Keratin fibres derived from tannery industry wastes for flame retarded PLA composites

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Abstract

In this work, keratin fibres (KFs) were recovered from tannery industry wastes and reused for preparing completely green materials based on poly(lactic acid) (PLA) composites. A specific process for extracting and treating KFs as reinforcing and flame retardant agents for PLA was used. KFs were characterized by scanning electron microscopy, thermogravimetric analysis (TGA) and total nitrogen content by Kjeldahl method. PLA was compounding using both KFs at different contents and KFs in combination with a traditional flame retardant, namely, aluminium trihydroxide (ATH), in order to exploit the joint action between these two species. PLA composites were studied by scanning electron microscopy, thermogravimetry in nitrogen and air, UL94 classification, dynamical-mechanical, mechanical and rheological measurements. As a result, a good KF/polymer matrix adhesion was observed. Thus, PLA passes from V2 with only KFs (3 phr) to V0 classification when KFs are added in combination with 30 phr ATH. Tensile strength was increased by 16%, strain at break by 40% and tenacity by 66% when ATH content was reduced from 50 phr down to 30 phr in joint combination with 3 phr KF content. Rheological measurements in simple and oscillatory shear flows showed that KFs reduced the viscosity of the investigated materials, improving the processability of composites.

Keywords: Keratin fibres; flame retardant; thermal stability; PLA; tannery wastes.

1. Introduction

As it is well known, the industrial and agriculture activities produce a considerable waste amount, mainly concerning the high volumes of fibres and fibrous materials. Several efforts have been carried out in the word in order to reduce such problem. However, the high cost of the specific treatments for fibres, processing difficulties and development of desired properties for producing useful products are still the main issues to consider when preparing materials reinforced with fibres from industrial wastes [1-2]. A great number of investigations have been published in the polymeric materials research area on natural fibres as reinforcing agents from the agriculture industry for over 40 years. These reports have been focused on cellulosic fibres as biofibres due to their positive environmental impact, non-abrasive properties, economical production and low specific weight [3-4]. As an example, cellulosic composites have been extensively used in the automotive industry for producing fibre-reinforced composite polymeric materials ever since 1957 [3, 5-6]. The properties of these composites (natural fibre/polymer matrix) depend on different parameters such as fibre type, fibre content, fibre pre-treatment, fibre/polymer matrix compatibility and processing [7-9]. As far as fibres derived from animals are considered, in the last decade, both industrial and academic researchers have paid a great attention to keratin fibres (KFs) from poultry feathers. Indeed, it has been found that KFs can effectively act as reinforcing agent for polymers, increasing their Young's modulus, tensile strength, flexural modulus, and hardness. KFs have also reported to increase polymer thermal stability better than cellulosic fibres [10-12].

On the other hand, tannery industry is a high pollutant emission sector. The wastes derived from this sector have a strong negative environmental impact due to the high content of the organic matter in the effluents or solids [13]. During tannery leather process, the beamhouse stage is the first step to tanner leather; in this stage different operations are involved; one of them is the ***liming*** step that requires several alkaline products, which chemically attack the keratin, causing skin swelling and hair detaching. From this operation, the wastes are handed as slurry, and then separated in solid and liquid parts. Sometimes the hair is partially removed through a mechanical operation halfway through the liming operation and it is thrown in sanitary fills [14-15]. However, wasted hair is considered an important keratin fibre source that can potentially have important applications in polymer materials.

To the best of our knowledge, in the literature there are no published papers on the use of KFs derived from tannery industry wastes as reinforcing and flame retardant agent in polymeric composites. Considering that poly(lactic acid) (PLA) is one of the main biopolymers produced and commercialized up to now, its applications are being addressed to different fields where flame retardant properties are required [16]. Thus, PLA/KF composites might be valuable and potentially green materials.

In this context, the present work assesses the potential of keratin fibres derived from tannery industry waste as both: flame retardant and reinforcing agent for PLA. A specific conditioning treatment for KFs was carried in order to make them suitable for the extrusion with PLA. The effect of keratin fibre content as well as the joint action with a halogen-free flame retardant (namely, ATH) on morphology, thermal stability, flame retardant, dynamic-mechanical, mechanical and rheological properties of the resulting materials was thoroughly investigated.

2. Experimental part

2.1 Materials

Poly(lactic acid) (PLA) INGEO 3251D was purchased from NarureWorks LLC; keratin fibres (KFs) were extracted as waste from Mexican tannery industry, fibre length of 1÷5 mm, measured with a stereomicroscope Nikon SMZ 1270; aluminium trihydroxide (ATH), industrial grade (99.5% purity), particle sizes of 1.0÷2.5 µm and surface area of 12 m^2/g was supplied by ABAQUIM, Mexico.

2.2 Keratin fibre treatment

As mentioned above, KFs (derived from hair skin bovine) were obtained from the slurry of by-products from the beamhouse stage during the tannery process of the Mexican industry. The slurry was rinsed and delimed in order to reduce the high alkalinity produced in the liming stage and degreased, these steps were carried out using tannery test drums. After degreasing, keratin fibres were dried initially outdoor and then in an oven at 40°C for 12h.

The total nitrogen content within keratin fibres (the main component) was assessed by Kjeldahl method. Briefly, this method consists in digesting sample in sulphuric acid, which converts nitrogen-based compounds (mainly, proteins, amines, organic compounds) into ammonia. Then, free ammonia is released by the addition of caustics, which are then expulsed by distillation and subsequently titrated [17]. The result of such analysis on KFs employed in the present study was 91.0 % total nitrogen in protein form.

2.3 Preparation of PLA composites by extrusion

PLA composites were obtained by extrusion process by using a twin-screw counter-rotating Leistritz Micro 27 extruder, L/D = 32 and 27 mm diameter with 8 heating zones. The counter-rotating intermeshing extruder was used because the compounding is forced to pass between two screws increasing pumping and melt pressure towards the die. In industry, co-rotating intermeshing is generally preferred by the higher output rate. Before extrusion, neat PLA was dried under vacuum, the operating pressure during the heating stage was 80 psi (0.5516 MPa) and 110°C for 30 min. In order to investigate the flame retardant effect of KFs on PLA, a reference sample using high traditional flame retardant additive content was prepared (namely, PLA_ATH_{50} sample). Samples with different KF content and samples using both KFs and ATH were prepared, as well. All ~~composite~~ materials were compounding under a temperature profile 165/165/175/175/185/185/190°C at 100 rpm rotational speed. Table 1 describes the composition of investigated materials.

Table 1. Formulations.

Sample	KF content [phr]	KF content [wt.-%]	ATH content [phr]	ATH content [wt.-%]
PLA	-	-	-	-
PLA_ATH_{50}	-	-	50	33.3
PLA_ATH_{30}	-	-	30	23.1
PLA_KF_{10}	10	9.1	-	-
PLA_KF_{5}	5	4.8	-	-
PLA_KF_{3}	3	2.9	-	-

PLA_KF_{10}/ATH_{30}	10	7.1	30	21.4
PLA_KF_5/ATH_{30}	5	3.7	30	22.1
PLA_KF_3/ATH_{30}	3	2.2	30	22.2

2.4 Preparation of PLA sample by injection moulding

Samples for flammability (125 x 13 x 3 mm^3), mechanical (specimen sizes according to the type I, thickness 3.1±0.1 mm described in the ASTM D638 standard) and dynamic-mechanical (60 x 13 x 3 mm^3) tests were obtained in an injection moulding machine Milacron TM55 model under the following conditions: 175/185/190/180°C temperature profile, 70 mm/s injection speed, 110 bar injection pressure and 20 s cooling time. All materials were dried under vacuum before injection moulding under the same conditions mentioned before for extruding PLA.

