

Influence of Ozone on Chemical Reactions During the Stabilization of Polyacrylonitrile as a Carbon Fiber Precursor

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ABSTRACT: Chemical shrinkage was used for the *in situ* measurement of the progressing chemical stabilization reactions and the influence of ozone during the stabilization of polyacrylonitrile. A method for evaluating the activation energy through the sensitivity temperature is presented. The calculated results show that the activation energies were 161.57 kJ/mol in air and 181.23 kJ/mol in ozone-enriched air. Therefore, the chemical reactions were postponed during stabilization in ozone-enriched air.

Ozone seemed to act in three ways: first, ozone promoted the formation of the serious skin-core structure. Second, ozone accelerated the chemical reactions and shortened the stabilization time at lower heating rates. Third, ozone postponed the chemical reactions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3990–3996, 2008

Key words: activation energy; differential scanning calorimetry (DSC); fibers

INTRODUCTION

It has been well established that polyacrylonitrile (PAN) fiber is one of the most suitable and widely used precursors for fabricating high-performance carbon fiber.^{1–3} The production process from PAN consists of three steps: (a) stretching to obtain a preferred orientation of the polymer molecule, (b) stabilization in air at a constant length or even with additional stretching, and (c) carbonization of the stabilized fiber in nitrogen. If we consider the residence times of the production process, we can see that stabilization is still the most time-consuming step, taking an hour and more.⁴ This stabilization is normally carried out in the temperature range 180–300°C in different atmospheres under tension for an adequate duration to render the fibers infusible and flameproof. Stabilization reactions have been observed *in vacuo*^{5,6} and in inert gases, such as nitrogen^{7,8} or argon,⁹ and also in air and oxygen-containing atmospheres.¹⁰ However, reports about the influence of ozone on the stabilization reactions have rarely been seen.

When PAN fibers are subjected to heat treatment, they undergo obvious changes in the length. The shrinkage is considered to consist of two categories: physical shrinkage and chemical shrinkage, or initial

shrinkage and secondary shrinkage.^{11–13} The two contributions can be clearly distinguished by a minimum in the first derivative curve⁴ (Fig. 1). The physical shrinkage below 180°C corresponds to entropic shrinkage and is due to oriented amorphous polymeric chains reverting to their random-coil configuration. The chemical shrinkage is mainly due to the cyclization and crosslinking reaction.¹² Some researchers have suggested that the shrinkage can be used as a parameter in the optimization of stabilization.^{1,4} Therefore, in this study, we mainly used shrinkage to investigate the progressing chemical stabilization reactions in air and ozone-enriched air. The influence of ozone is reported here.

EXPERIMENTAL

Precursor

The selected PAN precursor was supplied by Huitong Ltd. (Yangzhou, China) in tows of 3000 fibers with an average denier of 1.18 g/cc and a mean diameter of 12.4 μm. This precursor fiber was most probably a copolymer of acrylonitrile, methylacrylate, and itaconic acid.

Stabilization

The stabilization was carried out in a batch-scale furnace. A fixed length of precursor fiber was tied to Kevlar thread on both its ends. To monitor the shrinkage during stabilization, the Kevlar from one end was fixed, and the other end was passed over a

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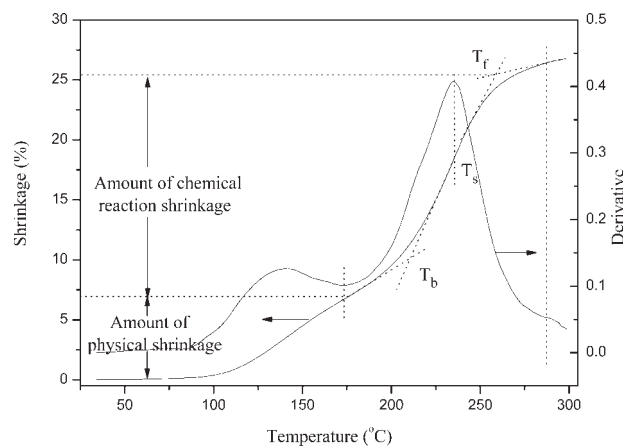


Figure 1 Typical shrinkage curve during stabilization without any load composed of contributions from physical entropy shrinkage and chemical shrinkage.

