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"The effect of sepiolite on the compatibilization of polyethylene-thermoplastic starch blends for environmentally friendly films"

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## **Abstract**

Green polyethylene is a new and attracting polymer from biobased resources (sugarcane) and identical properties to petroleum-based polyethylene. Its potential in the packaging industry is really promising. In this work we report the use of different compatibilizer systems for green polyethylene (from sugarcane) and thermoplastic starch (30 wt.% TPS) in order to increase ductile mechanical properties and biodegradable content. Typical petroleum-based graft copolymer of polyethylene with maleic anhydride (PE-g-MA) is used as reference compatibilizer and new compatibilizer systems are developed by using sepiolite. The obtained results show that sepiolite-based compatibilizers provide good compatibilization properties as observed by a remarkable increase in elongation at break and a noticeable size reduction of the

thermoplastic starch domains dispersed in the green polyethylene matrix as observed by scanning electron microscopy (SEM).

**Keywords:** polymer blends and alloys; green polyethylene; thermoplastic starch; sepiolite; compatibilizers.

#### 1.- Introduction.

The increase in environment concerns and petroleum depletion act as a driving force for the development of new environmentally friendly materials. Polyethylene is, together with polypropylene (PP) one of the highest consumption commodity plastics in the packaging industry due to their excellent barrier properties and their intrinsic chemical inertness. Nevertheless, polyethylene is a non-biodegradable petroleum-based polymer and, as a consequence, it is responsible for a high carbon footprint. "Green PE" is a commercial trade name (Braskem) of a biobased polyethylene obtained from bioethanol derived from sugarcane which is converted into ethylene by a dehydration process. Green PE shows a lighter carbon footprint if compared to petroleum-based polyethylene. CO<sub>2</sub> emissions for petroleum-based PE are 2.1 t CO<sub>2</sub>/t polymer while this value for Green PE is -2.5 which indicates that it fixes carbon so that, it contributes to lower CO<sub>2</sub> emissions. Several Life Cycle Assessment (LCA) studies have corroborated the positive effects of bio-PE on lowering the carbon footprint and reducing greenhouse gas (GHG) emission during life cycle compared to petroleum-based polyethylene.[1-3] Despite this, Green-PE is non-biodegradable and different approaches are being made in order to increase degradation rate. One of these approaches is based on blending polyethylene with starch due to its availability, low cost and biodegradation.

Starch is a natural polysaccharide mainly composed of amylose and amylopectin in different proportions. Amylose is a linear (or very low branched) polymer from glucose; it represents around 20-30% in starch and plays a key role in plant energy storage. On the other hand amylopectin is a highly branched polymer of glucose structure and represents about 70-80 wt. %. Starch appears in plants as granules with different size depending on the plant: i.e. potato starch granules range from 5 up to 100 µm while rice starch granules are considered the smallest vegetable powders with a particle size ranging from 7-9 µm. Starch is industrially used with plasticizers which provide easy processing and attracting properties and it offers great potential when blended with "commodity" and recycled polymers for high environmentally friendly solutions.[4-7] In general terms, starch is a readily available, cheap, renewable and fully biodegradable polymer; so that, its potential use is attractive for a wide variety of industrial sectors in which biodegradation is a key factor such as packaging industry, disposable products for hygienic and sanitary uses, etc.[8-10]

Polyethylene is a highly hydrophobic polymer while starch, in contrast, is a highly polar polymer so that their blends are not compatible. Several studies show that the addition of TPS to low density polyethylene (LDPE) leads to a decrease in mechanical properties, both tensile strength and elongation at break [11-14], which is representative for incompatibility between these two polymers; for this reason, it is necessary to compatibilize both polymers in order to obtain good balanced properties. Starch hydrophobization is an interesting issue from an industrial point of view due to its wide use in the food industry, packaging, papermaking, adhesives, cosmetics, etc. and its potential in polymer blending.[8, 15] The main approach to starch hydrophobization has been traditionally esterification but also alkenyl succinic anhydrides (ASA) and alkyl ketene dimers (AKD), widely used as hydrophobic sizings

