

Curing and Thermal Behavior of DGEBA in the Presence of Heterocyclic Derivatives of Stannanes

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Received 4 September 2006; accepted 17 January 2007

DOI 10.1002/app.26793

Published online 13 September 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The article describes the synthesis and characterization of heterocyclic derivatives of stannanes obtained by reacting 1 mol of biguanide (B) with 1 mol of phenylethyltindihydride (PED) or phenylmethyltindihydride (PMD) or phenylbutyltindihydride (PBD) or butylmethyltin dihydride (BMD) and their use as curing agents for diglycidyl ether of bisphenol-A (DGEBA). The derivatives so obtained have been designated as BPED or BPMD or BPBD or BBMD. Structural characterization of the derivatives was done by elemental analysis and spectroscopic techniques, viz. IR, ^1H NMR, ^{13}C NMR, ^{119}Sn NMR. These derivatives were used as curing agents to investigate the effect of structure on the curing and thermal behavior of

DGEBA. The curing behavior of DGEBA was investigated by differential scanning calorimetry in the presence of stoichiometric amounts of derivatives. A broad exothermic transition in the temperature range of 180–232°C was observed in all the samples. Thermal stability of epoxy resin, cured isothermally, was evaluated by recording thermogravimetric traces in nitrogen atmosphere. The percent char yield was highest in case of resin sample, DBPMD. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 228–235, 2008

Key words: synthesis; characterization; diglycidyl ether of bisphenol-A (DGEBA); curing; thermal behavior

INTRODUCTION

Epoxy resins have been commercially available for about 45 years and are now used in many major industrial applications, especially where major technical advantages warrant their somewhat higher cost with respect to other thermosets. The characteristics of toughness, low shrinkage on curing, high adhesion to many substrates, good alkali resistance, and versatility in formulation make epoxy resins widely used in adhesive, laminating, coating, and casting applications. The chemistry and technological applications of epoxy are voluminous, and there are many new developments each year. To meet some application requirements, several approaches have been used to enhance the thermal properties of epoxy resins.^{1,2}

The full characterization of the cure process of an epoxy resin involves many factors, that is, the properties and performance of the cured epoxy resin, which are dependent on the type of epoxy resin, the curing agent, and the curing conditions used. If the chemical structures of cured epoxy resins are constituted with aromatic rings, heterocyclic rings, or both, their thermal resistance is superior

to those of constituents with flexible or aliphatic chains.³

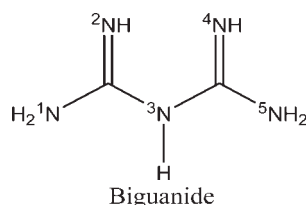
To prepare high-performance epoxies, many researchers synthesized polymeric networks with a liquid-crystalline order. The resulting networks could be used in new applications because of their mechanical, electrical, and optical properties.^{4–7} Liquid-crystalline epoxy networks were obtained mostly by chemical reactions between epoxy groups contained in the liquid-crystalline compounds and the curing agent. Another way to improve the thermal resistance of epoxy resins is to use a curing agent containing imide, urethane,⁸ or heterocyclic groups, such as hydroxyl-terminated imide compounds^{9,10} and imide acid.^{11,12}

Reaction of diglycidyl ether of bisphenol-A (DGEBA) with trialkyl or aryl phosphate followed by curing with 4,4'-diaminodiphenyl sulfone gave products with good thermal stability and flame resistance.^{13,14}

Synthesis and structural studies of neutral tetra coordinated tin compounds derived from ligands with strategically placed donor atoms (O, N, and S) have received considerable attention in the past.^{15,16} Major emphasis has been directed to understand the role of ligands as nucleophiles.

The chemistry of biguanide has provided a fertile field of chemical research ever since the first preparation of the parent base by Rathke.¹⁷

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The biguanide behaves as a strong chelating bidentate ligand for metal ions.^{18,19} It shows coordination either through imine nitrogen atoms (2 and 4 nitrogen atom of biguanide) or through amine nitrogen atoms (1 and 5 nitrogen atom of biguanide) to metals ions.¹⁹

In the views of the above, it was thought worthwhile to synthesize the derivatives of PhEtSnH₂, PhMeSnH₂, PhBuSnH₂, and BuMeSnH₂ by reacting these hydrides with biguanide, to develop the flame resistance cured epoxy and to study the curing and thermal behavior of epoxy resin (DGEBA) in the presence of different derivatives of tin-containing nitrogen atom.

