

Melt Processing of Polyacrylonitrile (PAN) Polymers

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Abstract

Carbon fibers are finding a wide variety of applications in the industrial sector, which encompasses the high-tech aerospace and defence areas, increasingly, the shipping, sporting, and medical fields as well. One of the major shortcomings that limit the potential widespread use of carbon fibers in commercial applications is their prohibitive cost, in comparison with other structural materials like glass fibres and steel. Polyacrylonitrile (PAN) polymer degrades before melting and thus melt spinning is not preferred. Current carbon fiber productions from acrylic fibers employ wet or dry spun PAN-based precursors that require expensive solvents and costly solvent recovery methods causing environmental pollution. Melting point of PAN can be reduced by disturbing intra and interchain interaction between nitrile groups. This can be achieved by incorporating suitable comonomers or by using plasticizers like water or organic solvents. Thus melt spinning becomes feasible and production cost can be minimized and it will be possible to produce low cost carbon fibre precursors. Melt spun PAN will be suitable for other applications like nonwovens, membranes, outdoor fabrics and filters.

Keywords: environmental pollution, low cost, melt spinning, polyacrylonitrile, wet or dry spinning

1. Introduction

Polyacrylonitrile-based textile fibers are well known and, indeed, currently account for nearly 6 billion pound per year worldwide [1]. A small fraction (~30 million pounds) of these materials is

used as a precursor to carbon fibers. It is well known that the free radically produced polyacrylonitrile displays a glass transition temperature (T_g) of around 105°C and a melting point of around 300°C . For PAN polymers the complex reaction of intra and intermolecular cyclization, which is referred to as ‘stabilization’ in the carbon fiber community, occurs at 220°C or higher and prevents thermoplastic fabrication by economical and environmentally attractive melt spinning process [2]. Hence (PAN) polymer precursor fibers are solution processed in the presence of toxic, environmentally unfriendly organic solvents [3,12,14,15]. Generally PAN polymers are processed by wet, dry or dry- jet-wet spinning methods. The solvents for polyacrylonitrile (PAN) generally belong to two classes. The first type consists of aqueous ionic-media such as ZnCl_2 and NaSCN . Secondly, polar organic liquids containing carbonyl ($\text{C}=\text{O}$) groups, such as dimethyl formamide and dimethyl acetamide, are used as solvents. These solvents are usually used in the range of 70–93 weight % and 7–30 weight % polymer to permit processing at temperatures well below the onset of the crosslinking reaction [4]. Large amount of solvent is required for processing small amount of solid polymer in solution spinning operation. This necessitates the recovery and reuse of the solvents and thus solution spun PAN fibre cost is very high. High cost PAN precursor fibre increases the cost of carbon fibres, as an illustration, carbon fibers could be up to 10 to 20 times the cost of glass fibers on a weight basis, although this ratio is lowered when normalized on a modulus basis [5]. Carbon-fiber composites cost is at least 20 times as much as steel, and the automobile industry is not interested in using them until the price of carbon fiber drops from \$8 to \$5 (and preferably \$3) a pound [6]. It is in this regard that melt spinning of PAN precursors seems to be the better alternative for reducing the cost of the final carbon fiber product. In the latter case, we are dealing with higher amounts of PAN concentration (100 weight % of the PAN polymer) as opposed to 7–30 weight % typically used

in solution spinning. The solvent-recovery process is eliminated (lowering the capital costs), which reduces the downstream processing costs and makes the PAN precursor manufacturing process an environmentally benign one. Moreover, it is believed that the melt-spun PAN fibers, as opposed to the conventional solution-spun fibers, would be essentially void-free, leading to less severe conditions and lesser times for the stabilization and carbonization steps, which translates to better savings for the entire process [5]. Generally two approaches [7] are used to reduce the melting point of PAN polymers and to prepare stable melt, which can be melt processed. First one is the use of suitable comonomers or termonomers [8-23] in particular amount to disturb the crystal structure and nitrile-nitrile interactions, so that stable melt can be formed at reduced temperatures. Second is the use of non-solvents for PAN polymer like organic plasticizers [24-33] or water [34-45] to decouple the nitrile-nitrile interactions. Different researchers [46-53] have modified the spinning machines aiming at high production rate, production of profiled fibres, and for improvement of the filament uniformity. On the cost basis, melt processable PAN is comparable with other commodity fibres like polyesters and polyamides [23]. Melt spun PAN can be used for manufacturing nonwovens, membranes [23], carbon fibre precursor [54-55], and electret filters [56].

