KEY PARAMETERS FOR CONSIDERATION IN THE DEVELOPMENT OF A CARBON FIBER RESEARCH LINE

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ABSTRACT

As the trajectory of the Carbon Fiber market indicates explosive growth to come, the opportunity to realize this full potential must be captured through achieving greater capacities in a more efficient and cost effective manner. Making use of emerging precursor materials will be integral to achieving a fiber suitable for widespread adoption in more demanding and large scale applications such as the automotive market. The processing technology to enable development of these alternative precursor options will be different by nature than standard Poly Acryl Nitrile (PAN) based carbon fiber processing technology. In this paper, Harper will discuss process technology advancements in research scale systems to enable flexibility, control and management of the development of alternative carbon fiber precursors. We will review key design considerations and technology solutions to facilitate most innovative areas of carbon fiber research today, such as fractional tow sizes, carbon nanotube containing carbon fibers, lignin, polyethylene and more.

1. INTRODUCTION

Although plant capacities continue to increase, the equipment configuration and process recipes for carbon fiber manufacture from PAN precursors has become fairly standard. Novel precursor materials, such as polyethylene[1,2,3], PAN/carbon nanotube[4,5,6], and lignin[7,8] are being developed at laboratory scale. For these and other new precursor materials to be processed to carbon fibers as commercial products, it will require thoughtful scale-up and data collection. This paper explains some of these scale-up challenges from a supplier's point of view.

2. DISCUSSION

2.1.1 Precursor format

Perhaps the most fundamental assessment of how the material will be handled throughout the carbon fiber production process is the format of the precursor material, both in an untreated state and as its physical properties change during the conversion process. Can the material support its own weight and be manufactured into a tow or yarn format, or is the precursor material weak and needs to be supported on a belt or bobbin throughout some or all of the heat treatment process

equipment? Additionally, it is critical to evaluate how these physical properties change while the material is heated, strained and converted.

The amount of force required and how is it applied to the various formats is mainly determined by the behavior of the precursor filaments under this applied force When discussing tow band format, the catenary of the tow is important. Catenary is the curve or droop that the tow assumes under its own weight when supported only at its ends as it is processed through each piece of equipment. This amount of droop is critical and is dependent on the lineal density of the tow, the force on the tow, any height difference in the entrance and exit of the equipment and the overall length of the tow from one support roll to the next; see Figure 1.

Theoretically speaking, this is an important calculation. However, practically speaking, there are minimum distances required to adequately heat treat the tows in each piece of equipment from the ovens through the furnaces. When considering production scale sized equipment, at least 5m heated length is required so any material at a minimum needs to be self supporting over this distance or it is not a practical precursor.

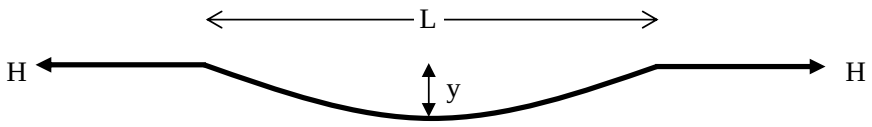

Figure 1. Droop (*y*) versus length (*L*) of a tow band.

The length of each piece of equipment and hence the overall floor space required for an installation is dictated by the required or anticipated residence time of the precursor material. Assuming the same residence time, tow filament count and decitex (dtex), material running at a line speed of 0.5m/min requires a much shorter length (L) than material running at 10 m/min. Therefore, the amount of force the tow would require to minimize the droop would be significantly more for the faster line speed due to this increased length. Comparing Figures 2 and 3, with the same force for both lengths, research line versus production line, the resulting droop is significantly higher for the longer length. Figure 4 demonstrates tow forces that are more realistic to production scale equipment. These forces are significantly higher, and yet the result is a significantly higher droop. The amount of droop also dictates the angle of attack for the incoming material and the design of the equipment so that the material does not drag on any surfaces, internal or external. Any surface the tow material touches increases the incidence of filament failures which degrade the overall properties of the finished product. Figures 2 and 3 demonstrate this phenomenon.

