MODELING OF THE MECHANICAL AGING BEHAVIOR OF PLA-BASED NONWOVENS AND MONOFILAMENTS UNDER FILTER APPLICATION-RELEVANT CONDITIONS

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Nonwovens and felts from synthetic fibers (polyester, polypropylene) or from glass fibers are the mostly used filter media in air filtration. These materials offer high efficiency, long service life and a good price-performance ratio. However the modern growing trend to replace petroleum-based fibers with bio-based and bio-degradable polymers dictates a new challenge for researchers, filter developers and manufactures.

Presented research focuses on exploring PLA fibers as an alternative material for applications in air filtration. Particular emphasis was made on the characterisation of the mechanical properties of PLA monofilaments under aging conditions, which are relevant for the applications as filter media, with an aim to quantify the biodegradability of the PLA-based materials. Also the air-filtration characteristics of the PLA nonwovens depending on the textile-media parameters have been tested.

Multiple methodologies have been used to characterise structural changes and mechanical properties of the PLA monofilaments before and after respective aging treatments. The results of the DSC analysis, tensile stress tests, 3D optical microscopy and scanning electron microscopy have been systematically evaluated. In on-going research similar aging conditions have been applied to PLA and blended nonwoven materials.



Figure 1: (a) Stress-strain diagram of PLA monofilaments before and after aging in a climate chamber (60°C, 80% humidity) for indicated number of days. (b) Optical microscopy image of PLA monofilament before (left) and after (right) aging in 1 mol NaOH solution (40°C, for 9 days).

Keywords

Biobased, PolyLactic Acid (PLA) Fibers, Spunbond, Monofilament, Hydrolysis, Filter Media, Air Filtration

Motivation and Background

In air filtration, filter media with high efficiency and long service life are required. The potential of filter media from fibers of polylactic acid (polylactide, PLA) as an alternative to petroleum-based synthetic fibers is considered in this research project. These filter media offer high efficiency, high durability and a good price-performance ratio.

In applications where mechanical and thermal requirements and long-term stabilities permit, replacement with biogenic fibers is increasingly required nowadays. This trend is already strong and currently affects many textile products, additionally to the filter media, e.g. coated fabrics and fiber composites. Irreversible social and political trends are key factors:

- increasing consumer awareness (e.g. desire for sustainable automotive materials),
- increasing legal regulations (in the case of conveyor belts see the current EU Directive 1935/2004 [1]),
- CO2 neutrality of products resulting from biogenic materials and, if necessary, biodegradation.

Against this background, the share of bio-based polymers in world production grew from 1.4 % to 2 % between 2011 and 2014 [2]. The same source assumes that this share will grow disproportionately above 4 % by 2020. The interest of the industry in bio-based materials is also influenced by the predicted developments of the plant capacities for bio-based polymers: Particular growth is expected here, in addition to the automotive sector, above all for the textile sector.

Various approaches to study the efficiency of PLA-based filters have been reported in literature. Within this project, the poor hydrolysis resistance of PLA under application relevant conditions has been analyzed and improved through the use of biobased blends. Systematic studies of the aging of the PLA monofilaments and nonwovens using a model connecting long-term relaxation with short-term relaxation measurements are expected to provide insights into aging and shelf life behavior of the PLA-filters.

Approach and Results

State of the art

Polylactides are aliphatic polyesters which are formed by ionic polymerization of lactide. Depending on the solidification method, PLA has comparable mechanical properties to polyethylene terephthalate (PET), but a lower melting and thus operating temperature. The methyl group of the repeating unit gives the polymer water-repellent nature and lowers water absorption, which is fundamentally advantageous with regard to use in filter media. The water contact angle on planar PLA surfaces (films, membranes) is typically in the order of 80°. PLA has a similar water contact angle as to PET (72°). The properties of the polylactides primarily

depend on molecular mass and degree of crystallinity. Higher molecular weight enlarges glass and melting temperatures and increases tensile strength and modulus of elasticity with reduced elongation at break [3], [4], [5]. The problem in this context is that the degradation sensitivity (hydrolysis) can be influenced already on the stage of production and processing of the polyester material.

