

Synthesis, Formulation, and Characterization of Siloxane-Modified Epoxy-Based Anticorrosive Paints

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ABSTRACT: Diglycidyl ether of bisphenol A epoxy (E) was modified with hydroxyl-terminated polydimethylsiloxane through a ring-opening addition polymerization reaction. The structural elucidation of the siloxane-modified epoxy resin (ES) was carried out with Fourier transform infrared, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectroscopy techniques. The physicochemical characterization of the synthesized resin (ES) was performed with standard methods. E and ES were subjected to paint formulation with the help of a rutile (TiO_2) pigment. The formulated paint systems were cured at room temperature with 1,6-diaminohexane (AH) and 1,3-diaminopropane (AP), which were used as curatives. The E-AH, E-AP, ES-AH, and ES-AP paint systems were ap-

plied to mild steel strips. The physicochemical and anticorrosive performance of the coated panels was evaluated with standard methods. The thermal analysis of these E-amine and ES-amine systems was carried out via thermogravimetric analysis. The effects of siloxane incorporation and amine curatives on the coating properties of the paint systems were also investigated. The ES-AP system exhibited good thermal and corrosion stability performance among all the E and ES paint systems. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4981–4991, 2006

Key words: coatings; resins; curing of polymers; cross-linking; polysiloxane

INTRODUCTION

Epoxy resins are an important class of polymeric resins. They exhibit low shrinkage, ease of cure and processing, excellent moisture, solvent, and chemical resistance, good electrical properties, and higher adhesive strength,^{1,2} which make them suitable for castings, adhesives, advanced composites, and coating applications.^{3–8} However, in the crosslinked state, they are intrinsically brittle^{4,5,9} with very low fracture energy.¹⁰ Also, they have comparatively low hydrophobicity¹¹ and poor weathering and thermal resistance.⁷ Major disadvantages for their application are their flammability^{3,12} and low impact resistance.^{8,13} The low pigment-holding ability and yellowing of epoxy resins further resist their wide application in paints and coatings.⁶ Recently, numerous attempts at the toughening of epoxy resins have been made with, for example, carboxy-, amine-, or hydroxyl-terminated acrylonitrile butadiene rubbers, functionally terminated acrylates, poly(phenylene oxide), and alkylene oxide.^{4,5,8,9,13} Such modifications improve the impact behavior of epoxy resins; however, in some cases, the presence of a high level of unsaturations in their structure has been found to provide sites for degradative reactions,⁹ and for

some other modifications, these systems have been found to be unsuitable for high-performance engineering applications.^{8,13} To overcome the drawbacks of such systems, extensive research efforts have been made to provide opportunities for the development of high-performance organic-inorganic hybrid polymers.^{3,13–18} The combination of organic and inorganic siloxane functionalities in a single component offers diverse and unique properties such as good processability, flexibility, durability, and toughness and high thermooxidative stability to the resin, along with good abrasion resistance, hardness, chemical resistance, weatherability, and UV resistance.^{14,15} These optimum characteristics have been obtained with the usage of inorganic siloxane polymers with acrylates, vinyls, acetoacetates, and epoxies.^{9,10,14,15,19–21} Siloxanes are known for unusual flexibility,²² high thermal stability and moisture resistance, good dielectric properties, excellent UV and chemical resistance,^{8,12,13,15,20,23–25} low toxicity,^{3,12} and high corrosion protective efficiency.¹⁵

The conventional methods used to introduce siloxanes into polymers involve a common blending process.^{7,26} Blending may increase the viscosity of the resin,^{6,7,24} and a larger amount of the solvent can be consumed in the preparation of the coatings; the evaporation of the excess solvent, during and after curing, may cause shrinkage and produce internal stresses in the coatings, causing leaching after a certain time. In the case of epoxy-siloxane blends, phase separation and bleeding of the silicon component occur, and this

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limits the use of larger silicone concentrations.^{6,7,24} The phase separation and low surface energy of silicone-polymer-modified epoxies hamper their use in surface coatings.⁶ Thus, to solve this problem, it is mandatory to incorporate a siloxane moiety into the polymer backbone through some chemical reaction.^{7,27} The incorporation of siloxane into epoxy through addition polymerization improves the aforementioned drawbacks.^{7,27}

In this study, diglycidyl ether of bisphenol A (DGEBA) epoxy (E) was modified by hydroxyl-terminated polydimethylsiloxane (HPDMS) through the incorporation of the latter into the former via ring-opening addition polymerization. The main objective of this research work was to investigate the possible use of siloxane-modified epoxy (ES) in the development of anticorrosive polymeric coatings and paints. The structure of E and ES was confirmed with Fourier transform infrared (FTIR), ¹H-NMR, and ¹³C-NMR spectroscopy analyses.²⁸ ES and E were further subjected to the formulation of anticorrosive paints. 1,6-Diaminohexane (AH) and 1,3-diaminopropane (AP) were used as curatives. The physicochemical analysis of E and ES was carried out by standard methods. The physicochemical and anticorrosive performance of the coated samples of the E- and ES-based paints were also evaluated. Thermal analysis was carried out via thermogravimetric analysis (TGA). The effects of the incorporation of HPDMS and the nature of the curatives on the aforementioned properties of the E- and ES-based paints were also investigated. The modification of E through siloxanes had a synergistic effect on the properties of the ES paints. Among all the E and ES paint systems, ES-AP exhibited superior thermal and anticorrosive properties.

EXPERIMENTAL

Materials

DGEBA E resin (LY 556; epoxy equivalent = 182.56, viscosity = 10,000 cP) was procured from Ciba Specialty Chemicals, Pvt., Ltd. (New Delhi, India), HPDMS (viscosity = 90–150 cSt, refractive index = 1.4057, density = 0.970 at 25°C; Aldrich, Milwaukee, WI) was used as a modifier. AP, AH (Merck, India), ethyl methyl ketone (Merck), TiO₂ (rutile), and phosphoric acid (S.D. Fine Chemicals, Mumbai, India) were used as such. Talc, mica, silica, and china clay (Shankar Dyes Chemicals, New Delhi, India) were used as extenders.