2. Solid State Structure of Acrylic Polymers

PAN polymers are produced by free radical polymerization which generally gives no or little stereo-regularity. A complete atactic polymer should have concentration of hetero, syndio and isotactic triads in the ratio of 2:1:1 which is found in case of PAN as 5:2:3, not markedly different from expectations for atactic case. The distinguishing feature of nitrile group is the very high dipole moment with a magnitude of 3.9 Debyes, which governs the chain conformation for

isolated PAN polymer chain. The key factor controlling the fiber structure is the interaction energy between nitrile groups, the interaction energy can be either attractive or repulsive depending upon the distance of separation. If the backbone chain were placed in a plane zigzag arrangement, then the adjacent nitrile groups would fall into a parallel alignment, thus giving the net repulsion. The chain potential energy can be lowered by placing the adjacent nitrile groups as far as possible and this will require that the backbone chain become helical (*Fig. 1*). In helical arrangement, all nitrile groups point outside and when nitrile group on other chain come closer, they get arranged in antiparallel orientation to give net attraction.

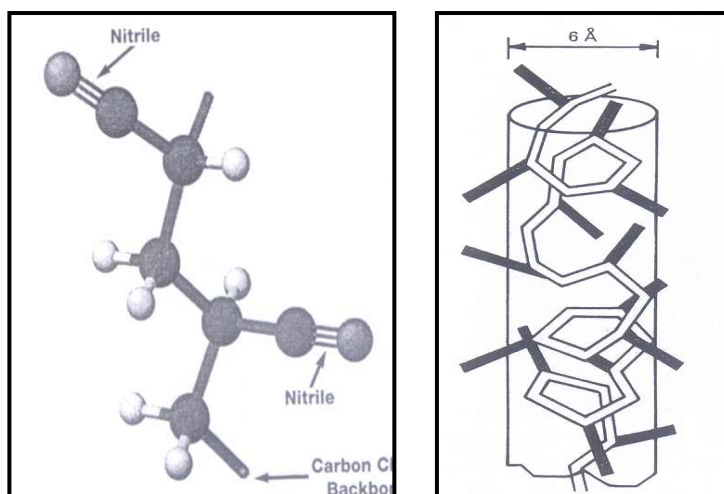


Fig. 1 Conformation for isolated PAN Chain

Two phase model is the framework for formulating structure-property relationship of fibers. The majority of textile fibers have a morphology that can be described by the classical two-phase model for semicrystalline polymers. For acrylic fibers, discrete amorphous and crystalline phases are not clearly seen. The PAN morphology has been described as “amorphous with high degree of lateral bonding” or as “two dimensional liquid crystalline-like structure with many defects” (*Fig. 2*)[7].

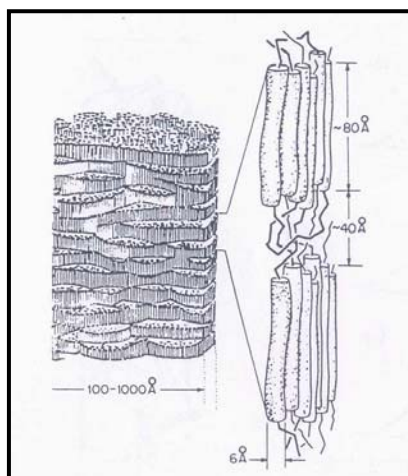


Fig. 2 Two phase model for PAN

3. Theories to Reduce Melting Temperature for Polymers

When PAN is analyzed by differential scanning calorimetry (DSC) using normal scanning rates of 20°C/min, the cyclization reaction produces a large exotherm and no melting is observed. PAN does not exhibit regular ‘melting’ thermograms, except when using DSC at a high ramp heating rate of 160 °C/min, where it shows what appears to be an endotherm prior to exothermic degradation reactions. The first order thermodynamic melting transformation, is defined by

$$\Delta T_m = \Delta H_m / \Delta S_m$$

Where ΔT_m , ΔH_m and ΔS_m are the temperature, enthalpy and entropy of melting, respectively. However, the increase in entropy during melting is small, which has little effect on lowering the T_m . To bring the melting point of the polyacrylonitrile below 200°C, the intramolecular interactions of the CN dipoles must be disrupted. This can be done chemically with the addition of comonomers. Addition of comonomers increases the distance between the CN pendant groups and disrupts the sequences of CN. In terms of equilibrium melting, the interchain interactions

