

The Influence of Tensile Rate on the Tensile Fracture Process of PA6

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Abstract. In this paper, we researched the influence of tensile rate on the tensile fracture process of PA6. The results showed that with the increase of tensile rate, the yield strength of PA6 was on the rise, and the elongation at break was on the decline. The elongation at break declined sharply when the tensile rate increased to 50 mm/min, it's because that under the tensile rate of 50 mm/min, the PA6 crystallinity decreased obviously after stretching, the lattice was damaged seriously, and there was also a sharp decline in capacity of molecular chain segments together with plastic deformation. In low-speed PA6 tensile process, for the two peak valleys of seven states crystallinity changing curve just respectively corresponded to the tensile states when two yield occurred in tensile process, we thought there was a certain relationship between double yield and crystal destruction. The phenomenon of double yield in low-speed tensile process might be accompanied with the destruction of the γ crystal.

Introduction

For the viscoelasticity of polymer materials and the close relationship among mechanical property, internal structure, and external factors[1-8], it's very important to research the influence of tensile rate to aggregation structure, mechanical property and partial response[9]. Chang' an Cai[10] studied the strain rate sensitivity of PBT, and finding the tensile strength of polymer increased with the increase of strain rate. High sensitive area was corresponded to the low tensile rate, medium sensitive area was corresponded to the medium stretching rate, and low sensitivity area was corresponded to stretching rate at high speed. Jie Yu [11] had studied the influence of loading rate on mechanical properties of PVC. When the tensile load speed was low, the size of the radiation extension area is larger, which was caused by controlled expansion of crack. By contrast, when the tensile load speed was high, the size of area is smaller, which was caused by rapid expanding of crack. With the increase of stretching rate, the movement of the PVC molecular chain increasingly was difficult, macromolecular configuration stretch smaller, therefore, the deformation produced by distance change between atoms became greater. As deformation rate increase, the essential force that made the sample produce the same deformation increased, and resulted in that the strength of the material showed higher. Jinjuan Fan[12] studied fracture microstructure of silicone rubber under different tensile rates, they found that under different tensile rates, the microscopic structure of crack propagation showed a parabolic characteristics mainly. With the increase of stretching rate, the depth and length of the parabola increased, as well as fracture surface was rough. When the stretching rate increased to a certain degree, smooth zone appeared secondary crack. PA6 belongs to semi crystalline polymer with a variety of crystal forms in the crystalline part, and all kinds of crystal forms can mutual transform under certain conditions [13-14]. In this paper, we researched the influence of tensile rate on the tensile fracture process of PA6, expecting to provide useful research foundation for the engineering practice and application of PA6.

Materials and Methods

Sample and Tensile Test. In this research, we used injection molding machine (PL860/290v, Wuxi Haitian Plastic Machinery Co., Ltd) to make the PA6(M3400, Guangdong Xinhui Meida Nylon Co., Ltd.) samples which were stretched by universal testing machine(WDW-10, Ji'nan Naier Test Machinery Co., Ltd). This experiment with reference to GB/T 10402-2006. The temperature level of 23°C was applied to tensile process and tensile rates, respectively, the tensile speeds were about to 10 mm/min, 20 mm/min, 50mm/min, 100mm/min, 200mm/min, 500 mm/min. After the tensile process which tested by using different samples with 10 mm/min tensile rate presented seven stages as shown in figure 5, we aborted the process. Then we kept the corresponding states and cut sample for testing.

Differential Scanning Calorimetry(DSC). The crystalline was analyzed by DSC (Q10, TA Instruments, USA). We cut the samples into 5mg, and tested them under nitrogen atmosphere protection with 10°C/min speed from 25°C up to 250°C. The crystalline was estimated by using the equation

$$X_c = \frac{\Delta H}{\Delta H_{100\%}} \times 100\% \quad (1-1)$$

Where X_c is the crystalline, ΔH is the melting enthalpy. $\Delta H_{100\%}$ is the melting enthalpy when crystalline is 100%, in this paper we use $\Delta H_{100\%}=190\text{J/g}$.