in the papermaking industry, have been used to provide hydrophobicity to starch.[16-18] The use of polyethylene-graft-maleic anhydride (PE-g-MA) gives good results as it provides dual polar-non polar behavior thus acting as a bridge between the immiscible polymers. PE-g-MA leads to some compatibilizing effects on high density polyethylene, low density polyethylene and ethylene-vinyl acetate copolymer with starch but phase separation also is detected.[19] On one hand, the polar component of PE-g-MA (polymer chain segments containing maleic anhydride) moves toward starch phase and it can interact with hydroxyl groups in the starch; on the other hand the non-polar component of PE-g-MA (polyethylene chains) rearrange toward polyethylene phase enabling some interactions.[11, 12, 20-22] In addition to PE-g-MA, other copolymers such as polypropylene-graft-maleic anhydride - PP-g-MA, poly(ethylene-co-glycidyl methacrylate) - PEGMA, poly(ethylene-co-vinyl alcohol) - EVOH, poly(ethylene-coacrylic acid)-PEAA, polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrenegraft-maleic anhydride (SEBS-g-MA) have been successfully used as compatibilizers for polymer-hydrophilic filler systems.[23-26] Sepiolite is a readily available, low cost magnesium silicate with a needle-shape characterized by high porosity and, consequently, high surface area. Sepiolite is a complex magnesium silicate [Si<sub>12</sub> O<sub>30</sub> Mg<sub>8</sub> (OH<sub>2</sub>)<sub>2</sub> (OH)<sub>4</sub>·6H<sub>2</sub>O] characterized by a hydrophilic fibrillar needle-shape porous structure with internal tunnels along the axis with a size of 0.37x1.06 nm<sup>2</sup> which provides a surface area up to 320 m<sup>2</sup> g<sup>-1</sup>.[27, 28] Due to its inorganic nature, it has been used as a plastic additive to improve mechanical, thermal and chemical barrier properties as other clays such as bentonite, organically modified nanoclays, halloysite nanotubes, etc.[29-33] In order to increase its compatibility with hydrophobic polymers such as polyethylene, sepiolite has been treated with different coupling agents such as

hydrophobic silanes.[34] Silanol groups in sepiolite surface can react with different chemicals to provide tailored functionalities.

In this work we report the manufacturing of films of polyethylene with 30 wt.% thermoplastic starch (TPS) by using different compatibilization systems: PE-g-MA, sepiolite and a combination of them. Hydrophobic silane (propyltrimethoxy silane, PTMS) is used to provide partial hydrophobicity to sepiolite. The effectiveness of the compatibilizing agent is evaluated in terms of the mechanical properties and the microstructure changes are followed by scanning electron microscopy (SEM). In addition, the effect of the starch on the overall biodegradation (controlled composting conditions) is studied in terms of weight loss with time.

## 2.- Experimental.

#### 2.1.- Materials.

Polyethylene-thermoplastic starch (TPS) blends containing 30 wt.% TPS were manufactured by using a biobased high density polyethylene (Green PE) grade SHA7260 (with a  $M_n$  of 10475 g mol<sup>-1</sup> and a  $M_w$  of 192099 g mol<sup>-1</sup>) by Braskem supplied by FKuR (FKuR Kunststoff GmbH, Willich, Germany). This FDA approved HDPE grade is characterized by a minimum biobased content of about 94%, a melt flow index of 20 g/10 min and a density of 0.955 g cm<sup>-3</sup>. With regard to the thermoplastic starch, a commercial grade Mater-Bi® NF-01 (Novamont Spa, Novara, Italy) was used to provide biodegradable content to films.

Sepiolite based compatibilizer was kindly supplied by Tolsa (Grupo Tolsa, Madrid, Spain). It was a polyfunctional additive PANSIL derived from high purity sepiolite supplied as a clear cream powder with uses in filler dispersion and reinforcing properties with polar polymers. Propyltrimethoxy silane (PTMS) supplied by Sigma

Aldrich was used as hydrophobic silane to selectively modify sepiolite surface. Polyethylene-*graft*-maleic anhydride (PE-*g*-MA) with a viscosity of 1700-4500 cP at 140 °C supplied by Sigma Aldrich was used as conventional compatibilizer. The total compatibilizer amounts were referred to thermoplastic starch content.

#### 2.2.- Compounding and film preparation.

PE-TPS blends containing 30 wt.% TPS were obtained in a micro extruder DSM Xplore at a temperature of 150 °C. The material remained 3 min at 100 rpm in the plasticization chamber. After this, a continuous film 25 mm wide and 25  $\mu$ m thickness was obtained at a controlled force of 700 N.

## 2.3.- Mechanical characterization.

Mechanical properties of PE-TPS films compatibilized with different systems were obtained in a Universal Test Machine Lloyd Instrument, model LR 30 K with a load cell of 500 N and a crosshead speed of 50 mm min<sup>-1</sup> following the guidelines of the UNE-EN-ISO 257-2 (sample type 2 and 10 mm sample width).

## 2.4.- Microscopic structure of sepiolite and PE-TPS blends.

Sepiolite needle-shape structure was evidenced by both SEM and TEM analysis. SEM characterization was carried out in a JEOL JSM-5410 microscope (JEOL, Peabody, USA) using secondary electrons with an acceleration voltage of 15 kV with prior sputtering with gold layer. TEM characterization was done in a JEOL mod. JEM-2010 microscope (JEOL, Peabody, USA) equipped with an image acquisition camera ORIUS<sup>TM</sup> SC600 TEM CCD (GATAN GmbH, München, Germany).

