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The Relationship between Process Technology, Structure Development and Fibre Properties in Modern Carbon Fibre Production

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The carbon fibre production based on polyacrylonitrile (PAN) is divided into two process steps: solution spinning of the precursor fibre and thermal conversion to the final carbon fibre. It is in the first step, the spinning of the precursor, where most of the properties of the final carbon fibre are determined. A high quality precursor is the key and a prerequisite for a high performance carbon fibre. The mechanical properties are mainly determined by the polymer that is used and by the structure of the fibres. As the polymer is taken here as fixed, the fibre formation process in solution spinning has to be evaluated. In recent years, the conventional wet-spinning technique is gradually replaced by the fast air-gap spinning technique. Therefore, PAN precursor producers have to transform their knowledge about wet-spinning to this new and promising way of fibre production. The evaluation of the structure formation process in precursor production is followed by a practical analysis of the theoretically derived results.

1. Introduction

Carbon fibres are use in combination with thermosetting or thermoplastic matrices for the application in lightweight design and construction (D'Almeida et al., 2009). Their combination of low density (1.8 g/cm³) and high strength as well as stiffness (around 4 GPa and 500 GPa) makes this material the ideal reinforcement for high-performance, lightweight parts in aeroplanes, wind power turbines and industrial applications.

PAN, as it is used in fibre production, is not meltable and therefore has to be dissolved in suitable solvents for the spinning procedure. The spinning process is a solution spinning procedure with take up speeds of 50 – 200 m/min. For making a carbon fibre from the PAN precursor, the precursor is at first treated for about 90 min at 200 – 300 °C in air. In this process PAN is converted into a ladder structure and is made incombustible. In the following carbonisation the fibre is treated for 1 – 2 min at first at around 700 °C and then at around 1600 °C under inert conditions. At the end of the process the fibre contains more than 95 %, usually around 99 % carbon. The reason for the high strength and stiffness is the regular turbostratic structure of the carbon layers, oriented along the fibre axis. Therefore a highly regular and oriented structure free of voids is already needed in the precursor fibre. (Masson, 1995)

The spinning of the precursor is realized in a solution spinning process (Figure 1). The polymer is dissolved in a suitable solvent to reduce the viscosity to a level at which spinning is possible (around 30 – 50 Pas). This targeted viscosity equals to a concentration of polymer in the dope of about 20 – 30 % in the case of organic solvents. The solution is thoroughly mixed and deaerated prior to pressing it through tiny holes of about 70 µm in diameter. Several thousands of these holes are in one nozzle, forming a bundle of single fibres called tow. In the following steps the molecules are aligned along the fibre axis and the solvent is removed from the forming fibre. This removal is, in the case of precursor production, done via a coagulation process in a non-solvent. The solvent diffuses out of the fibre, the non-solvent diffuses in. These conditions in this process step govern the speed of the coagulation and, by that, the final structure of the fibre. The strongest influence has the temperature and concentration of the dope and of the coagulation bath as well as the stretching of the filaments just behind the nozzle. (Masson, 1995)

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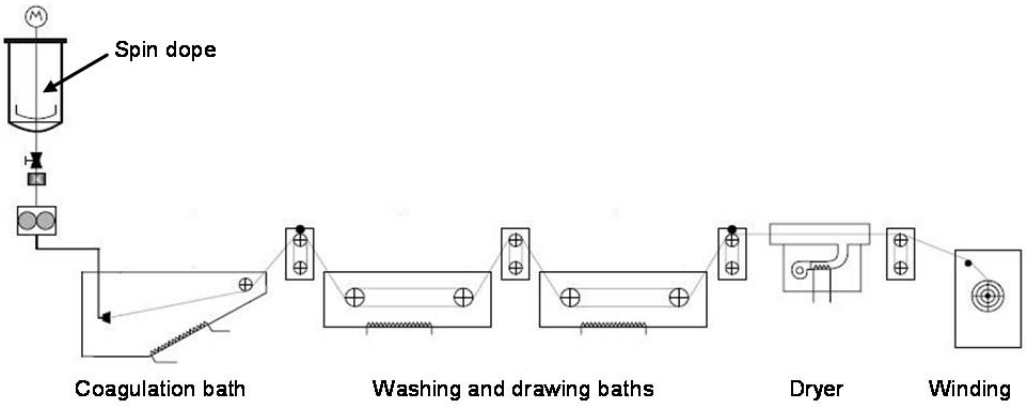

