Supplementary Information (SI) for Soft Matter.
This journal is © The Royal Society of Chemistry 2025

Electronic Supplementary Information

Impact of Cross-linking on the Time-temperature Superposition of Creep Rupture in Epoxy Resins

Atsuomi Shundo,[a]* Mika Aoki,[b] Satoru Yamamoto,[b] and Keiji Tanaka[a,b,c]*

[a] *Department of Applied Chemistry, Kyushu University, Fukuoka 819-0395, Japan*

[b] *Center for Polymer Interface and Molecular Adhesion Science, Kyushu University, Fukuoka 819-0395, Japan*

[c] *Department of Automotive Science, Kyushu University, Fukuoka 819-0395, Japan*

Contents

1. Stress-strain curves from tensile testing.

Fig. S1 shows the stress-strain (S−S) curves for (a) ER12, (b) ER6, and (c) ER2 at various temperatures ranging from 358 to 438 K. For all samples, the S−S curves exhibited initial elasticity, yielding, necking, and strain-hardening regions before rupture at lower temperatures. As the temperature increased, the yielding and necking regions became less pronounced. At higher temperatures, the stress initially increased with strain, reached a plateau or became less distinct, and then increased again before rupture. Such behavior is commonly observed in rubbery materials.[S1−S4] Notably, the rupture strain decreased in the order of ER12 > ER6 > ER2. This trend can be explained by considering that, as the diamine length, corresponding to the distance between cross-linking points, decreases, the population of chains in an extended state increases, making the chains more susceptible to scission.[S5−S7]

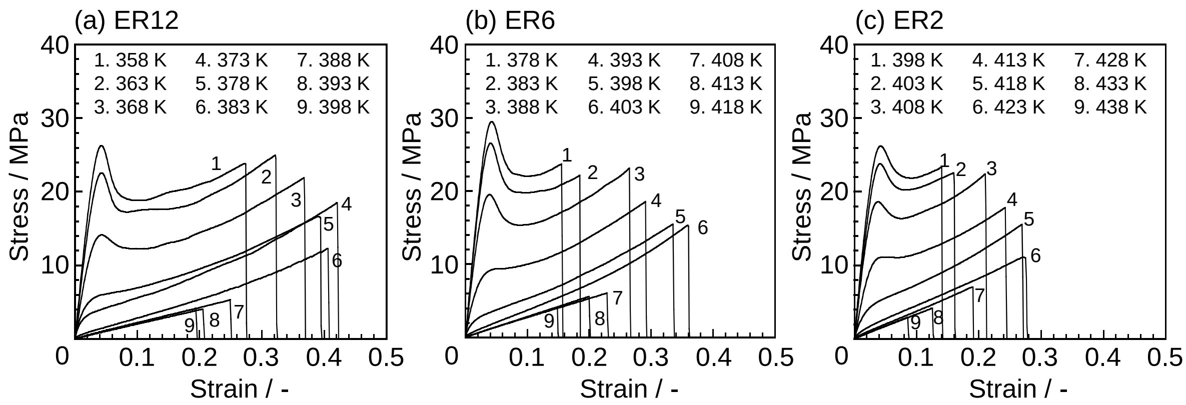

Fig. S1 Stress-strain curves for (a) ER12, (b) ER6 and (c) ER2 at various temperatures.

2. Time-domain curves of creep compliance.

Fig. S2 shows the time dependence of creep compliance, $J(t)$, for (a) ER12, (b) ER6, and (c) ER2 at various temperatures. At low temperatures, $J(t)$ for all samples initially remained almost unchanged over a certain period before starting to increase with time. As the temperature increased, the induction period disappeared and $J(t)$ increased steadily over time, eventually reaching a plateau. At higher temperatures, the $J(t)$ values were markedly higher and became independent of time. By horizontally and vertically shifting the high-temperature time-domain data to align with the data at the reference temperature (the glass transition temperature in this study), master curves were constructed, as shown in Fig. 2 of the main text.

