

# Methods for Lowering Loss Angle Tangent of Thin Polystyrene Films Obtained by Electrical Discharge in Styrene Vapor

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## Synopsis

The thin films of polystyrene obtained in an electrical discharge present a value of  $\tan \delta$  higher than that of traditional polystyrene films. It appears that oxygen is one of the factors bringing on this failure. A noticeable improvement of loss factor can be obtained either by addition of antioxidant or by reducing the electrodes spacing.

## INTRODUCTION

Thin films obtained by polymerization in an electrical discharge exhibit excellent insulating properties and constitute an original technological method for industrial manufacturing of capacitors. However, in this field of applications, their weakness is a value of dielectric loss angle tangent ( $\delta$ ) higher than that of traditional plastic films. In the following study we propose two methods which lead to an interesting reduction of dielectric loss factor.

## PREVIOUS RESULTS

The study of thin polymer film fabrication, especially film obtained from styrene, started at the Laboratoire de Génie Electrique de Toulouse (France), Equipe "Matériaux Diélectriques," in 1969. The following process<sup>1</sup> is used: An alternating voltage, with a frequency of a few kilohertz, is applied between two metal electrodes plunged in monostyrene vapor; the formation of a polymerized film can be observed on the electrodes or on a substrate (metallic or not) supported by one of them. It is interesting to note that the thickness of deposited polymer films is only a function of discharge duration as long as the electrical and thermodynamic parameters are kept constant. This makes it possible to obtain, if required, especially thin films ranging between a few hundred angstroms and a few microns. This property, together with a satisfactory dielectric strength, is of real interest for the fabrication of capacitors with high volume capacity.<sup>2</sup>

The study of frequency response of metal-polymer-metal (MPM) structures using such thin films has shown,<sup>3</sup> however, that loss factor  $\tan \delta$  is higher than that, measured under identical conditions, of commercial polystyrene obtained chemically and used in the fabrication of capacitors. As an example, at a frequency of 1 kHz, the latter has a loss factor close to  $10^{-4}$ , matched with a value ranging between 20 and  $40 \times 10^{-4}$ , depending on the quality of the deposit which

is determined by the experimental setup where the film is made. Figure 1 shows the variation of  $\tan \delta$  between 100 Hz and 100 kHz obtained with a deposit apparatus carefully designed and constructed the block diagram of which is shown in Figure 2. This setup has been used throughout the experiments described below.

### ROLE OF OXYGEN IN THE INCREASE OF LOSS ANGLE

A previous study, using infrared spectrophotometry, showed the existence of absorption peaks corresponding to  $-\text{OH}$  and  $>\text{C}=\text{O}$  groups (Fig. 3). These peaks do not exist in the spectrogram of commercial polystyrene obtained chemically,<sup>1</sup> which has lower values of  $\tan \delta$  than that made by our method, as has already been mentioned. This can be attributed to the presence of such radicals.

This interpretation is confirmed by the following experiment: Thin films were deposited with increasing oxygen pressures; the setup of Figure 4 was used. Table I shows the results obtained at a frequency of 1 kHz. Pressure values are given in torr.  $P_s$  is the styrene vapor pressure measured in the chamber by gauge J1, without oxygen;  $P_o$  is the oxygen pressure measured by gauge J2;  $P_{so}$  is the pressure of the oxygen-styrene mixture by gauge J1. Figure 5 shows the curves obtained under these conditions when the frequency was varied; they show clearly the negative action of oxygen during the deposit.

