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Flame retarded self-reinforced poly(lactic acid) composites of outstanding impact resistance

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Abstract: Impact resistant all-poly(lactic acid) composites were prepared by film-stacking of highly crystalline poly(lactic acid) (PLA) fibres with fully amorphous PLA films. The flammability of the self-reinforced PLA composites (PLA-SRCs) was effectively reduced by incorporating ammonium polyphosphate based flame retardant (FR) additive and montmorillonite clays in a weight ratio of 10 to 1 into the matrix layers. As low as 16 wt% FR content proved to be sufficient for achieving self-

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extinguishing behaviour, i.e. UL94 V-0 rating, and to achieve 50% and 40% reduction of peak of heat release rate and total heat emission, respectively. The introduction of FR additives improved also important mechanical properties compared to the FR-free all-PLA composite. The stiffness of the PLA-SRCs increased steadily with the FR contents of their matrix layers, furthermore, owing to the improved fibre-matrix bonding, prominent energy absorption capacity (impact perforation energy as high as 16 J/mm) was determined for the effectively flame retarded PLA-SRC.

Keywords: A. Polymer-matrix composites (PMCs); A. Polymer (textile) fibre; B. Impact behaviour; D. Mechanical testing.

1 Introduction

Poly(lactic acid) (PLA), being made from renewable resources, is one of the most extensively researched thermoplastic biopolymers. Thanks to its numerous advantageous properties, such as biodegradability, high degree of transparency, good strength and easy processability, PLA has significant potential to replace the conventional petrol-based thermoplastics in a wide range of applications.

Based on its mechanical strength and stiffness, PLA would be a promising candidate even for engineering applications (e.g. in construction or transportation fields), however, its inherent poor toughness [1,2] needs to be significantly improved in order to render PLA or its composites resistant to dynamic or impact stresses as well. Many studies have been conducted to overcome the brittleness of PLA by several approaches, such as chemical modification [3], blending with tougher resins or plasticizers [4,5], preparation of multi-layered film structures [6], fibre reinforcement [7,8] and use of woven structures [9,10]. However, these modifications generally affect the strength, stiffness, or degradability of PLA.

Self-reinforcement is a possible way to provide high impact resistance to polymers without compromising their inherent advantageous characteristics [11], still, this approach has not been employed to the brittle PLA substrate yet. *Nodo* et al. proposed the textile insert moulding technique, whereby PLA fabrics were attached to the surface of PLA resin by injection-compression moulding, and in the case of double textile insert mouldings recorded up to 400% improvement in impact resistance compared to the neat PLA resin [12]. For this method, however, both the (surface) position of the load bearing fabrics and the achievable maximum reinforcement content are limited, which encumbers the further enhancement of the impact resistance by this way. Although a few studies have already been published on the preparation of self-reinforced PLA composites (PLA-SRCs) by other techniques (such as compression moulding (film-stacking) [13,14,15] and hot compaction [16]), by which higher reinforcement contents are also achievable, the impact resistance of these all-PLA composite sheets have not yet been investigated.

Nevertheless, PLA is an easily flammable polymer, its heavy dripping implies increased fire danger during its burning [17,18]. Therefore, the flame retardancy of PLA based composites is indispensable when applications in electronics, transportation or construction are targeted. In our previous works, self-reinforced polypropylene composites (PP-SRCs) were successfully flame retarded by applying intumescent flame retardant (IFR) additive system in the matrix films of multi-layered composite plates manufactured by film-stacking method [19,20]. The effectively flame retarded PP-SRCs proved to have competitive mechanical performance with their additive-free reference composites even when prepared from secondary raw materials [21]. Based on these encouraging experiences, the preparation of PLA-SRCs in flame retarded form was also

targeted in this work to provide increased fire safety to the manufactured all-PLA sheets.

The flame retardancy possibilities of PLA have been comprehensively reviewed by *Bourbigot* and *Fontaine*, who revealed that the best performance can be provided through intumescence [22], however, the melt dripping is often still an issue. As for a solution, *Li et al.* reported the effective anti-dripping effect of montmorillonite (MMT) clays on PLA matrix when combined with IFR system [23].

In this study, the preparation of high-impact-strength all-PLA composites was the aim. Film-stacking and subsequent hot pressing of fully amorphous PLA films and cross-plyed reinforcing layers (composed of highly crystalline PLA multifilament yarns) was the selected method. The PLA-SRCs were flame retarded by incorporating IFR additive system in combination with MMT clays into the matrix films. The effect of the used FR additives was comprehensively studied on the morphology, flammability characteristics, and on the static- and dynamic mechanical properties of the manufactured PLA-SRCs.

2 Materials and methods

2.1 Materials

Ingeo™ Biopolymer 6302D type amorphous grade PLA, purchased from NatureWorks LLC (Minnetonka, MN, USA), was used as matrix material. The PLA resin was dried at 90°C for 8 h prior to processing.

