A novel cyclomatrix polymer based on (hydroxy phenoxy) phosphazenes and 2-methyl aziridine: some aspects of synthesis and adhesive heat resistance

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Tris(hydroxy phenoxy) cyclotriphosphazenes based on the reaction of hexachlorocyclotrisphosphazene, $(NPCl_2)_3$ with bisphenol-A, thiodiphenol and hydroquinone were prepared and characterized for degree of substitution of chlorine, product distribution and purity. Reaction of the residual chlorine atoms with 2-methyl aziridine (propylenimine) gave condensates, capable of storage under ambient conditions and curable on heating to give a crosslinked polymer stable up to 350°C. Characterization of the condensates and the adhesion strength of the cured polymer on Al substrates were studied.

(Keywords: hexachlorocyclotriphosphazene; bisphenol-A; thiodiphenol; hydroquinone; cyclomatrix polymer; adhesive heat resistance)

INTRODUCTION

Cyclomatrix poly(organophosphazenes) are a class of semi-inorganic, thermally stable systems currently causing interest due to their aerospace applications as high char laminates and as structural adhesives exhibiting a high degree of flame retardance and suppressed smoke evolution. All such polymers are formed by the reaction of hexachlorocyclotriphosphazene (HCP), $(NPCl_2)_3$, with a variety of multifunctional aromatic and heterocyclic organics. The development and evaluation of one such system based on a phosphazene modified epoxy has been reported by us earlier[1]. Common problems in the development of such systems are:

(i) intractability of the polymer precursors;

(ii) formation of a mixture of products instead of a single, pure intermediate (owing to the multifunctionality of the reactants);

(iii) gelation of the polymer matrix at very low degrees of conversion and the need for substantial post-curing to realize fully cured systems.

This has necessitated research and development on storable intermediates which could be processed at will without any loss of properties or formation of insolubles during storage.

In this paper, we report, for the first time, the development of such an intermediate which was formed in a two stage reaction in solution:

(1) Synthesis of a tris(hydroxy phenoxy) cyclotriphosphazene from HCP and a diphenol viz.: bisphenol A (BPA), thiodiphenol (TDP), or hydroquinone (HQ) (such intermediates and polyesters, thereof, are reported in literature as flame-retardant coatings[2–20].

(2) Reaction of the residual chlorine atoms with 2-methyl aziridine (propyleneimine).

The condensates, at both the stages, were characterized for product distribution, i.r., ^{31}P n.m.r., gross thermal stability (using t.g.a.) and d.t.a. in air. The propyleneimine condensates of the hydroxy phenoxy cyclo triphosphazenes could be stored under ambient conditions whereas on heating to 120°C, they crosslinked to give insoluble cyclomatrix polymers, stable up to 350°C in air. The adhesion strength of the cured polymer was evaluated at room temperature and at 250°C, with a soak time of 10 min, using lap-shear specimens made of an Al alloy. The overall reaction is shown in *Figure 1* and the curing mechanism in *Figure 2*. A possible side reaction occurring during curing (and confirmed by d.t.a.) involves liberation of HCl from the intermolecular reaction between the hydroxy aromatic residues and the unreacted chlorine atoms as shown in *Figure 3*.

EXPERIMENTAL

Materials

HCP was prepared by the standard process developed at VSSC. A freshly sublimed and recrystallized material (from hexane) m.p. 112°C–114°C was used in all the experiments. Reagent grade dioxane, tetrahydrofuran, and triethylamine were predried over KOH pellets, distilled and stored over Na. The diphenols were of the L.R. grade and were used as received. TDP was received as sample from the Crown Zellerbach Corporation, USA. 2-Methyl aziridine (propyleneimine) was (Fluka) used as received. L.R. grade Fe_2O_3 was dried at 150°C before use.

