

Tensile Mechanical Properties of PEEK Films Over a Wide Range of Strain Rates. II

N. D. ALBÉROLA, P. MÉLÉ, C. BAS

Laboratoire Matériaux Polymères et Composites, Université de Savoie, Campus Scientifique, Bâtiment IUT, F-73376 Le Bourget-du-Lac Cedex, France

Received 19 June 1996; accepted 18 September 1996

ABSTRACT: Tensile mechanical properties of poly(aryl ether ether ketone) (PEEK) films showing different thermal histories have been investigated at room temperature to point out the main key microstructural features governing properties over a wide strain rate range, i.e., from 10^{-5} to 300 s^{-1} . The strain rate sensitivity of the mechanical properties of amorphous PEEK films significantly depends on the analyzed strain rate range: i.e., 1) from 10^{-5} to 10 s^{-1} , the strain rate dependence of both apparent Young's modulus and yield stress is weak; and 2) from 10^{-1} to 200 s^{-1} , both parameters significantly increase. Thus, based on the definition of the relationships between temperature, strain rate, and frequency respectively used for tensile tests and dynamic mechanical spectrometry, it was shown that the mechanical behavior of PEEK films at room temperature could be governed by similar molecular mechanisms as those giving rise to the β_1 and β_2 transitions. The Eyring analysis shows that motions of five or six monomers are implied at the beginning of the plastic deformation of amorphous and semicrystalline PEEK films, while at higher strain rates, shorter chain segments are concerned. Thus, the crystalline phase only induces an increase in the stress level because of the reinforcement effect but does not modify the molecular mechanisms governing the plastic deformation of PEEK films at room temperature. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1053–1059, 1997

Key words: poly(aryl ether ether ketone) (PEEK); dynamic mechanical relaxation; mechanical behavior

INTRODUCTION

Few works deal with the tensile mechanical behavior of amorphous PEEK. Cebe et al.¹ have shown that amorphous PEEK films drawn at low strain rates, i.e., 0.5 s^{-1} , exhibit a high drawability even at low temperatures. Thus, strain at break of amorphous PEEK tested at 25°C is about 270% and it is not significantly decreased at an experimental temperature of -100°C .

Furthermore, Kemmish and Hay² have shown an increase in both the yield stress and stress at

break of amorphous PEEK aged at temperatures below T_g . Moreover, these authors have found a significant decrease in the fracture toughness of such aged samples with an increase in the aging keeping time.

Other amorphous polymers also show changes in the tensile mechanical behavior with an increase in the experimental temperature and the strain rate. The origin of such a transition in the mechanical properties has been attributed to the presence of various relaxational processes.^{3–6}

The influence of the reinforcement effect of the crystalline phase on the mechanical properties of semicrystalline PEEK was also analyzed.^{7–10} Thus, Cebe et al.⁹ have shown that the crystallinity ratio is not the only parameter governing the

Correspondence to: N. D. Albérola.

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/061053-07

mechanical behavior of such polymers. Thus, PEEK samples having the same crystallinity ratio but having undergone various thermal treatments exhibit different mechanical properties.

According to Chu and Schultz,¹¹ the fracture toughness of PEEK decreases with an increase in the size of spherulites. Furthermore, it was found that the tensile behavior of semicrystalline PEEK depends not only on the original morphology but also on both test temperature and strain rate.^{1,12-19} With a decrease in the experimental temperature, semicrystalline PEEK tested at low strain rates becomes more brittle. Then, samples annealed at 180°C for one hour and tested at -100 and +25°C show strains at break at about 70 and 240%, respectively.

According to Beguelin et al.,¹² the yield stress and the stress at break of semicrystalline PEEK both increase with an increase in the strain rate from $3 \cdot 10^{-2}$ to 300 s^{-1} . In this analyzed strain rate range, no significant change in the strain rate sensitivity of the Young's modulus can be observed by these authors.

