

# Novel Dibutyltin Oxide–Tributyl Phosphate Condensate as Accelerator for the Curing of the Epoxy Resin/4,4'-Diamino Diphenyl Sulfone System. I. Chemical Reactions and Properties of the Cured Resin

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**ABSTRACT:** A crystalline condensate of dibutyltin oxide and tributyl phosphate (Sn-P-c) was more effective than the stannous octoate and dibutyltin dilaurate in accelerating the curing of the epoxy resin/4,4'-diamino diphenyl sulfone (DDS) system, based on an equal tin concentration. Water took part in the reaction and played an important role in the morphology and mechanical properties of the cured resin when Sn-P-c was used as the accelerator. In the presence of Sn-P-c, water first reacted with glycidyl ether to yield glycerol ether; the yielded hydroxyl group may further catalyze the amino/epoxy group reaction. In the absence of water or polar hydroxyl additives, Sn-P-c did not completely dissolve in the resin systems, and the cured resin was translucent material with poor mechanical strength. In the presence of a small amount of water, the cured material became transparent. Both flexural strength and maximum deflection were increased greatly. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1229–1236, 2001

**Key words:** epoxy resin; condensate of dibutyltin oxide and tributyl phosphate; 4,4'-diamino diphenyl sulfone; catalyst

## INTRODUCTION

Epoxy resin/4, 4'-diamino diphenyl sulfone (DDS) systems are of great importance for high-performance composites and adhesives. However, owing to the electron withdrawing character of the sulfone group, DDS is sluggish toward the epoxy group, and therefore a high cure temperature is usually required. Lowering of the curing temperature is in many cases desirable for energy conservation or for the alleviation of the internal stress in the cured products.

Curing of epoxy resin with polyamine involves nucleophilic addition of the amino group to the epoxy group. Proton donors, such as water, alcohols, phenols, and acids, are known to exert an “electrophilic assistance” for this reaction.<sup>1</sup> Lewis acids, such as boron trifluoride monoethylene amine, organotransition metal complexes, stannous carboxylates, and stannic organophosphates are known to be used for accelerating the curing of epoxy resin/aromatic amine systems.<sup>2–5</sup>

The condensation products of organotin oxides or chlorides and di- or trialkyl phosphates are able to catalyze the polymerization of various epoxides.<sup>6–9</sup> The reaction proceeds through coordination of the epoxy oxygen to the electron deficient tin atom and a nucleophilic attack by alkoxide.<sup>4</sup> As the reaction mechanism for the addition

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of amino group to epoxy group is similar to that for the polymerization of epoxide, it is expected that the condensates of organotin oxide and trialkyl phosphate would be effective for accelerating the curing of epoxy resin with polyamines.<sup>10</sup>

In the present article, we report the catalytic effect of a novel condensate of organotin oxide and trialkyl phosphate for the curing of epoxy resin/DDS systems. The interactions between the components in the system were studied using the technique of differential scanning calorimetry (DSC), and through the study of the model compound. The influence of water on the morphology, and flexural properties of the cured thermoset were emphasized.

## EXPERIMENTAL

### Materials

The epoxy resin was Epon 828, supplied by Shell Company. DDS, a chemical reagent from Beijing Chemical Factory, was pulverized to pass through a 200 mesh sieve, and dried in vacuum at 100°C for 2 h before use. Phenyl glycidyl ether (PGE) was supplied by Yueyang Chemical Corporation. It was distilled under reduced pressure, and the fraction of 95–96°C/2 mm Hg was used. Dibutyltin oxide was supplied by Beijing Elf Atomchem Polystab Co., Ltd. It was dried in vacuum at 80–90°C for 4 h. Tributyl phosphate, stannous octoate, and dibutyltin dilaurate (DBTDL) were analytical reagents supplied by Beijing Chemical Factory. Glycerol was an analytical reagent and was dried over anhydrous potassium carbonate before use.

### Preparation of the Crystalline $\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ Condensate (Sn-P-c)

The mixture of  $\text{Bu}_2\text{SnO}$  and  $\text{Bu}_3\text{PO}_4$  (mole ratio 1:2) was heated at 140–180°C until dibutyltin oxide disappeared and the mixture became soluble in acetone. It usually took 4–18 h for this to happen, depending on the reaction temperature. The resulting yellow liquid was cooled to room temperature, and a needle-like crystalline product was formed. The product was purified by recrystallization from acetone or from hexane.