2.4 Characterization

The morphology of PLA and corresponding materials was studied using a JEOL JSM-7600F Scanning Electron Microscope (SEM). Fractured pieces were gold-metallized in order to make them conductive. Flame retardant properties were assessed following the UL94 classification in vertical configuration according to the ASTM D3801 standard [18]. Mechanical tests were carried out using a tensile Instron machine 5565 at 50 mm/min crosshead speed, following the ASTM D638 standard [19]. Thermogravimetric analysis (TGA) was carried out by a TA-Instrument Q5000 IR Discovery calorimeter under a heating rate of 10°C/min in nitrogen and air atmospheres; the experimental error was ±1°C and ±0.01 wt.-%. Temperatures at 10 wt.-% loss ($T_{10\%}$), at maximum weight loss (T_{max}) and final residues at 600°C were assessed. Rheological measurements were performed in a stress-controlled TA-Instrument G2 rheometer using parallel-plates (25 mm diameter); all tests were carried out at the temperature of 190°C and gap of 0.75 mm, under Small Amplitude Oscillatory Shear flow (SAOS) measurements. The oscillatory tests were performed in linear viscoelastic regime (5% strain). Dynamic-mechanical analysis were carried out in a TA-Instrument Q800 analyser with a frequency of 1.0 Hz, amplitude of 10 μm and heating speed of 3°C/min using a dual cantilever geometry at 30-110°C temperature range; storage modulus (E′) was assessed and the experimental modulus error was ±1%.

3. Results and discussion

3.1 Morphology

Figure 1 displays the SEM micrographs of the fractured surfaces for PLA (A), KFs (B), PLA_KF_{10} (C) and PLA_KF_{10}/ATH_{30} composites (D). According to the micrograph reported in Figure 1A, PLA exhibits a fragile fracture, since fracture planes are well defined, characterised by flat surfaces and no deformation is visible; thus, the observed morphology is characteristic of rigid and fragile materials. Figure 1B depicts a typical morphology of KFs [20-22]: fibres with cylindrical shape having a diameter of approximately 43 μm and characterised by overlapped layers on the surface (cuticle) are observable. In order to study keratin fibre morphology, several micrographs were taken (*see* Figures S1-S5 included in the Supplementary Material), same cylindrical shapes with different fibre diameters from 16 up to 83 μm (43 μm, average diameter) were observed; this variability can be ascribed to the natural source of KFs (hair skin bovine).

The morphology of PLA loaded with KFs (10 phr) is reported in Figure 1C; KFs lie in different fractured planes with respect to the matrix, without interstices between keratin fibre and polymer; the above morphology suggests that such fibres is likely to act as mechanical reinforcement for PLA. When ATH is added to the formulation (namely, PLA_KF_{10}/ATH_{30} sample), no interstices around fibre and good adhesion between keratin fibres and polymer matrix are clearly observed (*see* Figure 1D). According to this finding, it is reasonable that KFs have somewhat chemical or physical interactions with PLA matrix, regardless of the ATH presence.

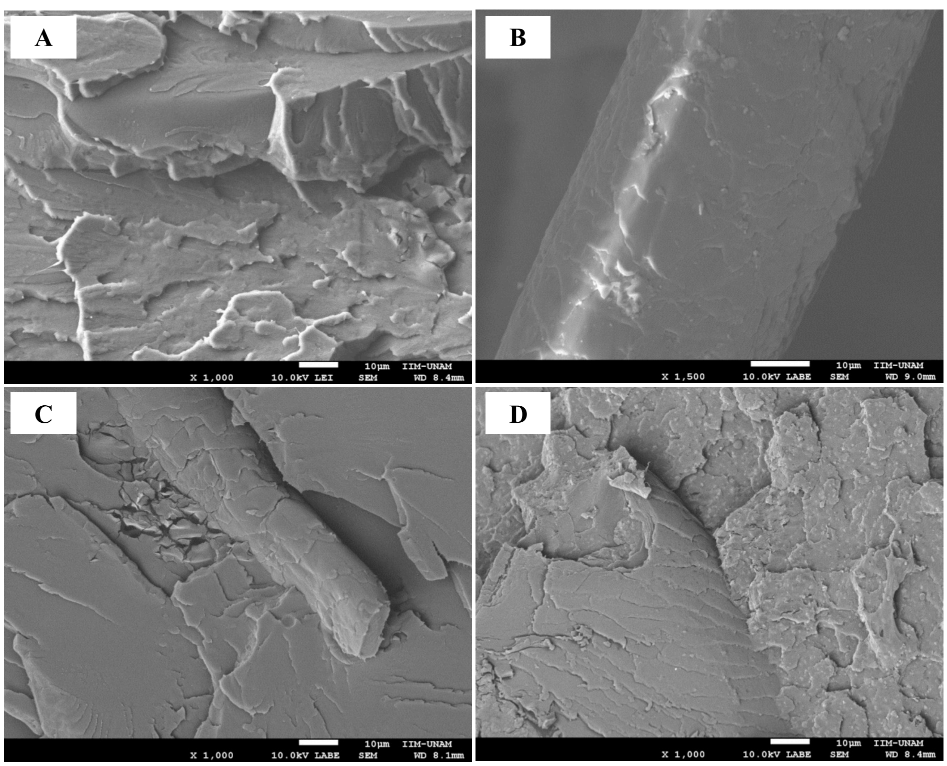


Figure 1. SEM micrographs of A) Neat PLA (1000X) and B) KF (1500X), C) PLA_KF_{10} (1000X) and D) PLA_KF_{10}/ATH_{30} (1000X) composites.

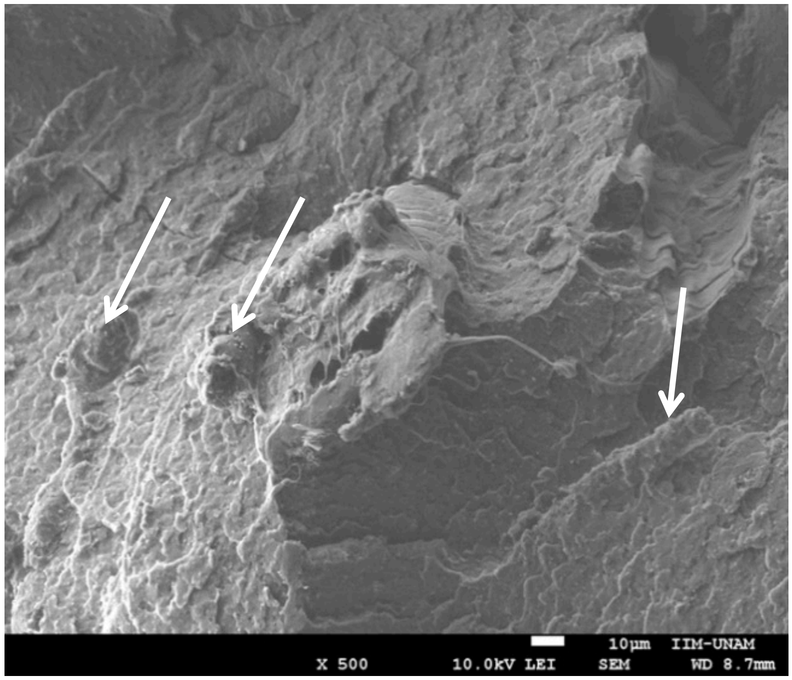


Figure 2. SEM micrograph of PLA_KF_{10}/ATH_{30} composite at 500X.

Figure 2 shows PLA_KF_{10}/ATH_{30} morphology in a different point with respect to that reported in Fig 1D at 500X magnification; it is interesting to observe that KF surface is homogeneously coated by the polymer (pointed out by white arrows) and fibres appear embedded within the matrix; no empty holes caused by the fibre pull out are observed. According to the observed morphologies, KFs exhibit a very good adhesion with polymer, probably due to the hydrophobic feature with high aspect ratio typical of KFs; therefore chemical or physical bonds can be possible, as already stated and observed in the literature [23-24].