between polar nitrile substituents, which must be incorporated in the PAN crystals, are expected to contribute primarily to the enthalpy of melting. The change in entropy upon melting, on the other hand, is associated mainly with disordering the intrachain PAN conformations. Another way of weakening the interactions between the CN dipoles is by surrounding the CN groups with other dipoles. Some of the molecules for this task would be water, which forms hydrogen bridges to the nitrogen atoms. Water is very mobile and it takes up little space and diffuses through the melt easily and rapidly. The polyacrylonitrile molecule becomes helical because of the strong electrical interactions between neighboring CN dipoles. The helices are not destroyed in the melt but the intramolecular interactions are diminished. Although it is a good option for the task, there are others also, including glycols and glycerin. These compounds form hydrogen bridges with the nitrile groups via their hydroxyl moieties. The reduction in the dipole interaction depends on the dipole moment. One attractive feature of the use of water and glycols is the fact that they can easily be removed from the fibers afterward. Flory proposed the theory for melting point depression of a polymer by diluents. This theory predicts the dependence of melting point on the volume fraction of the diluent, which in this case is the solvent.

$$1/T_m - 1/T_m^\circ = [RV_u / \Delta H_u V_1][V_f - XV_f^2]$$

Where,

T_m and T_m° are the melting points of the polymer with diluent and pure polymer respectively. R - Gas constant, ΔH_u - Heat of fusion per mole of crystalline repeat unit, V_u and V_1 - Molar volumes of the repeat unit and diluents, V_f - Volume fraction of the diluents, X - Polymer diluents interaction parameter. Flory asserts that comonomer interruption and shortening of the length of the crystalline monomer sequences, reduces the number and average size of crystallites. Because chain segments on the crystallite surfaces have larger free energy, smaller crystals with

a larger surface to volume ratio have a reduced melting point. Specifically, the crystallizable monomer sequence length decreases linearly with the addition of the comonomers,

$$1/T_m - 1/T_m^\circ = [R/\Delta H_u] * X_B$$

Where,

T_m and T_m° are the melting points of the copolymer and homopolymer, respectively, R - universal gas constant, ΔH_u - heat of fusion per mole of crystalline repeat unit, and X_B - mole fraction of the minor non-crystallizing comonomer. Furthermore, for non-random copolymers, Flory proposes that the melting point depression depends on the sequence propagation probability and not the overall comonomer composition (X_B). Eby, on the other hand, proposes that the comonomer may be partially incorporated into the crystal lattice as defects and extends Flory's theory by adding a parameter that accounts for the degree of lattice disruption. Eby states that the efficacy of the particular comonomer to depress the melting point is to a first approximation proportional to the molar volume of particular comonomer. Frushor developed a novel thermal analytical technique that utilizes water to depress the melting point of Acrylonitrile (AN) copolymers. As the water content is increased the melting point of the copolymer decreases continuously, till the critical concentration of water reached. The critical concentration shows dependence on the composition of the PAN. Incorporation of comonomer decreases the critical water concentration and also the melting point. Frushor demonstrated evidence in support of the Eby's theory with a melting point depression constant, which indicates the degree to which comonomers disrupt the crystalline lattice, based on the molar volume of their side groups. The melting point depression constant can be used in a generalized melting point equation for acrylic copolymers of any order

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = \sum_{i=1}^{n-1} K_i X_i$$

Where,

T_m and T_m° are the melting points of the copolymer and homopolymer, respectively, K_i and X_i are the melting point depression constants and the mole fraction of the i^{th} comonomer, and n is the order of the polymer ($n=2$ for a copolymer, 3 for terpolymer) [7].

4. Copolymerization to Impart Melt Processability

A small side group such as chlorine moiety of vinyl chloride, for example, or the absence of any side group as in ethylene, results in the disturbance of one nitrile-nitrile coupling due to the absence of nitrile group at that position. A large group, on the other hand, such as phenyl, sulfo-phenol, or halogenated phenyl group as an example can sterically hamper coupling over a considerable length of polymeric chain to which it is attached [8]. In 1954 Weinstock et al [9] produced copolymers of acrylonitrile and methacrylonitrile containing 15-30 parts of methacrylonitrile and melt processed into filaments. In another study [10], statistical (random) melt processable AN/MA copolymers were synthesized by solution, redox and suspension methods. The melt viscosity of 85/15 copolymer was fairly stable for 30 min (typical dwell time in an extruder) at 220°C. Char yield was independent of comonomers concentration and found to be approximately 50% which is ideal for carbon fiber production. Copolymers [11] of acrylonitrile and methyl acrylates were studied. It was found that increasing the MA content from 7 to 10 mol % or more causes the melt viscosity to drop by several orders of magnitude. As the amount of chain transfer agent and/or initiator increases, molecular weight and intrinsic viscosity decreases, this helps in melt spinning. Addition of photosensitive comonomers like

