


RESEARCH ARTICLE

Melt spinning of propylene carbonate-plasticized poly(acrylonitrile)-co-poly(methyl acrylate)

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Abstract

The primary use of poly(acrylonitrile) (PAN) fibers, commonly referred to as acrylic fibers, is in textile applications like clothing, furniture, carpets, and awnings. All commercially available PAN fibers are processed by solution spinning; however, alternative, more cost-effective processes like melt spinning are still highly desired. Here, the melt spinning of PAN-co-poly(methyl acrylate) (PMA) plasticized with propylene carbonate (PC) at 175°C is reported. The use of methyl acrylate (MA) as comonomer and PC as an external plasticizer renders the approach a combination of internal and external plasticization. Various mixtures of PAN and PC used in this work were examined by rheology, subjected to melt spinning, followed by discontinuous and continuous washing, respectively. The best fibers were derived from a PAN-co-PMA copolymer containing 8.1 mol-% of MA having a number-average molecular weight M_n of 34 000 g/mol, spun in the presence of 22.5 wt-% of PC. The resulting fibers were analyzed by scanning electron microscopy and wide-angle X-ray scattering (WAXS), and were subjected to mechanical testing.

KEYWORDS

melt spinning, PAN, plasticizer, polyacrylonitrile, textile

1 | INTRODUCTION

Poly(acrylonitrile) (PAN) fibers find application in carbon fiber (CF) production and various textile markets including indoor, outdoor, and work clothing; outdoor furniture; awnings; sails; carpets; and filtration.¹⁻⁷ All currently commercially available PAN fibers, whether for textile or CF purposes, are processed by solution spinning methods including dry-, wet-, or air-gap spinning utilizing *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethylsulfoxide or aqueous NaSCN solutions as solvent.⁸ Solution spinning is inherently more expensive than the cost-effective melt spinning. Since textile grade PAN fibers compete with cheaper melt-spun fibers, for example, polyesters, melt spinning is highly desired for PAN as well.⁹

Unfortunately, the melt spinning of PAN is impeded by the high melting point, T_m , of PAN at approximately 320°C,¹⁰ which is above the onset temperature of degradation, $T_{degr.}$, of around 200°C.¹¹ Since $T_{degr.}$ cannot be shifted to significantly higher temperatures, it is necessary to lower the T_m of PAN to allow melt spinning. This can either be achieved by external plasticization, that is, by the addition of solvents or oligomers, or by internal plasticization, that is, by copolymerization.

Examples for external plasticizers include DMF, DMAc, γ -butyrolactone,¹² propylene carbonate (PC),¹³ CO₂,¹⁴ water,¹⁵⁻¹⁷ acrylonitrile, mixtures of these solvents,¹⁶ ionic liquids,^{18,19} and acrylonitrile/acrylate-based oligomers.²⁰

Examples for internal plasticizers include common comonomers for PAN like methyl acrylate (MA)^{17,21-25} and vinyl acetate.²⁶ Melt-spun

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PAN-co-poly(methyl acrylate) (PMA) fibers containing ca. 10 mol-% of MA²⁷ with low-weight average molecular weights, M_w , of 40 000 to 60 000 g/mol²⁸ have been commercialized by BP as Amlon. Possibly due to yellowing of the fibers during high-temperature processing at around 210°C to 220°C, Amlon was discontinued after a few years.

Here, we present a combined approach consisting of both, internal and external plasticization, using MA as comonomer and PC as softener. It is characterized by spinning temperatures well below 200°C, obviation of a pressurized spinning plant, and a straightforward removal of PC by washing with water. MA was chosen as comonomer because of its very similar copolymerization parameters to acrylonitrile ($r_{AN} = 0.7-1.0$, $r_{MA} = 0.7-1.5$),^{25,29,30} offering access to statistical copolymers. PC was chosen because it is nontoxic and considered a green solvent.^{31,32} Furthermore, PC is a good solvent for PAN at elevated temperatures, but a bad solvent for PAN at room temperature, which facilitates the prehomogenization of PAN and PC at room temperature, that is, in a kneader, forming a nonsticky solvent-PAN mixture.

2 | EXPERIMENTAL

2.1 | Chemicals

Acrylonitrile, MA, and sodium persulfate were purchased from abcr GmbH, Germany. Sodium metabisulfite, PC, iron (III) sulfate, and aluminum sulfate hydrate were purchased from Alfa Aesar, Germany. Sulfuric acid was purchased by Acros Organics, Germany. All chemicals were used as received.