smooth pulley and connected to a weight corresponding to a tension of 0.0013cN/dTex (Fig. 2). The movement of the weight was monitored by a displacement pickup and converted to percentage shrinkage values. The results so obtained are referred to as *free shrinkage* because the tension on the fibers was extremely small. The change in the Kevlar length was negligible in the range of temperatures studied. Output from displacement pickup was amplified and noted by a paperless recorder every second. The gas flow rate was 3 L/min, and the concentration of ozone was 6 mg/L. The heating rate (ϕ) in air varied between 0.25 and 10°C/min. The Kevlar would be destroyed in ozone-enriched air with a ϕ of 0.25°C/min. Therefore, ϕ in ozone-enriched air varied between 0.5 and 10°C/min.

Density

Density was measured at 25°C with the suspension method. Mixtures of toluene (*density* = 0.866 g/cc) and carbon tetrachloride (*density* = 1.585 g/cc) were used for fiber density in the 1.00–1.6 g/cc range.

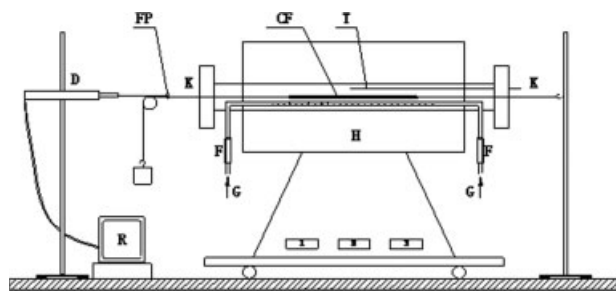


Figure 2 Apparatus used for percentage shrinkage measurements. CF = PAN fiber; D = displacement pickup; F = flowmeter; FP = fixed point; G = purge gas; H = three-zone furnace; K = Kevlar; R = paperless recorder; T = thermocouple.

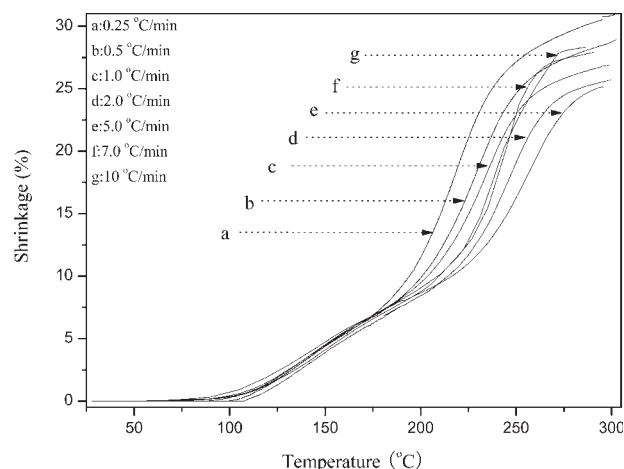


Figure 3 Free-shrinkage behavior during the stabilization of PAN fibers under linear treatment in air.

After mixing, the solutions containing chopped fiber sample were allowed to stand overnight. Regulations with appropriate liquids continued until the fiber floated in the center of the solution. The density of resulting solution was then determined with a density meter, and this density was extrapolated to be the density of the fiber specimen.

Other analyses

The cross sections of stabilized fibers were observed by a CMM-55 metallographic microscope (Shanghai Chaufang Optical Instrument Co., Ltd., Shanghai, China). Before observation, the fibers were embedded in epoxy resin and then made into 1 mm thick sections. Differential scanning calorimetry (DSC) of PAN fibers was carried out on a Netzsch STA 409 instrument (Germany). ϕ varied between 0.5 and 10°C/min.

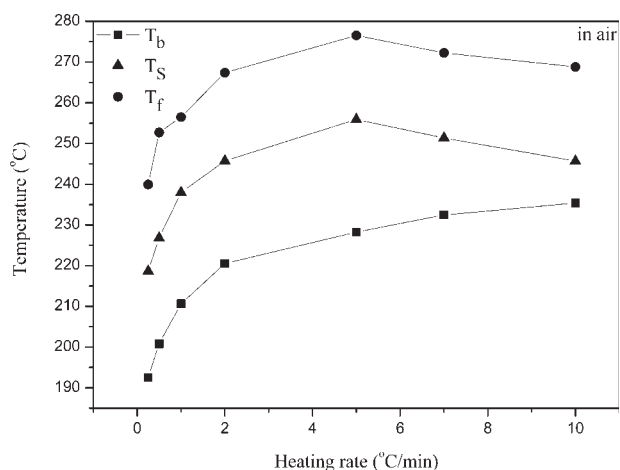


Figure 4 T_b , T_s , and T_f of chemical shrinkage as a function of ϕ .