Figure 1: Wet spinning process for the production of carbon fibre precursors

In the recent years many researchers have proposed an alternative configuration of the nozzle. In the air-gap spinning process the nozzle is placed some millimetres above the coagulation bath and the filaments are extruded vertically into the bath. The advantages of this configuration are the higher possible speeds and the denser fibre structure that is formed. However, up to now the number of filaments per nozzle is limited to around 6.000. Since the coagulation behaviour is affected by this change in the configuration, air-gap spinning has to be evaluated separate from the conventional wet spinning process. (Gupta et al., 1996)

With respect to the production of high quality carbon fibres, the first centimetres behind the nozzle are the critical ones in the spinning process. This is also documented in the scientific literature: Many papers deal with the influence of dope temperature (Masson, 1995), bath temperature (Knudsen, 1963), dope concentration (Ziabicki, 1976), bath concentration (Hou et al., 2006) and amount of stretching (Baojun et al., 1986) on the structure. However, since there are many influencing factors, the results are not comparable to each other and usually disregard the interdependence between the parameters.

2. Theoretical comparison of wet-spinning and air-gap spinning

2.1 Stretching of the fibre behind the nozzle

The dope is pumped with an average velocity $\bar{v}$ through the nozzles and is drawn out of the coagulation bath by the first pair of rollers, called godets, with a velocity v_1. The ratio $\frac{v_1}{\bar{v}}$ is defined as the jet stretch. The jet-stretch values can be smaller than, equal to and bigger than 1. A value smaller than 1 would suggest that the fibre is not stretch at all. This is not true. When the dope is pressed through the nozzles the polymer molecules are not randomly distributed anymore. Since this is not the favourable state with the lowest energy level, this energy is released after having passed though the nozzle. The polymer solution relaxes. Due to this, the dope swells at the end of the nozzle and increases its diameter. Since the mass flow is constant, the velocity decreases as a consequence. This velocity is called the free velocity v_f. Therefore, the take-off velocity has to be compared to the free velocity instead of to the mean velocity in the nozzle. The ratio $\frac{v_1}{v_f}$ is also called “true jet stretch”. (Paul, 1968)

The degree of swelling to the diameter D_f as indicated in Figure 2 depends on several factors. It increases with increasing the viscosity of the solution and the mean velocity in the nozzle, but it decreases with increasing the length and diameter of the single nozzle. For producing a good precursor at low cost, high spinning speeds are favourable. However, increasing the true jet stretch induces higher stresses into the fibre and may lead to rupture. Therefore the nozzle has to be designed in that way that the Barus effect is relatively small (i. e. high v_f) and high take-off velocities do not induce high stresses. (Paul, 1968)

For comparing wet spinning and air gap spinning the effects inside the nozzle and outside the nozzle have to be discussed separately. The above mentioned elastic deformation of the molecules within the nozzle and the influence of diameter and length of the nozzle are described by the so called inner spinning procedure. Comparing wet-spinning and air-gap spinning no systematic difference regarding the inner spinning procedure can be detected. The effects and conditions behind the nozzle are summarised in the outer spinning procedure. Influencing factors can be the temperature behind the nozzle, the medium (gas or liquid) or other forces acting on the fibre. (Lechner et al., 2009)

