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THE DIELECTRIC PROPERTIES OF ROSIN-MALEIC ANHYDRIDE RESIN

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(*Received May* 19, 1961)

ABSTRACT. The dielectric properties of rosin-maleic anhydride resin have been measured over the temperature range of 25°C to 170°C and the frequency range of 1 Kc/s to 500 Kc/s. Within this range of temperature and frequency it behaves as a polar resin in the anomalous dispersion range. Its dielectric constant *vs* temperature curve shows however a peculiar behaviour at high temperatures. At about 150°C dielectric constant values attain a maximum after gradually rising with temperature in the normal way of polar resins. But above this temperature a sudden and steep rise in the permittivity is observed. An attempt has been made to explain this peculiarity on the basis of its estimated rotor dimension and infrared absorption spectrogram.

INTRODUCTION

Rosin plays an important part in the production of several semi-synthetic resins. It is widely used as a modifier in the production of so-called modified synthetic resins, such as rosin modified phenol formaldehyde resins or alkyds. Another type of synthetic resin derived from rosin is the rosin-maleic anhydride adduct formed by the method of Diels-Alder reaction known as the "diene synthesis". This method of synthesis involves a "diene" system i.e. a system having conjugated double bonds reacting with a component having an ethylenic linkage flanked by carbonyl or carboxyl groups in such a manner that the "diene" system opens up and the terminal carbons become affixed at the double bond of the ethylenic linkage.

The chemical structure of rosin or abietic acid shows that it possesses a conjugated system of double bonds and consequently it reacts with maleic anhydride giving an addition compound. In fact, this diene synthesis confirms the presence of the conjugated double bonds in the structure of the abietic acid molecule. It should be noted that this compound is the partial anhydride of a tribasic acid and hence its acid value must be reduced and this is usually done by esterification with any polyhydric alcohol like glycerol, mannitol, pentaerythritol etc.

Now X-ray studies on the rosin maleic-anhydride resins and ester gum by Beal and co-workers (1932) have revealed that they show precisely the same rings which are associated with raw rosin. Esterification with glycerol or reacting it with maleic anhydride does not change its inherent character.

Because of the large size of the esterified rosin-maleic anhydride molecule, its rotation as a whole, when placed in the rapidly alternating electric field, is unlikely. Obviously, if dielectric loss occurs due to orientation it may only be due to contributions from side groups attached to the main molecule. Although rosin has been found to be present in this resin as a constituent unit, its freedom of rotation has been severely restricted by a pair of carbon-carbon bonds with the maleic anhydride on the one hand and by its linkage with the pentaerythritol molecule through the esterification of its carboxyl group on the other.

From a previous study of the dielectric properties of rosin it has been observed by the authors (Sen and Bhattacharya, 1958b) as well as by Kitchin and Muller (1928) that the dimension of its rotating unit is about 4.6Å which is in close agreement with the actual dimension of the abietic acid molecule calculated on the basis of its accepted chemical structure. This agreement led the authors to the obvious conclusion that the rotation of the entire abietic acid molecule was responsible for its dielectric behaviour. But a similar study in the case of ester gum (Sen and Bhattacharya, 1958a) or copal ester (Sen and Bhattacharya, 1960) revealed a different story. In both the cases the dimensions obtained for the rotating units were exactly the same as that of a hydroxyl group. The presence of hydroxyl groups in these resins was also confirmed from their infra-red absorption spectrograms. These evidences tend to suggest that instead of the whole molecule the hydroxyl groups in these resins are probably the rotating units. Hence it is inferred that when molecules of abietic acid (rosin) or copalic acid (copal) combine (e.g., by esterification with glycerol) to form larger molecules, their rotation as a whole is restricted and only the rotation of smaller groups can occur in the investigated range of frequency. In this context it is therefore of interest to study the dielectric properties of rosin-maleic anhydride adduct in relation to those of rosin and obtain the dimension of its rotating units.

EXPERIMENTAL

The same experimental procedure as was followed in the case of other resins and the details of which appeared elsewhere (Sen and Bhattacharya, 1958a, 1958b) has been employed. The sample used in this investigation was a pentaerythritol ester of the rosin-maleic anhydride adduct manufactured by the Imperial Chemical Industries Ltd., London, and sold under the trade name of Bedesol—74.

The results of measurements of dielectric constant ϵ', dielectric loss ϵ'' and power factor tan δ at different temperatures and frequencies are shown graphically in Figs. 1, 2 and 3. Quite contrary to our expectation, these graphs give clear evidence of the typical polar nature of this resin. The loss factor-temperature and the power factor-temperature curves shown in Figs. 2 and 3, are the usual absorption curves of a polar meterial. These curves begin to rise at a comparatively higher temperature viz, about 100°C for almost all the frequencies except that of 1 Kc/s. The loss peaks are also more or less of the same heights.