ABP was found to be desirable for photo cross linking the fibre to make precursors that will have enough mechanical strength to resist fusing during stabilization step and more suitable composition was found to be AN/MA/ABP in the molar ratio of 85/14/1. Jorkasky et al [12] described multi-polymer comprising about 85% to 92% by weight polymerized acrylonitrile monomer and about 8% to 15% by weight copolymerized olefinically unsaturated monomer like acrylates, methacrylates, acrylamide, vinyl acetate, vinyl chloride, etc. 85AN/15MA polymer resin having molecular weight of about 55,000 was melt spun at a temperature (224 °C) to achieve melt flow without degradation in a screw extruder. Curatolo et al [13] described the method of forming melt processable copolymers comprising methacrylonitrile (10 to 80%) and acrylonitrile (20 to 90%) for producing multiaxially oriented films. Polymerization of methacrylonitrile and acrylonitrile was carried out by incremental addition of methacrylonitrile, as it is less reactive than acrylonitrile to control the sequence length of each comonomer in the resulting polymer. It was found that the amount of comonomer is very important but at the same time the sequence length of monomers and comonomers in the polymeric chain plays vital role in deciding melt processability. Smierciak et al [14] details the process of 'starved' or 'scavenged' emulsion polymerization in which the rate of addition of acrylonitrile, methacrylonitrile and olefinically unsaturated monomers are controlled and are kept less than or equal to the rate of polymerization. This process claims that it is possible to produce homogeneous terpolymer in which the units of acrylonitrile, methacrylonitrile and olefinically unsaturated monomers are interdispersed randomly throughout the polymerized chain in relatively small monomer units resulting in a thermally stable melt processable multipolymer. Their latter patent [15] details the process of making melt processable multipolymer by starved polymerization technique, comprising 50-95% polymerized acrylonitrile and 5-50% polymerized olefinically unsaturated

monomer. Three types of acrylic copolymers [16] were prepared containing 5-25 mol % Methyl Acrylate (MA), Vinyl Acetate (VAc) and Acrylamide (AM) comonomers by aqueous precipitation polymerization method. It was observed that the decomposition temperature of AN/MA increases significantly with the increase of MA content. The effect of various comonomers on delaying the decomposition/cyclization reactions varied in the order MA>VAc>AM. With increased comonomer content, it was observed that the decomposition temperature of AN/MA increases, that of AN/VAc increases first and then it is decreased, whereas, in the case of AN/AM it is initially decreased and then it is increased. Incorporation of 15 mol % of MA can improve the decomposition temperature to 321°C and depress the melting point to 174°C. In another study [5] three different kinds of comonomers MA, Isobutyl Acrylate (IBA), and AM were studied. It was seen that MA was found to be suitable for enabling the melt processing of PAN, in terms of melt viscosity, time stability, and char yield. Below 10 mol % of MA, the PAN copolymer exhibited no flowability, even at very low molecular weights (20,000). The long-range order inherently present in PAN is speculated to be broken down at a critical value of about 10 mol % MA at 220°C in the PAN-based system, enabling its melt flowability. The molecular weight cutoff for the 90/10 mol % AN/MA system was about 50,000 at 220°C, whereas it was increased to about 100,000 in the presence of 15 mol % MA comonomer. AM comonomer was not found to improve the melt processability of the PAN system because of extensive crosslinking and IBA was not suitable due to low char yield. Another study [17] revealed that emulsion polymerization of 85-88 mole % AN, 11-14 mole % MA, 1 mole % acryloyl benzophenone (ABP) gives the melt processable acrylonitrile copolymer suitable for carbon fibre precursor. In another study [18] 2, 3, 4, 6 arm star polyacrylonitrile homopolymer and copolymer were synthesized and studied for their thermal behavior. Thermal analysis

