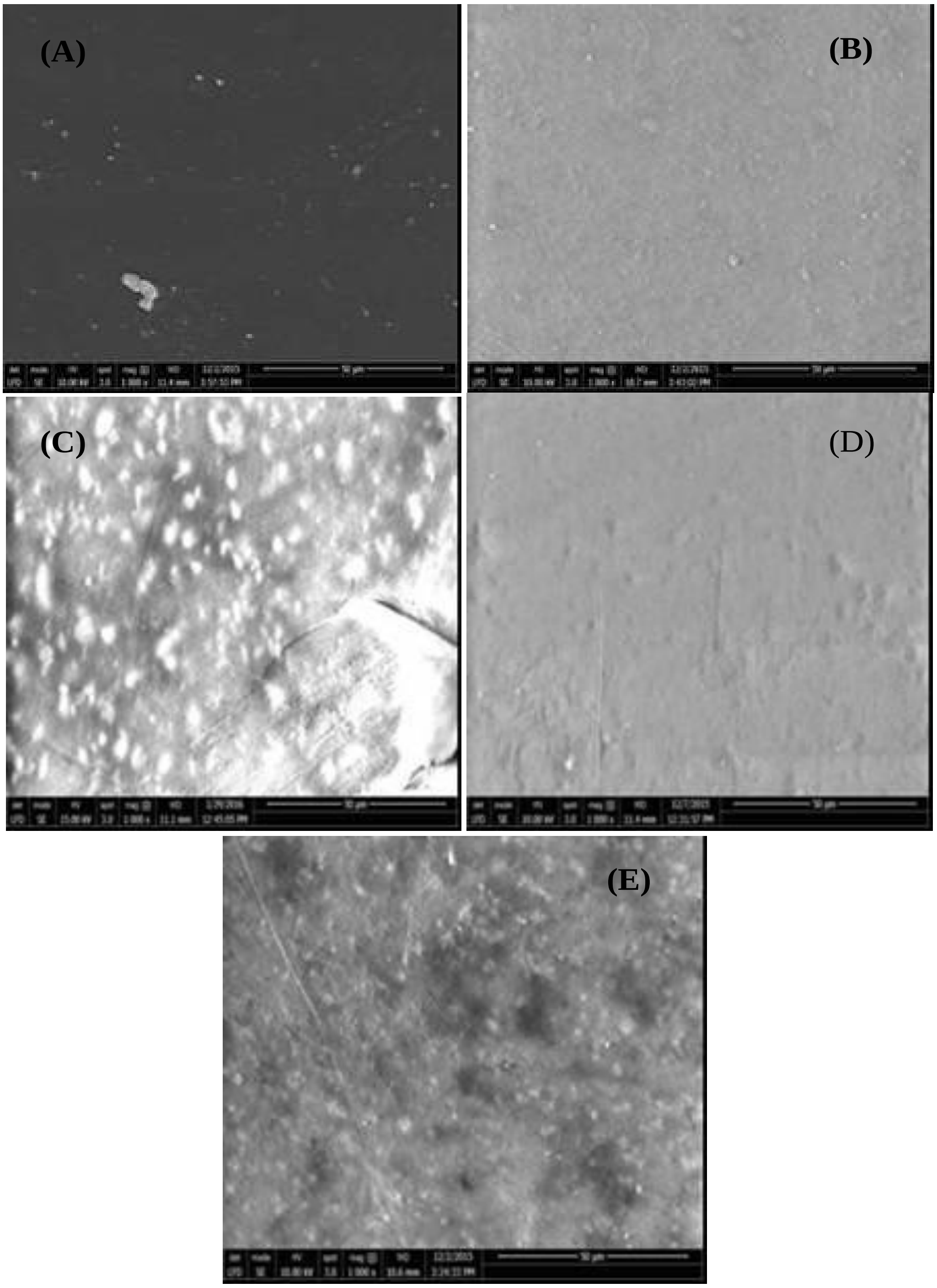


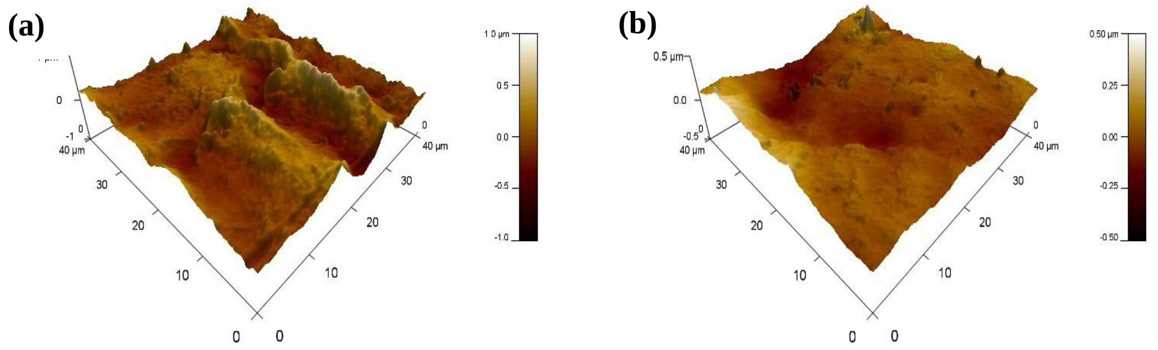
Fig.8. SEM micrographs of : (A) TPS, (B) PP/30TPS /C16-Mag, (C) PP/20TPS/ C16-Mag/2.5MA-g-PP, (D) PP/20TPS/C16-Mag/7 MA-g-PP and (E) PP/C16-Mag/30TPS/ 5MA-g-PP