3.2 Thermal stability

Thermal properties of keratin fibres were assessed and compared with those of ATH by TGA under nitrogen and air. Figure 3 displays the weight loss as a function of temperature under nitrogen atmosphere (TG and dTG curves in A and B, respectively) and Table 2 discloses the collected data.

According to Figure 3, KFs loss 10% weight (Figure 3A) at 233°C ($T_{10\%}$ in Table 2). The main degradation step occurs at 304°C (T_{max}, *see* dTG curve in Figure 3 and Table 2); at that point, the weight loss rate is 0.58%/°C. Meanwhile at 282°C ATH shows its main degradation step (T_{max}) with a weight loss rate of 0.79%/°C. At 600°C, KFs and ATH left 24.2 and 65.8% of final residue, respectively.

In air (Figure 4 and Table 2), the main degradation of KFs undergoes two steps, the former with a T_{max} of 340°C (with 0.43%/°C weight loss rate) and the latter at 556°C (with 0.51%/°C weight loss rate). In the meantime, ATH degrades in air by a single step having a T_{max} of 313°C, with 0.87%/°C weight loss rate.

According to the collected data by TGA, KFs have proven to be thermally stable both in nitrogen and air. This finding is probably due to its chemical structure; indeed, keratin is a protein with a complex quaternary structure rich of amino acids and disulphide bonds that upon heating releases volatile species such as NH_3, CO_2, and SO_2 as well as produces H_2S able to induce the formation of phenol-based compounds at approximately 300°C. The latter compounds are thermally stable structures at very high temperatures [25]. This behaviour seems to be a specific feature of some proteins such as whey proteins, caseins and hydrophobins, as already demonstrated [26-29].

(A)

(B)

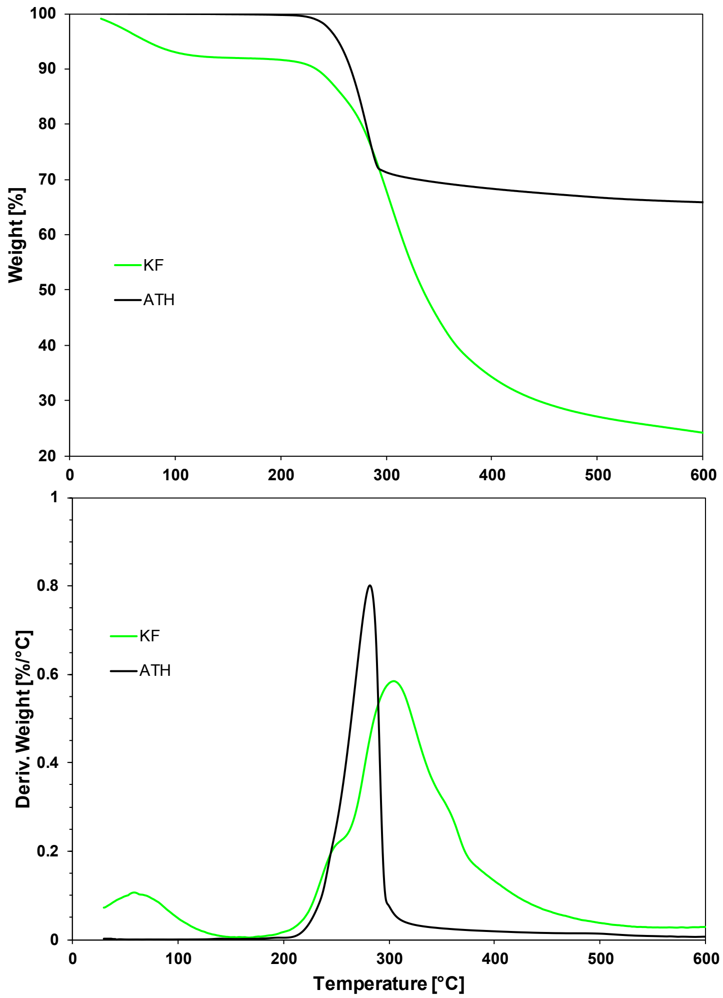


Figure 3. TG (A) and dTG (B) curves of KFs and ATH in nitrogen.

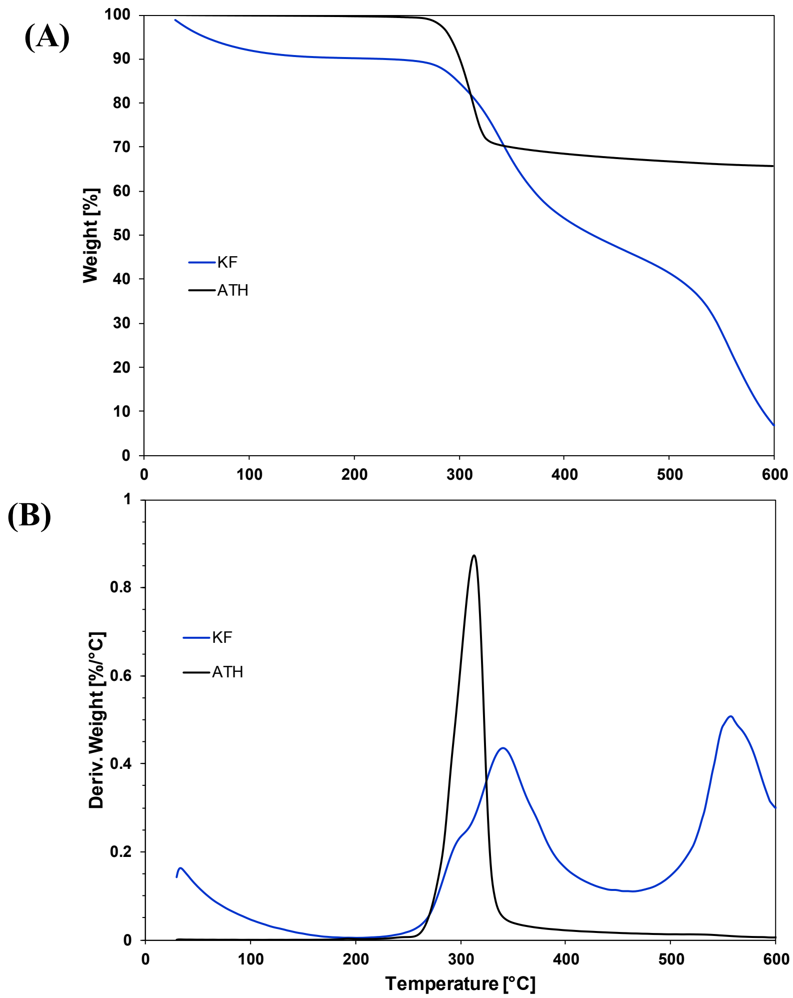


Figure 4. TG (A) and dTG (B) curves of KFs and ATH in air.

Table 2. TGA data of neat KFs and ATH in nitrogen and air.

Sample	Nitrogen			Air		
	$T_{10\%}$ [°C]	T_{max*} [°C]	Residue at 600°C [%]	$T_{10\%}$ [°C]	T_{max*} [°C]	Residue at 600°C [%]
KFs	233	304	24.2	220	340, 556	7.0
ATH	266	282	65.8	301	313	65.8

*From derivative curves (Figures 3B and 4B).

As far as PLA and KF-based composites are concerned, Figures 5 and 6 reports the TG (A) and dTG (B) curves in nitrogen and air, respectively.

In nitrogen, neat PLA degrades through a single decomposition step, without leaving any residue at 600°C. Indeed, 0.3% reported in Table 3 can be considered negligible, taking into account the experimental error on weight in TGA (*see* Experimental Part).

