

Dielectric Loss Features of Some Epoxy Resins

MERRILL COHEN, *Medium Steam Turbine Generator & Gear Dept., General Electric Company, River Works, Lynn, Massachusetts*, LEOS. KOHN, *Large Steam Turbine-Generator Dept., General Electric Company, Schenectady, New York*, and DAVID I. MACDONALD,* *Medium Steam Turbine Generator & Gear Dept., General Electric Company, River Works, Lynn, Massachusetts*

INTRODUCTION

This article is concerned with the effect of composition on some of the electrical properties,^{2,4,21,34,46} specifically the power factor, dissipation factor, and other dielectric loss features of epoxy resins.^{12-14,25,26,30,38,45,49,52} The power factor of an insulating material is usually of secondary consideration to such properties as electric strength which is the actual criterion of electric failure. However, it becomes an important index in certain high voltage applications and in high frequency insulation since it is an indication of electrical losses to be expected in the insulation and of the dielectric heating to be encountered.

It should be pointed out that this study is concerned only with pure epoxy resins. In actual insulation systems, particularly in resin-bonded mica, glass and other heterogeneous insulations, other factors, such as voids, may affect the power factor of the system much more than the resin itself. It should also be emphasized that power factor is a separate property of an insulating material and may have no direct correlation with dielectric strength or service life.

Although the power factor is in actuality the sine of δ , the loss angle, it is quite common to express power factor loss measurements in terms of the tangent of δ the so-called loss tangent or dissipation factor. This procedure will be followed here. At low values of δ , the two expressions are equivalent. Furthermore, the values of $\tan \delta$ are not limited to less than unity, even though materials with high values of $\tan \delta$ would not normally be considered good candidates for most types of insulation. An alternate description of $\tan \delta$ is the ratio of the so-called dielectric loss factor to dielectric constant.

A power factor or power loss occurring in an insulation exposed to an alternating electric field is a direct function of the ability of the insulating material to reverse polarity as directed by the change in phase of the elec-

* Present address: Direct Energy Conversion Operation, General Electric Company, River Works, Lynn, Massachusetts.

tric current. This may be thought of in part as the movement of electric dipoles in the polymer structure trying to be in phase with the alternating current. The dielectric absorption occasioned by interaction of the electric field of the current and that of the dipoles in their directed movement contributes greatly to the power factor loss. Another way of describing the power factor loss is by the heating due to the friction of dipoles moving according to the dictates of the changing alternating current through the viscoelastic polymer medium.

The dipoles may be on an electronic, atomic, or molecular level. However, at the low A. C. power frequencies (60 cycle) with which this work is concerned, only the molecular polarizations or dipoles are of concern. The others possess such a high relaxation frequency that, for all practical purposes, they are in phase with the alternating current at all times. The power factor is usually associated either with the movement of simple molecular dipoles or of sections of the polymer chain containing these dipoles. In the case of such a polar resin as an epoxy resin, these dipoles arise from such groups as hydroxyl, ether, epoxy, chlorine, acid, and the various groups introduced by the hardeners employed, such as carboxyl, ester, amino, etc.

Another contribution to the power factor is the presence of ionizable materials in the resin system,^{2,4,7,21-23,31,32,34,35,42,43,46,47} which leads to conduction losses⁴³ and resulting I^2R heating. These materials may be in the epoxy resin polymer chain or be a major component of the unreacted hardeners. They may also result from polar, nonreactive impurities present in the hardeners and in most resins. The latter are especially likely to appear in the bisphenol A epoxy resins because of their method of manufacture; i.e., the condensation of epichlorohydrin with bisphenol A in the presence of alkali.

Another source of saltlike materials arises as a result of the cure of epoxy resin with amines, particularly the tertiary amines.^{5,36,41}

A last factor is the presence of moisture which is known to increase the power factor^{23,28,37,39,42,53} and the A. C. conductivity of plastics.

As mentioned above, voids and the presence of more than one material phase will also contribute to the power factor through interfacial polarization, but this was not considered to be an important factor in the homogeneous resin systems studied herein.

This article is specifically concerned with four aspects of the (60 cycle/sec.) dielectric loss properties of bisphenol A-based epoxy resins at room temperature and elevated temperatures: (1) the power factor (or dissipation factor) characteristics of some conventional epoxy resins cured with various hardeners; (2) the power factor (or dissipation factor) characteristics of some flexibilized epoxy resins; (3) the power factor (or dissipation factor) characteristics of some epoxy resins with reduced hydroxyl content; (4) the power factor (or dissipation factor) characteristics of some epoxy resins of different molecular weight. Except for the work on acetylated resins, the data reported herein was carried out several years

ago on epoxy resins commercially available at that time. While the trends observed in the change of power factor of dissipation factor with molecular structure and temperature are pertinent to today's resins, the absolute values of power factor observed today may be lower because of advances in purifying the resins and hardeners.

This observation, which is supported by some recent data, has been found to be especially true of the higher power factor, unmodified, epoxy resin systems and less pertinent to the low power factor systems.

EXPERIMENTAL PROCEDURES

Preparation of Polyester Resins

The linear polyesters were prepared by heating 3-2 or 6.5-6 molar ratios of acids to glycol under nitrogen to 200-220°C. until distillate ceased coming off, followed by heating under vacuum to 150°C. (10 mm.). In some runs a benzene flash azeotrope method was employed up to 200°C. to hasten the removal of water. Glyceryl adipate (acid equivalent weight = 151-156) and trimethylolethane adipate (acid equivalent weight = 167) were prepared by heating one mole of polyol with three of acid.

The acid equivalent weights of the lower molecular weight polyesters were within a few percent of the theoretical. The acid equivalent weights of the higher molecular weight polyesters averaged about 75-80% of the theoretical. This was due to the large effect of slight loss of glycol (in the nitrogen stream and during water removal) and the resulting effect of small amounts of unreacted acid on the acid equivalent weight of these systems.