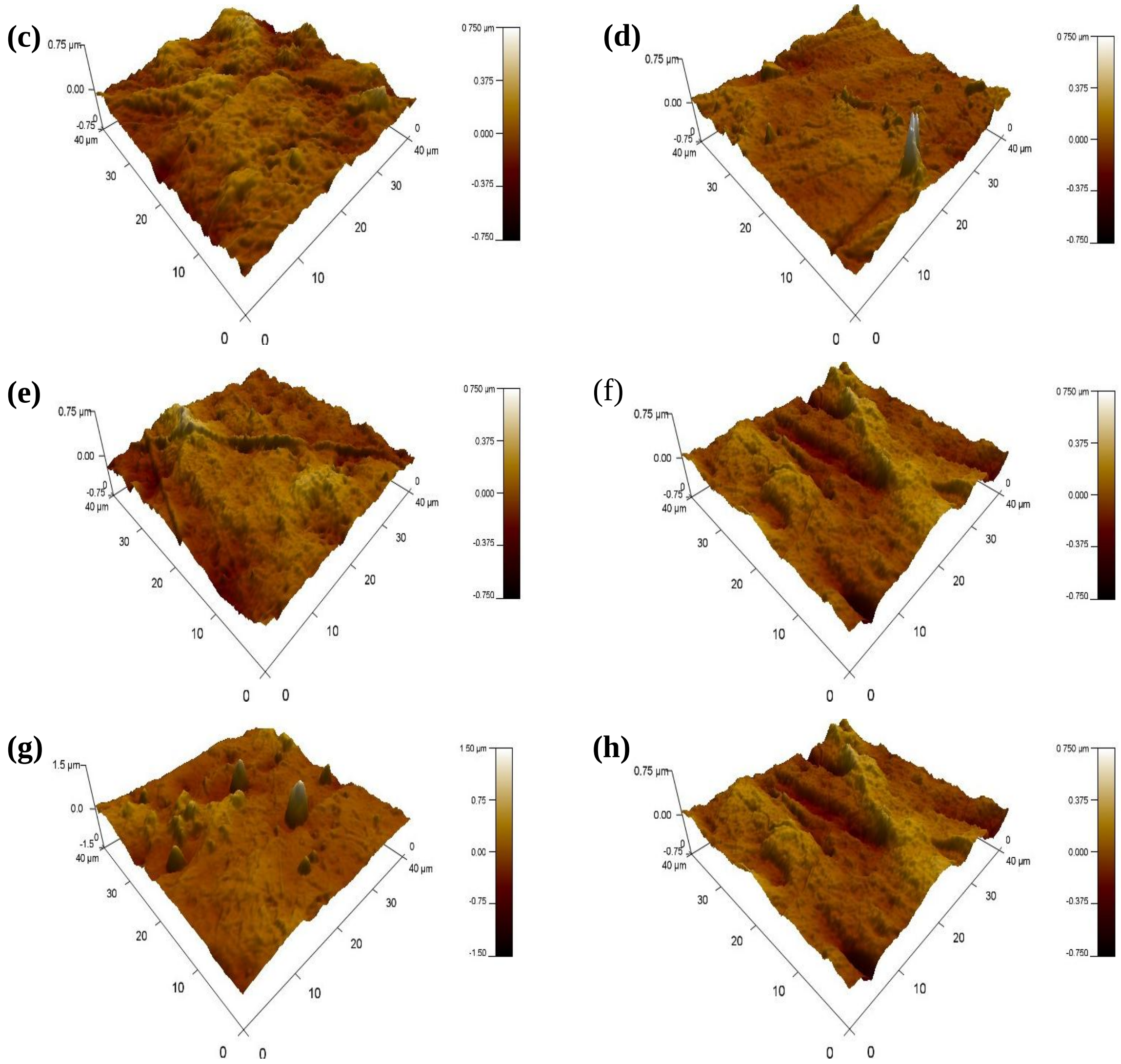
Mechanical Properties

It is now generally recognized that the mechanical properties of polymer-clay nanocomposites are intimately related to the properties of the polymer matrix, particle loading, clay particle size and morphology with interfacial adhesion between clay and polymeric matrix. So, mechanical properties of hybrid composites are strongly related to the interfacial adhesion between clay particles and matrix, as above mentioned. The effect of adding TPS and organoclay on tensile properties of polypropylene are measured and summarized in Table 3. These results indicate that the addition of TPS and the incorporation of organoclay without compatibilizer agent, (PP/TPS/C16-Mag), led to obtain materials with higher modulus (1185.0 MPa, at 30 wt% of TPS). In this case, this latter property was not found even in the pure polymer matrix. The improvement of the Young's modulus can be due to the intercalated structure of clay which has been increased the dispersion of clay in the polymeric matrix. This result was as well evidenced by XRD analysis. Therefore, the addition of organoclay revealed that is able to reinforce the PP/TPS.

For the samples containing different percentages of MA-g-PP as compatibilizer agent (2.5, 5.0, 7.0 and 10.0 wt%) in the presence of organoclay and without TPS leads to a neat increase in the Young's modulus values when the materials were prepared with 7.0 and 10.0 wt% wt of MA-g-PP for which the modulus value was found to be equal to 1135 and 999 MPa, respectively. This improvement in the Young's modulus may be explained the exfoliated structure process while the addition of MA-g-PP compatibilizer enhances the interfacial adhesion between PP and organoclay.

