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Starch from plant extract to plastic component

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Abstract

Polypropylene (PP) and Polyethylene (PE) are considered to be the most consumed polymers nowdays. In fact, they are part of the major components of plastic waste, in addition to their insoluble in water and even more hydrophobic, The end of life of polyolefins is particularly harmful for the environment. The main of our work is to introduce a polysaccharide in the polyolefin blend to cause partial biodegradation of our system, with conservation and improvement of their properties. Several PP / PE blends were prepared in different levels of thermoplastic starch (TPS). All the blends 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/bio-composites were studied by means of dynamic rheological behavior (DRB), Fourier transform infrared (FTIR) spectroscopy, Melt flow index (MFI), Izod impact (unnotched) tests, Thermogravimetry (TG), and Scanning Electron Microscopy (SEM).

Keywords: blend, bio-polymeres, polyolefin, and starch;

1. Introduction

Starch is an inexpensive, renewable, and natural polymer, It can be blended with synthetic polymers to lower the cost and to confer partial environmental degradability of the blends, [1, 2], it has disadvantages such as poor mechanical properties, high water solubility, high temperatures resistant and brittle in addition to poor flow characteristics, [3] .Chemically, Starch is a polysaccharide of chemical formula $(C_6H_{10}O_5)$ n. It is composed of glucose molecules linked by α (1,4) bonds and sometimes (1,6), it has generally been established that starch is a heterogeneous material containing two microstructures—linear (amylose) and branched (amylopectin). Amylose is essentially a linear structure of _-1,4 linked glucose units, and amylopectin is a highly branched structure of short _-1,4 chains linked by _-1,6 bonds. Fig. 1 shows the chemical structure and a schematic representation of amylose and amylopectin ,with different forms of starch grains. Physically, most native starches are semi-crystalline, having a crystallinity of about 20–45% [4], Amylose and the branching points of amylopectin form amorphous regions. The short-branched chains in the amylopectin are the main crystalline component in granular starch. Crystalline regions are present in the form of double helices with a length of ~ 5 nm. [5]. starch decrease weakness of biodegradable plastic, we put blend between thermoplastic starch and synthetic materials such as LLDPE, HDPE, PP and others Synthetic materials. Have advantages such as high mechanical properties, high temperature resistance, High flow properties and cheap and hydrophobic [6], Biodegradable plastic from TPS/synthetic material blend has a problem. The problem is incompatibility between hydrophilic starch and hydrophobic synthetic, which results in weak functional properties. Due to the incompatibility. Recently, many researchers have done much work to improve the compatibility of the blends, such as the modification of polymer and/or the introduction of compatibiliser and/or the modification of starch [7]. starche can be plasticized by glycerol or with another plasticizer as glycols, sorbitol, xylitol, fructose, glucose, urea and maltose, this plasticization provides a material called Thermoplastic Starch (TPS) which can be used in the molten state as a conventional thermoplastic polymer while being biodegradable however, its properties are still below to the ones obtained from classical polymers. TPS can be mixed with a synthetic polymer to reduce the use of synthetic polymers, such as high density polyethylene (HDPE), polypropylene (PP), low density polyethylene (LDPE), behaves in a manner similar to conventional polymer-polymer blends. The strategy used here to obtain a material with good properties is to examine precisely the interface/morphology relationship [8]. In this work, we prepared the thermoplastic starch by turbo-mixer, and PP/HDPE blend by Single-screw extruder, Then, we prepared the blends/bio-composites by internal mixer, were studied by different means of characterization, aims to investigate the effect of thermoplastic starch on the properties of polypropylene (PP) and high density polyethylene (PEHD) blend.

2. Experimental

2.1. Materials used

The Isotactic polypropylene, semi-crystalline, MFI = 3,4 (g/10 min), (2,16 g at 230 °C), was supplied by Basell .The high density polyethylene , MFI = (2, 5- 4,5) g/10 min (190°C/2,16 kg), was supplied by Complexe CP2 k. The Corn Starch Containing 30 wt% amylose and 70 wt% amylopectin was supplied by Sigma-Aldrich. The Glycerol, Density of 1,25g/cm3, was supplied by biochem.

