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Development of a biocomposite based on green polyethylene biopolymer and eggshell

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Abstract

In this investigation a fully biobased composite material has been obtained using a biobased polyethylene obtained from sugar cane as matrix and eggshell (ES) as filler. ES was studied in order to replace mineral carbonate calcium as polymer filler, which is commonly used. In order to do this the ES has been chemically modified and then its potential for the development of a biocomposite was evaluated. The filler adhesion to the polymer matrix has been improved using titanate particle treatment which has been chosen between silane and zirconate. The use of titanate as coupling agent enlarges the range of operating temperatures and also improves the interfacial bonding as it is displayed in impact fracture surface. Mechanical, thermal and rheological analysis were carried out in order to analyze the effect of the modified ES loading percentage. Thermal analysis showed a proportional effect of the filler load over the degradation temperature and an inversely effect over the enthalpy. Effect of the modified ES content on mechanical properties of PE/ES was also studied. The results showed that the modified CaCO₃ can effectively improve the mechanical properties of bio PE, improving stiffness, hardness, flexural and tensile modulus. The amount of filler increases the viscosity, this fact specially hinders the processing processes which work with low shear rates.

Keywords: Polymer-matrix composites; Particle-reinforcement; Thermomechanical; Thermal properties; Eggshell

1. Introduction

Due to the high costs, environmental awareness and risks of petroleum-derived products in recent years there is a growing trend in the research, development and application of biocomposites [1-3]. Biocomposite materials are those wherein at least one of the components, either the matrix or the reinforcement, comes from renewable resources. A green polyethylene biopolymer made from sugarcane ethanol has been used as biocomposite matrix and chicken eggshell (ES) has been used as filler. Green polyethylene presents the same performance and characteristics as resins made from non-renewable raw materials. The ES is an industrial byproduct most of which is produced by comparatively few businesses, but industries that have this problem generate very large quantities of ES. One of the most affected industry by this problem is hatchery for both egg and poultry meat production where the quantity of ES to be disposed of it is considerable. Many alternatives have been used in order to obtain a profit of the ES, it has been used as a source of calcium for animals or it has been composted in order to make soil mixes used in organic farming for certain plants that require high levels of calcium, but these uses do not consume the large amount of ES generated.

Mineral calcium carbonate (CaCO_3) is one of the most used inorganic fillers in polymer composites [4]. Several authors like Ghabeer [5], Toro [6, 7] and Kang [8] have replaced the mineral calcium carbonate by ES developing bio-compounds. Others like Ramdani [9] and Fombuena [10] have used other natural sources in order to obtain the calcium carbonate. These studies are based in the high content of calcium carbonate present in the ES (95% by weight) [11]. All these previous studies worked with polymers obtained from petrochemical sources, but in the present work both components are from natural sources. There is a new trend in replacing inorganic fillers with organic fillers such ES since they present low densities, high filling levels, non-abrasiveness, renewable nature and the most important, they have a very low cost. It also must be considered the new more stringent environmental policies that are forcing the industries such as packaging, construction and automotive industries to develop new materials in order to replace traditional composite materials consisting of a plastic matrix and inorganic reinforcement.

The behavior of filled polymers is a complex issue since the composite is influenced by many factors such as filler content, filler characteristics and interfacial adhesion. Polyethylene is a hydrophobic polymer, while ES is a hydrophilic filler [12]. Coupling agents have been added to the filler, in order to achieve a greater interaction

between the polymer matrix and the filler. The coupling agents provide a hydrophobic surface to the filler which increases the adhesion with hydrophobic polymers [13].

The aim of this study is to investigate the viability of a new full bio-composite material made from green polyethylene biopolymer filled with eggshell as bio-filler.

2. Experimental details

The investigation presented in this paper has been divided in two stages.

In the first phase the properties of 6 distinct combinations of PE with calcium carbonate filler are compared: unloaded PE, PE loaded with commercial calcium carbonate, PE filled with eggshell with no additives and treated with silane, titanate and zirconate. Thus, it is intended to determine which coupling agent is more convenient. Then, in the second experimental part, six concentrations of ES treated filler (0, 5, 10, 20, 30 and 40%) have been studied in order to determine which one provides the best characteristics.

2.1 Materials and sample preparation

A high-density polyethylene grade SHA7260 supplied by Braskem (São Paulo, Brasil) has been used as polymer matrix, which is a green polyethylene biopolymer made from sugarcane. The main characteristics of SHA7260 are shown in Table 1. The eggshell was obtained from brown eggs kindly supplied by local bakery. The most suitable coupling agent has been chosen between three possible alternatives: titanium (IV) isopropoxide 80%, trimethoxysilane (98%) and zirconium (IV) bis(diethyl citrate) dipropoxide (86%), all of them were supplied by Sigma–Aldrich (Sigma-Aldrich Química, S.A., Madrid, Spain).

Properties	SHA7260
Melt Flow Rate [g/10 min)]	20
Density [g/cm ³]	0.956
Tensile Strength at Yield [MPa]	29
Flexural Modulus [MPa]	1350
Shore D Hardness	64
Notched Izod Impact Strength [J/m]	25
Vicat Softening Temperature [°C]	124

Table 1: Polymer matrix characteristics

First, raw material eggshell was washed and dried for 24 hours in an oven at 70°C in order to eliminate contaminants and odour, then it was milled and passed through a sieve with a 25 µm mesh using an ultra-centrifugal Mill ZM 200 provided by Retsch (Düsseldorf, Germany). Coupling agents were added to ES powder when appropriate in a 0.7% in weight in a bioethanol solution, then the slurry was taken on a wide tray and put into an oven at 30°C in order to

remove bioethanol by evaporation. The mixture was kept in the oven for one day and then the treated ES particles were powderized. The bioPE, the calcium carbonate either mineral or eggshell and the coupling agents, when appropriate, were mixed using a twin screw co-rotating extruder. For the first stage all the mixtures were prepared with a load of calcium carbonate or eggshell of 20% in weight. For the second stage, six different concentrations in weight of the filler were prepared (0, 5, 10, 20, 30 and 40%). The samples prepared for this work are listed in Table 2. The extruder is divided into four barrels, the profile for the four barrels was set to: 170, 170, 175, 180°C and the outer diameter of the screws is 30mm. After blending, the composite was pelletized in order to be injected. Tensile test, DMA and impact specimens were obtained with injection molding using a Meteor 270/75 injection machine of Mateu & Solé® (Barcelona, Spain) at 200°C injection temperature.

