SHEETS OF POLY (LACTIDE) / O-MMT PREPARED BY ONE –STEP REACTIVE EXTRUSION-CALENDERING PROCESS

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Abstract:
In this study, a reactive extrusion-calendering process was used in order to manufacture OMMT-based (2.5 wt.%) PLA-REX sheets with a nominal thickness of 1 mm. During processing, the properties of the melt were stabilized and enhanced by the addition of 0.5 wt.% of a styrene-acrylic multi-functional-epoxide oligomeric reactive agent. Rheological experiments highlighted the creation of a possible continuous chemical bonding from the MMT organo-modifier to the PD,L-LA matrix. As a result, a better intercalated-dispersed morphology of the filler into the polymer matrix was observed by TEM analysis. Finally, OMMT-based PLA-REX samples showed semi-ductile behaviour under uniaxial tensile loading after one week storage at room temperature.

1. Introduction

In today's world of awareness of environmental situation and of "green" chemistry, commercial poly(lactic acid) grades (PD,L-LA) have been viewed as promising materials. Defined as a bio-based and biodegradable polymer, PD,L-LA is widely used in short-life eco-friendly applications. However, its brittleness in usual storage/service conditions limits its large-scale commercialisation. Addition of 2.5 wt.% of organically modified montmorillonite clays (OMMT) into PD,L-LA matrix showed positive results to overcome these drawbacks. However, significant degradation of the initial polymer matrix during melt processing was observed leading to competitive effects between polymer properties enhancement and degradation [1, 2]. As a result, it has been shown that PD,L-LA melt properties can be stabilized during processing. Addition of 0.5 wt.% of a styrene-acrylic multi-functional-epoxide oligomeric agent (SAmfE) through reactive extrusion technique counteracts the degradations of the PD,L-LA matrix by chain extension and branching reactions [3], increasing thereby the melt viscosity and the melt strength of the initial material. Therefore, reactive extrusion process seems to be an attractive solution to melt compound OMMT with PD,L-LA.

Our research group works on a project which goals are to assess the final properties (thermal, rheological, mechanical, fracture behaviour) of biocomposites obtained through one-step reactive extrusion process. In this communication are discussed the scaling up from

laboratory to pilot plan scale of these materials. Mechanical properties complemented by TEM and SEM analysis of the resulting extruded materials are thereafter determined.

2. Experimental

2.1. Materials

A commercial PD,L-LA extrusion grade (PLA 4032D®) supplied by NatureWorks (Belgium) characterized by a D lactide ratio of 98:2 was used in this study. Previous measurements reported a molecular weight (MW) of 181 kg.mol^{-1}, a polydispersity index of 2, a T_g and T_m of 60 ºC and 170 °C, respectively [1,3]. An OMMT clay (Cloisite 30B®) purchased from Southern Clay Products (USA) in powder form was used as a filler. Methyl-tallow-bis-2-hydroxyethyl ammonium groups (MT2EtOH) (MW= 404.8 g·mol^{-1}) are used as organo-modifier which weight loss on ignition is about 30 wt.% (ASTM D5630-01) [1]. A SAmfE agent (Joncryl-ADR-4300F®), kindly supplied by BASF (Germany) in flake form, was used as a reactive agent. Its T_g shifts around 56 ºC, its MW in the vicinity of 5443 g·mol^{-1} and it is defined by an epoxy equivalent weight of 433 g·mol^{-1} [1,3].

2.2. Melt compounding

Two different PD,L-LA-based masterbatches were initially prepared in order to avoid handling and processing issues of the OMMT powder and SAmfE flakes. Prior to processing, PD,L-LA pellets were dried using a dehumidifier (DSN506HE, Piovan) (dew point = -40ºC) at 80ºC for 3h and kept under the same conditions during extrusion process. OMMT were dried at 130ºC for 22 hours using a convection oven J.P. Selecta and SAmfE flakes were stored overnight at room temperature under vacuum.