EXPERIMENTAL

Materials

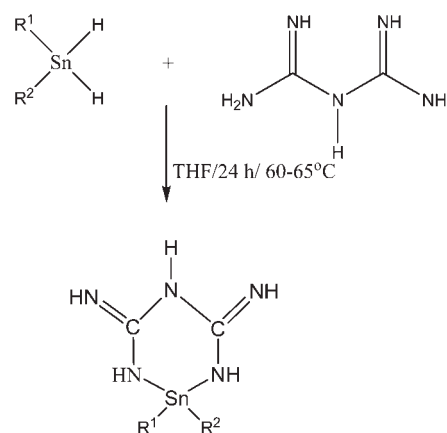
Diglycidyl ether of bisphenol-A (DGEBA, Grade LY556 having an epoxy equivalent 177) was procured from Hindustan Ciba Geigy (Maharashtra, India). Tetramethyltin, tetraethyltin, tetrabutyltin, phenyltin trichloride, trimethyltin chloride, and butyltin trichloride (Sigma Aldrich Chemical Pvt. Ltd., New Delhi, India) were used as such. Phenylmethyltin dichloride, phenylethyltin dichloride, phenylbutyltin dichloride, butylmethyltin dichloride,²⁰ and biguanide²¹ were prepared as reported in literature. Phenylmethyltin dihydride (PhMeSnH₂), phenylethyltin dihydride (PhEtSnH₂), phenylbutyltin dihydride (PhBuSnH₂), and butylmethyltin dihydride (BuMeSnH₂) were prepared from the corresponding chlorides by reaction with LiAlH₄ in accordance with the literature method.²² The biguanide base was obtained by treating the biguanide sulfates with alcoholic NaOH. All the solvents were dried and distilled by reported methods.

Synthesis of derivatives

Synthesis of BPED: To a stirred solution of phenylethyltin dihydride (0.510 g, 2.25 mmol) in dry THF (~ 60 mL), biguanide (0.227 g, 2.25 mmol) was added. The mixture was refluxed for 24 h. It was then concentrated under vacuum. To the concentrated liquid was added *n*-hexane. A yellow-colored solid was precipitated out, which was separated and dried.

The similar procedure was used for the reactions of the other stannanes with biguanide in the molar ratio of 1 : 1. The results of these reactions are summarized in Table I.

The reaction scheme for synthesis is as follows:



where R¹ = Ph, R² = Et; R¹ = Ph, R² = Me; R¹ = Ph, R² = Bu.

Four derivatives were synthesized by reacting biguanide with phenylethyltin dihydride (BPED)/phenylmethyltin dihydride (BPMD)/phenylbutyltin dihydride (BPBD)/butylmethyltin dihydride (BBMD).

Characterization

IR spectra were recorded using Shimadzu FTIR 8700 Spectrophotometer. ¹H NMR, ¹³C NMR, and ¹¹⁹Sn NMR were recorded on a Bruker 300 MHz spec-

TABLE I
Analytical Data

Sr. no.	Compound : Ligand (g)	Molar ratio at refluxing time 24 h	Products, color	Analysis : Found (%)			
				C	H	N	Sn
1.	PMD : B 0.479 (2.25) ^a : 0.227 (2.25)	1 : 1	BPMD, yellow paste	34.5 [34.9] ^b	4.6 [4.2]	22.4 [22.6]	38.6 [38.3]
2.	PED : B 0.510 (2.25) : 0.227 (2.25)	1 : 1	BPED, yellow paste	36.4 [37.1]	4.5 [4.7]	21.1 [21.6]	35.9 [36.6]
3.	PBD : B 0.574 (2.25) : 0.227 (2.25)	1 : 1	BPBD, yellow paste	40.6 [40.9]	5.2 [5.4]	20.1 [19.9]	33.3 [33.7]
4.	BMD : B 0.434 (2.25) : 0.227 (2.25)	1 : 1	BBMD, yellow paste	28.7 [29.0]	5.6 [5.9]	23.9 [24.1]	40.5 [40.9]

^a Values within parentheses are given in mmol.

^b Values within square brackets indicate calcd. in %.

