Continuous plasticized melt-extrusion of polyacrylonitrile homopolymer

Sudith Kanishke Atureliya and Zahir Bashir*
Courtaulds Research, 72 Lockhurst Lane, Coventry CV6 5RS, UK
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In this work, it is shown that polyacrylonitrile (PAN) powder which had been plasticized by propylene carbonate (PC) could be 'melted' and extruded continuously into filaments. The 'molten' extrudate solidified on-line as a result of cooling, without the need for coagulation. In this respect, PAN–PC solutions behaved differently when compared with other solutions commonly used in the wet-spinning of PAN fibres. Spontaneous solidification on cooling meant that the filament could be wound-up on a take-up system without the need to pass it through a coagulation bath. The solidification occurred as a result of the rapid crystallization of the PAN from the propylene carbonate solution. The X-ray diffraction pattern of the solidified filament (which contained 40–50 wt% of solvent) was different from that of the dry PAN powder, indicating that a different polymorph had been formed. Drawing of the filaments, however, led to the normal hexagonal polymorph. A PAN:PC (50:50 by wt) 'melt' had a shear viscosity comparable with that of a conventional thermoplastic such as extrusion-grade polyethylene. The plasticized melt showed shear-thinning behaviour.

(Keywords: polyacrylonitrile; propylene carbonate; plasticized melt-extrusion; rheology; shear thinning; X-ray diffraction)

INTRODUCTION

As polyacrylonitrile, $-[CH_2-CH(CN)]_n-$, cannot be melt spun, fibres are usually wet spun. Thus a typical industrial spinning process involves extruding a 10–30 wt% PAN solution (in solvents such as $ZnCl_2$ (aq) or dimethyl sulfoxide) into a coagulation bath[1]. The regenerated fibres are then washed, heat-stretched and finally dried. PAN-based fibres find applications in textiles and as carbon-fibre precursors. The homopolymer, however, is rarely used and one or two comonomers are usually present in small quantities in most commercially produced fibres[1,2]. The comonomers are added as dye sites (in textiles) or as exotherm moderators (in carbon-fibre precursors)[2]. For the purposes of this study, we have used the homopolymer as it crystallizes better than the copolymer and hence the underlying principles of this work can be more clearly understood.

A recent patent application reports the processing of PAN by using a 'crystallizing solvent'[3], i.e. a solvent from which the polymer crystallizes at some temperature, preferably ambient. It should be noted that 'crystallizing solvent' used in this context is not meant to refer to the solvent's ability to crystallize. This definition would exclude many of the solvents for this polymer, such as pure dimethylsulfoxide (DMSO) and pure dimethylformamide (DMF). The polymer is soluble in these liquids at room temperature.

While certain polymers such as polyethylene crystallize from all known solvents of the polymer, there appear to be very few reported cases of PAN crystallizing from a single-component organic solvent. A well documented example, however, is the crystallization of PAN from propylene carbonate[4]. PAN can also crystallize from solvent mixtures such as dimethylformamide–acrylonitrile[5].

PAN is not soluble in propylene carbonate (PC) at room temperature, but it dissolves in this solvent above about 130–150°C. Holland *et al.*[4] showed that polymer single crystals are formed on cooling a dilute PAN–PC solution. In our previous work[6], it was shown that the cooling of solutions of PC containing up to 20 wt% PAN led to the formation of thermoreversible gels. Furthermore, it was demonstrated that PAN powders could be blended with liquid PC and compression moulded, in the same way as a conventional thermoplastic material[7], to yield a plasticized 'gel-film'.

X-ray diffraction studies carried out on these PAN–PC gels and gel-films indicated the presence of crystallites[6,7]. It was also postulated that the solvent may be incorporated in the crystallite lattice by dipolar interactions between the carbonyl group of the PC and the nitrile groups of the PAN[7]. Further work showed how these compression-moulded gel-films could be 're-melted' and drawn uniaxially or biaxially to give oriented films, using the phenomenon of flow-induced chain extension and crystallization[8]. However, the use of compression moulding is limited because it is a batch process. It is the purpose of this present work to demonstrate how PC-blended PAN powders can be 'melted' and extruded continuously in the same way as a thermoplastic material, to produce filaments which can then be drawn.

