

VISCOELASTIC BEHAVIOR OF THE NON-HOOKE DEFORMATION BEFORE YIELDING IN UNIAXIAL DRAWING OF AMORPHOUS POLY(ETHYLENE TEREPHTHALATE)*

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Abstract Viscoelastic behavior of the non-Hooke deformation of amorphous PET film before yield was investigated in the temperature region 74–80.5°C around the glass transition temperature. The film specimen was drawn to yield point followed by unloading to zero stress, then the residual deformation was held constant, while the subsequent evolution of the stress was recorded. An induction period was found in the course of stress evolution followed by a stress step-increase. The induction period decreases with increasing drawing temperature with an activation energy of 1.10 MJ/mol · K, which is attributed to the time needed for the relaxation of rubbery deformation through cooperative internal rotations. At temperatures lower than 74°C, there is no stress increase or the induction period becomes too long to be observed. Thus the nature of anelasticity in the non-Hooke region before yielding is attributed to stress induced rubbery deformation. The experimental results are interpreted in terms of Perez' rheological model of a series connected Hooke spring and a Voigt element consisting of a parallel connected elastic spring and a dashpot.

Keywords Pre-yield deformation, PET, Uniaxial drawing, Non-Hooke deformation, Viscoelasticity, Stress induced rubbery deformation

INTRODUCTION

Deformation of amorphous polymers at temperatures below, around and above their glass transition temperature T_g , in the pre-yielding and post-yielding regions has been studied extensively. In the case of amorphous Poly(ethylene terephthalate) (PET) one has to choose the condition of drawing so that no crystallization and no rubbery flow of the polymer take place during deformation, in order to simplify the interpretation of experimental results. The appearance of a stress peak on the engineering stress-strain curve of uniaxial drawing below T_g has been attributed to the disruption of cohesive entanglement present in the polymer before drawing^[1, 2], and the post-yielding deformation has been shown to be rubbery deformation under the drawing conditions that no crystallization and no necking of the specimen took place^[3, 4]. As the post-yielding deformation is of the nature of rubbery deformation, it is viscoelastic. The nature of deformation in the non-Hooke region up to yielding is not clear and not much studied. Perez^[5] showed that the non-Hooke deformation at room temperature of polymethylmethacrylate (PMMA) before yielding is anelastic from the observation that when drawing was stopped at yield and unloading to zero stress was performed while holding the un-recovered deformation of the specimen constant, an evolution of a stress step was observed. He interpreted this stress evolution phenomenologically by a rheological model of a Hooke spring series connected to a viscoelastic Voigt element. On bringing the stress to zero after deformation in the non-Hooke region, the relaxation of the Hooke spring is

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instantaneous, while the relaxation of viscoelastic deformation of the Voigt element takes time so that some residual deformation remained. On holding the residual deformation constant the interaction of the Hooke spring and the Voigt element leads to an evolution of stress. This interesting viscoelastic behavior on unloading of non-Hooke deformation before yielding of an amorphous polymer has not been studied in detail. Previously published work deals mostly with the unloading behavior after post-yield large deformation^[6, 7]. The experiments here deal with deformation under drawing stress in short time periods, i.e. less than 15 seconds, and then the load is released immediately to zero stress after drawing is stopped. Thus, no long term deformation effects are involved, which are usually studied in the experiments on creep under constant load and stress relaxation under constant deformation in time periods of hours at room temperature for PMMA ($T_g = 110^\circ\text{C}$).

The aim of the present work is to confirm the observation of Perez on the phenomenon of stress evolution for the case of amorphous PET and to study the effect of drawing temperature on the phenomenon, which is new and not mentioned in Perez's work. It is hoped that this will pave the way to an understanding on molecular level of the nature of non-Hooke deformation of amorphous polymers.

