Fiber formation and properties of polyester/lignin blends

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ABSTRACT: Thermotropic liquid crystalline polyesters with varied chemical structure are synthesized by melt transesterification polycondensation. They are employed as matrix for blends with lignin materials to obtain melt-spinnable precursors for carbon fibers. The lignin samples are carefully purified by fractionation, enzymatic removal of reducing sugars, and subsequent modification of the terminal OH groups. Effective melt blending is achieved with liquid-crystalline aromatic–aliphatic polyesters having melting ranges that match the softening temperature of the lignin fractions, which is necessary to prevent thermal decomposition of the lignin. Polyester/lignin blends are partially compatibilized, phase-separated materials. The polyester/lignin materials are melt-spun successfully. The fiber properties depend on the lignin purification process. X-ray scattering reveals that orientation in lignin-containing fibers is maintained. First experiments show that the fibers can be converted successfully to carbon fibers by thermal annealing procedures. © 2019 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2019**, *136*, 48257.

INTRODUCTION

Advanced composite materials with high performance are the base for lightweight construction parts for applications in, for example, automotive, aircraft, and space industry. Carbon fibers are key components in these materials to achieve the required outstanding composite properties.[1] A variety of efforts including tailoring precursor systems, optimization of fiber preparation, and pyrolysis treatments have been made to improve the mechanical properties of standard carbon fibers from poly(acrylonitrile) (PAN), other synthetic polymer precursors, cellulose, or pitch.[2,3] The need to reduce the high costs for performance carbon fibers resulted in intensive studies to exploit cheaper and renewable sources. One of the main options appeared to use lignin (besides cellulose) as natural product. The lignin content in wood is 20–30 wt %. During cellulose refinement, lignin is produced as by-product in large amounts of up to 50 bill tons per year.[4] This raw lignin is used directly or is refined by pulping processes. So far, only small amounts of lignin (about 2 wt %) are used in material applications, for instance as flame retardant, adhesive or polymer constituent.[5–7]

The particular structure of lignin depends on its natural source (type of wood) as well as the pulping procedure.[8] It is characterized by a highly branched, semiaromatic structure with high molar mass and dispersity, as well as a huge number of terminal functional groups.[9] It is chemically rather heterogeneous and consists of infusible parts with high molar mass ($M_n >$ 5000 g/mol) mixed with lower molar mass components that soften above the glass transition temperature (T_g). T_gs of Kraft lignins are typically above 200 °C and are superimposed by thermal decomposition. Due to that reason and due to heterogeneity it is complicated to spin lignin from the melt yielding weakly oriented fibers with poor mechanical properties.[2] However, the first reports on carbon fiber precursors spun from lignin date back to 1969.[10]

In the past, many efforts were undertaken to improve the spinnability of lignin either from the melt or from solution, in particular including: (1) chemical modification of the lignin, and (2) mixing lignin with synthetic polymers to ease processability. The chemical modification of the terminal aliphatic and aromatic OH groups interrupts the hydrogen bonds and reduces T_g which

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results in better fusibility and processability in the melt. It has been demonstrated that conversion of OH groups in lignin by reaction with acetyl chloride, cinnamoyl chloride and methacryloyl chloride yielded materials that could be melt-spun into fibers as precursors for carbon fibers.[11] Nordström et al.[12] used the permeate of membrane-filtrated fractionated hardwood Kraft lignin as softener for lignin to achieve melt spinnability. Lignin has been used together with PAN in solution spinning procedures yielding fibers with higher tensile strength and ductility compared to fibers spun from pure lignin.[13]

The first efforts to use synthetic polymers as softeners for lignin to enhance processability were described for poly(ethylene oxide) (PEO).[10,14–16] Furthermore, the polyester poly(ethylene terephthalate) (PET), the polyolefin poly(propylene), and other synthetic polymers were employed as matrix for hardwood lignin and thermally spun into fibers that were subsequently thermally stabilized and carbonized.[3,16,17]

However, the mechanical properties of these carbon fibers are still to be improved due to the generation of more irregular rather than perfectly graphitized carbon structures typical for carbon fibers from PAN precursors.[2] Recent reports showed that fractionation of lignin into a water-soluble and water-insoluble fraction followed by treatment with the enzyme laccase might be a suitable way to reduce the heterogeneity and to enhance the spinnability of a lignin/PAN blend from solution.[5] The brittleness of the resulting fibers is avoided in sub-μm fibers obtained by electrospinning from solution.

The concept pursued here combined the use of carefully purified lignin fractions together with a tailor-made polymer matrix that is able to impose orientation on to the branched lignin molecules. The high orientability of thermotropic liquid crystalline polyesters (LCP) in melt spinning[18,19] was employed to force the branched lignin molecules into orientation. The study included both, design of lignin structures by fractionation, purification, and subsequent chemical modification, as well as synthesis of tailor-made thermotropic LCP with stepwise varied structure. Lignin samples and LCP were melt-mixed in a mini-twin screw extruder and the compounds were evaluated with respect to melt spinnability in a laboratory melt spinning system. The fibers were characterized with respect to the thermal decomposition behavior and mechanical properties.

EXPERIMENTAL

Materials

Starting materials for the polyesters: poly(ethylene terephthalate) (PET) (type K36, Thüringische Faser AG, Schwarza, Germany), hydroquinone (HQ, 99.5%, Merck KgA), 4-hydroxybenzoic acid (HBA, for synth., Merck KGaA), 6-hydroxy-2-naphthoic acid (HNA, 98%, TCI), isophthalic acid (IPA, 99% Sigma–Aldrich), suberic acid (SuA, >98%, Sigma–Aldrich), terephthalic acid (TPA, 98%, Sigma–Aldrich), vanillic acid (VA, 97%, Sigma–Aldrich), and the polycondensation catalyst zinc acetate (ZnAc₂, 99.9%, Sigma–Aldrich) were used as received. The solvents chloroform (99.98%, Fisher Chemical), pentafluorophenol (PFP, 99%, ABCR), toluene (for analysis, 99.9%, Acros Organics) and acetone (99.9%, Merck KGaA), as well as the acid chlorides for

lignin modification cinnamoyl chloride (98%, Sigma–Aldrich) and methacryloyl chloride (97%, Sigma–Aldrich) were also used as received.

The phenolic compounds were converted into the acetates by reaction with a mixture of acetic anhydride (Ac₂O, for synth., 98%, Merck KGaA) and acetic acid (AcA, 100%, Merck KGaA) catalyzed by sulfuric acid (>95%, Fisher Chemical). The phenolic compound (0.65 mol) was added into a dry round-bottom flask equipped with condenser together with Ac₂O (1.59 mol per OH group), AcA (250 mL) and two drops of H₂SO₄ (96%). The mixture was refluxed carefully for 5 h, cooled down overnight and the white precipitate was separated by filtration. Reprecipitation with n-butyl acetate (for anal., 99.5%, Merck KGaA) gave pure products as verified by ¹H NMR spectroscopy. Thus, p-acetoxybenzoic acid (pAOBA), 6-acetoxy-2-naphthoic acid (ANA), acetoxyvanillic acid (AVA), and hydroquinone diacetate (HQDA) were received. Resorcinol diacetate (RESDA, 1,3-diacetoxy benzene, 98%, Alfa Aesar) was a liquid and distilled under reduced pressure prior to use.

