

SEM OBSERVATION OF THE CRAZING FOR POLYPHENYLQUINOXALINE FILMS DURING *IN SITU* STRETCHING*

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Abstract The crazing of polyphenylquinoxaline (PPQ-E) films during *in situ* stretching has been observed by SEM. The crazing phenomena and craze morphology of PPQ-E films were interpreted. The strain values at critical crazing and yielding and the craze stability of PPQ-E samples depend on the thermal-dealing condition for the samples. From the point of view of cohesional entanglements and energy absorbed by samples, the experiment results were explained.

Keyword PPQ-E, Crazing, Physical aging, Cohesional entanglement, *in-situ* stretching, SEM

INTRODUCTION

Crazing is a characteristic of polymers — when a glassy polymer is stretched, crazes can be found on the surface and in the interior of the material. The craze plane is vertical to the direction of tensile stress. On further stretching, crazes will develop into cracks and lead to the fracture of polymer materials^[1]. There are lots of reports studying the crazing of glassy polymers by SEM or TEM^[2-11]. The majority of polymers studied are PS, SAN, PC, PMMA, or epoxy resin etc. But only a few of studies reported on polymers with high performance and high-temperature resistance.

It is well known that polyphenylquinoxaline (PPQ-E) is a heteroaromatic polymer with many excellent properties; its chemical structure is depicted in Fig. 1. It is mainly used as gas separation membranes in H₂ monitors, or as coating for electrical wire in submerged electric motors, or as a highly sensitive element in capacitance transducers for measuring liquid levels under high temperature and pressures and so on^[12-14]. Meanwhile, the crazing of PPQ-E has never been reported before. So studying its crazing is not only necessary for PPQ-E but also has a certain theoretical value and wide applicability. In this paper, the crazing of PPQ-E films during *in situ* stretching has been studied by SEM.

EXPERIMENTAL

PPQ-E synthesized in the laboratory was cast into a film 0.07 mm in thickness, and the film was then cut into dumbbell-shaped samples, the linear part of which was approximately 4.8 mm × 2.2 mm. The samples were annealed at 323°C for 1.5 h in nitrogen gas in order to eliminate past

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mechanical history, then quenched to room temperature. Some quenched specimens were annealed again at 280°C for 1.5 h to give sample 1; the other quenched specimens were annealed at 200°C for 1.5 h to give sample 2, and both were slowly cooled to room temperature. Thus, two groups of samples (cf. Table 1) with different heating processes were obtained.

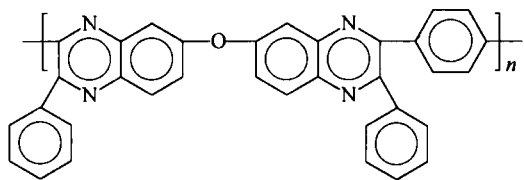


Fig. 1 The chemical structure of polyphenylquinoxaline (PPQ)

Table 1 The heating condition of two groups of samples of PPQ-E

Sample number	Heating condition
1	Annealed at 323°C for 1.5 h, quenched to room temperature, then annealed at 280°C for 1.5 h and slowly cooled to room temperature
2	Annealed at 323°C for 1.5 h, quenched to room temperature, then annealed at 200°C for 1.5 h and slowly cooled to room temperature

The crazing of samples during *in situ* stretching with a strain rate of 0.02 min⁻¹ was observed using a Hitachi S-570 SEM with a tensile-testing installation. Meanwhile, the displacement-load curve during stretching was given by a computer system. Samples were coated with gold by the sputtering technique prior to SEM examination.

The glass transition temperature of the sample which was annealed at 323°C for 1.5 h then slowly cooled to room temperature was measured using a Perkin-Elmer Model DSC-2 differential scanning calorimeter with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The DSC curve in Fig. 2 shows that the glass transition temperature (*T_g*) of PPQ-E is 298°C. Therefore, in our experiments, the annealing of samples at 323°C was a thermal treatment above *T_g* in order to erase the past history, and the subsequent annealing at 280°C or 200°C, respectively, was a process of sub-*T_g* annealing, or so-called physical aging. An example of craze occurring in the PPQ-E under stress is shown in a TEM micrograph (Fig. 3.).

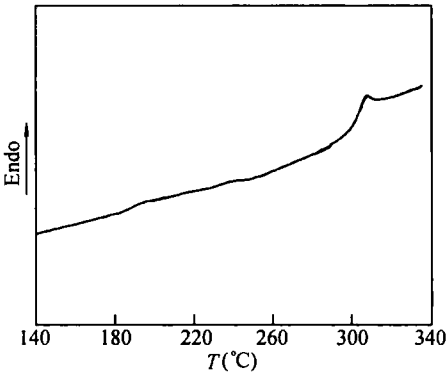


Fig. 2 The DSC curve of polyphenylquinoxaline (PPQ-E) using a heating rate of 10°C/min

