

Investigation of the hardener with latent and rapid curing based on phenol-amine salts for applications to cyanate ester resins

著者	Ueyama Junji, Ogawa Ryo, Tsuge Akihiko, Endo Takeshi
journal or publication title	Journal of Applied Polymer Science
volume	138
number	43
page range	51286-1-51286-7
year	2021-06-17
その他のタイトル	Investigation of the hardener with latent and rapid curing based on phenol-amine salts for applications to cyanate ester resins.
URL	http://hdl.handle.net/10228/00008921

doi: <https://doi.org/10.1002/app.51286>

Investigation of The Hardener with Latent and Rapid Curing Based on Phenol-Amine Salts Useful for Applications to Cyanate Esters Resins

Junji Ueyama^{†,‡}, Ryo Ogawa[†], Akihiko Tsuge[‡], Takeshi Endo^{*,§}

[†]Functional Polymers Development Laboratory, R&D Division, ADEKA Co., 20 Showanuma, Shobu-cho Kuki-shi, Saitama 346-0101, Japan

[‡]Department of Applied Chemistry, Graduate School of Engineering, Kyushu Institute of Technology, 1-1 Sensui-cho, Tobata, Kitakyushu 804-8550, Japan

[§]Molecular Engineering Institute, Kyushu Institute of Technology, 1-1 Sensui-cho, Tobata, Kitakyushu 804-8550, Japan

KEYWORDS: Cyanate Ester, Thermal Latent, Hardener, Curing Agent, Phenol-Amine.

ABSTRACT: We have developed curing agents that have good storage stability for cyanate ester resins and can be cured efficiently even at low temperatures around 100°C. It was focused on phenol-amine salts, which consisting of basic aliphatic amines that react immediately with cyanate esters at room temperature and weakly acidic phenols that are used as curing catalysts. But, due to the equilibrium between phenol and amine, the curing reaction of cyanate esters could not be controlled by simple molecules only. In order to control the curing reaction of cyanate esters, moreover, molecular motions suppression by polymers was used in combination. The suppression of molecular motions for hardener was evaluated by T_g, then those storage stability and reactivity to cyanate esters were studied. PSM-EPEDA, in which is composed of ethylenediamine-epoxy adducts and novolac phenolic resin, was showed great storage stability against cyanate esters due to its suppression of molecular motions, in addition, it showed efficient and rapid curing at around 100°C.

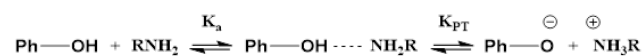
Cyanate ester resins are high-performance thermosetting resins which can be characterized by high strength, high heat resistance and high dielectric properties due to formation of triazine structure by cyclo-trimerization. Hence, it is able to supplement the heat resistance and dielectric properties that cannot be satisfied only with epoxy resins, in which is widely used industrially as the thermosetting resins, and it is especially used in aerospace and electronic materials. The history and application of cyanate ester resins are summarized by Harmerton et al.^{1,3}

Although trimerization of aryl cyanate occurs around 200°C without catalyst, complete curing needs long time and high temperature. Therefore, in general, metal-catalysts such as copper acetylacetonate are employed to complete curing. On the other hand, since metal-catalyst is used by melting in cyanate ester resins, the catalyst cannot be melted immediately during curing, and reached complete curing 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 °C in a short time.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.⁵⁻⁸ Recently, Palmese and Oyama have been utilized organic

catalysts without metal.⁹⁻¹¹ On the other hand, there are few reports on the latent hardener with storage stability for cyanate ester resins¹², despite the fact that they are high-performance resins with great potential., because of the difficult reaction control for cyanate ester resins.

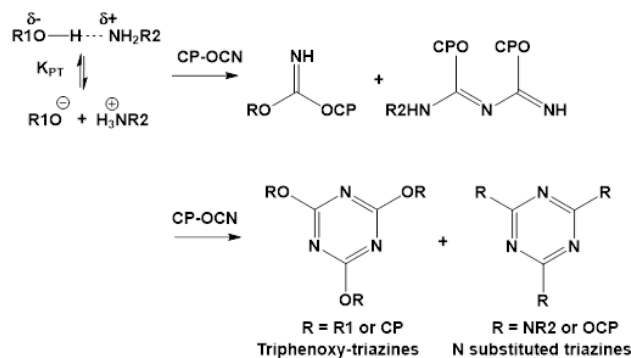
In this study we show thermal latent curing agents for cyanate ester resins, which consist of phenol-amine salts whose dynamics is suppressed by polymer effect. Especially, the latent curing agents found in this study consist of aliphatic amines, in which are also used for low-temperature curing of epoxy resins, but are not conventionally applicable to cyanate ester resins because they react and cure immediately, as reported by Bauer et al.¹³ Basic amines are known to form phenol-amine salts with the weakly acidic phenols, in which used as co-catalyst to cure the cyanate esters resins. Furthermore, the phenol-amine salts exist in the equilibrium state between the amine and the phenol as shown in Scheme 1.¹⁴⁻¹⁷ In other words, phenol-amine salts consisting of simple phenols and amines cannot provide storage stability in cyanate ester resins. Therefore, we attempted to suppress molecular dynamics by polymeric effect and evaluated its storage stability and reactivity using novolac phenolic resin and some amines.