Furthermore, we have attempted also to study the influence of TPS with compatibilizer in the presence of organoclay. So, it was found that the Young's modulus decreases as its content of TPS is increased for the PP/10TPS/C16-Mag/5MA-g-PP, PP/20TPS/C16-Mag/5MA-g-PP and PP/30TPS/C16-Mag/5MA-g-PP.





Fi.g.9. Images obtained by AFM in close contact mode for: (a) PP, (b) TPS, (c) PP/C16-Mag, (d) PP/C16-Mag/30TPS, (e) PP/C16-Mag/20TPS/10MA-g-PP, (f) PP/C16-Mag/10TPS/5MA-g-PP, (g) PP/C16-Mag/20TPS/5MA-g-PP and (h) PP/C16-Mag/30TPS/5MA-g-PP

Using different percentages of MA-g-PP with 20 wt% of TPS in the presence of organoclay, an increase in Young's modulus was as well observed for the content of 7 wt% of MA-g-PP compatibilizer for which the modulus value was found to be equal to 1123 MPa. On the other hand, in the absence of compatibilizer for this formulation, the Young's modulus drastically decreased to 627 MPa. Consequently, the increasing of the Young's modulus for this material may be explained by the good dispersion of the organoclay with its exfoliated structure associated to interactions developed by MA-g-PP as compatibilizer.

For the tensile strength, elongation at yield and at the break decrease for all samples (See Table 3). This can probably be justified by the low tensile strength presented by the pure starch for which the modulus value was estimated to about 1 MPa as reported in the literature [53]. The starch may probably contribute to the strengthening of tensile value because the glycerol acts as a plasticizer agent. In this case, it can also be noted that the tensile strength and elongation at yields are greater than the tensile strength at break confirming the high rigidity of the obtained materials [54].