PE-TPS blends' samples were subjected to cryogenic conditions with liquid N<sub>2</sub> and after 30 min, they were cryogenically fractured. After this, fractured surfaces were immersed in HCl solution (6 N) at room temperature for 3 h in order to selectively extract the thermoplastic starch rich domain. After the extraction process, samples were washed with distilled water, dried and stored in a vacuum desiccator. After this, samples were sputter-coated with a gold layer and subsequently observed in a scanning electron microscope (SEM) JEOL JSM-5410 (JEOL, Peabody, USA) using secondary electrons with an acceleration voltage of 15 kV.

## 2.5.- Disintegration of PE-TPS films.

Evaluation of the degree of disintegration of PE-TPS films was carried out under simulated composting conditions at laboratory-scale following the guidelines of the UNE-EN-ISO 20200:2004. According to this, squared samples sizing 25x25 mm² were cut and mechanically mixed with a biodegradable material to simulate controlled composting conditions. Composition of the synthetic solid waste was (in wt.% dry basis): wood sawdust (40), rabbit-feed based on alfalfa (30), mature compost (10), corn starch (10), corn oil (4) and urea (1). After this, distilled water up to 55 wt.% was added to synthetic solid waste. The mature compost consisted on a mulch fertilizer (aging less than 4 months) with a moisture content of about 30% and a pH in the 6-7 range. The samples were placed on a polyester mesh container to allow direct contact with the composting media as well as easy extraction. PE-TPS films were subjected to aerobic degradation at a constant temperature of 58 °C. The weight of the samples was monitored in terms of the composting time up to a maximum period of 56 days.

#### 3.- Results and discussion.

# 3.1.- Sepiolite modification and characterization.

Sepiolite nanoclays, with a needle-shape structure (Fig. 1), offer attracting possibilities for compatibilization of immiscible polymer systems. Sepiolite is characterized by a high surface area which is due to presence of longitudinal tunnels. In addition the surface electrical charge is negative as a consequence of the silanol groups with hydroxyl functionality which can react with different chemical groups to provide particular functionalities to sepiolite surface.

## Figure 1

The surface treatment of sepiolite with a hydrophobic silane (propyltrimethoxy silane-PTMS) provides some hydrophobic groups so that, silane-treated sepiolite is characterized by high porosity, unreacted hydroxyl groups and hydrophobic attached groups as observed in Fig. 2.

# Figure 2

For this reason, sepiolite needles can establish interactions between hydroxyl groups in thermoplastic starch as well as with hydrophobic polyethylene chains and this is intensified by the high surface area as reported in LDPE-starch systems with silane-treated (vinyl silane) sepiolite.[35] These interactions could lead to good compatibilizing effects. Fig. 3 shows TEM images of untreated (Fig. 3a & 3b) and silane-treated (Fig. 3c & 3d) sepiolite needle-shapes. It can be clearly observed the longitudinal axis in which, the tunnels are formed as a consequence of alternating

structures of tetrahedral-octahedral-tetrahedral plates which play a key role in the high surface are of sepiolite.

# Figure 3

## 3.2.- Mechanical properties of PE-TPS with different compatibilizing systems.

As thermoplastic starch (TPS) is a plasticized polymer material, it can provide plasticizing effects when blended with high density polyethylene. Polyethylene films are characterized by a tensile strength of about 14 MPa. The addition of 30 wt.% TPS leads to a small decrease in tensile strength up to values of 13.5 MPa for the uncompatibilized blend. It can be clearly observed that the use of the different compatibilizer systems (PE-g-MA and sepiolite at different concentrations and a combination of both at a fixed content of 5 wt.%) intensifies the plasticizing effect since in all the cases, the tensile strength is reduced up to values in the 9-12 MPa range thus indicating that all the compatibilizing systems used are efficient as observed in Fig. 4.

# Figure 4

Similar tendency can be observed with the Young's modulus. High density polyethylene is characterized by a modulus of about 600 MPa (Fig. 5). The only addition of 30 wt.% TPS provides a plasticizing effect as indicated by a decrease in the modulus up to values of 500 MPa; nevertheless, the plasticization effect is more intense if the PE-TPS blend is compatibilized (the Young's modulus is reduced up to values in the 340-470 MPa range) thus indicating that the plasticizing effect is more intense due to increased interactions between polyethylene chains and plasticized starch chains.

Despite the decrease in these mechanical resistant properties are useful to validate the compatibilizing effect of the different compatibilizing systems, it is not possible to observe clear differences between the different compatibilizer systems and their relative amount.