Sample	Description
PE	bioPE
ES	Eggshell
PE-20Cal	bioPE + 20% commercial CaCO ₃
PE-20ES	bioPE + 20% untreated ES
PE-20ES-Sil	bioPE + 20% ES silane treated
PE-20ES-Zir	bioPE + 20% ES zirconate treated
PE-5ES-Tit	bioPE + 5% ES titanate treated
PE-10ES-Tit	bioPE + 10% ES titanate treated
PE-20ES-Tit	bioPE + 20% ES titanate treated
PE-30ES-Tit	bioPE + 30% ES titanate treated
PE-40ES-Tit	bioPE + 40% ES titanate treated

Table 2: Samples list

2.2 Characterization techniques

In order to analyze the obtained blends a complete characterization has been carried out. The chemical analysis of major and minor elements was made by X-ray fluorescence (XRF) using a Philips MagiX PRO Model PW 2440 X-ray Fluorescence Spectrometer, a Rhodium (Rh) anode is used in the X-ray tube together with a beryllium window. The calorimetric analysis was performed using a DSC Mettler-Toledo DSC 821e (Mettler-Toledo S.A.E., Barcelona, Spain). The specimens were placed in sealed aluminum cups with weight varying from 7 to 10 mg for each sample. Samples of 2–3 mg were subjected to a heating (30–290°C at a rate of 10°C min⁻¹) under nitrogen atmosphere (with a flow rate of 40 ml min⁻¹). The thermal analysis was completed with a Thermogravimetric analysis (TGA) of the composite in order to obtain the changes of the physical and chemical properties of the materials as a function of the temperature. A Mettler-Toledo 851e-TGA-SDTA system (Mettler-Toledo Inc., Schwerzenbach, Switzerland) apparatus was employed for the thermogravimetric tests. The sample weight in all tests was approximately 10 mg.

Tests were performed in dynamic mode from room temperature to 900°C, at a heating rate of 20°C min⁻¹ and under nitrogen atmosphere in order to prevent thermo-oxidative reactions (20 ml min⁻¹).

Flexural, tensile, hardness and impact test were carried out in order to mechanically characterize the samples. The flexural and tensile tests were carried out using a universal flexural test machine ELIB 30 (S.A.E. Ibertest, Madrid, Spain). Flexural and tensile tests were done according to ISO 178:2011 [14] and ISO 527-1:2012 [15] respectively. Flexural tests were carried out at a speed of 5 mm·min⁻¹ and with a load cell of 5 kN. A 50mm·min⁻¹ crosshead speed was used to determine tensile strength, elongation at break and elastic modulus starting from the tensile graph. Shore D hardness was obtained in a durometer Model 676-D (J. Bot Instruments, Barcelona, Spain) according ISO 868:2003 [16]. The Charpy impact test was done in order to determine the fracture toughness of the materials. The impact test was conducted using a fully instrumented Metrotec test machine (San Sebastian, Spain) with a Charpy pendulum with an energy of 1 J according to UNE-EN ISO 179-1:2011. All specimens were tested at room temperature. Five test pieces of each sample were used, the presented values were determined as the average of the five values.

Qualitative observation of surface morphology of the aggregate and of the resulting composite was analyzed with a Scanning Electron Microscopy (SEM) supplied by FEL mod. Phenom (FEI Company, Eindhoven, The Netherlands) with an applied voltage of 5 kV. In order to observe the samples it was necessary to coat them with a gold–palladium alloy in a sputter coater EMITECH mod. SC7620 (Quorum Technologies Ltd., East Sussex, UK).

The rheological analysis of the materials has been carried out using a capillary rheometer model Rheoflizer MT (Thermo Haake, Germany) at 180 and 200°C. After charging the barrel five minutes were allowed to reach thermal. The measurements were done using a die with 1mm diameter and with L/D ratios of 10. The shear rates were varied between 100s⁻¹ and 10000s⁻¹. The viscosity values for each material correspond with the average of the five experimental tests. No end-correction was made since the aim was not to determine the viscosity values, it was to determine the general trends for a comparative study.

The study was done in order to determine the general trends for a comparison, so no end-corrections were made which allow to determine the real viscosity values.

2.3 First stage. Selection of the coupling agent

As discussed above, the study was divided into two distinct stages. In the first stage it is determined the appropriateness of the use of a coupling agent that improves adhesion of ES to the polymeric matrix. In the first stage the tests performed are: XRF, DSC,

2.4 Second stage. Study of the filler loading percentage.

After the study of the coupling agent selection, an analysis of the filler loading percentage has been done. With the selected coupling agent, it has been compared the thermal, mechanical and rheological properties for different percentages of ES. The studied concentrations of ES in PE varied within the range of 0 to 40% by weight (0; 5; 10; 20; 30; and 40 wt. %). The objective when producing filled compounds is to balance the properties for optimum performance.