Many studies have been reported on the enhancing mechanical properties such as the increase of the tensile strength and modulus [16,22,55,56]. Chen *et al*. [57] have examined the effects of clay and found that MMT showed greater exfoliation and increased modulus than all other smectites. This is attributable to its high aspect ratio. Clay nanocomposites have also been created from TPS blended with other biodegradable polymers or not biodegradable [58-60]. In this case, the blends of TPS and poly(caprolactone) (PCL) seem to be mostly studied when compared to the poly(olefin) materials. In fact, only one study [59] was reported in the literature about the clay containing blends of TPS and PP and essentially focusing the rheological properties without any description of the mechanical properties. Moreover, it has also been shown that the addition of organoclay to gelatinized starch inhibits starch retro-degradation or slow recrystallization and water loss by interactions between the clay and starch and by restricting the motion of plasticizer around the amylose chains [61].

Table 3. Tensile properties of neat PP, PP/C16-Mag, PP/TPS/C16-Mag and compatibilized nanocomposites

Sample	**Young's modulus (MPa)**	**Tensile strength (MPa)**		**Elongation (%)**	
		at yield	at break	at yield	at break
PP	955 ± 0,2	26,4 ± 0,3	22 ± 0,1	9,55 ± 0,6	12,5 ± 0,6
PP/C16-Mag	907 ± 0,8	24,8 ± 0,6	22,7 ± 0,4	9,66 ± 0,3	14,9 ± 0,9
PP/TPS/C16-Mag	871 ± 0,5	13,5 ± 0,5	12,8 ± 0,3	2,65 ± 0,3	3,1 ± 0,1
PP/TPS/C16-Mag	627 ± 0,6	13,4 ± 0,6	12,3 ± 0,4	3,1 ± 0,4	3,35 ± 0,4
PP/TPS/C16-Mag	1185 ± 0,1	17,8 ± 0,2	16,7 ± 0,3	3,86 ± 0,5	4,1 ± 0,5
PP/C16-Mag/MA-g-PP	928 ± 0,2	25,9 ± 0,8	24,5 ± 0,2	8,15 ± 0,9	8,15 ± 0,7
PP/C16-Mag/MA-g-PP	912 ± 0,2	24,7 ± 0,6	24,4 ± 0,4	8,2 ± 0,4	8,2 ± 0,9

PP/C16-Mag/MA-g-PP	1135 ± 0,1	23,9 ± 0,8	23,6 ± 0,5	6,5 ± 0,1	6,65 ± 0,7
PP/C16-Mag/MA-g-PP	999 ± 0,5	24,0 ± 0,2	22,7 ± 0,6	7,53 ± 0,6	8,2 ± 0,6
PP/TPS/C16-Mag/MA-g-PP	1089 ± 0,1	20 ± 0,7	19,9 ± 0,8	6,9 ± 0,4	7,2 ± 0,7
PP/TPS/C16-Mag/MA-g-PP	649,5 ± 0,5	16,1 ± 0,3	15,8 ± 0,2	7,2 ± 0,4	7 ± 0,6
PP/TPS/C16-Mag/MA-g-PP	1123 ± 0,1	14,4 ± 0,8	14 ± 0,8	4,7 ± 0,8	4,76 ± 0,8
PP/TPS/C16-Mag/MA-g-PP	795 ± 0,4	17,6 ± 0,8	16,8 ± 0,4	6,1 ± 0,1	6,8 ± 0,2
PP/TPS/C16-Mag/MA-g-PP	797 ± 0,2	19,6 ± 0,8	19,2 ± 0,7	7,3 ± 0,2	7,4 ± 0,3
PP/TPS/C16-Mag/MA-g-PP	649 ± 0,2	16,1 ± 0,3	5,81 ± 0,2	7,25 ± 0,4	7 ± 0,6
PP/TPS/C16-Mag/MA-g-PP	685 ± 0,2	15,3 ± 0,3	15,3 ± 0,3	4,95 ± 0,3	4,95 ± 0,3

At higher starch loadings as in TPS/polyolefin blends, mechanical properties are usually poor [62] since, these mechanical properties of the TPS are dominant. In spite of the increasing number of studies on starch blends, there is a lack of publications exploring blends containing large fractions of TPS, which is sustainably desirable as a biodegradable blend compounds.

Thermal properties

Regarding the thermal study carried out in this work, it concerns the comparative TG-DTA analysis of four samples including the pure polypropylene, TPS with two samples PP/30TPS/C16-Mag and PP/30TPS/C16-Mag/5MA-g-PP. So, Figure 10 depicts the thermal stability curves recorded in the temperatures, ranging from 20 to 600°C. The presence of TPS induces a weakness towards the thermal stability of our materials. For PP alone, the peak of heat flow curve, observed at 168°C, corresponds to the melting temperature of PP. Polypropylene exhibits mainly two endothermic peaks at the temperatures ranging from 400 to 450°C, due to its decomposition. The Tg of PP could not be observed in the DTA thermogram because it is lower than the range temperature measurements.