# Figure 5

If we observe the effect of the different compatibilizer systems and their respective amounts we can observe that the best plasticizing effect (highest elongation at break values) are obtained with the combined system based on polyethylene grafted maleic anhydride (PE-g-MA) with sepiolite (5 wt.% with different sepiolite:PE-g-MA ratios) as in all cases, the elongation at break is higher than 600%. Elongation at break of HDPE films is relatively low, with values of about 22%. By blending with 30 wt.% thermoplastic starch, the plasticizing effect is clearly evident as the elongation at break increases more than fourfold up to values of about 90%. Despite this, the use of PE-g-MA as compatibilizing agent leads to a remarkable increase in elongation at break as observed in Fig. 6. Addition of 1 wt.% PE-g-MA promotes a remarkable increase in elongation at break with values over 300% thus indicating a noticeable compatibilizing effect. This is a consequence of the interactions of the PE-g-MA compatibilizer as it can interact with both polyethylene and starch thus acting as a bridge between the two immiscible components. Polyethylene is highly hydrophobic whilst thermoplastic starch is highly hydrophilic. Maleic anhydride groups in PE-g-MA are highly polar and they can establish strong interactions with hydroxyl groups in the thermoplastic starch. On the other hand, the polyethylene phase in PE-g-MA can interact with polyethylene chains. For this reason, PE-g-MA acts as a link between the two immiscible components thus allowing to reduce the stress concentration effect of the dispersed immiscible thermoplastic starch phase. It is important to remark that this effect is more intense with 3 and 5 wt.% PE-g-MA addition as the elongation at break is over 600% (Fig. 6). In the case of sepiolite, similar tendency can be observed. The addition of 1 wt.% silane-treated sepiolite gives an elongation at break value of about 100% thus indicating the compatibilizing effect. But it is the addition of 3 and 5 wt.% silane-treated sepiolite what provides clear compatibilizing effects as the elongation at break is increased up to values of about 260% and 480% respectively.

## Figure 6

The overall effects are a remarkable increase in compatibilization between non-polar polyethylene and the highly polar thermoplastic starch. Finally, when the two compatibilizer systems are combined (5 wt.% total content with different sepiolite:PE-g-MA) the compatibilization effect is intensified so that for all sepiolite:PE-g-MA ratios the elongation at break is increased to values over 600%. Although the global compatibilizing efficiency of PE-g-MA is higher than that of the sepiolite it is important to consider this since sepiolite is a low cost, biocompatible additive with potential uses in the active packaging industry due to presence of nanometric tunnels in which, active components, can be embedded and released at a controlled rate.[36, 37]

## 3.3.- Effect of compatibilizers on the morphology and composting of PE-TPS blends.

As we have described above, compatibilizers have a positive effect on mechanical properties of polyethylene-TPS blends. Polyethylene has a remarkable hydrophobic behavior due to its structure whilst thermoplastic starch (plasticized starch) is characterized by high hydrophilicity. Immiscibility can be detected by phase separation thus leading to a randomly dispersed component into the main component as observed in other immiscible or partially miscible systems. For this reason it is expectable high immiscibility between the two components at a micro-scale level. This immiscibility can be clearly observed in Fig. 7a and Fig. 8a for uncompatibilized PE-TPS blends. Thermoplastic starch appears as a disperse phase with spherical shape (6-8 µm in diameter) and it is also possible to identify spherical voids corresponding to removed TPS particles during the HCl pre-treatment which is able to selectively remove thermoplastic starch. This blend morphology is matrix-droplet type and it has been reported that phase inversion occurs for high TPS contents.[38]

The compatibilization effect can be clearly observed as a reduction of the particle and/or void diameter as detected in Fig. 7b and Fig. 8b for the PE-TPS system compatibilized with PE-g-MA. As it can be obtained from high magnification images, the particle/void diameter is reduced up to average values of less than 2  $\mu$ m. The use of sepiolite as compatibilizer also leads to a remarkable decrease in the TPS domain size with average particle/void of about 2.5  $\mu$ m (Fig. 8c). In the case of the combined PE-g-MA/sepiolite compatibilizing system we observe a synergistic effect as the TPS domain size is reduced to values of about 1  $\mu$ m as it can be detected in Fig. 8d.