EXPERIMENTAL

Samples

Amorphous PET sheets of about 200 mm width and 0.15 mm thickness were produced by melt extrusion at 290°C through a slit die followed by quenching onto a chilled roll at 20°C . Its viscosity average molar mass is 1.63×10^4 . The density of the sheet is 1.3363 g/cm^3 and the birefringence is less than 2×10^{-4} indicating no measurable amount of crystallinity and orientation. The specimens used for uniaxial drawing had a gauge length of 25 mm and a width of 5 mm. Before drawing, the specimen was heated to 92°C for 8 min and then quenched in ice water to erase its thermal history. Its T_g was 74.5°C , taken as the midpoint of the step endothermic curve of a DSC measurement at 20 K/min.

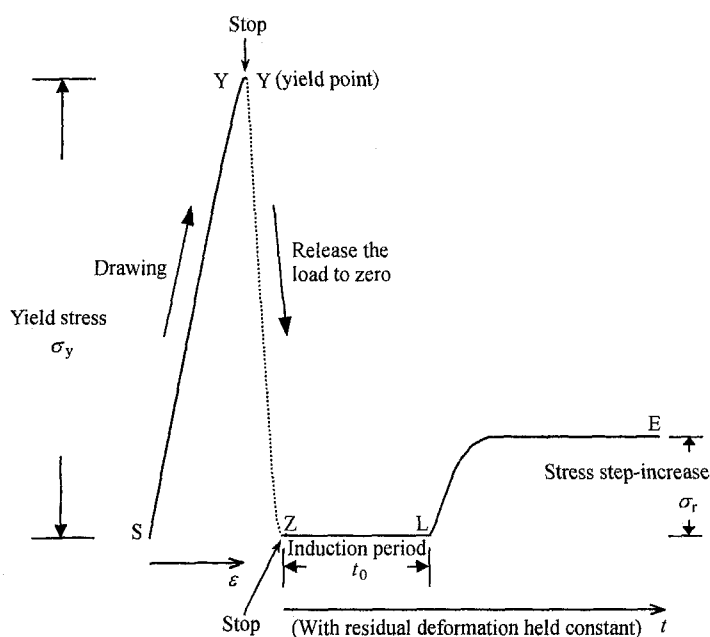


Fig. 1 Schematic showing the experimental procedure and stress observed. The film is uniaxially drawn (curve SY) at a constant rate and stopped at Y (yield point), then the load is released (curve YZ) immediately to zero at Z, and while the residual deformation at Z is held constant, the evolution of stress (curve ZE) is recorded, in which an induction period ZL is seen.

Uniaxial Drawing

Uniaxial drawing was performed on a self-made tensile tester equipped with a temperature-programmed chamber. The amorphous specimen was first heated in the chamber for 15 min at the desired drawing temperature to allow thermal equilibration, and then drawn at a constant cross-head speed of 30%/min to the yield point (the stress peak position of Fig. 1). At this instant the movement of the clamp of the drawing machine was stopped, and without any pause the clamp was set to move in reverse direction at the same speed as drawing, so as to reduce the load (the applied force) to zero, and then the clamp motion stopped. While the residual deformation was held constant the subsequent evolution of the stress was recorded.

RESULTS AND DISCUSSION

The uniaxial drawing of the amorphous PET specimen in its glass state starts with a Hooke region where the deformation and the applied stress follow a linear relation, i.e. Hooke's law. Preliminary experiments done by Jingshu Shen in this laboratory show the following results. When drawing at 10%/min at room temperature (23°C) is stopped within the Hooke region, stress 25 MPa deformation 0.8%, and then the deformation is held constant, the stress value does not decay in the time periods of 5 min, the stress decrease being 4% in 77 min. If the clamp of the drawing machine is set to move in the reverse direction to reduce the stress to zero, the deformation will decrease instantaneously and completely to zero. When drawing proceeds beyond the Hooke region, stress 37 MPa deformation 1.2%, and is then stopped with the deformation held constant, stress relaxation is observed, showing a stress decrease of 4% in the time period of 5 min. As the difference is not in temperature but a small difference in the extent of deformation or applied stress before the drawing is stopped, this viscoelastic behavior (stress relaxation) of non-Hooke deformation is induced by stress not by temperature. When the drawing proceeds further, the nominal stress shows a rounding over leading to a drop of the stress value, i.e. the specimen yields, thus a stress peak is shown in the engineering stress-strain curve. When drawing is performed on the specimen in rubbery state, i.e. at a drawing temperature above T_g , no stress peak will occur as shown in Fig. 2, where nine stress-strain curves for drawing at temperatures from 74–80.5°C are presented. From these curves we can locate the value of T_g of our sample under the drawing conditions to be 75.5°C, above this temperature the sample was in the rubbery state.

