

Effect of tow size on solvent extraction from PAN fibers during wet spinning- A MATLAB-based FDM study

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Abstract

Residual solvent content in the precursor fibers from polyacrylonitrile (PAN) is one of the key parameters that severely affects the mechanical properties of resultant carbon fibers to a large extent. Although its significance is well-known, the influence of precursor tow size (i.e., number of filaments) on the kinetics of solvent removal is not yet reported. In order to develop the relationship for better PAN precursor spinning line design, a computational model using MATLAB is presented. The model uses a finite difference method (FDM) approach using Fick's second law of diffusion for dynamically determining the residual solvent content in fibers after passing through various units. It is assumed that the multifilament tow takes the shape of a cylindrical geometry, considering hexagonal closed packing (HCP). The models were simulated for 1K, 2K, and 3 K precursor fiber tows passing a typical wet-spinning line. The model data values are also verified with consistent data recorded from Gas Chromatography-Mass Spectrometry (GC/MS) equipment. According to the data presented, solvent removal efficiency significantly reduces as tow size increases, while the washing unit operation is the most influential on extraction due to longer retention times. While significant size reduction occurs in the stretching unit but its influence on solvent reduction is not comparable with the washing unit. This paper presents a theoretical and reliable methodology for optimizing spinning plant parameters, selecting appropriate units, and developing higher-quality PAN precursors for high-performance carbon fiber applications.

Keywords:

Carbon Fiber, Polyacrylonitrile (PAN), Wet-Spinning, Finite Difference Method, Solvent Diffusion, Process Modelling.

Citation

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1.0 Introduction

The residual solvent content in PAN fiber is a very crucial parameter for the high-strength Carbon fiber production process. The high-solvent content severely affects the morphology of the PAN precursor, which results in microvoids in the carbon fiber [1]. Thus, an optimal quantity of solvent is desirable in the PAN precursor fiber for optimal strength and modulus in carbon fibers. Various spinning parameters, such as tow size (number of filaments), spinning bath concentrations, spinning line design, and spinning speed, have a direct influence on the solvent content in PAN precursor fibers [2,3]. As reported by Gao et al, the higher spinning line speed resulted in higher PAN precursor strength, but due to the presence of higher solvent content (~820 ppm), it resulted in lower strength in carbon fiber [4].

However, the PAN fibers spun at a lower spinning speed resulted in comparatively lower strength in the PAN precursor along with lower solvent content (~493 ppm) in it, resulting in higher strength in the Carbon fibers. This study shows the great significance of solvent content in PAN precursor that significantly affects the carbon fiber properties, where higher solvent content results in a higher number of microvoids in carbon during the heat treatment process. Though the importance of solvent content can be observed, the minor increase in it from ~500 ppm to 820ppm drastically reduces the strength in carbon fibers, but this study is only limited to the effect of one influential factor. However, the influence of other factors is yet to be known, which can help researchers and industry professionals to further improve the properties of the carbon fiber. Thus, this literature gap opens up an opportunity for further research in the related field.

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In this work, a MATLAB-based study is performed along with experimental verification to understand the effect of tow size and spinning unit components on the solvent content present in PAN precursor fibers during the spinning process. The effectiveness of the different types of unit and their effect on solvent extraction capability is also studied through the model. Further, the predicted values from the program were compared with the experimental values of the solvent content obtained through GC/MS. Based on the predicted values & experimental values, an optimized spinning line design is also applied and verified.

2. Experimental

Polyacrylonitrile copolymer (Mw: 100 kg/mol) was procured from Technorbital Pvt Ltd. N,N-Dimethyl acetamide (DMAc) solvent of commercial grade is used in the study was procured from Balaji amines Pvt Ltd. PAN fibers for the experimental sample preparation were prepared using a wet-spinning machine with 3 different spinneret sizes of (1000 holes) 1K, (2000 holes) 2K, and (3000 holes) 3K with a polymer dope concentration of 20%. The spinning parameters, such as jet-ratio (0.8), total draw ratio (4), take-up speed (1m/min), and bath temperatures (90 °C), were kept the same for all tow sizes.