X-ray Diffraction (XRD). The XRD (X'Pert PRO, PANalytical B.V) which was copper target, test angle is about $10^\circ < 2\theta < 400^\circ$ with 20/min scan rate and 40 kv accelerating voltage. At same time, we used Jade to do peak separation method and curve-fitting analysis.

Nuclear Magnetic Resonance Spectroscopy (NMR). At room temperature, the main parameters ^{13}C resonant frequency of the NMR (AVANCE III; Bruker Corporation) was 47.47MHz. The CP (cross-polarization) time was 1.5ms, rotational speed was 4kHz, and relaxation time was 6s. We could obtain both crystalline area and amorphous area signal at the same time though ^{13}C CP/MAS/HPDEC (cross-polarization, magic angle spinning and high-power decoupling method) method.

Results and Discussion

The Influence of Tensile Rate on PA6 Aggregation Structure and Tensile Property

The XRD curve of PA6 was shown in Fig. 1. The curve without stretching was absolutely sharp and the characteristic peak was obvious which meant the crystal structure was structured. When the tensile rate was 10 mm/min, compared with the one without stretching, the curve of characteristic peak was move to left, which meant that lattice distance increased slightly. But when the stretching rate increased to 50 mm/min, the XRD curve was smooth and the characteristic peak disappeared, which meant the crystal structure was damaged obviously.

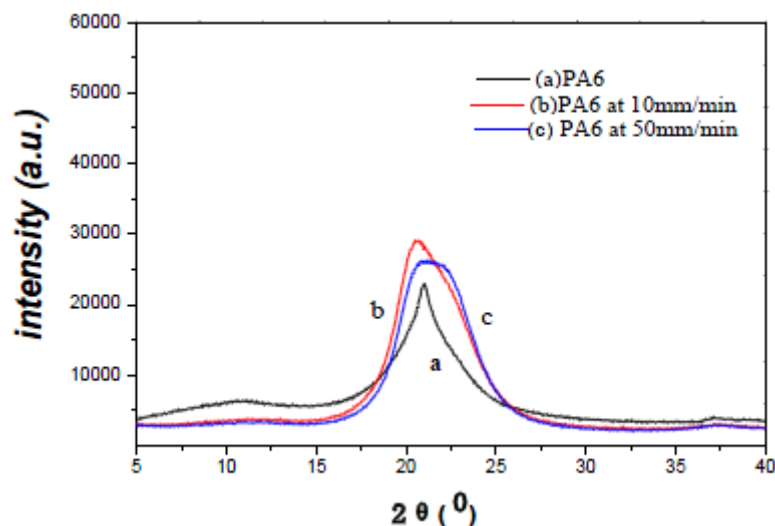


Fig. 1. X-ray diffraction patterns of pure PA6 with different tensile rate
a: No tensile; b: tensile rate 10mm/min; c: tensile rate 50mm/min

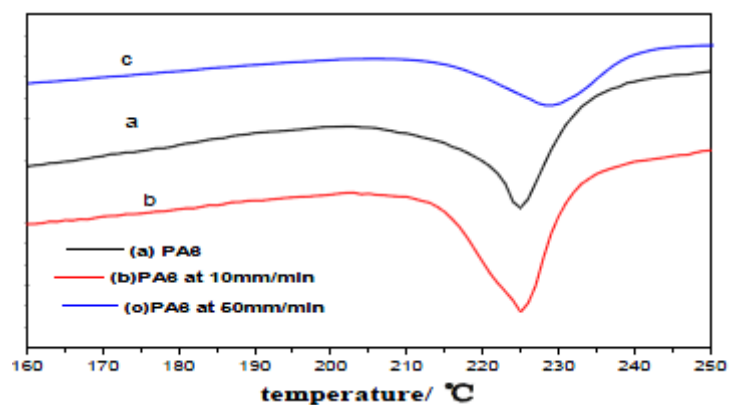


Fig. 2. DSC curves of PA6 with different tensile rate
a: No tensile; b: tensile rate 10mm/min; c: tensile rate 50mm/min

Table 1. DSC results of PA6 with different tensile rate

Sample	$\Delta H/(J/g)$	$X_c/\%$
PA6	63.86	33.61
PA6 at 10mm/min	66.58	35.04
PA6 at 50mm/min	36.71	19.32

Fig. 2. and Table 1. showed that the crystallinity of PA6 after tensile fracture was higher than the one without stretching when tensile rate was 10mm/min. But the when tensile rate was 50mm/min, crystallinity of PA6 after tensile fracture decreased significantly. By the increase of stretching rate, PA6 lattice damage was serious and lattice distance was increased gradually with the decrease of crystallinity.