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* To whom correspondence should be addressed

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EXPERIMENTAL

Polymer and solvent

PAN homopolymer was produced by the free-radical polymerization of acrylonitrile (from Aldrich)[9] by using a slurry method. The inherent viscosity of the polymer, measured in DMF at 25°C, was 1.5 dl g^{-1}. The tacticity was determined by use of ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy, and this indicated an essentially atactic polymer[9]. The polymer was in the form of a dry, white powder.

The propylene carbonate (obtained from Aldrich) was a clear, colourless liquid at room temperature, and had a boiling point of 240°C and a freezing point of -55°C. Propylene carbonate appears to be a non-toxic solvent, having the approval of the US Food and Drug Administration for its use in comestics[10].

Blending of PAN powder with propylene carbonate

It has been shown that the PAN powder produced by slurry polymerization is very porous, having a void content of $\approx 65\%$ by volume[7]. Hence, the powder can absorb a large volume of PC by capillary action and if this liquid can be distributed evenly throughout the powder, a well plasticized material can be obtained. Heating such a plasticized powder under a slight pressure gives a bubble-free 'melt'[7].

A PAN:PC (50:50 by weight) blend was used in this study. In the previous work, a pestle and mortar was used to blend the liquid PC with the powder[7]; in this work, a food blender was employed for the same purpose.

Extrusion of monofilaments

A Rosand capillary rheometer was used initially as a ram extruder for monofilament spinning. A 1 mm diameter die, of length 16 mm and with an entry angle of 180°, was used to extrude a monofilament at 190°C. The diameter of the piston was 15 mm, with typical piston speeds used for extruding the filaments being 2–10 mm min^{-1}. The extruded filaments were unoriented and were examined to determine the colour (a sign of degradation), die swell, and extrudate smoothness; X-ray diffraction measurements were also carried out on these materials.

Oriented filaments could be produced by using either a wind-up system to draw the fibres on-line, or the extruded filament could be collected first without drawing, and then reheated and drawn at a later stage.

X-ray diffraction behaviour of extruded and drawn filaments

Wide-angle X-ray diffractograms were obtained for three types of PAN sample. The first was obtained for the undrawn monofilament, which still contained approximately 40–50% by weight of the solvent. (It is estimated that there was a 10 wt% loss of PC due to evaporation during the extrusion process, hence, the extruded filament contained somewhat less solvent than the 50 wt% added originally to the powder.) An equatorial diffractogram was recorded for a (4×) post-drawn filament, and for comparison, a diffractogram of the PAN powder, as produced by the polymerization reaction, was also recorded.

Nickel-filtered CuKα radiation was generated by the use of a Philips PW1730 generator, employing an operating voltage and current of 40 kV and 40 mA, respectively. The diffractograms were obtained using a Philips 1050/81 diffractometer, with the samples being irradiated in the symmetrical-reflection mode. A crystal-monochromated detection system was used to collect the diffracted beam. Radial scans of the samples were carried out over the region $2\theta = 4$–$40°$, with the data collected at 0.02 degree intervals, with counting for 1 s at each step. Peak positions were determined by the use of the Philips APD 1700 (Version 4) software which controlled the system.

Fibre diffraction patterns were also recorded on photographic film using a flat-plate camera, and were obtained from the following samples:

(a) an extruded PAN–PC filament, collected without wind-up;
(b) an extruded filament, which was post-drawn slightly at 120°C to induce necking, in which the necked region was examined and;
(c) an extruded filament, which was post-drawn 4× at 120°C, in which the highly drawn region was examined.

Rheological measurements

The Rosand double-barrelled rheometer was used to study the rheology of PAN:PC (50:50 by weight) blends at different temperatures and shear rates. The Rabinowitsch and Bagley corrections were applied to the data[11,12]. The double-barrel arrangement of this rheometer allows the two experiments needed for the Bagley correction (i.e. using long and short dies) to be carried out simultaneously. The two dies used were 16 and 0 mm in length, both having a diameter of 1 mm and an entry angle of 180°. The shear rates used were in the range 10–10^4 s^{-1}. Measurements at each of the chosen shear rates were performed twice in order to check reproducibility.