Scheme 1. The equilibrium between phenol and amine



At First, as phenol-amine salts consisting of monofunctional compounds, pCr-DPEA (m.p. 76°C) which composed *p*-cresol (pCr) and 2,2-diphenylethyl amine (DPEA), and oCr-BA (liquid at r.t.) which composed *o*-cresol (oCr) and benzylamine (BA), were prepared (see Supporting Information (SI)). Then those phenol-amine salts were mixed with 4-cumylphenol cyanate ester (CPCy) which be monofunctional cyanate ester. Zundel and co-workers reported that there is equilibrium between phenols and amines, and mostly in equilibrium with K_{pt} .¹⁴ Actually, oCr-BA and pCr-DPEA were shown to be in the hydrogen-bonded state and in the ionic-bonded state, which is ammonium and phenoxide (SI). The IR spectrum of pCr-DPEA in the solid state below 76°C strongly suggests that the ion dissociated state is preferred, on the other hand, the hydrogen bonding state dominates in the molten state at 80°C (SI). On the other side, regarding the reactions of phenols or amines with the cyanate ester, cyanate esters does not only react with weakly acidic phenols¹⁸ to form the triazine via an intermediate imino carbonate, but nucleophilic amines also react rapidly to give cyanate-amine adducts or triazines substituted with amino groups.¹⁹⁻²¹ In the case of the addition of equal amounts of aromatic amines and phenols to cyanate esters, it has been found out that the products contain the imino carbonates and the cyanate-amine adducts in the ratio of 1:2. When pCr-DPEA was dropped into the liquid of CPCy, CPCy immediately has been reacted with a large exotherm. This mixture was found out to include imino carbonate, cyanate-amine adduct and a small amount of triazine by its IR spectrum. (SI, Scheme 2).

Scheme 2. Reaction mechanism between cyanate ester and phenol-amine salt



As the result of model experiments by monofunctional compound it seems difficult to give latency for (to) cyanate esters under only this condition. We attempted to develop a melt-type thermal latent hardener that can control the reaction by suppressing the molecular motions using the characteristics of polymers. The curing agents were prepared using several amines and PSM which is novolac phenol (SI), in addition, in the same phenol-amine salt combinations, Tg was used to be confirmed how the ratio of the OH of phenol to the N of amine (OH/N) affects the sup-

pression of molecular motions (Figure. 1). Finally, we evaluated the reactivity and storage stability between them and the cyanate esters.

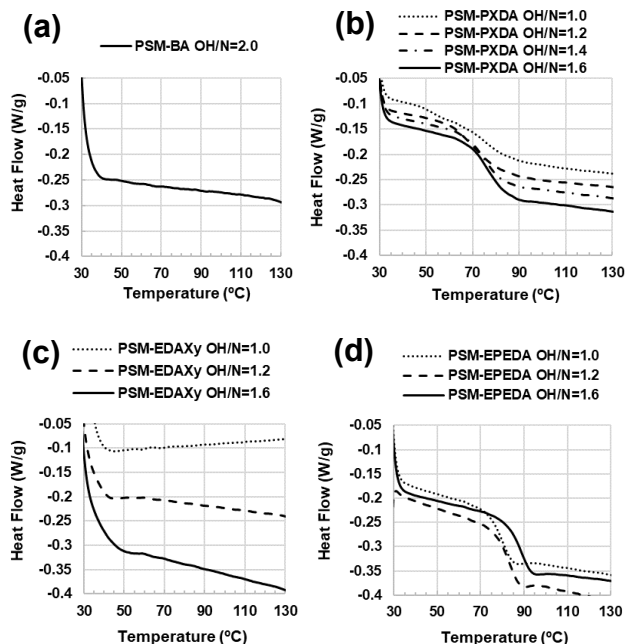


Figure 1. DSC curves of the hardener consisting of novolac type phenol resin and amines: (a) Benzylamine, (b) *p*-xylenediamine, (c) *p*-xylylene-ethylenediamine, (d) Oligomers of ethylenediamine and bis-A epoxy resin. ; Results of 2nd DSC after raising the temperature to 200°C at 10°C/min and then cooling it down to 25°C under N₂.

