

Effects of main chain rigidity on nonlinear dynamic viscoelasticity and fatigue performance for polymeric fibres

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Fatigue performance of polymeric fibres with different molecular chain rigidity was investigated based on zone nonlinear dynamic viscoelastic analyses under tension-type cyclic straining. Poly(vinyl alcohol), Nylon 6 (poly(ϵ -caprolactam)), poly(ethylene terephthalate), poly(*p*-phenylene terephthalamide) and Vectran (a copolyester of *p*-hydroxy benzoate (HBA) and 2-hydroxy-6-naphthoic acid (HNA)) fibres were used as specimens. Nonlinear dynamic viscoelasticity and fatigue performance of polymeric fibres strongly depended on the chain rigidity. The polymeric fibres with rigid molecular chains showed pronounced nonlinear viscoelastic characteristics compared with those with flexible ones. Also, based on the zone nonlinear dynamic viscoelastic analyses, it was found that the nonlinear viscoelastic behaviours of polymeric fibres was predominantly induced in the recovery process rather than in the tensile process during a single period of cyclic deformation, and the more remarkable nonlinear viscoelastic behaviour was exhibited in the zone with higher strain rate. The polymeric fibre which exhibited remarkable nonlinear dynamic viscoelasticity showed extremely poor fatigue performance. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Fatigue behaviours of polymeric solids have been studied on the basis of the classical fracture mechanical methods¹. However, this approach did not consider the inherent properties of polymeric materials such as viscoelasticity. The authors proposed a novel method for analysis of fatigue characteristics on the basis of the nonlinear dynamic viscoelastic measurement during the fatigue process^{2–5}. Several attempts have been made on the relationship between the nonlinear viscoelasticity and the structural characteristics for polymers^{6–8}. For example, crystalline polymers often exhibit greater nonlinear viscoelasticity than glassy polymers⁶, due to the presence of a heterogeneous structure composed of crystalline and amorphous phases. It was observed that the nonlinear behaviour of oriented polyethylene became pronounced around the α_c -crystalline relaxation temperature⁷. On the other hand, some facts have been found about the relationship between the fatigue performance and the structural characteristics for polymers, for example, the fatigue performance of polymers strongly depends on their molecular chain entanglement density and molecular weights⁹.

The understanding of how polymer structure affects chain flexibility has been a major focus of polymer science since its inception. Much progress has been made in this area on both theoretical and experimental fronts¹⁰. Polymer chains exhibit various conformations from tight coils to highly extended structures such as rigid rods and rigid helical

chains. The parameters used for evaluating the degree of chain flexibility are usually different for ‘flexibility’ versus ‘stiff’ chains¹⁰. For flexible polymers, the most common parameter in use is Flory’s characteristic ratio, C_∞ , defined as

$$C_\infty = \lim_{N \rightarrow \infty} \frac{\langle R^2 \rangle}{Nl^2} \quad (1)$$

where $\langle R^2 \rangle^{1/2}$ is the unperturbed mean-square end-to-end distance, N is the number of main chain bonds of length, l ¹¹. A value of C_∞ is equal to 1 for the freely jointed flexible chain, and the larger value is indicative of greater departures from freely jointed characteristics, i.e., diminished flexibility. The Kratky–Porod wormlike chain model is widely used for describing conformational characteristics of less flexible chains^{12,13}. The polymer is viewed as a semi-flexible strings of overall ‘countour length’, L , with a continuous curvature.

The chain is subdivided into N segments of length ΔL . The persistence length, q , is defined as

$$q = \lim_{\psi \rightarrow 0} \frac{\Delta L}{1 - \cos \psi} \quad (2)$$

and is thus a measure of tendency for segments in the polymer chain to remember the orientation of adjoining segment in the chain. Since there is no unique parameter which can describe the chain stiffness from flexible polymer to rigid rod-like polymeric chains, the rigidity index on the basis of photoelastic measurement was employed in order to quantitatively describe chain flexibility. However, there is almost

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no effort to be made upon the relationships among the nonlinear viscoelasticity, the fatigue behaviour and the rigidity of molecular chains for polymers though the mechanical properties of polymers depend, to a great extent, on their chain rigidity, for example, the modulus of polymers generally increases with an increase in their chain rigidity¹⁴. In this study, the authors made an attempt to reveal the relationships among nonlinear viscoelasticity, fatigue behaviour and rigidity of molecular chains for polymeric fibres based on the zone nonlinear dynamic viscoelastic analysis, a new approach for the nonlinear dynamic viscoelastic analysis proposed by the authors⁵.

