Epoxysiloxane Casting Resins

A Study in Geometry and Functionality

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Epoxysiloxanes are readily prepared by the platinum-catalyzed addition of silane hydrogen compounds to the double bond of allyl 2,3-epoxypropyl ether [allyl glycidyl ether (*2*)]. The resulting glycidoxypropyl siloxanes are stable organofunctional silicon compounds containing epoxy groups with a reactivity similar to commercial glycidyl ethers of phenols and alcohols.

Epoxysiloxanes are uniquely adapted for a study of the influence of geometry and functionality on properties of epoxy castings since individual members of branched, linear, and cyclic epoxysiloxanes are readily prepared, the epoxysiloxanes are low viscosity fluids that are readily handled for casting, and curing mechanism of glycidoxypropyl siloxanes are similar to those of commercial organic glycidyl ether resins.

Comparisons of properties of the various epoxysiloxanes cured with 4,4′-methylenedianiline indicate that increasing cross linking was obtained in going from branched to linear to cyclic polyepoxysiloxanes. Only in the cyclic series was there marked increased evidence of cross linking with increase in functionality. The higher cyclic epoxysiloxanes appear especially promising as new epoxy compounds for preparation of high temperature plastics.

PREPARATION OF EPOXYSILOXANES

Hydrolysis of dichloromethylsilane in toluene gave a mixture of linear and cyclic methylhydrogen siloxanes. The cyclic tetramer, pentamer, and hexamer were recovered by fractionation of the volatile portion (*3*):

$n\mathrm{MeHSiCl_2} + \mathrm{H_2O} \rightarrow \mathrm{HCl} + (\mathrm{MeHSiO})_n, n = 4, 5, 6,$ etc. A small proportion of cyclic trimer was recovered by cracking $(\mathrm{MeHSiO})_n$ residue at 330° to 350° C.

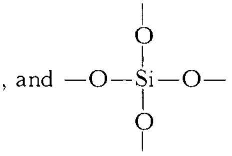
Cohydrolysis of dichloromethylsilane with chlorodimethylsilane gave a mixture of linear siloxanes from which the first five members were isolated by fractionation.

$$\mathrm{MeHSiCl_2} + \mathrm{Me_2HSiCl} + \mathrm{H_2O} \rightarrow \mathrm{HCl} + \mathrm{HMe_2SiO}(\mathrm{SiMeHO})_n\mathrm{SiMe_2H}, n = 0,1,2,3,4$$

Cohydrolysis of chlorodimethylsilane and dichlorodimethylsilane gave a mixture of linear dimethylsiloxanes, end-blocked with $\mathrm{HMe_2SiO}$. The first five members of this series were isolated by fractionation.

$$\mathrm{MeHSiCl} + \mathrm{Me_2SiCl_2} + \mathrm{H_2O} \rightarrow \mathrm{HCl} + \mathrm{HMe_2SiO}(\mathrm{SiMe_2})_n\mathrm{SiMe_2H}, n = 0, 1, 2, 3, 4$$

Cohydrolysis of silicon chloride and excess chlorodimethylsilane with isopropyl alcohol and water gave the neopentamer $\mathrm{Si(OSiMe_2H)_4}$ and dineo-octamer $\mathrm{(HMe_2SiO)_3SiOSi(OSiMe_2H)_3}$.

For shorthand purposes, the $\mathrm{HMe_2SiO_{0.5}}$ group is designated M′, HMeSiO as D′, $\mathrm{Me_2SiO}$ as D, and  $\begin{array}{c} | \\ \mathrm{O} \\ | \\ \mathrm{-O-Si-O-} \\ | \\ \mathrm{O} \\ | \end{array}$ as Q. The various siloxanes may then be represented as follows:

$(\mathrm{D'})_n$	Cyclic polyfunctional
$\mathrm{M'D'}_n\mathrm{M'}$	Linear polyfunctional
$\mathrm{M'D}_n\mathrm{M'}$	Linear difunctional
$\mathrm{M'(QM'_2)}_n\mathrm{M'}$	Branched polyfunctional

Properties of the silane hydrogen siloxane intermediates are summarized in Table I.

