Evaluation of dynamical behavior of epoxy resins in the curing process by X-ray photon correlation spectroscopy

Thermoset epoxy resins are indispensable materials for modern industry because of their excellent mechanical properties, high adhesion to various substrates, and excellent heat and chemical resistance. They are used in various materials, such as versatile adhesives, fiber reinforced materials, and high-performance coatings. In the production process, efficient energy use in the thermosetting process is becoming more important, for which optimization of curing conditions is required. Thus, it is necessary to properly understand the kinetics of the thermosetting process.

The thermal curing reaction is typically initiated by mixing two reactive components together and increasing the temperature to induce a cross-linking reaction. The effect of temperature on the isothermal curing reaction is fairly complex. The curing reaction is more likely to occur at high temperatures, thereby resulting in faster curing; however, it does not guarantee the hardness of the cured materials. For certain epoxy resins, when high-temperature curing is preceded by a low-temperature curing process, the cured material has a higher glass transition temperature T_g. Temperature affects the cross-linking network formation, and consequently, density and heterogeneity.

We examined the microscopic dynamics of a catalytic epoxy resin during the isothermal curing process at two different temperatures (100°C and 150°C) by X-ray photon correlation spectroscopy (XPCS) [1]. Previous rheological measurements indicated that both the curing process at 100°C and 150°C reached the gel point within 1 h, and solidification was almost complete. Thus, we focused on the first 2 h of the curing process and investigated its microscopic dynamics by XPCS.

XPCS measurements were performed at SPring-8 **BL03XU**. A sample was irradiated with partially coherent X-rays generated by passing the X-ray beam through a pinhole of 20 μm diameter, and the scattered X-rays were detected using a two-dimensional detector mounted approximately 8 m at the back of the sample. In the XPCS measurements during the curing process, we analyzed the fluctuation of the speckle patterns scattered from the dispersed tracer particles in the epoxy resin, which was a mixture of bisphenol A diglycidyl ether (BADGE) as the base resin and 1-(2-cyanoethyl)-2-undecylimidazole (C11ZCN) as the catalyst. The samples in the liquid state were enclosed in cells designed to have a homogeneous temperature using aluminum foil as window materials [2], placed in a heat bath of 100°C or 150°C, and the change in dynamics during the curing process was measured.

The XPCS results showed that a marked slowing down of dynamics was observed with the progress of thermal curing under both 100°C and 150°C temperature conditions. However, significant differences were observed between the curing process at 100°C and that at 150°C. The time dependence of the characteristic relaxation rate Γ in the 100°C curing process at the scattering wave vector $q = 0.0325\ \mathrm{nm}^{-1}$ is shown in Fig. 1(a). The kinetics were clearly distinguished into regions (I)–(III). This indicates that the thermosetting reaction proceeds in three sequential steps: (I) oligomerization by bonding between monomers, (II) gelation by the cross-linking reaction between oligomers, and (III) densification of the cross-linked structure, which shows a clear difference in dynamics. On the other hand, in the 150°C curing process, there was no clear regional division of dynamics, and a gradual attenuation of dynamics was observed, as shown in Fig. 1(b). In this curing, oligomerization and gelation proceeded simultaneously, and no clear change in dynamics appeared.

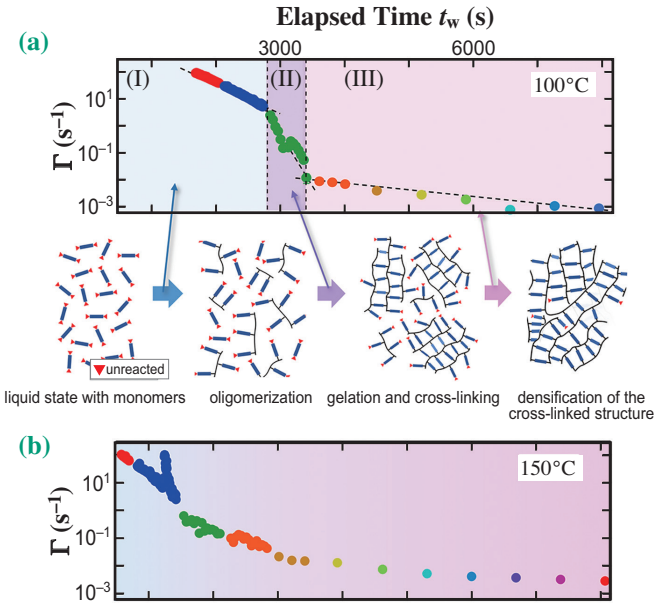

Fig. 1. Time dependence of the characteristic relaxation rate Γ at $q = 0.0325\ \mathrm{nm}^{-1}$ in the 100°C **(a)** and 150°C **(b)** curing processes. The schematic illustrations of the changes in the structure of the epoxy resin during the 100°C curing process are shown in (a).

