

Dielectric Behavior of Sulfonic Acid-Polystyrene Films

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Synopsis

The dielectric properties of partially sulfonated polystyrene films (15% degree of sulfonation) in their dry and slightly wet (4.7% by weight of water content) states were measured over the frequency range between 10^2 and 10^6 Hz with temperature as a parameter. Loosely crosslinked (1% divinyl benzene) polystyrene films were synthesized and sulfonated with chlorosulfonic acid to a 15% degree of sulfonation. Films containing more than 15% sulfonation were very brittle. Dielectric constant and loss data of these sulfonic acid films are presented at various temperatures and are correlated in terms of Cole-Cole plots. The dielectric response characteristics of these films find application in the electroformation of sulfonated polymer electrets, which have been shown to possess a high degree of polarizability and are capable of storing large amounts of electric charge.

INTRODUCTION

Surprisingly, little work has been published on the dielectric behavior of strongly acid polymeric films even though these polyelectrolytes have high dielectric constants. Zundel and Metzger^{1,2} studied hydration stages within sulfonic acid films by means of IR spectrography. Later, Zundel³ comprehensively reviewed the fundamental nature of the hydrated sulfonic acid molecule and its polarizability in polystyrenesulfonic acid. Urban and Wallace⁴ recently reported the dielectric properties of dry and wet commercial polystyrenesulfonic acid-polyethylene desalination membranes.

Lately, there has been widening interest in permanent internal polarization within sulfonated polymer electrets and in their charge storage and discharge mechanisms. Dry polystyrenesulfonic acid membranes were polarized under vacuum at an elevated temperature of 60°C in the presence of a d.c. field ranging from 1.25 to 5.0 kV/cm.⁵ Large amounts of internal electric charges were measured and found to be directly proportional to the dielectric properties and concentration of the styrenesulfonic acid content. Because of the large macroscopic dipole moments generated within sulfonated polymer membranes, a large negative electric charge or potential was induced at the membrane surface. This negative surface potential could repel organic molecules which form negative particles or foulants in water.⁶ Thereupon, this imposed electret effect may greatly increase the lifetime of

polystyrenesulfonic acid-incorporated polymer membranes used in desalination. These sulfonated polymer films also made good electrets when immersed in electrolytically conducting aqueous solutions such as 0.1*M* NaCl. Substantial progress was also reported by Murphy⁷ who described a series of experiments on the effect of electrified sulfonated polymer films on the clotting of blood and demonstrated that negative sulfonated electrets can prevent thrombus formation and thus can be used as blood-compatible materials.

In this paper, results are presented of measurements of the dielectric behavior of synthesized sulfonic acid-polystyrene films with a 15% degree of sulfonation in their dry and slightly hydrated (4.7% by weight water content) conditions. Dielectric constant and loss data of these partially sulfonated polystyrene films have been recorded in the low-frequency range between 10² and 10⁵ Hz at various temperatures. Cole-Cole⁸ plots have been used to correlate these dielectric response data. Dielectric results measured here will find application in determining the optimum charge storage capacity of sulfonated polymer membrane electrets.

EXPERIMENTAL

Sulfonic Acid Films

Partially sulfonated polystyrene films were prepared from a 20% solution of loosely crosslinked (1% divinyl benzene) polystyrene in benzene on glass plates, followed by sulfonation by the method of Chen.⁹ Polystyrene films were dried under vacuum for 24 hr and then swollen in *n*-heptane for another 24 hr prior to sulfonation. These loosely crosslinked polystyrene films were then immersed in chlorosulfonic acid for an 8-min period and subsequently washed with sulfuric acid of progressively decreasing concentration. These films were converted to the hydrogen form by equilibration with 1*N* HCl for at least 8-hr and then washed with deionized water. Degree of sulfonation was determined from exchange capacity measurements. Films containing 15% by weight of styrenesulfonic acid were used in our measurements; films containing more than about 15% sulfonation were found to be very brittle and unsuitable for dielectric measurements. Film samples were cut into discs, 2.54 cm in diameter and, on the average, 0.29 mm thick.

