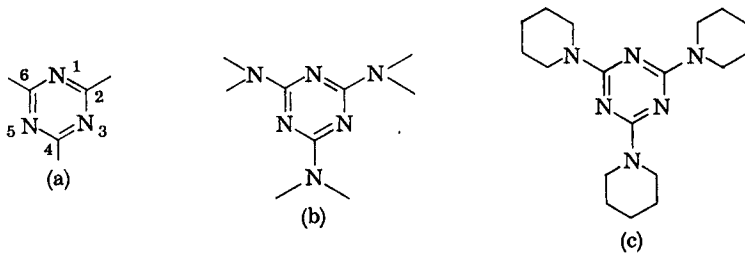
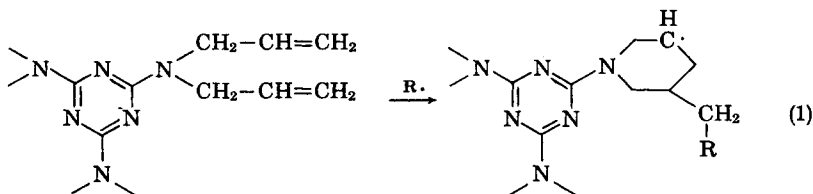


results in stable entities, such as 2,4,6-tripiperidino-*s*-triazine (c), the stability of which has been attributed¹ to steric restrictions of the pendent cyclic groups which prevent interaction of their alkyl hydrogens with the *s*-triazine ring.



It is known that free radical reaction involving two allyl groups bonded to one nitrogen atom can proceed by inter-intramolecular polymerization to yield piperidino-type rings. For example, linear homopolymers result² from polymerization of diallylamine in an acidic aqueous medium. Hence, it was considered that polymerization of molecules which contained the *s*-triazine nucleus linked to at least two such nitrogen atoms could lead to thermoset resins consisting of a mesh of *s*-triazine rings linked through piperidino rings as shown in eq. (1).



In addition to the expected stability of polyhexaallylmelamine, appreciable retention of mechanical properties was to be expected at elevated temperatures as a consequence of the high degree of crosslinking.

At least three factors were considered to contribute toward the anticipated electrical properties: (1) freedom from —NH— groups which occur in conventional melamine-formaldehyde resins, (2) low basicity of the completely alkylated melamine derivatives, and (3) the high density of crosslinking. Polymers from hexaallylmelamine might be expected to be similar at room temperature to the thermoplastic hydrocarbon polymers, such as polystyrene, with respect to dielectric properties. However, the thermoset nature of the allylmelamine resins would be responsible for appreciable retention of the dielectric properties at elevated temperatures.

The extent to which such expectations were realized will be apparent from the results and discussion which are presented.

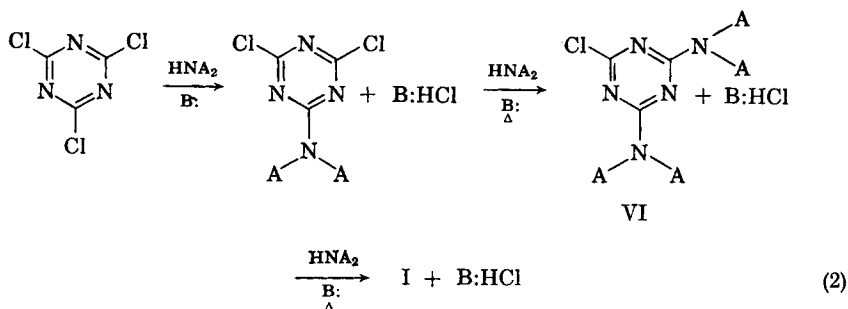
RESULTS AND DISCUSSION

Monomers

The following monomers were synthesized by the stepwise substitution reaction³ of the chlorine atoms of cyanuric chloride with secondary amine:

(I) 2,4,6-tris(diallylamino)-*s*-triazine (i.e., hexaallylmelamine); (II) 2,4-bis(diallylamino)-6-piperidino-*s*-triazine; (III) 2,4-bis(diallylamino)-6-di-*n*-propylamino-*s*-triazine; (IV) 2,4,6-tris(allyl-*n*-propylamino)-*s*-triazine; (V) 2-diallylamino-4,6-bis(di-*n*-propylamino)-*s*-triazine; (VI) 2,4-bis(diallylamino)-6-chloro-*s*-triazine; (VII) 2-chloro-4,6-bis(di-*n*-propylamino)-*s*-triazine.

Hexaallylmelamine monomer (I), for example, was synthesized by the reaction of cyanuric chloride with diallylamine in the presence of an acid acceptor. This is presented schematically in eq. (2), where A represents allyl and B: represents a base.



The intermediates can be isolated. The electrical properties of chloro-*s*-triazine derivatives differ significantly from those of the fully substituted melamine. For example, the dissipation factor at 25°C. and 60 cycles/sec. for hexaallylmelamine is less than 0.0001, compared with 0.46 for a sample of the intermediate 2,4-bis(diallylamino)-6-chloro-*s*-triazine (VI). The corresponding values of the dielectric constant are 2.62 and 12.7, respectively. For this reason great care was taken to ensure complete reaction in the preparation of fully substituted melamine monomers. This consideration was to be of particular importance in the preparation of polymers, the electrical properties of which were to be measured.

The method of synthesis and the analyses characterize the individual monomers. With one exception (VII), all are colorless, viscous liquids at room temperature, and while some (II, IV, V, VI) crystallize below room temperature, hexaallylmelamine and III form glasses at -78°C. The similar chemical structures and high molecular weights make differentiation difficult by boiling point (ca. 160°C. at 0.1 mm. Hg pressure), or by infrared or ultraviolet spectroscopy. The refractive indices change regularly with structure, so that the contribution to the refractive index of groups attached to the *s*-triazine ring increases in the order: dipropylamino- < allylpropylamino- < diallylamino- < chloro- = piperidino-. Three of the monomers (III, IV, V) could not be resolved from a mixture of equal parts of the monomers by vapor-phase chromatography (VPC) by using a 6-ft. silicone column at 240°C.

The properties and analytical data for the monomers are summarized in Tables I and II.

TABLE I
 Properties of Monomers

Monomer	M.W. (theoretical)	Melting point, °C.	n_D^{25}	VPC relative retention time ^a
I	366	glass at -78	1.5390	1.29
II	354	> -78 < R.T.	1.5501	1.92
III	370	glass at -78	1.5234	1.39
IV	372	<R.T.	1.5182	1.41
V	378	> -78 < R.T.	1.5102	1.41
VI	305.5	> -78 < R.T.	1.5500	0.78
VII	313.5	42-43	1.5147	0.86

^a Versus dibutyl sebacate = 1.00.

