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Natural fiber-induced degradation in PLA-hemp biocomposites in the molten state

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Abstract

The effect of small amounts (≤ 3 wt.%) of short hemp fibers on stability of a poly(lactic acid) (PLA) in the molten state is investigated through time-resolved rheology. The decrease over time of the zero-frequency complex viscosity was correlated to severe hydrolytic degradation of the PLA matrix. A kinetic model that accounts for thermal degradation and hydrolysis was fitted to the experimental viscosity data. The significant fiber-induced hydrolysis is due to traces of residual water bound to the fibers inside the composites after the processing steps. A significant mitigation of the fiber-induced PLA hydrolysis can be obtained by carefully drying the hemp fibers before melt compounding and (to a lesser extent) by subjecting the fibers to an alkaline treatment. On the other hand, if the interest is a shorter persistence in the environment, natural fibers can be exploited to accelerate degradation of biocomposites.

Keywords

A. Biocomposite; A. Natural fibers; B. Viscosity; D. Rheology.

Introduction

Bio-polymers are polymers derived from natural sources and/or able to degrade in environmental conditions. This class of ecofriendly plastics has been receiving a great deal of attention since the end of past century [1]. Due to their generally moderate performances and high costs, bio-polymers can benefit from the addition of a reinforcing phase. If the filler too comes from renewable sources and is biodegradable, then the overall environmental sustainability is preserved and the material is referred to as “green composite” [2-6]. As far as thermoplastic green composites are concerned, the high moisture uptake of natural fibers represents a problem during the melt state compounding in case of matrices susceptible to hydrolysis, such as bio-polyesters or bio-polyamides [7]. Surprisingly, excluding some notable exceptions [8-13], the effect of the processing step(s) on the performances of thermoplastic green composites has not received the deserved attention in the recent literature. Actually, the topic is intriguing and it is worth of further in-depth investigations. On the one hand, matrix degradation induced by natural fibers has a detrimental impact on the material properties. On the other hand, the same phenomenon can be in principle a desired feature, as it can be exploited to accelerate biodegradation in matrices, for example, susceptible of hydrolysis. The present study fits in this frame, providing a detailed study of the degradation processes of poly-(lactic acid) (PLA) filled with low amounts (≤ 3 wt.%) of short hemp fibers. PLA is a biodegradable polyester coming from renewable resources, which is often proposed as a potential substitute for many commodity petroleum-based thermoplastics due to its appreciable mechanical and barrier properties [14]. The

biodegradability of PLA, which is basically due to its potentially hydrolysable ester bonds, is highly desirable as end-of-life option, but it turns out to be a problem during high temperature processing steps, when the combined action of temperature, residual moisture, and mechanical stresses promotes degradation and, as a consequence, a decrease in mechanical performances [15-18]. The detrimental effect of the process might be further worsened in the presence of natural fibers due to their own additional moisture. Hemp fibers are being increasingly used as a substitute for glass and carbon fibers for the reinforcement of thermoplastic matrices for automotive, building and furniture industries due to their cheapness, low density, non-abrasiveness against mixing and molding equipments, and safe handling [19, 20]. In our study, the PLA/hemp fibers composites were prepared by conventional melt compounding using a twin-screw extruder. The fibers were subjected to two common pretreatments such as vacuum-drying and mercerization. The latter consists in an alkaline treatment and it is typically carried out to improve natural fiber adhesion with a host polymer [21]. The effect of the hemp fibers on the kinetics of matrix degradation in the melt state was investigated, as well as the role of fiber drying and alkaline treatment. Time-resolved rheological analyses were carried out to elucidate the pro-degradative effect of the fibers. This technique represents an easy and yet powerful tool for gathering information on changes in the molecular architecture of polymers due to degradation phenomena in the melt state [22, 23]. Rheological data were modeled assuming the occurrence of hydrolysis and thermal degradation. This enabled us to highlight the relevance of the first mechanism, strictly related to the presence of the fibers. Finally, the importance of fiber drying and the effects of mercerization on hemp fiber water-holding capacity are also discussed.

Experimental

2.1. Raw materials

Extrusion grade PLA (INGEO 2003D, 96% L-lactic acid) was purchased from Nature Works USA. It has density $\rho=1.24 \text{ g/cm}^3$ and melt flow index MFI=6 g/10 min (at $T=210^\circ\text{C}$ with 2.16 kg weight).

Raw hemp fibers (*Cannabis Sativa L.*) were provided by AssoCanapa (Carmagnola, Turin, Italy). They are technical fibers falling in the category of *bast fibers*, i.e. obtained from the outer cell layers of the stems of the hemp plant. Their morphology has been recently investigated in detail [E1]. For what we are concerned here, the selected fibers can be depicted as a tangle of strands and bundles of primary elementary fibers (bundle diameter $\sim 10^2 \mu\text{m}$; elementary fiber diameter $\sim 10 \mu\text{m}$) held together by an interphase mainly consisting of pectin and hemicellulose (Figure 1.a).

2.2. Alkaline treatment on the fibers

The hemp fibers were first cleaned with distilled water to remove external impurities and dirt, and then soaked in a 5 wt.% NaOH solution at room temperature. The treatment lasted 30 min, which was sufficient for ensuring an effective removal of the non-cellulosic substances from the pristine bundles and promotes the individualization of the elementary fibers [24]. After treatment, the fibers were washed again with distilled water and neutralized with 1 wt.% acetic acid and dried overnight in a vacuum oven at 80°C . The appearance of the fibers before and after the treatment is shown in Figure 1. Hereinafter, alkali-treated and untreated fibers will be referred to as “TF” and “UF”, respectively.