Apparatus

I.r. spectra were recorded using a Perkin Elmer model 283 spectrophotometer. T.l.c. of the condensates were run using silicagel-G coated glass plates. P n.m.r. spectra were recorded using a Jeol JNM-MH-100 spectrometer, while ^{31}P n.m.r. spectra were recorded using a Jeol FX-90 Q spectrometer operating at 36.23 MHz in the FT mode, with a sweep width of 5000 Hz, using 85% H_3PO_4 as the external standard. T.g.a. and d.t.a. traces were obtained

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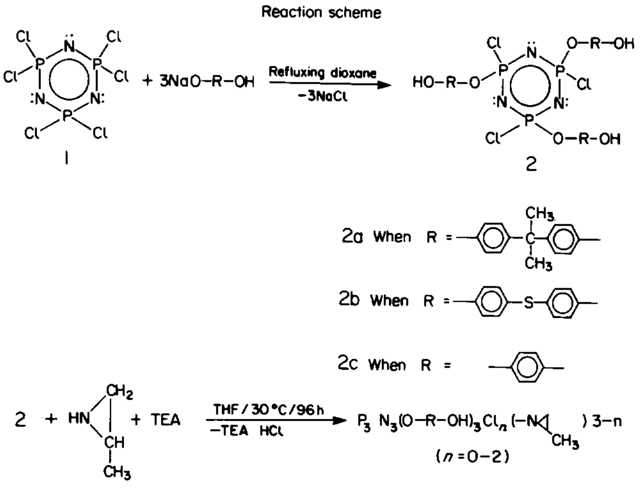


Figure 1 Overall reaction scheme

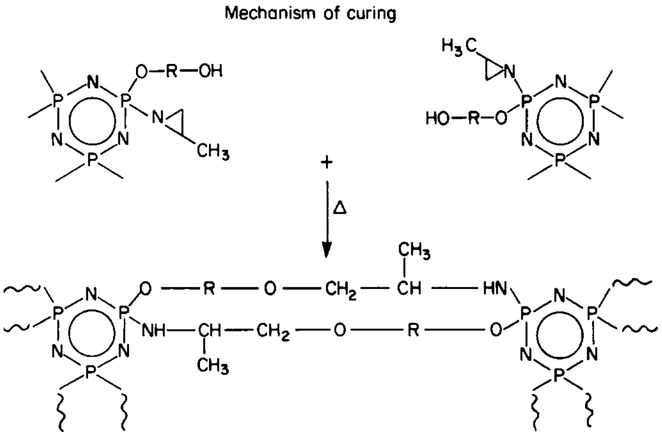


Figure 2 Mechanism of curing

from a duPont thermal analyser model 990. Lap shear strength values were evaluated by a Hounsfield-W-Model Tensiometer at a pulling rate of 3 mm min^{-1}.

Synthesis of **2a**, **2b** *and* **2c**

Sodium (2.3 g, 0.1 mol) was weighed into dry toluene (50 ml) and was heated to reflux. The molten sodium was globulized by vigorous shaking of the contents followed by rapid cooling to room temperature. Toluene was carefully decanted and the sodium globules were immediately covered by dry dioxane (225 ml). BPA (22.8 g, 0.1 mol) was added to this dispersion and was dissolved by gentle shaking. The system was refluxed with stirring (magnetically), with a calcium chloride guard-tube on top of the condenser, to remove moisture. Formation of the monosodium salt was complete in 3 h and a dense white slurry of the salt in dioxane resulted. HCP (11.6 g, 0.033 mol) was added to this slurry in the form of its solution in dioxane (20 ml) over a period of 10 min with stirring at room temperature. After complete addition, the system was refluxed for 20 h. It was then cooled, the NaCl precipitate was filtered out, dried and weighed. The filtrate was treated with hexane (1 litre) to precipitate the condensate, **2a**. It was redissolved in THF and reprecipitated with hexane, (yield 80%).

The condensates **2b**, and **2c**, were prepared in a similar fashion, using TDP and HQ respectively.

Characterization of **2a**, **2b** *and* **2c**

The weight of sodium chloride indicated the overall degree of substitution (*DOS*) of chlorine atoms. However, it was not helpful in analysing their composition. Hence the condensates were characterized by %CHN analysis, i.r., ^{31}P n.m.r. and t.l.c.

CHN analysis. All the condensates exhibited analytical values very close to those expected for tris substitution as shown in *Table 1*.

I.r. (*KBr*) (*cm*$^{-1}$). **2a**: 3500–3300 (s; broad, –OH), 1620, 1500, 1450 (s; C=C, aromatic); 1380–1370 (m-CH_3 deform, isopropyl); 1250 (vs, C–O str.); 1200 (vs; P–O–C asym. str.); 1170 (vs, PNP asym. str.); 960 (s; P–O–C sym. str.); 880 (s; PNP sym. str.); 600–560 (s, P–Cl str.).