As reinforcement, Ingeo™ Biopolymer PLA Yarn, kindly supplied by Noyfil SA - Radici Group (Stabio, Switzerland), was used. Each yarn consisted of 144 continuous filaments with a filament diameter of $20.5 \pm 0.8 \mu\text{m}$, with a crystalline melting

temperature of 174°C and with a tensile yield stress of 102.4 ± 5.8 MPa, an ultimate tensile strength of 258.3 ± 16.6 and a strain at break of $44.6 \pm 4.1\%$.

Exolit AP462 (received from Clariant GmbH, Frankfurt am Main, Germany), a melamine resin micro-encapsulated ammonium polyphosphate (APP) based additive with an average particle size (D50) of 20 μm , was used as flame retardant (FR) agent. Exolit AP462 was applied in combination with non-treated montmorillonite (MMT) clay, Nanofil[®] 116 (Rockwood Clay Additives GmbH, Moosburg, Germany).

2.2 Preparation of composites

Reference and flame retarded PLA-SRCs were manufactured by the film-stacking of cross-plyed reinforcing PLA fibre layers with neat and FR additive containing matrix films, respectively. The composition of the flame retarded matrix films was determined based on preliminary experiments executed on PLA mixtures of different FR compositions. Favourable performance/load balance was found in the case of combined application of APP (Exolit AP462) and MMT in a weight ratio of 10 to 1, thus this formulation was selected for preparation of flame retarded films.

65 ± 5 μm thick matrix films were produced from the amorphous PLA granules (Ingeo[™] 6302D) by film extrusion technique using a Labtech LCR 300 laboratory flat film line (Labtech Engineering Co., Samutprakarn, Thailand). In the case of the FR containing films, in order to ensure adequate dispersion, APP and MMT were compounded with the PLA granules using a Labtech Scientific LTE 26-44 modular twin screw extruder (Labtech Engineering Co., Samutprakarn, Thailand) and then granulated prior film extrusion. Matrix films were extruded with two loading levels of FRs, 33 wt% (i.e. 30 wt% APP + 3 wt% MMT) and 22 wt% (i.e. 20 wt% APP + 2 wt% MMT), respectively. Accordingly, the FR contents of the manufactured flame retarded

composites (PLA-SRC_FR10 and PLA-SRC_FR16), calculated by the actually measured fibre contents, added up 9.9 wt% (~10 wt%) and 15.8 wt% (~16 wt%), respectively. The codes and composition of the prepared composite sheets are summarized in **Table 1**.

The manufactured matrix films proved to be fully amorphous even after processing (as found from DSC measurements), therefore it was concluded that, below the initial melting temperature of the crystalline phase of the reinforcing PLA yarn (152°C), the composite processing temperature need to be determined principally with respect to the temperature dependent viscosity (fluidity) of the matrix materials. Accordingly, the processing temperature of 140°C was selected for composite preparation. Nevertheless, the applied FRs noticeably increased the fluidity of PLA, as found by measuring the MFI values of the flame retarded films at the composite processing temperature (140°C) (indicated in **Table 1**). It is assumed that APP induced unintended hydrolytic reactions during hot processing (extrusion and flat film extrusion) causing a decrease in molecular weight of PLA.

11 plies of 65 ± 5 μm thick matrix films and 10 PLA filament layers were laminated onto a 6 mm thick aluminium core (300 x 300 mm) in a filament winding process to obtain cross-ply configuration, as shown in **Figure 1**. The filament-wound, laminated packages were consolidated by compression moulding in a laboratory hot press (custom construction). The processing conditions such as temperature, pressure and time were optimized in terms of morphological and tensile mechanical properties; accordingly the following steps were found to be optimal; at first the packages were held for 180 s between the preheated press plates set to 140°C, then compressed for 180 s under a pressure of 1.8 MPa and finally cooled to 45°C under pressure. 2.20 ± 0.15

mm thick SR-PLA composite sheets with a nominal reinforcement of 53.5 ± 1.5 wt% were manufactured (**Table 1**).

2.3 Characterization methods

2.3.1 Morphology

The construction and consolidation quality of the SR-PLA composites were examined by reflection light microscopy (Olympus BX51M, Olympus Co., Tokyo, Japan) on polished cross sections of the sheets.

2.3.2 Flammability tests

The flame retardant performance of the prepared composite samples was characterized by *limiting oxygen index* (LOI) measurements according to the ASTM D 2863 standard. The LOI value expresses the lowest oxygen to nitrogen ratio where specimen combustion is still self-supporting.

Standard *UL-94 flammability tests* (ASTM D 635 and ASTM D 3801) were also performed on the composite specimens. UL-94 classification is used to determine dripping and flame spreading rates.

Mass loss type cone calorimeter tests were carried out by an instrument delivered by Fire Testing Technology Ltd. (East Grinstead, West Sussex, United Kingdom) using the ASTM E 906 standard method. Specimens ($100 \text{ mm} \times 100 \text{ mm} \times 2.20 \pm 0.15 \text{ mm}$) were exposed to a constant heat flux of 50 kW/m^2 and ignited using a spark igniter. Heat release values and mass reduction were continuously recorded during combustion.

