Electronic Supplementary Information

Effect of Heterogeneous Network on Glass Transition Dynamics and Solvent Crack Behavior of Epoxy Resins

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Contents

1. Fourier-transform infrared spectroscopy.

Fig. S1 shows time evolution of FT-IR spectra for the mixture of HDGEBA and CBMA during the pre-curing process at 283, 296, 323 and 353 K. Each panel also contains a spectrum obtained after middle-curing at 373 K for 1 h. For the initial stage of curing, the spectrum can be characterized by two absorption bands at 4,524 and 4,940 cm^{-1}. The former band is assignable to a combination of the stretching and bending vibrations of epoxy groups, while the latter one is due to a combination of the stretching and bending vibration modes of primary amino groups.[S1] The absorbance for both bands decreased with increasing pre-curing time, indicating that the primary amino and epoxy groups were consumed by the epoxy-amine reaction. After middle-curing at 373 K which was above the glass transition temperature (T_g), the two bands disappeared. The resultant spectra were totally identical with one another for epoxy resins pre-cured at 283, 296, 323 and 353 K.

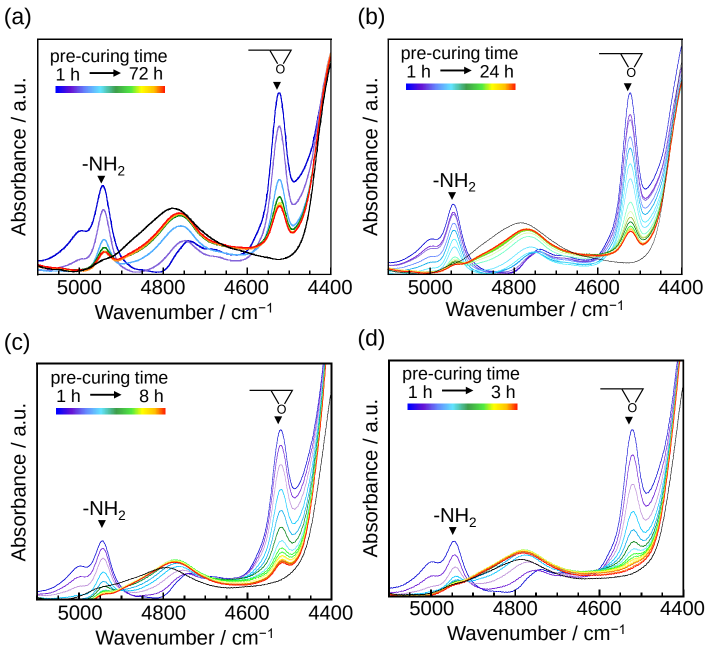

Fig. S1 Time evolution of FT-IR spectra for the mixture of HDGEBA and CBMA during the pre-curing process at (a) 283, (b) 296, (c) 323 and (d) 353 K. A black curve in each panel denotes a spectrum obtained after middle-curing at 373 K for 1 h.

The concentration of epoxy groups ([E]) and primary ([A_1]), secondary ([A_2]) and tertiary amino groups ([A_3]) was estimated on the basis of the absorbance for the bands at 4,524 and 4,940 cm^{-1}. They are written as follows;

$$[\mathrm{A}_1]_0 = [\mathrm{A}_1] + [\mathrm{A}_2] + [\mathrm{A}_3] \tag{1}$$

$$[\mathrm{E}]_0 = [\mathrm{E}] + [\mathrm{A}_2] + 2[\mathrm{A}_3] \tag{2}$$

where, [E]$_0$ and [A_1]$_0$ are the initial concentration of epoxy and primary amino groups, respectively. By using equations (1) and (2), [A_2] and [A_3] can be given by the following equations;[S2, S3]

$$[\mathrm{A}_2] = [\mathrm{E}]_0 (\beta B - \alpha) \tag{3}$$

$$[\mathrm{A}_3] = [\mathrm{E}]_0 \left(\alpha - \beta \frac{B}{2}\right) \tag{4}$$

where, α, β and B can be written as;

$$\alpha = \frac{[E]_0 - [E]}{[E]_0}, \quad \beta = \frac{[\mathrm{A}_1]_0 - [\mathrm{A}_1]}{[\mathrm{A}_1]_0}, \quad B = \frac{2[\mathrm{A}_1]_0}{[\mathrm{E}]_0}$$

The [E]$_0$ and [A_1]$_0$ values can be calculated by the feed ratio between HDGEBA and CBMA. The α and β values correspond to the consumption rate of epoxy and primary amino groups, respectively. The [E] and [A_1] values can be determined on the basis of the absorbance of bands at 4,524 and 4,940 cm^{-1}, which are arisen from epoxy and primary amino groups, respectively, in the FT-IR spectra.[S4] Thus, the [E] and [A_1] values, which were experimentally obtained, together with the known parameters ([E]$_0$ and [A_1]$_0$) provide the values of α, [A_2] and [A_3].[S2–S4]

