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Fatigue Behavior of Segmented Polyurethanes under Repeated Strains

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Fatigue time dependences of dynamic storage modulus (E') and loss modulus (E") of three kinds of segmented polyurethaneures (SPUs) and their blend were investigated. For component SPUs, a plateau-like region has been observed in the E' vs. fatigue time curve at intermediate fatigue times, but the E' vs. fatigue time curve of the blend has shown a monotonical decrease in almost all the fatigue time region. This difference is originated from the diffrence of the higher order structure between the component SPUs and the blend.

KEYWORDS : Segmented polyurethane / Fatigue behavior / Dynamic modulus / Stress-strain behavior

INTRODUCTION

It is well known that segmented polyurethane (SPU) has been widely put to medical uses, such as artificial hearts and the valves.[1] Studies on the tensile and fatigue properties as well as blood compatiblity are very important to use materials for biomedical purposes. Although several research groups[2,3] have reported the fatigue properties of polyurethanes, the studies on the fatigue properties of SPUs are still a few at present. As well known,[2-4] SPUs are multiblock copolymers composed of soft and hard segment blocks, and form a two-phase structure where hard segment domains act as physical crosslinks. We have studied[5] the structure and viscoelastic properties of SPUs and their blends by using three kinds of samples differing in the molecular weight of poly(tetramethylene glycohol) (PTMG) of the soft segment block (M_s). The 1:1 blend made of the components with the highest and lowest M_s have a structure where two different networks coexist.[5] Each network is composed of hard and soft segment domains, and both networks are interwoven similar to interpenetrating polymer networks (IPNs).[5,6] Since the mechanical and viscoelastic properties of SPUs are closely related to the morphology, the 1:1 blend might be expected to show different fatigure behavior compared with those of the component SPUs. It is very intersting to investigate how the higher order structure affects the fatigue properties from the academic point of view. For biomedical applications, this study is also important to obtain the information for molecular design of the SPUs with good fatigue properties. In this study, we have investigated fatigue properties of segmented

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polyurethaneureas (we also abbriviate these as SPUs) and the blend specimen.

EXPERIMENTAL

Three kinds of SPUs differing in M_s were supplied from Toyobo, Co. as dimethylformamide (DMF) solutions. The SPUs are multiblock copolymers composed of hard and soft segment blocks.[2-4] The soft segment block is composed of a sequence of PTMG and 4,4'-diphenylmethane diisocyanate (MDI), and the hard segment block in a sequence of MDI and 1,2-diaminopropane (DAP). The sample code and the number-average molecular weight of PTMG in the soft segment block (M_s) are summarized in Table I, together with those of blend sample SPU-1/5(1/1). SPU-1 has the lowest M_s and SPU-5 the highest M_s. SPU-1/5(1/1) is 1:1 (by weight) blend of SPU-1 and SPU-5, and the mixing was carried out in solution. The film specimens for mechanical measurements were prepared from the solution by cast method. The samples with dimension of 10 mm×5 mm×(0.1~0.3 mm) were used for tensile tests. Stress (σ)-strain (ε) curves of SPUs were measured by using a Orientec tensile tester (RTM 250) with crosshead speed (v) of 50 mm/min at 25°C. The fatigue time dependences of the dynamic Young's modulus (E') and loss modulus (E") were measured by using a Rheometrics Solids Analyzer (RSA II) at angular frequency (ω) of 100 s^{-1} at 30°C. Dynamic strain amplitude superimposed on the static extension was applied to the sample with dimension of 2 mm×1 mm×(0.1~0.3) mm. The constant force of 0.98 N was applied to samples for the static extension. The extension rate (λ_d) in dynamic oscilation was 1.09, 1.25 and 1.44.

Table I. Sample code and number-average molecular weight of poly(tetramethylene glycohol) (PTMG) of soft segment block (M_s) of segmented polyurethaneureas (SPUs).

Sample	M_s
SPU-1	850
SPU-3	1350
SPU-5	2000
SPU-1/5(1/1)	1270

RESULTS AND DISCUSSION

Stress-strain curves of SPUs

Fig. 1 shows the stress (σ)-strain (ε) curves of the component SPUs. Here, ε was calculated with the extension rate (λ_s) by $\varepsilon = \ln\lambda_s$. The true stress σ, was calculated with λ_s, force (F) and initial cross-sectional area (S_0) by $\sigma = F\lambda_s/S_0$. As seen from the figure, each curve falls on a line with slope of unity at low strains. As stated previously, M_s of SPU-5 is the highest, and M_s decreases in order of SPU-3 and SPU-5. The initial Young's modulus (E_0), which can be obtained as a stress value on the extrapolated straight line at $\log\varepsilon = 0$, increases with decreasing M_s. The value of E_0 for each sample agrees well with