showed that T_g was found to lie in the range of 85-95°C, with no clear trend and bulk material showed no improved melting. Copolymers [19] of AN/ MA and AN/MA/ABP terpolymers having higher and lower molecular weights were synthesized at molar ratios of 85/15 and 85/14/1, respectively. This study has identified the temperature and time dependence of shear viscosity η as well as the temperature and angular frequency dependence of complex viscosity η^* . Results suggest that copolymerization with ABP significantly increased the thermally induced kinetics of crosslinking for high molecular weight terpolymer and melt stability was found to be less. AN/ MA copolymer and both terpolymers appeared to be suitable for melt processing at temperatures between 200 and 220°C. AN–MA copolymer [20] in the molar ratio 85/15 containing 5–25 wt% of microencapsulated phase change materials (Micro-PCMs) were melt spun. It was found that, melt flow index initially increases for low concentration of Micro-PCM as they act as plasticizers and then reduces as the Micro-PCM hinders the chain mobility. It was also found that with increasing the concentration of Micro-PCM, fibre crystallinity and mechanical properties reduces. Hutchinson et al [21] studied the structure–property relationships between melt-processable high-acrylonitrile copolymer (MPHAC) and commercially available dry spun Dralon filaments. In these cases, the tenacity was found to be highly dependent on the degree of order present in the melt spun filaments. The Dralon fiber has shown a relatively high index of paracrystallinity (IP), but lower tenacity than does MPHAC, since paracrystalline order (PO) is presumably driven by the interaction between dipoles, an AN sequence length of approximately 36 in Dralon, as opposed to 13 in the MPHAC filament. Short AN sequence in MPHAC leads to high paracrystalline order in these fibers. The PO increases with draw ratio, while hot godet draw imparts a significantly higher degree of PO. Finally, no significant changes in molecular weights were observed between initial MPHAC resin pellets and “melt” processed

filaments. The orientation and crystal size study [22] of a series of melt-spun high acrylonitrile AMLON (commercial melt processable PAN) was carried out. It was found that orientation of the AMLON fibers is as good as or better than that of commercial solution-spun fibers. Post-drawing has a dramatic effect on molecular orientation. Heat setting was found to increase the crystal size without sacrificing orientation. Higher molecular weight increases orientation. While commercial solution-spun fibers have rough grooves and an irregular shape, the melt-spun fibers are relatively smooth and cylindrical. The cross-section of the fiber can be adjusted easily by die design. In another study [23] it was found that the tenacity of Amlon (commercial melt processable PAN) fibers were on average higher than a commercial solution spun fiber.

5. Melt Spinning Using Organic Plasticizers

Green et al [24] describe the process, in which acrylonitrile polymerization was carried out in presence of plasticizers like cyclic ethylene carbonate or tetramethylene cyclic sulfone or N-acetylmorpholine to produce melt processable plasticized PAN polymer. For emulsification of polymer/plasticizer mixture, non-solvent like hexane or heptane was used during polymerization. This method resulted into melt processable PAN/plasticizer mixture containing 30-60% PAN and remaining plasticizer. In another patent [25] a mixture of 40-65% PAN was mixed with plasticizers like ethylene cyclic carbonate or gamma-butyrolactone or ethylene cyclic sulfite and then melt processed. Hare et al [26] detail the process of making PAN fibres having crimp and resilience like natural wool fibres. Melt spinning of PAN homo and copolymers having polymer concentrations of about 40-70% plasticizers like N-acetyl morpholine, keeping spin stretch ratio more than 30, spinning was carried out at 1000-7000 ypm. Filaments were then allowed to shrink in hot water or air under slight or no tension conditions to yield crimped fibres. Farago et al [27]

