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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 $CaCO_3$ can effectively improve the mechanical properties of bioPE, 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.

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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 et al. [5], Toro et al. [6,7] and Kang et al. [8] have replaced the mineral calcium carbonate by ES developing bio-compounds. Others like Ramdani et al. [9] and Fombuena et al. [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

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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).

First, raw material eggshell was washed and dried for 24 h in an oven at 70 °C in order to eliminate contaminants and odor, 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 30 mm. 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.

Table 1
Polymer matrix characteristics.

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 2
Samples list.

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

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 50 mm 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 ISO 179-1:2011 [17]. 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. Flexural tests were carried out at a speed of 5 mm min^{-1} and with a load cell of 5 kN. A 50 mm 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

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