

Polyesters from Bisacid A2. Electrical Properties of Glass Fiber Laminates

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Synopsis

The preparation and purification of bisacid A2, the preparation of crosslinkable polyesters from bisacid A2, and some of the properties of the resulting resins and laminates have been reported in earlier communications.¹⁻⁷ This paper reports the surface and volume resistivities of laminates according to B.S. 2782 as well as their dielectric loss and permittivity at 23°C over a frequency range of about 9 decades and discusses the significance of the results.

INTRODUCTION

There exists a theoretical analogy in all dynamic stress systems. This is borne out by the fact that the mathematical treatment is identical irrespective of the specific force field employed.

Some workers have determined both mechanical and dielectric relaxation spectra with the aim of correlating these and of obtaining a structural interpretation. Among their papers the following should be mentioned: An article by Koppelman⁸ which lists among its nine references individual and team contributions from Würstlin, Thurn, Wolf, Becker, Sommer and others; a general review paper by Koppelman,⁹ dealing with the molecular interpretation of relaxation processes—mechanical as well as dielectric—read at a meeting of physicists in Höchst (1965) and subsequently published, containing 42 references; a review article by Hoffman¹⁰ which also quotes basic reading sources to which might be added Fröhlich's book on the *Theory of Dielectrics*¹¹; a review article by Mikhailov and Sazhin¹² containing 46 references; Mathes' chapter in the book on *Engineering Design for Plastics*¹³; and Deutsch, Hoff, and Reddish's review paper of 1951.¹⁴ As far as polyesters are concerned, the classical paper by Reddish¹⁵ on poly(ethylene terephthalate) deserves especial mention since it is one of the earliest exhaustive reports, including a structural interpretation, of the dielectric relaxation spectrum of a specific material which covers both a wide frequency and a wide temperature range and established the "contour map" type representation of dielectric properties of polymers.

Although Koppelman and his colleagues concerned themselves mainly with PVC and acrylics, Koppelman's researches are also notable for the

introduction and systematic examination of pressure as a further variable in dielectric relaxation spectra *in addition to* temperature, and for using the results for molecular interpretations based upon cooperative translational effects of chain elements and upon free volume concepts.^{16,17}

The determination of dynamic spectra sheds light on the molecular and morphologic structure of materials in that it identifies peaks of energy absorption in terms of frequency at constant temperature or in terms of temperature at constant frequency. Both variables may be accommodated in three-dimensional plots showing characteristic response surfaces. The frequency at an absorption peak represents the mean value for the inverse relaxation time of the volume elements upon which the specific force fields acts. In the case of dielectric loss spectra the volume elements involved are electrical dipoles.

The importance of temperature effects becomes obvious when it is borne in mind that relaxation processes can only take place when two preconditions are fulfilled: (a) The energy supplied to the process must be sufficient to enable a volume element to surmount the activation energy barrier which separates neighboring energy valleys (which in turn represent alternative stable states); (b) the volume element must possess sufficient freedom of movement to enable it to effect the transition, that is to say, there must be enough free volume and the jump into the next energy valley must be unimpeded by other obstructing volume elements.

In the case of polymers, there exists the further proviso that any volume element about to change its position requires cooperation from neighboring volume elements to which it is spatially related or even chemically attached. All these preconditions are interdependent. Thus, an increase in temperature energizes the volume elements, increases free volume owing to thermal expansion, reduces the activation energy barrier in relation to the enhanced energy of the diffusing volume element, and facilitates cooperation between neighboring volume elements on statistical grounds.

Clearly, therefore, for any process to occur at all, it is necessary that a certain minimum temperature be exceeded. The most important threshold temperature is the glass transition temperature beyond which the movement of main chain segments becomes significant. Below this temperature it is, however, possible that movements may occur which represent secondary transitions and show up as additional absorption peaks. The secondary transitions involve vibrational or rotational motions of local side chains.

The present investigation was carried out at room temperature (23°C) only, and therefore the relaxation phenomena were restricted to those which are assigned to secondary transitions. Since more or less densely crosslinked systems are involved, only minor effects were anticipated, namely, those which reflect crosslink density (degree of freedom) and minor, though conceivably significant, differences arising from the varying hydrophobicity of the constituent groups and the number of actual dipoles present.