2.3.3 Mechanical tests

Comparative *static tensile tests* were performed on rectangular composite specimens of $20 \text{ mm} \times 120 \text{ mm}$ (width \times length) (the gauge length was 70 mm) using a

Zwick Z020 universal testing machine (Zwick GmbH & Co. KG, Ulm, Germany) with a crosshead speed of 5 mm/min.

Comparative *static 3 point bending tests* were performed on rectangular specimens of 20 mm × 80 mm using a Zwick Z020 universal testing machine. The crosshead speed was 5 mm/min and the span length was 64 mm.

Instrumented falling weight impact (IFWI) tests were performed using a Fractovis 6785 instrument (Ceast, Instron Ltd., High Wycombe, United Kingdom) on the following settings: maximal energy: 228.64 J, diameter of the dart: 20 mm, diameter of the support rig: 40 mm, weight of the dart: 23.62 kg and drop height: 1 m. Square specimens with dimensions of 70 mm × 70 mm were subjected to IFWI tests. From the IFWI tests the specific perforation energy (E_p [J/mm]) and the ductility factor (D_r [%]) were determined. The ductility factor was calculated as the ratio of the total impact energy (E_{max}) to the energy absorbed until the maximum load (E_{Fmax}). E_{Fmax} represents mainly the energy required to initiate fracture in the specimen and corresponds to the deformation at yield, while E_{max} indicates the total energy absorbed until ultimate deformation.

$$E_p = \frac{E_{max}}{h} \quad [\text{J/mm}] \quad \quad D_r = \frac{E_{max} - E_{Fmax}}{E_{max}} \cdot 100 \quad [\%]$$

E_{max} : total energy of break [J], h : thickness of the specimen [mm], E_{Fmax} : energy at maximal force [J]

All the above listed mechanical tests were performed at room temperature and at least five specimens were tested in all cases.

Dynamic mechanical analyses were performed using a Q800 dynamic mechanical analyser (DMA, TA Instruments Inc., New Castle, DE, USA) to determine the storage modulus and loss modulus as a function of temperature for the prepared PLA samples.

Dual cantilever mode was applied with a span length of 35 mm. The width and length of the specimens were approximately 10 mm × 55 mm (cut by water jet), respectively. The scanning range of temperature was 20°C-160°C a heating rate of 1°C/min and a frequency of 1 Hz with a 0.02% deformation were selected.

3 Results and discussion

3.1 Morphology of reference and flame retarded PLA-SRCs

The morphology of the consolidated PLA-SRCs was investigated by optical microscopy. Images of the cross sections of the multilayer composites are shown in **Figure 2**. Apparently, all the composites are well consolidated. This was also confirmed by density measurements; accordingly, the density of all the prepared PLA-SRCs is above 93% of the theoretical maximum, indicating that the optimized processing parameters are adequate to obtain well-consolidated self-reinforced PLA composites.

3.2 Flammability characteristics

The flammability characteristics of the manufactured PLA-SRCs were examined by UL-94 tests, LOI measurements and mass loss calorimetric analyses. The obtained flammability test results are summarized in **Table 2**. The dripping of non-reinforced PLA specimens of 2 mm thickness is so intensive that no horizontal burning rates can be determined. The UL-94 rating of the FR-free PLA-SRC is HB, in horizontal position the PLA-SRC specimens burn with fairly high flame spreading rate ($v_{\text{flame}}=43.5$ mm/min) accompanied with intensive dripping until reaching the second mark. The use of FR matrix films with 22 wt% additive (APP + MMT) content proved to be sufficient to hinder the PLA-SRC's ability to burn horizontally. Although the flaming combustion of the PLA-SRC_FR10 specimens holds only for a couple of seconds also in vertical position (UL-94V), due to some drips of flaming particles the UL-94 rating remains V-

2. In contrast, the dripping is fully suppressed when matrix films with 33 wt% FR content are applied to form flame retarded PLA-SRC (PLA-SRC_FR16). Self-extinguishing behaviour can be observed after ignition both in horizontal and vertical position; the PLA-SRC_FR16 composite meets the requirements of the V-0 rating of the standard UL-94 flammability test. Furthermore, for this composite a LOI value as high as 34 vol% was measured. In the previous literature, at the same additive level (16 wt% IFR system) noticeably lower LOI values were reported [24], or in other words, to reach the LOI value of 34 vol% in PLA matrix, higher loadings of IFR additives were needed [25]. Considering the results obtained from the cone calorimeter tests (**Table 2**), it can be seen that already 10 wt% FR content reduces the pkHRR by 45% compared to the additive-free reference composites, however, in order to achieve significant reduction of tHR and to obtain noticeable amount of charred residue after combustion, the higher, 16 wt% FR loading was needed. Shorter TTI values were measured for all the composites than for the non-reinforced PLA reference, which is the consequence of the faster volatilization of the thin upper layers of the multi-layered structures compared to that of the thick bulk polymer.

