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Relaxation of Chain Extension of Amorphous PET Fiber Above the Glass Transition Temperature

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Abstract: The recovery of amorphous PET fiber in global chain orientation but nearly random segmental orientation (GOLR) state was studied by the hot shrinkage measurement above the glass transition temperature. The relaxation curves in the form of di-exponential decay were acquired and the change of two special times with the variation of treating temperature and residual recovery ratio η' was discussed.

Keywords: GOLR state PET, recovery of chain extension, hot shrinkage measurement.

The average relaxation time for segmental orientation is considerably shorter than that for chain extension[1,2], due to the difference of the ability to move between segments and chains. So in certain time intervals, an almost total relaxation of the segmental orientation can take place with little relaxation of global chain extension. Under the controlled conditions[1,3], high global chain orientation but nearly random segmental orientation (GOLR) state can be achieved. Through the hot shrinkage measurement of GOLR samples, the relaxation of global chain orientation can be studied.

The poly (ethylene terephthalate) (PET) fiber used in this study came from Beijing Institute of Fiber, P. R. China. The fiber was spun with a take-up velocity of 1000m/min at *ca.* 285°C, which had the viscosity-average molecular weight $M_\eta=1.6\times10^4$ and the density $\rho=1.337\text{g/cm}^3$. Very little birefringence $\Delta n=6.0\times10^{-3}$ as well as large maximal recovery ratio $\eta_{max}=42.4\%$ could prove that the PET fiber is in GOLR state [1].

The GOLR state PET sample was cut into a small string of *ca.* 10-12cm attached in the end with a thin nickel wire (diameter of 0.3mm and length of 85mm) which has neglectable coefficient of linear thermal expansion ($\sim12.5\times10^{-6}$/K at room temperature). The weight of the wire was so small (0.05g) that it hardly affected the recovery of the sample, meanwhile this chosen weight of metal wire made sure that the fiber didn't crimp during the course of recovery. Length recovery of the PET fiber was carried out in the oven at selected temperature which had a fluctuation of $\pm0.1^\circ$C. The dimensional change of the samples could be detected through a cathetometer with the precision of 0.01mm.

The recovery ratio was defined as the ratio of the length change of the sample in the course of recovery, Δl, to specimen's original length, l_0:

$$\eta = \Delta l / l_0 \qquad (1)$$

The residual recovery ratio η_t' was presented by the difference between maximal recovery ratio η_{max} and the recovery ratio at the time t, η_t:

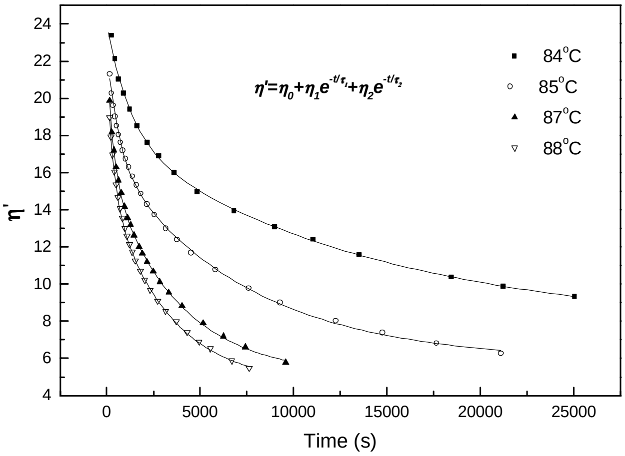
$$\eta_t' = \eta_{max} - \eta_t \qquad (2)$$

After the specimens were remained in the oven at 115°C for 30 min, all of the strain would be recovered. So the maximal recovery ratio $\eta_{\max}$ can be measured at this temperature.

In the other study about the recovery of deformed polymer[4], the relaxation step of the global chain extension was described in the form of single exponential decay. However, in our experiments, the relaxation of global chain extension didn't get along with this rule. According to the result of the Voigt-Kelvin Model[5], the relaxation of polymer should be described in the form of exponential decay, where every special time τ_i corresponds to one structure unit.

$$\eta' = \eta_0 + \sum_{i=1}^{n} A_i (e^{-t/\tau_i}) \qquad (3)$$

Figure 1 The fitting curves of the GOLR state PET fibers recovering above *Tg*, in the form of di-exponential decay; (the points are the data from experiments and the solid lines are fitting curves)



All the data of the PET samples relaxing above T_g were fitted in di-exponential decay, $\eta' = \eta_0 + \eta_1 e^{-t/\tau_1} + \eta_2 e^{-t/\tau_2}$ and the result seemed to be good. The dependency of all the result is more than 0.95.The fitting curves of the recovery represented by di-exponential decay are shown in **Figure 1**.