2.3. Composites preparation

The fibers were shortened to lengths of 5-10 mm using a grinder, and then they were compounded with PLA. The mixing apparatus was a co-rotating twin-screw extruder (mod. PTW 24 by Thermo Haake) with parallel intermeshing screws (diameter 24 mm, length-over-diameter ratio 40) endowed with three mixing blocks. The polymer pellets were loaded with a dosing device, while fiber flocs were manually added through a vent/feed section at around half of the screws' length. Samples at UF content $\Phi = 0.75$, 1.5, 2.25, and 3 wt.% were obtained by dilution of a master-batch prepared in a previous step. All extrusions were performed at a screw speed of 100 RPM while insufflating dry nitrogen into the sealed hopper. A uniform temperature profile at $T = 180^\circ\text{C}$ was kept along the extruder, while the die was kept at $T = 170^\circ\text{C}$. Before extrusion the polymer was dried overnight at 80°C under vacuum. To assess the effect of fiber drying and alkaline treatment, samples at $\Phi = 3$ wt.% of dried UF and TF were also prepared. Disk-shaped specimens (diameter 25 mm, height 2 mm) suited for rheological analyses were obtained by compression molding (LP-20B, LabTech Engineering Ltd). The mold was pre-heated at $T = 205^\circ\text{C}$. The procedure consisted in a 2-minute warm up period without applying pressure, to allow the softening of the pellets, followed by a 3-minute stage at a pressure of about 160 bar for compacting the softened pellets. The pressure was maintained while cooling down to about 50°C , that is below the T_g of PLA (55 - 60°C), and the samples were finally removed from the mold.

2.4. Characterization techniques

Rheological analyses were carried out using a stress-controlled rotational rheometer (AR-G2 by TA Instruments) in parallel plate geometry (diameter 25 mm). All measurements performed out at $T = 180^\circ\text{C}$ in nitrogen atmosphere on samples previously dried at $T = 80^\circ\text{C}$ overnight under vacuum. Sequences of small amplitude

oscillatory shear (SAOS) tests were performed for monitoring the degradation kinetics of samples in the melt state. The elastic (G') and viscous (G'') shear moduli were recorded at strain amplitude low enough to be in the linear regime, which was preliminarily estimated through strain scan experiments (reported as Supplementary material).

Thermo Gravimetric Analysis (TGA) was performed on the fibers using the Q500 analyzer by TA Instruments. The samples were heated under nitrogen flow from room temperature up to $T = 100^\circ\text{C}$ (heating rate of $20^\circ\text{C min}^{-1}$), then the temperature was kept constant at $T = 100^\circ\text{C}$ for monitoring the weight losses during time.

Results and discussion

3.1. PLA degradation in the presence of hemp fibers via rheology

Degradation phenomena were investigated by performing consecutive frequency scans on the same sample. The typical outcome of this testing protocol is shown in Figure 2 for pure PLA and the composite at $\Phi = 2.25\%$ of non-dried UF.

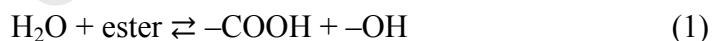
The moduli and magnitude of the complex viscosity, η^* , progressively decrease while testing. The reduction is more pronounced for the composite, meaning that the fibers promote matrix degradation. The low frequency plateau of the complex viscosity, η_0^* , can be taken as a reference for monitoring the advancement of degradation. The time evolution of η_0^* is shown in Figure 3.a for samples at different fiber content.

The pro-degradative effect of the fibers is obvious: the higher the Φ , the faster and more significant the drop of η_0^* . The initial slope of the curves provides a measure of the rate of the degradation phenomenon. The latter can be defined as $\dot{d} = |\Delta\eta_0^*(0)|/\Delta t$, where the numerator is the difference between the η_0^* values recorded during the first and

second frequency scan, and Δt is the time interval elapsing between such measurements. Similarly, the difference between the η_0^* values collected during the first and the last frequency scan, $\Delta\eta_0^*(\infty)$, can be taken as an estimate of the overall magnitude of degradation. As reported in Figure 3.b, both \dot{d} and $\Delta\eta_0^*(\infty)$ linearly grow with the amount of fibers, which confirms the key role of the latter in promoting PLA degradation. On the other hand, the data in Figure 3.a converge to a common value of ~ 6000 Pa s for $t \rightarrow 0$ (see dashed lines). This means that, once removed the effect of fiber-induced degradation, the fibers only have a negligible effect on the rheology of the samples. This is not surprising: in very dilute micro-composite such as those addressed in this study, the filler only causes a negligible increase of the viscoelastic functions with respect to the pure matrix because of the hydrodynamic interactions among the particles [25].

3.2. Modelling of PLA degradation kinetics induced by hemp fibers

From a chemical point of view, different degradation reactions have been postulated in the literature for PLA [26], but in the temperature range considered in this study, hydrolytic degradation can be considered the predominant mechanism [27]. The process consists in the hydrolysis of the ester bonds along the backbone of the PLA chain. It requires the presence of water according to the following reaction:



