Cyclomatrix Poly(organo Phosphazenes)—Some Aspects of Synthesis, Characterization and Adhesive Heat Resistance

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Synopsis

Structure-property relationships of a phosphazene-modified epoxy-based cyclomatrix system were studied using aromatic diamine condensates of hexachlorocyclotriphosphazene $(PNCl_2)_3$ and a diglycidyl ether of bisphenol-A. Synthesis and characterization of the condensates and difficulties associated with these aspects are described. Adhesive heat resistance and thermal stability are reported as functions of the "active hydrogen" content of the condensates, molar ratios of the epoxy and "active hydrogen," and amine structures. Modification of the —OH groups formed in the amine–epoxy reaction via cyanoethylation and transesterification was not effective in improving high-temperature adhesion. The polymer systems were stable up to 380°C in air, exhibited higher char contents at elevated temperatures, and were optically clearer when compared with the corresponding nonphosphazene systems. Presence of phosphazene rings was also helpful in lowering the cure time and temperature.

INTRODUCTION

Cyclomatrix poly(organophosphazene)s, which consist of a network of phosphazene rings coupled by multifunctional organic residues at the phosphorus atoms, form a class of heat-resistant, flame-retardant, ablative polymer systems useful as structural adhesives and coatings. The basic polymer precursors, hexachlorocyclotriphosphazene $(PNCl_2)_3$, 1, and octachlorocyclotetraphosphazene $(PNCl_2)_4$, are amenable to a variety of modifications involving the reaction of their chlorine atoms in simple substitutions and polymer-analogous reactions. Products from the former type of reactions are well known as flame-retardant additives[1–32] for textile fibers based on rayon,[11,13–16,22,24,25,29,31] terylene,[12,27] and urethane[7] and as heat stabilizers for polymers based on acetals,[6] benzoxazoles,[26] epoxy-novolacs,[23,30,32] etc. Likewise, cyclolinear and cyclomatrix systems involving phosphazene-modified phenolics,[33–49] polyurethanes,[50–55] polyesters,[56–65] aramids,[66] and others,[67–74] including silicones and chitosan, have been reported as thermally stable polymer systems. Notable work in this direction is due to Kawamura et al. Syntheses of 1 based multifunctional epoxides and their networks with different types of amines and anhydrides have also been reported.[75–95]

A common feature of such references is their availability only in the form of patents and paucity of detailed information on structure-property correlations. It is probably owing to the formation of a cluster of products rather than a single one (due to the multifunctionality of the reactants) and difficulties in their isolation and characterization. However, because of their importance as proven

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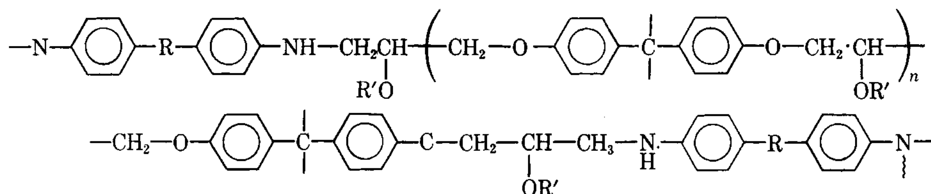
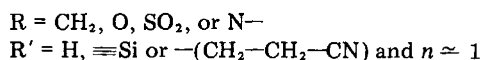
high-temperature performance materials, studies on phosphazene-modified epoxies are of current interest. Most of these deal with the synthesis of 1 based epoxides which could be crosslinked with amines and anhydrides. Since the epoxy resins are commercially available in various grades, the present study was aimed at the formation of multifunctional amine condensates of 1 and comparison of these condensates as crosslinkers for one grade of epoxy resin, in improving the thermal stability and adhesive heat resistance of the cyclomatrix systems formed.

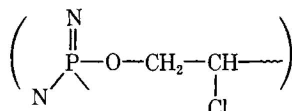
An idealized cyclomatrix polymer system is shown in Figure 1. For the current study, the portion —X—⊚—X— corresponds to the following structure:





R = CH_2, O, SO_2, or N—
R′ = H, ≡Si or —(CH_2—CH_2—CN) and $n \simeq 1$

Owing to practical difficulties in getting complete substitution of the chlorine atoms on 1 by the amines, the polymer network is not fully connected and contains unreacted "Cl" on some of the phosphorus atoms. The crosslink density of the networks could be further modified by the reactions of the —NH and the secondary —OH groups (generated *in situ*, as shown in Fig. 10) present in it and in terms of the "oxirane/active H" ratio of the reactants. It is also possible for the unreacted chlorines present in the network to undergo post-cure reactions with the oxirane groups, under heat activation, giving rise to



type of structures.[96]

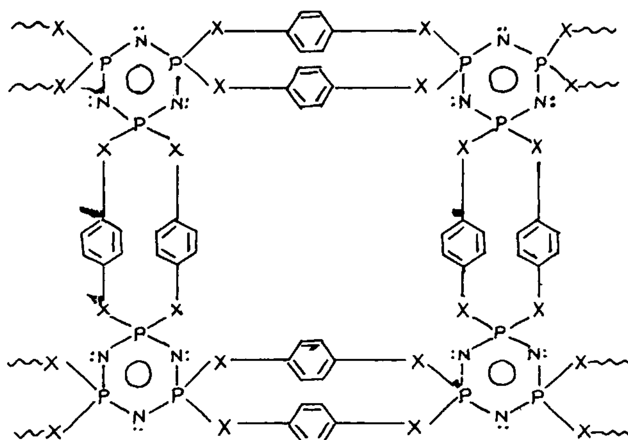


Fig. 1. Network structure of a cyclomatrix poly(organophosphazene).

EXPERIMENTAL

Materials

Hexachlorocyclotriphosphazene (1) was prepared using a standard process developed at the Polymers and special chemicals Division, VSSC. A freshly recrystallized material (from hexane), mp 113–114°C, was used in all the experiments. Reagent-grade tetrahydrofuran and triethylamine were predried over KOH pellets, distilled, and stored over sodium. 4,4′-Diamino diphenyl methane (2), other diaramines, tetraethoxy silane and acrylonitrile were of LR grade and used as received. The epoxy resin was a diglycidyl ether of bisphenol-A (epoxy equivalent = 190 g), supplied by M/s Ciba Geigy. It was dried under vacuum at 120°C, before use.

Apparatus

A Perkin-Elmer Model-283 IR Spectrometer was used to record the IR spectra of the condensates cast as thin films on NaCl plate from their solutions in THF. TLC of the condensates were studied using silica–gel-coated glass TLC plates. ^{31}P NMR {H} spectra were recorded on a JEOL-FX 90Q Spectrometer operating at 36.23 MHz in FT mode with a sweep width of 2500 Hz. TGA traces were recorded by a Stanton-Redcroft TR-01 Model Thermal Analyzer while DSC thermograms were recorded using a DuPont thermal analyzer model 990. Lap-shear strength values were evaluated by a Hounsfield-W Model Tensiometer, at a pulling rate of 3.18 $mm \cdot min^{-1}$.

Synthesis of Condensates Based on 1 and 2

Four types of condensates, viz., 4, 5, 6, and 7 were prepared using 2/1 molar ratio of 2, 3, 4, and 6, respectively, as 10 $g \cdot dL^{-1}$ solutions in THF, in presence of a 5.0% molar excess of triethylamine (HCl acceptor). 25 mmol of 1 were used in all the experiments. The reaction was carried out at 30°C by mixing solutions of 1 and 2 in THF and adding triethylamine (there was an initial rise in temperature to 55°C; the system was cooled down to 30°C, using ice water). The rate of formation of triethylamine hydrochloride, which corresponds to the % of chlorines reacted in the formation of these condensates (as shown in Fig. 2) could be used to calculate the overall degree of substitution (DS). The curves indicate that under the reaction conditions, it is difficult to get DS > 3.8. Use of the excess of 2 or triethylamine was not helpful in increasing the value of DS. Refluxing conditions led to the formation of THF-insoluble films. The condensates were stored as their solutions in THF after filtering out the triethylamine hydrochloride since evaporation of the solvent again favored formation of THF insolubles, especially when DS was 3 and below. The insolubles are most likely the cyclo linear and ionic structures as shown in Figure 3.