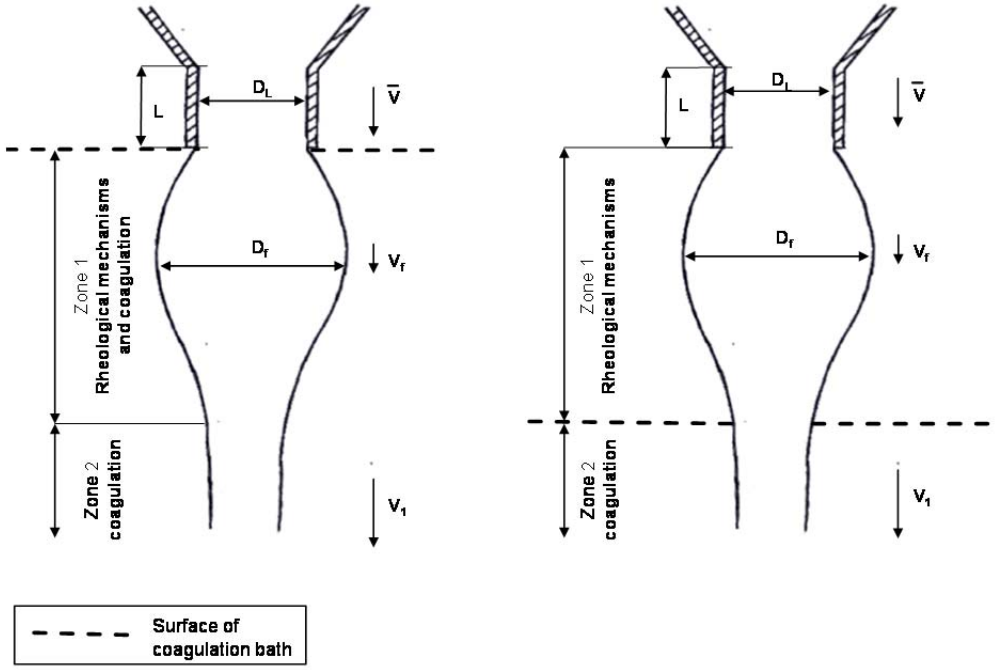

Figure 2: Fluid dynamics in the nozzle and in the forming fibre for wet-spinning (left) and air-gap spinning (right) partly based on (Falkai, 1981)

The outer spinning procedure is especially of importance when it comes to the difference of wet and air-gap spinning. Once the dope exits the nozzle in wet spinning, it is in contact with the liquid coagulant. This dramatically influences the coagulation behaviour. In total this affects the maximum take-off speed. To understand this the acting forces have to be evaluated (see equation 1). If the force F_{ges} with which the take-off godet has to pull the fibre exceeds the strength of the fibre, it breaks.

$$F_{ges}(x) = F_{rheo} + F_{coag}(x) - F_{grav}(x) \quad (1)$$

F_{rheo} is the rheological force that acts onto the fibre. This only applies when the viscous fibre is stretched. F_{coag} consists of several factors acting from the environment onto the fibre. The most prominent influence has the hydrodynamic resistance of the coagulation bath. This force is also referred to as the drag force. F_{grav} applies in case of the air-gap spinning process where the fibre is extruded vertically downwards into the coagulation bath.

The rheological force is influenced by the temperature of the polymer solution. In precursor production a low coagulation bath temperature is necessary to decrease the coagulation rates in order to guarantee a homogeneous, void free fibre structure (Wilms et al., 2012). In wet-spinning the fibre temperature at the exit of the nozzle is the same as that of the coagulation bath. Low temperatures cause high viscosities and therefore high rheological forces needed for stretching. In the air-gap spinning process the temperature of the forming fibre is similar to that of the dope, which is generally high in order to allow a higher dope concentration. The high dope temperature leads to lower viscosities and therefore lower rheological forces needed.