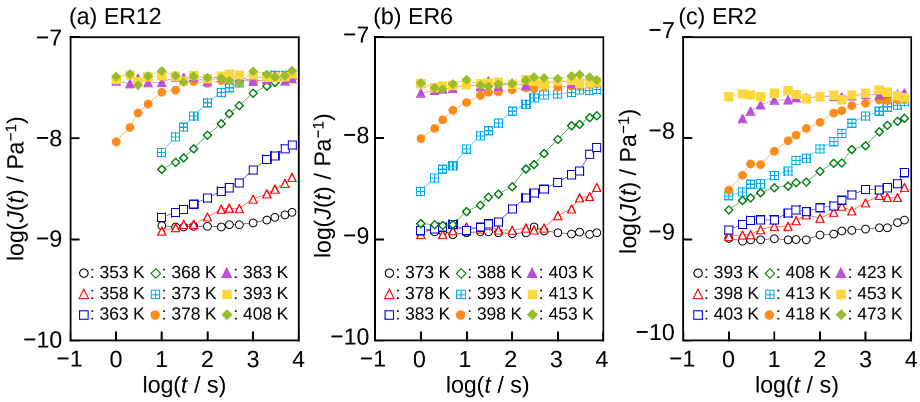

Fig. S2 Time dependence of $J(t)$ for (a) ER12, (b) ER6 and (c) ER2 obtained at various temperatures.

3. Rupture time plotted against imposed stress.

Creep tests were conducted under high stress levels, exceeding the linear response regime. The $J(t)$ value increased continuously until the specimen ruptured, as shown in Fig. 4 of the main text. The rupture time (t_{rp}) was acquired at various temperatures. Fig. S3 shows the relationship between t_{rp} and the imposed stress (σ) for (a) ER12, (b) ER6, and (c) ER2 at various temperatures. For all samples, t_{rp} decreased as σ value and temperature increased. By applying horizontal shifting, these plots were superimposed to create a master curve, as shown in Fig. 5 of the main text.

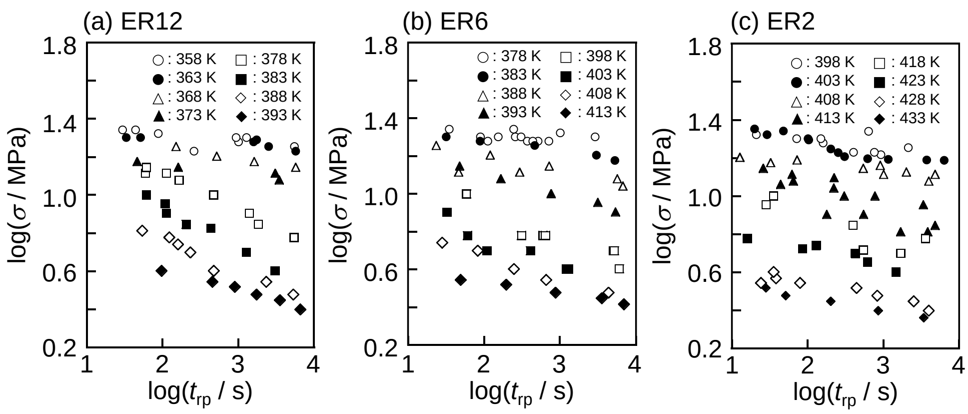

Fig. S3 Plots of rupture time against imposed stress for (a) ER12, (b) ER6 and (c) ER2 obtained at various temperatures.

4. References.

S1 T. L. Smith, Ultimate tensile properties of elastomers. II. Comparison of failure envelopes for unfilled vulcanizates. *J. Appl. Phys*., 1964, **35**, 27–36.

S2 T. L. Smith, Ultimate tensile properties of elastomers. I. Characterization by a time and temperature independent failure envelope. *J. Polym. Sci. A*, 1963, **1**, 3597–3615.

S3 T. L. Smith and J. E. Frederick, Ultimate tensile properties of elastomers. IV. Dependence of the failure envelope, maximum extensibility, and equilibrium stress-strain curve on network characteristics. *J. Appl. Phys.*, 1963, **36**, 2996–3005.

S4 T. L. Smith and W. H. Chu, Ultimate tensile properties of elastomers. VII. Effect of crosslink density on timetemperature dependence. *J. Polym. Sci. A*, 1972, **10**, 133–150.

S5 D. Wang, A. A. K. Klaassen, G. E. Janssen, E. de Boer and R. J. Meier, The detection of radicals in strained, high-modulus polyethylene fibres. *Polymer*, 1995, **36**, 4193–4196.

S6 B. Crist Jr., J. Oddershede, J. R. Sabin, J. W. Perram and M. A. Ratner, Polymer fracture—A simple model for chain scission. *J. Polym. Sci., Polym. Phys. Ed*, 1984, **22**, 881–897.

S7 R. Puthur and K. L. Sebastian, Theory of polymer breaking under tension. *Phys. Rev. B*, 2002, **66**, 024304.