# Figure 7

## Figure 8

Other important feature for films used in the packaging industry is the potential biodegradability due to the high volume of waste generation of this industrial sector. It is true that the use of green polyethylene from sugarcane represents an attracting market

(lowering the carbon footprint, CO2 fixation, etc.) but green polyethylene is not biodegradable or compostable. For this reason, blends of polyolefins with thermoplastic starch are interesting as TPS is biodegradable.[39] Fig. 9 shows biodegradation under controlled composting conditions for PE-TPS blends with different compatibilizing systems (all graphs corresponds to 5 wt.% compatibilizer). As it can be observed, green polyethylene is not composted in a period length of 56 days while its blends with thermoplastic starch (30 wt.% TPS) are characterized by a high biodegradation in the 22.5-30 wt.%. Biodegradation by composting of all PE-TPS blends is characterized by an initial induction stage, in which, a relative small weight loss is detected (this stage takes about 7 days); after this initial stage a high degradation rate occurs between 7 and 21 days and, finally, after 21 days, the weight loss tends to stabilize to a constant value. Uncompatibilized PE-TPS blends tend to stabilize degradation at a weight loss of about 22.5% and all compatibilized systems tend to stabilize degradation at higher values in the 25-28 wt.%. In the case of the PE-TPS blend compatibilized with PE-g-MA, degradation occurs up to values of about 28.0% which is the maximum weight loss observed for all the tested systems in the degradation period considered in this study. This maximum degradation could be directly related to the compatibilization effect as PE-g-MA acts as a bridge between polyethylene chains and plasticized starch chains and this good interaction could lead to partial degradation of some polyethylene chains linked with starch. With regard to the sepiolite and hybrid (sepiolite+PE-g-MA) compatibilized PE-TPS blends, degradation by composting occurs at a extent of a weight loss of 26 wt.% and 27 wt.% respectively thus showing interesting properties from a degradation point of view.

## Figure 9

## 4.- Conclusions.

Needle-shape sepiolite clays show an interesting compatibilizing effect on green polyethylene/thermoplastic starch (PE-TPS) blends containing 30 wt.% TPS. Silanol groups located at sepiolite surface offer good reactivity which is highly useful to provide the required functionalities to the sepiolite compatibilizer. Polyethylene is highly hydrophobic while thermoplastic starch is characterized by high hydrophilicity; for this reasons, a good compatibilizer must contain both hydrophobic and hydrophilic groups to act as a bridge between the two immiscible blend's components. This dual functionality is typical of graft copolymers used for polymer compatibilization as in the case of polyethylene graft maleic anhydride (PE-g-MA) which is highly used as compatibilizing agent. Surface modification of sepiolite with hydrophobic silane (propyletrimethoxy silane- PTMS) provides hydrophobic groups thus leading to a dual functionality sepiolite which is able to act as a bridge between hydrophobic polyethylene chains and hydrophilic plasticized starch chains.

The usefulness of silane-treated sepiolite as compatibilizer for PE-TPS blends has been corroborated by a remarkable increase in elongation at break of films from 90% (uncompatibilized PE-TPS blend) up to values of about 260% and 480% for PE-TPS blends compatibilized with 3 wt.% and 5 wt.% silane-treated sepiolite respectively. In addition, compatibilization is detected though SEM analysis. Uncompatibilized PE-TPS blend shows a clear phase separation which is evidenced by the presence of disperse spherical particles and voids corresponding to the thermoplastic starch domain with an average size of 6-8  $\mu$ m; on the other hand, the PE-TPS blend compatibilized with silane-treated sepiolite (5 wt.%) shows a remarkable decrease in the particle/void size to values around 2.5  $\mu$ m.

Although compatibilization with silane-treated sepiolite is lower than that observed with conventional copolymers such as PE-g-MA, it is important to remark that sepiolite is a low cost, readily available, biocompatible additive which can be easily modified to tailored functionalities and this could represent an attracting issue in the packing industry.

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## Figure legends

**Figure 1.-** SEM images (10000X) showing the typical needle-like structure of a) untreated sepiolite and b) silane-treated sepiolite.

**Figure 2.-** Schematic representation of a) longitudinal tunnels on sepiolite structure responsible for high surface area, b) sepiolite surface with silanol groups and chemical structure of propyletrimethoxy silane- PTMS and c) Presence of both hydrophobic and hydrophilic groups on silane-treated sepiolite surface.

**Figure 3.-** TEM images at different magnifications for a) & b) untreated sepiolite needles and c) & d) silane-treated sepiolite needles.

**Figure 4.-** Tensile strength for PE-TPS blends (30 wt.% TPS) in terms of the compatibilizer system and the compatibilizer amount in comparison to individual polyethylene and uncompatibilized PE-TPS blends.

**Figure 5.-** Young's modulus for PE-TPS blends (30 wt.% TPS) in terms of the compatibilizer system and the compatibilizer amount in comparison to individual polyethylene and uncompatibilized PE-TPS blends.

