POLYACRYLONITRILE-LIGNIN BLENDS AS PRECURSORS FOR POROUS CARBON FIBERS

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ABSTRACT

Polyacrylonitrile/lignin blends were spun by use of solvent wet spinning. The precursor fibers have been characterized by IR, rheometer, tensile tests and density calculation. Afterwards the fiber have been stabilized by means of a batch device and the stability indexes (S.i.) were assumed through differential scanning calorimetry.

Key Words: Lignin, Polyacrylonitrile, Porosity, Carbon Fiber

1. INTRODUCTION

Carbon fibers (CF) have long been known for their excellent combination of low weight and high mechanical stability. For this reason, CF are already highly relevant for lightweight construction in transportation and textile construction.[1, 2, 3] In the light of the energy revolution and the necessary new mobility and energy storage concepts, there is a special interest in innovative material and process developments for novel multifunctional CF.

Commercial CF are most commonly made of polyacrylonitrile copolymer precursors with molecular weights ranging from 70,000 and 200,000 g/mol using dry spinning, solvent wet spinning or gel spinning processes.[4] The spun precursors are then transferred to CF by successive thermal treatments of stabilization (200-300 °C, under oxygen) and carbonization (up to 1600 °C, under inert gas).[5] Despite the increase in CF production of more than 10 % per year [6], the high manufacturing costs prevent an expansion of use, i. a. in the transport sector. An important reason for this is the high price of petroleum-based PAN, which is approx. 51 % of the total CF price.[7] Therefore, more cost-effective precursors for the production of CF must be brought into focus in order to achieve broader market suitability.[8]

Lignin is the second most common biopolymer in nature and is therefore available in nearly unlimited quantities.[9] Its chemical structure and functionalities vary according to plant species and wood pulping method and thus influence the resulting fiber properties.[10] However, due to its low price and high carbon content (approx. 65 %), this renewable raw material has long been of great interest for the production of CF precursors. For a long time, research concentrated on melt spinning, whereby limitations often occurred due to rough filament surfaces and pores.[8]

In this study, the high-strength properties of wet-spun PAN-based CF will be combined with the structural limitations of lignin to produce porous CF. These should be suitable for the incorporation of energy storage materials and thus ensure functional integration into a fibrous and thus load-bearing CF battery.

2. EXPERIMENTAL

2.1 Materials

Lignosulfonate (LS) with a low sulfonate content (< 4 %) and a molecular weight approx. 10,000 g/mol and dimethyl sulfoxide (DMSO, 99 %) were purchased from Sigma-Aldrich. Dimethylformamide (DMF, 99 %) was purchased from BCD Chemie GmbH Hamburg. Further an institute's own polyacrylonitrile (PAN) homopolymer with Mn = 119,000 g/mol, and a polydispersity of 2.7 was used.

2.2 Spinning solution and wet spinning process

The reference spinning solution was prepared from 18 wt% PAN and 82 wt% DMF/DMSO (70:30). PAN/LS blend solutions were provided analogous to the reference and additionally 1, 2, 5, 10, 15 and 20 wt% LS (related to PAN) were added respectively. The solutions were homogenized by stirring at 60 °C and then degassed under vacuum. The fiber spinning was conducted by use of a wet-spinning pilot plant by Fourné Polymertechnik GmbH (figure 1) consisting of one coagulation bath, three washing baths, one drying and one sizing unit and a winder.

Figure 1. Wet-spinning pilot plant by Fourné Polymertechnik GmbH

Therefore the spinning solutions were heated to 70 °C and extruded through a filter (50 µm) and a spinneret with 1008 holes and 70 µm hole diameters. Here the spinneret was immersed in the coagulation bath and fiber was converted with a jet stretch of 1.0 (without stretching). The fibers were subsequently drawn within the washing baths to an overall ratio of 1:4.0, dried and finally sized with Torsinol ZSB.

2.3 Fiber stabilization

Table 1. Stabilization temperature programs

TP 1	Initial heating ramp: 20-230 °C @ 7 K/min, 230 °C (60 min)
TP 2	TP 1 + second heating ramp: 230-250 °C @ 5 K/min, 250 °C (60 min)
TP 3	TP 2 + third heating ramp: 250-270 °C @ 5 K/min, 270 °C (60 min)

The stabilization process was performed on a laboratory scale with a custom made batch tool. The PAN and PAN/LS precursor fibers were stabilized using three different temperature programs (TP) under air atmosphere at forced convection due to an air flow of 100%. After finishing the TP, the samples were taken directly from the furnace to avoid temperature effects during cooling. The temperature levels of the three TP's are shown in table 1 and figure 6.

