

Effect of aggregation structure on non-linear dynamic viscoelastic characteristics of oriented high-density polyethylenes under cyclic fatigue

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Non-linear viscoelastic properties under cyclic fatigue for oriented high-density polyethylenes (HDPEs) with different molecular aggregation states were discussed in terms of the non-linear viscoelastic parameter (NVP). Non-linear viscoelasticity of the oriented HDPEs became dominant with an increase of imposed strain amplitude, and fatigue strength decreased with an increase in the magnitude of NVP. Also, in the case of the same magnitude of NVP, the fatigue strength of the oriented HDPE drawn at the crystalline relaxation temperature, T_{α_c} (drawing temperature, $T_d = 353$ K) was greater than that of the oriented HDPEs drawn at the other temperatures, because PE drawn at T_{α_c} had the most stable aggregation structure. Higher-order structural change during the fatigue process by cyclic straining for the oriented HDPE at $T_d = 353$ K was not so apparent compared with that for the oriented HDPEs prepared at the other temperatures. In the case of the oriented HDPE at $T_d = 300$ K, composed of crystallites with small dimensions, the larger the magnitude of imposed strain amplitude, the greater the increase in crystallite size and/or the orientation of molecular chains to the direction of cyclic deformation occurring with cyclic straining. Also, that became more dominant with an increase in the magnitude of imposed strain amplitude. In the case of the HDPE drawn at a higher temperature than T_{α_c} ($T_d = 383$ K), the HDPE was composed of crystallites with large dimensions, and the crystalline disordering accompanying the decomposition of lamellar crystals into the small fragments occurred at the initial stage of cyclic fatigue. The magnitude of NVP for the oriented HDPEs increased with an increase in the degree of strain concentration in the amorphous and/or crystallite boundary regions in the case of fatigue experiments at 300 K. Thus, it is reasonable to conclude that the non-linear viscoelasticity of the oriented HDPEs under cyclic fatigue at 300 K mainly originated from the deformation of the amorphous and/or crystallite boundary regions. Also, it was clarified that the appearance of non-linear viscoelasticity remarkably reduced the fatigue strength.

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INTRODUCTION

The fatigue behaviour of polymeric materials, which is closely related to the non-linear viscoelasticity being accompanied by irreversible structural change, is very important with respect to industrial applications. Non-linear viscoelastic behaviour accompanying the irreversible structural changes for crystalline polymers appears even at small strain or stress level. Some studies concerning static and dynamic non-linear viscoelasticity have been carried out, and various models were also proposed in order to explain the non-linear viscoelastic behaviour of polymeric materials^{1–5}. Catsiff *et al.*¹ constructed a master curve for nylon using the non-linear factors which involved the scale factor, F , as a

factor to reproduce the actual creep behaviour at low stress level, i.e. the characteristic retardation time, τ , as a lateral shift factor, and the instantaneous elongation, E_0 as a vertical shift factor. Bauwens² proposed two approaches (analytical and ladder mechanical models) to describe the non-linear creep behaviour of glassy polymers. These models showed a better fit to experimental data than the stretched exponential law. Also, the relaxation master curves in a non-linear region for the crosslinked polyester resins was studied by Tieghi *et al.*³ Litt and Torp⁴ studied the mechanical non-linearity for glassy polycarbonate as a function of strain amplitude and temperature based on dynamic mechanical and stress-relaxation measurements, and found that strain made relaxations active. Rahaman and Scanlan⁵ studied the non-linear viscoelastic properties of glassy polymers and semi-crystalline polymers using the torsion pendulum. They reported that the β and α relaxation processes of glassy polymers were well described in terms of the mechanical model consisting of a number of Maxwell

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elements in parallel and a modified Maxwell element containing a non-linear dashpot, respectively.