Each of the separate siloxane fractions was added to allyl-2,3-epoxypropyl ether in the presence of platinum (*4*). The exothermic reaction was controlled conveniently by adding the silane to allyl 2,3-epoxypropyl ether and platinum in refluxing toluene (*2*). Excess allyl 2,3-epoxypropyl ether was removed by stripping to 150° C. at 1 mm. of mercury. The residue was filtered from active carbon to give the finished epoxysiloxane as listed in Table II.

Table I. SiH Siloxane Intermediates

SiH Compound	B.P., ° C.	Pressure	d^{25}	n_D^{25}	% Silane Hydrogen Observed	% Silane Hydrogen Theory
M′M′	71-2	1 atm.	0.754	1.3763	1.47	1.49
M′DM′	122-4	1 atm.	0.827			0.96
$\mathrm{M'D_2M'}$	169-70	1 atm.	0.862	1.3851	0.68	0.71
$\mathrm{M'D_3M'}$	94-8	15 mm.	0.880	1.3886	0.55	0.56
$\mathrm{M'D_4M'}$	91-5	2 mm.	0.899	1.3915	0.484	0.47
M′D′M′	116-18	1 atm.	0.825	1.3770	1.50	1.54
$\mathrm{M'D_2'M'}$	40-1	7 mm.	0.867	1.3804	1.58	1.57
$\mathrm{M'D_3'M'}$	70-2	7 mm.	0.889	1.3836	1.54	1.59
$\mathrm{M'D_4'M'}$	62	1.3 mm.	0.910	1.3860	1.59	1.60
$\mathrm{QM_4}$	188-90	1 atm.	0.884	1.3841	1.17	1.22
$\mathrm{M'(QM_2')_2M'}$	103-5	0.6 mm.	0.939	1.3920		1.15
$\mathrm{D_3'}$	92-5	1 atm.	0.968	1.3765	1.65	1.67
$\mathrm{D_4'}$	134	1 atm.	0.987	1.3860	1.67	1.67
$\mathrm{D_5'}$	169-70	1 atm.	0.996	1.3889	1.66	1.67
$\mathrm{D_6'}$	75-7	8 mm.	0.996	1.3924	1.68	1.67

Table II. Epoxysiloxanes

Epoxysiloxane	d^{25}	n_D^{25}	Visc., Cs.	Equivalent Weight/Epoxy Obsd.	Equivalent Weight/Epoxy Calcd.
MM′	0.915	1.4267	3.5	262	262
M′M′	0.995	1.4499	10.8	182	181
M′DM′	0.992	1.4442	11	222	218
$M'D_2M'$	0.991	1.4389	11	263	255
$M'D_3M'$	0.992	1.4359	12	286	292
$M'D_4M'$	0.997	1.4348	14	312	329
M′D′M′	1.038	1.4564	29	192	178
$M'D_2'M'$	1.060	1.4597	45	192	177
$M'D_3'M'$	1.084	1.4649	94	182	176
$M'D_4'M'$	1.088		105	179	175
D_3'	1.114	1.4628	98	174	174
D_4'	1.119	1.4635	135	175	174
D_5'	1.120	1.4660	160	179	174
D_6'	1.122		225	175	174
D_n' (linear)	1.130		12,300	182	174
QM_4'	1.053	1.4542	45	196	196
$M'(QM_2')_2M'$	1.088		113	204	204

PROPERTIES

Viscosity. Viscosities of the epoxysiloxanes are shown in Figure 1. Diepoxylinear siloxanes show little increase in viscosity with added dimethylsiloxy spacers. (Dimethyl silicones increase only approximately 0.5 centistoke with each added unit.) Polyepoxylinear siloxanes show a more rapid increase in viscosity. The pentamer was known to be partly condensed during an unduly prolonged reaction time.

Branched chain polyepoxysiloxanes fall on the curve for linear isomers if the central silicons are neglected—i.e., neopentamer *vs.* linear tetramer, and dineo-octamer *vs.* linear hexamer.

Cyclic polyepoxysiloxanes have much higher viscosities than comparable linears. It is believed that this is a measure of their true viscosity (not due to partial opening of cyclics to linears) because the preparations are reproducible within ±5 centistokes. Infrared spectra of the cyclic trimer and tetramer indicate retention of these ring structures.

Gel Time and Exotherm with Methylenedianiline. Epoxysiloxanes were warmed to about 100° C., mixed with stoichiometric 4,4′-methylenedianiline, and 25 grams of mix placed in a 25-mm. test tube immersed in an oil bath at 150° C. A thermometer immersed to within 1/2 inch of the bottom served to indicate temperature and point of gelation. Zero time was taken at 130° C.