The presence of KFs, regardless their content (namely, 3, 5 or 10 phr), significantly anticipates PLA thermal degradation, as well evidenced comparing the $T_{10\%}$ values reported in Table 3. In spite of this, PLA/KF T_{max} remains almost constant and KFs induce the formation of a final residue at 600°C that is a function of their content in composite. KFs reduce the weight loss rate with respect to neat PLA; PLA_KF_3, PLA_KF_5 and PLA_KF_{10} formulations showed weight loss rates of 2.3, 2.3 and 2.1%/°C, respectively, that are significantly lower than that of PLA, namely 2.6%/°C (Figure 5B). When only ATH is added to polymer matrix (PLA_ATH_{50} and PLA_ATH_{30}), the anticipation of PLA degradation is more evident, 316 and 310°C for PLA_ATH_{50} and PLA_ATH_{30}, respectively, with respect to 369°C for neat PLA, but at the same time ATH favours the formation of a significant residue at T_{max} (23.3 and 16.5%) that is thermally stable up to 600°C (Figure 5A). The addition of ATH also contributes to reduce the weight loss rate: namely, 2.1 and 2.2 vs. 2.6%/°C for PLA_ATH_{50}, PLA_ATH_{30} and PLA, respectively (Figure 5B).

The KF/ATH formulations (PLA_KF_{10}/ATH_{30}, PLA_KF_5/ATH_{30} and PLA_KF_3/ATH_{30}) exhibited an analogous behaviour to that of samples containing only ATH (PLA_ATH_{50} and PLA_ATH_{30}) in terms of T_{max} and $T_{10\%}$.

~~Unfortunately, some antagonist phenomenon occurred for the formation of a thermally stable residue, as well visible comparing the values of the residues reported in Table 3.~~

However, KF/ATH formulations showed lower weight loss rate than PLA and PLA/ATH formulations (Figure 5B). As an example, when KFs are added at the lowest content (PLA_KF_3/ATH_{30}), the weight loss rate is 1.6%/°C, significantly lower than those of PLA, PLA_ATH_{50} and PLA_ATH_{30} (2.6, 2.1 and 2.2%/°C, respectively).

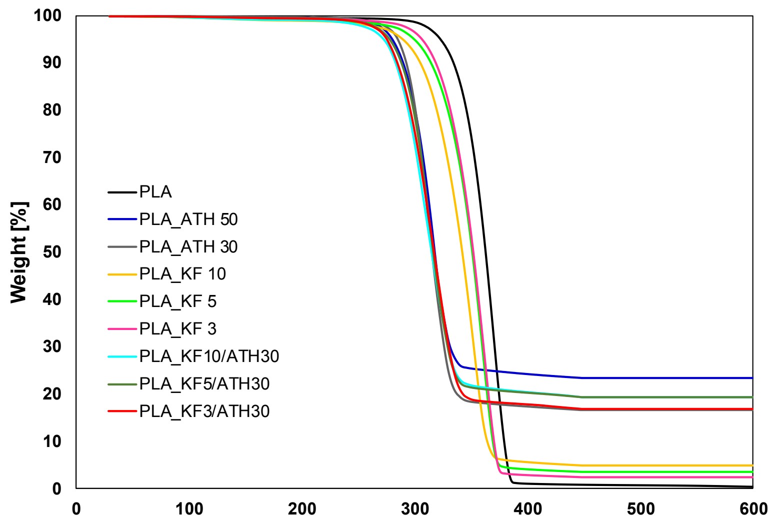
Thermal analysis in nitrogen has pointed out that the KF presence in combination with ATH exhibited similar thermal stability in terms of $T_{10\%}$ and T_{max} with respect to the reference sample (PLA_ATH_{50}) and even lower weight loss rate.

In air (Figure 6) the thermo-oxidation of PLA and composites occurred through a single step, similarly to what observed in nitrogen (*compare* Figures 5A and 6A). Once again, the presence of KFs in combination with ATH, regardless of their content, promotes the anticipation of PLA degradation as well as the formation of a thermally stable residue at 600°C. This behaviour is ascribed to the ATH presence, since T_{max} for PLA_ATH_{50} and PLA_ATH_{30} was 344 and 304°C, respectively. Meanwhile, when KFs are added without ATH, T_{max} values were 395, 395 and 385°C (PLA_KF_{10}, PLA_KF_5 and PLA_KF_3).

With respect to weight loss rate in air (Figure 6B), the lowest value was observed in PLA_ATH_{50} composite (1.5%/°C). Similar results were showed when KFs is added in combination with ATH (1.7, 1.7 and 1.8%/°C for PLA_KF_{10}/ATH_{30}, PLA_KF_5/ATH_{30} and PLA_KF_3/ATH_{30}, respectively).

According to Figure 6 and Table 3 (TGA in air), the thermal stability of formulation containing KFs in combination with ATH is nearly similar to that of PLA_ATH_{50} in terms of T_{max} and weight loss rate.

(A)



(B)

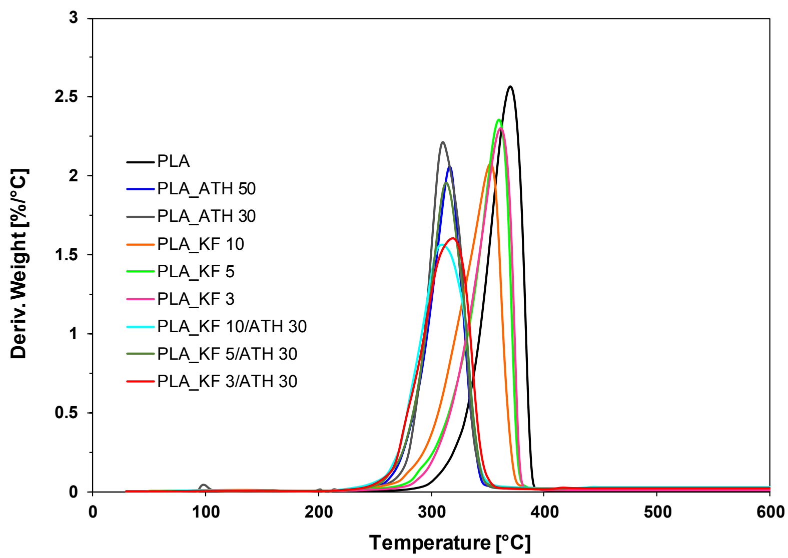


Figure 5. TG (A) and dTG (B) curves of neat PLA and composites with KFs and ATH in nitrogen.