2.2 | Characterization

NMR spectra were measured on a Bruker Ultrashield 400 Plus at 303 K. (¹H-NMR: 400 MHz, ¹³C-NMR: 101 MHz; ext. standard: tetramethylsilane). Spectra were analyzed using the MestReNova v.6.0.2-5475 program, Mestrelab Research. Differential scanning calorimetry (DSC) measurements were carried out under air on a TA Instruments Q2000 Differential Scanning Calorimeter with a heating rate of 10 K/min. Rheology was measured on a Physica MCR 501 using a heating element manufactured by Anton Paar, Austria under nitrogen. Rheology samples were prehomogenized according to section 2.5. Measurements were carried out using parallel plates in a distance of 1 mm. For mechanical testing of the fibers, 20 single filament measurements of each sample were conducted on a Favimat, Textechno, Germany. The clamping length was 25 mm, the test speed was 20 mm/min. SEM micrographs were taken on a Zeiss Auriga scanning electron microscope using a Quorum Technologies sputter with a Pt/Pd target. Samples were sputtered with Pt/Pd, 5 nm in thickness. The micrographs were taken at acceleration voltages of 3 kV and working distances between 6 and 8 mm in the secondary electron mode (Everhardt-Thornley detector). X-ray scattering was measured on a D/MAX Rapid II manufactured by Rigaku, using 40 kV and 30 mA Cu-

K_α-Irradiation ($\lambda = 0.15406$ nm). A shine monochromator and an image plate detector were used. The scanning rate was 0.2° min⁻¹; the scanning step was 0.1°. All fibers were aligned in a fiber sample holder. The crystallinity was calculated on the basis of the following formula:

$$I_c = \frac{\sum I_c}{\sum (I_c + I_a)}, \quad (1)$$

where I_c is the intensity of the crystalline reflections and I_a is the intensity of the amorphous reflections. For integration of the peak areas, the method developed by Gupta and Singhal was used.³³ The preferred orientation (P. O.) of the crystallites of PAN was calculated according to:

$$\text{P.O.} = \frac{180^\circ - B}{180^\circ}, \quad (2)$$

where B is the full width at half maximum of the (100) reflection of the hexagonal lattice of PAN.³³ Size exclusion chromatography measurements were performed on a 1260 Infinity device from Agilent Technologies equipped with a Multi-Detector-Suite viscosimetry and refractive index detector. A 50 mm precolumn and a 300 mm mixed B column (Agilent Technologies) were used as stationary phase, DMAc containing 5 g/L LiBr was used as mobile phase. The column temperature was set to 50°C, the flow rate was 0.75 L/min, and the sample concentration was 2 mg/mL. Chromatograms were interpreted using conventional calibration against poly(methyl methacrylate) polymer standards.

2.3 | Precipitation Copolymerizations

Precipitation polymerizations were carried out in a 5 L glass reactor connected to a thermostat under argon atmosphere at 56°C in aqueous, acidic medium (0.03 M molar sulfuric acid solution). The initiator system consisted of sodium persulfate, sodium metabisulfite, and catalytic amounts of iron (III) sulfate and aluminum sulfate hydrate. 1/20 of the total monomer amount was initially placed in the reactor together with 760 mL of a 0.03 M sulfuric acid solution, the rest of the monomers and the aqueous initiator solution was added dropwise over a period of 5 hours using peristaltic pumps from KNF Simdos. Thereafter, the reaction mixture was stirred for 1 hour. The copolymer was filtered off and washed twice with demineralized water, then twice with methanol. Finally, the PAN-co-PMA was placed in a heating oven overnight at 80°C to evaporate all volatiles. Isolated yields ranged from 950 to 1100 g of PAN-co-PMA corresponding to 80 - 95% of the theoretical amount.

2.4 | Drying of PAN-co-PMA

PAN-co-PMA was dried over a period of 1 to 2 days either at 70°C in a Heraeus vacutherm VT 6130 M vacuum oven connected to a vacubrand rz-16 vacuum pump, or in a Christ Alpha 2-4 LSC freeze dryer connected to a vacubrand rz-16 vacuum pump. The residual water content was determined by Karl Fischer titration, which was performed on an 899 Coulometer and an 885 Compact Oven SC manufactured by Methrom AG at 140°C. The resulting water content was <0.1 wt.-%.

2.5 | Prehomogenization

Prehomogenization was achieved by mixing the dried PAN-co-PMA having a water content <0.1% with anhydrous PC either in a Mortar or in a Werner & Pfleiderer batch kneader under nitrogen. Due to the poor solubility of PAN in PC at room temperature, a uniform, doughy mixture was obtained (Figure S1).

2.6 | Melt spinning

Fibers were melt-extruded using a Haake MiniLab II twin-screw extruder with a capacity of ca. 7 mL. A monofilament spinning nozzle with a diameter of 0.5 mm was used. The fibers were wound on a winder with a maximum speed of 600 m/min by Georg Sahn GmbH.

2.7 | Removal of the Plasticizer

Removal of the PC was achieved discontinuously by winding the fibers around a glass vial and then putting them in stirred demineralized water at 90°C for 5 minutes. For the continuous washing trial, a wet-spinning line manufactured by Dienes GmbH consisting of two drawing baths filled with demineralized water at a temperature of 95°C to 98°C and two washing baths filled with demineralized water at ~75°C and 25°C was used. The processing master speed was 5 m/min. In the first drawing bath, the fibers were stretched by 60%.