RESULTS AND DISCUSSION

We shall discuss the continuous extrusion of PC-plasticized PAN melts and compare this technique with the other more traditional spinning processes that are used for this polymer. After comparing the X-ray diffraction patterns of the PAN powder with the unoriented solvent-containing extrudate and the drawn filaments, the viscosities of plasticized PAN melts will be briefly discussed.

Plasticized extrusion of filaments

When the extrudate emerged from the long die, it was a transparent fluid; it showed die swell, and as it cooled further downstream, it turned into a solid filament, see *Figure 1* (left). It is remarkable that the extruded filament was bubble-free. Zwick, who studied the possibility of extruding polymer solutions that gel or solidify on-line, mentions that it is difficult to make bubble-free spinning dopes with polymer contents greater than approximately 25%[13]. Our method of absorbing a latent solvent such as PC into the porous powder, followed by heating under some pressure, appears to be successful in producing bubble-free melts. This has been explained in greater detail in a previous publication[7].

The diameter of the solidified filament when it was not wound up was ≈ 1.5–2.0 mm (due to the die swell). In fact, the extrudate behaved very much like the melt of a conventional thermoplastic polymer, such as

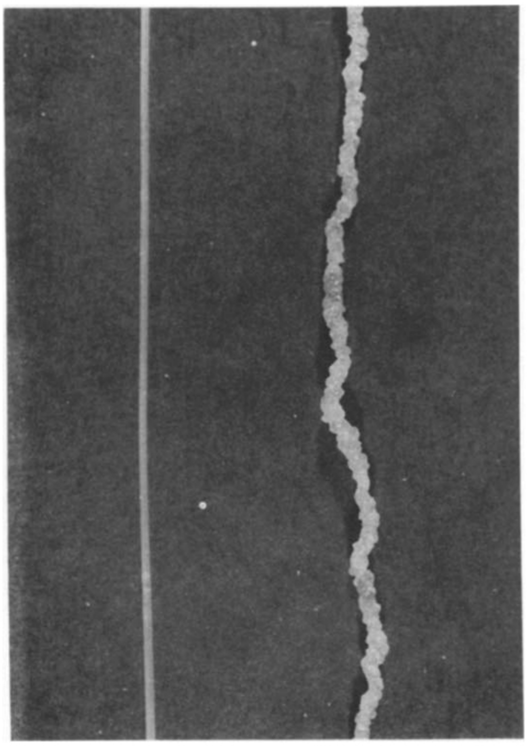

Figure 1 PAN filaments produced by a plasticized melt-extrusion technique: left, smooth, bubble-free filament (as extruded) with die swell, and right, extrudate distortion due to melt fracture at high shear rates. Note both filaments contain the solvent

polyethylene. The occurrence of die swell indicated that any chain extension caused by both the elongational flow field at the capillary entrance and the shear field in the die was rapidly lost at the exit. More direct evidence obtained from X-ray measurements (discussed below) confirmed that the 'as-extruded' filament was unoriented.

At very high shear rates, the familiar extrudate distortions such as melt fracture and 'shark-skin', which can occur during the melt extrusion of thermoplastic polymers, were observed. *Figure 1* (right) shows a solvent-containing filament which was extruded at a shear rate which led to melt fracture. During extrusion trials, it was found that melt fracture occurred at lower shear rates with high-molecular-weight PAN, when other conditions such as temperature and polymer concentration were kept constant.

The colour of the extrudate varied from virtually colourless (but translucent), to yellow, depending on the polymer sample and the extrusion conditions. Although the extrusion temperature and the residence time influenced the colour, much of this was inherent in the polymer and was produced during the polymerization process. Even when PAN powders are dissolved in solvents such as DMSO and DMF (at room temperature), the solutions are invariably tinted yellow. Thus, PAN fibres produced from wet spinning are also yellow-tinted. This is, of course, of no great concern if the fibres are to be used for carbonization but for textile applications it can be undesirable. In previous work, we found that the chromophore that causes colour in PAN, although very intense, is actually only present in small amounts[9]. We believe that, although the PAN–PC extrusion method necessarily involved heating, the colour was not induced solely because of exposure to heat, as it was already present in the polymer. In our experience, different polymerization conditions give polymers which show different susceptibilities to yellowing. Of course, prolonged exposure to heat always caused further yellowing, whatever the nature of the initial polymer.