Dielectric Measurements

The dielectric measurements were made as a function of frequency at various temperatures. Apparatus for the measurements is shown schematically in Figure 1. A G.R. bridge Type 716-3 was used in conjunction with G.R. oscillator Type 1210-C and G.R. tuned amplifier, Type 1232-A as a null-detector. A platinum clad electrode assembly was connected in series with a 1000 pF standard capacitor to the bridge.

Each film disc was vacuum dried at 55°C prior to testing. Dielectric tests were carried out in a vacuum oven maintaining temperature within 0.4°C.

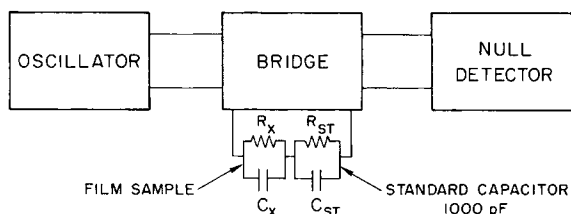


Fig. 1. Schematic diagram of apparatus to measure dielectric properties of sulfonic acid-polystyrene films.

The film weight was measured before and after the tests, and then averaged. The film water content, expressed as moles of hydrated water per equivalent of sulfonic acid group, n , is given by

$$n = \frac{(m_w/m_D)55.5}{Q} \quad (1)$$

where Q is the sulfonation degree given in milliequivalents of sulfonic acid groups per gram of dry film, and m_w and m_D are the hydrated and dry film weight, respectively; m_D was measured after vacuum drying at 70°C for 48 hr. The film in this virtually dried condition is referred to as dry. The thickness of the films was measured with a Gaertner cathetometer M-930 to within 0.001 mm.

Film capacitance C and dissipation factor D were measured in the frequency range 10^2 through 10^5 Hz. Since both C and D averaged relatively high, the 1000-pF standard capacitor C_{ST} , D_{ST} was added in series with the sample to bring the measured capacitance C_M and dissipation factor D_M to within the measuring range of the bridge. Then, the unknown film capacitance and dissipation factor were calculated from the values of C_M , D_M , C_{ST} , and D_{ST} . Dielectric constant ϵ' and loss ϵ'' are computed from film capacitance and dissipation factor:

$$\epsilon' = \frac{Cd}{\epsilon_r A}; \quad \epsilon'' = D \cdot \epsilon' \quad (2)$$

where $\epsilon_r = 8.85 \times 10^{-14}$ F/cm, the absolute dielectric constant of vacuum or dry air; d = distance between electrodes, in cm; A = electrode area, in cm^2 .

Electrode polarization represents a serious error in dielectric measurements, especially at low frequencies. In order to record meaningful results, electrode polarization effects and the magnitude of the impedance of lead effects were minimized.

In Figure 2 is shown the frequency dependence of dielectric constant of dry sulfonic acid-polystyrene films at various temperatures. All four curves display a deviation, due to electrode polarization, which occur only at frequencies lower than 100 Hz. Measured values of dielectric constant at frequencies below 1000 Hz were corrected for electrode polarization effects. Cole-Cole plots⁸ were constructed using the values at frequencies

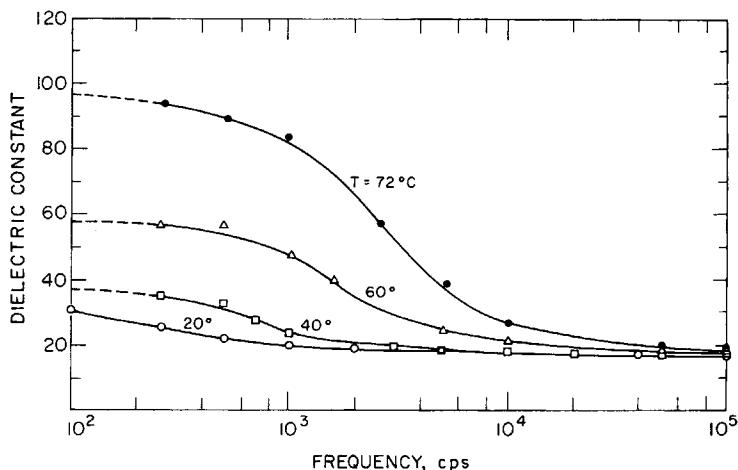


Fig. 2. Frequency dependence of dielectric constant of dry sulfonic acid-polystyrene film at various temperatures.