For TPS, the first shift, at around 100°C, is produced by water evaporation. The second shift starts at 284°C and is usually accompanied by the glycerol evaporation. For the pure glycerol has a boiling point of 290°C but, in this case, starch possesses hydrophilic nature with involving all hydroxyl groups that are directed outside of the ring [63]. This structure promotes direct interactions of starch and glycerol by forming hydrogen bonds and subsequently lowering the volatility of glycerol in the plasticized starch appearing at 284°C.

This process continued gradually up to 300°C where the thermal degradation of starch is occurred (oxidation of the partially decomposed starch).

When the modified clay (C16-Mag) is added to the PP/TPS blend, its thermal stability was found to be significantly enhanced. Therefore, this property was accompanied by a decrease in the decomposition temperature (T_d) of PP since, it was shifted from 438°C to 409°C. This result indicated that the T_d of PP was strongly affected by the blending with TPS. On the other hand, the adding of the compatibilizing agent (MA-g-PP) to the PP/TPS/C16-Mag mixture induces rather a neat increase in the decomposition temperature (T_d) shifting from 409 to 439°C with the material newly obtained. The enhanced thermal stability of layered silicate nanocomposites is essentially explained by the lower permeability of oxygen atoms and the lower diffusibility of the degradation products obtained from the polymer bulk due to the exfoliated clay in its previous composites clay present in the initial composite materials [64,65]. By adding the MA-g-PP, the adhesion between TPS and PP is again strongly induced further improvements in the compatibility process of the blend.

Figure 10 shows a peak, related to the melting temperature of the polypropylene phase with its nanocomposite. It can be noted that the melting temperature of the polypropylene phase is equal to 168°C while those of the PP/TPS/C16-Mag formulation, containing 5 wt% of organoclay and 30 wt% TPS, is only equal to 166°C. In the same way, the PP/TPS/C16-Mag/MA-g-PP formulation, containing 5 wt% of organoclay, 30 wt% TPS and 5 wt% MA-g-PP, the resulting melting point is slightly lower than the previous mixture and equal to 165°C. This decrease in the melting temperatures can be explained by the reduction in the crystallite size, caused by the intercalation of the TPS chains with PP macromolecules between clay platelets. Indeed, the presence of the TPS in these materials can be one of the main species contributing to the decrease of the melting points of the PP phase. On the other hand, the decrease of the PP melting point, in the mixture can also be ascribed to the strong interactions of the organoclay filler, PP and TPS phases.