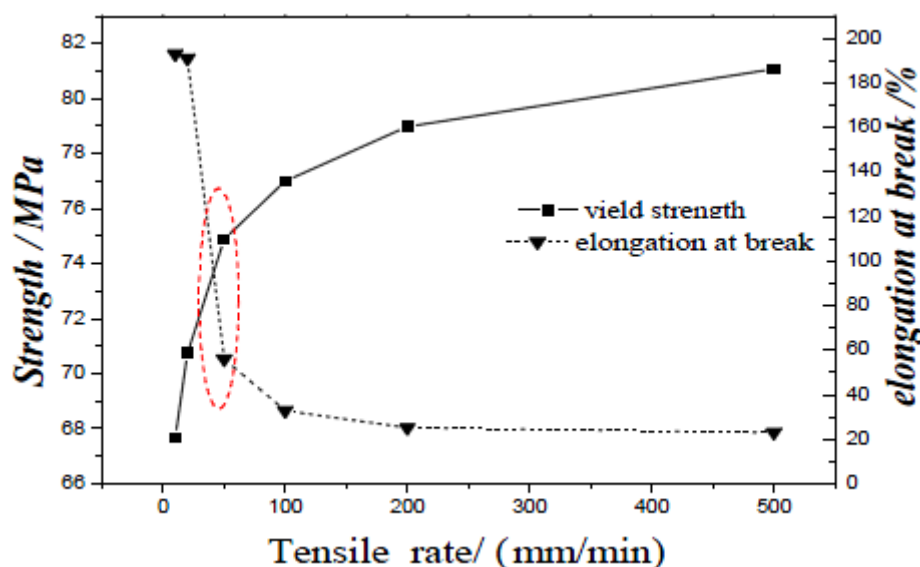


Fig. 3. Relationship between yield strength and elongation at break of stretch rate.

From Fig. 3, it can be seen that the yield strength of PA6 was on the rise with the increase of stretching rate, which was in line with the theory of Eyring on the linear relationship between the yield strength and tensile rate. However, the elongation at break decreased with the increasing of tensile rate. The findings showed that when the tensile rate was 50mm/min, the crystallinity of PA6 after tensile fracture decreased significantly, lattice damage was serious and there was also a sharp decline in capacity of molecular chain segments together with plastic deformation. All above factors were caused by the sharp decrease of elongation at break.

The Phenomenon of Double Yield in Low-Speed Tensile Process

Fig. 4 shows the load-displacement curves of PA6 under different tensile rates. There were always presented double yield phenomenons when the tensile rates were 10mm/min and 20mm/min. After the local necking appeared in the first yield deformation, we continued stretching the PA6 sample, and finding that the sample occurred second local necking at the same area of the first local necking again until the necking fracture. There was no double yield phenomenon when tensile rate was more than 50mm/min. The polymer in the same local internal structure was with the increase of the action time took on superimposing changing process. Butler[15-16] studied it though small angle and wide angle X-ray scattering synchronization technology, and finding that polymer for the first yield could be restored which corresponded to the imperceptible chain slip. But the polymer could not be restored at second yield which corresponded to the lamellae rupture caused by Coarse chain slip. Although the mechanism of double yield phenomenon had not yet completely clear, we could affirm that the occurrence of double yield was inevitably related to the aggregation structure. In this paper, after the tensile process which tested by using different samples with 10 mm/min tensile rate presented seven stages as shown in Fig. 5, we aborted the tensile process and studied the relationship between aggregation structure and double yield at this stage.

