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The influences of silicone finishes on thermooxidative stabilization of PAN precursor fibers

DONGBING JIN*, YING HUANG‡, XIANGLUAN LIU, YUNZHAO YU
National Key Lab of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China
E-mail: ying2huang@yahoo.com.cn

The influences of functional polysiloxanes bearing epoxy or amino groups on the thermooxidative stabilization process of the PAN precursor fibers were studied. Structural changes were investigated by FT-IR spectroscopy. It was found that formation of the conjugated ladder structure in the precursor fiber was promoted by the functional polysiloxanes. Meanwhile heat releasing in the thermooxidative stabilization process was depressed. It seems that the coatings of the functional polysiloxanes on the fibers retarded oxygen diffusion into the PAN precursor fibers. The functional polysiloxanes did not affect carbonization in an inert atmosphere following the thermooxidative stabilization process.

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1. Introduction

High strength high modulus carbon fibers are mostly based on polyacrylonitrile (PAN) precursor fibers. [1, 2] Stabilization of PAN precursor fibers by controlled heating in the temperature range of 180 to 300°C under tension in an oxidative atmosphere is considered to be a key step in the manufacture of carbon fibers [3]. Chemical reactions involved in the thermooxidative stabilization stage, which result in the formation of the conjugated ladder structure, are cyclization, dehydrogenation, aromatization, oxidation and crosslinking [4, 5]. They are influenced by the medium and the temperature of treatment, as well as pretreatment of the precursor fiber [6–10].

Usually a spin finish is applied to the acrylic precursor fibers to reduce entangling, to reduce fiber-to-metal adhesion, to decrease static charge build up and increase filament cohesion. Functionalized polysiloxanes are extensively used in spin finishes for PAN precursor fibers [11–13].

In the study of the thermooxidative stabilization of PAN fibers, we noticed that the functional polydimethylsiloxanes not only are good lubricants for the fiber, their influences on the chemical reactions in the thermooxidative stabilization process of the precursor fiber are also meaningful. This article is to report the effects of epoxy- and amino-modified polydimethylsiloxanes on the structure change and the heat releasing in the thermooxidative stabilization process.

2. Experimental

2.1. Materials

The PAN precursor fiber used in this study was provided by Shanxi Institute of Coal Chemistry, Chinese Academy of Sciences. It was produced from a specialty copolymer of acrylonitrile (AN), methyl acrylate and a small amount of acrylic acid for carbon fiber manufacture, with each tow consisting of 3000 filaments.

The epoxy-modified polydimethylsiloxane (EPS) was synthesized in this lab through hydrosilylation of allyl glycidyl ether with poly (dimethylsiloxane-co-methylhydrosiloxane) in the presence of a platinum catalyst. The epoxy group content was 0.51 mmol/g, and the kinetic viscosity at 25°C was 2400 cp. The amino-modified polydimethylsiloxane (APS) was prepared through copolymerization of octamethylcyclotetrasiloxane and aminopropylmethyl- dimethylsiloxane. The amino group content was 0.3 mmol/g, and the kinetic viscosity at 25°C was 2000 cp.

2.2. Cleaning and treatment of the PAN precursor fiber

The PAN precursor fiber was extracted with toluene for 24 h in a soxhlet extractor, and then extracted with methanol for 24 h to remove any contaminants. It was then dried in vacuum at 60°C for 4 h. The cleaned PAN precursor fiber was treated by dipping in 2% solution of EPS or APS in toluene for 30 min. The liquid was then squeezed out by pressing with a rubber roll until the holdup of the solution reached 50 wt%. The treated fiber was dried in a vacuum oven at 60°C for 4 h. After

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*Graduate School of CAS.
‡Author to whom all correspondence should be addressed.

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the treatment, the thin coating of the polysiloxane on the fiber was 1 wt% based on the fiber weight.

2.3. Stabilization of PAN precursor fibers

The PAN precursor fibers were stabilized by heating in an air-circulated oven at 200°C for one hour. After cooling to the room temperature, samples were taken for IR and TGA studies.

2.4. Measurements

PAN fiber samples were finely grounded with KBr; pellets were pressed for IR studies. FT-IR spectra were recorded on a Perkin-Elmer model 1600 IR Spectrometer.

