Effect of Physical Aging on Fracture Behavior of Polyphenylquinoxaline Films

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ABSTRACT: The influence of physical aging on the tensile fracture behavior of notched Polyphenylquinoxaline (PPQ-E) samples has been studied. The dependence of fracture stress and strain on physical aging has been explained. The glass transition temperature (T_g) and the endothermic peak at the end of T_g transition with different physical aging were characterized using differential scanning calorimetry (DSC) and the results have also been explained. The morphology of fracture surface was observed by scanning electron microscopy (SEM). © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1275–1279, 2000

Key words: physical aging; fracture; DSC; SEM; polyphenylquinoxaline; tensile; films

INTRODUCTION

Physical aging is a phenomenon known as the structure recovery where the enthalpy and the volume change with time and/or temperature as the material progresses from a metastable equilibrium value to true equilibrium value. The properties associated with the structure recovery are changed.[1–6] In fact, physical aging occurs also when an amorphous polymer held above its glass transition temperature (T_g) is slowly cooled to below T_g.[7]

Physical aging affects the deformation process and the fracture, which is the last state of deformation process. Some papers discussed the effect of physical aging on fracture behavior. Arnold[8] found that the strain to failure decreased with increasing the aging time on fracture behavior of polystyrene (PS). Ye and Shen[9] reported similar result on poly(methylmethacrylate) (PMMA). However, Crissman and McKenna[10] observed that the strain to fracture do not change with the aging time in studying the creep rupture of PMMA.

It is well known that the failure process of polymer is a relaxation process.[11,12] The failure occurs before the yielding point for brittle polymers. But for ductile polymers, the failure always occurs after the yielding point. Thus, the effect of large strain on failure process is complex for ductile polymer. Large deformation will release the effect of prephysical aging and produce a new aging process,[1,13,14] which derived from large deformation is equivalent to molecular motion above T_g. The new aging effect is an unpredictable factor for ductile polymer. Although samples with different conditions of physical aging undergo large deformation, they have no comparability due to the new aging effect. In order to avoid the effect of new aging process on polymers, it is necessary to choose a suitable experimental method. Generally, the notched method is used in

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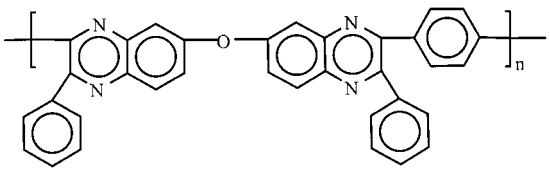

Figure 1 The chemical structure of polyphenylquinoxaline.

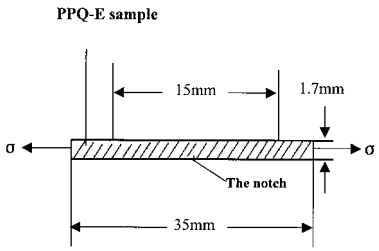

Figure 2 The schematic presentation of a notch specimen for tensile test.

impact tests. In order to solve the problem, we used the tensile test method for notched specimens in our experiments.

Polyphenylquinoxaline (PPQ-E) is an aromatic helerocyclic polymer; its chemical structure is expressed in Figure 1. PPQ-E has many potential usages due to its high performance, which is mainly used as a gas separation membrane in an H_2 monitor.[15] It can be used as a coating to cover the wire in submerged electric motors and can also be used as a high sensitive element in capacitance transducers for measuring liquid surface under high temperature and pressures, and so on.[16] It is also a ductile polymer at room temperature, its deformation mechanism is both of crazing and shear yielding.[17]

In the present paper, tensile tests have been performed on PPQ-E samples with two different states of physical aging. To observe the morphology of fracture surface, scanning electron microscopy (SEM) was used. Differential scanning calorimetry (DSC) was used to characterize physical aging of the samples. The effects of physical aging on fracture behavior were determined.

EXPERIMENTAL

Materials and Specimen Preparation

PPQ-E synthesized in the laboratory was casted to form a 0.05 mm thickness film. The film was then cut into rectangular specimens of 35 mm long and 1.7 mm wide. The specimens were notched on one side perpendicular to the direction of length with a sharp razor. The notch length was approximately 0.2 mm as shown in Figure 2.

Heating Process

The above specimens were annealed at 320°C for 1.5 h in nitrogen gas to eliminate past mechanical history and then were classified into two sets: one set of specimens was quenched in steel to room temperature at 18°C, which was denoted as sample 1. The other set was also quenched to room temperature but annealed again at 280°C for 1.5 h and then slowly cooled to room temperature at 18°C in nitrogen gas with the average cooling rate of 1.5°C/min, which was denoted as sample 2 (see Table I).

Tensile Properties Test

The tensile properties of the samples were tested using Shinkch tensile Test Machine with a strain rate of 3.3% min^{-1}. The length of specimen between the two clamps of the tensile machine was about to 15 mm. The load-displacement curve during deformation was generated. Five specimens were tested for each set of samples and the average values were reported.