Electrical Measurements

The electrical and physical properties of the resin mixtures were measured on cast sheets, usually $5 \times 5 \times \frac{1}{8}$ in. These were prepared in a mold made by forming Teflon-coated aluminum, backed with an adhesive to the shape of an open box and adhering the aluminum to a steel plate. Once the plate was leveled in an oven to assure uniform thickness in the casting, good castings could easily be made from this simple mold.

After painting on 2-3 in. silver electrodes, the dissipation factors were measured at room temperature and at 100°C. and above in a small air-circulating oven. Samples were left at temperature for $\frac{1}{2}$ hr. before measurements were made. Checks with thermocouples at 125-150°C. on the sample indicated that equilibrium temperatures in the resin were set up approximately 4°C. below the fixed oven air temperature within $\frac{1}{2}$ hr. and reported temperature readings were corrected for this factor. Power factors were measured at 10 volts/mil. on a Schering bridge.

Proportions of Hardeners Used

The epoxy content of the polyester-epoxy mixtures was calculated as that available after the epoxy-carboxyl reaction had occurred—one epoxy

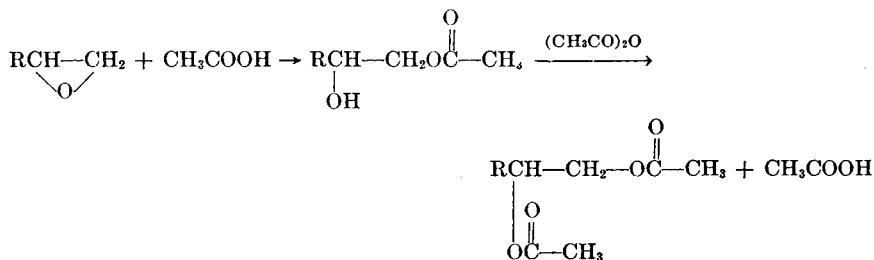
group consumed per carboxyl. An additional amount of 10% of the final epoxy content was estimated lost by the epoxy-hydroxyl reaction. Unless otherwise noted in the data, the amounts of various hardeners added to the polyester-epoxide resins were calculated on the "final" epoxy content as follows: *m*-Phenylenediamine, 15 parts/0.5 equivalents of epoxy; glyceryl adipate, 0.9 equivalents/1 equivalent epoxy; BF₃.monoethylamine, 9 parts/1 equivalent epoxy; pyromellitic anhydride-maleic anhydride mixture (21 g. pyromellitic anhydride to 19 g. maleic anhydride, 0.9 equivalents total anhydride/1 equivalent epoxide).

These proportions were set up by consideration of the amount of catalyst normally used with those commercially available epoxide resins whose epoxy content approximates 0.5 equivalent/100 g. of resin. The tetrapropenyl succinic anhydride used in this study is one of the isomeric dodecyl succinic anhydrides available for epoxy resin cures.

Modifications of Resins with Acetic Anhydride⁴⁴

Solid epoxy resin A—epoxy equivalent equal to 490 (100 g., 0.28 equivalents of hydroxyl according to the manufacturer) was dissolved in 100 ml. toluene and any water in the resin removed by azeotropic distillation. A solution of 100 ml. toluene and 156 g. acetic anhydride (1.53 m.) was prepared and a small amount of solution (20 ml.) distilled off to remove any acetic acid. The epoxy resin-toluene solution was then added dropwise over a period of 1.5 hr. to the anhydride solution at 115–120°C. in a 500 ml. flask fitted with Dean-Stark trap and condenser. The acetic acid formed was simultaneously removed as a toluene-acetic acid azeotrope by distillation. After the addition of resin was completed, the mixture was distilled until approximately 260 ml. of distillate had been removed. The residue was then vacuum distilled with final heating occurring at 157°C., 4 mm.

The resin was then used without further purification. Epoxy equivalents were estimated on the basis of the change in weight due to the acetylation, assuming 100% reaction. Although the theoretical epoxy equivalents were used to calculate the amount of hardeners to be added to the acetylated resins, a few subsequent experiments with resins of measured initial epoxy content and known hydroxyl content indicated that 7–20% of the original epoxy groups were consumed by side reactions during the acetylation procedure, i.e., by reactions such as



In one of these experiments, a small amount of acidic impurity, corresponding to 0.16% by weight of acetic anhydride, remained after the acetylation reaction. Infrared examination of one of these acetylated products indicated essentially a total absence of hydroxyl.

EPOXIDE ANALYSIS

Epoxide equivalents were either furnished in the manufacturer's literature, or measured by the pyridinium hydrochloride method.^{3,24} A 1-2 g. portion of resin was refluxed for 20 min. in 20 ml. of a solution of 16 ml. concentrated HCl diluted to one liter with pyridine. The resin solution was titrated with 0.1*N* alkali to the phenolphthalein endpoint. Acetone or alcohol was used to keep the resin in solution during the initial part of the titration. Dark colored solutions (for which a pH meter was necessary to determine the titration endpoint) could be avoided by carefully shaking the resin-pyridinium hydrochloride reaction mixture so that the resin dissolved in the warm pyridine solution before the refluxing began. The epoxide equivalent was determined by dividing the weight of resin by the equivalent amount of HCl consumed.

Although recent work²⁹ has shown that the accuracy of this method can be improved upon somewhat by using excess methyl alcohol as a solvent during the titration and by using methanolic alkali, the accuracy of the method used is deemed sufficient (probably within a few per cent of true values) for the purpose of this investigation.

EXPERIMENTAL RESULTS

Power Factor and Dissipation Factor as a Function of Curing Agent

Typical 60 cycle power factor vs. temperature curves of some cured epoxy resins are shown in Figure 1. At moderate temperatures, the polar groups are more or less rigidly locked in by the three-dimensional cross-linked polymer structure. The dipoles can hardly follow the field. There is little dipole-field interaction, little frictional heating and the power factor is low. As the ambient temperature increases, the resin relaxes (comparable to a second order transition in thermoplastics) and the dipoles are free to more easily follow the change in imposed A. C. field. The power factor accordingly rises. At still higher temperatures, the power factor drops. Here, loosening of the polymer structure and the attendant lowering of the viscosity of the polymer causes the frictional forces to decrease so that the power factor decreases. Finally, the power factor may rise rapidly as the temperature increases more and more. Here, ionic conduction,⁴³ as well as molecular movement involving normally sluggish, large, dipole-containing molecular segments, are a major contributing factor to the power factor.