 TABLE II
 Monomers: Analytical Data

Monomer	Carbon, %		Hydrogen, %		Nitrogen, %		Chlorine, %	
	Found	Theory	Found	Theory	Found	Theory	Found	Theory
I	68.79	68.85	8.31	8.20	22.95	22.95	—	0
II	68.08	67.67	8.44	8.47	23.87	23.73	—	0
III	^a		^a		^a		—	
IV	67.85	67.71	9.53	9.74	22.94	22.56	—	0
V	67.44	67.33	10.14	10.22	22.21	22.44	—	0
VI	58.82	58.92	6.65	6.55	22.84	22.92	11.74	11.62
VII	57.24	57.39	8.72	8.99	22.26	22.32	11.24	11.30

^a Not determined.

Polymerization of Hexaallylmelamine

An investigation was made of the bulk polymerization of hexaallylmelamine with the use of a variety of free radical-producing initiators. Samples were degassed and sealed *in vacuo* before being heated, and temperatures were so chosen⁴ that the half-life of each initiator was approximately 10 hr. Di-*tert*-butyl peroxide and 2,5-dimethyl-2,5-di(*tert*-butylperoxy)-*n*-hexane (Lupersol #101 technical grade, Lucidol Division, Wallace and Tiernan, Inc., Buffalo, N. Y.) were found to be effective in producing hard, uncracked, and transparent colorless solid polymer by using 2-10% of initiator with the monomer at 130°C. for 24 hr. On the other hand, benzoyl peroxide, azobisisobutyronitrile, and cumene hydroperoxide were ineffective. Intense electron radiation at 0°C. and at -78°C., intense x-ray irradiation at 130°C., and thermal treatment of the monomer below 200°C. produced insignificant changes.

The polymerization of hexaallylmelamine in nitrogen at 130°C., with 2% 2,5-dimethyl-2,5-di(*tert*-butylperoxy)-*n*-hexane, was monitored by infrared spectroscopy and by a dynamic mechanical method, torsional braid analysis.^{5,6} Decreases in intensity of infrared bands at 3085, 1643,

997, and 918 cm.^{-1} were attributed to the polymerization process and formed the basis for an estimate of chemical conversion. The mechanical properties, assessed by torsional braid analysis, were those for a composite made up of the polymerizing material supported by a glass braid formed from six strands taken from 181-301 glass cloth (United Merchants Industrial Fabrics, Division of Davis Mills Corp., New York, N. Y.). This composite may well be considered to be an elementary part of glass fiber-resin composites (e.g., glass cloth- and glass filament-wound resin structures) in which a new thermosetting resin is likely to be evaluated.

The percentage chemical conversion, and changes in mechanical rigidity and mechanical damping, throughout the isothermal polymerization are presented graphically in Figure 1. Since the half-life of the initiator is

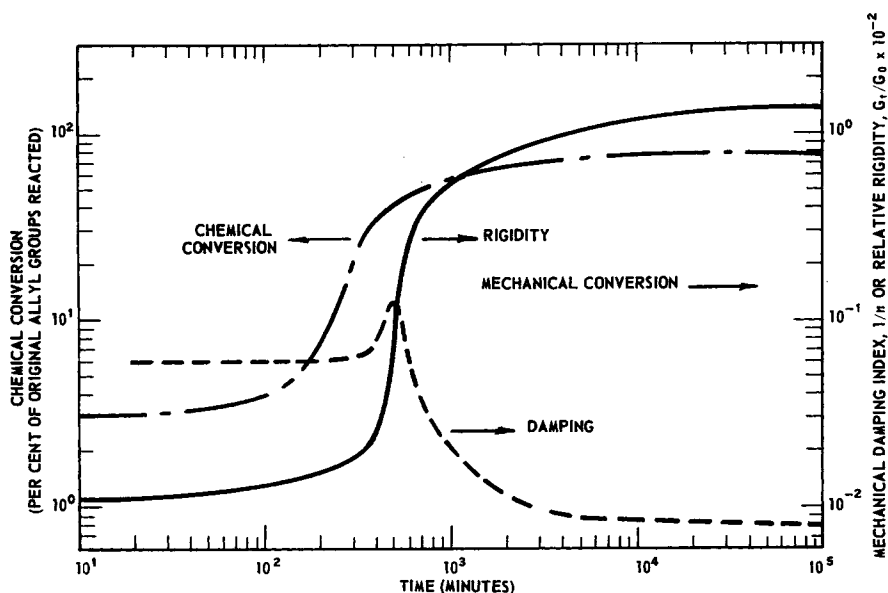


Fig. 1. Polymerization of hexaallylmelamine at 130°C.

probably less than 10 hr. at 130°C. and since thermal polymerization is slow at this temperature, it is not surprising that chemical conversion increases but slowly after several days. When the mechanical properties do level off there remains substantial (ca. 22%) residual unsaturation. Conversion could be increased without apparent degradation by heating at higher temperatures, and reaction was approximately complete (as indicated by infrared analysis) within 24 hr. at 300°C. Isothermal experiments demonstrated that hexaallylmelamine results in a glassy material at 130°C. (i.e., with low mechanical damping) only after a day of polymerization at 130°C. Therefore prolonged curing cycles, generally with 2% of 2,5-dimethyl-2,5-(*tert*-butylperoxy)-*n*-hexane, were used throughout the preliminary studies on allylmelamine polymerization. Exotherms would be

expected to attend the polymerization of bulk samples and would further the cure by thermal reaction.