The MATLAB model based on the finite difference method (FDM) analysis is developed, which determines the diffusion of the dimethyl acetamide solvent in the baths as a function of time and radius of the tow size. The objective is achieved by solving Fick's second law-based mass diffusion equation, considering each filament acting as the nodal point. One more assumption taken for this theoretical study is considering the multifilament tow forms a cylindrical shape as per the hexagonal close packing (HCP) theory in the form of multiple layers under tension. This assumption is taken to simplify the theoretical framework & considering that this form is most suitable for maximum packing efficiency and uniformly distributing the stretching load.

The experimental verification of solvent content from the wet-spun fibers of different tow sizes was done with a Gas chromatograph and mass spectrometer (GC/MS), Shimadzu GC/MS QP2010. 5g samples of the final processed fiber samples were taken & tests were performed using the headspace method. The solvent content obtained from the GC/MS is normalized with the pure DMAc solvent value (taken as standard). The detailed method of normalization and GC/MS reports is represented in the supplementary information.

3. Results and Discussion

The model for the tow geometry is developed based on the HCP theory, which gives the highest packing fraction (74%) and also conforms with the material behaviour to attain the lowest surface area under tension [5,6]. During this transition, the multifilament tow forms the structure by

forming multiple layers covering the layers underneath it and preventing their direct contact with the outside medium [7]. Figure 1 represents the schematic of the layering formation by the multifilament tow under tension.

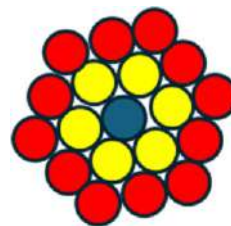


Figure 1: Schematic of the Hexagonal pack structure formed by multifilaments

With reference to the HCP theory for the formation of such cylindrical structure in multilayer form, the number of layers can be determined by the number of multifilaments present in it [8]. Thus, the number of layers obtained from 1K, 2K, and 3K filaments are obtained to be 18 layers, 26 layers, and 32 layers, respectively. Moreover, based on the HCP theory, the effective radius before any effect of the jet-ratio & draw ratio for the tows of 1K, 2K, and 3K can also be calculated (as per equation 1), and determined to be 3.16mm, 4.47mm, and 5.47mm, respectively [9].

$$R_{\text{eff}} = r \times \sqrt{N} \dots (1)$$

Where, R_{eff} is the effective radius of the Tow,

r is the radius of the single filament, and

N is the number of filaments

For efficient and faster calculation of the concentration reduction during the various processes, Fick's second law of mass diffusion from a cylindrical geometry system is employed, due to its ability to link concentration with time and spatial dimension. The law states that the rate of change of concentration with respect to time can be determined from the double spatial derivative of the concentration. The governing equation for the same for cylindrical geometry is represented in equation 2 [10].

$$\frac{\partial C}{\partial T} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{1}{x} \frac{\partial C}{\partial x} \right) \dots (2)$$

Where, C is the solvent concentration,

x is the spatial dimension,

D is the diffusion coefficient of the solvent in the outside medium, and

T is the time.

Though the equation is compatible with solving the cylindrical geometry system, but it requires the system to be homogeneous for computation. While in cylindrical geometry, a structure formed by multifilament tow is bound to have gaps in between due to its 74% packing efficiency.

Along with that, the bigger geometry requires a higher value of time difference, which severely affects the accuracy of the system, while lower time difference values may result in higher computing time. Thus, to reduce the computing equations and increase efficiency, the discretization of the cylindrical system is done along a single axis (along the radial direction). The discretized form of the governing equation is represented in equation 3 [11].

Governing equation:

$$C_i^{m+1} = C_i^m + \frac{D\Delta t}{\Delta r^2} \left[\left(1 + \frac{\Delta r}{2r_i}\right) C_{i+1}^m - C_i^m + \left(1 - \frac{\Delta r}{2r_i}\right) C_{i-1}^m \right] \dots (3)$$

Where, C_i^m is Concentration at radial position $r_i = i\Delta r$ and time $t_n = n\Delta t$,

D is the Diffusion coefficient of the DMAc solvent in the water ($1.41 \times 10^{-9} \text{ m}^2/\text{s}$) [12],

Δr is the Spatial step size,

Δt is the Time step size, and

r_i is Radial position, $r_i = i\Delta r$.

m is a step for time, and

i is the spatial step.