Melt compounding of the OMMT clays and PD,L-LA resin was performed in a co-rotating twin-screw extruder 25 mm (L/D = 36), (KNETER 25X24D, COLLIN) in order to manufacture a masterbatch of OMMT (referred to as MBC). The feeding rate of OMMT was adjusted to the polymer resin in order to obtain a nominal dosage of 10 wt.% of OMMT. The screw speed was set to 120 rpm, the estimated residence time was 1.5 min and the extruder was operated by starve feeding. The following temperature profile was used: 140ºC (feeding zone), 160ºC (melting zone) and 165ºC (metering zone and die). Once the extrusion line started and stabilized with raw PD,L-LA material, PD,L-LA and OMMT were introduced simultaneously in the hopper of the feeding zone under a N_2 blanket (2.5 bars). Vacuum was applied in the metering zone to remove any volatiles resulting from the extrusion stage. The extrudate was quenched in cold-water and then granulated. The exact composition of the resulting masterbatch was determined by calcination (ASTM D5630-01).

A single screw extruder 30 mm (L/D ratio = 25), (IQAP-LAP E30-25D, IQAP Technologies) was used to melt compound SAmfE agent with the PD,L-LA resin, to obtain a masterbatch of SAmfE (referred to as MBS). Prior to processing, the reactive agent and PD,L-LA resin were rapidly physically mixed to obtained a nominal dosage of 5 wt.% of SAmfE. The screw speed was set to 60 rpm, the estimated residence time was 1 min and the extruder was operated by groove feeding. The following temperature profile was used: 130ºC (feeding zone), 132ºC (compression zone) and 135ºC (metering zone and die). Low temperatures have been used in order to avoid premature reactions between SAmfE epoxy groups and PD,L-LA functional

groups [3]. Then, the mixture was introduced in the hopper of the feeding zone, once the production line was started and stabilized with raw PD,L-LA material. The extrudate was quenched in cold-water and then granulated. The exact composition of the resulting masterbatch was quantitatively determined by Fourier transform infrared spectroscopy analysis (FTIR) using the Beer-Lambert law.

2.2.1. Laboratory scale mixing: internal mixer

PD,L-LA pellets and both masterbatches were dried overnight at 55ºC under vacuum in order to remove any excess moisture. Prior to melt compounding, dried PD,L-LA, MBC and MBS were physically mixed according to table 1; samples were distinguished by the type and amount of masterbatches. Then, each mixture was melt blended in an internal mixer (Brabender Plastic-Corder W50EHT) with a mixing chamber volume of 55 cm^3, at 180 ºC and with a screw rotation speed of 50 rpm. A continuous flow of N_2 (3.5 bars) was introduced into the mixing chamber in order to minimize degradation. For each preparation, torque and temperature vs. mixing time were monitored for 35 min in order to follow the evolution of the reactions. Once the different materials were introduced into the mixing chamber, the torque increased considerably. Then, the initial high torque peak rapidly decreased due to the melting of the materials. A completely molten state was observed for all samples within 4 minutes. This time was considered as the starting point of the experiments.

Mixing process	Sample nomenclature	Nominal OMMT amount [wt.%]	Nominal SAmfE amount [wt.%]
- Internal mixer - One-step reactive extrusion calendering	PLA	0	0
	PLA-C	2.5	0
	PLA-REX	0	0.5
	PLA-REX-C	2.5	0.5

Table 1. Nomenclature used for all materials processed and analyzed in the current study.

2.2.2. Pilot plan scale: one-step reactive extrusion-calendering process

Prior to drying, PD,L-LA pellets and both masterbatches were physically mixed according to table 1. Then, all different mixtures were separately dried at 80ºC for 3 hours in a dehumidifier (DSN506HE, Piovan) (dew point = –40ºC) prior to processing and kept under the same conditions during the whole process. An identical extruder as described in the MBC preparation section was used to perform REX-Calendering process. The screw speed was 40 rpm, the residence time was 4.5 min and the extruder was operated by starve feeding. The following temperature profile was used: 150°C (feeding zone), 170°C (melting zone) and 175°C (metering zone and die). The production line was started and stabilized with raw PD,L-LA material prior to the introduction of the different mixtures in the hopper of the feeding zone under a N_2 blanket (2.5 bars). Vacuum was applied at the metering zone to remove volatiles resulting from the reactions. Sheets with a nominal thickness of 1 mm and a nominal width of 100 mm were calendered (TEACHLINE CR72T, COLLIN). The chill roll ($\varnothing$=72 mm) temperature was set to 50 ºC with a rotation speed of 1.25 rpm. The exact composition of the resulting sheets in OMMT clays and SAmfE agent was determined by calcination (ASTM D5630-01) and FTIR analysis, respectively.