A typical synthesis procedure was as follows: 83.80 g  $\text{Bu}_2\text{SnO}$  (0.337mol) and 179.5 g (0.674mol)  $\text{Bu}_3\text{PO}_4$  were charged into a three-necked glass flask equipped with a distillation

**Table I** Analytical Results of Sn-P-c

Mole Ratio from <sup>1</sup> H-NMR <sup>a</sup>	$-\text{OCH}_2$	$-\text{CH}_2$	$-\text{CH}_3$
	10	62	36
Molecular weight (by VPO)	1400		
Melting point (°C, by DSC)	129		
Melting enthalpy (J/g, by DSC)	37.2		

<sup>a</sup> The mole ratio of group  $-\text{OBu}$  to  $-\text{Bu}$  in Sn-P-c is calculated as:  $(10 \times 4.5)/(10 + 62 + 36 - 10 \times 4.5) = 5/7$ .

head connected with a receiver through a condenser. The mixture was reacted at 153–158°C for 14 h. The crystalline product was filtered and recrystallized from acetone. The yield was 62.5 g (23.7%). The analytical results of Sn-P-c are given in Table I.

### Characterization

The DSC analysis was conducted on a TA 2100 Modulated Differential Scanning Calorimeter at a heating rate of 10°C/min under nitrogen atmosphere. Infrared spectra were taken on a PE-2000 Fourier Transform Infrared Spectrometer with a resolution of 2  $\text{cm}^{-1}$ . The conversion of the epoxy group was calculated according to the extinction of the 915  $\text{cm}^{-1}$  band with the phenyl band (1594  $\text{cm}^{-1}$ ) as the internal reference.

The <sup>1</sup>H-NMR analysis was carried out on a Bruker DMX 300 MHz NMR Analyzer. The spectrum was recorded at 300 K in  $\text{CDCl}_3$  with the pulse delay,  $D_1$ , set as 5 s, and tetramethyl silane (TMS) as the standard.

A three-point bending test was performed at room temperature according to the standard GB 1042-79 to determine the flexural properties of the cured resins. The specimens were 4 × 6 × 55  $\text{mm}^3$  rectangular bars. The measurement was conducted on an Instron 1122 Mechanical Analyzer. The support span was 48 mm, and the crosshead speed was 10 mm/min for the flexural strength determination, and 2 mm/min for the flexural modulus determination. The average value was taken from five specimens.

The morphology of the thermosets was investigated on a Hitachi S-530 Scanning Electron Microscope (SEM). The fracture surface was gold-sputtered before the observation.

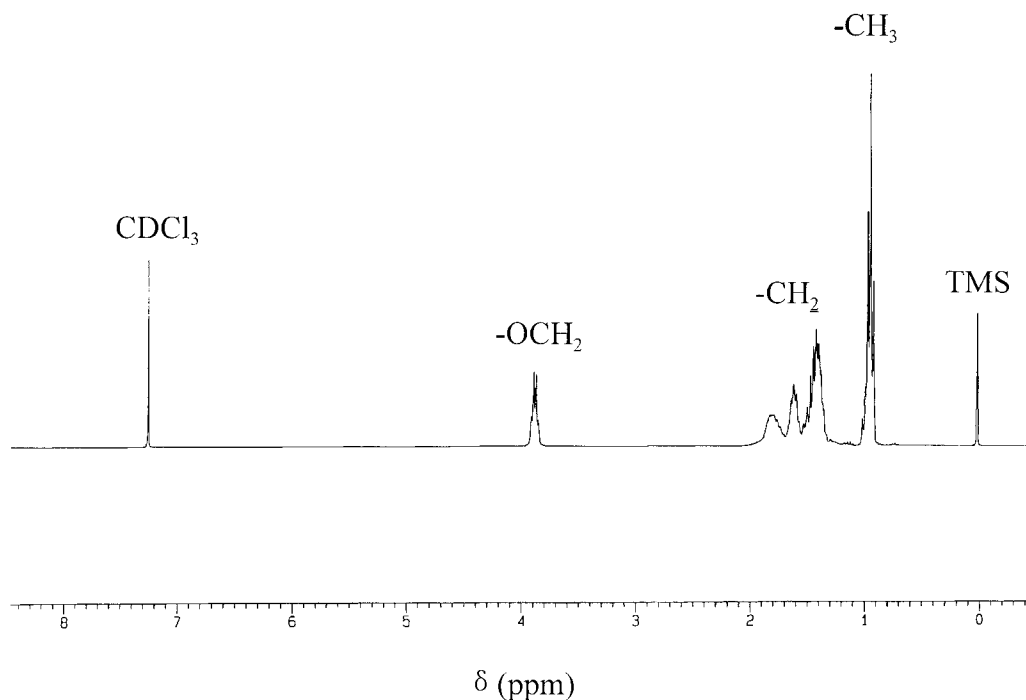


Figure 1  $^1\text{H-NMR}$  spectrum of Sn-P-c.