3 | RESULTS AND DISCUSSION

3.1 | Synthesized PAN-co-PMA copolymers

To identify a PAN-co-PMA copolymer suited for melt spinning, we synthesized a variety of copolymers (Table 1). Since particularly the comonomer content and the molecular weight of a copolymer influences its melt spinnability, the amount of MA was varied between 6.4 and 13.3 mol-%, a promising range in view of previous work on PAN-melt-spinning,^{15,16,20,34-36} while the number-average molecular

weight (M_n) was varied between 19 000 and 47 000 g/mol, typical for melt-spun polymers like polyamides and polyesters.^{37,38} The polydispersity index \bar{D} ranged from 2.1 to 4.0. The glass transition temperature (T_g), the melting point (T_m) and the onset of the degradation reactions (T_{deg}) ranged from 98°C to 105°C, 225°C to 263°C and 277°C to 297°C, respectively. An exemplary DSC measurement is shown in Figure S2. After synthesis and the evaporation of methanol used for washing, the PAN copolymers had a residual water content of 0.6 to 1.2 wt.-%. For rheology studies and melt spinning trials, they were further dried using either freeze-drying or drying in a vacuum oven at 70°C. The target water content was less than 0.1 wt.-%, which was achieved after 48 hours with both methods (Figure S3).

3.2 | Rheology of different PAN copolymers

Mixtures of PC and the different PAN copolymers were examined for their melt spinnability by oscillatory rheology measurements. First, the linear viscoelastic (LVE) region was determined by measuring an amplitude sweep, in which the amplitude of the deformation (γ) was varied while keeping the temperature (T) and angular frequency (ω) constant. Figure 1 illustrates the amplitude sweep of PAN5 mixed with 22.5 wt.-% PC, which was the mixture that ultimately led to the PAN fibers with the highest tensile strength.

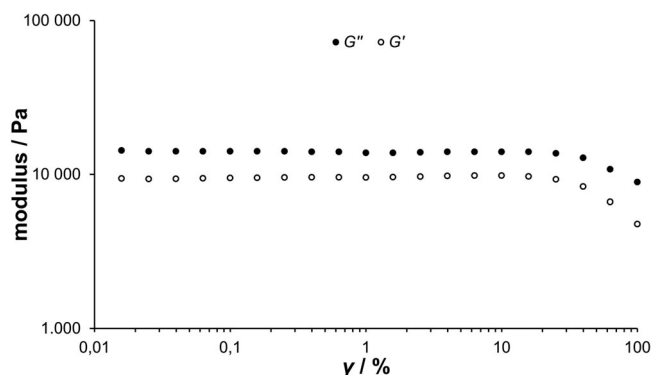


FIGURE 1 Amplitude sweep of PAN5 (8.1 mol-% MA, $M_n = 34\ 000$ g/mol, $\bar{D} = 4.0$) mixed with 22.5 wt.-% PC at $T = 175^\circ\text{C}$, $\omega = 10$ rad/s

TABLE 1 Comonomer content, molecular weights, polydispersity indices \bar{D} and glass transition temperatures (T_g), melting points (T_m), and onset temperatures of degradation (T_{deg}) of various synthesized PAN-co-PMA copolymers

PAN	MA/mol-%	M_n /g/mol	M_w /g/mol	\bar{D}	$T_g; T_m; T_{deg}/^\circ\text{C}$
PAN1	6.4	30 000	115 000	3.9	104; 263; 277
PAN2	7.8	31 000	102 000	3.3	100; 242; 286
PAN3	8.1	19 000	59 000	3.1	105; 230; 282
PAN4	8.1	32 000	106 000	3.3	102; 228; 288
PAN5	8.1	34 000	135 000	4.0	99; 235; 285
PAN6	8.1	46 000	178 000	3.9	103; 230; 291
PAN7	9.8	20 000	51 000	2.5	101; 231; 284
PAN8	9.8	34 000	90 000	2.7	101; 227; 290
PAN9	13.3	23 000	48 000	2.1	100; 229; 289
PAN10	13.3	47 000	114 000	2.4	98; 225; 297

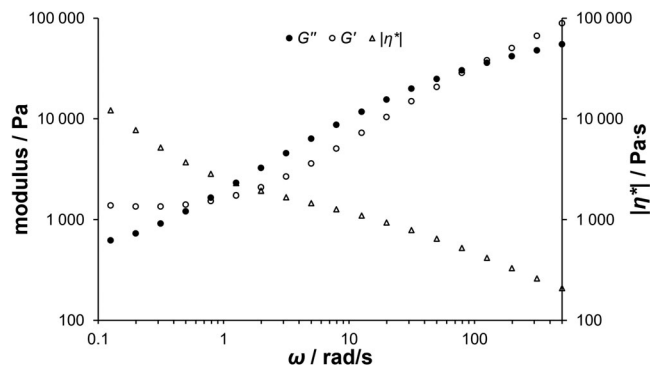


FIGURE 2 Frequency sweep of PAN5 (8.1 mol-% MA, $M_n = 34\,000$ g/mol, $D = 4.0$) mixed with 22.5 wt.-% PC at $T = 175^\circ\text{C}$ and $\gamma = 0.5\%$