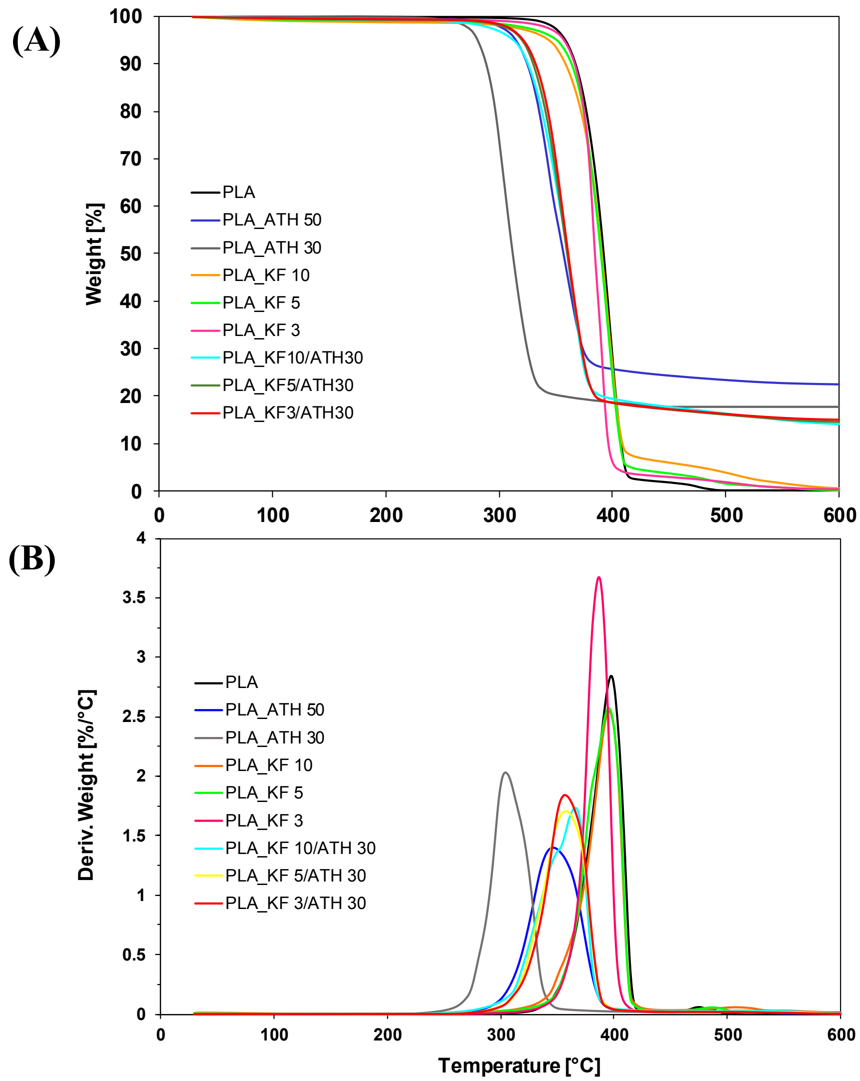


Figure 6. TG (A) and dTG (B) curves of PLA and composites with KFs and ATH in air.

Table 3. TGA data of neat PLA and composites in nitrogen and air.

Sample	Nitrogen			Air		
	$T_{10\%}$ [°C]	T_{max*} [°C]	Residue at 600°C [%]	$T_{10\%}$ [°C]	T_{max*} [°C]	Residue at 600°C [%]
PLA	334	369	0.3	367	397	0.0
PLA_ATH$_{50}$	290	316	23.3	325	344	22.5
PLA_ATH$_{30}$	292	310	16.5	288	304	17.7
PLA_KF$_{10}$	305	359	4.8	358	395	0.5
PLA_KF$_{5}$	315	360	3.6	364	395	0.1
PLA_KF$_{3}$	319	362	2.5	366	385	0.3
PLA_KF$_{10}$/ATH$_{30}$	285	310	19.3	325	365	14.2
PLA_KF$_{5}$/ATH$_{30}$	288	313	19.3	330	358	14.6
PLA_KF$_{3}$/ATH$_{30}$	285	319	16.8	332	355	15.0

*From derivative curves (Figures 5B and 6B).

3.3 Flammability

Flammability of PLA and KF-base composites was assessed in terms of resistance to a flame application in vertical configuration, following the UL94 classification. Table 4 summarises the collected data. In detail, neat PLA is a high flammable material resulting as not classifiable in UL94 classification (NC in Table 4). Indeed, during combustion, PLA vigorously burns with intense dripping; by this way, flaming drops ignite cotton. The observed behaviour does not allow PLA passing such test and to reach the highest performances (namely, V0 classification).

In order to investigate the effect of KFs on flammability of PLA composites, reference samples, namely, PLA_ATH$_{50}$ and PLA_ATH$_{30}$ were tested, as well. Indeed, according to the collected results and published in the literature [30], PLA_ATH$_{50}$ has been classified as V0 and PLA_ATH$_{30}$ as V2. These results show the high content of ATH that is required to reduce flammability properties of PLA.

When KFs are used as flame-retardants for PLA at different contents (3, 5 and 10 phr), the corresponding materials have proven to be classified as V2 (Table 4). These results indicate that KFs can be used at low content (3 phr) for reducing PLA flammability, analogously to what occurs using 30 phr ATH, even though the highest performances (V0 classification) are not reached. Higher flame retardant levels have been found when KFs were combined with ATH in new formulations having the advantage to contain a lower amount of ATH with respect to the reference (30 *vs*. 50 phr, Table 1). Regardless of KF content, PLA_KF$_{10}$/ATH$_{30}$, PLA_KF$_{5}$/ATH$_{30}$ and PLA_KF$_{3}$/ATH$_{30}$ composites reached V0 classification.

Figure 7 displays some digital pictures of the samples tested following the UL94 classification; more precisely, pictures in Figures 7A, 7B and 7C refer to composites containing 10, 5 and 3 phr content of KFs and Figures 7D, 7E and 7F to composites containing the same KF content with 30 phr of ATH. It has been observed that the samples containing KFs without ATH exhibited a more intense phenomenon of dripping with respect to the counterparts containing also ATH or only ATH (Figures 7G and 7H). As far as PLA flame retardancy is concerned, Bourbigot and Fontaine reviewing several papers on flame retardancy of PLA [16] concluded that ATH acts as efficient flame retardant i) by diluting flammable compounds released by PLA in the gas phase, ii) by partially absorbing the combustion heat for promoting its dehydration with consequent water vaporisation, as well as iii) by forming an insulating layer of Al_2O_3.

Regarding the flame retardant mechanism conceivable for KFs, it is well known that wool has inherent low flammability, due to the high nitrogen and sulphur content in the amino acid skeleton, disulphide bonds and crosslinking level between adjacent chains [31]. An analogous mechanism and similar conclusions have been proposed for the combustion of KFs derived from poultry feathers due to their chemical structure and amino acid type and content [32-33]. According to these statements and to the flammability data reported in Table 4, it is reasonable to ascribe a similar action mechanism also to KFs from tannery industry.

Comparing the flame retardant properties achieved by using KFs, derived from tannery industry wastes, and other natural fibres in polymer composites, some previous research works have pointed out that milled keratin fibres obtained from poultry feathers in elastic polyurethane foams (10 and 16% of KF content) improved their limiting oxygen index (LOI) values and reduced the burning rate in horizontal position test [32]. Coconut fibres (10 phr) in combination of aluminium trihydrate (30 phr) in a starch-based biocomposite, reduced the burning rate according to UL94 horizontal position test and slightly increased the LOI value~~; these results were attributed to coconut fibres induced some charring activity~~ [33]. Ramie fibres combined with ammonium polyphosphate (APP) at 40 wt.% in PLA composites showed V0 in UL94 classification and an increased LOI value [16].

From an overall consideration, the results collected here employing KFs have demonstrated their higher potentialities as flame retardant agents for PLA composites even at low content (3phr) with respect to the other fibres.

Table 4. Flammability data of neat PLA and composites following the UL94 classification (sample thickness=3 mm).

Sample	UL94 classification
PLA	NC*
PLA_ATH_{50}	V0
PLA_ATH_{30}	V2
PLA_KF_{10}	V2
PLA_KF_{5}	V2
PLA_KF_{3}	V2
PLA_KF_{10}/ATH_{30}	V0
PLA_KF_{5}/ATH_{30}	V0
PLA_KF_{3}/ATH_{30}	V0

* NC: Not classifiable.