Synthesis of Condensates Based on 1 and Other Diaramines

Condensates similar to 6 were prepared with 1 and benzidine, 1 and 4,4′-diaminodiphenylether (ODA) and 1 and 4,4′-diaminodiphenylsulfone (SDA). While the reaction conditions were similar (RT) in the case of benzidine and ODA, lower solubility of SDA in THF required refluxing conditions (15 h).

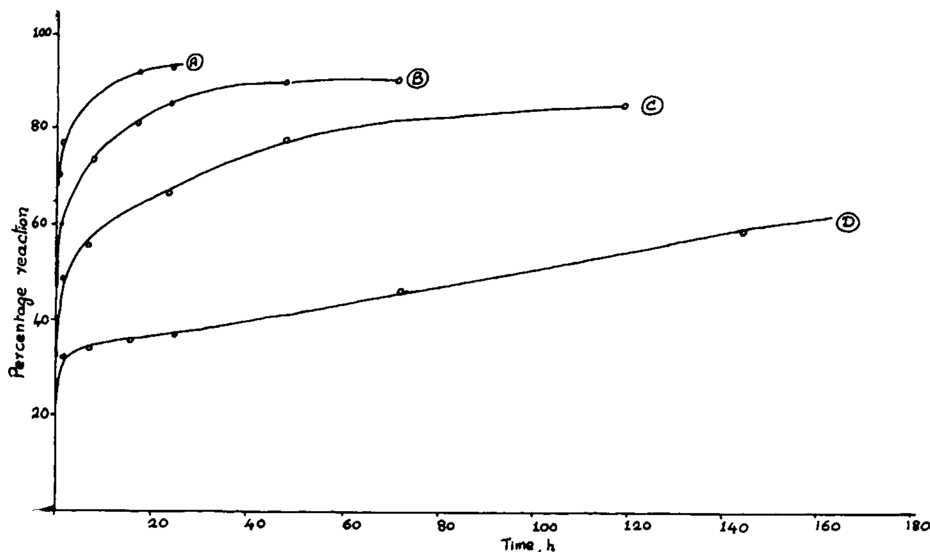


Fig. 2. Percentage reaction of the chlorines of 1 with MDA as a function of time (ex. wt of the triethylamine hydrochloride)—reaction temp 30°C, molar ratio of MDA/1: 2.0 (A), 3.0 (B), 4.0 (C), 6.0 (D).

Overall degree of substitution of the chlorines was 3.2 (benzidine), 2.9 (SDA), and 3.7 (ODA). The condensates were stored in solution in THF.

Characterization of the Condensates 4–7

In the formation of the above condensates from 1 and 2, the weight of triethylamine hydrochloride indicated the overall DS, but lent no information regarding their composition. Since results of elemental analysis were equally ambiguous (they were not different for the condensates and spuriously formed cyclo linear products), TLC, IR, and ^{31}P NMR techniques were used for characterizing the condensates.

(i) IR spectra (neat) of the condensates were similar and showed the following absorption peaks:

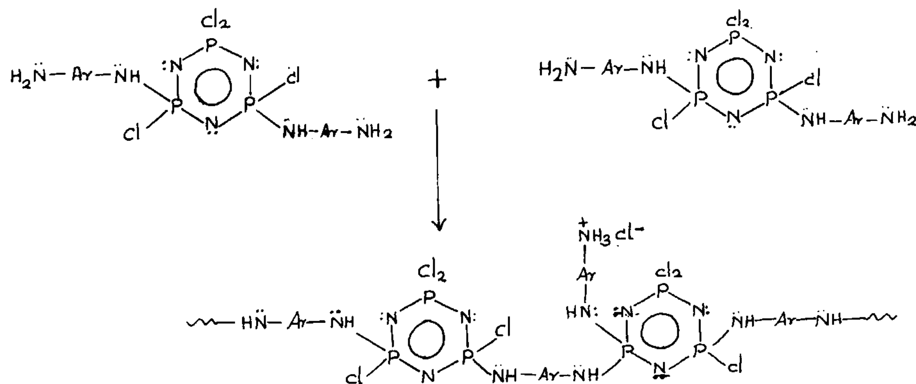
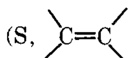


Fig. 3. Spurious structure, insoluble in the reaction medium, formed during the storage of the condensates of 1 with the diaramines.

IR (*neat*) $(cm)^{-1}$ 3360 and 3320 (m, —NH2 and —NH), 3020 and 2920 (s, —CH/Str), 1620, 1520, and 1460 (S, 

aromatic), 1440 (m, —CH_2 scissoring), 1270 (m, H—N—C/Str), 1180 (s, PNP asym/Str), 950 (s, PNC sym/str), 815 (s, 1,4-substitution), 765 (s, PNP sym/Str). The PNP/Str peaks were well resolved for 6 and 7 while they appeared as broad bands for 4 and 5.

(ii) TLC (silica gel; toluene/dioxane/ethyl acetate: 6/5/4, 30°C) of the condensates, when developed with iodine vapor, showed the presence of unreacted 2 in all cases. With respect to the spot corresponding to 2, R_f values of other spots and probable structures causing them were the following:

R_f value	Nature of the spot	Shown by condensates	Probable contribution from
0.7—0.71	Weak	7, 6, 5	Hexakis substitution
0.58	Strong	7, 6, 5	Tetrakis substitution
0.35	Weak	7, 6	Tris substitution
0.17	Strong	5, 4	Bis substitution
0.06—0.09	Strong	7, 6, 5	Soluble cyclo linear products

4 could be eluted up completely and the spot from this with R_f = 0.17 could be resolved further into three spots of equal intensity with R_f values of 0.21, 0.176, and 0.135. They seem to indicate mixed mode of substitution by geminal, non-geminal-*cis* and non-geminal-*trans* in its composition.

(iii) PMR spectra of the condensates in ($^2H_6$ DMSO) were not informative since the peaks due to —NH and —NH_2 were indistinguishable from each other, and there was interference from unreacted 2. On the other hand, ^{31}P NMR {H} spectra (THF/$2H_6$ DMSO, 20°C) recorded using 10 mm diam tubes and 500 scans in FT mode, shown in Figures 4–7 were useful in indicating the complexity of these systems when DS $\leq$ 3.0 and in assigning peaks helpful in calculating the

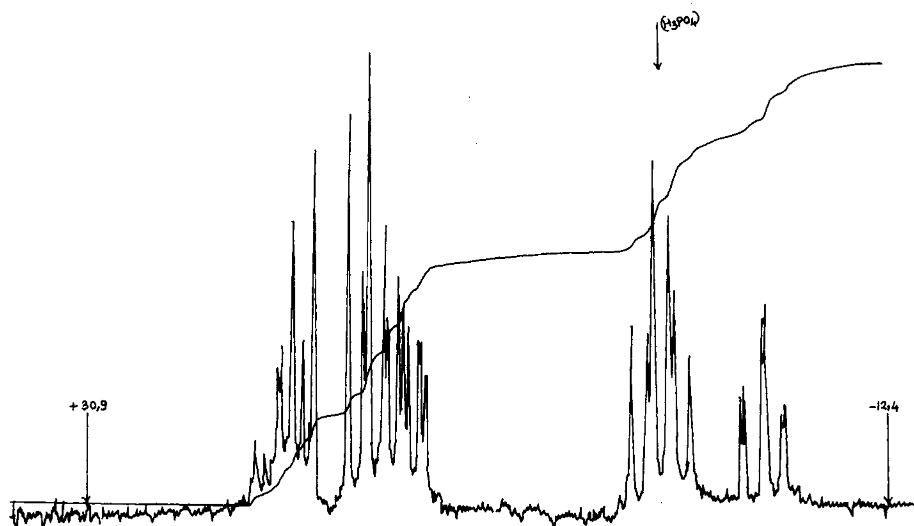


Fig. 4. ^{31}P NMR (THF/$^2H_6$ DMSO; 25°C) of 3.

