REVIEW ARTICLE

Manufacturing of Acrylic Fibres with Desirable Properties to Make Carbon Fibres - Review

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ABSTRACT: Any precursor used to make carbon fibres is subjected to very high temperatures to remove all the elements except carbon. The type of precursor to be used, the orientation of polymer chains within the structure and the tensile strength are of highest priority. The selection of co-monomers, the ideal path to produce PAN polymer and the parameters affecting Acrylic fibre properties have been reviewed in this paper.

KEYWORDS: PAN polymer, Wet spinning, Acrylic fibres

1. INTRODUCTION

Carbon fibres can be manufactured from precursors like PAN, mesophase pitch, viscose rayon, vinylidine chloride and phenolic resins of which the latter two have not been commercially viable. The starting material is the fibre itself. The ideal features of precursors required for manufacturing of carbon fibres are easy conversion to carbon fibre, high carbon yield and cost-effective processing.

The application of carbon fibres determines as to which precursor is to be used; for example, Viscose rayon based carbon fibres are not suitable for applications where high tensile strength and high modulus are required, since they are more porous[1]. Commercially, PAN-based carbon fibres production is common due to the good carbon yield and wide range of tensile strength and modulus that can be obtained with a feasible process.

The modulus of carbon fibre is directly proportional to the modulus of PAN fibre from which it is produced[2]. Thus, considering the precursor properties is very important.

Fibres with non-round cross section cannot withstand a high draw ratio during spinning, stabilization and carbonization due to stress concentration. Circular fibres experience Poisson's contraction when exposed to tensile forces[3]. The properties affected by this are lustre, mechanical and other physical properties.

The aim is to understand the manufacturing of acrylic fibres to be converted into carbon fibres with an objective of reviewing the properties of acrylic fibre and determine the desirable conditions for it to be converted into carbon fibres.

2.1 METHODS FOR POLYMERIZATION:

The PAN polymer can be synthesized by several methods using acrylonitrile and the selected co-monomers employing free radical mechanism. They are:

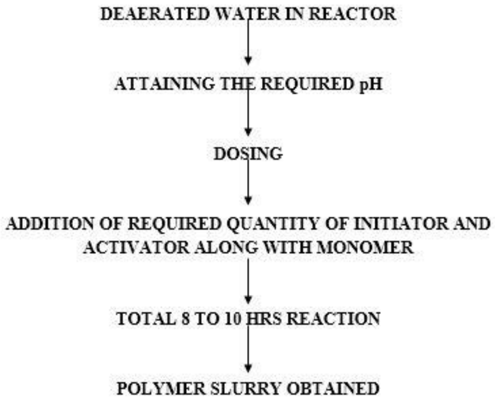
a. Solution polymerization (When the dope is prepared directly during the process of polymerization)

b. Bulk polymerization (It is an auto-catalytic process and not used commercially)

c. Emulsion polymerization (It is generally restricted to modacrylics and not relevant for a carbon fibre precursor)

d. Aqueous dispersion or Slurry polymerization (The most common method used for textile fibres)[5].

Figure 1: Aqueous slurry polymerization



PAN based polymer precursor can be classified into pure homo-polymer and co-monomer. The homopolymer PAN product is difficult to process into carbon fibres because the initial oxidation stage of the process cannot be easily controlled owing to sudden and rapid evolution of heat, coupled with a relatively high initiation temperature. Such heat may result in poor properties of carbon fibres due to the chain scission from the thermal shock. Thus no record of homopolymer being used for carbon fibre production exists[6].

On the other hand, co-monomers play an important role in the stabilization process and in enhancing the segmental mobility of polymer chains which results in better orientation and mechanical properties of the precursor and the resulting carbon fibres. They also help in reducing the temperature of initiation of cyclization.

2.2 SELECTION OF CO-MONOMERS:

Some of the preferred neutral co-monomers include vinyl esters, methacrylic acid and methyl methacrylate, although vinyl esters are not suitable for carbon fibres. These co-monomers can be termed as plasticizers as they break up the structure making the polymer more readily soluble in the spinning solvent, improving the quality of spinning and modifying the fibre morphology. Acrylonitrile and MA is considered to be the ideal pair since they both exhibit same