Synthesis of the HPDMS-modified epoxy resin (ES)

Calculated weight percentages of HPDMS (10, 20, 25, 30, and 40) and E resin were placed in a three-necked,

round-bottom flask equipped with a magnetic stirrer, thermometer, and nitrogen inlet tube in the presence of a few drops of phosphoric acid used as a catalyst. The reaction mixture was maintained at 80°C along with constant stirring. The progress of the reaction was monitored by thin-layer chromatography through the determination of the epoxy equivalent and hydroxyl value at regular intervals. As the reaction proceeded, the epoxy equivalent gradually increased and became constant at 345 upon the completion of the reaction. The increase in the epoxy equivalent (from 182.56 to 345) indicated a decrease in the oxirane content, supporting the idea that the chemical reaction took place between the E ring and siloxane to form ES along with the presence of residual epoxide rings.

ES was synthesized with various weight percentages (10, 20, 25, 30, and 40) of HPDMS by the aforementioned procedure to optimize the amount of siloxane with respect to the E resin. ES resins of different compositions were subjected to physicochemical analysis. No significant change in the value of the epoxy equivalent was observed as the reaction for the synthesis of ES (beyond and below 25 wt % HPDMS) proceeded, and this indicated a negligible reaction between E and HPDMS. An abnormal increase in the physicochemical characteristics, such as the viscosity and specific gravity, was also observed (>25 wt % HPDMS), and this ruled out the possibility of using the aforementioned systems further.

The structure of ES was further confirmed with FTIR, ¹H-NMR, and ¹³C-NMR spectral analysis (Figs. 1–4).

Formulation of the HPDMS-modified E-based paint

ES (25 wt %) was subjected to paint formulation. TiO₂ (rutile; 15 wt %), used as a pigment, along with a predetermined quantity (30 wt %) of ES, was dissolved in ethyl methyl ketone and placed in a ball mill machine; talc (0.2 wt %), mica (1.0 wt %), silica (1.0 wt %), and china clay (2.0 wt %) were used as extenders. All the ingredients except the hardener were mixed and homogenized in a ball mill for 8 h at 1400 rpm in the presence of glass beads of a specific size. The fineness of the grind was checked with a Hegmann gauge to get the fineness value of 8–10 μm (ASTM D 1210).²⁴ Similarly, plain E-based paint was developed, which further served as a control. Each of the paint systems (E and ES) was mixed with a solution of a predetermined amount of a curing agent (20 wt %), AH or AP, to prepare the precondensate of the E-amine or ES-amine system, which was further stirred at 80°C in ethyl methyl ketone for 20 min.

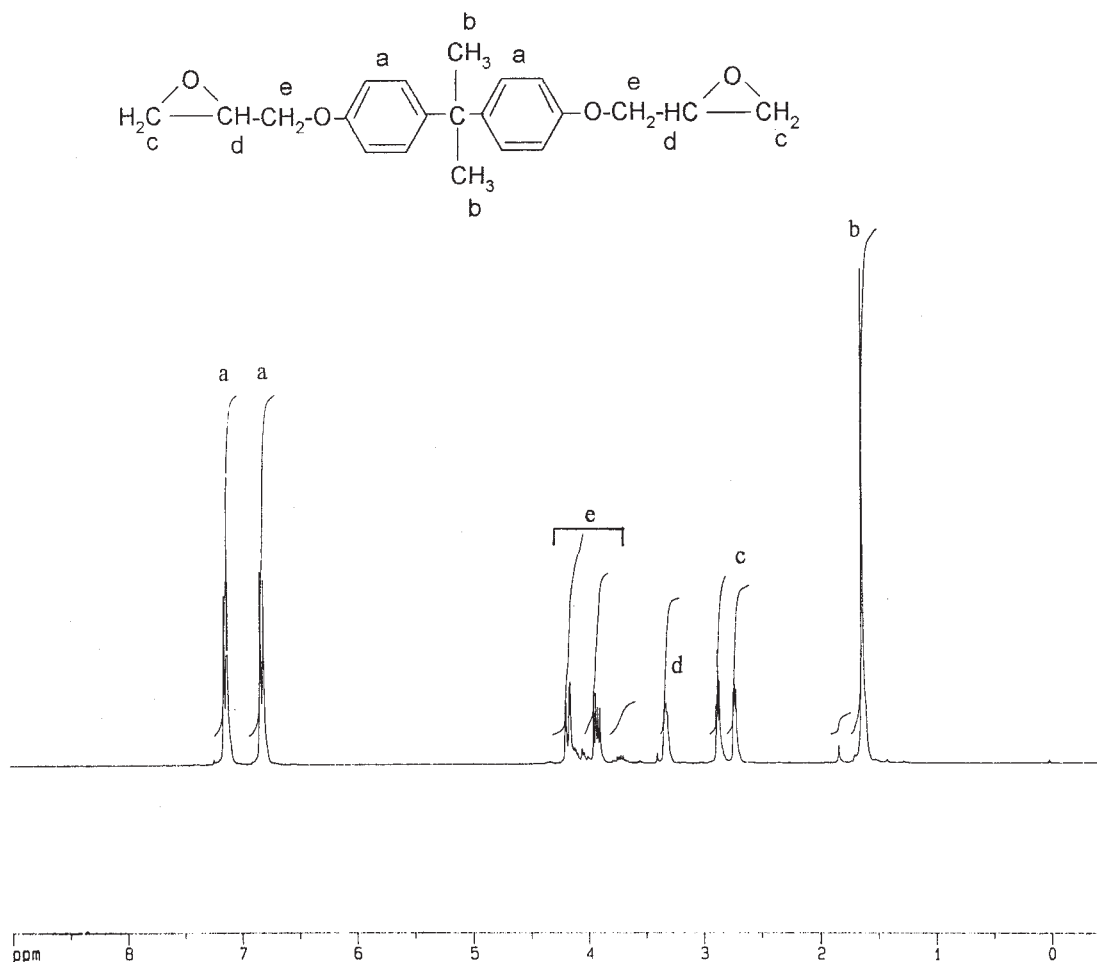


Figure 1 $^1\text{H-NMR}$ spectrum of E.

