Synthesis and Characterization of Siloxane-modified Epoxy Resin

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Abstract: Epoxy resins of the EBS, a bis-p-phenol S modified diglycidyl ether of bis-p-phenol A and the ESBS, a siloxane modified EBS epoxy resin were prepared. Both structures of EBS and ESBS were elucidated with IR, ^{1}H NMR, and ^{13}C NMR. The near perpendicular comformation of two phenyl rings of sulfone has been introduced into the epoxy resins of EBS and ESBS for the increase of the T_g. Some curing and thermal characteristics of these modified EBS and ESBS epoxy resins were studied. The curing patterns of EBS and ESBS indicated the similarity with that of the DGEBA epoxy resins. T_g measurements resulted an increasing order of the ESBS (T_g of 141 °C), EBS (T_g of 135 °C) and then followed by Epons 1004 (T_g of 104 °C), 1001 (T_g of 101 °C) and 828 (T_g of 100 °C) in samples tested under the same conditions. Thus the substantial improvement of the thermal stability of the modified epoxy resins was indicated. Compatibility characteristics of the EBS and ESBS as indicated by the SEM/EDX is that an ESBS up to 30 % of the siloxane content was found to be compatible but not miscible with the Epon, a phenolic epoxy resin of DGEBA.

Keywords: Sulfone-epoxy EBS, Silopane-epoxy ESBS, SEM/EDX, Compatibility, Immiscibility.

Introduction

The phenolic epoxy resin which is based on the diglycidyl ether of bis-p-phenol A (DGEBA) is one of the basic and commercial epoxy resins, and it has been used extensively in electronic print circuit boards and aerospace applications, etc. (Schwartz et al. [1], Billmeyer [2], and Lee et al. [3]). The advanced high-functional materials are needed to meet the demands of the thermal stability, good weatherability and the overall performances (Wang et al. [4], Chang et al. [5], and Chen et al. [6]). Some research works are using Novolac epoxy resins and some are using fracture toughing agents (Wang et al. [7]), epoxy-terminated poly (aryl ether sulfone), PES (Iijima et al. [8]), and PES with hydroxyl, amino-, and chloro- terminal groups (Yamanaka et al. [9] and Herdrick et al. [10]), as well as the uses of the matrix toughing agents of CTBN (carboxy terminated butadiene acrylonitrile) (Backnall [11]), or its amino derivative (ATBN) (Kinloch et al. [12]), PPO [poly(oxypropylene oxide)] (Pearson et al. [13]), and in form of encapsulants (Wang et al. [14]).

Others such as PAEK (poly aryl ether ketone) (Jane el al. [15]) and other thermoplastics of polyetherimide and polysiloxane copolymers (Riew et al .[16], Bauer et al. [17], and Riew et al. [18]) as modifiers for epoxy resins were also in use.

The high functional epoxy resin based on the liquid DGEBA with the aryl sulfonyl group of bis-p-phenol S , abbreviated as EBS, and the siloxane modified epoxy resin with poly (methyl phenyl siloxane) (PMPS) on the EBS, abbreviated as ESBS, were designed. It is intended to introducing the unique spatial arrangement of two aryl rings into the resin structure. The bis-p-phenyl sulfonyl group has shown (Huang et al. [19] and Dickinson et al. [20]) the near perpendicular ring configurations which may provide additional spatial arrangement other than the bis-p-phenol A configurations for the EBS. This rather rigid aryl sulfonyl group may restrict the ring movement (Freitag et al. [21, 22], Fennhoff et al. [23], Westeppee et al. [24] and Aiken et al. [25]) thus resists the backbone movement as the temperature increases. This may provide the needed increase of the glass transition temper-ature (Tg) of the resin .

Furthermore, the incorporation of siloxane into the epoxy resin as in the ESBS, is intended for enlarging the siloxane application and introducing the excellent siloxane properties (Beylen et al. [26],

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Babu et al. [27], Kajiyama et al. [28], Noll [29] and Smith [30]) into the epoxy resins where normally are not available from the carbon-based polymers.

It is also intended to improve the compatibility of carbon-based and silicon-based polymers. Polymeric material with both carbon-and silicon-based moieties may provide some functions of the both moieties and it may be used as the interphasing agent for coblending applications and for the study the compatibility of the both polymers.

With this intention, syntheses of EBS and ESBS were carried out and the general characteristics of sulfone-and/or siloxane-modified epoxy resin can be carried out with the incorporation and comparisons of the corresponding DGEBA of Epon 828 and 1000's series. The measurements of Tg's and conversions (the curing character) of the epoxy specimens, may provide the curing properties for comparisons and application considerations. Specimens of the fracture surfaces of these synthsized epoxy resins, the EBS and the ESBS, in the matrix of Epon 828, may reveal compatibility of the silicon-based epoxy resin with the sulfonyl (containing S element) and siloxane (containing Si element) moieties in its components, while the carbon-based epoxy resin of the DGEBA forming the matrix does not. The observation of S and Si elements can therefore be used for the study on the compatibility in this system through the use of the SEM (Watt [31]) and the SEM /EDX .

Experimental

1. Materials

Epon 828, a DGEBA epoxy resin was obtained from Shell Corporation, locally and bis-phenol S was purchased from Merck Co. Poly (methyl phenyl siloxane) (DC 3074), was the gift from Dow Corning Taiwan.

2. General procedure for the epoxy resin preparation

2.1 The EBS, the epoxy resin of Epon 828 with bis-p-phenol S

EBS epoxy resin was prepared with the addition of bis-p-phenol S (BPS) to the Epon 828 in the one to two molar ratios. Reaction was carried out in the flask with a stirrer and heating facility which was maintained the temperature of 90 °C for 4 hrs under the inert atmosphere. The reaction mixture was then washed with chlorinated solvent after the mixture was cooled to ambient temperature and a yield of 95 % was obtained.

2.2 The ESBS, the epoxy resin of siloxane modified EBS

ESBS, the siloxane-containing epoxy resin was carried out with EBS and DC 3074, (Mol. Wt. of 1800, 17 % methoxy content) (Lin et al. [32]) in 30 % weight ratio with 0.5 % of catalyst of the Du Pont Tyzor TPT at the temperature of 110 °C for 3 hrs under the inert atmosphere. Other ratios of 10 to 50 % were also prepared accordingly.

Purification was carried out by washing the product with xylene for the removal of unreacted DC 3074. Yield was 93-95 % .

2.3 Curing Procedure

Epoxy resins in formulation in various compositions were mixed and the curing procedures were conducted as follow.

