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The deformation mechanism of polyphenylquinoxaline films

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Abstract

The deformation mechanism of polyphenylquinoxaline (PPQ-E) film has been studied by theoretical prediction and microscopic observation. The entanglement density, estimated from the plateau modulus on the dynamic mechanical property curves, was used to predict the deformation mechanism of PPQ-E. Polarized light microscope (PLM) was used to observe the morphology of the PPQ-E film during tensile deformation. It is found that the deformation mechanism of PPQ-E is both crazing and shear yielding, which is in agreement with the prediction by entanglement density. The craze morphology of PPQ-E is mainly of fibril craze consisting of micro-fibrils and micro-voids as observed by transmission electron microscope (TEM). The interface between the bulk and craze is distinct. Multiple crazes, blunting of craze tips and homogeneous deformation zones have also been observed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyphenylquinoxaline; Entanglement; Deformation mechanism

1. Introduction

The deformation mechanism of amorphous polymers mainly involves crazing and shear yielding [1–4]. The crazing process of polymers can be recognized by that (1) crazes are usually initiated in the zone of chain segments weakly bonded and loosely packed and with structure defects under a dilatational stress field and (2) craze growth gives rise to strain-softening of the craze/bulk interface and strain-hardening of craze fibrils. Shear yielding is the flow of the molecular chains along the tensile direction or the slipping of the inter-molecular chains. During the process of shear yielding, the volume of polymer does not change. The deformation mechanism of polymers is determined not only by strain rate and temperature, but also by the polymer's intrinsic properties, such as critical entanglement molecular weight, entanglement density and chain stiffness [5].

Polyphenylquinoxaline (PPQ-E) is an aromatic heterocyclic polymer with high performance. Its glass transition temperature is 298°C. The chemical structure of PPQ-E is shown in Fig. 1. It is mainly used to coat wire for submerged electric motors. It will form PPQ-E-metallic complexes with high catalytic activity and be transformed into conductor. It may be used as pervaporation and UF membranes, and highly sensitive element in capacitance transducers for measuring liquid surface under high temperatures and pressures [6]. However, only few studies on its deformation mechanism have been reported. In addition, the entanglement density of the polymer is estimated by plateau modulus from dynamic rheological analysis other than dynamic mechanical analysis. In the present paper, entanglement density of PPQ-E was estimated from the plateau modulus on dynamic mechanical property and was used to predict its deformation mechanism. The morphology of PPQ-E during stretching was observed with polarized light microscope (PLM), while the craze morphology of PPQ-E was observed by means of transmission electron microscope (TEM).

2. Experimental

2.1. Material and specimen preparation

PPQ-E was synthesized in the laboratory of Fengcai Lu and was cast into a film of 0.05 mm thick. Rectangular specimens with the experimental area of 15 mm long and 2.0 mm wide were cut from the film.

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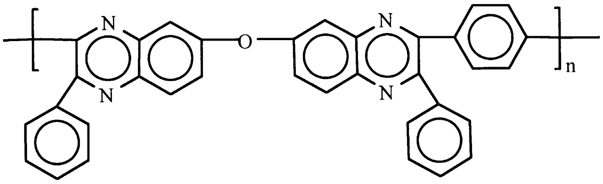

Fig. 1. Chemical structure of PPQ-E.

2.2. Morphology observation during stretching

The morphology of PPQ-E film during tensile deformation with a strain rate of 0.2% min^{-1} was observed with a BH-2 PLM polarized light microscopy.

2.3. Dynamic mechanical property analysis

The dynamic mechanical properties were measured with a Scientific IV Mode DMTA. Master curves were plotted according to the principle of time–temperature superimposing technique.

2.4. TEM observation of craze morphology

Thin film specimens of PPQ-E (~0.8 μm) suitable for TEM observation were prepared according to the method reported in literature [3]. The craze morphology was observed by the use of a TEM, H-800 TEM.