Characterization

FTIR spectra of the synthesized resins were taken on a model 1750 FTIR spectrophotometer (PerkinElmer Cetus Instruments, Norwalk, CT) with a NaCl cell. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on Bruker Spectrospin model DPX 300-MHz instrument with deuterated chloroform (CDCl_3) and deuterated dimethyl sulfoxide as solvents and tetramethylsilane as an internal standard. The thermal analysis of these resins was carried out via TGA (TGA-51, TA Instrument, New Castle, DE) under a nitrogen atmosphere.

Preparation and testing of the coatings

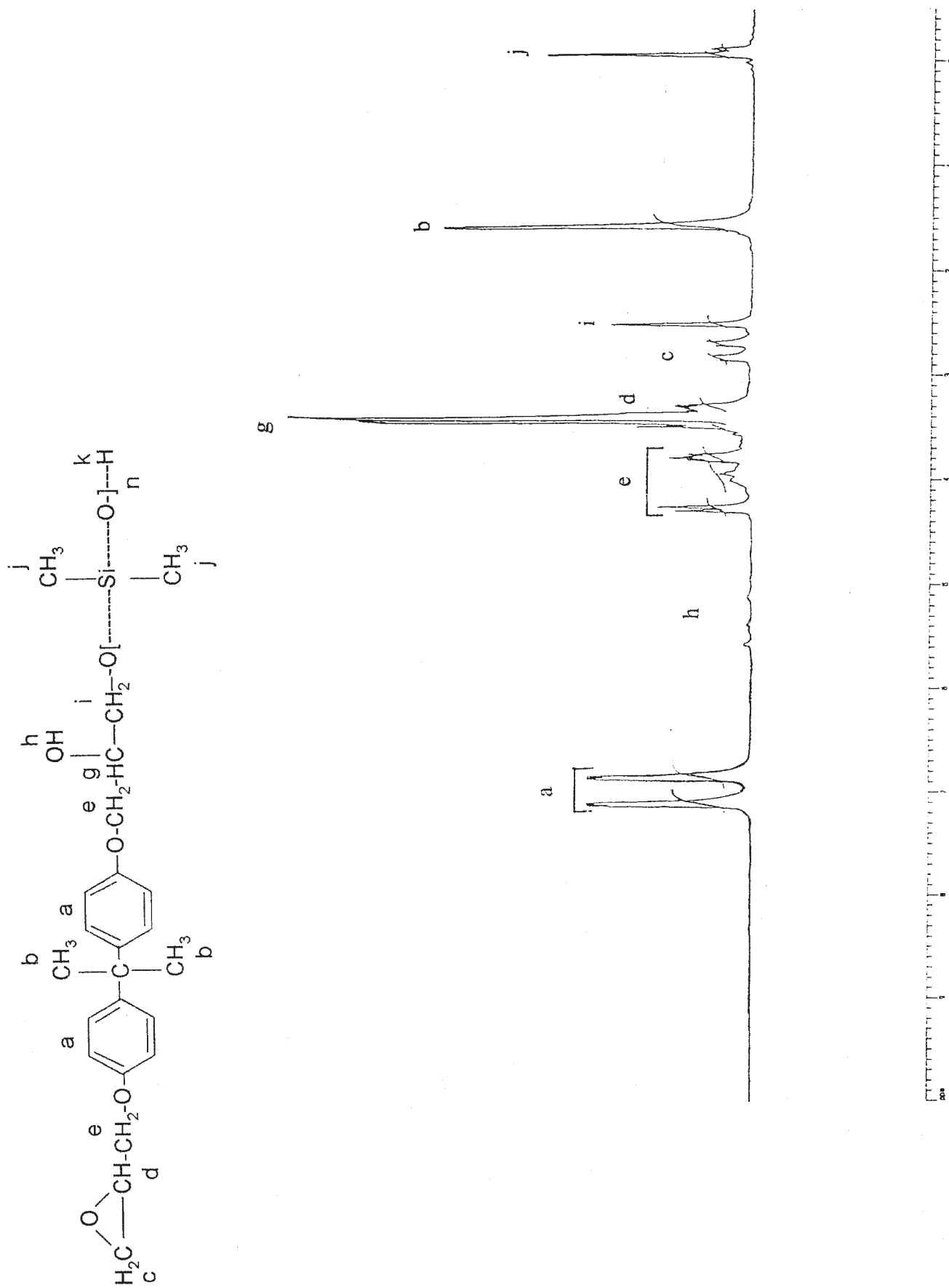
A precondensate solution of the E- or ES-curing agent paint system in ethyl methyl ketone was applied by a brush, at room temperature, to commercially available mild steel strips of standard sizes: $30 \times 10 \times 1 \text{ mm}^3$ for chemical (corrosion) resistance testing and $70 \times 25 \times 1 \text{ mm}^3$ for gloss testing, scratch hardness testing (BS 3900), bending testing (ASTM D 3281-04), and impact resistance testing (IS : 101 part5/s.3,1988). The specu-