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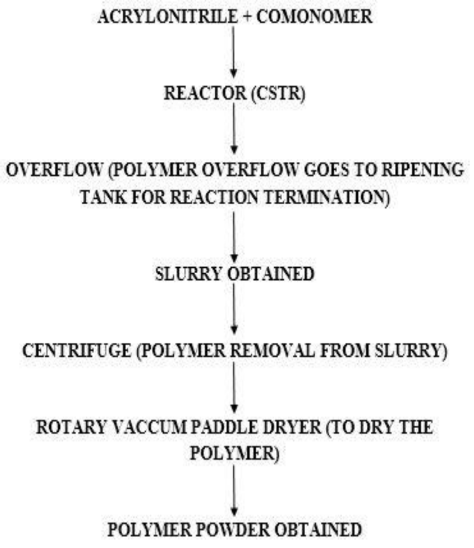
polarity, resonance and stearic hindrance. Carboxylic acids are also very effective co-monomers since the presence of carboxylic group affects the ease of oxidation, exothermicity and carbon yield of some precursors[7]. The other studied co-monomers include acrylamide and sodium acrylate. The effectiveness of the different co-monomers in reducing the initiation temperature of cyclization can be expressed in the decreasing order as:

Itaconic acid > methacrylic acid > acrylic acid >acrylamide[8].

Figure 2: Polymerization process flow chart



3. SPINNING PROCESS:

Wet spinning is used for most commercial PAN based carbon fibre precursor processes and is gradually being replaced by air gap (dry jet wet) spinning. Melt spinning of a plasticized PAN has been used but is yet to become a commercial process.

The dope is pumped through spinneret into the coagulation bath which is mixture of solvent (DMAc) and non-solvent (Water) with desired composition and temperature[9]. The spinneret has holes through which the dope comes out and fibre formation occurs. The spinneret hole is made such that it will have a conical entry to reduce the pressure drop while dope entry in jets[10]. Cleaning of the spinneret is important since blocked holes will introduce unevenness in extrusion which leads to the higher variation in filament properties. The concentration of dope should be optimized since very low concentration will lead to high recovery cost and high concentration will lead to polymer processing issue mainly because of increased viscosity. Line speed in coagulation and tension is gradually applied to newly formed tow with stretching continuing throughout the process to orient along the axis.

PAN coagulates in the spin bath. Initially skin formation takes place and then the spin bath diffuses through the centre of filament giving porous gel network formed by separation of polymer solution into a polymer and solvent rich phase. Structure is a gel network of interconnected polymer fibrils separated by voids of size about 0.3micrometre or greater[11]. The rate of diffusion depends on temperature and concentration. Coagulation rate is controlled to limit internal pores formation, surface defects and skin core[12]. Stretching is limited by rate of coagulation and speed of fibre drawing (fibres stretch more in gel state because the occluded solvent limits the cohesive forces between molecular chains thereby allowing the chains to unfold and form an oriented network with a reasonable distribution of pores and void sizes)[13].

Irrespective of solvent or coagulation system used in wet spinning, a fibrillar structure is generated in an oriented form during coagulation. The porosity is initially controlled by coagulation and subsequently reduced by stretching and drying. The cross-section relates to the volume transfer rate of spin-bath liquid (non-solvent) into fibre versus outward transfer of solvent. The fibre skin limits the volume that fibre can occupy and if less volume of solvent diffuses out, we obtain a kidney shaped cross-section.

4. ACRYLIC FIBRES WITH HIGH ORIENTATION INDEX:

The production of high tenacity acrylic fibres requires high molecular weight polymer (with an order of magnitude equal to 10^5)[14]. The factors that affect the physico-mechanical properties of fibres are the selection of co-monomer while producing PAN polymer, the method of polymerization, the type of reactor used for polymerization, reaction parameters, the moisture content of PAN polymer powder obtained after drying, the type of solvent used for dope preparation, the filtration of dope, type of spinneret used, coagulating conditions, type of finish oil used, drying and drawing.

4.1 EFFECT OF FIBRE FORMING CONDITIONS:

The important fibre-forming conditions are type of spinning bath, spinning temperature, drawing temperature, drawing ratio, and heat- treatment conditions.

The microvoid content of filaments that are obtained by spinning into aqueous baths is in many cases markedly larger than the microvoid content of filaments obtained by spinning into non-aqueous baths. Reduced spinning and drawing bath temperatures are favourable to improved fibre microstructure[15]. Drawing of filaments results in great improvement of fibre microstructure. The temperature of heat treatment in the dry state has an important meaning for the formation of the internal microstructure. The heat treatment in the wet state markedly changes the internal micro-structure of both water- swollen gel-like filaments and dried filaments.

A consideration of the relation between small-angle scattering power, which is a measure of the relative content of micro-voids of colloidal dimensions, and the properties of the fibre, such as specific gravity, cross-sectional aspect, degree of water retention, and dyeability, leads to a better understanding of the meaning of the internal micro structure of acrylic fibre. [16]

4.2 EFFECT OF COAGULATING BATH CONDITIONS:

The parameters to be considered are solvent concentration in the bath and the bath temperature. When the bath temperatures (above 50°C) and the solvent concentration is high (above 70 wt%), the flux of solvent outward is greater than the flux of solvent inward leading to swelling of the fibre giving us a circular cross section. However, this also leads to an increase in the void content thus affecting the linear density of the fibre.

