POLY(LACTIC ACID) (PLA) BASED NANO-STRUCTURED FUNCTIONAL FILMS FOR PERSONAL CARE APPLICATIONS

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ABSTRACT

Replacing petro-based materials in personal care sector with renewable biodegradable counterparts is a correct strategy for taking care of the environment. Textured films are currently used in several applications in contact with skin, such as diaper and napkins. Poly(lactic acid) (PLA), fully renewable and compostable, with an intrinsic anti-microbial property, has enormous potentialities but it is necessary processing it by flat die extrusion to obtain flexible films. The plasticization of selected polymeric blends, obtained by using biodegradable and partially biobased polyesters as well as a citrate, and the control of melt viscosity by proper additives during extrusion were thus investigated.

Key Words: Poly(Lactic Acid), Personal Care, Extruded Films, citrate, melt viscosity

1. INTRODUCTION

The production of flexible films by using compostable plastics can be important because they can be used for preparing low apparent-density packaging. Moreover, biodegradable films can be used in diapers and femcare sanitary pads, to produce renewable and compostable products.

To increase the flexibility of PLA it is possible to add a low molecular weight plasticizer [1-2] or blending it with a flexible polymer such as poly(butylene adipate-co-terephthalate) (PBAT) [3-4]. In the latter case, the use of a proper compatibilizer was demonstrated to be important for a better modulation of properties thanks to the achievement of a phase morphology characterized by a lower dimension of the dispersed PBAT phase and an increased adhesion [5-6].

In applications such as flat die extrusion or blow extrusion it is important the fine tuning of melt viscosity and melt strength. In these cases, the use of chain extenders, much used in the field of polyester processing [7], can be fundamental. In some cases, the use of plasticizers with reactive groups having a low number of reactive groups per molecule (two or three) can allow better modulating PLA based compounds viscosity, limiting also the migration of the plasticizer from the final film thanks to its partial grafting to PLA [8]. The use of a compatibilizer bearing epoxide groups that decreases the melt flow rate of PLA based blends was also demonstrated to be effective for improving the processability by blown film extrusion [9]. On the other hand, the necessity of increasing the melt strength of pure PLA was yet investigated by several authors often using modifiers with epoxide moieties [10-12].

Flat die extrusion consists of an extrusion through a linear die of adjustable thickness (die gap) usually between 3 and 1.4 mm. This technology allows the production of polymeric films (with thicknesses higher than 50 microns) and consists of the extrusion of the molten polymer through a die of rectangular geometry. The material comes out from the die in the form of a molten film that is immediately in contact with a thermostatic roller to allow cooling and solidification. Due to the movement of the roller, the film undergoes elongation with a consequent reduction in thickness. The film then passes through a second roller and to a measuring, cutting and winding station.

The operating parameters to be controlled during flat die extrusion are the extrusion and windup rolls temperatures, distance between die and the first roll and the draw ratio (ratio between windup roll speed and polymer speed at the die exit). All these parameters have a big influence on the final product characteristics (morphology and mechanical properties).

In flat die extrusion, as well as in blown extrusion, the necessity of increasing the melt viscosity of PLA-based blends is often an issue.

Films produced by flat die extrusion can be used to produce diaper top-sheets. Diaper top-sheets are generally made by using polyolefins with a specific patterning of holes on the surface allowing the controlled passage of liquids through the film.

Bio-nanocomposites based on poly(lactic acid) (PLA) and chitin nanofibrils (CN) are considered important because they can allow to combine anti-microbicity with improved mechanical strength [13,14]. Moreover, having CN the same structure of extracellular matrix (ECM) is widely used in tissue engineering also as scaffold for soft and hard human tissues [15]. In any case the addition of chitin nanofibrils needs a specific procedure, that much affect the final properties. The presence of chitin nanofibrils affects processing and some authors report that it leads to an increase in melt viscosity and melt strength [16-19].

In the present paper the plasticization of PLA/PBAT blends was studied by using different plasticizers. Moreover a pre-composite consisting of chitin nanofibrils/poly(ethylene glycol) was added to disperse chitin nanofibrils in the plasticized blend and the viscosity in the melt was controlled by measuring the torque. The addition of different melt strength enhancers in different compositions was then considered to increase the extrusion viscosity maintaining the mechanical properties typical of a flexible film.

