Deformation of PS, PPE, and Their Alloys During Reversed Tension–Compression for Study on Fatigue Behavior

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ABSTRACT: Fatigue tests in reversed tension–compression were carried out on the sample of polystyrene (PS), poly(oxy-2,6-dimethyl-1,4-phenylene [poly(phenylene ether) (PPE)], and their alloys. The dynamic loss modulus, storage modulus, tan δ, and surface temperature of the specimens were continuously measured by a viscoelastometer during the fatigue tests. Fatigue lives and analysis of the samples by electron microscopy were also measured. The mechanical work, heat generated, and percent of work that appears as heat (PWAH) were calculated by the equations derived by viscoelastic equations and heat transfer. PWAH was in the range from 40 to 65%. The fatigue lives and PWAH were longer and larger for PPE and PPE-rich alloys than for PS and PS-rich alloys, respectively. The cleavage energy of the polymer chain calculated from the decrease of molecular weight before and after the fatigue test were much smaller compared to the total mechanical work. The entanglement densities observed before and after the test were the same. The majority of the work due to structural deformation is thought to be consumed by formation of striation and microscopically irreversible deformation. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 2279–2286, 1997

Key words: fatigue; dynamic loss modulus; heat generated; mechanical work; striation

INTRODUCTION

There have been many studies on the mechanical properties under various kinds of stress systems and for various modes of fatigue crack propagation. The fatigue behavior of polymer systems is far less well studied than that of metals. The reason is that polymers have not been used as materials which must withstand heavy duty. On the other hand, the use of polymers in durable structural applications has increased substantially in recent years. A better understanding of "aged polymer" and their long-term deformation and failure behavior is therefore required.

The earliest review on fatigue in organic materials was published by Dillon in 1950,[1] wherein an outline of fatigue testing was presented. Plumbridge studied the fatigue of organic materials and metals together in 1972.[2] Manson and Hertzberg reported their studies of fatigue in polymers on the role of molecular structure.[3] Bucknall and Kambour, famous for their studies on the fracture of various polymers, reviewed and discussed the general discussions on deformation behavior and micromechanisms in detail.[4,5] In 1980, Hertzverg and Manson published the book titled *Fatigue of Engineering Plastics* and reviewed the studies on fatigue behavior.[6] In the field of metal fatigue, the study on crack propagation during the fatigue test is the most important, where the crack propagation speed ($\partial a/\partial N$) is measured as a function of the number of loading

cycles. Many polymer fatigue studies follow the above procedure.

Poly(oxy-2,6-dimethyl-1,4-phenylene)[poly-(phenylene ether)(PPE)] and polystyrene (PS) were selected as the experimental materials for the present study for two reasons: First, among the polymeric materials used as engineering plastics, PPE is prominent for its high glass transition temperature (211°C), ductile property, and flame retardancy. Second, as PPE is also known to be perfectly miscible with PS, the contents of PPE in alloys can be continuously changed. PPE/PS alloys play an important role in various commercial applications and they will be the polymers serving as load-bearing materials. Various fatigue data are already available for PPE and PS.[7-9] However, few reports are known where the fatigue of organic materials is discussed as the relation between macroscopic data such as fatigue life to microscopic and molecular deformations, such as the decrease of molecular weight, change of polymer chain configuration, entanglement density, and striation.[10]

The present work investigated the assumptions that (1) the reduction of mechanical strength by fatigue is accompanied by the degradation and other damages in the polymer structure and (2) the structure deformation includes both chemical degradation such as cleavage of the main chain and physical damages such as striation and crack formation. The continuous viscoelastic method[11-13] was applied to analyze the structure deformation, and the total energy during the fatigue test was calculated.

EXPERIMENTAL

Materials

PPE (M_w = 69,800, injection grade) and PS (M_w = 189,000, injection grades commercially available) were provided by Asahi Chemical Industry Co. PPE/PS polymer alloys were prepared by blending in a 30 mm corotating twin-screw extruder (Werner & Pfleiderer) at 110 rpm. Process temperatures were varied from 240 to 260°C depending on the PPE/PS composition. Five sheets of the press-molded polymers were prepared for fatigue tests, then cut into smooth dumbbell-shaped specimens. Before the specimens were used for the fatigue test, they were carefully polished by hand to avoid surface crazing.