3.3 Mechanical properties

The tensile behaviour of the reference (non-reinforced) PLA sheet and the prepared (FR-free) PLA-SRC are compared in **Figure 3a**. It can be seen that the stress-strain curves of the two materials are of different character: rigid failure is characteristic to PLA, while its self-reinforced composite shows ductile behaviour. The tensile yield stress (46.4 ± 1.7 MPa) of the PLA-SRC is by 23% lower than that of the unreinforced PLA sheet, but the measured value is in good agreement with the performance of other PLA-SRCs reported in the literature [13,15]. This can be explained by the cross-ply

configuration of the PLA-SRC (only 50% of the yarns, i.e. about 26 wt% of the composite are involved in the load transfer) and by the fact that the reinforcing PLA fibres with a failure strain of about 45% are much more ductile than the embedding matrix. As a consequence, the fibres become detached from the matrix before reaching their maximum yield stress and deform freely. This fibre debonding from the matrix occurs when the applied stress overcomes the interfacial bond strength between the matrix and the fibre, as also found by *Li* and *Yao* in the case of all-PLA composites [13]. Considering the stress-strain curves recorded during three-point bending up to 10% deflection (**Figure 3b**), the manufactured PLA-SRC shows better performance than the non-reinforced PLA reference; in respect to the flexural strength a characteristic 14% increase, while in respect to the flexural modulus a 6% increase was measured.

The tensile and flexural strength and initial moduli of the prepared PLA-SRCs are presented in **Figure 4a** and **b**, respectively. As it can be seen from the results, the tensile properties being fibre dependent are less affected by FR presence in the matrix, whereas the flexural properties being matrix dependent are lowered with FR additives. The experimental results plotted in **Figure 4a** (Young's modulus values of 10 specimens of each composite type) have been statistically tested, and the null hypothesis that the slope of the regression line for the Young's modulus values of the composites of increasing FR contents is zero ($H_0: \beta_1=0$) has been rejected ($p = 0.007$), so it was concluded that there is an increase in initial tensile modulus with increasing FR addition. The decreasing yield stress values (**Figure 4a**) measured for the flame retarded SRCs can be also connected to the increasing Young's modulus i.e. stiffness of the embedding matrix layers as a function of their FR contents, which results in somewhat

earlier slip of the ductile PLA fibres from the rigid flame retarded matrices. Nevertheless, the altogether 15% reduction of yield stress, measured for PLA-SRC_FR16 compared to the additive-free reference composite (PLA-SRC), can be considered as a fairly slight loss in mechanical performance for such an effectively flame retarded polymeric composite. The use of FRs resulted in more noticeable reduction of the flexural strength of the composites (shown in **Figure 4b**), still at 16 wt% loading of additives the flexural strength of the manufactured self-reinforced composite (56 MPa) is comparable with that of the non-reinforced PLA sheet (60 MPa, see in **Figure 3b**).

The observed trends in the mechanical characteristics of the prepared PLA-SRCs are supported by the visual observations of the failed specimens. Photographs taken of the composites after tensile testing are shown in **Figure 5**. In the case of the FR-free PLA-SRC significant fibre pull-out reveals that the matrix and the reinforcement broke at different strains, about 3% and 23%, respectively. Similarly, in the case of the 10 wt% FR containing composite also the matrix broke first, than the fibres were pulled out and continued to elongate until failure occurred, in this case, however, the noticeable vertical crack propagation indicates somewhat increased fibre-matrix adhesion. On the contrary, in the case of the PLA-SRC_FR16 sample the matrix and the fibres undergo about the same strain (35%) during deformation, their concurrent failure indicates strong bonding [13,26]. These observations can be explained by the balance of two competing phenomena. On the one hand, the FR particles decrease the fibre-matrix adhesion, and thus the interlaminar shear strength between them [21]. On the other hand, the noticeably better fluidity of the FR-containing matrix films at the composite processing temperature (see in **Table 1**) can result in better impregnation and thus in

superior interfacial bonding in the case of the flame retarded PLA-SRCs. It is presumed that in the case of the 10 wt% FR containing PLA-SRC the former effect dominates, while at 16 wt% FR content, the latter one prevails.

The impact strength of the PLA-SRCs was evaluated based on IFWI tests performed on square composite specimens with thicknesses ranging from 2.05 to 2.35 mm at room temperature. Typical thickness-related fractograms are shown in **Figure 6a** and the corresponding thickness-related perforation energy values and ductility factors are plotted in **Figure 6b**, respectively. Accordingly, significantly increased impact resistance is expressed by the flame retarded PLA-SRCs compared to the very low impact absorption capacity (0.5 ± 0.1 J/mm) of the inherently very brittle non-reinforced PLA (not shown in Figures). The outstanding perforation energy values of the self-reinforced PLA composites reveal prominent (more than one order of magnitude) improvement in impact resistance. The IFWI fractograms, shown in **Figure 6a**, help the main impact damping mechanisms of the PLA-SRCs to be understood. In the case of FR-free PLA-SRC, after reaching the maximum load a great amount of energy is absorbed progressively, as also indicated by the corresponding relatively high ductility factor of about 50%. In correlation with the tensile failure behaviour, such impact fracture character can mainly be attributed to noticeable interfacial delaminations (debonding) indicating insufficient interlaminar adhesion between the layers. In contrast, as shown in **Figure 6a**, with increasing FR contents increasing amount of energy was required to initiate fracture in the composites specimens and almost instantaneous impact failures (accompanied with decreased ductility factors) were recorded for the flame retarded PLA-SRCs. It is suggested that in these cases the fibre fracture occurs almost simultaneously with the matrix fracture, and thus the impact