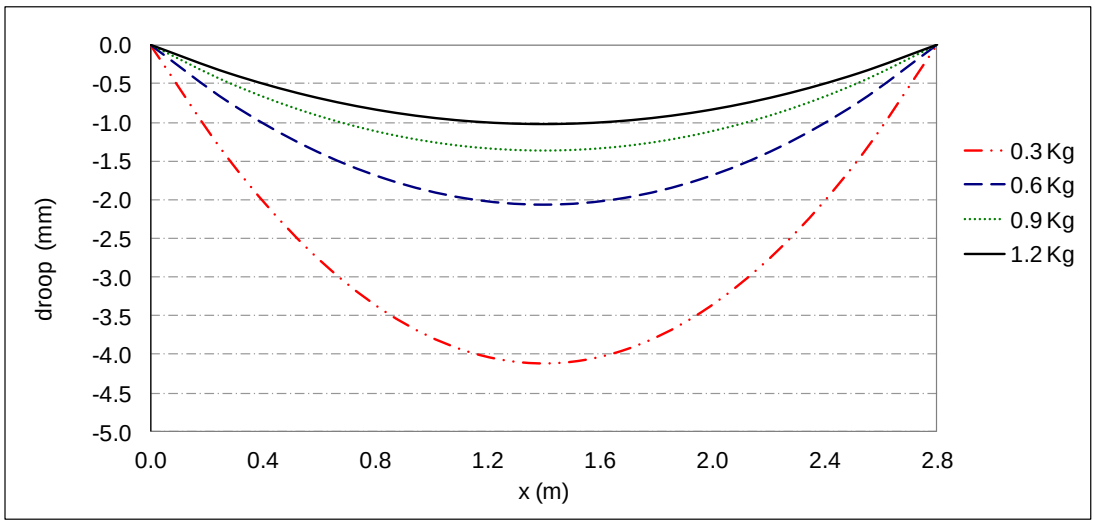

Figure 2. Catenary versus Force – 12k, length sized for 120sec residence time, 0.5m/min

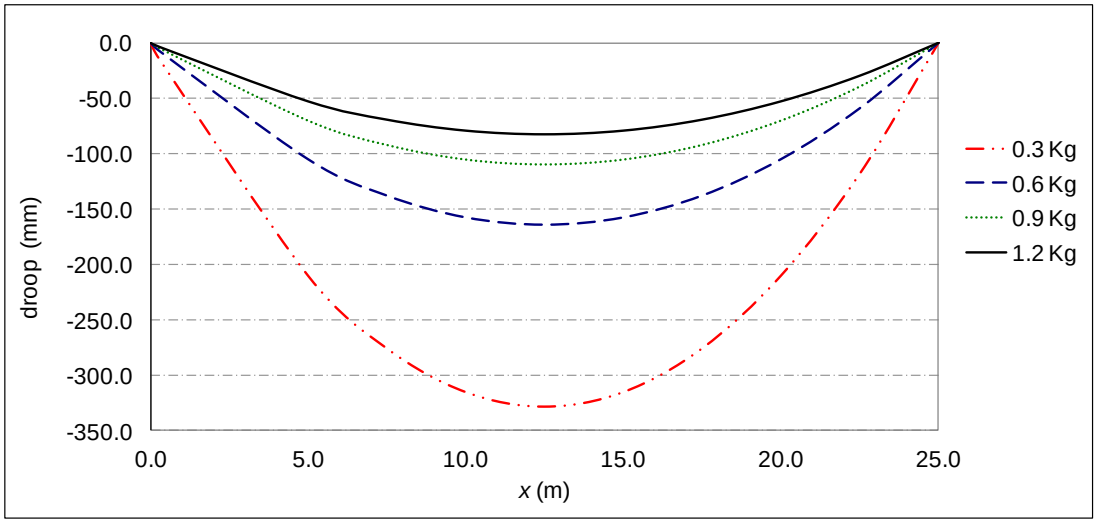

Figure 3. Catenary versus Force – 12k, length sized for 120sec residence time, 10m/min