DSC Analysis

The T_g and the endothermic peak at the end of T_g of samples 1 and 2 were measured using TA 2100 Modulated DSC with heating rate 10°C/min under nitrogen gas. Only first heating curves were recorded for study physical aging effects.

Morphology Observation

The fracture surface of the samples were observed using a Hitachi S-530 Scanning Electron Micro-

Table I Heating Condition of Two Kinds of Samples for PPQ-E

Samples	Heating Conditions
1	Quenched to room temperature after annealed at 320°C for 1.5 h
2	Quenched to room temperature after annealed at 320°C for 1.5 h, annealed at 280°C for 1.5 h again, then slowly cooled to room temperature

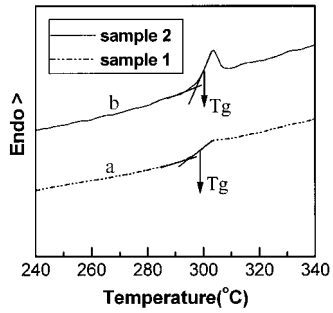

Figure 3 The DSC curves for two samples.

scope. The fracture surfaces were sputter coated with gold prior to examination.

RESULTS AND DISCUSSION

Analysis of DSC Curve for Two Samples

The DSC curves of these samples with different physical aging are shown in Figure 3. On curve of sample 1, it can be seen that there is only T_g transition at 298°C and no obvious endothermic peak at the end of T_g transition. However, curve of sample 2 shows that not only T_g transition at 299.8°C but also the obvious endothermic peak at the end of the glass transition appears. The T_g of sample 2 is higher about 2°C than that on sample 1. All the results are related to physical aging of samples as discussed next.

Over the past three decades, the essence of physical aging was progressively revealed. On a basis of free volume theory, free volume of polymer decrease with physical aging.[1,2] On a molecular level, it is considered that physical aging makes segments packed tightly by motion of polymer chains or local segments configuration rearrangements of molecular chains for noncrystalline polymer.[2–4] Research on enthalpy relaxation and density with physical aging has supplied enough evidence that physical aging leads to increase in the degree of packing of polymer chain and reduction in molecular mobility.[5,6] In view of molecular interaction, a new interpretation is that local nematic interaction between neighboring segments of a few monomer units can be formed during physical aging.[18,19]

For sample 1, the annealing above T_g temperature and then the quenching to room temperature made molecular chains freeze at the state of above T_g. The molecular chains had no chance for rearrangement. But sample 2 was annealed again at 280°C (below T_g) for 1.5 h and then was slowly cooled to room temperature. The Sub-T_g annealing and the slow cooling processes were in fact structure relaxation process of molecular segments. In this case, molecular segments had chance to repack and to form stronger and more local nematic molecular interaction. Therefore, in the heating process of DSC, sample 2 at the end of the glass transition will absorb more energy to overcome the potential energy resulted from stronger local nematic interaction between segments. As a result, not only T_g temperature slightly shifts towards higher temperature but also the endothermic peak is obvious. The endothermic peak is caused by the changes in structure from a nonequilibrium state to metastable state during physical aging. So, the endothermic peak results from the changes in the repacking structure, specifically in local nematic molecular interaction between segments.

Tensile Properties of Two Samples

The nominal stress-strain curves of notched samples with two different heating conditions are shown in Figure 4. Figure 4 shows that fracture of the quenched sample and the Sub-T_g annealed sample occurs before yielding. This result shows that the two samples exhibited macroscopic brittle fracture.

The values of the fracture strain ε_b, the fracture stress σ_b, and the fracture energy E_b, which was attained through integration on the nominal stress-strain curve for the sample, are shown in Table II. The values are different for two samples. Here, E_b expresses energy absorbed by the sample in unit volume.

Although both the samples fractured in macroscopic brittle manner, sample 2 has higher value

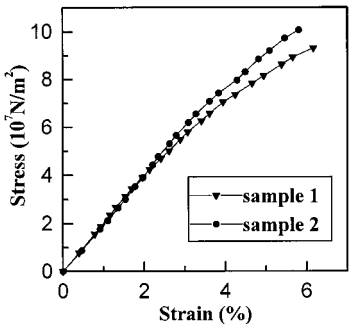

Figure 4 The nominal stress-strain curves of tensile test for single-edge notched samples.

Table II Fracture Stress, Strain to Break, and Deformation Energy of Samples 1 and 2

Samples	1	2
ε_b, %	6.16 ± 0.21	5.71 ± 0.16
σ_b, 10^7 N/m^2	9.32 ± 0.18	10.07 ± 0.27
E_b, 10^5 J/m^3	33.21 ± 0.04	31.98 ± 0.04

of fracture stress, lower value of fracture strain, and lower fracture energy than sample 1. The difference of E_b between sample 1 and 2 is a real response of physical aging on fracture behavior. Also this is a response of the difference between the structure of sample 1 and 2 on fracture behavior. Sample 1 and 2 have the same molecular weight, the topological entanglement in sample 1 and 2 is identical, and the effect of the topological entanglement on tensile properties of sample 1 and 2 is identical.[20] For the two samples, the main difference of structure results from physical aging. According to the view of the molecular interaction,[18,19] local nematic interaction between segments during physical aging increases. According to the view point of molecular mobility,[3–5] the packing degree of polymer chains in sample 2 is tighter and molecular motion will be more constrained, so molecular mobility is decreased. Thereby, in the tensile process, compared with samples 1, tensile stress of sample 2 increases, the fracture strain decreases, and fracture energy decreases.

