OVERVIEW OF 100 FILAMENT BENCH SCALE SPINNING METHODS FOR EXPERIMENTAL PAN-BASED PRECURSOR FIBER

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Introduction

The use of carbon fiber in composites and other applications has grown exponentially as the demand for lighter and stronger materials has increased. Numerous carbon fiber producers, including Hexcel, Mitsubishi, Toho Tenax, Toray, and Zoltek, all have production capability of PAN precursor fiber(1), however, such industrial-scale capabilities require massive quantities of precursor dope. For development of experimental fibers, a scaled-down bench scale spin line with industrial characteristics, but allowing for quick change over between dope formulations, is desired. The goal of bench scale spinning is to facilitate small scale spinning operations with fiber characteristics comparable to those produced on a large scale.

The University of Kentucky Center for Applied Energy Research is one of the few research centers in the country to maintain and operate an on-site, fully commissioned (2007), bench-scale (100 ft long) multifilament polyacrylonitrile (PAN) precursor fiber spinning line housed in a secure 5000 ft^2 facility. The line is capable of producing up to 1 lb of fiber per working day, using experimental precursor dopes, which are prepared in-house with varying compositions of polymer. Production of 100 filament precursor tow, as seen in Figure 3 below, with minimal time and effort required for changeover, allows for the efficient testing of the "spinnability" of experimental dopes, as well as subsequent thermal processing. The advantages of a bench scale system continue with the ability to dial-in the processing parameters of experimental dopes on a small scale, reducing time and cost for production, while optimizing dope characteristics. Favorable dope characteristics, to be discussed later, lead to superior precursor fiber, which can further be optimized by tuning the spinning parameters on-the-fly. The UK CAER spin line operates at approximately 100 ft/min, enabling tow re-stringing without stopping the line. Spinning parameters include: filtration sequence, spinnerette geometry, wet spinning, air-gap spinning, spinning temperature, coagulation, and wash bath(s) temperature, composition and residence time, cold stretching, hot water drawing, steam drawing, etc, all of which contribute to the final fiber properties.

Experimental

The production of quality experimental precursor tow requires that the spin line be an ever-changing system. Current experiments with dope formulation and spin line setup have led to several new observations concerning changes to the system which promote a more consistent precursor fiber, as far as qualitative and quantitative properties are concerned.

The preparation of the spinning dope is one of the most critical steps in the spinning of precursor fiber. It is well known that several factors influence the "spinnability" of a dope, including polymer concentration, heating cycle, molecular weight distribution, filtration, stable drip length, etc. Regarding concentration, it has been found that the concentration of polymer within the dope controls the effectiveness, efficiency, and economics of the spinning process(1). If the concentration is too high, the viscosity will be high, and there will be an increase in the propensity to form gels and other die blocking agglomerates. Therefore, the viscosity of the PAN precursor dope must be tuned, or dialed-in, for proper spinning, but also enable efficient de-aeration of the dope. Figure 1 presents capillary rheology results on a typical spin dope. Significant shear thinning is clear. Shear rates of approximately 10^3 1/sec are typical during extrusion of the dope through the spinnerette. Figure 2 depicts the steady shear viscosity of PAN dopes of varying composition. 18wt% PAN, a known spinnable dope, has a repeatable viscosity of 80 Pa-sec at a shear rate of 1 (1/sec) at room temperature. Knowledge of desired viscosity allows for the use of experimental polymers to formulate new spinnable dopes.

A purpose-built, temperature controlled, zero-head, dope mixer allows for the production of 800 mL of quality spin dope. Continuous stirring of the PAN/DMAc suspension while heating and eliminating the opportunity for skinning of the heated polymer solution with the use of a zero-head space floating piston results in a spin dope of homogeneous, repeatable quality, as can be seen from the repeatable viscosity measurements for dope mixes 2-4 in Figure 2.

The spinline begins with a pneumatically pressurized dope inlet system (2 – 200 mL stainless steel syringes – enabling continuous dope charging), which pre-filters, and introduces the dope into the metering pump at a constant inlet pressure. The metering pump provides a constant flow of dope through a sintered metal filter cup to remove gels and other agglomerates. At the extruder head, the dope is again filtered through a screen pack, and flows through the breaker plate to the spinnerette plate. For wet-jet spinning, nascent fibers emerge from the spinnerette face, which immediately begin to coagulate into a tow of 100 individual filaments.