3. Results and discussion

Entanglement is an important feature of polymers, which is one of the key factors controlling rheological, viscoelastic, solid mechanical and adhesive properties of polymers. The entanglement junctions confine the motion of chain molecules during deformation under applied stress as transient 'cross-link' points. Donald and Kramer [7] believed that the deformation of polymers had very strong correlation with entanglement density. For polymers with low chain entanglement density, the deformation mechanism is mainly crazing due to the fact that if the molecular weights between entanglement junctions are large, the maximum extension ratio of chains will be large too. On the other hand, for polymers with high entanglement density, the deformation mechanism is mainly shear yielding. For polymer with middle entanglement density, both crazing and shear yielding may be the case. Wu [8] considers that chain density as an important parameter of polymer is a primary factor, which decides the intrinsic brittleness and toughness. The brittleness/toughness of a

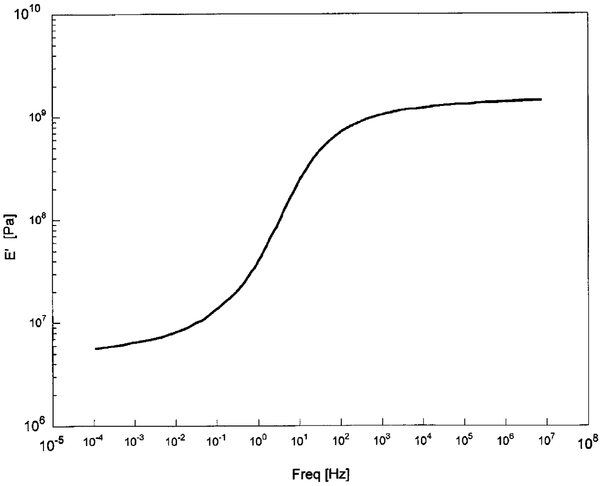

Fig. 2. Master curve of dynamic mechanical property of PPQ-E at 315°C.

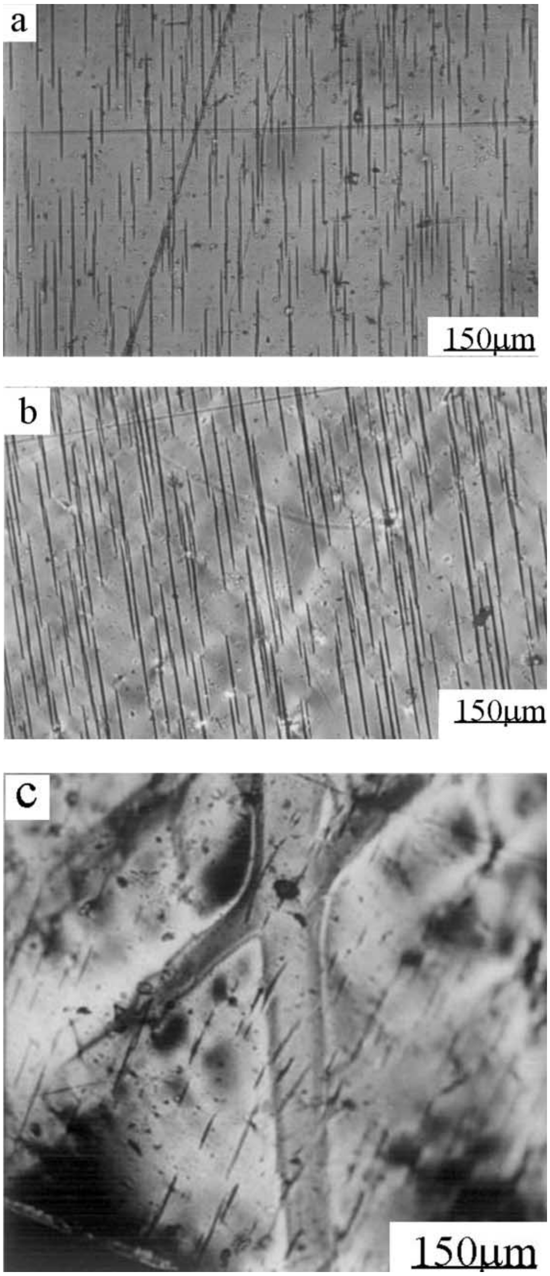

Fig. 3. PLM micrographs of PPQ-E films during stretching: (a) crazing; (b) micro-shear bands; (c) shear bands. σ and arrow represent the tensile load and its direction, respectively.