This description⁴² of a power factor vs. temperature model of a thermo-setting epoxy resin, although admittedly an oversimplified one, is supported

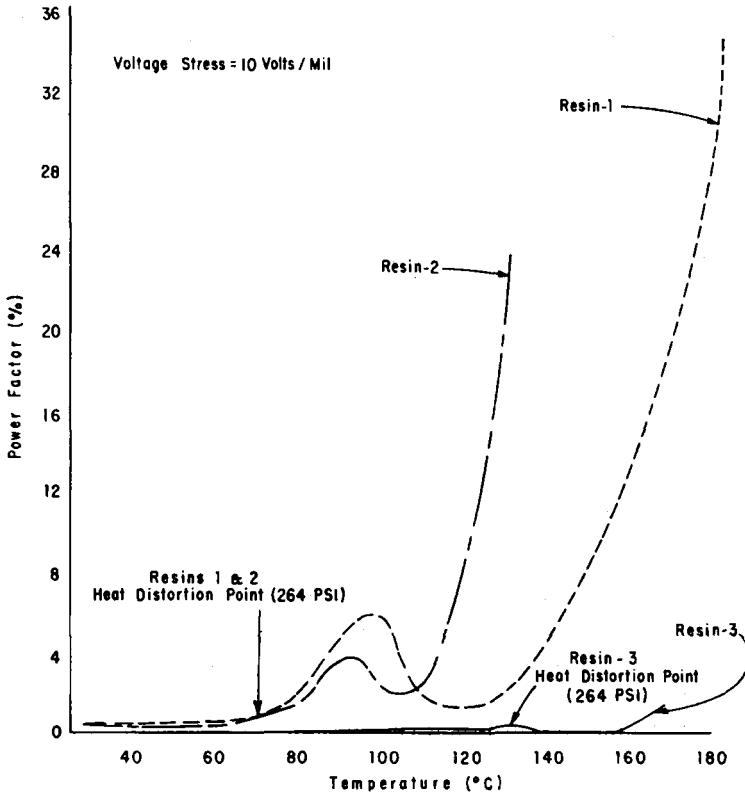


Fig. 1. 60 cycle power factor of some typical epoxy resin systems.

by similar features in other models theorized for the power factor vs. temperature dependence of thermoplastics such as polyethylene terephthalate³⁹ and other materials.^{4,8,9,21-23,27,32,34,35,46,47,50}

It is interesting to note that the 60-cycle power factor often starts to rise rapidly in the region of thermal softening^{9,14,22,38,50} or heat distortion point (Fig. 1). Although the latter measurement is an arbitrary one (taken at 264 psi fiber stress), it does denote a general region of softening temperatures and, therefore, the change in power factor is in accordance with the physical model relating to power factor changes. Finally, it should be pointed out that the behavior of the power factor of epoxy resins beyond the heat distortion point will vary, as will be discussed later, from hardener to hardener. Some curves rise rapidly while others rise at a much lower rate.

Table I gives some loss tangent and heat distortion point data of a low molecular weight liquid bisphenol A-based epoxy resin (epoxy equivalent equal to approximately 200) cured with a variety of hardeners.

The main deductions that can be drawn from the data are that the dissipation factor (and therefore the power factor) tends to rise with tempera-

TABLE I
Dissipation Factor of Various Epoxy-Hardener Combinations

Hardener	Amt. hardener, phr	Cure time, hr.	Cure temp., °C.	tan δ at various temp. ^a	Approximate heat distortion point, °C. (264 psi)
Glyceryl adipate	68.5	16	150	0.0035 (25°C.) 2.2 (125°C.)	<25
<i>m</i> -Phenylenediamine	15.0	16	150	0.0045 (25°C.) 0.005 (116°C.)	150
Mixture of 21 parts pyromellitic dianhydride + 19 parts maleic anhydride	46.5	16	150	0.013 (25°C.) 0.0095 (117°C.)	>200
BF ₃ -monoethylamine	4.5	16	150	0.0035 (25°C.) 0.028 (117°C.)	177
Piperidine	5.0	24	60	0.0034 (25°C.) 0.27 (125°C.)	120
2-Ethylhexanoate salt of tris(dimethylaminomethyl)phenol (Shell Catalyst D)	10.5	17	125	0.83 (165°C.)	92
		4	60	0.0037 (25°C.)	
		17	125	0.49 (125°C.)	
Phthalic anhydride	66.5	16	150	0.0021 (25°C.)	120
				0.053 (117°C.)	
				0.11 (148°C.)	
				0.053 (117°C.)	
Tetrapropenyl succinic anhydride ^b	118.0	16	150	0.12 (148°C.)	70
				0.057 (25°C.)	
				0.39 (125°C.)	
				0.19 (145°C.)	

^a Measurements made at 60 cycles/sec.; 10 volts/mil.; 1/8 in. thick sample.

^b One of the isomeric forms of dodecenyl succinic anhydride.

ture but does not rise excessively until temperatures beyond the heat distortion point are reached.³⁸ At room temperature, most of the loss tangents were fairly comparable. Also, anhydride-cured resins (when fully cured) gave lower loss tangents above their heat distortion points than the amine- or acid-cured systems that were evaluated.