Differential scanning calorimetry (DSC) was carried out on Mettler-Toledo 822^e differential scanning calorimeter at a heating rate of 10°C/min with a nitrogen flow or a air flow of 100 ml/min. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer pyris-1 TGA Thermogravimetric Analyzer in the range of 50–900°C at a heating rate of 10°C/min under a nitrogen flow of 30 ml/min.

3. Results and discussion

3.1. Effect of polysiloxane on the structure change of the PAN fiber in the thermooxidative stabilization process

In order to illustrate the effect of the functional polysiloxane on the structure change of the PAN fiber in the process of thermooxidative stabilization, the fiber was thoroughly cleaned by extraction with solvents, and then the polysiloxane was applied in known concentrations. To eliminate the effect of temperature fluctuation, a series of samples were treated simultaneously in an air-circulating oven at 200°C for one hour. After heat treatment, FT-IR spectra were taken for evaluating the proceeding of structure change.

As shown in Figs 1 and 2, a new moderate intense absorption band at 1600–1610 cm^{-1} and a weak band at 1700 cm^{-1} appeared for all PAN fiber samples treated at 200°C. Morever, a broad absorption band from hydroxy groups located at 3200–3700 cm^{-1} became much more stronger after heat treatment. The band at 1600–1610 cm^{-1} is due to the vibration of the conjugated C=C/C=N bonds of the fully-cyclized ladder polymer [14–16]. The band at 1700 cm^{-1} can be attributed to the vibration of the C=O bonds formed by addition of carboxyl group to nitrile group of the neighboring AN unit. These changes in the FT-IR spectra indicate that oligomeric cyclization of nitrile groups, dehydrogenation and aromatization, as well as oxidation took place during the heat treatment.

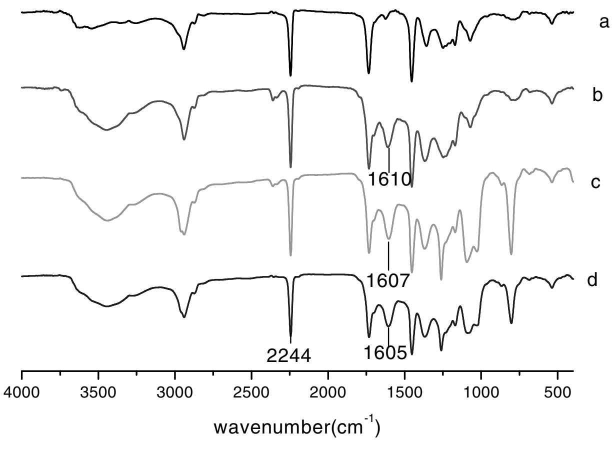


Figure 1 FT-IR spectra for the PAN precursor fibers: (a) original, (b) heated at 200°C for 1 h in air, (c) coated with 1 wt% EPS and heated at 200°C for 1 h in air, and (d) coated with 1 wt% APS and heated at 200°C for 1 h in air prior to the measurement.

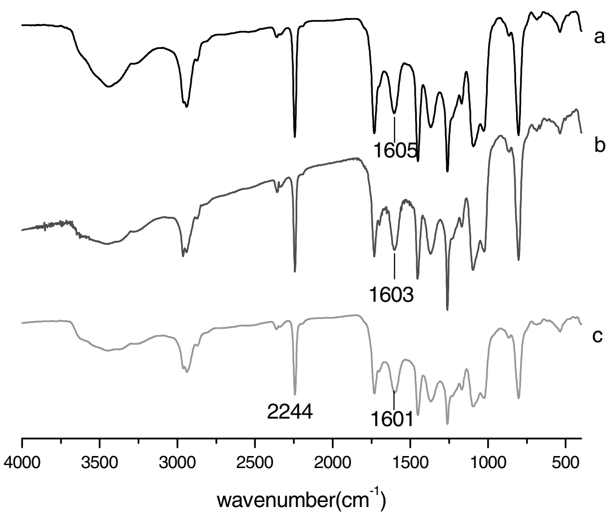
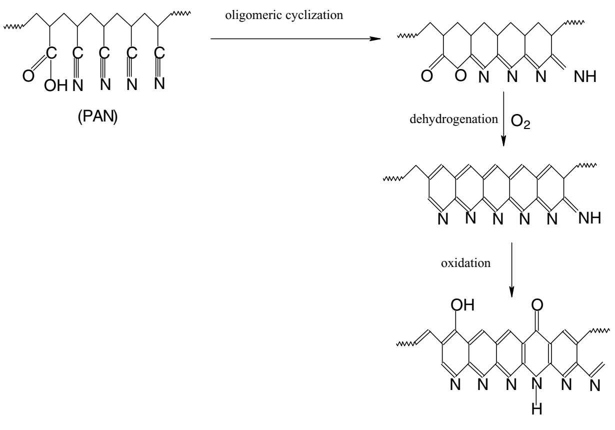


