RELEVANCE OF INNER-STRESS TO ORIENTATION OF PAN FIBERS DURING THE THERMAL TREATMENT AT 120 to 160℃

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Introduction

During the conversion from Polyacrylonitrile fibers to carbon fibers, the thermal treatment prior to the stabilization is employed to restrain or improve the preferred oriented structure of PAN fibers[1], which is carried out at the temperature of 120 ~ 180℃ in an air atmosphere for 2 ~ 4 min before the initiating of chemical reactions[2,3]. The appropriate tension applied on fibers could be beneficial to fibers [4, 5], however, in our previous study, the temperature and time of the treatment also have a remarkable influence on the result of tensional influence. In this study, the effect of temperature and treat period on inner-stress of PAN fibers, and the relevance of inner-stress to oriented structure were discussed.

Experimental

PAN 3K fibers that used in this study were produced by Courtaulds company of U.K., its chemical constitutes (weight proportion) AN: IA: MA is 92.8:1.2:6.0, and the diameter and elongation are 12.48μm and 9.94%, respectively.

The inner-stress was detected by a strain gauge, which registered on a recorder. One of the ends of the sample fibers was fixed on the stainless steel arm, and a clip that was hooked on the strain gauge, enlaced the other one. The length of those fibers was kept at 20cm. After adjusting the tension of the sample fibers to zero at room temperature, the samples were inserted into the oven, in which the temperature for the isothermal treatment of the fibers was keeping at 120, 130, 140, 150 and 160℃, respectively.

Then, the work was re-done and the samples under different heat treatment period of each isothermal process were selected. The orientation of PAN crystal was determined using the azimuthal scans at 2θ = 17° by Rigaku X-ray diffractmeter. The width at half-maximum intensity (H) was used as an index of orientation, which was used to calculate the parallelism of the crystalline part of structure by the following equation [6]:

$$P = (180-H)/180\times100\%$$

Results and discussion

The relationship between inner-stress and heat treatment period in the range from 0 to 20 min at each isothermal process was shown in fig.1. The inner-stress increased rapidly at the initiating of the treatment and then decreased gradually with the extending of period during each isothermal process.

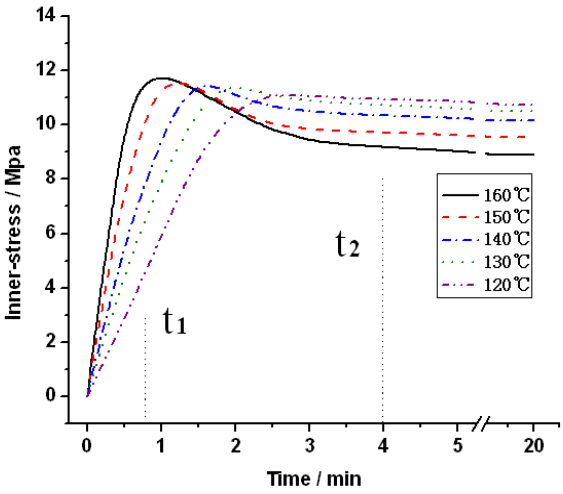

Fig.1 The relationship between inner-stress and heat treatment period

Another information could be obtained from Fig.1 that the increasing and falling velocity of the inner-stress at the higher temperature treatment were faster than others that treated at the lower ones. The increasing velocity (v) and peak time (t_p) of each process were exhibited in Fig.2.

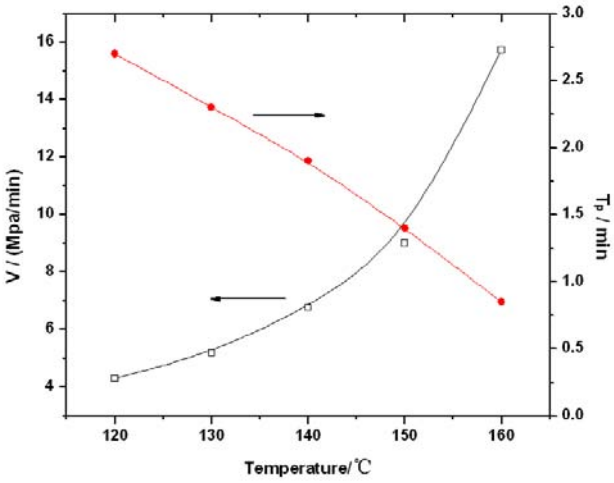

Fig.2 The climbing velocity (v) and peak time (t_p) of each process

The climbing velocity increased and the t_p decreased exponentially along with the raise of temperature, which were due to the improved activity of PAN chains affected by the higher temperature. However, the chemical reactions did not initiate before 160℃, so the changes of inner-stress with temperature or time were because of the evolvement of the physical structure.