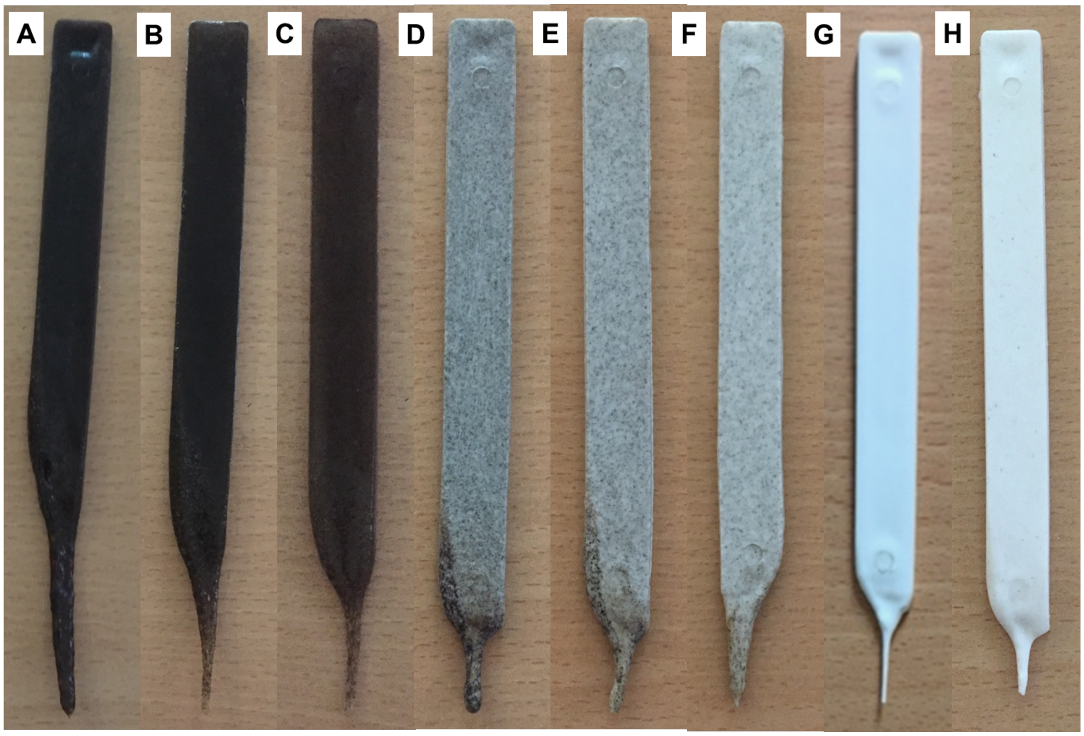


Figure 7. Digital pictures of samples under investigation after UL94 tests: A) PLA_KF$_{10}$, B) PLA_KF$_5$, C) PLA_KF$_3$, D) PLA_KF$_{10}$/ATH$_{30}$, E) PLA_KF$_5$/ATH$_{30}$, F) PLA_KF$_3$/ATH$_{30}$, G) PLA_ATH$_{30}$ and H) PLA_ATH$_{50}$.

3.4 Dynamic-mechanical behaviour

Figure 8 displays the storage modulus (E′) as a function of temperature for neat PLA and investigated composites. Both PLA and composites show a remarkable transition from glass to viscoelastic zone in 55-70°C range. E′ under glass transition temperature (30°C) is strongly depending on ATH content: namely, for the composite having the highest ATH content, the highest E′ was measured (6082 *vs*. 3810 MPa for PLA_ATH$_{50}$ and PLA, respectively). The composites containing 30 phr ATH with different KF content, 10, 5 and 3 phr, showed values 5372, 5132 and 5225 MPa, respectively, that are slightly lower than that containing only ATH (5492 MPa). KF amounts did not show a significant effect on E′, particularly at low loadings.

The storage modulus showed values of 4291, 3803 and 3934 MPa when 10, 5 and 3 phr KFs are added (PLA_KF$_{10}$, PLA_KF$_5$, PLA_KF$_3$). These results point out that ATH content determines the tendency to store energy below glass transition temperature (T_g); therefore, composites containing ATH exhibit higher stiffness with respect to composites with only KFs. This trend is in agreements with that already observed in the literature [34]. For all investigated composites PLA storage modulus hence mechanical properties downfall in between 60-70°C.

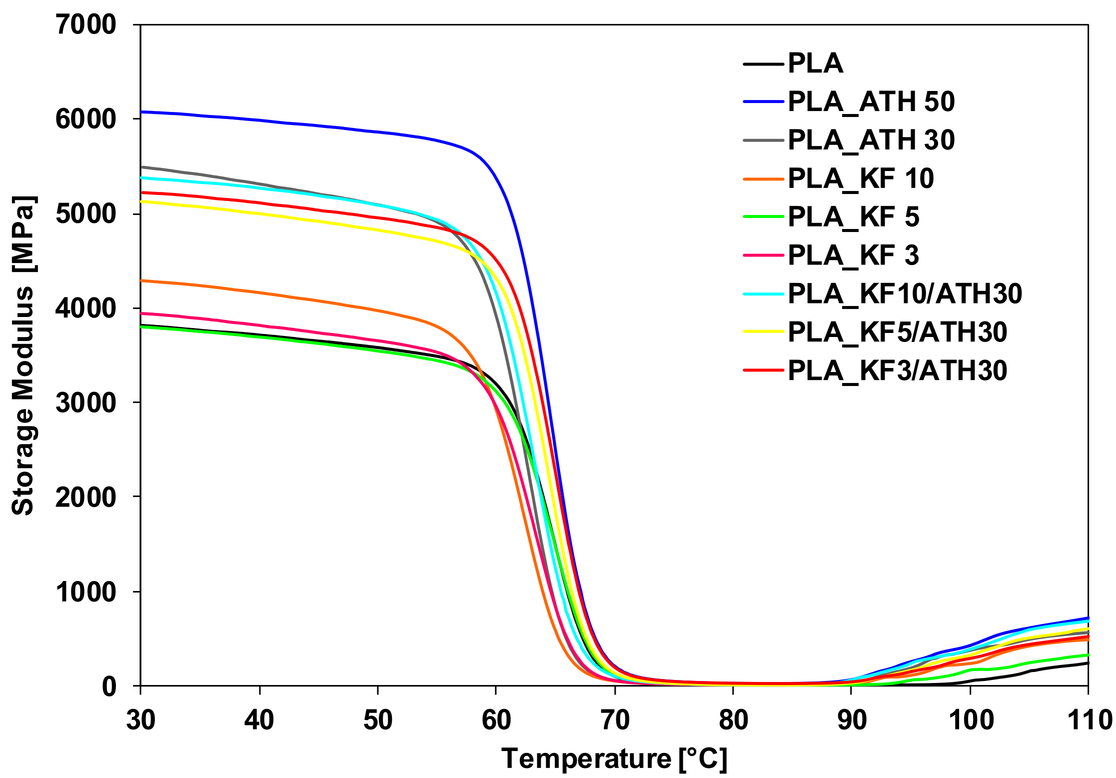


Figure 8. Storage modulus (E′) as a function of temperature for neat PLA and composites.

3.5 Mechanical properties

Table 5 discloses the mechanical properties of investigated materials. As it is well known, composites can exhibit deteriorated mechanical properties with respect untreated polymer if a higher filler content is added to the formulation. A clear example was observed in PLA loaded with 50 phr ATH with respect to neat PLA. Tensile strength, strain at break and tenacity of PLA_ATH$_{50}$ are lower than those of neat PLA. On the other hand, PLA Young's modulus has been remarkably increased (+43%) due to the high ATH content (2413 *vs*. 1695 MPa for PLA_ATH$_{50}$ and PLA, respectively).

Taking in account that the reference sample contains a flame retardant, mechanical properties of the composite materials using KFs and ATH were compared to those of PLA_ATH$_{50}$ and PLA_ATH$_{30}$. According to the collected data (Table 5), PLA Young's modulus is not significantly affected when 10, 5 and 3 phr KFs are added as fillers to polymer matrix (1717, 1692, 1768 *vs*. 1695 MPa for PLA_KF$_{10}$, PLA_KF$_{5}$, PLA_KF$_{3}$ and PLA, respectively).

PLA tensile strength is reduced when the highest KF content (10 phr) is used, from 56 to 28 MPa with respect to PLA_ATH$_{50}$. However, lower KF contents (5 and 3 phr) exhibit similar tensile strength values with respect to PLA_ATH$_{50}$ (58 and 53 MPa for PLA_KF$_{5}$ and PLA_KF$_{3}$ samples, respectively). The strain at break and tenacity are significantly affected by KF content; indeed, when the highest KF content is used (10 phr), strain at break is reduced from 3.2 to 2.2% and tenacity passes from 0.9 to 0.3 MPa in comparison with PLA_ATH$_{50}$.