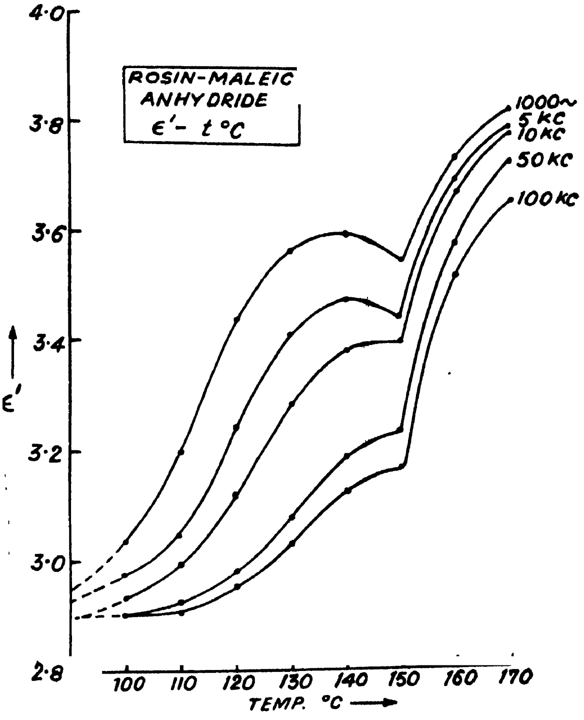

Fig. 1

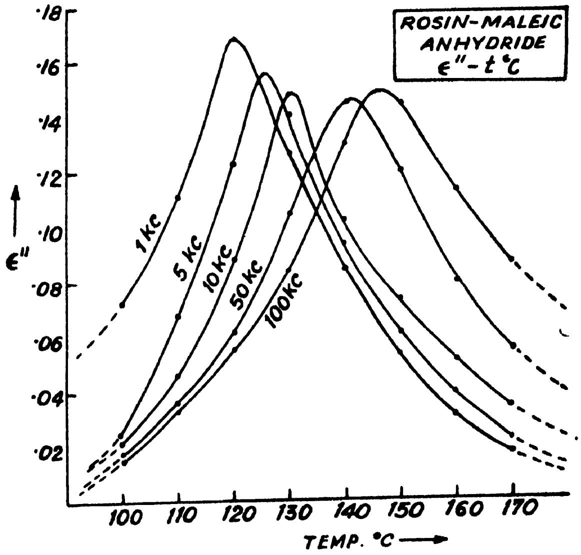

Fig. 2

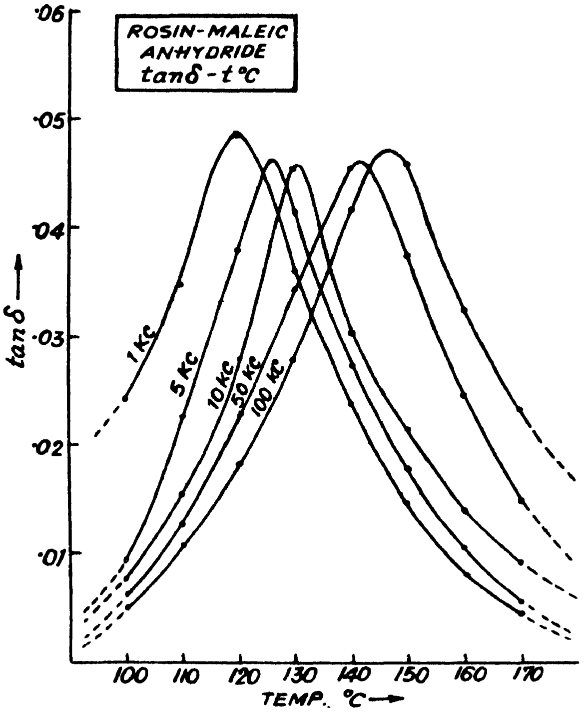

Fig. 3

But the dielectric constant-temperature graphs show a peculiar behaviour. It may be noticed from Fig. 1 that the permittivity for all the frequencies begins to rise from about 100°C in the usual way and attains a maximum at temperatures between 130°C to 150°C. But peculiarly enough, after 150°C it is found to make

