Affect of Dope Additives on Finishing Behavior of Carbon Fiber Precursors

Chen Hou, Cheng-Guo Wang, Liang Ying, Hua-Su Cai

Carbon Fiber Center, College of Materials Science and Engineering, Shandong University, Jinan 250061, People's Republic of China

ABSTRACT: Finishing kinetics of acrylic precursor fibers was studied by using a new CGB finish. Effects of dope additives including polyvinyl pyrrolidone, glycerol, and polyvinyl acetate on finishing behavior of acrylic precursors were contrastively discussed. Diffusion coefficients for the finish were calculated from the Crank's equation. It is shown that the precursor fibers applied with the CGB finish do not give fluffs, broken, and adhered precursors. The increase of the finish uptake values is greater around the glass transition temperature, and the changes of uptake become less prominent as the finish bath temperature above the glass transition temperature. By use of the dope additives, the finish uptake values are enhanced; the diffusion coefficient for the finish is higher; the activation energy required for the finish is lower; the extent being greatest for the fibers containing polyvinyl pyrrolidone. The properties of the finished precursor fibers containing polyvinyl pyrrolidone are the best. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2752–2755, 2003

INTRODUCTION

Application of the finish is an important aftertreatment stage for carbon fiber precursors production. In the industrial processes for carbon fiber production, the oxidative stabilization and the carbonization operation usually encounter troubles, such as adhered or fused precursors, fluffs on precursors, and precursor breakage due to the frication between precursors and machinery surface. Such troubles lead to poor quality and performance of the resultant carbon fibers.[1,2] The above-mentioned troubles are variable, depending on the finish variants applied to the precursors. A finish should therefore smooth the surface of the fibers, but also ensure a certain degree of adhesion of the tow and prevent antistatic charges that impair the processing of water-repellent fabrics. Moreover, the finish should give the fibers an attractive hand. Various methods for eliminating such adhered or fused precursors by applying silicone oils have already been proposed.[3–5] but the hydrophilicity of silicon oils is apt to accumulate static charge and cause precursors fluffs and breakage. Incorporating various additives into the spinning dope can improve effect of the finish.[6] To our knowledge, there are only few reports on application of finish in precursors, but there is almost no report on effect of the dope additives on finishing behavior of carbon fiber precursors. In this study, a new CGB finish not containing silicone oils for precursors was introduced. Finishing kinetics of acrylic fibers containing polyvinyl pyrrolidone, glycerol, and polyvinyl acetate as dope additives was contrastively studied. The activation energy of finishing behavior of these fibers was also calculated.

EXPERIMENTAL

Materials

The precursor fibers used for finishing were continuous filaments spun on a laboratory-made wet-spun apparatus. The precursors had methyl acrylate as the main comonomer unit, and had the following elemental analysis: C, 66.54; N, 25.61; H, 6.73; O, 1.12. The fibers were produced from a 20 wt % solution of acrylonitrile/methyl acrylate copolymer in dimethyl sulphoxide (DMSO). The 20 wt % copolymer solution was deaerated, filtered, and then pumped through a spinneret (1000 holes, 0.06 mm/hole, $L/D = 1.2$) to a coagulating bath. The coagulating bath composition and temperature were 60% DMSO and 20°C, respectively. The wet-spun filaments were washed and drawn in three steps in a water bath, followed by finished with a new CGB finish. The finished filaments were dried to collapse them, further drawn in steam, set, dried, and wound to PAN precursors. The jet stretch was 0.5 and the overall draw ratio was 14.

The dope additives (4% on the weight of acrylonitrile/methyl acrylate copolymer) for this study include polyvinyl pyrrolidone, glycerol, and polyvinyl acetate.

Correspondence to: C. Hou (chenhou0825@163.net).