energy is mainly dissipated by fibre stretching, effective dispersion of impact loading and fibre rupture. The ability of PLA fibres to stretch under tension can provide substantial support to the composites during impact loading [12], and thus the increased fibre-matrix bonding obtained for the flame retarded PLA-SRCs largely contributes to the effective energy dissipation in the multi-layered composites. As a consequence, the achieved outstanding perforation energy value of 16 J/mm renders the effectively flame retarded PLA composite (PLA-SRC_FR16) competitive with other shock-resistant polymeric composites, such as SR-PP composites [27].

In order to investigate the thermo-mechanical stability, an important applicability issue, the PLA-SRCs were examined by DMA (and compared with the performance of unreinforced PLA). The effect of temperature on the storage moduli is plotted in **Figure 7a**. The storage moduli of the PLA-SRCs were measurable until $\sim 152^{\circ}\text{C}$, which is the starting temperature of crystalline melt of the reinforcing fibres. All the PLA-SRCs exhibit higher maximum storage modulus than the non-reinforced PLA reference (2940 MPa). It can be also noticed that the stiffness of PLA-SRCs consistently increased with their FR content. In the case of the PLA-SRC_FR16 composite a 27% improvement in maximum storage modulus was measured when compared to the additive-free PLA-SRC, which can also be in connection with its better consolidation quality [27]. The unusual simultaneous improvement in stiffness and impact resistance is the result of the significant difference between the physical characteristics of PLA as a bulk material and PLA fibres. While the former one is a rigid and brittle material, after drawing the obtained PLA fibres become ductile besides that their strength and stiffness also increase in the direction of orientation. Consequently, PLA fibres can act both as reinforcing and toughening agents in the embedding brittle matrix.

The PLA-SRCs showed also superior mechanical performance as a function of temperature. While above its T_g (about 55°C) the storage modulus of the non-reinforced PLA decreased below 10 MPa, in the case of the effectively flame-retarded PLA-SRC (PLA-SRC_FR16) the storage modulus remained above 400 MPa even up to 110°C. Based on these results, it can be established that the thermo-mechanical stability of the manufactured PLA-SRCs, especially when flame retarded, is comparable [28] or even overcomes that of PP-SRCs [29].

The corresponding loss modulus results in the temperature range of 30 to 80°C are shown in **Figure 7b**. The peaks of loss modulus curves, i.e. the glass transition temperatures (T_g), of PLA-SRCs shifted to higher temperatures comparing to that of unmodified PLA. The relatively lower T_g in the case of PLA-SRC_FR16 compared to the other composites is in connection with the decreased molecular mass of the APP containing PLA film, as also proposed based on its increased MFI value (see **Table 1**).

The increased storage moduli accompanied with decreased loss modulus values and the less ductile fracture behaviour observed during both tensile and IFWI tests all indicate enhanced fibre-matrix interaction, and thus better reinforcing efficiency imparted by the PLA fibres to FR containing matrices [30]. This increased interfacial adhesion provides elastic character and toughness for the flame retarded PLA-SRCs.

4 Conclusions

The preparation of flame retarded self-reinforced PLA composites proved to be a promising way to overcome two serious drawbacks, brittleness and flammability, of PLA, simultaneously. Self-reinforced PLA composites were manufactured by film stacking of highly crystalline PLA multifilament yarns and fully amorphous PLA matrix films, also in flame retarded form. Self-reinforcement provided PLA with outstanding

impact resistance without compromising its strength, stiffness or biodegradability, while the combined application of IFR additives and MMT clays in the matrix films resulted in significantly reduced flammability compared to the readily combustible PLA. A review on inorganic polyphosphates by *Kulakovskaya* et al. [31] claims that APP is a nontoxic and biodegradable compound; its degradation by hydrolysis leads to ammonium phosphates which are common plant nutrients. Therefore, it is supposed that the used APP based FR additive may influence but not hinder the biodegradation of the all-PLA composites.

FR loading of 16 wt% ensured self-extinguishing behaviour for the PLA-SRC both when horizontally or vertically ignited, i.e. UL94 V-0 rating, a LOI value as high as 34 vol% was achieved, and a 50% reduction of pkHRR and a 40% of tHR were measured by cone calorimeter. The PLA fibres are the main load bearing substances, therefore the FR particles in the matrix films did not cause noticeable deterioration in the tensile and flexural strength of the PLA-SRCs, in contrast, the stiffness of the composites increased with increasing additive contents. Furthermore, enhanced consolidation quality was obtained in the case of the flame retarded PLA-SRCs as a result of the significantly increased fluidity of the matrix films in the presence of the used FRs. Consequently, the impact resistance of the PLA-SRCs further increased with the FR loading; the effectively flame retarded composite (PLA-SRC_FR16) exhibits an outstanding perforation energy of 16 J/mm.