Polyhexaallylmelamine

Unfilled castings of polyhexaallylmelamine are difficult to machine. The values for flexural strength (3500 psi at 23°C.) and flexural modulus (0.4×10^6 psi at 23°C.) are low, probably as the result of difficulties in preparing defect-free test samples, but mechanical properties are retained at elevated temperatures. For example, the deflection temperature under load is greater than 260°C. The material cracks under the pressure used in obtaining a value for the Barcol hardness, but by use of the Rockwell M scale of hardness a value of 120 was obtained without fracture of the speci-

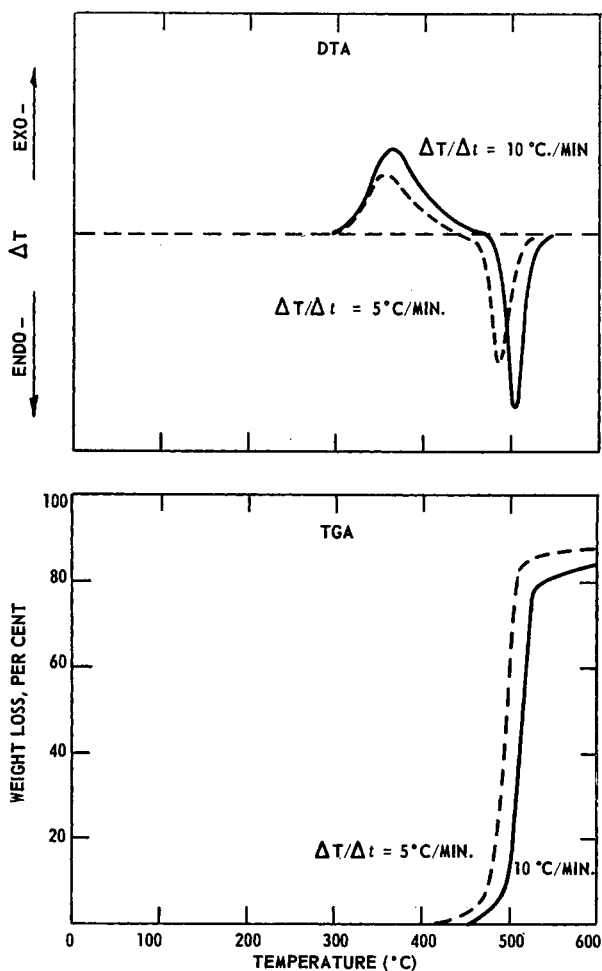


Fig. 2. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of polyhexaallylmelamine.

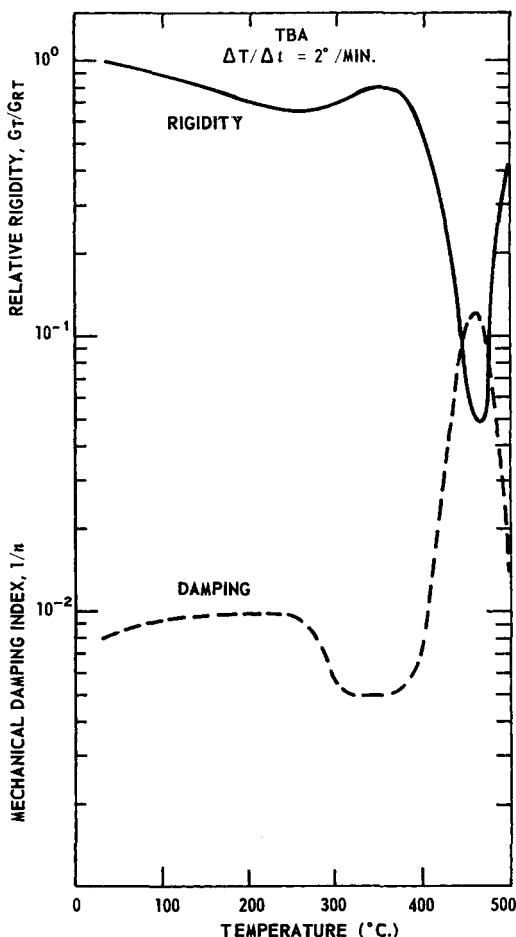


Fig. 3. Torsional braid analysis (TBA) of polyhexaallylmelamine.

men. High inherent internal stress was made apparent by examination with a polarizing microscope which revealed low level overall and more severe localized strain patterns. The coefficient of linear expansion of the polymer from -30 to $+30^\circ\text{C.}$ was $4.52 \times 10^{-5}^\circ\text{C.}^{-1}$.

A preliminary assessment of the thermal stability of polyhexaallylmelamine was made using four techniques. Polymer was formed in nitrogen by heating the monomer with 2% of 2,5-dimethyl-2,5-di(*tert*-butyl peroxy)-*n*-hexane at 130°C. for 64 hr. The results for changes in weight by thermogravimetric analysis (TGA),⁷ heat content by differential thermal analysis (DTA),⁸ and mechanical properties (rigidity and mechanical damping) by torsional braid analysis (TBA)^{5,6} for the polymer as it was heated to 500°C. in nitrogen over a period of several hours are presented in Figures 2 and 3. Polyhexaallylmelamine loses little weight and rigidity below 370°C. but degrades shortly thereafter. Degradation is

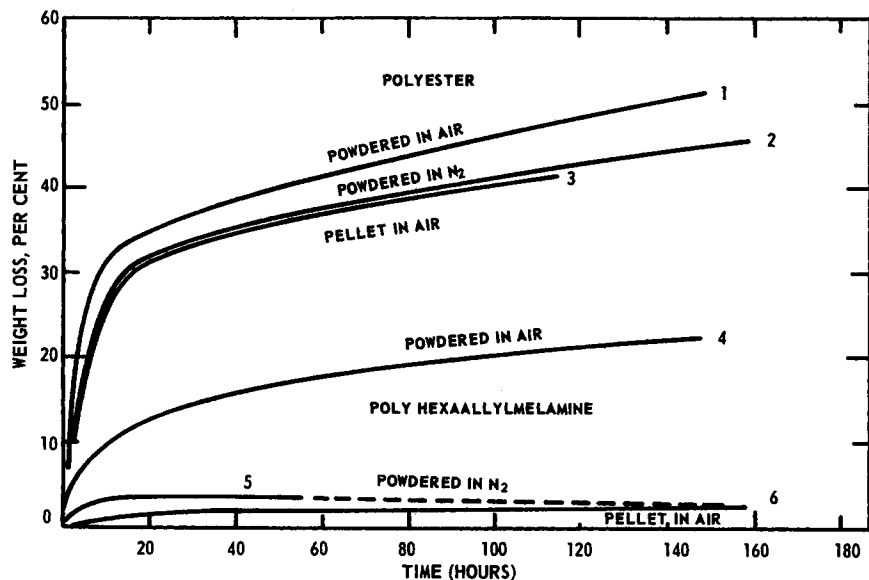


Fig. 4. Isothermal (370°C.) gravimetric analyses of polyhexaallylmelamine and a heat resistant polyester.

apparent from the drastic loss of weight, the violent endotherm, and the drop in rigidity and maximum in mechanical damping. Since parallel analysis by infrared spectroscopy showed that the disappearance of unsaturation is the only chemical change apparent below 370°C., the exotherm which occurs above 300°C. is attributed to thermal polymerization of unreacted allyl groups.

