CLS system: Rapid curing systems with cyanate ester resins.

Junji Ueyama, Ryo Ogawa,

New curing systems for epoxy resins

In general, curing of epoxy resins by amines, which are typical thermosetting resins, takes time. This is due to the reaction mechanism and reaction rate between the epoxide and curing agent [3]. Epoxy resins and curing agents are often used as one-component types for curing at high temperature and as two-component types mixed just before use for curing at low/ambient temperature, mainly from the viewpoint of storage stability. In order to achieve rapid curing with one -component type, the control of the stability control is most important technology.

We call the epoxy resin adhesives used in our laser ultra-rapid curing system the "CLS system" (Curing system of Latent hardener and Specialty epoxy resin). The CLS system enables thermoset ultra-rapid curing adhesives using a new compounding technology that combines original epoxy resins and latent hardeners with a highly reactive cyanate ester resins.

1. Cyanate ester resins and curing agents

Cyanate ester resins have been researched and developed since the 1950s as thermosetting resins with high heat resistance, low dielectric properties, mechanical strength and chemical resistance, based on the formation of a triazine structure by cyclo-trimerization. Cyanate ester resin was derived from phenol and developed in 1976 as Triazine A (bisphenol A dicyanate ester) for printed circuit boards. However, due to its purity, Triazine A had problems regarding moisture resistance in the process. Since the 1980s, various phenol-based high-purity cyanate ester resins have been produced. After many years of research and development, cyanate ester resins have been used in space, aerospace, high-gain antennas, High-Speed Civil Transport (HSCT) and Superconducting Supercollider taking advantage of its characteristics since the 1990s [2].

In general, the trimerization of allyl cyanate ester resins occurs slowly at around 170-200 ºC without catalyst, so that high temperatures and/or long time are required for complete curing. Therefore, in general, metal-catalysts such as cupper acetylacetonate are employed to complete curing. On the other hand, since metal-catalysts are used by melting in cyanate ester resins, the catalyst cannot be melted immediately during curing, so the curing products are with catalyst residue. Moreover, the particles formed by catalyst residue in cured resins are not preferred. Therefore, an alkylphenol such as nonylphenol as a co-catalyst is often employed. It also works as the solvent for metal-catalyst, thus, it could promote further cyclo-trimerization to cure the resin completely at about 170 ºC in a short time [3,4]. Some studies on more efficient curing catalysts, such as metal species and hydrogen-donating co-catalysts to expand the application process have been reported [5-7]. A recent study by Palmese et al. reported the use organic ionic liquids without metal as curing agents [8]. On the other hand, although cyanate ester resins are a high-performance resin with potential, there are few reports on low-temperature curing and one-component curing because of difficultly of reaction control [9].

Meanwhile, polymerization reactions involving addition reactions of cyanate ester resins are highly reactive and can react with acidic or basic compounds. For example, trimerization reaction with weakly acidic phenols, via an intermediate imino carbonate. Reactions with aromatic amines, which are basic compounds, are known to give triazines substituted with amino groups via isourea intermediates [10] (Figure 1). Especially, Reactions with amine compounds, which are basic compounds, are intense and are often accompanied by a large reaction heat upon mixing. Hence, when cyanate esters and   amines are reacted, the reaction must be controlled and cured.
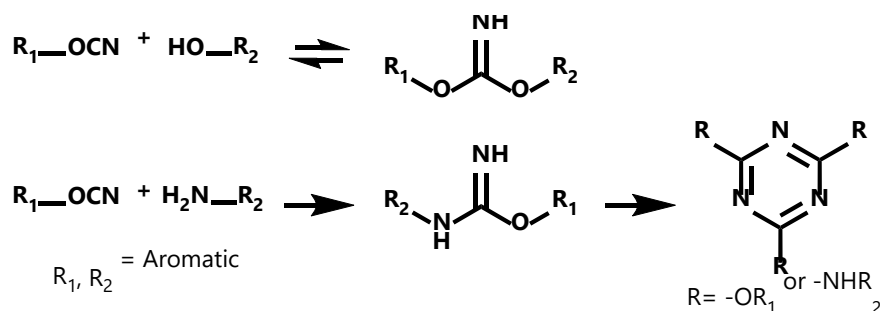
Figure 1 Reaction of cyanate esters with phenols and amines.