Here we assume that the hemp fibers promote hydrolytic degradation of the PLA matrix because of the water bound to the hydroxyl groups of the main hemp constituents,

namely cellulose, hemicelluloses, pectins, and lignins [28]. In addition to hydrolysis, strictly thermal degradation mechanisms also take place, as proved by the viscosity decrease noticed also for pure vacuum-dried PLA (see Figure 4). Speranza *et al.* specifically addressed PLA degradation in the molten state, proposing a kinetic model that takes into account both hydrolysis and thermal degradation [29]. They derived the following set of equations for the rate of change of ester groups (c_e) and water (c_w) concentration in the samples:

$$\frac{dc_e}{dt} = -k_h c_e c_w - k_T c_e \quad (2)$$

$$\frac{dc_w}{dt} \cong -k_h c_e c_w \quad (3)$$

where k_h and k_T are the hydrolytic and thermal kinetic constants. The first term in the right side of equation (2) represents the rate of hydrolysis, whereas the second term accounts for thermal degradation. The approximate equality in equation (3) derives from having neglected the loss of water through the sample surface. In case of rheological tests in parallel plate geometry, the latter corresponds to the lateral surface of the disk-shaped samples, which are thin enough to justify the assumption. Since there is one ester group per monomer in the PLA chain, the time-dependent ester concentration obtainable by solving the set of equations (2) + (3) can be easily transformed in the time evolution of the PLA number average molecular weight, $M_n(t)$, through the following relationship [30]:

$$M_n(t) = \left(\frac{1}{M_0} - \frac{c_e(t)}{\rho} \right)^{-1} \quad (4)$$

where M_0 is the molecular weight of the PLA monomer and ρ is the PLA density. The time evolution of the average molecular weight reflects on the rheological properties, which progressively decrease because of degradation. Since other rheological effects of the fibers have been excluded, we can ascribe the decrease of η_0^* uniquely to the decrease in molecular weight. The scaling law between the zero-shear viscosity (η_0) and the weight average molecular weight (M_w) can be hence used:

$$\eta_0 \sim M_w^{3.4} \quad (5)$$

Replacing η_0 with η_0^* according to the Cox-Merz rule [31], which was verified to work quite well at low shear rate/frequency ($< 10^0 \text{ s}^{-1}/\text{rad s}^{-1}$), and introducing the polydispersity index $z = M_w/M_n$, we get:

$$\eta_0^*(t) = c \cdot (z \cdot M_n(t))^{3.4} \quad (6)$$

where c is a constant. In Equation (6) the origin of the time dependence of the complex viscosity has been highlighted.

Together with equations (2)-(4), Equation (6) can be used to fit the experimental data in Figure 3.a and provide useful information on hemp fiber-induced hydrolytic degradation of molten PLA. Of the various parameters and initial conditions of the problem, some are known or available in literature, while others can be estimated by using them as fitting parameters. Among the known/available parameters, there are the molecular weight of the monomer ($M_0 = 0.071 \text{ kg mol}^{-1}$) and the density of PLA at $T = 180^\circ\text{C}$ ($\rho =$

1120 kg m⁻³, according to the suppliers). The initial values of PLA average molecular weight and polydispersity index can be found in the literature. We set $M_n(0) = 100$ kDa and $z = 1.7$, which are averages of the values reported in [32] and [33] for the specific PLA grade used in this study. According to Mohd-Adnan *et al.* and Gorrasi & Pantani, we neglect variations of the polydispersity index during degradation [34, 35]. Through equation (4), $M_n(0)$ allows to evaluate $c_e(0)$, which is necessary to solve the system of differential equations (2) + (3). In conclusion, only four parameters remain to be estimated: k_T , k_h , the parameter c of equation (5), and the initial concentration of water carried by the hemp fibers, $c_w(0)$.

The fitting of Equation (6) to the experimental η_0^* data was carried out with a simple MATLAB code. The model nicely fits the experimental data for all the composites ($R^2 > 0.995$). The calculated time dependences of the functions c_e , c_w , M_n , and η_0^* are shown in Figure 4 for the PLA/hemp composite at $\Phi = 2.25$ wt.%. Similar results were obtained on all the other samples based on non-dried UF and are provided as Supplementary material in Appendix A.

Ester and water concentration decrease over time (Fig. 4.a and b) due to the advance of hydrolysis and thermal degradation. The consequent reduction in the average molecular weight (Fig. 4.c) is reflected in the decrease of the viscosity, which is well predicted by the model (Fig. 4.d). The fitting parameters are shown in Figure 5 together with those derived for the other samples at different hemp content.

The parameters k_T , k_h , and c do not depend on fiber loading. This is expected, as they reflect features of the matrix alone: k_T and k_h , are the kinetic constants of the degradation reactions and, as such, they are specific for PLA at the selected temperature; c is the conversion factor required to pass from molecular weight data to

viscosity ones (see Equation (6)), and it is not affected by the presence of the fibers in the studied systems. For the system considered in this study at $T=180^{\circ}\text{C}$ we found: $k_T = 2.96 \pm 0.08 \times 10^{-9} \text{ s}^{-1}$; $k_h = 1.17 \pm 0.06 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$; $c = 1.52 \pm 0.03 \times 10^{-4} \text{ Pa s (mol kg}^{-1})^{3.4}$. Such values are only slightly higher than those derived by Speranza *et al.* on a different grade of PLA (IngeoTM 4032D by NatureWorks), in which the water responsible for hydrolysis was that naturally present in non-dried samples [29]. The authors quantified the initial water content in their samples in traces of order of $2\div 5 \text{ mol m}^{-3}$. This value is incidentally of the same order of magnitude as those found in the present study, where the specimens were dried before rheological tests and the water responsible for PLA hydrolysis was that bound to the hemp fibers (indeed, $c_w(0) \sim \Phi$). In other words, the kinetics of hydrolysis in our PLA/hemp composites is comparable to that of non-dried PLA samples.