The opposite behaviour has been observed with lower KF contents (5 and 3 phr). Strain at break increases from 2.2 to 4.4 and 4.0% and tenacity passes from 0.9 to 1.2 and 1.1 MPa for PLA_KF$_{10}$, PLA_KF$_{5}$ and PLA_KF$_{3}$, respectively.

Similar mechanical behaviour has been observed when KFs are added in combination with ATH. Using the same ATH loading (30 phr) and 10 phr KFs (PLA_KF_{10}/ATH_{30} in Table 5), PLA tensile strength, strain at break and tenacity are similar to sample with only 30 phr ATH. However, with low KF contents (PLA_KF_3/ATH_{30} and PLA_KF_5/ATH_{30} samples), tensile strength, strain at break and tenacity are higher than those of PLA_ATH_{30}. In this regard, KF restrict and slightly improve the mechanical properties depleted when adding ATH alone, even at low contents (PLA_KF_3/ATH_{30} and PLA_KF_5/ATH_{30} samples). However, the KFs alone are not so efficient to enhance PLA mechanical properties due to the low concentrations used in this study. In general a significant improvement employing fibres as reinforcing agent has been reported for systems at high contents such as nylon fibres in NR/SBR composites [36], hemp fibres in polylactide [37] and kenaf fibres on Mater-Bi® composites [38].

According to the collected data, it is possible to conclude that high KF loadings with or without ATH produce a rigid and fragile material; conversely, low KF content allows for preparing less rigid materials. It is likely that somewhat fibre-polymer physical interactions favouring a better stress transfer [39] occur in these materials thanks to the KF/PLA good adhesion of KFs with polymer matrix, as already observed by SEM.

Table 5. Mechanical properties of neat PLA and composites.

Sample	Young's modulus ±σ [MPa]	Tensile strength ±σ [MPa]	Strain at break ±σ [%]	Tenacity ±σ [MPa]
PLA	1695±49	80±4	6.2±0.5	2.6±0.4
PLA_ATH_{50}	2431±112	56±6	3.2±0.3	0.9±0.2

PLA_ATH_{30}	2464±64	49±8	2.7±0.4	0.6±0.2
PLA_KF_{10}	1717±133	28±5	2.2±0.3	0.3±0.1
PLA_KF_{5}	1692±86	58±2	4.4±0.2	1.2±0.1
PLA_KF_{3}	1768±149	53±9	4.0±0.5	1.1±0.3
PLA_KF_{10}/ATH_{30}	2073±102	43±3	2.8±0.3	0.6±0.1
PLA_KF_{5}/ATH_{30}	1910±158	63±2	4.4±0.1	1.4±0.1
PLA_KF_{3}/ATH_{30}	1941±113	65±5	4.5±0.4	1.5±0.3

3.6 Rheological behaviour

Flow behaviour of neat PLA and composites was investigated under continuous simple and small amplitude oscillatory shear flows (SAOS). Figure 9 depicts the shear viscosity as a function of shear rate of PLA and composites (Figure 9A) and the complex viscosity versus frequency for small amplitude oscillatory shear tests (Figure 9B). In Figure 9A, Neat PLA shows a mild shear-thinning behaviour at low shear rates (0.01-0.10 1/s). However, at higher shear rates (1.0-100 1/s), PLA exhibits a pronounced shear-thinning behaviour. All samples exhibit shear-thinning behaviour, which is consistent with reports for similar systems of fibre-reinforced polymer composites such as nylon in NR/SBR composites [36] and sisal in polypropylene [40]. PLA_ATH_{50} exhibits the highest shear viscosity of all samples at low shear rate ranges (0.01-0.10 1/s). At the same time, PLA_ATH_{50} shows a more pronounced shear-thinning behaviour in the second decade (0.10-1.0 1/s); on the contrary, in the last decade (10-100 1/s) a more pronounced shear-thinning behaviour is clearly observed. Samples containing ATH at 30 phr show a similar behaviour and their curves almost overlap (PLA_ATH_{30}, PLA_KF_{3}/ATH_{30} and PLA_KF_{5}/ATH_{30}), indicating that when ATH is added, KF at low contents does not significantly affects the rheology of the system except for the sample containing 5 phr KFs which shows a viscosity reduction, evidencing that there is a minimum content of KFs to effectively reduce the viscosity of the systems when ATH is present in the matrix. As far as KF-based composites are concerned, Figure 9A shows that KF presence and content significantly affects PLA rheological behaviour. At low shear rate ranges (0.01-0.1 1/s), shear viscosity decreases by increasing KF content. Indeed, PLA_KF_{10} shows a lower shear viscosity than that of PLA_KF_5 and the PLA_KF_3 and the lowest value with respect to all the formulations under investigation. It is reasonable to guess that, at high KF content (higher fibre-polymer matrix contact), fibres are well oriented and contribute to better orientate PLA chains under flow testing [41]. It is important to highlight that, at high shear rate ranges, KF/PLA composites exhibit a mild shear thinning behaviour that is fundamental during transformation processes such as extrusion and injection moulding. In oscillatory flow (Figure 9B), the complex viscosity does not show shear thinning behaviour but its reduction due to the KF content is analogous to that observed in simple shear flow (*compare* Figures 9A and 9B).

On the other hand, all samples containing both KFs and ATH show a higher viscosity than their counterparts containing only KFs in both simple shear and oscillatory flow. However, KF at high content (PLA_KF_{10}/ATH_{30}) shows similar diminishing effect on the viscosity for samples with 30 phr of ATH, as previously discussed, confirming that high KF content contributes in an important way to decrease the viscosity of the composites. On the basis of the collected rheological results, it is possible to conclude that KF presence and content contribute to decrease the viscosity of the composites in a remarkable way, favouring and making easier their processability. This is likely due to the higher orientation of KFs near the shearing walls, causing a reduction in the bulk viscosity, as previously reported in some cases of other fibre-reinforced polymeric composites [41].