2.   One-component cyanate ester resin compositions with latent curing agents

Cyanate ester resins react violently with bases such as aromatic amines and are particularly dangerous when reacting with aliphatic amines. Therefore, the CLS system is controlled the reaction and curing temperature nucleophilicity of amines and acids, and the polymer effect as the molecular motions suppression. In general, acids and bases are in equilibrium, and the equilibrium constant is determined by the acid and base selected and varies depending on the environment and temperature. For example, the equilibrium state of amine and phenol was reported in detail by Zundel et al. [11, 12] (Fig. 2). Here, when benzylamine and p-cresol are mixed at equal mol, the equilibrium state product is obtained as a liquid. On the other hand, equal mol mixtures of phenylethylamine (m.p. 48 °C) and p-cresol (m.p. 32 °C) give salts having melting point at 76 °C. When these salts are mixed with cyanate ester, it can be confirmed that they react instantly with a significant exothermic. The reaction of aromatic amines, phenol and cyanate ester resins was also described by Jensen et al. [13]. In other words, the formation of salts by simple acid/base reactions is not sufficient. Therefore, by also utilizing the control of molecular motion by polymers, it will be possible to control the reaction of amines, phenols, and cyanate ester resins.

The latent hardener has a Tg of around 80 °C (Fig. 3) and does not react when mixed with liquid bisphenol E cyanate ester resins, as indicated at the characteristic peak around 2200 cm^{-1} originating from the stretching vibration of the -OCN group (Fig. 4). The DSC measurement results of the mixture of the latent hardener and the bifunctional cyanate ester resin are shown in Fig. 5. Essentially, cyanate ester resins and amine compounds react instantaneously with significant exotherm as soon as they are mixed. However, we have succeeded not only in controlling the

reactivity of the curing agent by latent technology, but also in making the hardener react at the moment it melts.

$$R_2{-}NH_2 \; + \; HO{-}R_2 \; \rightleftarrows \; R_2{-}NH_2 \ldots HO{-}R_2 \; \rightleftarrows \; R_2{-}\overset{\oplus}{N}H_3 \ldots \overset{\ominus}{O}{-}R_2$$
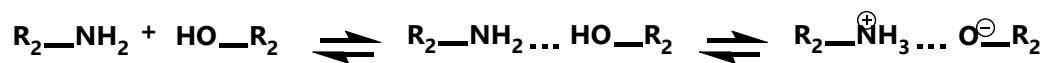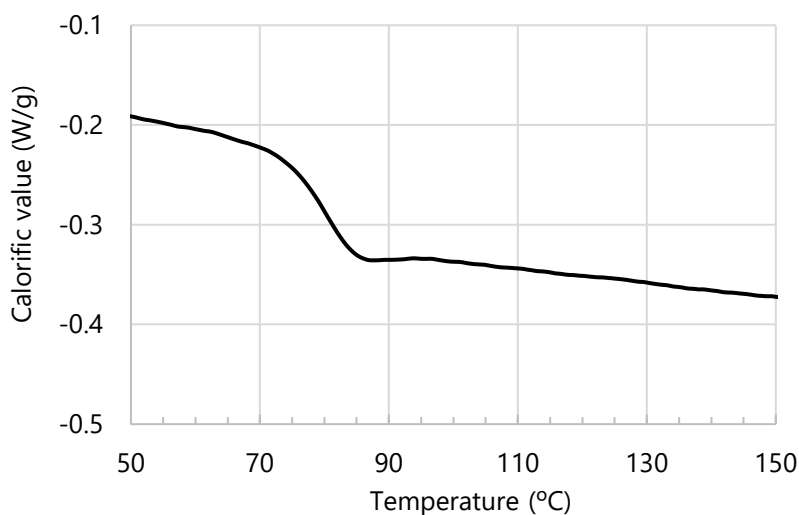
Figure 2 Equilibrium reaction between phenol and amine.