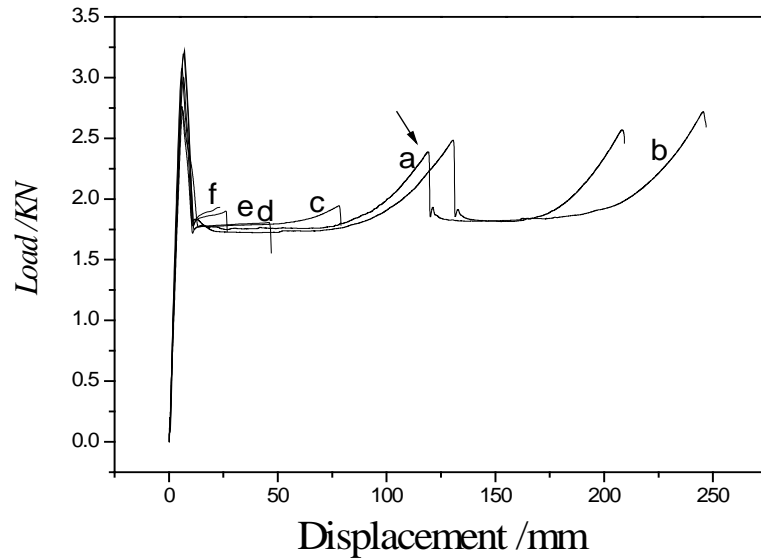


Fig. 4. Load-displacement curves of PA6 at different tensile rate
a.10mm/min;b.20mm/min;c.50mm/min;d.100mm/min;e.200mm/min; f.500mm/min

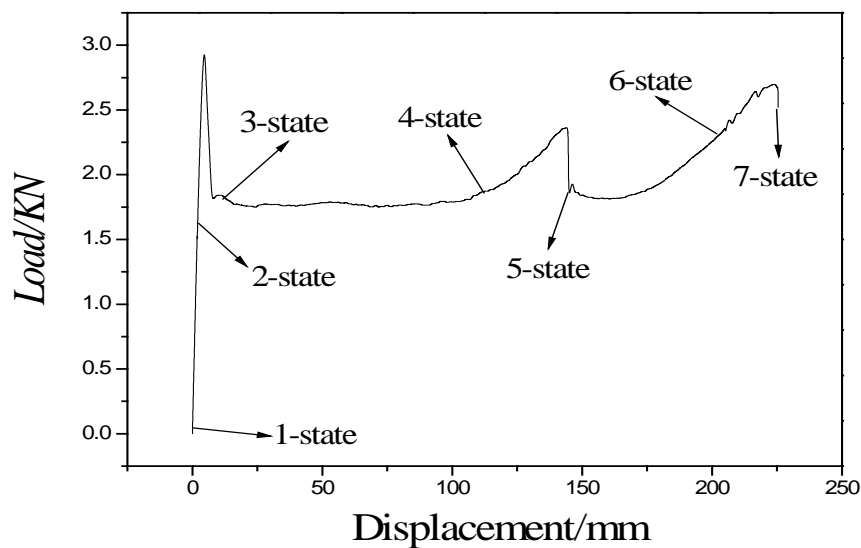


Fig. 5. Different tensile strain state in load-displacement curves of PA6 at 10mm/min tensile rate:
(1)1-state;(2)2-state;(3)3-state;(4)4-state;(5)5-state; (6)6-state; (7)7-state

Fig. 6. shows the XRD, from tensile state1 to 7, the sharp degree of PA6 crystal characteristic peak reduced gradually. It could be seen that the PA6 crystal structure was changed constantly with continuous tensile process and the crystal structure was broken. We treated the XRD figures of seven different tensile states by Sub-peak fitting method [17]. Fig. 7. shows that in the spectrogram of PA6, the 2θ values were about 20° and 23° . There were two characteristic peaks of α crystal and respectively corresponded to the crystal plane (200) and (002). The 2θ value was 21° , the γ crystal characteristic peak corresponded to the crystal plane (200). The result of Sub-peak fitting was shown in Fig. 8. At the stages 1, 2, 3 and 4 there were not double yield occurred yet, α crystal accounted for 75% and γ crystal accounted for 25%. But the stages 5, 6 and 7 presented phenomenon of double yield already, the γ crystal was totally disappeared.