The LVE region for this mixture at 175°C ranged from $\gamma = 0.015\%$ to 15.8%. For the following rheological measurements, γ was consequently set to 0.5%, which was well in the LVE region for all tested PAN/PC mixtures. The loss factor ($\tan \delta$), which is the quotient of the loss modulus G'' over the storage modulus G'

$$\tan \delta = \frac{G''}{G'} \quad (3)$$

was larger than 1, verifying viscoelastic fluid properties at $T = 175^\circ\text{C}$ and $\omega = 10$ rad/s (Figure 2), which is a prerequisite for melt spinning. Also, shear thinning was observed (Figure 2), which is again a prerequisite for fiber spinning. Notably, at low ω -values, $\tan \delta$ was less than 1, indicating that the mixture behaved like a gel at low shear rates. This is not an issue for melt spinning, as shear in an extruder is generally high.

A cross-over, defined as $\tan \delta = 1$, was observed at $\omega \approx 0.75$ rad/s; above this value $\tan \delta$ remained larger than 1 up to $\omega \approx 99$ rad/s. The second crossover observed at $\omega \approx 99$ rad/s indicates that the PAN/PC mixture loses its spinnability above a certain shear stress at the spinneret. This second crossover at high shear stress seems to be typical for plasticized PANs.¹⁸

Based on the amplitude and frequency sweep shown in Figure 1 and Figure 2, a temperature sweep from 150°C to 190°C was conducted in order to find a suited processing window for a given PAN/PC mixture. For this temperature sweep, γ was set to 0.5% to stay within the LVE region while ω was set to 10 rad/s, since the PAN/PC mixture shown in Figure 2 had the highest $\tan \delta$ at this ω -value. In order to be suitable for melt spinning, the $\tan \delta$ must be >1 , and the complex viscosity $|\eta^*|$ should be in the range of 200 to 1500 Pa s.³⁹

Figure 3 illustrates the temperature sweep for PAN4 containing 8.1 mol-% MA (M_n of 34 000 g/mol, D of 4.0), mixed with 22.5 wt.-% PC. Above 157°C , $\tan \delta$ was larger than 1. $|\eta^*|$ was less than 1500 Pa s above 172°C . Consequently, the mixture was melt-spinnable in a processing window between 172°C and 190°C .

Applying the same temperature sweep for all synthesized PAN-co-PMA copolymers containing different amounts of PC allowed for

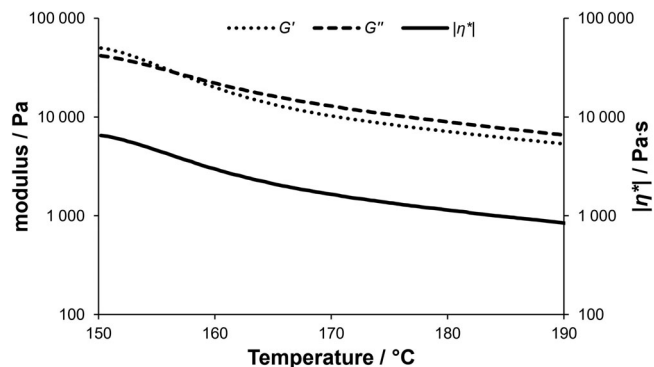


FIGURE 3 Temperature sweep between 150°C and 190°C for PAN5 (8.1 mol-% MA, $M_n = 34\,000$ g/mol, $D = 4.0$) mixed with 22.5 wt.-% PC. $\gamma = 0.5\%$, $\omega = 10$ rad/s, heating rate = 1 K/min

identifying a set of melt-spinnable PAN/PC mixtures for which $\tan \delta$ was >1 and $|\eta^*|$ was in a range of 200 to 1500 Pa s (Figures S4–S12).

In general, the target spinning temperature was 175°C to minimize the coloration of the fibers. Table 2 lists the highest $\tan \delta$ values achieved at 175°C for all synthesized PAN-co-PMA copolymers mixed with PC. Copolymers containing less than 8.1 mol-% MA were not melt-spinnable; the same was true for copolymers with 8.1 mol-% MA but comparably high number-average molecular weights ($M_n = 46\,000$ g/mol $D = 3.9$). For melt spinning, it is of utmost importance that the PAN/PC mixtures do not degrade for at least 20 minutes, which is the approximate residence time of the PAN/PC mixture inside the extruder. This can be verified by measuring a time sweep, in which the viscosity $|\eta^*|$ should stay below 1500 Pa s, and $\tan \delta$ should stay above 1 for said 20 minutes. A time sweep over 45 minutes at 180°C of PAN4 mixed with 22.5 wt.-% PC is shown in Figure S29, where $|\eta^*|$ increases from 850 to 1500 Pa s over 44 minutes, with $\tan \delta$ being larger than 1 throughout the entire measurement. Spinning temperatures of up to 180°C are therefore easily feasible.