Fatigue Test

A servohydraulic testing machine, manufactured by Orientec Corp. (type: vFA-1KNA), was used for loading reversed tension–compression and measuring viscoelastic properties simultaneously. It was conducted with a load control at 10 Hz, appropriate for maintaining a fairly good isothermal condition as well as to shorten the testing time. The storage modulus, loss modulus, and tan δ were continuously measured by a load cell and displacement sensor. The temperature of the specimens was measured by a radiation thermometer and a thermocouple. A block diagram of the fatigue tester is shown in Figure 1.

Tensile Test and Microscope Observation

Tensile specimens were cut from compression-molded sheets and tests were performed on an Instron (Model 1127) in accordance with ASTM D638 using a crosshead speed of 5 cm/min at room temperature. The displacement, which was one of the most important conditions in the fatigue test, was determined by using the results of the tensile tests in order that the specimen was not compressed at any time during the fatigue test. The surface of the specimens after the fatigue test were observed by an ultrasonic microscope (Hitachi Kenki, HSAM-200) and a scanning electron microscope (Topcon SEM 500).

THEORETICAL TREATMENTS AND EXPERIMENTAL DATA ANALYSIS

The work of deformation during the fatigue test is expressed as follows:

$$W_M = \int_0^{2\pi/\omega} \sigma d\gamma = \int_0^{2\pi/\omega} \sigma \frac{d\gamma}{dt} dt \qquad (1)$$

where W_M is the work due to mechanical deformation; σ, the stress; γ, the strain; and ω, the angle velocity. The dynamic stress and strain can be written, using the complex modulus (E^*), dynamic storage modulus (E'), and dynamic loss modulus (E''), as eq. (2):

$$\sigma(t) = E^*\gamma = \gamma_0\{(E' \cos \omega t - E'' \sin \omega t)$$
$$+ i(E' \sin \omega t + E'' \cos \omega t)\} \quad (2)$$

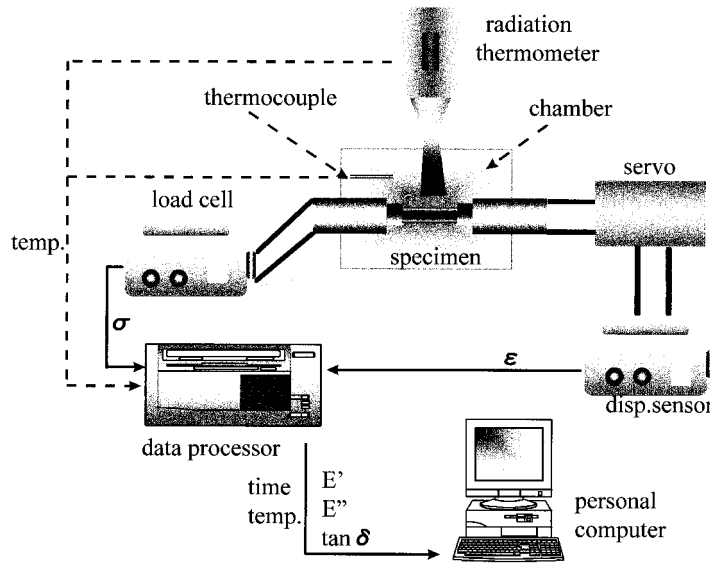where γ_0 is the maximum strain. On the other

Figure 1   Block diagram of fatigue tester.

hand, the displacement of the specimen during the fatigue test was

$$\gamma(t) = \gamma_0 \exp(i\omega t) \tag{3}$$

The work is, therefore, calculated by real parts of eqs. (1)–(3):

$$W_M = -\gamma_0^2 \omega \int_0^{2\pi/\omega} \{E' \cos(\omega t)$$

$$- E'' \sin(\omega t)\} \{\sin(\omega t)\} \, dt \tag{4}$$

The work during a cycle is

$$W_M = \pi\gamma_0^2 E'' \tag{5}$$

The average work during the test is

$$W = \pi\gamma_0^2 f \int_0^{t_f} E''(t) \, dt \tag{6}$$

where f is the frequency, and t_f, the fatigue time.