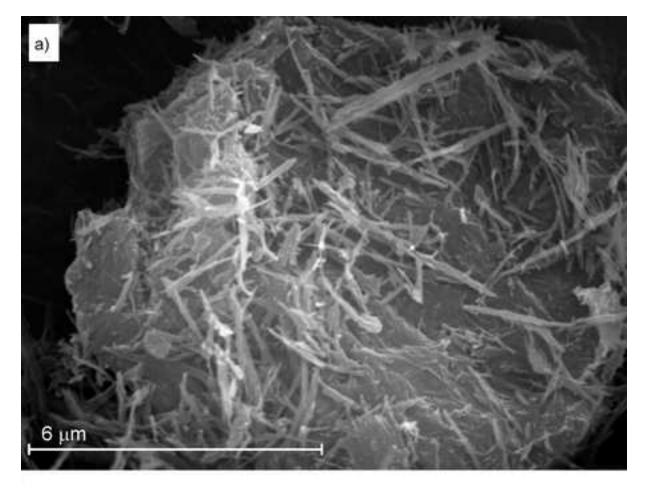
**Figure 6.-** Elongation at break for the PE-TPS (30 wt.% TPS) blend in terms of the compatibilizer system and the compatibilizer amount in comparison to individual polyethylene and uncompatibilized PE-TPS blends.

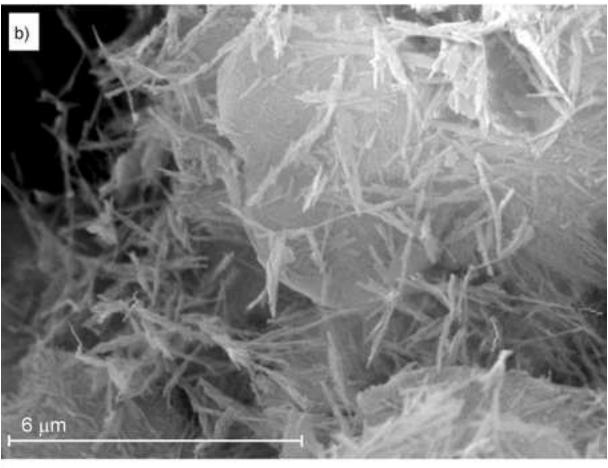
**Figure 7.-** SEM images of PE-TPS (30 wt.% TPS) blends with different compatibilizer systems (1000X): a) uncompatibilized, b) compatibilized with 5 wt.% PE-*g*-MA, c) compatibilized with 5 wt.% sepiolite and d) compatibilized with 5 wt.% sepiolite+PE-*g*-MA with a sepiolite:PE-*g*-MA ratio of 1:1.

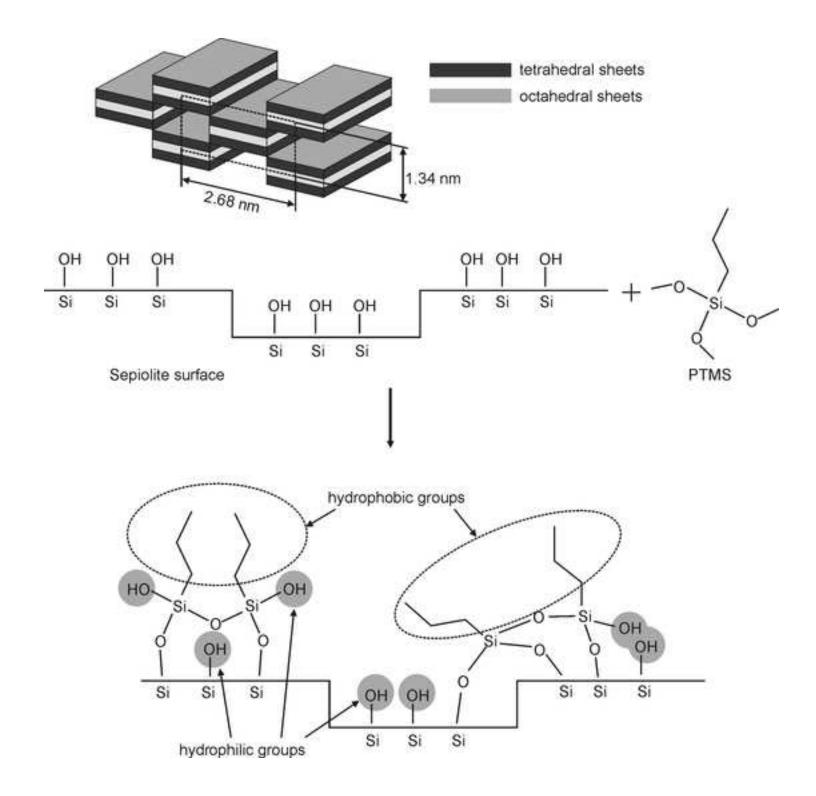
**Figure 8.-** SEM images of PE-TPS (30 wt.% TPS) blends with different compatibilizer systems (5000X): a) uncompatibilized, b) compatibilized with 5 wt.% PE-g-MA, c)