## RESULTS AND DISCUSSION

### The Crystalline Sn-P-c

Dibutyltin oxide is an inorganic polymer, which is insoluble in common organic solvents. The polymer chain of  $-\text{Bu}_2\text{SnO}-$  can be severed by reaction with tributyl phosphate. When the condensation of dibutyltin oxide and tributyl phosphate was carried out at high temperatures, for example at  $240\text{--}250^\circ\text{C}$ , pyrolysis took place, and the obtained products were very active for catalyzing the polymerization of epoxides.<sup>8</sup> Although the pyrolysis products were active for accelerating the cure of the epoxy resin with aromatic amine too, they were not soluble in the epoxy resin.

In order to improve the solubility of the Sn-P-c in the epoxy resin, we used a mild temperature for the condensation. When dibutyltin oxide and tributyl phosphate were reacted in the temperature range of  $140\text{--}180^\circ\text{C}$ , a crystalline condensation product was obtained. The yield of the product was influenced by the ratio of the reactants and the heating temperature. The composition and the melting temperature of the crystalline product, however, were not influenced by the reaction conditions.

Sn-P-c is easily soluble in common solvents such as hexane, benzene, acetone, and chloro-

form. It shows a melting peak at  $129^\circ\text{C}$  in the DSC curve. The average molecular weight by VPO was 1400. In the  $^1\text{H-NMR}$  spectrum (Fig. 1), only the signals for the Sn-Bu and the P(O)-OBu structure could be identified. The signal at 3.85 ppm is due to the methylene protons adjacent to oxygen in butoxy groups, while the rest of the protons in butoxy groups, together with the butyl protons attached to tin, give rise to signals in the range of 0.7–1.7 ppm. The molar ratio of the P(O)-OBu group to the Sn-Bu group in Sn-P-c is 5:7, according to the integration of the  $^1\text{H-NMR}$  signals. Based on the above results, an empirical formula for Sn-P-c is suggested, as shown in Figure 2.

### Acceleration of the Cure of Epon 828/DDS Systems by Organic Tin Compounds

We used the gelation time as an index for the comparison of the curing rate of the Epon 828/

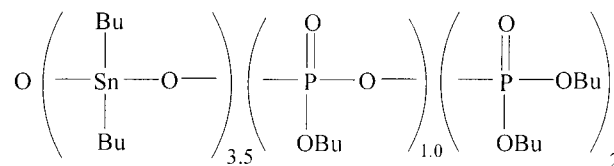


Figure 2 Empirical formula of Sn-P-c.

**Table II** The Catalytic Effect of Organotin Compounds for the Epon 828/DDS System<sup>a</sup>

Catalyst			Conversion of Epoxy Group by IR	
Compound	Concentration (phr)	Gelation Time at 140°C (min)	Curing Conditions °C/min	Conversion (%)
None	—	190	180/270	96.5
Sn-P-c	2.0	65	140/270	95.0
Stannous octoate	1.34	109	140/270	90.8
DBTDL	2.92	117	140/270	90.0

<sup>a</sup> DDS 32 phr; water absorbed by the components was not purposefully removed.

DDS systems. The reaction was very slow at 140°C for the system without a catalyst. It is shown in Table II that stannous octoate and DBTDL were able to accelerate the curing of the Epon 828/DDS system, and Sn-P-c was more effective in comparison with the stannous salt and the organotin compound, based on an equal tin concentration.