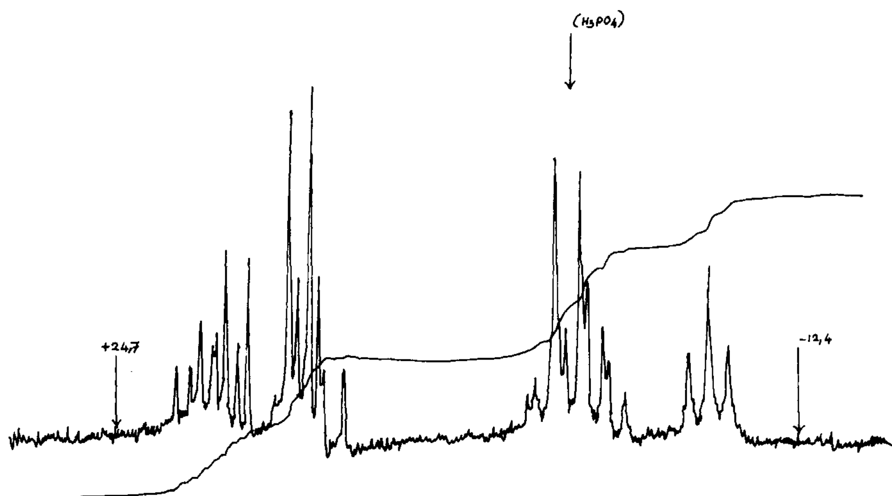


Fig. 5. ^{31}P NMR (THF/$^{2}H_6$ DMSO; 25°C) of 4.

active "H" functionality of the condensates (excluding that contributed by the presence of unreacted 2).

Geminal mode of substitution of "Cl" by aniline in 1 has been recorded in the literature.[97–101] 2 may be expected to behave like aniline in this regard. However, the spectra of 4 and 5 seem to indicate a mixed mode of substitution. Thus, in the case of 4 geminal substitution would be indicated by a doublet (D) due to PCl_2 and a triplet (T) due to PR_2 (R = HN—◎—CH_2—◎—NH_2), the T occurring at a higher (more negative) field and a T:D ratio of 2.0. Nongeminal substitution by *trans* mode would have caused a T(PCl_2) and a doublet of doublet (DD) of PClR while nongeminal *cis* mode would have shown a T(PCl_2) and D(PClR). The actual spectrum is, however, more complicated and suggests

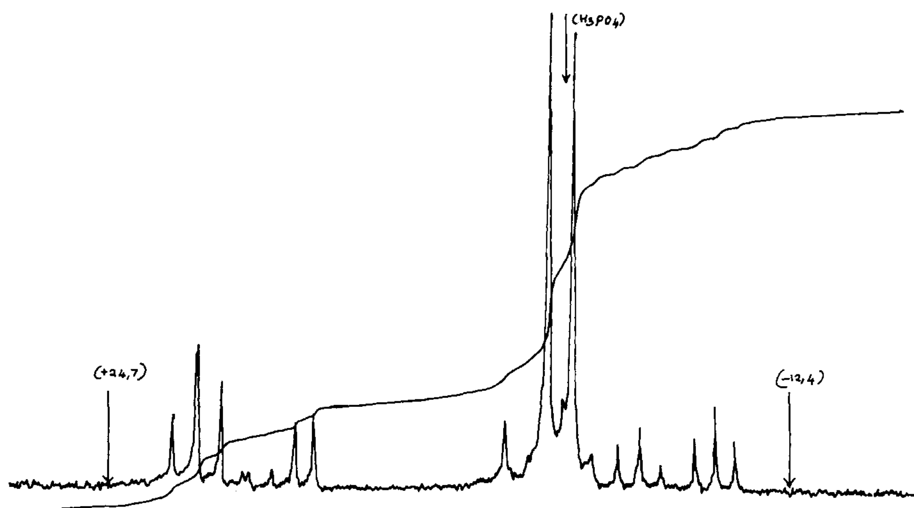


Fig. 6. ^{31}P NMR (THF/$^{2}H_6$ DMSO; 25°C) of 5.

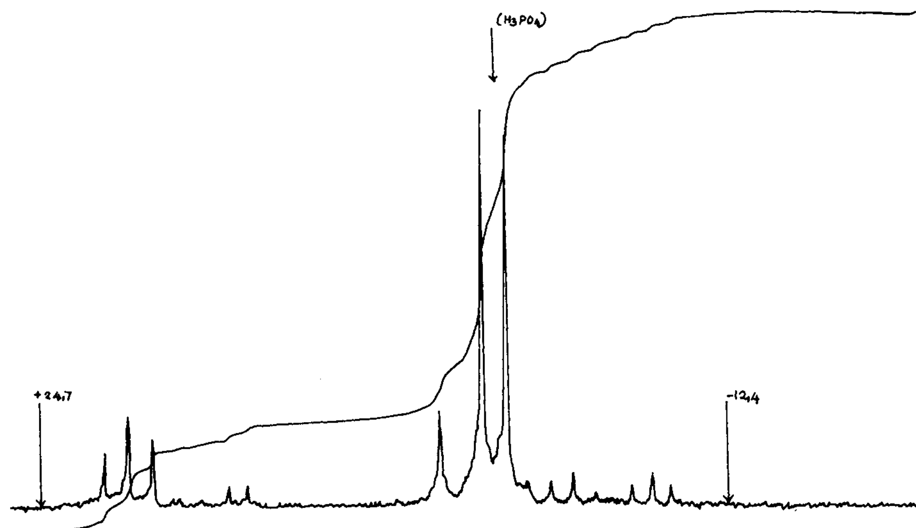
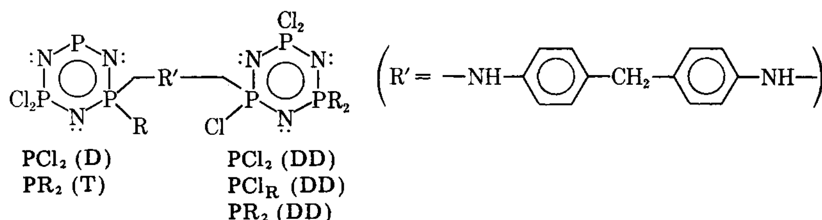


Fig. 7. ^{31}P NMR (THF/$^2H_6$ DMSO; 25°C) of 6.

mixed mode of substitution. The presence of extra DD(PClR) and T(PR2) could have been caused by soluble cyclolinear structures like



In a similar way, the spectrum of 5 suggests the presence of a mixed mode of substitution and a probable makeup of 4 and 6 in its composition. 6 and 7 exhibited relatively simpler spectra. Assigning the singlet (S) at 3.08 ppm to "PR_2" from the hexakis-substituted product and the T and D at 19.2 ppm and 0.12 ppm, respectively, to the "PCl_2" and "PR_2" from tetrakis substitution (geminal), the spectra indicate that both 6 and 7 are similar in composition and contain, predominantly, the geminally substituted $N_3P_3Cl_2(MD)_4$ (where MD represents the once-reacted MDA, —NH—Ar—NH_2). Minor peaks due to lower degrees of substitution and soluble cyclo linear structures are present in lower concentration in 7. The major peaks also help in calculating the ratio X of $N_3P_3Cl_2(MD)_4/N_3P_3(MD)_6$ and the overall DS. Thus, comparing the S(PR_2) of $N_3P_3(MD)_6$ with the T(PCl_2) of $N_3P_3Cl_2(MD)_4$, $X = 6.0$ in 6 and 9.0 in 7. It could also be shown that, in 6, the two major structures contribute to 64% of the total DS while, in 7, it becomes 80%. Thus, assuming a DS of 3.0 for the presence of products with lower degrees of substitution, the overall DS of 6 becomes 3.80 while that of 7 works out to 4.03. These values are in good agreement with those given by the weight of triethylamine hydrochloride. (It should, however, be remembered that 7 contains larger amounts of unreacted 2). D(PR_2) from these condensates was not used for comparison since it contains appreciable contribution from the "PR_2" absorption of condensates with DS ≤ 3. The positions, multiplicities, and $^2J_{PNP}$ coupling constants of the peaks are shown in Table I.