An estimate of the thermal and oxidative stability of the homopolymer was also made by comparison with a commercial heat-resistant polyester resin. This unsaturated polyester contains triallyl cyanurate as the cross-linking agent. Examination of the powdered resins by TGA in nitrogen and in air established the superior thermal stability of polyhexaallylmelamine in an inert atmosphere, but also showed its sensitivity to an oxidizing atmosphere. The same conclusions were drawn from isothermal experiments in which powdered samples and pellets of the two resins were compared at 370°C. The latter results, summarized graphically in Figure 4, show that whereas polyhexaallylmelamine is thermally stable at 370°C., it is oxidatively unstable at 370°C. The polyester is thermally unstable at 370°C. It is evident from Figure 4 that an apparent stability in air can exist for polyhexaallylmelamine when the ratio of surface area to volume is at a minimum.

Since the brittleness of unfilled cast polyhexaallylmelamine resulted in generally impractical mechanical properties, attention was directed to the evaluation of the polymer in the form of glass cloth-reinforced laminates. Such a laminate was prepared from partially polymerized, bodied hexa-

TABLE III
Thermal and Oxidative Properties of Glass Cloth-Reinforced Thermoset Resin Laminates

Property	Atmosphere	Conditions			Epoxy ^a	Phenolic ^b	Silicone ^c	Polyester ^d	Allylmelamine	
		Temp., °C.	Time, hr.	Temp. tested at, °C.					Hexa- ^e	Tetra- ^f
Flexural strength, psi (Flexural modulus, 10 ⁶ psi)	Air	23		23	54,000 (3.1)	40,000 (2.6)	38,000 (2.3)	57,000 (3.1)	36,000 (3.1)	63,500 (2.8)
	Air	260	1/2	260	5,700 (0.5)	31,000 (2.2)	11,000 (1.1)	32,000 (2.8)	34,000 (2.8)	52,000 (2.7)
	Air	260	192	260	Delamination	10,000 (1.6)	17,500 (1.8)	16,500 (2.4)	1,200 (0.3)	24,000 (1.9)
	N ₂	345	192	260	—	16,500 (2.0)	10,000 (1.5)	12,500 (2.6)	28,500 (2.5)	31,000 (2.5)
Weight loss, %	Air	260	192	—	9.7	14.6	0.9	14.5	13.7	6.0
	N ₂	345	192	—	—	11.8	1.3	25.1	3.6	1.7

^a Typical commercially available laminate satisfying the requirements of NEMA Grade G-11.

^b Typical commercially available laminate satisfying the requirements of NEMA Grade G-3.

^c Typical commercially available laminate satisfying the requirements of NEMA Grade G-7.

^d Heat-resistant grade, crosslinked with triallyl cyanurate.

^e Poly[2,4,6-tris(diallylamino)-s-triazine].

^f Poly(TAM); see text.

allylmelamine monomer (the experimental section gives details of the procedure). Immediately after curing at 130°C., the laminate was transparent; but on cooling slowly, minute cracks developed to the accompaniment of crackling sounds. Eventually at room temperature the laminate was white and opaque.

Table III includes a comparison of laminates prepared from hexaallylmelamine and the heat resistant polyester. On exposure in nitrogen at 260 and 345°C., the laminate from hexaallylmelamine lost less weight and retained a higher percentage of its original flexural strength than did the polyester. In the presence of air at high temperatures (260°C.), although the materials showed comparable weight losses, the polyester was superior with respect to retention of mechanical properties. The poor performance in air of the hexaallylmelamine product was attributed to numerous cracks which served as sites for penetration of the structure by oxygen.

Polymers Related to Polyhexaallylmelamine

In addition to hexaallylmelamine (I), related monomers (II, III, IV, and VI) could be polymerized to hard, transparent and uncracked castings by heating each monomer at 130°C. *in vacuo* or in nitrogen, with 2% of either di-*tert*-butyl peroxide or 2,5-dimethyl-2,5-di(*tert*-butylperoxy)-*n*-hexane.

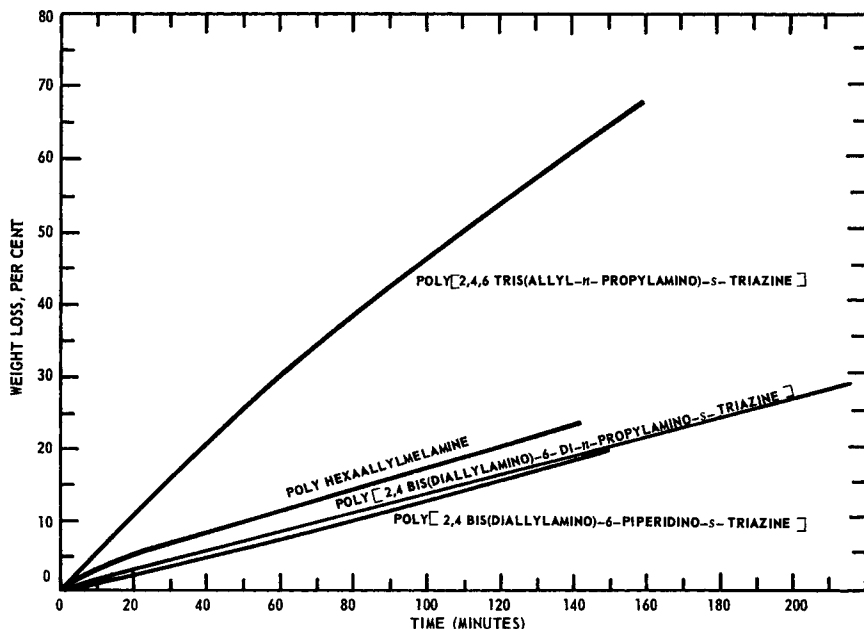


Fig. 5. Isothermal (405°C.) gravimetric analyses in nitrogen of polyhexa-, polytetra-, and polytriallyl substituted melamines.