EXPERIMENTAL

Specimens

In order to investigate the effect of polymeric chain rigidity on the nonlinear dynamic viscoelastic characteristics and the fatigue performance for polymeric fibres, five kinds of polymeric fibres with different degrees of rigidity of their molecular chains were used in this study, as shown in Figure 1. Also, Table 1 shows the density, the diameter and the mechanical properties of polymeric fibres used in this study. PVA (poly(vinyl alcohol)), Nylon 6 (poly(ϵ -caprolactam)) and PET (poly(ethylene terephthalate)) are the fibres composed of flexible chain polymers. Vectran (a copolyester of *p*-hydroxybenzoate (HBA) and 2-hydroxy-6-naphthoic acid (HNA)) and Kevlar (poly(*p*-phenylene terephthalamide)) are the fibres composed of rigid chain polymers. In this series of polymeric fibres, PVA, Vectran and Kevlar are in the category of ultrahigh modulus fibres.

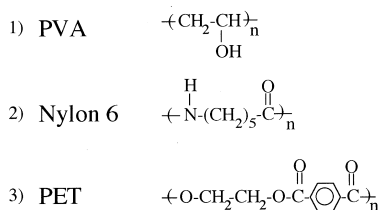
Evaluation of chain rigidity of polymeric fibres

Chain rigidity of polymeric fibres was evaluated based on their photoelastic characteristics^{15,16}. In the case of deformed crosslinked ideal rubber under small elongation, the stress-optical coefficient, *C*, can be given by equation (3)

$$C = \frac{\Delta n}{\sigma} = \frac{2\pi}{45kT} \frac{(\bar{n}^2 + 2)^2}{\bar{n}} (b_1 - b_2)_s \quad (3)$$

where σ , Δn , \bar{n} and *k* are stress, birefringence, average refractive index and Boltzmann's constant, respectively. Also, b_1 and b_2 are the principal polarizabilities of the 'statistical segment' parallel and perpendicular to the contour of the molecular chain. Then, the magnitude of $(b_1 - b_2)_s$ can

1. Polymeric fibers with flexible molecular chains



2. Polymeric fibers with rigid molecular chains

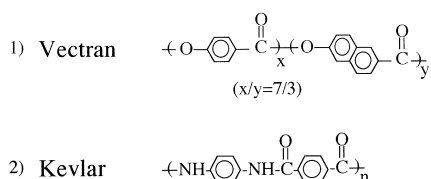


Figure 1 Chemical structures of polymeric fibres used in this study

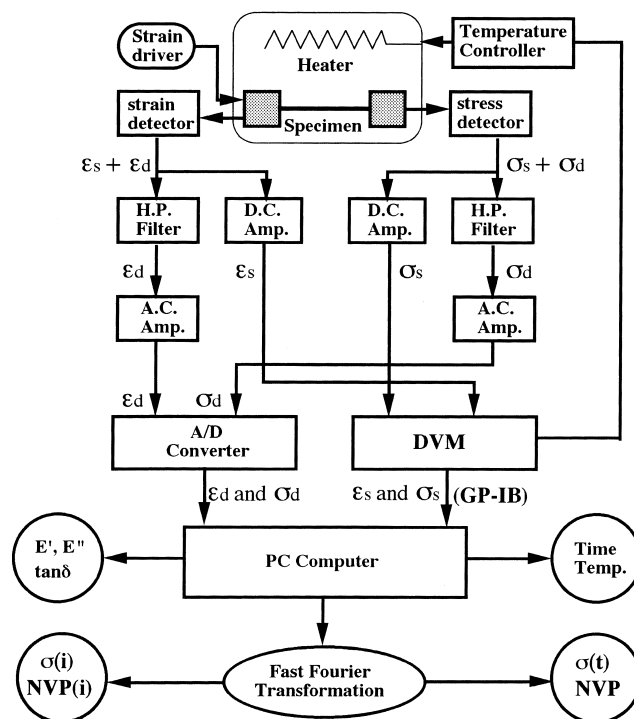


Figure 2 Block diagram of fatigue tester for investigation of nonlinear dynamic viscoelastic properties under cyclic fatigue test