Two types of lignin were used for the experiments: Kraft Lignin IAT from spruce (type Indulin AT, Westvaco Corp., CT), abbreviated IAT, and Organosolv Lignin from spruce (Kehlheim Company, Germany), abbreviated OC.
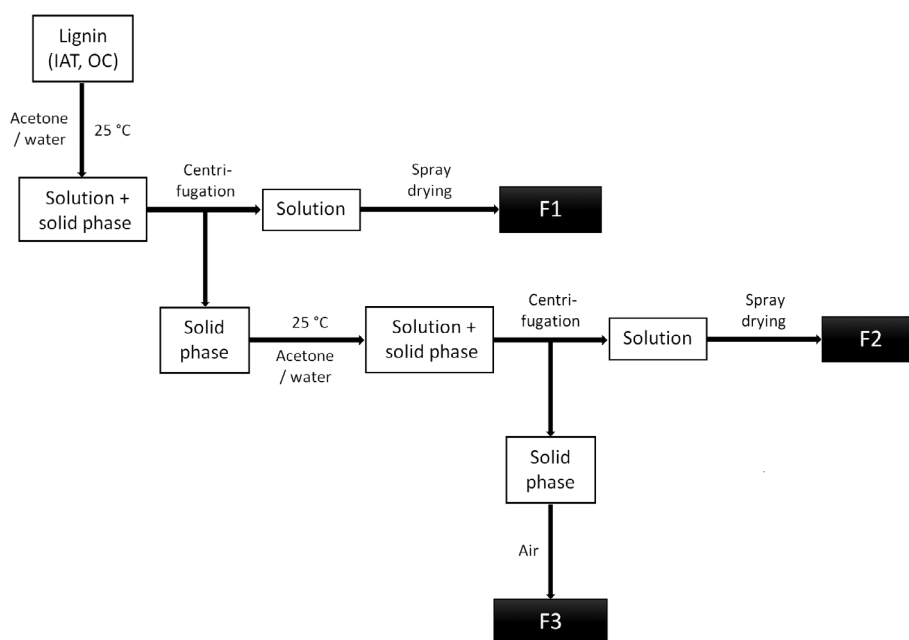
Lignin Fractionation

The fractionation of lignin was carried out in acetone/water mixtures with different composition. In a first step, lignin (200 g) was dissolved in acetone/water (30/70 vol/vol) mixture (2 L). After stirring for 2 h at room temperature, the nondissolved part was separated by centrifugation (Hettich Rotixa 190, 4500 U·min⁻¹, 30 min). Fraction 1 (F1) was extracted by spry-drying of the remaining solution of step 1 with a spray-dryer (Büchi 190, Switzerland). After that, the insoluble part of the lignin of step 1 was stirred in 2 L of an acetone/water (50/50 vol/vol) mixture (step 2). The undissolved part of step 2 was separated again by centrifugation. Fraction 2 (F2) was extracted by spry-drying of the solution of step 2. For IAT and OC, the solid residues after centrifugation are designated Fraction 3 (F3). Figure 1 illustrates the fractionation procedure schematically.

Removal of Reducing Sugars from Lignin Fractions

Fractionated lignin (2.0 g) was suspended in buffer solution (40 mL, pH = 5.0, 1/15 M, Sörensen phosphate buffer). Additionally, an enzyme mixture of 40 μL xylanase (30 kU, Ecopulp TX800A, AB Enzymes GmbH, Darmstadt, Germany) and 400 μL cellulase (8.8 kU, Metaplus L, DSM, the Netherlands) were added to the preheated suspension and shaken at 50 °C for 3 h. As control, the same procedure was carried out without enzyme addition. After incubation, the reaction mixture was cooled to 4 °C and centrifuged for 20 min at 5000 rpm (Megafuge-8, Heraeus, Germany) to separate the solid and liquid phase. The solid fractions were washed three times with deionized water (20 mL).

After completing the enzymatic treatment, all solid fractions were frozen at − 80 °C and freeze-dried for 24 h. The supernatant solution was used to determine the release of sugars. Therefore, the reducing groups were photometrically measured by the 3,5-dinitrosalicylic acid (DNS) method described by Miller.[20]

Figure 1. Fractionation procedure used for purification of lignin samples (F1: fraction 1; F2: fraction 2; F3: fraction 3).

Monosaccharides (D-xylose, D-glucose) were used as a standard for the calculation of free reducing sugars with the corresponding calibration curve.

Chemical Modification of Lignin Fractions

The lignin fractions were chemically modified by acetylation with acetic anhydride, by reaction with acetyl chloride, and by reaction with cinnamoyl chloride and methacryloyl chloride according to procedures adapted from Steudle et al.[11] The acetylation procedure is given in the following: the lignin sample (2.5 g), predried in a desiccator over P_2O_5 together with sodium acetate (0.013 g; 1.58 mmol) as catalyst was given into a 100 mL round bottom flask with magnetic stirring bar. Ac_2O (2.32 mL, 0.025 mol) and AcA (12.5 mL, 0.219 mol) were added under stirring and the flask was closed by a reflux condenser. The reaction was carried out under reflux typically for 5 h. After cooling, the mixture was precipitated into ice water. The product was filtered off, rinsed several times with deionized water, and was finally dried under reduced pressure at 40 °C overnight resulting in a light yellow product. Typical ^{1}H and ^{13}C NMR spectra are shown in the Supporting Information (SI), Figure SI-1–SI-3.

Synthesis of Thermotropic Polyesters

The fully aromatic liquid crystalline copolyesters were synthesized by transesterification polycondensation in the melt as reported earlier in detail.[21,22] A general description of the procedure is given in the following: the predried monomers TPA (5.90 mmol) or IPA (6.38 mmol), RESDA (7.11 mmol) or HQDA (7.57 mmol), pAOBA (11.82 mmol or 10.88 mmol, respectively) and the catalyst $ZnAc_2$ (0.1226 mmol) were filled in a three-necked round-bottom flask equipped with nitrogen inlet, mechanical stirrer, and distillation head. The flask was degassed by three vacuum-nitrogen cycles. The polycondensation was started by inserting the flask in a preheated metal bath at 230 °C under nitrogen flow and stirring. The temperature was raised

gradually to T_{max} (depending on the polymer between 330 and 350 °C) within 30 min. Then, the pressure was reduced gradually to $2 \cdot 10^{-3}$ mbar and the polycondensation proceeded for further 30 min to 3 h. Finally, the flask was exerted from the bath and the polymer was removed mechanically.

Poly(ethylene terephthalate-co-oxybenzoate) (PET/HBA) was prepared according to the procedure of Jackson and Kuhfuss[23] by melt transesterification with AOBA as described earlier.[24]

Melt Mixing of Lignin Fractions with Polyesters

Melt mixing was carried out with the small-scale twin screw extruders DSM Micro 5 Compounder and DSM Micro 15 Compounder (DSM, The Netherlands) requiring sample amounts of 4 g and 15 g, respectively. The lignin samples were predried over P_2O_5 overnight in a desiccator, the polyesters were predried under reduced pressure in an oven at 100 °C for 4 h. The temperature of the blending experiments was adjusted to the melting ranges of the polymer used (HBA/HNA: 290 °C; HBA/IPA/HQ: 290 °C; PET/HBA: 200 °C; HBA/VA/SuA/HQ: 200 °C). Blending was carried out at that temperature with a rotational speed of 200 rpm for 5 min. Thereafter, the blend was extruded out as strand.

Melt Spinning of Fibers

The polyester/lignin blends were dried in a vacuum oven at 80 °C for 10 h before spinning. The single fiber melt spinning experiments were carried out using a piston-type spinning device constructed at Leibniz-Institut für Polymerforschung Dresden e. V. The setup was reported earlier in detail.[25,26] The spinning experiments were performed at a temperature of 210 °C, and a volume throughput of 0.39 and 0.78 $cm^3 \cdot min^{-1}$ (mass throughput approximately 0.5 and 1.0 $g \cdot min^{-1}$), respectively. The diameter (D) of the capillary hole and the ratio (L/D) of the capillary length (L) to capillary diameter were 0.2 and 2, respectively.

Approximately 10 g of sample were fed under nitrogen atmosphere into the cylinder. After heating up and melting the extrusion was started. The single fibers were wound up with take-up speeds of 50 m·min⁻¹ and 100 m·min⁻¹, respectively. The variable distance between die and winder was 1.0–1.2 m. Monofilaments with diameters of approximately 70, 100 and 140 μm (fineness: 5–20 tex) were obtained.