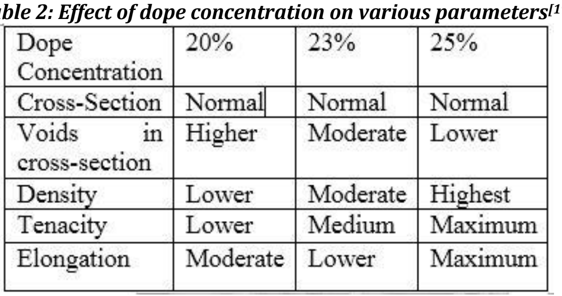
Figure 3: Micro voids formation [17].

In contrast, at lower coagulation temperatures and typical solvent concentrations (below 70 wt%), the outward diffusion of solvent is higher and the perimeter of filament in contact with

non-solvent is solidified early. As the outward diffusion of solvent continues, the filament collapses resulting in a non-circular (bean-shaped) cross-section.[18]

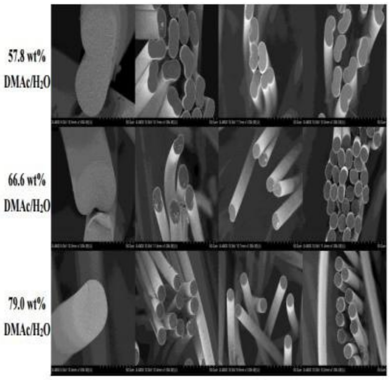
Extensive research has been carried out to obtain circular cross section with minimum voids by altering the solvent concentration and temperatures of coagulating bath. Best results were obtained when the solvent concentration was kept high and the temperatures low (below 20°C).

Table 2: Effect of dope concentration on various parameters[19].



Dope Concentration	20%	23%	25%
Cross-Section	Normal	Normal	Normal
Voids in cross-section	Higher	Moderate	Lower
Density	Lower	Moderate	Highest
Tenacity	Lower	Medium	Maximum
Elongation	Moderate	Lower	Maximum

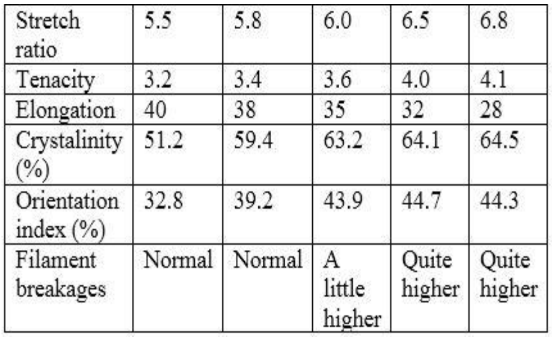
Figure 4: Effect of solvent concentration on the fibre cross-section[20]



4.3 EFFECT OF DOPANT CONCENTRATION:

The parameters to be considered here are the solvent concentration in the dope and the amount of additives. Higher the solvent concentration, lower is the dope concentration. Dope is prepared by adding suitable solvents to the polymer solution which is allowed to stand and then deaerated by heating and subjecting to vacuum and finally sent to the spinning line after filtration. The dope concentration depends on the molecular weight of the polymer and the solubility in chosen solvent and is usually kept below 25%[21]. Higher the additives, less is the tenacity of acrylic fibres.

Table 3: Effect of stretch ration on various parameters.[19]



Stretch ratio	5.5	5.8	6.0	6.5	6.8
Tenacity	3.2	3.4	3.6	4.0	4.1
Elongation	40	38	35	32	28
Crystalinity (%)	51.2	59.4	63.2	64.1	64.5
Orientation index (%)	32.8	39.2	43.9	44.7	44.3
Filament breakages	Normal	Normal	A little higher	Quite higher	Quite higher

High dope concentration gives more economic recovery but it is not favoured because:

1. Dope will be too viscous to pass through the spinneret at required rate
2. It will be more likely to form gels which are difficult to filter out and block the equipment.

4.4 EFFECT OF STRETCHING (DRAWING):

On stretching, the amorphous and crystalline region gets oriented along the fibre axis and voids get elongated. Molecules within the chain slide past one another and align parallel, enabling cross-linking to form by dipole interactions forming two dimensional rod structures. Stretching of the fibres increases the orientation of polymer chains within the structure leading to higher tensile strength. The parameters to be considered are the stretch ratio and the stretching temperatures. The crystalinity and the orientation index of fibre improves significantly on increasing the stretch ratio. However, a stretch ratio above 6 usually leads to fibre breakage and thus it is kept below 6.[22] The temperature on the other hand affects the tenacity. The elongation is unaffected. At higher temperatures the tenacity of acrylic fibres decreases leading to fibre breakages.