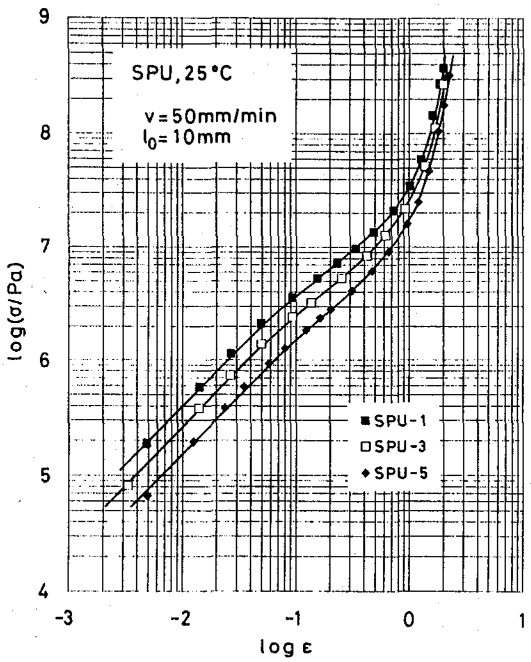

Fig. 1. Stress (σ)-strain (ε) curves of SPU-1, SPU-3 and SPU-5.

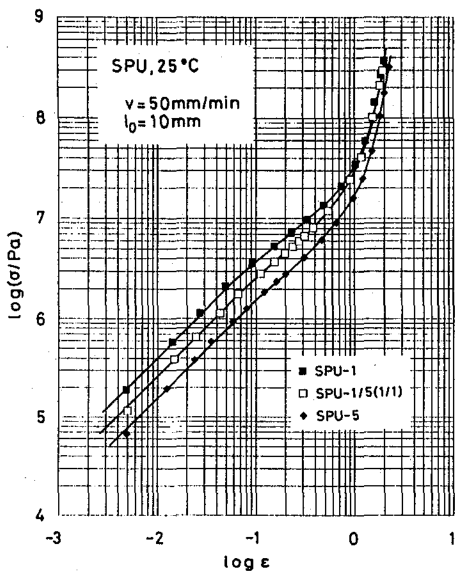

Fig. 2. Stress (σ)-strain (ε) curves of SPU-1, SPU-5 and the blend SPU-1/5(1/1).

the value of dynamic Young's modulus (E') in the leathery plateau region.[5] The slope of each curve slightly decreases at middle starins, but the slope becomes steep in the high strain region. The shape of the σ-ε curve of each specimen is almost identical. In Fig. 2, the σ-ε curve for the blend sample SPU-1/5(1/1) is shown together with the curves for the component SPUs. As seen in Table I, M_s of SPU-3 and SPU-1/5(1/1) was almost identical to each other, but the morphology of the two specimens is quite different: SPU-3 has the two-phase structure where hard segment domains are dispersed in the continuous soft segment phase, while the blend has an IPN-like structure composed of two interpenetrating networks, both of which are composed of hard and soft segment domains.[5] The σ-ε curve of the blend lies between two curves for the components in the wide strain range, although the curve overlaps with that of SPU-1 at very high strains. The value of E_0 of the blend agrees well with the plateau value of E', and is almost the same as that of SPU-3 having almost the same M_s as the blend. These show that the morphological difference between SPU-3 and SPU-1/5(1/1), i.e., the difference in the number of networks existing in the system, affects neither the shape of the σ-ε curve nor the value of E_0, but E_0 clearly depends on M_s of the specimens.

Fatigue properties of SPUs

Figs. 3 and 4 respectively show plots of E' and E" against fatigue time (or repetition number, n) for SPU-1 measured at dynamic strain amplitudes (λ_d-1) of 0.09, 0.25 and 0.44.