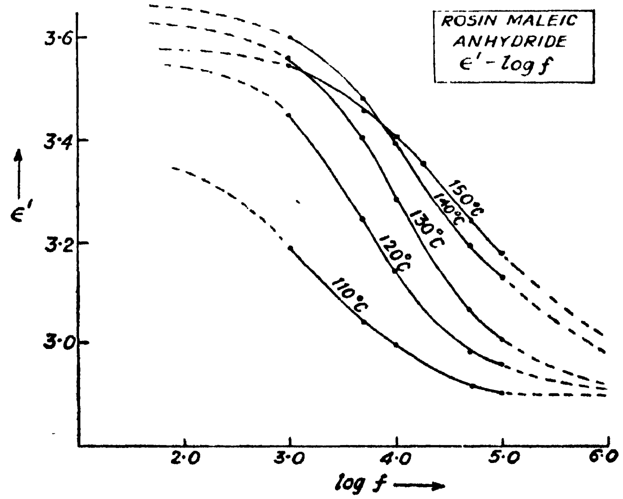

Fig. 4

a sudden and steep rise again. Measurements were carried out up to 170°C only as it was apprehended that the resin might polymerize after that temperature. This peculiar behaviour can only be explained on the supposition that at temperatures higher than 150°C the resin becomes unstable and more and more dipoles are somehow set free which now increase the orientation polarization and make the permittivity to rise. Hence an estimation of the size of the rotating unit is considered interesting in this case.

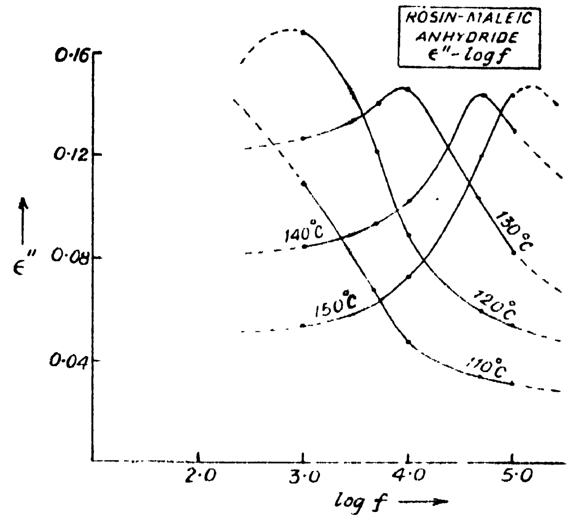

Fig. 5

The radius of the rotating unit was estimated from the calculated relaxation time at the temperature of loss maximum corresponding to a particular frequency and the melt viscosity at that temperature. The melt viscosity of this resin at

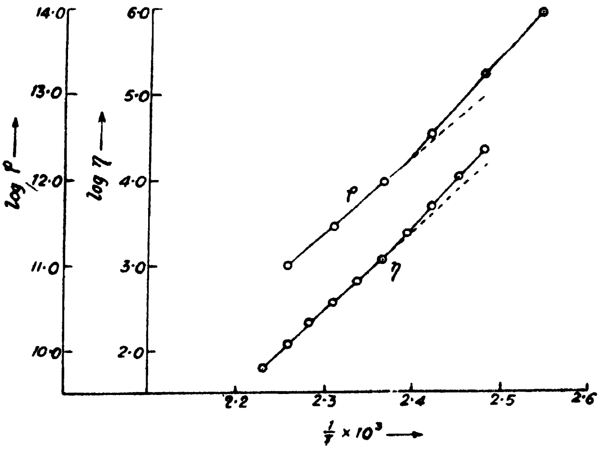

Fig. 6

different temperatures was measured by the same method as reported earlier (Sen and Bhattacharya, 1957) and the results are shown in Table I. Fig. 6 shows the logarithm of viscosity plotted against the reciprocal of absolute temperature and the graph is a straight line. For the sake of comparison the logarithm of resistivity is also plotted against the reciprocal of absolute temperature using the same scale. The conductivity and resistivity data appear in Table II. Once again the slopes of both these graphs are found to be the same. Upto the temperature of 170°C, however, none of these graphs shows any abnormality to indicate any likely polymerization within this temperature region.