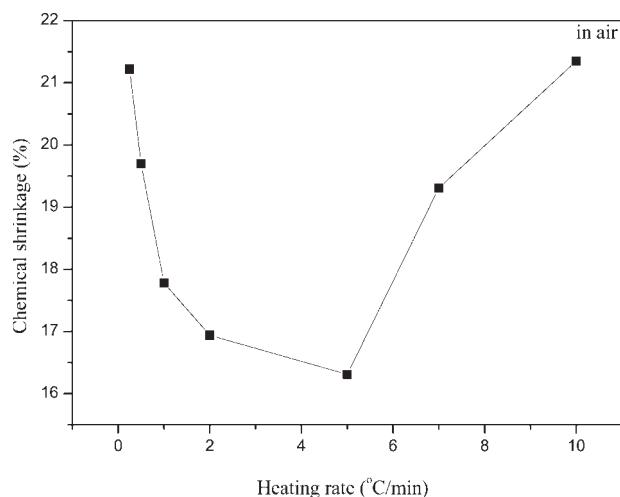


Figure 5 Amount of chemical shrinkages as a function of ϕ .

RESULTS AND DISCUSSION

Influence of ϕ on the stabilization of PAN fibers in air

Figure 3 shows the free-shrinkage behavior of PAN fibers under dynamic heating conditions in air. The curves indicated that increasing ϕ had a little effect on the amount of physical shrinkage but had a significant effect on the amount of chemical shrinkage. Therefore, the influence of ϕ on the chemical shrinkage was investigated. According to the analytical method (Fig. 1), some results were obtained.

The effect of ϕ on the beginning temperature (T_b), sensitivity temperature (T_s), and final temperature (T_f) during the stabilization of PAN in air is shown in Figure 4. Clearly, increasing ϕ increased T_b . This increase, expected to be a parabolic function according to the Kissinger theory of calorimetric measurement, was confirmed only up to a maximum.⁴ Our experimental results accorded with this theory. However, T_s and T_f showed a maximum with a ϕ of 5°C/min. The decreases in T_s and T_f may be explained by the overheating of the fiber yarn, which was an arrangement of some thousands of monofilaments surrounded by air as the heat source, in analogy to the technical arrangement with convective heating. The time of heat transfer was shortened with increasing ϕ . Therefore, the temperature of the heating gas was not that of the fiber at higher ϕ 's. The fiber temperature was higher because of overheating by the reaction heat as a consequence of insufficient heat transfer. This overheating effect must be avoided in the stabilization process because it will not only introduce additional defects in the fiber but can also produce fiber ignition.⁴ The conclusion to be drawn is that ϕ should not be higher than 5°C/min during the stabilization of PAN in air.

Figure 5 shows the effect of ϕ on the amount of chemical shrinkage during the stabilization of PAN in air. The amount showed a minimum with a ϕ of 5°C/min. The reason may be that at lower ϕ 's, the skin-core structure was more and more evident with increasing ϕ (Fig. 6). The diffusion of oxygen was