Initial conditions:

$$C = C_i^m \text{ at } 0 < r \leq R_{\text{eff}} \dots (4)$$

$$C = 0 \text{ at } r > R_{\text{eff}} \dots (5)$$

Boundary conditions:

$$C = 0 \text{ at } r > R_{\text{eff}} \text{ for } 0 < \Delta t < T \dots (6)$$

Therefore, the calculation of the concentration profile with reference to time & spatial dimension (radius) is done for various tow sizes (1K, 2K, and 3K filaments) to determine the solvent reduction in the various components of the wet-spinning line. For normalization, the determination of the solvent profile is done by designing a line with similar components arranged in the same arrangement and at similar speeds to give a similar draw ratio. Therefore, the effect of line designing on the solvent extraction from the various tow can be compared. The designed spinning line for the solvent extraction calculation consists of 2 coagulation baths, 2 stretching units, and 1 washing unit respectively. The flow diagram of the line is represented in Figure 2, and details of processing parameters are given in Table 1.

Table 1: Parameters of wet-spinning line for solvent extraction

S. No.	Unit	Parameters		
		Temperature (°C)	DMAc Concentration (%)	Residence time (s)
1	Coagulation Bath-1	30	70	120
2	Coagulation Bath-2	30	0	41.63
3	Washing unit	90	0	570
4	Stretch Bath-1	90	0	24.27
5	Stretch Bath-2	90	0	17.65

The calculation of the solvent extraction from the various tow sizes (1K, 2K, and 3K) is performed according to the FDM model with respective initial and boundary conditions. Figure 3 represents the solvent reduced from the various tows at different stages of the wet-spinning line. The effect of layering formed due to a larger number of filaments on solvent extraction was found to be prominent at all stages. The initially reduced value of solvent in 1K, 2K, and 3K filaments after the coagulation bath was found to be 71.5%, 74.1%, and 75.3% respectively. This also correlates well with the coagulation theory, where a single filament undergoes a double diffusion process and coagulates to form the semi-solid gel fiber structure [13]. The residual solvent content in 2K and 3K was obtained to be the same, while 1K shows a comparatively lower value, indicating the role layer structure formed by the tows and their critical limit, which reduces solvent extraction efficiency due to more number of layers. Thus, it also indicates that the major factor responsible for the solvent extraction difference between 2K and 3K mainly depends upon the further components of the spinning line, which are responsible for stretching and washing of the fibers. As shown in Figure 3, the reduction in solvent concentration is more prominent in the subsequent units of the wet-spinning machine. One noteworthy observation is in the solvent reduction data after washing units, where no further notable reduction was observed for the 1K filament yarn. This indicates the efficient washing & solvent extraction in the washing unit. Thus, the difference between the stretching unit and washing unit can be observed from the plots. Though the stretching unit does reduce the fiber size, which exposes the new surface, but residence time remains less. While the washing unit has a much higher residence time, no reduction occurs in size. Still, this prolonged time is enough to efficiently extract the solvent from the tow. For better understanding, the comparative simulation video of both the stretching unit and washing unit for 1K is illustrated as SV1K and WV1K in the supplementary information.

While the higher number of layers present in 2K and 3K showed resistance to the washing process, in comparison to 1K showed a very drastic reduction in the average solvent concentration of yarn. Moreover, the model is also tuned to