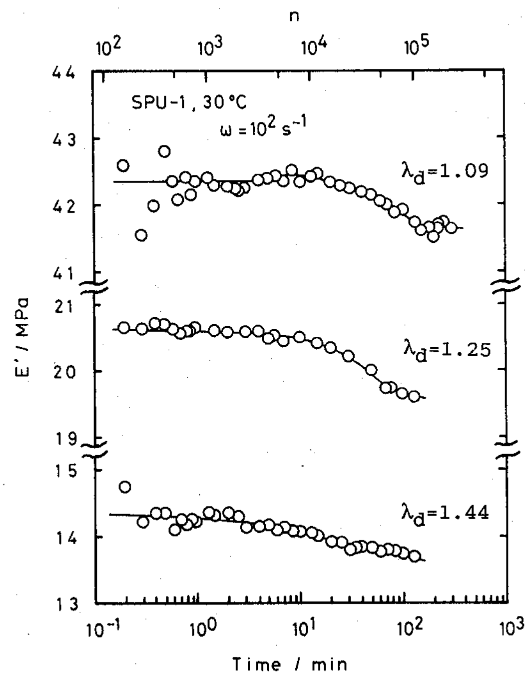

Fig. 3. Fatigue time dependence of dynamic Young's modulus (E') of SPU-1 at dynamic strain amplitudes (λ_d-1) of 1.09, 1.25 and 1.44.

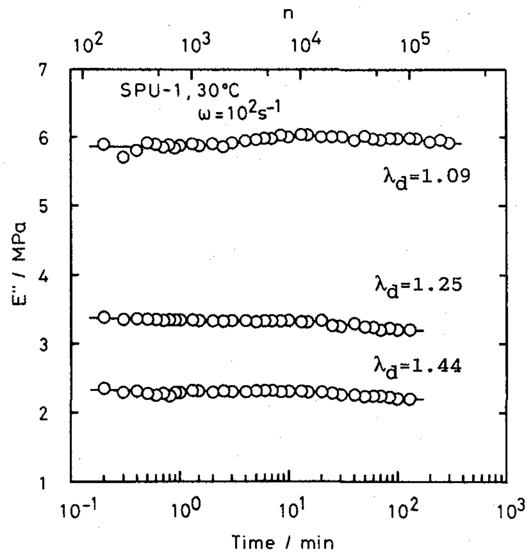

Fig. 4. Fatigue time dependence of dynamic loss modulus (E'') of SPU-1 at dynamic strain amplitudes (λ_d-1) of 1.09, 1.25 and 1.44.

The magnitude of E' at early fatigue times decreases with increasing λ_d. As shown in Fig. 1 (and also in Fig. 2), SPU-1 shows nonlinear σ-ε behavior at ε higher than 0.1, which corresponds to λ_s=1.1. In the early stage of the nonlinear region, the increase of σ with ε (the slope of the curve) is lower than that in the linear region at low ε. As mentioned before, constant static force of 0.98 N was applied to each sample in this experiment. Although the stress level of each sample depends on the cross-sectional area, we can estimate the order of magnitude of σ to be 10^7 Pa, which corresponds to λ_s of 1.4. The application of the static force must move the σ-ε relation of the specimen to the nolinear region where the ε dependence of σ becomes weak. This implies that the decrease of E' at short fatigue times with λ_d is caused by the increase of nonlinear character in σ-ε relation. As shown in Fig. 3, the value of E' with λ_d=1.09 is almost constant in the initial stage of the fatigue test, although the data points are a little scattered. At fatigue time of about 10 min, E' starts to decrease. The similar behavior is observed for the E' vs. fatigue time curves with λ_d=1.25 and λ_d=1.44. The degree of the decrease of E' with λ_d=1.09 at long times is almost identical to that with λ_d=1.25. However, the degree of the decrease of E' with λ_d=1.44 is comparably small. The decrease of E' would be closely related to a structural change of the samples as will be discussed later. The breakdown of the structure at long fatigue times at larger repeated strains is reduced, because the breakdown of structure has already occured in the initial stage at short times. Fig. 4 shows that no effect of fatigue can be seen in E'' vs. fatigue time plots of the samples.

Fig. 5 shows fatigue time dependence of E' for the component SPUs with λ_d=1.25. The shape of the curves of SPU-3 and SPU-5 is quite different from that of SPU-1 discussed above. The E' vs. fatigue time curve of SPU-3 shows a rapid decrease at short times, and

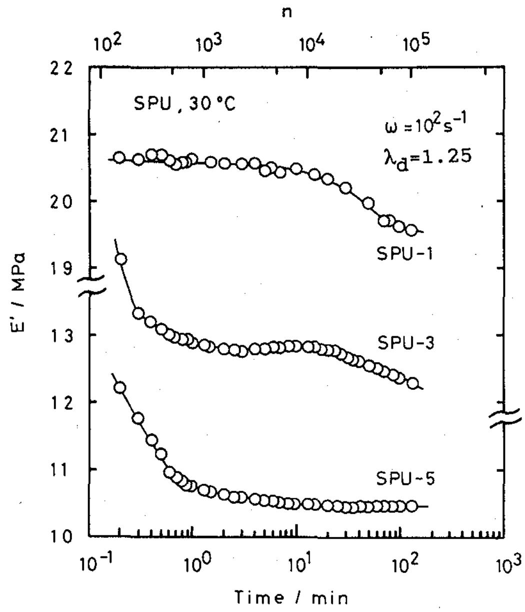

Fig. 5. Fatigue time dependence of dynamic Young's modulus (E') of SPU-1, SPU-3 and SPU-5 at dynamic strain amplitude (λ_d-1) of 1.25.