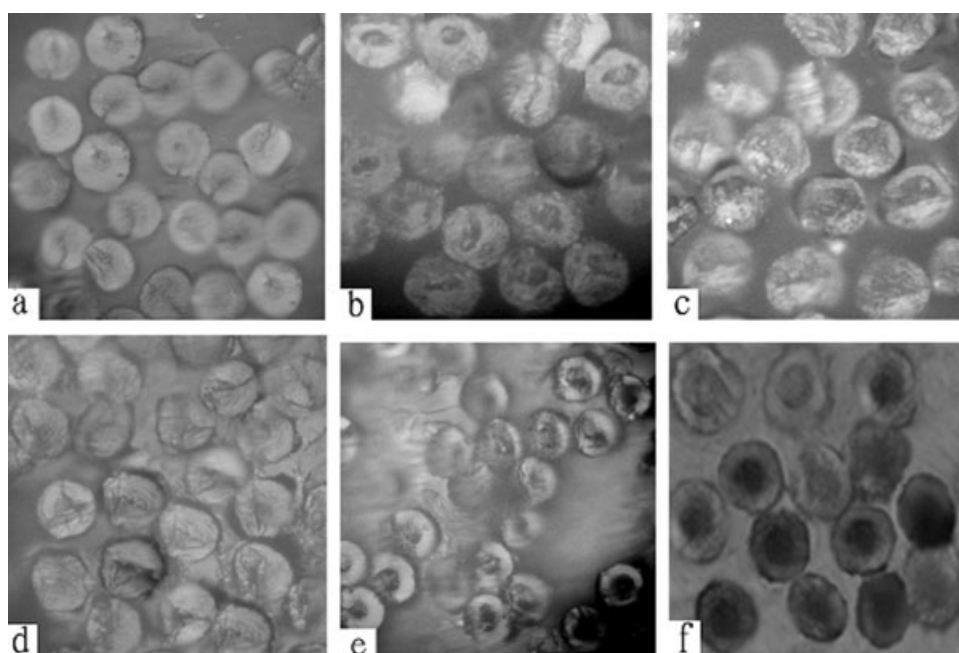


Figure 6 Cross sections of the stabilized fibers: (a) 0.5°C/min in air, (b) 2°C/min in air, (c) 10°C/min in air, (d) 0.5°C/min in ozone-enriched air, (e) 2°C/min in ozone-enriched air, and (f) 10°C/min in ozone-enriched air.

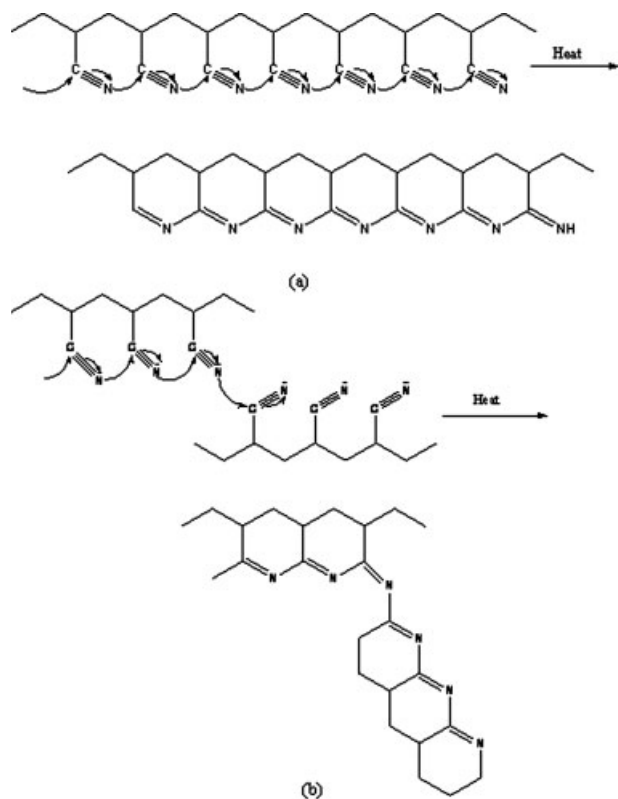


Figure 7 Stabilization reaction schemes: (a) intramolecular cyclization and (b) intermolecular crosslinking cyclization.

inhibited, and the degree of intramolecular cyclization decreased. Consequently, the amount of chemical shrinkage diminished. However, at higher ϕ 's, because of the intermolecular crosslinking reactions, which are presumed to occur to a higher extent at increasing rates, contributed to the chemical shrinkage,⁴ the amount of chemical shrinkage increased. It seemed to be that at ϕ 's lower than 5°C/min, the intramolecular cyclization was the main reaction. Above 5°C/min, intermolecular crosslinking became obvious because of the crosslinking of unmodified nitriles between the adjacent molecular chains, as explained in the structural diagram (Fig. 7).

Influence of ϕ on the stabilization of PAN fibers in ozone-enriched air

Figure 8 shows the free-shrinkage behavior of the PAN precursor fibers under dynamic heating conditions in ozone-enriched air. The figure indicates that the increase in ϕ had a significant effect on the amount of chemical shrinkage at ϕ 's lower than 5°C/min but a small effect at ϕ 's higher than 5°C/min.