The monofilament extrudate from the rheometer could be drawn on-line, to give fibres of approximately 30–40 μm diameter, by using a wind-up attachment. A hot cabinet for on-line drawing at high temperatures was not available, but it is expected that drawing the fibres in a heated zone should give even finer filaments. A large amount of the solvent evaporated during the spin-line drawing process and the remainder could be removed by convection air-heating or by extracting the PC in a hot-water bath.

Although we have restricted ourselves in this work to describing the plasticized extrusion of the PAN homopolymer, the behaviour of the common industrially used PAN copolymers (such as those containing 1–10 wt% methyl acrylate comonomer) should be briefly noted. Powders of the copolymers could also be similarly plasticized and extruded by using this technique. In fact, the copolymers were generally easier to extrude than the homopolymer, as they had a lower viscosity, which meant that lower temperatures and compositions with higher polymer contents could be used. The extruded filaments of the copolymers also showed die swell, but were transparent even after solidification, whereas the homopolymer filaments always became turbid as soon as they cooled.

X-ray diffraction patterns of PAN powder and PAN–PC filaments

Figure 2a shows the wide-angle X-ray diffractogram of PAN powder as obtained from the polymerization reactor. This generally displays two prominent reflections corresponding to 5.30 Å and 3.04 Å, which has been interpreted as arising from crystallites containing rod-like chain segments packed in a hexagonal fashion[14].

Figure 2b shows the diffractogram obtained from the extruded filament, i.e. the monofilament extruded without wind-up which still contained approximately 40–50 wt% solvent (i.e. the filament in *Figure 1* (left)). This diffractogram also indicates the presence of crystallites in the filament. The rapid crystallization of the PAN from propylene carbonate solution is undoubtedly the cause for the spontaneous solidification of the 'molten' filament, downstream of the die exit, without any coagulation. The corresponding diffraction pattern (shown as an inset in *Figure 2b*), confirms that the 'as-extruded' filament in *Figure 1* (left) was unoriented.

Remarkably, the diffractogram of the unoriented filament (*Figure 2b*) is different from that of the dry reactor powder (*Figure 2a*). It can be seen that the PC-containing filament shows new peaks when compared with the reactor powder. In particular, the single peak at $2\theta \approx 17°$ in the powder has become a doublet in the PAN–PC filament. Double peaks at 5.3 and 5.1 Å, such as those in *Figure 2b*, have usually been observed in specimens such as single-crystal mats made from sedimenting single crystals grown from dilute PC solutions[15,16], and in PAN–PC gels[6,7]. For example, Hinrichsen and Orth[15] have reported a diffraction pattern of a single crystal mat which resembles that shown in the inset in *Figure 2b*. This has been interpreted as arising from an orthorhombic, instead of the usual hexagonal, polymorph[15–17].