It appears therefore that the presence, practically unavoidable, of residual oxygen between the electrodes is a factor in the deterioration of  $\tan \delta$ . It has to be noted though, and this is important, that the formation of polar groups

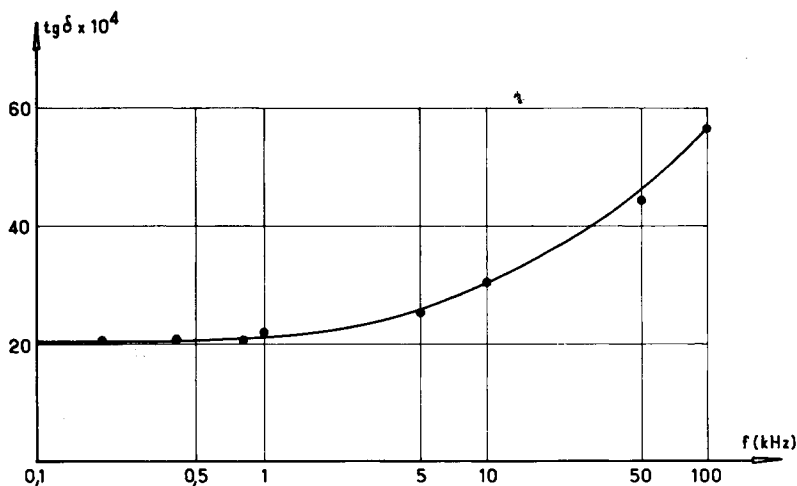


Fig. 1. Variation of  $\tan \delta$  with frequency.

TABLE I

$P_s$	0.27	0.25	0.25
$P_o$	1.2	1.3	1.45
$P_{so}$	0.5	0.7	1
$\tan \delta$	$52 \times 10^{-4}$	$70 \times 10^{-4}$	$80 \times 10^{-4}$