3. Results and discussion

3.1 First stage. Selection of the coupling agent

X-ray fluorescence spectrometry (XRF) has been used for the determination of chemical composition of all the calcium carbonate additives used in this study, Table 3 shows the concentration of major-element concentrations, and Table 4 shows the concentration of the different oxides present in the material. The composition of commercial CaCO_3 is calcium which oxide represents the 99.8% of total, the rest are traces of magnesium, phosphorus and strontium. The eggshell presents a less pure composition because it is from natural source, its composition may vary according to the feed of the hen and it is also contaminated by the inner membrane of the egg. The main component in eggshell is also calcium, which oxide represents the 97.68% of total, the remaining includes mainly magnesium oxide, and to a lesser extend oxides of, sulfur, phosphorus, aluminum, potassium, chlorine, strontium, and silicon. The composition of the treated eggshell confirms treatment applied percentage (20%) for all the applied treatments (silane, titanate and zirconate).

	CaCO₃ (%)	ES (%)	ES-Sil (%)	ES-Tit (%)	ES-Zir (%)
Ca	72.53	69.82	68.21	69.69	69.77
O	27.35	28.96	29.05	28.91	28.88
Mg	0.10	0.50	0.75	0.59	0.52
S	-	0.26	0.23	0.23	0.23
P	0.01	0.19	0.19	0.20	0.18
K	--	0.07	0.08	0.06	0.06
Cl	--	0.06	0.06	0.05	0.05
Al	--	0.08	0.18	--	--
Si	--	0.03	0.25	0.02	0.03
Sr	0.02	0.04	0.04	0.04	0.04
Ba	--	--	--	--	0.05
Na	--	--	0.96	--	--
Ti	--	--	--	0.21	--
Zr	--	--	--	--	0.20

Table 3. Major-element concentrations obtained by XRF in fillers

	CaCO₃ (%)	ES (%)	ES-Sil (%)	ES-Tit (%)	ES-Zir (%)
CaO	99.80	97.68	95.38	97.36	97.60
SrO	0.02	0.04	0.05	0.05	0.05
SO₃	--	0.66	0.57	0.58	0.57
SiO₂	--	0.07	0.54	0.05	0.06
P₂O₅	0.01	0.43	0.43	0.45	0.42

Na₂O	--	--	1.29	--	--
MgO	0.16	0.83	1.24	0.97	0.86
K₂O	--	0.08	0.10	0.08	0.07
Cl₂O₃	--	0.06	0.06	0.05	0.05
Al₂O₃	--	0.15	0.34	--	--
BaO	--	--	--	--	0.05
ZrO₂	--	--	--	--	0.27
TiO₂	--	--	--	0.41	--

Table 4. Oxides obtained by XRF

The influence of the coupling agent on the calorimetric properties has been investigated by DSC study of the composites. Figure 1 depicts the dynamic temperature thermograms which were shifted vertically for ease of presentation, thermal properties such as melting temperature (T_m), enthalpy of melting (AH_m) and the degradation temperature (T_d) are listed in Table 5. All the specimens for the DSC analysis were obtained after the injection molding of the samples. All the DSC curves are characterized by the presence of a peak around 135°C which is the value of the melting of the PE component of the composite. In composite materials, this value is slightly modified due to the presence of other components. The most remarkable case is the specimen treated with titanate (PE-20ES-Tit) since there is a decrease of the melting temperature until 132.72°C. Analyzing the values of the enthalpy it is noted that the higher value is reached for the unloaded PE (146.67 J/g), the rest of the composites present similar values (around 130 J/g) except the ES treated with titanate (PE-20ES-Tit) which presents a significant drop compared to the rest (105.44 J/g). The values of the degradation temperature are also similar for all samples (around 235°C) except for the ES treated with titanate in which the degradation is delayed 15°C reaching a value of 252.76°C. Therefore the titanate used as coupling agent for the PE-20ES composite increases its temperature working range and reduces the energy required to melt the compound.

	Normalize Enthalpy (J/g)	Melting Temperature (°C)	Degradation Temperature (°C)
PE	146.67	135.08	233.20
PE-20Cal	126.60	134.25	234.84
PE-20ES	130.02	135.79	236.57
PE-20ES-Sil	130.00	136.41	236.37
PE-20ES-Tit	105.44	132.76	252.76
PE-20ES-Zir	128.63	136.06	236.89

Table 5. DSC results for raw PE and composites with different coupling agents

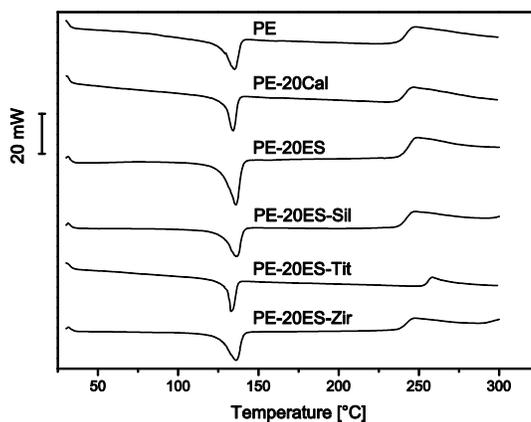


Figure 1

The weight loss of a polymer as a function of temperature can be determined by the TGA technique. It is interesting to determine the weight loss due to thermal degradation since it is an irreversible process. The TGA analysis has been performed for all the studied materials and for the ES powder, all the thermograms are presented in Figure 2. The raw bioPE is degraded in a single step beginning at 470.11°C and ending at 508°C, presenting a weight loss of 91.78%.

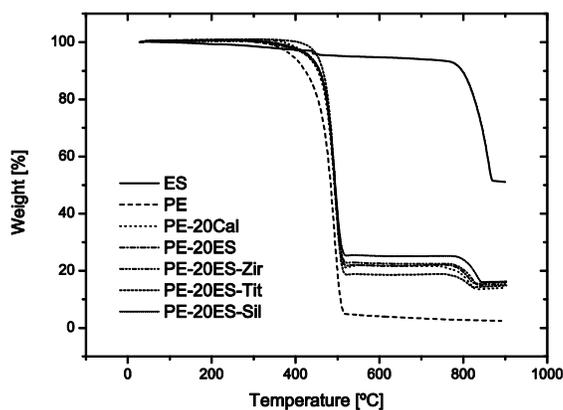


Figure 2

The curve of the thermogram of neat ES shows a slight decrease in mass, at 275°C the organic component of the ES is degraded with a weight loss is 2.895%. At 750°C there is an abrupt weight loss of 41.81% due to the loss of CO₂ from the ES carbonate, according to equation 1. After that, there is a very negligible weight loss and the sample is transformed to stable calcium oxide.