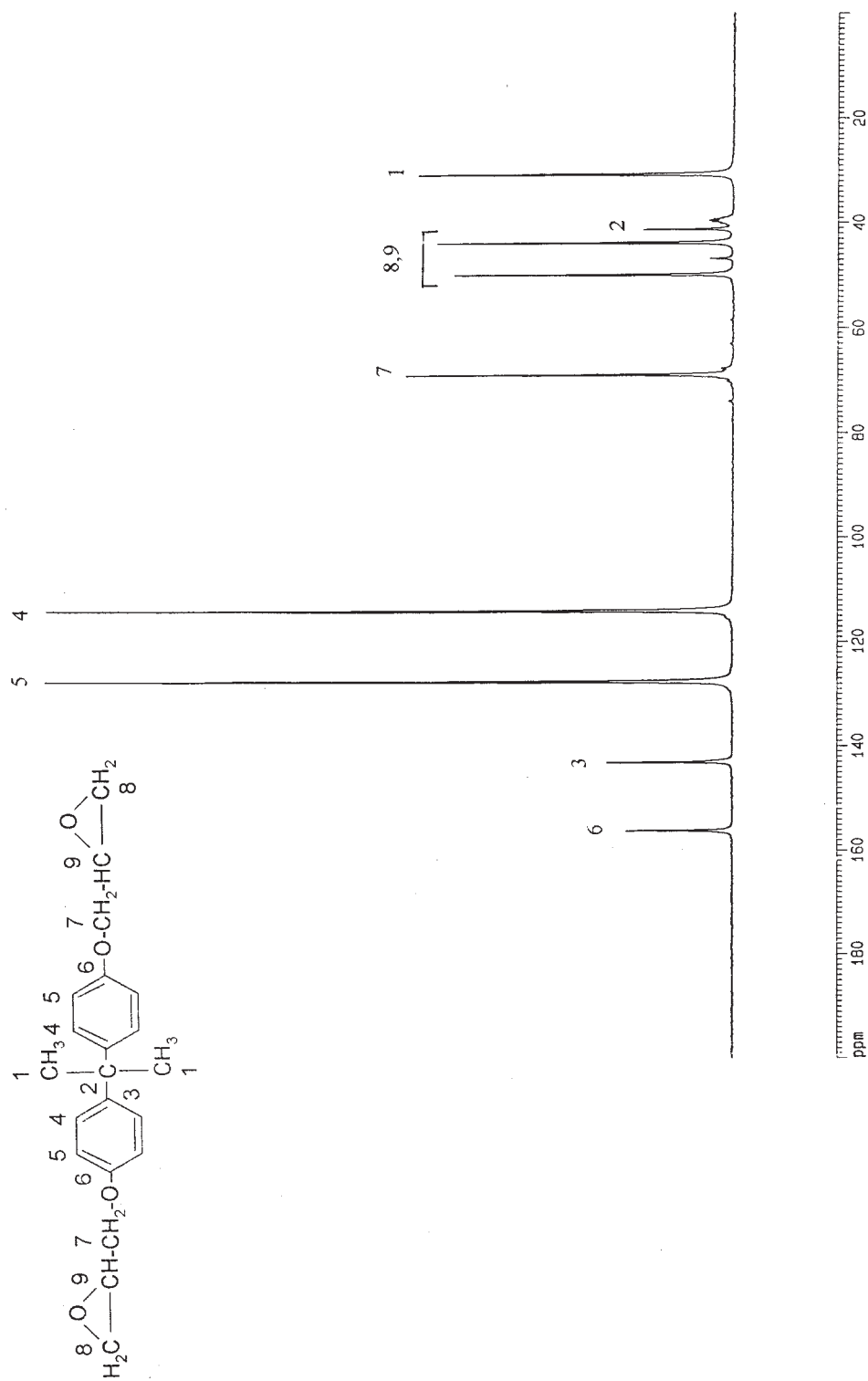
lar gloss was determined at 45° with a model RSPT 20 glossmeter (Digital Instruments, Santa Barbara, CA). The coating thickness was measured with a model 345 elcometer (Elcometer Instruments, Manchester, United Kingdom). The thickness of these coating was between 140 and $175 \mu\text{m}$. The dry-to-touch (DTT) and dry-to-hard (DTH) times were also noted (Table I).

Corrosion tests were performed in water, acid (5 wt % HCl), alkali (10 wt % NaOH), NaCl (3.5 wt %), ethyl methyl ketone, and xylene by the placement of samples in 3-in.-diameter porcelain dishes in the aforementioned media. Periodic visual examinations were conducted until the films showed evidence of softening or deterioration. The aforementioned coating properties of the paints were evaluated only after 8 days of application over the substrate.

RESULTS AND DISCUSSION

Scheme 1 shows the chemical reaction between DGEBA E and HPDMS to form ES. The proposed structure for ES was confirmed by spectroscopic anal-

Figure 2 $^1\text{H-NMR}$ spectrum of ES.

Figure 3 ^{13}C -NMR spectrum of E.