Measurements

Size Exclusion Chromatography. Size exclusion chromatography (SEC) of the polyesters was performed in a modular SEC with HPLC-pump (Series 1200, Agilent Technologies), separation column PL MiniMIX-D (Agilent Technologies), differential refractometer (Knauer, Germany), using pentafluorophenol/chloroform (PFP/CHCl₃) 33/67 (vol/vol) as eluent with a flow rate of 0.3 mL min⁻¹ at 45 °C. Lignin fractions were analyzed with an SEC setup of HPLC pump (Series 1200, Agilent Technologies), RI detector (K-2301, Knauer, Germany) using a PolarGel-M separation column (300 x 7.5 mm, PL) and a mixture of dimethyl acetamide (DMAc)/LiCl (3 g·L⁻¹ LiCl) as eluent at a flow rate of 1.0 mL·min⁻¹ at 25 °C. In both cases, narrowly distributed polystyrene was used as standard for calibration to calculate the relative molar masses.

Solution Viscosity of Polyesters. Solution viscosities of the polymers were determined by an Ubbelohde viscometer (SI Analytics CT 72/2) with capillary I in PFP/CHCl₃ mixture (1/1 vol/vol) as eluent at 25 °C using a polymer concentration of 0.5 g·dL⁻¹. The inherent viscosity was calculated using the relation $\eta_{inh} = \ln \eta_{rel}/c$ [dL·g⁻¹].

Nuclear Magnetic Resonance Spectroscopy. ¹H (500.13 MHz) and ¹³C (125.74 MHz) NMR spectra were recorded using an Avance III 500 NMR spectrometer (Bruker Biospin) at 30 °C. The polyesters were measured in a mixture of CF₃COOD (TFA-d)/CDCl₃ (1/1 vol/vol) and the lignin samples in DMSO-d₆ as solvent. The spectra were referenced on the solvent signal (CDCl₃: δ(¹H) = 7.26 ppm; DMSO-d₆: δ(¹H) = 2.5 ppm; δ(¹³C) = 39.6 ppm).

³¹P NMR spectroscopy (Bruker Nanobay 400, 162 MHz) was employed to determine the Oh content. Data processing was done with the Bruker software TopSpin 3.1. The samples were prepared by dissolving water-free lignin samples (20 mg) in a mixture (700 μL) of CDCl₃/nondeuterated pyridine (1/1.6 v/v).

Elemental Analysis. Elemental analysis was performed using a Vario Micro Cube (Elementar Analysensysteme GmbH, Langenselbold, Germany).

Chemical Analysis of Lignin. *Klason lignin content.* Lignin (0.5 g) was dissolved in sulfuric acid (72%) for 2 h at room temperature. After that, the solution was diluted by water (575 mL) and heated under reflux for 4 h. The solid phase was separated with a sintered glass disc (POR 3, 10–16 μm), washed and dried at 105 °C.

Ash. The ash was determined by heating to 600 °C under air until weight constancy.

Functional groups. The determination of the functional groups (phenolic and aliphatic hydroxyl groups, carboxylic groups) was carried out after phosphitilation by ³¹P NMR spectroscopy. The samples were prepared by dissolving water-free lignin samples (20 mg) in a mixture (700 μL) of CDCl₃/nondeuterated pyridine (1/1.6 vol/vol). Dissolution was ensured by shaking for 15 min at room temperature. After dissolution, 200 μL of stock solution, containing the internal standard cyclohexanol (0.03 mmol·mL⁻¹, δ: 144.9 ppm) and the NMR relaxation agent chromium(III)acetyl acetonate (5 mg·mL⁻¹) were added. After mixing, the phosphitilation reagent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphosphalane (150 μL) was injected through a septum into the closed vial. The sample was shaken for 45 min at room temperature and then transferred into a 3 mm-NMR tube and measured. The content of functional groups was then calculated as described in the literature.[27–29]

Differential Scanning Calorimetry (DSC). DSC experiments were performed by a Discovery DSC 2500 (TA Instruments) under nitrogen atmosphere with a heating and cooling rate of 10 K·min-1. The glass transition temperatures (T_g) and melting temperature maxima (T_m) were determined from the second heating run to eliminate the thermal history of the sample.

Wide-Angle X-Ray Scattering (WAXS). The solid-state structure of blends and fibers was examined by WAXS. The X-ray diffractometer D8 Discovery (Bruker-axs) equipped with the 2D-detector Vantec (detector distance = 95 mm, accumulation time = 3600 s) was used with CuKα radiation (monochromatic beam, λ = 0.1542 nm). Radial intensity distributions were measure in the range of 2Θ = 3–55°, step-width $\Delta 2\Theta$ = 0.02°, azimuthal intensity distributions at 2Θ = 20° with a step-width of $\Delta\psi$ = 0.5°.

Thermogravimetric Analysis (TGA). TGA experiments were carried out with a TGA Q5000 (TA Instruments) under nitrogen in the temperature range between 30 and 800 °C with a heating rate of 10 K·min⁻¹.

Pyrolysis GC/MS. Pyrolysis-GC/MS (Py-GC/MS) analysis of the lignin samples was performed on an Agilent 7890D 5977 MSD, Agilent). Lignin (300 μg) was given into a quartz capillary tube and pyrolized (Frontier Lab EGA/ Py 3030D) at 450 °C. Separation was achieved on a ZB-5MS capillary column (30 mm × 0.25 mm) using a temperature program of 50–240 °C and a heating rate of 4 K·min⁻¹. Compounds were identified using the NIST 2014 mass spectral library. The hydroxypropyl/guajacyl/syringyl (H/G/S) ratio was determined as described by Faix et al.[30]

Scanning Electron Microscopy. The extruded samples and fibers examined were cut at −180 °C with the ultramicrotome EM UC7 (Leica Microsystems). The cut surfaces were then observed with a Zeiss Ultra Plus SEM with an acceleration voltage of 3.00 kV, aperture size of 30 μm and magnification of 1000×.

Mechanical Testing of Fibers. Fineness. The fineness Tt of a fiber is defined as mass per length, the unit 1 tex is given by the fiber mass of 1 g at a length of 1000 m. Before mechanical

characterization, the fineness was calculated as an averaged value determining the masses of three different pieces at fiber lengths of 10 cm.

Mechanical Characterization. The tensile strength tests (force elongation behavior) were carried out at room temperature in accordance to ASTM D2256 by a testing machine Zwick Roell Z0.5 (Zwick, Germany) under defined test conditions (gauge length: 50 mm; preload: 1 cN; test speed: 20 mm·min^{-1}).

RESULTS AND DISCUSSION

Lignin Fractionation and Chemical Modification

Softwood Kraft lignin (IAT) and Organosolv lignin (OC) were chosen as starting materials because they are easily available from the most often used pulping process and they contain generally only small contents of syringyl basic units. Syringyl units contain two methoxy groups. In the generally accepted opinion, these substituents disturb the formation of ordered graphitic layers during carbonization and result therefore in irregular carbon fibers.[2] Thus, it is advantageous to avoid lignin materials with high number of substituted subunits in the initial selection of starting materials.

Fractionation of the starting lignin was carried out to achieve a higher purity and homogeneity of samples. It was expected that this will result in more homogeneous melting which is necessary to achieve melt-spinnable compounds. The samples were chemically analyzed after fractionation. For application as carbon precursor the Klason lignin content, residual ash, amount of H, G and S units, functional groups and molar masses of the fractions were of interest.

Table I shows the proportion of non-acid soluble lignin (Klason lignin), the remaining ash fractions as well as the elemental analysis of the individual fractions.

The content of Klason lignin in both samples increased from fraction F1 to fraction F3. Fraction F1 was dissolved with the largest amount of water in the mixture. Therefore, it contained the highest amounts of remaining sugars and low molar mass parts of lignin that were not included in the Klason lignin value. Overall, the IAT sample had a higher content of Klason lignin and thus, higher lignin content. The ash content that is primarily caused by the digestion methods decreased from fraction F1 to fraction F3. Fraction F3 of IAT lignin was almost without ash, while the OC lignin had higher ash content. The carbon content in both lignins determined by elemental analysis was the highest in fraction 2 (IAT F2C1: 64.85%; OC F2: 66.23%).