The relationships between fatigue behaviour and non-linear viscoelasticity on the basis of the hysteresis energy loss for various solid polymers, for instance, plasticized poly(vinyl chloride)⁶, unoriented high density polyethylene (HDPE)⁷, oriented HDPE^{8,9} and short glass fibre reinforced composite¹⁰ have been extensively investigated by the authors. It has been revealed that the fatigue lifetimes of solid polymers decreased with an increase in non-linear viscoelasticity, estimated by hysteresis energy loss which was dissipated for fatigue damage. Moreover, the authors proposed the non-linear viscoelastic parameter (NVP) being evaluated on the basis of Fourier analysis of the higher-order stress wave, because the non-linear viscoelasticity based on hysteresis energy loss had only provided information about the apparent and gross non-linear viscoelasticity. The physical importance on NVP under cyclic fatigue was discussed, and it was concluded that the magnitudes of NVP for the annealed and isothermally crystallized HDPEs were closely related to both the magnitude of spherulite deformation and the degree of strain or stress concentration at the spherulite or crystallite interface¹¹. Also, the effect of crystalline relaxation on non-linear viscoelasticity during fatigue process for the oriented HDPE was investigated¹². Non-linear viscoelasticity at the α_1 -crystalline relaxation temperature was lower than that at room temperature, its fatigue strength was lower than those at the other ambient temperatures, because the intermosaic block region, being very sensitive to the imposed strain or stress, was selectively deformed as well as was the amorphous region. Since both crystalline and amorphous regions were deformed at the α_2 -crystalline relaxation temperature, the magnitude of NVP became lower than that at the α_1 -crystalline relaxation temperature.

In this study, the effect of molecular aggregation state on non-linear dynamic viscoelastic properties of the oriented HDPEs was investigated on the basis of NVP, and the relationship between non-linear viscoelasticity and structural change during the cyclic fatigue process was also discussed.

EXPERIMENTAL

Specimens

The polymer used in this study was HDPE (Hizex 7000F, Mitsui Petrochemical Co.) with $M_w = 260\,000$. In order to obtain oriented HDPEs with different molecular aggregation states, HDPEs were stretched up to the draw ratio of 5.3 at the drawing temperatures T_d of 300 K (room temperature), 353 K corresponding to the α_2 -crystalline relaxation temperature of HDPE¹³⁻¹⁵ and 383 K. The draw ratio was defined as the ratio of the cross-sectional areas of the samples before and after drawing.

Fatigue test and estimation of non-linear viscoelasticity

Figure 1 shows a block diagram of the fatigue tester used to investigate non-linear dynamic viscoelastic properties. The fatigue test was carried out using a fatigue tester which allowed continuous measurement of dynamic viscoelastic functions during the fatigue process. The strain and stress signals were detected by the semiconductor displacement sensor and the load cell, respectively. The magnitude of the mechanical loss

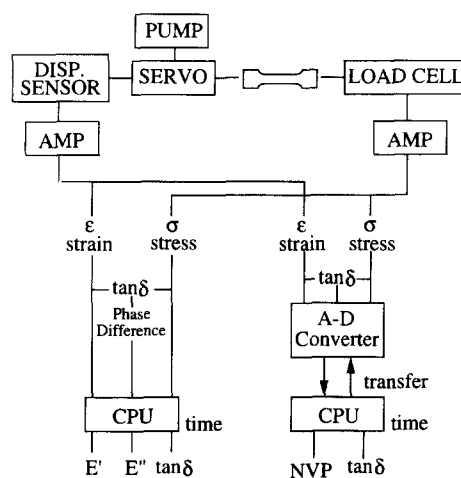


Figure 1 Block diagram of fatigue tester for investigation of non-linear dynamic viscoelastic properties under cyclic fatigue

tangent, $\tan \delta$, was obtained from the phase difference between stress and strain signals under cyclic straining. The magnitudes of E' and $\tan \delta$ were apparent ones which included the contribution of higher order term of response stress. The fatigue tests were performed under conditions of a testing frequency of 10 Hz and an ambient temperature of 300 K. The magnitude of dynamic strain amplitude, ϵ_d , was in the range 2.0–4.0%. The magnitude of initial static stress to hold the tension–tension mode was 40 MPa. The imposed strain and response stress signals were collected with an AD converter. Since this AD converter had a large memory, this could be used as a digital storage memory. The digital data were transferred to the personal computer, and the degree of non-linear viscoelasticity was estimated on the basis of the NVP¹¹, which was defined as follows:

$$NVP = \frac{\sqrt{a_2^2 + b_2^2} + \sqrt{a_3^2 + b_3^2} + \dots + \sqrt{a_{10}^2 + b_{10}^2}}{\sqrt{a_1^2 + b_1^2}} \quad (1)$$

where a_n and b_n ($n = 1, 2, 3 \dots$) were the coefficients of a Fourier series of stress signals.

Wide angle X-ray diffraction

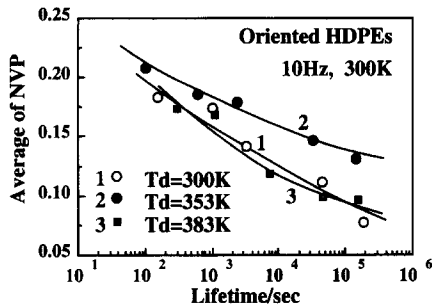
The change of crystalline state in the specimens during the fatigue process was investigated on the basis of wide angle X-ray studies at room temperature using an X-ray diffractometer with a rotating anode source (40 kV, 200 mA) (RU-300; Rigaku Co.). Assuming that the distribution function for lattice distortions and the shape factor are Lorentzian, the crystallite size, D_{hkl} and the lattice distortion factor, g_{hkl} along the hkl lattice direction were evaluated on the basis of Hosemann's paracrystal analysis¹⁶.