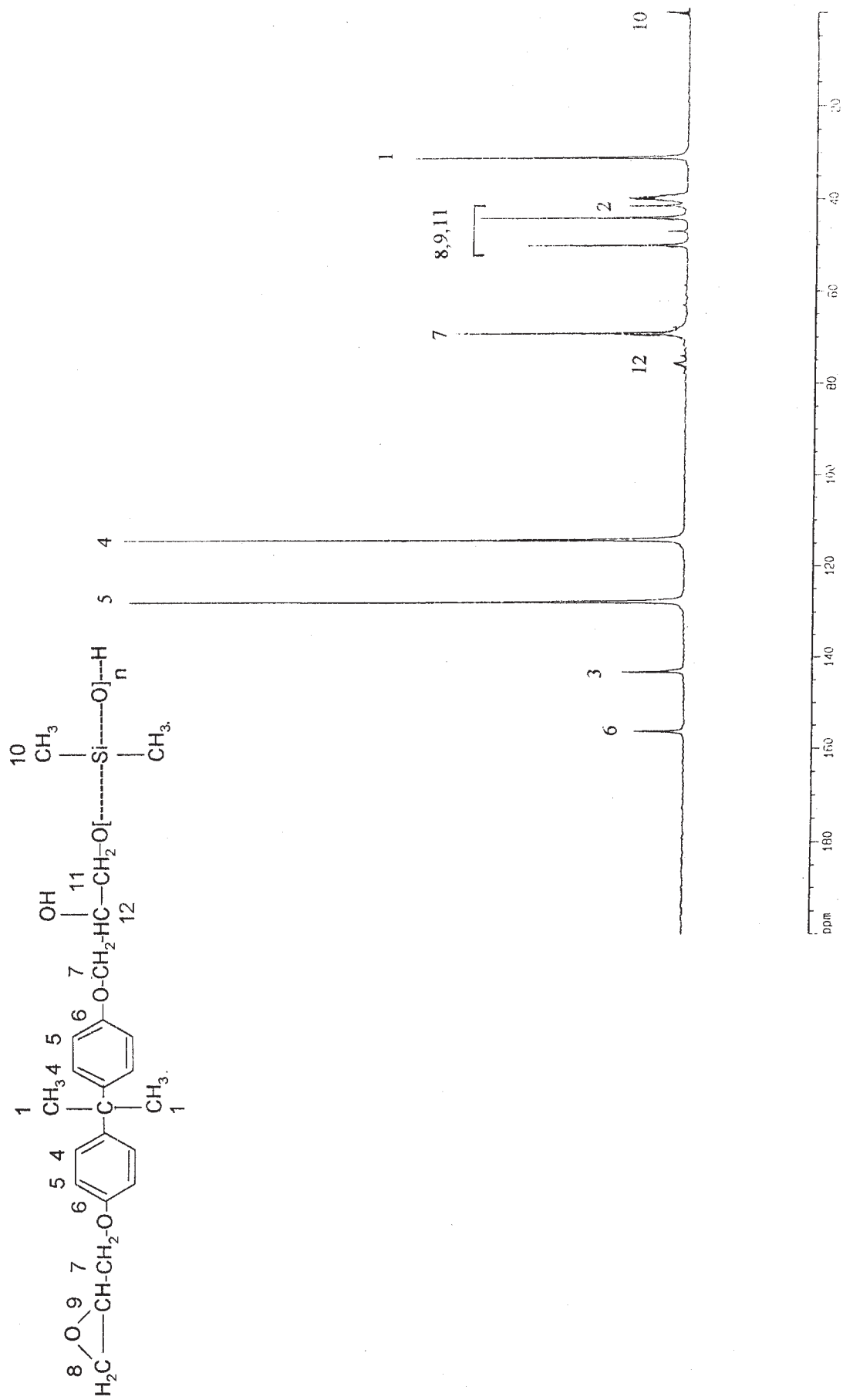


Figure 4 ^{13}C -NMR spectrum of ES.

TABLE I
Physicomechanical and Anticorrosive
Performance Evaluations

Characteristic	System			
	E-AH	ES-AH	E-AP	ES-AP
DTT (h)	5	2	5.5	1.5
DTH (h)	8	4	9	3
Gloss at 45°	60	69	59	72
Scratch hardness (kg)	1.5	4	1.4	5
Impact resistance (150 lb./in.)	Pass	Pass	Fail	Pass
Bending test (1/8 in.)	Pass	Pass	Fail	Pass
Chemical				
NaOH (10 wt %, 10 days)	c	b	c	a
HCl (5 wt %, 10 days)	d	c	d	b
NaCl (3.5 wt %, 10 days)	d	c	d	b
H ₂ O (45 days)	b	a	c	a
Butanone (60 h)	d	c	d	b
Xylene (60 h)	b	b	c	a

a = unaffected; b = slight loss in gloss/film was not affected; c = loss in gloss/film was affected; d = film swelling.

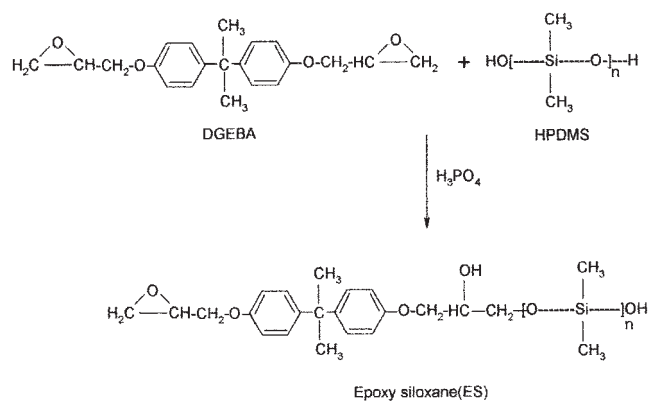
ysis (IR, ¹H-NMR, and ¹³C-NMR). It is also supported by physicochemical analysis results discussed in a later section.

