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The production and properties of polylactide composites filled with expanded graphite

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ABSTRACT

Composites have been produced by melt-blending biodegradable polylactide (PLA) with commercially available expanded graphite (EG). Using different techniques of addition, the manifold effects of EG on PLA molecular, thermo-mechanical and fire-retardant properties were evaluated. The EG nanofiller provides PLA composites with competitive functional properties. They have a high rigidity, with Young's modulus and storage modulus increasing with EG content. They also have excellent thermal stability while preserving the glass transition and melting temperature of the original PLA matrix. Purification and pre-dispersion of EG nanofiller proved beneficial for preserving PLA molecular weights and led to improved mechanical performance. The presence of dispersed graphene nanolayers in PLA significantly accelerated the polyester crystallization process. The flame retardant properties also displayed improvements with a large decrease in the maximum rate of heat release as recorded by cone calorimetry, whereas the horizontal burning test (UL94 HB) was successfully passed revealing non-dripping and char formation.

1. Introduction

Polylactide or poly(lactic acid) (**PLA**) is currently receiving considerable attention for conventional uses, such as packaging materials as well as production of fibres, and more recently, as composites for technical applications. Having a principal position on the market of biodegradable polymers, PLA is undoubtedly one of the most promising candidates for further developments; it is not only biodegradable but also produced from renewable resources [1–4]. With a tremendous increase in production capacity over the past years, PLA is potentially interesting for engineering applications (electronic and electrical devices, mechanical and automotive parts, etc.), but it is required the tailoring of its properties to reach the end-user demands. For further applications, the profile of PLA properties can be tuned by combining this polyester matrix with different dispersed phases: (nano)fillers, impact modifiers, flame retardants, plasticizers, other polymers, etc. [3,5–10].

The production of filled-PLA grades using various types of micro- or nano-mineral fillers, surface-modified or not, can be an interesting solution to reduce PLA global price and to improve some specific properties such as rigidity, dimensional stability, heat deflection temperature, processability, etc. [5–11].

Nanocomposites with improved properties (stiffness, thermal stability, fire retardancy, lower permeability, etc.) have been recently obtained by melt-blending PLA with different nanofillers such as organo-modified layered silicates (**OMLS**), carbon nanotubes (**CNTs**), polyhedral oligomeric silsesquioxanes (**POSS**), etc. [5–7,12–14].

The polymer nanocomposites filled with nanosized carbonaceous fillers such as CNTs were proved to exhibit a remarkable balance of performances in terms of mechanical, fire resistance, electrical conductivity and barrier properties [15]. Generally, the high cost of CNTs has limited their extensive use in industrial sectors and other alternatives are to be considered.

Graphite combines the lower price and the layered structure of clays with the superior thermal and electrical properties of CNTs. It can be thus an alternative to both clays and CNTs to make polymer composites with competitive multifunctional properties. Graphite is consisting of graphene nanosheets [15,16] and has thermal and

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electrical characteristics usually associated with metals which make it suitable for applications where its properties like heat stability, lubricant ability, thermal and electrical conductivity are required.

An important number of studies have been recently carried out on dispersion of expanded graphite (**EG**) and exfoliated graphite nanoplatelets (**GNP**) in engineering or commercial polymers such as poly(phenylene sulfide), polyamide 6, epoxy resins, poly(methyl methacrylate) or polypropylene [17–21]. In all cases the natural graphite must undergo chemical treatments to allow the polymer chains entering between the nanofiller layers. EG reinforced/conductive polymer composites were prepared using various techniques [17–22]: *in situ* polymerization, mixing in solution, melt-compounding, etc. At the same time, many works have been devoted to the exfoliation of previously intercalated graphite using different methods [19,23,24]: microwaves, radiofrequency wave treatment, sonication, milling, etc.

In other context, an accelerated nucleating process in the presence of EG was identified for different polymer–EG composites [17]. Currently, the use of PLA in technical applications (e.g., injection moulded articles) is limited because PLA has a slow crystallization rate when it is compared with many other thermoplastics [25]. In our opinion, this represents one of the limits of PLA for a larger utilization and it is believed that new PLA grades with improved properties are needed.

For increasing PLA crystallization rate different methods such addition of nucleating agents (talc, nanoclays, stereocomplexes, derivatives of carboxylic and fatty acids, etc.) can be considered [25]. In this context, it is worth mentioning that a recent study performed by Drzal group has shown that the polymer composites prepared by mixing in solution PLA with GNP are characterized by advanced nucleating properties [26].