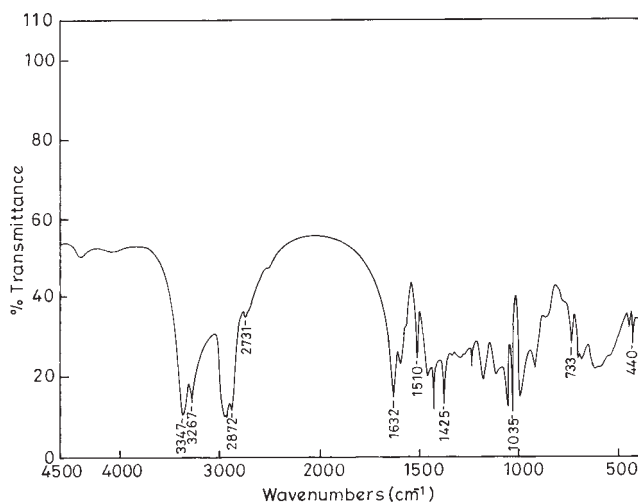


Figure 1 FTIR spectrum of BPED.

trometer using CDCl_3 as solvent and tetramethylsilane as internal standards. Elemental analysis was carried out using EURO EA 3000 elemental analyzer. Tin was estimated by standard method.²³

Curing studies

TA 2100 thermal analyzer having a 910 DSC module was used to record DSC scans at $10^\circ\text{C}/\text{min}$. For curing studies, samples were obtained by mixing DGEBA with stoichiometric amounts of derivatives dissolved in methyl ethyl ketone. After thorough mixing, the solvent was removed under vacuum and the freshly prepared samples were used for recording DSC traces in nitrogen atmosphere at a programmed heating rate from room temperature to 350°C . 5 ± 2 mg of samples were used in each experiment. DSC scans of isothermally cured samples were also recorded to determine the effect of

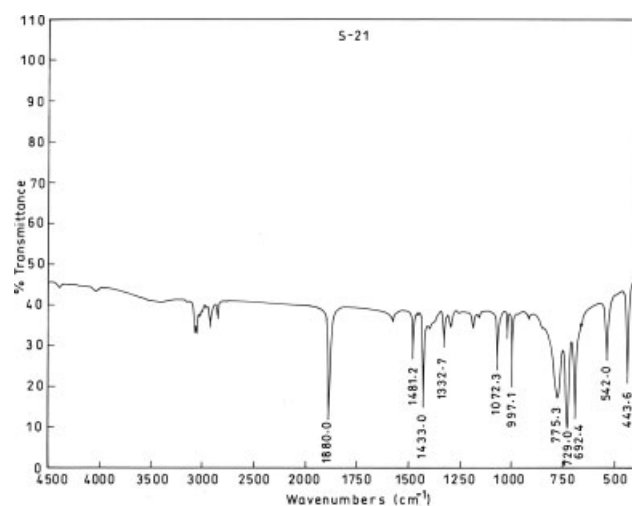


Figure 2 FTIR spectrum of PED.

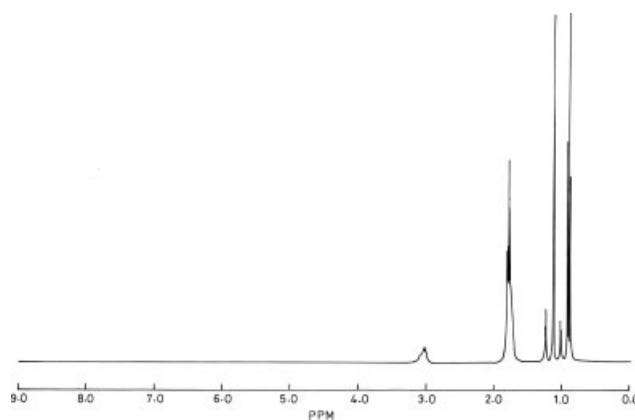


Figure 3 ^1H NMR spectrum of BBMD.

network structure on the glass transition temperature. The curing mixtures of DGEBA and derivatives (BPED, BPMD, BPBD, and BBMD) have been designated by the introduction of prefix D to the letter designation of derivatives such as DBPED, DBPMD, DBPBD, and DBBMD, respectively.

Thermal stability

Thermal stability of the resins cured isothermally by heating ($175 \pm 20^\circ\text{C}$) for 2 h in an air oven in the presence of various derivatives was evaluated by recording TG/DTG traces in nitrogen atmosphere (flow rate $60 \text{ cm}^3/\text{min}$) using a Rheometric Thermal Analyzer. A heating rate of $20^\circ\text{C}/\text{min}$ and powdered samples of 10 ± 2 mg were used in each experiment.