detail the polymerization for melt processable PAN homo and copolymers in dimethyl sulfoxide or succinonitrile or dimethyl sulfoxide dimethyl sulfone as plasticizers for the polymer. This plasticized melt was spun at very high spinning speed up to 4000 ypm. Opferkuch et al [28] proposed the method of melting PAN homo and copolymers at atmospheric pressure using organic liquids, having dielectric constant preferably higher than 30. The melt thus formed was used for making textile filaments and molds using commercial melt processing machines. Daumit et al [29] describe the melt spinning of polyacrylonitrile using plasticizers comprising acetonitrile, C1-C4 monohydroxy alcohol and water for manufacturing PAN as a carbon fibre precursor. In another patent [30] the use of nitromethane and nitroethane in place of acetonitrile was suggested for melt plasticization of acrylic copolymers. Similar patent [31] details the melt spinning of PAN copolymer for carbon fibre precursor. PAN copolymer was melted using 14-21% acetonitrile and 15-23% water as plasticizer, then extrusion was carried out in the filament form followed by plasticizer evaporation and drawing. The process claims that the resulting filaments are ideal from carbon fibre precursor point of view. Bashir et al [32] studied the compression molding of concentrated solutions of polyacrylonitrile (PAN) in two organic solvents; gamma butyrolactone (gBL) and ethylene carbonate (EC). It was found that these solvents form the complexes with PAN polymeric chains. Differential scanning calorimetry showed gel-melting endotherms on heating and crystallisation exotherms on cooling for compression molded films. Kanishke et al [33] described the plasticized extrusion of the PAN homopolymer and propylene carbonate (PC). The plasticized melts showed shear-thinning behaviour. It was feasible to extrude the PAN-PC (50:50) 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 (~ 5-10 min) which is 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. In another study [17] carbon dioxide (CO₂) was used as plasticizer for AN copolymers to an extent that facilitates processing at reduced temperatures. A batch saturation method to absorb CO₂ in AN copolymers was developed. Reduction in processing temperature was found to be directly proportional to the amount of CO₂ absorbed.

6. Melt Spinning Using Water

In 1952 C. D. Coxe [34] first discovered that water can hydrate the pendant nitrile groups of PAN, by decoupling the nitrile-nitrile associations. The melting point thus, can be significantly lowered, and hydrated PAN can be melt extruded without significant degradation. Such hydrated form of PAN could be extruded using elevated temperature and pressure resulting in fibrillar material suitable for making paper or in strands of fused and sintered or foamed particles. However, such a process was unable to produce fibres for textile applications. George et al [3] developed the continuous method for making fibrous filamentary material suitable for paper products. In this method, PAN polymer is mixed with water containing sodium carboxymethylcellulose, this mixture is heated in the pressurized vessel and extruded in restricted area where high velocity steam is directed in transverse direction to the extrudate imparting it suitable draw ratio. The bonded fibrils so formed can be separated by beating or other abrasive methods. For the first time Blickenstaff [8] provided the clear understanding of water-polymer interactions at different time, temperature and pressure conditions and details, substantially single phase hydrated melt using appropriate amount of water and temperature, comprising polymers or copolymers of acrylonitrile containing at least 80 mol % of acrylonitrile

units. The filaments spun from such a composition are characterized by sheath-core structure (due to very fast evaporation of water from filament surface), surface striations, micro voids in core and diffused visible light reflectivity. Density of sheath was higher than core, which led to high bending modulus of the filament. Drawback of the process was that the loop tenacity of these filaments was poor. Due [35] to voids in core, these fibres required large amount of dye to achieve desired shades and obtention of heavy shades such as blacks and navy blues was impracticable. To overcome this problem, acrylonitrile copolymer was prepared using suitable amount of hydrophobic and hydrophilic comonomers. Single phase fusion melt was then prepared using amount of water in the lower half of range necessary to provide melt. This melt was then extruded in steam pressurized zone where rate of evaporation of water from filament surface was controlled by saturated steam and hydrophilic monomer in the copolymer structure to give void free filaments. Hirotaka et al [36] detail the process of making homogeneous single phase melt of PAN homo and copolymers. In this process, polymer/water crumbs containing 30-60% by weight of PAN polymer was dewatered at 140° C above its autogenous pressure to yield homogeneous melt containing 70% polymer concentration. Coleman et al [37] propose the use of terpolymer containing 80-95 weight percent of acrylonitrile, 4-19 weight percent of hydrophobic monomer and 1-10 weight percent of hydrophilic monomer. Goodman et al [38] suggested the addition of 3-7% compatible solvents like 2-pyrrolidone ethylene carbonate and tetramethylene sulphone in the single phase hydrated melt of PAN to improve the loop tenacity of the filaments. With this invention still solvent recovery and pollution problem were not solved. Cline et al [39] state that PAN copolymer containing 91% AN and 9% other comonomers with 23 µeq/g enolizable groups, 15-70 µeq/g thioether ends and 3 µeq/g oxidizable hydrolysis fragments shows better single fusion hydrated melt stability and good melt color. Porosoff [40] provided a