Figure 2: Hypothetically designed wet-spinning line for solvent extraction

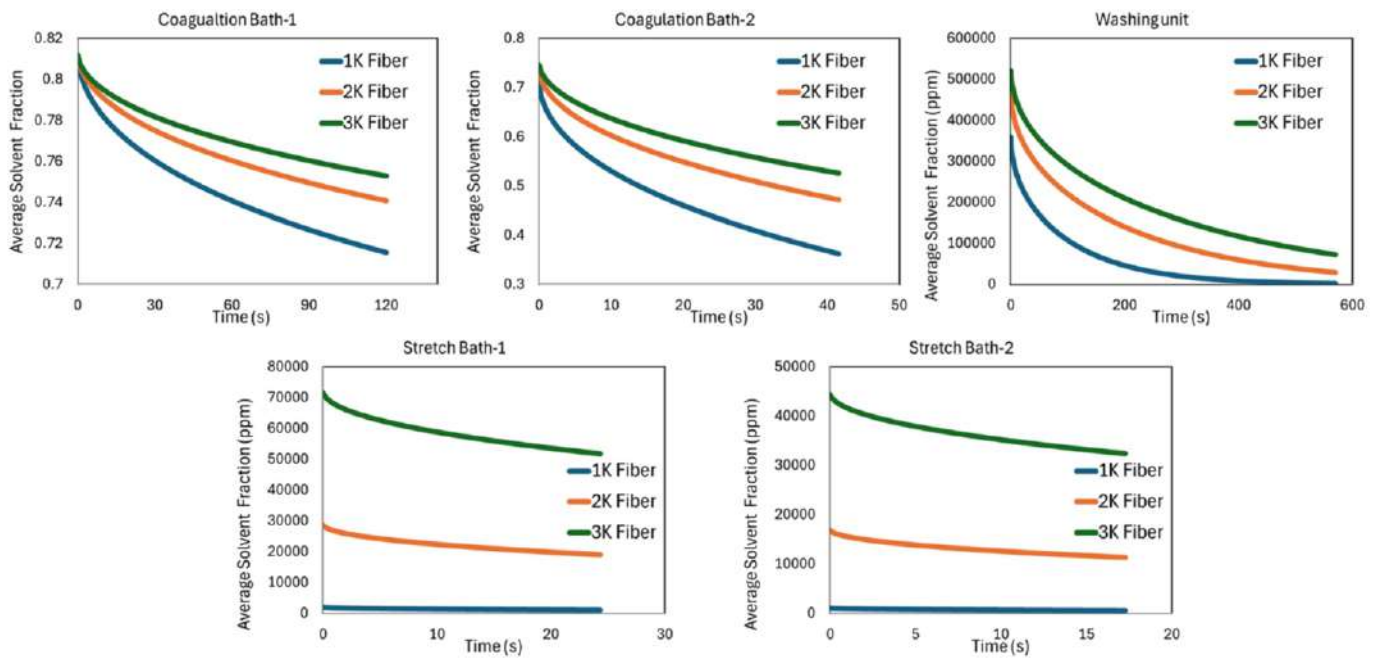


Figure 3: Solvent extraction profile for 1K, 2K, and 3K filaments at various stages

determine the penetration of the water into the core filaments of the yarn is also performed. The 2D colour map plot of the 1K, 2K, and 3K filament yarns after passing through the stretching units and washing unit is represented in Figure 4. It can be clearly observed that the reduction in the concentration is obtained in the washing unit only with a more prominent reduction obtained in 1K than in 2K and 3K. While the clear distinction of solvent extraction can be made in comparison to 1K and 2K & 3K filament yarns in both the stretching units & washing unit. Due to the smaller yarn size & less number of nodal points, 1K showed a drastic and faster reduction in the concentration values than 2K & 3K [14]. It is anticipated that a similar effect will also take place with the actual yarn samples.

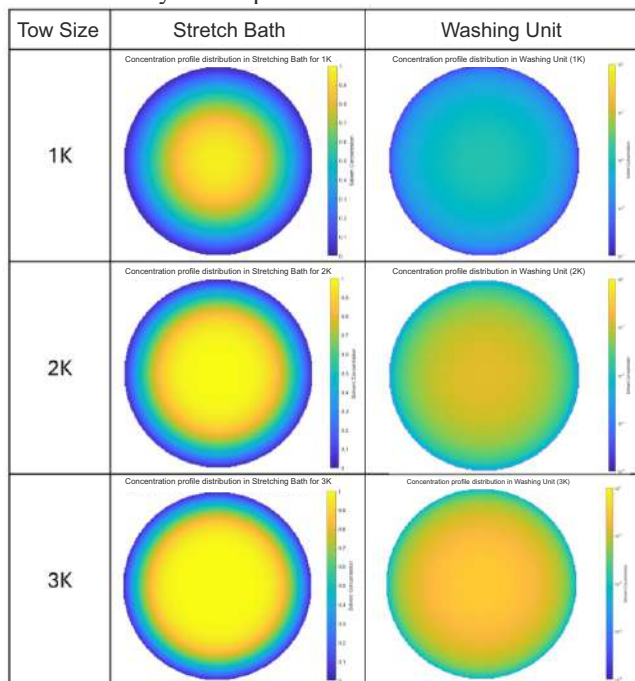


Figure 4: Solvent concentration reduction in: (A) Stretching unit, (B) Washing unit