3.3 | Spinning of PAN-co-PMA/PC mixtures, removal of the plasticizer

In order to demonstrate the spinnability of the PAN-co-PMA/PC mixtures with suitable rheological properties, monofilament spinning trials were performed. The goal was to identify a mixture that yields fibers with adequate mechanical properties at high winding speeds. Furthermore, the external plasticizer PC had to be removed within reasonable time, that is, within 5 minutes.

Table S1 summarizes the mechanical properties of the best fibers for each PAN-co-PMA/PC mixture with the plasticizer still incorporated. The corresponding tensile strength-elongation diagrams are shown in Figures S13 to S19. The best fibers were derived from PAN5 containing 8.1 mol-% MA ($M_n = 34\,000$ g/mol, $D = 4.0$) mixed with 22.5 wt.-% PC and had a tensile strength of 24.0 ± 2.0 cN/tex (280 ± 20 MPa) and a Young's modulus of 670 ± 100 cN/tex (7.9 ± 1.2 GPa). The highest winding speed, 600 m/min, was also

TABLE 2 Summary of the processing windows, $\tan \delta$, and $|\eta^*|$ at 175°C for mixtures of the synthesized PAN-co-PMA with PC

PAN	MA/mol-%	M_n /g/mol	\bar{D}	PC/wt.-%	Processing window/°C	$\tan \delta$ at 175°C	$ \eta^* $ at 175°C/Pa s
PAN1	6.4	30 000	3.9	50	-	0.5	220
PAN2	7.8	31 000	3.3	30	-	0.9	720
PAN3	8.1	19 000	3.1	20	178-190	0.9	1690
PAN4	8.1	32 000	3.3	22.5	162-190	1.2	1030
PAN5	8.1	34 000	4.0	22.5	172-190	1.3	1350
PAN6	8.1	46 000	3.9	30	-	0.9	5400
PAN7	9.8	20 000	2.5	10	165-190	1.5	870
PAN8	9.8	34 000	2.7	20	169-190	2.0	1140
PAN9	13.3	23 000	2.1	10	150-190	3.9	230
PAN10	13.3	47 000	2.4	30	166-190	2.1	1030

Note: For every PAN sample, only the PAN/PC mixtures that led to the highest $\tan \delta$ -value are shown.

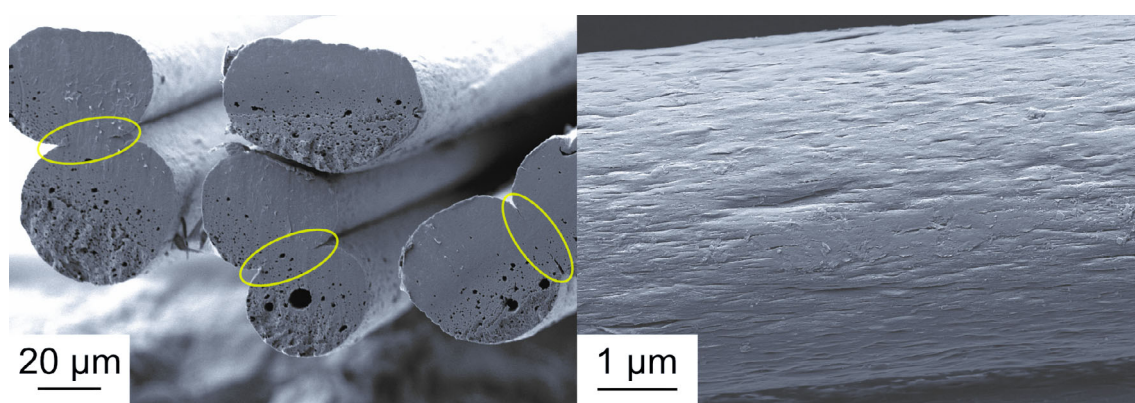


FIGURE 4 Cross section and surface SEM micrographs of PAN9 fibers (13.3 mol-% MA, $M_n = 23\,000$ g/mol, $\bar{D} = 2.1$) plasticized with 10 wt.-% PC during spinning applying a winding speed of 200 m/min and washed at 80°C for 10 minutes. The yellow ellipses highlight the filament fusing of the fibers [Colour figure can be viewed at wileyonlinelibrary.com]

achieved with this mixture, which was the upper winding speed limit of the employed winder. Overall, the mechanical properties were surprisingly good with the PC still incorporated. Nevertheless, for textile applications, the PC needs to be washed out, as it can cause skin irritation. In view of the good solubility of PC in water, washing was accomplished with demineralized water. The best-suited washing temperature was identified by determining the PC content in a PAN/PC-fiber (PAN: 13.3 mol-% MA, $M_n = 47\,000$ g/mol, $\bar{D} = 2.4$; 30 wt.-% PC) over time at 70°C, 80°C and 90°C, respectively, via $^1\text{H-NMR}$ (Figure S20). As expected, the PC was washed out significantly faster at 90°C than at lower temperatures; after 5 minutes at 90°C, the PC content in the copolymer determined by NMR was below 0.3 wt.-%. (Figure S21).