Small angle X-ray scattering (SAXS)

In order to evaluate the magnitudes of long period and scattering peak intensity for the unfatigued and fatigued samples, SAXS profiles were obtained using an X-ray diffractometer with Ni-filtered Cu K_α radiation (RU-200; Rigaku Co.). A position sensitive proportional counter was used as the scattering photon counter. SAXS peak intensity affords information about both the density

Table 1 Crystal structural parameters of the oriented HDPEs with different molecular aggregation states before fatigue test

Sample	D_{110} (nm)	D_{200} (nm)	g_{110} (%)	g_{200} (%)	L (nm)	SAXS peak intensity (a.u.)
Drawn at 300 K	8.2	4.6	4.39	1.75	—	—
Drawn at 353 K	11.3	9.4	1.74	1.55	21.3	7.90
Drawn at 383 K	16.0	14.6	1.23	1.46	29.2	9.22


Figure 2 Relationships between fatigue lifetime and the average value of NVP for the oriented HDPEs with different molecular aggregation states

difference between the crystalline and amorphous regions and the crystallinity.

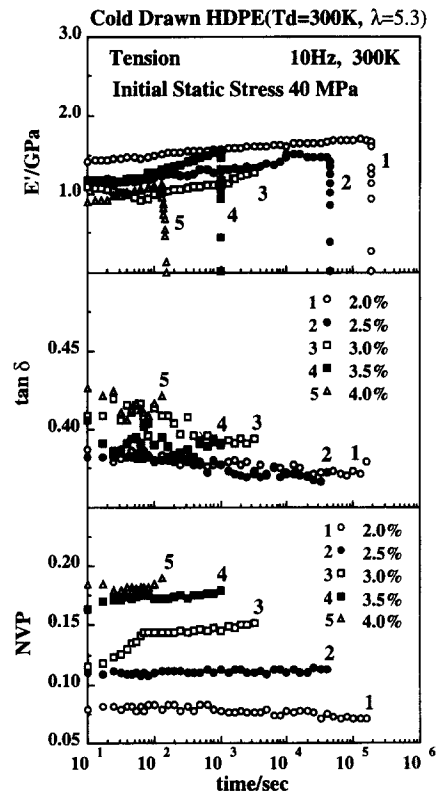
RESULTS AND DISCUSSION

Crystalline states of oriented HDPEs

Table 1 shows the crystallite size, D_{hkl} , the lattice distortion factor, g_{hkl} , the long period, and the SAXS peak intensity for the oriented HDPEs drawn at different temperatures. In the case of the cold drawn HDPE ($T_d = 300$ K), the crystallite sizes were very small, and the crystallites were largely distorted. Since the long period and the SAXS peak were not observed, it is reasonable to consider that the boundary between the crystalline and amorphous regions was not apparent. On the other hand, in the case of the oriented HDPE at a higher temperature than the crystalline relaxation temperature ($T_d = 383$ K), the crystallite sizes were largest and the lattice distortion factors along the 110 and 200 directions were smallest among the oriented HDPEs. Since both the long period and the SAXS peak intensity for the oriented HDPE ($T_d = 383$ K) were largest among the samples studied here, it might be confirmed that the boundary between the crystalline and amorphous regions became distinct and lamellar crystals were decomposed into larger fragments, resulting in the formation of a distinct fibre structure with an increase in the drawing temperature, as reported previously¹⁵.

Relationships between fatigue lifetime and non-linear viscoelasticity of oriented HDPEs

Figure 2 shows the relationship between fatigue lifetime and the average value of the NVP from the onset of cyclic fatigue until the fatigue failure for the oriented HDPEs drawn at different drawing temperatures. All the oriented HDPEs showed a remarkable decrease in fatigue lifetime with an increase in the average value of NVP. Thus, it became apparent that the appearance of non-linear viscoelasticity effectively reduced the fatigue strength of the oriented HDPE. A similar trend was also reported


Figure 3 Variations of E' , $\tan \delta$ and NVP of the oriented HDPE ($T_d = 300$ K) with time during fatigue process as a function of dynamic imposed strain amplitude

for the annealed and isothermally crystallized HDPEs in a previous report¹¹. Therefore, it can be concluded that the NVP can be used as an index of fatigue lifetime or fatigue strength for polymeric solids. At the same magnitude of NVP, the magnitude of fatigue lifetime for the oriented HDPE ($T_d = 353$ K) was greater than for the others. This result may arise from the facts that the drawing at 353 K, corresponding to the crystalline relaxation temperature T_{α_c} , provides both the greatest degree of orientation and little defects in the crystalline region, while the drawing at 300 K causes many defects in the crystalline region, and that at 383 K causes both over-growing crystallites and a low degree of orientation.