The tow then continues down a sequence of seven coagulation/wash baths, also containing a DMAc/DI water solution, which provide gentle coagulation of the fiber while inter-bath godet stations provide the appropriate stretch ratios. Coagulation plays an important role in the development of quality precursor fiber through the removal of excess solvent, resulting in a dense fiber. Mass transfer during coagulation, however, is a delicate process that must be balanced to avoid yielding large voids within the fiber, common when coagulation occurs too quickly and the fiber forms a rigid skin around a gel core, which later collapses, causing voids and decreased mechanical properties. The goal of coagulation is

for the solvent to diffuse radially from the inside of the fiber to the coagulation bath, resulting in uniform solvent concentration across the fiber and therefore uniform shrinking in the radial direction (2). Coagulation conditions and temperatures have a strong effect on the final cross sectional shape of the fiber (3). The coagulation/wash baths consist of solutions made of distilled water and DMAc, with decreasing concentrations of DMAc as the fiber progresses down the line. The slow ramping of the coagulation baths toward pure distilled water coupled with the chilled bath temperatures promotes a slow, homogeneous coagulation and an even densification of the fiber. However the low temperature can promote bean shaped fiber (3).

Following coagulation, the line ends with a hot water stretch bath containing DI water heated to approximately 85 °C and a keyhole furnace fitted with a steam generator, which can additionally provide a steam stretch before final take-up onto a traversing winder. A heated roller godet system has also been incorporated at the end of the line to facilitate proper drying of the fiber tows prior to take-up winding.

The final solidified, densified, and dried fiber tow is traverse-wound onto 3" OD cores at the end of the spinline (Figure 3).

Analysis of the fiber after take-up allows for the determination of the cross-sectional shape and diameter prior to stabilizing and carbonizing. The average diameter for the fiber in Figure 4 was found to be 20.4 µm and the cross sectional area to be slightly "bean-shaped". This occurs, as described previously, due to coagulation conditions. This can be remedied by adjusting conditions, from coagulation bath composition, or temperature, to bath residence time, all of which affect the rate at which the fiber coagulates.

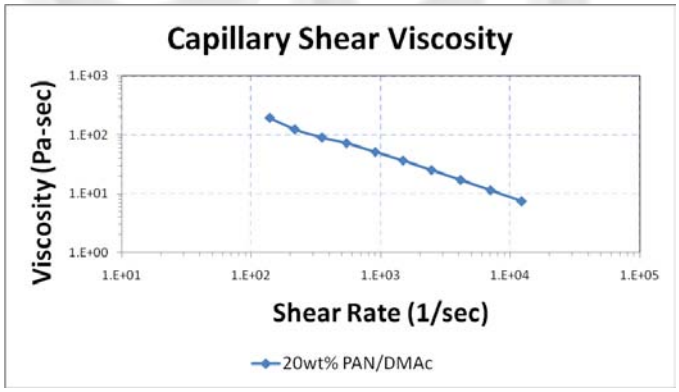

Fig. 1 Capillary shear viscosity of 20wt% PAN dope as a function of shear rate at 25°C.

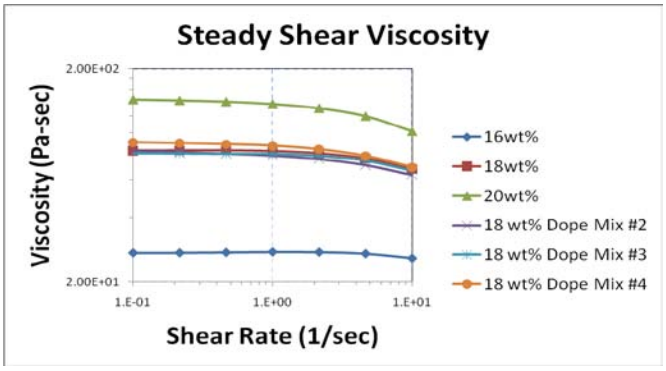

Fig. 2 Steady shear viscosities of PAN dopes of varying composition shown as a function of shear rate at 25°C.

Fig. 3 Close up of 100 two PAN precursor fiber traverse-wound on a 3" cardboard core

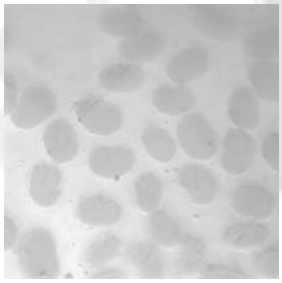

Fig. 4 Cross section of PAN fiber magnified x1000

Conclusions

The spin line at the University of Kentucky Center for Applied Energy Research is capable of producing significant amounts of experimental precursor PAN fiber tow from a variety of polymer variations, and allows for the rapid testing and development of new dopes with minimal time and expense.

References

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