higher than 1000 Hz where the electrode polarization is presumed negligible. Then, the values of the static dielectric constant ϵ_0 and the characteristic frequency f_m were determined from these Cole-Cole plots.

RESULTS AND DISCUSSION

The dielectric constant of the dry sulfonic acid-polystyrene film containing 15% styrenesulfonic acid is given in Figure 2 as a function of frequency at various temperatures. The dashed portions of the curves are extrapolated data. All four curves display a similar shape. The dielectric constant decreases with increasing frequency passing through a point of inflection. The point of inflection determines the position of characteristic frequency f_m . The precise locations of characteristic frequencies were found by means of Cole-Cole plots which are presented in Figure 3. The position of f_m moves toward higher values as the temperature increases. This shift is probably due to the decrease of film microviscosity at the higher temperatures.

At higher frequencies all the curves in Figure 2 approach an asymptotic value of about 18. This value is much higher than the square of the refraction index, which for this sulfonic acid film is 2.4. Therefore, additional dispersions are predicted at frequencies greater than 10^5 Hz. As shown in Figure 3, the width of the dispersion region, $\epsilon_0' - \epsilon_{00}'$, increases from 12 at 20°C to about 80 to 72°C.

Figure 4 shows the dielectric constant versus frequency at various temperatures for the slightly hydrated ($n = 1.0$) sulfonic acid film. This slightly wet film also displays a dispersion in our frequency range similar to that of the dry film. The curves shown in Figure 4 pass through inflection points, and the position of f shifts with increasing temperature toward higher values.

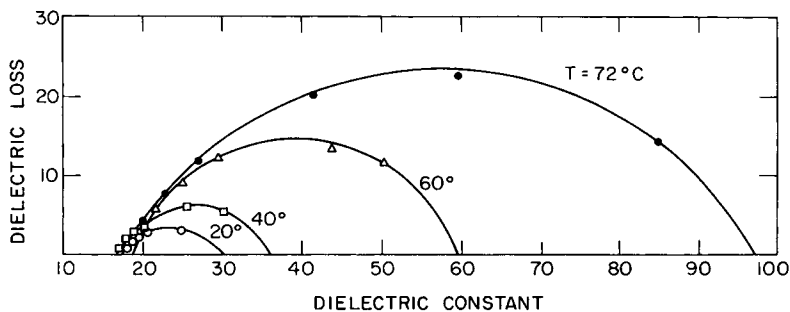


Fig. 3. Cole-Cole plots for dry sulfonic acid-polystyrene film at various temperatures.

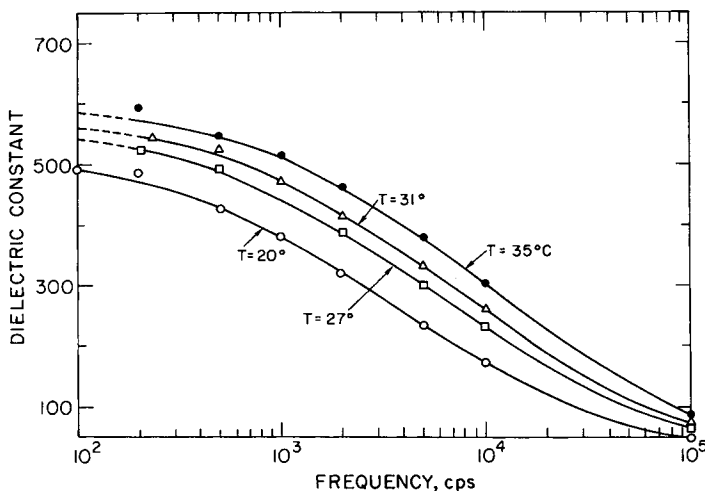


Fig. 4. Frequency dependence of dielectric constant of wet ($n = 1.0\%$ or 4.7% by weight water content) sulfonic acid-polystyrene film at various temperatures.