be calculated from the stress-optical relaxation experiments. Also, the difference of the principal polarizabilities in the monomer $(b_1 - b_2)_m$ can be calculated from the polarizabilities of chemical bonds in the monomeric unit^{17,18}. Then, the rigidity index¹⁵, *Z*, for a molecular chain was defined as equation (4)

$$Z = \frac{(b_1 - b_2)_s}{(b_1 - b_2)_m} = \frac{45kT\bar{n}C}{2\pi(\bar{n}^2 + 2)^2(b_1 - b_2)_m} \quad (4)$$

Equation (4) means that one statistical segment is composed of monomer units. Though equation (3) is strictly suitable for ideal rubber, this method to evaluate their chain rigidity has been applied to the uncrosslinked amorphous polymers^{15,19,20}. In this study, the relaxation experiments of stress and birefringence of polymeric fibres were carried out at room temperature under the condition of the initial tensile strain of 3%.

Fatigue tester

Figure 2 shows the block diagram of the fatigue tester which enables the in situ measurement of nonlinear dynamic viscoelasticity during fatigue process²⁻⁵. The specimen of single fibre was placed into a specimen chamber with the temperature controller under dry nitrogen purge. A sinusoidal strain with a variable magnitude of strain amplitude was imposed to the specimen at frequencies of 3.5, 11 and 35 Hz. The signals of the imposed strain and the response stress were separated into the static and the

Table 1 Mechanical properties of the polymeric fibres used in this study

	ρ (g/cm ³)	<i>d</i> (μ m)	σ_b (GPa)	<i>E</i> (GPa)	ϵ_b (%)
PVA	1.30	21	2.5	49	4.3
Nylon 6	1.14	28	0.91	3.9	19
PET	1.39	23	1.1	14	19
Vectran	1.41	23	3.5	74	3.8
Kevlar	1.45	12	3.2	75	3.9

ρ , density; *d*, diameter; σ_b , breaking stress; *E*, tensile modulus; ϵ_b , breaking strain

dynamic components by high-pass filters. The dynamic signals were amplified and converted into digital data with a high-speed 2-channel A/D convertor, then sent to a personal computer and analysed by fast Fourier transformation (FFT).

Nonlinear dynamic viscoelastic analysis⁵

When the uniaxial sinusoidal dynamic strain, $\epsilon(t)$, with angular frequency, ω , as given by equation (5) is imposed to the polymeric specimen, the response stress, $\sigma(t)$, can be expanded by a Fourier series as shown in equation (6).

$$\epsilon(t) = \epsilon_0 \sin(\omega t) \quad (5)$$

$$\sigma(t) = \sigma_1 \sin(\omega t + \delta_1) + \sigma_2 \sin(2\omega t + \delta_2) + \dots + \sigma_j \sin(j\omega t + \delta_j) + \dots \quad (6)$$

where ϵ_0 is the imposed strain amplitude, and σ_1 and δ_1 are the fundamental stress amplitude and phase difference angle, respectively. $\sigma_2, \sigma_3, \dots$, and $\delta_2, \delta_3, \dots$ are the higher harmonic stress amplitudes and the phase difference angles, respectively. The nonlinear viscoelastic parameter, NVP^{2-5} , which represents the degree of nonlinear dynamic viscoelasticity, is defined by equation (7).

$$NVP = \frac{\sigma_2 + \sigma_3 + \dots + \sigma_i + \dots + \sigma_n}{\sigma_1} \quad (7)$$

where the number of higher harmonics, n , was taken into consideration up to 100 since the higher harmonics over 100 were very small and could be ignored.