Unfortunately, the fibers of PAN-co-PMA/PC mixtures containing PAN with 13.3 mol-% of MA fused together during washing at temperatures $\geq 80^\circ\text{C}$ (Figure 4). Furthermore, some cavities were present in the cross section of these fibers. Filament fusing was no issue with the fibers prepared from PAN-co-PMA having lower MA content; however, fibers derived from PAN3 containing 8.1 mol-% of MA and the lowest molecular weight ($M_n = 19\,000$ g/mol, $\bar{D} = 3.1$) were also

not washable. Due to their brittleness, they could not be unwound from the bobbin.

The mechanical properties of the discontinuously washed PAN-fibers are shown in Table 3. The corresponding force-elongation diagrams are shown in Figures S22 to S25. Plasticizer-free PAN5 fibers containing 8.1 mol-% of MA ($M_n = 34\,000$ g/mol, $\bar{D} = 4.0$) displayed the best tensile strengths and Young's moduli up to 31.2 ± 2.7 cN/tex (370 ± 30 MPa) and 770 ± 40 cN/tex (9.1 ± 0.5 GPa), respectively. The PAN4 fibers ($M_n = 32\,000$ g/mol, $\bar{D} = 3.2$) had only slightly lower tensile strength and Young's modulus than the fibers prepared from PAN5, the mechanical properties of both PAN4 and PAN5 fibers were in the range of typical commercial textile PAN-fibers. Compared to the unwashed PAN-co-PMA fibers (Table S1), the washed PAN-fibers in Table 3 had better tensile strength and a smaller diameter.

SEM images of the cross section of washed PAN4 fibers (Figure 5) revealed a porous structure. Nevertheless, the mechanical properties of these fibers were already comparable to those of commercial textile PAN. We assume that these pores stem from the discontinuous washing process at a fixed fiber length. Washing of a fiber containing a polymer-plasticizer mixture in water is driven by the

TABLE 3 Mechanical properties of selected PAN fibers after PC removal

PAN	Winding speed/m/min	Fineness/dtex	Elongation/%	Tensile strength/cN/tex	Tensile strength/MPa	Young's modulus/cN/tex	Young's modulus/GPa
PAN3	250	Not determinable (n. d.), fiber to brittle for unwinding from the bobbin					
PAN4	200	2.3 ± 0.4	13.8 ± 1.2	28.0 ± 1.6	330 ± 20	680 ± 30	8.0 ± 0.4
PAN5	600	2.3 ± 0.4	12.1 ± 0.7	31.2 ± 2.7	370 ± 30	770 ± 40	9.1 ± 0.5
PAN7	250	6.5 ± 3.6	13.8 ± 2.5	13.1 ± 1.2	150 ± 15	490 ± 50	5.8 ± 0.6
PAN8	250	4.5 ± 1.1	19.2 ± 1.8	18.9 ± 2.1	220 ± 25	550 ± 30	6.5 ± 0.4
PAN9	200	n. d., fibers disintegrated during washing at 90°C					
PAN10	600	n. d., fibers disintegrated during washing at 90°C					

Note: The PC was removed with demineralized water at 90°C for 5 minutes. Fibers were wound around a glass vial multiple times in order to maintain constant length during washing.

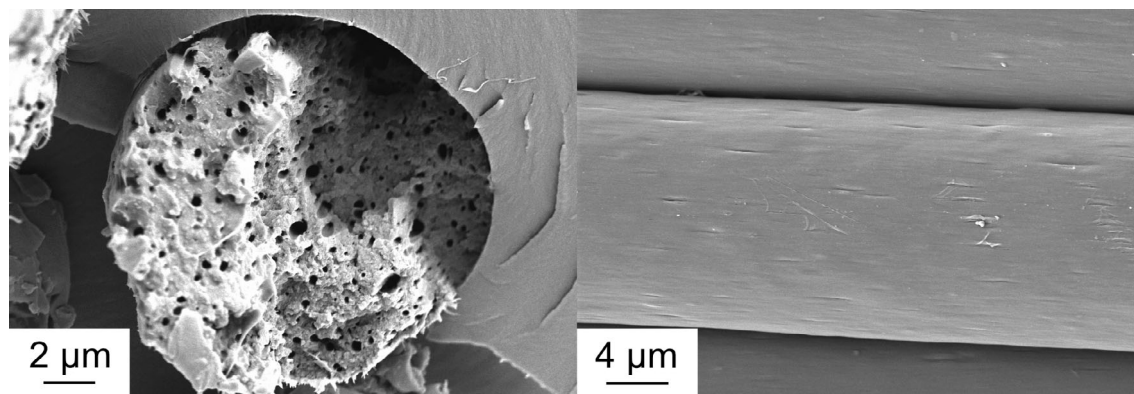


FIGURE 5 Cross section and surface SEM micrographs of PAN4-fibers (8.1 mol-% MA, $M_n = 32\,000$ g/mol, $D = 3.3$) plasticized with 22.5 wt-% PC, spun at a winding speed of 150 m/min, after washing at 90°C for 5 minutes. For the cross section image, the fibers were embedded in an epoxide matrix, which was then broken in order to see cavities and pores