On the other hand, the heat flow during the fatigue test is as follows:

$$\frac{\partial T}{\partial t} = a \, \frac{\partial^2 T}{\partial x^2} + \frac{q_E}{\rho C_p} - \frac{q_U}{\rho C_p} \tag{7}$$

where T is the temperature (K); ρ, the density (kg m^{-3}); q_E, the amount of heat generated (Ws^{-1} m^{-3}); q_U, the amount of radiation heat (Ws^{-1} m^{-3}); C_p, the specific heat (J kg^{-1} K^{-1}); and a,

the heat diffusion coefficient (m^2 s^{-1}). If the gradient of the temperature along the x-axis (length of specimen) is able to be assumed to be negligible ($\partial T/\partial x = 0$), eq. (7) follows:

$$q_E - q_U = \rho C_p \, \frac{dT}{dt} \tag{8}$$

As the difference between the specimen and the circumstance temperatures is small at the early stage of the experiment, the second term can be neglected. Only the heat generated per second was calculated in the first place as the first approximation. After about 10 min, the specimen temperature was constant and the curve of time/temperature showed a plateau.

The total heat transfer from the specimen to the atmosphere is expressed as follows:

$$q_U = U(T - T_C)A/V \tag{9}$$

The heat calculation as the second approximation was achieved by using q_E and q_U calculated as the first approximation. The procedures were done repeatedly to obtain the heat generation and transfer. The work due to heat is summarized as follows:

$$W_T$$

$$= \frac{1}{t_f} \int_0^{t_f} \left(\rho C_P \, \frac{dT}{dt} + U(T(t) - T_C)A \right) V \, dt \tag{10}$$
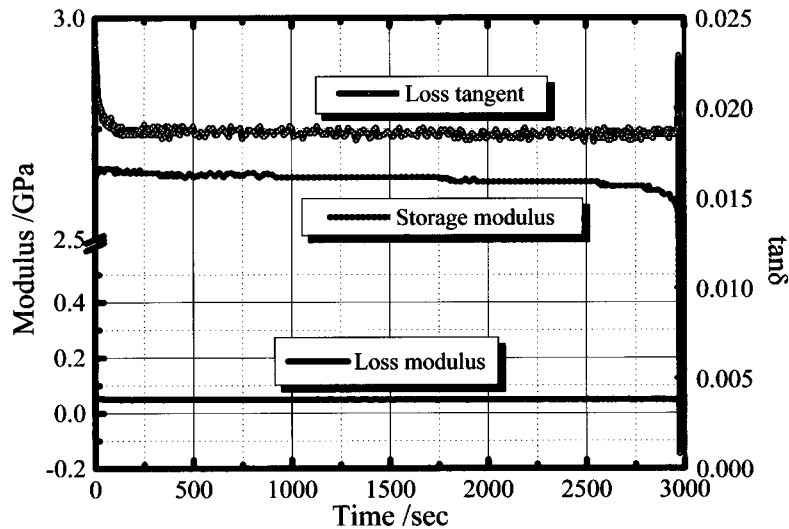
Figure 2   Dynamic, loss modulus, and tan δ during fatigue test.

The total mechanical work can be divided into two terms: heat generated and structural deformation (W_s):

$$W_M = W_T + W_S \qquad (11)$$

RESULTS AND DISCUSSION

The average stress during the fatigue test was 11.8 MPa, which was approximately 20% of the yield stress (58.8 MPa) of the PPE50 polymer alloy. The maximum and minimum stresses of the experiment were about 20 and 2–3 MPa, so as not to loosen the sample. The dynamic storage modulus, dynamic loss modulus, tan δ, and surface temperature were continuously measured during the fatigue experiments as shown in Figure 2. The dynamic storage modulus decreased in the initial stage because of the increase of temperature and it slightly decreased even though the temperature was constant during the experiments. It is suggested that the deformation occurred from the initial stage to the final stage of the fatigue test. The loss modulus increased suddenly just before fracture. However, details of the sudden increase were very difficult to observe because the time (fatigue time) could be not predicted accurately enough to stop the test just before the increase.

Preliminary experiments were achieved in order to make clear the relation between the displacement and temperature of the specimen. The experimental condition under which the specimen was softened by the elevated temperature is unsuitable; 0.50–0.60 of displacement was selected because the surface temperatures of the specimen were in the range 30–50°C, which were low enough compared to the glass transition temperature and high enough to measure the temperature increase accurately.

Fatigue times of the three kinds of alloys were observed as a function of displacement. The fatigue lives rose proportionally to the increase of the displacement and increased with increasing the contents of PPE as plotted in Figure 3. The larger the displacements were, the smaller the fatigue lives. The result was as expected.