Then, a thermal treatment was applied to all extruded sheets in order to relax residual stresses and to avoid excessive defects during sample cutting. They were heated to 60 ±1 °C for 40 min in an identical convection oven as previously described and thereafter quenched in an ice water bath (2 ±2 °C) for 15 min. Samples were rapidly extracted from the centre of the

quenched film, parallel to the main axis of the machine direction (MD). Prior to testing, all samples were stored at room temperature during one week in order to reproduce possible manufacturing storage conditions. All samples are listed in table 1.

2.4. Characterization techniques

To observe the silicate layers dispersion, Transmission Electron Microscopy (TEM) (Jeol JEM-2011) experiments were performed under vacuum with an accelerating voltage of 200 kV. Thin samples (~100 nm thickness) were cut using an ultramicrotome (Ultra-Reichert 701, Reichert Technologies) coupled with a diamond blade at room temperature.

Dynamic rheological measurements of all the material were performed using an oscillatory rheometer (AR-G2, TA Instrument) equipped with parallel-plate geometry of 25 mm diameter and with a gap of 1 mm. Tests were conducted at 180°C under controlled deformation conditions (0,2%, LVR). Prior to testing, all samples were dried overnight at 55 °C under vacuum and kept during tests under nitrogen flow to minimize oxidation and to maintain a dry environment. Dynamic frequency sweeps were carried out over an angular frequency (ω) range of 628.3–0.06283 rad·s^{-1}.

The mechanical characterization was performed according to the ASTM D638 standard, using type I specimen extracted from the centre of the sheet, parallel to the MD direction. All the tests were conducted at room temperature (23 ± 2°C) using a universal testing machine (SUN 2500, GALDABINI) equipped with a 5 kN load cell. The crosshead speed was set to 10 mm.min^{-1}. Deformations were measured with a video extensometer (OS-65D CCD, MINSTRON) coupled with a Messphysik Windows-based software. The Young's Modulus (E), yield strength (σ_y), yield strain (ε_y) and strain at break (ε_b) were calculated from the engineering stress-strain curves. All the values reported are average reading of five valid tests. The fractured surface of all tensile specimens was inspected by Scanning Electron Microscopy (SEM) (JEOL JSM-5610). All the tests were performed with an accelerating voltage of 12 kV and under vacuum. Therefore, samples were coated with a thin layer of gold in argon atmosphere using a BAL-TEC SCD005 Sputter Coater.

3. Results and discussion

3.1. Laboratory scale process monitoring

Effect of the OMMT and SAmfE addition on the PD,L-LA torque profile over prolonged mixing times (35 min) is shown in figure 1. The torque was used as a basic rheological response of the PD,L-LA resin with respect to the reactive process. Although not displayed in figure 1, the bulk temperature of all samples underwent fluctuations over the whole process. By increasing mixing time, the bulk temperature increased from 180 to 215 °C until 17 min. Afterwards, it monotonically decreased to 200 °C with further mixing time. This behaviour may be attributed to the mechanical shearing effects and the exothermic nature of the different reactions.

