RESEARCH ARTICLE

Effect of Wet-Spinning Parameters and Spin-Finish Application on Production of Polyacrylonitrile Precursor for Carbon Fibre Production

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ABSTRACT: The precursor fibre should possess the required properties to be heat treated to form carbon fibres. The polyacrylonitrile (PAN) precursor fibre properties are hugely dependent on wet-spinning and post wet-spinning finishes. The temperature and stretch conditions affect the orientation and resultant mechanical properties. The spin finish oil applied gives an ease of operation and better performance. This article deals with establishing effects of major parameters like temperature, stretch and finish application to use certain PAN precursor for making carbon fibres, followed by some basic experimentation related to improvised formulation of spin finish oil for PAN precursor fibre.

KEYWORDS: Polyacrylonitrile precursor, Spin finish, Wet-spinning, Thermal stretch

1. INTRODUCTION

PAN is the most popular precursor for carbon fibre manufacturing as it has a continuous carbon backbone and the nitrile groups are ideally placed for cyclization reaction to occur, producing a ladder structure polymer. The carbon content in the acrylonitrile (CH_2=CHCN) monomer is 67.9%. Due to such a high carbon content PAN precursors give a carbon yield of 50-55% coupled with the ability to produce high tenacity and high modulus fibres, making it a highly popular precursor in the carbon fibre industry. Wet-spinning of polyacrylonitrile (PAN) fibres is the most widely used system in manufacture of acrylic fibres [1]. Parameters of wet-spinning play a major role in achieving the desired properties of PAN fibres (to be used as precursor for carbon fibres). Temperature during wet-spinning, stretch conditions, spin finish application are few parameters discussed in this article [2].

The PAN polymer is mixed with an organic solvent in a high shear homogenizer with rigorous mixing for several minutes under vacuum[3]. The mixture is then subjected to dissolution. The dissolution process starts in a mixer where the temperature is monitored (60 to 90˚C) under vacuum and agitation [4]. Once the polymer is dissolved completely, it goes for dope de-aeration operation to remove any air-bubbles trapped during dope preparation [5]. The de-aerated dope then goes through several stages of filtration through various in-line filters [6]. The filtration is very critical for fibre properties as any trapped particle or gels in the dope can create defects in the filament and reduce the tensile strength. Once the dope is completely filtered, it is sent for the dope extrusion which is again a controlled process with flow rate, temperature and pressure as the parameters. The speed of all the fibre line rollers is set as desired and the spinning process starts. The coagulation process is carefully monitored for the processing parameters (temperature, concentration and flow rate[7]. The concentration of solvent is kept in decreasing order for gradual coagulation. After complete coagulation, fibre is washed in water with different temperature and stretched simultaneously.

The temperature of water in these baths is monitored [8]. Next bath is filled with spin finish oil. The fibres then go on for the drying process. The initial dryer is kept at about 90˚C for excess and free moisture removal [9]. The next dryer is kept within the range 120 to 140˚C for removal of bound moisture. The fibres are then given a hot stretch and wound on creels [10].

This paper aims to study the effect of wet-spinning parameters and spin-finish oil used on the polyacrylonitrile precursor for carbon fibres. The underlying objective is to optimize the process of acrylic fibre spinning process suitable for carbon fibre production.

1.1 EFFECT OF TEMPERATURE AND STRETCHING

Temperature is a key variable controlling the diffusion of solvent and non-solvent. As in most diffusion processes, an increase in temperature increases the diffusion of solvent and non-solvent. The temperature change might be in coagulation bath or in the polymer-spinning solution [11]. The diffusion rate for the solvent increases faster than the rate for the non-solvent. For acrylic-fibre-spinning systems, the coagulation baths are normally within a temperature range of 0 to 50°C and the polymer spin solution is between 25 and 120°C.

On stretching, the amorphous and crystalline region gets oriented along the fibre axis and voids get elongated [12]. Molecules within the chain slide past one another and align parallel, enabling cross-linking to form by dipole interactions forming two dimensional rod structures [13]. The orientation or stretch given to the wet-spun acrylic fibre is very important in altering the fibre structure and enhancing fibre properties. On increasing the overall stretch, the ratio of denier/filament reduces.

The fibre temperature is increased above the wet glass transition temperature, and the fibre is stretched 3 to 12 times between set of rollers with hot water as the heating

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medium. In this stretching process the orientation of the fibrillar network formed in the spin bath is increased and the fibre strength is increased. [14]

1.2 EFFECT OF SPIN-FINISH APPLICATION

A spin finish or lubricant is applied to synthetic fibres for ease of processing during manufacturing. Synthetic fibres easily generate electrostatic charge while they rub against each other or different machine parts[18]. This charge can cause major problems in processing. Electrostatic charge build-up can cause fibres to repel or attract each other. They can also stick to the machine parts they come in contact with. This can disrupt yarn formation and lead to non-uniform PAN precursor tows. The primary function of a spin finish is to eliminate the build-up of static electric charges on fibres during processing. A spin finish can reduce the amount of friction to a level which avoids problems such as end-breaks in fibres[19]. Ensuring a continuous filament tow is necessary to obtain optimum yield of carbon fibres. [20] At the same time, the spin finish should be compatible with the fibre. The layer of spin finish should not hamper any of heat treatment processes for the final carbon fibre production [21].