Composites containing PE and Calcium Carbonate present the two steps described before for the single components. The first step in the composites is more pronounced and shows the weight loss caused by the decomposition of the PE which starts at about 470°C, the average weight loss for all composites is about 78% by weight, which corresponds to the percentage of PE in the mixture (80%). The end of this first weight loss region is variable, the unloaded PE is the one that presents a shorter region (508°C). These results agree with the obtained by Fombuena in CaCO₃ composites obtained from seashell [10]. Compounds with ES behave all the same, regardless of the treatment the ES has received and whether it has been treated or not, in all of them the decomposition of PE is extended approximately 1°C more as shown in Table 5, so this increase of rate can be considered negligible. The second step is less marked since it is due to the CO₂ released by the decomposition with heat of the CaCO₃, either it is from natural (ES) or chemical source. From a thermal point of view, the ES is a good bio-filler for polymeric industry since it is degraded at higher temperatures than processed ones.

Table 6 summarizes the mechanical properties obtained by tensile, flexural, impact and hardness tests for the first part of the study. All PE–filler composites showed a higher tensile modulus compared with the PE. This effect is more pronounced in PE-ES composites especially those treated with silane (20% increase) and titanate (19% increase). The addition of the CaCO₃ induces the decrease of the tensile strength. The decrease in tensile strength is due to the poor adhesion of the filler-matrix and the agglomeration of filler particles. The tensile strength decrease is the same for all CaCO₃-PE compounds studied, regardless whether the used filler is from chemical or natural source or the coupling agent used. The elongation at break feature is drastically reduced by the addition of the filler. This effect is more pronounced for natural filler (ES) regardless of the treatment it has been subjected to, but there is no significant variation between the different values of elongation for the different composites with ES. So, this parameter does not provide information for the selection of a coupling agent, but confirms the poor or no compatibility between the components, so there is no stress transfer phenomenon and the filler particle acts as a stress concentrator which leads to an early fracture [18].

	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation (%)	Flexural Modulus (MPa)	Flexural Strength (MPa)	Shore D Hardness	Charpy's impact energy (kJ/m²)
PE	373 ± 8.6	19.6 ± 0.2	520 ± 8.8	804 ± 30.0	23.9 ± 0.2	56.6 ± 0.5	0.28 ± 0.02
PE-20Cal	372 ± 12.7	16.8 ± 0.7	45.5 ± 2.0	785 ± 50.6	22.6 ± 0.5	56.6 ± 2.1	0.19 ± 0.01
PE-20ES	402 ± 21.5	17.1 ± 0.1	20.3 ± 0.8	826 ± 75.8	24.3 ± 0.6	57.4 ± 1.5	0.16 ± 0.01

PE-20ES-Sil	445 ± 11.8	16.9 ± 0.3	17.4 ± 0.1	946± 27.0	24.8 ± 1.2	57.0 ± 1.2	0.16 ± 0.01
PE-20ES-Tit	439 ± 11.5	17.4 ± 0.6	17.3 ± 3.3	1021± 52.8	25.2 ± 0.3	57.8 ± 1.6	0.16 ± 0.01
PE-20ES-Zir	390 ± 17.0	19.6 ± 0.2	20.6 ± 1.4	826± 31.3	24.0 ± 0.6	57.0 ± 1.2	0.16 ± 0.01

Table 6. Mechanical properties for raw PE and ES composites with different coupling agents

The flexural properties present more information in order to select the most suitable coupling agent. The commercial calcium composite (PE-20Cal) presents a decrease of the flexural modulus. In contrast when the calcium comes from ES powder its addition increases the stiffness of the bioPE since it increases flexural modulus of all the composites. The composites PE-20ES-Sil and PE-20ES-Tit present higher variations, specially the titanate which increases the flexural modulus a 26.93% respect to the unfilled PE. This comparison between treated ES composites shows the effect of the coupling agent over the filler since all the ES particles present the same size and geometry. The flexural strength presents a similar behavior, it decreases in PE-20Cal composite, but it increases for ES composites. In this case there are not significant differences between the composites.

The mechanical properties are completed with the study of hardness and resilience. There is no significant differences in shore D hardness between the unfilled polymer and the composites regardless whether it is chemical calcium carbonate or eggshell. In the case of eggshell coupling agent does not influence on the hardness either. However, the addition of calcium carbonate to PE brittles the composite due to the brittle nature of the reinforcing material. This effect occurs in all the composites, but it is a bit more pronounced in the ES composites. The coupling agent in the ES composites does not affect the ability of the material to absorb the impact energy.