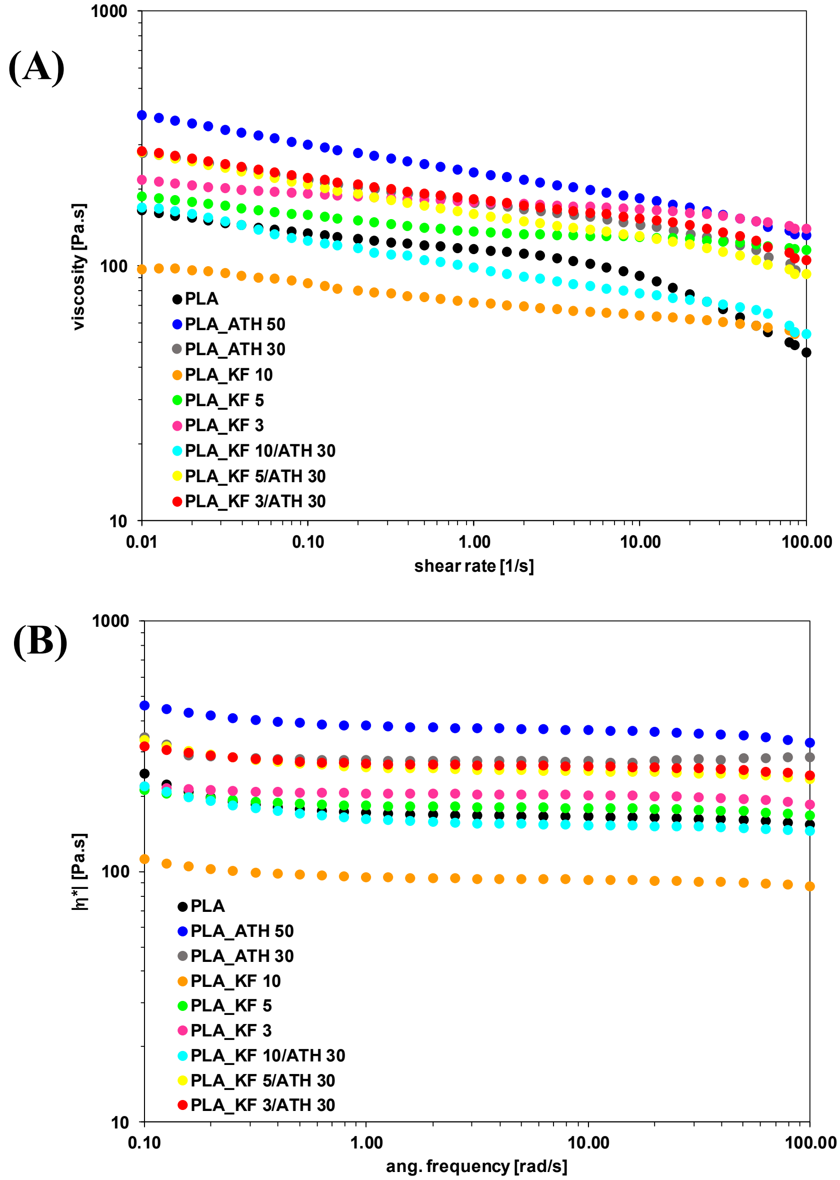


Figure 9. A) Simple shear viscosity as a function of shear rate and B) Small amplitude oscillatory shear test showing the complex viscosity as a function of oscillatory frequency of net PLA and composites.

Figure 10 reports the storage modulus (G') as a function of angular frequency under small amplitude oscillatory shear flow (SAOS) measurements of neat PLA and investigated composites. According to the plotted data in the 1.0-100 rad/s frequency range, most of the composites exhibit a G' modulus comparable with that of neat PLA, with the exception of PLA_ATH_{50} and PLA_KF_{10}/ATH_{30}; indeed, PLA_ATH_{50} shows the highest modulus in the whole frequency and PLA_KF_{10}/ATH_{30} exhibits the lowest one. However, in the 0.1-1.0 rad/s frequency range, G' value slightly depends on the composition of the investigated materials. Indeed, composites loaded with only KFs (regardless of their content) show a decrease of G' whereas the others containing both KFs and ATH exhibit an increase of G', with respect to neat PLA. In addition, comparing the curve slopes at low frequency in Figure10 (values listed in Table 6), neat PLA, PLA_ATH_{50} and PLA_KF_3/ATH_{30} show the lowest values that are almost equal, suggesting that these blends might behave as neat PLA during transformation process. The sample with the highest slope value is PLA_KF_3, this could be associated with poor particle-matrix interactions for this particular sample with low KF content, which is consistent with the measured mechanical properties. Indeed, this sample did not improve tensile strength with respect to the high loaded ATH sample (PLA_ATH_{50}).

According to SAOS flow tests composites containing both KFs and ATH exhibit a higher elastic behaviour than those loaded with only KFs, as observed for the viscosity in both simple shear and oscillatory flow tests (*see* Figures 9A and 9B).

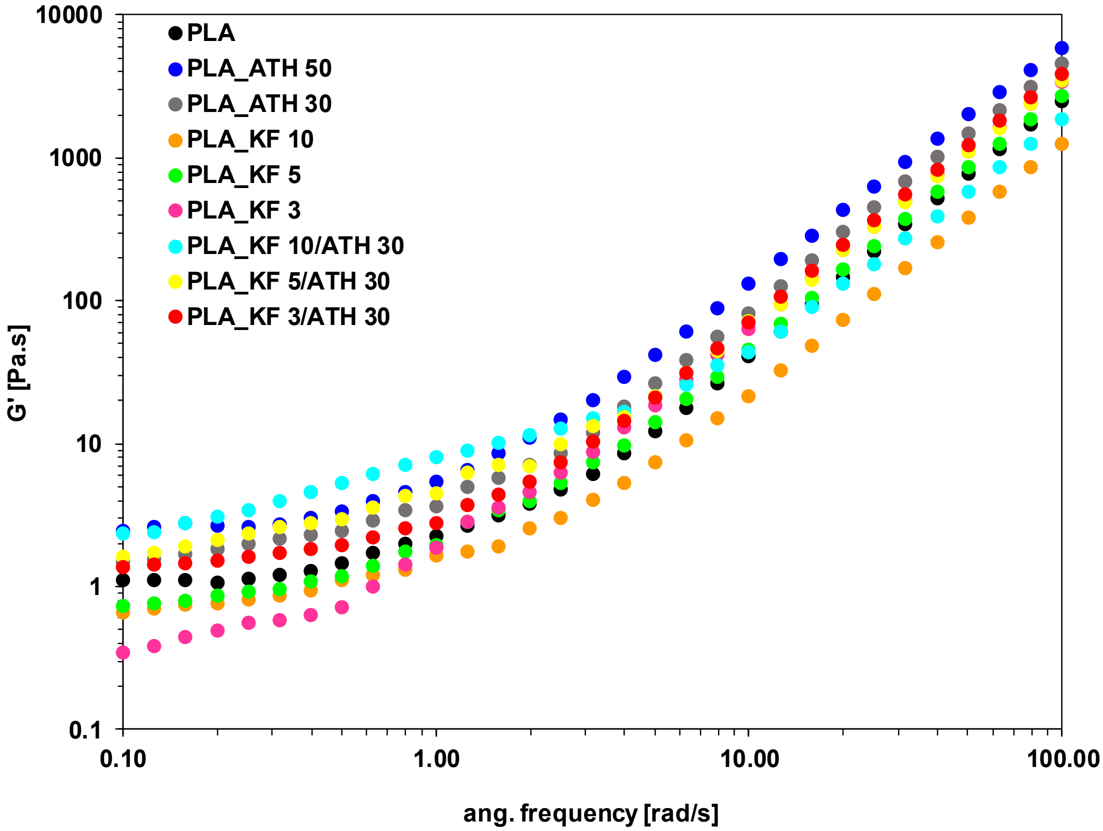


Figure 10. Storage modulus (G') as a function of angular frequency in SAOS flow of neat PLA and composites.

Table 6. Slope values of curves reported in Figure 10 in the low frequency range.

Sample	Slope in the 0.1 a 1.0 rad/s range
PLA	0.27
PLA_ATH_{50}	0.26
PLA_ATH_{30}	0.39
PLA_KF_{10}	0.33
PLA_KF_5	0.39
PLA_KF_3	0.60
PLA_KF_{10}/ATH_{30}	0.57

PLA_KF_5/ATH_{30}	0.45
PLA_KF_3/ATH_{30}	0.28

4. Conclusions

Poly(lactic acid) composites based on keratin fibres recovered from tannery industry wastes were prepared by melt-extrusion. The joint action with a traditional halogen-free flame retardant (namely, aluminium trihydroxide) was investigated. KFs have proven to be well embedded in polymer matrix as well as exhibit a good adhesion with PLA.

KFs have conferred remarkable flame retardant properties to PLA. Indeed, a low KF content (3 phr) has proven to be efficient for passing from NC (not classifiable) to V2 classification, according to the UL94 standard. Further improvements have been achieved exploiting the joint action between KFs (3 phr) and ATH (30 phr). With this formulation, PLA reached the V0 classification, the same categorization obtained for the target sample containing 50 phr ATH, but exhibiting higher mechanical properties i.e. tensile strength increased by 16%, strain at break by 40% and tenacity by 66% when ATH content was reduced from 50 phr to 30 phr + 3 phr KF content. Thus, replacing 20 phr ATH with 3 phr KFs has proven to be very advantageous from an economical and environmental point of view.

On the other hand, the formulations containing higher KF contents exhibited better flow properties, making easier the PLA processing.

The present work set the bases for a new application of the KFs derived from tannery industry wastes; indeed, it has been demonstrated that it is possible to easily prepare completely green polymeric composites with remarkable flame retardant and mechanical properties that might be exploited in electrical, electronic and automotive fields such as manufacturing flame retardant panels, cabinets or protective housing parts.

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