Figure 5 shows the frequency dependence of dielectric loss for slightly wet ($n = 1.0$) sulfonic acid film at various temperatures. All four curves display a deviation from a standard bell-shaped dielectric loss curve. This deviation, due to electrode polarization, seems to occur only at frequencies lower than 1000 Hz.

Polarizations were calculated using the Kurosaki¹⁰ equation for specific polarization:

$$P_n = \frac{2\epsilon'^2 + 1}{9\epsilon'^2\rho} + \frac{\partial\epsilon'}{\partial n} \quad (3)$$

where ϵ' is measured dielectric constant; ρ is the specific gravity of sulfonic acid film; and $\partial\epsilon'/\partial n$ is the variation of dielectric constant with the change of water content. In the dry condition ($n \approx 0$), $\bar{P}_n \approx 0.32$. At the slightly wet condition ($n = 1.0$), $\bar{P}_n \approx 40$. This large difference points out that the hydrated water causes the sulfonic acid film to increase drastically in its degree of polarizability.

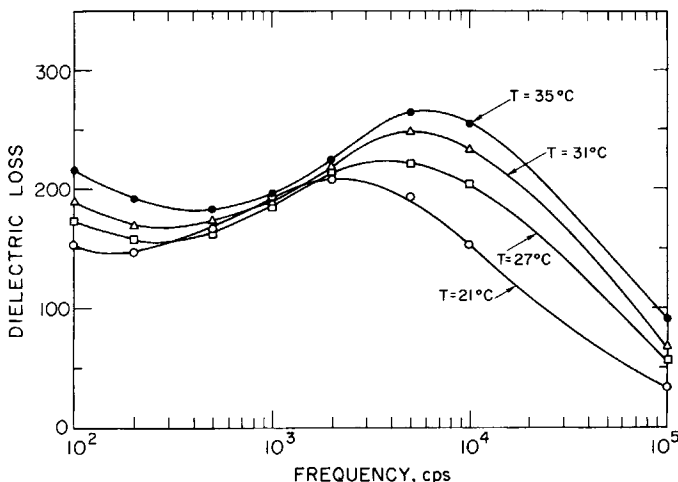


Fig. 5. Frequency dependence of dielectric loss of slightly wet ($n = 1.0\%$ or 4.7% by weight water content) sulfonic acid-polystyrene film at various temperatures.

One explanation for this abrupt increase of specific polarization is that in the dry film the hydrogen ions are associated with $-\text{SO}_3^-$ groups by strong ionic bonds. Since the dry sulfonic acid group is stiff and difficult to polarize, P_n^* is low.

As the water is sorbed by the film, the $-\text{SO}_3^- \text{H}^+$ groups hydrate into $\text{SO}_3^- \text{H}_3\text{O}^+$ ($n = 1$) and then into $-\text{SO}_3^- \text{H}_5\text{O}_2^+$ ($n = 2$), $-\text{SO}_3^- \text{H}_7\text{O}_3^+$ ($n = 3$), etc. The hydrogen ions begin to dissociate from the $-\text{SO}_3^-$ groups and associate with water molecules.¹¹ Since the hydrated sulfonic acid group is now flexible and polarizable, \bar{P}_n is high.

Results suggest that the presence of sorbed water in sulfonic acid polystyrene films gives rise to a specific water-induced relaxation process, which is characterized by high dielectric constant, loss, and increment $\Delta\epsilon'$. Its characteristic frequency occurs in the vicinity of 10^3 Hz, as indicated in Figure 4, and its experimental activation energy is computed to be 11.5 kcal/mole $\pm 10\%$.