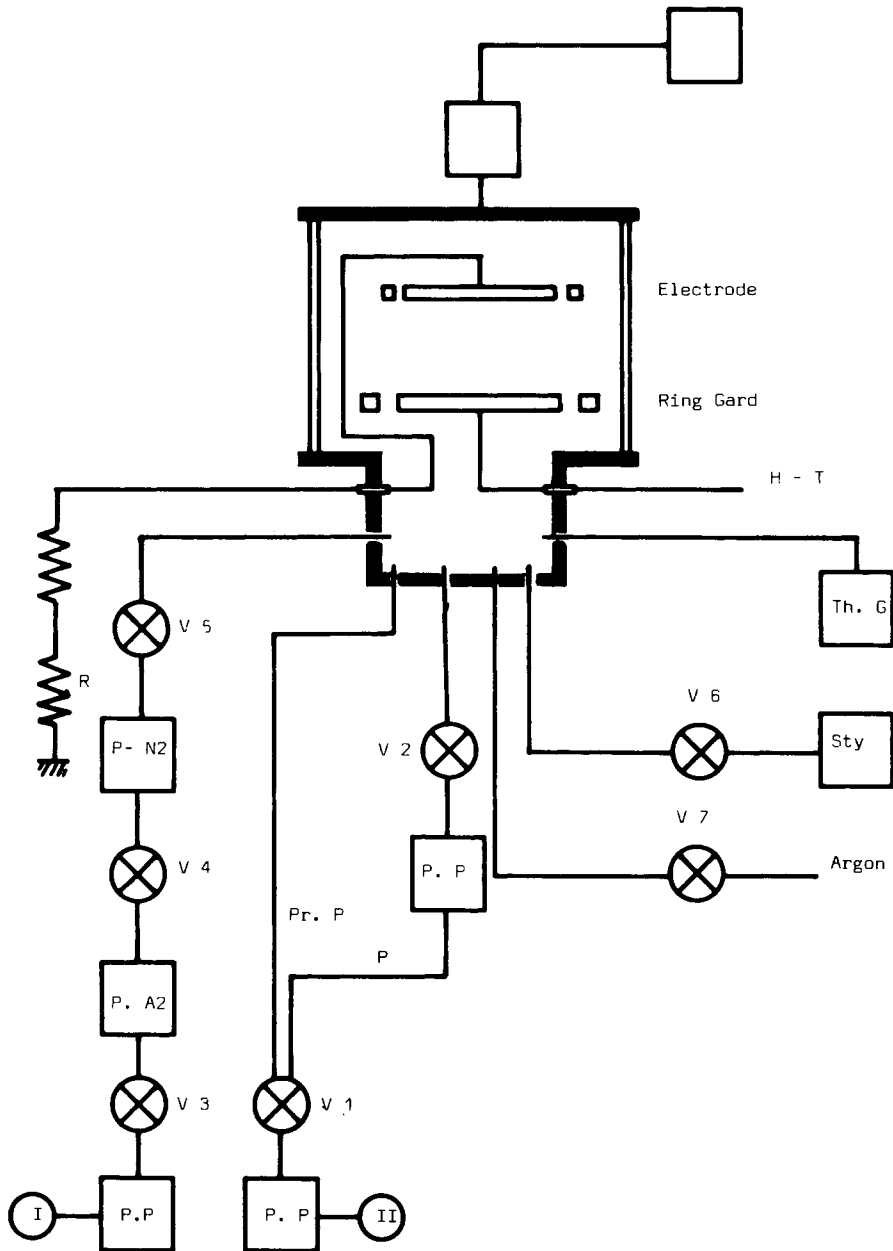


Fig. 2. Block diagram of the experimental setup for polymer film deposit. Sweeping circuit I: P.P. = primary pump; V2, V4, V5 = insulating valves; P.Az = zeolite trap; P.N<sub>2</sub> = liquid nitrogen trap. Primary vacuum circuit II: P.P. = primary pump; P.D. = diffusion pump (secondary vacuum); V<sub>1</sub>, V<sub>2</sub> = insulating valves; V<sub>6</sub> = needle valve for monomer input; V<sub>7</sub> = argon input valve; Sty = liquid styrene tank; S. Th = thermocouple gauge; H.T. = high-voltage connection; K = protection resistance on ground end sude; G<sub>p</sub>, J.C. = variable capacity gauge.

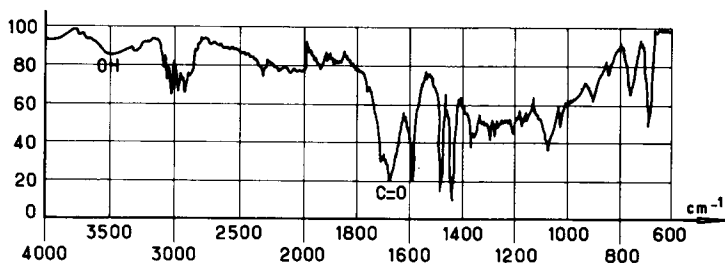


Fig. 3. Infrared spectrogram taken with a thin film obtained from monostyrene.

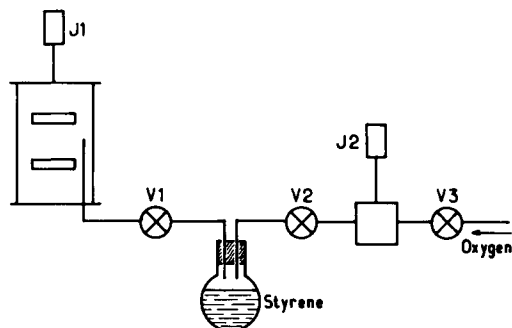


Fig. 4. Experimental setup for polymer film deposit with oxygen-containing atmosphere.

TABLE II

Catechol, ppm	50	1000	1500	3000	5000	10 000	100 000
$\tan \delta \times 10^4$	20	23	30	22	28	24	10

responsible for loss increase necessitates two complementary elements: (1) the presence of residual oxygen in the discharge (this does not preclude a partial oxidation of the monomer before its introduction in the discharge chamber), and (2) the existence of free radicals likely to react with this oxygen, which can be explained, as will be seen, by unsaturated bond breaking within the chain, under ionic bombardment. These two factors, of independent origins but with linked and complementary consequences, are those we tried to modify with a view of lowering the dielectric loss factor.<sup>4</sup>

## LOWERING OF $\tan \delta$ BY CONTROLLED ADDITION OF STABILIZER

### Results Obtained

After having observed an increase of dielectric loss when the 50 ppm of catechol usually contained in the monostyrene was removed, we added increasing quantities of this stabilizing substance. Table II shows results obtained with a frequency of 1 kHz. More complete results with different frequencies are reported on the curves of Figure 6.