The surface and volume resistivity measurements, as distinct from the dielectric measurements, are static and not dynamic in nature. They are not suitable for purposes of structural interpretations, but they do give an indication as to the suitability of an insulating material under the chosen test conditions (500 V, 23°C). These test conditions, though arbitrary, are reasonably representative of applied static electric fields for which plastics are commonly considered as insulating materials.

EXPERIMENTAL

The dielectric measurements were carried out on two sets of instruments: one set in the electronic engineering department of the Polytechnic of the South Bank and the other set in the Physics Research Department of I.C.I. Plastic Division. The two sets of results were identical up to 1 MHz, which was as far as the Polytechnic instruments ranged. The I.C.I. instruments continued measurements up to 600 MHz.

The Polytechnic instruments comprised (a) a C3060 Precision Decade Capacitance Bridge, to cover the frequency range from 80 Hz to 80 kHz; this instrument is fully described in a technical instructions booklet provided by the makers (H. W. Sullivan Ltd., England), and its theory is based on the fundamental ideas of Brooks and Holtz¹⁸ and of Deacon and Hill.¹⁹ (b) A Wayne Kerr Capacitance/Conductance Bridge B201, to cover frequencies from 100 kHz to 1 MHz; this instrument is also described in an appropriate instruction manual (No. TP 20/2) provided by the makers.

The I.C.I. instruments consisted of (a) a modified Hartshorn and Ward capacitance bridge as described in a recent paper by Reddish and his colleagues²⁰ which covered the radio frequency part of the spectrum up to 100 MHz; (b) a reentrant cavity apparatus developed by Reddish and his colleagues from that described by Parry,²¹ to cover frequencies from 100 to 600 MHz.

The surface and volume resistivities of polyester laminates were determined according to B.S. 2782, Part 2, Methods 202A and 203A, on a 20-Million Megohmmeter as described in the manual supplied by the instrument makers (Electronic Instruments Ltd., Richmond, Surrey, England).

All specimens were glass-reinforced polyester sheets made from a liquid resin containing 48% styrene, except for the commercial resin of high acid value, which contained only 31% styrene.

RESULTS

There is a general pattern in all dielectric loss curves (Figs. 1-4). After a slight initial decrease in loss between 60 Hz and 1 kHz, a broad peak is ascended which reaches a maximum between 1 and 10 MHz, whereupon the dielectric loss decreases again.

There are, however, differences in the amplitudes of the curves. It was thought that these might correlate to one or more of the following factors:

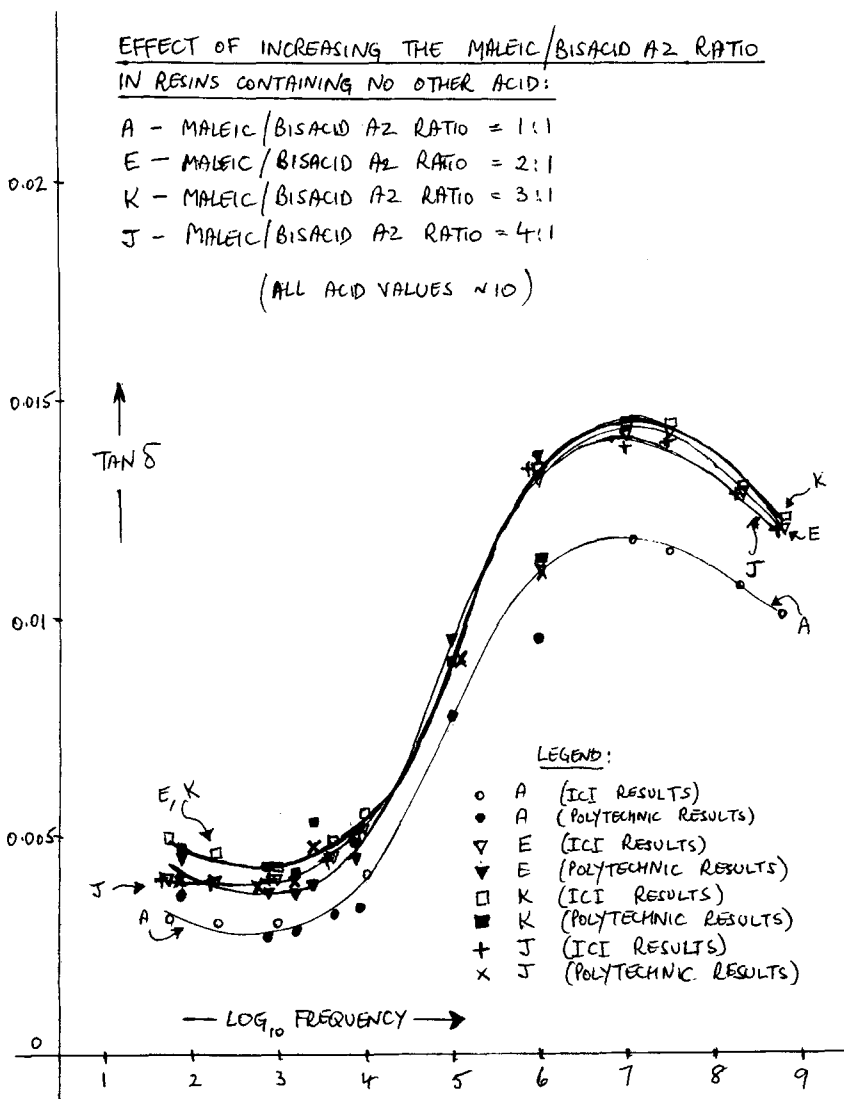


Fig. 1. Variation of $\tan \delta$ with frequency of polyester laminates. Effect of increasing the maleic/bisacid A2 ratio in resins containing no other acid: (A) maleic/bisacid A2 ratio = 1:1; (E) maleic/bisacid A2 ratio = 2:1; (K) maleic/bisacid A2 ratio = 3:1; (J) maleic/bisacid A2 ratio = 4:1. (All acid values ~ 10 .)

(i) variation in acid value at constant composition; (ii) the use of different maximum temperatures during the cocondensation reaction at constant composition and constant acid value; (iii) changes in maleic/bisacid A2 ratio in the series of resins where these were the only acids involved in the cocondensation reaction (series II resins); (iv) differences due to commercial scale and laboratory scale production.