EXPERIMENTATION WITH SPIN FINISH OIL

Table 1: General Components of Spin-Finish Oil

Component	Function
Lubricants	To enhance the sliding of the fibres against one another
Emulsifiers	To bind the components in the finish
Antistatic agents	To reduce static charge build-up
Cohering agents	To promote adherence between fibre strands to prevent hairiness and lapping.
Antioxidants	To give the fibres the ability to resist the formation of insoluble resinous compounds in the presence of oxygen
Antifoam agents	To prevent generation of foam
Wetting agents	To reduce surface tension of spin finish solution
Bactericides	To prevent degradation of spin finish composition

2 MATERIALS AND METHODOLOGY

For comparative study of spin finish oil suitable for PAN precursor fibres, initially we made a solution consisting of commercial silicon oil and epoxy compound having fixed solid content [22]. This is the reference solution-Reference solution. Based on general composition for spin finish oil, another formulation was prepared. The formulation prepared consisted of:

Silicon Oil, Surfactant, Acid (to maintain the required pH), Antibacterial agent, Epoxy based Lubricant and Water. The spin finish solution was prepared and its properties were checked. To compare the properties of the solution made with the reference solution, we diluted it to lower the solid content and further filtered it to achieve the desired solid content. This is- Formulation 1.

A third solution was prepared with inherently lower solid content and we used hot water instead of room temperature water. This solution was then filtered. This is- FORMULATION 2. All the solutions made were checked for their solid content, viscosity and the behavior with change in shear rate.

The viscosity of a fluid can be calculated by the following formula:

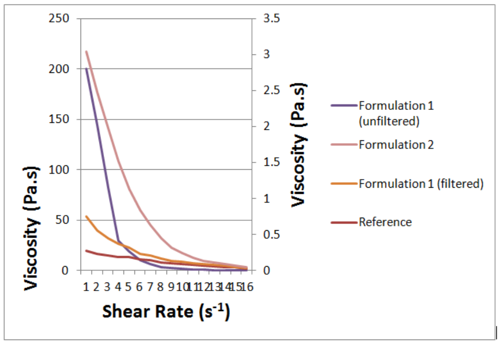
Viscosity = Shear stress/ Shear rate

3. RESULTS AND DISCUSSIONS

The properties of all the solutions are summarized below (Table 2). Based on these properties, the viscosity of each solution was plotted with respect to changing shear rate.

Table 2: Testing of Spin Finish Oil

Test for	**Property tested**	**Value**	**Method/ Machine used**
SOLUTION 1	Solid Content	26.38%	Gravimetry
	Viscosity	0.16 poise (at 10 RPM)	Brookfield Viscometer
	Behavior with changing shear rate	0.246 poise (at 10 s^{-1})	Rheometer
	pH	5.36	pH meter
SOLUTION 1 (Unfiltered solution)	Solid content	24.10%	Gravimetry
	Viscosity	0.22 poise (at 10 RPM)	Brookfield Viscometer
	Behavior with changing shear rate	2.2 poise (at 10 s^{-1})	Rheometer
	pH	4.4	pH meter
SOLUTION 2 (Filtered solution)	Solid content	21.69%	Gravimetry
	Viscosity	0.20 poise (at 10 RPM)	Brookfield Viscometer
	Behavior with changing shear rate	0.3 poise (at 10 s^{-1})	Rheometer
	pH	4.4	pH meter
SOLUTION 3 (Solution with lower solid content)	Solid content	23.7%	Gravimetry
	Viscosity	0.22 poise (at 10 RPM)	Brookfield Viscometer
	Behavior with changing shear rate	0.138 poise (at 10 s^{-1})	Rheometer
	pH	4.62	pH meter



Graph 1: Behavior of spin finish solutions with changing shear rate

All the solutions prepared are shear thinning in nature. This property is useful especially when we want the solution to be sufficiently viscous at the same time to form a thin layer on the fibre surface. The prepared solution (Formulation 1) behaved similar to the solution containing commercial silicon oil and epoxy resin. Using just the REFERENCE

SOLUTION for spin finish application gives all round performance of the spun fibre; hence the prepared solutions are compared to the same. Formulation 1 is therefore a good composition for spin finish application than FORMULATION 2, since its behavior is close to the REFERENCE SOLUTION. This was a simple experimentation to establish basic properties required in spin finish oil for optimum performance of PAN precursor fibres.

4. CONCLUSION

Commercial production of carbon fibres using PAN precursor gives a yield of less than 50%, whereas the theoretical char yield of PAN is 68% [23]. The yield can be increased if properties like temperature, stretching and spin finish application are optimized, that also determine the overall performance of the PAN precursor. The polymerization and wet-spinning processes must be optimized such that near-defect free, uniform fibres coagulate out of the spinning bath to form perfect PAN precursor fibres, subsequently forming carbon fibres eventually. Parameters such as temperature and stretching are crucial since they control the crystallinity and the orientation of the fibres [24]. To ensure that the fibres do not break during the further processes and to reduce the static charge generation, adequate application of spin finish oil is a necessity. Hence, such parameters must be monitored in the wet-spinning of PAN to produce a suitable precursor for carbon fiber [25].

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