2b: 3600–3350 (s; broad, –OH), 1600, 1500, 1450 (s; C=C, aromatic); 1250 (vs; C–O str.); 1200 (vs, P–O–C asym. str.); 1160 (s, PNP asym. str.); 1120 (s, CH deform.); 1100–1085 (s, C–S–C str.); 970 (s, P–O–C sym. str.); 880 (s, PNP sym. str.); 790–770 (s, CH out of plane); 610–570 (vs; P–Cl str.).

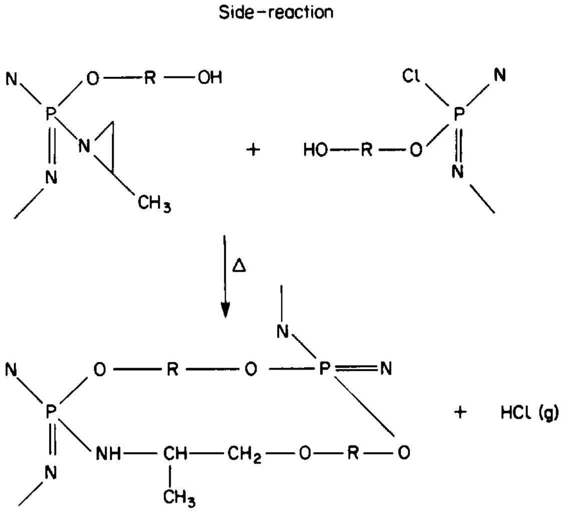


Figure 3 A possible side-reaction during curing

Table 1 Elemental analysis of and the degree of substitution of chlorine atoms (*DOS*) in **2a**, **2b** and **2c** (formed from refluxing dioxane, 20 h, at phenol/HCP ratio = 3.0)

		Elements analysed (%)						D.S.	
		C		H		N			
Sl. No.	Phenol (condensate)	Calculated for DS = 3	Observed (anal.)	Calculated for DS = 3	Observed (anal.)	Calculated DS = 3	Observed (anal.)	Based on wt of NaCl	Based on % C
1	BPA (**2a**)	58.34	55–56.1	4.88	5.10	4.55	4.48	2.80–2.86	2.6–2.7
2	TDP (**2b**)	48.35	45.0	3.02	3.40	4.70	4.50	2.97	2.55
3	HQ (**2c**)	32.95	32.6	3.20	3.60	6.41	5.96	3.0	2.86

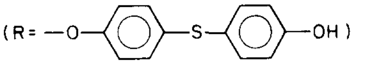
2c: 3600–3350 (s, broad, -OH); 1500 (s, C=C; aromatic); 1250 (s; C–O str.); 1200–1150 (s, broad, POC and PNP asym. str.); 970 (s, P–O–C sym. str.); 875 (s, PNP sym.); 580–530 (vs; P–Cl str.).

T.l.c. silica gel; hexane/acetone 7:3 and toluene/hexane/acetone 1:2.6:1, 30°C. T.l.c. of **2a**, **2b** and **2c** with the above solvent systems indicated the presence of products with more than a single degree of substitution in the case of **2a** and **2b**. **2c** showed only a single spot under these conditions. R_f values and probable structures contributing are shown in *Table 2*.

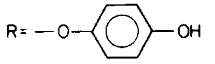
^{31}P n.m.r. {H} (dioxane/$CDCl_3$, 20°C). Spectra indicated a complex product composition in all three cases with contributions from condensates of lower degrees of substitution, apart from the expected ones.

2a *(HCP/BPA condensate).* The spectrum of **2a** revealed a non-geminal pattern of substitution and the presence of the tris and bis substituted condensates as the major ingredients (90%). A strong singlet at 18 ppm is attributed to the tris condensate, while a doublet–triplet pair in the 21 to 25 ppm range ($J_{PNP} = 64$ Hz) is attributed to the bis condensate. (One peak of the doublet is probably merged with the singlet.) Multiplets that occur in the 2–7 ppm range are in all probability, due to the presence of hydrolysed cyclic structures. The spectrum indicated that the bis condensate was present to the extent of 15% in the product composition.