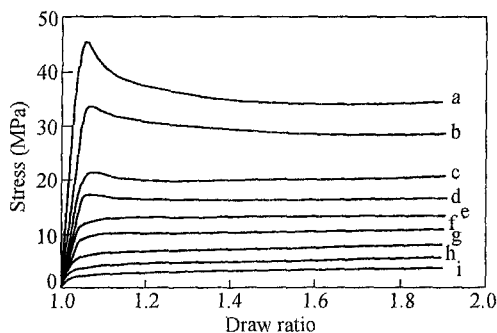
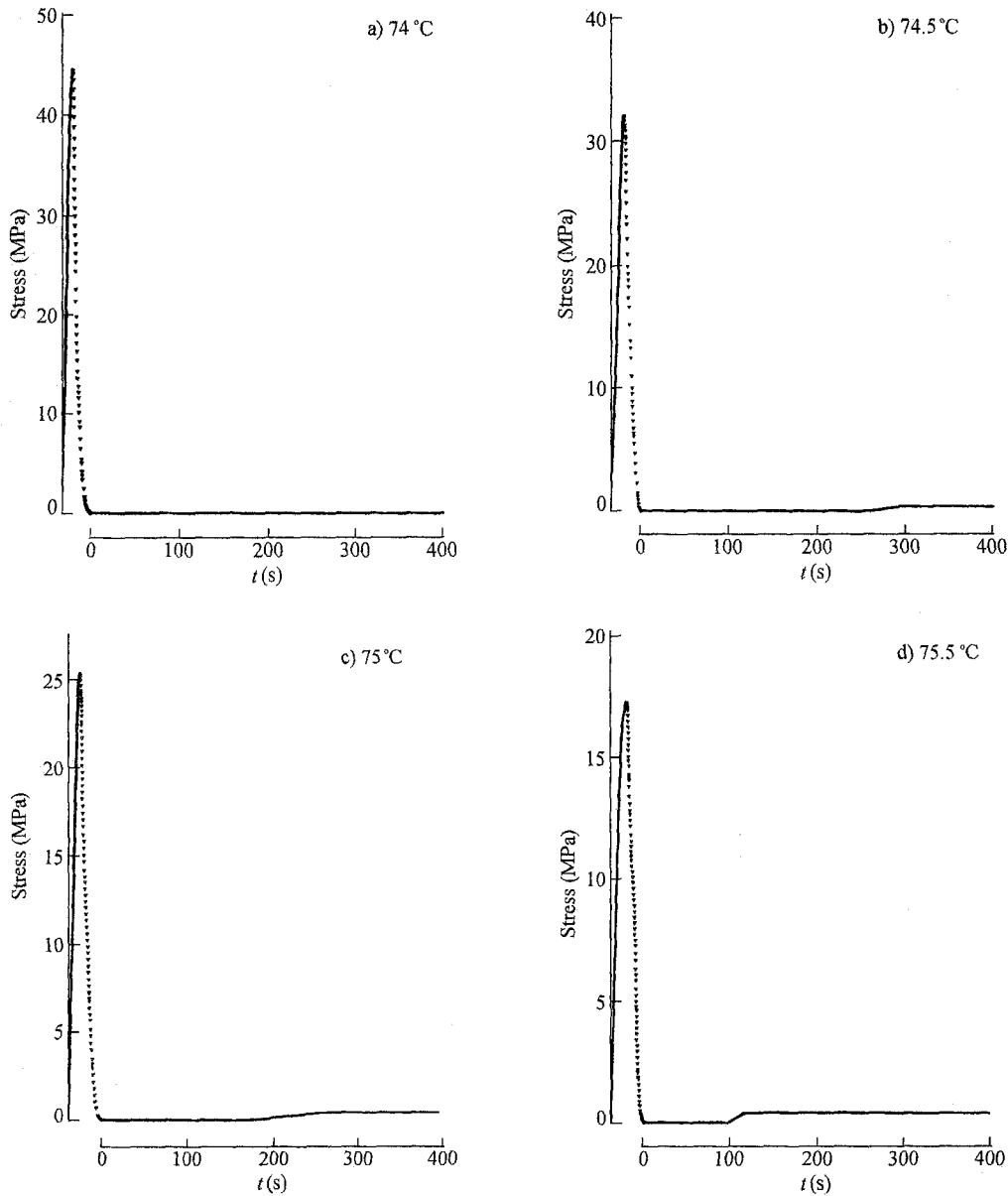


