



Property tuning of poly(lactic acid)/cellulose bio-composites through blending with modified ethylene-vinyl acetate copolymer



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ABSTRACT

The effect of addition of an ethylene-vinyl acetate copolymer modified with glycidyl methacrylate (EVA-GMA) on the structure and properties of poly(lactic acid) (PLA) composites with cellulose micro fibres (CF) was investigated. Binary (PLA/CF) and ternary (PLA/EVA-GMA/CF) composites obtained by melt mixing in Brabender mixer were analysed by SEM, POM, WAXS, DSC, TGA and tensile tests. The miscibility and morphology of PLA/EVA-GMA blends were first examined as a function of composition: a large rise of PLA spherulite growth rate in the blends was discovered with increasing the EVA-GMA content (0–30 wt%) in the isothermal crystallization both from the melt and the solid state. PLA/EVA-GMA/CF ternary composites displayed improved adhesion and dispersion of fibres into the matrix as compared to PLA/CF system. Marked changes of thermodynamic and tensile parameters, as elastic modulus, strength and elongation at break were observed for the composites, depending on blend composition, polymer miscibility and fibre-matrix chemical interactions at the interface.

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1. Introduction

Blending of biodegradable polymers and natural fibres offers the possibility of obtaining new types of eco-friendly biodegradable composites with a wide application potential in several advanced technological sectors (Cheung, Ho, Lau, Cardona, & Hui, 2009; Khalil, Bhat, & Yusra, 2012). Poly(lactic acid) (PLA) is well known as a biocompatible and biodegradable polymer obtained from natural resources, with application potential superior to petrochemical polymers as concerning energy consumption, environmental impact and life-cycle (Jamshidian, Tehrani, Imran, Jacquot, & Desobry, 2010). However, the costs of production, processability and some low mechanical performances of PLA still constitute limiting factors for its applications. Accordingly, a large number of investigations have been focused on the preparation of new composite or hybrid systems based on natural and synthetic polymers combined with various types of fillers. In particular, large attention

has been addressed to the formulation of biodegradable polymer composites containing fibres (on a wide scale of sizes) derived from natural and renewable resources (Bledzki & Jaszkievicz, 2010; Nishino, Matsuda, & Hirao, 2004; Suryanegara, Nakagaito, & Yano, 2009). In this respect, composites with nano-sized fibres are being extensively investigated for their peculiar mechanical and thermal properties which allow for such unique systems huge application potential (Herrera, Salaberría, Mathew, & Oksman 2015; Pracella, Haque, & Puglia, 2014; Spinella et al., 2015).

The addition of natural fibres to polymers contributes to markedly increase the stiffness and the strength of the material, especially for low fibre content, as well as to modify the crystallization behaviour of the matrix and gas permeability (Battezzore, Alongi, & Frache, 2014; Lezak et al., 2008; Mathew, Oksman, & Sain, 2006). However, due to the general lack of compatibility between fibres and matrix, the interfacial adhesion is generally low, limiting the final mechanical performances of these systems. To improve the filler-matrix interactions and thus the composite properties various strategies can be used, which include surface modification of fibres and/or matrix, growth of polymer chains on the fibre surfaces, addition of a compatibilizing/coupling agent, or even blending of the matrix polymer with another polymer.

Different methods of fibre modification have been reported aimed at optimizing the physical and mechanical characteristics of PLA composites with various types of fibres, such as flax

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(Andersons, Spārniņš, & Joffe, 2006), hemp (Hu & Lim, 2007), bamboo (Okubo, Fujii, & Thostenson, 2009), jute (Plackett, Andersen, Pedersen, & Nielsen, 2003), kenaf (Cho et al., 2007), henequen, oat husks and others (Lezak et al., 2008). It has been shown that the fibre treatment by alkali and silane improved the tensile mechanical properties and impact strength due to a better adhesion between treated fibres and matrix (Huda, Drzal, Mohanty, & Misra, 2008). The effect of various types of compatibilizers (reactive or not), plasticizers and modified polymers on the mechanical properties has also been analysed for several composites of PLA (Avella et al., 2008; Masirek, Kulinski, Chionna, Piorowska, & Pracella, 2007; Serizawa, Inoue, & Iji, 2006; Wong, Shanks, & Hodzic, 2004).

Another opportunity to modify and improve the properties of polymer/fibre composites is offered by the methods of blending and compatibilization with a second polymer component which displays complementary properties and can contribute to improve the fibre dispersion through effective interactions at the interface (Oyama, 2009). The use of polymer blends as matrices in composite systems may offer several advantages, whether improving processability and widening the spectrum of properties and applications, as well as reducing the costs of raw materials. 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. (Henderson, 1993). EVA can be modified by insertion of functional groups along the chain, i.e. by grafting or copolymerization with unsaturated monomers, such as maleic anhydride (Yin, Zhang, & Yao, 2006). In a previous study we demonstrated that mixing a glycidyl methacrylate grafted EVA copolymer (EVA–GMA) with CFs gave rise to interfacial reactions between the components, resulting in enhanced fibre dispersion and improvement of the polymer matrix properties (Haque & Pracella, 2010). In fact, the epoxy groups of EVA–GMA chains can react with both COOH and OH end groups of polyester chains, and with OH groups of cellulose. Moreover, due to its rubber-like behaviour EVA–GMA is expected to improve the tensile and impact behaviour of the materials (Nagarajan, Zhang, Misra, & Mohanty, 2015). Addition of nanocrystalline cellulose to EVA was found to enhance tensile and optical properties (Elanthikkal, Gopalakrishnanpanicker, Varghese, Guthrie, & Francis, 2013; Ma, Jiang, Hoch, Dong, & Chen, 2015). Moreover, the presence of EVA in composites can improve the resistance to water absorption, as shown for composites of polypropylene with cellulose fibres (Espert, Vilaplana, & Karlsson, 2004).