The temperature of the polymer during the fatigue test was measured by a radiation thermometer and a thermocouple. The accuracy of the tem-
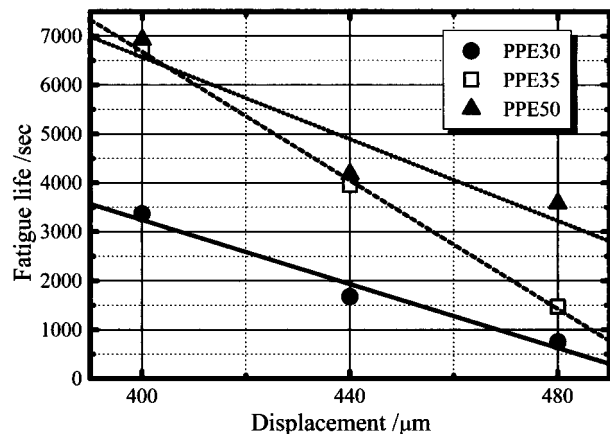

Figure 3   Fatigue time of PPE/PS alloys.

Table I   Viscoelastic Results of Fatigue Experiments for PC, PPE, PS, and PPE/PS Alloys

Polymer and Alloy	Strain Factor (%)	Heat Generated per Second (mW/g)	Mechanical Work per Second (mW/g)	Percent of Work That Appears as Heat (PWAH) (%)	Total Heat Energy (J)	Total Loss Energy (J)
PS	0.50	12.6	30.4	41.6	65.0	156.2
	0.55	17.5	40.8	42.1	167.7	400.8
	0.60	22.4	49.7	45.1	120.6	267.3
PPE30	0.50	14.3	28.1	50.9	166.1	326.4
	0.55	17.6	30.8	57.1	101.8	178.2
	0.60	28.4	45.0	60.8	70.9	116.6
PPE35	0.50	27.4	52.5	51.3	373.0	726.6
	0.55	35.2	62.4	56.5	240.6	426.2
	0.60	30.8	50.6	60.9	89.2	146.4
PPE50	0.50	15.4	27.6	55.7	184.5	331.1
	0.55	19.0	32.9	57.6	137.1	238.0
	0.60	24.6	42.5	57.9	152.7	263.6
PPE	0.50	12.9	21.6	59.7	40.6	67.8
	0.55	16.6	26.6	62.4	52.9	84.8
	0.60	21.7	32.3	65.2	53.8	82.5
PC	0.50	17.9	26.5	67.4	55.5	82.2
	0.55	25.8	38.5	66.8	86.6	129.3
	0.60	20.1	27.9	71.9	54.3	75.4

perature measured is very important in this study because the heat generated per unit time is calculated by the temperature and the percent of work that appears as heat (PWAH) is also determined as mechanical work per unit time by the heat generated per second. Two kinds of equipment for measuring the temperature were used and the standard deviation with a thermocouple (σ = 0.040 K) was smaller than with a radiation thermometer (σ = 0.056 K).

It was also expected that the heat generated per second and the mechanical work per second increased with increasing the displacement. As listed in Table I, the former increased from 12.6 W/g at 0.50% displacement to 22.4 W/g at 0.60% for PS and 12.9 W/g at 0.50% displacement to 21.7 W/g at 0.60% for PPE. However, there is little effect of PPE contents on the heat generated per second. On the other hand, higher mechanical works per second calculated by the loss modulus were observed for PS (40.9 W/g at 0.55% displacement) and the PS-rich alloys than for PPE (32.9 W/g at 0.55% displacement) and PPE-rich alloys.

Mechanical work per unit time calculated from the loss modulus during the fatigue test decreased with increasing PPE contents as shown in Figure 4. Conversely, the heat generated per unit time