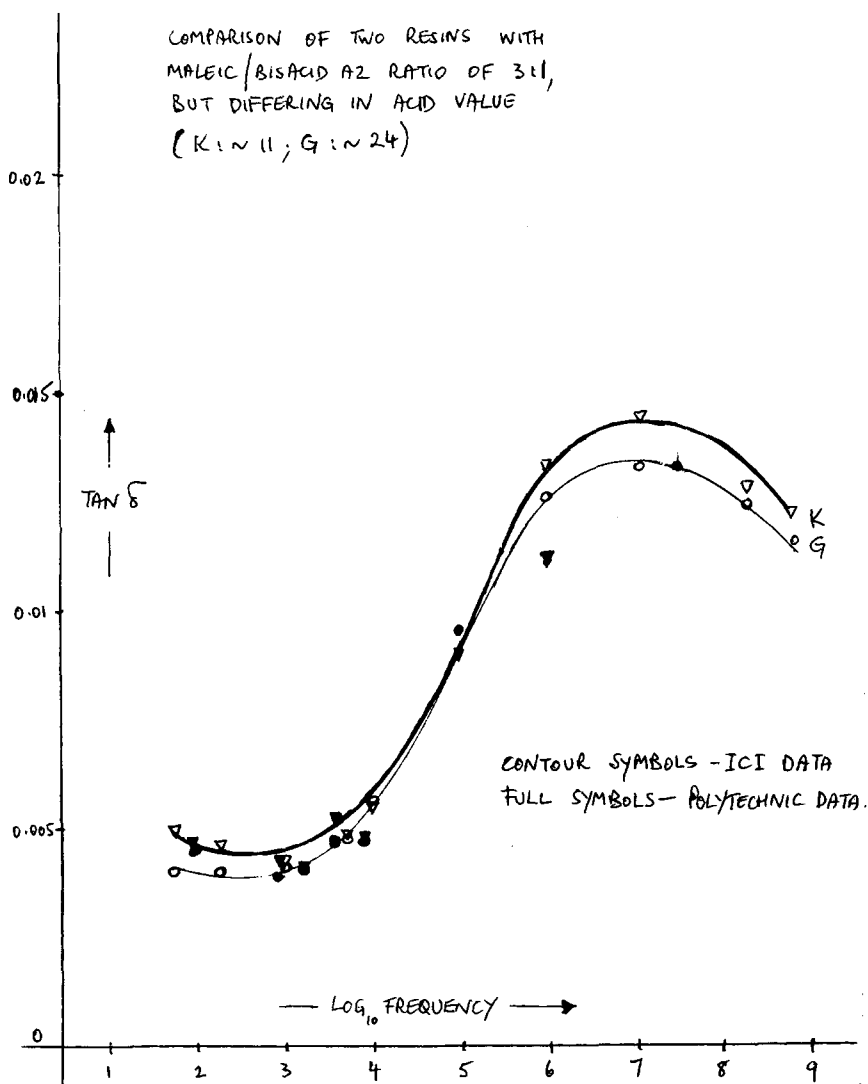


Fig. 2. Variation of $\tan \delta$ with frequency of polyester laminates. Comparison of two resins with maleic/bisacid A2 ratio of 3:1, but differing in acid value (K: ~11; G: ~24). Contour symbols, ICI data; full symbols, polytechnic data.

In order to investigate and interpret these factors, the results are presented in Figures 1 to 4. The loss spectra were determined at 23°C only, and it is appreciated that contour maps involving a wide temperature range as well as a wide frequency range would be necessary in order to describe the full dielectric behavior pattern of a material. Examples of this technique are given in references 14 and 15.

Permittivities were determined up to 1 MHz. These are set out Table I. It is seen that the minute and linear decrease in permittivity

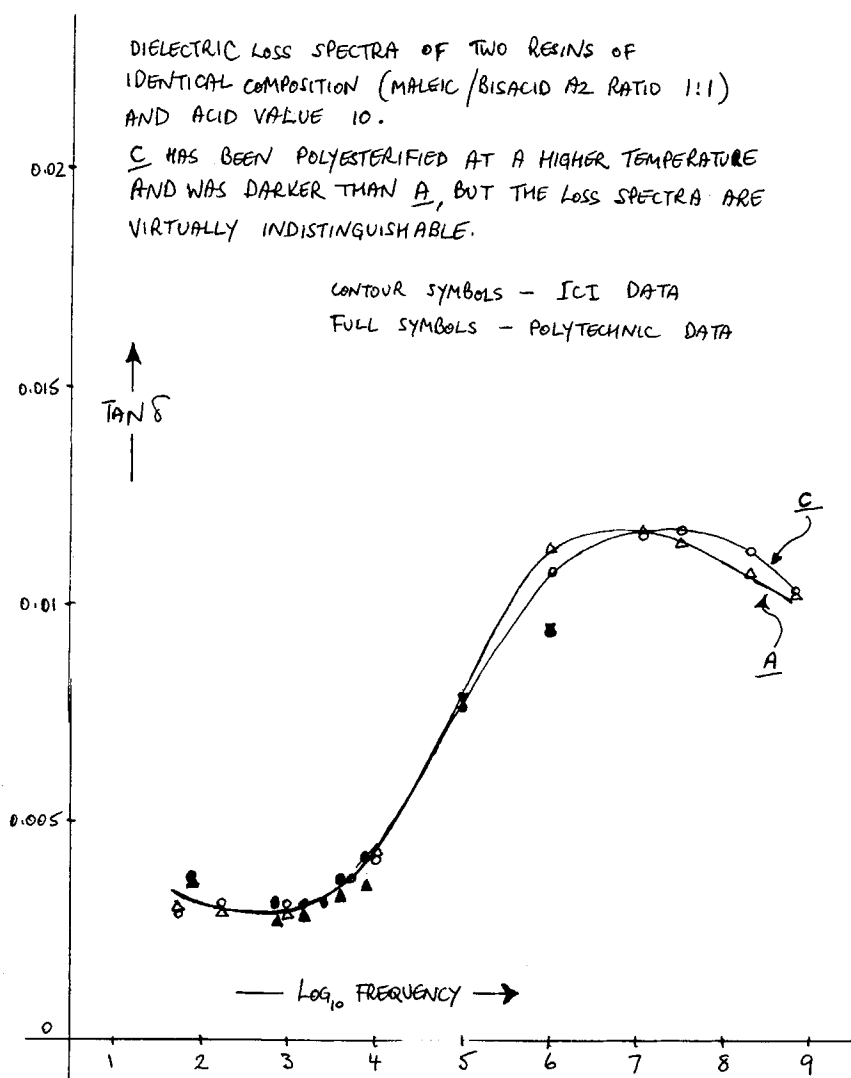


Fig. 3. Variation of loss tangent with frequency of polyester laminates. Dielectric loss spectra of two resins of identical composition (maleic/bisacid A2 ratio 1:1) and acid value 10. C has been polyesterified at a higher temperature and was darker than A, but the loss spectra are virtually indistinguishable. Contour symbols, ICI data; full symbols, polytechnic data.