The effect of ϕ on T_b , T_s , and T_f during the stabilization of PAN in ozone-enriched air is shown in Figure 9. The changing trend of T_b was the same as that

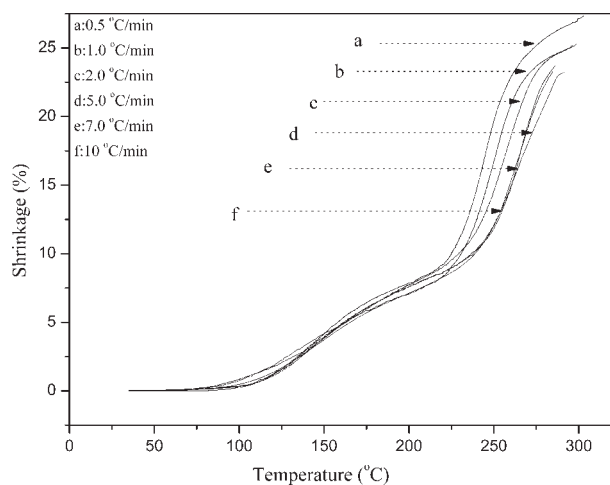


Figure 8 Free-shrinkage behavior during the stabilization of PAN fibers under linear treatment in ozone-enriched air.

in air. However, T_s and T_f did not show an evident maximum. They did not change obviously at ϕ 's higher than 5°C/min. A possible reason is that the ozone was a strong oxidant and the chemical reaction rate accelerated during the stabilization of PAN in ozone-enriched air. The serious skin-core structure was quickly formed at higher ϕ 's (Fig. 6), and the diffusion of oxygen was prohibited. Therefore, the chemical reactions finished early, and ϕ had little effect on the chemical shrinkage at ϕ 's higher than 5°C/min. It seems to be that ϕ should not be higher than 5°C/min during the stabilization of PAN in ozone-enriched air because the serious skin-core structure will deteriorate the mechanical properties of resulting carbon fibers.

Figure 10 shows the effect of ϕ on the amount of chemical shrinkage during the stabilization of PAN in ozone-enriched air. The difference between in air

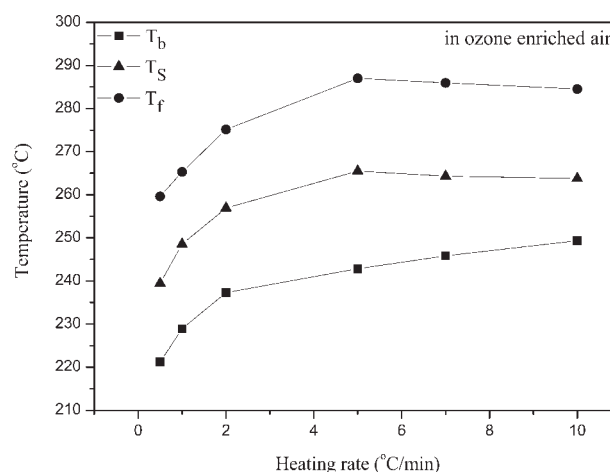


Figure 9 T_b , T_s , and T_f of chemical shrinkage as a function of ϕ .

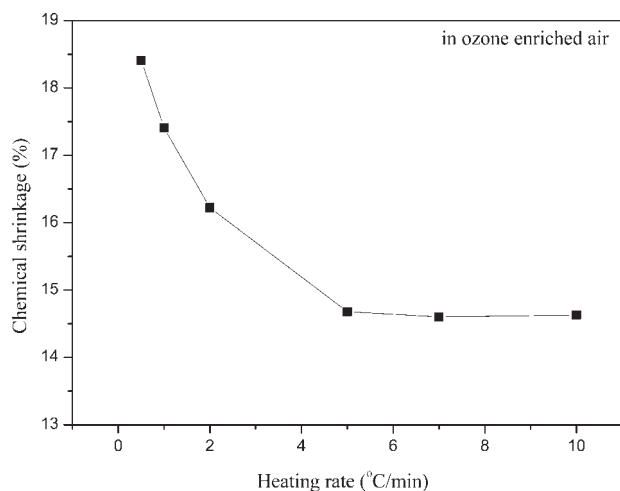


Figure 10 Amount of chemical shrinkage as a function of ϕ .

and ozone-enriched air was that chemical shrinkage did not change obviously at ϕ 's higher than 5°C/min in ozone-enriched air. The reason may be that the higher degree of surface cyclization inhibited the intermolecular crosslinking reactions. Therefore, the amount of chemical shrinkage did not increase with increasing ϕ .