The coagulation forces act onto the fibre along the entire way through the coagulation bath. The only difference between air-gap spinning and wet spinning is the place where the deformation of the fibre and therefore acceleration of the coagulation liquid occurs. The deformation of the fibre takes place at the position where the dope can be stretched in the easiest way. This is the case close to the nozzle, where the core of the forming fibre is still liquid. In the case of wet spinning this area is within the coagulation bath, in air-gap spinning it is in the air gap. Therefore the coagulation force is negligible in the air-gap spinning process whereas in wet spinning it considerably contributes to the forces induced into the fibre.

In air-gap spinning additionally the gravimetric forces have to be considered. They increase with increasing air-gap height. It is therefore important to limit the height to what is needed for stress relaxation according to the Barus effect. An increasing the height further leads to fibre breakage in the air-gap.

Summing up it is obvious that the forces acting onto the fibre are smaller in the air-gap spinning procedure compared to conventional wet-spinning. However, the higher possible spinning speeds are not only a consequence of the smaller forces. Also the stresses have to be evaluated. As discussed earlier, in wet spinning the dope immediately interacts with the coagulation bath and forms a solid shell. By diffusion and coagulation mechanisms this solid shell moves inwards. The liquid, easily deformable core is quickly getting smaller. In the case of air-gap spinning the dope, when exiting the nozzle, interacts with the gas inside the air-gap. Minor amounts of solvent evaporate leading to an ultra thin but rigid membrane on the forming fibre. The core remains liquid in the air-gap. The deformation in the stretching process takes place in the area where the dope is still liquid. This area is considerably larger in the air-gap spinning procedure. Looking at the cross section of the fibre this induces smaller stresses in case of air-gap spinning. Looking at the length of the liquid area this leads to smaller draw rates which leads to a less pronounced increase in the induced stresses.
In addition, the larger liquid area in the air-gap spinning procedure gives way to a relaxation of any induced stresses. Besides, in the case of wet spinning the hydrostatic pressure acts against the tendency to swell and therefore decreases the Barus effect. The hydrostatic pressure therefore suppresses balancing the stresses. (Baojun et al., 1986)
In total a combination of lower forces acting onto the fibre, lower stress levels and better relaxation of stresses leads to a higher possible deformation of the fibre. This leads to higher take-off speeds and, in the end, to more productive processes.

2.2 Structure development in the coagulation bath

The general structure of a PAN precursor fibre is shown in Figure 3. The molecules are arranged in a helical structure and form aligned and unordered areas. These areas together form fibrils, which build up the polymer network of the fibre. The fibrils are separated by voids which should be smaller than 0.2 µm in diameter for a high quality carbon fibre. The arrangement of fibrils and voids is the result of the coagulation just behind the nozzle.

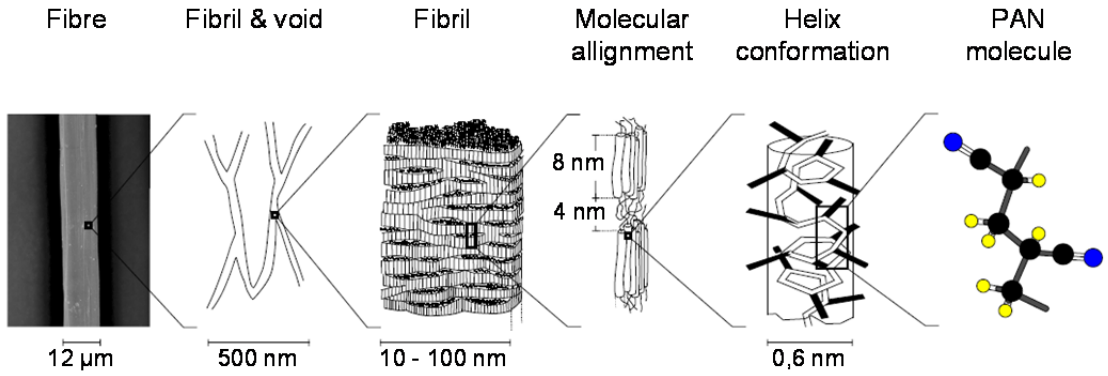

Figure 3: Fibre structure of a PAN precursor, partially based on (Masson, 1995)