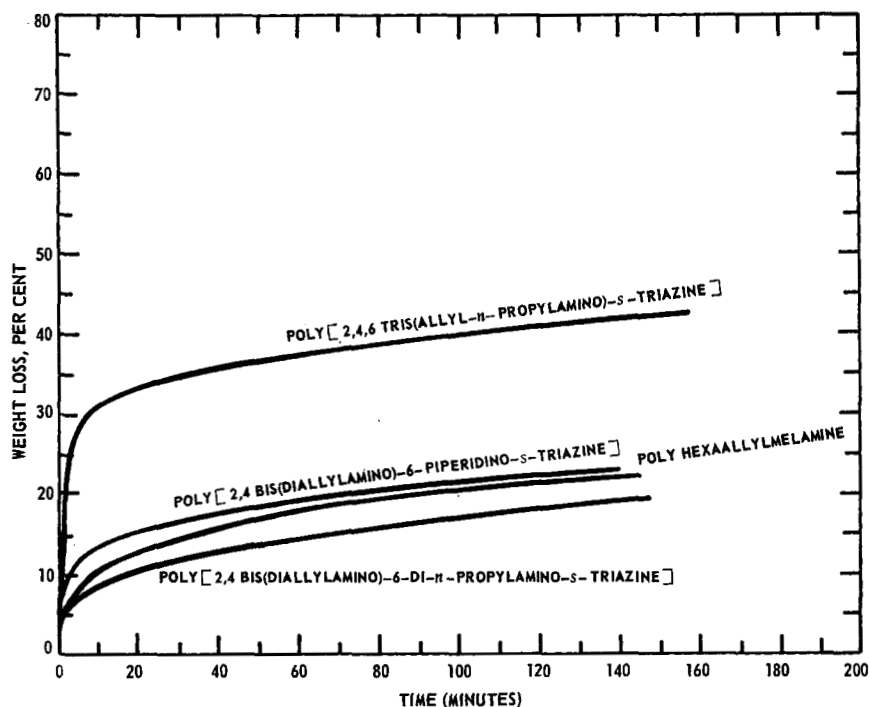


Fig. 6. Isothermal (370°C.) gravimetric analyses in air of polyhexa-, polytetra-, and polytriallyl substituted melamines.

It was considered that internal strain in the polymers, together with crazing in glass cloth-filled laminates, might be reduced by using less highly functional monomers than hexaallylmelamine. This would follow as a consequence of the decreased shrinkage which would occur on polymerization. Hence a series of laminates was prepared from blends of three monomers, I, II, and V, such that the average functionality varied from 6.0 to 3.3 allyl groups per *s*-triazine ring. Decreased crazing accompanied decreasing functionality so that the laminate from the least functional blend (3.3) was transparent and uncrazed. However, this laminate suffered some loss in strength at elevated temperatures (flexural strength was 61,500 psi at 25°C. and 29,500 psi at 260°C.; flexural modulus was 3.6×10^6 psi at 25°C. and 2.6×10^6 psi at 260°C.). Further examination of copolymers which contained the diallylamino monomer (V) demonstrated that its incorporation as an ingredient of heat-resistant copolymeric systems was detrimental. For example, in contrast with polyhexaallylmelamine, such copolymers were affected by organic solvents (e.g., toluene-carbon tetrachloride mixtures). The low reactivity of the allyl systems was quite apparent from the low number-average degree of polymerization which resulted from the bulk polymerization of V. Isothermal gravimetric analyses of some of the powdered homopolymeric resins were performed in nitrogen at 405°C. and in air at 370°C. The results (Fig. 5 and 6)

demonstrate that polymers from the tetraallylmelamine monomers (II, III) have the same order of stability in nitrogen and in air as polyhexaallylmelamine, whereas that from the triallyl monomer (IV) is less stable.

For these reasons polymers from 2,4-bis(diallylamino)-6-piperidino-*s*-triazine (II) warranted further study.

Glass Cloth-Reinforced Laminates of Poly[2,4-bis(diallylamino)-6-piperidino-*s*-triazine]

Initial attempts to prepare glass cloth-reinforced laminates using bodied monomer from analytically pure monomer (II) resulted in only partially transparent, somewhat crazed specimens. Although these possessed interesting mechanical and electrical properties, two weaknesses were apparent: (1) vulnerability to oxidative attack at temperatures greater than 200°C. in air and (2) sensitivity of the dielectric properties to water vapor. Craze imperfections, together with capillaries in the edge of the laminates which were caused by machining, were at first held responsible for the sensitivity to environmental conditions. The craze imperfections appeared inside the laminates as small, right-angled crosses with axes corresponding to the two weave directions of the glass cloth; they resulted as a consequence of rupture of the bonding of the glass to the resin. For further development a large batch of monomer was prepared in a pilot plant which provided a mixture of 2,4-bis(diallylamino)-6-piperidino-*s*-triazine (94.7%) and hexaallylmelamine (4.8%) in a total yield of greater than 95% of theory, based on cyanuric chloride. After numerous attempts, a reliable procedure was obtained for preparing craze-free and transparent glass cloth-reinforced laminates using the batch preparation. The procedure is described in the experimental section. In the figures and tables polymers resulting from the batch preparation are designated poly(TAM), whereas those from the analytically pure monomer are designated poly[2,4-bis(diallylamino)-6-piperidino-*s*-triazine].

TABLE IV
Thermomechanical Behavior of Poly(TAM) Glass Cloth-Reinforced Laminates

Conditioning	Temp. tested at, °C.	Flexural strength, psi (flexural modulus, 10 ⁶ psi)	
		Laminate A ^a	Laminate B ^b
23°C./—	23	63,500 (2.8)	50,500 (3.1)
100°C./1/2 hr.	100	58,000 (2.8)	50,000 (3.3)
150°C./1/2 hr.	150	54,000 (2.8)	46,000 (3.2)
200°C./1/2 hr.	200	56,000 (2.8)	48,500 (3.2)
220°C./1/2 hr.	220	52,000 (2.7)	52,000 (3.3)
260°C./1/2 hr.	260	52,000 (2.7)	49,000 (3.1)
300°C./1/2 hr.	300	43,500 (2.6)	46,000 (3.0)

^a Cured 64 hr. at 130°C.

^b Cured 64 hr. at 130°C.; post-cured 2 hr. at 350°C.