Zone nonlinear dynamic viscoelastic analysis

Although the sinusoidal dynamic strain is often used to simplify the calculation for the viscoelastic analysis, the sinusoidal strain shows different strain rate during one period of cyclic deformation. For this reason, the nonlinear viscoelastic responses during one cyclic deformation can be expected to exhibit different behaviours in each step of deformation since the nonlinear viscoelastic responses generally depends on the imposed strain rate^{6,8}. However, the NVP given by equation (7) only represents the average degree of nonlinear viscoelasticity during one period of cyclic deformation. In order to investigate the nonlinear viscoelasticity in the different stages or different zones during one period of cyclic deformation, the authors

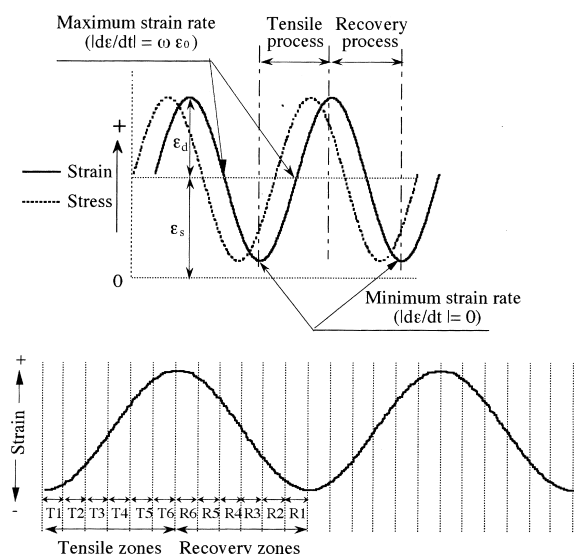


Figure 3 Principle of zone nonlinear dynamic viscoelastic analysis

proposed a new approach based on zone nonlinear dynamic viscoelastic analysis⁵. Figure 3 shows the principle of zone nonlinear dynamic viscoelastic analysis. If one period of cyclic deformation is divided into $2m$ zones (m is an integer), that is, m tensile zones and m recovery zones, m equations for tensile process and another m equations for recovery process can be obtained as given by equation (8).

$$\sigma(i, t) = \sigma_1(i) \sin[\omega t + \delta_1(i)] + \sigma_2(i) \sin[2\omega t + \delta_2(i)] + \dots + \sigma_j(i) \sin[j\omega t + \delta_j(i)] + \dots \quad (8)$$

where i is the zone number such as T3, R4, etc., shown in Figure 3. In this study, each period of cyclic deformation was divided into 12 zones, i.e., six tensile and six recovery zones ($i = T1, \dots, T6, R6, \dots, R1$). Then, the zone nonlinear viscoelastic parameter, $NVP(i)$, which represents the degree of nonlinear dynamic viscoelasticity in the i th zone, is defined as equation (9)

$$NVP(i) = \frac{\sigma_2(i) + \sigma_3(i) + \dots + \sigma_i(i) + \dots + \sigma_n(i)}{\sigma_1(i)} \quad (9)$$

where the number of higher harmonics, n , was also taken into consideration up to 100 as mentioned in equation (7).

The strain rate can be given by equation (10)

$$\frac{d\epsilon}{dt} = \omega \epsilon_0 \cos(\omega t) \quad (10)$$

Therefore, the maximum of absolute value of strain rate appears at $t=0$ and $t=\pi/\omega$, that is, $(d\epsilon/dt)_{\max} = \omega \epsilon_0$, $(d\epsilon/dt)_{\min} = -\omega \epsilon_0$ and the minimum value of strain rate does at $t=\pi/2\omega$ and $t=3\pi/2\omega$, that is, $|(d\epsilon/dt)|_{\min} = 0$. The average strain rate of each zone shown in Figure 3 can be calculated by equation (11).