TABLE I
Details of the ^{31}P NMR Spectra of 1 + 2 Condensates

Condensate No.	No. of multiplets	$\delta_{=PCl_2}$ (ppm)	$\delta_{=PClR}$ (ppm)	$\delta_{=PR2}$ (ppm)	$^2J_{PNP}$/Hz
3	1 DD	20.50	—	—	48
	1 D	19.20[a]	—	—	48
	1 DD	—	13.70	—	45
	1 DD	—	14.25[a]	—	45
	1 D	—	16.20[a]	—	45
	4 T	—	—	0.29[a]	
				−0.55[a]	45
				−5.70[a]	
4	1 D	20.80	—	—	52
	1 D	18.20[a]	—	—	50
	1 DD	19.30	—	—	48
	3 D's	—	14.75[a]	—	45
		—	14.25	—	48
		—	12.90	—	45
	2 D's	—	—	0.25[a]	52
		—	—	−2.30	48
	2 T's	—	—	−0.87	48
		—	—	−7.40[a]	45
5 and 6	1 T	19.95[a]	—	—	52
	1 D	—	14.00	—	45
	1 S	—	—	3.08[a]	—
	1 D	—	—	0.12[a]	52
	2 T's	—	—	−4.10	48
				−8.30	45

[a] Major peaks.

The J values are in good agreement with those reported by Keat[103] and those calculable according to Finer.[104]

(iv) Gross thermal stability of the condensates 4–7 was checked by TGA. Results shown in Figure 8 indicate good thermo-oxidative stability up to 250°C, a plateau region with 65% char between 350°C and 500°C and a residual char content of 25% above 700°C in all cases. DSC thermograms of the condensates (in N_2, heating rate, $10°C{\cdot}min^{-1}$) did not show any major physical transitions up to 300°C.

Preparation and Application of Adhesives Based on 3 and Condensates

THF solutions of the condensates (containing unreacted 2 in varying amounts) were used after determining the concentration ($g{\cdot}dL^{-1}$). A known weight of condensate in THF was first concentrated to 50% of its original volume by warming to 40°C and applying vacuum. (This helps in driving off excess triethylamine which may otherwise catalyze homopolymerization of 3.)[102] It was then mixed with calculated amounts of 3, tetraethoxy silane, and/or acrylonitrile. The resulting solution was warmed to 50°C and degassed to give a clear viscous liquid. Bonding surfaces of the adherends based on B51-SWP aluminum, whose dimensions are shown in Figure 9 were prepared by grit blast, degreasing with trichloroethylene and chromic acid etch.[97] They were dried in an incubator at

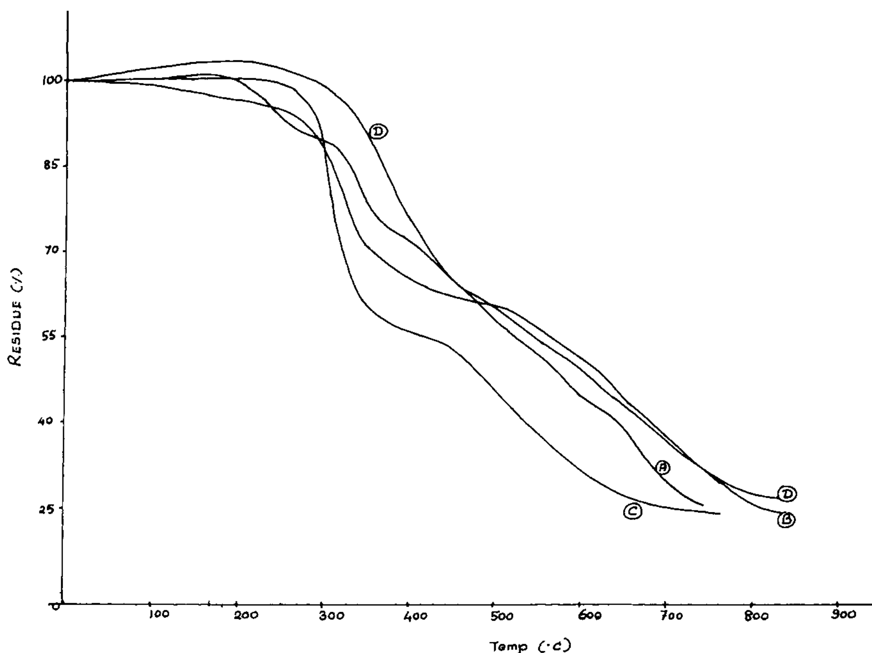


Fig. 8. TGA traces of the 1 + 2 condensates: (A) 4; (B) 5; (C) 6; (D) 7; medium-static air, heating rates 4°C·min^{-1}.

60°C. The warm, unprimed surfaces of the specimens were smeared with the adhesive and kept pressed against each other, using teflon tape, at room temperature for 48 h (to ensure gelation) followed by oven cure at 120°C for 15 h. Glue line thickness (calculated from the weight of the adhesive, its specific gravity, and bonded area) was controlled to be in the range of 0.15–0.25 mm. The bonded specimens were tested without "conditioning." In all experiments, a portion of the adhesive polymer was cast and cured in bulk in the same manner, for getting analytical samples.

Adhesion Studies

It is of interest to note that amine–epoxy reactions generally proceed without side reactions[105] and the secondary —OH groups liberated in these reactions (Fig. 10) do not react with residual epoxy groups under mild conditions.[106–108] However, they may catalyze the amine–epoxy reactions by forming ternary in-

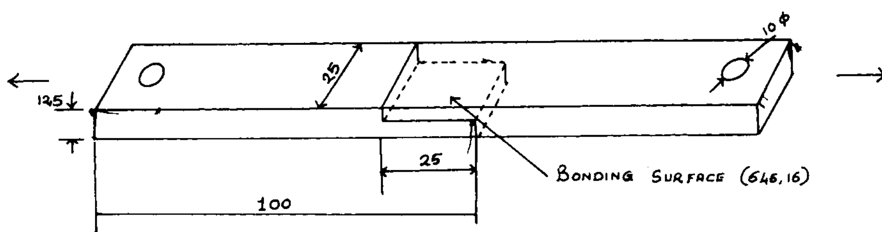


Fig. 9. Dimensions of the lap-shear specimen.

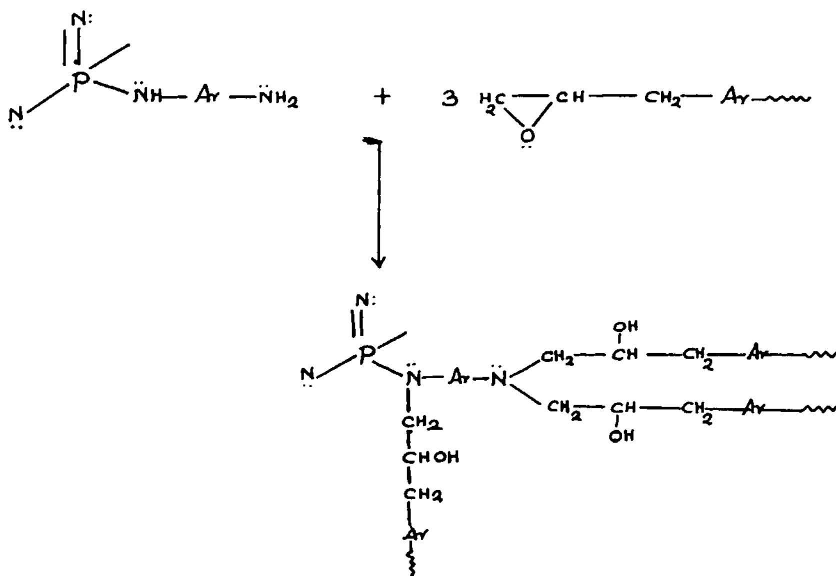


Fig. 10. Generation of secondary—OH groups in the amine–epoxy reaction.

termediate complexes.[109] The effect of some formulation variables involving such reactions on the adhesive heat resistance and thermal stability of the polymer network is given below. An average of eight values (standard deviation 1.20 at RT and 0.90 at 275°C) was taken in plotting the results.

Oxirane/Active Hydrogen Ratio (R′)

The crosslink density of the cyclomatrix network was altered by varying the R′ between 0.80 and 1.50, thus covering both epoxy-deficient and epoxy-excess systems. The number of active hydrogens were calculated based on the overall DS of the chlorine atoms in the condensates (ex. triethylamine hydrochloride). $N_3P_3Cl_{(6-n)}(MD)_n$ and the amount of unreacted 2. Lap-shear strength of adhesives based on the condensates 4–7 at 30°C and 275°C (after soaking for 7 min) are shown in Figures 11(a) and (b). The results indicate better performance of adhesives based on 6 and 7 (with DS > 3) and lower sensitivity to change in R′ in the case of 6, where the unreacted 2 is present in lower concentration. Off-stoichiometric compositions exhibited better gross thermal stability (350–380°C) and higher char contents (30%) in either case. However, there was a distinct difference between the two series in that the maximum values were associated with R = 1.50 in the case of 7 and R = 0.85 in the case of 6. TGA traces shown in Figures 12 and 13 also indicate that the overall thermal decomposition occurs in two major steps, with a plateau region of stability in between 400°C and 500°C containing 60% residue.