Unfortunately, to the best of our knowledge, investigations on PLA–EG composites have not been conducted so far to evidence the overall effect conferred by EG addition on main PLA properties. Generally, addition of nanofillers can provide PLA with specific properties but sometimes triggers problems such as loss of mechanical and thermal properties, degradation of the polyester matrix, etc., aspects that need to be considered when targeting a potential application [8,10].

In this regard and to add graphite's properties to a biodegradable polymer matrix of high interest like PLA, the aim of this paper is to present an experimental screening with different approaches directed to the synthesis of PLA–EG composites. To obtain “green” products with specific end-use properties, commercially available EG was added to PLA by direct dosing or as masterbatch (**MB**) using the melt-compounding technology and the resulting composites were characterized in detail for highlighting their performance.

2. Experimental

2.1. Materials

Poly(L,L-lactide) – hereafter called PLA, was kindly supplied by NatureWorks LLC. Characteristics of PLA are as follows: number average molecular weight, $M_{n(PLA)} = 88500$, index of polydispersity, $M_w/M_n = 1.8$, D isomer content: <2%.

EG was supplied by Timcal Belgium S.A. as TIMREX BNB90. According to the technical sheet the principal characteristics of this specific grade of graphite are: mean diameter (d_{50}) = 36 μm, dimension of primary particles = 35 nm, density (xylene) = 2.24 g/cm^3, specific surface area BET = 28.4 m^2/g.

Ultranox 626A (bis (2,4-di-t-butylphenyl) pentaerythritol diphosphite) supplied by GE Specialty Chemicals was selected as thermal stabilizer (it will be noted **U626**) and used at preferred percentage of 0.3 wt% in PLA, except in the case where EG was added as MB.

2.2. Processing

Before processing by melt-blending, PLA was dried overnight at 80 °C under vacuum. To minimize the water content for melt-blending with PLA, all additives were previously dried and then directly used for melt-compounding. EG was dried for 24 h at 105 °C, but due its thermal stability, higher temperatures and shorter times of drying can be used.

The EG (as received) and thermal stabilizer were mixed together with PLA pellets at 200 °C under moderate mixing (cam blades) by using a Brabender bench scale kneader (model 50 EHT) following a specific procedure: 3 min premixing at 30 rpm-speed in order to avoid an excessive increase of the torque during melting of PLA, followed by 7 min mixing at 70 rpm. For the sake of comparison, the neat PLA was processed in similar conditions of melt-compounding like the composites containing up to 12% EG.

A MB (PLA – 30% EG – 2% U626) has been performed using higher mixing time (5 min feeding and premixing, up to 10 min mixing with came blades). The previously dried MB was re-dispersed in the same PLA matrix. Throughout this paper, all percentages are given as wt%.

In a second step, selected PLA–EG compositions (with 3% and 6% EG) were performed after previous treatments of the nanofiller. Because EG is an industrial product which could contain some metallic ions or other impurities (details in section 3.1), in a typical procedure, EG was mixed for 1-h by magnetic stirring in demineralised water (the initial pH level of the solution was about 5–5.5), step followed by filtration and washing. The nanofiller was carefully washed several times with water (it will be noted **w-EG**) until the pH level of solution was neutral and finally, filtrated and dried for melt-mixing with PLA.

Plates (~3.1 mm thickness) were manufactured by compression moulding at 190 °C by using an Agila PE20 hydraulic press. More specifically, the material was first pressed at low pressure for 240s (3 degassing cycles), followed by a high-pressure cycle at 150 bar for 150 s. The resulting samples were then cooled under pressure (50 bar). Specimens for tensile, Izod impact and horizontal burning tests were obtained from plates by using a milling-machine in accordance with ASTM D 638-02a norm (specimens type V), ASTM D 256-A norm (specimens $60 \times 10 \times 3$ mm^3) and ASTM D 3801/UL94 HB (specimens $127 \times 12{,}7 \times \sim 3.1$ mm^3), respectively. The specimens for cone calorimeter testing (plates $100 \times 100 \times 3$ mm^3) were performed under similar conditions by compression moulding.

2.3. Characterization

2.3.1. Size exclusion chromatography (SEC)

Isolation of PLA from selected compositions for molecular weight parameters determination was carried out by first dissolving the samples in chloroform. As precaution, to assure the protection of SEC columns a centrifugation step (30–60 min at 4000 rpm) was supplementary used in the case of the samples containing EG. Then, the catalyst residues were removed by liquid–liquid extraction with a 0.1 N HCl aqueous solution and PLA was recovered by precipitation in an excess of heptane. After filtration and drying, PLA solutions were prepared in THF (10 mg polymer/5 ml solvent). Molecular weight parameters (number average molar mass, M_n, and polydispersity index, M_w/M_n) of pristine PLA and PLA extracted from the studied composites were determined by SEC using the procedure described elsewhere [8].