PLA was reported to be compatible in the melt with poly(vinyl acetate) (PVAc) and EVA copolymers (Gajria, Dave, Gross, & McCarthy, 1996; Yoon, Oh, Kim, Chin, & Kim, 1999). 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% (Ma et al., 2012). It was concluded that the morphology of the blends could be tuned by varying the EVA amount and VA content in the copolymers, since the EVA particle size and rubber cavitation in the PLA matrix were responsible for the toughening mechanism of the blends. Further, it has been shown that blending of PLA with EVA–GMA copolymer and cellulose fibres causes significant variations of rheological properties and biodegradability, enhancing the degradation rate of composites in composting conditions as compared to neat PLA (Fortunati, Puglia, Kenny, Haque, & Pracella, 2013). In the present paper, we investigated the effect of polymer miscibility on the morphology and physical/mechanical behaviour of PLA/EVA–GMA blends and their composites with cellulose fibres of different type, obtained by melt mixing. The main aim of the work was to design new PLA based composites with controlled processability, improved fibre dispersion and tuneable properties, by exploiting both the reactivity of EVA–GMA (toward cellulose)

Table 1
List of samples.

Sample code	Composition (wt%)		
	PLA	EVA–GMA	CF
PLA/EVA–GMA 95/5	95	5	–
PLA/EVA–GMA 93/7	93	7	–
PLA/EVA–GMA 85/15	85	15	–
PLA/EVA–GMA 70/30	70	30	–
PLA/EVA–GMA 50/50	50	50	–
PLA/EVA–GMA 30/70	30	70	–
PLA/CF 70/30	70	–	30
PLA/EVA–GMA/CF 75/5/20	75	5	20
PLA/EVA–GMA/CF 65/5/30	65	5	30
PLA/EVA–GMA/CF 60/10/30	60	10	30
PLA/EVA–GMA/CF 55/5/40	55	5	40
PLA/EVA–GMA/CF 50/20/30	50	20	30
PLA/EVA–GMA/CF 35/35/30	35	35	30
PLA/EVA–GMA/CF 20/50/30	20	50	30
EVA–GMA/CF 70/30	–	70	30

and the favourable interactions of PLA with vinyl acetate units. The morphology, phase interactions, crystallization processes, as well as thermal degradation and tensile properties of PLA/CF and PLA/EVA–GMA/CF ternary composites were thus analysed as a function of blend composition and fibre content.

2. Experimental

2.1. Materials

Poly(lactic acid) (PLA), trade name Hycail HM 1011, specific gravity 1.24 g/cm³, MFR (190 °C/2.16 kg) = 2–4 g/10 min 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 fibres (CFs), trade name Technocel 165 (bulk density: 0.07–0.12 g/cm³), were kindly supplied by NEUCHEM (Milan, Italy) and used as received without any further treatment.

2.2. Preparation of blends and composites

PLA/EVA–GMA blends, PLA/CF and PLA/EVA–GMA/CF composites were prepared by melt mixing in a Brabender Plasti-corder internal mixer at 180 °C, using a mixing speed of 60 rpm. For the preparation of ternary composites PLA was first melted into the mixer and then EVA–GMA was added; after 5 min mixing the cellulose fibres were loaded into the molten blend and mixing was continued for 10 min. For all samples the torque moment was recorded during the mixing process as a function of time. Before mixing PLA and CFs were dried under vacuum for 6 h at 90 °C and EVA–GMA, at 60 °C. The prepared samples are listed in Table 1. In order to analyse the phase composition of PLA/EVA–GMA blends, films (thickness: 40–50 μm) of blends with 15, 20, 30, 50 and 70 wt% EVA–GMA were prepared by hot pressing between two Teflon sheets at 170 °C under a load of 7 × 10³ kg for 3 min, and then extracted with acetone: the PLA used is soluble in acetone, whereas EVA–GMA is insoluble. The films were soaked in acetone for three days, dried and then examined by scanning electron microscopy and FTIR analysis, in order to control the morphology of the matrix phase and the presence of PLA after extraction.

2.3. Microscopy

Scanning electronic microscopy (SEM) was used to analyse the surfaces of injection moulded samples (see Section 2.7) freeze fractured in liquid nitrogen. The sample surfaces were sputter coated with fine layer of gold in an Edward Sputter Coater and analysed

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