Jones et al.¹⁵ have shown a drastic transition from ductile to brittle behavior at about -15°C for semicrystalline PEEK tested at 5 m/s. According to Medellin-Rodriguez and Phillips,²⁰ such a transition could be related to the subglass relaxation shown by PEEK. Karger-Kocsis and Friedrich¹⁴ have also shown such a drastic transition at 115°C for semicrystalline PEEK drawn at 10^{+3} mm/min . According to these authors, this transition could be related to both the glass transition of PEEK and the heat generation within the sample, leading to an adiabatic drawing.

Such two kinds of mechanical behavior have been also observed for other semicrystalline polymers, in particular, for isotactic polypropylene.²¹⁻²⁴ According to Rolando et al.,^{21,22} the drastic transition could result from the decrease in the length of time necessary to adjust and absorb the applied load on increasing the strain rate. Then, the two types of tensile behavior could result from two kinds of mechanical relaxational processes. For Jang et al.,²³ this could result from the two kinds of deformation mode. Thus, at high deformation rates or at low temperatures, crazing in the crystalline phase is favored; while at low deformation rates or at high temperatures, shear yielding predominates. According to such an interpretation, it is of interest to report microscopic observations of deformation modes in semicrystalline PEEK performed by Plummer and Kausch.¹³ It was found that semicrystalline PEEK drawn at $2 \cdot 10^{-2} \text{ s}^{-1}$ at room

temperature exhibits a bimodal deformation mode. With an increase in the experimental temperature, shear yielding predominates; and at temperatures higher than T_g , no crazing was observed.

Based on the microstructure analysis reported in Part I of this article,²⁵ the aim of this work is to obtain evidence for the main microstructural parameters that govern the elastic and plastic behaviors of amorphous and semicrystalline PEEK films at room temperature and over a wide strain rate range, i.e., from $5 \cdot 10^{-5}$ to $3 \cdot 10^{+2} \text{ s}^{-1}$.

EXPERIMENTAL

Materials

Sheets of amorphous PEEK films with thickness of 100 and 250 μm were provided by ICI Company. The average molecular weight and polydispersity index determined by the Laboratoire des Hauts Polymères (Université Catholique de Louvain-la-Neuve, Belgium)²⁵ are $\overline{M}_w = 38,000 \text{ g/mol}$ and $I_p = 2.2$, respectively.

As described in Part I of this article, as-received films were dried at 145°C for six hours under vacuum. Then, to erase the previous thermal history and to give the same isoconfigurational state at each sample, specimens were heated for 10 min at a temperature higher than the glass transition temperature and then quenched at room temperature.

Semicrystalline PEEK samples were obtained by annealing as-received films at different temperatures, i.e., 200, 250, and 320°C for various keeping times.

The amorphous PEEK film is designed as Q, and the annealed samples as A, followed by the annealing temperature. The microstructure of amorphous and semicrystalline samples was discussed in Part I of this article. Table I lists the various annealing treatments undergone by the samples and the corresponding weight crystallinity ratios issue from wide angle diffraction analysis (see Part I).²⁵

Tensile test measurements were carried out on dog-bone-shaped specimens (5 mm wide and 33 mm long in the gauge section).

Uniaxial Tensile Tests at Low Strain Rates

Uniaxial tensile tests at low strain rates were performed at room temperature in an Adamel Lho-

Table I Nomenclature, Annealing Conditions, and Weight Crystallinity Ratio

Sample	Annealing Conditions	Weight Crystallinity Ratio (%)
Q	Dry and freshly quenched sample	0
A200	Sample Q annealed for 1 h at 200°C, then quenched	24
A250	Sample A200 annealed for 1 h at 250°C, then quenched	28
A320	Sample Q annealed for 30 min at 320°C, then quenched	33

margy testing machine. Five replicates were run at each strain rate. The reported data are the average values. Measurements were made at various crosshead speeds ranging from 0.1 to 900 mm/min. Because the gauge length is 33 mm, these crosshead speeds imply strain rates from $5 \cdot 10^{-5}$ to $5 \cdot 10^{-1} \text{ s}^{-1}$. The load-elongation curves were converted into engineering stress-strain plots by dividing the measured load of the sample by the initial cross-sectional area of the sample and the elongation by the original gauge length.

For each strain rate, the following parameters are determined: the apparent Young's modulus E ; the engineering yield stress σ_y ; and yield strain ϵ_y . The apparent Young's modulus E was calculated from the initial slope of the stress-strain plot.