2.2. Sample preparation

The preparations of blends are composed of three steps: first, preparation PP/PE and. Secondly, preparation of thermoplastic starch and finaly, production of blend/bio-composite.

2.2.1. Preparation of PP/HDPE

The formulation used to prepare the PP/PEHD blend containing 80 wt% of polypropylene and 20 wt% of high density polyethylene; it was prepared through melt-mixing procedure, which uses an intermeshing single-screw extruder, the four heating zones of the extruder were maintained at 170, 180, 190, 190 °C, and the screw speed was 60 rpm [10].

2.2.2. Preparation of thermoplastic starch (TPS)

Figure (1) shows the physical and chemical structures of starch

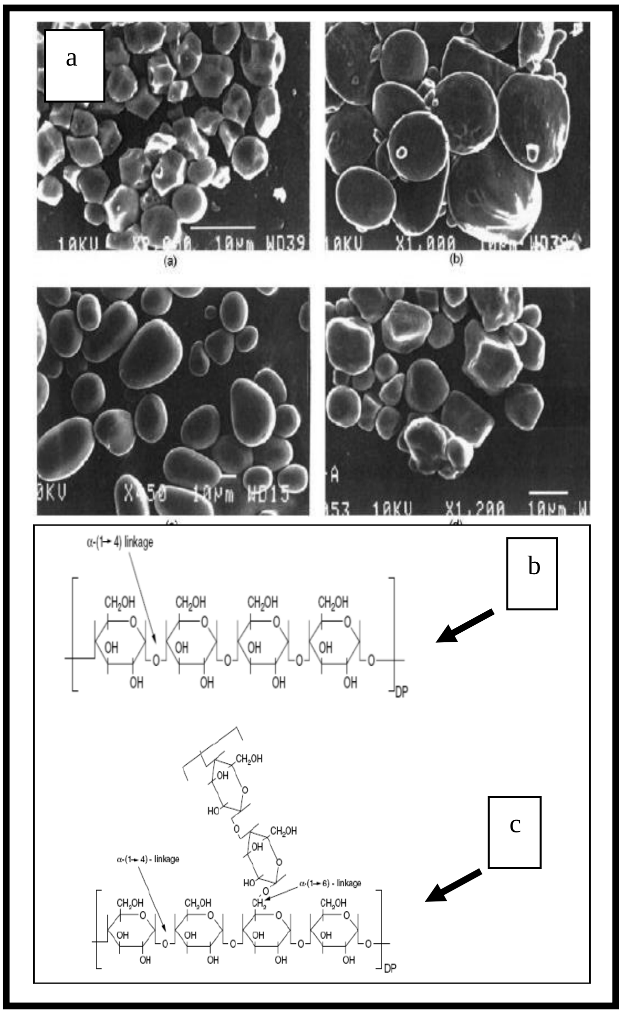

Figure 1. Physical and chemical structure of starch, (a) SEM images of granule, (b) amylose, (c) amylopectin

TPS was prepared using two procedures: first, the starch was premixed with glycerol and water , The formulation used was contained 54 wt% of native corn starch, in addition to 23 wt% of glycerol and 23 wt% of water [9] . The starch powder was introduced into a turbo-mixer.after that, the water was slowly added under stirring. After finishing from adding water, then, the glycerol is added slowly with agitation; the mixture was then placed in a ventilated oven at 150 ◦C for 20 min. To allow the evaporation of water, then the dry blend obtained was 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 [10].