RESULTS AND DISCUSSION

All the derivatives were yellow in color, soluble in polar solvents, viz. chloroform, dimethylsulfoxide, and tetrahydrofuran, but insoluble in nonpolar solvents, viz. carbon tetrachloride and hexane.

Figure 1 shows FTIR spectrum of the BPED and Figure 2 shows FTIR spectrum of PED. The IR spectra of phenylmethyltin dihydride, phenylethyltin dihydride, phenylbutyltin dihydride, and butylmethyltin dihydride showed characteristics bands approximately at 2968, 2926, and 2877 cm^{-1} due to $\nu(\text{C-H})$ of alkyl groups. These bands were observed nearly at the same positions in all the derivatives. A sharp absorption observed in the range $1880\text{--}1820 \text{ cm}^{-1}$ was due to $\nu(\text{Sn-H})$ of stannanes. The IR spectra of the biguanide ligand showed bands at 3420 and $3347\text{--}3267 \text{ cm}^{-1}$ assigned to νNH_2 and νNH , respectively. The respective bands observed at 1633, 1556, and 1457 cm^{-1} had been assigned $\nu(\text{C=N})$ and $\nu(\text{NCN})$. An absorption band due to C=N stretching observed at $\sim 1633 \text{ cm}^{-1}$ both in biguanide and in all the derivatives suggested that imine functions

TABLE II
¹H NMR Spectral Data of Derivatives

Sr. no.	Derivatives	Phenyl protons	—NH	¹ CH ₂ ² CH ₃	—CH ₃	¹ CH ₃ ² CH ₂ ³ CH ₂ ⁴ CH ₂ Sn
1.	BPMD	7.51–7.45 (5 H, m)	3.6–3.9 m (4 H, br)	—	1.0	—
2.	BPED	7.48–7.37 (5 H, m)	3.5–3.7 m (4 H, br)	0.9 q (1), 1.3 t (2)	—	—
3.	BPBD	7.31–7.26 (5 H, m)	3.3–3.0 m (4 H, br)	—	—	0.6 t (4), 1.5–1.2 m (1, 2, 3)
4.	BBMD	—	3.2–2.9 m (4 H, br)	—	1.1	0.9 t (4), 1.9–1.7 m (1, 2, 3)

(=NH) were free and had not been involved in the bond formation. In spectra of ligand bands observed at 1556 and 1457 cm⁻¹ due to ν NCN are observed at 1510–1513 and 1426–1430 cm⁻¹ in derivatives. In all derivatives two bands were observed at ~ 3267 and 3347 cm⁻¹ due to —NH— groups. The two bands were observed due to the fact the two —NH— groups of the ligand moiety were directly linked to the Sn atom, whereas the other three —NH— groups were not linked to the Sn atom and hence showed different stretching absorptions.

The absorption at ~ 3420 cm⁻¹ due to ν NH₂ mode was absent in all derivatives indicating further that NH₂ group had been involved in the bond formation. The band due to (C—N) stretching (which was observed at 1080 cm⁻¹ in IR spectra of the biguanide) observed at ~ 1035 cm⁻¹ in the derivatives. In all the derivatives bands nearly at 440 cm⁻¹ were observed due to ν Sn—N mode. Further, absence of the band due to ν Sn—H mode in all the derivatives clearly indicated that both the hydrogen bonded to tin had been used in the dehydrocoupling reaction with biguanide.

Because of the presence of band due to ν Sn—N mode and absence of band due to ν Sn—H mode in all the derivatives, and further, due to strong chelating nature of biguanide,^{9,10} it is proposed that formation of chelate ring has taken place. The same can be concluded from the IR spectra of all Cu and Ni complexes using the criterion given by McLellan and Kedzia.²⁴

¹H NMR spectrum of the BuMeSnH₂ showed a multiplet in the range δ 1.3–0.2 due to intermixing of the butyl and methyl protons. A signal observed at δ 4.3 was due to hydrogen directly attached to Sn atom. ¹H NMR spectra of PhEtSnH₂, PhMeSnH₂, and PhBuSnH₂ showed a multiplet in the range δ 7.4–7.1 due to phenyl protons. In case of PhMeSnH₂, a signal observed at δ 0.4 was due to methyl protons directly attached to tin ²J (Sn—H = 4.5 Hz). A signal observed at δ 5.0 was due to hydrogen attached with tin ³J (HC—SnH = 3 Hz). In case of PhEtSnH₂, the signal centered at δ 1.1 was due to the intermixing of methylene and methyl protons of ethyl group. A signal observed at δ 5.2 is due to protons attached to Sn atom. In case of PhBuSnH₂, a multiplet was observed in the range δ 1.6–0.8 due to butyl protons

attached to tin. A signal observed at δ 5.8 was due to hydrogen directly attached to tin.