It is important to observe that the $c_w(0)$ values of Figure 6 represent the initial water content in the molten specimens at the beginning of rheological tests. As such, they are not easily correlated to the water content of the pristine hemp fibers. The latter can be quantified through TGA analysis. Isothermal tests carried out on the UF at $T = 100^{\circ}\text{C}$ indicate a water content of $\sim 7 \text{ wt.}\%$, which corresponds to $\sim 43 \text{ mol m}^{-3}$ per each percentage point of fibers in the composite. Such a value is much higher than what derived with the model ($\sim 1 \text{ mol m}^{-3}$ per percentage point of fibers, see Figure 5). This means that most of the water bound to the fibers is lost during the various steps experienced until the beginning of the rheological tests, namely: (i) melt mixing step, when which the fibers are loaded in the extruder and rapidly heated up to $T = 180^{\circ}\text{C}$; (ii) compression molding step; (iii) drying step of the samples prior to rheological tests, carried out at $T = 80^{\circ}\text{C}$ under vacuum overnight; (iv) heating and melting of the samples

in N₂ atmosphere to perform the rheological tests. Speranza *et al.* also found a significant drop in the water content of their samples when passing from the condition of not dried pellets (~250 mol m⁻³) to that of molten specimens for rheological tests (2÷5 mol m⁻³) [29].

3.3. Mitigation of PLA degradation through hemp drying and alkaline treatment.

The previous results demonstrate that even small amounts of natural hemp fibers exert a non-negligible pro-degradative effect on PLA in the melt state. Since the effect increases with fiber content, and keeping in mind that the amount of fibers in green composites is usually much higher than those considered in this study, it is useful to evaluate possible strategies to mitigate fiber-induced degradation phenomena of polymer matrices susceptible to hydrolysis. In the following, the effects of fiber drying and alkaline treatment carried out prior to melt compounding are addressed.

The water content of UF and TF, either dried or not, is shown in Figure 6 as measured through isothermal TGA tests at $T = 100^{\circ}\text{C}$ in N₂ atmosphere. Since in this temperature window the volatilization of organic compounds of the hemp is unlikely [36], the recorded mass changes can be ascribed to the loss of adsorbed water.

All samples start losing weight since the early stages of the test, when the temperature is still well below $T = 100^{\circ}\text{C}$. After this initial drop, which lasts about 5 minutes, the weight reaches a constant value that depends on drying and alkaline treatment. Drying removes a considerable fraction of water, and a further reduction is achieved with the alkaline treatment. This is in line with the finding by Pejic *et al.*, who reported a decrease in water retention power of NaOH-treated hemp fibers with respect to untreated ones [37].

Once assessed that both fiber drying and alkalization reduces the bound water of hemp fibers, the effect of these pre-treatments on the degradation kinetics of the PLA/hemp composites was investigated by using the same procedure adopted in the previous section. The results are shown in Figure 7; the fitting parameters are summarized in Table 1.

Both the rate and magnitude of the η_0^* decrease are significantly reduced if the fibers are dried before the melt compounding step. The effect is even more pronounced if the fibers were alkali-treated before drying. Looking at Table 1, c , k_T and k_h remain close to the values derived in the previous section for samples containing UF not subjected to any pre-treatment. Again, this is reasonable considering that none of these parameters is related to the fibers. The main effect of drying is a reduction of the amount of the initial water carried by fiber in the composites. Further decrease in $c_w(0)$ is achieved by performing the alkaline treatment, and the kinetics of the sample with dried TF approaches that of pure PLA.

Conclusions

The detrimental effect of small amounts ($\Phi \leq 3$ wt.%) of inherently hydrophilic short hemp fibers on the high temperature stability of a polymer susceptible to hydrolysis such as PLA was discussed. Samples at different fiber content prepared by melt compounding were subjected to a simple rheometric protocol consisting in repeated frequency scans. This enabled us to monitor the degradation kinetics by looking at the changes in the rheological functions. It was found that the fibers have a negligible effect on the rheological behavior of the as-prepared samples, but they significantly speed up degradation in the molten state. In particular, η_0^* roughly halves in about two hours for

the composite at only 3 wt.% of hemp. The decrease in the zero-frequency complex viscosity reflects the reduction of the average molecular weight of the polymer, which was modeled using kinetic equations that accounts for both thermal degradation and hydrolysis. Fitting the experimental $\eta_0^*(t)$ data enabled us to compute the kinetic constants of thermal degradation and hydrolysis, and the water content of the hemp fibers at the beginning of rheological tests. k_T and k_h resulted of the same order of magnitude as reported in literature for pure PLA [29]. Regarding the amount of water responsible for the observed degradation, it was found to be of order of $\sim 1 \text{ mol m}^{-3}$ per percentage point of fibers. This value is much lower than what measured through TGA on the pristine fibers ($\sim 40 \text{ mol m}^{-3}$ per percentage point of fibers). The discrepancy is due to the loss of most of the bound water during the thermo-mechanical history experienced by the fibers during sample preparation. Overall, the presence of even small amounts of hemp fibers accelerates PLA degradation to an extent similar to that of residual water in non-dried pure PLA. Finally, we showed that drying the fibers prior to melt compounding with PLA allows significantly reducing the pro-degradative effect of the fibers, and that further benefits in this sense can be obtained by subjecting the fibers to alkaline treatment. On the contrary, one can be interested in exploiting the phenomenon and using hygroscopic natural fibers for accelerating bio-degradation of polymer matrices susceptible to hydrolysis.

Declaration of Competing Interest

The authors declare that there is no conflict of interest.

Appendix A. Supplementary material

The following are the Supplementary data to this article:

Strain sweep experiments. Strain sweep experiments were performed to identify the range of linear viscoelasticity. The results are shown below as a function of strain amplitude γ for the unfilled PLA and UF-filled samples at different Φ .