2. MATERIALS AND METHODS

Materials. The poly(lactic acid) (PLA) used in this paper is Ingeo 2003D from NatureWorks, poly(butylene adipate-co-terephthalate) (PBAT) is Ecoflex F Blend C1200 from BASF; acetyl tri-n-butyl citrate (ATBC) and Poly(etylene glycol) 6000 (PEG6000) were purchased from Aldrich; Biostrength 700 (BS) is an Arkema product; Joncryl ADR-4468 (Joncryl) is a BASF product; calcium carbonate (CC) is OMYACARB 2AV kindly provided by OMYA (Avenza, Italy).

To prepare the composite PEG6000 was added to concentrated chitin nanofibrils (CN) water suspension provided by MAVI SUD and stirred for two hours at room temperature. The amount was calculated considering that in the final pre-composites the weight ratio of PEG6000 and CN was 1:1. The obtained semiliquid emulsion was dried in a ventilated oven at 50°C up to constant weight to obtain a solid.

Methods. The extrusion of the PLA 2003D (IngeoTM Nature Works) in the presence of plasticizers and other additives was carried out, after drying the material in an oven at 60°C for 16 h, using a TwinLab II Haake ™ Rheomex CTW 5 laboratory screw extruder. The extrusion was carried out at 190°C and at 110 rpm for one minute. The torque meaurement were performed at 20, 40 and 60 seconds during the extrusion. After extrusion, the molten material was transferred through a preheated cylinder into the Haake ™ MiniJet II mini injection molding injection molding machine to obtain Haake type III test specimens for tensile testing. The injection molding was carried out at 180°C, 700 bar, holding time of 20 seconds, mold temperature of 35°C. Tensile tests (ASTMD638) were carried out using a universal INSTRON 5500R test machine with a 10 kN load cell at a speed of 10 mm/min.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Regarding the mechanical properties of the extruded materials, it was evident that the ATBC was the best plasticizer (Table 1). In fact it allowed a consistent reduction of the elastic modulus of the material, but keeping the stress at break at 27 MPa and improving the elongation at break at 380%. The properties are similar to those obtained by using PEG6000, but the advantage of ATBC is its renewability.

The blending of PLA with PBAT in a 70/30 blend was effective for improving the PLA properties resulting in a more ductile material, showing a decreased Modulus and an elongation at break of 180%. The plasticization with ATBC resulted advantageous to further modulate flexibility reducing the Modulus at 0,3 GPa, thus obtaining a flexible film. These results were used to prepare films based on plasticized PLA/PBAT blends by flat die extrusion (Figure 1).

Table 1. Composition and tensile properties of blends

Blend composition	**E (GPa)**	**σ_y (MPa)**	**ε_y (%)**	**σ_b (MPa)**	**ε_b (%)**
PLA pure	3,5 ± 0,4	-	-	61,4 ± 2,3	2,7 ± 0,3
PLA + 20%PEG6K	0,3 ± 0,1	15,6 ± 2,0	4,5 ± 0,4	27,3 ± 0,6	370 ± 10
PLA + 20% ATBC	0,9 ± 0,5	19,7 ± 3,6	3,8 ± 0,6	27,1 ± 2,7	380 ± 20
PLA70/PBAT30	2,0 ± 0,2	48,1 ± 3,2	4,1 ± 0,2	20,3 ± 5,8	180 ± 20
PLA70/PBAT30 + 20%ATBC	0,3 ± 0,05	12,6 ± 8,0	5,2 ± 0,7	16,8 ± 0,6	210 ± 60
PLA70/PBAT30 +4%CN/PEG6000 +18%ATBC	0,13 ± 0,3	-	-	20,1 ± 0,2	490 ± 8
PLA70/PBAT30 +4%CN/PEG6000 +16%atbc+2%BS	0,15 ± 0,2	7,6 ± 5,2	5,6 ± 1,3	21,1 ± 1,5	335,4 ± 17,0
PLA70/PBAT30 +4%CN/PEG6000 +14%atbc+4%BS	0,10 ± 0,1	20± 4	5,1 ± 0,6	19,1 ± 0,6	370 ± 20

(a) **(b)**

Figure 1. (a) flat die extrusion facility at University of Pisa (DICI) and (b) flat die extruded film based on plasticized PLA/PBAT

The addition of CN determined an increase in elongation at break and a strong reduction of Modulus (Table 1). The addition of BS, as melt strength regulator, determined an increse in

yielding stress, but the elongation at break was not significantly modified as well as elastic modulus and stress at break. The results are in agreement with a good dispersion of CN in the plasticized blend thanks to the methodology set up for pure PLA [13,14].
The addition of CN was found to decrease much the viscosity in the melt (Table 2) of the belnds, reasonably because of polyester hydrolisis. The viscosity was lower when also a plasticizer was added. BS was added because it could allow to control well the viscosity in the melt, conterbalancing the occurring chain scission.