2.4 Characterization

Spinning solution viscosity measurements were performed by use of a HaakeMars rheometer at 70 °C and 1 Hz in oscillation mode. Infrared spectroscopy using a FTIR Nicolet 6700 from Thermo Scientific was employed for non-destructive structure elucidation. The shapes and diameters of the precursors and the stabilized fibers were measured using a AXIOImager.M1m (Zeiss) microscope. Filament tensile tests were carried out by means of Favimat+ (Textechno Herbert Stein GmbH) with Vulkollan® clamps, clamping pressure: 5 bar, clamping length: 20.0 mm, number of tests: 30, test speed: 20.0 mm/min (PAN filaments) and 2.0 mm/min (stabilized fibers). Stabilization indexes (S.i.) were assessed using a Mettler Toledo Stare 1 DSC. The fibers have been scanned in the temperature range 150-400 °C using a heating rate of 5 K/min. The S.i. were calculated using the heat release related to exothermic DSC peaks using the following equation:

$$S.i. = \frac{h_0 - h_S}{h_0} * 100$$

where h_0 and h_S are specific heat released in DSC thermograms of the precursor fiber and the stabilized fiber. The amounts of h_0 and h_S were calculated by integrating the total area under exothermic peaks to spline curve between the borders of 230 °C and 380 °C.

3. RESULTS AND DISCUSSION

3.1 Precursor fibers

Figure 2. Wet spun PAN and PAN/lignin (5, 10 and 15 wt%) blend fibers

Employing wet spinning process PAN fibers and PAN/lignin blend fibers (1, 2, 5, 10, 15 and 20 wt% LS addition) with 1008 filaments and a draw ratio of 1:4.0 could be spun each with several hundred meters. The used PAN and PAN/lignin solutions were examined by rheological measurements and the results are shown in figure 3 (left). Except for the 5 wt% LS sample, an increase in viscosity was observed with increasing amount of lignin addition. Figure 3 (right) shows the IR absorption bands of pure PAN with 3000-2920 cm^{-1} (C-H) and 2240/1450 cm^{-1} (N-H) and pure lignin with 3600-3000 cm^{-1} (wide, OH) and 1590/1500 cm^{-1}

(aromatic C=C). The PAN and the PAN/lignin blend fibers show exclusively bands of pure PAN and unexpected no increase in OH and aromatic carbon bands with increasing lignin content. Since the penetration depth of the stimulating IR radiation using ATR technique is just a few 100 nm,[11] only the outer area of the filaments can be examined. The used LS is very good soluble in water and thus it was completely washed out of the filament edge areas (during the coagulation and washing steps) even with a high lignin addition of 15 wt%. Therefore no IR typical lignin bands were detected.

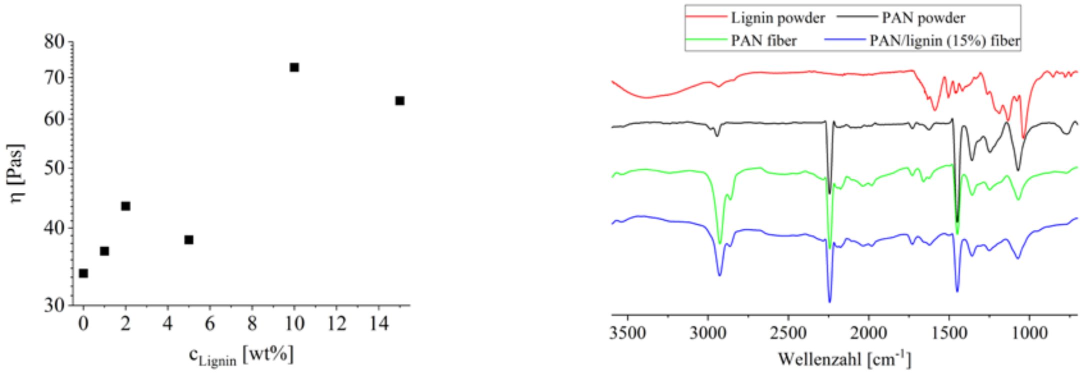

Figure 3. Viscosity measurements of the spinning solutions (left)
FTIR analyses of PAN, lignin and blend fibers (right)