TABLE I
Equilibrium Finish Uptake Values for Precursor Fibers

Fiber code	Dope additive	T_g/°C	Finish uptake/(mg/g)								
			45°C	55°C	65°C	75°C	80°C	85°C	90°C	95°C	100°C
T	no	94	4.8	5.9	7.3	8.9	10.2	12.3	14.2	23.7	24.1
TP	polyvinyl pyrrolidone	80	5.6	7.9	10.4	13.7	28.8	29.1	29.2	29.9	30.1
TV	polyvinyl acetate	85	5.2	7.1	9.1	11.2	14.2	26.3	27.7	28.1	29.6
TG	glycerol	88	5.1	6.9	8.9	11.1	13.2	15.1	26.7	27.2	27.9

A new CGB finish is a mixture of different components in the form of aqueous emulsion. The prepared finish comprises 25 or more percent by weight of the reaction product of a saturated aliphatic dicarboxylic acid, and a monoalkyl ester of an ethylene oxide adduct of bisphenol A; and 40 to 50 wt % of the product from the reaction of oleic acid diethanol amide, and the condensate of adipic acid, and the ethylene oxide adduct of hydrogenated castor oil; and about 15 wt % of the ethylene oxide adduct of the product from the reaction of diethylenetriamine and stearic acid; and about 20 wt % of the mixture of the adduct and the ethylene/propylene oxide block copolymer. The finish is resistant against heat and forms film on fiber surface so as to impart superior detachability between fiber strands. Such finish performance remarkably minimizes the troubles relating to the above-mentioned defect.

Finishing

The precursor fibers consisting of 1000 monofilaments were treated with the 4% solution of the CGB finish emulsion while under longitudinal restraint. The finish bath temperature was ranged from 45 to 100°C. After finishing for a definite time, the sample were dried at 100–140°C, and then prepared into the precursor fibers.

Characterization

The glass transition temperature (T_g) of the finished precursor fiber was recorded on a DT 40 thermal analyzer in nitrogen using a heating rate of 10°C/min.

The finished precursor fiber was dried and conditioned at 25°C. A known amount of the finished fiber was dissolved in 25 mL of dimethyl formamide (DMF), and the optical density of the solution was determined on a spectrophotometer (Unicam SP 600). A standard plot of concentration vs. optical density was obtained, taking the known concentration of the finished solution. From the standard plot, the amount of the finish in the fiber was calculated.

Diffusion coefficient (D_a) was calculated using the Crank's method[7] by measuring the finish uptake of the fiber with time intervals of t from the finish bath. Crank's equation is represented as

$$D_\alpha = \pi \alpha^2 C_t t^1 C_\infty / 16$$

where D_a is the diffusion coefficient, C_t is the finish uptake at time t, C_∞ is the equilibrium finish uptake, a is the radius of the fiber, and t is the finishing time.

The fineness and mechanical properties of PAN precursors were measured by an XQ-1 tensile-testing machine (made in Donghua University, Shanghai, China) at a crosshead speed of 0.5 mm/min with a testing length of 2 cm and load cell of 0.2 cN. In each case, at least 30 sample filaments were tested, and the average of 30 filaments was taken for each experiment.

RESULTS AND DISCUSSION

Effect of dope additives on finish uptake of precursor fibers

An influence of temperature on the finish uptake of the precursor fibers was studied by varying the finish bath temperature from 45 to 100°C, and the finishing time was controlled at 5 min. The glass transition temperature (T_g) was also determined. The fiber code and composition and experimental results are given in Table I. The values of glass transition temperature of the fibers show a trend of decrease with addition of the dope additives. The equilibrium finish uptake values of the fibers containing the dope additives are higher compared to those of fibers without additives. The finish uptake values increase with an increase of the finish bath temperature and the increase of uptake becomes less prominent when the temperature is above the glass transition temperature, but the increase is greater around the glass transition temperature. For example, T fiber shows a T_g at 95°C and TP fiber at 80°C. T fiber shows the finish uptake values of 14.2 mg · g^{-1} at 90°C and 23.7 mg · g^{-1} at 95°C, whereas TP fiber shows finish uptake 13.7 mg · g^{-1} at 75°C and 28.8 mg · g^{-1} at 80°C.