Figure 3 DSC curve of latent hardener.
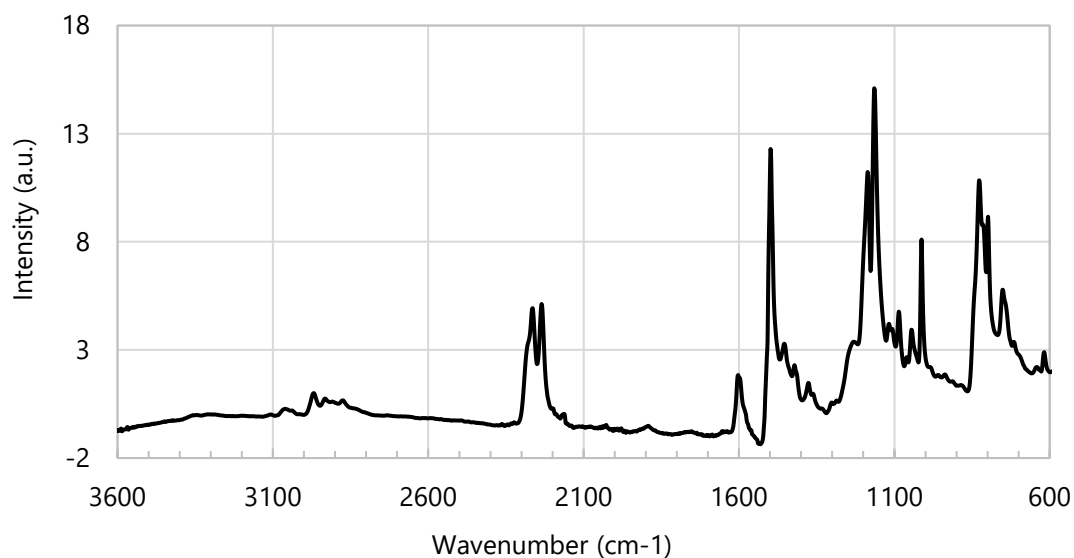
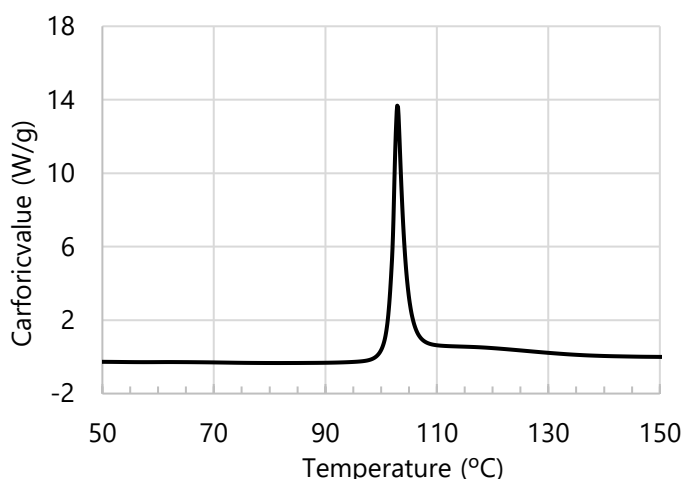Figure 4 IR spectra for mixture of cyanate ester resins and latent hardener.

Figure 5 DSC curve with mixture of bisphenol E cyanate ester and the latent hardener.