up to about 10 kHz is a common feature and, equally, that a small but significant drop occurs in the subsequent transition region which coincides with the loss peak. Had the permittivities been determined beyond 10 kHz as far as 1000 MHz, one would have expected a sigmoid overall curve to appear in which the linearity beyond the transition region mirrors the linearity prior to the transition region.

The volume and surface resistivity results are given in Table II.

TABLE I
Permittivities from 80 Hz to 1 MHz at 23°C^a

Freq.	log ₁₀ freq.	Permittivities								
		A	B	C	D	E	F	G	J	K
80 Hz	1.9	3.56	3.96	3.68	3.94	3.65	3.81	3.81	3.63	3.71
800 Hz	2.9	3.55	3.91	3.66	3.93	3.63	3.79	3.79	3.61	3.70
1.6 kHz	3.2	3.55	3.91	3.65	3.91	3.62	3.78	3.78	3.61	3.70
2.4 kHz	3.4	—	3.89	3.64	3.91	3.61	—	—	—	—
4 kHz	3.6	3.54	3.88	3.64	3.90	3.61	—	3.77	3.61	3.68
8 kHz	3.9	3.53	—	3.63	3.90	3.61	3.74	3.76	3.61	3.65
100 kHz	5.0	3.52	3.80	3.62	3.86	3.58	3.73	3.74	3.56	3.61
1 MHz	6.0	3.49	3.73	3.59	3.82	3.54	3.70	3.69	3.53	3.58

^a Sample letters A to K refer to resin compositions; these are given in Table II; their respective thicknesses are 1.60, 1.52, 1.65, 1.58, 1.58, 1.62, 1.53, 1.56, 1.54 mm.

TABLE II
Volume and Surface Resistivities of Laminates

Sample	Composition	A.V.	Styrene, %	Volume resistivity, (ohm cm) ×10 ⁻¹⁴	Surface resistivity, ohm ×10 ⁻¹³
D	maleic/phthalic resin 1:1 (lab-made)	10	48	2.1	4.1
B	maleic/phthalic resin 1:1 (commercial)	34	31	1.8	9.4
F	bisphenol- glycol resin (commercial)	10	48	2.6	6.7
A	maleic/bisacid A2 resin 1:1 (sl. over- cooked)	10	48	2.6	4.1
C	maleic/bisacid A2 resin 1:1	10	48	1.3	4.3
E	maleic/bisacid A2 resin 2:1	10	48	2.8	2.3
K	maleic/bisacid A2 resin 3:1	10	48	4.4	11.0
G	maleic/bisacid A2 resin 3:1	24	48	3.3	11.0
J	maleic/bisacid A2 resin 4:1	10	48	4.6	11.0

DISCUSSION

While surface and volume resistivity determinations yielded no information which would allow of unambiguous structural interpretation, the dielectric properties, especially the loss tangent, were somewhat more fruitful in this respect. The general significance of dynamic spectra (of which