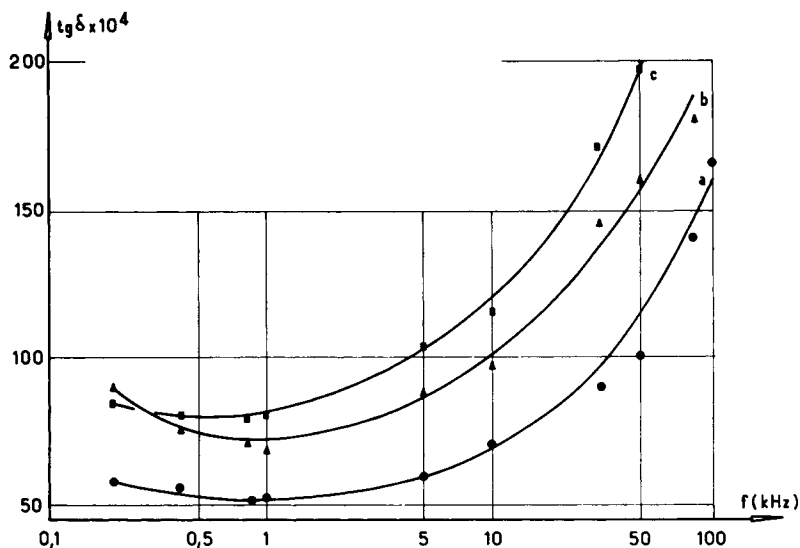


Fig. 5.  $\tan \delta$  as a function of frequency (sample prepared with excess oxygen): (a)  $P_s = 0.27$  torr;  $P_o = 1.20$  torr;  $P_{so} = 0.50$  torr. (b)  $P_s = 0.25$  torr;  $P_o = 1.30$  torr;  $P_{so} = 0.60$  torr. (c)  $P_s = 0.25$  torr;  $P_o = 1.45$  torr;  $P_{so} = 1$  torr.

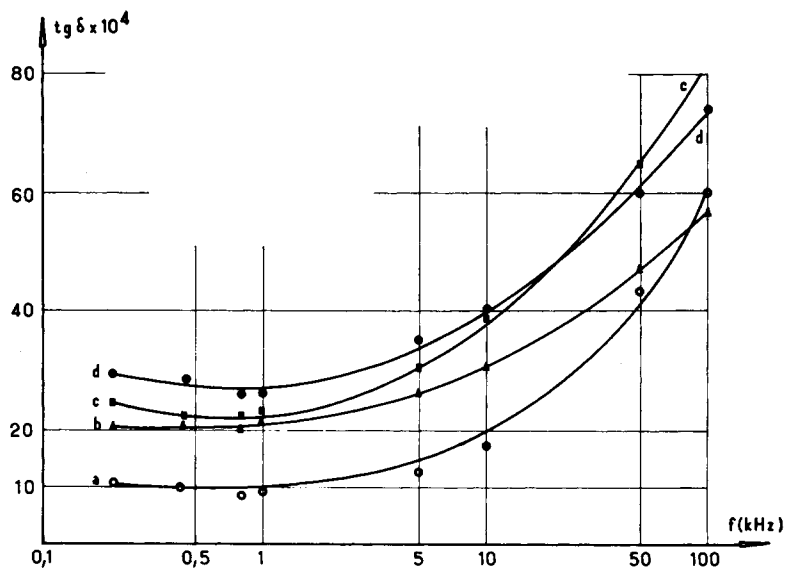


Fig. 6. Variation of  $\tan \delta$  with frequency for different catechol concentration in styrene: (a) 100,000 ppm; (b) 50 ppm; (c) 1000 ppm; (d) 10,000 ppm.

