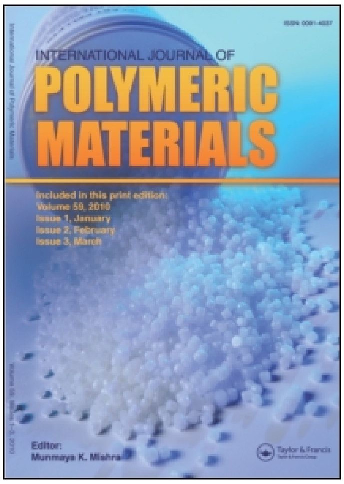

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In this article, lyocell fiber is used as a precursor for carbon fiber. The mechanical properties of lyocell fiber and tenacity of carbon fiber from this precursor have been determined. Gray-relation analysis is used to investigate the relation between precursor's properties and the strength of the carbon fibers. The results suggested that the strength, force at breaking, and fineness of precursor have greater influence on the strength of carbon fibers than precursor's elongation, and modulus.

Keywords: lyocell fiber, precursor, carbon fiber, strength, gray-relation

INTRODUCTION

Cellulose-based carbon fiber has some unique applied qualities, such as lower density, high strength and stiffness, excellent ablation, and keeping fine mechanical properties at high temperature. As such, it is a kind of high-performance material and used in some special fields. Because its mechanical performance is poorer than PAN-based carbon fiber, its application and development were greatly limited. Therefore, how to improve cellulose-based carbon fiber's mechanical properties, especialy its strength, has been the focus in this field.

It is known, that carbon fiber's quality greatly depends on its precursor; some physical features of precursor, such as voids, flaws, and son on may be passed down from precursors to the resulting carbon fiber in the process of making carbon fiber. So, a good precursor is

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precondition to producing high-performance carbon fiber [1–2]. Studies indicate that a good precursor for carbon fiber should generally meet the following conditions: fine denier, high strength, circular cross-section, and homogeneous physical structure [3]. Lyocell fiber, a new type of cellulose fiber, observably, agrees with these features [4]. Thus, it may be potentially good precursor for producing high-performance cellulose-based carbon fiber. In addition, the use of lyocell process in producing cellulose fiber display the advantages of this process and manufactures lyocell fiber with high strength, high modulus, and controlled fineness. In order to improve the final carbon fiber's strength, it is necessary to figure out the most effective factors affecting the making of carbon fibers, and understand the effect of properties of precursor on the strength of the carbon fiber. It will finally be instructive in optimizing the production process of precursor in order to improve its quality. In this article, the gray system theory has been used to analyze the relationship between the property parameters of precursor and the strength of carbon fiber. It will provide important reference for the manufacture of the precursor for carbon fiber.

GRAY RELATION ANALYSIS METHOD

Compared to the traditional theoretical analysis, gray relation analysis investigates the relationship between behavior data and affecting factors in a given system. It is mainly used to analyze the effects of all factors in the system, judge which factors are important and which are subsidiary, and provide in accordance the basic principles for the production and control of real projects. The detailed procedures are listed as follows:

The Pretreatment for the Testing Data

For a matrix with N factors and M levels:

$$X^0 = \begin{bmatrix} x_1^0(1) & x_1^0(2) & \dots & x_1^0(m) \\ x_2^0(1) & x_2^0(2) & \dots & x_2^0(m) \\ \dots & \dots & \dots & \dots \\ x_N^0(1) & x_N^0(2) & \dots & x_N^0(m) \end{bmatrix}$$

In order to make those data comparable, it is necessary to delete the dimension and the difference in quality of the original experimental data with some special methods, which include the initialization transform of the experimental data, calculation of the average value, and standardization transform, and so on.

The initialization transform of the experimental data's as follows:

$$\overline{x_i^0} = \frac{1}{m}\sum_{t=1}^{m} x_i^0(t) \quad (i = 1, 2, 3, \ldots, N)$$

$$x_i^1(t) = \frac{x_i^0(t)}{\overline{x_i^0}} \quad (i = 1, 2, 3, \ldots, N)$$

Then, the matrix can be changed into:

$$X^1 = \begin{bmatrix} x_1^1(1) & x_1^1(2) & \ldots & x_1^1(m) \\ x_2^1(1) & x_2^1(2) & \ldots & x_2^1(m) \\ \ldots & \ldots & \ldots & \ldots \\ x_N^1(1) & x_N^1(2) & \ldots & x_N^1(m) \end{bmatrix}$$

Determining the master series $x_i^1(t)$ and subsidiary series $x_i^1(t)$ in the studied system, then calculating the absolute value of the difference between the Elements Corresponding to each Master Series and Subsidiary Series:

$$\Delta_{ij}(t) = |x_i^1(t) - x_i^1(t)| \quad (j = 1,\ 2,\ \ldots,\ \mathrm{N})$$

