

Novel Rapid-Cure Adhesives for Low Temperature Using Thiirane Compound

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ABSTRACT: We investigated improvement of workability (viscosity), storage stability, and curing ability of thiirane resin for adhesive applications. The viscosity of bisphenol-F thiirane resin was lower than that of bisphenol-A thiirane resin, especially at low temperatures, thus improving ease of handling. Addition of diphenyl decyl phosphite improved its storage stability to a level similar to that of bisphenol-A epoxy resin. The curing of bisphenol-F thiirane resin increased three times faster by adding 2,4,6-tris(dimethylaminomethyl)phenol (DMP-30) as a tertiary amine. In applications of this new thiirane resin as civil and architectural adhesives, a superior curing ability at low temperature was attained. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2953–2957, 2001

Key words: thiirane (episulfide); epoxy; adhesives; rapid-cure; low temperature

INTRODUCTION

Epoxy resin has been widely used in industry because of its high mechanical properties and high adhesive strength. However, its slow curing speed at low temperatures ($<5^{\circ}\text{C}$) is unacceptable, in spite of its superior storage stability. Epoxy adhesives for use below 5°C have never been developed. The reason can be attributed to the low reactivity of the epoxy group. However, epoxy-comparable adhesives for low temperature are strongly desired in cold regions and at wintertime. Thiirane (episulfide) compound has been known to have higher reactivity than that of epoxy compound because of its higher cyclic strain. Moreover, addition products of epoxy and thiirane with amine are alcohol and thiol, respectively. Because thiol has a higher reactivity than that of alcohol, rapid-cure adhesives for low temperature can be obtained by the use of thiirane compound.

Although some experiments using thiirane compound as adhesives have been conducted, all of those have failed as a result of two major problems: high viscosity and poor storage stability.^{1–3} Its high viscosity can be attributed to the high crystallinity of the thiirane moiety. In addition, the high reactivity of the thiirane moiety, which brings about rapid cure, also degrades the storage stability.

Therefore, to develop rapid-cure adhesives by using thiirane compound, our work focused on the following three points: (1) the reduction of viscosity (crystallinity) for easy handling, (2) the improvement of storage stability while retaining the rapid-cure speed, and (3) the acceleration of cure at low temperature, below 5°C .

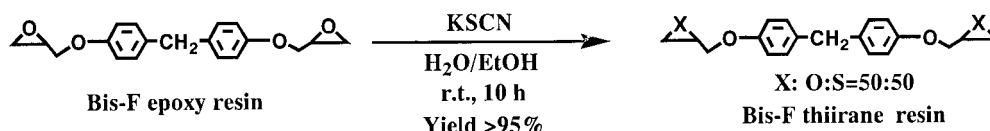
EXPERIMENTAL

Materials

Diglycidylethers of bisphenol-A and bisphenol-F (Asahi Denka Kogyo K.K. under the trade name

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Scheme 1 Synthesis of bisphenol-F thiirane resin from bisphenol-F epoxy resin

EP-4100 and EP4901, respectively) were used. Weight per epoxy equivalent of EP-4100 and EP4901 were 190 and 170 g/eq, respectively. Potassium thiocyanate, and 2,4,6-tris(dimethylaminomethyl)phenol (DMP-30) were purchased from Tokyo Kasei Kogyo Co., Ltd. Ethanol and toluene were purchased from Kanto Chemical Co., Inc. Triphenylphosphite, diphenyl monodecylphosphite, bis(nonylphenyl)pentaerythritol diphosphite, and tributylphosphite were purchased from Johoku Chemical Co., Ltd.

Synthesis of Thiirane Resin Containing 50% of S Unit (General Procedure)

To a solution of 58.8 g (0.605 mol) of potassium thiocyanate in 75 mL of ethanol and 100 mL of water, 187 g (1.1 equiv.) of bisphenol-F diglycidylether was added dropwise for 1 h. Then, after the reaction mixture was vigorously stirred at room temperature for 10 h, the organic layer (upper layer) was separated and 100 mL of toluene was added. The toluene solution was washed with brine, dried over MgSO_4 , and evaporated, to give 180 g of bisphenol-F thiirane resin containing 50% of S unit as a pale yellow liquid.

IR (neat): 2997, 2923, 1610, 1585, 1509, 1493, 1453, 1298, 1242, 1177, 1114, 1034, 915 (epoxy), 824, 787, 754, 713, 639, 615 (thiirane) cm^{-1} .