process for preparing PAN fibre which comprises extruding a single phase fusion melt of acrylonitrile copolymer and water through spinnerets directly into the steam pressurized solidification zone wherein temperature, pressure and saturation of steam is maintained so as to keep extruded filament in plasticized form and then drawn to spin stretch ratio of at least 25 and generally in the range of 25-250. Filaments thus produced have shown straight and loop tenacity of textile interest. Kreauling et al [41] developed two stage drawing process, for single fusion melts of PAN copolymer. In this process as spun filaments were drawn to draw ratio of at least 5 in first stage and to achieve total draw ratio of at least 25, by maintaining appropriate draw ration in the second stage of drawing. Straight and loop tenacity of the resulting filament was comparable to the commercial PAN filaments. In another study [42] low molecular weight copolymers of acrylonitrile having number average molecular weight in the range of 6000-15750 was melt spun from homogeneous fusion melt of an acrylonitrile copolymer and water. The stretch ratio of at least 25 was applied to extruded filaments in steam pressurize zone. Filaments were having the properties of textile interest. DeMaria et al [43] described a process for producing an acrylonitrile polymer fibre from a single phase melt of acrylonitrile polymer and water. This single phase melt comprising 83.2 parts by wt. of acrylonitrile terpolymer and 16.8 parts by wt. of water was extruded in to a steam pressurized solidification zone maintained under conditions of temperature (167°C), pressure (13 psi) and saturation that enabled the nascent extrudate to solidify, and to retain sufficient water to remain in a stretchable plastic state. The extrudate was wetted in the solidification zone with hot water and stretched in at least two stages to provide the molecular orientation. The total stretch ratio achieved using wetting with two hot water sprays was 50.88 as compared to 25.68 when no hot water wetting was used. The resulting filament from the modified process had significantly higher straight tenacity, hot-wet initial

modulus and was void-free. Streetman et al [44] developed the self crimping melt spun PAN fibre for better aesthetic value, based on differential thermal shrinkage principle. This method uses a heterogeneous mixture of 80-90% PAN copolymer and 10-20% incompatible polymer like commercially available acrylonitrile grafted starch or polypropylene, then spinning this hydrated mixture followed by heat treatment to give self crimping filaments. In their latter patent [45] they have covered other incompatible polymers like Polyethylene, Nylon and Polyesters.

7. Modifications in Spinning Machines

Different researchers have modified the spinning machines aiming at high production rate, production of profiled fibres, and improvement in the uniformity of filaments. Pfeiffer et al [46] successfully spun the hydrated melt of PAN copolymer of kinematic molecular weight in the range of 30000-60000 through spinneret plates having orifice diameter in the range of 60-160 micron and orifice density of 18 per sq.cm. to increase productivity. Pfeiffer et al [47] developed the new spinneret plates having 25-50 orifices per sq.cm. and capillary diameter of 200-400 micron for spinning homogeneous fusion melt of polyacrylonitrile and water. This design increased the productivity by 180%. Pfeiffer et al [48] have shown that, a spinneret plate having multiple capillaries per counter-bore can be effectively used to melt spin fusion melt of acrylonitrile polymer and water without sticking together. Production rate can be increased by providing large plurality of orifices in the single spinneret assembly. At the same time it becomes difficult to maintain uniform back pressure over all the orifices and leads to non-uniform diameter of extruded filaments. Siegman et al [49] designed the spinneret assembly wherein tapered passageways and distribution chambers of diminishing length are arranged in such a manner as to provide uniform backpressure over all the orifices, so that extruded filaments of

uniform diameter can be produced. Pfeiffer [50] designed the spinneret assembly for spinning hollow PAN fibre from hydrated single fusion melt. In another patent Pfeiffer et al [51] developed fibres of open cross sectional shape by inserting removable pin in the counter bore of the spinneret, from single fusion melt of PAN copolymers. Klausner et al [52] described the process of continuous extrusion of single fusion melt of PAN in horizontally disposed extruder. In the said process, porous plug of composition to be extruded is formed between compression zone and melting zone. Linear rate of advancing for porous plug was equal to the rate at which condensed vapors move towards the feed zone so as to prevent water escape. Young et al [53] developed the vertically disposed compression zone and claimed the advantages that, polymer powder as well as granules can be processed, pressure generated in the compression zone is sufficient to provide single fusion melt and hence no need of auxiliary pumps, no need of forming porous plug and the fibres spun thereof have less bubble counts.