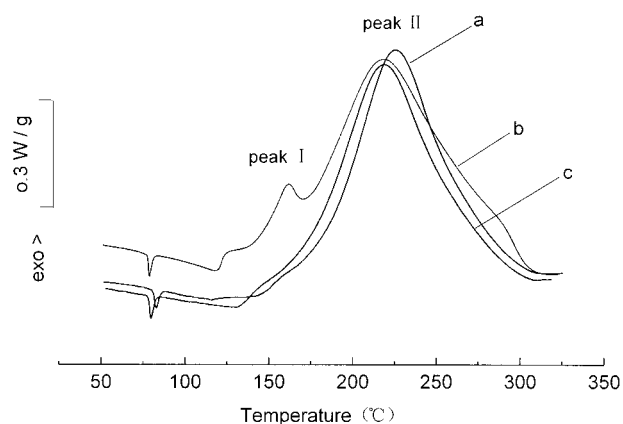
Figure 3 shows the DSC thermograms for the Epon 828/DDS, Epon 828/DDS/Sn-P-c, and Epon 828/DDS/DBTDL systems. The curing agent DDS was in stoichiometric ratio, i. e., 32 parts per 100 parts of resin by weight (phr). The small endothermic peaks around 83°C can be attributed to the fusion of a crystalline impurity existing in DDS.<sup>11</sup> The catalytic effect is seen from the downward shift of the onset temperature and the exothermic peak. The main peak for the epoxy/amine reaction was shifted from 225 to approximately 218°C in the presence of the catalyst.

From the onset temperature of the DSC thermograms and the conversion of the epoxy group

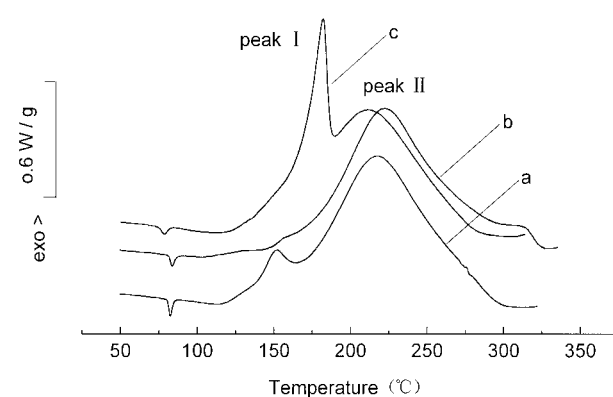
given in Table II, it can be seen that with the addition of 2 phr of Sn-P-c, the curing temperature of the Epon 828/DDS system can be lowered by around 40°C.

#### Reaction of Water in the Curing System with Sn-P-c as Accelerator

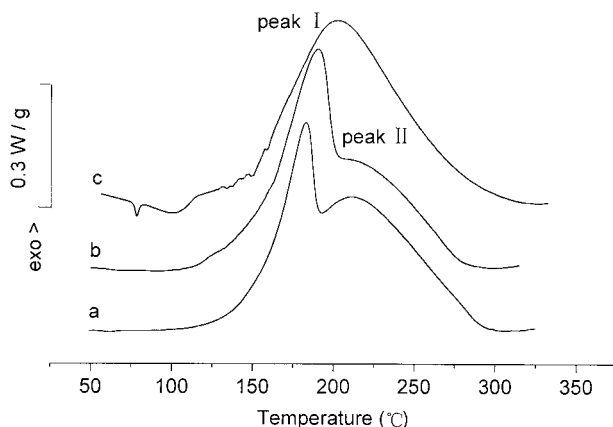
In the DSC curve for the resin catalyzed by Sn-P-c (Fig. 4, curve a), there is a significant exothermic peak at 152°C. This peak was attributed to the reaction of water. Moisture could be absorbed by the resin and the curing agent. It was also absorbed on the aluminum DSC sample pan. The exothermic peak was depressed to a shoulder (Fig. 4, curve b) when the sample pan and the sample were dried at 75°C for 15 min in a good vacuum before scanning. On the contrary, when 2.4 phr of water was introduced to the sample, the area of the first exothermic peak increased greatly, and the peak position was shifted to 182°C (Fig. 4, curve c).



**Figure 3** DSC thermograms for (curve a) Epon 828/DDS, (curve b) Epon/828/DDS/2 phr Sn-P-c, and (curve c) Epon 828/DDS/2.9 phr DBTDL.



**Figure 4** DSC thermograms for (curve a) Epon 828/DDS/2 phr Sn-P-c, (curve b) Epon 828/DDS/2 phr Sn-P-c with the components carefully dried, and (curve c) Epon 828/DDS/2 phr Sn-P-c/2.4 phr water.



**Figure 5** DSC thermograms for (curve a) Epon 828/DDS/2 phr Sn-P-c/2.5 phr glycerol, (curve b) Epon 828/DDS/2 phr Sn-P-c/7.8 phr glycerol, and (curve c) Epon 828/DDS/7.8 phr glycerol.

The presence of Sn-P-c was the necessary condition for the reaction of water. For the Epon 828/DDS system without catalyst, or with a weak catalyst such as DBTDL, no exothermic peak for the reaction of water was present in the DSC curves.