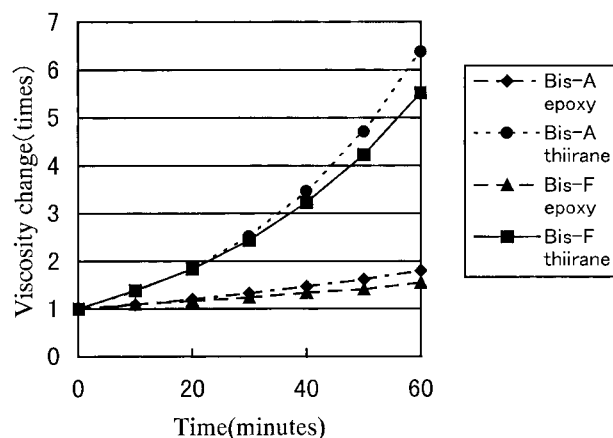


Figure 1 Cure behavior of thiirane resins (S = 30%) and epoxy resins at 5°C.

$^1\text{H-NMR}$ (270 MHz, CDCl_3) δ in ppm: 7.05 (m, 4H, phenyl), 6.83 (m, 4H, phenyl), 4.15 (m, 2H, $-\text{CH}_2-$), 3.89 (m, 4H, $-\text{O}-\text{CH}_2-$), 3.32 (m, 2H, $-\text{CH}-\text{O}-$), 2.88 (dd, 1H, epoxy- CH_2), 2.74 (dd, 1H, epoxy- CH_2), 2.60 (dd, 1H, thiirane- CH_2), 2.26 (dd, 1H, thiirane- CH_2).

Curing of Thiirane Resin

Modified alicyclic polyamine, as a hardener, was added to the resins with vigorous stirring for 30 s, after which samples were cured at various temperatures. The curing ability was estimated by the change of viscosity under cure. The storage stability was estimated by the change of viscosity after heating at 70°C for 24 h.

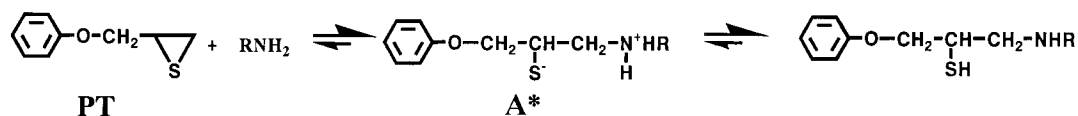
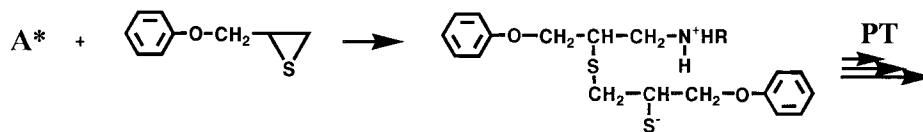
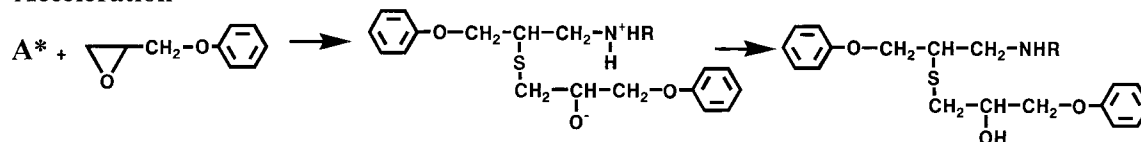
Measurements

Infrared (IR) spectra were performed on a Perkin-Elmer model 2000FTIR (Perkin Elmer Cetus Instruments, Norwalk, CT). $^1\text{H-NMR}$ spectra were performed on a JEOL model CSX-270 W (JEOL, Peabody, MA). Viscosity was measured on a Tokyo Keiki Co. model Visconic (EHD) as a Brookfield Synchro-Lectric Viscometer (cone-plate version, 3° cone; Brookfield Instruments). The flexural strength and compressive strength were evaluated using Shimadzu model 10TE (Shimadzu, Tokyo, Japan) according to ASTM D790 and D695, respectively. Approximately five specimens were tested for each condition and the results averaged.