Figure 2 FT-IR spectra for the PAN precursor fibers: (a) coated with 1 wt% EPS, (b) coated with 2 wt% EPS, and (c) coated with 3 wt% EPS. All fiber samples were heated at 200°C for 1 h in air prior to the measurement.



Scheme 1 Main reactions of the PAN precursor in the thermooxidative stabilization stage.

The structure change of PAN in the thermooxidative stabilization process is shown in Scheme 1.

To quantify the structural conversion from PAN to conjugated ladder polymer, we use the IR conversion index, which is expressed in terms of the relative intensities of the vibration bands associated with the PAN and the ladder structure [17]:

$$A = I_{\mathrm{C=C/C=N}}/(I_{\mathrm{C\equiv N}} + I_{\mathrm{C=C/C=N}}) \qquad (1)$$

where $I_{\mathrm{C=C/C=N}}$ is the measured absorption intensity for the conjugated C=C/C=N bonds at 1600–1610 cm^{-1} and $I_{\mathrm{C\equiv N}}$ is that for the unreacted nitrile groups at 2244 cm^{-1}.

TABLE I The effect of functional polysiloxanes on the conversion of the PAN fiber[a]

Sample code	Polysiloxane	Concentration of polysiloxane on PAN fiber (wt%)	IR band for C=C/C=N (cm^{-1})	$I_{C=C/C=N}/I^{b}_{C\equiv N}$	Conversion index (%)
0-0-1	–	0	1610	0.72	41
A-1-1	APS	1	1607	0.81	45
E-1-1	EPS	1	1605	0.76	43
E-2-1	EPS	2	1603	0.91	48
E-3-1	EPS	3	1601	0.95	49

[a] The conditions for the heat treatment: 200°C, 1 h in air.

[b] The ratio of peak height.

The effect of functional polysiloxanes on the conversion of PAN in the thermooxidative stabilization process is summarized in Table I. It is seen that enhancement of the conversion index by coating the fiber with APS and EPS was meaningful, and it became more remarkable as the concentration of the polysiloxanes increased. The formation of the conjugated ladder structure during the heat treatment was promoted by the functional polysiloxanes remarkably.

3.2. Heat releasing during the thermooxidative stabilization

The oligomeric cyclizations of nitrile groups, dehydrogenation and aromatization, as well as oxidation are all exothermic reactions. Heat releasing during the thermooxidative stabilization process was investigated by DSC measurements. In Fig. 3, the DSC thermograms obtained in air for the PAN precursor fiber and the fibers coated with 1 wt% of EPS or APS are shown. The thermograms obtained in nitrogen are shown in Fig. 4.

We can see a great difference between the DSC thermograms obtained in air and in high purity nitrogen: in the thermograms obtained in air there are mainly two exothermic peaks at 290 and 335°C respectively, while only a single exothermic peak at 290°C was found in the thermograms obtained in nitrogen. According to a previous work [18], dehydrogenation reactions could take place over the whole stabilization process. The exothermic peak at about 290°C in air should be related basically with the oligomeric cyclization of nitrile groups and dehydrogenation reactions, while the exothermic peak at 335°C should be related with the oxidation and dehydrogenation in air. The plateau situated at still higher temperature region in the thermograms obtained in air should be related with the dehydrogenation, aromatization and oxidative reactions, which continued after cyclization of the nitrile groups.