Uniaxial Tests at High Strain Rates

Tensile experiments at high strain rates ranging from 10 to 200 s^{-1} were carried out at room temperature by means of a new tensile VHS 56 servo-hydraulic machine purchased from Schenck Company.

Special grips were developed for testing polymer films. The dog-bone-shaped sample was gripped to a piston rod, which is displaced at a velocity from 0.1 to 20 $\text{m} \cdot \text{s}^{-1}$. The position of the piston and then the displacement of the sample versus time can be assessed by both the usual transducer and an optical extensometer. The load was measured versus time by means of a piezoelectric crystal ring of 250N in the fixture assembly and placed on the fixed end of the specimen. For each strain rate, such an instrument provides

the evolution of both load and specimen displacement versus time. Such curves are converted into usual engineering stress-strain plots according to the method described above. For each measurement, apparent Young's modulus E , engineering yield stress, σ_y and yield strain ϵ_y were determined.

RESULTS AND DISCUSSION

Amorphous PEEK Films

Figure 1 shows the engineering stress-strain curves of amorphous PEEK films, recorded at various strain rates, i.e., $5 \cdot 10^{-5}$, 0.5, and 230 s^{-1} .

In the analyzed strain rate range, the amorphous PEEK film exhibits a ductile mechanical behavior, whatever the strain rate is. Stress-strain curves exhibit a yield point, followed by a drop in stress before necking occurs. For samples drawn at strain rates lower than 1 s^{-1} , hardening becomes noticeable at about 120–140% engineering strain. With increasing the strain rate, it can be noted that yield stress and stress at break both increase, while strain at break decreases.

Figure 2 shows the evolution of the apparent Young's modulus with the logarithm of the engineering strain rate for the amorphous PEEK films. For strain rates lower than 1 s^{-1} , the apparent Young's modulus is almost constant; while for strain rates higher than 1 s^{-1} , it tends to markedly increase.

Moreover, it can be noted that the apparent moduli of the sample at low and high strain rates

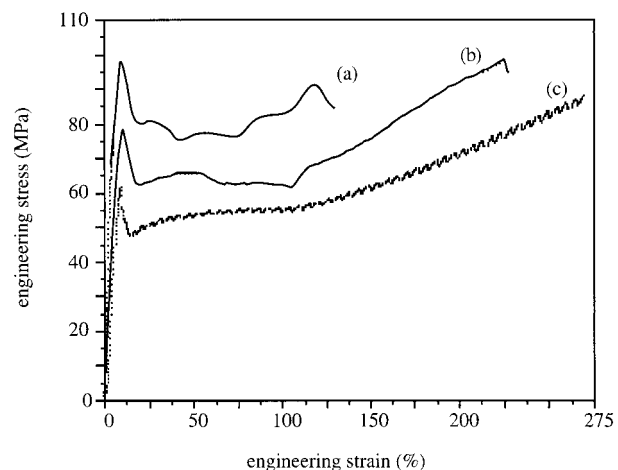


Figure 1 Engineering stress-strain curves of amorphous PEEK drawn at (a) 230 s^{-1} , (b) 0.5 s^{-1} , and (c) $5 \cdot 10^{-5} \text{ s}^{-1}$.

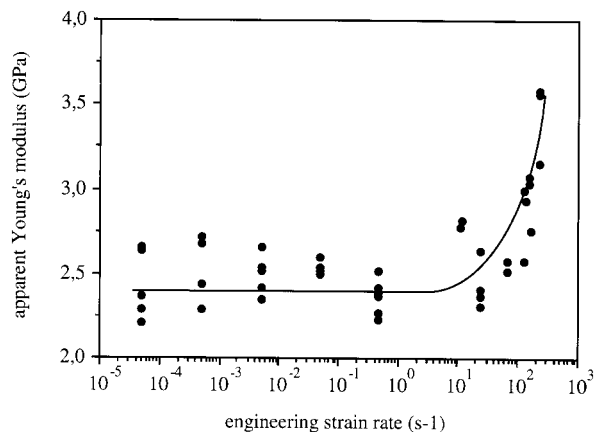


Figure 2 Evolution of the apparent Young's modulus with the logarithm of the engineering strain rate for the amorphous PEEK.