From these Tg, it was found that higher OH/N is increased the inhibition of molecular motions of the hardener. While PSM-PXDA showed a clear Tg due to the suppression of bifunctional amine, PSM-EDAXy resulted in an unclear Tg despite an even higher contents of amine functional groups and showed less suppression of molecular motions than PSM-PXDA. Increasing the contents of amine functional groups in a molecule was not simply influenced for motions inhibition. For PSM-BA (OH/N = 2.0) and PSM-PXDA with each OH/N, the latency was evaluated in two methods (Figure 2). (1) the amount of reaction of cyanate groups was estimated by IR after mixing each hardener with the monofunctional cyanate ester CPCy and (2) the amount of amine extracted from each hardener into CDCl₃ was quantified by ¹H-NMR. PSM-BA which molecular motions be not restrained was rapidly reacted with CPCy. PSM-PXDA (OH/N is 1.0) also reacted with CPCy due to the inadequate suppression of molecular motions. On the contrary, PSM-PXDA (OH/N is more than 1.2) showed improvement for latency against CPCy.

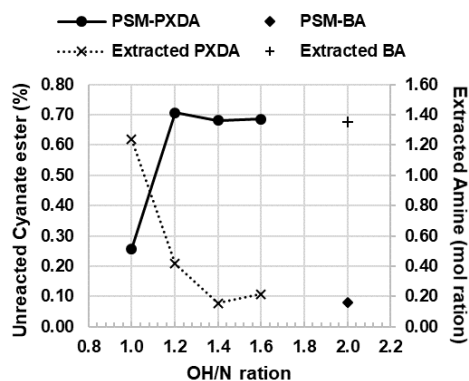


Figure 2. Amount of extracted amines and unreacted cyanate: Amount of unreacted cyanate ester was estimated from the height of cyanate stretching vibration peak (2264 cm^{-1}) as compared with the height of CPCy (100%). The amount of extracted amine was estimated from the amine concentration of the original sample prepared ($1.18 \times 10^{-4}\text{ mol/L}$).

The latency of PSM-PXDAs and PSM-EPEDAs in terms of bifunctional cyanate ester DCBE has been examined by IR and DSC (Figure 3, 4).

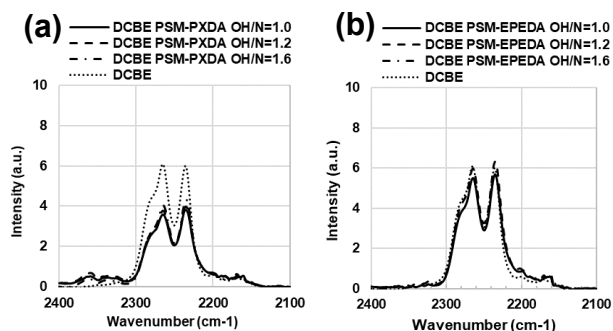


Figure 3. IR spectra of (a) PSM-PXDAs and (b) PSM-EPEDAs mixed with DCBE: normalized by methylene peak (2969 cm^{-1}).

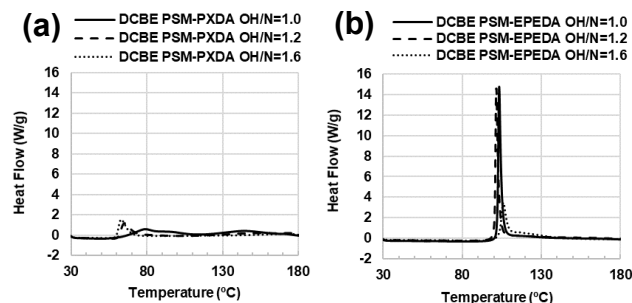


Figure 4. DSC curves of (a) PSM-PXDAs and (b) PSM-EPEDAs mixed with DCBE.

The compositions of PSM-EPEDAs with DCBE were almost the same as intensity of the cyanate ester's stretching peaks of DCBE itself because of the suppressed molecular motions of PSM-EPEDAs, but the mixtures of PSM-PXDA and DCBE showed a decrease in the peak intensity as in the case of CPCy because of insufficient suppression of molec-

ular motions for the hardeners regardless of whether cyanate esters is monofunctional or bifunctional. On DSC spectra, the compositions of PSM-PXDA and DCBE showed very weak exotherm. The thermal behavior is considered to be caused by in-complete curing reaction due to cross-linking reaction occurring inside the hardener. In contrast, the PSM-EPEDA's (OH/N of 1.0 and 1.2) mixtures with DCBE showed instantaneous large exothermic reactions ($>200\text{ J/g}$) at higher than T_g . It indicates that PSM-EPEDA is well latent against the cyanate esters and reacts efficiently above the T_g , in which molecular motions inhibition is removed. In the case of PSM-EPEDA (OH/N is 1.6), inhibition of curing against cyanate ester (97 J/g) was observed. It seems that the excess free phenol groups were cross-linked with cyanate ester, resulting in partially incomplete curing.