Power Factor and Dissipation Factor of Flexibilized Epoxy Resins

The method chosen for flexibilizing the resins involved the use of carboxyl-terminated linear polyesters^{5,15,18,19,40,52} of the ethylene glycol and propylene glycol adipate series. The carboxyl-terminated polyesters were either prereacted with fluid low molecular weight epoxy resins (epoxy equivalent = 200) by heating at 150°C. until the acid was essentially consumed before addition of the hardener, or merely mixed into the resin along

TABLE II
Dissipation Factors of Some Flexibilized Epoxy Resins

Polyester used ^a	Cure of mixture	Polyester acid eq. wt.	Eq. ratio (epoxy/carboxyl) ^b	Polyester reacted or unreacted ^c	Hardener used ^d	Condition of cured resin ^e	Sample temp., °C.	tan δ^f	Sample temp., °C.	tan δ^f
None	16 hr., 150°C.				Glyceryl adipate	H	25	0.0035	125	2.2
PGA	16 hr., 150°C.	260	3	R		F		0.071	114	9.9
EGA	16 hr., 150°C.	242	5	R		Barely F		0.055	113	8.7
EGA	16 hr., 150°C.	965	3	R		F		0.130	102	8.1
EGA	16 hr., 150°C.	965	5	R		F		0.023	111	7.7 ^g
PGA	16 hr., 150°C.	893	11	U		F		0.077	117	4.1
PGA	16 hr., 150°C.	893 ^h	20	U		Barely F		0.063	117	4.1
None	16 hr., 150°C.				<i>m</i> -Phenylenediamine	H	25	0.0045	116	0.005
EGA	16 hr., 135°C.	242	3	U		H		0.008	114	0.99
EGA	16 hr., 135°C.	893	3	U		F		0.053	117	9.9
EGA	16 hr., 150°C.	965	5	R		F		0.035	103	9.6
EGA	16 hr., 150°C.	965	7	R		H		0.024	102	0.3
None	16 hr., 150°C.				Pyromellitic-maleic anhydrides	H	25	0.013	117	0.0095

PGA	16 hr., 150°C. ^b	893	3	U		F	0.028	113	6.6
PGA	16 hr., 150°C.	893	5	R		H	0.037	116	8.1
None	16 hr., 150°C.					H	25	117	0.028
EGA	16 hr., 110°C.	242	3	U	BF ₃ ·ethylamine	H	0.020	111	7.5 ^c
EGA	16 hr., 150°C.	242	3	R		H	0.012	111	7.6
EGA	16 hr., 100°C.	965	3	R		Resin not fully cured			

^a PGA refers to propylene glycol adipate. EGA refers to ethylene glycol adipate.

^b The equivalent ratio refers to the epoxy/carboxyl ratio of the epoxy resin and polyester.

^c Unreacted mixtures (U) refer to mixtures of polyester, hardener, and resin. Reacted mixtures (R) refer to mixtures where the polyester and epoxy resin were prereacted before addition of the hardener.

^d See experimental section for methods used to calculate amounts of hardeners used.

^e The condition of the cured resin refers to its room temperature flexibility (F) or rigidity (H).

^f All measurements made at 60 cycles/sec., 1/8 in. thick sample, 10 v./mil.

^g Measured at 6 v./mil.

^h In this mixture, the amount of hardener was in 10% excess over that calculated by methods given in experimental section.

with the hardener. There did not seem to be a large difference in dissipation factor ($\tan \delta$) between the two methods used, as far as gross effects were concerned. Prereaction did present the limitations of increasing the viscosity of the medium before the addition of hardener. Also, in some cases, particularly where the low molecular weight, high acid content, polyester resins were used as flexibilizers, care had to be taken to prevent gellation due to the acid-catalyzed hydroxyl-epoxy side reaction^{20,41} increasing the functionality of the system to a value greater than two. The experimental data on the flexibilized resins is given in Table II.

From our previous discussion, data in Table I and the work of others,^{13,38,40} it would be expected that the effect of introducing flexibility into the molecule (comparable to heating the resin above its heat distortion point) would be to increase the dissipation factor and the power factor. This was certainly shown to be the case, even at room temperature, where the cured resin itself is rigid. Of course, the contribution due to the polar nature of the polyester itself, the increase in dipolar hydroxyl content from the epoxy-carboxyl reaction and any unreacted carboxyl would also increase these dielectric loss properties.

A word about the various flexibilizer-curing agent combinations is in order. At a given epoxy/carboxyl ratio, the higher molecular weight polyesters are more effective in promoting flexibility. This is understandably due to the fact that the rigid epoxy chains are more fully separated by the higher molecular weight polyesters. Furthermore, because of their higher molecular weight, these polyesters lead to a greater amount of flexibilizer per (cured) resin volume.

Another interesting point is the flexibilizing effect of the different hardeners. Glyceryl adipate which is internally flexibilized itself, for example, required much less additional polyester flexibilizer to give room temperature flexibility than did the quite rigid *m*-phenylenediamine.

$\text{BF}_3 \cdot \text{ethylamine}$ did not fully harden some of the polyester-epoxy mixtures. This may be due to traces of moisture or alcohol in the polyester which occasionally have been known to cause inhibition of cure with this hardener. As a side note, hydroxyl⁵¹ has also been known to cause an acceleration of certain $\text{BF}_3 \cdot \text{ethylamine}$ -epoxy resin cures.

The Power Factor and Dissipation Factor Characteristics of Epoxy Resins With Reduced Hydroxyl Content

Since published data on other hydroxyl-containing resins and plastics^{11,47,48} had indicated that a reduction in dielectric loss factor and power factor could be expected by chemical conversion of hydroxyl groups, it was deemed of interest to examine epoxy resins where the hydroxyl was chemically modified to less ionizable, less mobile, organic functional groups. One would expect some⁴² but not a complete reduction in the power factor, because of the contribution of functional groups and ionizable impurities theoretically not affected by hydroxyl-conversion reactions. Also, the con-

verted hydroxyl groups would still be polar and therefore afford a dipole moment and dielectric loss.

The reaction chosen was that of acetylation⁴⁴



Under the proper acetylation reaction conditions, a majority of the epoxide groups remain unaffected although some side reactions (see Experimental Section) that consume epoxide groups do occur.