As a typical example, 2 % of amine hardener was added to the resin mixture of Epon 828, EBS, (or ESBS) in weight ratios of 90 to 10, or in other ratios. The well mixed resins was then placed in the aluminum foils or Teflon coated sample holders which had been preheated at 80 °C and the specimens were placed in an oven of 120 °C for one hour and then post-cured at 130 °C for one hour.

3. Characterization

Structure elucidations on the EBS and ESBS were conducted with IR for the functional groups of sulfone and oxirane and with ^{1}H NMR and ^{13}C NMR for the hydrogen and carbon distributions, respectively. IR spectra were obtained with Jasco IR-700. And ^{1}H NMR and ^{13}C NMR spectra were obtained with Bruker AM-300WB FT-NMR.

Thermal analysis was conducted with DSC for the measurements of the activation energy of the curing process and TMA was used for the glass transition temperature measurements. Perkin Elmer DSC-2 and TMS-2 were used for the DSC and TMA measurements, respectively.

Fractural surface morphology was determined by SEM and EDX/SEM and photograms were obtained from Canscan DCV-3 with EDX. Specimens were fractured with hands after the specimens were cooled with liquid nitrogen.

Results and Discussion

1. Synthesis of EBS, the epoxy resin of the bis-p-phenol S modified DGEBA

The epoxy resin of DGEBA (Epon 828 or DER 331) with bis-p-phenol A is known as Epon 1000's or DER 664 (Lee et al. [3]). The corresponding epoxy resin of DGEBA with bis- p-phenol S was synthesized and was abbreviated as EBS. The structure of EBS is

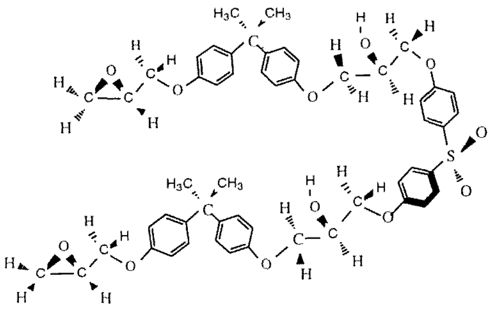


Figure 1(a). Structure of the EBS, the bis-p-Phenol S modified Epoxy resin of DGEBA.

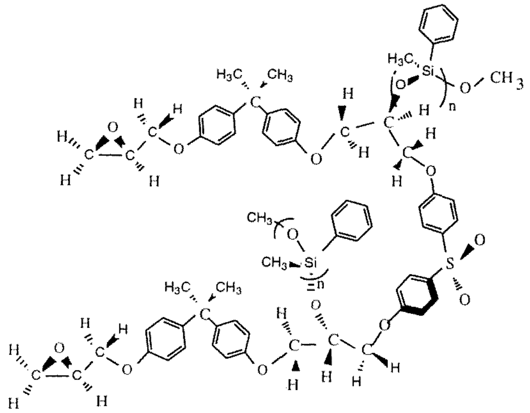


Figure 1(b). Structure of the ESBS, the siloxane modified EBS Epoxy resin.

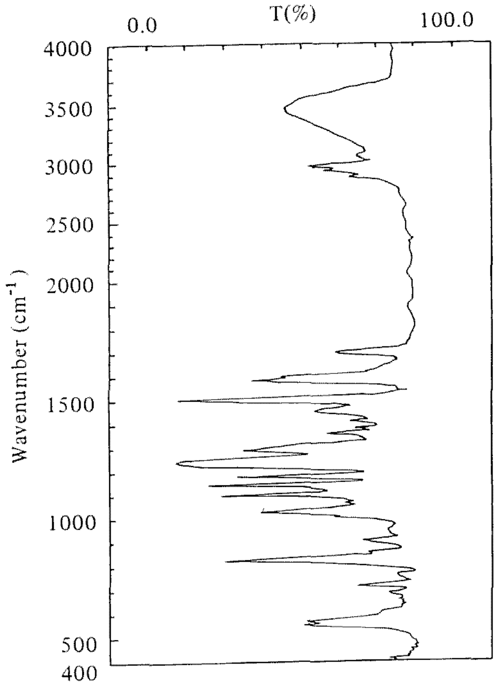


Figure 2. The IR spectrum of the EBS.

shown in Figure 1(a).

The structure of synthesized EBS was analyzed by IR, ^{1}H-NMR and ^{13}C NMR. The IR of EBS, shown in Figure 2, has the absorptions of 913, 836 cm^{-1} for oxirane and 1359, 1148 cm^{-1} for the sulfonyl group among other absorptions.

The ^{1}H NMR of EBS is shown in Figure 3(a). The noticeable glycidyl $-OCH_2-$ protons have the chemical shifts centered at 3.9 and 4.2 ppm. This is the typical pattern of glycidyl group as it is splitted by the hydrogen attached to the asymmetrical oxirane carbon and this pattern can also be seen in the Epon 828 in Fig. 3(b). The integration ratios of these protons in respect to the dimethyl group on the bis-p-phenol A, shown in Table 1, are in agreement with the structure of the EBS of the two to one addition of DGEBA and the bis-p-phenol S. The structure with this ratio of the EBS is shown as in Fig. 1(a).

The ^{13}C NMR spectra of EBS and the reference Epon 828 are shown in Figures 4(a) and (b). The oxirane carbons of the glycidyl group are shown with the chemical shifts of 44.6 and 50.1 ppm, respectively.

Figure 5 shows the assigned chemical shifts of the ^{1}H NMR and the ^{13}C NMR for the structure of synthesized epoxy resin of EBS.

With these instrumental data, the structure of the EBS is therefore confirmed.

2. Synthesis of the ESBS, the epoxy resin of the siloxane-modified EBS

With the assured structure of the bis-p-phenol S modified epoxy resin, EBS, the siloxane incorporation synthsis of the epoxy resin of EBS with the poly (methyl phenyl siloxane) (PMPS) of DC 3074 was carried out with various weight ratios of DC 3074 and the EBS epoxy resins. The condensation reaction of methoxy group of the siloxane with the hydroxyl group of the EBS was resulted the product of siloxane modified epoxy resin of ESBS.

- The structure of the 30 % siloxane modified epoxy resin, as an illustration for the ESBS series of the compounds, was determined with the IR, ^{1}H NMR and ^{13}C NMR as follow:

The IR spectrum of this ESBS showed the absorptions of Si-Ar at 1590, 1428 cm^{-1} and 1359, 1148 cm^{-1} for the sulfonyl group. Si-OMe at 2945 and 487 cm^{-1} and oxirane at 912 and 836 cm^{-1}.