As shown in figure 1, the torque values at 4 minutes of the OMMT-based samples were lowered as compared to the PLA and PLA-REX samples. This trend may be attributed to the plasticizing effect induced by the low MW of the MMT organo-modifiers on the polymer matrix [2]. Regarding PLA and PLA-C samples, a monotonous decrease in the torque was observed over mixing time. This behaviour was expected and resulted from a decrease in the MW of the initial PD,L-LA resin due to the effect of several degradation processes [3,4].
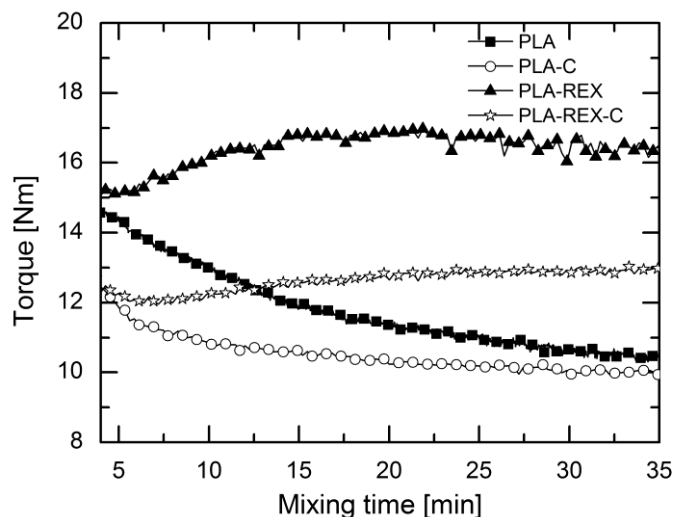
Figure 1. Effect of the OMMT and SAmfE addition on the PD,L-LA torque at 180 °C in an internal mixer.

As expected, a significant increase followed by a stabilization of the torque values was observed when PD,L-LA resin was mixed with SAmfE agent. This was due to an enhancement of the melt properties and of the initial resin molecular weight due to chain extension and branching reactions [3]. In contrast, a slower and lower increase in the torque values over mixing time was measured for PLA-REX-C samples as compared to PLA-REX samples. Due to their low MW, a higher diffusivity of the MMT organo-modifier functional groups towards SAmfE epoxy groups may be expected in the melted bulk as compared to the macromolecular polymeric chains. Therefore, premature reactions between OMMT and SAmfE might occur mitigating further possible reactions between PD,L-LA functional groups and SAmfE epoxy groups. Hence, the enhancement of the melt properties and molecular weight of the initial polymer resin may be reduced leading to lower torque values.

3.2. Scaling up to pilot plan: one-step reactive extrusion-calendering process

As a result of the inability to monitor the reaction profile during the scaling up, rheological tests have been performed to determine the flow properties of all the samples manufactured by REX-Calendering process. Complex viscosity ($|\eta^*(\omega)|$) and storage modulus ($G'(\omega)$) curves referenced at 180ºC are shown in figure 2. Except for PLA-REX samples, the terminal (Newtonian) region was observed for all samples at relatively high ω and was followed by the shear-thinning regime for further ω increase. This behaviour is generally observed for linear polymers resulting from relatively fast stress relaxation processes. In contrast, the terminal region of PLA-REX samples was not reached within the experimental window due to a broadest flow transition.

Regarding PLA-C samples, slight decrease in the zero shear viscosity (η_0) and in the melt strength (G' values) were observed as compared to PLA samples. Similar to the internal mixing process, this trend may be attributed to a possible loss of MW resulting from several degradations of the polymer matrix during the melt blending process [4]. On the other hand, a slight increase in $|\eta^*(\omega)|$ and $G'(\omega)$ were revealed in the low ω region. This behaviour may be attributed to a modification of the stress relaxation processes at low frequencies resulting from the interaction of the OMMT in the polymeric chain motions.
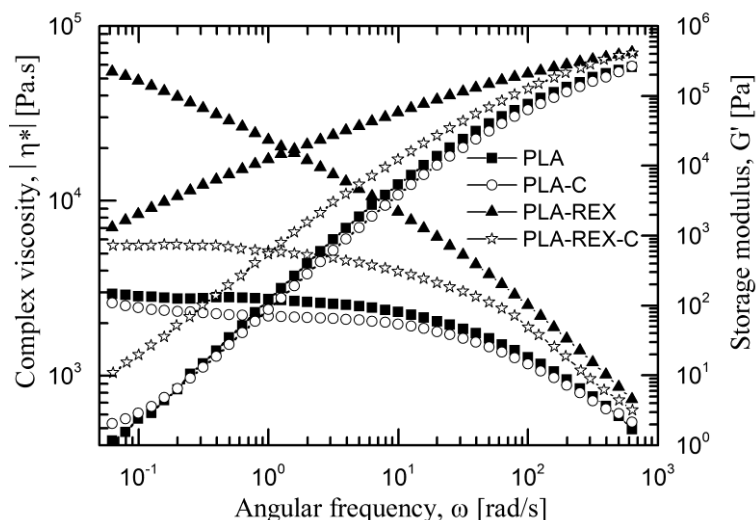
Figure 2. Rheological curves at 180 ºC of all the samples prepared by REX-Calendering process.