had no relation to the PPE contents. As the entanglement density of PPE is much higher than that of PS, the work per unit time is thought to be higher for PPE than for PS because the work is considered to be due to friction between the adjacent polymer chains and the higher entanglement density causes friction. It is possible that the tendency is due to the test frequency for the loss
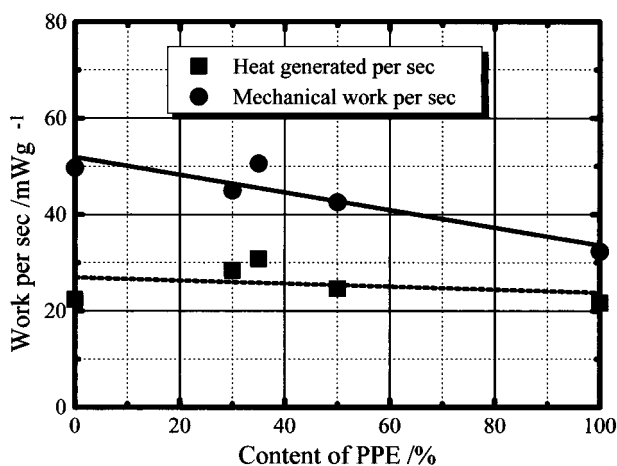
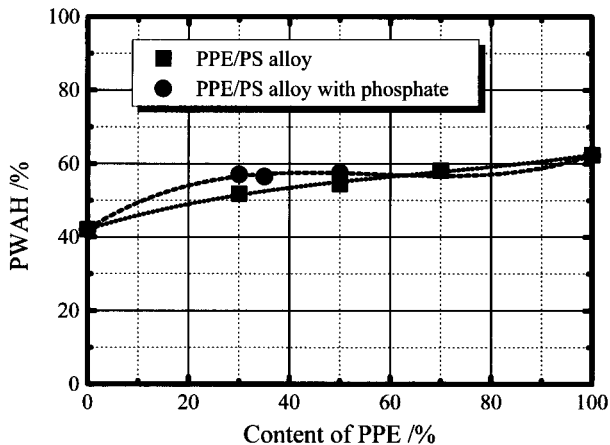**Figure 4**   Work per second as a function of content of PPE.

Figure 5 PWAH of PPE, PS, and their alloys with and without phosphate.

modulus is decided by the relaxation time of the polymer.

In any case, the percent of the work that appears as heat (PWAH) was 41–45% for PS and 60–65% for PPE and gradually increased with increase of the content of PPE in the PPE/PS alloys. In Figure 5, the PWAH of two series of specimens was plotted as a function of PPE content in the case that the displacement was 0.55%. One was PPE, PS, and their alloys with no solvent and the other with triphenylphosphate which had a strong interaction with the PPE chain.[14] PWAH increased with increase of the PPE contents in both cases. It means that about 50–60% of the MWPS calculated by the dynamic loss modulus during the fatigue test converted to heat and 40–50% of the energy was considered to be consumed in the structural deformation such as the cleavage of chains, crack formation, three-dimensional configuration, and other deformations. It is unexpected that the PWAH was about half of the total mechanical work calculated from the loss modulus. Similar experiments have been reported for the purpose of studying the mechanical strength of the polymer.[15]

The values and the tendency of PWAH were the same for the polymers blended with organic phosphate. The quantitative data were better for the blended polymer than for the polymer without phosphate. The surface of the molded specimens with the phosphate were better because it improved the lesser processability of PPE and its alloys.

Mechanical works per unit time and heat generated per unit time decreased with decrease of the PPE contents. The larger the mechanical work

per unit time is, the larger the structural damage of the polymer is thought to be. The fatigue lives are, therefore, expected to show the same tendency as that of the PWAH. The fatigue life of PS was shorter than that of PPE in this study. It has been known that the fatigue life of PS is shorter than that of PPE in the case of the notched specimen.[16,17]

Although much experimental data for the fatigue lives have been reported, there are few articles where the fatigue life of PS, PPE, and their soluble alloys is discussed from the chemical point of view.

About 50% in the case of PS and 40% in the case of PPE of the total mechanical work was consumed by structural changes during the fatigue tests. The molecular weight (M_W) of mechanically aged polymers has been reported to be smaller than that of the virgin polymer.[18–21] The M_W before and after fatigue tests was measured and the bond energy equivalent to the polymer chain breaking off was calculated. The molecular weight after the fatigue test of 1756 s was smaller than before the fatigue test, as expected; the molecular weight of PPE dropped from 63,000 to 48,000 during this test. The mechanical strength of PPE strongly depends on its molecular weight. The minimization of the PPE molecular weight is important to optimize the melt flow during the molding process. Additional loss of molecular weight leads to a significant decrease in impact strength.

The number of the polymer chains which cleaved during the fatigue tests were relatively small (5.65×10^{17} for PS and 3.10×10^{18} for PPE) because the molar weights of the polymer were extremely large compared to ordinary chemicals. The total energies of the breaking off were smaller than was the energy due to the loss modulus, as listed in Table II.