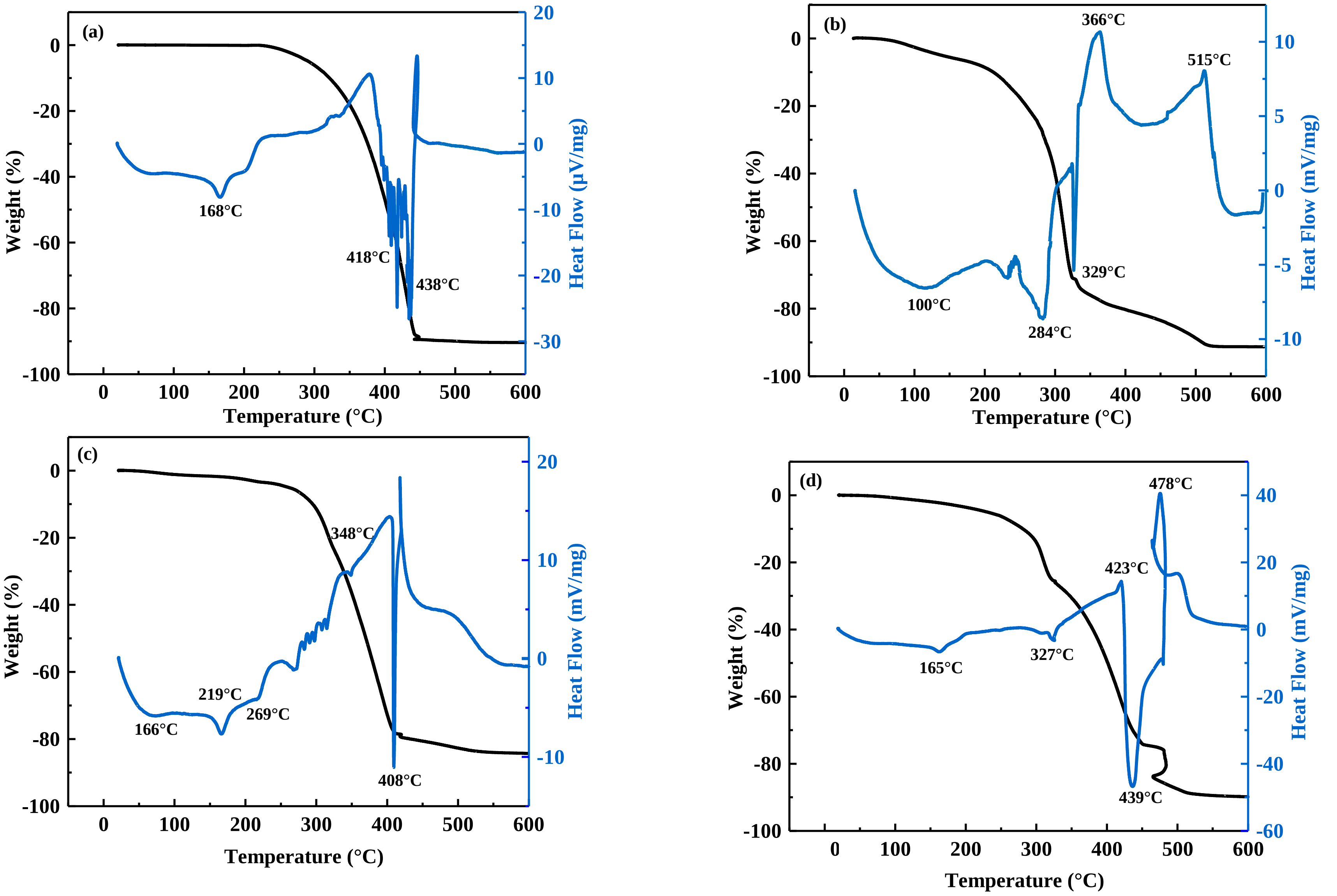


Fig.10. TG-DTA curves of: (a) PP, (b): TPS, (c) PP/C16-Mag/30TPS and (d) PP/30TPS/C16-Mag/5MA-g-PP

4. CONCLUSIONS

Polypropylene/organo-Maghnite clay nanocomposites in the presence of MA-g-PP as compatibilizer and thermoplastic starch (TPS) were prepared by melting technique and the influences of various factors on the properties of these materials were studied. The main conclusions are given below:

The XRD-diffraction and SEM revealed that the modified Maghnite (Algerian clay) was well-dispersed in the polymer matrix with an intercalation and an exfoliation processes. The organically modified clay dispersed in the TPS phase as well as located at the interface between TPS and PP when the amount of TPS increases. In this case, it can be noted that a good intercalation of clay is obtained for PP/C16-Mag/TPS and a complete exfoliation of this clay was performed by a simple addition of MA-g-PP compatibilizer to the mixture previously indicated.

The mechanical properties of the PP/C16-Mag/TPS samples were significantly improved (with 30 wt% of TPS). These properties seem to be strongly influenced by the TPS and the amounts of compatibilizer agents. In this case, the use the compatibilizing agents appear as compounds of choice particularly when they are associated to the maleic anhydride content which is appropriately introduced to the mixture since, if the amount of this last ingredient was increased, the desired mechanical properties of the obtained blend becomes significantly decreased. This is probably attributable to the degradation of maleic anhydride molecules in the TPS and PP particles during the elaboration of the blends. In this case, it can be taught that the interactions between glycerol, starch, organolay, and PP occur in order to elucidate how the resulting complex composite system requires further studies in order to establish definitively the mechanism governing these properties.

By TG-DTA curves, a reduction of the melting points for the nanocomposite was observed and the decomposition temperature was again improved by simple addition of MA-g-PP compatibilizer. Finally, the addition of clay is as well another possible route to elaborate starch-based plastics by combining the clay and MA-g-PP compatibilizer allowing to obtain homogeneous and transparent TPS and other organoclays may also be advantageously introduced in the packaging industry.

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