5 CONCLUSION

The PAN polymer should be produced by aqueous slurry polymerization technique following free-radical chain polymerization mechanism since it is most suitable for textile fibres. Co-monomers should be used instead of using pure homopolymer. Acrylonitrile and methacrylic acid is considered as the ideal pair. The solvent used in dope preparation should be compatible with the PAN polymer to avoid lump formation. Dissolution, de-aeration and filtration of the dope is very critical. The polymer used for fibre production should have high molecular weight. Non-aqueous baths for spinning cause less microvoid formation as compared to aqueous baths. The spinning and drawing temperatures should be low to support the ideal microstructure formation. The solvent concentration in the coagulating bath should be high and bath temperature should be low. The solvent solubility and the dope should be high and the concentration should be kept below 25%. The stretch ratio during spinning should be kept below 6

REFERENCES

[1] Soo-Jin Park, Gun-Young Heo Precursors and Manufacturing of Carbon fibres, 2015, pp.31-66

[2] E. Ashley Morris, Matthew C. Weisenberger and Gregory Wilson Rice, Properties of PAN fibres solution spun into a chilled Coagulation Bath at High solvent Compositions, Fibres 3.4, 2015, pp. 560-574

[3] Morris, Elizabeth Ashley. "Bench-scale, Multifilament Spinning Conditions Effect on the Structure and Properties of Polyacrylonitrile Precursor Fiber." (2011).

[4] Peter Morgan, Taylor and Francis, Carbon Fibres and their Composites, 2005

[5] Odian, George. Principles of polymerization. John Wiley & Sons, 2004.

[6] Carrott, P. J. M., et al. "Preparation of activated carbon fibres from acrylic textile fibres." Carbon 39.10 (2001): 1543-1555.

[7] Peebles LH, Carbon fibres Formation, Structure and Properties, CRC Press, Boca Raton, 1995.

[8] Bajaj, P., T. V. Sreekumar, and K. Sen. "Thermal behaviour of acrylonitrile copolymers having methacrylic and itaconic acid comonomers." Polymer 42.4 (2001): 1707-1718.

[9] Capone,G.J. Wet-spinning Technology, 1995, pp. 69-103 In Acrylic fibre technology and applications

[10] Tsai, J.S. Su, W.C. 1991, Control of cross section shape for PAN fibre during wet-spinning

[11] M.A. Rahman, A.F.I., A. Mustafa, B.C. Ng, H. Hasbullah, M.S.A. Rahaman and M.S. Abdullah, The Effect Of Coagulation Bath Temperature On The Mechanical Properties Of Pan-Based Carbon Fiber. P. 169-179.

[12] Juan Chen, C.-G.W., Xing-Guang Dong, And Huan-Zhang Liu, Study On The Coagulation Mechanism Of Wet-Spinning Pan Fibers. Journal Of Polymer Research, 2006. 13: P. 515-519.

[13] Jin-Shy Tsai, W.-C.S., Control Of Cross-Section Shape For Polyacrylonitrile Fibre During Wet-Spinning. Journal Of Materials Science Letters, 1991. 10: P. 1253-1256.

[14] Er. A.K. Tripathy, Dr. Divya Hiran Effect of process parameters on tenacity of acrylic fibres

[15] Mitsubushi Rayon Co.Ltd, Chem Abstract 1986

[16] Heyi Ge, H.L., Juan Chen, Chengguo Wang, The Skin-Core Structure Of Poly(Acrylonitrile-Itaconic Acid) Precursor Fibers In Wet-Spinning. Journal Of Applied Polymer Science, 2007.

[17] J. Ferguson, C.D., G.R. Mckay, Rheological And Coagulation Features In The Wet Spinning Process. Journal Of Non-Newtonian Fluid Mechanics, 1980. 6: P. 333-338.

[18] Takahashi M., Nukushina Y.;Kosugi S. 1964 Effect of fibre-forming conditions on the microstructure of acrylic fibre, Text. Res. J, 34, 87-97

[19] Law, S.J. Mukhopadhyay, S.K. 1996 Investigation of wet-spun acrylic fibre morphology by membrane technology technique.

[20] Gong-Qiu Peng, Y.-F.W., Yong-Gang Yang, And Lang Liu, A Novel Method For Investigating The Structural Uniformity Of Polyacrylonitrile Nascent Fibers. International Journal Of Polymer Anal. 2008.

[21] Christopher J.S. Petrie, A.P., Spinning Viscosity. Journal of Non-Newtonian Fluid Mechanics, 1995. 57: P. 83-101.

[22] Lawrence, Carl A., ed. Advances in yarn spinning technology. Elsevier, 2010.