Fig. 2 Engineering stress-strain curves under different drawing temperatures
a) 74°C; b) 74.5°C; c) 75°C; d) 75.5°C; e) 76.5°C; f) 77.5°C; g) 78.5°C;
h) 79.5°C; i) 80.5°C

When the drawing below T_g is stopped just at the yield point, then the clamp is set to move in the reverse direction immediately to reduce the stress to zero, and stopped there to maintain the residual deformation constant, an evolution of stress was actually observed. The residual deformation after unloading, i.e. the non-Hooke part of the deformation under drawing being not relaxed during unloading (in ca. 10 s), amounts to 5%–10% of the deformation before the drawing is stopped. It is interesting to note that for such evolution of stress an induction period was observed which was very sensitive to the temperature of drawing. The induction period decreases with increasing temperature of drawing. The results are shown in Fig. 3 and summarized in

Table 1. The following characteristics of the phenomenon are to be noted. (i) After drawing is stopped, the process of stress release on reversing the motion of the clamp occurred apparently in two steps when the drawing temperature was higher than 75.5 °C. Evidently the first step of stress reduction is faster than the second step. It is reasonable to attribute the first step to the release of stress of the Hooke spring according to Perez’s model. As the reversed motion of the clamp was not fast enough, before the Hooke spring had completely recovered to the undeformed state some recovery of the deformation of the Voigt element occurred, which contributes to the second step of the stress release. If the reverse motion of the clamp could be done at a much faster rate, we would expect much less release of stress of the Voigt element and subsequently a higher evolved stress step than actually observed. (ii) The induction period, t_0 , for the evolution of stress step-increase, after the specimen was held under constant residual deformation at zero stress, appears highly sensitive to the temperature of drawing.



(Figure 3, to be continued)