Besides their indisputable environmental benefits such as renewable source and probable biodegradability, the manufactured self-reinforced PLA composites prove to have competitive mechanical characteristics with conventional petrol-based polymeric composites, both in respect to static (tensile and flexural strength and stiffness) and

dynamic mechanical properties (impact resistance and temperature dependent storage modulus), especially when flame retarded.

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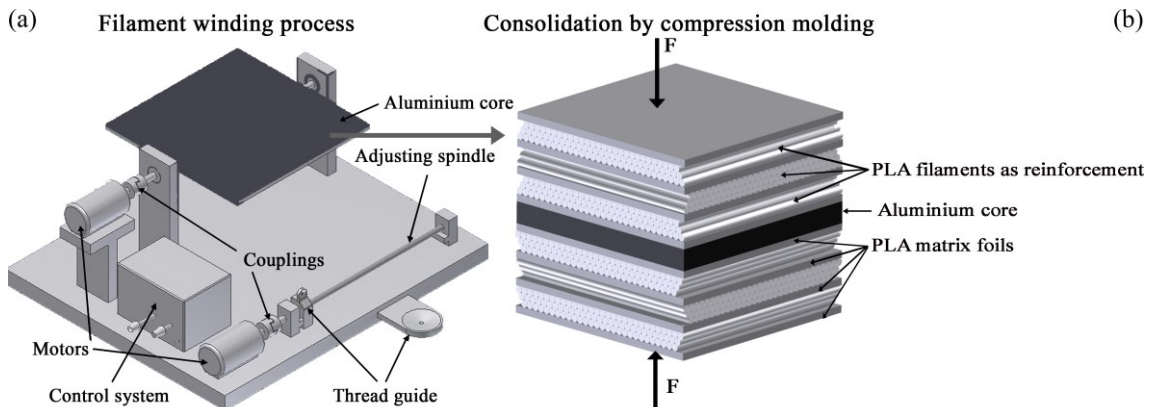


Figure 1 Preparation of cross-ply SR-PLA composites (a) with filament winding and (b) with subsequent compression moulding (theoretical lay-up)