For the similar exhibition of the five curves in Fig.1, the sample fibers that heat at 140℃ was selected for orientation characterization and the results was displayed in Fig.3. Compared to the changes of inner-stress in Fig.1, the orientation degree had a contrary trend. While the stress increased during the initiate process before t_p and decreased slowly after t_p, the orientation reduced before t_p and increased after t_p. Then, the sample fibers at the same time ($t_1$and t_2) but different temperatures as shown in Fig.1, was selected for orientation characterization and the result were exhibited in Fig.4. At the time of t_1, the five curves did not reach their peak time, the orientation degree decreased and the inner-stress increased with the raise of temperature. At the time of t_2, exceeding t_p, the inner-stress and orientation degree had the opposite trend to the one of t_1.

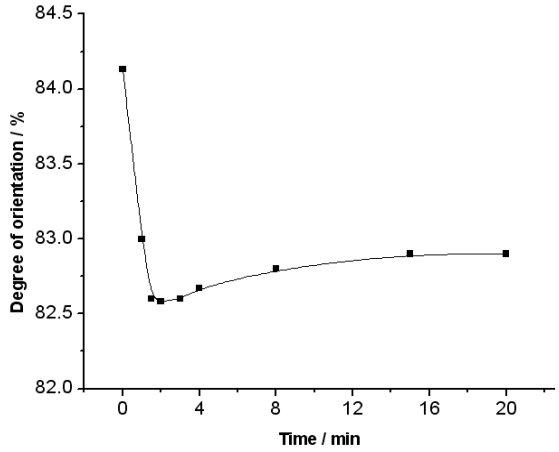

Fig.3 The change of orientation degree with the thermal period at 140℃

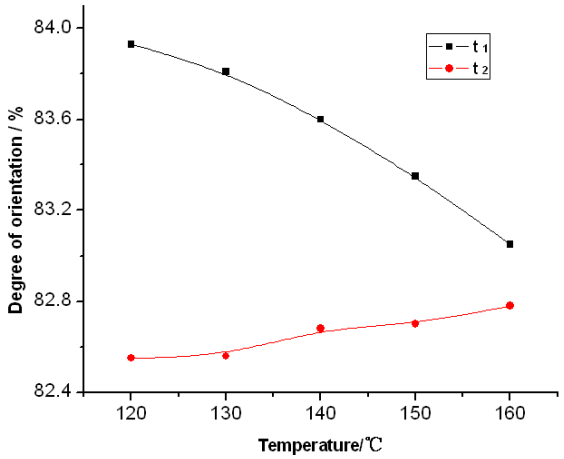

Fig.4 The change of orientation degree with the temperature during the same period

The results indicated that the disorientation resulted in the increase of inner-stress and the orientation of PAN crystal led to the slowly decrease of the stress, and the higher temperature, the more remarkable of the effect. The change of inner-stress is the results of the competition between disorientation and orientation of PAN fibers. When the temperature exceeds the glass transition temperature（T_g）, the activity of PAN chains is improved obviously, and the serious orientation structure of PAN fibers that formed by the stretching during the spinning process are weakened [7, 8]. The disorientation results in the increase of inner-stress. At the condition that the length of fibers are kept during the heat treatment, the stress will be accumulated in fibers, and when the force is too strong, the PAN crystal may be induced to orientate gradually along the fiber axis to counteract the increasing of the force, which leads to the decrease of the inner-stress.

Conclusion

Being thermal treated before stabilization, PAN fibers will disorients spontaneously at the initiate of the process before t_p, when the inner-stress reaches to the maximum. However, if the heat time exceeds t_p, the PAN crystal will be induced to orientate gradually along the fiber axis, and the raise of temperature will intensify the effect. Consequently, the heat-treated process before stabilization can carry out at an appropriate higher temperature and the time should exceed t_p. On the one hand, the disorientation could be replaced by the orientation of PAN crystal; on the other hand, the sufficient treat period will increase the activity of PAN chains, which will benefit for stretching fibers to improve the preferred oriented structure.

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