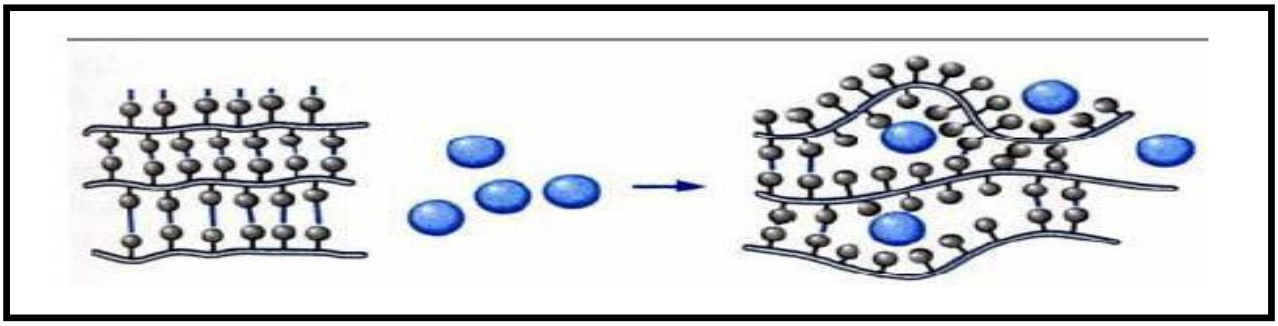

Figure 2. Schematization of the plastification mechanism at the molecular level.

2.2.3. Preparation of bio_blends

All the blends were prepared through a melt-mixing procedure, using Mixer interns Haake Rheomix 600 and Contrarotating 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, the proposed structure is in Figure (3).

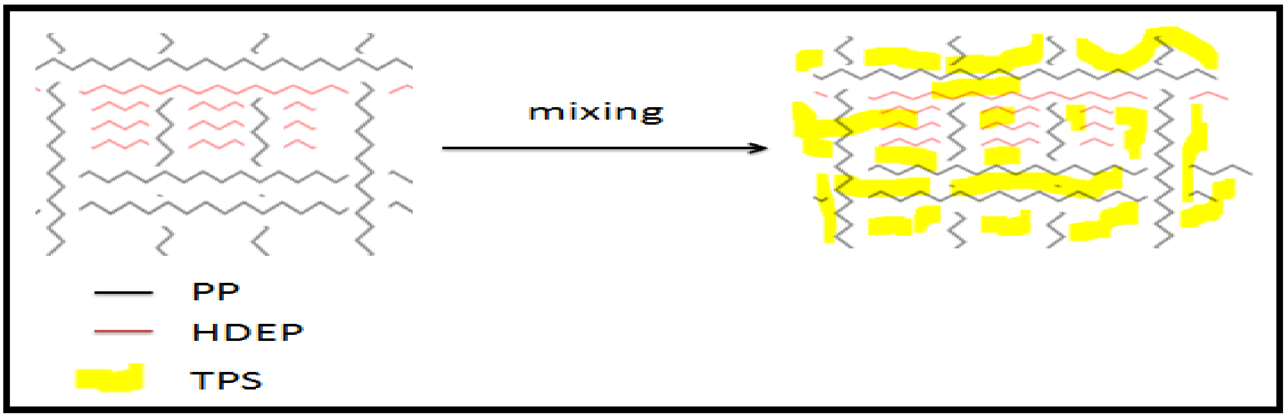

Figure 3. The virtual structure of PP/HDPE/TPS bio_blend

2.3. Characterization

2.3.1. Dynamic rheological analysis technique:

The study represents the dynamic rheological behavior (DRB) of materials and evaluation of the crosslinking or branching reaction, The Brabender" plastograph "is the most suitable for this study, The Brabender used PLASTI-CORDER type, is used for the production of PP/HDPE/ TPS blends.

2.3.2. Fourier transform infrared spectroscopy

Fourier Transform Infrared Analysis is a method based on the exploitation of vibration bands characteristic of carbonyl groups. The spectra are produced on polymer films a few tens of microns thick. *The* apparatus used is a PERKIN-ELMER FTIR spectrometer working in transmission and reflection. The information is digitized (microprocessor) and stored with the possibility of recording spectra on diskettes. The resolution is 4 cm-1 for a field of study of 4000 to 450 cm-1

2.3.3. Mechanical properties

Measurements of the mechanical properties, such as tensile strength and Elongation at break, the specimens were prepared according to ASTM D4812. ISO 180 standard, For each sample five measurements were made and the results were their average value.