diffusion of water into the fiber, and diffusion of the plasticizer into the water and out of the fiber. During discontinuous washing at a fixed length, the washed-out plasticizer might leave cavities and pores behind, simply due to the low mobility of the polymer chains. In continuous washing, the fibers are usually stretched. The diffusion process is therefore different since cavities and pores are squeezed out. To verify this, we conducted a continuous washing trial of the melt-spun PAN4/PC fibers on a wet spinning line.

The washing conditions had no significant effect on the mechanical properties of the fibers. The tensile strength of the continuous washed PAN4 fibers was 25 ± 2 cN/tex, which is within the SD of the discontinuously washed fibers. Its Young's modulus was 760 ± 30 cN/tex, which is only slightly higher than that of the discontinuously washed fibers (see Table 3). However, the washing conditions had in fact an influence on the porosity of the fibers. Figure 6 shows a SEM image of the cross section and the surface of continuously washed PAN4-fibers, which were stretched by 60% during washing. In contrast to the fibers prepared by discontinuous washing (Figure 5), the cross section of these fibers was virtually defect-free without pores and cavities. This can also be seen in Figure S26, where light microscope images of the cross-sections of the continuously washed fibers are shown.

3.4 | Wide-angle X-ray scattering analysis

As discussed above, the plasticized fibers already had surprisingly good mechanical properties, especially a high Young's modulus, which typically indicates crystallization. According to Bashir et al PAN and PC can cocrystallize in an orthorhombic polymorph.⁴⁰ The same group showed that upon removal of the PC, the typical hexagonal modification of PAN is reobtained. Furthermore, Atureliya et al showed, that PAN can crystallize in its hexagonal modification from the orthorhombic polymorph in 50:50 PAN/PC-fibers upon drawing the fibers.¹³

In Figure 7, the X-ray diffractograms obtained by wide-angle X-ray scattering (WAXS) of PAN4-fibers (8.1 mol-% MA) with 22.5 wt-% PC incorporated are compared to the same fibers after continuous washing. The corresponding WAXS diffraction images are shown in Figures S27 and S28. After removal of the PC, the typical diffractogram of PANs hexagonal lattice with its characteristic reflection at $2\theta = 17^\circ$ (100) and the weaker reflection at $2\theta = 30^\circ$ (110) was obtained in accordance to Bashir's findings.⁴¹ The crystallinity of this PAN-fiber was 54%, the P. O. of the crystallites was 94%.

The PAN/PC fiber also showed the (100) reflection, though slightly shifted to $2\theta = 17.2^\circ$, which points toward smaller crystallites. The (110) reflection at $2\theta = 30^\circ$ was less pronounced. There was also