Non-linear dynamic viscoelasticity and structural change during the fatigue process for oriented HDPE ($T_d = 300$ K)

Figure 3 shows the time dependence of E' , $\tan \delta$ and NVP for the cold drawn HDPE ($T_d = 300$ K) during the fatigue process at 300 K as a function of dynamic imposed strain amplitude. The magnitudes of E' and $\tan \delta$ increased and decreased with fatigue time, respectively, and these behaviours became more prominent

with an increase in the magnitude of imposed strain amplitude. Therefore, it is reasonable to consider that the increase in crystallite size and/or the orientation of molecular chains along the direction of cyclic deformation occurred with cyclic straining, resulting in an increase of strength for the specimens. The magnitude of $\tan \delta$ increased slightly with the magnitude of imposed strain amplitude. The increase in $\tan \delta$ might be due to the contribution of non-linear viscoelasticity, because an increase in viscous contribution to the mechanical loss factor is very small due to the almost constant specimen temperature during cyclic fatigue. The magnitude of NVP as an index of non-linear viscoelasticity increased and fatigue lifetime markedly decreased with an increase in imposed strain amplitude. This apparently indicates that the non-linear viscoelastic characteristics become more prominent as the imposed strain amplitude increases.

Figure 4 shows the imposed strain amplitude dependences of the crystallite sizes, D_{110} and D_{200} , the SAXS peak intensity and the long period, L , for the cold drawn HDPE ($T_d = 300$ K) after fatigue fracture. The appearance of the long period and the increase in SAXS peak intensity at around 2.0% of ϵ_d clearly indicate that the apparent one-phase structure of the cold drawn HDPE was changed into a fibre structure with a repeating distance after cyclic fatigue. This structural transformation apparently occurred above the imposed strain amplitude of 3.0%. This structural change corresponded well to the change of NVP with the imposed strain amplitude, as shown in Figure 3, i.e. the magnitude of NVP increased with the increases in the crystallite sizes, the SAXS peak intensity and the long period. Therefore, the actually larger strain was imposed on the

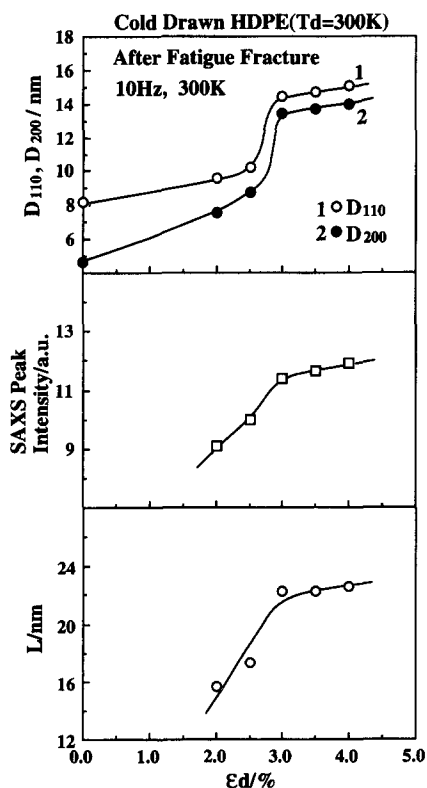


Figure 4 Values of the crystallite sizes, the SAXS peak intensity and the long period for the cold drawn HDPE ($T_d = 300$ K) after fatigue fracture as a function of imposed strain amplitude

amorphous or intercrystallite regions because the fraction of those regions decreased with an increase in the fatigue process. Therefore, it can be concluded that non-linear viscoelasticity during the fatigue process for the cold drawn HDPE ($T_d = 300$ K) may arise mainly from the deformation at the amorphous and/or crystallite boundary regions rather than that at the crystalline region itself.