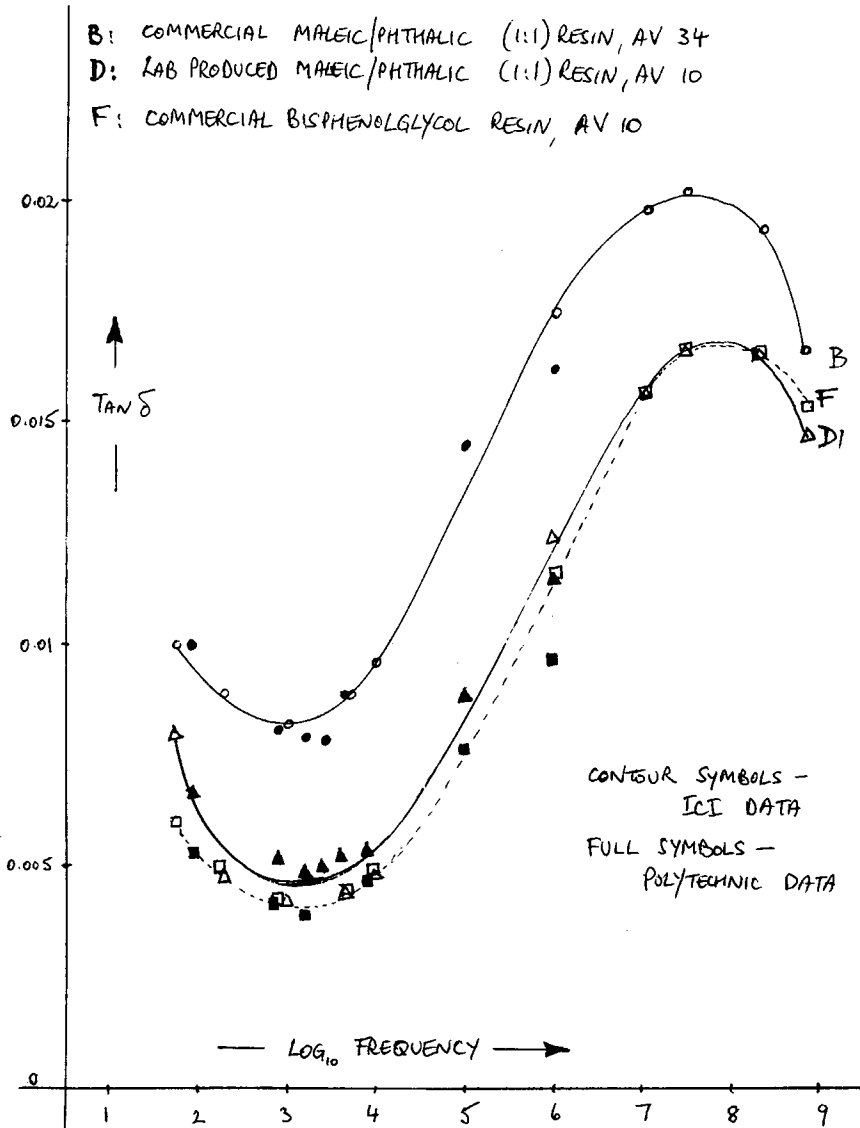


Fig. 4. Variation of $\tan \delta$ with frequency of polyester laminates: (B) commercial maleic/phthalic (1:1) resin, AV. 34; (D) lab-produced maleic/phthalic (1:1) resin, AV. 10; (F) commercial bisphenolglycol resin, AV. 10. Contour symbols, ICI data; full symbols, polytechnic data.

dielectric loss spectra are representative) have already been discussed prior to the description of apparatus and presentation of results.

The results make it possible to draw a number of conclusions:

As regards the *loss spectra*, there exists a clear general pattern: An initial decreasing loss (possibly indicating a peak in the ultralow frequency range which is not readily evaluated on standard equipment) reaches a

minimum and changes to an increasing loss around 1 kHz, followed by a steep rise between 10 and 100 kHz and a peak between 1 and 10 MHz, which is in turn followed by a steep drop beyond about 10 MHz.

The curves are almost identical for all polyesters based on maleic and bisacid A2 in the molar ratio region of 1:1 to 3:1. At 4:1, the shape is the same, but the curve is uniformly displaced downward by about $0.002 \tan \delta$ units (Fig. 1).

Polyesterifying identical charges to different final acid values produced no significant differences in the dielectric spectra of maleic/bisacid A2 resins of ratio 3:1 (Fig. 2). Neither did minor changes in the heating schedule during polyesterification of a maleic/bisacid A2 resin of ratio 1:1 produce any identifiable changes. Despite the fact that one of the resins (A) had been overheated by some 30°C for about 1 hr and that its color had darkened as a consequence, it was not possible to detect any significant differences in the spectra (Fig. 3).

