



# Evolution of self-generating porous microstructures in polyacrylonitrile-cellulose acetate blend fibres



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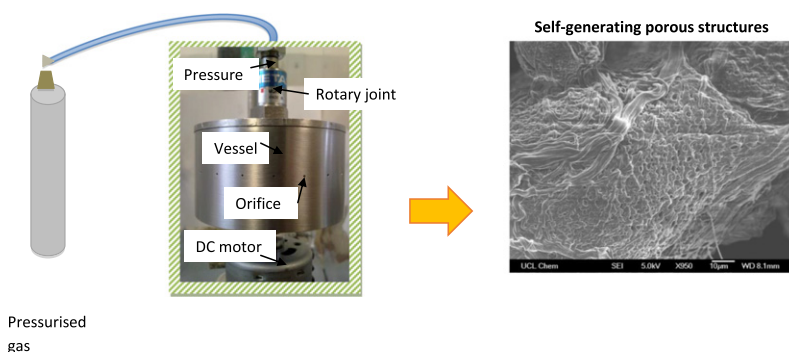
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## HIGHLIGHTS

- Gyration under pressure was used to spin polyacrylonitrile-cellulose acetate blend fibres.
- Self-generating porous structures were obtained by controlling working pressure.
- Artificial porous fibrous structures were made by leaching and etching.
- Structural evolution in polyacrylonitrile-cellulose acetate blend fibres is explained.
- A mathematical model has been developed to predict fibre diameter.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Polyacrylonitrile (PAN), cellulose acetate (CA) and polyacrylonitrile - cellulose acetate (PAN-CA) fibres were formed in single and binary solvents which were subjected to gyration under pressure. Fibres in the diameter range 200–2000 nm were generated using a rotating speed of 36,000 rpm and a working pressure of  $3 \times 10^5$  Pa. Long fibre morphologies with isotropic distribution of fibre orientation were obtained from PAN polymer solutions with a concentration of 5–15 wt%. Short fibre morphologies with anisotropic distribution of fibre orientation were produced for CA polymer solutions with a concentration of 25 wt% and below this concentration polygonal beads were generated. PAN-CA fibre bundles were generated and these showed remarkable self-generating porous characteristics when the working pressure was changed from 1 to  $3 \times 10^5$  Pa. For comparison, porous PAN-CA fibres were also generated by solvent etching and porogen leaching techniques and in these the etching time and porogen concentration influenced the pore size of the generated fibres. Fourier transform infrared and Raman spectroscopies were performed to elucidate the bonding characteristics in the fibres. Release characteristics of the porous fibrous structures were studied using vanillin as the active ingredient. A mathematical model which allows the evaluation of the fibre diameter as a function of rotating speed and working pressure is presented and this helps to understand the solvent mass transfer taking place during fibre forming.

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## 1. Introduction

Porous fibres are excellent candidates for enhanced photocatalytic activities owing to their high surface area, attendant dispersions of catalyst functions and superior mass transport. It has been shown that

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TiO<sub>2</sub>/SiO<sub>2</sub> porous fibres had significantly enhanced photocatalytic activity and photodegradation of rhodamine compared to TiO<sub>2</sub> nanoparticles and Degussa P25 [1]. Highly porous graphitic fibres are widely used as a counter electrode in dye sensitised solar cells with high photoconversion performance. Using porous fibres is an ideal strategy for improving the surface of electrodes which in turn influences the rate of electrochemical reaction [2]. These designed architectures have been also exploited in lithium ion batteries and supercapacitors which offer improved energy and power density [3,4]. The potential use of porous polycaprolactone fibres in tissue engineering scaffolds has been reported by evaluating mouse osteoblast cell growth in them and results show excellent cell attachment and proliferation [5,6].

A plethora of methods have been used to generate porous fibres and increase their porosity. Of these, the phase separation method is widely reported, where selected removal of one polymer after spinning a polymer blend from solutions is used to generate multi-phase fibres [7]. Here, when the polymer blend solution becomes thermodynamically unstable and if one of the dispersed phases can be accessed and removed easily without collapse, then internal pores could be created in the fibres [8]. Another method involves using porogens during fibre forming and subsequent leaching out the porogens is done post-processing. For example, removing CaCO<sub>3</sub> in PAN/CaCO<sub>3</sub> fibres using an extraction bath containing HCl/water at various temperature and time intervals can generate porous structures [9]. Alternatively, pores could be formed using a humid environment, in this case water molecules from the atmosphere condense on the surface to leave imprints on fibres [10,11]. However, these methods are not robust and lack simplicity, most of them require post-processing which is time consuming and costly. In addition, the residual additives used in such operations could affect the quality of formed fibres.