Determining the maximum and minimum value of $\Delta_{ij}(t)$ and calculating the Relation Coefficient $\mathrm{L}_{ij}(t)$:

$$L_{ij}(t) = \frac{\Delta_{ij}(t)_{\min} + k\Delta_{ij}(t)_{\max}}{\Delta_{ij}(t) + k\Delta_{ij}(t)_{\max}} \qquad (\mathrm{K}, \text{resolution factor}, 0.1 \leq \mathrm{k} \leq 1, \text{ taking } \mathrm{K} = 1 \text{ in this work}).$$

Calculation of the correlative degree R_{ij} of each subsidiary series $\mathrm{x}_j{}^1(t)$ to the master series $\mathrm{x}_i{}^1(t)$:

$$R_{ij} = \frac{1}{m}\sum_{t=1}^{m} \mathrm{L}_{ij}(t)$$

Comparing the value of R_{ij} and listing its order from large to small, all factors in the system can be easily analyzed.

EXPERIMENTAL

Raw Materials

50% NMMO (N-methylmorpholine-N-oxide, from BASF) used as a solvent; antioxidant n-propyl gallate (A.R. from the second plant of Shanghai Chemical Corporation), and wood pulp (DP = 700).

Spinning Process and the Manufacture of Precursor

Using lyocell process (dry-jet-wet spinning) to produce lyocell fiber precursor for carbon fiber, the concentration of cellulose is about 9% in the dope; the diameter of spinneret is about 0.08 mm (210 holes); coagulation bath medium is diluted NMMO water solution (5%) and its temperature is 18°C.

The weighted pulp power and NMMO (containing 0.1% antioxidant) are poured into the dissolving tank and mixed at 90°C. When completely swollen, they are heated and stirred under vacuum to remove the excess water. At last the dope is extruded with N_2 though the 210-hole spinneret into the coagulation bath. After cleaning and drying, the filaments obtained can be used directly as the precursor for carbon fiber.

The Preparation of Carbon Fiber

On the oxidation line, the lyocell fiber is washed with pure water, acid, and carbonization catalyst. After five different temperature procedures, the precursor is over-treated at 800°C and 1300°C sequentially. The carbon fiber is thus obtained.

Testing of Fiber Samples

Lyocell fiber fineness is determined with an XD-1 linear density tester (China Textile University, Shanghai), and the mechanical properties are tested with an XQ-1 single filament electric tenacity tester (China Textile university, Shanghai) at the condition of 20°C and R.H.65%. The sample trapped length is 20 mm, drawing rate 3 mm/min, and the testing frequency 35 times for each sample. For the carbon fiber, its fineness is mensurated in a JSM-5600LV SEM electric microscope (JEOL Co. Japan); its mechanical properties are tested with electric tenacity tester by paper flame method. Sample trapped length is 10 mm, drawing rate 1 mm/min, and the testing frequency 35 times for each sample.

RESULTS AND DISCUSSION

The Properties of Precursor and the Final Carbon Fiber

Like viscose fiber, lyocell fiber is one of the regenerated cellulose fibers. The fiber with circular cross-section, homogenized skin-core structure, and high strength can be made through lyocell process [4–5]. All the features just mentioned are very important as a good precursor for carbon fiber. But the precursor produced by viscose process hardly meets them, so lyocell process may make high-quality cellulose precursor for carbon fiber. Table 1 lists some performance parameters of lyocell fiber and the lyocell-based carbon fiber.

Gray-Relation Analysis

Use average value method to pre-treat the data listed in Table 1 and consider the strength of carbon fiber as the master series and the mechanical properties parameters of precursor fiber as the subsidiary series. The resolution factor K is equal to 1, then

$$X_j^0 = \begin{bmatrix} 1.08 & 1.20 & 1.30 & 1.46 & 1.62 & 1.82 & 2.65 \\ 3.04 & 3.93 & 3.06 & 3.20 & 3.32 & 4.45 & 3.68 \\ 4.60 & 5.90 & 6.20 & 8.30 & 9.40 & 8.60 & 10.20 \\ 60.10 & 55.8 & 43.80 & 36.50 & 28.60 & 41.10 & 33.10 \\ 3.29 & 4.72 & 3.99 & 4.68 & 5.40 & 8.11 & 9.87 \end{bmatrix} \tag{1}$$

$$X_j^0 = [3.85\ 6.11\ 3.94\ 4.28\ 5.03\ 6.75\ 5.74] \tag{2}$$

TABLE 1 The Mechanical Properties of Lyocell Fiber and the Strength of Lyocell-Based Carbon Fiber