It is generally accepted that mild coagulation conditions are favourable for a homogeneous and dense structure. Mild coagulation means that the diffusion speeds are low and that the inward diffusion is considerably lower than the outward. The slow coagulation is a prerequisite for the formation of a dense network. In the gel state, which is a state between a homogeneous solution and phase separation, tie molecules connect the fibrils. These connections limit the size of the voids and, in addition, facilitate the load transmission. (Knudsen, 1963)
The diffusion coefficients depend on the fibre structure. Diffusion is faster in the liquid dope than in a coagulated, solid shell. Therefore it is important to control the coagulation in order to keep the diffusion coefficient constant across the fibre. In the case of air-gap spinning, the rate of diffusion is determined by the outer membrane that is formed in the air-gap. In conventional wet spinning the structure of the membrane is determined by the coagulation conditions and later controls the diffusion and by that also the coagulation conditions. Because of the different layout of the outer part of the forming fibre, also the changes in further coagulation that are induced by stretching the fibre are varying. In air-gap spinning the shell of the fibre is thin but dense. When stretching this, it becomes even denser. The type of diffusion through a dense layer is different from the one through a porous structure. Through a dense skin the diffusion happens through free volume of molecular size, the so called activated diffusion. This type of diffusion is considerably slower than the one through pores. Since PAN has a hydrophobic nature diffusion

of the organic solvents is always faster than that of water. This effect is even more pronounced when diffusion only takes place in the manner of activated diffusion. Therefore, when stretching the fibre in air-gap spinning, the coagulation becomes even milder and a more homogeneous and dense fibre structure is evolving. (Baojun et al., 1986)

The structure of the shell in wet spinning is porous. Due to the swelling of the fibre just behind the nozzle the pore size increases. Therefore, in case the fibre is extruded freely the coagulation is hard because of the high diffusion speeds. Stretching the fibre reduces the pore size and the coagulation becomes milder. This holds true until the fibre is stretched beyond a specific limit. This limit is reached at a jet-stretch ratio of about 1. If the fibre is further stretched structural effects open up the rather thick and inflexible shell and the diffusion rate is increased again. Therefore, wet-spinning under mild conditions is only possible up to jet stretch ratios of 1. (Baojun et al., 1986)

3. Experimental evaluation

3.1 Materials and equipment

For evaluating the differences in spinning PAN with conventional wet spinning and air-gap spinning processes, commercial PAN polymer from company Dralon GmbH, Dormagen / Germany was used. It was dissolved in DMSO from Overlack GmbH, Moenchengladbach / Germany. The solution was prepared by thoroughly mixing PAN and DMSO and leaving it in a barrel for at least 24 h at room temperature for deaerating the dope. The dope was then sucked into a piston pump (500D Syringe Pump, Teledyne Isco, Lincoln NE / USA) and then extruded. Different multifilament nozzles where used. The fibres were spun into a coagulation bath, either in a wet spinning setup or with an air-gap. After the fibres were guided out of the coagulation bath they were directly wound on a bobbin. The coagulation bath was constantly at room temperature and contained 50 wt.% DMSO and 50 wt.% water. The schematic setup and a picture are shown in Figure 4.