The upward shift of the exothermic peak by introduction of water to the system can be accounted for by the change of the activity of the catalyst. Sn-P-c is a Lewis acid in nature. Coordination of the electron-donating  $H_2O$  molecules to Sn-P-c makes the catalyst less active for the reaction.

The reaction of water resulted in the hydrolysis of the epoxy group to form glycerol ether. Phenyl glycidyl ether was used as model compound to demonstrate the reaction of water in the presence of Sn-P-c. For example, a mixture of 15.0 g (0.10 mol) PGE, 1.80 g (0.10 mol) water, 0.30 g Sn-P-c, and 30 mL toluene was refluxed for 4 h, and a needle-like crystalline product (mp 53.9°C) was obtained. It was identified as phenyl glycerol ether by  $^1H$ -NMR spectrum and mass spectroscopic analysis.

#### Reaction of Alcohol with Epoxy Resin Catalyzed by Sn-P-c

The DSC curve for the Epon 828/DDS/Sn-P-c/glycerol system is given in Figure 5. The area of the first exothermic peak increased as the amount of the introduced glycerol increased. The peak position increased in the same trend, which was 183°C when 2.5 phr glycerol was introduced (Fig. 5, curve b), and 190°C when 7.8 phr glycerol was

introduced (Fig. 5, curve b). Etherification should take place, because similar etherification products have been reported in the literature.<sup>12</sup> As alcohols are not reactive enough toward epoxy groups, the first exothermic peak did not appear in the absence of the catalyst (Fig. 5, curve c).

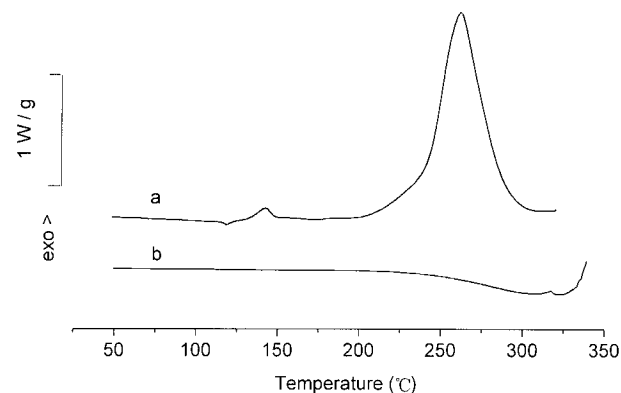
Therefore, we believe that the hydrolysis of the epoxy group should be followed by the etherification reaction of the yielded hydroxyl group with the epoxy group. The exothermic peaks for the hydrolysis and the etherification reaction were overlapped, and the peak position was dependent upon the kind and the concentration of the electron-donating substances.

#### Polymerization of the Resin Catalyzed by Sn-P-c

When DDS was omitted from the system, there were two exothermic peaks in the DSC thermogram for the Epon 828/Sn-P-c mixture (Fig. 6, curve a). The first small peak at 143°C was attributed to the hydrolysis of the epoxy group by absorbed moisture, and the heat of the reaction was 6.9 J/g.

It should be pointed out that the first peak for the Epon 828/Sn-P-c mixture was around 10 degrees lower than that for the Epon 828/DDS/Sn-P-c mixture (Fig. 4, curve a). The difference of the peak position can be accounted for, again, by the change of the catalytic activity with the composition of the system. DDS is a weak electron donating substance. Therefore, the catalytic activity of Sn-P-c for the hydrolysis of the epoxy group was depressed by DDS.

The second peak at 262°C was attributed to the polymerization of the epoxy group, the peak temperature of which was much higher than that for



**Figure 6** DSC thermograms for (curve a) Epon 828/4.25 phr Sn-P-c and (curve b) Epon 828 without catalyst.

**Table III Mechanical Properties and Epoxy Conversion of the Epon 828/DDS/Sn-P-c Thermosets<sup>a</sup>**

Code	Sn-P-c (phr)	Additive (phr)	Cure Conditions (°C/min)	$\alpha^d$ (%)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Maximum Deflection (mm)
1	0	—	180/270	96.5	144.0 ± 9.6	2.38 ± 0.05	7.89 ± 0.97
2 <sup>b</sup>	2	—	140/270	91.3	95.3 ± 6.9	2.26 ± 0.06	3.98 ± 0.59
3 <sup>c</sup>	2	—	140/270	94.3	169.5 ± 5.5	2.60 ± 0.05	8.06 ± 1.11
4 <sup>c</sup>	2	Water (1)	140/270	96.7	172.5 ± 4.0	2.42 ± 0.05	11.47 ± 0.68

<sup>a</sup> DDS was 32 phr.