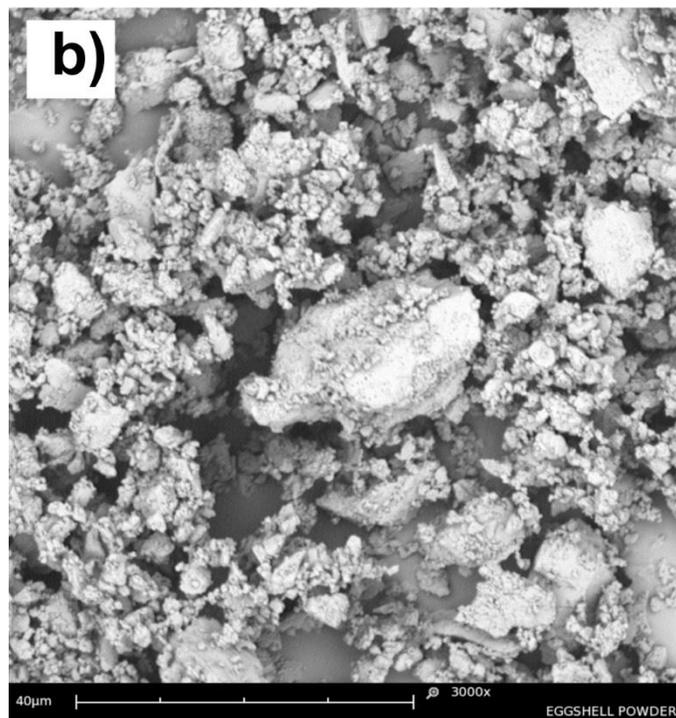
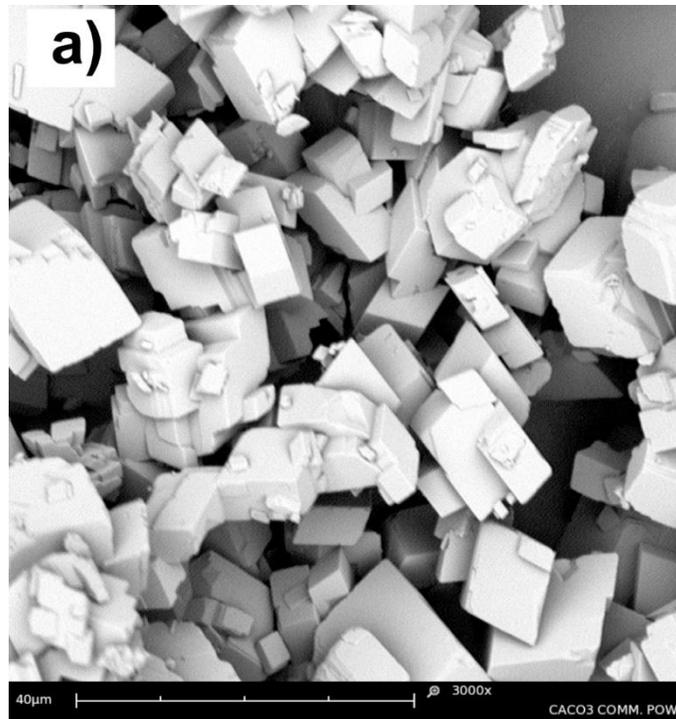


Figure 3

Figure 3 provides the SEM micrographs of the different used fillers. Commercial calcium carbonate is shown in Figure 3a, the unique presence of calcite crystals is observed which exhibits the characteristic rhombohedral morphology with smooth surface. The particle size is homogeneous and there is a uniform size distribution. The

micrograph of natural calcium carbonate presents a completely different morphology compared to commercial calcium carbonate (Figure 3b). This is because their origin is completely different, natural CC is obtained by a milling process of eggshell, while the commercial one was acquired from precipitate processes. As observed the eggshell powder particles have irregular shape and a wide particle size, resulting of the comminution process used. The particle surface is rough with a high surface irregularity.

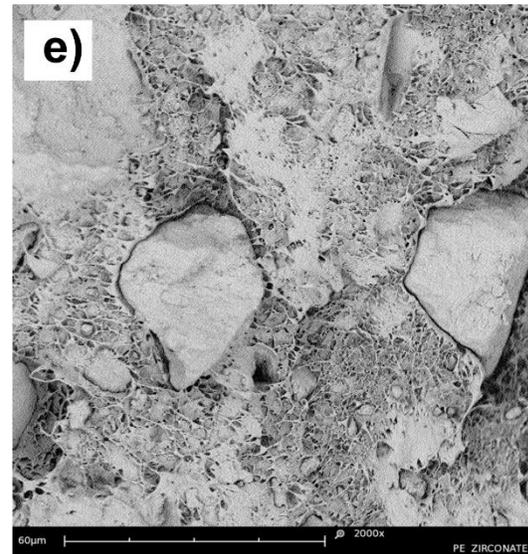
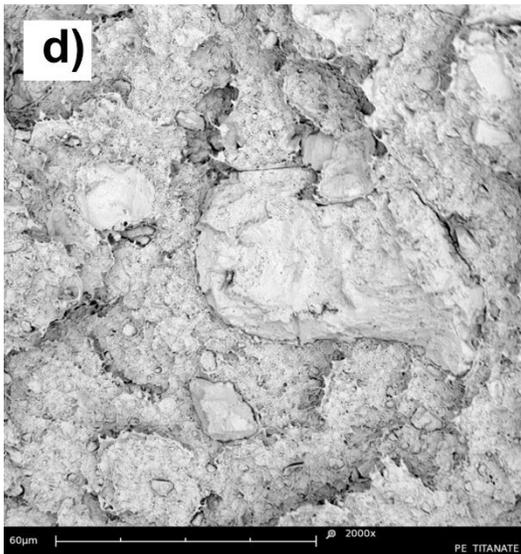
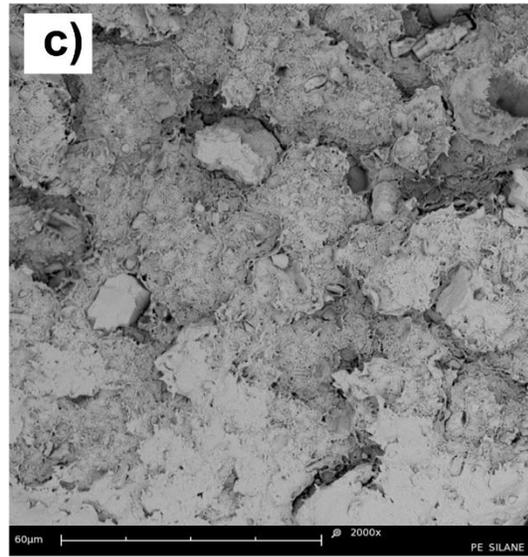
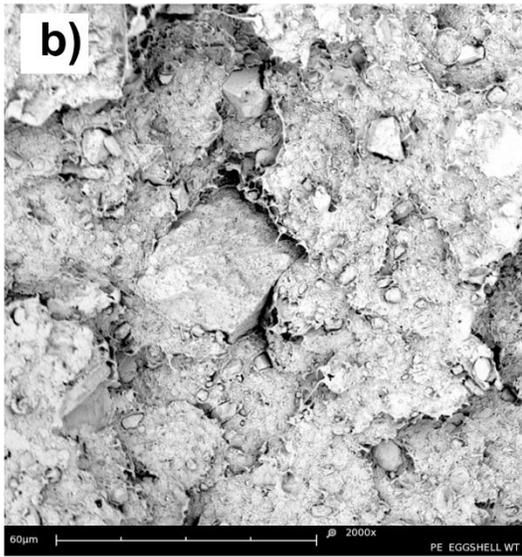
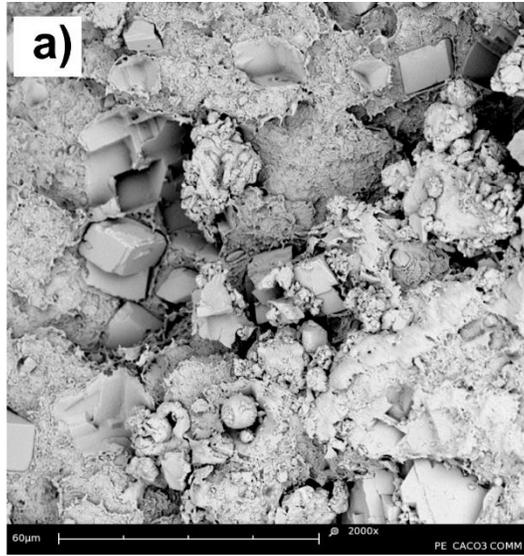