This can be explained by taking into account the glass transition temperatures of these fibers. The finish uptake is dependent on the amount of the finish molecules penetrating into the amorphous and disori-
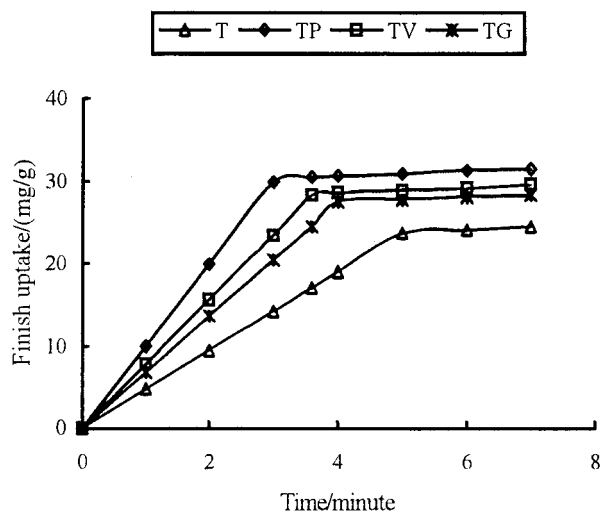
Figure 1   Effect of time on finish uptake of fibers.

ented region of the fibers.[8] Above T_g, the polymer chain segmental mobility occurs, the glass-like amorphous region changes into an elastic one, permitting the finish molecules to migrate into the fiber to a greater extent for level finishing.[9] The addition of spinning dope reduces T_g. This is presumably because of a reduction in dipole interaction due to the irregularly disposed pendant groups.[10] The low glass-transition temperature eases the finish diffusion and provides more sites accessible to finishing. The introduction of the dope additives loosens the compact structure of the fibers, and there is more amorphous content and less orientation in the fibers with additives. Hence, the dope additives favor good diffusion of the finish molecules.

Finish Uptake as a Function of Time

The rate of finishing for the fibers was determined by determining the finish uptake at the different time intervals, and the finish bath was kept at 95°C. Figure 1 shows the finish uptake vs. time plots. The finish uptake increases quickly as time increases, and such a change becomes less prominent as the time is beyond 5 min. T fibers reach the maximum finish uptake value in 5 min, whereas TP, TV, and TG fibers take 3, 3.6, and 4 min, respectively, to reach equilibrium. The rate of finishing of TP, TV, and TG fibers is faster compared to that of T fiber.

The literature reports that the diffusion of finish into acrylic fibers is controlled by to a considerable extent the polymer composition, the segmental mobility of the polymer chain, and the free volume of the fibers.[11] The isotacticity of polymer chain of the spinning dope decreases largely, and the free volume of the fibers increases with addition of the dope additives; the extent is greater by addition of polyvinyl pyrrolidone, so the rate of finishing of TP fiber is fastest.

TABLE II
Diffusion Coefficient and Activation Energy Values for Fibers Finished at 95°C

Fiber code	$D_a \times 10^{14}/(m^2/s)$	$\Delta E/(kJ/mol)$
T	2.08	29.1
TP	3.47	17.9
TV	2.89	21.2
TG	2.61	23.4

The diffusion coefficient values were calculated by using the Crank's method according to the parameters in Figure 1. It is evident from Table II that the diffusion coefficient values for the fibers containing the dope additives are higher compared to the fibers without additives, and the diffusion coefficient value of TP fiber is the highest. For example, T fiber has a D_a value of $2.08 \times 10^{-14} m^2 s^{-1}$, but TP fiber has a value of $3.47 \times 10^{-14} m^2 s^{-1}$.

From the Arrhenius equation, the expected relation between the diffusion coefficient and the absolute temperature is given by the following equation:

$$\ln Da = -\Delta E/RT + C$$

where Da is diffusion coefficient, ΔE is the activation energy, T is the absolute temperature, R is the gas constant, and C is a constant. The plot of $\ln Da$ vs. $1/T$ is a straight line above T_g of the fibers.[12] The activation energy calculated from the slope of the straight line gives a value of 29.1 kJmol for the T fiber (Fig. 2). Similarly, the activation energy of TP, TV, and TG fibers was also calculated. TP, TV, and TG fibers show the lower values, i.e., 17.9, 21.2, and 23.4 kJ/mol, respectively (Table II). The value of ΔE of the TP fiber is the lowest. ΔE may be the energy required for migration or replacement of the finish molecules already combined with the finish affinitive positions.[13] The presence of the dope additives in TP, TV, and TG fibers could plasticize the structure internally, so that
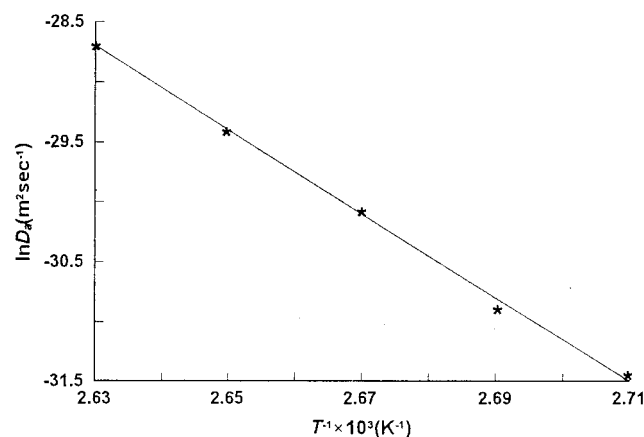