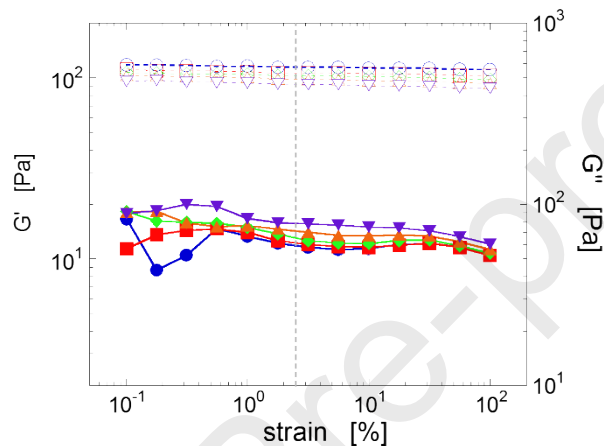


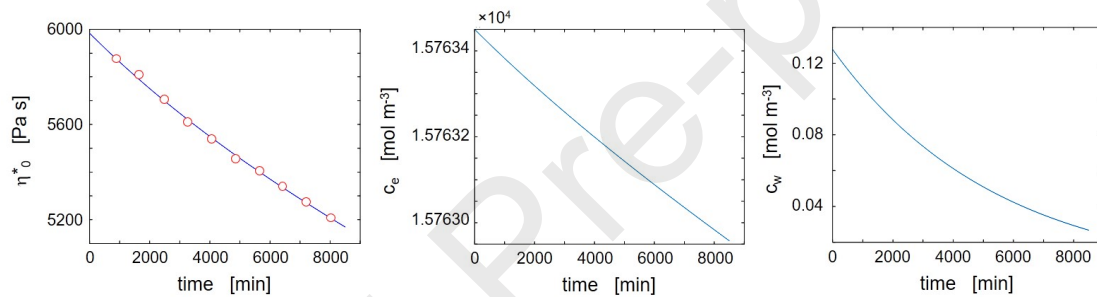
Fig. S1. Elastic (full symbols) and viscous (empty symbols) moduli collected during strain scan experiments carried out at $T = 180^{\circ}\text{C}$ and frequency $\omega = 0.1 \text{ rad s}^{-1}$. Datasets refer to the unfilled PLA (blue circles) and composites at 0.75 (red squares), 1.5 (green diamonds), 2.25 (orange triangles), and 3 w.% (purple reverse triangles) of UF. Vertical dashed line identifies the strain amplitude of 2.5%, which was selected for all SAOS experiments.

The moduli are stable between $\sim 1\%$ and $\sim 30\%$. Below 1% the oscillation amplitude is too low and the signal of the elastic modulus is noisy; above 30% the elastic modulus starts decreasing, meaning that the linear viscoelastic limit is exceeded. A common strain amplitude of 2.5% was hence selected for all SAOS experiments (see dashed gray line in Fig. S1).

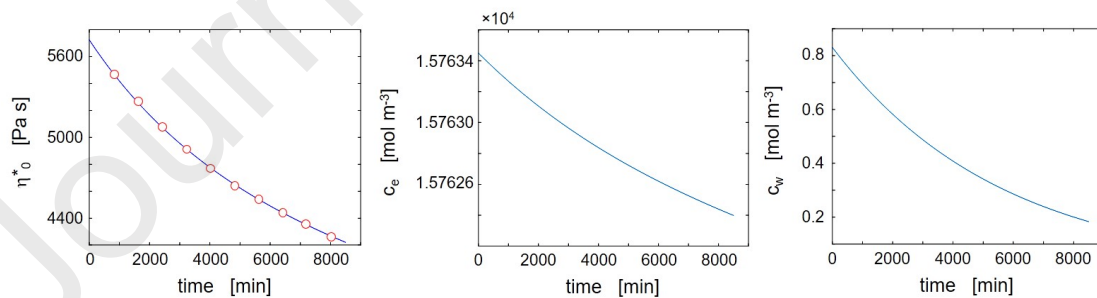
Time dependence of the functions η_0^* , c_e , and c_w . The results of the fitting procedure are shown below for all the samples (excluded the one at $\Phi=2.25$ wt.%, whose plots are reported in the main text, see Fig. 4).

For each sample, from left to right we report (i) the fitting to the complex viscosity data (η_0^*), (ii) the time evolution of the ester concentration (c_e), and (iii) the time evolution of the water concentration (c_w).

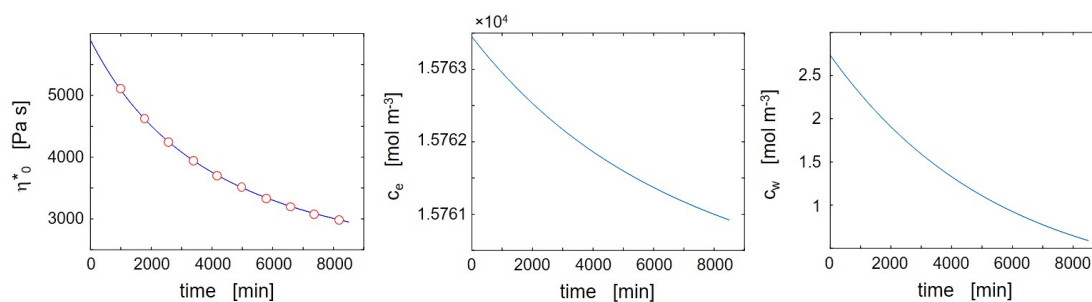
Unfilled PLA:



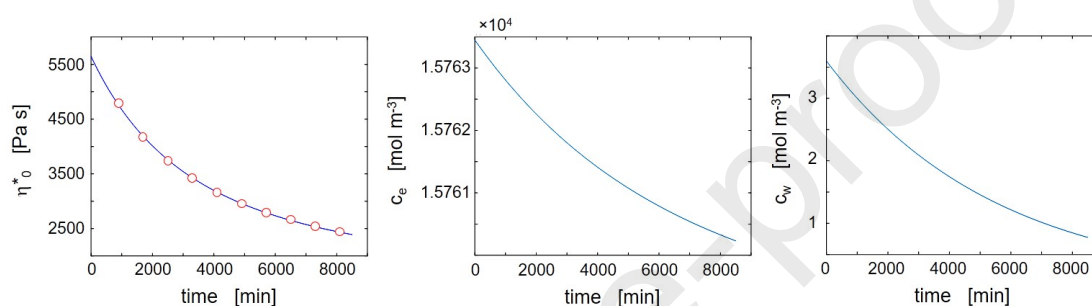
Composite at $\Phi=0.75$ wt.% (non dried UF)



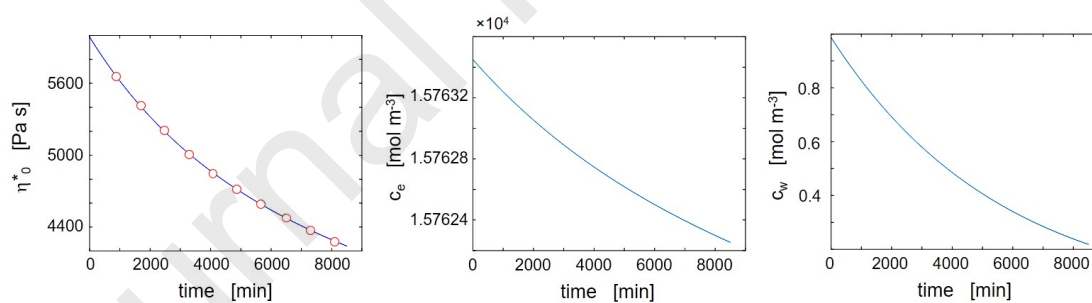
Composite at $\Phi=1.5$ wt.% (non dried UF):



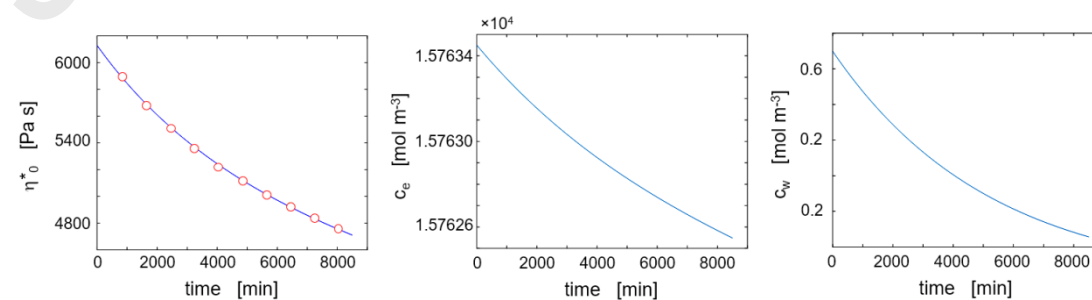
Composite at $\Phi=3$ wt.% (non dried UF):



Composite at $\Phi=3$ wt.% (dried UF):



Composite at $\Phi=3$ wt.% (dried TF):



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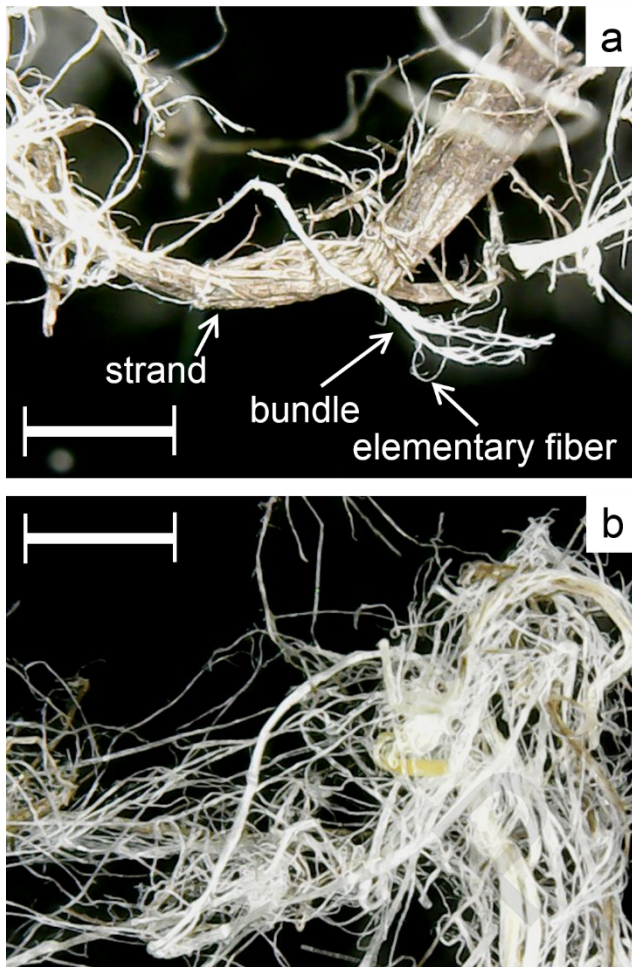


Fig. 1. Untreated (a) and alkali-treated (b) hemp fibers. The hierarchical structure of the fibers is highlighted in (a). Scale bars are 500 μm .