Figure 4 presents the filament fineness and the filament densities of the spun PAN and PAN/lignin fibers with increasing LS contents. The fineness of the blended fibres shows a slight increase in weight up to 5 wt% LS due to the addition of lignin and above a weight stagnation (figure 4 left). This is an indication that above 5 wt% LS the lignin washout (during coagulation and fiber stretching) counteracts weight gain with further LS addition. The lignin leaching can already be observed during the spinning process by discoloration of the coagulation and water baths. Simultaneously, for low LS contents the filaments have significantly higher cross-sections, whereby the filament densities decrease from 1.07 g/cm³ (0 wt% LS) to 0.79 g/cm³ (2 wt% LS) and increase significantly above 5 wt%. Since LS, which is evenly distributed in the spinning solution, is washed out of the filaments and thus the filament densities decrease compared to the reference, especially for low LS concentrations, LS represents a promising mechanism for physical pore formation during the spinning process.

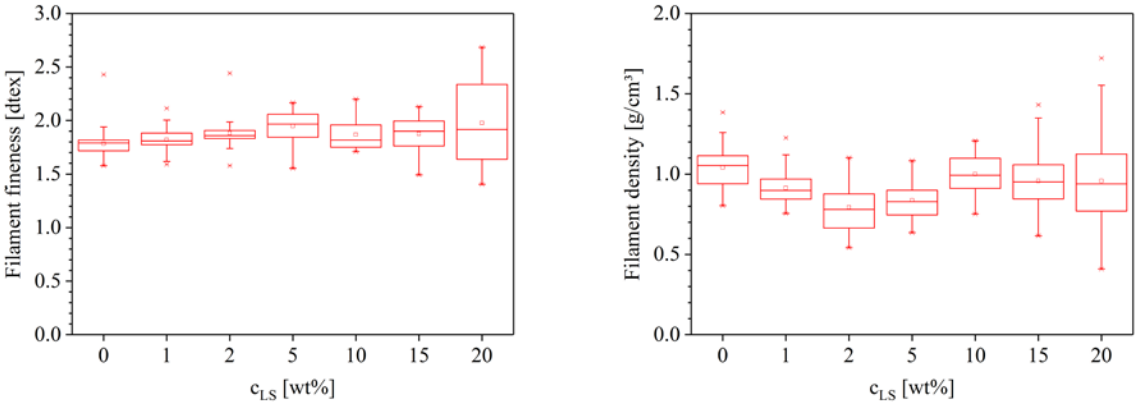

Figure 4. Filament finesses (left) and filament densities of the precursor fibers (right)

In order to convert the precursors to CF during the thermal stabilization and carbonization process steps, the fibers must have sufficient mechanical properties despite the reduction of densities due to the addition of LS. To examine the mechanical properties, tensile elongation tests were carried out for each LS content and the results of the maximum tensile forces are shown in figure 5 (left). All fibers up to 15 wt% LS show tensile strengths between 2.98 and 2.49 cN/tex and are thus only 10 % below the reference value of pure PAN filaments. Thus the LS modification of the precursors should not result in any mechanical fiber limitations for the further process steps. Despite almost constant maximum tensile strengths, the PAN/lignin blends show a significant decrease in maximum elongation above 2 wt% LS addition (figure 5 right). It can be assumed that the regular storage of the cross-linked three-dimensional lignin between the linear PAN chains reduces their extensibility and thus the overall extensibility.