Since the fatigue test was carried out in tension-tension cyclic fatigue, it was necessary to investigate whether or not the higher-order structural change originated from the crystalline structural change during the creep process under the application of constant stress. Figure 5 shows the creep strain dependence of crystallite size, D_{110} , for the specimens subjected to a certain static tensile stress with and without cyclic

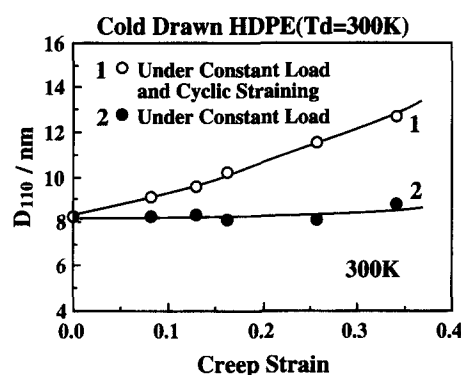


Figure 5 Plots of the crystallite size D_{110} of specimens subjected to constant load with and without cyclic straining against the extent of creep strain

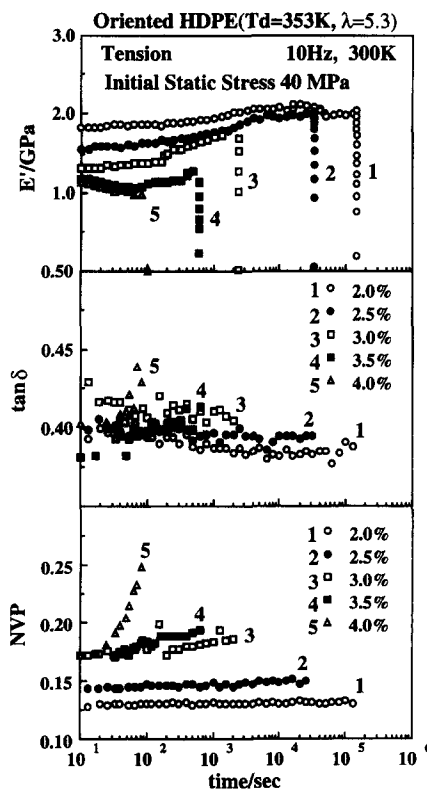


Figure 6 Variations of E' , $\tan \delta$ and NVP for the oriented HDPE ($T_d = 353$ K) with time during fatigue process at the various dynamic imposed strain amplitudes

Table 2 Crystal structural parameters, the average magnitude of NVP and fatigue lifetime (t_f) of the oriented HDPE ($T_d = 353$ K) after fatigue fracture

ϵ_d (%)	Average NVP	t_f (s)	D_{110} (nm)	g_{110} (%)	L (nm)
Original	—	—	11.3	1.74	21.3
2.0	0.130	143 450	13.1	1.62	22.7
2.5	0.146	33 600	12.0	1.49	22.5
3.0	0.179	2400	11.9	1.65	21.2
3.5	0.186	620	15.6	1.45	23.4
4.0	0.208	110	15.7	1.33	24.1

straining. The crystallite size, D_{110} , of the specimen subjected to tension–tension cyclic fatigue increased with an increase in the extent of creep strain. On the other hand, that of the sample subjected to constant load was not markedly changed with the extent of creep strain. Figure 5, then, apparently indicates that the crystalline structural change is accelerated by dynamic cyclic straining.

Non-linear dynamic viscoelasticity and structural change during the fatigue process for oriented HDPE ($T_d = 353$ K)

Figure 6 shows the fatigue time dependences of E' , $\tan \delta$ and NVP for the oriented HDPE ($T_d = 353$ K) as a function of imposed dynamic strain amplitude under the conditions of the measuring temperature of 300 K and the initial static tensile stress of 40 MPa. The magnitude of E' decreased and that of $\tan \delta$ increased slightly with the magnitude of imposed strain amplitude. In the case of small imposed strain amplitude, E' showed a maximum and $\tan \delta$ showed a minimum just before the fatigue failure. These typical behaviours for brittle failure indicate a considerable increase in the contribution of the elastic term, such as orientation of molecular chains under cyclic fatigue^{6,7}. In the case of the fatigue test at large imposed strain amplitude, the magnitude of E' decreased and that of $\tan \delta$ increased monotonically in the initial stage of the fatigue test. These are typical behaviours for ductile failure^{6,7}. The magnitude of NVP increased with the magnitude of imposed strain amplitude. In particular, at a high magnitude of imposed strain amplitude, the magnitude of NVP apparently increased with fatigue time. Therefore, it is reasonable to consider that the fatigue behaviour is strongly related to the non-linear viscoelastic characteristics.