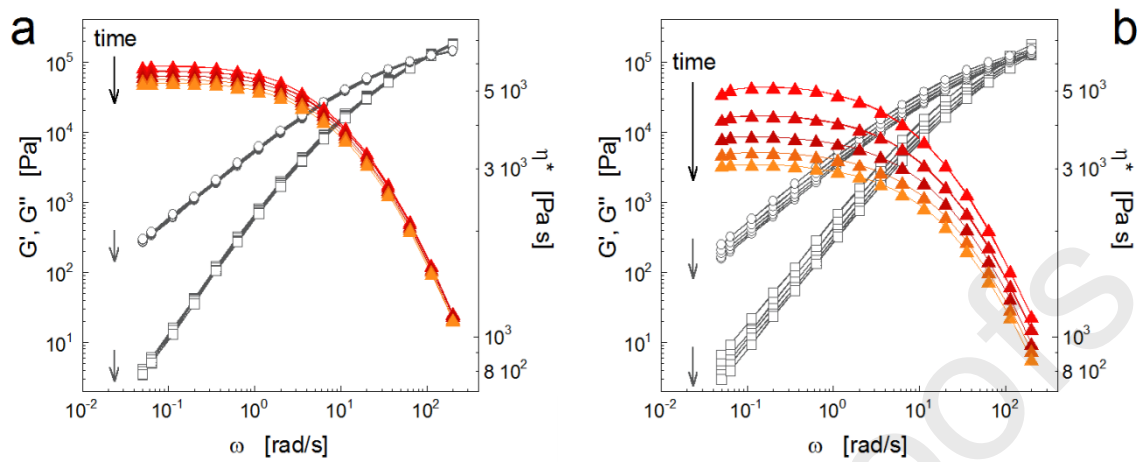


Fig. 2. Decrease of the complex viscosity (full triangles) as collected through consecutive frequency scans over ~ 2 hours for (a) pure PLA and (b) PLA/hemp composites at 2.25 wt.% of non-dried UF. The elastic and viscous moduli are reported as grey squares and circles, respectively.

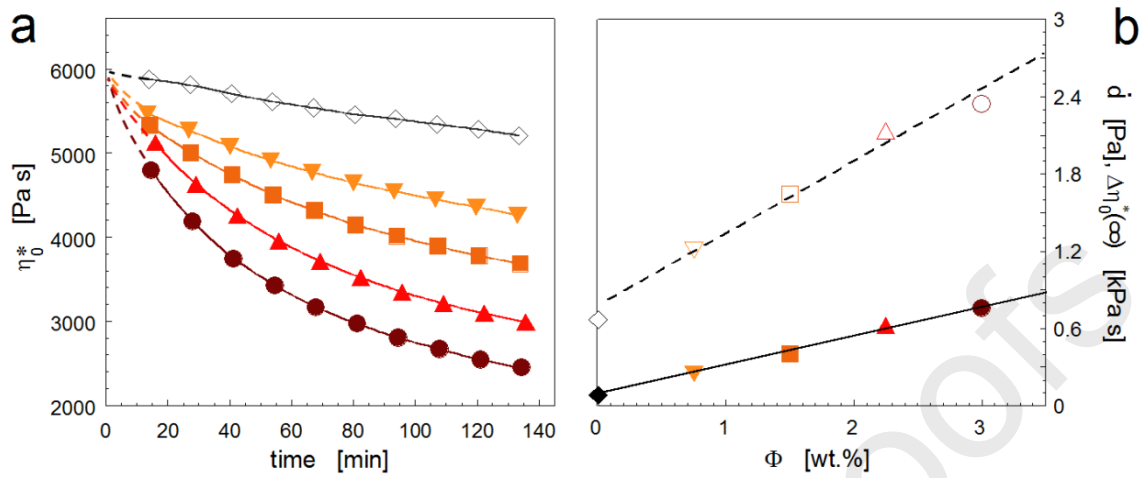


Fig. 3. a) Time evolution of the zero-frequency complex viscosity for neat PLA (diamonds, empty symbols) and composites (full symbols) at 0.75 (reverse triangles), 1.5 (squares), 2.25 (triangles), and 3 w.% (circles) of UF. Lines are guide for the eye. b) Rate (full symbols) and extent (empty symbols) of degradation as a function of fiber content. Lines are linear fitting to the data.

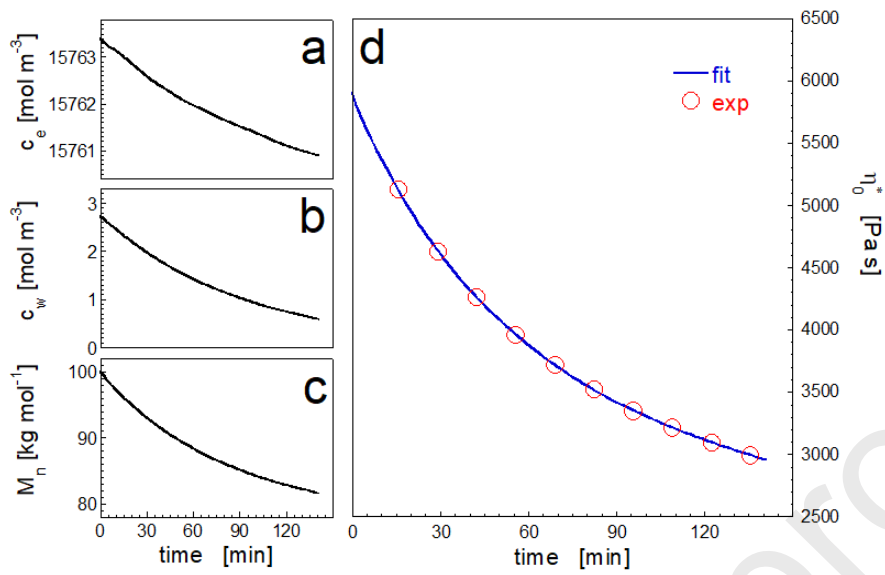


Fig. 4. Time evolution of (a) ester concentration, (b) water concentration, (c) PLA number average molecular weight, and (d) zero-frequency complex viscosity as obtained by fitting the set of Equations (2)-(6) to the experimental η_0^* data for the PLA/hemp sample at $\Phi = 2.25$ wt.% (circles).