In previous work[7,8], it was suggested that in PAN

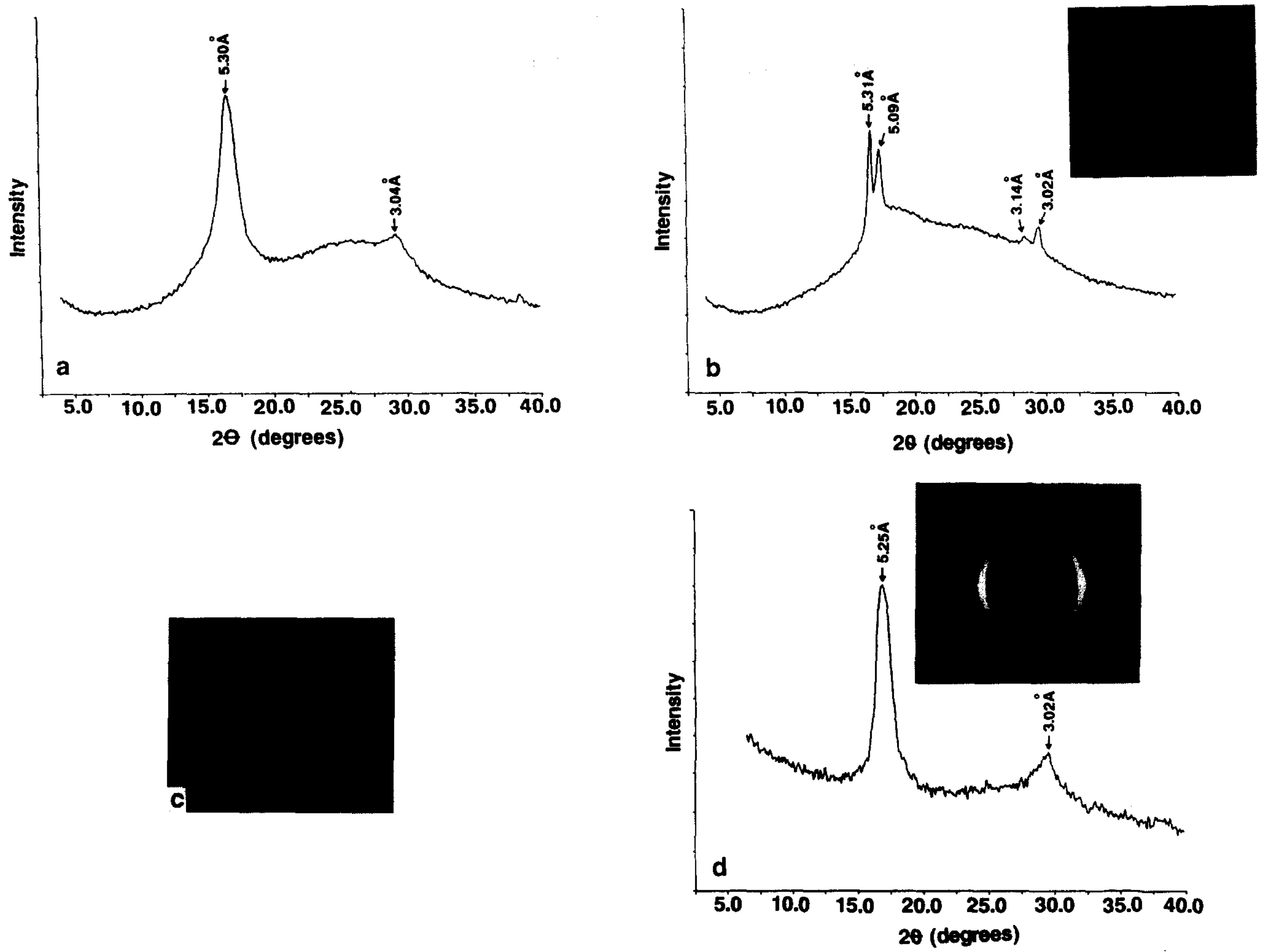

Figure 2 (a) X-ray diffractogram of PAN powder obtained from the polymerization reactor. (b) X-ray diffractogram of the undrawn PAN–PC filament (inset shows the corresponding diffraction pattern; the two rings correspond to 5.31 and 5.09 Å). (c) X-ray diffraction pattern of the necked region of a slightly drawn PAN–PC filament (fibre axis is vertical). (d) Equatorial X-ray diffractogram of a (4 ×) post-drawn PAN–PC filament (inset shows the corresponding diffraction pattern, with the fibre axis vertical).

samples (such as PAN–PC gels) where diffractograms similar to *Figure 2b* were observed, an orthorhombic polymorph, in which the solvent had co-crystallized with the polymer, may be present. Herbert *et al.* have shown that when the solvent was extracted from the PAN–PC gels, the diffraction pattern resembled that of the original reactor powder[18]. This was taken as strong evidence to support the view that a new polymorph was formed in the gel, not merely due to crystallization from the solvent, but also due to the active participation of the solvent in the crystallite lattice. One possible explanation of how this could occur was that solvent was incorporated by dipolar interactions between the carbonyl group of the PC and the nitrile groups of the PAN, thus leading to an enlarged orthorhombic lattice[8].

Figure 2c shows the diffraction pattern obtained from the necked region of a slightly drawn PAN–PC filament (draw ratio was approximately 1.2:1). The peaks in the diffraction pattern correspond to 5.3 Å (innermost arc), 5.1, 3.1 and 3.0 Å (the last two arcs are faint but can be better seen in the original negative). These are, in fact, the four peaks shown in the diffractogram of the unoriented filament (see *Figure 2b*). The diffraction pattern shown in *Figure 2c* allows us to conclude that all four peaks are equatorial.