As expected, a significant increase in $|\eta^*(\omega)|$ and in the melt strength were observed for PLA-REX samples. This behaviour has been attributed to an increase in the molecular weight combined with the presence of long chain branching (LCB) topology leading to a better cohesive network formation [3]. Nevertheless, drastic changes in these flow properties were observed with the incorporation of OMMT. Beside a significant decrease in the $|\eta^*(\omega)|$ and $G'(\omega)$ values at low ω, the terminal region was reached at relatively high ω. According to the internal mixing process, a possible interaction of the OMMT into the reactivity of the SAmfE epoxy groups towards PD,L-LA functional groups may be expected. Premature reactions between organo-modifier functional groups and epoxy groups might inhibit branching reactions, allowing only chain extensions. Therefore, due to a possible increase in the molecular weight, η_0 and the melt strength were slightly increased but the resulting polymer featured all the characteristics of a linear one. As compared to PLA-C samples, the effect of the OMMT on the rheological response of the PLA-REX-C samples was not appreciated within the experimental window. Such transition might be shifted to lower ω justifying thereby a stronger interface between the OMMT and the polymer matrix and a higher dispersion.

3.3. Morphological characterization

TEM micrographs of the samples processed by REX-calendering process are shown in figure 3. Regarding PLA-C samples, the micrograph show principally clay agglomerations. In contrast, PLA-REX-C samples presented a higher degree of intercalation and delamination of the silicate layers.
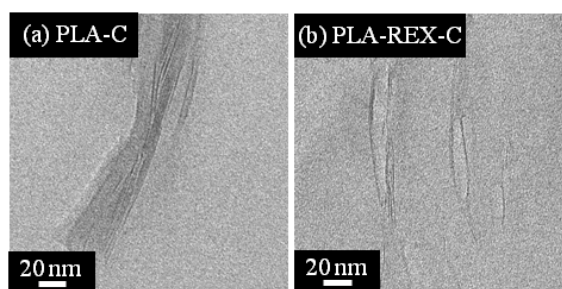
Figure 3. TEM Micrographs of (a) PLA-C and (b) PLA-REX-C samples prepared by REX-Calendering process.