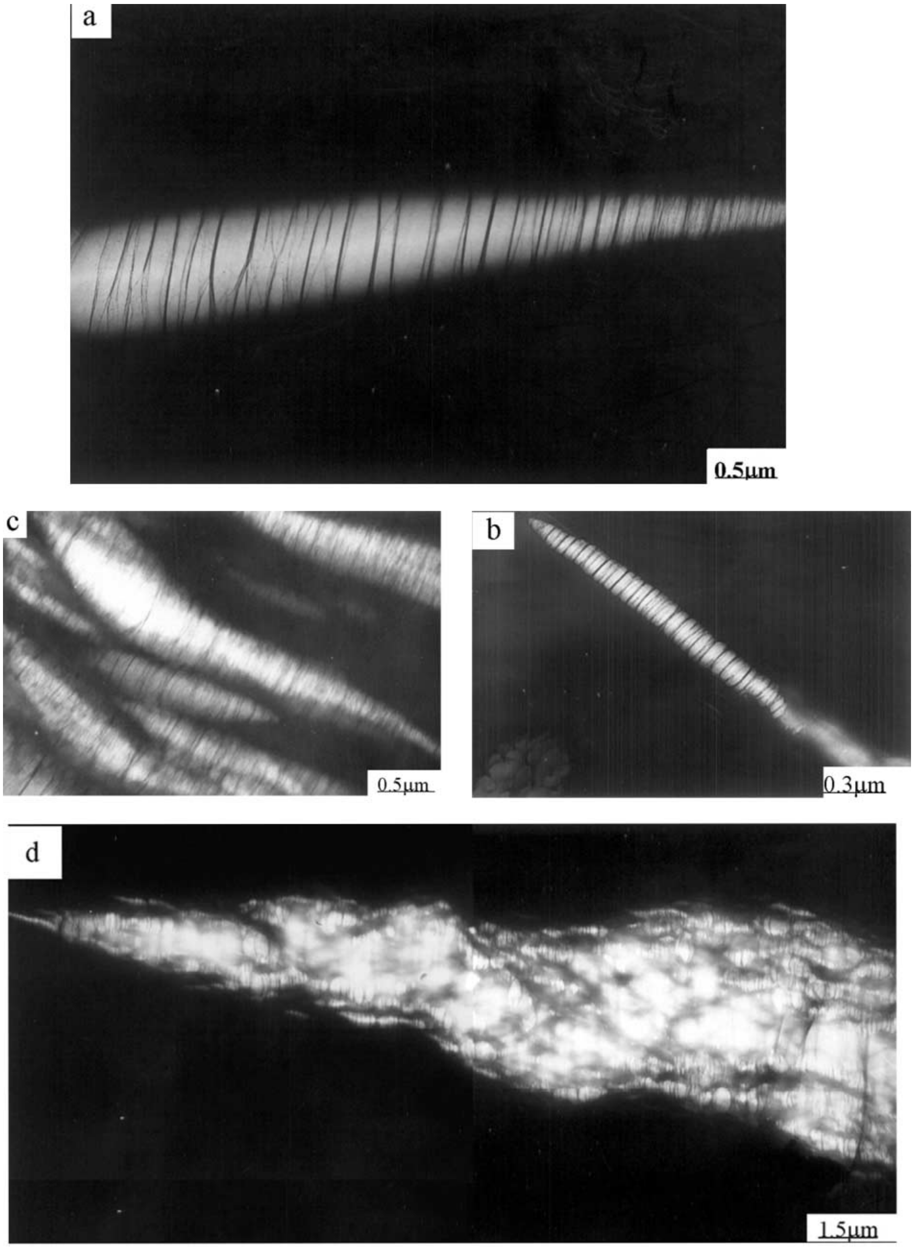

Fig. 4. Craze morphology of PPQ-E thin films: (a) fibril craze; (b) blunting in the tip of craze; (c) multiple crazing; (d) homogeneous deformation zone.