Polyacrylonitrile (PAN) is a well-known precursor for carbon fibres, it has a high carbon yield as well as outstanding mechanical properties [12,13]. PAN is a semi-crystalline synthetic polymer obtained through free radical polymerisation of acrylonitrile. The non-meltable ladder structure obtained through cyclisation of PAN molecules is very crucial to avoid melting during carbonisation. The cyclised network of hexagonal carbon nitrogen rings are formed with nitrile groups through a thermal free radical mechanism [14]. Nitrile groups in PAN also have a large dipole moments and provide high cohesive energy density and chain stiffness which result in excellent tensile strength. Cellulose acetate (CA) is a semi-synthetic polymer derived from cellulose which is the most common biopolymer used in biomedical applications such as tissue engineering and drug delivery [15–17]. Cellulose acetate is derived from esterification of cellulose, which is obtained by reaction of cellulose with acetic anhydride and acetic acid in the presence of sulphuric acid.

Pressurised gyration is an attractive method concurrently using centrifugal spinning and solution blowing to form large quantities of nanofibres [18]. The process depends on the concentration of the solute-solvent mixture, rotating speed of the gyration vessel and the working pressure across an orifice to generate fibres on a scale range from nano- to micro-. Thus, this method offers not only control of the polymeric nanofibre diameter and length but also their size distribution [18]. A mathematical model illustrating how the fibres are generated in this process has been described by considering rotational and blowing frames of the spinning process [19]. It is an uncomplicated but efficient technique permitting simultaneous generation of a multitude of polymer nanofibres with regular morphology [20–22]. In addition, pressurised gyration has shown to generate functional microbubbles (rather than fibre) that could be used in drug delivery, antimicrobial vesicles and biosensing [23,24].

The current work discovers a new route to form well characterised self-generating porous polyacrylonitrile-cellulose acetate composite fibres using pressurised gyration. This forming process relies on the destabilising centrifugal force and the dynamic fluid flow acting against the stabilising surface tension of the polymer solution to form fibres at

very high speed. By carefully tuning one of the process parameters, working pressure, porous composite fibres were obtained. Here we use the well-known synthetic polymer polyacrylonitrile in combination with a semi-synthetic polymer derived from natural cellulose to form porous structures. Moreover, for comparison, in this study porous fibres are also made from post-processing techniques such as porogen leaching (sodium chloride) and solvent etching. We describe in detail plausible explanations for forming porous fibrous structures using these routes. Taking vanillin as a model material, the release characteristics of active ingredients from these structures in de-ionised water is studied and findings discussed. We give details of the mechanism of sorption of such active ingredient molecules and their release profile from the porous fibrous structures.

## 2. Materials and methods

### 2.1. Materials

Polyacrylonitrile (PAN) ( $M_w = 150$  kDa) and cellulose acetate (CA) ( $M_w = 30$  kDa) were used as received from Sigma Aldrich, UK. Acetone and dimethylformamide (DMF) were obtained from Sigma Aldrich, UK. Vanillin (Kosher) was purchased from Sigma Aldrich, UK and used as received.

### 2.2. Solution preparation and characterisation

Various concentrations of PAN solutions (5, 10, 15 wt%) were prepared by dissolving PAN powder in DMF and mixing using a magnetic stirrer for 24 h at ambient temperature (~20 °C). Similarly, various concentrations of CA solutions (15, 20, 25 wt%) were prepared by dissolving CA in acetone/DMF solvent mixture. These solutions were subjected to rigorous mixing by a magnetic stirrer until CA was completely dissolved. In addition, 10 wt% PAN-CA composite polymer solution was prepared in acetone/DMF solvent mixture. Various ratios of solvent mixture were used for this study. Of these the 2:1 ratio was chosen as an optimum mixture for this work.

The prepared polymer solutions were characterised by measuring their physical properties such as viscosity and surface tension (Table 1). A Kruss tensiometer K9 was selected and used for measuring the surface tension of the solutions (Wilhelmy plate method). A Brookfield viscometer was used to measure the viscosity of the polymer solutions. All equipment was calibrated before use and all measurements were performed at ambient conditions (20 °C and 42% relative humidity).

### 2.3. Fibre preparation

Fibres of PAN, CA and PAN-CA were prepared using pressurised gyration. The experimental set up used at the ambient temperature in this study is schematically illustrated in Fig. 1. It consists of a rotary aluminium cylinder vessel with ~60 mm diameter and ~35 mm height. There are approximately 20 orifices located on the wall of vessel, and each is ~0.5 mm in diameter. The features of orifices (number, dimensions and shape) and vessel could be customized. The vessel is driven by a DC motor which connects at the bottom of vessel, and it could

**Table 1**  
Polymer solutions' physical properties obtained at ~20 °C.

Polymer solution	Surface tension (mN/m)	Viscosity (mPa s)
5 wt% PAN	52.5	200
10 wt% PAN	56.0	760
15 wt% PAN	58.0	1090
15 wt% CA	57.0	75
20 wt% CA	59.0	230
25 wt% CA	61.0	650
10 wt% PAN-CA	53.0	740

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