Furthermore, a significant difference in dynamics fluctuation was observed between the curing process at 100°C and that at 150°C. Figures 2(a) and 2(b) show representative two-time correlation functions at 100°C and 150°C, respectively, which show the time variances of dynamics. In the two-time correlation function, a constant width of the band on the diagonal line indicates that the dynamics is stable. As shown in Fig. 2(a), the function during the 100°C curing process at t_w~1 h shows gradual fluctuation. On the other hand, the function during the 150°C curing process at t_w~1.3 h shows intermittent fluctuations as shown in Fig. 2(b), which indicates that fast and slow dynamics, the difference between which is very large, coexist. Similar intermittent fluctuations were observed for more than an hour during the 150°C curing process, whereas it was observed for about 600 s (Fig. 1(a-II)) of the gelation process during the 100°C curing process. These dynamical behaviors indicate that the 100°C curing process proceeds under relatively dynamically stable conditions, whereas the 150°C curing process proceeds under dynamically unstable conditions. From the instability appearing in the two-time correlation function, the spatial heterogeneity of the dynamics can be quantitatively evaluated as "dynamic heterogeneity" [3,4]. The cured product obtained by curing at 150°C showed a greater dynamic heterogeneity than the cured product obtained by curing at 100°C.

The chemical reactions during the curing process were examined by the Fourier transform infrared (FTIR) spectroscopy, which showed that about 80% of the reactive groups reacted during the 100°C curing process, whereas only 40% reacted during the 150°C curing process. The density of the cross-linking network structure of the resin after curing was also examined by ^{1}H-pulse nuclear magnetic resonance (NMR) spectroscopy, and the results showed that the density of cross-linked components was more than three times higher in the 100°C curing than in the 150°C curing.

These experimental results showed that in the 100°C curing process, reactions proceeded step by step to form a dense network structure (Fig. 3(a)), whereas in the 150°C curing process, the formation of chemical bonds at an early stage prevents molecular motion, resulting in curing with many unreacted groups remaining (Fig. 3(b)). These differences in the network formation should lead to the difference in glass transition temperature.

The dynamical behaviors observed in this study have not been observed in macroscopic rheological measurements. There are various materials produced by the formation of cross-linked networks. Similar analysis can be applied to the curing process using ultraviolet light as well as heat, and similar principles are also used to mold many three-dimensional printing materials. By focusing on the dynamic fluctuations during the curing process, we expect to produce high-performance materials by more efficient molding methods.

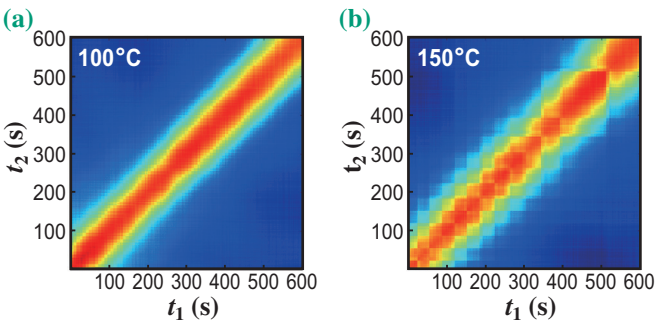

Fig. 2. Two-time correlation function at $q = 0.0325$ nm^{-1} in the 100°C ($2825 < t_w < 3425$ s) **(a)** and 150°C ($5007 < t_w < 5607$ s) **(b)** curing processes. Both have almost the same time-scale dynamics, but the fluctuations are quite different.

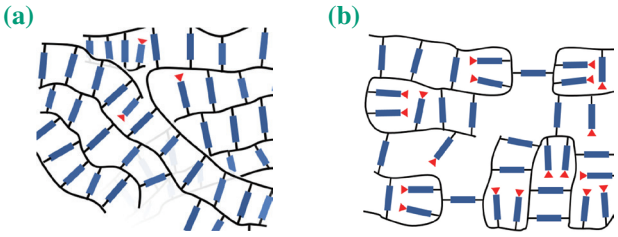

Fig. 3. Schematic illustration of the structure of the epoxy resin obtained by the 100°C **(a)** and 150°C **(b)** curing processes.

Taiki Hoshino[a,b,*], Yasushi Okamoto[c] and Atsushi Yamamoto[c]

[a] International Center for Synchrotron Radiation Innovation Smart, Tohoku University
[b] RIKEN SPring-8 Center
[c] DENSO CORPORATION

*Email: taiki.hoshino.c7@tohoku.ac.jp

References

[1] *T. Hoshino, Y. Okamoto, A. Yamamoto and H. Masunaga: Sci. Rep.* ***11*** *(2021) 9767.*
[2] T. Hoshino *et al.*: Polymer J. **45** (2012) 94.
[3] T. Hoshino *et al.*: Phys Rev Lett **124** (2020) 118004.
[4] K. Kanayama *et al.*: Phys. Rev. Research **4** (2022) L022006.