Finally, *Figure 2d* displays the equatorial diffractogram and diffraction pattern of a 4 × drawn PAN–PC filament. This diffractogram shows peaks at 5.25 and 3.02 Å, and is similar to that obtained for the dry polymer powder (see *Figure 2a*), corresponding to the hexagonal polymorph. Similarly, the diffraction pattern of the (4 ×) drawn filament (shown as an inset in *Figure 2d*) showed just two intense equatorial arcs, which corresponded to 5.3 and 3.0 Å. The presence of an unoriented amorphous halo should also be noted. Drawing the filament to even higher draw ratios resulted in the same peaks, except that the equatorial arcs in the diffraction pattern in *Figure 2d* became shorter in arc width, and the amorphous halo disappeared. The transformation from *Figure 2c* to the diffraction pattern in *Figure 2d* has already occurred as the result of a draw ratio of 4:1.

It is worth remarking that the photograph shown in *Figure 2d* resembles the 'standard' diffraction pattern of oriented PAN that is observed by most workers[8,14,19]. For example, Houtz[19] and Bohn *et al.*[14] have shown diffraction patterns, similar to that of *Figure 2d*, that were obtained from highly drawn PAN fibres, produced by wet-spinning. This has been attributed to the hexagonal packing of rod-like PAN chains, which possess no chain-axis order[8,14].

The general transformation indicated by the diffraction patterns shown in *Figure 2* may be summarized as follows: unoriented, hexagonal polymorph (PAN powder)→solvated, orthorhombic polymorph with no chain-axis order (extruded, undrawn filament)→oriented, hexagonal polymorph with no chain-axis order (highly drawn filament). Thus, there appear to be two consecutive polymorphic transitions, induced first by the presence of solvent in the extruded filament, and secondly by the drawing process.

In our previous work[8], a similar transformation was observed in going from PAN powder, to PAN–PC gel-films (made by compression moulding the PC-plasticized PAN powder) and finally to drawn films. It was postulated that a solvated, orthorhombic polymorph was formed in the PC-containing gel-film, with drawing leading to the solvent being squeezed out, thus causing a return to hexagonal packing. A similar explanation can be offered here in the case of these continuously extruded PC-plasticized filaments.

Comparison of plasticized melt-spinning with other spinning techniques used for PAN

The most commonly used techniques for producing PAN fibres include wet-spinning, dry-jet wet-spinning and dry-spinning. This subject has been reviewed by Gupta *et al.*[1]. In wet-spinning, the fibres are regenerated by coagulation, i.e. by a phase transformation due to a change in composition, caused by the presence of a non-solvent for the polymer in the coagulation bath. A dope used for wet-spinning will not usually solidify if extruded into air. In normal wet-spinning, the spinnerette is immersed in the coagulation bath and this allows the spinning of over 50000 filaments from a single jet[1]. Dry-jet wet-spinning is a variation of this technique in which the jet is not immersed in the coagulation bath so that the filaments pass through a short air gap before reaching the bath[1]. In dry-spinning, the solution is extruded into a heated chamber where the solvent is vaporized; again, the filament is generated by a phase transformation that occurs due to a change in the composition. This time, however, it involves removal of the solvent by thermal means. For best results, the solvent for dry-spinning should be very volatile, so that it evaporates on-line very rapidly.

Plasticized melt-spinning may appear to have some similarities with dry-spinning in that the filaments can be stretched on-line with the simultaneous removal of solvent by vaporization. However, it is different from dry-spinning because the filament can also be generated simply by cooling of the extrudate, and there is no need for solvent vaporization. It is this aspect that makes it similar to true melt-spinning. Hence, plasticized melt-spinning shares the features of both dry-spinning (presence of solvent) and melt-spinning (solidification due to cooling). Unlike wet-spinning, however, melt-spinning only allows hundreds, or possibly a few thousand, fibres to be spun from a single jet.