Previous research in fiber production focused on the processing of low-melting grades. In the filament spinning of PLA with a denier of 3 dtex per filament, speeds of 5,000 m/min have already been achieved (NatureWorks). Other studies, at the US-American University of Tennessee in Knoxville for example, document filament velocities up to 4,700 m/min, with the best properties (e.g. orientation degree, crystallinity, strength) in the range between 2,000 and 3,000 m/min [6]. Similar results have been shown by experimental studies of the German Leibniz Institute of Polymer Research Dresden (IPF) on spinning experiments with PLA [7] [8].

It was found out that in a speed range between 1,000 and 5,000 m/min the maximum values with regard to orientation degree, crystallinity, breaking stress and modulus of elasticity were reached at filament velocities between 2,500 m/min and 3,500 m/min. These parameters increase steadily depending on the stretch ratio. In contrast, the elongation falls continuously as expected. Orientation and crystallinity also depend significantly on the degree of modification of the PLA polymers. This was shown by spinning experiments with D-lactid portions in the range of 1.8-16.5 % [9]. With a rising D-lactide content, the crystallinity decreases as the degree of orientation increases.

The spinning speeds were varied between 1,000 m/min and 10,000 m/min. In the period of 2007-2012, STFI already carried out initial work in several research projects concerning the development of spunbonded nonwovens from renewable raw materials (IW073083, IGF15926BR/1, MF100005). The general processability of the (at this time) available biopolymers of PLA, copolymers and blends were amongst other things investigated in conjunction with biofilms using spunbond and meltblown technology. In addition to the spinning stability and the spinning speeds, in particular the parameters in the thermal (calender) and the mechanical (spunlacing or needle punching) solidification process could be thoroughly tested and significantly improved.

PLA nonwovens as filtermedia in air filtration

Nonwovens from PLA and its blends with PBS have been produced via melt spinning process. The polymers to be processed must fulfill the basic condition: spinning and stretching capability. In the spunbond process the polymers is melted in an extruder. The polymer melt gets through nozzles by means of a cold air stream, gets mechanically stretched and deposited directly onto a screen belt without tearing. After depositing the filaments into an unconsolidated surface, this surface is subsequently solidified in some way (thermally or mechanically), Figure 2.



Figure 2: Spunbond plant Reicofil[®]4.5 with different technology units for web bonding in STFI

In the meltblown process, which is also depending on the polymer melting process step, finest filaments are made from a polymer melt which is being exposed to hot air directly at the nozzle exit. The intensive effect of the hot air directly at the nozzle exit causes a filament-air mixture and produces finest filaments in a range of < 1 μ m to about 10 μ m.

The media was characterised and first tests with regads to the separation of solid particles in air filtration have been carried out (Table 1 and 2).

Trial nr. [NaCl]	Grammage (g/m²)	Raw gas 1+2 (-)	Clean gas (-)	Retention (%)	Standard deviation (-)	CV (coefficient of variation) (-)	particle size 0.4 µm (%)
260/16	100.8	110,000	73.20	33.4	4.25	12.73	31.3
62/18	139.2	109,860	101.60	7.5	1.72	23.07	4.5
405/18	123.2	110,520	91.70	17.0	2.06	12.11	14.1
624/18	99.0	110,640	99.64	9.9	1.82	18.45	7.4

Table 1: Characterization of PLA filter media for separation of solid particles in air filtration for NaCl

Table 2: Characterization of PLA filter media for separation of solid particles in air filtration for SAE-fine dust

Trial nr. [SAE-fine]	Grammage (g/m²)	PTI-fine raw gas 1+2	PTFI-fine clean gas	Retention (%)	Pressure difference (Pa)	gravimetric separation efficiency (%)
260/16	100.8	80,413	3,350	95.9	44	95.9
62/18	139.2	80,078	28,625	64.1	14	67.5
405/18	123.2	80,525	15,564	80.7	16	79.7
624/18	99.0	80,487	17,563	78.3	24	76.7

Biodegrability and hydrolysis of PLA

It should be noted that in the context of bio-based (or biogenic) materials, the aspect of biodegradability is often cited. Although filter media are incinerated after use in the prior art, and thus biodegradation is of minor importance, this characteristic relates to wastes from production and manufacture. Therefore, it should be noted that PLA basically has biodegradability due to the molecular structure. An appropriate environment can be realised in industrial composting plants where the degradation takes place within a few months [10]. PBAT and PBS are also biodegradable. However, the CO2 neutrality of the biogenic filter medium is given in all cases and thus, a clear added value compared to commercially available materials can be demonstrated.