8. Cost Analyses and Potential Market for Melt Spun PAN

The benefits of melt processing, aside from mechanical enhancements, are cost driven. The least expensive manufacturing route is synthesis of the polymer followed by direct conversion to fibers. Cost predictions of melt processable high acrylonitrile are based on raw materials and estimated conversion costs for poly ethylene terephthalate, polypropylene, and polyamides. The results are presented in Table 1[23]. PAN scores over other two predominant precursors for carbon fibres namely viscose rayon and pitch, mainly because of the following advantages, 1) Its structure permits faster rate of pyrolysis without much disturbance to its basic structure and to the preferred orientation of the molecular chains along the fiber axis present in the original fiber 2) It decomposes before melting 3) Higher degree of preferred orientation is possible during spinning 4) It results in high carbon yield (50-55%) when pyrolyzed to 1000°C and above [2].

Comparative study of [54] Mitsubishi® PAN (95% PAN, 5% methyl acrylate) pre-spun fiber, isotropic pitch and Amlon® (80% PAN, 20% methylacrylate) which is a melt spinnable PAN precursor, was carried out to produce carbon fibers. However, heat treatment trials showed that standard oxidative stabilization of a melt-spun PAN is likely to require process times in the order of days and concluded that slight modifications of the chemical compositions of isotropic pitch and Amlon® PAN are likely to make them practical for industrial applications. Grove et al [55] explored the feasibility to produce carbon fibers using water plasticized melt spun PAN based precursors and succeeded to gain reasonable strength, up to an average of 15 cN/dtex, Young's modulus from 1080 to 1310 cN/dtex, and sonic moduli in excess of 1000 cN/dtex from experimental acrylonitrile-based, plasticized melt spun precursors. Thermoplastic polyacrylonitrile [23] is likely to find application in the larger field of composites and carbon carbon composites. Due to the exceptional UV resistance in high acrylic fibers, their fabrics will find use in many outdoor applications. Primarily, products include awnings, convertible automobile covers and marine textiles woven mainly from ring-spun yarns. To date, almost all acrylic fiber nonwovens are constructed from wet-lay, air-lay or carding processes. However, the amount of melt spun nonwoven production (at least in the U.S. and Canada) has steadily increased. A thermoplastic polyacrylonitrile would potentially open up the melt spun industry to acrylic for fabrics, filtration and high tech products including carbonized fabrics. Membranes are constructed in many forms for specific properties and applications. One of the methods that pertain to fibers is hollow fiber membranes (HFM). HFMs are advantageous because they allow a high modulus composite with high surface area. Dugan [56] disclosed the electret filters made up of multicomponent splittable fibers such as melt processable polyacrylonitrile as one and

polypropylene as other which lie towards more negative side on the tribo-electric series as compared to polyacrylonitrile.

Polymer type	Raw Cost (¢/lb)	Conversion cost (¢/lb)	
		Resin	Fibre
PET	36	40	Staple 19, Filament 27
Polypropylene	22	15	N/A
Nylon-6	72	53	Filament 21
Nylon-66	117	21	
Amlon (Melt Processable PAN)	30	45-65	Staple 20 to30, Filament 30 to 45

Table1. Raw materials and conversion costs for major thermoplastic polymers

9. Conclusion

Polyacrylonitrile shares a huge market as textile fiber, as well as carbon fiber precursor. By using melt spinning, the problems of environmentally harmful solvents, higher capital and operating costs can be solved. Melt-spinning is inherently less expensive than solution-spinning because it eliminates the extra cost of solvent handling and it also operates at much higher throughputs. Two approaches can be used to reduce the melting temperature for melt spinning of the PAN polymers, namely; 1) use of a melt assistant, such as water, or other organic plasticizers and 2) the use of suitable comonomers to reduce the long-range order, simply by increasing their concentration and subsequently reduce melting point as well as to give stable melt for processing. Experimentally, positive birefringence values has been found for melt spun PAN, which indicate high orientation of the polymeric chains in melt spun fibers. Again the cross-section of the fiber can be adjusted easily by die design. Melt spinning of PAN can significantly reduce the cost of carbon fibers. Moreover, it is believed that the melt-spun PAN fibers, as opposed to the conventional solution-spun fibers, would be essentially void-free, leading to less

severe conditions and lesser times for the stabilization and carbonization steps, which translates to better savings for the entire process. Apart from carbon fiber precursor, melt spun fibers can be used in spun bonded nonwovens and other applications which will give low cost products.

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