The resin chosen for modification by these methods was a high molecular weight solid epoxy resin, resin A, melting near 70°C., with an appreciable hydroxyl content (0.28 equivalent/100 g. according to the manufacturer's technical literature). The principal hardening agents investigated were glyceryl adipate, tetrapropenyl succinic anhydride, diethylene triamine

TABLE III
Modified Epoxy Resins Cured with Glyceryl Adipate
and Tetrapropenyl Succinic Anhydride

Epoxy resin	Eq. ratio hardener ^a	Hardener	Sample temp., °C.	tan δ ^b	Sample temp., °C.	tan δ ^b	Cured resin ^c
Resin A	0.9	Glyceryl adipate	25	0.003			Hard
Resin A, modified with acetic anhydride	1.1	Glyceryl adipate					Resin did not fully cure
Resin A	0.9	Tetrapropenyl succinic anhydride	25	0.002	115 145	0.054 0.076	Hard
Resin A, modified with acetic anhydride	1.1	Tetrapropenyl succinic anhydride	25	0.004	115 145	0.005 0.074	Hard
Resin A	1.0	Methylene dianiline	25	0.001	80 120 150	0.002 0.004 0.090	Hard
Resin A, modified with acetic anhydride	1.2	Methylene dianiline	25	0.004	80 120 150	0.010 0.019 0.290	Hard

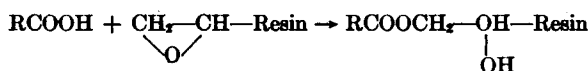
^a The equivalent ratio in the case of the acidic polyester is the ratio of equivalents of carboxyl to those of epoxy. In the case of anhydrides, the equivalent ratio was the ratio of moles of anhydride to equivalents of epoxy, and with amines, the ratio of equivalents of amine hydrogen to equivalents of epoxy. The difference in epoxy/hardener ratio between the acetylated and nonacetylated resins was due to loss of epoxy during the acetylation reaction. When the resin mixtures were prepared, the theoretical epoxy content of the acetylated resin calculated from the epoxy and hydroxyl content of the parent resin were used to estimate the amount of hardener. The values reported herein have been corrected for the measured epoxy content, subsequently determined.

^b All measurements were made at 60 cycles/sec. and 10 v./mil, 1/4 in. samples.

^c The cure was 15 hr. at 150°C.

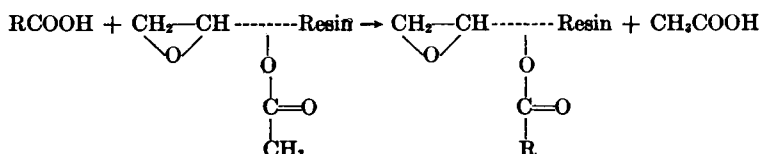
and methylene dianiline. The experimental results with an acetylated, present day, bisphenol A epoxy resin are given in Table III. However, a logical comparison of the power factor data of acetylated and unacetylated resins is complicated by the curing behavior observed for the acetylated resin.

In the first place, the acetylated resin failed to completely cure with the carboxyl terminated glyceryl adipate. This was unexpected since one of the curing mechanisms possible⁴¹

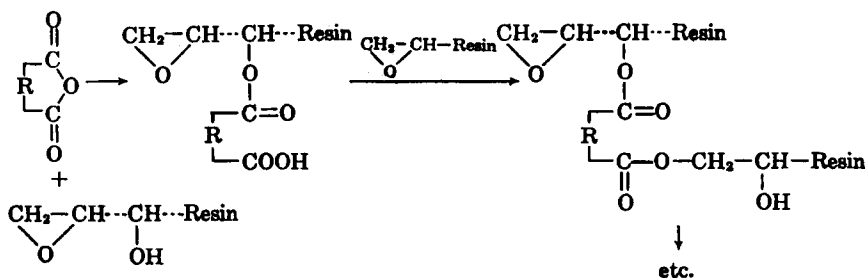


should not be affected by loss of initial hydroxyl.

Infrared analysis of the heated, acetylated epoxy resin-glyceryl adipate mixture still revealed the presence of considerable epoxy. This, coupled with the odor of acetic acid during the cure, indicated that the primary reaction of the hardener was a carboxyl interchange reaction instead of the desired epoxy-carboxyl reaction, the reaction being driven by the volatilization of acetic acid.



On the other hand, the acetylated resin could apparently be more fully cured with tetrapropenyl succinic anhydride, which was also surprising since the uncatalyzed anhydride curing mechanism^{16,17,20} would require the presence of hydroxyl to initiate the cure, i.e.,



Similar reactions have been reported for nonhydroxyl-containing epoxies and phthalic anhydride^{17,20} and have been attributed to impurities reacting with the anhydride to form the free acid and initiate the cure. It is felt that the cure of the acetylated resin can be explained by a similar mechanism or by traces of hydroxyl arising (see Experimental Section) from side reactions of the epoxy group during the acetylation reaction.

This "impurity" theory would account for an observation made several years ago on the noncuring of certain acetylated epoxy resin systems with

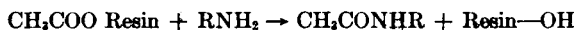
tetrapropenyl succinic anhydride at 150°C. Another contribution to the apparent noncuring of the acetylated resin-anhydride systems would arise from the volatilization of anhydride from small samples during heating, before the anhydride could react with the epoxy resin. The decreased rate of reaction could easily be attributed to lack of initial hydroxyl.

Although one can theorize methods whereby the anhydrides could cure specific lots of acetylated resin, the apparent greater ability of tetrapropenyl succinic anhydride to cure the acetylated resin, as compared to glyceryl adipate, cannot be presently explained; particularly since the anhydride cure proceeds through a carboxyl (monoester) intermediate. Limited experiments using increased equivalent ratios of carboxyl to epoxy to compensate for the doubled "potential carboxyl" content of an anhydride, as compared to its parent carboxylic acid, have also thus far failed to satisfactorily explain this discrepancy.

Bulk experiments with several primary and tertiary amines indicated that, except for the more volatile amines, they would harden the acetylated resin but generally at much slower rate than the nonacetylated resin. Also, in contrast to the nonacetylated resins, thin films cast from solution and heated in an oven could only be cured when amines of extremely low volatility, such as methylene dianiline, were used. This is presumably due to volatilization of most of the hardener from the thin films before it could react with the epoxide.