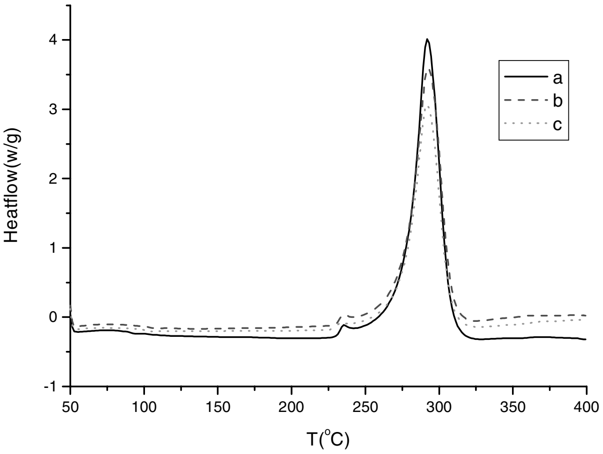


Figure 4 DSC thermograms for the PAN precursor fibers obtained in nitrogen: (a) the virginal fiber, (b) coated with 1 wt% EPS, and (c) coated with 1 wt% APS.

In Figs 3 and 5, we can see a notable reduction of heat releasing in the DSC thermograms obtained in air especially in the high temperature region when the fiber was coated with the functional polysiloxanes. The reduction of heat releasing became more significant as

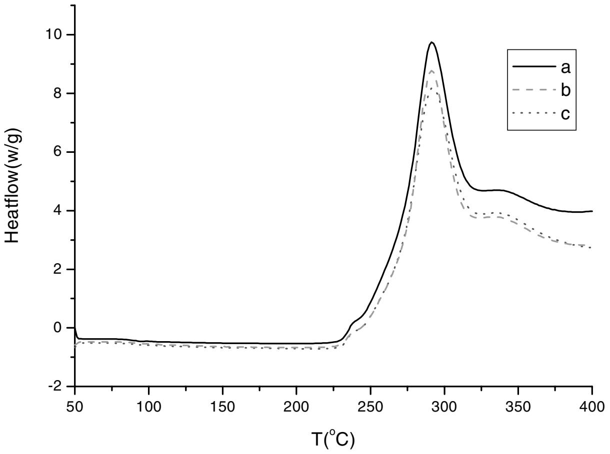


Figure 3 DSC thermograms for the PAN precursor fibers obtained in air: (a) the virginal fiber, (b) coated with 1 wt% EPS, and (c) coated with 1 wt% APS.

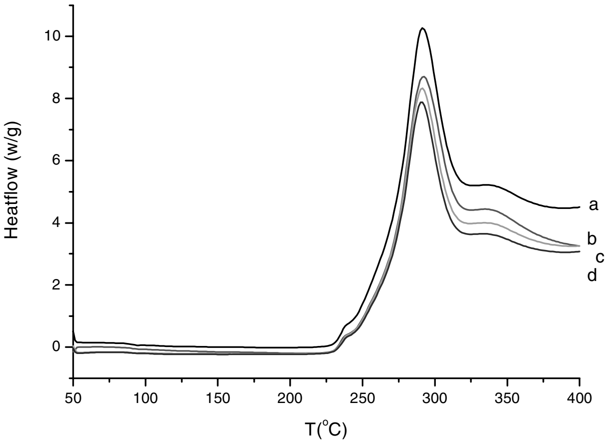


Figure 5 DSC thermograms obtained in air for the PAN precursor fibers coated with: (a) 1 wt% EPS, (b) 2 wt% EPS, and (c) 3 wt% EPS.

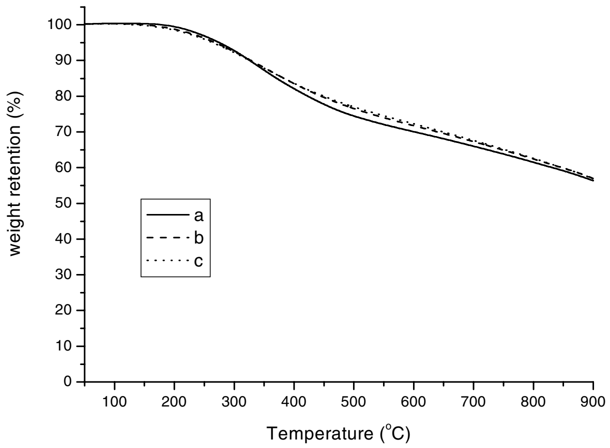


Figure 6 TGA diagrams for the PAN precursor fibers: (a) coated with 1 wt% APS, (b) coated with 1 wt% EPS, and (c) neat PAN fiber. The samples were treated at 200°C for 1 h in air prior to the measurement.

the concentration of EPS on the fiber surface increased (Fig. 5).