The ability of two sets of PPQ-E samples to deform under an applied load depends on the repacking structure of PPQ-E. The characteristic of fracture surface of the PPQ-E samples can reflect their tensile fracture behavior.

Morphology of Fracture Surface for Two Samples

The morphology of the fracture surface of sample 1 is shown in Figure 5. The fracture was coarse and showed brittle manner. Yet some localized ductile character of the fracture morphology can be observed. That was induced by the higher fracture strain. This means that the structure of sample 1 is loose because the chains were frozen in the glassy state. The morphology of fracture surface of sample 2 is shown in Figure 6. The fracture surface is smooth. This reflects more compact structure of the annealing sample due to the fact that molecular chains have a chance to repack. On the one hand, the above results manifest that the morphology of fracture surface partly represents the changes in structure derived from physical aging. On the other hand, the above results show the effects of the changes in structure due to physical aging on tensile fracture behavior.

CONCLUSION

Physical aging in PPQ-E generates obvious endothermic peak on DSC curves. The endothermic peak results from the repacking structure into stronger local nematic molecular interaction between segments. This changes in structure affects tensile fracture behavior of PPQ-E, and leads to an increase in break stress and a reduction in fracture energy and break strain. Simultaneously, the morphology features of fracture surface are also affected by the local molecule interaction.

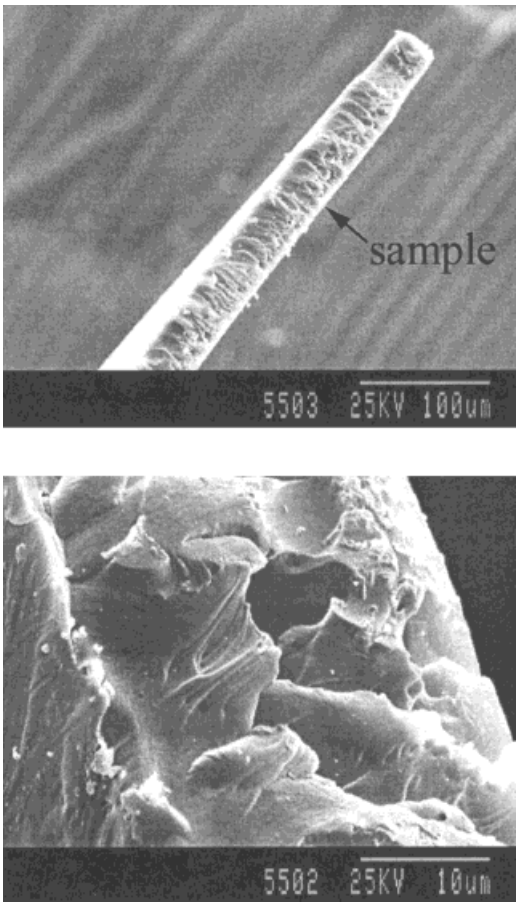

Figure 5 The SEM micrographs of fracture surface of sample 1.

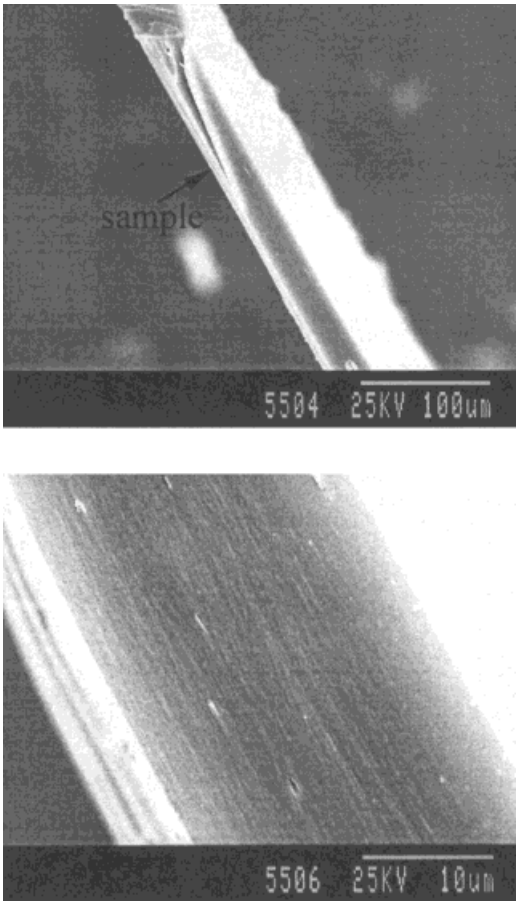

Figure 6 The SEM micrographs of fracture surface of sample 2.

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