The slowness of the amines in curing the acetylated epoxy resins can be attributed to the lack of initial hydroxyl groups. With primary or secondary amines⁴¹ and probably with tertiary amines, the acceleration of the amine-epoxy reaction by hydroxyl would be largely lost. Also, with tertiary amines, the reduced extent of the hydroxyl-epoxy reaction⁴¹ would probably play an even more significant part in reducing the rate of cure. The slower rate of cure of the acetylated resins, even as compared to normally low hydroxyl content, low molecular weight epoxy resins, is probably associated with the much lower epoxy content of the acetylated resins and with the correspondingly lower amounts of hardener used.

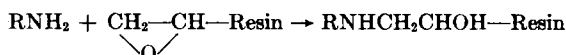
Even though the loss of some epoxy groups during the acetylation would account for some of the observed retardation of rate, it is not considered sufficient to account for the full extent of the retardations of cure observed. Infrared analysis of diethylenetriamine-acetylated resin films indicated that a further reaction leading to retardation or inhibition of cure of the acetylated resin with primary and secondary aliphatic amines could be ascribed to amidation.^{1,33}



The dissipation factor of the acetylated resin cured with tetrapropenyl succinic anhydride was lower at certain elevated temperatures than that of the cured unacetylated resin. The opposite was true of the methylene dianiline-cured resins. As stated above, no attempt has been made to explain these differences, since the unknown extent of the side reaction with

these cures precludes any true comparison with the unacetylated resins or between the acetylated resins cured with the different hardeners.

Thus, even though one might expect a difference on comparing the anhydride cured samples, in which the hydroxyl content is not changed appreciably during the cure,¹⁷ with the amine cured samples, in which there is an increase,



it is not known whether the observed changes are due to the products of the side reaction, slightly different amounts of hardeners used with the acetylated resins, or different cure mechanisms involving groups other than epoxies.

Power Factor and Dissipation Factor as a Function of Molecular Weight

Since the power factor of the cured epoxy resins seemed to be closely allied with the degree of rigidity of the epoxy resin polymer, our attention was turned towards resins of increased molecular weight. Because of their reduced epoxy content, the increased proportion of epoxy resin in these higher molecular weight epoxy resin mixtures would lead to a higher phenyl content and, with most of the hardeners investigated in the work, to more rigid resins, even in spite of the correspondingly lower crosslinking density.

Two types of hardeners were used in these studies, an acid-terminated ester, glyceryl triadipate or trimethylolethane triadipate and anhydride hardeners such as tetrapropenyl succinic anhydride and phthalic anhydride. This choice was aimed at observing any effect of hydroxyl content, i.e., carboxylic acids form hydroxyls during cure, while anhydrides do not appreciably increase the overall hydroxyl content.^{16,17,20} Also, the degree of flexibility afforded by the hardeners themselves would be quite different, decreasing in the order glyceryl adipate \cong trimethylolethane adipate > tetrapropenyl succinic anhydride > phthalic anhydride.

Commercially available epoxide resins of differing molecular weight were used for the resinous components in the mixtures. As pointed out above, this work was carried out several years ago, on epoxy resins available at that time. The experimental results are shown in Table IV. Table IV also gives some of the approximate hydroxyl contents calculated for the cured resins.

Examination of the data obtained from the resins cured with glyceryl adipate revealed a marked decrease in elevated temperature dissipation factor and power factor with the very high molecular weight resins. This is understandably due to an increase in rigidity because of the nature of the cured resin changing from one of a highly flexible polyester to one of a more rigid phenyl-containing ether.

Even though the amount of hydroxyl estimated in the acidic polyester-cured samples is an approximation, in view of the assumptions involved

in the calculation, the errors involved are probably small. The hydroxyl content can safely be estimated to be in comparable amounts in all the resin mixtures and could not account for the change in power factor observed. The effect of hydroxyl on power factor and dissipation factor in these mixtures, is, therefore as expected, secondary to the structural effects. Although an abrupt decrease in loss tangent or power factor above an epoxy equivalent of 564 was observed, a more gradual transition would be expected. The reason for this is not known, and may have been due to impurities of some type in some of the higher molecular weight resins used. That this may be a real effect involving the result of increased rigidity being counterbalanced by increased hydroxyl content is not ruled out, but would involve more extensive studies with other series of epoxy resins. The effect of decreasing power factor with prolonged cure¹⁴ beyond 16 hr. at 150°C. seems definite, but secondary to the structural effects pointed out above.

Although the effect of change in hardener/resin ratio has been minimized by using comparable epoxy/carboxyl ratios, this is still considered an important variable in determining elevated temperature power factor, as seen by the data for resin E—trimethylolethane adipate mixtures.

With tetrapropenyl succinic anhydride, we again had a marked drop-off in dissipation factor (or power factor) with increasing molecular weight of the epoxy resin used. Here, the reduction occurred at a lower molecular weight of epoxy resin used. That this was due to structural changes in the resin and not hydroxyl content is quite apparent from the fact that the resin mixtures of highest hydroxyl content have the lowest loss tangent. The importance of fully curing the lower molecular weight resins with this slow curing anhydride may be seen from data on resins B and C.

A practical point of interest is that these anhydride-cured resins have rather low power factors at temperatures far above their heat distortion points. Furthermore, the presence of a very small amount of high molecular weight resin effected a marked decrease in elevated temperature power factor with tetrapropenyl succinic anhydride cures and an increase in rate of cure. This allows the use of more handleable, fluid, lower molecular weight resins.

The lowering of the elevated temperature power factor of the low molecular weight resins by addition of small amounts of higher molecular weight resins was felt to be largely due to the benefit of initially added hydroxyl. The higher molecular weight resins thereby increased the crosslinking density and rate of cure by affording a highly polyfunctional polymerization initiator.

A further factor leading to a higher state of cure (and lower power factor or loss tangent) with the higher molecular weight resin mixtures would be a lesser extent of volatilization of unreacted anhydride¹⁷ with the faster curing materials.