Figure 3 shows the ¹H-NMR spectrum of BBMD. In ¹H NMR spectra of derivatives, the NH protons were observed as broad signal¹⁰ at δ 3.9–2.9 and signal due to Sn—H protons was absent in all the derivatives. The observance of the NH protons as a signal and absence of signal due to the hydrogen atoms attached to tin confirmed that both the hydrogens bonded to tin had been used in the dehydrocoupling reaction with biguanide. The HNMR spectrum of BBMD showed triplet at δ 0.9 due to methylene group attached to tin, whereas a complex multiplet at δ 1.9–1.7 was resulted from the intermixing of the peaks due the protons of the rest part of the butyl group. A sharp singlet was obtained δ 1.1 due to the methyl group attached to tin. A broad peak was observed at δ 3.2–2.9 for —NH— group.

The ¹H NMR signals of all other derivatives were observed at their usual positions and have been shown in Table II. The proton integration area was consistent with the molecular formula.

Figure 4 shows the ¹³C NMR spectrum of the BBMD. ¹³C NMR spectrum of BuMeSnH₂ showed the signals at δ 26.4, δ 25.7, δ 24.4, and δ 13.6 due to ¹C, ²C, ³C, ⁴C carbons (¹CH₃²CH₂³CH₂⁴CH₂Sn) of the butyl group and a signal at δ 6.9 due to methyl carbon attached with tin.²⁵

¹³C NMR spectra of PhEtSnH₂, PhMeSnH₂, and PhBuSnH₂ showed signals in the range δ 137.9–127.9 due to carbons of the phenyl group. These were observed at their usual positions. Further phenyl car-

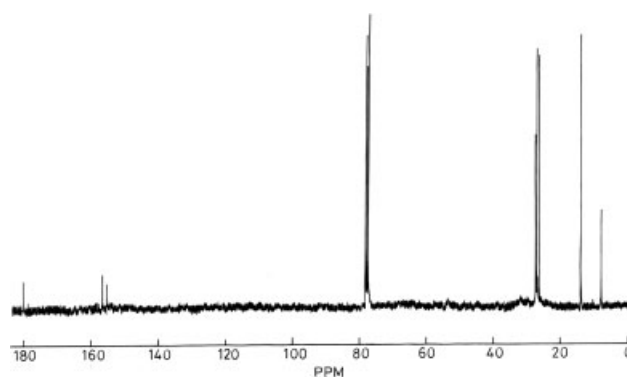


Figure 4 ¹³C NMR spectrum of BBMD.

TABLE III
 ^{13}C NMR Spectral Data of Derivatives

Sr. no.	Derivatives	Phenyl carbons	$^1\text{CH}_3^2\text{CH}_2^3\text{CH}_2^4\text{CH}_2\text{Sn}$	C=N	CH_3	$^1\text{CH}_2^2\text{CH}_3$
1.	BPMD	139.5 (C ₁), 137.2 (C ₄), 128.7 (C ₂ , C ₃ , C ₅ , C ₆)	–	157.5, 156.8	8.8	–
2.	BPED	139.1 (C ₁), 137.8 (C ₄), 128.3 (C ₂ , C ₃ , C ₅ , C ₆)	–	157.9, 157.1	–	10.4 (1), 17.7(2)
3.	BPBD	138.5 (C ₁), 137.2 (C ₄), 127.9 (C ₂ , C ₃ , C ₅ , C ₆)	δ 26.9 (1), δ 26.5 (2), δ 26.1 (3), δ 14.3 (4)	158.3, 157.5	–	–
4.	BBMD	–	δ 26.7 (1), δ 26.2 (2), δ 25.5 (3), δ 13.9 (4)	156.2, 155.4	7.4	–

bons to tin could not be distinguished and assignment had been made by analogy only.²⁵ In case of PhMeSnH₂, the methyl carbon appears at δ 7.2, whereas the methylene and methyl carbons in case of PhEtSnH₂ appear at δ 12.3 and δ 10.4, respectively. In case of PhBuSnH₂ the signals due to butyl carbons appear at δ 26.3, δ 25.4, δ 24.8, and δ 13.8.