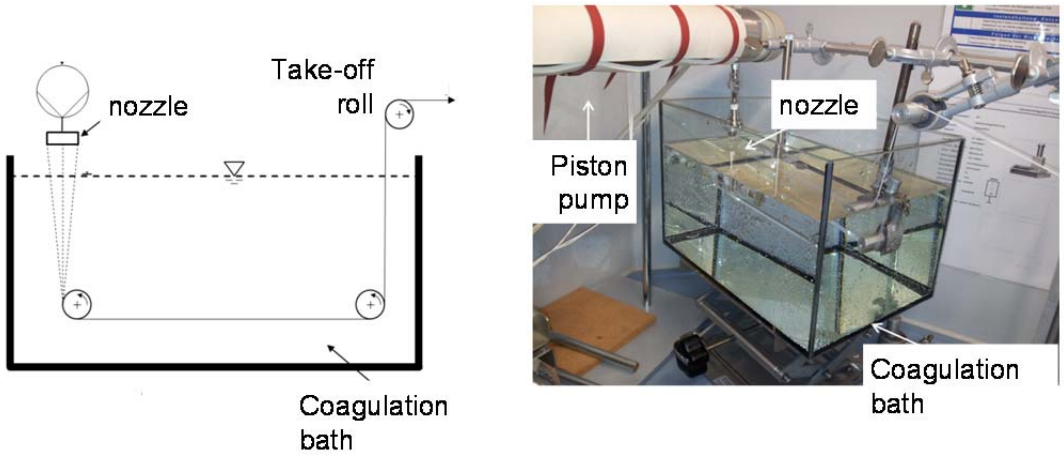

Figure 4: Experimental setup: Scheme (left) and photography (right)

3.2 Results

Using a 20 wt.-% PAN, 80 wt-% DMSO solution with a 120 hole nozzle with each hole 70 µm in diameter the possible take off velocity of the fibre was almost double as high for the air-gap spinning compared to wet spinning (10.3 m/min compared to 6.4 m/min). This equals jet-stretch ratios of 4.0 and 2.4, respectively.

All fibres that were spun have a dense and nearly void-free structure. In the air-gap spinning process the change of fibre shape can be observed clearly. For a high quality, high strength carbon fibre it is important to have a round cross section. This can only be achieved by mild coagulation conditions. In Figure 5 images that were taken with a light microscopy are shown.

In the light microscopy images it is obvious that the fibre diameter decreases with increasing jet-stretch ratio. This is a direct consequence of the law of conservation of mass. In addition the transition from oval, almost kidney-shaped to nearly round cross sections can be observed. Besides, the inner structure of the fibre is becoming more and more homogeneous and dense as the jet-stretch ratio increases.

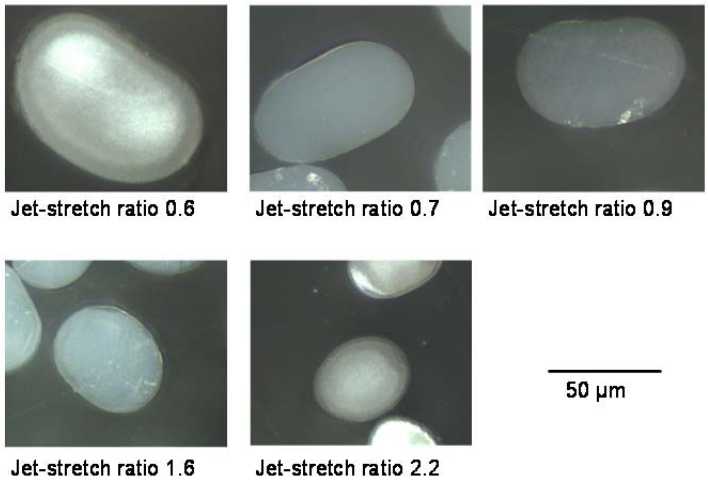

Figure 5: Light microscopy images of air-gap spun fibres with different jet-stretch ratios

4. Conclusion

The precursor spinning is the key process for producing high quality, high strength carbon fibres. The emerging air-gap spinning technology has several advantages over the conventional wet spinning procedure. In the theoretical part of this paper an in-depth comparison of the two technologies regarding the fibre forming processes was presented. In air-gap spinning higher spinning speeds can be achieved due to lower forces, stresses and increased stress relaxation. In addition the diffusion and coagulation can be controlled in an easier way. The mild coagulation conditions are the prerequisite for a dense, void-free structure and a round fibre cross-section. Fibres with these properties can be further processed to high quality carbon fibres.

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