Influence of ozone on stabilization

Typical cross-section micrographs of fibers stabilized at different ϕ 's to 300°C are reproduced in Figure 6. Electron micrographs of shadowed replicas of the sections indicated that the core areas were depressed and, therefore, softer than the material in the skin areas. The skin-core structure became more and more evident with increasing ϕ during stabilization in air, and it was more serious in ozone-enriched air

than in air. Therefore, it seems to be that ozone could promote the formation of the serious skin-core structure.

Density is believed to be a good indicator of the extent of stabilization.^{14,15} It was observed that for successful carbonization, the stabilized fibers should reach a precursor-dependent critical density.¹⁶ The density evolutions in air and ozone-enriched air from room temperature to 300°C at different ϕ 's are shown in Figure 11. The densities of PAN stabilized in air continue to decrease because the stabilization degree decreased with increasing ϕ . In ozone-enriched air, because of the formation of the serious skin-core structure, the densities did not change evidently at ϕ 's higher than 5°C/min.

Also, at ϕ 's lower than 2°C/min, the density and amount of chemical shrinkage were quite equivalent during the stabilization of PAN in air and ozone-enriched air at the same ϕ (Figs. 5, 10, and 11). However, the temperature range of the chemical shrinkage was shortened in ozone-enriched air (Figs. 4 and 9). In other words, ozone could accelerate the chemical reactions and shorten the stabilization time at lower ϕ 's.

Figure 12 shows the free shrinkage during the stabilization of PAN in air and ozone-enriched air with a ϕ of 2°C/min. The shrinkage between 100 and 180°C was due to physical shrinkage.¹² Therefore, the difference between in air and ozone-enriched air was small. However, above 180°C, shrinkage set in earlier in air. The same trend was shown by the density change at different stabilization temperatures (Fig. 13). The densities rose rapidly at temperatures beyond 200°C in air. However, the temperature was postponed about 20°C in ozone-enriched air. T_b , T_s , and T_f were higher in ozone-enriched air than in air (Figs. 4 and 9). All of these phenomena may indicate

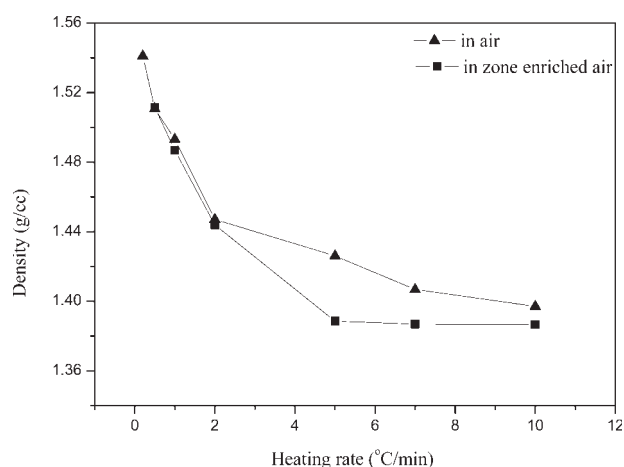


Figure 11 Effect of ϕ on the density of stabilized PAN fibers.

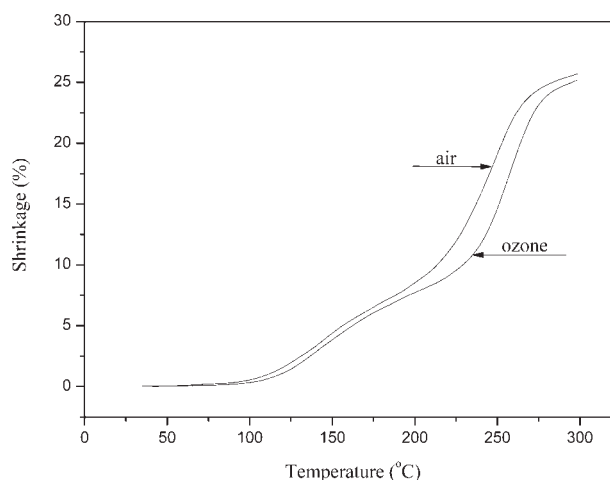


Figure 12 Free shrinkage on heating in air and ozone-enriched air with a ϕ value of 2°C/min.