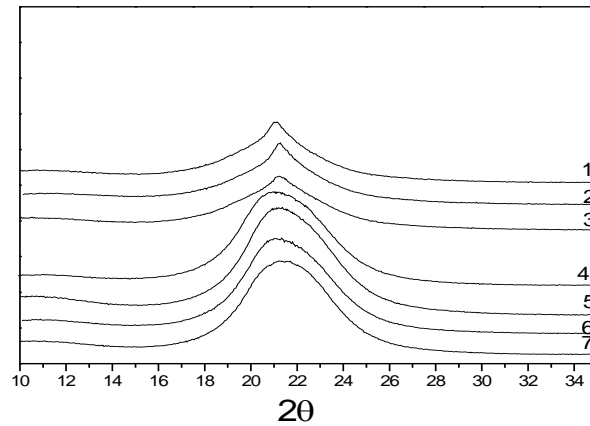


Fig. 6. X-ray diffraction patterns of PA6 at different tensile strain state : (1)1-state;(2)2-state;(3)3-state;(4)4-state;(5)5-state; (6)6-state; (7)7-state

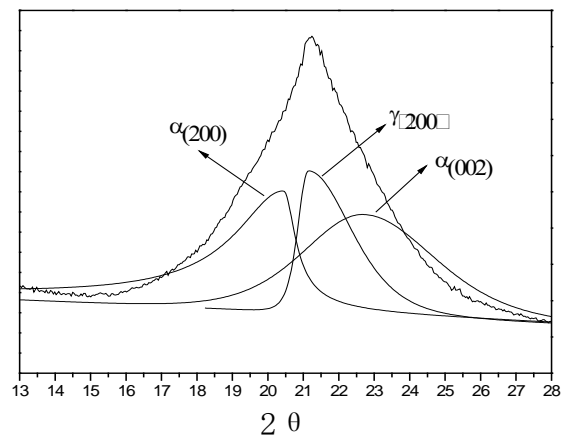


Fig. 7. Deconvolution curves of the X-ray diffraction curve of PA6

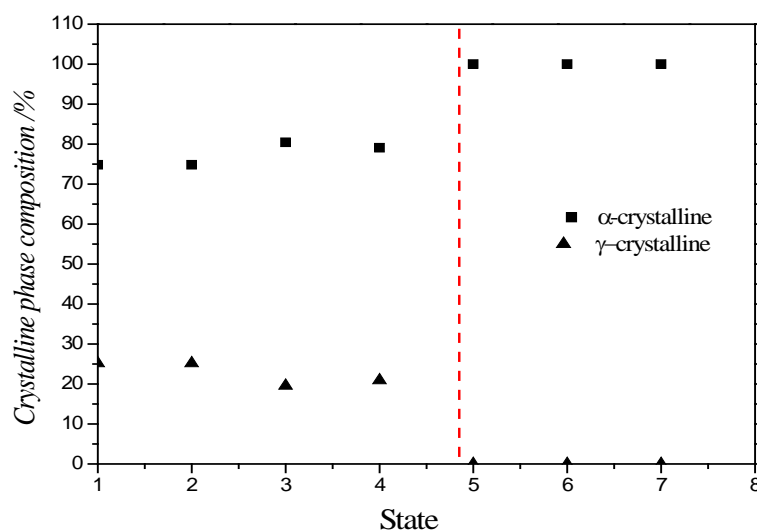


Fig. 8. Change of PA6 crystal structure upon tensile process.

It could be seen that we could do some further research about the change of PA6 crystal structure through the spectrogram of ^{13}C CP/MAS [18-19]. Fig. 9. and Table 2 show that under the tensile stage of 5, the γ crystal C2 peak which corresponded to chemical shift 32.3 ppm was disappeared

basically and under the tensile stage of 1, the γ crystal C1 peak which corresponded to chemical shift 38.5 ppm was less than the signal of tensile state 1 obviously. The conclusions further illustrated the γ crystal was gradually disappeared in the process of low tensile rate. Combined with XRD analysis, we thought that the phenomenon of double yield in low-speed tensile process might be accompanied with the destruction of the γ crystal.