Table 2 summarizes the crystal structural parameters (the crystallite size, D_{110} , the lattice distortion factor, g_{110} and the long period, L), the magnitude of NVP and fatigue lifetime for the oriented HDPE ($T_d = 353$ K) at various imposed strain amplitudes. The magnitudes of the crystal structural parameters such as D_{110} , g_{110} and L did not change apparently up to $\epsilon_d = 3.0\%$ in comparison with those for the original unfatigued samples. These results, then, indicate that the crystalline structural change induced by cyclic fatigue was not prominent under the small magnitude of imposed strain amplitude. On the other hand, the magnitude of NVP increased with an increase in the magnitude of imposed strain amplitude, even if the magnitude of applied strain amplitude was less than 3.0%. Therefore, it is reasonable to conclude from Table 2 that the non-linear viscoelasticity during the fatigue process for the oriented HDPE ($T_d = 353$ K) mainly originates from the deformation of

amorphous and/or crystallite boundary regions by cyclic straining. On the other hand, in the case of large imposed strain amplitudes of 3.5 or 4.0%, the magnitudes of the crystallite size, D_{110} , the long period, L , and the SAXS peak intensity for the fatigue-fractured sample became larger, and the lattice distortion factor, g_{110} , became smaller than those for the original unfatigued one. These structural changes may be explained by the fact that the molecular motions activated by the internally generated heat, i.e. a part of viscoelastic energy loss, tend to improve the unstable structural state in the intermosaic block region and/or in the main chain, resulting in more stable packing of molecules. Therefore, it can be finally concluded from Table 2 that non-linear viscoelasticity during fatigue process for the oriented HDPE ($T_d = 353$ K) originates from the deformation of amorphous and/or crystallite boundary regions rather than that in the crystalline phase itself.

Non-linear dynamic viscoelasticity and structural change during the fatigue process for oriented HDPE ($T_d = 383$ K)

Figure 7 shows the variations of E' , $\tan \delta$ and NVP with time during the fatigue process as a function of imposed strain amplitude for the oriented HDPE ($T_d = 383$ K). The magnitudes of E' and $\tan \delta$, especially at the initial stage of the fatigue test, decreased and increased with the magnitude of imposed dynamic strain amplitude, respectively. The magnitude of NVP increased consistently with the magnitude of imposed strain amplitude. In particular, in the case of large imposed strain amplitude, the magnitude of NVP was very large, and increased abruptly with fatigue time compared with that at small imposed strain amplitude. Thus, the

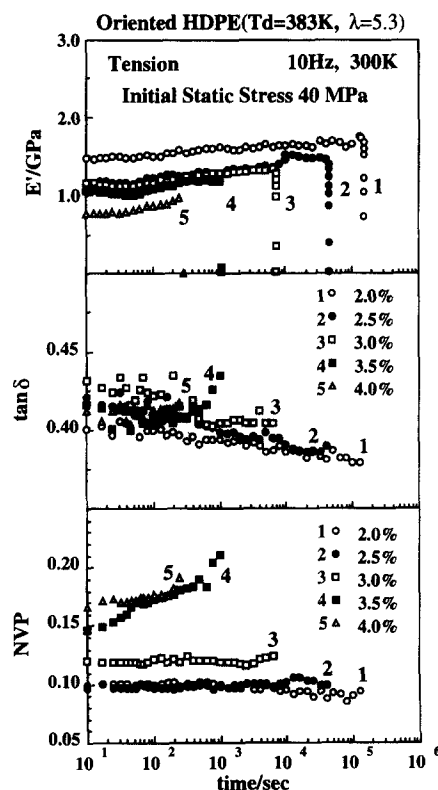


Figure 7 Variations of E' , $\tan \delta$ and NVP for the oriented HDPE ($T_d = 383$ K) with time during fatigue process as a function of imposed strain amplitude

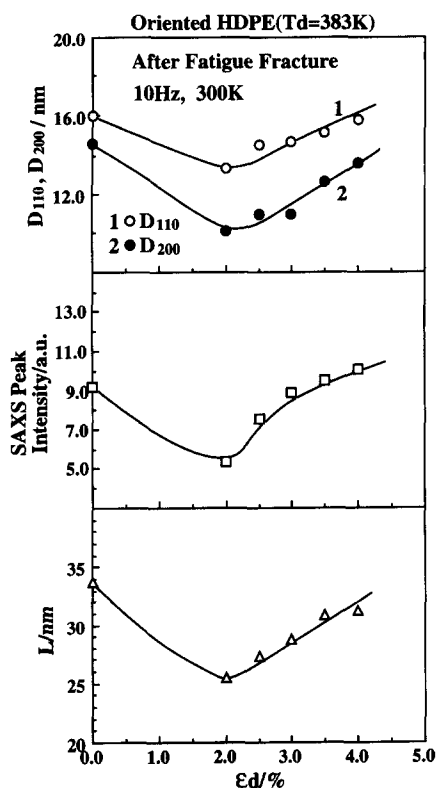


Figure 8 Changes of the crystallite sizes, the SAXS peak intensity and the long period for the oriented HDPE ($T_d = 383\text{K}$) after fatigue fracture as a function of imposed strain amplitude