a broad peak in the intermediate time region and a decrease of E' again at long time are observed. On the other hand, the curve of SPU-5 shows a rapid decrease of E' in the short time region, and the slope of the curve becomes very small at long times. The rapid decrease of E' in the short time region can be observed in SPU-3 and SPU-5, while the decrease is not observed for SPU-1. In the time region up to 10 min, the subdivision process of the hard segment domains into smaller domains continues to occur.[3] In the initial stage of fatigue tests, large hard segment domains are subdivided into small domains. The decrease of E' at short times observed for SPU-3 and SPU-5 corresponds to the breakdown of large domains. However, when the breakdown of the hard segment domains proceeds to some extent, the rate of the subdivision of the hard segment domains becomes slower so long as constant strain amplitude is imposed on the system. The slow rate range of sudivision process corresponds to the plateau-like region in modulus-fatigue time curves observed for all component SPUs. It is suggested that the initial drop of E' must exist for SPU-1, although the drop was not actually observed in Fig. 3 (nor in Fig. 5). As will be discussed below, the two-phase structure of SPU-1 is not so orderly as those of SPU-3 and SPU-5. This might imply that the the breakdown of the hard segment in SPU-1 will occur rapidly compared with those of SPU-3 and SPU-5, and then the decrease occurs at times shorter than the time scale measured by the experiments (~0.1 min). The decrease of E' in the long time region ovserved in SPU-1 and SPU-3 may be attributed to the effect of the phase mixing process between smaller hard and soft segment domains.[2,3] The degree of phase mixing of as-cast film decreases in order of SPU-1, SPU-3 and SPU-5, since the degree of phase mixing between hard and soft segment domains decreases with increasing M_s.[2-4]

SPU-5 has the most orderly two-phase structure. This suggests that the phase mixing followed by the subdivision process is difficult to occur for SPU-5. The reason why the decrease in the long fatigue time region is not observed in the experimental time scale for SPU-5 is due to the slow breakdown of the hard segment domians because of their tight phase-separated structure composed of the hard and soft segment domains. In the case of SPU-3, the degree of the phase separation lies between those of SPU-1 and SPU-5, and therefore the decrease of E' is observed in both early and late stages of the fatigue experiment. Fig. 6 shows E" vs. fatigue time curves of SPUs with λ_d=1.25. Although a decrease of E" is observed in the early stage of fatigue time for SPU-3, the curve shows almost constant value at long times. E" of SPU-1 and SPU-5 shows no change in the values over an entire time range examined here.

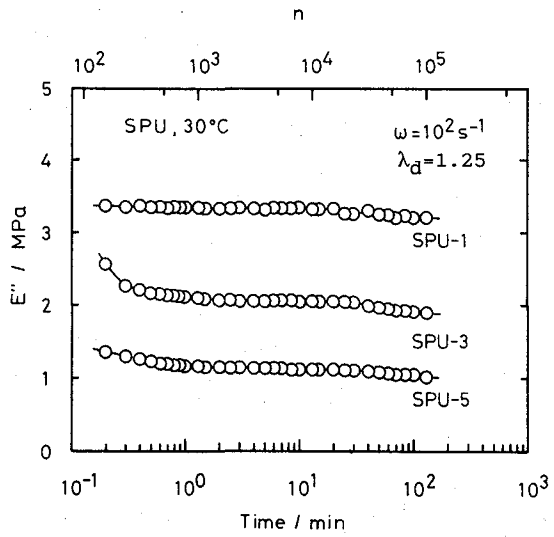

Fig. 6. Fatigue time dependence of dynamic loss modulus (E") of SPU-1, SPU-3 and SPU-5 at dynamic strain amplitude (λ_d-1) of 1.25.