Figure 4

The SEM micrographs of the impact fracture of the composites are shown in Figure 4. It is interesting to study the internal structure of the composites since the mechanical behavior is consequence of it. Figure 4a displays the micrograph of the bioPE blended with commercial CaCO_3 . A reasonably even distribution of CaCO_3 in the PE matrix of the composite was detected. In the picture, a rough surface of the matrix can be observed due to the fracture process. The matrix surface presents some holes caused by the detachment of filler which indicates poor adhesion between the two components. So, there is lack of interaction between the filler and the matrix. The gaps around the filler particle also indicate the deficient interaction of the components. This gap causes a discontinuity in the material and it acts as a stress concentrator, so the composite material becomes more brittle. Figure 4b shows the picture of the fracture surfaces of PE/ES untreated. Morphological analysis using SEM clearly shows the difference in the morphology of the compounds if it is used commercial CaCO_3 or ES. It is noted that the ES particles which are within the PE matrix present a great dispersion and variety of sizes. The interface between the ES particle and PE matrix is obvious. In Figure 4c the ES has been treated with silane, but in the SEM picture there is no evidence of the coupling agent over the morphology since there is not interaction between the load and the matrix. The composite of the Figure 4d has been treated with titanate, and it presents variations. There are peaks in the matrix which indicate plastic deformation of the matrix before rupture. The filler is dispersed over the matrix with several sizes. The area between the matrix and the filler is narrower, as consequence of the coupling agent, this justifies the increase of the flexural modulus. Figure 4e depicts the composite of bioPE-ES modified with zirconate where adhesions between the matrix and the filler are observed, this justifies the increase in elongation compared to other composites, but, the embrittle effect is not completely eliminated. The improvement of the adhesion is a key factor, poor interfacial region weakens the composite. Toro [6] pointed that when a crack is generated due to an impact it is propagated towards poor interfacial regions, so the composite is broken easily.

After studying the obtained results it has been determined that the best coupling agent is the titanate. The titanate is the coupling agent which presents better thermal characteristics, it decreases the melting temperature, so it is easier to melt the composite and it also increases the degradation temperature. The mechanical properties of PE-20ES-Tit are not particularly outstanding over the other ES composites, except the stiffness which is clearly better than the other composites. The rest of the mechanical properties have been improved over raw PE, but all the treated

composites presents similar values. In the SEM micrographs a better adhesion of the filler to the matrix is observed, which justifies the higher values of flexural modulus over the other composites.

3.2 Second stage. Study of the filler loading percentage.

Once the coupling agent has been chosen the second stage of the investigation consists in an analysis of the best percentage of ES loading as filler in bio-PE. Thermal, mechanical and rheological analysis has been done.

The incorporation of ES in the composites presents a dilution effect over the enthalpy, as shown in the DSC results in Table 7. In the studied composite, the enthalpy and the amount of ES load are inversely proportional. The reduction of enthalpy means that the heat needed to melt the polymer is reduced, so there is a reduction of power needed and therefore during the extrusion and injection molding processes there is a cost saving. The melting temperature does not present variation nor correlation with the amount of filler. In contrast, the degradation temperature shows an increasing trend with the amount of filler. Figure 5 shows the typical thermogravimetric curves for PE and ES composites for different filler content. Figure 5 shows the two steps described before for all the composites, the first step corresponds to the decomposition of the PE. The weight loss in the first step matches with the amount of the PE in the composite. After the first step, the amount of ES was very close to the theoretical filler content, which indicates that the filler was well distributed in the matrix.