#### Addition of High Proportion of Catechol Prevents Formation of $-\text{OH}$ and $>\text{C}=\text{O}$ Groups

This is indicated in the infrared spectrogram of Figure 7 where  $-\text{OH}$  and  $>\text{C}=\text{O}$  peaks are no longer observed. This results in a noticeable improvement

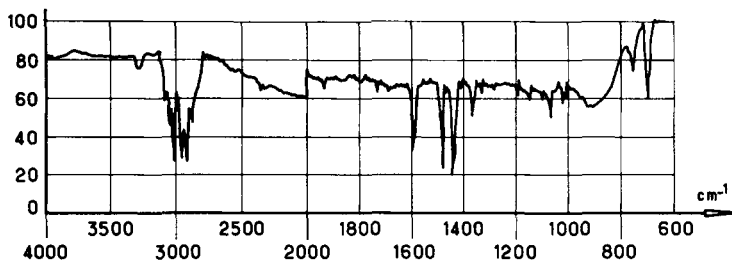


Fig. 7. Infrared spectrogram taken on film obtained from monostyrene containing 100,000 ppm catechol.

of loss factor, probably due to catechol antioxidation action, the role of which is to fix the oxygen.<sup>5</sup> When this substance is present in high enough quantities, it traps the oxygen in place of the free radicals of the polymer chain. Nevertheless, it was not possible for us to determine whether this action took place during film growing or before styrene vapor ionization within the liquid monomer.

### DECREASE IN TAN $\delta$ BY MODIFICATION OF DISCHARGE SETUP

As noted above, free radicals must exist during film formation in order for the oxygen to be fixed and to create polar groups. The existence of these free radicals is evidently related to the action of ionic bombardment in the discharge. We thought that free-radical density should decrease with the energy of bombarding particles on the film and that under such conditions a lowering of loss factor  $\tan \delta$  should be observed.

#### Theoretical Study of Influence of Electrode Spacing on Incident Energy of Ions in Discharge

Previous studies<sup>1</sup> have pointed out the mechanisms of the discharge and of thin film growing. Within the discharge, the electrons colliding with styrene molecules in the electrode gap produce positive ions; the latter bombard the cathode with a certain energy. The more energetic ones are likely to break the chemical bonds in the polymer chain. We tried to show the influence of electrode spacing  $d$  on ion energies, this parameter being the easiest to adjust in practice. To make the problem simpler, we computed ion speed in the electrode gap assuming a dc applied voltage. In this case, the electrodes are well differentiated, which makes it possible to separate the action of electrons and that of the ions.<sup>1,6,8</sup>

The discharge in which polymerization is produced is of the glow type; it is characterized by the existence between the anode and the cathode of different regions. Their extent depends on the pressure and on electrode spacing  $d$ . Potential difference  $V_A$  between these electrodes is nearly equal to the sum of the cathode drop  $V_c$  and ionization potential  $V_I$ :

$$V_A \approx V_c + V_I$$

Cathode drop is localized in the cathode region of length  $d_c$ ; in this region the

electrons are strongly accelerated and reach their maximum energy; it is there that positive ions are mostly formed. Then they are accelerated and bombard the cathode. These ions have a speed

$$V = K^+E$$

where  $K^+$  and  $E$  are, respectively, the average mobility of the ions and the electric field in the cathode zone. It follows that  $V = K^+ V_c/d_c$  and the mean kinetic energy of an ion is

$$E_c = \frac{1}{2} M(K^+)^2 V_c^2/d_c^2$$

$M$  being the ion mass. This expression shows that ion energy is proportional to the square of the mobility. Now it can be shown that at constant temperature  $K^+p$  (the product of mobility and pressure) is constant.<sup>6,7</sup> Using this result and values already given of this product,<sup>1</sup> the computation showed us<sup>4</sup> that when the electrode spacing decreases, the mobility decreases faster, which lowers energy  $E_c$ .