Transesterification of Secondary —OH Groups

Tetraethoxy silane, 8, was reacted with the secondary —OH group liberated in the amine–epoxy reaction, in part or completely, under heat activation in the adhesives prepared with the condensates at a constant R′ value of 1.15 (Fig. 14).

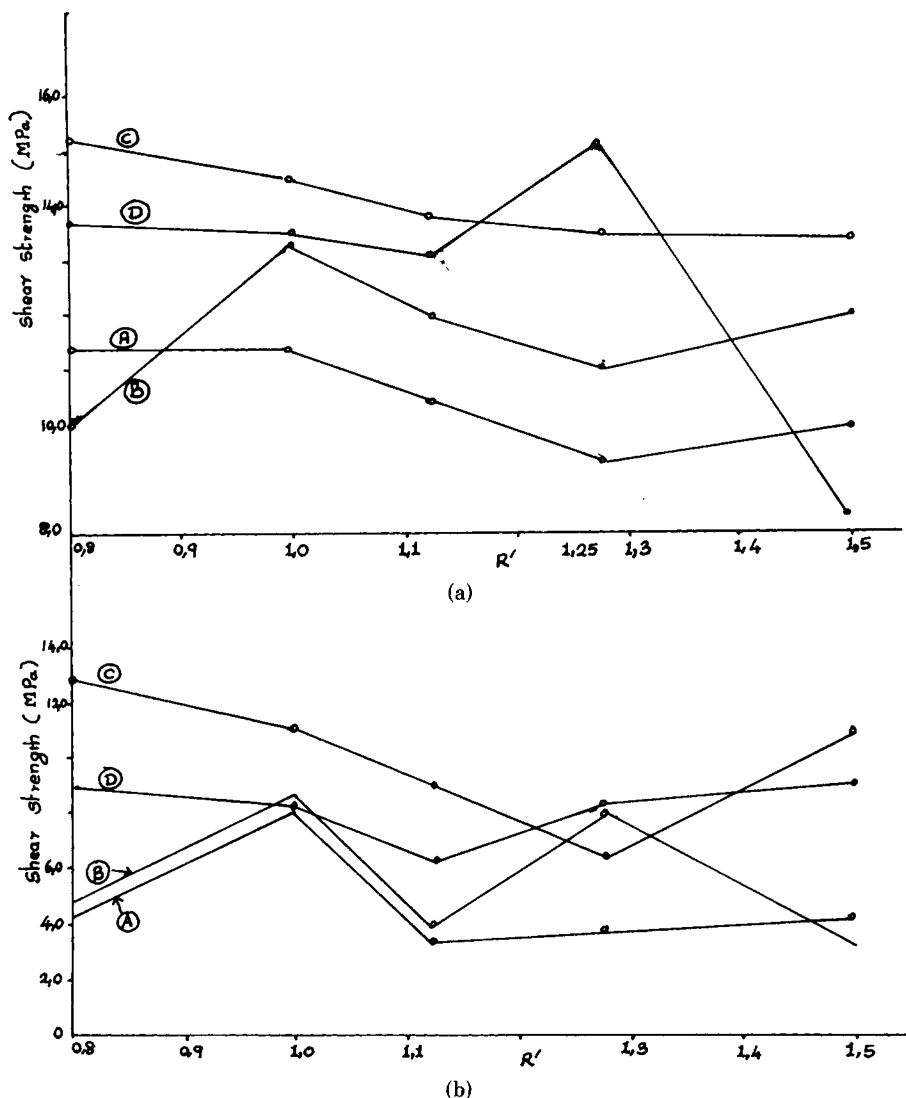


Fig. 11. Effect of R′ on the lap-shear strength of the adhesives based on 3 and the condensates 4–7: (a) values at 30°C and (b) values at 275°C with a soak time of 7 min; adhesives based on: (A) 4; (B) 5; (C) 6; (D) 7.

Adhesion strength of the specimens, cured under similar conditions, was evaluated as a function of the percentage of —OH groups reacted as above, (Fig. 15) both at 30°C and at 275°C (after soaking for 7 min). It was interesting to observe that while at 30°C, shear strength of the adhesives based on these condensates did not differ much with this variable (except in the case of 7 at 100% reaction of the OH groups), the difference was much pronounced at high temperatures. Thus, transesterification was helpful in increasing the adhesion strength when the degree of substitution of the 1 + 2 condensate was ≤3.0 (probably owing to the ease of availability of the —OH groups: Spurious reactions involving P—Cl + Si—OEt are not likely to occur since, even under refluxing conditions, 1 was not reacting with 8) whereas it was drastically decreasing the adhesion strength in the case of 6 (wherein the reaction is probably not occurring at all under the

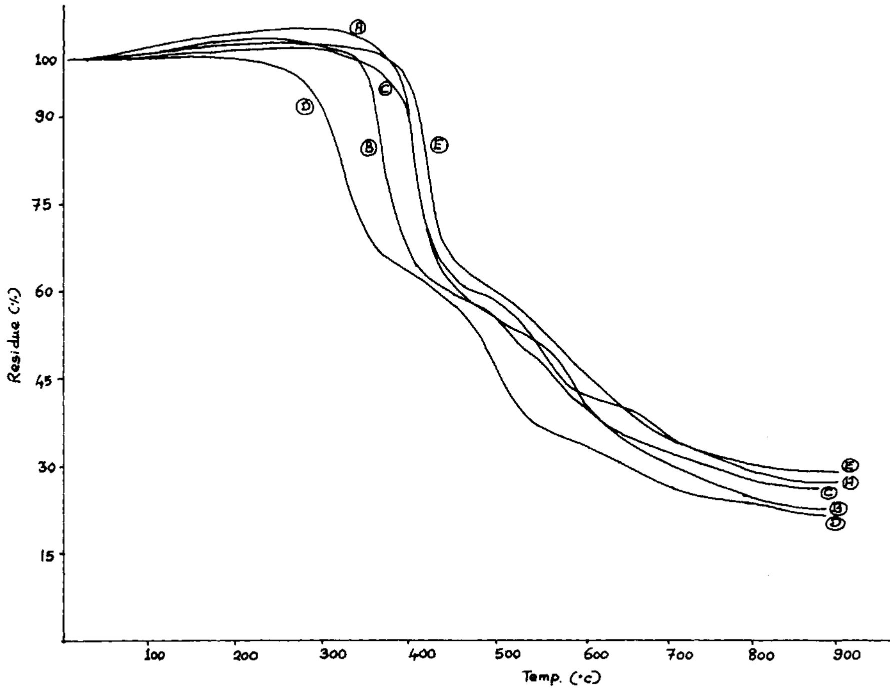


Fig. 12. Effect of R′ on the thermal stability of adhesives based on 3 and 6. TGA in static air at a heating rate of 4°C·min^{-1}. Values of R′: (A) 1.50; (B) 1.25; (C) 1.15; (D) 1.00; (E) 0.85.