With the more rigid phthalic anhydride the effect of adding small amounts of higher molecular weight resin was much smaller and not as

TABLE IV. Dissipation Factor of Epoxy Resins of Varying Molecular Weight

Resin	Epoxy eq. wt.	Eq. ratio carboxyl ^a or anhydride	Cure	Sample temp., °C.	tan δ^b	Calculated hydroxyl concentration (eq./100 g.) in cured resin
A. Glyceryl adipate curing agent ^c						
B	202	0.906	16 hr. 150°C.	25	0.0035	0.31
				126	2.8	
C	200	0.902	72 hr. 150°C.	25	0.0039	0.31
				126	1.9	
			16 hr. 150°C.	25	0.0028	
D	564	0.907	72 hr. 150°C.	25	0.0041	0.39
				126	1.5	
			16 hr. 150°C.	117	1.7	
E	1007	0.900	72 hr. 150°C.	25	0.0026	0.38
				126	1.8	
B. Trimethylolethane adipate curing agent						
E	1007	0.885	16 hr. 160°C.	25	0.0011	0.38
				117	0.11	
E	1007	0.928	16 hr. 150°C.	120	0.39	0.38
				130	0.92	
E	1007	0.928	16 hr. 150°C.	25	0.0008	0.38
				121	0.13	
C. Tetrapropenyl succinic anhydride curing agent ^d						
B	202	0.900	16 hr. 150°C.	25	0.057	0.036
				119	0.99	
C	200	0.900	80 hr. 150°C.	145	0.19	0.036
			16 hr. 150°C.	125	0.39	
			4 hr. 130°C.	145	0.19	
			80 hr. 150°C.			

apparent. This may be due to the fact that the effects of increased rate of cure and crosslinking density would be most apparent with slower curing, more flexible systems of the tetrapropenyl succinic anhydride type. With the phthalic anhydride cures, any changes in rigidity due to the crosslinking density and phenyl content would be masked by the large phenyl content of the hardener itself, the relatively faster rate of cure and the softening effect of diluting the higher crosslinking epoxy group density in the lower molecular weight resin with higher molecular weight resin.

As noted above, because of the change in the purity of commercially available resins and hardeners in recent years, the high dissipation values reported herein would be considerably lower with today's resins, but the trends observed as a function of molecular weight would be the same. In fact, relatively pure grades of tetrapropenyl succinic anhydride will not

TABLE IV (continued)

Resin	Epoxy eq. wt.	Eq. ratio carboxyl ^a or anhydride	Cure	Sample temp., °C.	tan δ ^b	Calculated hydroxyl concentration (eq./100 g.) in cured resin
100 pts. C		0.900	16 hr. 150°C.	145	0.043	0.089
60 pts. D						
100 pts. C		0.900	16 hr. 150°C.	125	0.018	0.048
10 pts. D				145	0.053	
D	564	0.895	16 hr. 150°C.	25	0.0025	0.23
				147	0.035	
E	1007	0.900	16 hr. 150°C.	25	0.003	0.27
				120	0.009	
				147	0.049	
D. Phthalic anhydride curing agent						
C	200	0.900	16 hr. 150°C.	117	0.053	
				148	0.11	
			32 hr. 150°C.	117	0.053	
				148	0.12	
100 pts. C		0.900	16 hr. 150°C.	117	0.028	
10 pts. D				146	0.12	

^a The equivalent ratio is the ratio of equivalents carboxyl or moles anhydride to equivalents of epoxy.

^b Measurements made at 10 v./mil, 1/8 in. thick samples.

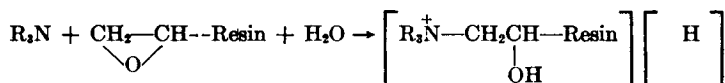
^c The hydroxyl content was calculated by adding the initial hydroxyl content (from available technical literature) and the hydroxyl formed by the carboxyl-epoxy reaction, assuming complete reaction, and assuming that no hydroxyl-carboxyl and little hydroxyl-epoxy reaction occurred.

^d The hydroxyl content was calculated on the basis of no change from initial hydroxyl content during the cure.^{16,17,20}

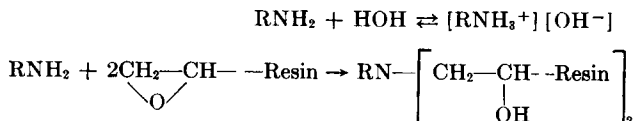
cure today's epoxy resins of low molecular weight within 15 hr. at 150°C. without the addition of polyhydroxy initiator or acidic or basic catalysts.

The previously mentioned lower power factor and dissipation factor of the anhydride-cured resins at elevated temperatures above the heat distortion point, as compared to amine and acidic polyester cured resins, deserves some comment. The higher elevated temperature power factors of the amine-cured resins can in large part be attributed to the presence of ionizable materials or so-called "polyelectrolytes"⁴³ arising in the cure.

While these ionizable materials would most naturally arise in cures with tertiary amines



or would be present with amine salt-curing agents, their presence in the case of primary amines can arise either by direct ionization or by going through a tertiary amine stage.



Even though the extent of both these reactions is admittedly small, the effect of a small amount of ionizable impurity on the elevated temperature power factor is probably large.^{42,43}

With the acidic polyesters, the combination of flexibility plus the possibility of unreacted ionizable carboxyl probably contributes to the high power factor observed. However, the anhydride cured materials presumably have some unreacted carboxyl, in the form of monoester.^{16,17} Therefore, the rather low loss factors of such anhydride-cured resins in the flexible region above the heat distortion point indicates that other factors, possibly hindered dipolar rotation of some type, may be involved.

Although not elaborated on by the present data, a small variation in hardener content might be expected to have a significant effect on the elevated temperature power factor as well as on other properties.¹⁰ This effect has also been shown to be appreciable on some of the heat aging properties of phthalic anhydride-cured resins.¹⁷ This would be particularly true of amine-accelerated anhydride cures where the curing mechanism imposes a rigid stoichiometry of one mole anhydride to one equivalent of epoxy.^{10,41} In the uncatalyzed resins studied here, the optimum stoichiometry was considered to be less than 1.0, primarily due to the side epoxy-hydroxyl and epoxy-epoxy reactions.