3. Curing Temperature Control and Curing Process with Latent hardener in CLS Systems

The CLS system consists of a combination of epoxy resin, cyanate ester resin and latent hardener. As described above, our latent hardener technology enables this one-component system, and the curing temperature can also be controlled by the amine species of the latent hardener (Figure 6). The curing temperature of latent hardener using highly reactive aliphatic amines is approximately 70 °C, that of simple aliphatic amines is approximately 90 °C, and that of aliphatic amines modified with controlled structure is approximately 120 °C.
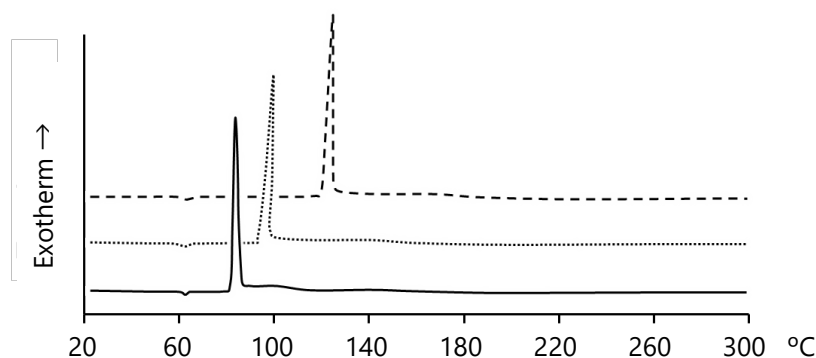

Figure 6 DSC curves with each latent hardener ;
solid line: highly reactive aliphatic amine
dotted line: simple aliphatic amine
dashed line: structure-controlled aliphatic amine

We are also investigating the curing process of the CLS system by using corresponding monofunctional model compounds. Since cyanate esters and epoxides do not react even at 180 °C, the expected reaction is between amines and cyanate esters or epoxides, although cyanate esters react much more rapidly due to the difference in reaction rates. The detailed reaction between cyanate esters and amines has only been reported by Bauer et al. for aromatic amines [12],

but there are no detailed reports for aliphatic amines. When cyanate esters are in excess, most of the reactions with aliphatic primary and secondary amines lead to trimerization via cyanate amine adducts, according to an analysis of the elementary reactions of cyanate esters with amines (Figure 7). The reaction with aliphatic amines is similar to that of aromatic amines, but the aliphatic amine reacts more rapidly, especially when primary amines are used. Furthermore, cyanate-amine adducts consisting of primary amines are unstable and dissociate in solution within a several hours (Figure 8). The reaction with tertiary amines is considerably slower than the reactions with primary and secondary amines, but it has been shown to promote gradual trimerization of cyanate esters at room temperature.
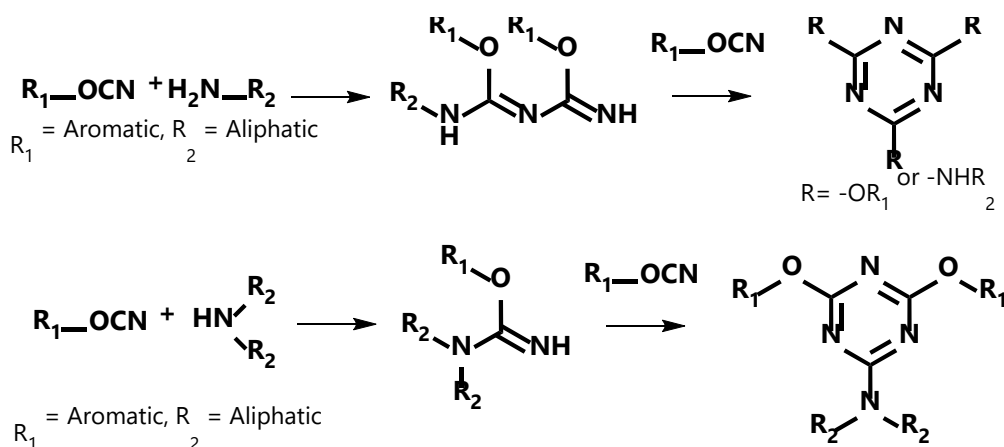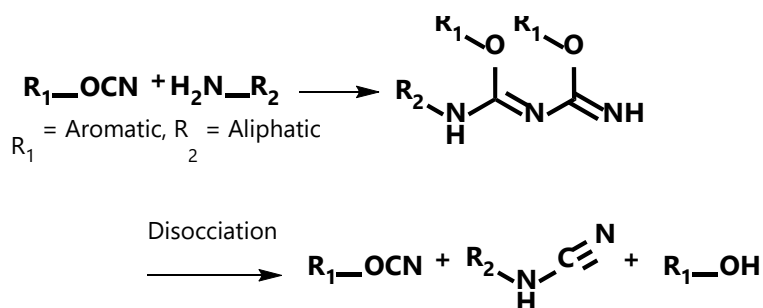
Figure 7 Reaction of cyanate ester s and amines.