2.3.4. Thermogravimetric analysis (TGA)

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

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

The scanning electron microscope uses a thin electron beam, emitted by an electron gun. Electromagnetic lenses focus the electron beam on the sample. Thanks to the scanning electron microscope, it is possible to see the surface of objects, bacteria, materials ... The great depth of field is an asset of this microscope. The resolution (1 nanometer). surfaces of the various fractured specimens were examined by scanning electron microscope (phillips X L20) operating 10-15 KV.

2.3.6. Melt flow index (MFI)

Melt flow index was 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. Results and discussion

3.1. Behavior during mixing

The internal mixer, in addition to permitting the mixing of polymers in a molten medium, is also a measuring tool that makes it possible to follow the evolution of the material subjected to shear and temperature. The two parameters measured are the temperature of the mixture and the engine torque. We will limit this study to torque according to time, Figures (4) show the evolution of the torque as a function of time. We observe at the beginning , an increase in the couple, resulting from the strength of the mixture which has not yet reached the melting state and then a slight decrease corresponds to the beginning of the melting of the polymer having the lowest melting temperature, it is the polypropylene/polyethylene blend , at this time the melting temperature of the blend is not yet reached, the couple follow its increase and with the shear and the temperature of the chamber the couple decreases until reaching a stable value, the incorporation of the thermoplastic starch in the PP / PE mixture is accelerated the increase of the torque this can be due to the existence of granule of rigid starch, in the stability stage of the couple we noticed that the TPS additive to the PP/HDPE blend decreased the viscosity of our system, and this can be due to the free volume which is found in the TPS and which is formed by the presence of the glecyrol. The similar evolution of the torque for all the mixtures during the residence time in the mixer may be an indication of the non-degradation during the implementation.