Table 2. Composition and torque data at 20, 40 and 60 s of extrusion

Blend composition	**Torque at 20 s (N*cm)**	**Torque at 40 s (N*cm)**	**Torque at 60 s (N*cm)**
PLA pure	121± 12	120 ± 11	118 ± 10
PLA + 2% CN	61 ± 2	55 ± 3	48 ± 3
PLA70/PBAT30 + 20%ATBC	50± 3	55± 4	58± 4
PLA70/PBAT30 +4%CN/PEG6000 +18%ATBC	37 ± 8	38 ± 9	38 ± 6
PLA70/PBAT30 +4%CN/PEG6000 +16%ATBC+2%BS	60 ± 3	60 ± 3	59 ± 3
PLA70/PBAT30 +4%CN/PEG6000 +14%ATBC+4%BS	68 ± 3	65 ± 2	64 ± 3
PLA70/PBAT30 +4%CC+4%CN/PEG6000 18%ATBC+2%BS	60± 3	57± 5	56± 4
PLA70/PBAT30 +4%CC+4%CN/PEG6000 18%ATBC+2%Joncryl	31 ± 2	31 ± 2	32 ± 1

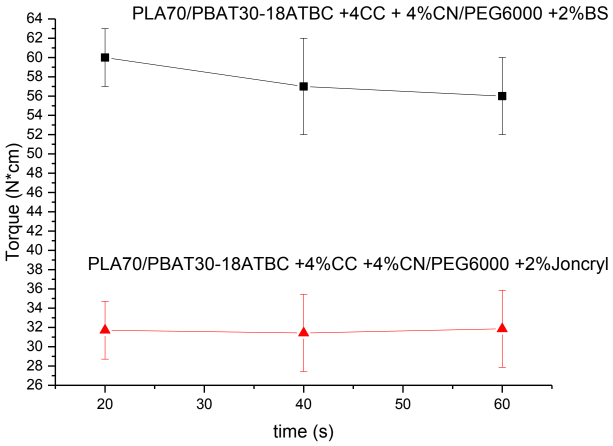

Figure 2. Torque data recorded as a function of time during extrusion of plasticized PLA/PBAT blends containing CC and CN with BS (squares) or Joncryl (triangles)

In literature the chain extenders based on copolymers containing epoxide groups and commercialized by BASF with the tradename Joncryl are well known and were yet used in PLA/PBAT blends in blowing extrusion formulations [20]. Joncryl was compared with BS and torque measurement indicated that it resulted not effective in increasing the viscosity of the blend (Figure 2). The difference between the two additives is certainly explainable considering their different structure. The reactivity of Joncryl is linked to epoxide groups present on its structure, that should react with polyester terminals to increase its molecular weight. Generally epoxide groups react better with carboxylic groups than with hydroxyl groups.

BS is an acrylic copolymer based on methyl methacrylate and butyl acrylate monomers. The reactivity of BS is based on a different mechanism, not completely known, but reasonably based on a radical mechanism starting from this copolymer that is reported to be miscible in PLA [21-22]. The possibility of improving the processability and properties of PLA/PBAT blends thanks to the occurring of controlled radical reactions was yet evidenced by Coltelli et al. [5].

4. CONCLUSION

Formulations and conditions for producing flexible films highly renewable based on plasticized PLA/PBAT blends were identified. ATBC was selected as the most promising plasticizer.

The dispersion of chitin nanofibrils in the plasticized blends was possible thanks to the preliminary preparation of a pre-composite, however this addition resulted in extensive hydrolysis of the polyesters. To increase melt viscosity it was necessary to add chain extenders or melt strength enhancers. To select the most promising, the torque behavior of a chain extender based on epoxy groups (Joncryl) was compared with a melt strength enhancer based on an acrylic commercial copolymer (BS). The latter allowed to maintain higher the viscosity of the blends. Mechanical properties of bionanocomposites treated with increasing content of BS showed an increase in yielding stress, but the elongation at break was not significantly modified as well as elastic modulus and stress at break. The results are in agreement with a good dispersion of CN in the plasticized blend.

These results can be promising in view of preparing innovative and renewable films for applications in contact with skin in the personal care and sanitary sector.

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