PSM-EPEDAs was evaluated the storage stability to cyanate ester with IR (Figure 5).

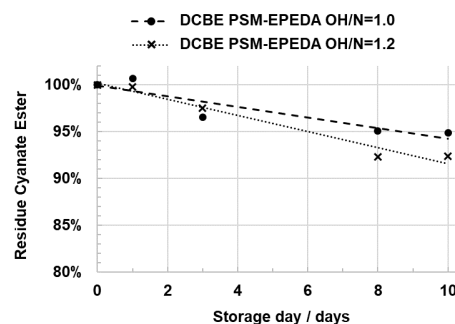


Figure 5. Storage stability with PSM-EPEDAs to cyanate ester under 25°C . : Standardized on the cyanate peak intensity immediately after prepared the compositions.

It has been found that the PSM-EPEDAs maintains the excellent storage stability ($>90\%$) against cyanate ester even after 10 days.

In summary, we have demonstrated the latent curing agent that gives storage stability to cyanate ester resins by employing both the usage of phenol-amine salts and the effect of the polymer and achieving a one-component system of cyanate ester and curing agent. It should be noted that PSM-EPEDA has excellent storage stability against cyanate esters and an efficient curing reaction at around 100°C . This rapid and efficient curing with the latent curing agents and cyanate esters could be applied to composite systems with epoxy resins used for adhesives and other applications. The finding here could solve the tedious and long curing time.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Materials, measurements, synthesis of latent curing agents, and experimental methods (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: endo.takeshi328@mail.kyutech.jp.

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

I would like to thank Kyushu Institute of Technology, Molecular Engineering Institute, and ADEKA Co. for giving me the opportunity to conduct this research, also thank the members of Molecular Engineering Institute for their advice in writing this paper.

REFERENCES

- (1) Hamerton, I., Chemistry and Technology of Cyanate Ester Resins, Blackie Academic and Professional, Glasgow (1994).
- (2) Fang, T., Shimp, D. A. (1995) *Prog. Polym. Sci.* **20**, 61-118.
- (3) Hamerton, I., Hay, J. N. (1998) *Polymer Int.*, **47**, 465-473.
- (4) Hi-Tech Polymers Inc. (1989) US Patent 4,847,233.
- (5) Osei-Owusu, A., Martin, G.C. (1992) *Polym. Eng. Sci.* **32**(8), 535-541.
- (6) Li, W. Liang, G., Xin, W. (2004) *Polym. Int.*, **53** (11), 869-876.
- (7) Gomez, C.M., Recalde, I. B., Mondragon, I. (2005) *Eur. Polym. J.* **41**, 2734-2741.
- (8) Remiro, P.M., Caba, K. D. L., Mondragon, I., Riccardi, C. C. (2010) *J. Appl. Polym. Sci.* **49**, 1441.
- (9) Kobayashi, T., Isono, M., Oyama, T., Takahashi, A. (2012) *J. Network Polym., Jpn.* **33**, 130-139.
- (10) Izu, K., Tokoro, Y., Oyama, T., (2020) *Polymer.* **52**, 1245-1252.
- (11) Throckmorton, J., Palmese, G. (2016) *Polymer.* **91**, 7-13.
- (12) Shimp, D.A. and Christenson, J.R. (1990) *Plastics-Metals-Ceramics*, ed. Hornfeld, H.L., SAMPE, p.p. 81-94.
- (13) Bauer, J., Bauer, M., (2001) *Macromol. Chem. Phys.*, **202**, 2213-2220.
- (14) Albrecht, G. and Zundel, G. (1984) *J. Chem. Soc., Faraday Trans. 1*, **80**, 553-561.
- (15) Menger, F. M. and Barthelemy, P. A. (1996) *J. Org. Chem.*, **61**, 2207-2209.
- (16) Ogoshi, H., et al., (1998) *J. Phys. Org. Chem.*, **11**, 737-742.
- (17) Solgadi, D. et al, (2000) *Phys. Chem. Chem. Phys.*, **2**, 893-900.
- (18) Pankratov, V. A., Vinogradova, S. V., Korshak, V. V., (1977) *Russian Chemical Reviews.*, **46**, 278-295.
- (19) Tsuchiya, K., Endo, T., (2014) *J. Polym. Sci. Part A: Polym. Chem.*, **52**, 699-706.
- (20) Neitzel, M., Zinner, G., (1981) *Arch. Pharm. (Weinheim)*, **314** (1), 2-9.
- (21) 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.