The samples after fractionation were analyzed for their hydroxypropyl (H), guajacyl (G), syringyl (S) ratios by pyrolysis-GC/MS. The data are summarized in Table I. The dominant building units in all fractions were G units, as expected for softwood lignin (>98%).[31] Fractionation influenced the ratio of building units. It was found that fractions F2 and F3 did not contain S units anymore (see Table I). This can be explained by the better cleavability of β-O-ethers of S units in comparison to G units.[32] The proportion of H units decreased continuously from fractions F1 to F3, and the sample OC F3 was completely free of H and S, and thus consisted only of G units.

Table I. Chemical Characterization of the Lignin Fractions

Fraction	Klason-Lignin (wt %)	Ash (wt %)	Ratio H/G/S (wt %)	Elemental analysis (wt %)
IAT F1	69.9	5.46	4.0 95.5 0.5	C: 58.37 H: 5.45 O: 36.1
IAT F2C1	87.8	1.82	2.5 97.5 0	C. 64.85 H: 5.46 O: 29.69
IAT F3	95.1	0.64	1.0 99.0 0	C: 64.39 H: 5.60 O: 30.01
OC F1	68.8	9.65	5.0 94.0 1.0	C: 55.74 H: 5.04 O: 39.22
OC F2	78.8	2.93	2.0 98.0 0	C: 66.23 H: 5.69 O: 28.08
OC F3	85.8	1.95	0 100.0 0	C: 57.35 H: 5.23 O: 37.42

End group analysis of the fractions revealed the existence of different contents of functional groups. The ratio of the different functional groups in the samples is illustrated in Figure 2.

The content of aliphatic hydroxyl groups in both lignin types decreased slightly from fractions F1 to F3, correlating to the enhanced carbon content. This is originated from the higher molar mass of F3 compared to F1. The higher the molar mass, the less OH groups can be detected. It is also expressed by the increasing Klason lignin value shown in Table I. Accordingly, the proportion of polysaccharides was reduced. In IAT lignin, a slightly lower content of phenolic groups with increasing fraction number was observed, while it was higher in the OC lignin fractions. This result can be explained by the different production routes and the associated different bond cleavages. The content of carboxyl groups as well as the content of methoxy groups in both lignins decreased from fraction F1 to F3. This is particularly important for the generation of carbon fibers as methoxy groups influence the resulting carbon structure after pyrolysis and result in reduced regularity of the structure.[2]

The molar masses of the lignins were analyzed by SEC using conditions that are usually applied in literature.[33] It is generally accepted that the conditions used so far bear a high number of problems. The use of linear polymers as calibration standards does not take the branched structure of the lignin into account and yields large deviations of the calculated relative molar masses to real values. This might be overcome by application of advanced methods like asymmetric flow-field fractionation,[34] which was beyond the scope of the present study. Therefore, we just used linear calibration and RI detection. The relative molar masses obtained allowed a comparison of the fractions. The results are summarized in Table II. It was noticed that the relative
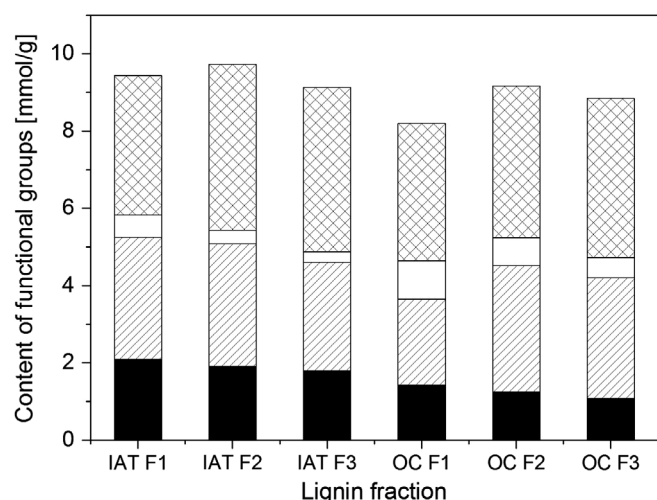
Figure 2. Content of functional groups in the lignin fractions prepared. ▨, OCH_3; ▢, COOH; ▧, phenolic OH; ■, aliphatic OH.

molar masses raised with increasing fraction number (note that fraction IAT F1 still contained a high molar mass fraction that was not completely soluble in the eluent DMAc/LiCl). Removal of reducing sugars also increased the molar mass moderately, while acetylation only broadened the dispersity Đ (see Table II).

It can be noted that the fractionation of Kraft and Organocell lignins allowed the control of building units, functional groups, and molar masses. From all the results it could be concluded that fractions F2 and F3 were best suited for use in carbon fiber precursors and blending with aromatic polyesters.

Additionally, it was examined whether or not enzymatic treatment contributed to further purification of the lignin fractions by removal of reducing sugars and if the removal of sugars would

have an effect of the later results in blending, fiber spinning, and subsequent properties of the fibers. It was supposed that sugar components in the lignin fractions would disturb fiber spinning and subsequently the formation of carbon fibers with regular structure. The lignin fractions IAT F1-3 were treated with enzymes as described in the Experimental section. Enzyme mixtures containing cellulases (Metaplus) and xylanases (Ecopulp) were selected. In all enzymatically treated lignin fractions, a release of sugars by the respective enzyme could be noticed (Figure 3). The highest amount of sugars was released from IAT F1, while fraction IAT F2 contained the lowest amount. It was also noted that the combination of both enzymes (Ecopulp and Metaplus) yielded in each case, but particularly for IAT F1 and IAT F3, the highest release of sugars. The combination of both enzymes showed the highest values for the release of sugars (IAT F1 and IAT F3). The fraction IAT F2 had the lowest sugar release. Only Metaplus could achieve an additional cleaning effect on this fraction.

The fractionated lignins (without enzyme treatment) were further chemically modified by acetylation and, in selected cases, by reaction with methacryloyl chloride and cinnamoyl chloride as reported by Steudle et al.[11]

Acetylation was performed by reaction of the respective lignin fraction with acetic anhydride/acetic acid as more facile method, in contrast to Steudle et al.[11] who employed reaction with acetyl chloride in pyridine. The conversion was followed semiquantitatively by ^{1}H NMR spectroscopy. Figure SI-4a depicts the region of broad acetyl proton signals (2.2–1.2 ppm) and of methoxy proton signals (4.0–3.2 ppm). The latter were not affected by acetylation and were used as intensity reference. The enlarged plot (Figure SI-4b) reveals that after a reaction time of 5 h the main conversion was finished and increased only slightly after that time. Therefore, 5 h were selected as optimum reaction time.
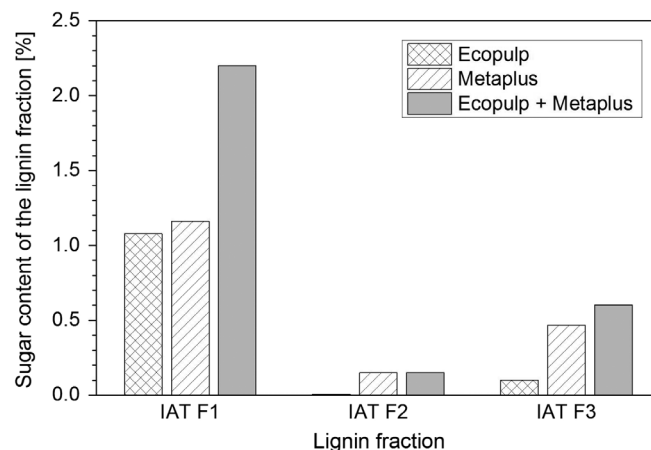
The glass transition temperatures depended accordingly on the reaction time (i.e., conversion), as illustrated in Figure 4. Only lignin fractions IAT F2C1/C2 and IAT F3 showed a clearly distinguishable T_g in DSC, while fraction OC F1 did not. Acetylation significantly reduced T_g (Figure 4, Figure SI-10) and reached a minimum at 5 h acetylation time with a value of 140 °C.