	Normalized Enthalpy (J/g)	Melting Temperature (°C)	Degradation Temperature (°C)
PE	146.7	135.1	233.2
PE-5ES-Tit	137.2	137.4	245.7
PE-10ES-Tit	131.4	135.0	258.8
PE-20ES-Tit	105.4	132.8	252.9
PE-30ES-Tit	100.5	133.9	257.0
PE-40ES-Tit	84.79	135.2	259.8

Table 7. Summary of the values obtained by DSC with different ES contents

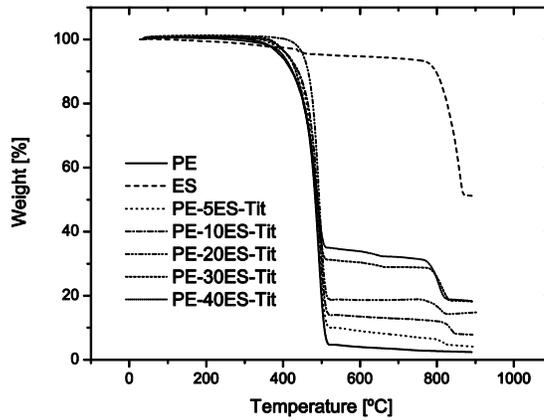


Figure 5

The mechanical properties obtained by tensile and flexural tests of PE and eggshell composites are summarized in Table 8. The flexural modulus increases evidently with the content addition of filler, the increase is moderate until a percentage of 30% of ES with an increase respect unfilled material of nearly 30% reaching an average value of 1,038.62MPa. Adding a 10% more of filler, the flexural modulus is fired up until an increase higher than 88% respect the unfilled material. When the filler content is low there is a better dispersion and the distance between filler particles is large, so it affects the flexural modulus independently. But, as the eggshell content increases the space between particles decreases. So, the effect of each filler particle over the flexural modulus is superposed, which lead to the flexural modulus increasing evidently.

	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation (%)	Flexural Modulus (MPa)	Flexural Strength (MPa)
PE	373 ± 8.6	19.6 ± 0.2	520 ± 8.8	804 ± 30.0	23.9 ± 0.2
PE-5ES-Tit	396 ± 13.3	19.2 ± 0.4	58.1 ± 2.5	855 ± 94.9	24.2 ± 0.5
PE-10ES-Tit	408 ± 7.9	18.6 ± 0.5	35.5 ± 6.1	879 ± 44.0	25.0 ± 0.2
PE-20ES-Tit	439 ± 11.8	17.4 ± 0.6	17.3 ± 3.3	1021 ± 71.5	25.2 ± 0.3
PE-30ES-Tit	562 ± 80.3	16.6 ± 0.3	10.7 ± 0.6	1038 ± 81.7	25.8 ± 0.2
PE-40ES-Tit	616 ± 87.9	14.7 ± 0.5	6.98 ± 1.1	1513 ± 155.1	25.8 ± 0.5

Table 8. Tensile and flexural properties of PE/ES composites with different Eggshell contents

Table 8 also shows that Young's modulus increases in the blends with the increase of ES filler concentration. The elastic modulus of elasticity ranged from 373.01 to 616.39 MPa for eggshell ratio between 0% and 40%, respectively. The increase for composites containing 40wt. % ES is nearly 65%. The high intrinsic stiffness of the

ES provides an increasing stiffness to the composite with the increasing filler loading compared to polymeric material. This fact is also present in other studies such Ghabeer's [5] and Toro [6] where the ES has been added into a polypropylene matrix. It is observed that the tensile strength for the composites decreases with increasing filler content. The decrease is caused by the interfacial adhesion between the PE matrix and the ES filler which is critical in the strength of particulate-filled polymer composites since it enables the transference of a small section of stress to the filler particle during deformation. The elongation at break for the composites decreases as the filler content increases because the addition of ES powder causes a stiffening and hardening of the composite. This reduction indicates the incapacity of the filler to support the stress transfer from the polymer to the matrix which shows a poor compatibility between the components. Similar observations on the variation of elongation at break have been reported by Doufnoune and Shuhadah [19, 20] for other filled polymer systems.

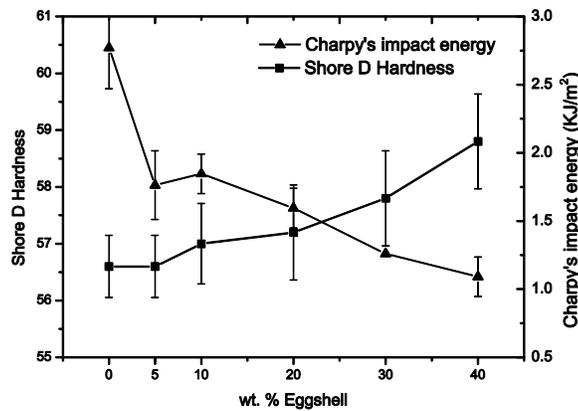


Figure 6

Figure 6 shows the Shore D hardness and the Charpy Impact Energy values of the composites. The hardness increased gradually as the %wt ES addition is increased. This is due to increment in the polymer matrix of the percentage of ES which is hard and brittle. A substantial improvement in hardness values was obtained in the reinforced polymer matrix in comparison with the unreinforced polymer matrix. This is in line with the earlier works of Suwanprateeb [21]. The toughness of the composites is degraded by the brittle nature of the reinforcing materials (ES) as it is shown in the impact results. As the percent eggshell particle addition increases in the composites the impact energy absorbed decreases. The impact energy of the composites is degraded by the brittle nature of the reinforcing materials (ES). There is a clear drop in the toughness of the samples respect of the unloaded sample.

With an addition of 5% wt. of ES a decrease of 36.36% is obtained. But the drop between loaded samples is low, this indicates a good interaction between the polymeric matrix and the biofiller.