The thermal and oxidative properties of the laminates were assessed in terms of changes in mechanical and electrical properties, and of changes in weight which occurred on exposure to nitrogen and to air at elevated temperatures. Table III includes comparative data for poly(TAM), polyhexaallylmelamine, and for commercially available epoxy, phenolic, silicone and polyester glass cloth-reinforced laminates. Table IV contains thermomechanical data for two poly(TAM) laminates, one cured at 130°C. and the other further cured by heating at 350°C. in a press. This particular post-cure, at nearly the maximum temperature of isothermal stability for the system, was chosen to ensure complete chemical conversion. Torsional braid analyses indicated that the system is mechanically stable at 350°C., while infrared analyses demonstrated that chemical conversion was indeed complete. In agreement with the torsional braid analyses the laminates appeared not to be damaged by the severe thermal treatment. While the mechanical properties of the post-cured laminate showed virtually no change with temperature up to at least 300°C., those of the laminate cured only at 130°C. must be considered excellent, too. These uncrazed laminates are oxidatively more stable at 260°C. in air than the crazed specimens obtained in initial experiments. Data are presented in Table V and should be compared with those of Table III. Changes in electrical

TABLE V
Properties of Glass Cloth-Reinforced Poly(TAM) Laminates Aged in Air at 260°C. and Tested at 260°C.

Aging at 260°C., hr.	Laminate A ^a			Laminate B ^b		
	Flexural strength, psi	Flexural modulus, 10 ⁶ psi	Weight loss, %	Flexural strength, psi	Flexural modulus, 10 ⁶ psi	Weight loss, %
0.5	51,000	2.8	—	47,500	3.2	—
24	49,000	3.0	0.6	48,000	3.3	0.6
48	48,500	2.9	1.1	40,500	2.9	1.2
96	43,500	2.7	2.1	42,500	2.7	2.3
192	24,000	1.9	5.4	20,000	1.9	6.0
500	2,000	0.5	14.9	2,000	0.6	14.2

^a Cured 64 hr. at 130°C.

^b Cured 64 hr. at 130°C.; post-cured 2 hr. at 350°C.

properties due to temperature and atmospheric oxidation at 200°C., as measured by dielectric constant and dissipation factor at two frequencies (60 and 10⁶ cycles/sec.), are presented graphically in Figures 7 and 8. The effect of cycling between room temperature and 200°C. on the same parameters (at 60 cycles/sec.) is shown in Figure 9. The influence of temperature and aging in air at 200°C. on the surface, volume, and insulation resistances is presented in Figures 10 and 11. These data show that the glass-resin composites have dielectric and insulation properties at least equal to those of the best thermoset resins presently available. Values for

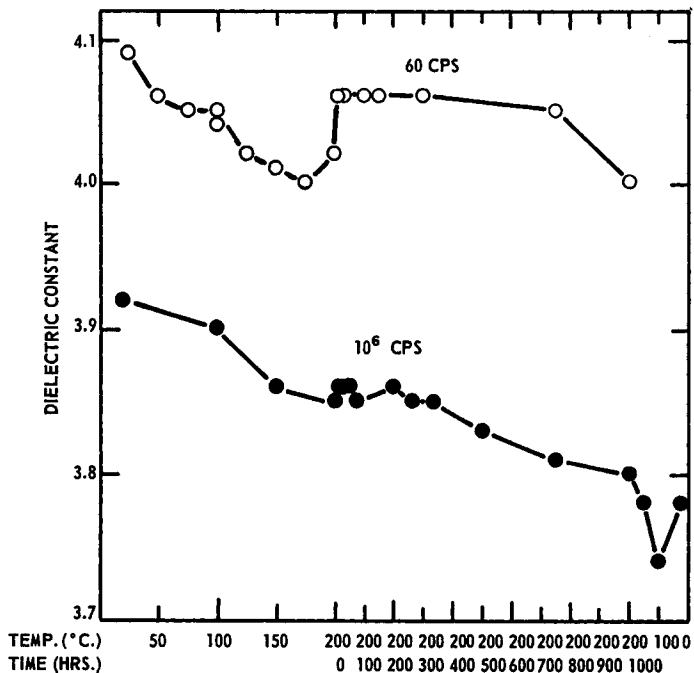


Fig. 7. Dielectric constant at 60 and 10⁶ cycles/sec. of poly[2,4-bis-(diallylamino)-6-piperidino-s-triazine] glass cloth-reinforced laminates aged in air at 200°C.

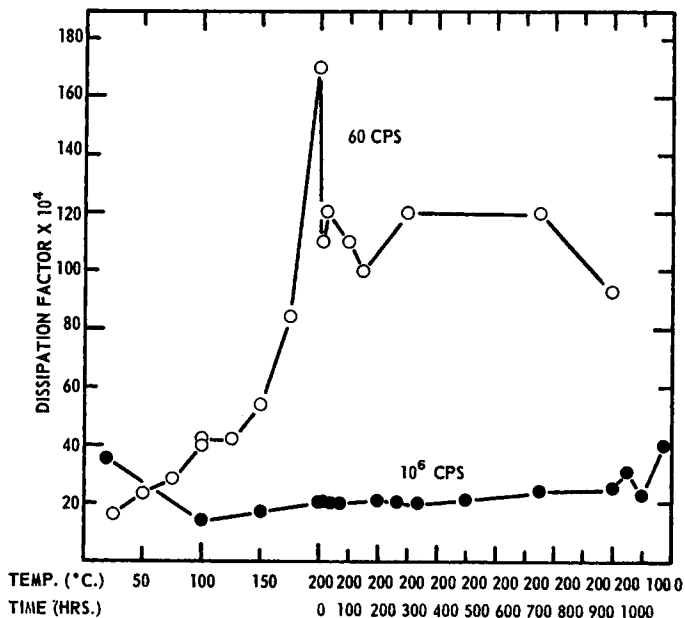


Fig. 8. Dissipation factor at 60 and 10⁶ cycles/sec. of poly[2,4-bis-(diallylamino)-6-piperidino-s-triazine] glass cloth-reinforced laminates aged in air at 200°C.

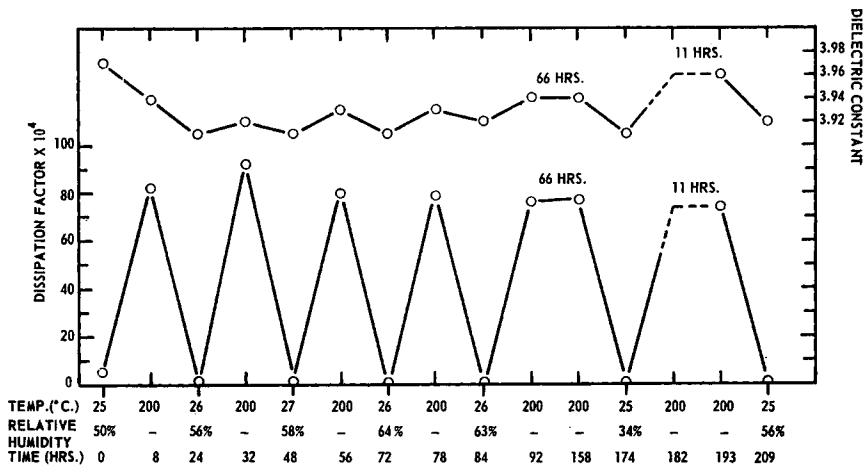


Fig. 9. Dielectric constant and dissipation factor at 60 cycles/sec. of a poly[2,4-bis-(diallylamino)-6-piperidino-s-triazine] glass cloth-reinforced laminate cycled between room temperature and 200°C.