RESULTS AND DISCUSSION

Synthesis of Thiirane Resin

Thiirane compound is known to be easily prepared from the corresponding epoxy compound.⁴ Generally, the reaction of epoxy resin with potassium thiocyanate or thiourea in polar solvents such as water and/or alcohol gave the thiirane resin quantitatively. Reaction of bisphenol-F epoxy resin with potassium thiocyanate in a mixture of water and EtOH at room temperature for

Addition**Oligomerization****Acceleration**

Scheme 2

10 h gave bisphenol-F thiirane resin with 50% thiirane unit at over 95% yield (Scheme 1). Furthermore, the substitution ratio of O to S was controllable from 1 to 100%. These thiirane resins were relatively odorless (based on the presence of the sulfur atom).

The crystallinity of bisphenol-A thiirane resin was higher than that of bisphenol-F thiirane resin, a result that may be attributed to bisphenol-F thiirane resin having many kinds of isomers. Bisphenol-A thiirane resin containing 50% of S unit was solid, whereas bisphenol-F thiirane resin containing 100% of S unit was liquid. Thus, bisphenol-F thiirane resin was easier to handle, especially at low temperatures. However, although curing became faster with increasing thiirane content, the viscosity rose and became hard to handle, and the storage stability was decreased. The curing of bisphenol-F thiirane resin that has 30% of thiirane moiety was sufficiently rapid, in addition to its ease of handling and good storage stability.

Cure Behavior of Thiirane Resin

In the curing of thiirane (S unit = 30%) or epoxy resin with 60 parts of modified alicyclic polyamine as a hardener (Fig. 1), the viscosity change at 5°C was used as the index of curing rate. The curing of thiirane resins was faster than that of corresponding epoxy resins. The curing rate of bisphenol-F thiirane resin was almost the same as that of bisphenol-A thiirane resin.

The rapid-cure reaction can be attributed to the high reactivity of the thiirane moiety and thiol group (thiolate anion), generated by the reaction of the thiirane group with amine during cure. Moreover, the reactivity of thiirane was thought to be further accelerated by the presence of the epoxy group, as reported previously (Scheme 2).⁵

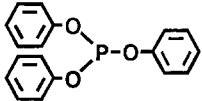
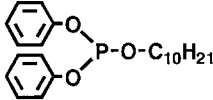
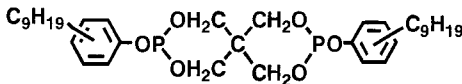
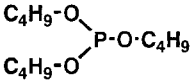
Generally, although the cure reaction terminates as a result of reaching equilibrium when only thiirane compound was present, the cure reaction can be accelerated by the retardation of the equilibrium when epoxy compound was also present.

Improvement of the Storage Stability of Thiirane Resin

By using the viscosity change of thiirane resin, after heating at 70°C for 24 h, as the index of storage stability, effects of various kinds of additives were estimated. Dehydration agents and trapping agents of thiol that may be generated by the reaction of thiirane with water during storage, such as isocyanate compound, phosphorus compound, and phenolic antioxidant as additives, were investigated. Phosphite compound was confirmed as the best compound for improvement of storage stability. The effect of adding various phosphites (1 mol %) to bisphenol-A thiirane resin (S = 30%) was further investigated (Table I).

This result indicated a correlation between the trapping ability of the phosphorous atom to the

Table I Effect of Adding Phosphites (1 mol %) to Bisphenol-A Thiirane Resin (S = 30%)

Additives	Viscosity change at 70°C after 24h (times)	
None	1.3	<p>Electron Density</p> <p>UP</p> <p>UP</p> <p>Steric hindrance</p> <p>Mutual solubility</p>
	8.24	
	1.05	
	1.81	
	1.43	
Bisphenol-A Epoxy	1.0	

thiol group and mutual solubility of phosphites to bisphenol-A thiirane resin. The trapping ability increased with increasing electron density of the phosphorous atom and with decreasing of its steric hindrance. That is to say, its trapping ability increased with increasing number of alkoxy groups and with decreasing number of phenoxy groups. On the other hand, mutual solubility in-

creased with increasing number of phenoxy groups. Phosphite, which has two phenoxy groups and one alkoxy group, was the most suitable compound for this cure system. Adding diphenyl decyl phosphite improved its storage stability to almost the same level as that of bisphenol-A epoxy resin. The use of phosphite compound did not affect the cure behavior of thiirane resin; that is, the stor-