The ^{1}H NMR showed the hydrogens of the

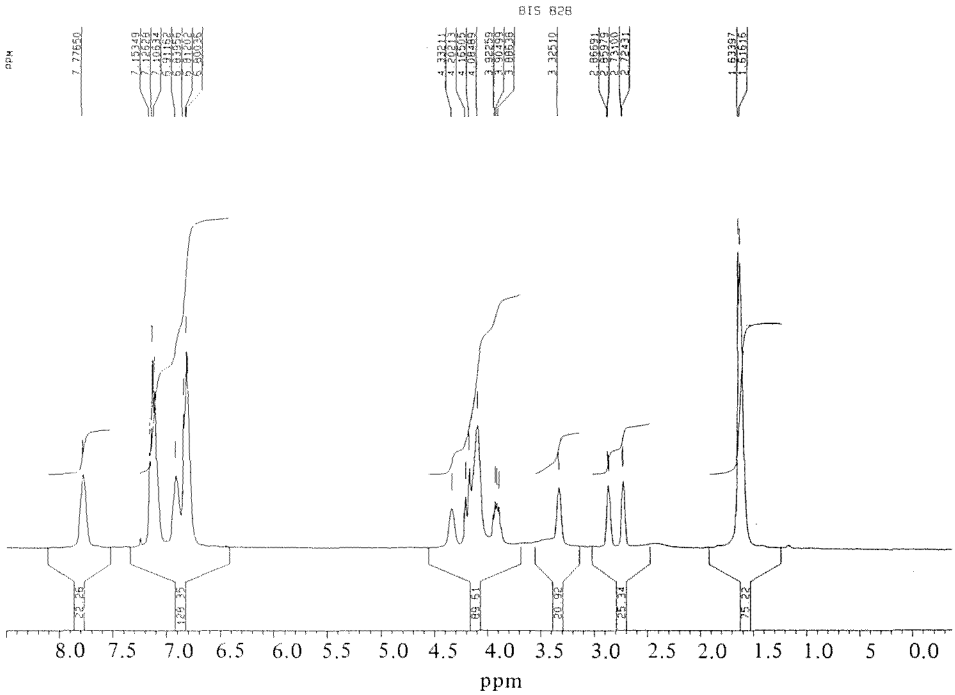


Figure 3(a). The ^{1}H NMR spectrum of the EBS.

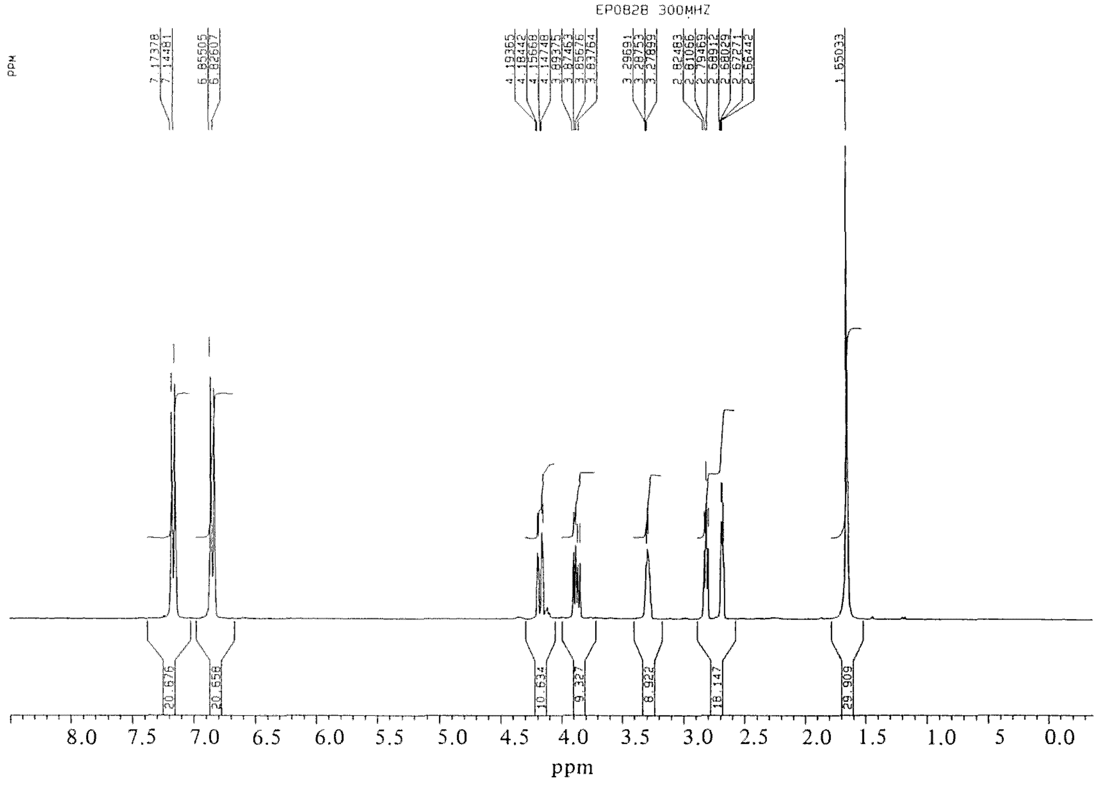


Figure 3(b). The ^{1}H NMR spectrum of the Epon 828.