Table II. Relative Molar Masses (SEC) and Glass Transition Temperatures T_g (DSC, Second Heating) of Lignin Fractions

Sample	M_n (g·mol^{-1})	M_w (g·mol^{-1})	M_w/M_n	$T_{g,DSC}$ (°C)
IAT F1	106 000	132 000	4.41	n. det.
	2600	4400		
IAT F2C1[a]	3500	17 000	4.85	198
IAT F2C2[b]	3400	14 000	4.11	206
IAT F2C1-E	4200	19 500	4.64	
IAT F2C1-Ac	2800	15 000	5.35	144
IAT F2C1-E-Ac	2350	17 500	7.44	150
IAT F2C2-Ac	1500	16 500	11.00	150
IAT F3	5900	23 000	3.89	200
IAT F3-Ac	1000	8500	8.50	151
OC F1	2300	9700	4.40	n. det.
OC F2	3700	10 000	2.70	n. det.
OC F3	4200	12 000	2.85	n. det.

[a] Charge 1.
[b] Charge 2; n. det.: not detectable, mostly overlapped by thermal decomposition.

Figure 3. Released sugar upon enzymatic treatment of lignin fractions.
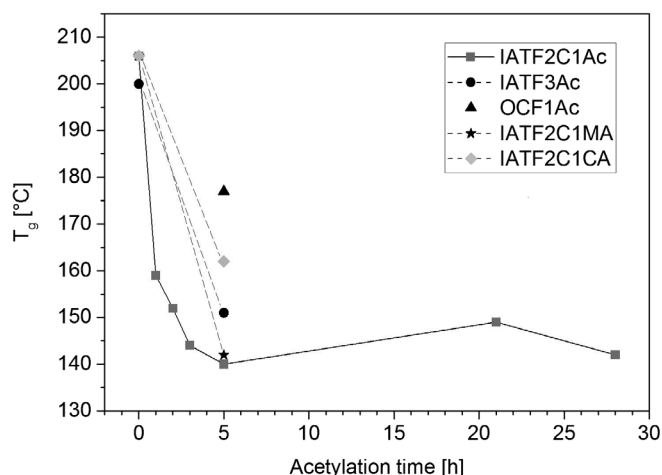
Figure 4. Influence of the modification time on the glass transition temperature T_g of different lignin fractions. Ac, acetylation; CA, reaction with cinnamoyl chloride; MA, reaction with methacryloyl chloride. Note that fraction OC F1 unmodified did not show an observable T_g. For sample names please see Table II.

Longer reaction times obviously led to consecutive reactions that slightly increased again T_g. These results indicated that acetylation significantly decreased the processability temperature of the lignin fractions.

The reaction with methacyloyl chloride (IAF F2C2-MA) resulted in crosslinked products without observable T_g, while reaction with cinnamoyl chloride (IAT F2C1-CA) moderately reduced T_g.

Synthesis of Thermotropic Polyesters

The chemical structure of the copolyesters explored as matrix for lignin was chosen considering earlier research concepts for aromatic copolyesters[35] as well as recent reports on thermotropic LCP with biobased suberic acid units into account.[36,37] It was presumed that copolyesters without aliphatic content will be more suitable to generate fibers with high carbon content and regular structure than semiaromatic copolyesters. Their chemical structure was varied systematically to reduce the melting range by the well-known concepts, for example, by introduction of nonsymmetric, m-substituted monomers.[35,42] The variation is outlined in Figure 5. The copolyesters were prepared by

(a)
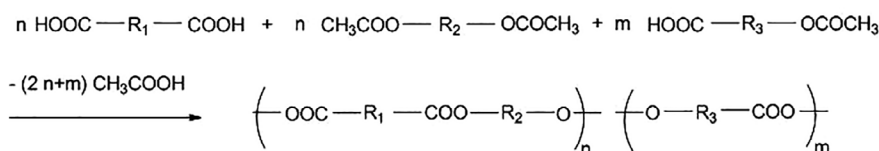
(b)
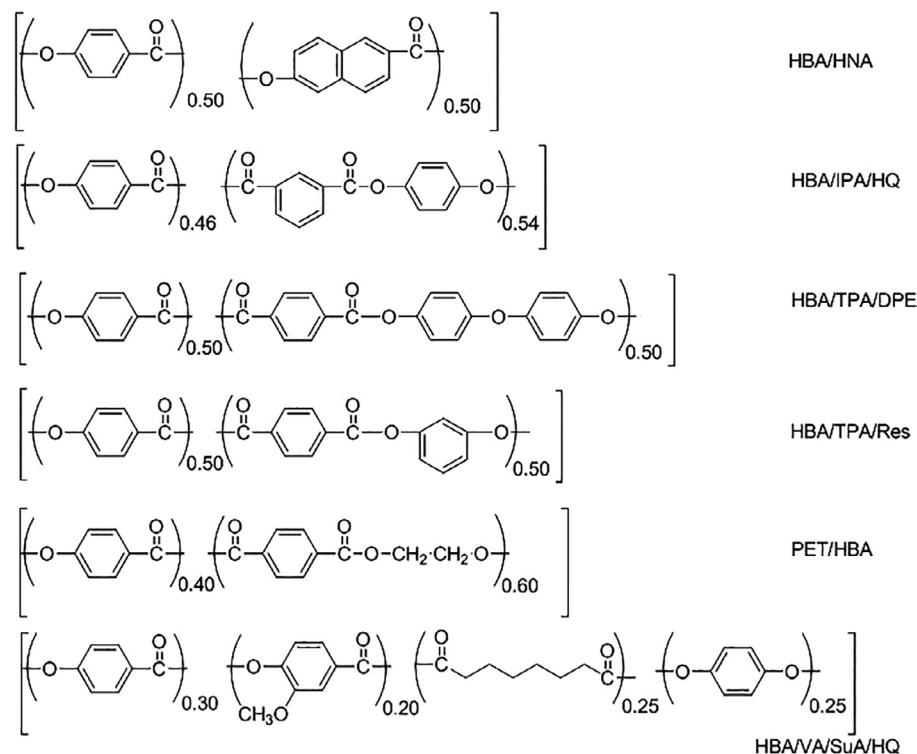
Figure 5. Copolyesters explored as polymer matrix for lignin: (a) general synthesis route; (b) chemical structures of the copolyesters synthesized and studied.

transesterification polycondensation of dicarboxylic acids with aromatic acetylated diols and acetoxycarboxylic acids as given in the general scheme also in Figure 5.

During polycondensation, acetic acid is evolved and removed from the melt by applying reduced pressure. The final reaction temperature depended on the melting range of the polyester that is influenced by the chemical structure. Fully aromatic copolyesters (HBA/HNA; HBA/IPA/HQ; HBA/TPA/RES; HBA/TPA/DPE) required a final temperature of 330 °C, while semiaromatic copolyesters were synthesized by moderate temperatures (PET/HBA: 275 °C; HBA/VA/SuA/HQ: 260 °C). The heating conditions have to be chosen thus to avoid formation of poly(hydroxybenzoic acid) homopolymer which is insoluble and not meltable without thermal decomposition below 500 °C.[38–40]

The chemical characterization of the copolyesters studied is summarized in Table III. The ^{1}H NMR spectra of five soluble copolyesters are given in Figure SI-5–SI-9. The spectra allowed determination of the molar composition of the copolyesters and supported the successful synthesis.

The relative molar masses of the copolyesters were obtained by SEC. The elution curves indicated unimolar distributed samples as expected for regular polycondensations. It can be noted that the molar masses relative to PS calibration standards were high enough to ensure that the properties will not depend anymore on the molar mass. The high dispersities Đ were caused by the long transesterification times and were expected for the reaction conditions used. Table III also outlines the thermal behavior as examined by DSC. The respective DSC curves are given in Figure SI-10. The fully aromatic copolyesters (with high carbon content) had melting ranges around 300 °C (HBA/HNA; HBA/TPA/RES; HBA/TPA/DPE) or even higher (HBA/IPA/HQ), while the semiaromatic polyesters PET/HBA and HBA/VA/SuA/HQ melt at around 200 °C and 180 °C, respectively. These values clearly indicate that the semiaromatic polyesters may be better suited for melt blending with the lignin fractions because their melting ranges match the glass transition ranges of the lignins better than in case of the fully aromatic copolyesters. However, first blending experiments were also performed with the fully aromatic ones.