Spectral analysis

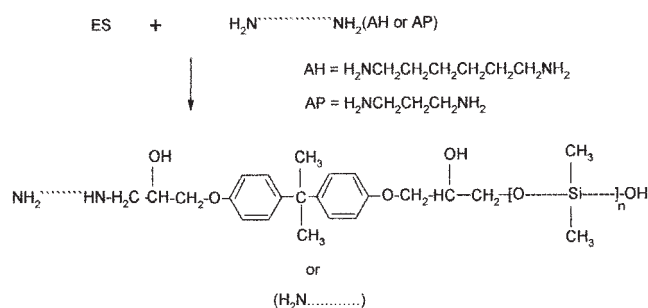
The spectral analysis of pure E and ES is discussed, and the important characteristic peaks are given (Figs. 1–4)

Pure E (IR, cm⁻¹)

1297–1184 (C—O—C, aryl alkyl ether, asymmetric stretching), 1087 (aryl alkyl ether, symmetric stretching), 2962 (—CH₃ of quaternary carbon), 3056.5, 1582, 787, 750 (aromatic rings, stretching), 2929 (—CH₂ symmetric stretching), 2872 (—CH₂, asymmetric stretching), 972.4–915.8 (oxirane ring), 1381 [(CH₃)₂C], 3487.9 (—OH), 1158–1085 (Si—O—Si, stretching), 2958, 1245, 805 (Si—CH₃).^{19,22}



Scheme 1 Synthesis of ES.



Scheme 2 Modification of ES with a diamine curative (AH or AP).

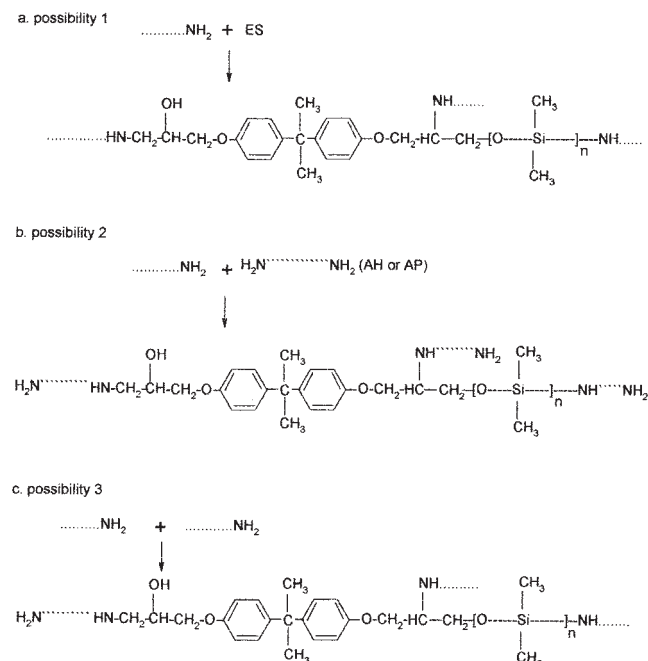
metric stretching), 2872 (—CH₂, asymmetric stretching), 972.4–915.8 (oxirane ring), 1381 [(CH₃)₂C].¹⁹

ES (IR, cm⁻¹)

1297–1184 (C—O—C, aryl alkyl ether, asymmetric stretching), 1087 (aryl alkyl ether, symmetric stretching), 2962 (—CH₃ of quaternary carbon), 3056.5, 1582, 787, 750 (aromatic rings, stretching), 2929 (—CH₂ symmetric stretching), 2872 (—CH₂, asymmetric stretching), 972.4–915.8 (oxirane ring), 1381 [(CH₃)₂C], 3487.9 (—OH), 1158–1085 (Si—O—Si, stretching), 2958, 1245, 805 (Si—CH₃).^{19,22}

Pure E (¹H-NMR, CDCl₃, δ, ppm)

7.14–6.8 (aromatic ring protons), 4.19 (—CH₂—O—Ar), 3.33–3.30 (—CH, oxirane), 2.8–2.7 (—CH₂, oxirane), 1.8–1.6 (—CH₃)



Scheme 3 Possible curing reactions of ES with an amine curative (AH or AP).

TABLE II
Physicochemical Analysis of E and ES

System	Epoxy equivalent	Hydroxyl value	Specific gravity	Refractive index
E	182.56	—	1.1506	1.5685
ES	345.00	18	1.2553	1.5885

ES ($^1\text{H-NMR}$, CDCl_3 , δ , ppm)

7.11–6.8 (aromatic ring protons), 5.58 (OH), 4.28–4.24 (CH—OH), 4.19 ($-\text{CH}_2-\text{O}-\text{Ar}$), 3.55–3.48 ($-\text{CH}_2-\text{OH}$), 3.33–3.29 ($-\text{CH}$, oxirane), 2.8–2.69 ($-\text{CH}_2$, oxirane), 2.5 ($\text{CH}_2-\text{O}-\text{Si}$), 1.56 ($-\text{CH}_3$), 0.064 ($-\text{CH}_3-\text{Si}$).^{19,28}

Pure E ($^{13}\text{C-NMR}$, dimethyl sulfoxide, δ , ppm)

49.79 (CH_2 , oxirane), 43.7 (CH, oxirane), 68.86 ($\text{CH}_2-\text{O Ar}$), 156, 142.9, 127.4, 113.8 (aromatic ring carbons), 41.16 [$-\text{C}(\text{CH}_3)_2$].

ES ($^{13}\text{C-NMR}$, dimethyl sulfoxide, δ , ppm)

49.79 (CH_2 , oxirane), 43.7 (CH, oxirane), 68.86 (CH_2-OAr), 156, 142.9, 127.4, 113.8 (aromatic ring carbons), 41.16 [$-\text{C}(\text{CH}_3)_2$], 73.8–71.3 (CH—OH), 46.78 ($\text{CH}_2-\text{O}-\text{Si}$),³ 26.3 (CH_3-Si).

FTIR spectra of ES, compared with those of plain E, showed that the bands at $972.4\text{--}915.8\text{ cm}^{-1}$ for the oxirane ring shortened; a broad and pronounced band appeared at 3487.9 cm^{-1} , which was characteristic of the hydroxyl group. The bands at $1158\text{--}1085\text{ cm}^{-1}$ for Si—O—Si significantly indicated the presence of siloxane in the ES system. However, in the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of ES, the appearance of characteristic peaks for OH (5.58) and CH_3-Si (0.064; Fig. 2) as well as the peak for $-\text{CH}_2-\text{O}-\text{Si}$ (2.5) confirmed that a chemical reaction occurred between E and HPDMS to form ES. Peaks for Si— CH_3 , $\text{CH}_2-\text{O}-\text{Si}$, and $-\text{CHOH}$, which appeared at 26.3, 46.78, and 73.8–71.3 in $^{13}\text{C-NMR}$, further supported the siliconization of E.