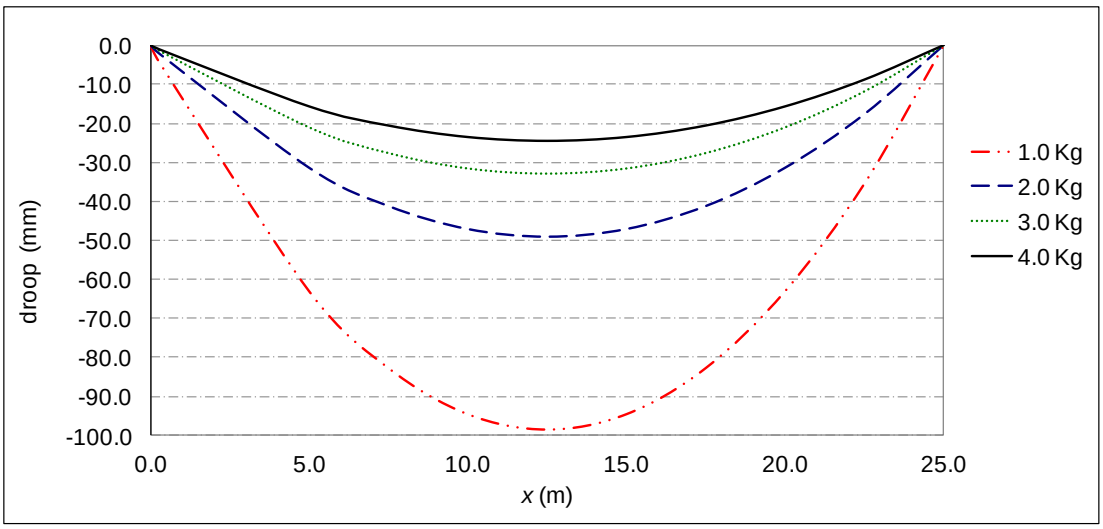

Figure 4. Catenary versus Force for typical forces in a production scale system – 12k, length sized for 120sec residence time, 10m/min

As Figure 4 demonstrates, higher force on the tows results in lower droop through the equipment. There are limitations, however, on the maximum force that can be applied per tow per number of tows that the equipment or material can handle. Practical limitations are currently around 2000 kg total force for 3 meter long rolls. This is not an absolute limit, because the roll diameters could be increased but this would result in a volumetric efficiency penalty, and a significant capital cost increase.

There are also practical limitations on the minimum amount of force that can be applied to a tow on the very small end of the spectrum. It is very difficult to apply <10g of force to a tow that has 15-20 filaments. A significant problem with very small filament count tows is that the distribution of the force across all of the filaments is nearly impossible to attain, especially in batch processing as described in Section 2.2.1.1. Invariably some of the filaments are supporting the majority of the load and can fail. When dealing with filament counts of less than 50, every filament break is significant.

As Figure 3 shows, materials under low force may have large and impractical catenaries in production scale equipment. Most stabilization ovens use convection heating, and the air flow causes tows to move around. If the droop dimension is similar to the spacing between adjacent tows, then there is a tendency for tows to entangle. The oven can be designed to have larger spaces between adjacent tows, but this compromises the volumetric efficiency. For practical plant designs, catenaries should be no more than about 30 mm in stabilization ovens and 60 mm in carbonization furnaces.

Table 1 shows the correlation between dTex and required tension to have a 60mm droop in a 12k fiber over a distance of 25m. This would be the minimum tension per dTex that the tow would need to be able to support to be practical.

dTex	Force (kg)
0.5	0.63
1.0	1.26
1.5	1.89
2.0	2.52

Table 1. Force versus dTex for 12k tows to maintain 60mm of droop

2.2 Stabilization

The stabilization process varies widely from one precursor to the next and is a necessary step prior to carbonization. The main goal of stabilization is the formation of a thermally stable ladder polymer that will then prevent the precursor from deforming or melting at carbonization temperatures.

For some materials, such as polyethylene, a thermo-chemical stabilization stage in fuming sulfuric acid or chlorosulfonic acid to sulfonate the fiber is necessary prior to carbonization. Sulfonation is also necessary to increase the yield potential of the fiber from < 1% up to 70% or higher[3].

For other materials, such as lignin, PAN and PAN/carbon nanotube, a thermo-oxidative stabilization stage in an air atmosphere is necessary prior to carbonization.

Future stabilization techniques and equipment could further change if current research results in significant improvements from current techniques.

2.2.1 Stabilization – Batch or Continuous Processing

This is a fundamental choice in the development program. The key parameters are 1) anticipated residence time, 2) quantity of available precursor, and 3) desire to control either tension or strain.

2.2.1.1 Batch

For residence times greater than 20 minutes, batch stabilization can be representative of larger scale equipment time/temperature profiles; although the process is in constant tension and not constant strain. The material is held static, and a constant force (constant tension) is applied versus a variable force (constant strain). For batch stabilization, accurate temperature control and uniformity within the reaction volume are important. The rate of reaction is dependent on a number of factors including the co-monomers and tends to be highly sensitive to temperature[8]. This behavior can be mapped using differential scanning calorimetry (DSC)[9].

When designing a batch oven for research and development purposes, it is advantageous to be able to be able to control and vary the rate of change of temperature within the volume to mimic zone to zone temperature variations and travel time between zones on a continuous line. The goal of batch processing on a research and development size scale should be to try to mimic this continuous process as close as possible in order to deduce the “real world” behavior of the

precursor and to garnish interest from industry to try the new precursor material if it performs well in the laboratory. Additionally, for research flexibility, a wide range of temperatures is advantageous to be able to accommodate future precursors that may have unusual temperature ranges when compared to typical precursors. Current researchers are using stabilization temperatures as high as 350°C[4] and current oxidation ovens designed and installed by Harper International are rated as high as 400°C for stabilization processes.