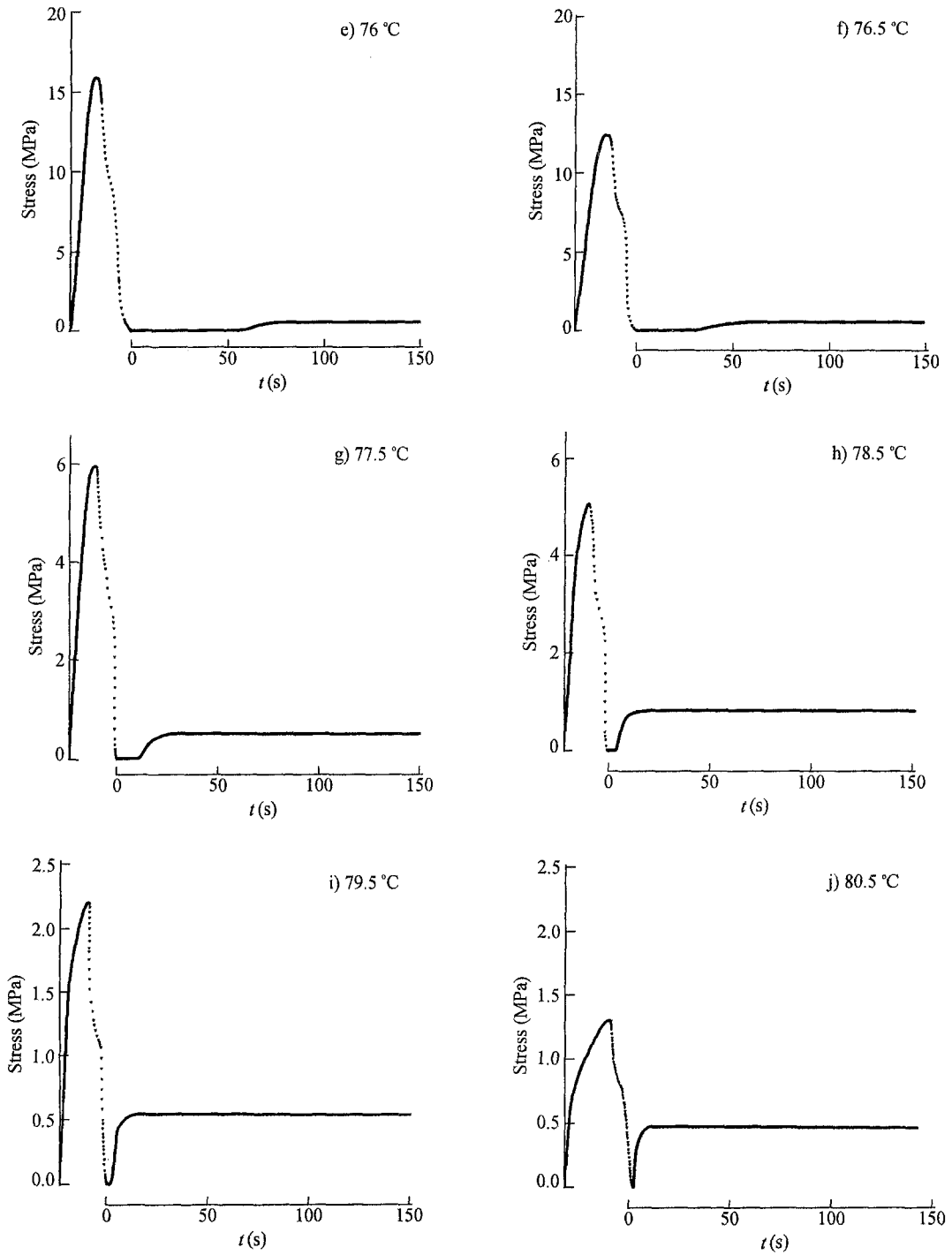


Fig. 3 Experimental drawing stress and the stress step-increase at different drawing temperatures

This appearance of an induction period for stress step-increase and its temperature dependence were not mentioned by Perez^[5], as he observed the evolution of stress step-increase on uniaxial drawing of PMMA at 27°C, which is some 90°C below its T_g . The present results show that above 80.5°C, being only 6°C above T_g , the induction period is practically zero, while below 74.5°C, i.e. just below its T_g , the induction period becomes very

long (250 s). This is the reason that when this sample of PET was drawn uniaxially at room temperature, no such stress evolution was observed. These results are not in agreement with Perez's result^[5] for drawing of PMMA at 27°C. A plot of $\lg(1/t_0)$ versus $1/T$ gives a straight line as shown in Fig. 4, the activation energy for the process involved as evaluated from the slope of the straight line amounts to 1.10 MJ/mol · K. (iii) The rate of increase of stress in the step increases with increasing temperature of drawing. (iv) The height of stress step-increase, σ_r expressed as a fraction of the yield stress σ_y , σ_r/σ_y , increases with increasing drawing temperature, the value lying between 1.3% for drawing at 74.5°C and 37% for drawing at 80.5°C given the same speed of reversed clamp motion used.