2b *(HCP/TDP condensate).* A spectrum of **2b** was indicative of a mixed mode of geminal and nongeminal substitution of the chlorine atoms by TDP, the latter mode predominating. Thus there was a major singlet at 18.06 ppm, due to the tris nongeminal product, a system of double doublets (DD) at 24.4 ppm (PCl_2; $J_{PNP} = 73$ Hz and 20 Hz), 14.63 ppm (PR_2, $J_{PNP} = 64.8$ Hz and 20.25 Hz) and a third one merging with other peaks around 18 ppm range



The presence of a nongeminal biscondensate was indicated by a triplet at 20.4 ppm ($J_{PNP} = 25$ Hz) whose complimentary doublet again merged with other peaks at the 18 ppm range. The spectrum also contained spurious peaks, in minor quantities, at +2 ppm owing probably to hydrolysed cyclic structures.

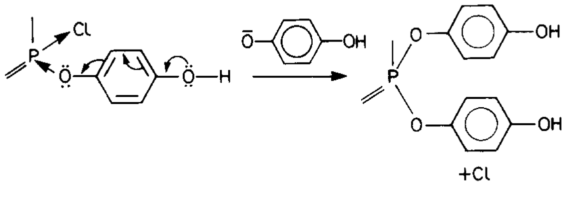
2c *(HCP/HQ condensate).* A spectrum of **2c** predominantly indicated a geminal mode of substitution with this phenol. The spectrum contained a system of 3 DDs, at 24 ppm (PCl_2, $J_{PNP} = 70$ and 30 Hz), at 18 ppm, (PClR; $J_{PNP} = 55$ Hz and 30 Hz) and at 15 ppm (PR_2, $J_{PNP} = 70$ Hz and 55 Hz) where  .

As suggested by t.l.c. and CHN analysis, the spectrum confirmed the presence of a single product with a degree of substitution of 3. Additional peaks present at the 18 ppm region implied a minor contribution from the nongeminal mode of substitution. This could be the reason for the middle DD remaining more intense than the other two and poorly resolved. The percentage of the nongeminal product works out to be 10% of the total.

Table 2 T.l.c. analysis of **2a**, **2b** and **2c**

Sl. No.	R_f	Relative intensity of the spot	Observed in the condensates	Probable contribution from
1	0.35–0.50	major	**2a**, **2b**, **2c**	tris-substitution
2	0.11–0.15	minor	**2a**, **2b**	bis-substitution
3	0.06–0.08	minor	**2a**, **2b**	mono-substitution

The predominantly geminal mode of substitution in the case of hydroquinone was a curious observation. Phenols are generally expected to undergo a nongeminal mode of substitution. The strange behaviour of hydroquinone could be ascribed to the activation of the chlorine atoms present in the once reacted P atoms by the -OH group of the diphenol in the nucleophilic substitution by another phenol moiety as shown below.



The $^{+}$R effect is probably partially transmitted in case of TDP and is blocked in the case of BPA.

Synthesis of **3a**, **3b** *and* **3c**

2a (9.2 g, 0.01 mol) was dissolved in dry THF (50 ml). Triethylamine (3.08 g, 0.0315 mol) and propyleneimine (1.8 g, 0.0315 mol) were mixed in THF (10 ml). The mixture was slowly added to the solution of **2a** over a period of 5 min. The system became warm and tirethylamine hydrochloride started precipitating out. The flask was stoppered air-tight and kept at room temperature for 4 days with occasional shaking. The precipitate was filtered and weighed. The filtrate was added to 500 ml hexane and the precipitated condensate was isolated. It was redissolved in THF and reprecipitated with hexane. The product was dried in vacuum at 50°C for 1 h to give a pale yellow powder (yield 9.1 g (90%)). **3b** and **3c** were prepared under similar conditions.

Characterization of **3a**, **3b** *and* **3c**

Elemental analysis. The *DOS* of the chlorine atoms on **2a**, **2b** and **2c** by propyleneimine was calculated from the weight of the triethylamine hydrochloride formed during the synthesis of **3a**, **3b** and **3c** and by the CH and N% analysis. There was good agreement between the values as shown in *Table 3*. The overall reactivity of the chlorine atoms on **2a**, **2b** and **2c** was affected by the electron releasing capacity of the phenol moiety. Thus the order of reactivity was **2c** > **2a** > **2b** which is in tune with the electron releasing capacity of the phenols viz. HQ > BPA > TDP.

In no case, was a *DOS* of 3 achieved under the observed reaction conditions. Use of higher reaction temperatures (up to 67°C) led to the premature formation of insoluble compounds.