polymer is controlled by crazing/shear yielding, respectively. Generally, the entanglement density of a polymer will determine its plateau modulus. The plateau modulus is obtained by dynamic rheological analysis [9]. Here, the plateau modulus is determined by dynamic mechanical properties. The master curve of dynamic mechanical properties of PPQ-E at 315°C is shown in Fig. 2. It exhibits that the plateau modulus of PPQ-E is 5.88 MPa (E') in the tensile mode. The relation between shear modulus (G') and tensile modulus (E') is

$$E' = 3G' \tag{1}$$

and the plateau modulus of PPQ-E for shear mode is 1.96 MPa. The entanglement density is calculated according to Eq. (2)

$$V_e = \frac{N_A G_0^n}{RT} \tag{2}$$

where V_e is the chain entanglement density, N_a the Avogadro constant, R the gas constant and G_0^n the plateau modulus of the melt at temperature T. The V_e value of PPQ-E is $2.4 \times 10^{26}\ \mathrm{m}^{-3}$ or $0.400\ \mathrm{mmol\ cm}^{-3}$. It is in the intermediate zone between crazing and shear yielding. Therefore, the deformation mechanism of PPQ-E may be crazing or shear yielding, or both crazing and shear yielding.

During in situ observation of stretching PPQ-E film under applied stress, at 3% strain, a few crazes perpendicular to tensile direction was observed in the stress concentration zone such as the tip of a sample and the surface scrape. With further stretching, at 5% strain, lots of crazes were observed as shown in Fig. 3a. Then, the growth of micro-shear bands at the tip of craze developed at 9% strain (see Fig. 3b). This is a typical example of craze terminated by micro-shear band. This may be the reason that, why PPQ-E exhibits better toughness. Subsequently, when the strain approached 10%, shear deformation band developed, as shown in Fig. 3c. The angle between it and tensile direction is about 45°. The direction of craze inside shear band had changed and it was derived from shear flow of a part of molecular chain under tensile stress. Finally, fracture of the material occurred at strain of 20%. The above results indicate that the deformation of PPQ-E is extensive and competitive between crazing and shear yielding. This is in accordance with the deformation mechanism predicted by entanglement density.

By TEM observation, the craze morphology of PPQ-E is typical fibril craze consisting of fibrils and micro-voids as shown in Fig. 4a. Actually, the morphology of a crazed material consists of two phases. The continuous phase is fibril and the disperse phase is micro-voids. Thus, the material will absorb more energy during deformation. The interface between bulk and craze is obvious. The craze fibrils array along the direction of applied stress. Craze fibril at mid-rib is the slimmest, i.e. fibril has maximum extension ratio along mid-rib. The ahead tip of developed craze is blunted by homogeneous deformation zone, as shown in Fig. 4b. Multiple craze is also observed, as shown in Fig. 4c. The two kinds of deformation together create better ductility for PPQ-E. Homogenous deformation zone (HDZ) is also observed. Meanwhile, small fibril crazes that appear inside the HDZ are shown in Fig. 4d. Those results indicate that crazing is the dominant deformation mechanism in thin film of PPQ-E, while HDZ is competitive with craze in thin films. This is a reflection of correlation between entanglement density and micro-deformation mechanism. Further discussion about this will be given in another paper.

4. Conclusion

The entanglement density of PPQ-E may be estimated by its dynamic mechanical properties. The deformation mechanism of PPQ-E is both crazing and shear yielding on the basis of theoretical prediction of entanglement density and PLM observation during stretching. The craze morphology is a typical example of fibril craze, while HDZ coexists with fibril craze. Simultaneously, multiply crazing and shear blunting at tip of craze are also observed.

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