non-linear viscoelasticity became apparent with the magnitude of imposed strain amplitude; also, the larger imposed strain amplitude made the fatigue lifetime shorter. Thus, it is reasonable to consider that the irreversible structural change related to non-linear viscoelasticity occurred markedly during the fatigue process under large imposed strain amplitude.

Figure 8 shows the plots of the crystallite sizes, D_{110} and D_{200} , the SAXS peak intensity, and the long period, L , for the oriented HDPE ($T_d = 383\text{K}$) after fatigue fracture at 300 K against the magnitude of imposed strain amplitude. In a range of small imposed strain amplitudes, the crystallite sizes, the SAXS peak intensity and the long period of the fatigue fractured samples were smaller than those of the unfatigued original one. This may indicate that the decomposition of unstable larger lamellar crystals into smaller crystalline fragments occurred due to fairly preferential deformation of the intermosaic region, since the fatigue test was carried out at the α_1 -crystalline relaxation temperature, 300 K.

Figure 9 shows the fatigue time dependence of the crystallite sizes, D_{110} and D_{200} , the SAXS peak intensity, and the long period, L , at the small imposed strain amplitude of 2.0%. The crystallite sizes, the SAXS peak intensity and the long period markedly decreased at the initial stage of the fatigue test and remained almost constant until the fatigue fracture. This indicates that the unstable larger lamellar crystal was decomposed into smaller crystalline fragments or mosaic blocks and that the larger fibrous structure became the smaller fibrous structure at the interfacial region of crystalline and amorphous phases by cyclic straining in the initial stage of fatigue test. On the other hand, as shown in Figure 8,

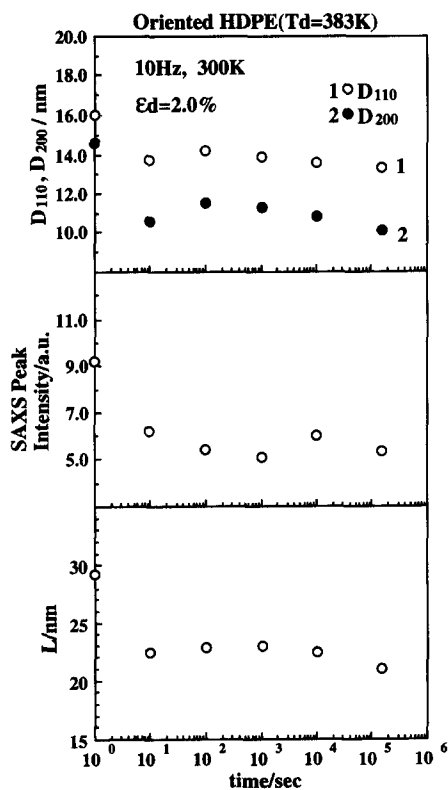


Figure 9 Variations of the crystallite sizes along the 110 and 200 lattice directions, the SAXS peak intensity and the long period for the oriented HDPE ($T_d = 383\text{K}$) with time during fatigue process at the dynamic imposed strain amplitude of 2.0%

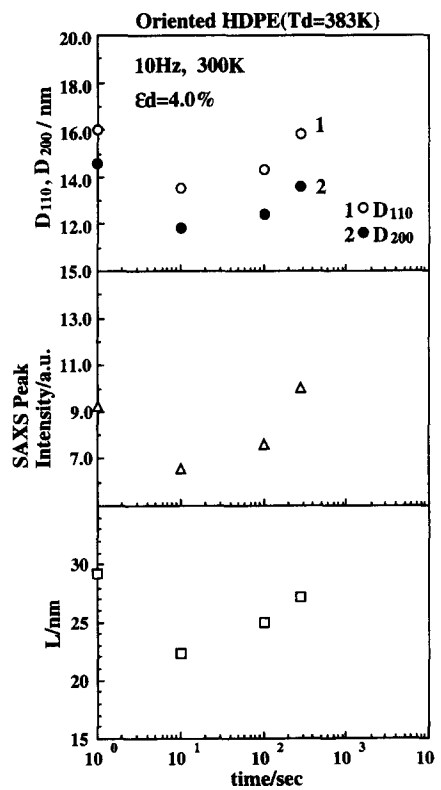


Figure 10 Fatigue time dependence of the crystallite sizes along the 110 and 200 lattice directions, the SAXS peak intensity and the long period for the oriented HDPE ($T_d = 383\text{K}$) at the dynamic imposed strain amplitude of 4.0%