2. Differential scanning calorimetry.

The HDGEBA and CBMA mixture was cured via three steps. The first step, named pre-curing, was performed under different conditions for three independent mixtures; 283 K for 72 h, 296 K for 24 h, 323 K for 12 h and 353 K for 3 h. The second step, named middle-curing, was performed under the same condition at 373 K for 1 h for the three resins after pre-curing, reaching a quasi-completion of the reaction. In the third step, epoxy resins were post-cured at 393 K for 2, 3, 6, 12, 24, 48 and 72 h. Fig. S2 shows DSC thermograms for epoxy resins prepared by (a) 283, (b) 296, (c) 323 and (d) 353 K pre-curing with middle-curing. After middle-curing, a baseline shift accompanied with an endothermic peak was observed. Once post-curing was performed at 393 K, the peak disappeared and the baseline shift moved to the higher temperature side. That is, the T_g value, which was defined as a midpoint of the baseline shift, shifted to the higher temperature side with increasing post-curing time (t_p). Fig. S3 shows dependence of t_p on T_g for the post-cured epoxy resins after middle-curing. The T_g value increased with increasing t_p and apparently leveled off after a certain time.

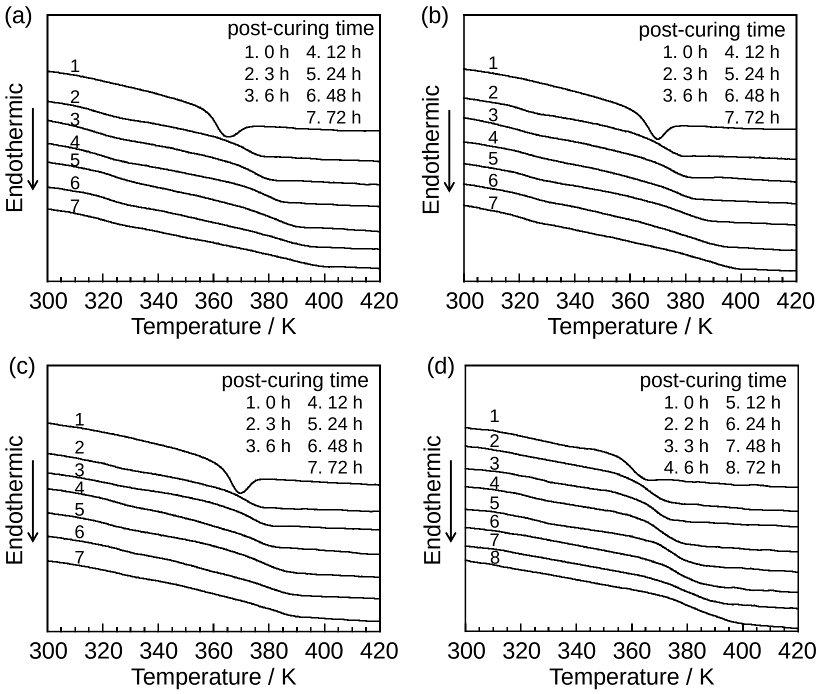

Fig. S2 DSC thermograms for the middle-cured epoxy resins with (a) 283, (b) 296, (c) 323 and (d) 353 K pre-curing at various post-curing times.

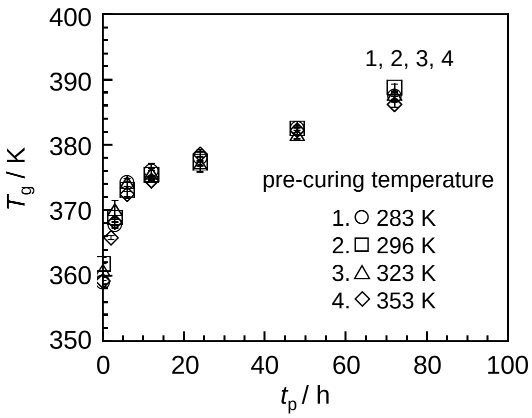

Fig. S3 Dependence of t_p on T_g for the post-cured epoxy resins.

3. Solvent swelling test.

The cross-linking density (ν) of epoxy resins at various stages of the post-curing was examined by the swelling test with THF, which is a good solvent, in conjunction with the Flory-Rehner equation (see main text). Fig. S4 shows t_p dependence of ν for the epoxy resins with the 283, 296, 323 and 353 K pre-curing followed by the middle-curing at 373 K. It showed a similar trend with the t_p–T_g relationship shown in Fig. S3, although the ν value at a given t_p was different, depending on the pre-curing temperature.