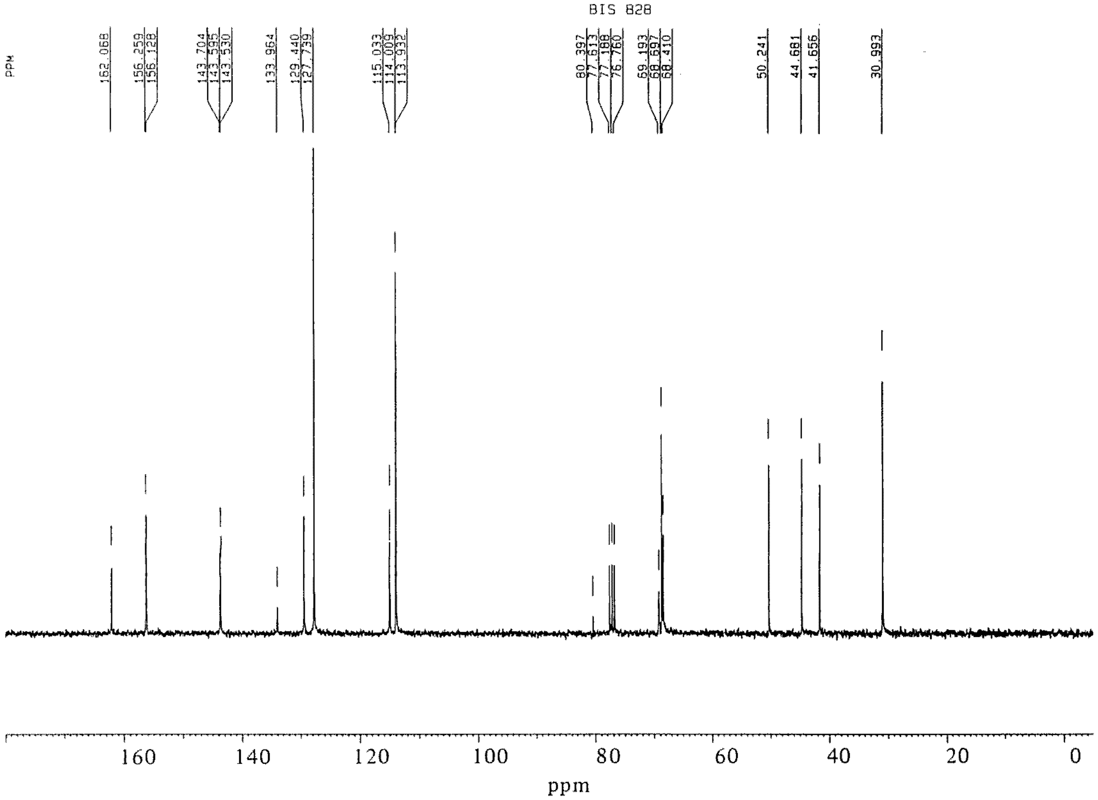


Figure 4(a). The ^{13}C NMR spectrum of the EBS.

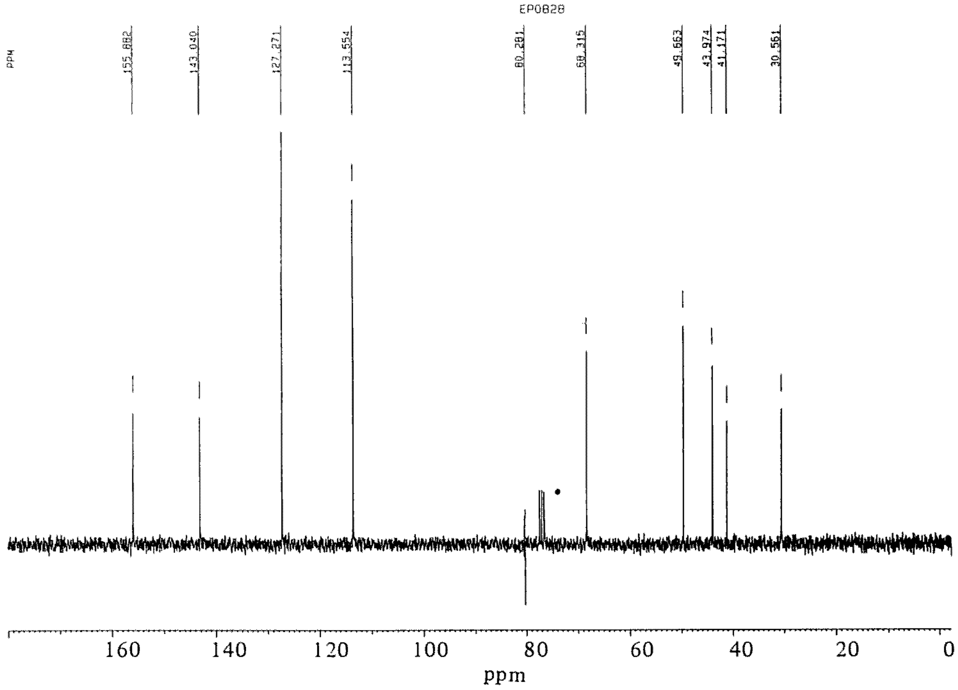


Figure 4(b). The ^{13}C NMR spectrum of the Epon 828.

Table I. The integration of glycidyl protons in respect to $(CH_3)_2$ C-group of the EPON 828, EBS and Epo:.y resins

Protons	Resins	Relative Peak Hight	Protons	
			Exp.	Theor.
	EPON 828	5.2	6	6
C $(CH_3)_2$	EBS	4.4	12	12
	ESBS	3.25	12	12
O / CH$_2$—C	EPON 828	3.35	3.87	4
	EBS	1.5	4.1	4
	ESBS	1.05	3.88	4
O / C–CH	EPON 828	1.67	1.87	2
	EBS	0.8	2.18	2
	ESBS	0.53	1.95	2

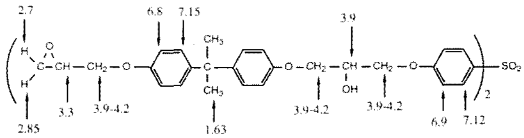


Figure 5(a). The chemical shifts (ppm) of ^{1}H NMR of EBS.

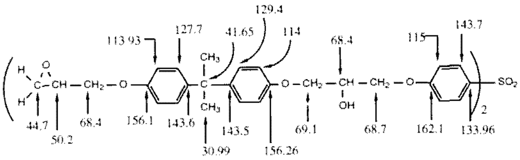


Figure 5(b). The chemical shifts (ppm) of ^{13}C NMR of EBS

glycidyl group has the chemical shifts, centered at 4.1 ppm for -O CH_2, and the chemical shifts, centered at 2.75 and 3.3 ppm for the oxirane protons. The assigned ^{1}H NMR chemical shifts to the ESBS are shown in Fig. 6(a).

The integration of glycidyl protons in respect to $(CH_3)_2C$- group of the bis-p-phenyl A in Epon 828 and in ESBS were shown in Table I with the excellent agreement. The ratios of glycidyl group to other groups as shown in Table I can be used for the confirmation of the epoxy group in the siloxane modified ESBS as well as sulfone modified EBS epoxy resins.

The ^{13}C NMR assignments of ESBS were shown in Fig. 6(b). It showed that the CH_3-Si of the poly methyl phenyl siloxane segment has the chemical shift at 0.4 ppm., and the phenyl-Si at 127.5-134.2 ppm. The glycidyl carbons showed at 44.6, 50.1 and 68.4 ppm.