<sup>b</sup> The components were dissolved in acetone and the solvent was then removed by stirring at 120–130°C in vacuum for 2 h before the curing.

<sup>c</sup> The mixture of Epon 828 and Sn-P-c was heated at 140°C for 30 min before addition of DDS and additives.

<sup>d</sup>  $\alpha$ : epoxy conversion measured by IR.

the addition of the amino group; the heat of the reaction was 375.5 J/g. In the absence of a catalyst the epoxy resin did not polymerize until the temperature reached 340°C, as shown by Figure 6 (curve b).

#### Reaction of DDS with Epoxy Resin Catalyzed by Sn-P-c

Addition of an amino group to an epoxy group is the main reaction for the curing. The main exothermic peak in the DSC thermograms of Figures 4 and 5 was contributed to by this reaction. It has been found that the peak position was strongly influenced by moisture content in the system. For the dehydrated mixture of Epon 828/DDS/Sn-P-c, the exothermic peak located at 222°C, for the normal mixture it located at 218°C, and it located at 211°C when 1 phr water was introduced to the system.

The onset temperature for the amino/epoxy group reaction is of importance for design of the cure regime. However, it cannot be determined in the DSC thermograms owing to the exothermic peak for the hydrolysis and the etherification.

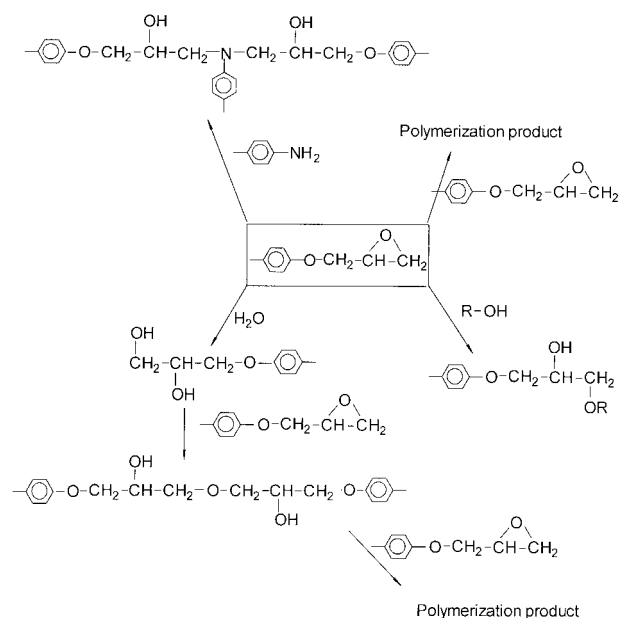
The presence of moisture is very important for the curing at moderate temperatures catalyzed by Sn-P-c. It can be seen in Table III that the conversion of a dehydrated Epon 828/DDS/Sn-P-c mixture after 270 min at 140°C was 91.3%, according to the change of the epoxy band in the IR spectrum. In the same conditions, the conversion was 94.3% for the normal mixture (the moisture absorbed by the components was not purposefully removed), and the conversion was 96.7% when 1 phr water was introduced to the mixture. In the following paragraphs, the effect of water on the curing of the Epon 828/DDS/Sn-P-c system will be discussed in more detail.

The reactions of the epoxy group in the presence of Sn-P-c are summarized in Figure 7.