and at room temperature are of the same order of magnitude as those measured at 1 Hz at temperatures higher and lower than the β transitions, respectively (Fig. 3). Thus, a sample drawn at a high strain rate and at room temperature could exhibit similar elastic properties as those displayed by a sample tested at low temperature, i.e., lower than -80°C , at 1 Hz. To correlate the dynamic mechanical modulus of the PEEK film with its tensile deformation behavior, it is useful to find the relationship between frequency and strain rate, respectively, used for dynamic mechanical measurements and tensile tests.²⁵ Obviously, the strain rates of the two kinds of tests are comparable in the initial region, i.e., for very small strains. To a first approximation, the strain rate in a tensile mode equivalent to such a frequency can be determined by the slope of the straight line joining the origin and the maximum

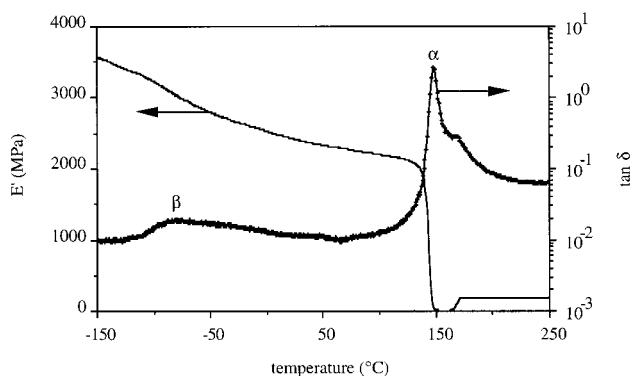


Figure 3 Dynamic mechanical spectrum of amorphous PEEK film (1 Hz).

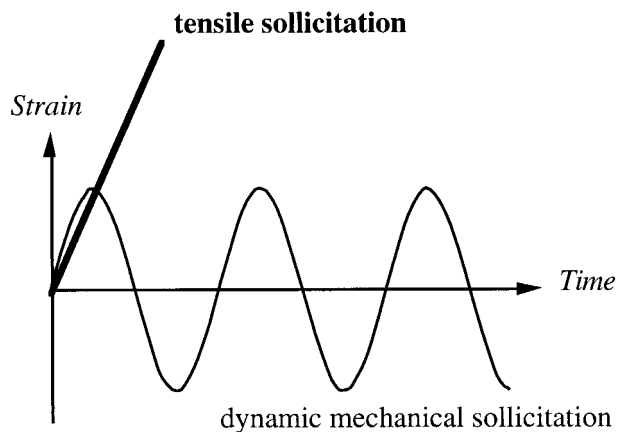


Figure 4 Equivalence between strain rate in tensile experiments and frequency in dynamic mechanical spectrometry.

of the strain²⁶ (Fig. 4). Thus, as the peak-to-peak amplitude is about $16\ \mu\text{m}$, an imposed frequency of 1 Hz corresponds to a strain rate in tensile mode of about $3.2 \cdot 10^{-3}\ \text{s}^{-1}$. Then, according to such a strain rate-frequency equivalence, a sample drawn in tensile mode at about $200\ \text{s}^{-1}$ at room temperature should exhibit similar micro-mechanical properties as those shown by the sample analyzed at 60,000 Hz at room temperature by dynamic measurements. Such a conclusion is in agreement with dielectric measurements²⁷ carried out on such a polymer, which give evidence for the location of β spectrum at about room temperature for such a frequency.

Accordingly, because both such an equivalence between strain rate and frequency and the frequency-temperature superimposition principle, the increase in the apparent Young's modulus shown by amorphous PEEK tested at high strain rates and at room temperature can be interpreted through the shift of the β spectrum towards the room temperature.