The contribution of the energy due to the breaking off was about several % of the whole energy loss during the fatigue test. The rest, 30% or more,

Table II   Difference of Mean Molecular Weights Before and After Fatigue Tests

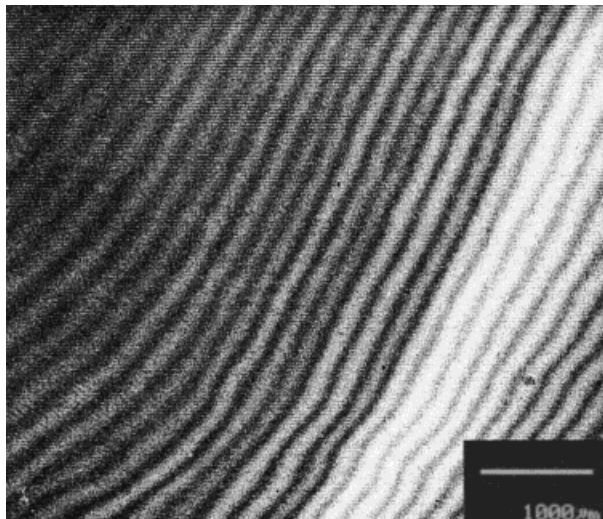|	PPE	PS
Before fatigue	6.35×10^4	2.10×10^5
After fatigue	4.70×10^4	1.75×10^5
Difference	1.55×10^4	3.5×10^4
No. of molecules cleavaged	3.10×10^{18}	5.65×10^{17}

Figure 6 Striation image modified photographs of scanning acoustic microscope by computer-modified command (direction of tension is the horizontal axis).

could not be measured. It seemed to be composed of the conformation energy such as the change of the entanglement density, the energy of the surface of very small cracks on the polymer surface, and other structural changes. The entanglement densities before and after the fatigue test were 11,160 and 9090, respectively. The change was so small that the three-dimensional structure did not affect the total energy loss during the fatigue test.

The values of the total heat generated and the total mechanical work were not constant and did not show a clear tendency that the content of PPE for the two energies depended on the two values which were the fatigue times and mechanical works per second. The fatigue striation on the surface of the polymer was observed by an ultrasonic microscope.[22]

Figure 6 shows the striation which was reported in articles already reported.[23,24] The striation is formed by an irreversible process during the cyclic loading test. The formation consumes the mechanical work but it cannot be estimated preciously.

CONCLUSION

In spite of the necessity to understand fatigue in polymers, the knowledge is not as well advanced as in the case of metals. The phenomenon of fatigue has achieved little fundamental analysis.

Many empirical works have been done, which may make the understanding of the fatigue phenomena move to the wrong direction. For instance, as mentioned in this article, it is generally known that the fatigue life of PS is shorter than that of PPE. However, the life of PPE becomes shorter when the molecular weight of the specimen subjected to experiments is not high enough for the "aged polymer" but is high enough for the virgin polymer. The mechanical strength strongly depends on the molecular weight, which is usually designed to be slightly larger than the threshold value of the molecular weight because the melt-flow property is very important in the industrial meaning.

Hertzberg and Manson noted in their book three major problems which have hindered the understanding of fatigue in polymers. They pointed out that chemical analysis as well as physical and mechanical consideration is indispensable to understand the fatigue which is an irreversible and nonlinear phenomenon. However, it is very difficult to discuss the mechanical property as a phenomenon related to the chemical structure of the polymer. In this study, the heat power is only 50–60% of the total mechanical work and only a small portion of the rest of the work can be explained as the chain cleavage, three-dimensionally structural deformations, and crack propagation. While the quantitative analyses were of limited precision, the results of this study nevertheless indicate that "fatigue" includes heat, chain scission, striation formation, the change of entanglement, and crack formation. The following conclusions are drawn from this work:

1. The percent of work that appears as heat (PWAH) was about 50–60% of the mechanical work per unit time (MWPS) and it increased with increase of the PPE contents in the range from PPE = 0 to PPE = 100.
2. The fatigue lives of PPE-rich alloys are longer than those of PS-rich alloys. It seemed to be caused by the dependence of the MWPS on the PPE contents.
3. The molecular weight decreased during the fatigue test. The molecular weight range, ΔM_W, is large enough to lower the mechanical strength but the cleavage energy was very small compared to the energy consumption during the fatigue test.
4. The macroscopically structural deforma-

tion such as striation was observed before crack propagation. It was thought to account for an appreciable percent of the total mechanical work.

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