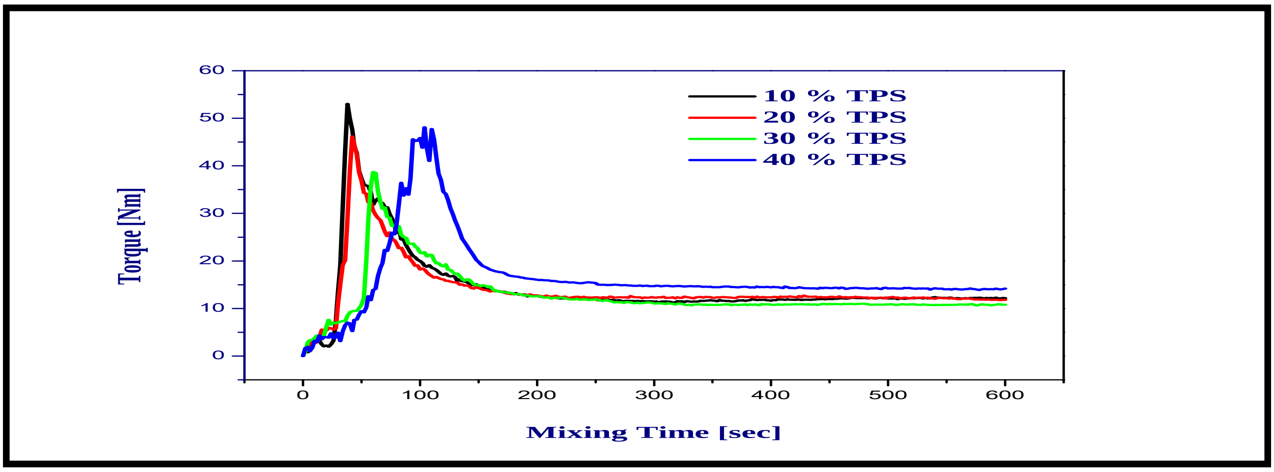

Figure 4. Melt torque of PP/HDPE/TPS blends

3.2. Fourier transform infrared (FTIR) spectroscopy

Fourier Transform Infrared (IRFT) analysis is a method based on the exploitation of vibration bands characteristic of carbonyl groups. The spectra are produced on polymer films a few tens of microns thick. A reference peak is chosen from the characteristic peaks of the polymer chain in order to be able to ignore the thickness of the sample (for example, 1166 cm $^{-1}$ in the case of polypropylene). With this method, a calibration is [11]. The characterization of FTIR spectra is of paramount importance, it makes it possible to predict the various phenomena that occur. Figure (5) shows the infrared spectra of PP/PE/TPS blend. The typical saccharide band region is noted between 950 cm^{-1} and 1200 cm^{-1}. It is characterized by the elongation vibrations of the C-C and C-O bonds present in amylose and amylopectin. the spectrum of PP / PE blend shows all the characteristic bands of this blend, A wide band between 3200 and 3800 cm^{-1} corresponds to the vibration of the O-H group. This band becomes more intense and wider, increasing the level of plasticized starch because of the increase in the level of O-H groups present in starch and glycerol.

A peak located around 1650 cm^{-1} attributed to the valence vibrations of the OH bond of the absorbed water. This peak becomes more intense for the blend with 30% of thermplastic starch because of the increase of the absorbed water molecules. on the surface of the starch.

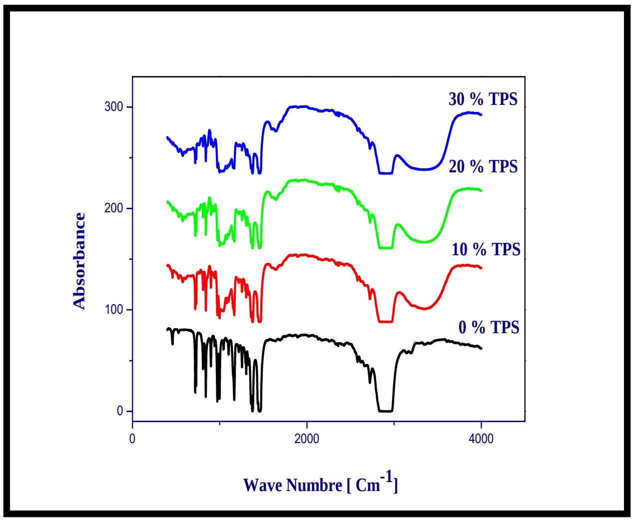

Figure 5. Spectra of PP/HDPE/TPS blends

3.3. Mechanical properties

The tensile test was carried out for the various formulations, the results obtained are shows in Figure (6). It is observed from the results, that the elongation at break increases after the addition of 10% of the thermoplastic starch. , then stabilized at 20%, then decreased after adding 30%, this can be explained by interactions that have been developed between the TPS and the PP / PE blend, and therefore an increase in viscosity is obtained after adding 10 and 20% TPS, this result is in agreement with that obtained in MFI (decrease of the melt flow index after the addition of 10 and 20% of TPS to the PP / PE mixture and consequently increase of the viscosity).

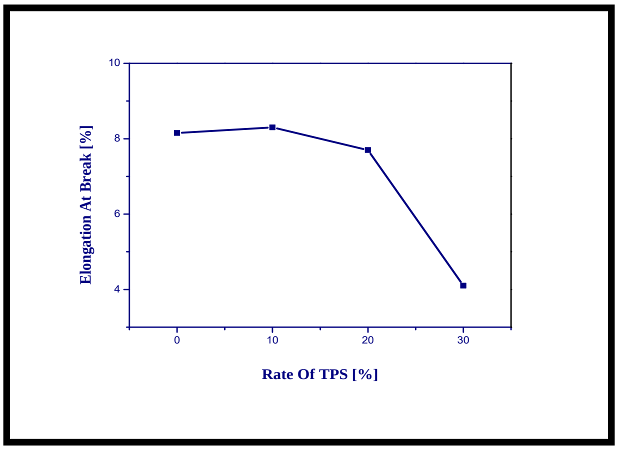

Figure 6. Elongation at break (%) for PP/HDPE blends containing different amounts of TPS

The tensile modulus and strength of the blends were decreased by additing of the TPS to the high-density polyethylene (PE), polypropylene (PP), polystyrene (PS), polylactic acid (PLA), and polycaprolactone (PCL) [12].