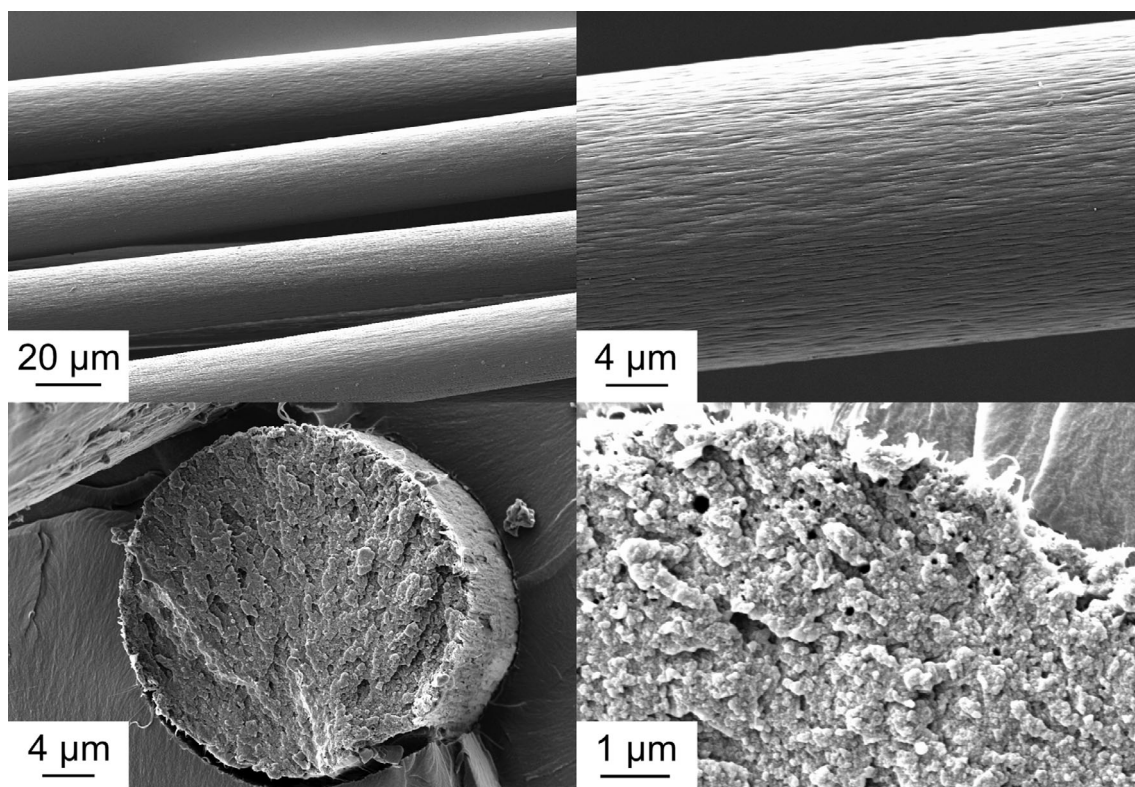


FIGURE 6 Cross section and surface SEM micrographs of PAN4-fibers (8.1 mol-% MA, $M_n = 32\,000$ g/mol, $\bar{D} = 3.2$) plasticized with PC after continuous washing and stretching by 60%. Fibers were embedded in an epoxide matrix, which was then broken

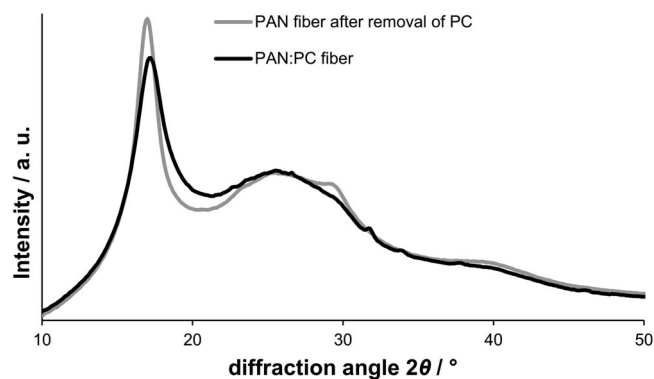


FIGURE 7 X-ray diffractograms of PAN4-fibers (8.1 mol-% MA) spun with 22.5 wt.-% PC. The black diffractogram represents fibers with the plasticizer still incorporated. The gray diffractogram represents fibers where the plasticizer has been removed continuously with demineralized water

a minor second crystalline phase present with a prominent reflection at 31.6° , which is probably addressable to residual sodium metabisulfite. The absence of the additional reflections of PAN/PC cocrystallization reported by Atureliya and Bashir^{13,40–42} suggests that the PAN4 crystallizes directly from the as-spun fiber. For the PAN/PC fibers reported by Atureliya et al, PAN crystallization only happened upon extensive fiber drawing,¹³ which suggests that the as-spun PAN4/PC-fibers are already highly oriented. In conclusion, the good

mechanical properties of PAN/PC fibers (Table S1) stem from the crystallization of PAN from the PAN/PC mixture.

4 | CONCLUSIONS

In summary, a melt spinning process for plasticized PAN-co-PMA with winding speeds of up to 600 m/min has been established using PC as a cheap, nontoxic, green plasticizer, and MA as comonomer. The plasticizer can easily be removed by washing in water. Rheological measurements imply that at least 8.1 mol-% of MA are necessary for melt spinning, whereas the upper limit of MA-content is below 13.3 mol-%, since fibers with 13.3 mol-% disintegrated during plasticizer removal. A lower comonomer content leads to better PAN-fibers; the best fibers produced were derived from PAN-co-PMA (8.1 mol-% of MA, $M_n = 34\,000$ g/mol, $\bar{D} = 4.0$) spun with 22.5 wt.-% of PC. After removal of the plasticizer, they had a tensile strength of 31.2 ± 2.7 cN/tex (370 ± 30 MPa), a Young's modulus of 770 ± 40 cN/tex (9.1 ± 0.5 GPa), a fineness of 2.3 ± 0.4 dtex (15.7 ± 1.4 μm) and an elongation at break of $12.1\% \pm 0.7\%$, which is adequate for textile applications. Higher molecular weight led to higher tensile strength and Young's modulus, but there is an upper technical limit in that for PAN-co-PMA with 8.1 mol-% MA, $M_n = 46\,000$ g/mol and $\bar{D} = 3.9$, no melt-spinnable PAN/PC mixture could be found. Removal of the plasticizer can be achieved by discontinuous or continuous washing, both methods lead to fibers with comparable mechanical properties.

However, discontinuous washing leads to a porous structure, whereas continuous washing leads to a compact fiber. Moreover, WAXS analysis of the fibers with 8.1 mol-% MA showed that PAN crystallizes from the as-spun PAN/PC fibers. After continuous washing, the fibers had a crystallinity of 54%, the P.O. of the crystallites was 94%.

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CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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