In batch testing of tow formats, the number of filaments in the tow is another important factor. At very low filament counts, it is difficult to apply force uniformly across the tow. When attaching a weight to a tow, the tendency is for some filaments to be longer than the others, and these longer filaments do not carry any force load, while a subset of neighboring filaments carry the entire load. Further, the lower the filament count, the greater the uncertainty from broken filaments, which are almost impossible to quantify. Therefore, for batch testing it is best to conduct testing on tows with at least 250 filaments, preferably greater than 500 filaments; even then, it is unknown how many of the filaments are supporting the load. For a test program, assuming a minimum requirement of 300 meters of a 500 filament tow at 1.3 dTex equates to 20 grams of material.

Porwal et al.[10] developed a probability model for the strength of a twisted yarn bundle with an ideal helical structure, which accounts for statistical Weibull fiber strength and frictional effects. They developed a load sharing rule, called the twist modified global load sharing (TM-GLS) rule. Global load sharing assumes that when a fiber breaks, the load from a broken fiber is locally lost at the break but is then gradually recovered over a length l_f away from the break by interfiber frictional shear forces. For the slipping fiber, the average developed tensile stress is shown in Equation 2.

$$\bar{T}_k = \frac{f\,P_k}{d_f} L \qquad [2]$$

Where:
T_k = tensile stress in the fiber
L = fiber section length between two breaks in layer k
f = coefficient of friction
P_k = interfiber contact pressure on layer k acting normal to the fiber surface
d_f = diameter of fiber

For an untwisted tow in a static (batch) process, P_k will be small, especially at low filament counts, so broken filaments will contribute little to the tensile strength.

In continuous processing, the tow will move around a series of rollers and P_k will vary from a maximum at the roll to a minimum at a distance halfway between the rolls. This implies there is local stress cycling in broken filaments that is present in continuous processing but not in batch processing. Further, in continuous processing filaments will rearrange from layer to layer in what is known as migration. Also, as the tow travels around a roll, outer layer filaments are at a larger radius than inner layer filaments and this produces local slipping between filaments. This slipping can result in filament breaks as well as the generation of static charges and consequent forces within the tow. These migration, slippage, and static phenomena all have implications for

overall tow tensile strength, and they are only present in continuous tow processing. These dynamic tow effects are influenced by precursor composition, filament cross-sectional shape, and the application of finish oils. With the complexities of these combinatory effects, there is little substitute for piloting the continuous process using at industrial scale pilot plant that is 300 mm wide or greater.

2.2.1.2 Continuous

Continuous processing has the material moving throughout the system and has more elaborate equipment that requires much more mass of precursor compared to batch processing, but has the advantage of controlled strain. Similar to batch processing, the rate of reaction tends to be highly sensitive to temperature and if not controlled properly, an exothermic reaction can occur in the material. Further, for research flexibility, a wide range of temperatures is also advantageous.

Continuous processing makes much larger samples possible as well. One typical oven design used for very small scale continuous stabilization uses a once through air approach with individual tubes for each pass. This provides for a very clean environment for the fiber, reduces buildup of toxic emissions inside the process chamber, reduces chances of exothermic reactions causing a fire and eliminates the need for a water suppression system. The design also allows for very quick changes in temperature and excellent accuracy and uniformity of the temperature within each pass[11]. All of which are critical for uniform properties along the tow bands.

For continuous testing of tow formats, the number of filaments in the tow should be at least 1.5k. To run a 1.3dTex, 1.5K tow at 0.5 meters per minute for one week requires 1 kg of material, so minimum mass requirements for continuous processing are two orders of magnitude greater than for batch processing. With these small filament tow counts, it is important to take into consideration the torque required to overcome any non-driven rolls. Joining of tows to make bigger tows can be problematic because the tows can separate during processing; two 1.5k's does not equal a 3k, although it can serve as a good approximation if insufficient material is available.

2.2.2 Atmosphere and Instrumentation

Control of the processing atmosphere is critical to a successful scale-up of carbon fiber processes.