Figure 5 shows the evolution of the yield stress with the logarithm of the strain rate for the amorphous PEEK film. At low strain rates, i.e., lower than $1\ \text{s}^{-1}$, σ_y obeys a linear function of the logarithm of strain rate. It is expressed by

$$\sigma_y = 80 + 1.9 \cdot \ln(\dot{\epsilon}) \quad \text{for } \dot{\epsilon} < 1\ \text{s}^{-1}$$

At the higher deformation rates, the strain rate sensitivity of σ_y is increased and can be expressed by

$$\sigma_y = 83 + 3.7 \cdot \ln(\dot{\epsilon}) \quad \text{for } \dot{\epsilon} > 1\ \text{s}^{-1}$$

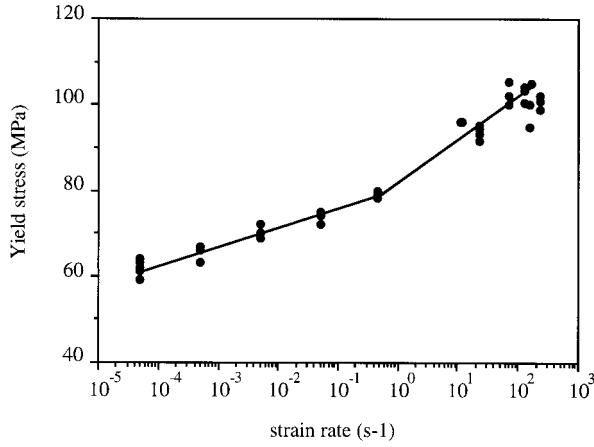


Figure 5 Plots of the engineering yield stress versus the logarithm of the engineering strain rate for the amorphous PEEK.

Then, it is of interest to correlate the different strain rate sensitivities of the beginning of the plastic deformation to the microstructure of the polymer. To a first approximation, this can be carried out by the Eyring equation, as follows²⁸:

$$\frac{\sigma}{T} = \frac{R}{V} \left\{ \frac{\Delta H}{RT} + \ln \left(\frac{2\dot{\epsilon}}{\dot{\epsilon}_0} \right) \right\}$$

where V is the apparent volume activation, T is the absolute temperature, ΔH is the activation energy, and $\dot{\epsilon}_0$ is the preexponential factor.

Table II reports the values of the activation volumes and the corresponding numbers of monomers of PEEK implied in the beginning of the plastic deformation of PEEK for the two analyzed strain rate ranges, i.e., from 10^{-5} to 1 s^{-1} and from 1 to 200 s^{-1} , respectively. Thus, at low strain rates (and at room temperature), the molecular process of the plastic deformation of PEEK is governed by molecular motions of chain segments composed by five or six monomer units. Such molecular motions could give rise to the β_2 relaxation, the highest temperature component of the PEEK β spectrum. At high strain rates (and at

Table II Values of the Characteristic Parameters Issued from the Eyring Analysis

Strain Rate Range (s^{-1})	PEEK	
	V (\AA^3)	Monomers Units
$1.10^{-5} < \dot{\epsilon} (\text{s}^{-1}) < 1.10^{+0}$	2100	5–6
$1.10^{+0} < \dot{\epsilon} (\text{s}^{-1}) < 2.10^{+2}$	1000	2–3

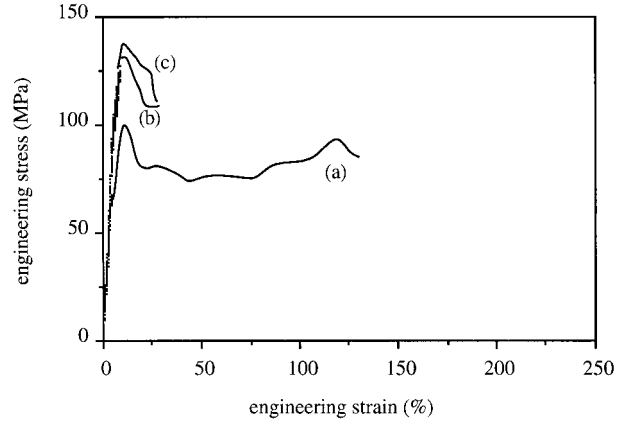


Figure 6 Engineering stress-strain curves of PEEK samples drawn at $5 \cdot 10^{-3} \text{ s}^{-1}$: (a) amorphous, (b) A200, and (c) A320 films.

room temperature), mechanical behavior of PEEK could affect molecular motions of shorter segments, i.e., two or three monomer units. Such local motions could give rise to the β_1 relaxation, the lowest temperature component of the PEEK β spectrum. Accordingly, we could suggest that the two kinds of mechanical behavior exhibited by PEEK at room temperature in the analyzed strain rate range could be governed by the bimodal character of the β spectrum.