$$\begin{aligned} \left(\frac{d\epsilon}{dt}\right)_{T1} &= \left(\frac{d\epsilon}{dt}\right)_{T6} = -\left(\frac{d\epsilon}{dt}\right)_{R6} = -\left(\frac{d\epsilon}{dt}\right)_{R1} = 0.250\omega\epsilon_0 \\ \left(\frac{d\epsilon}{dt}\right)_{T2} &= \left(\frac{d\epsilon}{dt}\right)_{T5} = -\left(\frac{d\epsilon}{dt}\right)_{R5} = -\left(\frac{d\epsilon}{dt}\right)_{R2} = 0.683\omega\epsilon_0 \\ \left(\frac{d\epsilon}{dt}\right)_{T3} &= \left(\frac{d\epsilon}{dt}\right)_{T4} = -\left(\frac{d\epsilon}{dt}\right)_{R4} = -\left(\frac{d\epsilon}{dt}\right)_{R3} = 0.933\omega\epsilon_0 \end{aligned} \quad (11)$$

The relationship between the strain rate and the $NVP(i)$ will be discussed in the following section.

RESULTS AND DISCUSSION

Rigidity of a polymer chain

Table 2 shows the photoelastic coefficients, average refractive indices, the difference of the principal polarizabilities in the monomer, $(b_1 - b_2)_m$, and rigidity indices, Z , for PVA, Nylon 6, PET, Vectran and Kevlar fibres. At first, the stress-optical relaxation experiments at room temperature was carried out and then the magnitude of C was

Table 2 Photoelastic coefficients, average refractive indices, polarizability difference, and rigidity indices for polymeric fibres used in this study

Polymer	C (Pa^{-1})	Average refractive index, \bar{n}	$(b_1 - b_2)_m$	Rigidity index, Z
PVA	2.28×10^{-13}	1.50	1.52×10^{-31}	4
Nylon 6	5.53×10^{-13}	1.52	4.62×10^{-31}	3
PET	3.28×10^{-12}	1.58	6.34×10^{-31}	12
Vectran	1.34×10^{-11}	1.66	7.28×10^{-31}	40
Kevlar	1.58×10^{-13}	1.65	7.40×10^{-31}	48

evaluated. The magnitude of Z was calculated on the basis of equation (3). The magnitudes of Z indicate that PVA and Nylon 6 fibres are consisted of flexible molecular chains, whereas Vectran and Kevlar fibres consist of rigid molecular chains. The Z value of PET was between the two kinds of fibres mentioned above. This indicates that a PET has a semi-rigid polymer chain since it contains rigid aromatic rings in its backbone chain.

Effect of rigidity of molecular chains on nonlinear viscoelasticity

Figure 4 shows the variations of the magnitude of NVP with the imposed dynamic strain amplitude for PVA, Nylon 6, PET, Vectran and Kevlar fibres at 303 K after 100 s from the start of fatigue test. It is apparent from Figure 4 that the nonlinear dynamic viscoelastic characteristics of these polymeric fibres were strongly dependent on their chain rigidities, that is, flexible, semi-rigid and rigid chain characteristics. PVA and Nylon 6 with flexible polymer chains exhibited smaller NVP values. On the other hand, Vectran and Kevlar with rigid polymer chains exhibited a higher NVP value than PET, PVA and Nylon 6. Also, with an increase in the magnitude of imposed strain amplitude, the NVP values for the Vectran and Kevlar with rigid chain showed a remarkable increase in comparison with that of the flexible ones. The semirigid PET exhibited an intermediate behaviour between these two characteristic fibres. Then, it is reasonably concluded that the nonlinear dynamic viscoelasticity of polymeric fibres was strongly affected by their chain rigidity.

Figure 5 shows the relationships between magnitude of NVP and rigidity indices for polymeric fibres. The NVP value did not show a remarkable change with an increase in the chain rigidity under smaller deformation conditions. However, it increased steeply with the chain rigidity under large cyclic deformation conditions. Therefore, it seems reasonable to conclude that the nonlinear viscoelasticity of polymeric fibres was very slight, and almost independent on the rigidity of molecular chains under smaller deformation conditions because the linear viscoelastic behaviour might be predominant in such small strain amplitude. By contrast, the nonlinear viscoelasticity of polymers showed a great dependence on their rigidity of molecular chains under larger cyclic straining amplitude.