### Experimental Results

Table III gives the results obtained for  $\tan \delta$  at 1 kHz for  $7 < d < 50$  mm. For such an important variation it has not been possible to keep a constant pressure. The other deposit parameters were unchanged. Practically, we could not bring the electrode spacing under 7 mm. For this value Figure 8 shows the variation of  $\tan \delta$  with frequency: at 1 kHz the loss tangent is  $7 \times 10^{-4}$ . This interesting result is confirmed by infrared spectrophotometric analysis. The spectrogram of Figure 9, taken with a film deposited with a 7-mm electrode spacing, shows the disappearance of the absorption peaks due to  $-\text{OH}$  and  $>\text{C}=\text{O}$ .

The experiment shows that this result cannot be improved by the addition of a high concentration of antioxidant; the result obtained is of the same order

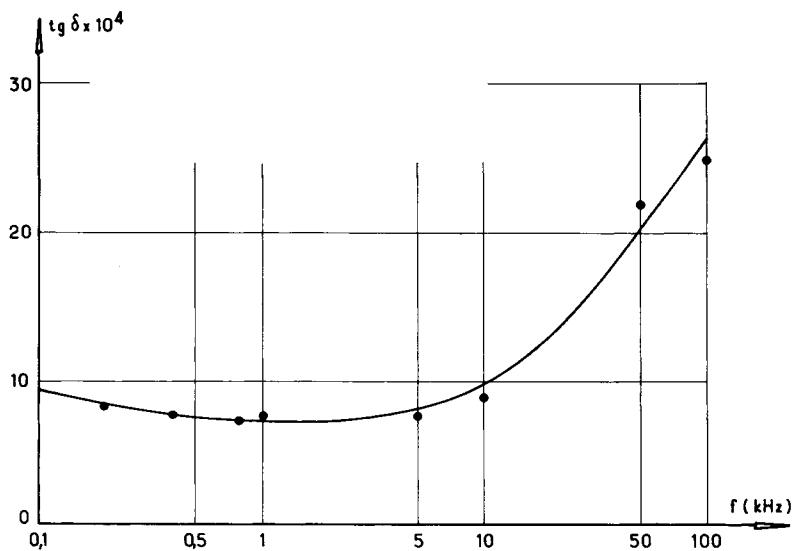


Fig. 8. Variation of  $\tan \delta$  with frequency (electrode gap length 7 mm).

TABLE III

Pressure, torr	$d$ , mm	$\tan \delta \times 10^4$
0.3	50	33-40
	40	20-30
	30	20-25
	30	19-23
0.6	20	12-16
	10	9-13
2.5	7	7-10

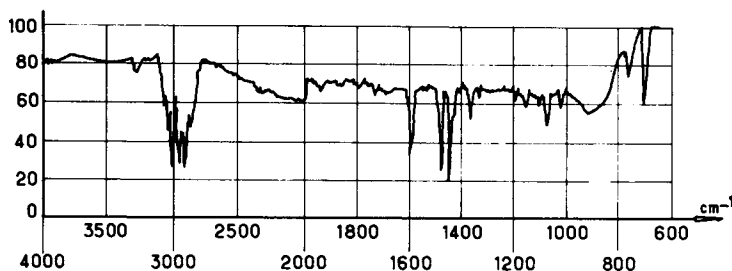


Fig. 9. Infrared spectrogram taken on film obtained from styrene with normal concentration of stabilizer and a gap length of 7 mm.

of magnitude as that obtained separately by the two methods. This corroborates our hypotheses: reducing the electrode spacing lowers the density of free radicals likely to react with oxygen. It is of no importance that the latter is or is not fixed by the catechol.

### CONCLUSIONS

The study showed that it is possible to reduce the loss tangent value by a factor ranging between 4 and 5. The two methods we have developed are both equivalent in preventing the formation of polar groups such as  $-\text{OH}$  and  $>\text{C}=\text{O}$  by inhibiting oxygen action during deposit. The  $\tan \delta$  reduction observed brings about no practical modification of the frequency response curve between 100 and 1000 kHz; it results in a translation of the whole curve toward the lower values of  $\tan \delta$ .

The choice of an adequate method for practical applications will be done by use of technological criteria following the considered application after a preliminary study of the other physical-chemical characteristics of the deposited films.

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