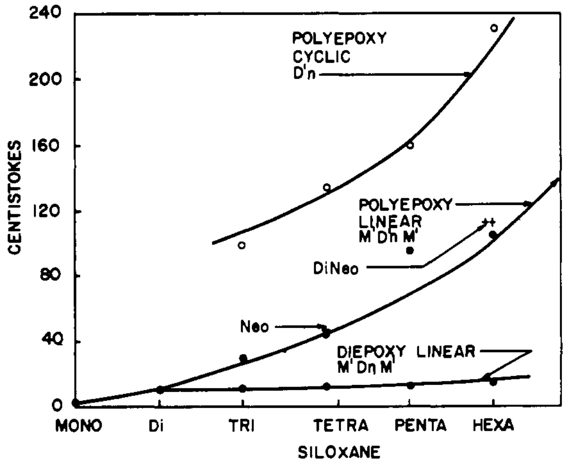


Figure 1. Viscosities of polyepoxysiloxanes

Gel times of the various polyepoxysiloxanes are shown in Figure 2. Linear structures occupy reasonable positions showing decreasing gel times with increasing functionality. Cyclic structures show little variation in gel time with increasing functionality. Branched structures fall on the curve for linear epoxysiloxanes of comparable viscosity.

Maximum exotherm temperatures (Figure 3) reached by linear epoxysiloxanes lie on a curve that is asymptotic to 280° C. Because epoxy equivalents and gel times in the cyclic series are the same, higher exotherms for cyclic trimer and tetramer may be caused by siloxane ring opening.

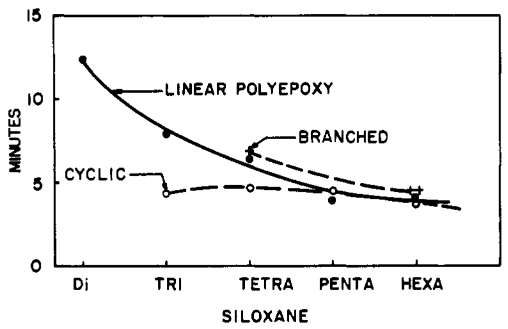


Figure 2. Gel time of epoxysiloxanes in oil bath at 150° C.

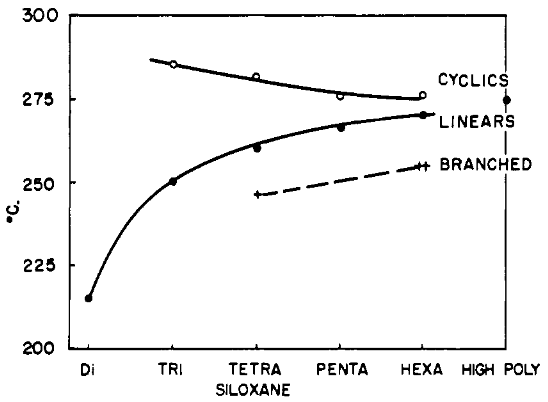


Figure 3. Maximum exotherms of epoxysiloxanes

4,4′-Methylene dianiline in oil bath at 150° C.

Castings. All data were obtained with stoichiometric amounts of 4,4′-methylenedianiline curing agent. Complete cure, as shown by heat distortion temperature, is reached in a few hours at 135° C. All samples were cured initially for 4 to 6 hours in an oven at 100° C., and postcured 16 hours at 135° C. Additional postcure (24 to 48 hours) at 150° C. gave no appreciable increase in heat distortion point.

Hardness was measured with a Barcol Impressor (GY2J 934-1 by Barber-Coleman Co.) recommended for soft metals and plastics.

Impact strengths were measured on notched bars by the Izod method (ASTM D 256-43T). Heat distortion points were determined by ASTM method D 648-45T (264 p.s.i., 2° C. per minute). Weight loss was measured on 1/2 X 1/2 X 1 inch castings in an air oven maintained at 500° ± 4° F. by a Sim Ply Trol control. All samples were run simultaneously to equalize any variations in oven temperature.