Polyester/Lignin Blends

In the starting experiments, melt blending of the polyesters with nonpurified alkali lignin resulted for processing temperatures at 290 °C (aromatic polyesters HBA/HNA and HBA/IPA/HQ) and at 200 °C (PET/HBA) in thermally decomposed, dark materials.

The glass transition temperatures T_g of the purified lignin fractions (if visible in DSC) were in the temperature range of slightly above 200 °C. Acetylation resulted in the drop of T_g depending on the reaction time to the range of 150 °C (compare Table II). Melt processing of these samples appeared possible at temperatures of about 20 K above T_g, that is, at about 220 °C. At higher temperatures, thermal decomposition starts. This fact results in a rather small processing window.

Table III. Chemical Characterization of Thermotropic Copolyesters Synthesized and Studied

| Sample	Molar composition (mol%)	Conditions vacuum phase T (°C) t (h)	Solution viscosity $\eta_{inh.}$ (dL·g^{-1})	M_n [a] (g·mol^{-1})	M_w [a] (g·mol^{-1})	M_w/M_n = Đ	EA[b] C Calc. Found (wt %)	EA[b] H Calc. Found (wt %)	EA[b] O Calc. Found (wt %)	T_g [c] (°C)	T_{max} [c] (°C)
HBA/HNA	50/50	350 3	Not soluble	Not soluble	–	–	74.48 72.79	3.47 3.45	22.05 23.76	102	283
HBA/IPA/HQ	46/27/27	350 3	0.94	16 200	57 000	3.52	70.00 69.65	3.36 3.26	26.64 27.09	125	353
HBA/TPA/RES	52/24/24	330 0.50	1.36	38 700	140 000	3.61	70.00 69.16	3.36 3.14	26.64 27.70	127	237/ 300
HBA/TPA/DPE	54/23/23	330 0.50	1.29	21 400[d]	63 400[d]	2.96[d]	71.24 70.60	3.51 3.19	25.25 26.21	117	293/ 310
PET/HBA After compounding	41/59	275 6	0.58	16 300 16 200	54 300 52 400	3.33 3.23	64.77 65.90	3.94 3.74	31.29 30.36	56	205
HBA/VA/SuA/HQ	31/20/25/24	260 1.25	0.95	23 400	82 000	3.51	69.25 67.07	5.16 4.37	25.69 28.56	56	–

[a] Relative molar masses as determined by SEC.
[b] Elemental analysis.
[c] Determined by DSC, second heating.
[d] Sample dissolved and reprecipitated.
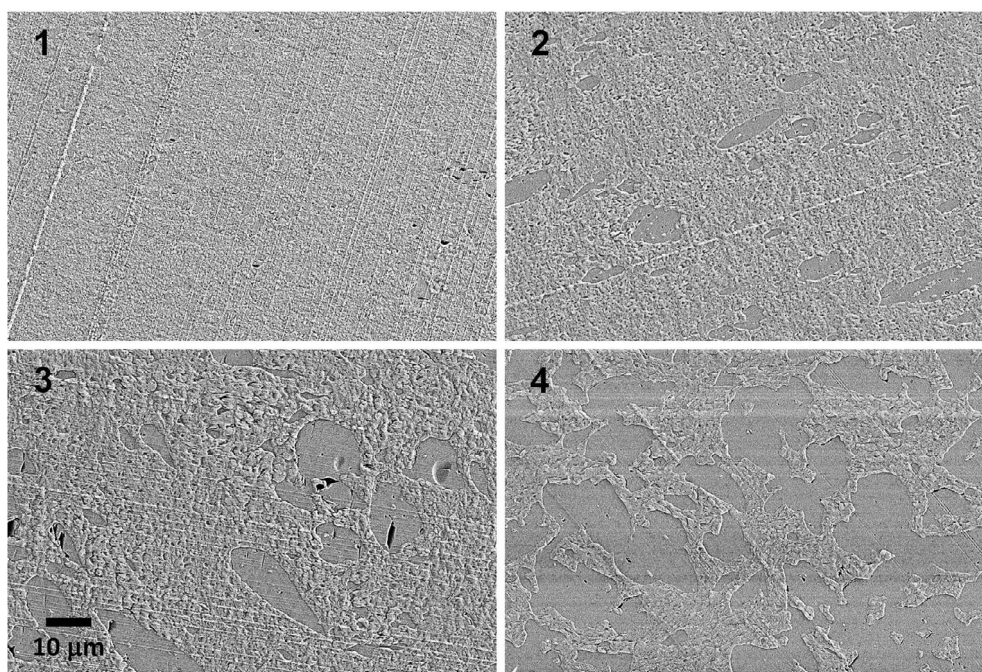
Figure 6. SEM images of cut, extruded strands of PET/HBA/lignin blends: 1: PET/HBA-IAT F2C1–5; 2: PET/HBA-IAT F2C1–10; 3: PET/HBA-IAT F2C1–20; PET/HBA-IAT F2C2–40.

The fully aromatic polyesters, that were regarded as preferred to generate carbon fibers because of their high carbon content, had very high melting ranges at around 290 °C independent of their structural variation, and also despite of the fact that older literature reported lower melting ranges.[41–43] Therefore, semiaromatic copolyesters (PET/HBA and HBA/VA/SuA/HQ) with melting ranges at about 200 °C were incorporated into the study. The DSC curves of all copolyesters examined are depicted in Figure SI-8, T_g and T_m values are summarized in Table III. Melt blending experiments were undertaken also with selected fully aromatic polyesters (HBA/HNA). Melt mixing with lignin fractions was executed at 290 °C and resulted in thermally impaired materials.

Melt extrusion of pure PET/HBA did not result in a reduction of relative molar mass (compare the molar mass values before and after extrusion in Table III). Blending experiments with different lignin fractions and PET/HBA were performed at 200 °C. From the results described in Lignin Fractionation and Chemical Modification section. it was derived that fraction IAT F2 would be the most suitable for blending experiments. Comparing blending of PET/HBA with 10 wt % IAT F1, F2 and F3 did not reveal significant differences. Therefore, all following blend experiments were undertaken with IAT F2. Blending was possible until IAT F2 concentrations of 40 wt % (see SI, Figure SI-11) yielding brownish samples. Figure 6 illustrates the morphology of these blend samples as SEM images of cross-sections of extruded strands.

The SEM images revealed clearly that lignin and the polymer formed demixed phases, that is, a heterogeneous morphology. A similar result was found before for blends of another polyester, poly(butylene succinate) with lignin.[44] Here, the lignin formed separate phases within the polymer matrix. The phase size ranged from 1 to 5 μm for 5 wt % IAT F2, 5 to 15 μm for 10 wt %, 8 to 21 μm for 20 wt %, until 9 to 36 μm for 40 wt % IAT F2 in the blend.

DSC investigations revealed that the T_gs of both, PET/HBA as well as IAT F2 were slightly shifted to each other in the blend (Figure 7), as it is typical for partial miscibility (that means, compatibilization) occurring by reactions between the blend partners in in thermodynamically demixed polymer blends.[45]

Mixtures of PET/HBA with acetylated IAT F2 showed an improved processability compared to those without acetylation (see photographic images in Figure SI-11). Blends with 40 wt % IAT-F2C2-Ac were easily achieved. The morphology of these blends appeared comparable to that of the blends with nonacetylated lignin, while the DSC curve of sample PET/HBA-IAT F2C2-Ac-40 showed indications of a completely disappeared lignin T_g (Figure 7), a strong hint of partial miscibility.