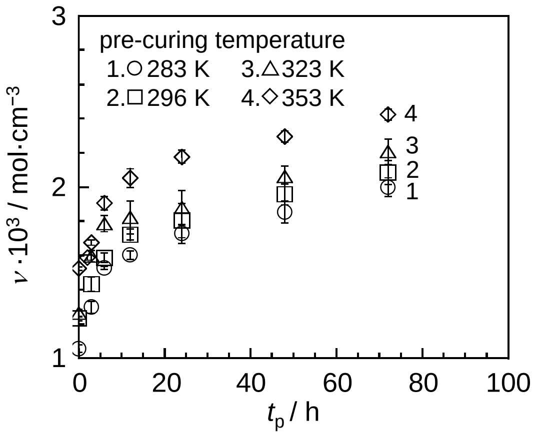

Fig. S4 Dependence of t_p on ν for the post-cured epoxy resins.

The swelling ratio (*Q*) of epoxy resins in THF was examined as a function of immersion time. The *Q* value was defined as the volume ratio of swollen and dried samples. Fig. S5 shows time dependence of *Q* for ER283, ER296, ER323 and ER353, which were post-cured epoxy resins after middle-curing with 283, 296 323 and 353 K pre-curing. For all samples, the *Q* value increased with increasing time and then reached an equilibrium after approximately 40 h. There was no significant difference in the swelling rate among the four samples. Thus, it seems most likely that the time at which the fracture occurred in the solvent stress crack test, as shown in Fig.9, was not directly related to the swelling rate.

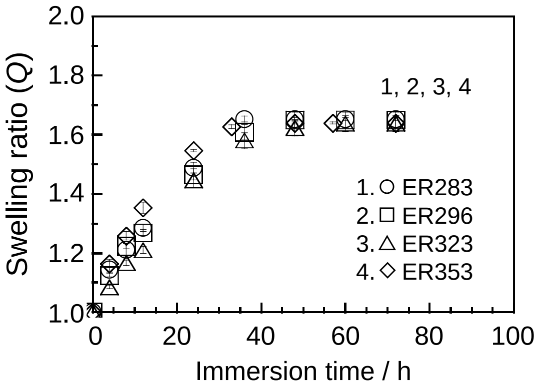

Fig. S5 Time dependence of *Q* for ER283, ER296, ER323 and ER353.

4. Dynamic mechanical analysis.

The segmental dynamics of ER283, ER296, ER323 and ER353 were examined by dynamic mechanical analysis (DMA). Fig. S6 shows temperature dependence of storage (*E*') and loss moduli (*E*'') for ER296 at various frequencies ranging from 0.1 to 110 Hz. An *E*'' peak, which was accompanied by the distinct change in *E*', was observed in the temperature range employed. Since the peak position shifted to the higher temperature side with increasing frequency, it is apparent that the *E*'' peak was arisen from a relaxation process. Taking into account the T_g value determined by differential scanning calorimetry, 373 K, the peak can be assigned to the segmental motion in the epoxy resin, namely the α-relaxation process.[S5] Such E'' peak due to the α-relaxation was also observed for ER296, ER323 and ER353. Base on the peak position, the relaxation time (τ^{DMA}) at a given temperature can be obtained. Semi-logarithmic plots of τ^{DMA} against the inverse temperature (T^{-1}), which was normalized by T_g, for ER283, ER296, ER323 and ER353 were given as Fig. 7(b) in the main text.

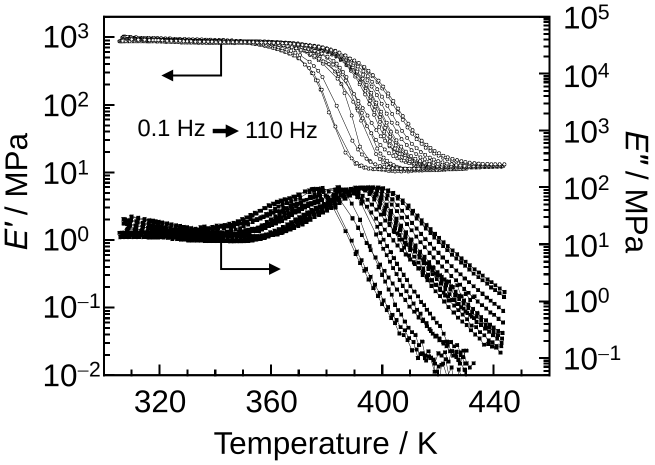

Fig. S6 Temperature dependence of storage (E') and loss moduli (E'') for ER296.

5. References.

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