Diepoxy Linear Siloxanes as Reactive Diluents. Diepoxy linear siloxanes were considered only as reactive diluents and flexibilizers for DER-331, a technical bis-phenol-A glycidyl ether with epoxy equivalent weight of 188, supplied by The Dow Chemical Co. Hardness and impact resistance of castings with 25% diepoxy linear siloxanes are shown in Figure 4. The hexasiloxane was relatively incompatible in the cured sample and showed discontinuities with lower epoxysiloxanes in trend of properties.

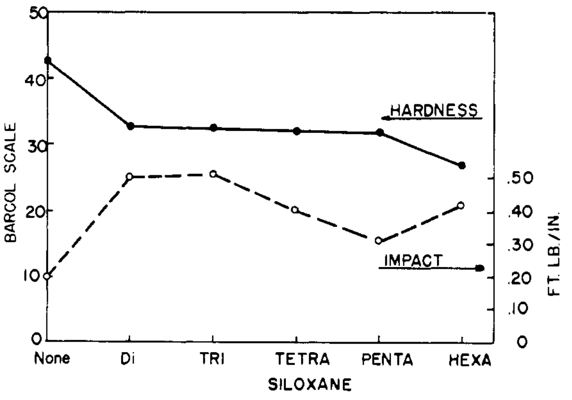


Figure 4. 75% DER-331, 25% diepoxy linear siloxanes
Hardness and impact strength

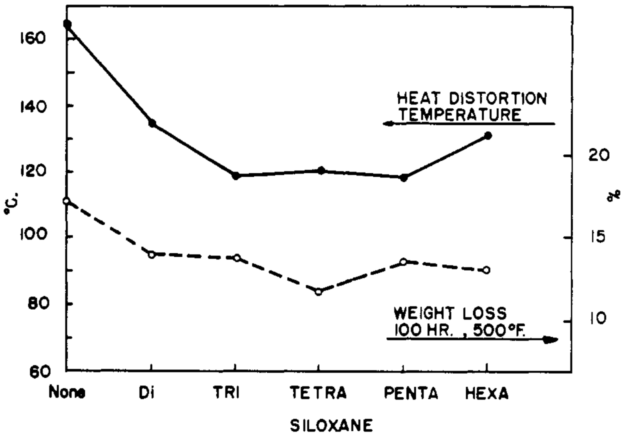


Figure 5. 75% DER-331, 25% diepoxy linear siloxanes
Heat distortion and heat stability

Heat distortion temperature and weight loss at 500° F. are shown in Figure 5. Although the diepoxy linear siloxanes cause lowering of the heat distortion temperatures, they do improve the heat stability of castings.

As the diepoxy linear siloxanes have almost the same viscosity, they may be considered to be roughly equivalent as reactive diluents for commercial epoxy resins. Possibly the best balance of properties is shown by the first member of the series. The diepoxydisiloxane has been introduced to the trade as Syl-Kem 90.

Polyepoxysiloxanes as Reactive Diluents. Mixtures of 25% polyepoxysiloxanes with DER-331 were completely compatible during cure with 4,4'-methylenedianiline. Hardness and impact strength of the castings are compared in Figure 6. Whereas the difunctional disiloxanes impart lower hardness and higher impact strength, higher polyfunctional siloxanes give physical properties that level out at approximately the same values as unmodified DER-331. Linears and cyclics are roughly equivalent in these properties.