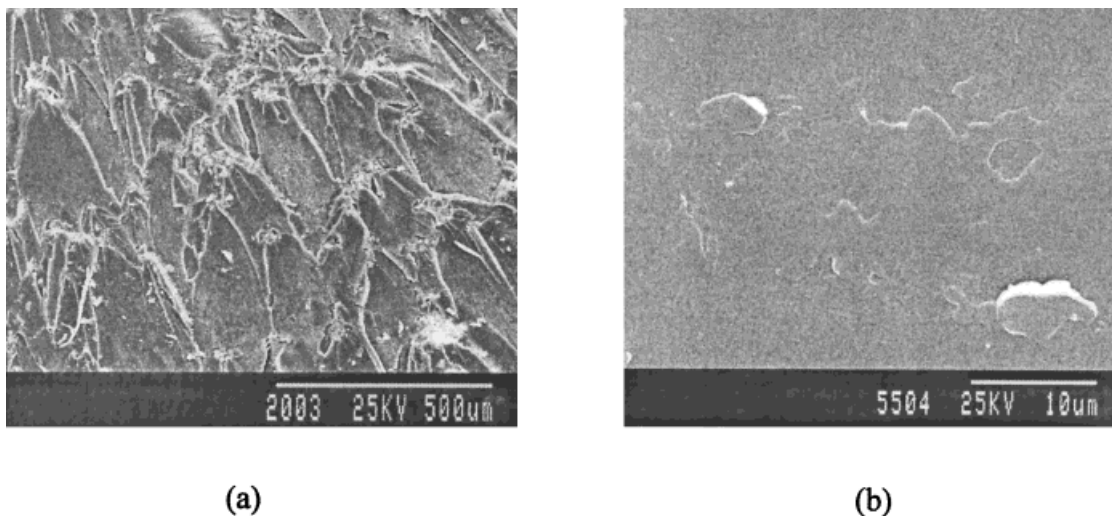
#### Dissolution of the Catalyst Sn-P-c

Sn-P-c did not completely dissolve in the Epon 828/DDS mixture in dehydrated conditions. Both Sn-P-c and the Epon 828 resin were soluble in acetone, and the mixture of the two solutions was clear. However, as the solvent was removed in vacuum, a part of the catalyst was precipitated out. Therefore, the cured resin of Epon828/DDS/Sn-P-c was turbid. Domains of around 50  $\mu\text{m}$  diameter were observed under SEM [Fig. 8(a)].

Dissolution of the catalyst in the Epon 828 could be improved by addition of a small amount



**Figure 7** Scheme of the reactions of the epoxy group catalyzed by Sn-P-c.



**Figure 8** SEM micrographs of the fracture surface of the Epon 828/DDS/Sn-P-c thermoset cured at 140°C for 4.5h. (a) The components were dissolved in acetone and the solvent was removed at 120–130°C in vacuum for 2 h before effecting the cure. (b) Sn-P-c was dissolved in Epon 828 with the help of a small amount of water before the introduction of DDS.

of water. When a few drops of water were added to the turbid mixture of Epon 828/Sn-P-c, the mixture became clear after heating at 140°C for 2 min. The amount of water needed for this transformation was less than 0.05 phr in the system. The transformation was a reversible process; as water was removed immediately by applying a vacuum, the transparency of the resin decreased again. It was found that the moisture absorbed from the atmosphere by the resin and the curing agent was enough to help the dissolution of the catalyst.

As discussed above, water would react with the epoxy group in the presence of Sn-P-c when heating continued. The reaction product of water with the epoxy group was glycerol ether. It was therefore expected that hydroxyl compounds would be helpful to improve dissolution of the catalyst in the resin. Complete dissolution of Sn-P-c was achieved with addition of 1 phr glycerol.

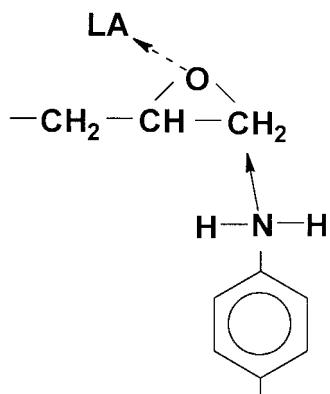
In order to make complete dissolution of Sn-P-c, in the practice, the mixture of Epon 828 resin (with moisture) and Sn-P-c was heated at 140°C for 30 min to effect the dissolution of Sn-P-c. During this process, a consumption of around 6% of the epoxy group was estimated by infrared spectroscopy. Then the curing agent DDS was introduced. In this way, transparent thermosets with good mechanical properties were obtained. The fracture surfaces of the thus formed thermosets are homogeneous in the SEM micrograph [Fig. 8(b)].

#### Mechanical Properties of the Cured Resin with Sn-P-c as the Catalyst

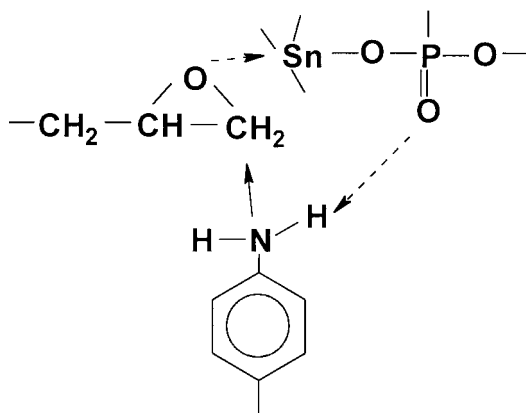
The presence of water was important to the mechanical properties of the cured resin when Sn-P-c was used as the catalyst. In the absence of moisture, curing of the Epon 828/DDS/Sn-P-c systems resulted in turbid materials with poor mechanical properties.