Semicrystalline PEEK Films

Figures 6 and 7 show the engineering stress-strain curves recorded for semicrystalline PEEK films annealed at 200, 250, and 320°C drawn at two strain rates, i.e., $5 \cdot 10^{-3}$ and about $2 \cdot 10^{+2} \text{ s}^{-1}$. For com-

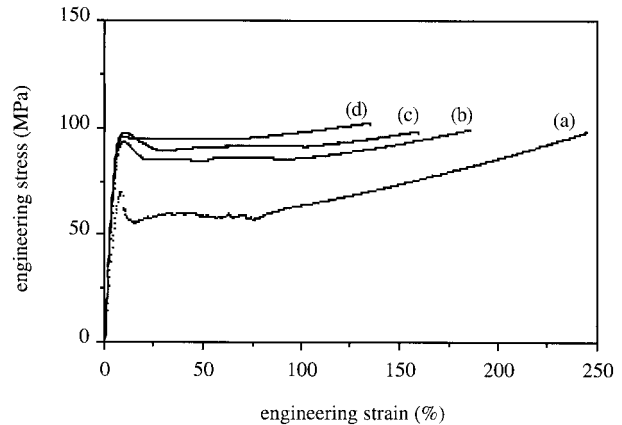


Figure 7 Engineering stress-strain curves of PEEK samples drawn at $2 \cdot 10^{+2} \text{ s}^{-1}$: (a) Q, (b) A200, (c) A250, and (d) A320 films.

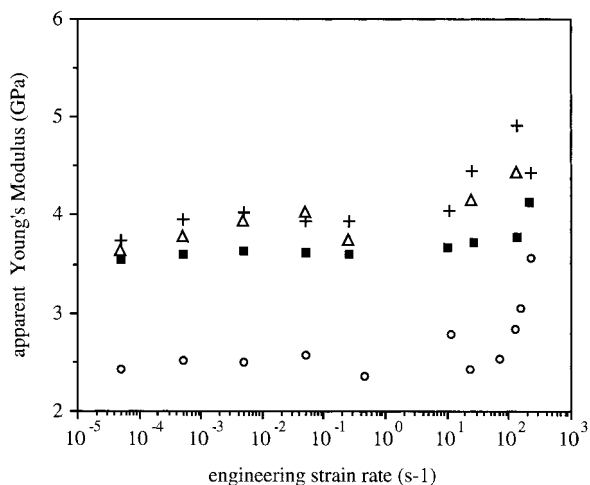


Figure 8 Evolution of the apparent Young's modulus with the logarithm of the engineering strain rate for the amorphous and semicrystalline samples: Q (\circ), A200 (\blacksquare), A250 (\triangle), and A320 ($+$) films.

parison, curves obtained for the as-received amorphous PEEK are superimposed.

At low strain rates, samples exhibit a ductile behavior, whatever the thermal history can be. With an increase in the annealing temperature, the following features can be noted: 1) the overall stress level increases; in particular, the yield stress and the engineering stress at break; and 2) the engineering strain at break decreases.

At high strain rates, i.e., for strain rates upper than 10 s^{-1} , semicrystalline films become more brittle; but shear yielding remains predominant.

Figures 8 and 9 show the evolution of the apparent Young's modulus and engineering yield stress, respectively, with the logarithm of the engineering strain rate for semicrystalline films. Data issue from the analysis of the amorphous film are given as references.