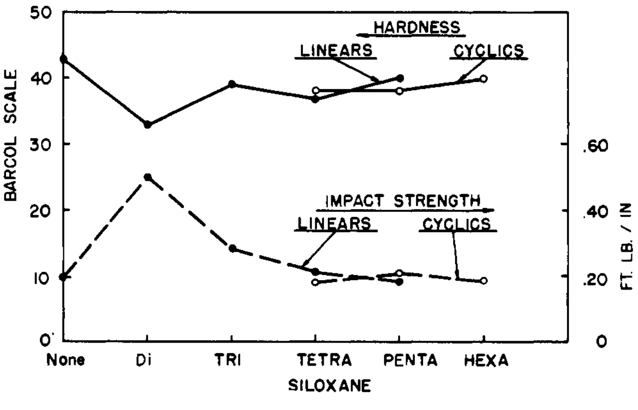


Figure 6. 75% DER-331, 25% polyepoxysiloxanes
Hardness and impact strength

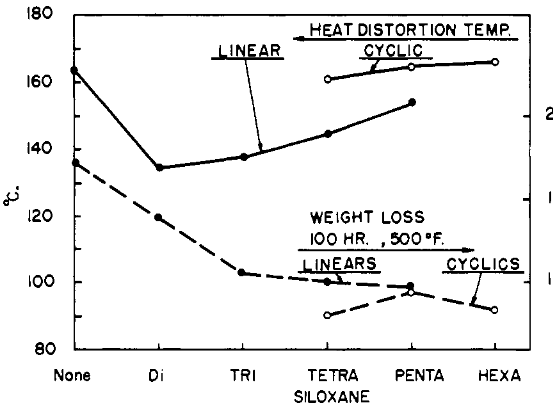


Figure 7. 75% DER-331, 25% polyepoxysiloxanes
Heat distortion and heat stability

Figure 7 shows that heat distortion temperatures and heat stability at 500° F. vary somewhat more with structure. Heat distortion temperature rises with increasing functionality, and cyclics are higher than linears. All epoxysiloxanes improve the heat stability of castings as shown by weight loss at 500° F. Stability increases with functionality, and cyclics show some advantage over linears.

Polyepoxysiloxanes as Casting Resins. The effect of structure and functionality on properties is more clearly shown in castings of the individual polyepoxysiloxanes with 4,4'-methylenedianiline curing agent. Hardness (Figure 8) increases regularly

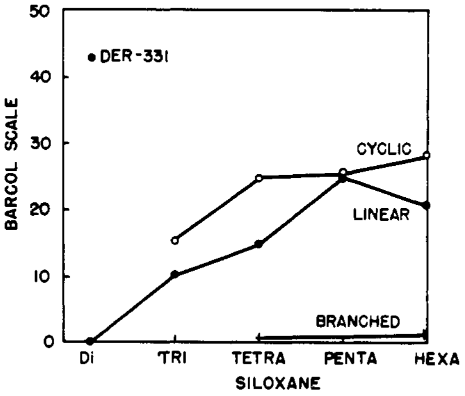


Figure 8. Polyepoxysiloxanes
Hardness

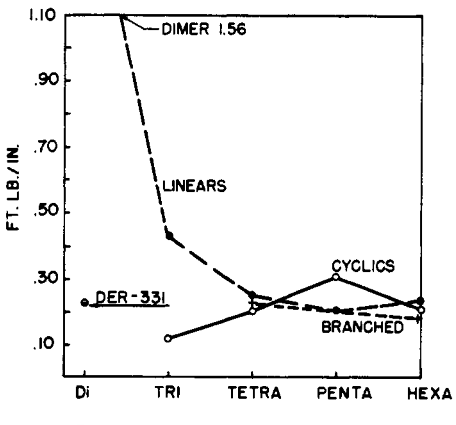


Figure 9. Polyepoxysiloxanes
Impact strength

with increasing functionality but does not approach that of DER-331. Cyclics give somewhat harder castings than linears while branched are very low. Impact strength (Figure 9) decreases rapidly with increasing functionality and levels off with tetramers at a value comparable to DER-331. Cyclic, linear, and branched siloxanes are roughly equivalent.

Heat stability as shown by weight loss in 100 hours at 500° F. (Figure 10) is about the same for linears above the trimer, but improves uniformly with increasing functionality of the cyclics. Branched isomers show highest weight loss, but all epoxysiloxanes are far more stable than the bisphenol epoxy resin.

Heat distortion temperatures of linear and branched polyepoxysiloxanes (Figure 11) level off at values far below that of DER-331. Cyclic siloxanes have sharply increasing heat distortion temperatures with increasing functionality.

Resistance to deflection with increasing temperature has been interpreted to be due to a combination of Van der Waal's forces between molecules, and chemical cross links that resist deformation (*1*). Figure 12 compares deflection *vs.* temperature of cyclic polyepoxysiloxanes and DER-331. The rigid backbone of the bisphenol epoxy resin allows high Van der Waal's forces to hold the casting in a rigid "frozen" state until a sharp distortion is observed at a given temperature. Epoxy siloxanes have a very flexible backbone with low Van der Waal's forces such that rigidity is maintained primarily through cross links with the curing agent. The rate of change in deflection with increasing temperature is less than with DER-331, but for the lower cyclics is much greater than might be expected for materials of such high functionality.

