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Effect of ethylene-co-vinyl acetate-glycidylmethacrylate and cellulose microfibers on the thermal, rheological and biodegradation properties of poly(lactic acid) based systems

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ABSTRACT

The properties and biodegradation behavior of blends of poly(lactic acid) (PLA) and ethylene-vinyl acetate-glycidylmethacrylate copolymer (EVA-GMA), and their composites with cellulose microfibers (CF) were investigated. The blends and composites were obtained by melt mixing and the morphology, phase behavior, thermal and rheological properties of PLA/EVA-GMA blends and PLA/EVA-GMA/CF composite films were investigated as a function of the composition. The disintegrability in composting conditions was examined by means of morphological, thermal and chemical analyses to gain insights into the post-use degradation processes. The results indicated a good compatibility of the two polymers in the blends with copolymer content up to 30 wt.%, while at higher EVA-GMA content a phase separation was observed. In the composites, the presence of EVA-GMA contributes to improve the interfacial adhesion between cellulose fibers and PLA, due to interactions of the epoxy groups of GMA with hydroxyls of CF. The addition of cellulose microfibers in PLA/EVA-GMA system modifies the rheological behavior, since complex viscosity increased in presence of fibers and decreased with an increase in frequency. Disintegration tests showed that the addition of EVA-GMA influence the PLA disintegration process, and after 21 days in composting conditions, blends and composites showed faster degradation rate in comparison with neat PLA due to the different morphologies induced by the presence of EVA-GMA and CF phases able to allow a faster water diffusion and an efficient PLA degradation process.

1. Introduction

The selection of biodegradable polymers offers the possibility of obtaining new types of eco-friendly and fully degradable composites with a wide application potential in several advanced technological sectors. Poly(lactic acid) (PLA) is well known as a biocompatible, bioresorbable and biodegradable polymer superior to petrochemical polymers from the viewpoint of energy consumption and life-cycle (CO_2 emission), since it can be obtained from natural resources. However, the cost of production and some low mechanical performances of PLA still constitute limiting factors for its applications. As a consequence, several investigations have been focused on the production of mixtures of biodegradable natural and synthetic polymers. The addition of polyolefin components with biodegradable polymers has also been examined for obtaining improved properties and reduced cost [1–3]. Moreover, the addition of natural fibers to polymers can be considered as an option to noticeably increase the stiffness of the resulting material and also the strength, especially for low fiber content [4–7]. However, due to the usual lack of proper fiber/matrix compatibility, the interfacial addition is not good enough, leading to a reduction in mechanical properties. To improve the filler–matrix interactions and thus the composite properties, various strategies can be used, which include surface modification of fibers [8–11], growth of polymer chains on the fiber surfaces [12], addition of a compatibilizing/coupling agent [13–15], or even blending of the matrix polymer with another polymer [16]. Another important opportunity to modify and improve the properties of these systems is offered by the methods of blending and (reactive) compatibilization with a second polymer component which displays complementary properties and can contribute to improve the fiber dispersion through effective interactions at the interface [17].

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Ethylene vinyl acetate (EVA) copolymers, due to their important rubber and resin properties are often used in blends with other polymers for various applications, especially in the field of packaging, adhesives/paper coatings, cable insulation, etc. EVA can be modified by insertion of functional groups along the chain, i.e. by grafting with maleic anhydride [18], or by copolymerization with unsaturated monomers, such as GMA (glycidylmethacrylate). In a previous study we demonstrated that mixing an EVA-GMA copolymer with cellulose fibers gave rise to interfacial reactions between the components, resulting in good fiber dispersion and significant changes of the polymer matrix properties [19]. In fact, the epoxy groups of EVA-GMA chains can react both with COOH and OH end groups of polyester chains, and with OH groups of cellulose. Moreover, due to its rubber-like behavior, EVA-GMA is expected to improve the tensile and impact behavior of the materials. The presence of EVA can also improve the resistance of the composites to water absorption, as shown for composites of polypropylene with cellulose fibers [20]. It is worth noting that a super-tough poly(lactic acid) material has been obtained by reactive blending of PLA with a poly(ethylene-co-glycidylmethacrylate) copolymer [21]. Recently, Ma et al. [22] reported on the toughening of PLA by blending with EVA copolymers with different vinyl acetate content. The compatibility between PLA and EVA was found to improve with increasing the vinyl acetate content and blends with higher impact toughness were obtained for a VA content of 50–60 wt.%. The authors concluded that the morphology of the blends could be tuned by varying the VA content in the copolymers and the EVA content in the blends, since EVA particle size and rubber cavitation in the PLA matrix are responsible for the toughening mechanism of the blends. Moura et al. [23] investigated the morphology, thermal and mechanical properties of EVA-g-PLA grafted copolymers obtained by reactive extrusion and the results confirmed that the biodegradability of these systems can be tuned modifying the composition.