Whatever the strain rate, the apparent Young's modulus and the engineering yield stress of semicrystalline films are respectively higher than those measured for the amorphous PEEK film. Thus, for a given strain rate, the values of these parameters increase with increasing the crystallinity ratio (see Part I).²⁵ Furthermore, both the apparent Young's modulus and the yield stress of semicrystalline film exhibit similar evolution with the strain rate as was observed for the amorphous sample. As a matter of fact, with increasing strain rate, semicrystalline films exhibit two kinds of mechanical behavior. Such a result apparently disagrees with the data of Beguelin et al.,¹² who have detected only one kind

of mechanical behavior of the semicrystalline PEEK. But we can recall that the strain rate analyzed by these authors is narrower than that of reported in this work, i.e., 10^{-3} to 300 s^{-1} in the work of Beguelin et al. and 10^{-5} to 300 s^{-1} in this article. Then, from the data of Beguelin et al., it is difficult to conclude to a bimodal character of the mechanical behavior of PEEK.

The Eyring analysis shows that activation volumes implied in the plastic deformation of semicrystalline PEEK are of the same order of magnitude as those calculated for amorphous PEEK films (Table II). Accordingly, it can be concluded that the crystalline phase does not modify either the molecular mechanisms or the length of backbone chains segments involved in the mechanical behavior. This phase only induces a reinforcement effect of the amorphous phase. In other terms, it seems that the beginning of the plastic deformation of PEEK at room temperature is unaffected by changes in the molecular motions of large segments of backbone chains, i.e., motions implied in the α relaxation, induced by the physical crosslinking of the amorphous phase by crystalline entities. Such a conclusion also supports the idea that the yield stress of semicrystalline PEEK films at room temperature is actually controlled by local molecular motions and then by the β relaxations. Moreover, according to both the microstructural (see Part I) and tensile properties analysis, it can be suggested that the eventual changes in the chain conformations and/or the magnitude of interactions between chains in-

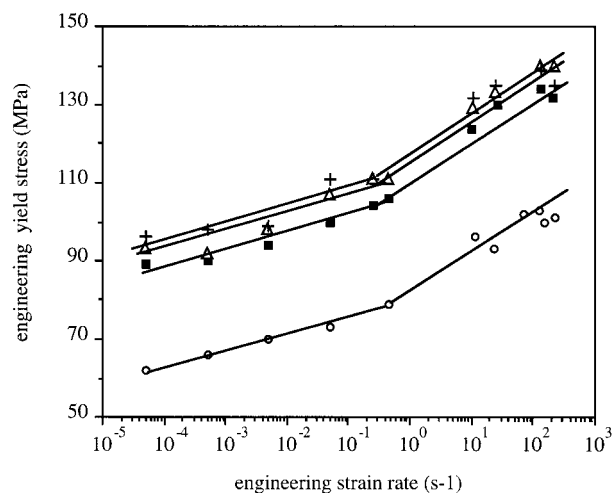


Figure 9 Plots of the engineering yield stress with the logarithm of the engineering strain rate for the amorphous and semicrystalline samples: Q (\circ), A200 (\blacksquare), A250 (\triangle), and A320 ($+$).

duced by the crystalline phase could not affect the molecular mechanisms implied at the beginning of the plastic deformation.

Furthermore, to interpret the changes in drawability induced by the annealing treatments, we must consider now, in addition, the degree of perfection of the crystalline entities. As a matter of fact, the overall drawability of such semicrystalline films assumed to be composite materials is governed not only by the mechanical properties of the amorphous phase but also by the plastic deformation ability of the crystalline phase, which is controlled by the crystal defect concentration. Then, the decrease in the engineering strain at break of PEEK films with an increase in the annealing temperature could result from an increase in the perfection degree of the crystalline phase. Such an interpretation was also proposed to explain the changes in the drawability of polypropylene films induced by thermal treatments.²⁴

CONCLUSIONS

The tensile mechanical behavior of amorphous and semicrystalline PEEK films was investigated at room temperature over a wide strain rate range, i.e., from $5 \cdot 10^{-5}$ to 300 s^{-1} . With an increase in strain rate, both amorphous and semicrystalline exhibit two kinds of mechanical behavior that can be related to the bimodal character of the β spectrum through the determination of the relationship between frequency of dynamic mechanical measurements and strain rate of tensile test. According to the Eyring analysis, the activation volumes implied at the beginning of the plastic deformation were determined for amorphous and semicrystalline PEEK films. Thus, at low strain rates, i.e., from $5 \cdot 10^{-5}$ to 10 s^{-1} , the beginning of the plastic deformation of both amorphous and semicrystalline PEEK films implies the motions of five or six monomer units; while at higher strain rates, shorter chain segments constituted of about two or three monomers are affected. Thus, the crystalline phase does not modify the length of the segments involved in the deformation. The ultimate properties of semicrystalline PEEK films are found to be controlled not only by both the microstructural parameters governing the mechanical behavior of the amorphous phase and the crystallinity ratio but also by the perfection degree of the crystalline phase, which increases with higher annealing temperature.