3.4. Mechanical Characterization

Typical engineering stress-strain curves of all the samples processed by REX-calendering process are plotted in figure 4.a. Their respective tensile parameters are summarized in table 2. In addition, SEM analysis was performed on the fractured plane of all the samples. Figure 4. b-d shows an overview of the fractured surface together with one detailed region. In figure 4.a, it should be noticed that all samples exhibited a local maximum in the engineering stress which can be defined as a yield point. As expected, PLA, PLA-C and PLA-REX samples exhibited craze nucleation which prevent the formation of a stable neck for further strain increase. As shown in the overview of figures 4.b and 4.c, the surface topography of these samples revealed a "hackled" pattern, characteristic of a brittle behaviour (c.f. table 2). Within the experimental error, σ_y and ε_y did not seem to be affected neither by the presence of LCB nor by the introduction of OMMT. However, a slight increase in E was revealed with the introduction of the latter as already reported in the literature [5]. PLA-C and PLA-REX samples exhibited a slight increase in ε_b as compared to their neat homologues. This trend was attributed to the formation of a larger content of highly localized process plastic yielding surrounding crazes, promoted by the irregularities present in the molecular pattern (LCB) or by the debonding of the OMMT agglomerates [5,6].
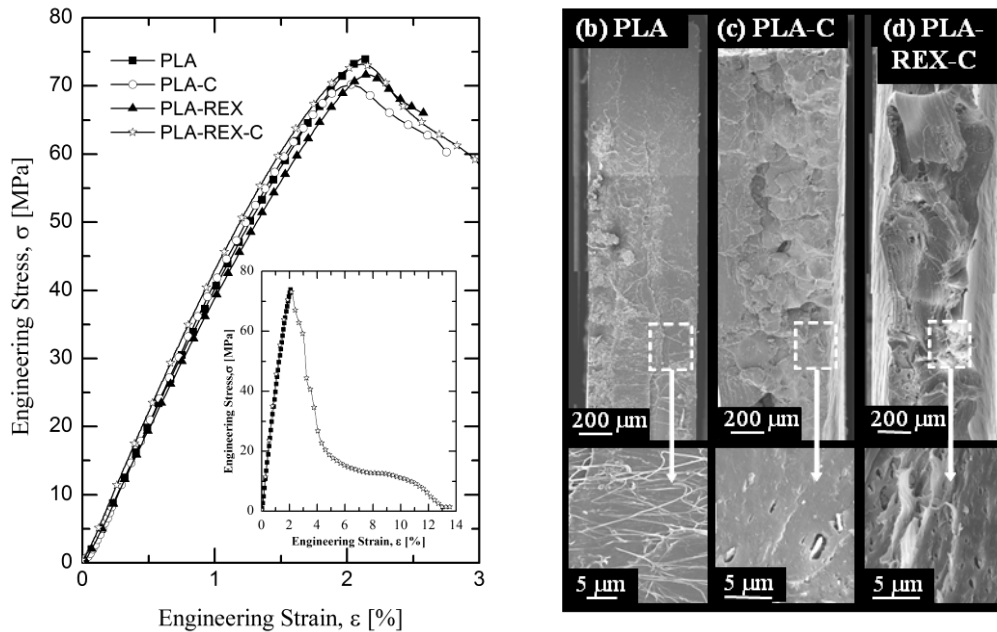
Figure 4. (a) Typical stress-strain curves at 10 mm.min^-1 and (b-d) SEM micrograph of the resulting fractured surfaces. PLA and PLA-REX samples presented similar surface morphology.

Sample Nomenclature	E [GPa]	σ_y [MPa]	ε_y [%]	ε_b [%]
PLA	3.5±0.1	74±2	2.2±0.1	2.2±0.1
PLA-C	3.7±0.1	73±3	2.17±0.01	2.8±0.1
PLA-REX	3.3±0.1	73±1	2.18±0.03	2.5±0.1
PLA-REX-C	3.9±0.1	72±2	2.3±0.1	7±3

Table 2. Uniaxial tensile parameters for REX-calendered samples at 10mm.min^-1.

In contrast, PLA-REX-C specimens featured semi-ductile behaviour. As shown in figure 4.d, the fractured surface exhibited extensive plastic deformation together with a significant reduction of the sample thickness. However, a significant proportion of microvoids are revealed resulting from a possible decohesion of the matrix around the fillers. Within the

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experimental error, σ_y and ε_y values remained unaffected as compared to the other materials. Nevertheless, a slight increase in E was measured. Under load, this trend was attributed to a better stress transfer from the polymer matrix to the OMMT as a result of the higher degree of OMMT intercalation-dispersion coupled with a possible strong chemical bonding between the fillers and the polymer matrix through SAmfE agent. In addition, after one week storage at room temperature, the higher drawability of this material might be due to a decrease in the rate of physical aging promoted by these last observations. However, this study is beyond the scope of this communication and more in-depth experiments are needed.

4. Conclusion

According to the reactive extrusion processing conditions used in the current study, the melt degradation occurring to a PD,L-LA matrix melt blended with OMMT clays was counteracted by the addition of a SAmfE reactive agent. It was revealed that premature reactions occurred between the MMT organo-modifier and the reactive agent. As compared to the OMMT-based PLA samples, this lead to the formation of a possible continuous chemical bonding between the filler and the matrix that would allow a higher intercalation-dispersion degree of the OMMT fillers into the OMMT-based PLA-REX samples. Finally, the latter samples showed semi-ductile behaviour under tensile loading after one week storage at room temperature.

Acknowledgments

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