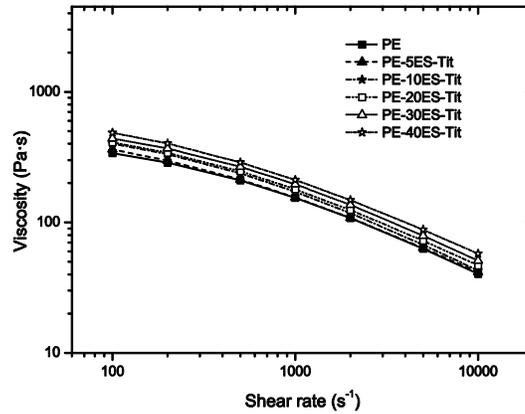


Figure 7

A rheological analysis of the composites under molten state allows to study the effect of the ES on the internal and processing properties. Figure 7 depicts the apparent viscosity curves of pure bioPE and bioPE+ES composites measured at 180°C as function of shear rate ranging from 100 to 10.000 s⁻¹. In all studied range there is a big dependence of viscosity from shear rate, all of the composites present a pseudoplastic behavior. The apparent viscosity of the composites increases as the ES content increases due the high specific area of the filler which prevent composite melt from flowing. The effect of the filler on the viscosity does not vary in all the studied range. High concentrated bioPE-ES composites would present difficulties due to high viscosity values especially in processes working at low shear rates such rotational molding or thermoforming. This issue is less important in manufacturing processes which work with high shear rates such injection molding since the viscosity decreases with shear rate at constant temperature.

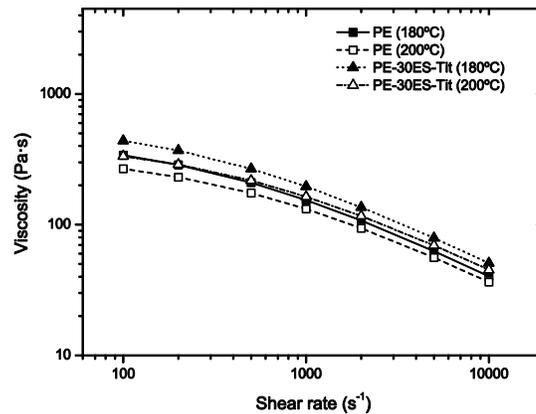


Figure 8

Shear viscosity decreases as temperature is increased, this effect is shown in Figure 8. The sensitivity to temperature is an important feature since it influences on the processing conditions. When temperature is increased there is thermal motion of the molecules which causes greater free volume in the polymer and as a consequence there is a decrease in intramolecular or intermolecular resistance associated with the viscosity [22].

4. Conclusions

This project was undertaken in order to develop a new composite from natural source which upgrade an industrial byproduct such as the eggshell. The eggshell presents a very similar chemical composition to mineral calcium carbonate as it has been confirmed in the XRF tests, so from a chemical point of view the ES is a suitable substitute. In the first part of the study different coupling agents were studied in order to identify the one which enhances the interaction between the polyethylene matrix and the eggshell filler. The melting point of the PE it is not significantly affected with the addition of calcium carbonate, but the degradation temperature is increased significantly when ES is modified with titanate. The addition of calcium carbonate in all the studied compositions reduces the enthalpy, since the CaCO_3 it is not fusible, this effect is also emphasized with the titanate modification. From the thermal analysis it can be concluded that ES is a good biofiller since it is not degraded at the processing temperatures of the matrix, the titanate is the best coupling agent of all the studied. The use of titanate improves the processability of the composite since it enlarges the manufacturing range temperature and also it is necessary less energy in order to melt the material. From the analysis of the mechanical properties it can be seen that calcium carbonate brittles the composites, it acts as stress concentrator since there is bad interaction between the load and the matrix. The addition of titanate as compatibilizer reduces the lack of adhesion between the components of the composite and improves

the mechanical behavior despite the brittle effect is not completely eliminated. In the first part of the study it can be concluded that the titanate is the best coupling agent between bioPE matrix and ES.

In the second part of the study PE-ES composites with different filler content were developed in order to determine the influence of the filler over the mechanical, thermal and rheological properties. The increasing percentage of ES in the composition decreases linearly the enthalpy and delays the degradation temperature, but it does not affect the melting temperature. The mechanical properties are also affected by the percentage of load, the tensile strength decreases as consequence of the bad adhesion between the matrix and the filler and the toughness is degraded due to the brittle nature of the ES.

In order to analyze the processability of the mixture a rheological analysis has been done. The apparent shear viscosity for all the investigated samples present a non-linear manner, the viscosity decreased with the increase of the shear rate, showing a shear thinning behavior. The addition of ES increased the apparent shear viscosity which hinders their processing at low shear rates, but manufacturing processes such extrusion or injection molding are suitable because they work at high shear rates.

In conclusion, waste such as the eggshell can easily be used as filler in order to obtain a new environmentally friendly material, which lowers the cost of a new and still expensive green polyethylene biopolymer.

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Figure Caption

Figure 1.- DSC thermograms for raw PE and composites with different coupling agents

Figure 2.- Thermogravimetric curves for raw PE and composites with different coupling agents

Figure 3.- SEM images (3000x) of filler added (a) commercial CaCO_3 , (b) milled eggshell

Figure 4.- SEM images (2000x) of impact fracture of the composites: (a) PE-20Cal, (b) PE-20ES, (c) PE-20ES-Sil, (d) PE-20ES-Zir, (e) PE-20ES-Tit

Figure 5.- Thermogravimetric curves for ES, raw PE and PE/ES composites in terms of the wt. % of ES

Figure 6.- Plot evolution of the Shore D hardness and Charpy's impact energy of PE/ES composites with different ES contents

Figure 7.- Rheological comparisons of raw PE and PE-ES composites with different ES contents (180°C)

Figure 8.- Temperature effect over rheological curves.

Table Captions

Table 1.- Polymer matrix characteristics.

Table 2.- Samples list.

Table 3.- Major-element concentrations obtained by XRF

Table 4.- Oxides obtained by XRF

Table 5.- DSC results for raw PE and composites with different coupling agents

Table 6.- Mechanical properties for raw PE and ES composites with different coupling agents

Table 7.- Summary of the values obtained by DSC with different ES contents

Table 8.- Tensile and flexural properties of PE/ES composites with different Eggshell contents