The tensile strength of the blends/bio-composites are shown in Figure (7) , We try to study the influence of TPS on the tensile strength of PP/PE blend, the impact strength decreased by adding of TPS according to [13] , the incorporation of TPS into PP/PEHD blend Has a negative impact on impact resistance, This is because The presence of starch granules which form a considerable distance with the PP/HDPE blend , Also note the penetration of starch thermoplastic starch between the

PP/ HDPE particles Which further weakened its mechanical properties.

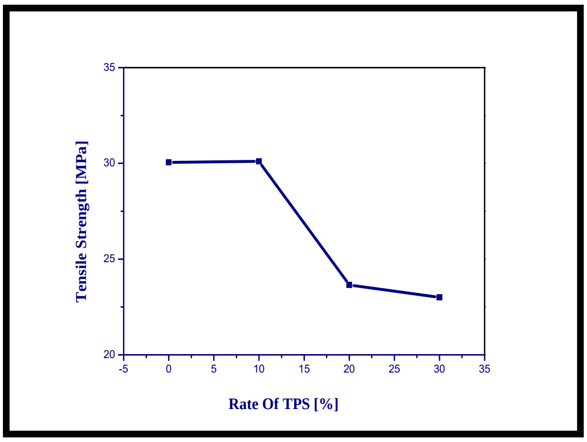

Figure 7. The effect of TPS on the tenseil strength of HDPE/PP blend

3.4. Thermal stability

The results of the blends/ bio-Composites are shown in Figure (8) . For the blend PP/PE, the initial thermal decomposition temperature (T_{onest}) was observed around 291 °C, and the temperature of maximum rate of masse loss was detected at 473 °C.

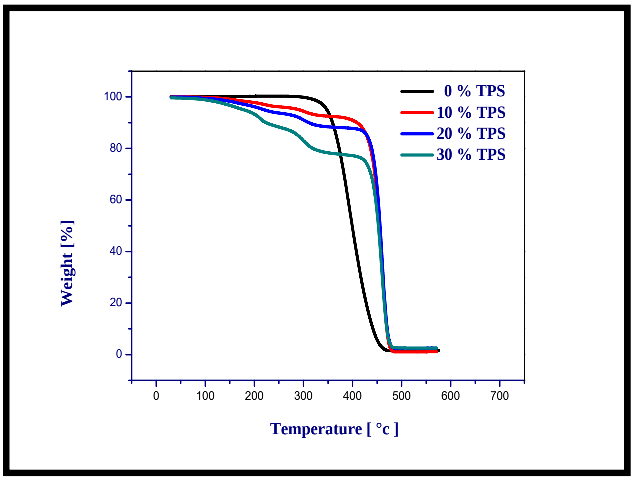

Figure 8. Thermal Stability of blends according to rate of TPS

As shown in the figure (8) , 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 Started at 180 °C, and it was produced due to the evaporation of glycerol. At 300◦C, the thermal decomposition of starch occurs according to (Shujun, Jiugao et al. 2005) [7].

The last shift was increased for the reference blend PP/HDPE , corresponds to the heat degradation of blend PP/HDPE. The thermoplastic starch decomposition products protect the blend PP/PE from heat degradation According to [14], As can be seen from Figure (8) , with the increase in starch content, the residue increased according to [15].

3.5. Melt flow index (MFI)

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 mixture according to [6] , Figure (9) , 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 [16], 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 an increase in viscosity is obtained.