^{13}C NMR spectra of products showed signals at δ ~ 158.3–155.4 due to the C=N group. The other ^{13}C NMR signals of the derivatives were observed nearly at their usual positions and have been summarized in Table III.

Figure 5 shows the ^{119}Sn NMR spectrum of the BBPD. ^{119}Sn NMR spectra of the derivatives of

BuMeSnH₂, PhEtSnH₂, PhMeSnH₂, and PhBuSnH₂ showed singlets at δ 120, δ 146, δ 177, and δ 147, respectively. The singlets appeared at downfield from that of stannanes and had been attributed to tetra-coordinated Sn atom.²⁶ The appearance of the signals at downfield from that of the dialkyltin dihydrides may be due to replacement of less electronegative hydrogen with more electronegative nitrogen atom.

Curing studies

The curing behavior of the mixture of derivatives and DGEBA were investigated by recording DSC traces. Figure 6 shows DSC scans of DGEBA in the presence of stoichiometric amount of derivative BPED at heating rate of 10°C/min under nitrogen atmosphere. In the DSC scan of DGEBA alone, no exothermic transition was seen in the temperature range of 50–350°C, thereby indicating the absence of curing or crosslinking. Also in the DSC scans of the derivatives alone no exothermic transition was observed.

In the DSC scans of derivatives mixed with varying amounts of DGEBA, an exothermic transition

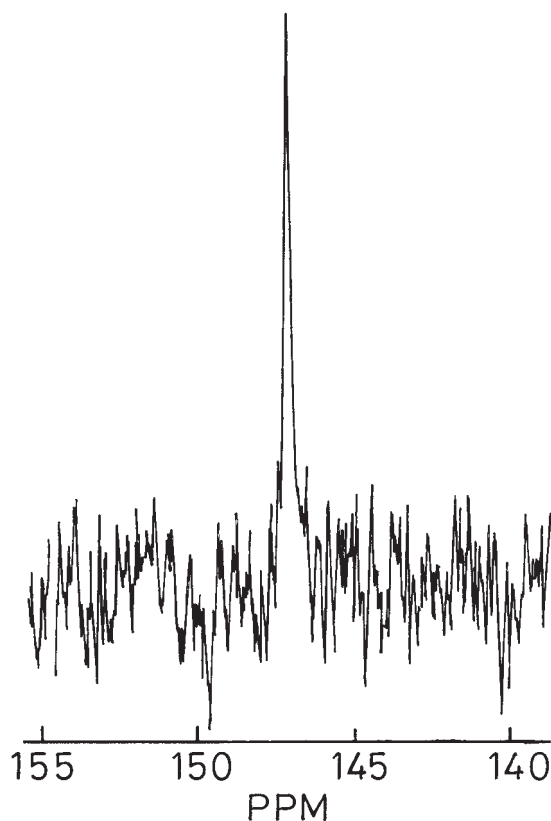


Figure 5 ^{119}Sn NMR spectrum of BPBD.

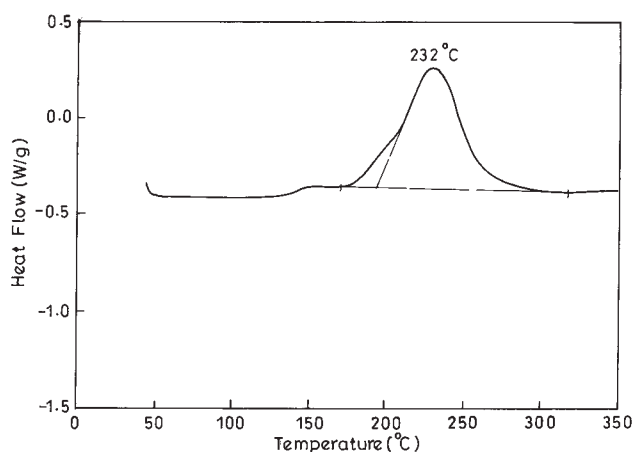


Figure 6 DSC scans of DGEBA in the presence of stoichiometric amount of derivative BPED at heating rate of 10°C/min under nitrogen atmosphere.

