

# Effects of deformation on the viscoelasticity of rubber

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It is a powerful method of investigation on the glass transition to control the relaxation time by a variable besides temperature. We have employed the tensile strain as a parameter to experimentally control the relaxation time of the system, and have chosen the rubber as a material because of its large deformability and nonfluidity[1]. The viscoelastic properties under deformation also serve important information in analyzing the mechanical behaviour of rubber upon large deformation up to fracture. In this study, the dynamic mechanical measurements are carried out on the stretched samples and the dependence of relaxation properties on deformation is discussed.

The material used is vulcanized rubber of synthetic cis-1, 4 polyisoprene kindly supplied by Toyo Tire & Rubber Co., Ltd. The samples are uniaxially stretched at 30°C up to the strain  $\gamma = 1.05 \sim 5.0$  and kept fixed afterwards. For  $\gamma \leq 3$ , the samples are cooled at 1K/min, while  $\gamma = 4.0$  and 5.0, they are quenched to -40 and -50°C, respectively, to prevent from crystallization before measurements, and then cooled at 1K/min. Dynamic mechanical measurements are performed with Rheogel-E4000(UBM Co., Ltd.) in a nitrogen gas atmosphere. The dynamic strain of small amplitude of the multiplexing frequencies  $f = 1, 2, 4, \dots, 256$  Hz is superposed on static strain  $\gamma$ . The complex Young's modulus  $E^*$  under deformation is defined by the ratio of the change in true stress to the change in strain, and the complex tensile compliance, by  $D^* = 1/E^*$ , and they are calculated assuming incompressibility.

Figure 1 shows the variation with strain of the temperature dependence of  $E^*$ ,  $D^*$  and  $\tan \delta$  at 16Hz on heating at 1K/min. The effect of crystallization during the measurements was observed only for  $\gamma = 5.0$  above -40°C. The real part of Young's modulus  $E'$  in the glassy state is about 4GPa with little dependence on strain (Fig.1a), while that in the rubbery state increases with increasing strain from about 1MPa for  $\gamma = 1.05$  to about 10MPa for  $\gamma = 4.0$ , as a result of well-known rubber elasticity. The temperature at which the imaginary part of Young's modulus  $E''$  reaches a maximum, about -56°C, and the maximum value of  $E''$  are almost independent of strain (Fig.1b). On the other hand, both the maximum temperature and the maximum value for  $D''$  decrease with increasing strain. These results indicate that the representative relaxation time  $\tau_X =$

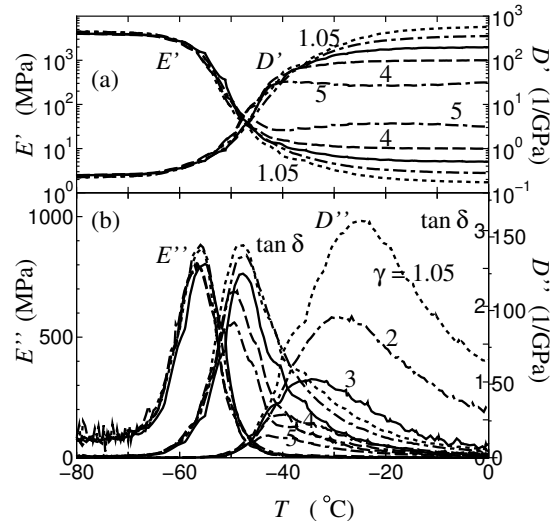


Figure 1: Temperature dependence of (a)  $E'$  and  $D'$ , (b)  $E''$ ,  $D''$  and  $\tan \delta$  for  $\gamma = 1.05 \sim 5.0$  at 16Hz in the heating process at 1K/min.

$\tau(E'')$  hardly depends on strain and that the representative retardation time  $\tau_D = \tau(D'')$  decreases with strain at a given temperature.

For a single relaxation time system, the relation among the unrelaxed modulus  $E_U = E(f \rightarrow \infty)$ , the relaxed modulus  $E_R = E(f \rightarrow 0)$  and the characteristic time is given by  $\tau_D = \frac{E_U}{E_R} \tau_X$ ,  $\tau_\delta = \sqrt{\frac{E_U}{E_R}} \tau_X$  (1), where  $\tau_\delta = \tau(\tan \delta)$ . In the present system, the ratio of  $E_U$  to  $E_R$  is about  $10^3$  and decreases with increasing strain, but the relation (1) holds only approximately because of the distribution of relaxation times and its asymmetric distribution. If we consider a viscoelastic model composed of a spring with modulus  $E_R$  and the generalized Maxwell model in parallel,  $\tau_X$  is given by the Maxwell elements, and  $\tau_D$ , approximately given by the combination of  $E_R$  and the Maxwell elements according to eq.(1). The results shown above can be interpreted by assuming that the Maxwell elements are not affected by strain but the rubber modulus  $E_R$  increases with increasing strain.

## References

- [1] Y. Miyamoto et. al., Phys. Rev. Lett. **88** (2002) 225504.