I.r. (KBr) cm^{-1} **3a**: 3500–3250 (m; broad -OH); 1620, 1510, 1470 (s; C=C aromatic); 1250 (vs; C–O str.); 1200–1160 (s, broad P–O–C asym. str. + PNP asym. str.); 1050 (s, C–N str.); 950 (vs; POC sym. str.); 905 (vs, PNC sym. str.); 880 (vs, PNP sym. str.); 550–590 (m; broad, P–Cl str.).

3b: 3350–3200 (m; br. -OH); 1600, 1500 (s; C=C arom.); 1400 (m, CH_3 deform); 1250 (vs. C–O str.); 1190 (vs, P–O–C asym. str.); 1165 (vs, PNP asym. str.); 1050 (s, C–N str.);

Table 3 Elemental analysis of **3a**, **3b** and **3c** and *DOS* of chlorines by 2 methyl aziridine (PI): (reaction conditions: THF solutions of **2a**, **2b** and **2c** at room temperature for 4 days; (PI/**2**) = 1.10; (PI/$Et_3 \cdot N$) = 1.0)

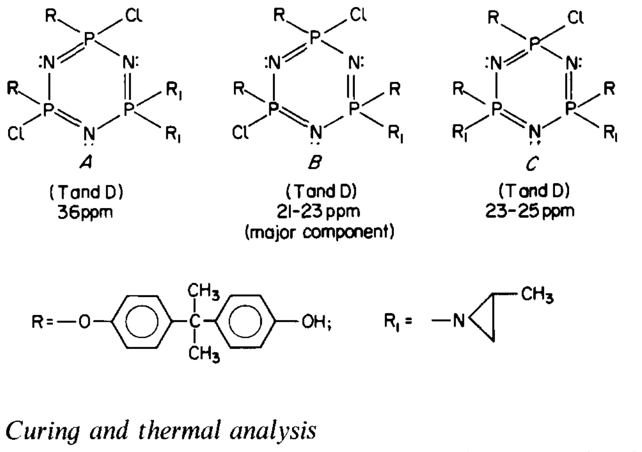
				C (%)		H (%)		N (%)	
Sl. No.	Condensate	Percentage reaction (ex. Et_3 N.HCl)	*DOS* of chlorines (ex. Et_3 N.HCl)	Calculated for the *DOS*	Observed	Calculated for the *DOS*	Observed	Calculated for the *DOS*	Observed
1	**3a**	54.8	1.65	60.91	61.05	5.68	6.3	7.47	7.5
2	**3b**	48.0	1.45	49.7	50.2	3.8	4.0	7.43	7.3
3	**3c**	64.5	1.96	45.78	46.00	4.31	4.4	11.53	12.00

945 (s, P–O–C sym. str.); 920 (s, PNC sym. str.); 870 (s, PNP sym. str.).

3c: 3400–3200 (m, br. –OH); 1510, 1460 (vs, C=C arom.); 1405 (s, CH_3 deform.); 1240 (vs; C–O str.); 1205 (vs; P–O–C asym. str.); 1170 (vs, PNP asym. str.); 1050 (s, C–N str.); 950 (m, P–O–C sym. str.); 875 (s, PNP sym. str.); 760 (s, CH, out of plane); 670 (m, P–Cl str.).

P n.m.r./($CDCl_3$). P n.m.r. spectra of the $CDCl_3$ solutions of **3a**, **3b** and **3c** were recorded. A spectrum of **3a** indicated the following diagnostic peaks; 'δ' (ppm): 7–7.5 (M, aromatic H); 4.3 (broad -OH); 1.8 (S, isopropyl H); 1.2–1.4 (M, H on aziridine ring); 1.0 (D, CH_3 on aziridine).

$^{31}P\{H\}$ n.m.r. (dioxane/$CDCl_3$) spectra of **3a**, **3b** *and* **3c** *at 20°C.* The propylenimine condensates **3a**, **3b** and **3c**, were considerably less soluble compared with condensates **2a**, **2b** and **2c**, leading to poorly resolved spectra. The spectrum of **3a** indicated a contribution to the extent of 10–12% from the bis-substituted structure present in **2a**. A triplet–doublet (T–D) combination at 36 ppm (J_{PNP} = 61.6 Hz) is ascribed to structure A shown below. Major multiplets occurring in the 20–24 ppm range were however, too complex to analyse. Apart from the presence of a tris nongeminal structure, indicated by a singlet at 25.4 ppm, there were overlapping multiplets arising due to structures of the types **B** and **C**, structure **B** predominating, as suggested by CH analysis and weight of triethylamine hydrochloride.