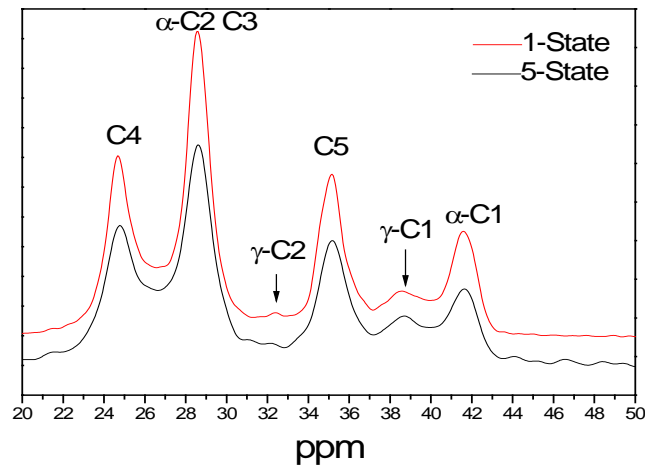


Fig. 9. CH_2 resonances of ^{13}C CPMAS spectra of different tensile strain state PA6

Table 2. ^{13}C Chemical Shifts of the Methylene Carbons in aggregation of PA6

	$\begin{array}{ccccccc} & & \text{H} & \text{H} & \text{H} & \text{H} & \text{O} \\ & & & & & & \\ \text{H}_2\text{N} & -\text{C}_1 & -\text{C}_2 & -\text{C}_3 & -\text{C}_4 & -\text{C}_5 & -\text{C}_6- \\ & & & & & & \\ & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \end{array}$				
phase	C1	C2	C3	C4	C5
α	41.6	28.5	28.5	24.6	35.1
γ	38.5	32.3	29.0	24.6	35.0
Amorphous	41.3	29.8	28.4	26.2	35.2

- a. In ppm relative to TMS. b. From ref 2: C3, C4 and C4 resonances were not individually assigned by the authors.

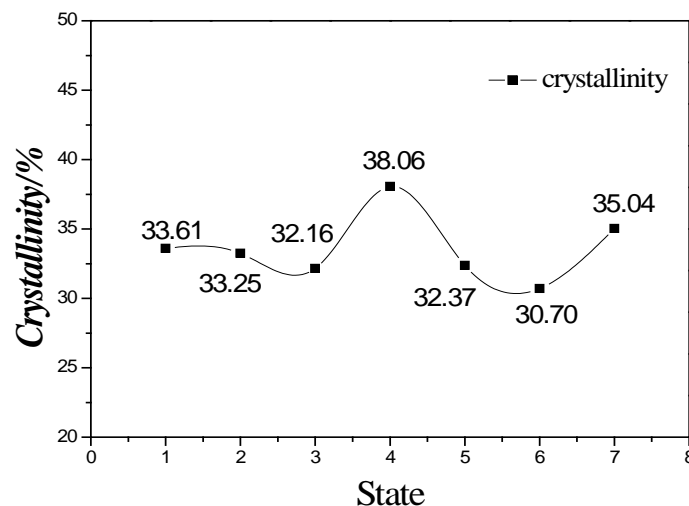


Fig. 10 Change of PA6 crystallinity upon tensile process.

Fig. 10. shows the changing trend of PA6 crystallinity upon seven tensile processes. The two peak-valleys of crystallinity changing curve just corresponded to the twice tensile states which were yielding. So we thought there was a certain relationship between double yield and crystal destruction. After the first yield, PA6 had experienced partial irreversible plastic deformation and molecular chain orientation arrangement, which caused the increase of crystallinity. In the process of second yield along with the decrease of crystallinity, which because of the obvious damage of the crystal structure, then the crystallinity was increased by the orientation hardening.

Conclusions

With the increase of tensile rate, the yield strength of PA6 was on the rise, and the elongation at break decreased. The elongation at break declined sharply when the tensile rate increased to 50 mm/min, it's because that under the tensile rate was 50mm/min, the PA6 crystallinity decreased obviously after stretching, the lattice was damaged seriously, and there was also a sharp decline in the capacity of molecular chain segments together with plastic deformation.

In low-speed PA6 tensile process, when two yield occurred in tensile process, the two peak valleys of seven sates in the crystallinity changing curve just respectively corresponded to the tensile states, we thought there was a certain relationship between double yield and crystal destruction. The phenomenon of double yield in low-speed tensile process might be accompanied with the destruction of the γ crystal.

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