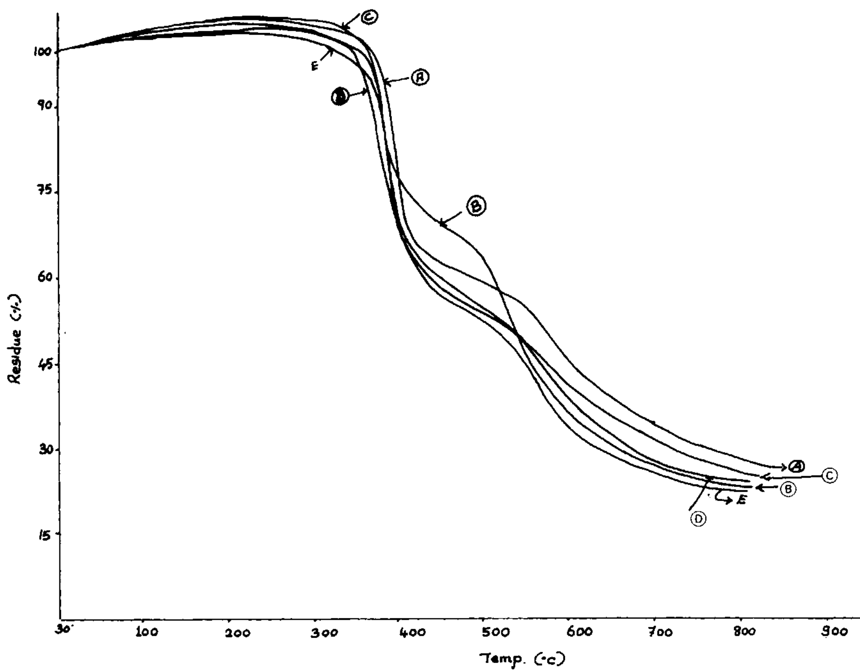


Fig. 13. Effect of R′ on the thermal stability of adhesives based on 3 and 7. TGA in static air at a heating rate of 4°C·min^{-1}. Values of R′:(A) 1.50; (B) 1.25; (C) 1.15; (D) 1.00; (E) 0.85.

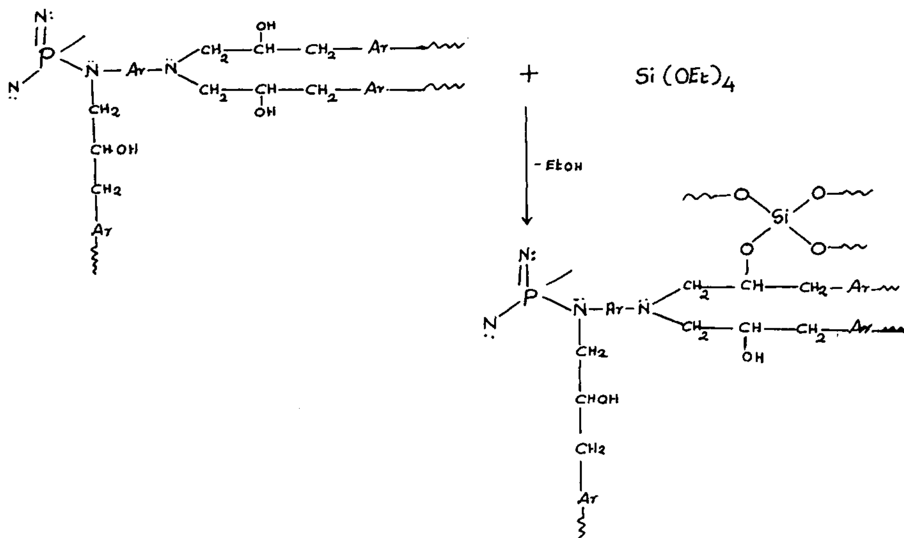


Fig. 14. Reaction of the secondary—OH group with $Si(OC_2H_5)_4$-transesterification.

curing conditions and the unreacted 8 is modifying the adherend surface). It was also interesting to note that the adhesive heat resistance of 7 based adhesives were better than those from 6 when the % of —OH groups reacted is 66% and above. It is likely to be due to the reaction of —OH groups generated from unreacted 2 present in this condensate in larger amounts. Gross thermal stability of adhesives from 6 and 7 (shown in Figs. 16 and 17) indicated marginally better performance of 7-based systems.

Cyanoethylation of —OH Groups

In a related study, a mixture of 8 and acryonitrile was used to modify the —OH groups in adhesive formulations based on 6, at an R′ value of 1.15. Since the conversion of —OH groups into β-cyanoethyl groups is amenable to catalysis by tertiary bases, the tertiary nitrogens formed in the amine-epoxy reaction may be expected to favor this reaction. (It is also possible for some of the $—NH_2$ groups to undergo this change. This was possibly avoided by first carrying out the amine–epoxy reaction and then adding acrylonitrile to the viscous liquid.) The pendant nitrile groups produced in such reactions was expected to improve adhesion strength. Results shown in Figure 18, however, indicate that, compared to a 0.0% and 100.0% modification of the OH groups by acrylonitrile, combined use of both 8 and acrylonitrile was better in improving the adhesion strength at 30°C (RT). High temperature adhesion was, however, not influenced by this modification, and, in the absence of 8, acrylonitrile was not effective in maintaining a high level of adhesion.

Soaking Temperature and Soak Time

Adhesives based on 6 and 7, prepared with R′ = 0.85, were evaluated for their heat resistance by soaking the specimens at different temperatures for constant

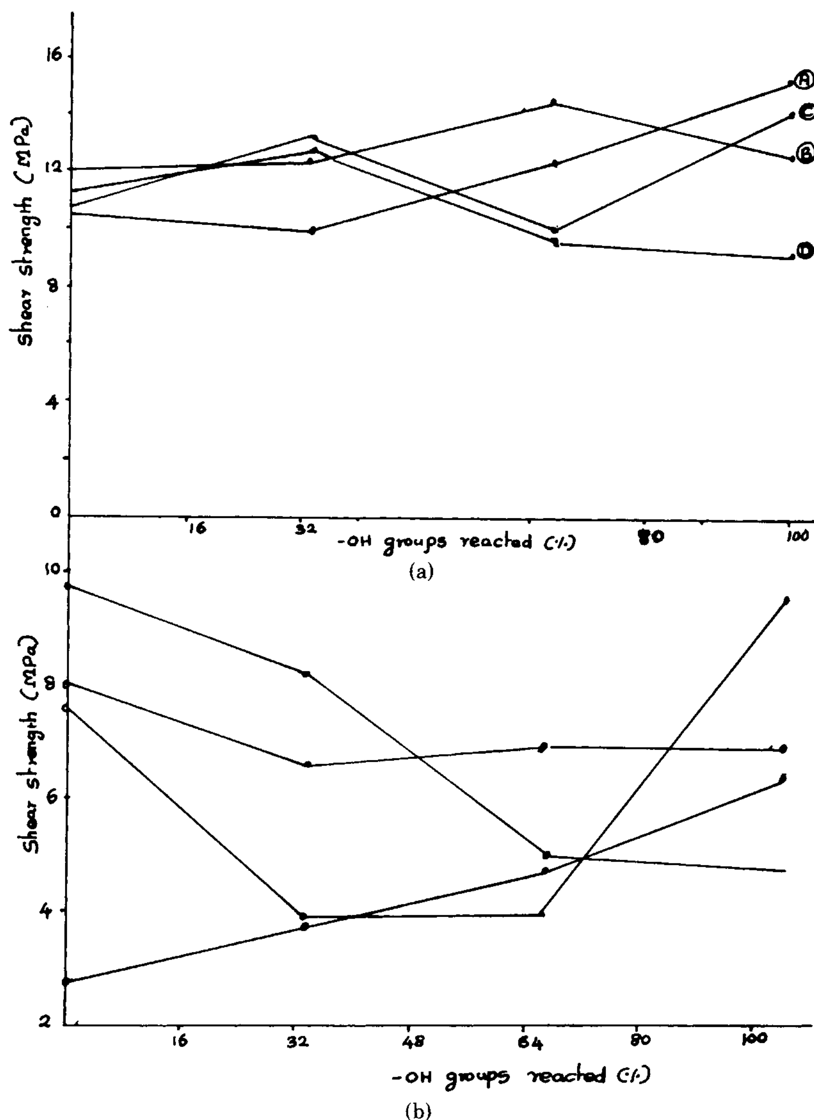


Fig. 15. Variation of the lap-shear-strength as a function of the % of —OH groups (produced in the reaction of 3 with the condensates 4–7) modified by transesterification with $Si(OC_2H_5)_4$: (a) values at 30°C; (b) values at 275°C with a soak time of 7 min; adhesives based on: (A) 4; (B) 5; (C) 6; (D) 7.

duration of time and by exposing the same to a high temperature environment for different time intervals followed by testing them at these temperatures. Results of this study, shown in Figures 19 and 20, indicated better performance of the 6-based systems and faster degradation of the same at 300°C.