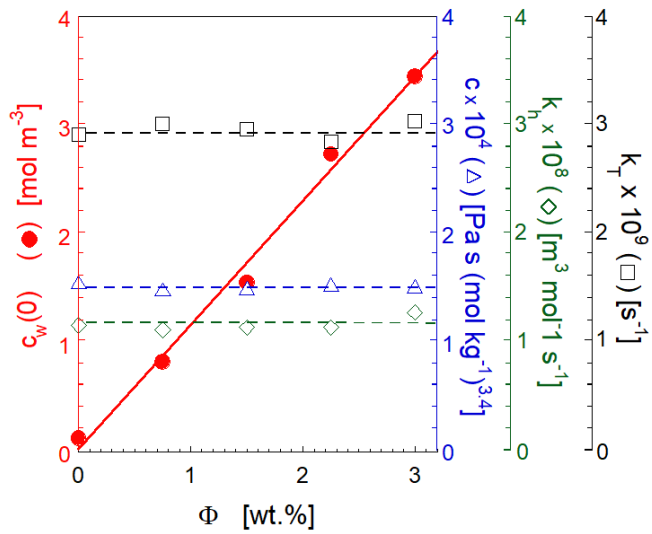


Fig. 5. Fitting parameters as a function of filler content: $c_w(0)$ (full circles, left axis), k_T (squares, right axis), k_h (diamonds, right axis), and c (triangles, right axis). Full line is the linear fit to the $c_w(0)$ data; dashed lines are the average values of the k_T , k_h , and c values computed at different fiber content.

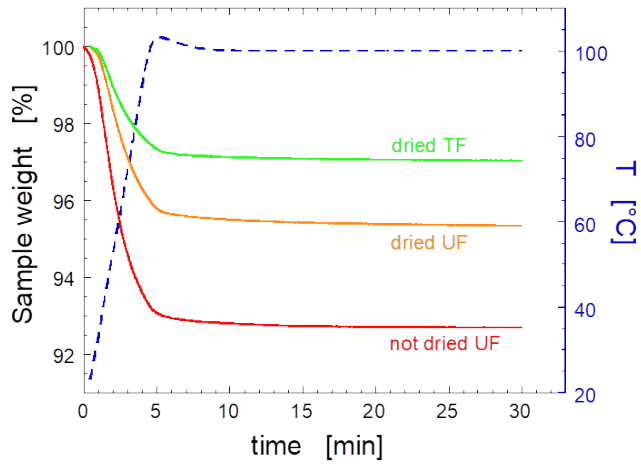


Fig. 6. Weight losses of UF and TF, either dried or not, as collected through TGA.

Dashed line shows the raise of the temperature (right axis).

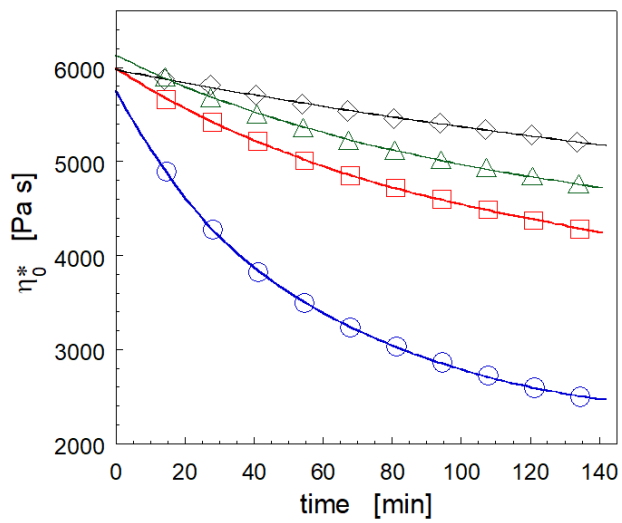


Fig. 7: Experimental data (symbols) and model predictions (lines) of the time evolution of zero-frequency complex viscosity of PLA/hemp samples at 3 wt.% of fibers: not dried UF (circles), dried UF (squares), and dried TF (triangles). The data of pure PLA are reported as well as reference (diamonds).

Table 1. Parameters computed by fitting Equation (6) to the experimental data of the time evolution of zero-frequency complex viscosity for PLA/hemp samples containing different types of fibers.

Type of fibers	c [Pa s (mol kg ⁻¹) ^{3,4}]	k_T [s ⁻¹]	k_h [m ³ mol ⁻¹ s ⁻¹]	$c_w(0)$ [mol m ⁻³]
not dried UF (same as in Figure 5)	1.52×10^{-4}	3.04×10^{-9}	1.28×10^{-8}	3.45
dried UF	1.56×10^{-4}	3.19×10^{-9}	1.26×10^{-8}	0.99
dried TF	1.58×10^{-4}	2.84×10^{-9}	1.21×10^{-8}	0.65

Highlights

- Short hemp fibers significantly accelerate hydrolysis of PLA in the molten state
- The key role of the water brought into the composite by the fibers is highlighted
- Fiber drying and alkaline pre-treatment mitigate fiber-induced PLA degradation
- Pro-degradative action of natural fibers can be exploited to promote biodegradation

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Credi author statement

VM: Investigation, Resources, Writing – Original Draft, Software; MSdL: Methodology, Formal analysis, Writing – Original Draft; RP: Investigation, Validation; FM: Resources, Software, Writing – Original Draft; GF: Conceptualization, Methodology, Writing – Original Draft, Supervision.

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