The results of flexural tests are given in Table III. In the experiment Code 2, the components were dissolved in acetone and the solvent was then stripped in vacuum by stirring at 120–130°C for 2 h. In this way, the moisture in the system was also removed. After that, the resin was cured at 140°C for 270 min and a turbid thermoset was obtained. Compared with the control specimen (Code 1; without catalyst and cured at 180°C for 270 min), introduction of 2 phr of Sn-P-c with removal of water absorbed by the components made a 34% loss in flexural strength of the thermoset. The presence of domains, as shown in Figure 8(a), acted as stress intensifying centers that weakened the mechanical strength.

In the experiments Code 3 and Code 4, the mixture of Epon 828 and 2 phr Sn-P-c was stirred at 140°C in the air for 30 min to effect the dissolution of Sn-P-c before introduction of the curing agent DDS. The presence of a small amount of water, even the moisture absorbed by the resin and the curing agent from the atmosphere, was effective to make the cured material transparent.



Scheme 1



Scheme 2

**Figure 9** Scheme 1: The nucleophilic attack of the amino group on the epoxy carbon atom promoted by electrophilic assistance mechanisms (Lewis acid). Scheme 2: The “pull-push” mechanism in the presence of Sn-P-c.

In this way, both flexural strength and maximum deflection of the catalyzed resins were increased greatly. The improvement in the mechanical properties of the thermoset by this treatment could be attributed to the better dissolution of Sn-P-c.

#### A Further Discussion on the Mechanisms

A number of reactions can take place in the Epon 828/DDS/Sn-P-c system, as discussed above. Water plays a great role when Sn-P-c is used as the

catalyst. The effect of water is twofold. First, moisture promotes the dissolution of Sn-P-c in the system, so that Sn-P-c can be effective. Moreover, the reaction product of water with the epoxy group, glycerol ether, is a proton donor, which also favors the amino/epoxy group reaction. The above two mechanisms may work together in a synergetic way.

It is known that the nucleophilic attack of the amino group on the epoxy carbon atom can be promoted by electrophilic assistance of a Lewis acid,<sup>1</sup> which is denoted as “LA” in Scheme 1 of Figure 9. The higher catalytic activity of Sn-P-c, compared to that of stannous octoate and dibutyltin dilaurate, may be related to the highly electron-deficient character of the tin atom substituted by the electron-withdrawing phosphate groups in Sn-P-c. Meanwhile, in the case of Sn-P-c as the catalyst, the space arrangement of the electron-deficient tin atom and the pyrophosphate moiety seems to make a “pull-push” mechanism work, as shown in Scheme 2 of Figure 9.

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#### REFERENCES

1. Rozenberg, B. A. *Adv Polym Sci* 1986, 75, 113.
2. May, C. A., Ed. *Epoxy Resins—Chemistry and Technology*; Marcel Dekker: New York, 1988.
3. Stoakley, D. M.; St Clair, A. K. *J Appl Polym Sci* 1986, 31, 225.
4. Lin, K. F.; Shu, W. Y.; Wey, T. L. *Polymer* 1993, 34, 277.
5. William, R. P.; Charleston, W. Va. US Pat. 3 281 376, 1966.
6. Nakata, T. In *Coordination Polymerization*; Price, C. C.; Vanderberg, J. E., Eds.; Plenum Press: New York, 1983; 55.
7. Otera, J.; Yano, T.; Kunimoto, E.; Nakata, T. *Organometallics* 1984, 3, 426.
8. Miura, K.; Kitayama, T.; Hatada, K.; Nakata, T. *Polym J* 1993, 25, 685.
9. Xu, J. J.; Hou, K. Y.; Song, R.; Li, L. P.; Yu, Y. Z. *Polym Bull* 1998, 40, 395.
10. Xu, J.; Yu, Y. CN Pat. Appl. No. 98101525.5, 1998.
11. Morgan, R. J.; Walkup, C. M.; Hoheisel, T. H. *J Appl Polym Sci* 1985, 30, 289.
12. Otera, J.; Niibo, Y.; Tatsumi, N.; Nozaki, H. *J Org Chem* 1988, 53, 275.