Table 1. The value of τ_1, τ_2, τ_2/τ_1 getting from samples treated at various temperatures (all the samples were of the same η'(20.3) to make sure the parallel results)

T (°C)	88	87	85	84
τ_1(s)	180	200	510	1600
τ_2(s)	1600	2000	4900	16000

τ_2/τ_1	9.3	10	9.6	10

Table 2. The value of τ_1, τ_2, τ_2/τ_1 getting from samples with different residual recovery ratio η' all treated at 88^{o} C

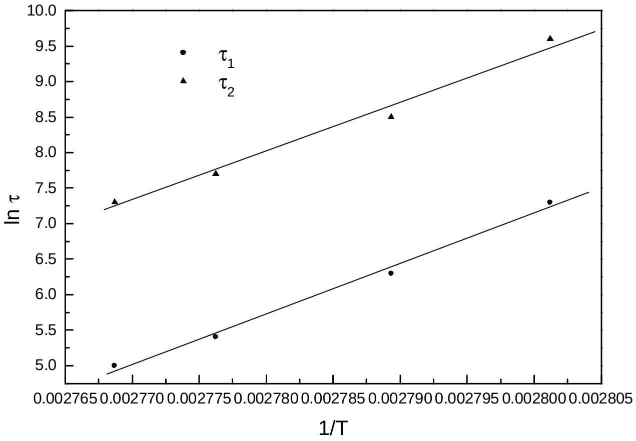
η' (%)	21.4	19.0	17.9	16.9	16.0	15.3
τ_1(s)	230	360	410	480	560	650
τ_2(s)	2700	3200	3300	3600	3800	4100
τ_2/τ_1	12	8.8	8.1	7.4	6.8	6.3

In our opinion, during the course of global chain extension recovery, only two structure units account for the most part of the affection for the recovery above *Tg* while other structures contribute rather less to it. Song *etc.*[3] discussed that the special recovery time τ_s for the segment is around 10~60s at 84°C according to infrared dichroism detection. However as shown in **Table 1**, the shorter special time τ_1 in our study is *ca.* 1600s at the same temperature, nearly 100 times as large as τ_s for the segment. It can be concluded that two special times τ_1 and τ_2 obtained from the fitting results correspond to the motion of two structure units with different lengths which could be the combination of a number of segments. Furthermore, it was reported in the literature[2] that the relaxation time for chain orientation would be about 100 times longer than that for segmental relaxation, while the values of τ_2 / τ_1 in our experiments are around 10. Because the movement of both two special structure units could be attributed to the recovery of global chain extension, the difference of mobility between these two structures should be obviously less than that between the segment extension and global chain extension.

As shown in **Table 1** and **Table 2**, two special times τ_1 and τ_2 increase with decreasing residual recovery ratio, η' and diminishing shrinkage temperature. However the ratio of two special times, τ_2/τ_1 remains unchanged with the variation of the temperature. It is clear that the effect of temperature on the mobility of both two structure units is identical, and followed results of activation energy can also verify this conclusion. Meanwhile **Table 2** demonstrates that τ_2 / τ_1 goes down with decreasing η', which means the shorter structure unit closes continuously to the longer one with the processing of the relaxation.

Figure 2 depicts the temperature dependence of the relaxation special time τ above *Tg* according to Arrhenius theory, and activation energy for both τ_1 and τ_2 can be calculated (Ea_1=580kJ/mol for τ_1 and Ea_2=610kJ/mol for τ_2). It can be seen that the activation energy for both two special structure units is very close. As discussed above, the effect of temperature on the mobility of two structures is the same on the whole.

Figure 2 Temperature dependence of two special relaxation times τ_1 and τ_2 of chain extension relaxation above *Tg*



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