Precursor's tenacity (CN/dtex)	Precursor's elongation(%)	Precursor's modulus (CN/dtex)	Precursor's load at breaking (CN)	Carbon fiber's strength (CN/dtex)
3.04	4.60	60.10	3.29	3.85
3.93	5.90	55.80	4.72	6.11
3.06	6.20	43.80	3.89	3.94
3.20	8.30	36.50	4.68	4.28
3.32	9.40	28.60	5.40	5.03
4.45	8.60	41.10	8.11	6.75
3.68	10.20	33.10	9.78	5.74

$$\overline{X_j^0} = [1.590\ 3.526\ 7.600\ 42.686\ 5.71] \tag{3}$$

$$\overline{X_i^0} = 5.1 \tag{4}$$

The following matrix can be obtained from Eqs. (1) and (3):

$$X_j^i = \begin{bmatrix} 0.679 & 0.775 & 0.818 & 0.918 & 1.109 & 1.145 & 1.667 \\ 1.160 & 1.115 & 0.868 & 0.908 & 0.942 & 1.262 & 1.044 \\ 0.605 & 0.776 & 0.816 & 1.092 & 1.237 & 1.132 & 1.342 \\ 1.408 & 1.307 & 1.026 & 0.855 & 0.670 & 0.963 & 0.775 \\ 0.576 & 0.827 & 0.699 & 0.820 & 0.946 & 1.420 & 1.713 \end{bmatrix} \tag{5}$$

Eq. (6) can be obtained from Eqs. (2) and (4):

$$X_i^1 = [0.7549 \quad 1.1980 \quad 0.7725 \quad 0.8392 \quad 0.9863 \quad 1.3235 \quad 1.1255] \tag{6}$$

Therefore

$$\Delta_{ij}(t) = \begin{bmatrix} 0.0759 & 0.4430 & 0.0455 & 0.788 & 0.0327 & 0.1785 & 0.5415 \\ 0.4051 & 0.0830 & 0.0955 & 0.778 & 0.0443 & 0.0615 & 0.0815 \\ 0.1499 & 0.4220 & 0.0435 & 0.2528 & 0.2507 & 0.1915 & 0.2165 \\ 0.6531 & 0.1090 & 0.2523 & 0.0158 & 0.3163 & 0.3605 & 0.3705 \\ 0.1789 & 0.3710 & 0.0735 & 0.0192 & 0.0403 & 0.0965 & 0.6055 \end{bmatrix} \tag{7}$$

$L_{ij}(t)$ can be calculated from Eq. (7)

$$L_{ij}(t) = \frac{\Delta_{ij}(t)_{\min} + k \times \Delta_{ij}(t)_{\max}}{\Delta_{ij}(t) + k \times \Delta_{ij}(t)_{\max}} = \frac{0.0158 + 1 \times 0.6531}{\Delta_{ij}(t) + 1 \times 0.6531} \tag{8}$$

So,

$$L_{ij}(t) = \begin{bmatrix} 0.9176 & 0.6103 & 0.9575 & 0.9139 & 0.9754 & 0.8044 & 0.5599 \\ 0.6063 & 0.9087 & 0.8935 & 0.9422 & 0.9591 & 0.9360 & 0.9106 \\ 0.8359 & 0.6222 & 0.9602 & 0.7384 & 0.7401 & 0.7920 & 0.7692 \\ 0.5121 & 0.8777 & 0.7378 & 1.0000 & 0.6900 & 0.6599 & 0.6535 \\ 0.8039 & 0.6532 & 0.9206 & 0.9949 & 0.9647 & 0.8923 & 0.5315 \end{bmatrix} \tag{9}$$

$$R_{ij} = \begin{pmatrix} 0.8199 \\ 0.8795 \\ 0.7797 \\ 0.7330 \\ 0.8230 \end{pmatrix} \quad (10)$$

from Eq. (10) the correlative order of the relative coefficients of precursor can be arranged in numerical sequence as following:

Strength (0.8795) > forces at breaking (0.8230) > fineness (0.9199) > elongate at breaking (0.7795) > modulus (0.7730).

Analyses and Discussion

From the results calculated earlier [6–8] it can be found that the strength of precursor, the force at breaking, and its fineness have great influence on the final carbon fiber prepared from this precursor; the elongation and initial modulus, however, have little effect on the strength of lyocell-based carbon fiber. Precursor's strength and the force at breaking mainly depend on its internal super-molecular structure and other physical structural effects. Fiber precursors made from lyocell process have higher orientation and crystalline degree and regular arrangement of cellulose molecular links. So, the strength of the precursor depends on the formation of fiber and physical avoids and imperfections formed during the coagulation of the fiber. What's more, the lacuna within the precursor fiber may be more or less directly transferred to the resulting carbon fiber [9]. Thus it is easy to understand from Griffith's rupture theory why the precursor's strength and the force at breaking have great influence on the strength of the carbon fiber. On the other hand, the great influence of precursor's fineness on the strength of carbon fiber is caused by the following fact: the smaller the fiber's diameter, the larger the surface area of fiber; then, catalyst can be easily absorbed in the stage of pretreatment, making the carbonization of precursor more homogeneous, and, at the same time, the tar produced during carbonization more easily eliminated; consequently, the final carbon fiber will have more homogeneous structure.

CONCLUSION

The effect of mechanical performance parameters on the strength of carbon fiber has been investigated with gray relation analysis method. The analytic results suggest that the strength, the force at breaking, and fineness of precursor fiber have great influence on the strength of carbon fiber, the elongation and modulus of the precursor, however, have indistinctive effect.

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