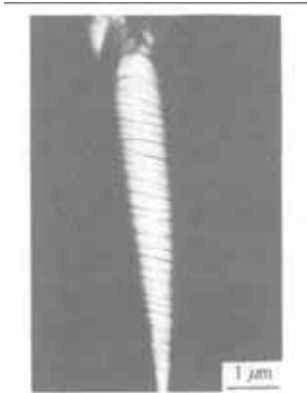


Fig. 3 Transmission electron micrograph of example of craze in PPQ-E

The crazeing features of these samples under tensile stress are summarized as follows. Sample 1 underwent sub- T_g annealing at 280°C for 1.5 h. Figure 4 shows that curve "a" is its nominal stress-strain curve. When strain reached 5.71%, slim and short crazes were in the minority, then crazeing propagated slowly with further stretching. Upon reaching a strain of 14.41% after the yielding point, crazes filled the whole view. These crazes were homogeneous in size and arranged regularly. Lengthy crazes crossing over the whole vision were not observed. Crazes grew separately and occasionally a few of them linked together. Crazeing developed rapidly under further loading. Figure 5 shows that at a strain of 15.67%, crazes arrange closely. Because the stretching extent is different on the surface, some crazes grow rapidly across the width, leading to fibril breakage and microcrack generation. At a strain of 17.60%, the sample was fractured.

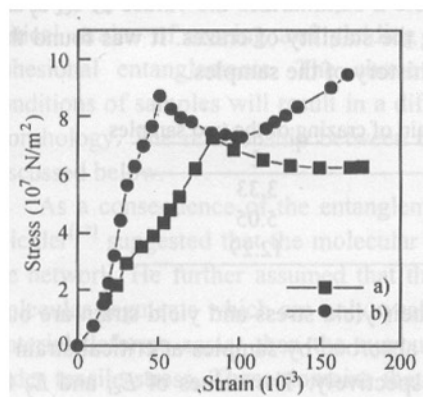


Fig. 4 The nominal stress-strain curves for a) sample 1 and b) sample 2

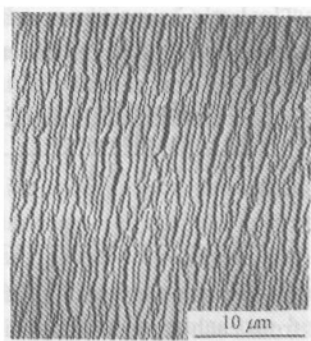


Fig. 5 The scanning electron micrograph of sample 1 at a strain of 15.67%

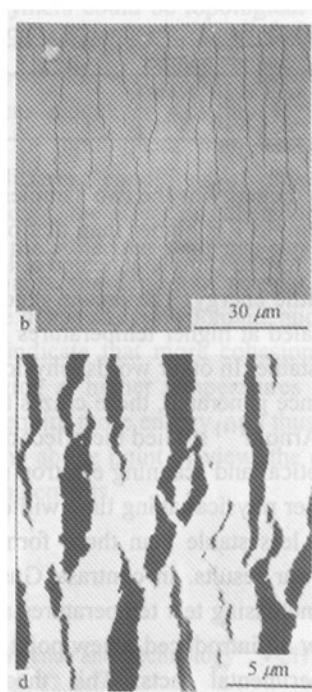
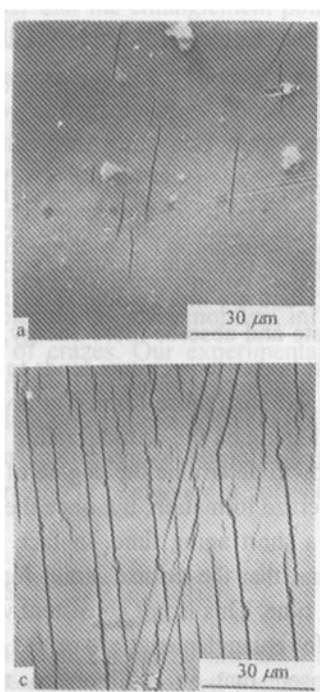


Fig. 6 The scanning electron micrographs of sample 2 at different strain values a) 3.33%, b) 5.55%, c) 11.93% and d) 14.18%

Sample 2 was aged at 200°C for 1.5 h. Its nominal stress-strain curve is shown as curve "b" in Fig. 4. It has high yield stress and low yield strain. The initial crazing appeared very early in this sample. A few crazes, which have formed at a strain of 3.33%, are slim and minute as shown in Fig. 6a. When strain reaches 5.55%, crazing developed rapidly with loading. Figure 6b shows that slim crazes arrange regularly and also propagate independently, without linking up or merging. As strain reaches 11.93%, most of the fibers in the crazes are broken across the whole view and can be found in Fig. 6c. At a strain of 14.18%, many microcracks that result from fibril breakage resulted in an intensely arranged network-like structure as shown in Fig. 6d. The breaking strain of the sample was 15.63%.

From the above experiments the critical strain of crazing, ϵ_c , the yield strain, ϵ_y , and the breaking strain, ϵ_b , of the samples can be determined. Table 2 summarizes the values of ϵ_c , ϵ_y and ($\epsilon_b - \epsilon_c$). The latter is a parameter used for characterizing the stability of crazes. It was found that the values of ϵ_c , and ϵ_y are both dependent on the thermal history of the samples.