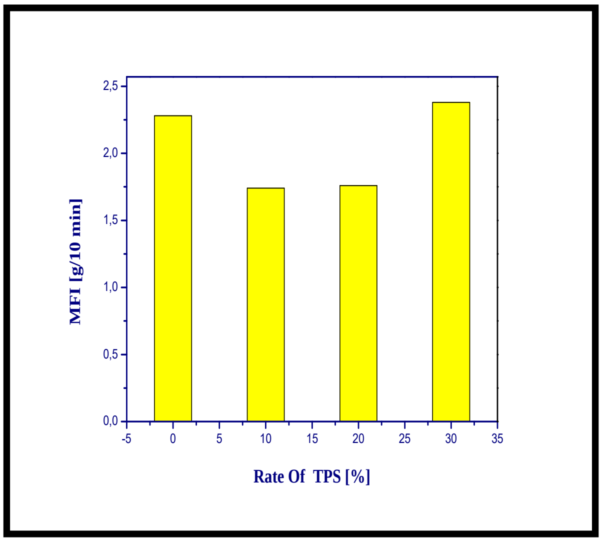

Figure 9. Melt flow rate value of biodegradable plastic

3.6. Morphology

By their immiscibility, the mixtures have different microstructures depending on the composition. There are two major classes: 1) a discrete structure of droplet type in a matrix and 2) 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 for close to phase inversion compositions or droplets of one phase are encapsulated in an oriented or co-continuous geometry of the other phase [17].

The phase morphology of PP/PE blend and their composites was investigated by SEM , Figure (10 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 seem to be more disordered and show a more pronounced curvature. The addition of thermoplastic starch tends to cover the mixture, as we observed in the figure (10 b,c,d). the addition of TPS up to 20% retain the mechanical properties of the blend, According to our study of mechanical properties, But the presence of a lot leads to weak mechanical resistance, Where we observe in Figure (10, d) The presence of starch between the molecules of the PP/HDPE blend In a homogeneous manner , Because many studies have shown that the presence of starch in plastic mixtures weakens the mechanical properties due to the presence of solid granules.

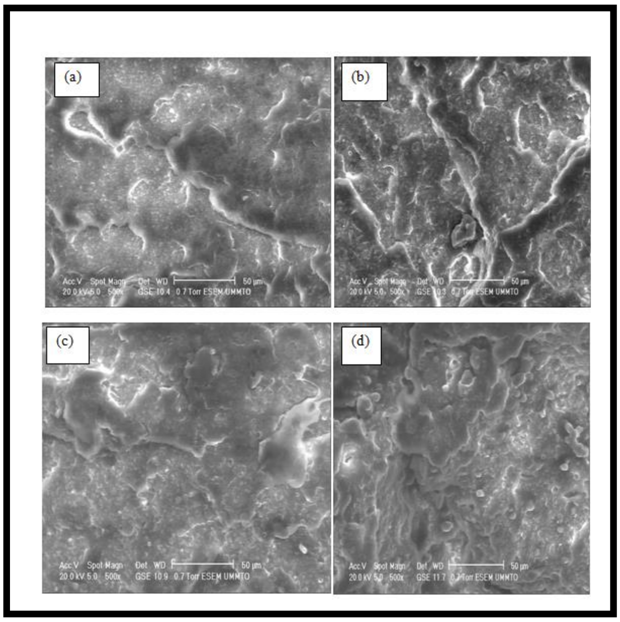

Figure 10. SEM images of (a) PP/HDPE; (b) PP/HDPE/10TPS; (c) PP/HDPE/20TPS; (d) PP/HDPE/30TPS

4. Conclusion

The study and application of polymer blends is one of the fastest growing areas in the science of macromolecular materials Polymer blends, this offer the attractive possibility of obtaining materials with interesting properties, The aim of adding starch to polymers was to obtain low-cost materials with high quality mechanical properties, as well as to promote microorganism activity on discarded artifacts, Through our study We concluded that the addition of 10% to 20 % of the starch to the plastic preserves many of the properties of this mixture , While adding 30 weakens the properties of the mixture , and as perspective , We speculate that adding less starch will improve its properties, especially the mechanical ones, as it can play a role of compatibilizer.

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