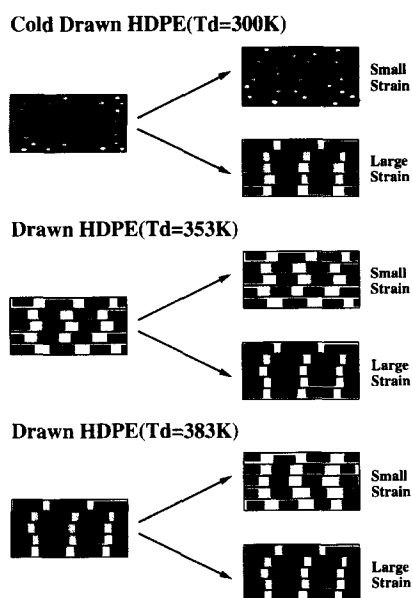


Figure 11 Schematic representation of higher-order structural changes by cyclic straining for the oriented HDPEs

the crystallite sizes, the SAXS peak intensity and the long period of the fatigue fractured samples increased gradually with an increase in imposed strain amplitude.

Figure 10 shows the fatigue time dependence of the crystallite sizes, the SAXS peak intensity and the long period at the large magnitude of imposed strain amplitude at 4.0%. Within a very short fatigue test of 10 s, the crystallite sizes, the SAXS peak intensity and the long period strikingly decreased. These results indicate that the decomposition of lamellar crystals into small fragments of the mosaic block occurred at the initial part of the fatigue test even at the large magnitude of imposed strain amplitude. Also, the crystallite sizes, the SAXS peak intensity and the long period increased with fatigue time. These structural changes may be explained by the fact that the molecular motions activated by the internally generated heat, i.e. a part of viscoelastic energy loss, tend to improve the unstable structural state in the intermosaic block region and/or in the main chain, resulting in more stable packing of molecules. With increases in the crystallite sizes, the SAXS peak intensity and the long period, the magnitude of NVP increased markedly, as shown in Figure 7. Therefore, it can be concluded that the increase in cyclic straining concentration at the amorphous and/or crystallite boundary regions results in both an increase in non-linear viscoelasticity and a decrease in fatigue strength.

CONCLUSIONS

The oriented HDPEs with different molecular aggregation states were prepared at the drawing temperature, T_d , of 300 K (room temperature), 353 K (crystalline relaxation temperature, T_{α_c} of PE) and 383 K above T_{α_c} . Non-linear viscoelastic properties of the oriented HDPEs during the fatigue process were investigated on the basis of the NVP. It has been revealed that the appearance of

non-linear viscoelasticity reduced fatigue strength of the oriented HDPE. Also, at the same magnitude of NVP, the fatigue strength of the oriented HDPE ($T_d = 353$ K) was greater than for the other HDPEs, because the crystalline state of the oriented HDPE ($T_d = 353$ K) was more stable towards the fatigue damage compared with the others.

Figure 11 shows a schematic representation of higher-order structural change under cyclic straining for the oriented HDPEs with different molecular aggregation states. In the case of the cold drawn HDPE ($T_d = 300$ K), the homogeneous phase turned into the two phases consisting of amorphous and crystalline regions by cyclic straining, and it became more dominant with the magnitude of imposed strain amplitude. Higher-order structural change of the oriented HDPE ($T_d = 353$ K) during the fatigue process hardly occurred until $\epsilon_d = 3.0\%$, while the improvement of the crystalline order took place above $\epsilon_d = 3.0\%$. In the case of the oriented HDPE ($T_d = 383$ K), the decomposition of unstable larger lamellar crystals into small fragments occurred at the initial stage of the fatigue test. Also, the increase in crystallite size and/or the orientation of molecular chains along the direction of cyclic deformation took place as the imposed strain amplitude increased. For all the oriented HDPEs, non-linear viscoelasticity under cyclic fatigue became dominant with the improvement of the crystalline order. Therefore, it can be concluded that non-linear viscoelasticity of the oriented HDPEs during the fatigue process originates from the deformation of the amorphous and/or crystallite boundary regions rather than that in the crystalline phase itself.

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