Blending of the partially biobased, semiaromatic LCP HBA/VA/SuA/HQ with 40 wt % IAT F2C2-Ac was also successful. This offers the opportunity to substitute PET/HBA by this biobased polyester in future works.
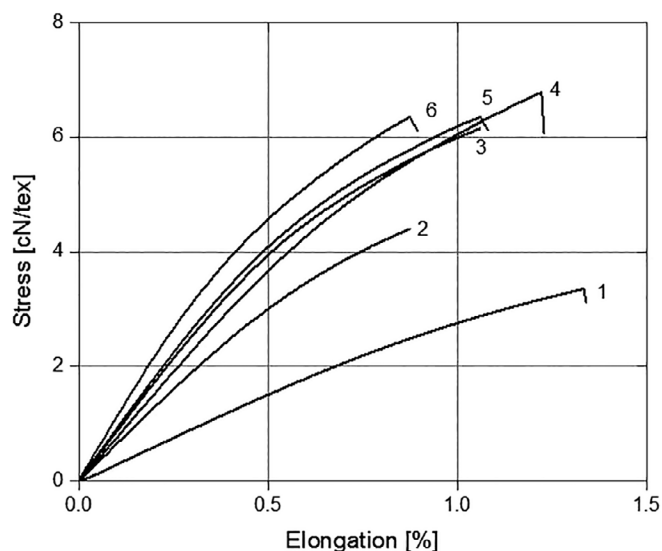
Fiber Spinning and Fiber Properties of LCP/Lignin Blends

The LCP PET/HBA, its blends with different lignin fractions as well as acetylated lignin fractions were examined with respect to the melt spinnability in a laboratory spinning equipment using a piston advance of 10 mm·min^{-1} and different winding speeds. At lower nozzle diameters high pressures were observed, but a nozzle diameter of 0.2 mm combined with winding speeds between 50 and 100 m·min^{-1} resulted in acceptable spinning pressure and formation of acceptable fibers.
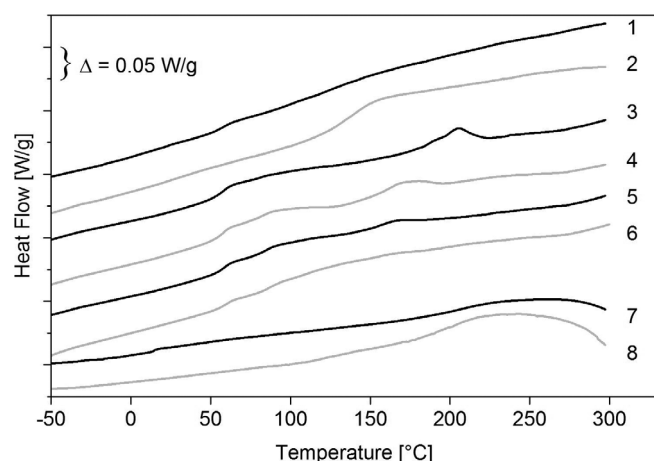
Figure 7. DSC curves (second heating cycle) of LCP/lignin blends: 1: PET/HBA-IAT F2C2-Ac-40; 2: IAT F2C1-Ac; 3: PET/HBA; 4: PET/HBA–IAT F2C1–5; 5: PET/HBA–IAT F2C1–10; 6: PET/HBA-IAT F2C2–20; 7: IAT F2C2; 8: IAT F2C1.

The pure PET/HBA was used as reference yielding fibers with an elongation at break of about 1% and a tensile strength of 7 cN/tex as shown in Figure 8. This specific characteristic of an LCP fiber caused that all fibers of LCP-lignin blends could be drawn with only small drawdown ratios. Blends with nonacetylated lignins were spinnable until lignin concentrations of 10–15 wt %. Fibers with IAT F1 showed the lowest tensile strength, which we attribute to the heterogeneity (high ash content, Table I) and incomplete melting behavior of this fraction, as discussed in 3.1 (Table II). PET/HBA-IAT F2 blends were better spinnable with increased tensile strength. Thus, PET/HBA-IAT F3-10 fibers had lower tensile strength than PET/HBA-IAT F2C1–10 fibers. Acetylation of fraction IAT F2 (IAT F2-Ac) yielded materials that were spinnable

Table IV. Relative Orientation of LCP and LCP/Lignin Blend Fibers Determined by WAXS

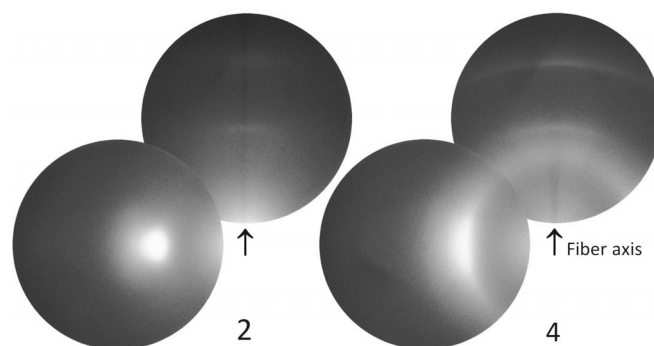| Sample	FWHM[a] (°)	O_{rel}[b]
PET/HBA (extruded)	53.4	0.703
PET/HBA (fiber)	18.4	0.898
PET/HBA-IAT F2C1-5 (fiber)	41.0	0.772
PET/HBA-IAT F2C1-10 (fiber)	45.3	0.748

[a] Full width at half maximum.
[b] $O_{rel} = (180° − FWHM)/180°$.

until lignin concentrations of about 40 wt %. The resulting fibers had tensile strengths comparable to blends with 10 wt % non-acetylated IAT F2, thus showing the significant influence of chemical modification. If the material was only extruded through the nozzle without drawing but applying shear, fibers with lower tensile strength were obtained (as expected). Additional orientation was achieved by spin drawing in the nozzle and increased the tensile strength (curve PET/HBA-IAT F2C2-Ac-40 "extruded" versus curve PET/HBA-IAT F2C2-Ac-40).

The visual appearance of the fibers is shown in the photographs in Figure SI-12.

The orientation of the melt-spun fibers was examined by WAXS. The lignin sample IAT F2 used for blending had an amorphous structure with a scattering maximum at $2\Theta \sim 21.5°$. The PET/HBA sample obtained after synthesis was a nonoriented nematic structure with scattering maximum at $2\Theta \sim 20°$. These structures are well known from literature.[46]

The relative orientation of fibers was calculated from the azimuthal distributions using the full width at half maximum (FWHM) values at $2\Theta \sim 20°$. An orientation of PET/HBA was already observed after simple extrusion (Table IV, Figure 9). This orientation was improved by melt-spinning (Figure 9, pattern [2], Table IV). PET/HBA-lignin blend fibers showed also orientation, but reduced compared to PET/HBA fibers (Figures 9 and 10, Table IV). The full width at half maximum (FWHM) depended on the lignin content and decreased with increasing content, showing that the highly branched lignin molecules disturbed the orientation of the LCP molecules. At present, it remains open

Figure 8. Stress–strain curves of PET/HBA and PET/HBA/lignin blend polyesterfibers (1: PET/HBA fiber; 2: PET/HBA-IAT F1C1–10 fiber; 3: PET/HBA-IAT F2C1-E-10 fiber; 4: PET/HBA-IAT F2C1-Ac-10 fiber; 5: PET/HBA-IAT F2C2-Ac-40 extrusion; 6: PET/HBA-IAT F2C2-Ac-40 extruded strand.