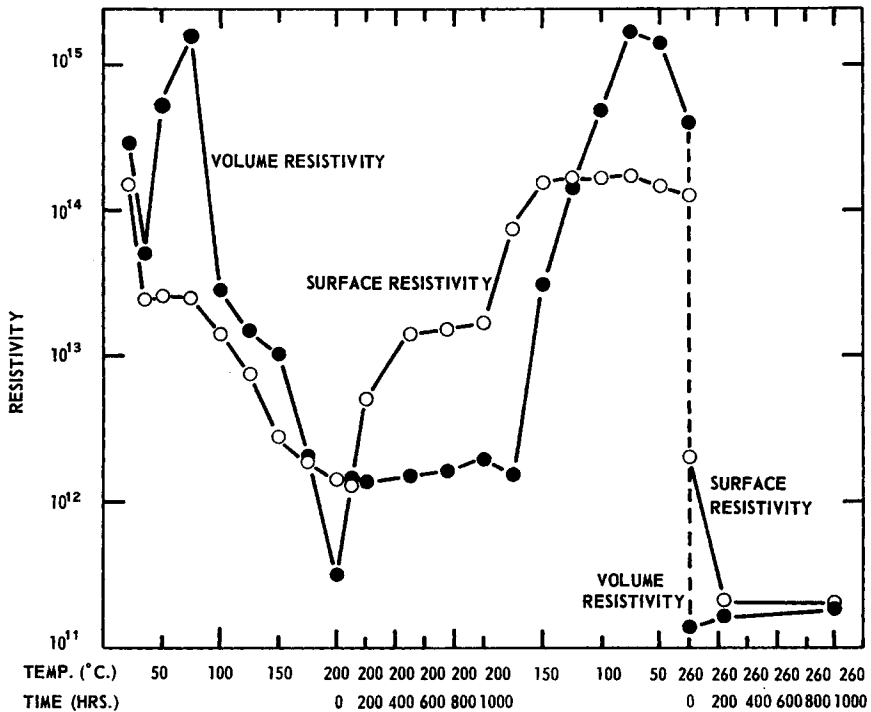


Fig. 10. Volume (ohm-cm.) and surface resistivity (ohm) of poly[2,4-bis-(diallylamino)-6-piperidino-s-triazine] glass cloth-reinforced laminates aged in air at 200°C.

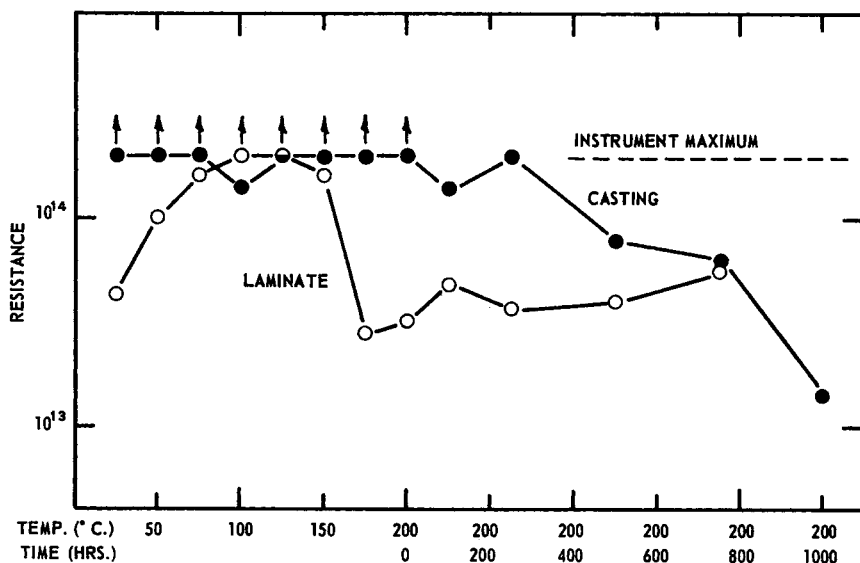


Fig. 11. Insulation resistance (ohm) of a poly[2,4-bis(diallylamino)-6-piperidino-s-triazine] glass cloth-reinforced laminate and unfilled casting aged in air at 200°C.

the dissipation factor of less than 0.001 at 60 cycles/sec. are especially noteworthy. The maximum in the dissipation factor at 60 cycles/sec. measured in Figure 8 after 1 hr. at 200°C., appears to be transient with time; this is not apparent in Figure 9 since measurements were made several hours after the laminate had attained 200°C. Differences in the dielectric values in the figures (Figs. 7-9) are otherwise attributable to the

TABLE VI

Influence of Relative Humidity on the Dielectric Properties at 60 cycles/sec. of a Poly[2,4-bis(diallylamino)-6-piperidino-s-triazine] Glass Cloth-Reinforced Laminate

Conditioning	Tested at	Dielectric constant	Dissipation factor
96 hr., 23°C., <1.4% R.H.	23°C., <1.4% R.H.	4.00	0.0005
40 hr., 23°C., 50% R.H. ^a	23°C., 23% R.H.	4.00	0.0006
96 hr., 35°C., 90% R.H. ^a	23°C., 48% R.H.	4.10	0.013

^a In addition to previous conditioning at lower relative humidity.

different specimens tested. The influence of water vapor on the dielectric properties at 60 cycles/sec. is demonstrated in Table VI. Since the dielectric properties could be almost restored to initial values by conditioning at low relative humidity, the effect of water vapor was considered to be due primarily to a physical process. The deterioration of dielectric properties with increasing relative humidity was not lessened for uncrazed samples having either machined edges or sealed edges. This behavior was in contrast with that for oxidative attack where increased resistance to oxidation

paralleled decreased crazing and lowering of the ratios of edge area to surface area. A noteworthy property for the glass cloth laminates was the excellent arc resistance (186 sec. at 23°C. compared with 128 sec. for an unfilled casting).