The structure of ES distinctly indicated the presence of three functionalities per molecular chain of ES. With one oxirane ring at one end and two hydroxyls, the pendant hydroxyl group formed during the E ring-opening reaction with HPDMS,¹³ as well as the terminal hydroxyl group of siloxane at the other end of the molecular unit (Scheme 1). These groups participated in the curing reactions.

The diamine curing agents (AH and AP) reacted with the oxirane ring of ES to subsequently form hydroxyl groups. The free amino group reacted with the terminal hydroxyls of the siloxane moiety of ES, the terminal oxirane ring of ES, the pendant hydroxyls formed during oxirane ring opening by the addition reaction of E with HPDMS,¹³ and those formed during

the curing reaction with the amine itself⁶ (Scheme 1). Scheme 1 reveals that the system could attain a high crosslink density after curing.

Physicochemical analysis

Table II (physicochemical analysis) shows that the epoxy equivalent decreased, whereas the specific gravity and refractive index increased, from plain E to the ES system. This trend was indicative of a chemical reaction occurring between DGEBA and HPDMS, which reduced the overall oxirane content and also led to an increase in the molar mass of ES in comparison with E. In the case of ES, the hydroxyl value was 18, and this also implied that hydroxyl formation due to oxirane ring opening occurred through the addition reaction of E with HPDMS.¹² The values for hydroxyl as well as the trend for other physicochemical properties further supported the idea that the siliconization of E was effectively carried in the due course of the reaction.⁸

Thermal analysis

The effects of siloxane incorporation and the curatives AH and AP on the thermal stability of E and ES were investigated with TGA studies (Fig. 5). In the TGA thermograms of all ES systems, the onset of degradation occurred in the range of $220\text{--}250^\circ\text{C}$, and this can be attributed to the evaporation of the trapped solvent or the loss of moisture. The weight-loss percentage (10–50 wt %) and the corresponding temperature of degradation for E—AH, E—AP, ES—AH, and ES—AP are given in Table III. For the same weight loss, the degradation temperatures were higher for the ES—AH and ES—AP systems than those of E—AH and E—AP, respectively. In other words, it can be inferred that the ES systems had higher thermal stability than the plain E curative systems. The siloxane (Si—O—Si) bond dissociation energy is higher than the C—C and C—O bond energy, as reported by earlier workers.^{14,25} The

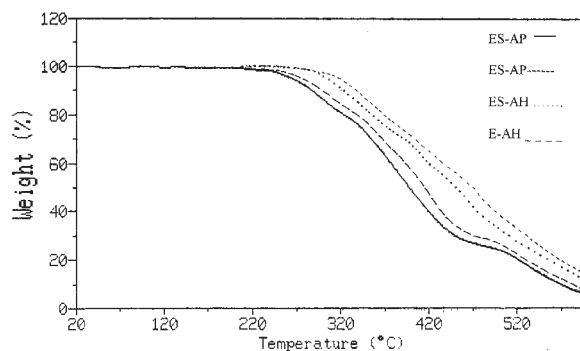


Figure 5 TGA thermograms of E—AH, E—AP, ES—AH, and ES—AP.

TABLE III
Percentage Weight Loss of E-AH, ES-AH, E-AP, and ES-AP at Different Temperatures by TGA

Weight loss (%)	Temperature (°C) for			
	E-AH	ES-AH	E-AP	ES-AP
10	295	322	286	339.5
20	339	356	324	379.0
30	367	391	353	403.0
40	391	421	378	430.0
50	414.5	451	395	473.0

stability of the inherent inorganic nature of the siloxane structure may stabilize the epoxy resin from heat.²⁵ The high energy of the siloxane bond, the low surface energy of silicones,^{3,12,14} and their partial ionic character may be responsible for substantial thermal stability.^{3,12,29,30} However, Table III also reveals that E-AH had higher thermal stability than E-AP, whereas, interestingly, for the same weight-loss percentage, ES-AP showed a considerably higher degradation temperature than ES-AH. In the case of the plain E curative system, E-AH paint was thermally more stable than E-AP. However, upon the incorporation of HPDMS, ES-AH showed a lower degradation temperature range than ES-AP. As discussed later, the number of crosslinks per unit of molecular chain length was higher for ES-AP than ES-AH. That is, ES-AP presumably had a higher crosslink density than ES-AH. In our earlier studies, we found that an increase in the crosslink density increased the thermal stability of the resins^{31,32} and also enhanced the coating properties of the resins. Consequently, ES-AP and E-AH attained a higher thermal stability than ES-AH and E-AP. The study conclusively reveals that E-AH and ES-AH can be safely used up to 245–255 and 275–285°C, respectively, whereas E-AP and ES-AP can be safely employed up to 240–250 and 290–300°C, respectively. Thermal stability studies revealed that these coatings systems could find applications in high-temperature environments.