Figure 8 Dissociation reaction of cyanate-amine adduct.

As a result of examining the reaction of epoxides with cyanate-amine adducts consisting of secondary amines, cyclized oxazolines and epoxy oligomers from adducts or phenoxides were observed (Figure 9). An interesting fact about this reaction is that the phenol generated by the thermal decomposition of the adduct activates the reaction of the adduct with the epoxide. As shown in Figure 10, when equal mol of phenol is added to the reaction of this adduct with epoxide, the reaction is significantly lower in temperature.

However, this reaction is minor in the reaction between cyanate ester and amine, and triazine structure formation by trimerization is by far the predominant reaction. Several reactions between the formed triazine and epoxide have been reported [14, 15], including the insertion reaction of the ring-opened epoxide into the triazine, isocyanurate formation by isomerization, and finally

oxazolidinone by reaction with the epoxide [16]. Based on the above elementary reaction analysis and previous reports, the curing process of the CLS system is shown in Figure 11, and its cross-linked structure is controlled by the ratio of components.
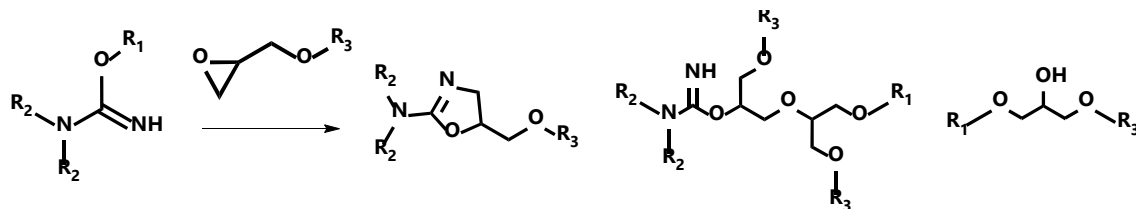

Figure 9 Reaction products of cyanate-amine adducts and epoxides.
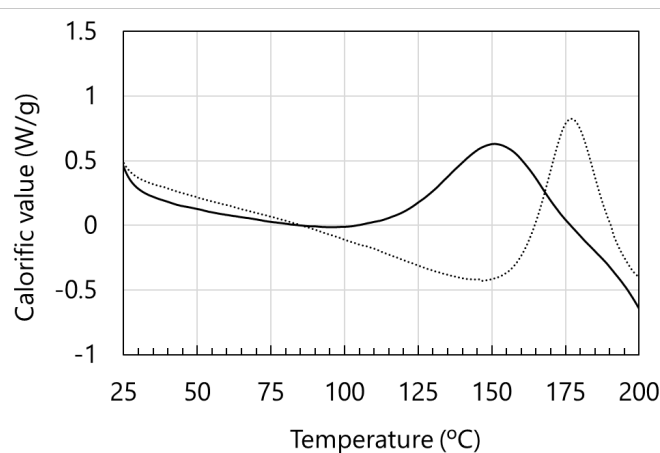