Thus, the FDM study clearly indicates the effectiveness of the function of the different units used for the wet-spinning process. Multiple process parameters, such as the effective radius of the tow, tow size, and residence time, play a significant role in the residual solvent content in the PAN fiber. However, without experimental validation, these results only give a superficial comparison of the PAN fiber properties with different tow sizes due to the wet-spinning line design. To validate the FDM results with the actual solvent content present in the fibers, the respective fiber samples were tested with a GC/MS machine. The DMAc solvent gives a solvent peak at 7-7.3 R-time in GC/MS, which is obtained from the analysis of the pure DMAc solvent. With reference to the peak properties of DMAc from the pure DMAc solvent (standard), the comparative content present in the yarns was determined to obtain the solvent content present in the fiber sample [15]. The solvent content in 1K, 2K, and 3K fiber tows was tested with GC/MS for the residual solvent content and is represented in Table 2.

Table 2: Residual solvent content in the fibers with different tow sizes

S. No.	Tow size	FDM predicted value (ppm)	Experimental value (ppm)	Difference (ppm)
1	1K	327.1	122.6	204.5
2	2K	11,258.1	10,889.5	368.9
3	3K	32578.5	26005.2	6573.7
4	2K-modified line	897.2	2597.8	-1700.6
5	3K-modified line	5464.4	5983.4	-519

From Table 2, it can be observed that the predicted solvent content values through the FDM model are in accordance with the experimental values obtained from the GC/MS values, indicating the FDM model is valid. It can be observed

that the reduction in the solvent content (in ppm) values holds good for the 1K and 2K filaments HCP model. Whereas above it (for 3K filaments), the packing must follow a different geometry due to their own weight, which increases the surface area & more contact points with the water, along with a reduced number of layers. Therefore, this study shows its direct application in the wet-spinning of PAN, where appropriate unit placement and type not only directly influence the mechanical properties but also the solvent content in the yarn as well.

Therefore, based on the information, the revised hypothetical wet-spinning line is designed with 2 washing units running at the same speed. Since washing is found to be more efficient in extracting the solvent from the stretching unit. The FDM results show that there will be a drastic decrease in the solvent content value in 2K filaments compared to 3K filaments. However, it is observed that the HCP theory gave a better prediction for the 3K filament result than the 2K. For experimental samples, the 2K and 3K filament yarns, right after washing from the washing units, were collected and washed again. The FDM-based value & experimental values obtained through GC/MS are represented in Table 2. It can be observed that the values are in good agreement and show reduced solvent values from the previous single wash values. This shows that through this theoretical framework approach, a wet-spinning line can be designed for high-strength PAN fiber, which may also result in high-performance carbon fiber with fewer microvoids in it.

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4. Conclusion

An FDM based computational model was successfully developed in this work to mimic and simulate the influence of tow size on solvent removal from PAN precursor fibers in the wet-spinning process. The results confirmed that smaller 1K tows are significantly more efficient in solvent removal than larger 2K and 3K tows, resulting in solvent content values as low as 327 ppm in 1K. The difference is caused by the smaller effective radius and fewer filament layers in the 1K tow, which decreases the diffusion path length for the solvent. The most important finding was the crucial role of the washing unit, whose longer residence time is indispensable for removing residual solvent from the tow's core since this is less effective with short-duration stretch baths. The predictions of the FDM model showed good agreement with the GC/MS experimental measurements, which validated the FDM model as a robust and inexpensive tool for process simulation. The present model provides valuable knowledge to engineers for better line design and process parameters, which reduces the need for extensive experimental trials and helps to customize the precursor properties for the synthesis of high-strength carbon fibers.

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