Figure 2   Plot of finishing uptake vs. finishing time.

TABLE III
Effect of the Dope Additives on the Properties of the Precursor Fibers

Fiber code	Fineness/ dtex	Tenacity/ (cN/dtex)	Elongation at–break (%)
Unfinished fiber	1.19	5.76	14.1
T	1.18	5.92	15.1
TP	1.09	6.27	17.5
TV	1.13	6.09	15.9
TG	1.11	6.17	16.4

lower energy is required for the migration of the finish. The lower activation energy happens to reflect the higher the finish uptake values for the fibers containing the dope additives.

Effect of the dope additives on properties of the precursor fibers

Because both the finish and the dope additives play an important role in the factors that affect properties of precursor fibers, it is necessary to study the properties of the finished precursor fibers. The fibers were dried at 100–140°C after finishing, and then were prepared into the precursors. Table III shows effects of the finish and the dope additives on properties of the precursor fibers.

The precursor fibers applied with the CGB finish give an attractive hand, and there are no fluffs, broken, and adhered precursors in them. In addition, the elongation at break of the finished precursors is enhanced, the extent being greater in the fibers containing the dope additives. The changes of the fineness and tenacity of the finished precursor fibers are less obvious. The properties of the finished precursor fibers containing polyvinyl pyrrolidone are the best.

CONCLUSIONS

Laboratory studies of finishing behavior of the precursor fibers have shown that the finished precursor fibers give an attractive hand, and there are no fluffs, broken, and adhered precursors in them by the application of the CGB finish. The finish uptake values increase with an increase of the finish bath temperature, and the increase is greater around the glass transition temperature. As the finish bath temperature is above the glass transition temperature, the increase of finish uptake becomes less prominent. Polyvinyl pyrrolidone, glycerol, and polyvinyl acetate were used as dope additives. The finish uptake values are enhanced by use of the dope additives. By a contrastiing study, the diffusion coefficient for the finish is highest and the activation energy required for the finish is lowest when polyvinyl pyrrolidone is used as the dope additive. In addition, the elongation at break of the finished precursors is enhanced, the extent being greater in the fibers containing polyvinyl pyrrolidone.

References

1. Dong, J.-L.; Zhao, Y.-M.; Chen, X.-T.; Cheng, X.-M. Process of Synthetic Fiber Production; Chinese Textile Industry Press: Beijing, 1996.
2. Mason, J. C. Acrylic Fiber Technology and Applications; M. Dekker: New York, 1995.
3. Masaki; Komatsubraa; Tanaka; Nakanishi; Nakagawa; Kanamori, U.S. Pat. 5783305 (1997).
4. Loew; Peter. U.S. Pat. 4382801 (1983).
5. Zhang, X.-Q.; Zhang, Q.-H.; Wang, J. Adv Fine Petrochem 2001, 2, 28.
6. He, M.-J.; Chen, W-X.; Dong, X.-X. High Polymer Physics' Fudan University Press: Shanghai, 2000.
7. Brody, H. Textile Res J 1965, 35, 844.
8. Bajai, P.; Munukutla, S. K. Textile Res J 1990, 60, 113.
9. Levine, C. A.; Traylor, T. G. J Appl Polym Sci 1961, 5, 606.
10. Bajai, P.; Sengupta, A. K.; Jain, P. C. Textile Res J 1980, 50, 218.
11. Rosenbaum, S. J Appl Polym Sci 1963, 7, 1225.
12. Bajai, P.; Padmanaban, M. Textile Res J 1985, 55, 352.
13. Gao, X.-S.; Wu, D.-C. The Applied Physics of Fiber; Chinese Textile Industry Press: Beijing, 2001.