Commercial interest in the composites would be heightened if laminates with properties similar to those described above could be made using an accelerated cure. Preliminary laminates formed from the same bodied monomer, by curing at 180°C. for 3 hr., had mechanical properties equal to those of the precursors.

EXPERIMENTAL

Preparation of Glass Cloth-Reinforced Laminates

The fluidity of the monomers at the curing temperature (130°C.) led to difficulties in the preparation of glass cloth-reinforced laminates by the "wet lay-up" or "hand lay-up" technique.⁹ Hence partially polymerized, bodied monomers were generally used. These were obtained by heating monomer with sufficient initiator to increase the viscosity and yet insufficient to cause gelation. The technique could be employed in consequence of the low rate of thermal polymerization of uninitiated monomer below 200°C. and the low efficiency of the initiators in the allylic polymerization process. For the same reasons the viscosity of the bodied monomer could be increased at will by removing unreacted monomer by vacuum distillation below 200°C. The following example is typical.

Viscous bodied monomer was prepared from 2,4-bis(diallylamino)-6-piperidino-*s*-triazine by heating the monomer with 0.3% of 2,5-dimethyl-2,5-di-*tert*-butylperoxy-*n*-hexane in nitrogen at 150–160°C. for 1 hr. The product was thoroughly degassed *in vacuo* at 150°C. before slowly cooling it *in vacuo*. Laminating resin was obtained by adding 1.7% more initiator to the cooled and degassed bodied monomer. An assembly for cure was made by using initiator-loaded bodied monomer and 12–14 plies of 181-301 glass cloth stacked front-to-front and back-to-back with the directions of warp parallel. A vinylaminosilane finish (301) was employed, since chemical coupling between the glass and resin was likely to occur. The assembly was wrapped in cellophane or polytetrafluoroethylene sheet and placed between two polished metal plates. The resin was cured in a press at 130°C. and 20 psi for 64 hr. In order to minimize thermal shock the cured laminate was permitted to cool slowly in the press. Laminates prepared according to this procedure contained about 30% of resin.

Test Procedures

Standard procedures were used throughout this research for measuring mechanical and electrical properties of the polymers and of their composites. A list of the standard testing procedures follows: ASTM-D-790, flexural strength and flexural modulus; ASTM-D-648, deflection temperature under load (DTL); ASTM-D-696, coefficient of linear expansion; ASTM-D-150,

dissipation factor and dielectric constant; ASTM-D-495, arc resistance; ASTM-D-257, volume and surface resistivity, and insulation resistance.

The dimensions of samples which were used for aging and flexural testing were $3 \times 0.5 \times (0.10-0.125)$ in.; the values reported are average values of three to five replicate determinations. The dimensions of samples for dielectric measurements at 60 cycles/sec. were $4 \times 4 \times (0.10-0.125)$ in., whereas for 10^6 cycles/sec. a disk with 1 in. radius was employed. For glass cloth-reinforced laminates, the results of testing specimens which had been aged in air depended on their geometry. It might be noted that the ratio of the area of machined edge to that of non-edge in all the specimens was high compared with the parent laminates. Thus the percentage loss of flexural strength on exposure to air at 260°C . was more than halved when samples for testing were cut away from the edge of an aged (260°C ., 5 days) sheet of laminate. On the other hand, the influence of geometry was low for the polyester.

CONCLUSIONS

An "ideal" heat-resistant resin system would have the electrical (dielectric and insulation) properties and the oxidative and thermal stability, of the silicone resins, but would also have the mechanical and thermo-mechanical properties which are associated with heat-resistant phenolic resins. Resistance to organic vapors and solvents would also be an asset. Glass cloth-reinforced laminates of poly[2,4-bis(diallylamino)-6-piperidino-s-triazine] are interesting materials which combine the advantageous properties of both the silicone and phenolic resin systems. The attractive properties of the new system include: thermal stability to almost 400°C .; high mechanical strength and modulus to at least 300°C . (and probably to almost 400°C .); and excellent electrical properties, especially dielectric and arc resistance.

It may be stated that a resin system has been developed which has certain advantages in comparison with materials heretofore available, and which would be useful in structural and electrical applications for long term service in air to 200°C . and for shorter periods of time to almost 400°C .

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Résumé

Des polymères thermodurcissables se forment lorsque l'hexaallylmélatmine et ses monomères dérivés, tels que la 2,4-bis-(diallylamino)-6-pipéridino-*s*-triazine sont polymérisés avec du peroxyde de di-*tert*-butyle ou le 2,5-diméthyl-2,5-di-(*tert*-butylperoxy)-*n*-hexane. Les nouveaux systèmes chargés de fibres de verre possèdent des propriétés avantageuses: une résistance mécanique élevée et un module élevé à hautes températures, de la résistance aux solvants et des propriétés électriques excellentes, spécialement en ce qui concerne la constante diélectrique, le facteur de dissipation et la résistance à l'arc. Bien que les résines laminées et renforcées au moyen de verre soient stables jusque 400° sous atmosphère d'azote, dans un milieu oxydant elles sont beaucoup moins stables. Néanmoins, ces nouveaux systèmes de résines possèdent certains avantages si on les compare aux résines de silicone et pourraient être utiles pour des applications structurales et électriques dans l'air au-dessus de 200°C.

Zusammenfassung

Wärmehärtende Polymere werden bei der Polymerisation von Hexaallylmelamin und verwandten Monomeren, wie 2,4-Bis(diallylamino)-6-piperidin-*s*-triazin, mit Di-*tert*-butylperoxyd oder 2,5-Dimethyl-2,5-di(*tert*-butylperoxy)-*n*-hexan gebildet. Zu den vorteilhaften Eigenschaften der neuen Systeme bei Füllung mit Glasgewebe gehören hohe mechanische Festigkeit und hoher Modul bei erhöhten Temperaturen, Lösungsmittelbeständigkeit, sowie ausgezeichnete elektrische Eigenschaften, besonders Dielektrizitätskonstante, Dissipationsfaktor und Bogenwiderstand. Glasgewebeverstärkte Lamine des Harzes sind in Stickstoff bis fast 400°C beständig; gegen Oxydation sind sie viel weniger stabil. Die neuen Harzsysteme besitzen im Vergleich zu Siliconharzen gewisse Vorteile und sollten als Bauelemente und für elektrische Anwendungen in Luft bis oberhalb 200°C brauchbar sein.

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