Obviously the dehydrogenation and oxidative reactions were retarded to some extent by the polysiloxanes layer. It is understandable that the polysiloxanes layer on the surface of PAN fibers can hinder the diffusion of oxygen into the PAN fibers and thus slows down the rate of these reactions.

The oligomeric cyclization, the dehydrogenation and aromatization, as well as oxidative reactions are all exothermic; from technical point of view, quick liberation of a large amount of heat in a short time period is harmful: it would result in fusion of the fibrils and breakdown of the polymer chains, and finally the quality of carbon fibers would be impaired. Therefore a reduction of heat releasing rate in the thermooxidative stabilization stage is advantageous for carbon fiber production. Use of the functional polysiloxanes as a coating of the PAN precursor fibers will make the thermooxidative stabilization easier to control.

3.3. Effect of the functional polysiloxanes on carbonization of the PAN precursor

In the process of carbon fiber production, thermooxidative stabilization of the precursor fiber is followed by carbonization in an inert atmosphere at 400–1000°C. To study the effect of the functional polysiloxanes on the carbonization, thermogravimetric analysis in high purity nitrogen was carried out. Prior to the TGA measurements, samples of the PAN precursor fiber and the fibers coated with 1 wt% of EPS or APS were first stabilized by a treatment in air at 200°C for 1 h.

As seen in Fig. 6, the difference between the TGA diagrams for the stabilized fibers of the original PAN precursor fiber and the fibers coated with functional polysiloxanes was marginal. Weight retention of three samples at 900°C was indistinguishable. Therefore, it is reasonable to assume that the functional polysiloxanes did not affect the carbon yield in the carbon fiber production.

4. Conclusions

The functional polysiloxanes bearing epoxy groups or amino groups are able to promote the formation of the conjugated ladder structure in the PAN precursor fiber in the thermooxidative stabilization process. Heat releasing during the thermooxidative stabilization can be depressed by a thin coating of the functional polysiloxane. It is likely that the polysiloxane layer retards diffusion of the oxygen into the PAN fibers and thus slows down the dehydrogenation and oxidative reactions. The functional polysiloxanes do not affect the carbonization of the stabilized precursor fiber in an inert atmosphere.

References

1. J. B. DONNET and R. C. BANSAL, “Carbon Fibers”, 2nd ed. (Marcel Dekker, New York, 1990).
2. A. K. GUPTA, D. K. PALIWAL and B. J. PUSHPA, *JMS-Rev. Macromol. Chem. Phys.* **31** (1991) 35.
3. W. WATT, *Carbon* **10** (1972) 121.
4. Z. BASHIR, *ibid.* **29** (1991) 1081.
5. S. DALTON, F. HEATLY and P. M. BUDD, *Polymer* **40** (1999) 5531.
6. G. HENRICI-OLIVE and S. OLIVE, *Adv. Polym. Sci.* **51** (1983) 3.
7. E. FITZER and D. J. MULLER, *Carbon* **13** (1975) 63.
8. M. M. COLEMAN and R. J. PETCAVICH, *J. Polym. Sci. Polym. Phys. Ed.* **16** (1978) 821.
9. E. FITZER, W. FROHS and M. HEINE, *Carbon* **24** (1986) 387.
10. T. H. KO and C. H. LIN, *J. Mater. Sci. Lett.* **7** (1988) 628.
11. Mitsubishi Rayon Co. Ltd., Japan Kokai Tokkyo Koho JP 60181323 (1985).
12. I. MASASHI and K. Y. MAKOTO, Japan Kokai Tokkyo Koho JP10102380 (1998).
13. K. MARUYAMA and R. KOIDE, US Patent US5726241 (1998).
14. A. J. CLARKE and J. E. BAILEY, *Nature* **243** (1973) 146.
15. R. LIEPINS, D. CAMPBELL and C. WALKER, *J. Polym. Sci.* **A 1** (1968) 3059.
16. H. KAKIDA and K. TASHIRO, *Polym. J.* **30** (6) (1998) 463.
17. Y. ZHU, M. A. WILDING and S. K. MNKHOPADHYAY, *J. Mater. Sci.* **31** (1996) 3831.
18. E. FITZER and D. J. MULLER, *Carbon* **13** (1975) 63.

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