Figure 9. 2D-WAXS patterns of 2: PET/HBA fibers, and 4: PET/HBA-IAT F2C1–10 blend fibers (with 10 wt % IAT F2C1).
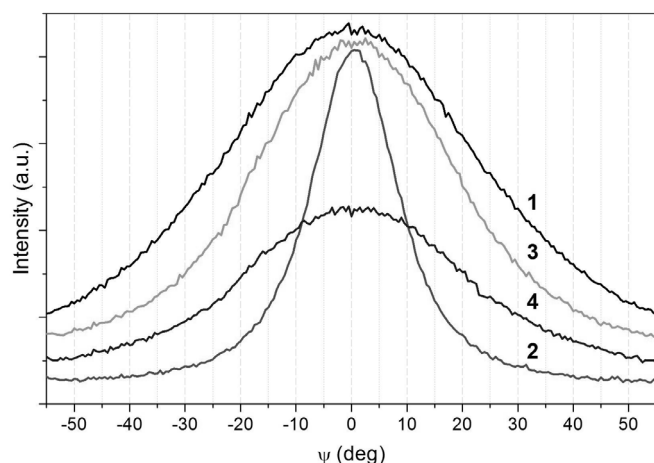
Figure 10. Azimuthal density distribution at $2\Theta = 20°$ in radial direction of 2D-WAXS patterns of: 1: PET/HBA extruded; 2: PET/HBA fibers; 3: PET/HBA/IAT F2C1–5 fibers; 4: PET/HBA/IAT F2C1–10 fibers.

whether or not the lignin molecules are incorporated into the orientation along the fiber axis.

Thermal Decomposition of the Lignin/Polyester Materials

The thermal decomposition behavior of the materials was studied by TGA under nitrogen to preevaluate the possible application as precursor for carbon fibers. All materials were examined and the complete summary of results is given in Table SI-1. The TGA mass loss and derivative curves in Figure 11 illustrate the main tendencies for the material system.

The aromatic–aliphatic LCP PET/HBA had the highest thermal stability with the main decomposition maximum at 460 °C and a second decomposition maximum at 528 °C which is assigned to post-carbonization. The lignin fraction IAT F2C2, in contrast, had the lowest thermal stability with multiple decomposition maxima. The decomposition already started below 200 °C. The main decomposition maximum occurred at 323 °C followed by two more weak maxima at higher temperature. Acetylation of the sample resulted in a shift of all maxima to higher temperature (start of decomposition at 222 °C; main maximum at 381 °C). Thus, TGA revealed the improved thermal stability of modified lignin fractions. The curves of the blends appeared as superimposition of PET/HBA and lignin fraction curves, where the main decomposition maximum of PET/HBA is shifted towards lower temperature (from 460 °C in PET/HBA to 430 °C in PET/HBA-IAT F2C1-40). It was noticed in the first derivative plots that the start of decomposition of the lignin blend partner was shifted to higher temperature.

The residue at 800 °C left after TGA was taken as first measure to evaluate the carbonization ability. The residue decreased in the order of lignin > acetylated lignin > PET/HBA-lignin blends > PET/HBA. Mixing lignin with PET/HBA did not significantly enhance the total residue of the blend. From that point of view, the aromatic–aliphatic structure (the same applies for HBA/VA/SuA/HQ) has shortcomings compared to completely aromatic structures (note the high residue yields of all aromatic polyesters in the range of 40 wt %, Table SI-1). The same
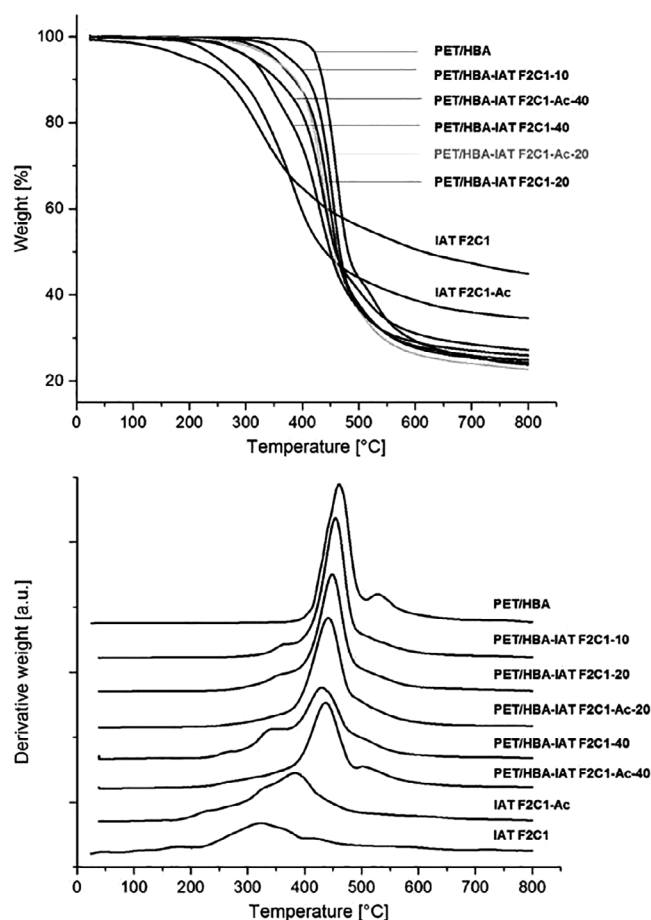
Figure 11. Thermal decomposition (TGA) of LCP; lignin fractions and PET/HBA-lignin blends.

behavior was observed for other lignin fractions. In blends with PET/HBA, the lignin appeared thermally more stable than the pure lignin samples, being a result of the melt compounding process and reactions that occurred there.

First experiments with carbonization until 1000 °C according to protocols of Kadla and coworkers[10] for carbonization of PET/lignin fibers proceeded positive and the formation of carbon with a D/G ratio of about 1.6 found with Raman spectroscopy. These results will be published separately.

CONCLUSIONS

In this study, novel precursors for carbon fibers based on lignin were developed. All steps of the preparation process have been addressed starting with synthesis and characterization of suitable polyesters (LCP), careful fractionation, modification and characterization of Kraft and Organocell lignin types, melt blending of the lignins with the polyesters, characterization of the blends, melt spinning of the blends and analysis of fiber properties. It was found that aromatic–aliphatic polyesters were the most appropriate polymer matrix for lignin blending. Lignin fractionation was found a necessary requirement to achieve completely meltable lignin samples that could be successfully melt mixed with the LCP. The resulting blends had a demixed morphology,

even though DSC revealed partial miscibility, that is, a compatibilized state. It was demonstrated that the LCP/lignin blends could be melt spun with a laboratory equipment resulting in fibers with mechanical properties typical for LCP. Acetylation of the lignin fraction enhanced the possible content of lignin in melt-spinnable blends to 40 wt % (while nonacetylated lignins were restricted to 10 wt % for spinnability). Removal of reducing sugars in the lignin gave an additional small contribution to improve spinnability.

Thus, it can be summarized that lignin purification and modification is indispensable for processability and provide a variable tool to tailor the processing properties. First carbonization experiments at 1000 °C were successful and yielded high carbon content and graphitic structures. These results will be published in a following contribution.

In summary, the novel concept of using LCP as matrix for lignin to obtain new carbon fiber precursors appears to provide potential for future work.

AUTHOR CONTRIBUTIONS

Dr. Doris Pospiech contributed to the idea of the collaboration project, collected and evaluated all data, and wrote the manuscript. Mr. Andreas Korwitz did the melt blending of fractionated lignins with the polyesters. Mrs. Kathrin Eckstein synthesized the LCP and prepared some of the figures of the manuscript. Dr. Hartmut Komber analyzed the samples by NMR spectroscopy and prepared all figures showing NMR spectra (mostly in the SI). Dr. Marcus Suckow modified the lignin fractions. Dr. Dieter Jehnichen did the WAXS measurements and their evaluation and prepared some of the figures. Dr. Albena Lederer contributed to the SEC analysis of lignin and polyester samples. Mrs. Kerstin Arnhold measured TGA and DSC curves of all samples. Mr. Michael Göbel performed 2D WAXS measurements. Dr. Martina Bremer contributed to the project idea and supervised Anton Hoffmann. Mr. Anton Hoffmann fractionated the starting lignins and analyzed the fractionated samples. Prof. Dr. Steffen Fischer contributed to the project idea, supervised Anton Hoffmann and wrote the manuscript together with Dr. Doris Pospiech. Dr. Anett Werner contributed to the project idea and performed the enzymatic treatments. Prof. Dr. Thomas Walther revised the manuscript (partially) and joined discussions. Dr.-Ing. Harald Brünig performed the melt spinning of fibers. Prof. Dr. Brigitte Voit contributed to the project idea and revised the manuscript.

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