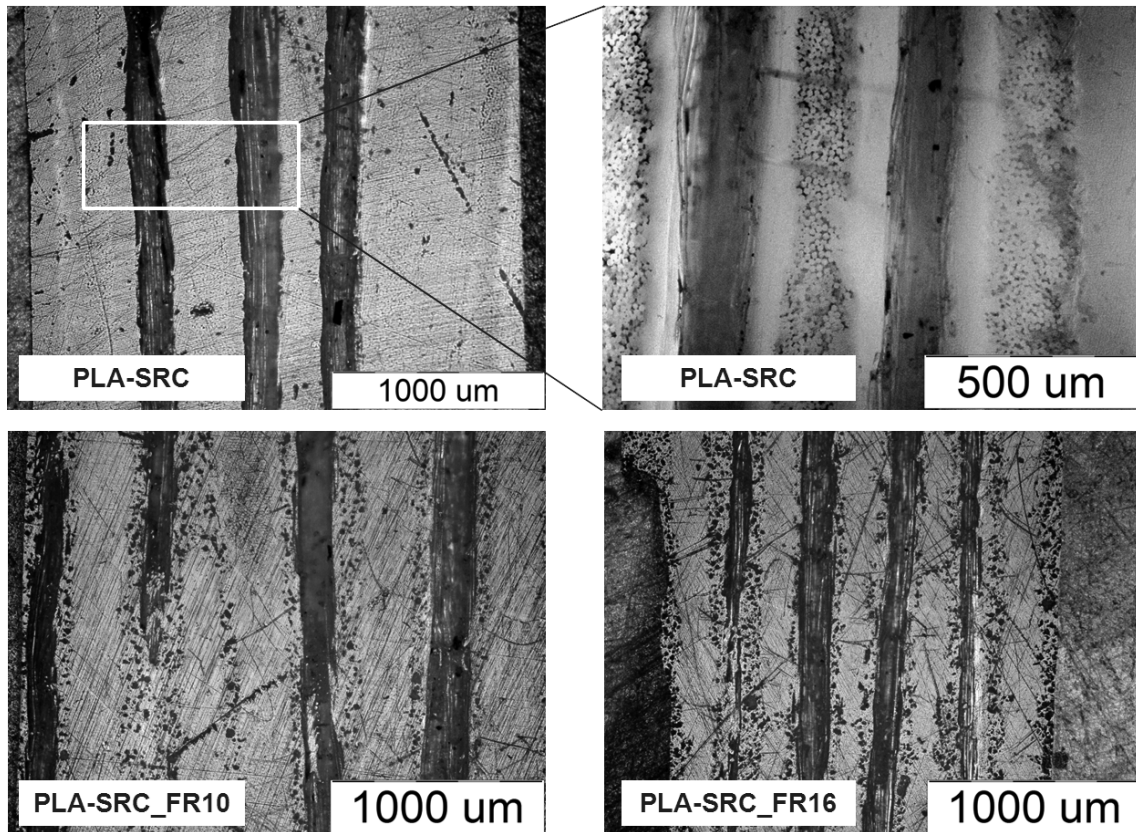


Figure 2 Optical microscopic images of the polished cross-sections of PLA-SRCs

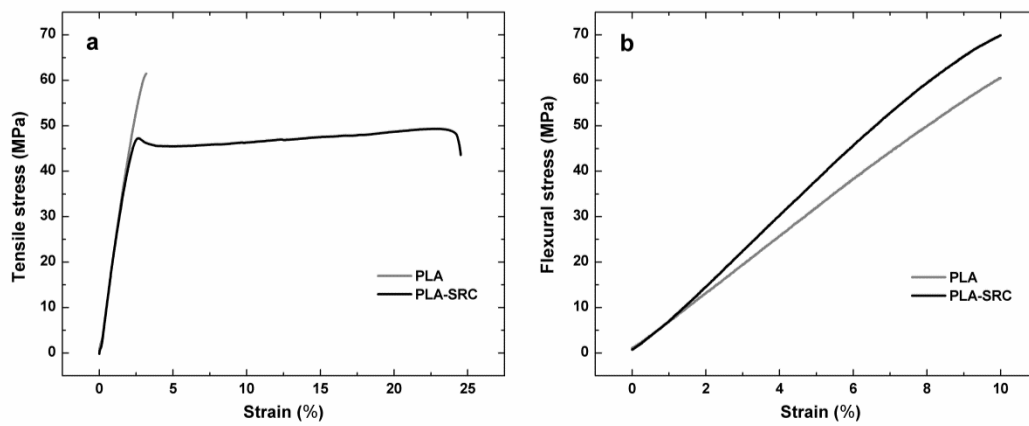


Figure 3 Characteristic stress-strain curves recorded during a) tensile and b) flexural test of non-reinforced PLA and PLA-SRC

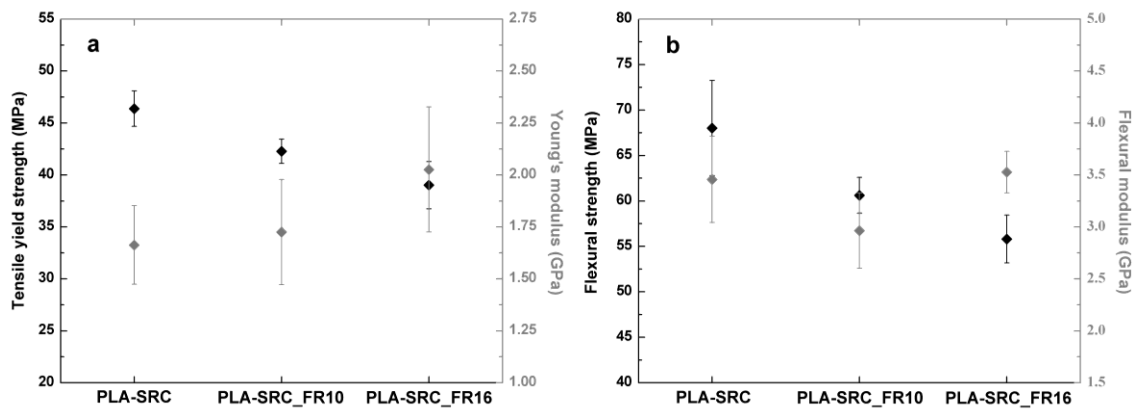


Figure 4 a) Tensile yield strength and Young's modulus and b) flexural strength and flexural modulus of PLA-SRCs

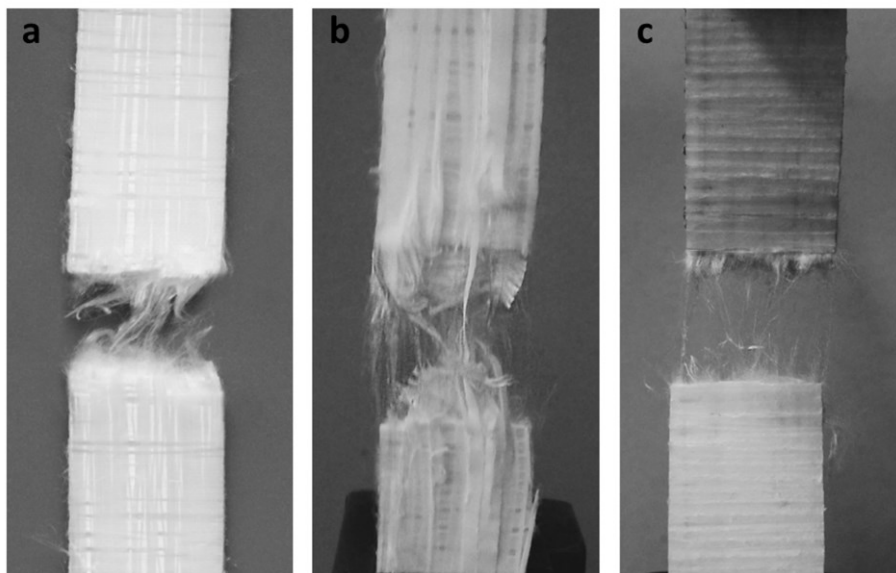


Figure 5 Photographs taken of the tensile test specimens: a) PLA-SRC, b) PLA-SRC_FR10 and c) PLA-SRC_FR16