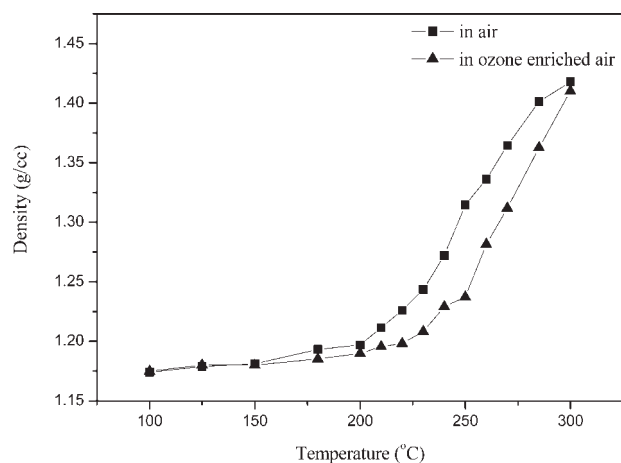


Figure 13 Effect of the stabilization temperature on the density of PAN fibers with a ϕ value of $2^\circ\text{C}/\text{min}$.

that the chemical reactions were postponed in ozone-enriched air. Fitzer and Muller¹⁷ investigated the influence of oxygen on the chemical reactions during the stabilization of PAN and observed that the consecutive cyclization of activated centers was inhibited by oxygen because of the increase in the activation energy (E). This reason may account for the phenomenon in our experiment. The question converts to how to obtain E in ozone-enriched air.

Evaluation of E

E was calculated from the temperature dependence of the peak maximum (T_m) of the exothermic reaction in a DSC curve on ϕ (K/min) according to Kissinger method,¹⁸ as described in eq. (1):

$$-\frac{E}{R} = \frac{d \ln(\phi/T_m^2)}{d(1/T_m)} \quad (1)$$

where, R is gas constant and ϕ is heating rate.

T_s obtained from the shrinkage curve denotes the temperature at which the chemical reactions occur most tempestuously. Therefore, T_s should be similar to the T_m . The method that uses T_s to calculate E in ozone-enriched air may be feasible.

The experimental results evaluated from DSC measurements with varied ϕ 's are compiled in Table I.

TABLE I
 T_m Values Derived from the DSC Curves of the PAN Precursor Stabilized in Air with Various ϕ Values

	ϕ ($^\circ\text{C}/\text{min}$)				
	0.5	1	2	5	10
T_m ($^\circ\text{C}$)	243.44	255.37	263.20	277.23	287.01
T_m (K)	516.44	528.37	536.20	550.23	560.01

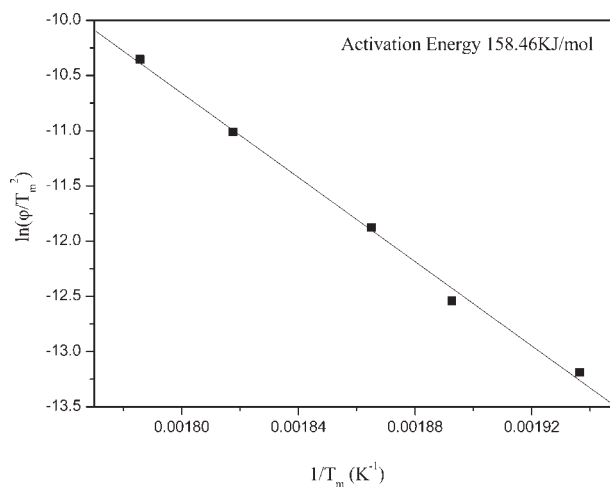


Figure 14 Evaluation of E from the DSC T_m .

T_m was strongly affected by ϕ . Thus, the Kissinger method could be used to evaluate E in air.