The introduction of this spatial arrangements of bis-p-phenol S in EBS and ESBS may be significant.

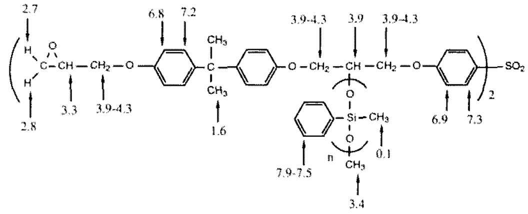
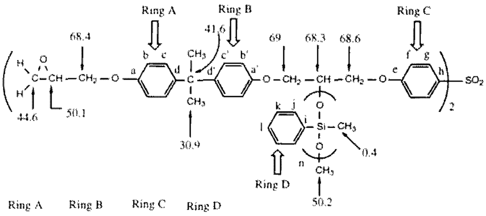


Figure 6(a). The chemical shifts (ppm) of ^{1}H NMR of ESBS.



Ring A	Ring B	Ring C	Ring D
a 156.0	a' 156.2	e 161.9	i 127.5
b 113.8	b' 113.9	f 114.9	j 130
c 127.6	c' 129.4	g 143.5	k 133
d 143.5	d' -----	h 134.1	l 134.2

Figure 6(b). The chemical shifts (ppm) of ^{13}C NMR of ESBS.

This addition of another dimensional phenyl rings may increase the impact strengths of the epoxy resins in applications. This additional mechanical strengths may be the results of the unique sulfonyl structured epoxy resins forming the additional dimensional networks or matrix with the general thermal curing process upon which epoxy oxiranes were self-polymerized after the initiation with the small amount of hardener in formulation.

3. Curing characteristics of the epoxy resins of EBS and ESBS

3.1 Curing Properties From DSC Measurements

With the structural confirmations of sulfonyl modified epoxy resin of EBS and its siloxane modified epoxy resin of ESBS, the curing properties of these two synthesized epoxy resins were studied with the incorporation of EBS and/or ESBS with the phenolic DGEBA's Epon 828. The selection of using available epoxy resin of Epon 828 has twofold proposes. The first, the curing properties of EBS and ESBS can be compared with the well established DGEBA system. Secondly, the compatibility of newly synthesized epoxy resins to the phenolic epoxy resin is important, if it is expected to be applicable in that system.

A typical DSC measurement of the EBS with a curing agent of an amine is shown in Fig. 7. Some curing properties from DSC studies with curing temperature range, curing time in min., and the activation

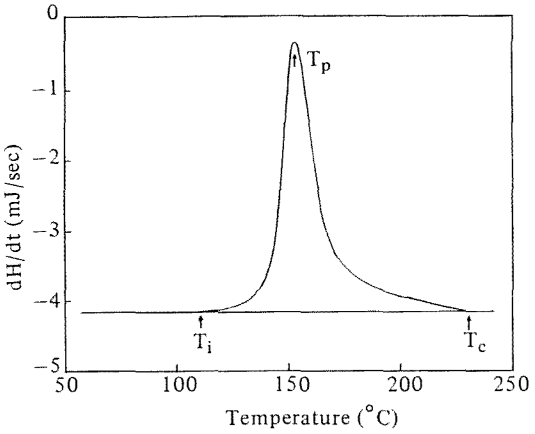


Figure 7. A typical dynamic DSC measurement of the EBS.

Table II. The curing properties of Epon 101, EBS and ESBS (30%) with 2% amine curing agent.

RESINS	Scan Speed (K/min)	Ti Initial Temp. (K)	Tp Peak Temp. (K)	Tc Final Temp. (K)	Curing Range (K)	Curing Time (min)	E_a^* (KJ/mol)
1001	10	389	412	446	57	5.7	
1001	20	400	422	474	74	3.7	
1001	40	413	445	523	110	2.8	52
1001	80	425	469	587	162	2.0	
EBS	10	395	417	457	62	6.2	
EBS	20	408	431	494	86	4.3	
EBS	40	417	451	528	111	2.8	60
EBS	80	429	469	566	137	1.7	
ESBS	10	405	424	459	54	5.4	
ESBS	20	411	434	479	68	3.4	
ESBS	40	428	445	513	85	2.1	84
ESBS	80	437	464	561	124	1.6	

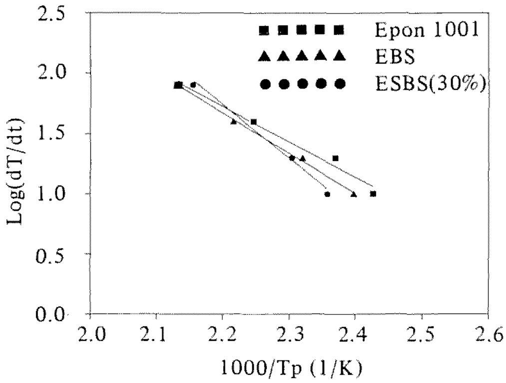


Figure 8. Reciprocal peak temperature as a function of logarithm heating rate for Epon 1001, EBS, and ESBS (30% PMPS).

energies of Epon 1001, EBS, and ESBS epoxy resins were listed in Table II. The activation energy is derived from the following equation (Morgan et al. [33]).

$$\log(dT/dt) = C - 0.4567\, E_a^*/RT_p \qquad (1)$$

The dT/dt is the heating rate and the Tp is the peak or maximum temperature of the thermogram. From Table II, the T_p's, K(°C), temperature curing ranges in K, and curing time in min., of Epon 1001 the EBS, and the ESBS (30 % of PMPS) are 412 K (139 °C); 57 K; 5.7 min., for Epon 1001 and in the same order of 417 K (144 °C); 62 K; 6.2 min., for EBS, and 424K (151 °C); 54K; 5.4 min., for the ESBS, respectively, at the heating rate of 10 °C/ min.

The activation energies, E_a^*, for Epon 1001, EBS, and ESBS are 52, 60, and 84 KJ/mol, respectively. These E_a^* were obtained from the graphic plots of these individual T_p's of the DSC measurements and were shown in Figure 8. The increasing activation energy for ESBS with E_a^* of 84 KJ/mol from that of 60 KJ/mol for the EBS can be resulted, for instance, from the large molecular weight addition of the PMPS oligomer and from the thermal stability of ESBS with higher T_i as listed in Table II as well.