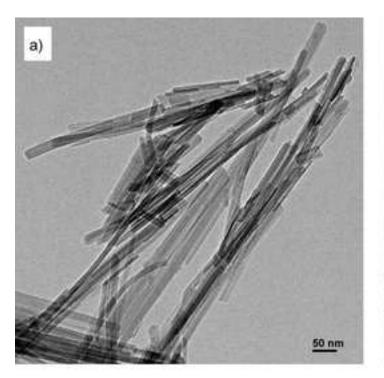
compatibilized with 5 wt.% sepiolite and d) compatibilized with 5 wt.% sepiolite+PE-*g*-MA with a sepiolite:PE-*g*-MA ratio of 1:1.

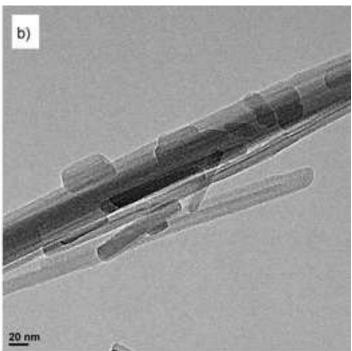
**Figure 9.-** Bio-disintegration of polyethylene and its blends with thermoplastic starch (uncompatibilized and compatibilized blends) in compost expressed as the weight loss as a function of time.