As many reports have pointed out^{21–24}, the nonlinear dynamic viscoelasticity of polymers depends, to a large extent, on the degree of deformation. A remarkable nonlinear dynamic viscoelasticity appeared under large cyclic deformation conditions because the irreversible structural changes were induced by the large-scale forced cyclic deformation^{21–24}. In the case of flexible chain polymer, the imposed cyclic deformation can be easily

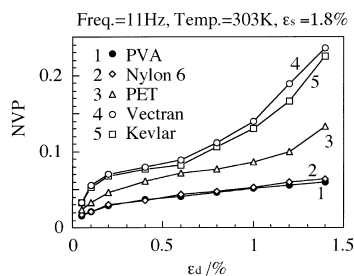


Figure 4 Relationships between NVP and the magnitude of imposed strain amplitude for PVA, Nylon 6, PET, Vectran and Kevlar fibres at 303 K after 100 s from the start of fatigue test under static strain of 1.8%

absorbed by the local or long-scale conformational rearrangement of molecular chains in an amorphous phase. In the case of rigid chain polymer, however, since the number of possible chain conformations decreases with an increase in the rigidity of molecular chains, the imposed cyclic deformation, especially the large one, could not be simply absorbed by the conformational rearrangement, that is to say, the slippage among rigid molecular chains would be induced by such large imposed cyclic deformation. This might be one of the reasons that the rigid chain polymers exhibited a greater nonlinear dynamic viscoelastic behaviour than the flexible ones.

Effect of rigidity of molecular chains on zone nonlinear viscoelasticity

Figure 6 shows a comparison of the zone nonlinear dynamic viscoelastic behaviour for PVA, Nylon 6, PET, Vectran and Kevlar fibres at 303 K after 100 s. from the start of the fatigue test. The zone nonlinear dynamic viscoelastic behaviour exhibited a great dependence on their chain rigidity for polymeric fibres, especially in the recovery zone. In the case of flexible chain polymers such as nylon 6 and PVA, the NVP(i) value in each zone was relatively small, and the NVP(i) behaviour in the recovery zones did not show a great difference with that in the tensile ones. In the case of rigid chain polymers such as Vectran and Kevlar, however, the NVP(i) value in the recovery zones was much larger than tensile zone, particularly in the recovery zones with higher strain rate, such as zones R3, R4 and R5. Also, it should be noticed that at the initial stage of a period of cyclic deformation, i.e. in zones T1–T4, the NVP(i) for each polymeric fibre showed almost the same value, that is to say, the nonlinear dynamic viscoelastic behaviour was almost independent on the rigidity of molecular chains in these stages. However, at the later stages of T5 and T6, the nonlinear dynamic viscoelastic behaviour exhibited a great dependence on the rigidity of molecular chains. According to the present data, we cannot yet give a satisfactory understanding on such a relationship between zone nonlinear dynamic viscoelastic behaviour and the rigidity of molecular chains. However, it seems reasonable to consider that the slight nonlinear dynamic viscoelastic behaviour might be still comparable to the linear one at the initial stage of a period of cyclic deformation due to the small magnitude of the imposed strain amplitude.

Also, it should be noticed that the maximum NVP(i) value was observed in zone R4, particularly under the larger strain amplitude and higher strain rate conditions, although the strain rate of zone R4 was equal to that of zone R3 at the macroscopic level. This indicates that the relaxation of polymers might play an important role here. Since at the initial stage of relaxation, the relaxation rate of molecular

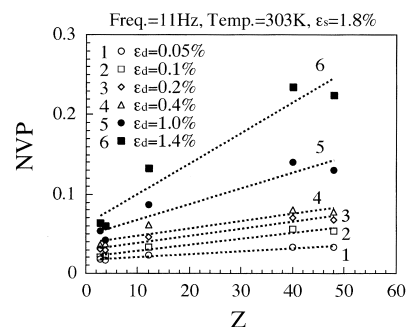


Figure 5 Relationships between rigid index of molecular chains, Z , and NVP under various imposed strain amplitudes at 303 K after 100 s from the start of fatigue test

chains was faster than that at the later stage, the movement of molecular chains during zone R4 would be faster than that during zone R3. For this reason, the actual strain rate of zone R4 was greater than that of zone R3 at the microscopic level. So the nonlinear viscoelastic behaviour in zone R4 was more remarkable than that in zone R3 for polymeric fibres.