Curing and thermal analysis

The products **3a**, **3b** and **3c** were crosslinked to a hard insoluble polymer when heated at 120°C for 8 h. The thermogram of the cured polymer in air indicated stability up to 350°C (*Figure 4*). Although there were no major differences in their thermal behaviour, the slight superiority of the **3c** based polymer over the other two could be attributed to the increased crosslink density resulting from the greater reactivity of the small HQ pendent groups, as compared with the bulkier TDP and BPA moieties. This is further reflected in their d.t.a. traces (*Figure 5*) taken in air at a heating rate of 5°C min^{-1}. They showed a similar behaviour with regard to the three major thermal events, the temperature range for which differed only slightly from one another. The first exotherm in the range of 150°C–190°C is attributed to the reaction between the phenol and the aziridine. The second exotherm at 220°C–250°C is ascribed to the side reaction wherein the phenol reacts with the residual chlorine atoms as shown in *Figure 3*. The decomposition exotherms occur in the range 325°C–350°C, with **3c** possessing the maximum stability which is in tune with the t.g.a. of the cured products. The thermograms of the precured **3a** in air and in N_2 (*Figure 6*) do not differ from that of the cured product indicating that during the thermal analysis the prepolymer undergoes curing. The thermograms of **3a**, in air and in N_2 at the same heating rate (5°C min^{-1}) indicated that, although thermal stability remains unaffected, there is a plateau region of stability with about 45% char content between 500°C–600°C in N_2 atmosphere. A similar comparison of the t.g.a. traces of **3a** before and after curing indicated that they do not differ from each other greatly, thus implying that the product had been cured during heating under the t.g.a. conditions.

Curing

The curing of the condensates **3a**, **3b** and **3c** was effected by heating them at 120°C for 8 h. We suggest that the mechanism of curing involves reaction of the phenolic – OH with the aziridine ring, opening up the latter and

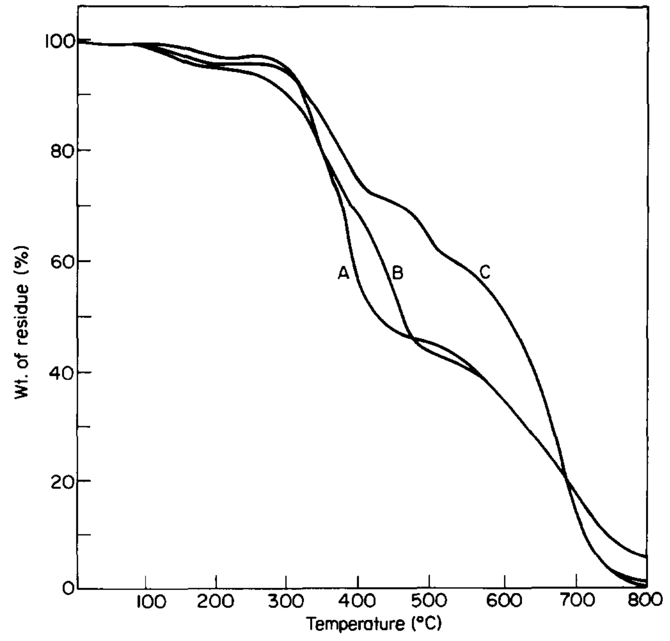


Figure 4 T.g.a. traces of **3a**, **3b**, **3c** (A, **3a**; B, **3b**; C, **3c**; heating rate = 4°C/min., medium was static air)

generating –NH groups (*Figure* 7). Support for this mechanism is provided by the i.r. spectra of the condensate, **3a**, recorded before and after curing (*Figure 8*). The broad band between 3600–3300 cm^{-1} in the spectrum of the condensate changed to a sharper band in the cured system due to the generation of –NH groups and the characteristic absorption bands of the aziridine ring at 1060 cm^{-1} and 700 cm^{-1} disappearing on curing. Similar results were observed in the case of **3b** and **3c**.