The preliminary experiments of the research partners involved in this paper have also shown the significant hydrolytic degradation of the PLA and the possibilities of blending in this context.

In an alkaline hydrolysis experiment (Figure 3), experimental nonwoven webs of PLA and a PLA/PBS blend material were stored for 20 hours at room temperature in NaOH solution. While both samples survive storage largely free of damage at a NaOH concentration of 4 g/l, pure PLA was completely degraded by storage in 40 g/l NaOH, while the blended material exhibits only slight hydrolytic damage.



Figure 3: Preliminary experiments on the present research work show the clear difference in degradation of pure PLA to PLA/PBS blend material alkaline hydrolysis (NaOH, 4 g/l (a) or 40 g/l (b), 20 h at RT)

The experimential results shown in Figure 3 display high hydrolytic instability of PLAmaterials as well as the possibility to improve the degradation behavior by blending.

Mechanical tests on PLA monofilaments

An essential aspect of the present research concerned the prediction of the product lifetime under real conditions of a filtration application and thus the evaluation of the various measures for the modification of the material properties. In this context, the standard examination methods (tensile test, DSC, SEM, optical microscopes) provide important information. Earlier studies on the degradation in certain environments

have focused mainly on medical or agricultural products and analyzed accordingly the in vitro degradation in physiological saline solution (e.g. [11]) or the enzymatic hydrolysis of PLA (e.g. [12], [13], [14]).

In general, the tensile tests can be used to define the mechanical tension and the standard deviation which are important data for all futher measurements. The results for the standard PLA monofilaments shown in Figure 4 have a high replicability. Therefore, the tensile tests can be defined as a suitable measurement method to describe the mechanical behavior of PLA monofilaments.



Figure 4: Results of tensile tests of PLA standard monofilaments

The data for the tensile tests show a clearly decreasing strength of the PLA monofilament in case of treatment in extreme milieus for an indicated number of days, like a climatic chamber with a temperature of 60°C and 80% humidity (Fig. 5).



Figure 5: Results of tensile tests of PLA monofilaments, treated in a climatic chamber with a temperature or 60°C and 80% humidity for indicated number of days

Some damages of the monofilament can already be seen via examination with optical microscopy. The diameter of a PLA monofilament, treated for nine days at 40 °C in 1 molar NaOH solution, notably decreases as shown in Figure 6.



Figure 6: Optical microscopy image PLA monofilament bevor (left) and after (right) treamtment in 1 molar NaOH solution at 40°C for 9 days

Experiments and model for predicting long-term mechanical stability of PLA fibers

Although not previously applied to PLA or PLA-based materials, there is a really interesting concept for the lifetime prediction of technical textiles like PET, which is completely based on the IGF-Project No. 16198 N by T. Bahners from the "Deutsches Textilforschungszentrum Nord-West" (DTNW) [15]. Bahners describes the evaluation of short-time relaxation measurements to define a relaxation master curve (RMC). The relatively complex course of the RMC describes the material behavior over many time decades and reflects the decrease in the modulus of the material as a function of the service life, but it is virtually impossible to record in its time evolution in real time. This evaluation method, in the following Schulz-Model, was designed by Schulz et al. [16] who used a Boltzmann theory based model of visco-elasticity by Persoz [17].

The RMC is described by a symmetrical s-shaped function (equation (1)), where the mechanical tension (Stress σ) is depending on the time t.

$$\sigma(t) = E_0 \varepsilon - (E_0 - E_\infty) \varepsilon \Phi(t)$$
(1)

Because of the assumption, the RMC is symmetrical s-shaped, the relaxation function can be expressed as integral over the Gauss normal distribution centered at a time τ , as shown in equation (2), where τ is the point of inflection.

$$\Phi(t) = \int_0^t \varepsilon * \Phi[(t-\tau);\varepsilon] d\tau = \frac{1}{\sqrt{2\pi}} * \int_{-\infty}^{V(\varepsilon,t)} e^{-\frac{z^2}{2}} dz$$
⁽²⁾

The whole equation for the RMC, transformed from mechanical tension $\sigma(t)$ to modulus E(t), is described by equation (3).

$$E(t) = \frac{\sigma(t)}{\epsilon} = E_0 - (E_0 - E_\infty) * \frac{1}{\sqrt{2\pi}} * \int_{-\infty}^{V(t)} e^{-\frac{z^2}{2}} dz$$
(3)