Figure 10 DSC curves for mixture between cyanate-amine adduct and epoxide.
solid line: with phenol
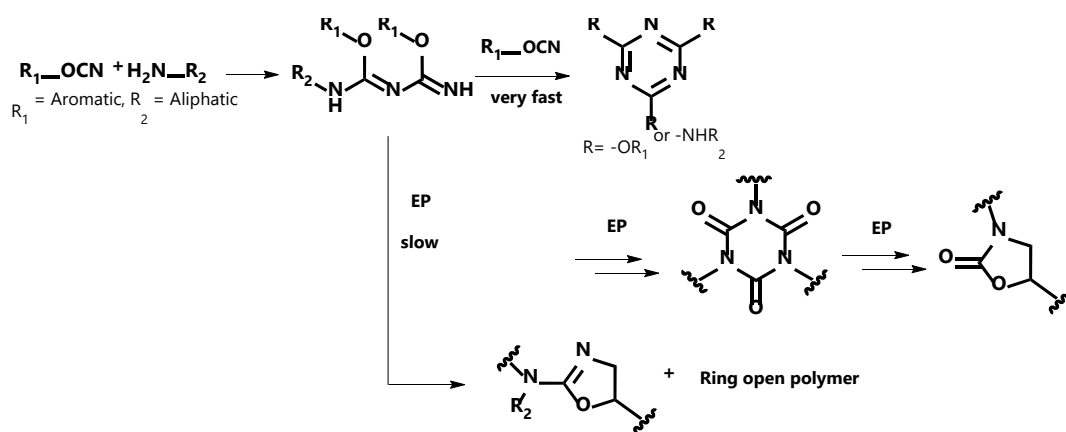dotted line: without phenol.

Figure 11 Proposed curing reaction process of CLS system.

Conclusion

We have succeeded to control the high reactivity of cyanate ester resins and amine compounds, which was conventionally considered to be difficult to control. Furthermore, we succeeded in developing the CLS system, a rapid curing system combining epoxy resin, cyanate ester resin and latent curing agents, and found that it has a new curing behavior not seen before.

In the future, we expect to develop a variety of applications utilizing the CLS system.

Bibliography

1. Takashi, K., (1985) Kobunshi Ronbunshu, 42 (9), 577-583
2. Hamerton I., Chemistry and Technology of Cyanate Ester Resins, Blackie Academic and Professional, Glasgow (1994)
3. Hi-Tech Polymers Inc. (1989) US Patent 4,847, 233
4. Osei-Owusu, A., Martin, G. C. (1992) Polym. Eng. Sci. 32 (8), 535-541 7.
5. Li, W. Liang, G., Xin, W. (2004) Polym. Int., 53 (11), 869-876
6. Gomez, C. M., Recalde, I. B., Mondragon, I. (2005) Eur. Polym. J. 41, 2734-2741
7. Remiro, P. M., Caba, K. D. L., Mondragon, I., Riccardi, C. C. (2010) J. Appl. Polym. Sci. 49, 1441
8. Throckmorton, J., Palmese, G. (2016) Polymer. 91, 7-13
9. Shimp, D. A. and Christenson, J. R. (1990) Plastics-Metals-Ceramics, ed. Hornfeld, H. L., SAMPE, p. p. 81-94
10. Bauer, J., Bauer, M., (2001) Macromol. Chem. Phys., 202, 2213-2220
11. Albrecht, G. and Zundel, G. (1984) J. Chem. Soc., Faraday Trans. 1, 80, 553-561
12. Menger, F. M. and Barthelemy, P. A. (1996) J. Org. Chem., 61, 2207-2209
13. Jensen, K. A., Holm, A., (1977) In The Chemistry of Cyanates and Their Thio Derivatives, Part 1, ed. Patai, S. Wiley, New York, 569-617
14. Bauer, M., Tänzer, W., Much, H., Ruhmann, R., (1989) Acta. Polym., 40 (5), 335-340
15. Bauer, M., Bauer, J., Ruhmann, R., Kühn, G., (1989) Acta. Polym., 40 (6), 397-400
16. Ohno, D., Kazuya, Z., Youji, K., Kazuyoshi, U., Hitoshi, H., (2016) Int. J. Org. Chem., 6, 117- 125