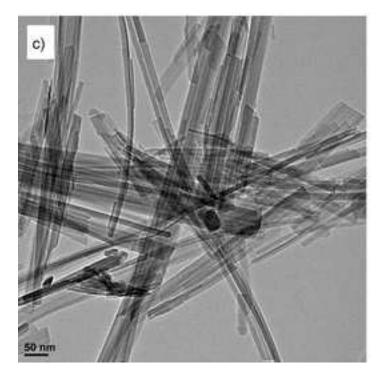


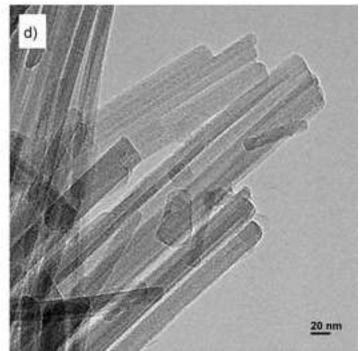


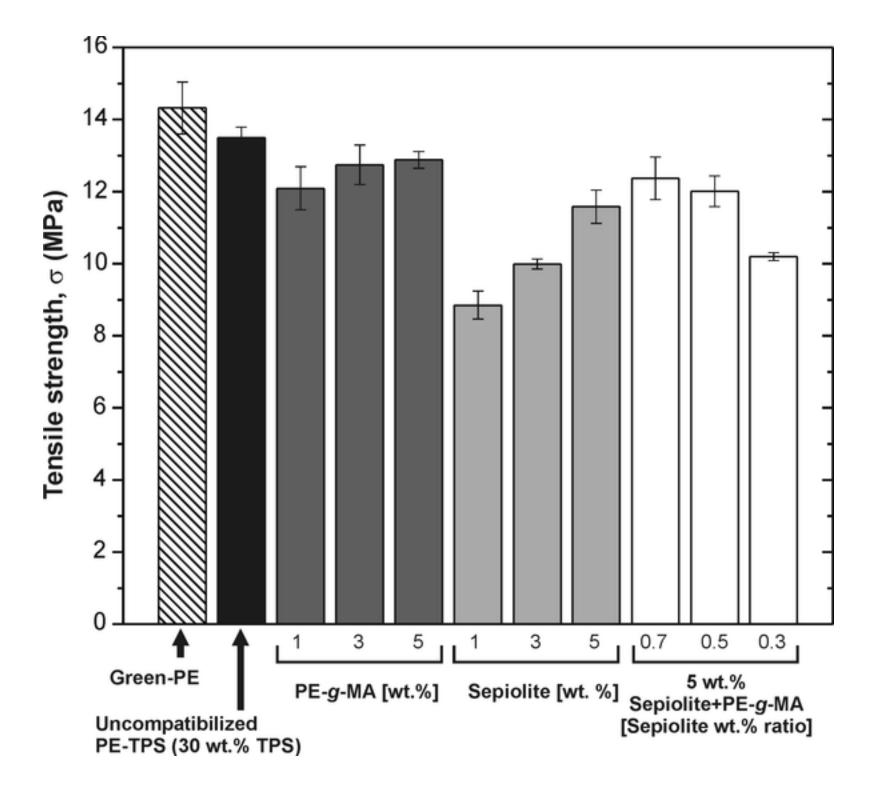


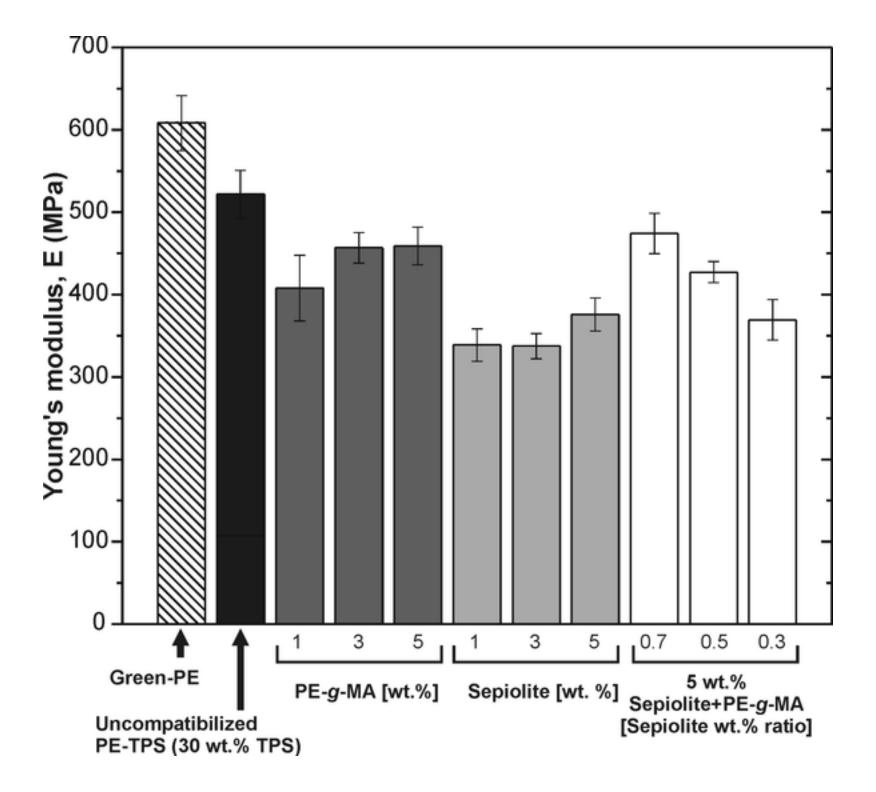












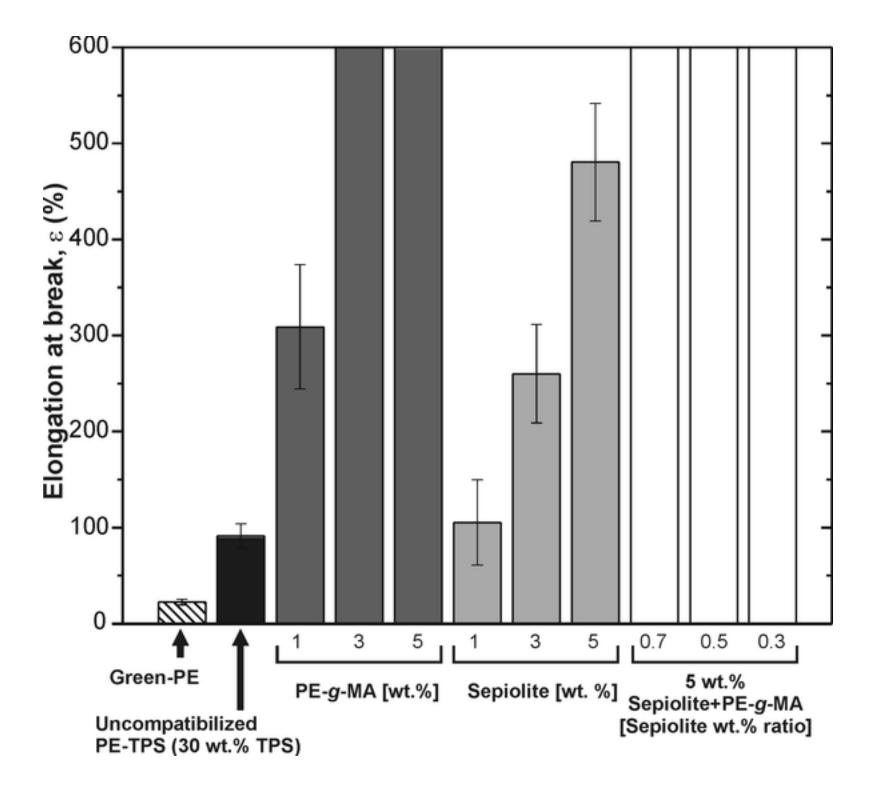


Figure 7