Effect of rigidity of molecular chains on fatigue performance

Figure 7 shows the relationships between the average value of NVP during fatigue test and fatigue lifetime for the

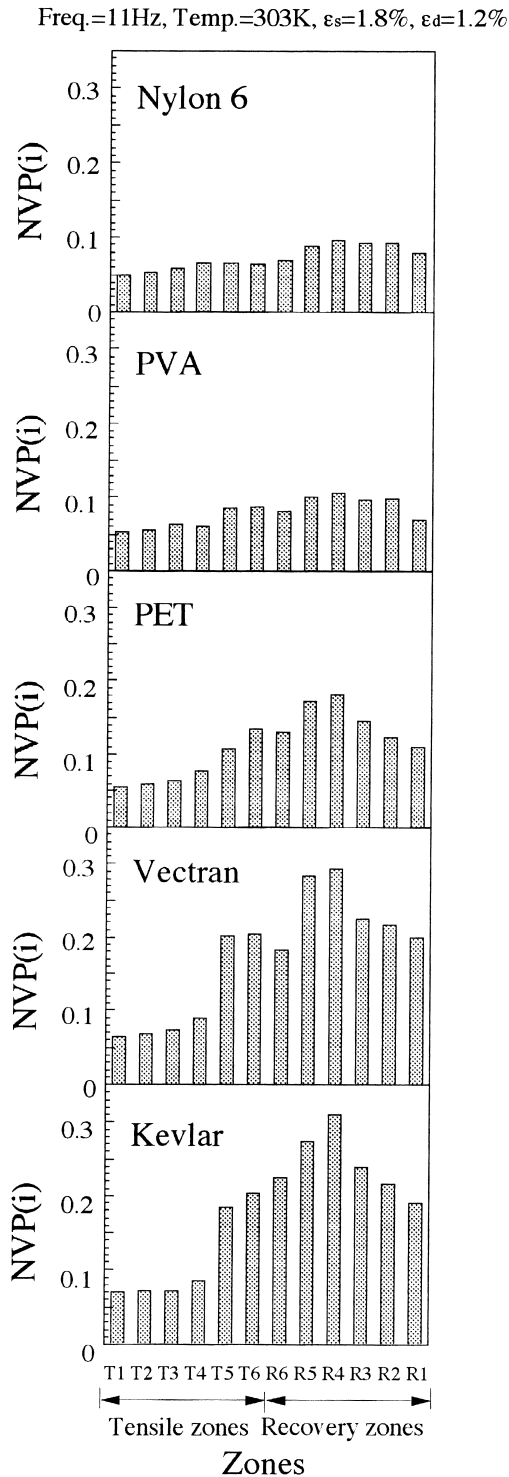


Figure 6 Variation of NVP(i) with deformation zones for PVA, Nylon 6, PET, Vectran and Kevlar fibres under static strain of 1.8% and the dynamic strain amplitude of 1.2% at 303 K after 100 s from the start of fatigue test

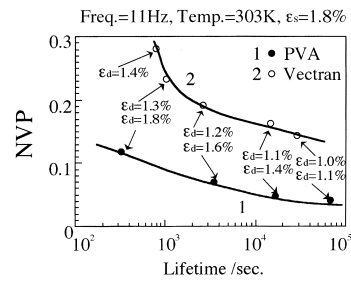


Figure 7 Relationships between NVP and fatigue lifetime for Vectran and PVA fibres under various imposed strain amplitudes at 303 K

Vectran and the PVA fibres under various imposed strain amplitudes at 303 K. The fatigue lifetime of the PVA fibre was much longer than that of the Vectran fibre, which exhibited a remarkable nonlinear viscoelasticity under the same magnitude of imposed strain amplitude.