TABLE IV
Results of DSC Scans of DGEBA in the Presence of Stoichiometric Amounts of Derivative (Heating Rate = 10°C/min) and Glass Transition Temperature (T_g) of Cured Resins

Sample designation	Molar ratio of DGEBA : Derivatives	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	T_g (°C)
DBPMD	1 : 1	185.8	196.4	238.1	308.5	177.1	189.4
DBPED	1 : 1	170.8	194.0	231.7	317.2	179.8	194.3
DBPBD	1 : 1	156.7	182.2	198.9	260.0	137.8	116.3
DBBMD	1 : 1	150.9	176.4	179.2	265.8	181.5	120.8

associated with crosslinking or curing was characterized by noting the following parameters:

- T_i = kick-off temperature, where the curing starts.
- T_{onset} = temperature where the first detectable heat is released. It was obtained by extrapolation of the steepest portion of curve to the base line.
- T_p = temperature of peak position of exotherm.
- T_f = temperature of the end of curing exotherm. This was taken as the temperature where the exotherm levels with the base line in the final stage of curve.
- ΔH = heat of curing, calculated by measuring the area under the exothermic transition.

The results of DSC scans are summarized in Table IV. The curing temperatures were dependent upon the structure of derivatives. Comparing the curing behaviors, the following trend of T_i , T_{onset} , and T_p was observed:

$$DBBMD < DBPBD < DBPED < DBPMD$$

The reaction of all the derivatives with oxirane ring of DGEBA is a nucleophilic addition, and pres-

ence of electron-donating Sn atom is expected to increase the nucleophilicity of the nitrogen atoms. Further, on the basis of the negative induction (-I) and positive induction (+I) of the aryl and alkyl groups, respectively, one would have expected that highest curing temperature was observed in resin cured with derivative BPMD.

DGEBA was cured isothermally in the presence of derivatives by heating in an air oven ($175 \pm 20^\circ\text{C}$ for 3 h) to determine the glass transition temperature. In the DSC scans of isothermally cured samples, no exothermic transition was seen, thereby indicating the complete crosslinking reaction; however, a shift in the baseline was observed in the DSC scans of cured samples. The glass transition temperature is dependent on the rigidity of polymer backbone as well as on the crosslink density. Highest value of T_g was obtained for cured resin DBPED.

The relatively highest value of the T_g , in case of DBPED, can be explained on the basis of the ΔH value and flexible aliphatic side chain. In case of DBPED, the value of ΔH was higher whereas the aliphatic side chain was smaller. The higher value of ΔH suggested higher crosslinking, and further, the presence of the smaller flexible aliphatic side chain and rigid phenyl ring suggested the higher T_g .

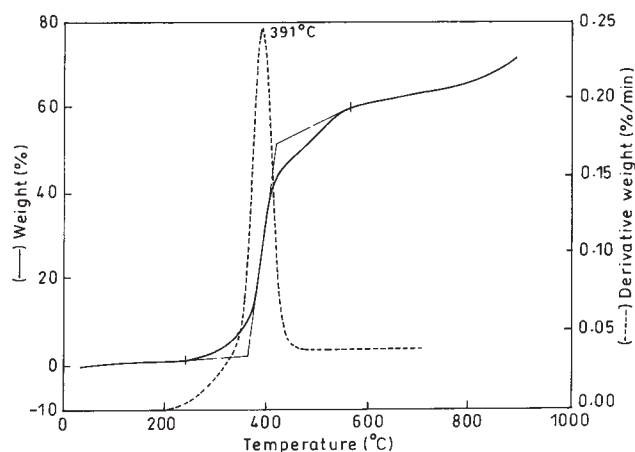


Figure 7 TG/DTG traces of DGEBA cured isothermally using derivative BPED at heating rate of 20°C/min under nitrogen atmosphere.

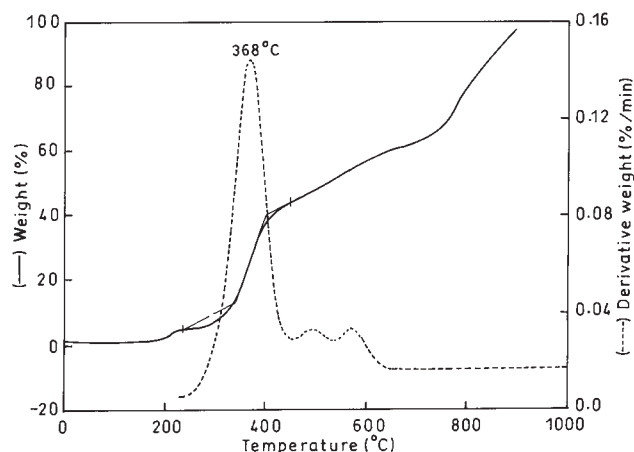


Figure 8 TG/DTG traces of DGEBA cured isothermally using derivatives BBMD at heating rate of 20°C/min under nitrogen atmosphere.