Adhesive preparation and evaluation of adhesive heat resistance

The condensates **3a**, **3b** and **3c** in solution, in THF, served as one component adhesive systems. A concentrated solution of the condensate was prepared in THF and was smeared as a thin film on the unprimed bonding surfaces of the adherends based on B51-SWP aluminium. (The adherend surfaces were prepared by grit blasting, degreasing with trichloroethylene and by chromic acid etching.) The bonding surfaces were kept tightly pressed against each other with teflon tape and were placed in an oven at 120°C for 8 h. Adhesives with Fe_2O_3 as filler were prepared in a similar fashion. The cured specimens were evaluated for their adhesion strength at room temperature and at 250°C with a soak time of 10 min, by the lap shear strength (*LSS*) measurement. An average of six values was taken for reporting (with a standard deviation of +85 psi at room temperature and 46 psi at 250°C). A similar evaluation was operated for **2a** for comparison.

The *LSS* values of the adhesives based on **3a**, **3b**, **3c** and **2a** with and without Fe_2O_3 as filler are given in *Table 4*. The values indicate a moderately good adhesion strength at room temperature and a good adhesive heat resistance at 250°C, especially in the case of the **3a**-based polymer. The poor adhesion strength exhibited by the **2a**-based system is attributed to a lower degree of crosslinking attained under the experimental conditions. (Crosslinking in the case of **2a** involves reaction of the phenolic –OH groups with the chlorine atoms on another molecule of **2a** liberating HCl, which requires a higher temperature, i.e. 220°C as shown by d.t.a.). The absence of adhesion promoting groups like –NH (present in case of **3a**, **3b** and **3c**) also accounts for the poorer adhesion. The evolution of HCl as the byproduct further impairs adhesion. The addition of Fe_2O_3 as filler improved the adhesion at high temperature especially for the **3b**- and **3c**-based systems. Ferric oxide, besides acting as a reinforcing filler, enhances adhesion by absorbing the HCl gas evolved during curing by the side reactions, which is otherwise detrimental to adhesion.

D.t.a. showed that the curing takes place in the temperature range 150°C–190°C. Hence, in one experiment, using **3a**, the curing temperature was raised to 170°C for 8 h. But the LSS values remained unaltered from those cured at 120°C for 8 h, showing that curing is almost complete at 120°C.

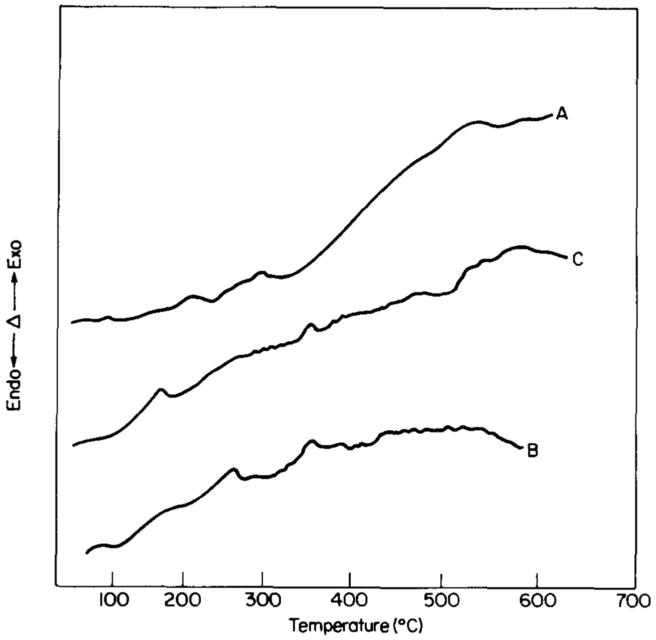


Figure 5 D.t.a. traces of **3a**, **3b** and **3c** (A, **3a**; B, **3b**; C, **3c**; heating rate = 5°C/min)