The fatigue time dependence of the blend sample SPU-1/1(1/1) is shown in Fig. 7 together with those of the component SPUs. The shape of the curve of E' vs. fatigue time is quite different from those of component SPUs. Furthermore, the shape also differs from that of SPU-3 which has almost the same M_s as the blend. The value of E' of the blend decreases rather steeply with fatigue time up to the fatigue time of about 30 min. The small peak appears on the E' vs. fatigue time curve at about fatigue time of 50 min, and E' again decreases with further increase of fatigue time. How the higher order structure affects the fatigue behavior of SPUs can be estimated by the comparison of the curve of the blend with that of SPU-3. The both have almost the same M_s but the morphology of SPUs is different: The blend has an IPN-like structure comprising two component SPUs, both of which are consisted of the hard and soft segment domains,[5] while SPU-3 is composed of a sigle network. Although a peak is observed for the both samples, the peak position is different from each other. In addition, the decrease of E' is observed separately in the

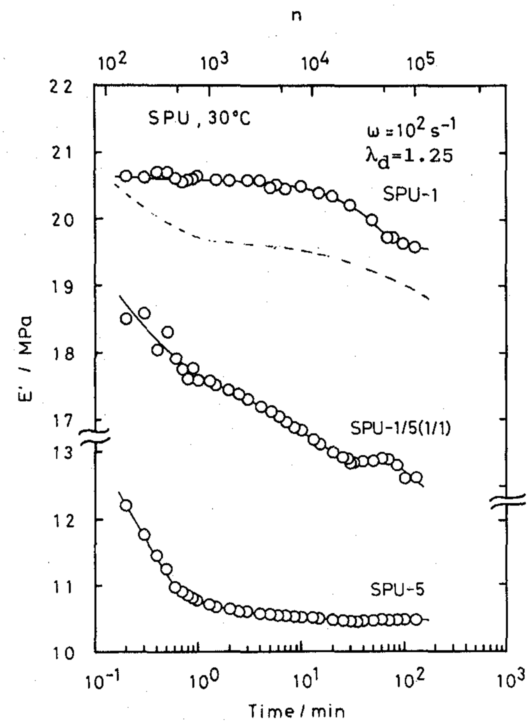

Fig. 7. Fatigue time dependence of dynamic Young's modulus (E') of SPU-1 and SPU-5 and the blend SPU-1/5(1/1) at dynamic strain amplitude (λ_d-1) of 1.25. Dashed curve represents the average value of E' of SPU-1 and SPU-5. The curve is shifted upward by 4 MPa.

short and long time regions for SPU-3, but the E' curve of the blend shows a monotonical decrease over almost all the time range. These diffrences will be originated from the diffrence of the higher order structure between two SPUs. The dashed line in Fig. 7 shows the fatigue time dependence of average value of E' for SPU-1 and SPU-5. The curve is shifted upward by 4 MPa. By comparing the calculated E' vs. fatigue time curve with that of SPU-3 in Fig. 5, one can see that the E' vs. fatigue time curve of SPU-3 is almost identical to the calculated curve. This is reasonable because the fatigue behavior appeared in E' vs. fatigue time curve is mainly controlled by M_s through the degree of the phase separation between the hard and soft segment domains for the component SPUs, as discussed before. However, the shape of the curve for the blend is quite different from that of the calculated curve. The monotonical decrease of E' curve of the blend sample will be caused by delaying of the decrease of E' of the components at short times and also shortening of the decrease of E' of the components at long times. This delaying and shortening will be due to the interaction between two networks exsiting in the blend. In Fig. 8 the E'' vs. fatigue time curves for the blend and their component SPUs are shown. The curves of the components shows constant values, while the curve of the blend shows a gradual decrease in the whole range of faitigue time. The shape of E'' curve of the blend is also different from that of SPU-3.

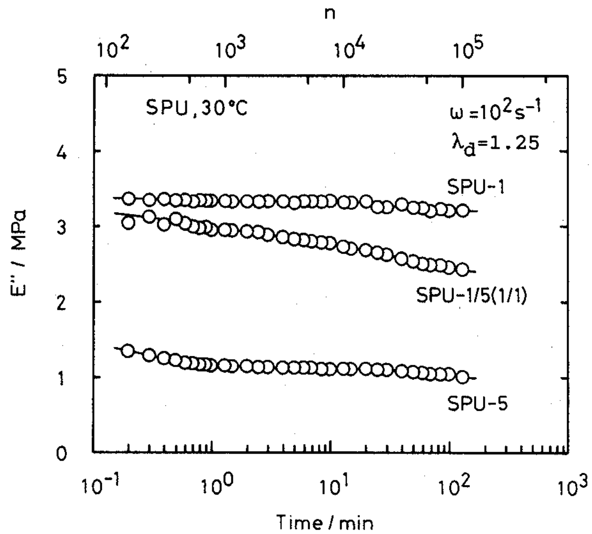

Fig. 8. Fatigue time dependence of dynamic loss modulus (E") of SPU-1 and SPU-5 and the blend SPU-1/5(1/1) at dynamic strain amplitude (λ_d-1) of 1.25

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