The curing range of the ESBS is 54K comparing to 62K for EBS and 57K for the corresponding DGEBA of Epon 1001 (Table II). This characterization of the narrowing curing range may be due to the flexible siloxane chains. The -O- Si bonding in the siloxane segment can move more freely and away from the oxirane at the curing temperature and therefore, it may facilitate the self-polymerization of the epoxy rings in ESBS, even though ESBS is stable thermally and starts to cure at higher temperature than the EBS. (T_i for ESBS is 424K (151 °C), for EBS is 417K (144 °C)).

This thermal curing similarity but with some differences as shown in DSC measurements (Table II) for the EBS and the ESBS in respect to the corresponding Epon 1001 may be important. This may indicate that the EBS and the ESBS can be incorporated into the DGEBA system for the applications without much of the process changes.

In addition, the various contents of PMPS in the forms of the ESBS were synthesized. Their fractional conversions as a function of temperature were shown in Fig. 9. Again only a few minor differences at the high conversion range of 70-90 % were observed and all three samples of 20 %, 30 %, and 50 % of PMPS in ESBS, showed with the rather similar

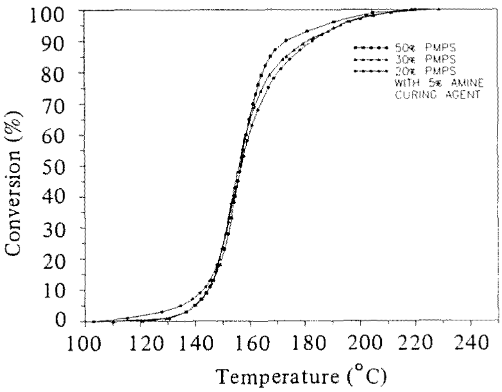


Figure 9. The fractional conversions as a function of temperature for various weight percent of PMPS in the ESBS.

patterns below 60 % conversions at the temperature of 158 °C and reached 100 % conversion at 220 °C.

3.2 Glass Transition Temperatures (T_g) From TMA Measurements

With the measurements of the above thermal property, the specimens of the EBS and the ESBS were incorporated with the Epon 828 for the following measurement .

Glass transition temperature, T_g, is an excellent indicator for the thermal stability of the epoxy formulated samples. Higher the T_g, higher the temperature for the epoxy applications. The measurements of T_g have been carried out by the thermal mechanical analyzer, TMA , and were shown in Fig. 10 and in Table III, in which EBS showed that it has the T_g of 135 °C and the ESBS (30 % PMPS) has the T_g of 141 °C., while the Epon 828 under the same conditions has the T_g of 100 °C. The addition of bis-p-phenol S has increased the T_g as expected. The siloxane modified epoxy resins as shown in Fig. 11 and Table III (ESBS without Epon 828 added, that is ESBS/Epon 828 of 100/0) tend to have slightly higher T_g's than that of EBS. For example, the individual T_g's of 135, 138, 150, 141, and 133 °C were for specimens with the increments of 0, 10, 20, 30, and 50 % of the PMPS in ESBS epoxy resins, respectively. The declining T_g at high content at the 50 % increment was mainly due to the overloading/mixing of the two systems. It is shown from this experiments, upper mixing limit is around 30 % of the poly (methyl phenyl siloxane) (PMPS) oligomer in DGEBA system.

The epoxy specimens of the ESBS/Epon 828 as shown in Table III indicated that specimens with higher segments of siloxanes have lower T_g's. For instant, with 50/50 ratio of ESBS/Epon 828, the T_g's are decreased from 135, 127, 123, 120, and 116 °C for PMPS of 0, 10, 20, 30, and 50 % in ESBS. And this is not unexpected, for the characteristics of the siloxane with high flexible chains of -O-Si-O- tends to facilitate the main chain motion in liquid DGEBA system of Epon 828 as the Tg temperature approaches.

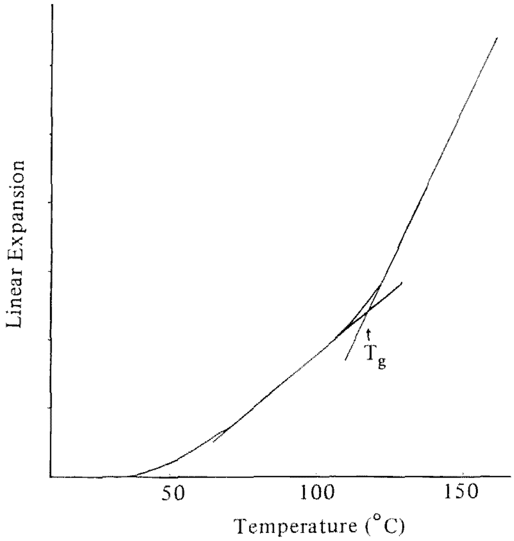


Figure 10. Thermomechanical analysis of 60/40 weight ratio of ESBS/Epon 828.

Table III. The effect of the PMPS on the glass transition temperatures of the compositions of ESBS and EPON 828.

Composition	PMPS Weight Percent (%)				
ESBS / EPON 828	0 (EBS)	10	20	30	50
0/100	100	100	100	100	100
10/90	118	115	118	111	110
25/75	116	118	112	116	115
40/60	126	125	121	117	113
50/50	135	127	123	120	116
70/30	139	117	122	123	...
85/15	...	127	123	...	130
100/0	135	138	150	141	133

4. Compatibility of siloxane-modified epoxy resin with Epon 828

One of the obstacles of incorporation of silicon-based polymers with the carbon-based polymers is the incompatibility as well as the immiscibility of the two. Thus limits the applications of siloxanes in modern plastics (Matzner et al. [34]).

In this experiments, over 35 different formulations of Epon 828/EBS/ESBS were prepared. for the tests of characterizations To facilitate the specimen

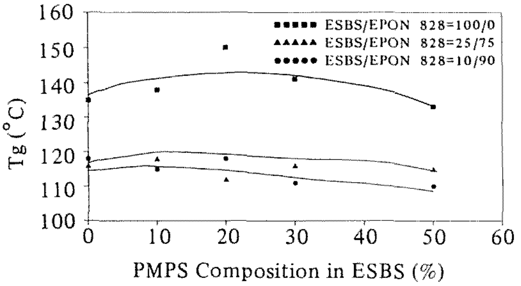


Figure 11. The effect of the PMPS on the Tg of the ESBS and Epon 828.

preparation, epoxy resins containing poly methyl phenyl siloxane contents ranged from 10, 20, 30, 50 % were first synthesized and the additions of these various siloxane contents in the forms of ESBS to the Epon 828 were intended to test the compatibility of siloxane-contained epoxy resins to the Epon resins. Specimens in percentage from 0 (Epon 828 only, without ESBS), 10 (10 % ESBS and 90 % Epon 828 by weight), 25, 40, 50, 70, 85 to 100 (ESBS alone without Epon 828) were prepared and all samples were mixed well and de-molded with ease after they were cured with the same 2 % by weight of the curing agent.