REFERENCES

1. P. Cebe, S. Y. Chung, and S. D. Hong, *J. Appl. Polym. Sci.*, **33**, 487 (1987).
2. D. J. Kemmish and J. N. Hay, *Polymer*, **26**, 905 (1985).
3. J. A. Roetling, *Polymer*, **6**, 311 (1965).
4. F. Riesch and B. Bouette, *Eur. Polym. J.*, **26**, 1071 (1990).
5. P. Zitek and J. Zelinger, *J. Appl. Polym. Sci.*, **14**, 1243 (1970).
6. D. Melot, B. Escaig, J. M. Lefebvre, R. P. Eustache, and F. Laupretre, *J. Polym. Sci., Part B, Polym. Phys.*, **32**, 1805–1811 (1994).
7. R. A. Chivers and D. R. Moore, *Polymer*, **35**, 110 (1994).
8. J. M. Barton, J. R. Lloyd, A. A. Goodwin, and J. N. Hay, *Brit. Polym. J.*, **23**, 101 (1990).
9. P. Cebe, S. D. Hong, S. Chung, and A. Gupta, *Thoughened Composites, ASTM STP 937*, 1987, p. 342.
10. A. Arzak, J. I. Eguiazabal, and J. Nazabal, *Polym. Eng. Sci.*, **31**, 586 (1991).
11. J. N. Chu and J. M. Schultz, *J. Mat. Sci.*, **24**, 4538 (1989).
12. Ph. Beguelin, M. Barbezat, and H. H. Kausch, *J. Phys. III Fr.*, **1**, 1867 (1991).
13. C. J. G. Plummer and H. H. Kausch, *Polymer*, **34**, 305 (1993).
14. J. Karger-Kocsis and K. Friedrich, *Polymer*, **27**, 1753 (1986).
15. D. P. Jones, D. C. Leach, and D. R. Moore, *Polymer*, **26**, 1385 (1985).
16. P. C. Dawson, G. M. Swallowe, and Z. Xinwu, *J. Phys. IV (C3)*, **1**, 701 (1991).
17. S. C. Chou, K. D. Robertson, and J. H. Rainey, *Experimental Mechanics*, 1973, p. 422.
18. A. Marquez-Lucero, C. G'Sell, and K. W. Neale, *Polymer*, **30**, 636 (1989).
19. S. Wu, *J. Appl. Polym. Sci.*, **46**, 619 (1992).
20. F. J. Medellin-Rodriguez and P. J. Phillips, *Polym. Eng. Sci.*, **30**, 860 (1990).
21. R. J. Rolando, W. L. Krueger, and H. W. Morris, *Plast. Rub. Proc. Appl.*, **10**, 245 (1988).
22. R. J. Rolando, W. L. Krueger, and H. W. Morris, *Plast. Rub. Proc. Appl.*, **11**, 135 (1989).
23. B. Z. Jang, D. R. Uhlmann, and J. B. Vander Sande, *Polym. Eng. Sci.*, **25**, 98 (1985).
24. N. Alberola, M. Fugier, D. Petit, and B. Fillon, *J. Mat. Sci.*, **30**, 860 (1995).
25. C. Bas, M. Fugier, and N. D. Alberola, *J. Appl. Polym. Sci.*, to appear.
26. C. Xiao, J. Y. Jho, and A. F. Yee, *Macromolecules*, **27**, 2761 (1994).
27. A. Jonas and R. Legras, *Macromolecules*, **26**, 813 (1993).
28. I. M. Ward, *Mechanical Properties of Solid Polymers*, 2nd Ed., Wiley, New York, 1983.