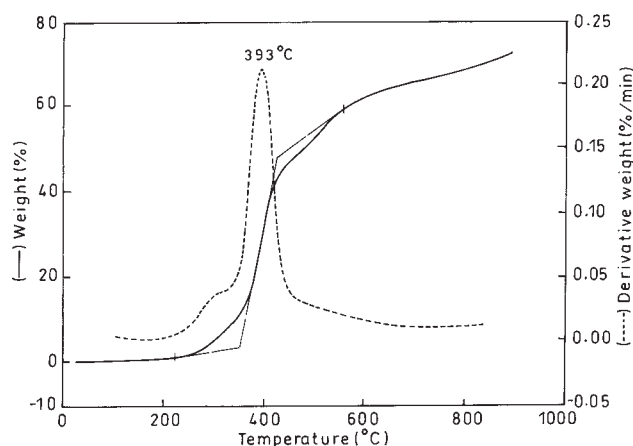


Figure 9 TG/DTG traces of DGEBA cured isothermally using derivatives BPMD at heating rate of 20°C/min under nitrogen atmosphere.

Whereas, in case of DBBMD, though the ΔH was highest, there was no rigid phenyl ring and two flexible alkyl groups were present, leading to the lowest T_g .

Thermal behavior

Figures 7–9 show TG/DTG traces of isothermal cured epoxy resins (DBPED, DBBMD, and DBPMD, respectively) recorded in nitrogen atmosphere. The initial decomposition temperature (IDT), temperature of maximum rate of weight loss (T_{max}), and final decomposition temperature (FDT) were noted from TG traces. A single-step decomposition was observed in all samples. The relative thermal stability of the cured resins was compared by determining percent char yield at 800°C. These results are summarized in Table V. All the samples were stable up to 350°C except the epoxy resin cured with only biguanide (DB), and a significant weight loss occurred only beyond this temperature. Highest char yield was obtained with epoxy resin cured with derivative BPMD.

In case of sample DB, the IDT, T_{max} , FDT, char yield, and LOI are significantly less than that for all other samples. This is because biguanide have flexible chain and does not have ring structure. This pro-

vides less thermal stability to the epoxy resins, whereas the compounds having ring structures provide more thermal stability to the epoxy resins.³

Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the resins in accordance with Van Krevelen and Hoftyzer equation.²⁷

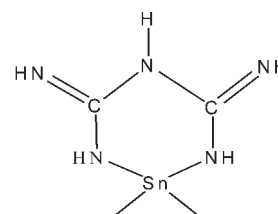
$$LOI = 17.5 + 0.4 CR$$

where CR = char yield.

All the samples had LOI values calculated based on their char yield higher than 28. On the basis of LOI values, such materials can be classified as self-extinguishing, i.e., flame-resistant resin.

CONCLUSIONS

The stannylbiguanides reported herein are a new class of SnN bonded compounds containing biguanide ligand in the structural framework. These are synthesized by the SnH/NH dehydrocoupling reactions and coordination via N-atom of the biguanide with secondary stannanes. Elemental and spectroscopic studies suggest the existence of the following tentative four-coordinated Sn structure.



Thermal stability of the cured epoxy resin was found to be dependant on the structure of network. Type of the mixture had a significant effect on the curing and thermal behavior. The highest peak exotherm temperature and highest char yield were observed for DBPMD. The glass transition was highest for epoxy resin cured with BPED. All the cured resins are flame resistant in nature.

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TABLE V
Results of TG/DTG Traces of DGEBA Cured Isothermally at Heating Rate 20°C/min

Sample designation	IDT (°C)	T_{max} (°C)	FDT (°C)	% Char yield at 800°C	LOI (%)
DBPMD	353.2	393.4	424.8	35.2	31.6
DBPED	362.4	390.7	417.5	34.5	31.3
DBPBD	382.7	402.3	426.1	30.4	29.7
DBBMD	340.2	367.9	400.5	20.5	25.6
DB	260.2	335.1	385.7	16.5	24.1

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