The compatibility of ESBS with Epon 828 seems to be excellent from these preparations, provided the siloxane contents in epoxy resin is not over 30 %.

5. SEM/EDX Study Upon the ESBS Epoxy Resin

Scanning electronic microscope (SEM) with EDX (energy dispersion X-rays) has been used for the compatibility study. Figures 12-15 showed the SEM photos of the fractured surfaces of these epoxy specimens.

Figure 12 (a) shows the fracture surface of Epon 828 and Fig. 12(b), of EBS with enlargement of 2,000. The fracture surface of the specimen was obtained from the hand breaking of the frozon sample. The EBS surface showed a smooth and small circular pattern while rough and large fractured surface were observed in the Epon. This smoothness on the surface may probably due to the structure of the near perpendicular conformation of two phenyl rings with the tetrahedral sulfonyl group in EBS (see Fig. 1), thus causes the polymeric chains to be aligned or arranged into more compact and/ or orderly structure. Figure 13(a) shows the surface of 100 % ESBS which has contents of the 30 % of PMPS. Random or disordered arrangements with some small circular pattern , probably formed from PMPS segment, can be seen in the ESBS specimen. This may show the specimens with the imcompatibility of the carbon-based and the silicon-based segments.

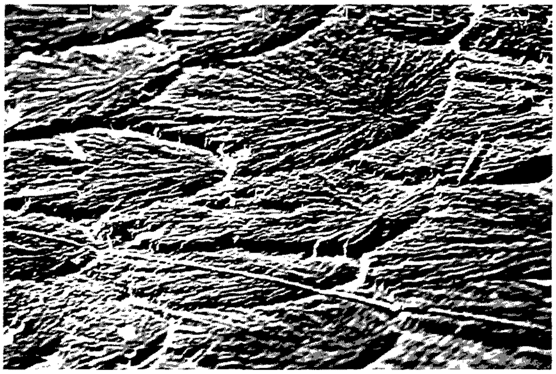


Figure 12(a). SEM photograph of Epon 828 (100%).

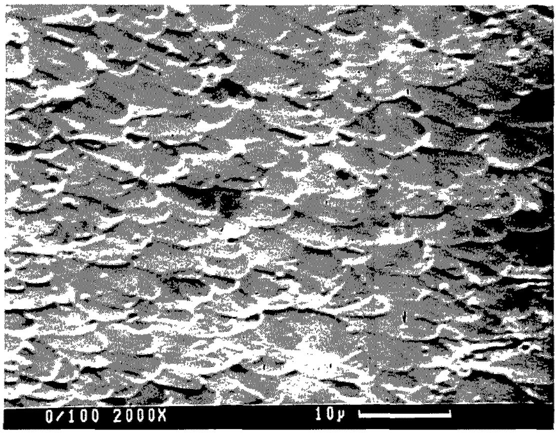


Figure 12(b). SEM photograph of EBS (100%).

And as shown in Fig. 13(b) of the specimen from 25/75 weight ratio of ESBS/Epon 828, a fewer circular segment in the 828 matrix was observed. This is the indication in which the increasing mutual compatibility of the two with the increasing portions of the Epon 828. On the other hand. with the increasing amounts of ESBS in the specimen, the surface of circular pattern are more profound as shown in Figures 14(a) and (b) with 50 to 70 of the weight ratios of ESBS in Epon 828 specimens. Therefore, it is concluded that ESBS and Epon 828 are compatible but not miscible from these SEM examination of the samples.

Upon obtaining these needed information on the compatibility and/or miscibility of the silicon-based and carbon-based polymers from the prepared EBS and ESBS samples., a further evaluations on the surface of the sample with the 50/50 weight ratio of the ESBS/Epon 828 were examined by EDX/SEM and the photo was shown in Fig. 15(a) and EDX electrogram in Fig. 15(b).

The EDX is utilized for the search of its individual component. Since the ESBS contains the sulfur

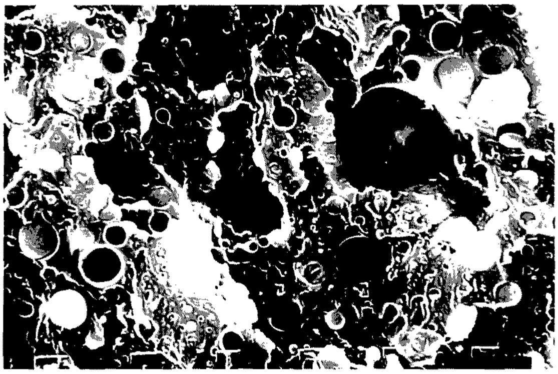


Figure 13(a). SEM photograph of ESBS (with 30% PMPS) (100%).

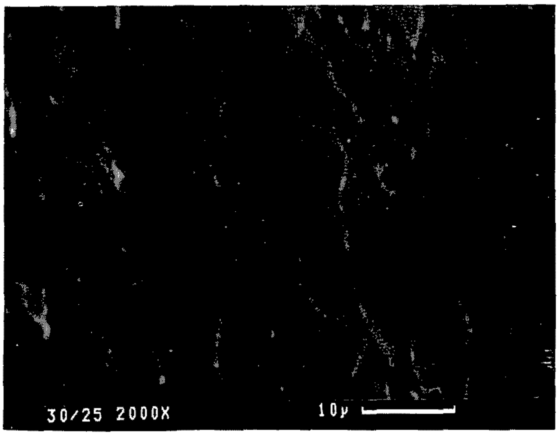


Figure 13(b). SEM photograph of ESBS (with 30% PMPS)/Epon 828 (25/75).

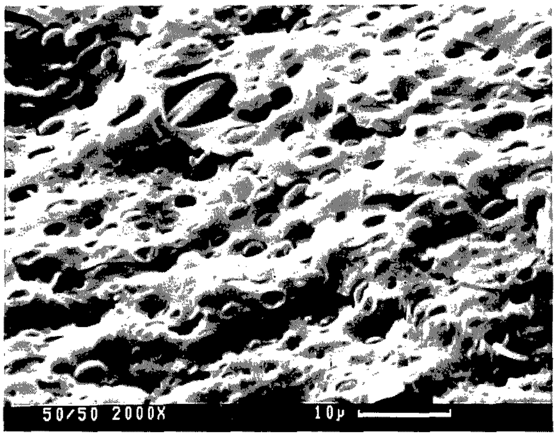


Figure 14(a). SEM photograph of ESBS (with 30% PMPS)/Epon 828 (50/50).