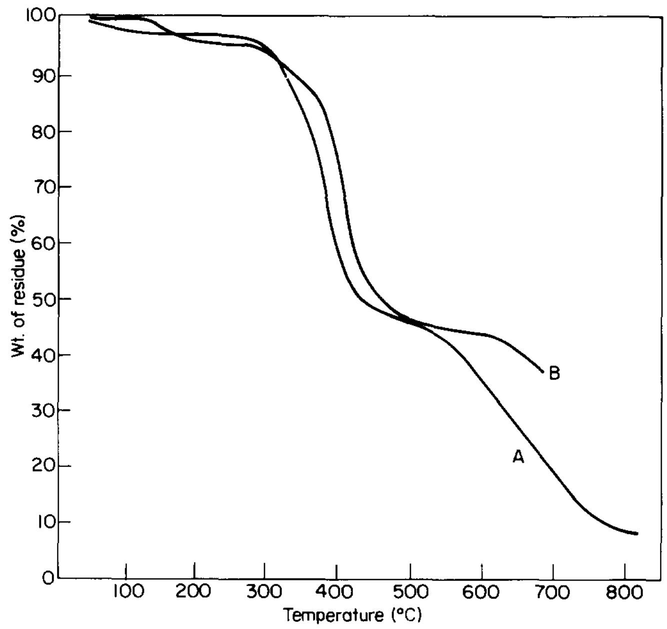


Figure 6 T.g.a. traces of **3a** in air and in N_2 (A, in air; B, in N_2; heating rate = 4°C/min)

Table 4 Lap-shear strength (*LSS*) of the one-component adhesive systems; effects of filler and high-temperature soaking (10 min)

Sl. No.	Adhesive based on the condensate	*LSS* of the plain system (psi)		*LSS* of the Fe_2O_3 filled system (psi)		
		At room temp. (30°C)	At 250°C	Filler concentration (phr of adhesive)	At room temp. (30°C)	At 250°C
1	**3a**	980	750	20	990	760
2	**3b**	506	185	10	735	660
3	**3c**	1030	85	20	1020	350
4	**2a**	200	poor	20	260	110

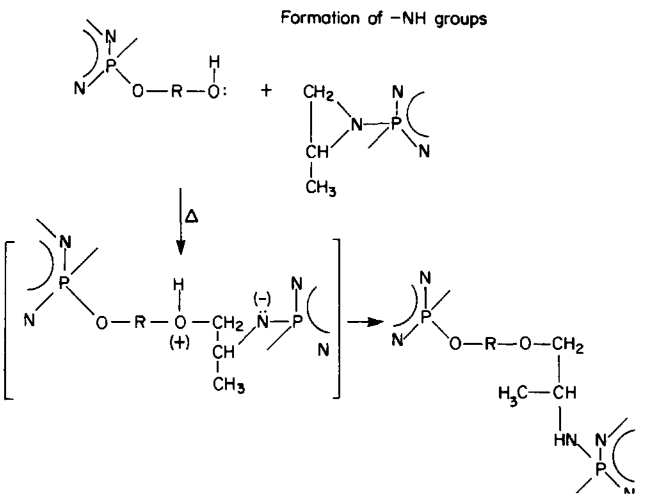


Figure 7 Formation of –NH groups during curing

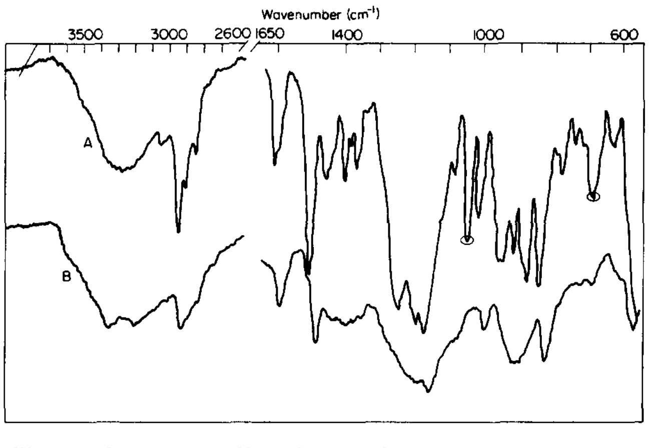


Figure 8 I.r. spectrum of **3a**, before and after curing (A, before curing; B, after curing)

CONCLUSION

A high temperature resistant, self curing, one component adhesive system was developed based on (2-methyl aziridinyl) (hydroxy phenoxy) cyclotriphosphazene, using three phenols, viz. BPA, TDP and HQ. The intermediates, which were mixtures of condensates of different degrees of substitution, were not separated but were identified by t.l.c. and ^{31}P n.m.r. studies. The systems showed moderately good adhesion, with a good retention of adhesion strength at high temperature. The cured systems were thermally stable up to 350°C and possessed improved char contents at high temperature (>600°C). However, the data generated are under specific reaction conditions and similar data, under other environments, will be required for a better evaluation of the system. A more uniform crosslink density and hence better thermal stability and adhesive heat resistance can be achieved if the components are separated at each stage of the reaction and the residual chlorine atoms are completely substituted by 2-methyl aziridine.

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