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Development of slate fiber reinforced high density polyethylene composites for injection molding

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ABSTRACT

During the last decade the use of fiber reinforced composite materials has consolidated as an attracting alternative to traditional materials due to an excellent balance between mechanical properties and lightweight. One drawback related to the use of inorganic fibers such as those derived from siliceous materials is the relative low compatibility with conventional organic polymer matrices. Surface treatments with coupling agents and the use of copolymers allow increasing fiber–matrix interactions which has a positive effect on overall properties of composites. In this research work we report the use of slate fiber treated with different coupling agents as reinforcement for high density polyethylene from sugarcane. A silane (propyltrimethoxy silane; PTMS) and a graft copolymer (polyethylene-graft-maleic anhydride; PE-g-MA) were used to improve fiber–matrix interactions on HDPE-slate fiber. The effect of the different compatibilizing systems and slate fiber content were evaluated by scanning electron microscopy (SEM), dynamic thermomechanical analysis (DTMA) as well as mechanical properties (tensile, flexural and impact). The results show that the use of silane coupling agents leads to higher fiber–matrix interactions which has a positive effect on overall mechanical properties. Interesting results are obtained for composites containing 30 wt.% slate fiber previously treated with propyltrimethoxy silane (PTMS) with an increase in tensile and flexural strength of about 16% and 18% respectively.

1. Introduction

In the last decade a remarkable increase in concern about the environment has been detected and different topics related to petroleum depletion, recycling, biodegradation, waste upgrading, etc. act as leading forces for the development of new and environmentally friendly materials. This situation has been particularly marked in the field of polymers and polymer-based composites which traditionally use petroleum-based polymers characterized by non-biodegradability. In the case of composite materials, research has been focused on the use of low environmental impact polymer matrices and reinforcing fibers [1–5].

Commodity plastics such as polyolefins (polyethylene, polypropylene, etc.) find attracting uses in medium to low technical applications due to excellent balance between overall properties (mechanical, thermal, chemical resistance, etc.) and easy processing by conventional techniques such as extrusion and injection molding. Nevertheless these polymers do not reach, in general, typical properties of technical or engineering polymers. For this reason, it is quite usual to reinforce commodity plastics (and also, engineering plastics) [6] with short or long fibers such as natural (flax, sisal, coir, jute, henequen, etc.) [7–13], inorganic (glass fiber) [14–17], synthetic (aramid, polyamide, polyester, etc.) [18], carbon fiber [19], etc. in order to provide them with improved properties such as stiffness, thermal resistance, shrinkage reduction in order to offer materials in the frontier line separation between commodity and engineering/technical plastics. Although glass fiber has been the most used reinforcing fiber for thermoplastics, in the last years new inorganic fibers have invaded the composite's industry as alternatives to glass and carbon fibers for industrial, medical, electrical, etc. applications [20]. This is the case of basalt fiber obtained from widely spread basalt mineral, which offers some advantages with regard to glass fiber by considering Life Cycle Assessment (LCA) approach or nature silica [21–24]. Another recent initiative is the slate fiber (SF) obtained from slate wastes.

Slate is a widely used material for roofing; this industry is characterized by a large waste generation (one ton end product could generate almost 30 tons of waste) thus leading to a high environmental impact. For this reason the survival of this industry is directly linked to its capacity to upgrade wastes [25]. Some

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attempts have been used in order to upgrade slate powder as filler for polymers [26] or even as a filler for thermosetting resins such as unsaturated polyesters or epoxies. Galicia (a region located in northwest Spain) is one of the largest producers of slate in Europe with about 90% production in Europe. Being aware of the high environmental impact of the generated slate wastes, important efforts focused on slate waste upgrading have been made in the last years. Mifibra is a Galician company which commercializes a novel fiber obtained from slate wastes with potential uses in composite's industry (pultruded bars and profiles, fabrics for laminates, isolation panels, twisted yarns, etc.). This contributes twice to environment: on one hand the large volume amounts of slate wastes are reduced and on the other hand, wastes represent the base material for fiber production with new and attractive industrial and technical uses.

The main aim of this work is manufacturing of new environmentally friendly thermoplastic reinforced composites by using high density polyethylene from sugarcane and slate fiber from slate wastes. Slate fibers treated with a hydrophobic silane namely, propyltrimethoxy silane (PTMS) are used in combination with and without conventional compatibilizer copolymer (polyethylene graft maleic anhydride, PE-*g*-MA) to evaluate the influence on overall properties for a fixed slate fiber content of 20 wt.%. In addition, the effect of the slate fiber content in the 5–30 wt.% on mechanical properties of HDPE-slate fiber composites is evaluated.