Modelling the RMC is done by the evaluation of a set of short-time relaxation measurements to define the unknown Parameters E_0 , E_{∞} and V(t), where V(t) is the integration limit with a scaling factor a as shown in equation (4).

$$V(t) = \frac{1}{a} * \left(\log(t) - \log(\tau)\right) = \frac{1}{a} * \log\left(\frac{t}{\tau}\right)$$
(4)

The set of short-time relaxation measurements contains the measurement of the mechanical tension σ for different elongations ε . The higher elongations represent the artificial aging of the material. By using a time shift Δt , depending on the elongation ε , the whole RMC can be designed by several short-time measurements. The first step to design the relaxation master curve using the Schulz-Model is to record the data for standard tensile tests (Figure 3). This is really important to valuate the data. If the standard deviation is to high, it will not be possible to get purposive results. This is the reason why monofilaments with a high regularity are used. By evaluating the data, the elastic area (straight line at the beginning of the curve) can be found. The choosen elongation ε for the short-time relaxation measurements need to be in this area, including one elongation ε at the end of the elastic area. The choosen elongations for the short-time relaxation measurements are:

For each elongation five repeated relaxations measurements are recorded where the mechanical tension σ is plotted against the time t (Figure 7).



Figure 7: Results of short-time relaxation measurements of PLA monofilaments

The data needed for the evaluation have to be transformed from mechanical tension σ in MPa to modulus E in N, additionally the significant areas are extracted and plotted against the logarithm of time log(t). The significant area, as shown in Figure 8, of the curve starts at the maximum mechanical tension and ends after 300 s.



Figure 8: Results of short-time relaxation measurements of PLA monofilaments transformed into modulus and plotted against time

By using the Schulz-Model, as shortly described previous in this chapter, it is possible to transfer the eight short-time relaxation measurements with differing elongation ε into one relaxation master curve (Figure 9).



Figure 9: Short-time relaxation measurements (left) and transfer into one relaxation master curve using an elongation depending time shift Δt (right)

In addition to the standard material (PLA basis), several treated PLA monofilaments have been studied. Different media (NaCl, H₂SO₄, VE) and a climate chamber with 50 % humidity at 50 °C have been used to treat the monofilaments for two weeks at 23 °C. The complete RMC's, based on the Schulz-Model and the equation (3), are shown in Figure 10.

$$E(t) = E_0 - (E_0 - E_\infty) * \frac{1}{\sqrt{2\pi}} * \int_{-\infty}^{V(t)} e^{-\frac{z^2}{2}} dz$$
(3)

The results show a high dependence from the treatment in the climate chamber, the material is less strong with a maximum modulus of about $E_{max,50^{\circ}C 50\%} \approx 800 N$ instead of $E_{max,Basis} \approx 1000 N$ for the basis material. On the other hand, the material lasts longer until the modulus reaches about the half of the maximum.



Figure 10: Relaxation master curves (RMC) for treated/basic PLA monofilaments

After the successful application of the Schulz-Model to PLA monofilaments, the model should be applied to PLA nonwovens. Therefore, the data for standard tensile tests are recorded using the DIN EN 29073-3. Interestingly Figure 11 shows that standard deviation for the nonwoven tested lengthwise (3,4 %) is much lower then for the nonwoven tested crosswise (17,9 %). Usally, standard deviation of about 10 % is expected for this kind of material. In the case of the lengthwise nonwovens it may be possible to define a purposive RMC by using the Schulz-Model.



Figure 11: Results of tensile tests of PLA standard nonwoven 405/18 lengthwise (left) and crosswise (right)

Conclusion and Outlook

In general, the tensile test is a partical method to define the mechanical properties of a technical textile.

The Schulz-Model is usable for the lifetime prediction of technical textiles in form of monofilaments. The results show the pronounced sensitivity to hydrolysis, as described before. During the treatment in a climate chamber, the molecule bonds break and lead to a lower modulur or mechanical tension. However, the longer service life is prolonged as a positive effect. There are still many different conditions that can be investigated to describe a larger area of filter application relevant conditions.

The biggest challenge is to applicate the model on textiles with low regularity. Futher studies on the lifetime prediction concentrate on a reduction of experimental work und a better application on unregular textiles.

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