Coating properties

Table I provides information about the coating properties of the resins. A considerable improvement was achieved in the DTT and DTH times of ES paint systems (ES-AH and ES-AP) in comparison with plain E-based paints (E-AH and E-AP). It was assumed that the upon the incorporation of HPDMS into DGEBA E, the molar mass of the systems increased. The increase in the molar mass was also supported by the physicochemical analysis results (Table II). Furthermore, upon curing with AH and AP, as explained earlier, ES became crosslinked. These factors contributed to an increased molar

mass and crosslink density of the resin, and this may be responsible for the lowering of the DTT and DTH times in ES-AH and ES-AP in comparison with the E-AH and E-AP paint systems.^{31–35} However, without HPDMS, the drying times (DTT and DTH) of the E-amine paint systems (E-AH and E-AP) varied comparably among themselves (Table I), the drying times of E-AH being lower than those of E-AP, whereas the ES-amine (ES-AH and ES-AP) paint systems showed a contrary trend, as explained later. The gloss at 45° increased upon the incorporation of siloxane. The scratch hardness and impact resistance along with the bending test values increased markedly upon the incorporation of HPDMS into E. This result was also in contrast to our expectations because siloxanes have unusual flexibility^{7,8,13,22} on account of the flexible Si—O linkages and mobile silicone chains; they possess poor mechanical characteristics.⁶ HPDMS was expected to behave as a flexibilizer.^{5,8,13} However, in this case, anomalous behavior was observed (Table I); HPDMS incorporation actually enhanced the physico-mechanical properties (Table I). It is assumed that in these paint systems, the siloxane behaves as chain entanglements rather than as a flexibilizer.¹³ The long, mobile siloxane chains assist in the formation of a highly crosslinked network between two ES molecular units (Scheme 1) through either of the amine curatives. As discussed earlier, the free amino groups may further react with the free pendant and terminal hydroxyls as well as a terminal epoxide ring (Scheme 1), leading to the formation of a highly crosslinked network and resulting in a tremendous increase in the scratch hardness, impact resistance, and bending test values (Table I). The gloss values were higher for ES-AH and ES-AP than for E-AH and E-AP for similar reasons; the highest value was achieved for ES-AP because of a highly crosslinked and dense structure. The systems were subjected to an anticorrosive performance evaluation under the influence of various corrosive chemicals. The ES paint (ES-AH and ES-AP) coated specimens showed a fair-to-satisfactory performance when immersed in HCl (5 wt %, 10 days), NaCl (3.5 wt %, 10 days) ethyl methyl ketone (60 h), and xylene (60 h) in comparison with E-AH and E-AP. ES-AP showed an outstanding performance under alkaline media; the coated panels remained unaffected in the presence of NaOH (10 wt %) for 10 days. The siloxane-incorporated systems remained unaffected in water for 45 days. This can be attributed to the hydrophobic nature of the silicones as well as the hydrophobic nature of the methyl groups, which hindered the ingress of water molecules.^{6,11} The highly crosslinked network of ES hindered the easy penetration of chemicals into the paint system and thus enhanced the anticorrosive performance of the

TABLE IV
Nomenclature for the Coating Systems

Curative	E	ES
AH	E-AH	ES-AH
AP	E-AP	ES-AP

ES-amine paints over plain E-amine paints, particularly the ES-AP system (as explained in the previous paragraph).

Interestingly, the ES-AH and ES-AP paint systems were highly antidust in nature. This inherent characteristic could be attributed to the low surface tension of siloxanes and outstanding surface properties of siloxane-containing polymers.^{4,7,27} The E-AH system showed improved physicomechanical performance over the E-AP system. E-AH showed a scratch hardness of 1.5 kg, an impact resistance of 150 lb/in, and a bending test values of 1/8 in., whereas E-AP showed a scratch hardness of 1.4 kg and failed the aforementioned values of the impact resistance and bending test. The ES-AP system showed better results than ES-AH (Table IV). The better properties of E-AH in comparison with E-AP can be correlated to its higher molar mass; AP (three carbons of propane) had a shorter chain length than AH (six carbons of hexane). In the case of ES cured with AH, the two ES molecular units were separated by six carbon atoms (AH), whereas in the case of ES cured with AP, the two ES units were three carbons (AP) apart (Scheme 1). In other words, in ES-AP, the two ES molecular units were in close proximity to each other in comparison with ES-AH. Thus, the number of crosslinks per unit of chain length, that is, the crosslink density, was presumably higher in ES-AP than ES-AH. As a result, the ES-AP system showed improved overall performance.³¹⁻³³ The proximity of two ES molecular chains due to the small chain length of AP (Scheme 1) may also have been responsible for restricting the free mobility of siloxane chains because of the steric hindrance¹² retarding its flexibilizing nature further; the siloxane units behaved only as chain entanglements, providing better properties to ES-AP than its counterparts (E-AH, E-AP, and ES-AH). The ES systems were keenly observed for 6 months. No phase separation and no signs of depigmentation or leaching were observed, as is common for ES; no yellowing or shrinkage was noticed for the ES paint systems, as mentioned earlier. This highlights that our paint systems have overcome some of the common drawbacks of ES systems, which have restricted their wide applications in paints and coatings. These remarkable inherent characteristics of ES-AH and ES-AP may be well attributed to the role of siloxane and amine curatives.

CONCLUSIONS

ES-amine paint systems showed a considerable improvement in the drying time (DTT and DTH) in comparison with that of plain E-amine paint systems. Contrary to our expectations, fairly good physicomechanical properties were achieved for ES paints, and this indicated that here the siloxane moiety provided chain entanglements instead of acting as a flexibilizer. An anticorrosive performance evaluation showed that ES-AP gave a satisfactory performance under the influence of the aforementioned corrosive media and, particularly, an outstanding performance in alkaline environments (10 wt % NaOH, 10 days), being unaffected. The thermal analysis through TGA confirmed that the incorporation of Si—O—Si units into the E backbone had a synergistic effect on its thermal stability. The curing agents AH and AP had a positive influence on the physicomechanical, anticorrosive, and thermal properties of the ES paints in comparison with those of plain E-amine paints. Our studies conclusively confirm that ES-amine systems may be well recommended to be used as anticorrosive paint systems for high-temperature applications.

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