While the shape of the curves for the standard maleic/phthalic (ratio 1:1) resins is identical, it was seen (Fig. 4) that the commercial resin with an acid value 34 had much higher losses (about 20% higher at the maximum, 40–50% at the minimum) than a laboratory-produced resin of the same composition but reacted to acid value 10. In the light of the results of Figure 2, it is not reasonable to assume that the difference in the curve positions is simply due to different acid values. It is much more likely that the much lower losses in the low acid value resin are due to the fact that its higher molecular weight demanded a correspondingly higher styrene content in order to obtain a manageable viscosity for the purpose of lamination. While all the other sheets had styrene contents of 48% on the liquid resin, sheet B was made from the high acid-value commercial maleic/phthalic polyester with a styrene content of only 31% on the liquid resin. The commercial bisphenolglycol polyester F (at 48% styrene content in the liquid resin) gave a spectrum similar to that of the laboratory-produced maleic/phthalic resin of equal styrene content and acid value.

One significant difference exists between the resins containing bisacid A2 as the sole saturated acid and the polyesters not containing bisacid A2: the resins with bisacid A2 all have lower losses in the low frequency part of the spectrum (say, between 60 Hz and 1 kHz.) The standard maleic/phthalic resins not only have much higher losses in the same region, but show a large increase in loss as the frequency is lowered from about 1 kHz to 60 Hz. This would suggest a massive loss peak for those resins at 0.1 to 1 Hz which is not indicated *in that region* for the bisacid A2/maleic resins. It is tempting to suggest this as a diagnostic feature, should bisacid A2/maleic resins become commercial materials in the future.

It is an obvious inference that in order to obtain low-loss resins, one should formulate a liquid resin such that it has a high styrene content. But this is limited by the high acid value and hence the low solution viscosity of commercial maleic/phthalic resins, the high acid value implying shorter processing times and paler products. Such resins are much too thin for laminating

purposes if diluted from, say, 31% to 48% styrene. Since bisacid A2/maleic resins are more readily reacted to lower acid values than standard resins, it is also possible to use more styrene for diluting the resin for subsequent laminating purposes, while maintaining a suitably high solution viscosity. In the end one has not only a dielectrically superior product, but also one in which the cheapness of styrene should partly offset the probable initially high cost of bisacid A2.

As regards *permittivity*, there is also a common pattern in the frequency dependence. In the range over which permittivities were determined (80 Hz to 1 MHz), there is a very slight decrease, generally of no more than 2% over the range. Deviations from linearity seem to appear at the high frequency end of this range. This is readily understood since the loss spectra show a transition region (an approaching peak) between 1 MHz and 10 MHz. One would therefore expect that an extension of the permittivity determinations to frequencies beyond 1 MHz would show a small but distinct drop in the transition region, followed by a symmetrical flattening of the curve thereafter, as is the case with real components of complex moduli generally.

The permittivity levels indicate that there is a slight trend to higher values with increasing maleic/bisacid A2 ratios in this series of resins and that overheating does not seem to cause any recognizable differences in this respect. The two maleic/phthalic resins (one commercial, the other laboratory produced) had permittivities which were well above those for the maleic/bisacid A2 resins. Evidently, phthalic anhydride gives more scope for polarizability than bisacid A2 in polyesters. The differences between the commercial and the laboratory-produced maleic/phthalic polyesters, although not great, were of the expected order: the commercial material (with the high acid value and the lower styrene content) had the higher permittivity.

The surface and volume resistivity data do not indicate an obvious connection between structure and resistivity, except that the surface resistivity appears to increase with increasing Maleic/bisacid A2 ratio, reaching a plateau at 3:1. The difference in acid value between 10 and 24 did not seem to affect results significantly. The highest surface resistivity (about 10^{14} ohm) in the high acid-value/low styrene commercial maleic/phthalic resin cannot be explained on the basis of what is known of its composition.

A high maleic content in maleic/bisacid A2 (series II) resins appears to produce a resistivity increase as the maleic/bisacid A2 ratio increases from 1:1 to 4:1. It would be wrong to attempt to read too much into the variations. The order of magnitude of resistivities is that which is normally associated with crosslinked polyester resins as a class of materials.

SUMMARY

The dielectric loss and permittivity of a group of glass reinforced polyester sheet laminates were determined at 23°C over a wide frequency range.

The polyesters included commercial standard resins as well as experimental resins based upon bisacid A2. The results showed that it was possible to interpret the dielectric frequency spectra on the basis of the known composition of the materials.

Surface and volume resistivities were also determined. Although these did not show any significant differences that could be correlated with differences in composition, the data fit in with those usually obtained from polyester laminates.

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