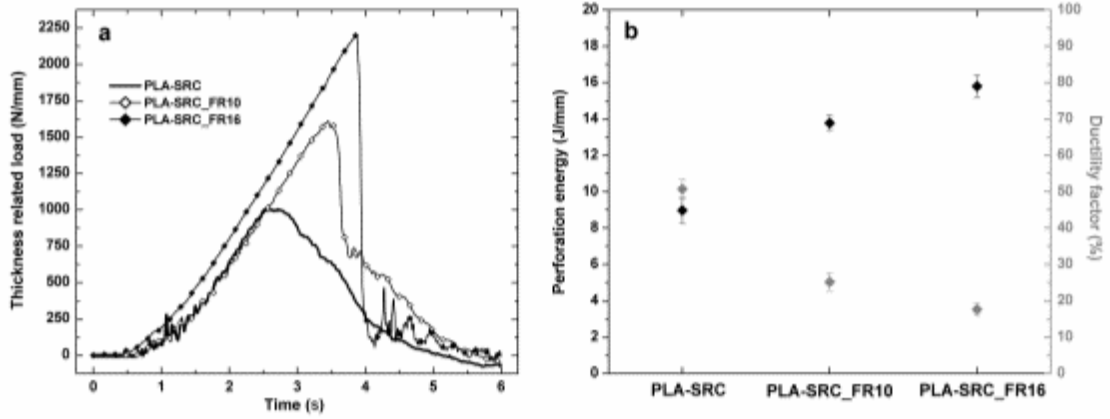


Figure 6 a) Typical thickness related load-time curves recorded during the IFWI tests and b) perforation energy and ductility factor of PLA-SRCs

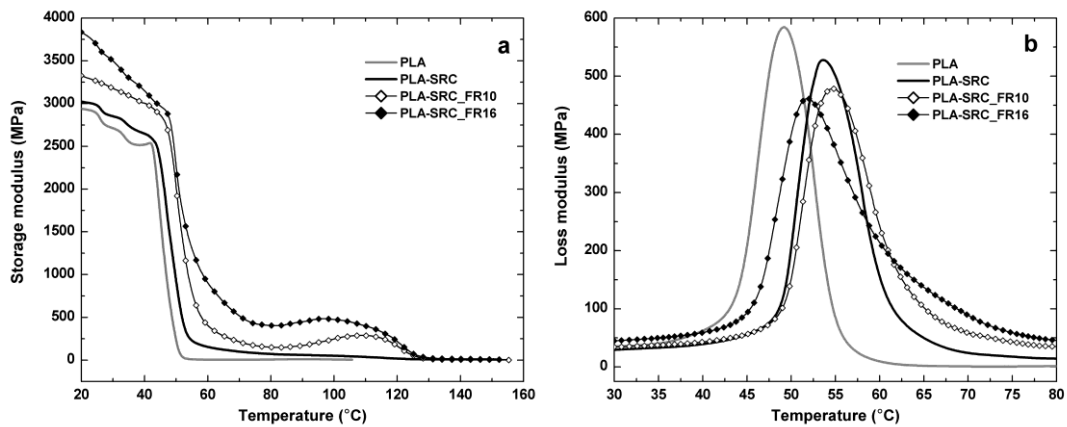


Figure 7 a) Storage modulus and b) loss modulus of PLA and PLA-SRCs

Table 1 Codes and composition of the prepared PLA-SRCs

Codes	PLA-SRC	PLA-SRC_FR10	PLA-SRC_FR16
Reinforcement content of the composite [wt%]	54	55	52
FR content of the matrix films [wt%]	0.0	22.0	33.0
MFI of the matrix films at 140°C/2.16kg [g/10 min]	0.73 ± 0.02	2.81 ± 0.22	5.52 ± 0.64
Overall FR content of the composite [wt%]	0	9.9	15.8

Table 2 Flammability characteristics of PLA and the PLA-SRCs

	PLA	PLA-SRC	PLA-SRC_FR10	PLA-SRC_FR16
UL-94	no rating	HB	V-2	V-0
rating	v_{flame} : not measurable	$v_{\text{flame}} = 43.5$ mm/min		
LOI	21	23	30	34
[vol%]				
TTI	31	20	18	18
[s]				
pkHRR	401	425	233	207
[kW/m ²]				
tHR	44.4	49.5	47.8	29.4
[MJ/m ²]				
residue	0.3	1.3	4.85	16.5
[%]				

v_{flame} : flame spreading rate [mm/min]; LOI: limiting oxygen index, TTI: time to

ignition; pkHRR: peak of heat release rate; tHR: total heat released

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