Structure of the Amine Component in the Condensates

Shear strength of adhesives based on ODA, benzidine and SDA were compared with that of 2. The adhesives were prepared with R′ = 0.85 and were evaluated

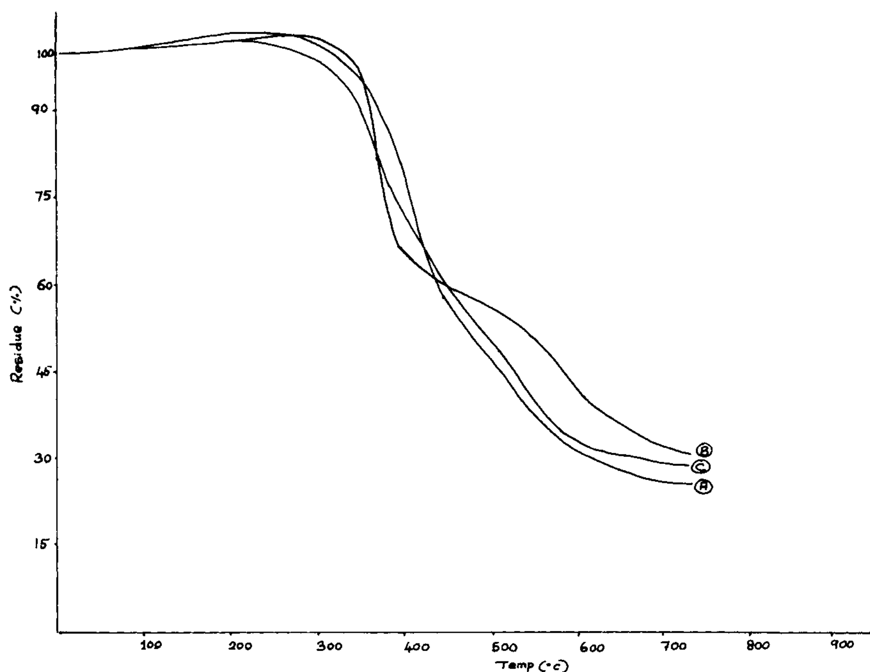


Fig. 16. Effect of siloxy modification of the —OH groups on the thermal stability of adhesives based on 3 and 6. TGA in static air, heating rate $4°C{\cdot}min^{-1}$ percentage of —OH groups reacted: (A) 0%; (B) 33.3%; (C) 100%.

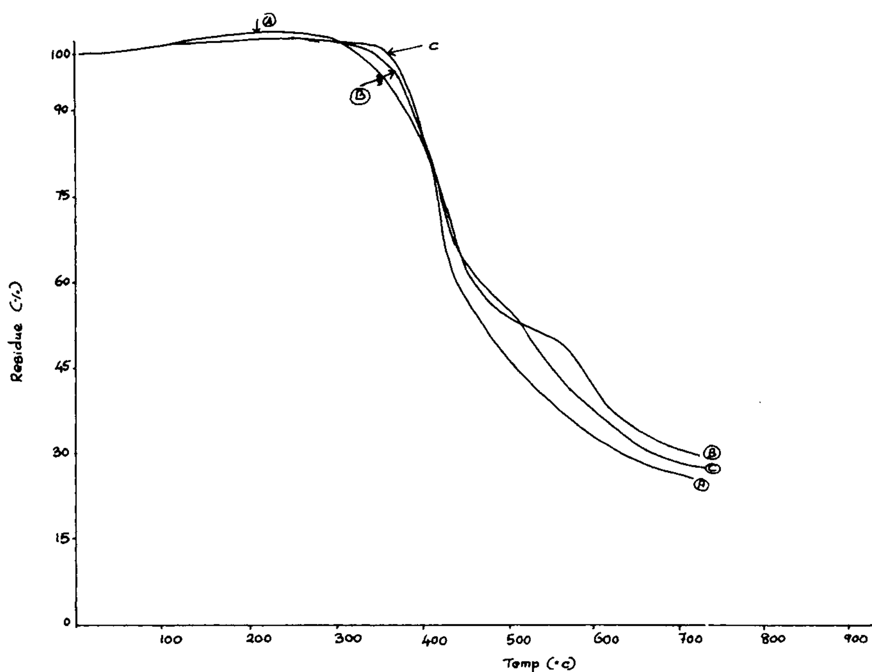


Fig. 17. Effect of siloxy modification of the —OH groups on the thermal stability of adhesives based on 3 and 7: TGA in static air, heating rate $4°C{\cdot}min^{-1}$, percentage of —OH groups reacted: (A) 0%; (B) 33.3%; (C) 100%.

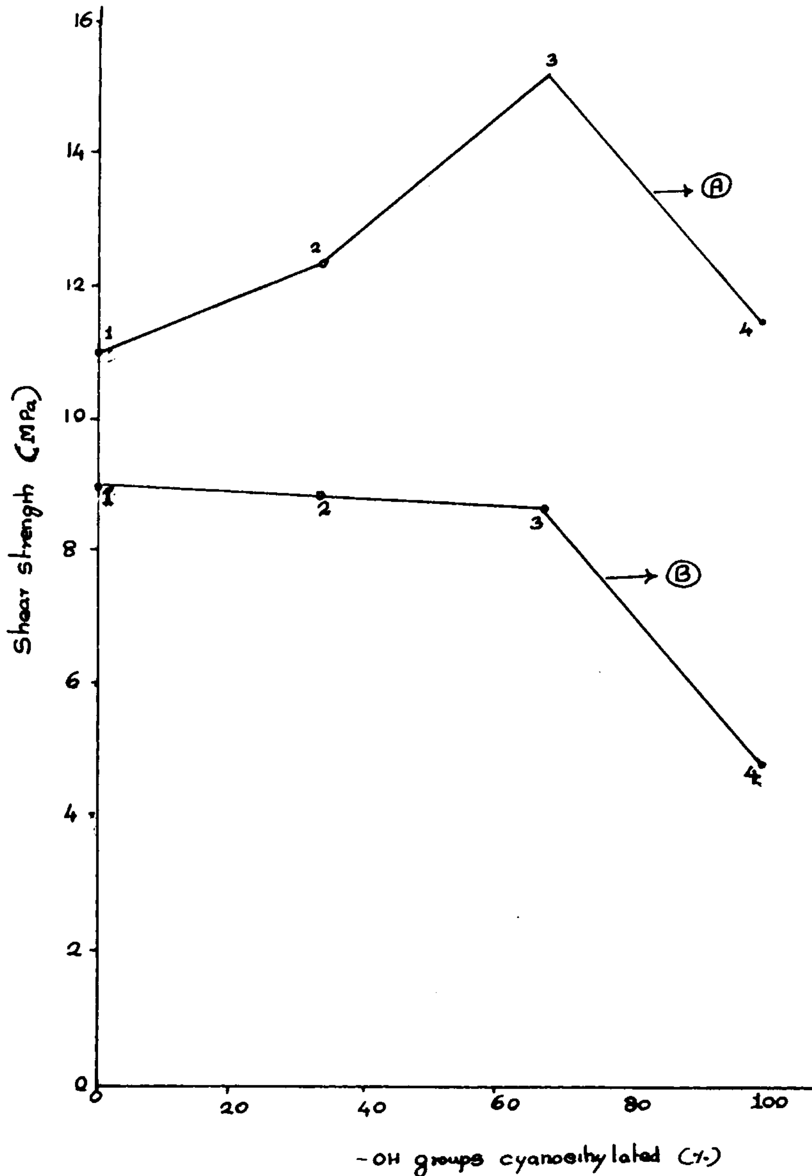
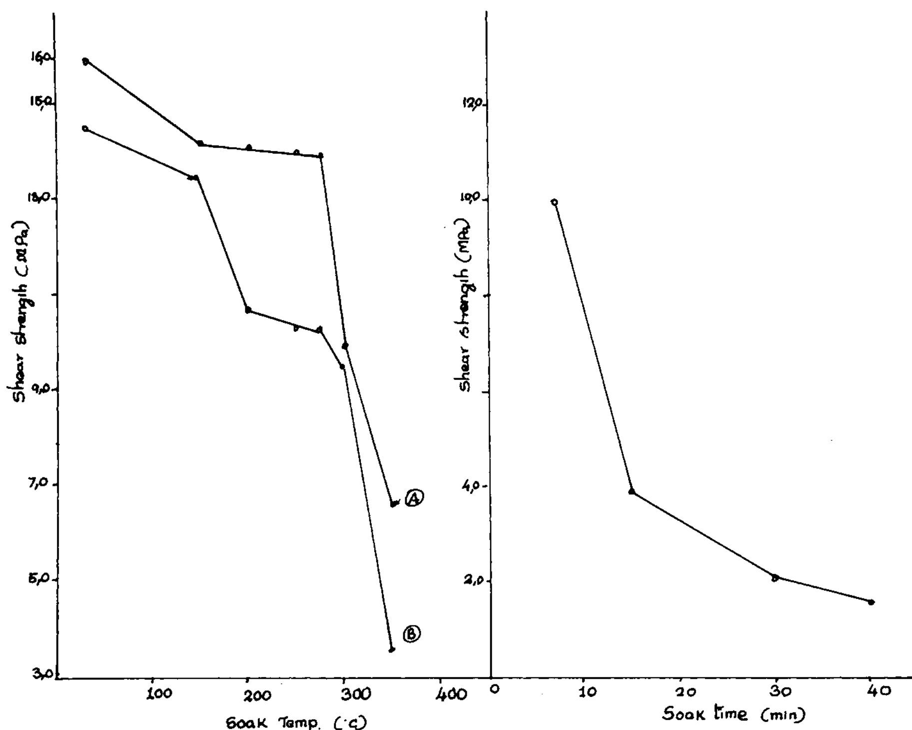