For the stabilization process it is critical to ensure that the toxic off gasses do not reach the LEL limit for each gas constituent. For some processes maintaining minimum O_2 content inside of the oven can also be important. However, measuring these values is problematic in the harsh environments inside the stabilization ovens. Samples can be taken of the off-gas to develop a better understanding of the concentrations of the constituents that would need abatement at high levels. The best time to determine this would be before designing the layout of the process line and not after. Fiber samples should be tested using FTIR, DSC and mass spectroscopy to help select and design the equipment needed. These tests also help to give a general idea of the behavior of the material prior to attempting to stabilize for the first time or to even determine if the material is worth pursuing with further studies

2.3 Carbonization

Generally, for all materials this process step will involve an inert atmosphere thermal ramp/soak. This process is done at high-temperatures, up to 1000°C in the low temperature furnace and up to 2000°C or higher in the high temperature furnace. For typical filament diameters; the required residence times are between 60 to 120 seconds in duration.

2.3.1 Stabilized precursor format

As with stabilization, it must be accessed whether the material will be processed in tow or in bulk format. For bulk format, there are limited options available in the market. Harper International currently supplies LT and HT furnaces with belts rated for temperatures up to 2000°C. When dealing with a tow format, the material must be able to withstand tensioning which is required for proper processing of the material. A lack of proper tensioning could result in material properties that are less than optimal.

2.3.2 Batch or Continuous Processing

Since required residence times are 120 seconds or less, and there is apt to be a benefit to using a multiple temperature ramp/soak, the use of batch processing, which is prevalent in much of the cited literature, is problematic. It is difficult, if not impossible, to get batch equipment with acceptable control of time at temperature at these time scales and this affects the final properties of the carbon fiber. It has been reported that trace oxygen decreases tensile strength at residence times of 100 minutes and carbonization temperatures between 1000 and 1500 C.[12] With PAN, as an example, excessive residence time during carbonization results in excessive mass loss and degradation of final properties, in particular if the integrity of the atmospheric control is sub optimum.

For continuous processing, achieving multiple temperatures in a single pass requires careful furnace design to avoid the higher temperature portions of the furnace swamping the lower temperature portions and thereby limiting the range of possible temperatures. With proper equipment, a strain can be imposed on the material during the carbonization process. Use of a second furnace in series enables a change in strain as the processing temperature increases.

2.3.2.1 Mixed mode testing

It is possible to use batch processing for stabilization and continuous processing for carbonization by connecting of the stabilized samples to a pull rope. This “quasi-batch” or mixed mode processing is an option but has limitations such as how to tension the stabilized sample, how to pull the sample through a furnace setup and how to handle the sample without damaging filaments; especially with very small filament tow counts. This method also complicates the control of strain or tension during the carbonization process. However, this mixed mode testing may be a consideration if floor space is very limited for the process equipment and would be a step closer to a continuous process than a strictly batch process.

2.3.3 Atmosphere and Instrumentation

For carbonization, it is important to maintain an inert environment, typically with nitrogen, to prevent the material from degrading and forming carbon monoxide in the presence of oxygen. This inert atmosphere is also important in protecting the high temperature furnace if it is a graphite furnace. These furnaces can come equipped with oxygen and dew point analyzers to monitor for the ingress of oxygen. It is also important to know what impurities are in the fiber that can have a detrimental effect on the furnace muffles. High levels of sulfur and chlorine can degrade/corrode the alloy muffle in the low temperature furnace which can then result in catalytic corrosion and erosion in the high temperature furnace if neither furnace is designed to compensate for the high sulfur levels.

It is important to balance the materials of construction, the impurities in the precursor, the chemistry of the precursor, the process recipe and any chemical additions related to this process recipe to provide the best optimization of operating conditions and equipment characteristics. This understanding of the chemistry of the precursor and impurities is also important to recognize if any of the impurities or off-gases can result in safety concerns, an example being sodium in the precursor that can form sodium cyanide in the carbonization furnaces.

3. CONCLUSIONS

In order to implement a successful research and development program with the intentions of either developing a commercial precursor or to scale up to a production sized plant it is important to understand your needs. For screening of candidate compositions, batch stabilization processing under static tension combined with standard analytical tests such as DSC can provide tension limitations, preliminary stabilization residence time, and carbon yield. The amount of material required is relatively small, on the order of tens of grams per sample.

For assessment of final carbon fiber properties such as tensile strength, continuous processing will provide several advantages. These include well controlled carbonization residence time, so that over-carbonization and consequent loss of properties does not confuse results. Also, continuous processing makes it possible to investigate dynamic tow effects such as migration, filament slippage, and the buildup and affects of static charge. These needs highlight the need for well-designed equipment. The equipment design is often further challenged by space/foot print constraints typical in research facilities, so it is important that equipment providers have a basic understanding of the process and pitfalls involved. Continuous processing requires being able to produce at least a few kilograms of each sample material.

Processing carbon fiber is a meticulous process that can take years to perfect, so it is important to get off on the right foot with equipment well matched to the individual research program needs and future goals.

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