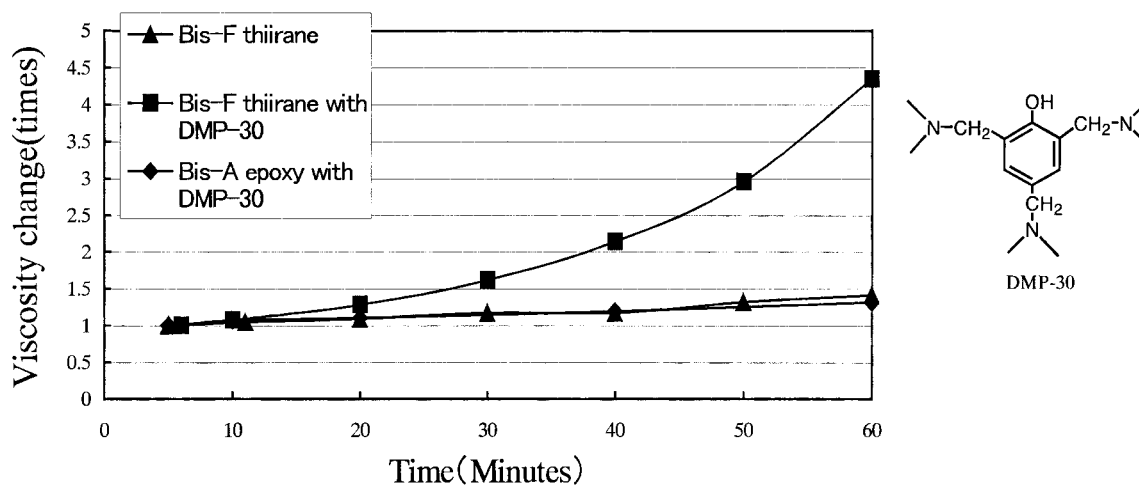
**Figure 2** Effect of adding DMP-30 (2 wt %) as a tertiary amine to bisphenol-F thiirane resin (S = 30%) at 0°C.

Table II Application of New Thiirane Resin to Civil and Architectural Adhesives

	Conventional Epoxy Resin for Low Temperature	New Thiirane Resin (S-content: 25%)
Cure condition	>5°C	> -5°C
Viscosity	High/<5°C	Low/<5°C
Working time	60 min/10°C	60 min/0°C
Gel time (tack-free)	>24 h/5°C	12 h/5°C
Cure time	1 week/5°C	2 days/5°C
Flexural strength	74.5 N/mm ² (25°C, 7 days)	20.6 N/mm ² (0°C, 2 days) 74.5 N/mm ² (0°C, 5 days)
Compressive strength	94.1 N/mm ² (25°C, 7 days)	71.5 N/mm ² (0°C, 7 days)

age stability could be improved while retaining the rapid-cure property.

Further Improvement of the Cure of Thiirane Resin

It was previously determined that adding tertiary amines to epoxy resin accelerates its cure.⁶ The effect of adding DMP-30 (2 wt %) as a tertiary amine to bisphenol-F thiirane resin (S = 30%) was investigated (Fig. 2).

The curing of bisphenol-F thiirane resin became three times faster by adding DMP-30 as a tertiary amine. This outcome is the result of the tertiary amine coordinating to the amine hardener and to the thiol generated by the reaction of thiirane with amine during cure, thus activating the attack of amine hardener and thiol to both the epoxy and the thiirane group.

Application

This novel rapid-cure resin can be applied to various purposes such as adhesives, sealants, coatings, laminates, caulking compounds, casting compounds, potting compounds, and encapsulation compounds. Applications of this new thiirane resin as civil and architectural adhesives were investigated (Table II). Although conventional epoxy resin for low temperature cannot be cured below 5°C, this new thiirane resin can be cured, even below -5°C. The viscosity of this new thiirane resin is much lower than that of the conventional epoxy resin below 5°C. The working time of this new thiirane resin was sufficiently long. The cure and gel times of this new thiirane resin were much shorter than those of the conventional epoxy resin. The flexural and compressive strength of this new thiirane resin, cured at 0°C, were almost the same as those of conventional epoxy

resin cured at 25°C. Superior curing and handling ability of this thiirane resin at low temperatures was proved for industrial application.

CONCLUSIONS

Rapid-cure adhesives characterized by superior curing and handling ability at low temperatures could be obtained by the following three breakthroughs:

1. Viscosity (crystallinity) can be reduced, by using bisphenol-F type resin.
2. Storage stability can be improved, while retaining rapid cure, by using diphenyl decyl phosphite as an additive.
3. Further acceleration of cure at low temperatures can be achieved, by using DMP-30 as a tertiary amine catalyst.

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