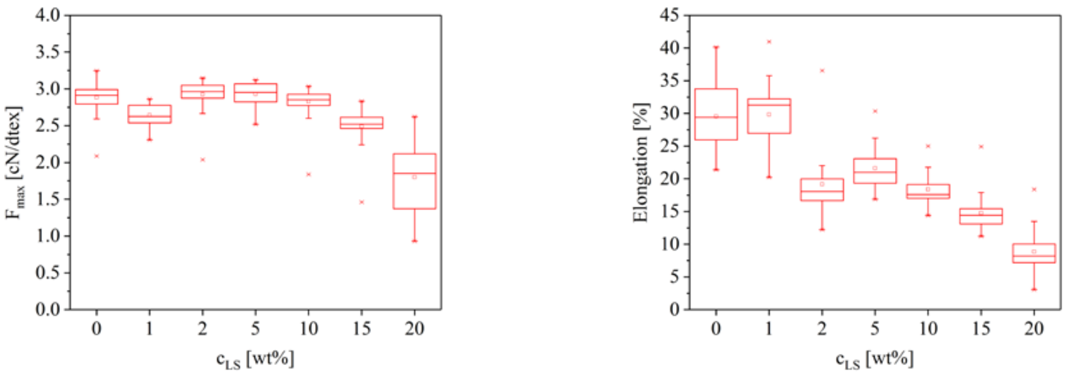

Figure 5. Tensile strength (left) and maximum elongation of the precursor fibers (right)

3.2 Stabilized fibers

Since the cross-linking of the polymerchains is the essential feature to ensure thermal stability in the carbonisation process, the precursor fibers of PAN and PAN/Lignin have been stabilized at different temperatures and residence times. Various process conditions tend to different degrees of stabilization which are expressed in the stabilization index (S.i.). The S.i. should reach a value of at least 50% [12, 13] to produce CF with best mechanical properties. This is supposed to be unlike for the production of porous fibers. High temperatures [14] and long dwell times [15] have been described as suitable conditions for the production of porous fibers. Precursor fibers with different lignin concentrations were treated at different temperatures and residence times to produce oxidized fibers with a low, mid and high S.i. which are shown in figure 6 (right).

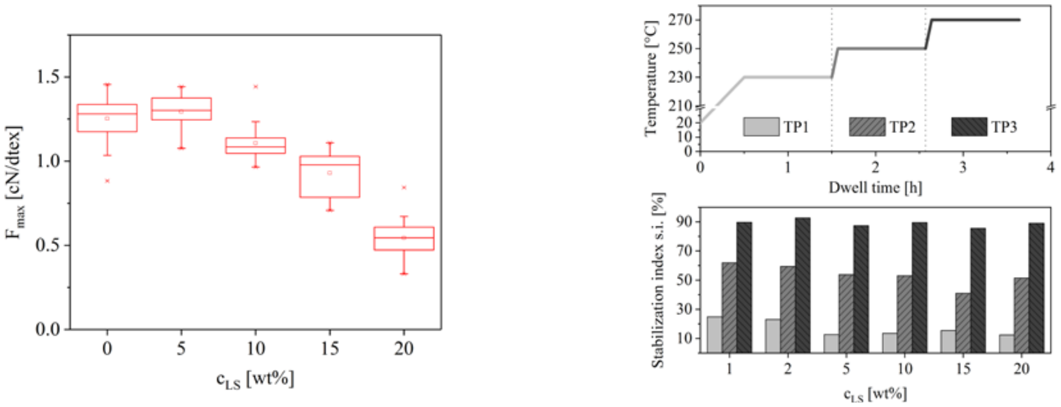

Figure 6. Tensile strength (left); temperature programs and stabilization indexes of the crosslinked fibers (right)

It can be seen, that all fractions reached a S.i. of at least 50% after TP 2 except of 15 wt% LS content. Thus stabilized fibers after TP 2 should be feasible in the carbonization process. In general the S.i. decreases with increasing lignin content. İt is assumed that fibers with a higher lignin content tend to incomplete crosslinking PAN polymerchains wich results in a slower reaction speed, caused by a variation of the degradation reactions as well as a steric hindrance of the spheric lignin molecules. Due to that reason the stabilized filaments show a decrease of tensile strength with increasing lignin content in the precursor after TP3. A strong decrease already occurs above 10 wt% lignin, resulting from the infections of the precursor filaments.

4. CONCLUSION

In this article PAN/Lignin blends, with 1008 filaments and 1-20 wt% lignosulfonate, were spun as CF precursors and extensive textile-mechanical investigations were carried out. Partially, these fibers have significantly lower fiber densities with sufficient mechanical strength for the further processing. Batch trials have been successfully performed for different degrees of stabilization. The effect of the degree of S.i. on pore formation in carbonization is currently being investigated and will be reported soon.

5. ACKNOWLEDGEMENT

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