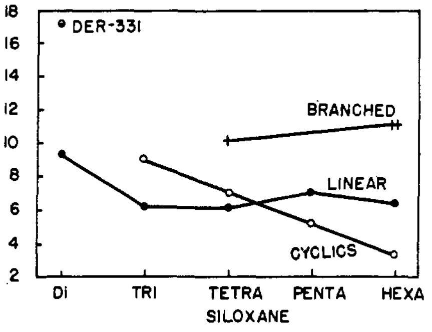


Figure 10. Polyepoxysiloxanes

Weight loss, 100 hours, 500° F.

Higher cyclic epoxysiloxane castings give complex deflection *vs.* temperature curves with no sharp distortion temperature. The rate of change in deflection of the cyclic hexamer is so low than there is no actual heat distortion temperature except by arbitrary definition of the 10-mil deflection point. This casting returned to its original shape when weights were removed, while DER-331 castings were permanently deformed.

DISCUSSION

Properties of epoxysiloxanes cured with methylenedianiline are interpreted in terms of nonpolar, flexible backbones of the epoxysiloxanes. The epoxy groups appear to have normal reactivity of glycidyl ethers.

Differences among branched, linear and cyclic epoxysiloxanes may best be attributed to differences in effective cross linking with the curing agent, with epoxy branched siloxanes being the least cross-linked, linears only slightly more, while cyclics increase rapidly in cross-linking ability from trimer to hexamer. It is improbable that appreciable proportions of unreacted epoxy groups were trapped in the gelled structure since cure temperature was generally above the heat distortion point. Additional postcure for 24 hours at 150°C. also gave little change in properties. Low degree of cross linking from highly polyfunctional molecules could result if adjacent groups within a molecule were cyclized internally by reacting with amine groups of the same molecule.

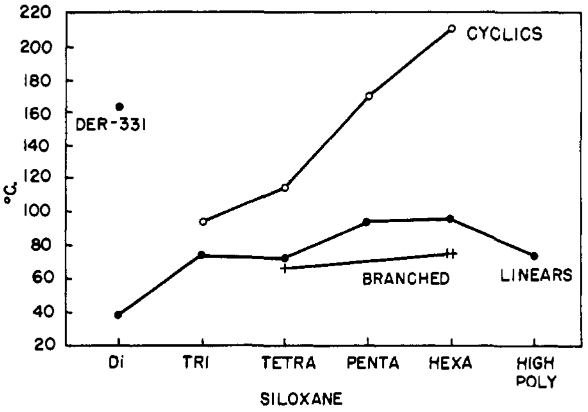


Figure 11. Polyepoxysiloxanes

Heat distortion temperature

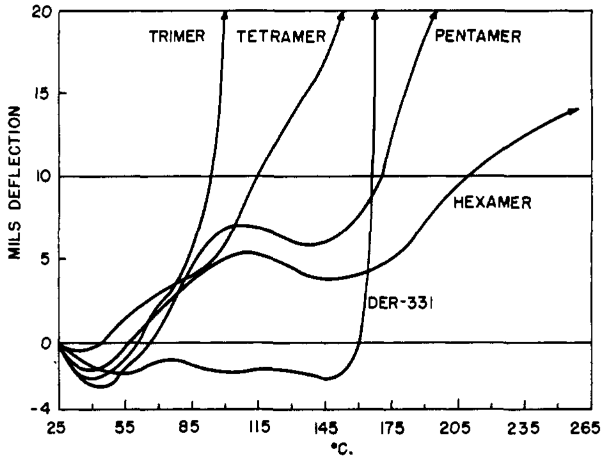


Figure 12. Polyepoxy cyclic siloxanes

Heat distortion curves

Linear diepoxysiloxanes similarly could bend back upon themselves to allow both epoxy groups to react with the same molecule of curing agent. They all, therefore, were of similar effectiveness as flexibilizers.

Molecular models demonstrate that the branched siloxane structures are most flexible allowing all epoxy groups to congregate in the area of a single molecule of 4,4′-methylenedianiline. Linear polyepoxysiloxanes have sufficient flexibility for most of the epoxy groups to congregate, while cyclics allow only two adjacent groups to react with a given 4,4′-methylenedianiline molecule.

Other curing agents have not been studied extensively, but it is possible that steric limitations of some curing agents such as pyromellitic dianhydride might give more effectual cross linking with even the linear polyepoxysiloxanes.

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