Figure 14 shows the values of $\ln \phi/T_m^2$ versus $1/T_m$ calculated from the experimental data, which fit a straight line quite well, as expected from theory. Thus, the maximum of error was smaller than $\pm 10\%$, as given in literature for the Kissinger method.¹⁷ By replacing T_m with T_s , we used the same method to evaluate E in air. The result is shown in Figure 15. With the overheating taken into account, ϕ 's were chosen between 0.25 and $5^\circ\text{C}/\text{min}$.

The E values in air calculated from T_m and T_s were 158.46 and 161.57 kJ/mol, respectively. The difference was very small. Therefore, the method that used T_s to calculate E seemed to be feasible. According to the previous method, E in ozone-enriched air was obtained as 181.23 kJ/mol, as shown in Figure 16. This result was consistent with our guess. Therefore, the reason that the chemical reactions were postponed during stabilization in ozone-enriched air may have been the increase in E .

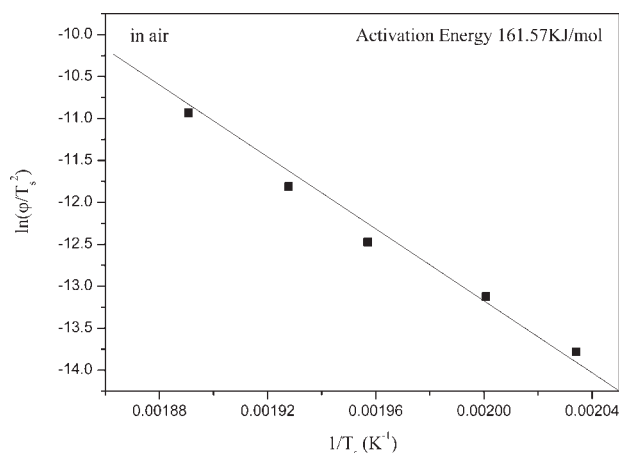


Figure 15 Evaluation of E in air from T_s .

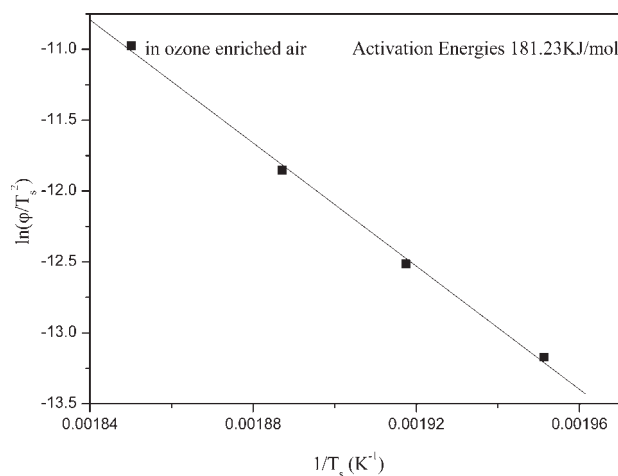


Figure 16 Evaluation of E in ozone-enriched air from T_s .

CONCLUSIONS

By conducting a series of free-shrinkage experiments of PAN fibers under different linear ϕ 's in air and ozone-enriched air, we observed that during stabilization in air, with increasing ϕ , the amount of chemical shrinkage showed a minimum with a ϕ of $5^\circ\text{C}/\text{min}$, and the density continued to decrease. At ϕ 's lower than $5^\circ\text{C}/\text{min}$, the intramolecular cyclization was the main reaction. At ϕ 's higher than $5^\circ\text{C}/\text{min}$, intermolecular crosslinking reactions became obvious. To avoid overheating, ϕ should be lower than $5^\circ\text{C}/\text{min}$. During stabilization in ozone-enriched air, at ϕ 's lower than $5^\circ\text{C}/\text{min}$, the amount

of chemical shrinkage and the density decreased with increasing ϕ . At ϕ 's higher than $5^\circ\text{C}/\text{min}$, they changed little.

The method for evaluating E from the shrinkage diagram was presented. The reason that the chemical reactions were postponed seemed to be that E was larger in ozone-enriched air than that in air. Ozone seemed to act in three ways: first, ozone promoted the formation of the serious skin-core structure. Second, ozone accelerated the chemical reactions and shortened the stabilization time at lower ϕ 's. Third, ozone postponed the chemical reactions because of the increase in E .

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