Other terms such as 'gel-spinning' and 'phase-separation-spinning' have also been used to describe processes similar to plasticized melt-spinning[13]. Zwick has attempted to give a generalized scheme for 'phase-separation-spinning' of various polymers from solution, where the phase separation on the spin line occurs as a result of heat transfer[13]. In the case of PAN, he tried spinning from mixed solvents, such as DMF/urea and DMSO/urea, which led to fibre formation without coagulation[13]. In these ternary systems, the author merely noted that there may be more than one kind of phase separation occurring and states that the urea tended to crystallize on cooling[13]. One single-component solvent, namely caprolactam, was also investigated by Zwick[13]. In this case, the polymer separated from the liquid solvent, and then the whole system solidified when the solvent froze (the freezing point of caprolactam is above ambient). In the case of PAN, Zwick seems to relate the regeneration of the fibre to the crystallization of the solvent rather than the polymer. In contrast, in the PAN–PC system described in this present work, the solvent's freezing point is well below room temperature, and crystallization of the polymer is clearly involved in the solidification of the filament. Additionally, we have also proposed that some of the solvent co-crystallizes with the PAN, but no separate crystallization of the pure solvent is involved. The PC that has not co-crystallized with the polymer exists as a liquid in the filament.

It is instructive to compare our PC-plasticized melt-extrusion technique with the water-plasticized extrusion method for PAN which is described in the patent literature[20–28]. Water is a non-solvent for PAN at room temperature, but it dissolves the polymer at elevated temperatures[20–30]. The main difference between the PC and the water system is that water only becomes a solvent for PAN at temperatures that are much higher than the boiling point of water at atmospheric pressure[21]. This obviously means that high pressure has to be applied in order to produce a PAN–water 'fusion melt'. One patent deals with how to maintain the pressure needed to prevent the water from evaporating and venting back through the feed zone of the screw extruder[26]. After extrusion, the filaments have to be carefully depressurized, in order to avoid the water flashing off and leaving a porous extrudate[27]. In contrast, PC dissolves PAN at a temperature of 130–150°C, which is much below its boiling point (240°C) at atmospheric pressure. Hence, in the PC-plasticized extrusion of PAN, extraordinarily high pressures are not needed and the extrudate does not have to be depressurized to prevent voiding. *Figure 1* shows that the extruded PAN–PC filaments contain neither air bubbles (from the melting of the plasticized powder), nor bubbles due to solvent vaporization at the die exit.

Interesting applications are possible for plasticized melt-spinning of PAN. We have extruded films from PAN–PC melts which could be drawn; again, such films are more difficult to produce by the coagulation route. An initial trial of the multifilament spinning of 40 fibres by using a screw extruder was also successful. It should also be possible to spin non-circular fibres (trilobal and multilobal), as well as fibres with hollow cross sections; such fibres may be desirable as precursors for carbon fibres, but cannot be produced as easily by wet-spinning techniques.

Rheological measurements, extrudability and thermal degradation

Figure 3 shows plots of the shear viscosity *versus* shear rate for the PAN:PC (50:50 by weight) samples measured at two temperatures. The curves show shear-thinning behaviour over the range of shear rates that were investigated. As expected, lower viscosities were obtained at higher temperatures. Over this range of shear rates, die swell occurred, but no elastic turbulence (i.e. melt fracture or 'shark-skin') was observed. Melt fracture at 200°C occurred only at shear rates which were greater than approximately 5000 s^{-1}.

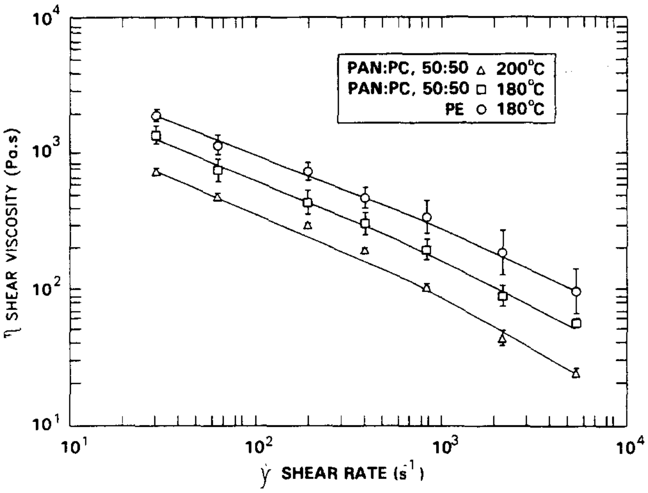

Figure 3 Plots of shear viscosity *versus* shear rate for a plasticized PAN:PC (50:50 by weight) sample at different temperatures; the corresponding plot of a standard extrusion-grade polyethylene at 180°C is included for comparison: (□) PAN:PC, 180°C; (△) PAN:PC, 200°C; and (○) PE