Lastly, these studies are concerned with 60 cycle frequencies and specific temperatures. At other frequencies and temperatures, the relative behavior of some of these systems may be somewhat different due to different dissipation factor vs. frequency and temperature profiles.

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Synopsis

At temperatures far below the heat distortion point, the dissipation factor (and therefore power factor) of epoxy resins is comparably low—in the order of 0.001–0.01. Internally flexibilized, polyester-modified resins may have higher loss tangents, in the order of 0.01–0.10, even at room temperature. At temperatures far above the heat distortion point, anhydride curing agents give lower dissipation factors than do amines or acids. With anhydride cures, the higher molecular weight resins investigated cure faster than the lower molecular weight resins, give lower elevated temperature power factors and loss tangents, and are tougher. With any hardener–epoxy resin system, the optimum elevated temperature power factor, weight loss on aging and heat distortion point will probably depend on a close examination of the optimum hardener/resin ratio.

With certain anhydride-cured low molecular weight epoxy resin systems, an increased rate of cure and lower elevated temperature power factor may be obtained by use of a small amount of higher molecular weight (polyhydroxy) epoxy resin. Attempts to compare the effect on power factor of changing the hydroxyl groups to less mobile dipoles by acetylation were unsuccessful, since the resulting acetoxy groups changed the cure mechanisms. However studies with resins of different molecular weights indicated that the effect of hydroxyl content on elevated temperature power factor is subordinate to other effects such as the rigidity of the cured resin system, rate of cure and ionic impurities. Acetylation of hydroxyl-containing epoxy resins may inhibit cure with some curing agents, due to side reactions of the resulting acetoxy group with specific hardeners.

Résumé

A des températures bien inférieures au point de distorsion, le facteur de dissipation (et dès lors le facteur de puissance) des résines époxydes est assez bas—de l'ordre de 0.001–0.01. Par plastification interne, des résines polyesters modifiées peuvent avoir des pertes tangentielles plus élevées, de l'ordre de 0.01–0.10, même à température de chambre. A des températures loin au-dessus du point de distorsion, les anhydrides de post-traitement donnent des facteurs de dissipation plus faibles que ne le font les amines ou les acides. Avec des agents à base d'anhydride, les résines de plus haut poids moléculaire étudiées se durcissent plus rapidement que les résines de plus bas poids moléculaire, donnent les facteurs de puissance plus faibles à température élevée et de plus faibles pertes tangentielles, et elles sont plus résistantes. Avec chaque système de résine époxy-renforcée, le facteur de puissance optimum à température élevée, la perte de poids par vieillissement et le point de distorsion à la chaleur dépendront probablement d'un examen serré du rapport optimum durcissant-résine. Avec certains systèmes de résines-époxy de faible poids moléculaire et d'anhydride, on peut obtenir un accroissement de la vitesse de durcissement; une diminution du facteur de puissance à température élevée en employant de faibles quantités de résine époxy (polyhydroxy) de plus haut poids moléculaire. Des essais de comparaison de l'effet du changement des groupes hydroxyles en dipôles moins mobiles, par acétylation, sur le facteur de puissance se sont révélés sans succès, étant donné que les groupes acétoxy-lés ont changé le mécanisme du post-traitement. Toutefois des études avec des résines de différents poids moléculaires montrent que l'effet de la concentration en hydroxyles sur le facteur de puissance à température élevée est subordonné à d'autres effets comme la rigidité du système de résine utilisé, la vitesse de traitement et des impuretés ioniques. L'acétylation des résines époxy renfermant des hydroxyles peut inhiber le post-traitement avec quelques agents durcisseurs, par suite de réactions secondaires du groupement acétoxy résultant avec des agents de durcissement spécifiques.

Zusammenfassung

Bei Temperaturen weit unterhalb des Wärmefestigkeitspunktes ist des Dissipationskoeffizient (und damit der Verlustfaktor) von Epoxydharzen verhältnismässig niedrig,

in der Grössenordnung von 0,001 bis 0,01. Bei innerer Weichmachung können polyester-modifizierte Harze sogar bei Raumtemperatur einen höheren Verlusttangens, in der Grössenordnung von 0,01 bis 0,10 besitzen. Bei Temperaturen weit oberhalb des Wärmefestigkeitspunktes liefern Anhydridhärter niedrigere Dissipationskoeffizienten als Amine oder Säuren. Bei Anhydridhärtung werden die untersuchten, höhermolekularen Harze schneller ausgehärtet als die niedrigermolekularen Harze, liefern niedrigere Verlustfaktoren bei erhöhter Temperatur und sind zäher. Bei jedem Härter-Epoxyharzsystem werden wahrscheinlich der optimale Verlustfaktor bei erhöhter Temperatur, Gewichtsverlust bei der Alterung und Wärmefestigkeitspunkt nur durch eine genaue Einstellung des optimalen Härter-Harzverhältnisses erhalten werden. Bei bestimmten anhydrid-gehärteten niedermolekularen Epoxyharzsystemen kann durch Anwendung einer kleinen Menge eines höhermolekularen Polyhydroxy-Epoxyharzes eine erhöhte Härtungsgeschwindigkeit und ein niedrigerer Verlustfaktor bei erhöhter Temperatur erhalten werden. Versuche, den Einfluss einer Umwandlung der Hydroxylgruppen in weniger bewegliche Dipole durch Acetylierung auf den Verlustfaktor festzustellen, blieben ohne Erfolg, da durch die gebildeten Acetoxygruppen der Härtungsmechanismus geändert wurde. Untersuchungen an Harzen mit verschiedenem Molekulargewicht zeigten jedoch, dass der Einfluss des Hydroxylgruppengehaltes auf den Verlustfaktor bei erhöhter Temperatur gegen andere Einflüsse, wie Starrheit des gehärteten Harzsystems, Härtungsgeschwindigkeit und Verunreinigung durch Ionen zurücktritt. Die Acetylierung von hydroxylhaltigen Epoxyharzen kann die Härtung mit gewissen Härtern wegen der Nebenreaktionen der gebildeten Acetoxygruppe mit spezifischen Härtern, verhindern.

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