Table 1. Yield stress σ_y , induction period t_0 and height of stress step-increase σ_r at different drawing temperatures, drawing speed 30%/min

Drawing temperature T (°C)	Yield stress σ_y (MPa)	Induction period t_0 (s)	σ_r/σ_y ($\times 100$)
74.5	32.0	250.4	1.3
75.0	25.3	174.0	1.8
75.5	17.2	96.0	2.4
76.0	15.9	56.0	3.2
76.5	12.4	30.0	4.3
77.5	6.0	10.8	8.5
78.5	5.1	4.0	16
79.5	2.2	1.2	25
80.5	1.3	0.4	37

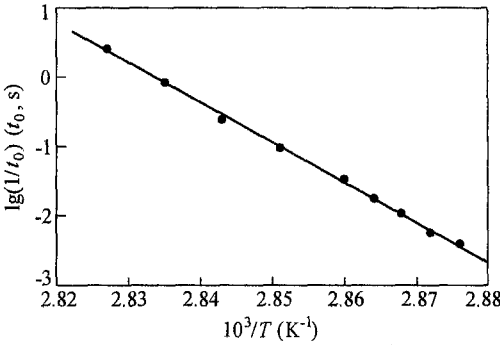


Fig. 4 A plot of $\lg(1/t_0)$ versus $1/T$
 t_0 being the induction period in s and T the drawing temperature in K

The existence of an induction period for the evolution of stress step-increase indicates a process involving two processes in succession, the induction process and the stress increasing process. The value of activation energy obtained seems to be fitted to cooperative internal rotations of successive bonds of the chain around the temperature of glass transition. If this interpretation is correct, this induction period is the time needed for the development of cooperative internal rotations for rubbery deformation or its reverse process here, the relaxation of rubbery deformation through cooperative internal rotations. Consequently, the anelasticity in the non-Hooke region in the uniaxial drawing of amorphous PET around its T_g is of the nature of rubbery deformation. In terms of Perez's model, on unloading to zero stress the Hooke spring element is totally and instantly relaxed. On the other hand, the relaxation of rubbery deformation of the Voigt element produced in non-Hooke deformation during drawing takes a much longer time after unloading. This relaxation of rubbery deformation of the Voigt element leads to a re-extension of the totally relaxed Hooke spring, thus creating a small stress step-increase, as the modulus of the Hooke spring is much larger than that of the Voigt element.

In the case of drawing at temperatures considerably below T_g the nature of anelastic deformation in the non-Hooke region may be analogously considered as stress induced rubbery deformation. In this case, on releasing

the load and maintaining the residual deformation constant, a step increase of the stress is not observed as the induction period becomes much longer than the time scale of the experiment. In other words, the relaxation of the rubbery deformation is frozen at the temperature of the experiment, similar to the frozen post-yield deformation below T_g which is of the nature of stress induced rubbery deformation^[3]. It has been clearly shown that when PMMA is unidirectionally compressed at 20°C^[8, 9] to an increasing degree of deformation and then released, the pre-yield deformation can be completely recovered on heating-up temperature scanning to 50°C, well below T_g , while the post-yield deformation is recovered completely only at T_g . This indicates that the deformation mechanism involves two components of molecular motions, one group of shorter relaxation times perhaps of cooperative internal rotations of a few main chain bonds for the pre-yielding anelastic deformation, and the other group of longer relaxation times known as α -relaxation for the post-yielding stress induced rubbery deformation.

CONCLUSION

A detailed study has been undertaken on the non-Hooke behavior of PET in the temperature region of 74–80.5°C around the glass transition temperature. When an amorphous PET film is deformed up to the yield point, two components of its deformation are commonly distinguished: Hooke and non-Hooke deformations. The Hooke deformation relaxes instantaneously and completely on unloading to zero stress. On the other hand, the non-Hooke deformation does not recover completely in such a process due to its much longer relaxation time, thus an evolution of stress step increase was observed for drawing temperatures higher than 74°C. An induction period was observed in the evolution of stress, which decreases with increasing temperature of drawing. An interpretation of the two successive processes involved is given. The first process is attributed to the time needed for the relaxation of rubbery deformation through cooperative internal rotations which lead to a re-extension of the totally relaxed Hooke spring, creating the second process of a step-increase in stress.

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