It is apparent from Figure 7 that the fatigue lifetime became shorter with an increase in NVP values in both the Vectran and the PVA fibres. Since the large NVP value corresponds to the fact that the irreversible structural changes occurred more frequently during cyclic deformation, the fatigue deterioration induced by such irreversible structural changes would proceed faster, and result in a shorter fatigue lifetime with an increase in NVP value. On the other hand, in the case of rigid chain polymers, they showed a rather greater nonlinear viscoelasticity and a much poorer fatigue performance due to the greater ease of the more remarkable irreversible structural change, since the imposed strain could not be dissipated elastically in a similar fashion to the flexible fibres. As discussed in our previous paper⁵, the crystalline polymers are, in general, composed of a relatively hard crystalline region and a relatively soft amorphous region. This indicates that the imposed dynamic strain is predominantly absorbed by the soft amorphous region rather than by the hard crystalline region^{23,24}. In the case of rigid chain polymers, since their amorphous regions consist of rigid molecular chains which lack the flexibility or elastic deformation, the large deformation could not be easily absorbed as in the case of the flexible ones^{25,26}. Therefore, the rigid chain polymeric fibres exhibited a remarkable nonlinear viscoelastic behaviour and poor fatigue performance.

Figure 8 shows the relationships between average value of NVP during fatigue test and the rigidity indices of molecular chains for the polymeric fibres under the same magnitudes of static and dynamic strains. As shown in Figure 8, the fatigue lifetime became shorter with an increase in the rigidity of molecular chains for polymeric fibres. It is reasonable to consider that with an increase in the rigidity of molecular chains, the chain entanglement density became lower, and the interaction among molecular

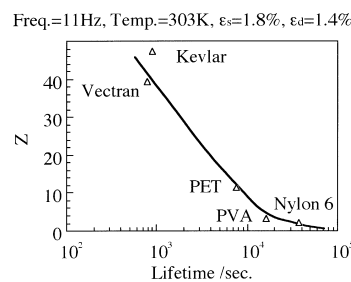


Figure 8 Relationship between rigidity index of molecular chains, Z, and fatigue lifetime for polymeric fibres under static strain of 1.8% and the dynamic strain amplitude of 1.4% at 303 K

chains became weaker^{8,27}. When a large cyclic deformation was imposed to the specimen with more rigid molecular chains, the internal friction caused by the slippage among molecular chains would be more prominent, and the fatigue deterioration induced by such internal friction would be more remarkable. For this reason, the fatigue performance became poorer with an increase in the chain rigidity for polymeric fibres.

CONCLUSION

The effect of main-chain rigidity on the nonlinear dynamic viscoelasticity and the fatigue performance for polymeric materials was discussed in this paper. The polymeric fibres with rigid molecular chains showed more remarkable nonlinear dynamic viscoelasticity and poorer fatigue performance than those with flexible molecular chains. Also, the zone nonlinear dynamic viscoelastic analyses were successfully applied to the analysis of nonlinear viscoelasticity and fatigue performance. The results from the zone nonlinear dynamic viscoelastic analyses revealed that the nonlinear viscoelasticity of polymeric fibres was predominantly induced in the recovery process rather than in the tensile process during one period of cyclic deformation, and the more remarkable nonlinear viscoelastic behaviour was exhibited in the zone with higher strain rate. The facts that polymeric fibres with rigid molecular chains exhibited remarkable nonlinear viscoelasticity and poor fatigue performance were considered due to the following reasons: (1) since the possible number of chain conformations became less with an increase in the chain rigidity, the large magnitude of imposed strain could not be absorbed simply by the conformational rearrangement in molecular chains; and (2) the physical chain entanglement density became lower with an increase in the rigidity of molecular chains. This indicates that the irreversible structural changes, which lead to the remarkable nonlinear viscoelasticity and the poor fatigue performance, might occur more easily or more frequently during a cyclic deformation in the case of rigid chain polymers.

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