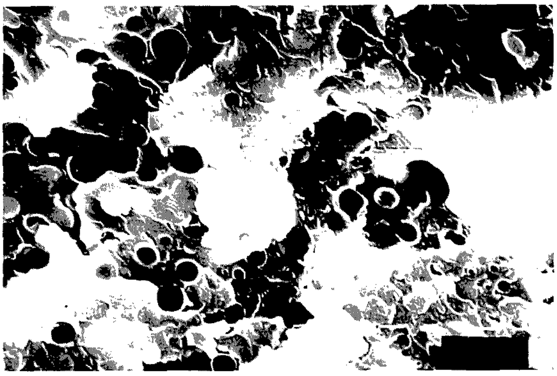


Figure 14(b). SEM photograph of ESBS (with 30% PMPS)/Epon 828 (70/30).

(S) in its sulfonyl segment and silicon (Si) in its siloxane moiety, and the Epon 828 does not, the identification of sulfur and silicon elements may shine the lights for the ESBS, either located in the circular region or on the matrix. The portions of the photo searched by the EDX are designated with three different arrows as shown in the Fig. 15(a). The EDX electrograms are shown in Fig. 15(b) and Fig. 16(a) and (b).

From these preliminary surface observations , the samples with low contents of siloxane-modified epoxy resins (ESBS) (Fig. 13(b)) in Epon 828, may be characterized as compatible and/or miscible of the two, and it may simply due to its low contents of ESBS in Epon 828.

With high contents of ESBS, the fractured surfaces did show the immiscibility as the existence of each individual circular patterns of the components of ESBS and Epon 828. These patterns of individual components are shown in Fig. 14 or Fig. 15(a).

Furthermore, upon the EDX examinations of these three individual surfaces, the sulfonyl (S atoms) and siloxane (Si atoms) groups are detected on all areas. This result has enhanced the phenomenon which indicated that these two resins are compatible, although immiscible, and two resins may be coating each other on the surfaces so that both S and Si elements are detected in all regions.

Therefore, it may be concluded that at high contents of ESBS, the siloxane modified epoxy resin is compatible to the sulfone-containing carbon-based EBS and DGEBA epoxy resin, though they are not miscible.

Compatibility of the synthesized ESBS and the EBS to other types of epoxy resins will be further investigated.

Conclusion

Syntheses of the epoxy resin of bis-p-phenol S with DGEBA, abbreviated as EBS and its siloxane-

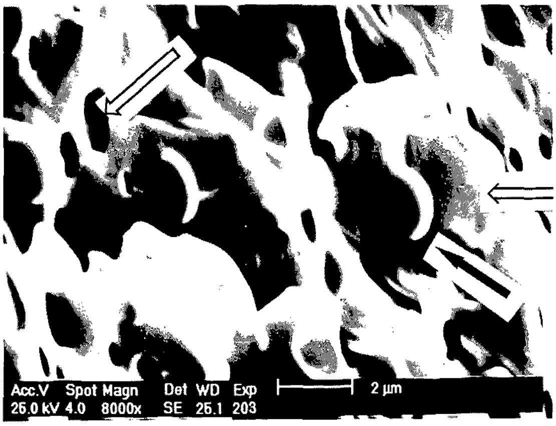


Figure 15(a). SEM photograph of ESBS (with 30% PMPS)/Epon 828 (50/50).

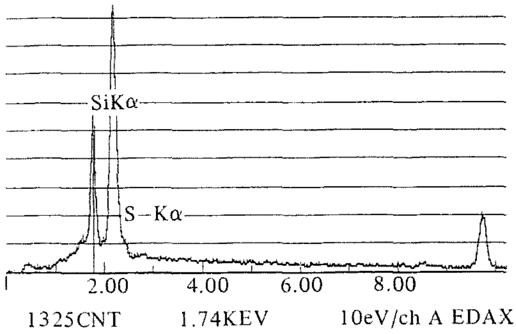


Figure 15(b). The EDX electrogram of circular region of SEM photpgraph of ESBS (with 30% PMPS)/Epon 828 (50/50).

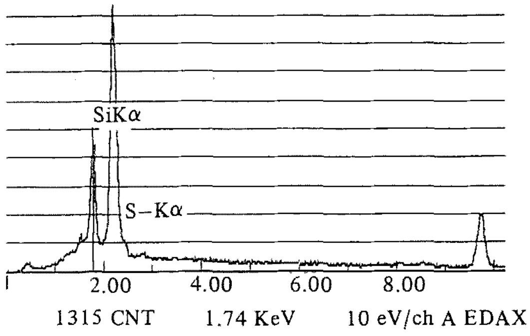


Figure 16(a). The EDX electrogram of matrix of SEM photograph of ESBS (with 30% PMPS)/Epon 828 (50/50).

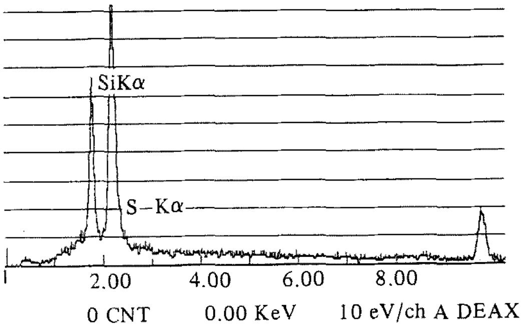


Figure 16(b). The EDX electrogram of circular region of SEM Photpgraph of ESBS (with 30% PMPS)/Epon 828 (50/50).

modified derivative with poly methyl phenyl siloxane, abbreviated as ESBS were carried out and their structures have been elucidated with IR, ^{1}H NMR and ^{13}C NMR. Both epoxy resins of EBS and ESBS have the higher Tg's than that of Epon 828 under the same curing conditions. The curing properties of the synthesized EBS and ESBS epoxy resins are compatible to those of the DGEBA epoxy resins of the corresponding counterparts of Epons 828 and 1000's. The siloxane-modified ESBS has good compatibility to EBS and to the DGEBA epoxy resins of Epon 828 and 1000's.

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