TABLE I

Viscosity-temperature data

Temperature		$\frac{1}{T} \times 10^3$	Viscosity η in poise	log η
t°C	T°K			
130	403	2.481	22,970	4.3612
135	408	2.451	11,000	4.0414
140	413	2.421	4,900	3.6902
145	418	2.392	2,340	3.3692
150	423	2.364	1,200	3.0792
155	428	2.336	635	2.8028
160	433	2.309	355	2.5502
165	438	2.283	210	2.3222
170	443	2.257	120	2.0792
175	448	2.232	60	1.7782

TABLE II

D.C. conductivity or resistivity-temperature data

Temperature		$\frac{1}{T} \times 10^3$	Conductivity K in mho cm^{-1}.	Resistivity ρ in ohm cm.	log ρ
t°C	T°K				
120	393	2.545	0.1042×10^{-13}	9.596×10^{13}	13.9821
130	403	2.481	0.5970×10^{-13}	1.675×10^{13}	13.2240
140	413	2.421	0.2935×10^{-12}	3.407×10^{12}	12.5324
150	423	2.364	0.1067×10^{-11}	9.369×10^{11}	11.9717
160	433	2.309	0.3339×10^{-11}	2.894×10^{11}	11.4614
170	443	2.257	0.1036×10^{-10}	9.654×10^{10}	10.9847

The results of calculation of the radius of the rotating units are shown in Table III.

TABLE III

Calculated relaxation time and radius of the rotator

Frequency in kc/s	Loss maximum temperature t_m in °C	Relaxation time τ in sec.	log η at t_m	Radius of the rotator in Å
5	126	2.80×10^{-5}	4.60 (extrapolated)	1.45
10	131	1.39×10^{-5}	4.30	1.45
50	142	2.76×10^{-6}	3.60	1.46
100	147	1.39×10^{-6}	3.27	1.51

From these results we find again that the same value of the dimension of the hydroxyl group is obtained here for the radius of the rotator in this resin. We should examine therefore if there is any possibility for this resin of containing hydroxyl groups as probable rotating units. As in the production of this resin pentaerythritol is employed it is not unlikely for some of the four hydroxyl groups of the pentoerythritol molecule to remain unesterified in the same way as some hydroxyl groups of glycerol were found to remain unesterified in ester gum (Sen and Bhattacharya, 1958a) and copal ester (Sen and Bhattacharya, 1960). Moreover this possibility may also provide an explanation for the observed phenomenon of abnormal rise in permittivity above 150°C. For some of these hydroxyl groups may form hydrogen bonds amongst themselves at ordinary temperatures and these may be disturbed only at temperatures above 150°C. Consequently

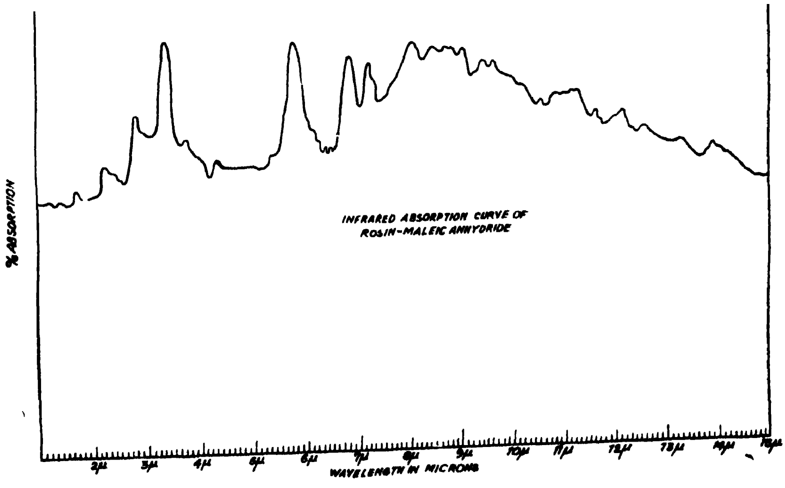

Fig. 7

upto 150°C only the free hydroxyl groups can contribute towards polarisation there being no contribution from the bonded hydroxyl groups. But at temperatures above 150°C these hydrogen bonds may break and the released hydroxyl groups may contribute further towards polarization thereby increasing the dielectric constant. Or, in the alternative there may be condensation-polymerisation above 150°C and the released water vapour may contribute towards increased dielectric constant.

The infrared absorption spectra of this resin was obtained in the manner indicated previously (Sen and Bhattacharya, 1960) and the spectrogram shown in Fig. 7. In this figure no absorption peak occurs at the wave length region of 2.93μ corresponding to the bonded hydroxyl group but the peak due to the free hydroxyl group occurs at about 2.78μ. The second explanation for increased values of dielectric constant above 150°C seems therefore reasonable. The free hydroxyl groups may be the unesterified hydroxyl groups of the pentaerythritol molecule as stated earlier. As chances of rotation of the entire resin molecule are remote, only side groups attached to the main molecule or segments of it are capable of orientation. Therefore hydroxyl groups attached to the molecule seem to be the probable rotating units.

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