It was feasible to extrude the PAN–PC plasticized melts up to 220°C, although at this temperature the effect of solvent vaporization became noticeable in the form of bubbles on the filament surface. Above 220°C, degradation reactions occurred, even for the short time-scale ($\approx$5–10 min) needed to empty the barrel. These degradation reactions led not only to discoloration of the fibre, but also to an increase in viscosity with time. Although it is commonly reported that PAN degrades by nitrile cyclization reactions, our previous work has indicated that interchain crosslinking reactions are equally feasible[9]; these may be induced by heat or base[9]. Only a small amount of crosslinking is necessary to transform the melt into a permanently crosslinked network, which results in a non-extrudable gel. Hence, although the boiling point of pure PC is 240°C, the limit for extrudability of PAN–PC melts is approximately 220°C. The optimum upper limit of the temperature working range is probably 200°C (especially when using a screw extruder), i.e. a temperature at which degradation reactions are not excessive. The possibility of crosslinking in PAN should be borne in mind when making rheological measurements at elevated temperatures.

Figure 3 also shows a shear viscosity–shear rate curve for a polyethylene (PE) melt extruded at 180°C. The PE used was a standard extrusion-grade polymer (BP Chemicals, Rigidex 006-60, $M_w = 130000$, $M_n = 20000$). The molecular weight of our PAN material is comparable to these values (the degree of polymerization is in fact lower). However, it can be seen that the neat PE melt has a viscosity which is higher, but still comparable to the PAN–PC plasticized melt. Expressed another way, the viscosity of PAN is exceptionally high, and a 50 wt% solution of the polymer is comparable to that of a PE melt at similar temperatures, even when the molecular weights are comparable. The reason for this is almost certainly the existence of nitrile dipolar interactions between the chains in PAN, with the latter being absent in a purely hydrocarbon polymer such as PE. Whereas the viscosity of PE would be dominated by the entanglement density, in the case of PAN it would be dominated by the nitrile–nitrile interactions between the chains, so that even a low-molecular-weight PAN will always be more viscous than a PE with an equivalent molecular-weight distribution.

CONCLUSIONS

The aim of this paper was to demonstrate the continuous plasticized melt-extrusion of PAN, with propylene carbonate being used as a plasticizer. Powders of PAN homopolymer, when blended with PC, could be processed in the same way as thermoplastic materials. Therefore, filaments could be extruded, and these subsequently solidified, even with the solvent present, without the need for any coagulation stage. The solidified filaments could either be drawn on-line, or could be 're-melted' and post-drawn. The solidification of the extrudate occurred as a result of the tendency for PAN to rapidly crystallize from propylene carbonate solution on cooling.

The X-ray diffraction results suggested that there was a transition from a hexagonal to an orthorhombic polymorph in going from the dry polymer powder to the unoriented PC-plasticized filament. In keeping with previous work on PAN–PC gels, it is believed that the orthorhombic form is a solvated polymorph. Most interestingly, it was observed that on drawing the extruded filament to a high draw ratio, there was a return to the hexagonal form. There was no evidence for any chain-axis order in the orthorhombic or hexagonal forms, so the crystallites were only 'laterally ordered'[14].

The rheological behaviour of a PAN:PC (50:50 by weight) blend was studied at temperatures of 180 and 200°C. The plasticized melts showed shear-thinning behaviour. The viscosities of the plasticized melts were lower, but comparable to those of neat melts of a standard extrusion-grade polyethylene.

This work demonstrates that instead of using wet-spinning technology, it would be feasible to use thermoplastic extrusion methods to extrude PAN fibres and films, although a system of solvent recovery would still be necessary for large-scale fibre spinning processes.

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