Fig. 18. Effect of siloxy modification and cyanoethylation of the —OH groups on the shear strength of adhesives based on 3 and 6. % ratio of unreacted: siloxy modified: cyanoethylated —OH groups: (1) 100:0:0; (2) 33.3:33.3:33.4; (3) 0:33.3:66.7; (4) 0:0:100. A: at 30°C; B: at 275°C.

for their heat resistance. The data, shown in Table II, indicate similar performance of the systems except in the case of SDA, which showed poor adhesion levels both at RT and at high temperatures. It may be attributed to lower degree of substitution and nonwetting characteristics contributed by the —sulfone groups. Gross thermal stability of the adhesives was good up to 320°C with maximum weight loss occuring between 350°C and 450°C. SDA-based adhesive exhibited a 43% residue at 700°C.



Figs. 19 and 20. (19, Left) Effect of soaking temperature on the shear strength of adhesives based on 3 and 6 (A) and 3 and 7 (B). R′ = 0.85; soak time = 7 min. (20, Right) Effect of soak time on the shear strength of adhesives based on 3 and 6. R′ = 0.85, soak temp 300°C.

Comparison of Data with Adhesives Containing No. 1

Adhesives were prepared based on 2 and 3 by varying R′ between 0.85 and 1.50 and one-third of the secondary —OH groups was modified by treating with 8. The systems were not gelling at RT and were cured first at 60°C for 24 h (to gel the system) and then at 120°C for 15 h. They were opaque in bulk compared to the transparent systems obtained with the condensates 4–7. This could be attributed to incompatibility of this adhesive system with 8 since similar adhesive compositions without 8 were transparent. Comparison of their shear strength at 30°C and 275°C (Fig. 21) indicated better performance of adhesives containing

TABLE II
Effect of the Amine Structure on the Adhesion Strength

Amine	DS of chlorines in the condensate with 1	Shear strength (MPa)	
		At 30°C	At 275°C[a]
2	3.48	15–16	10–11
SDA	2.95	3–3.5	0.7–0.8
ODA	3.70	18–19	12–12.5
BZD	3.20	13–14	6–6.5

[a] Soak time = 7 min.

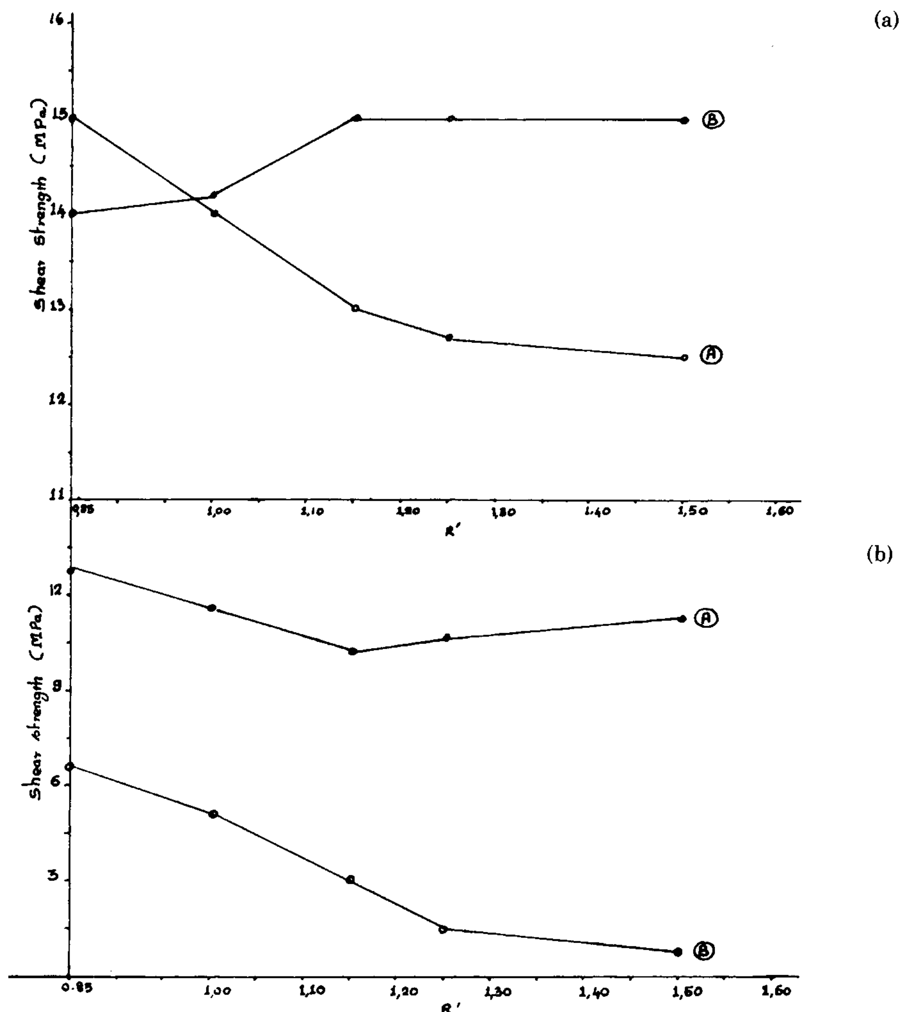


Fig. 21. Comparison of the adhesive heat resistance of the (a) phosphazene and (b) non-phosphazene–epoxy systems: (A) at 30°C; (B) at 275°C (soak time 7 min).

1 especially at $R' \geq 1$. Thermal stability of systems devoid of 1 were inferior and exhibited rapid decomposition above 350°C with practically no char content above 600°C.

CONCLUSION

Thermally stable polymer systems could be prepared based on 3 and multifunctional phosphazene–amine condensates. Adhesive heat resistance and thermophysical profile of these systems were good when the degree of substitution of the Chlorines in 1 by 2 was high and concentration of unreacted 2 was low in the condensates. Preparation of the condensates 4–7 was giving a mixture of products and DS could not be improved above 4.0. Condensates with DS $\leq$ 3.0 were prone to undergo spurious reactions forming THF insoluble films on

storage under ambient conditions. Substitution of the unreacted chlorines in these condensates with trifluoro ethoxy or phenoxy groups could be expected to improve their storability. However, this has not been studied. Likewise, the condensates 6 and 7 may be expected to perform better when freed from unreacted 2. Although modification of the secondary —OH groups was not effective in improving the thermophysical profile, it could help improve the high temperature ablation. Systems based on 1 were superior to the corresponding nonphosphazene systems, for their adhesive heat resistances especially in epoxy-rich compositions and were compatible with 8. Presence of a thermally stable, flexibilizing group (viz., —O—) in the diaramine, conferred better reactivity to its amino groups and higher levels of adhesion. The study is, however, of limited scope and data pertaining to durability of the adhesives under specific environments (other than thermal) will be useful to improve upon such systems.

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