In the present paper, we focused the attention on the thermal and rheological characterization and the biodegradation behavior of PLA/EVA-GMA blends and their composites with cellulose fibers (PLA/EVA-GMA/CF), obtained by melt mixing. The main aim of the work was that of analyzing the effect of compatibilization and composition on the degradability and disintegrability in composting conditions of PLA based composites. The morphology, the crystallization processes as well as thermal and mechanical properties of blends and ternary composites of PLA, EVA-GMA and cellulose fibers have been also examined as a function of composition and will appear in a forthcoming paper.

2. Experimental section

2.1. Materials

Poly(lactic acid) (PLA), trade name Hycail HM 1011, specific gravity 1.24 g cm^{-3}, melt flow index (190 °C/2.16 Kg) = 2–4 g 10 min^{-1} and melting point of 142 °C was supplied from Hycail.

Ethylene-vinyl acetate-glycidylmethacrylate (EVA-GMA), trade name Elvaloy AS, was an epoxy modified ethylene terpolymer obtained from DuPont.

Cellulose fibers (CF), trade name Technocel 500-1 (bulk density $\geq$ 60 g L^{-1}), were kindly supplied by NEUCHEM, Milan, Italy. These commercial fibers were used as received without any treatment.

2.2. Preparation of blends and composites

Blends of PLA/EVA-GMA and binary and ternary composites with cellulose fibers were obtained by melt mixing the components. Binary PLA/CF and ternary PLA/EVA-GMA/CF composites (total amount: 40 g) were prepared in a Brabender Plasticorder internal mixer at 180 °C, using a mixing speed of 60 rpm for 15 min. Firstly, PLA was melt and then EVA-GMA was added; after 5 min mixing, the cellulose fibers were added into the molten blend. For all samples torque moment was recorded during the mixing process as a function of time. Before mixing, PLA and CF were dried under vacuum for 6 h at 90 °C while EVA-GMA was dried at 60 °C. EVA-GMA/CF binary composites was also produced for comparison: EVA-GMA was melt and then the cellulose fibers were added. The prepared samples are listed in Table 1. The blends and composites were injection molded in oar shape test specimen by using a Proma WL-5 micro-injector (Torun, Poland) operating at 170/40 °C. Blend and composite films with 2 mm thickness were also obtained by hot pressing.

2.3. Characterization methods

Neat PLA, PLA blend and composite cross-sections performed in liquid nitrogen were investigated by field emission scanning electron microscopy (FESEM, Supra 25-Zeiss), after gold sputtering, (sputtering conditions: 20 mA for 40 s at 0.08 bar), by using an AGAR, Auto Sputter Coater. Thermogravimetric analysis (TGA, Seiko Exstar 6300) was performed on neat PLA, PLA blends and PLA binary and ternary composite samples as follows: 10 mg weight samples, nitrogen (250 mL min^{-1}) flow, temperature range from 30 °C to 900 °C, heating rate of 10 °C min^{-1}. Rheological tests have been performed in a rotational rheometer ARES, with parallel plate geometry ($\phi = 8$ mm). Dynamic measurements have been performed in order to analyze the viscoelastic properties of the materials. Preliminary strain sweep tests to determine the liner viscoelastic region have been done. Frequency sweep measurement at a temperature $T = 170$ °C) with a strain of 0.3% in the frequency range of 0.05–100 Hz have been performed.

2.4. Disintegrability in composting of PLA blends and composites

Disintegration study was carried out following the European standard ISO 20200, which considers the disintegration degree of plastic materials under simulated composting conditions in a laboratory-scale test at 58 °C, 50% of humidity and in aerobic conditions. A specific quantity of compost inoculum, supplied by Gesenu S.p.a., was mixed together with the synthetic biowaste prepared with sawdust, rabbit food, starch, sugar, oil and urea. The water content of the substrate was around 50 wt.% and the aerobic conditions were guaranteed by mixing it softly.

Samples of 20 mm × 20 mm × 2 mm were buried into the organic substrate at 4–6 cm depth in the perforated boxes and incubated at 58 °C. The tested samples were taken out at selected times, washed and dried in an oven at 37 °C for 24 h. The disintegrability value was obtained normalizing the sample weight, at different stages of incubation, to the initial one. Surface microstructure of blends and composites before the composting and at different days of incubation was investigated by field emission

Table 1
Material formulations.

Materials	PLA (wt.%)	EVA-GMA (wt.%)	CF (wt.%)
PLA	100	–	–
EVA-GMA/CF	–	70	30
PLA/CF	70	–	30
PLA/EVA-GMA(50/50)	50	50	–
PLA/EVA-GMA(70/30)	70	30	–
PLA/EVA-GMA/CF	60	10	30