Table 2 Craze stability, yield strain and critical strain of crazing of the two samples

Sample number	1	2
ϵ_c (%)	5.71	3.33
ϵ_y (%)	8.35	5.05
$(\epsilon_b - \epsilon_c)$ (%)	11.89	12.29

For the two samples aged at different temperatures their yield stress and yield strain are both different from each other as shown in Fig. 4. The energy absorbed by samples at critical strain of crazing and at yield strain was denoted as E_c , and E_y , respectively. The values of E_c , and E_y for these two samples can be calculated through integration of the nominal stress-strain curves and are shown in Table 3.

Table 3 Energy absorbed by samples at critical strain of crazing and yield point

Sample number	1	2
$E_c (\times 10^4 \text{ N/m}^2)$	141.1	73.7
$E_y (\times 10^4 \text{ N/m}^2)$	298.2	196.7

The absorbed energy of the two samples is also affected by the sub- T_g annealing process. The value of E_c of sample 1 is higher than that of sample 2. It is consistent with the trend of ϵ_c . These results show that for the sample annealed at lower temperature its initial crazing appears earlier and absorbs only a little energy. The crazes generate easily and are more stable. The initial crazing of the sample annealed at higher temperatures appears late and absorbs more energy, and the crazes formed are less stable. In other words, physical aging at higher temperature tends to delay the craze formation, but once generated, these crazes are less stable than those formed at lower temperature physical aging. Arnold^[11] studied the effect of physical aging on the brittle fracture behavior of PS, and also used optical and scanning electron microscopy to determine the degree of crazing. It was found that a longer physical aging time will delay the craze formation, but once the crazes formed, they were much less stable than those formed with a short aging time. In fact, this is in good agreement with our results. In contrast, Guster^[8] found that the critical strain for crazing of PS decreased with increasing test temperatures and aging time. This is not consistent with our results. Recently, Qian *et al.* introduced a new point of view for entanglement^[15, 16] on the basis of a large amount of experimental facts. This theory supposed that in addition to the topological entanglement of chains, there is another kind of chain entanglement termed as cohesional entanglement, which exists at the site of local nematic interaction between segments of a few monomer unit or three nearest neighboring chains. These cohesional entanglements may serve as physical crosslinks to cause the linear polymer to behave as a network. Thus, this kind of

cohesional entanglement point is different from the topological entanglement point. The linear density of cohesional entanglement is also larger than that of topological entanglement. As the cohesional entanglement is a weak interaction, the density of the cohesional entanglement point is strongly dependent on temperature. Therefore, the strength and quantity of that entanglement is obviously related to the thermal history of samples. Cohesional entanglement is important for the physical properties of a polymer around and below its T_g . Sub- T_g annealing can effectively change the cohesional entanglement for polymers. According to the point of view of cohesional entanglement, the sub- T_g annealing of samples at higher temperatures will form more stable cohesional entanglement points than that at lower temperatures, and more energy would be absorbed for disentangling the cohesional entanglement points. This is consistent with the results from energy studies. So we may conclude that the quantity of energy absorbed by a sample at critical strains of crazeing and yielding point is related to the condition of physical aging and cohesional entanglements. The above experimental results show that the different heating conditions of samples will result in a difference in the amount of crazes in unit area and the craze morphology. The relationship between crazeing and physical aging or cohesional entanglement is discussed below.

As a consequence of the entanglements of polymer chains an entangled network is formed. Michler^[17] suggested that the molecular mobility of local areas increases during the stretching of the network. He further assumed that the meshes of the entangled network contain lots of other molecular segments which are only weakly bonded and relatively loosely packed. This portion of material deforms easier than the surroundings, hence some small flow domains can be formed under tensile stress. These domains that act as craze nuclei lead to the initiation of crazeing. The flow domain is limited by the neighboring more strongly entangled chains. The density of flow domain depends on the cohesional entanglement density and the degree of activity of the domains.

We consider that the entanglement points of polymers could be topological or cohesional in nature. Yang and Berger believe that the topological entanglement of polymers decides their deformation mechanism, i.e. crazeing or shear flow^[6, 7]. We believe that the cohesional entanglement will affect the flow domain on Michler's model, as will the crazeing. Because the samples have identical molecular weight, the effect of topological entanglement on crazeing is identical. But for samples which have undergone different conditions of physical aging, their cohesional entanglement will be different. So in this case, the effect of cohesional entanglement on crazeing can be discussed. During sub- T_g annealing the molecular segments can be repacked and form cohesional entanglement points, which will change the degree of activity of the domains, decrease the molecular segment mobility, influence the density of flow domain, and therefore affect the occurrence of crazes. Our experimental results indicate that more cohesional entanglement points will be formed in samples during physical aging at higher temperatures or longer times, therefore the release of the entanglement points will require more energy, and thus the crazeing and yielding occur at higher critical strain values. From the above point of view, the energy absorbed by samples at crazeing is a behavior of cohesional entanglements.

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