2. Materials and methods

2.1. Materials

Base polymer for composites was high density polyethylene (HDPE) commercial grade SHA7260 from Braskem (BRASKEM, Sao Paulo, Brasil) supplied by FKuR (FKuR Kunststoff GmbH, Willich, Germany) with a minimum biobased content of 94% (as determined by ASTM D6866). It is characterized by a melt flow index (MFI) of 20 g/10 min at 190 °C and a density of 0.955 g cm^{-3} and it is suitable for injection molding.

Slate fiber (SF) from Mifibra (MIFIBRA S.L., Ourense, Spain) 15 mm in length and a diameter in the 15–23 μm range was used as reinforcing fiber for HDPE-based composites. Before composite manufacturing, slate fibers were washed with distilled water and subsequently they were placed in an oven at 350 °C for 3 h to remove organic sizings. Chemical characterization of slate fiber was carried out with X-ray fluorescence spectroscopy in a sequential X-ray spectrometer PHILIPS MAGIX PRO PW2400 equipped with a rhodium tube and a beryllium window. Results of chemical composition were analyzed by using the SuperQ analytical software. Table 1 shows a summary of the chemical composition of slate fiber obtained by XRF.

A hydrophobic silane coupling agent was used to improve fiber–matrix interactions: propyl trimethoxy silane; PTMS supplied by Sigma Aldrich (Sigma Aldrich, Madrid, Spain). A typical graft copolymer polyethylene-graft-maleic anhydride; PE-*g*-MA supplied by Sigma Aldrich was also used to increase compatibility between the inorganic slate fiber and the organic HDPE matrix.

Table 1
Chemical composition of slate fiber obtained by X-ray fluorescence spectroscopy.

Composition	wt.%
SiO_2	53.50
Fe_2O_3	15.70
Al_2O_3	15.11
CaO	10.05
TiO_2	3.02
K_2O	2.38
MnO	0.25

Table 2
Composition of HDPE-slate fiber composites and their code.

Code	HDPE (wt.%)	Silane type: slate fiber content (wt.%)	PE-*g*-MA (wt.%)
SF	80	Untreated: 20	–
SF-MA	78	Untreated: 20	2
SF-PTMS	80	Silane treated TMPS: 20	–
SF-PTMS-MA	78	Silane treated TMPS: 20	2

2.2. HDPE–SF composite manufacturing

Four different HDPE–SF composite formulations were manufactured by varying the compatibilizing system at a constant slate content (see Table 2).

Silane treatment was carried out as follows: 1 wt.% silane with respect to the slate fiber to silanize, was dissolved in a 50/50 water/methanol solution and the final solution was stirred for 10 min to ensure homogenization and hydrolysis of alkoxy groups. After this, slate fiber was immersed in this solution for 15 min and subsequently, slate fiber was removed and was washed with distilled water and dried at room temperature for 24 h.

HDPE–SF composites were manufactured with a twin screw extruder with 4 temperature stages (160 °C, 160 °C, 165 °C and 170 °C from the feeding to the dye) at a rotating speed of 40 rpm and subsequently pelletized. Standardized samples for testing were obtained with an injection molding machine Meteor 270/75 (Mateu & Solé, Barcelona, Spain) at an injection temperature of 190 °C.

2.3. Mechanical characterization of HDPE-slate fiber composites

HDPE–SF composites were characterized by standardized mechanical tests: tensile, flexural, hardness and impact. Tensile and flexural tests were carried out at room temperature in a universal test machine Ibertest ELIB 30 (S.A.E. Ibertest, Madrid, España) following the guidelines of the ISO 527-5 and ISO 178 respectively. A 5 kN load cell was used and the crosshead speed was set to 5 mm min^{-1}. Al least five samples were tested and average values of different parameters were calculated.

With regard to the impact test, a 1 J Charpy's pendulum (Metrotec S.A., San Sebastián, Spain) was used as indicated in the ISO 179:1993 standard. Five different notched samples ("V" notch type at 45° with a notch radius of 0.25 mm) were tested and average values of absorbed energy were calculated.

Hardness characterization was obtained with a Shore D durometer 673-D (Instrumentos J. Bot S.A., Barcelona, Spain) following the ISO 868. At least five different measurements were taken and average values were calculated.

2.4. Characterization of HDPE-slate fiber fractured surfaces

Fractured surfaces of HDPE–SF composites from impact tests were analyzed by scanning electron microscopy (SEM) with a FEI mod. Phenom (FEI Company, Eindoven, The Netherlands). All fractured samples were previously coated with a thin gold–palladium alloy with a sputter coater EMITECH model SC7620 (Quorum Technologies, East Suseex, UK).

2.5. DMA analysis of BioPE-Slate fiber composites

Mechanical dynamical properties of HDPE–SF composites were evaluated in an oscillatory rheometer AR G2 (TA Instruments, New Castle, EEUU) equipped with a DMA accessory (torsion mode) for solid samples. Samples sizing 40 × 10 × 4 mm^3 were subjected to a temperature program from −50 °C up to 100 °C at a heating