The original Debye theory assumes a single period of relaxation which is the same for all dipoles in the system. For liquids, this assumption is justified because all the molecules are independent of each other. This, however, is not the case with polar polymers where the dipoles are coupled to each other in many ways. The effect of this on dielectric properties is to spread the dispersion region on the frequency scale.

Accordingly, it was necessary to modify the original Debye equations, taking into account all this evidence. Equation (4) represents a subsequent modification of the original Cole-Cole plot developed by Davidson and Cole¹² and is generally involved when the distribution of relaxation times is not symmetric:

$$\epsilon^* = \epsilon' + \frac{\epsilon_0' - \epsilon_\infty'}{1 + (j\omega\tau_0)^\beta} \quad (4)$$

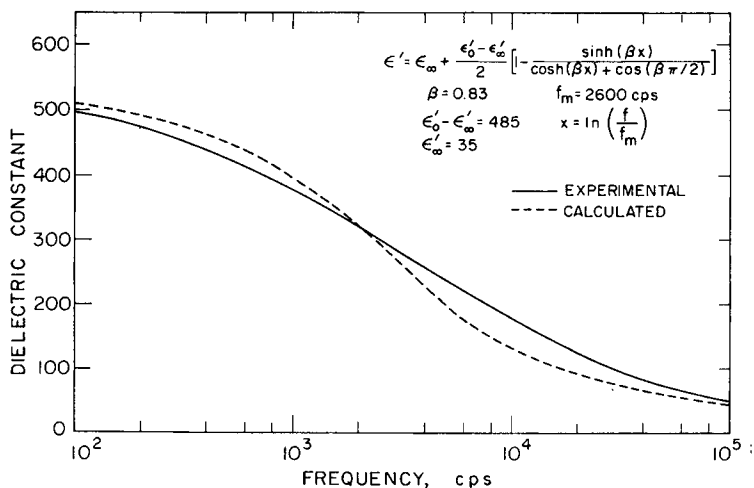


Fig. 6. Comparison of experimental and calculated dielectric constant vs. frequency relationship of slightly wet ($n = 1.0\%$ or 4.7% by weight water content) sulfonic acid-polystyrene film at 20°C .

From eq. (3), it can be shown that

$$f_m = \left(\frac{1}{2\pi\tau_0} \right) \tan \left(\frac{\pi/2}{\beta + 1} \right) \quad (5)$$

where τ_0 is the most probable relaxation time, f_m is the frequency for maximum dielectric loss, and β is an empirical constant characterizing the slope of the dielectric constant-versus-frequency curve and the shape of the bell-shaped dielectric loss-versus-frequency curve; β is usually given as a decimal fraction of 1, taking $90^{\circ} = 1$. Therefore, β can assume any value between 0 and 1. If $\beta = 1$, the case reduces to the Debye type of dielectric relaxation process with only one relaxation time possessed by all molecules.

The ϵ_0' and ϵ_{∞}' values are extrapolated values of the dielectric constant at zero and infinite frequencies. Extrapolation was done by means of the Cole-Cole method. According to this method, the experimental values of ϵ'' was plotted against the corresponding values of ϵ' at different frequencies. The points fell approximately on the circular arc loci, called the Cole-Cole arc. The points where the arc crosses the ϵ' axis are ϵ_0' and ϵ_{∞}' . The value of the constant β was determined by the angle $\beta\pi$, which corresponds to the angle between the radii of the arc to the points ϵ_0' and ϵ_{∞}' from the center of the circle.

Since eq. (4) represents the dependence of the complex dielectric constant ϵ^* on the angular frequency ω , it was desirable to calculate the dependence of its components ϵ' and ϵ'' on frequency. Thus, the calculated curves were compared to the experimental results and the degree of agreement found.

The expression giving the dielectric constant ϵ' as a function of frequency is

$$\epsilon' = \epsilon_{\infty}' + \frac{1}{2} (\epsilon_0' - \epsilon_{\infty}') \left[1 - \frac{\sinh(\beta x)}{\cosh(\beta x) + \cos(\beta\pi/2)} \right] \quad (6)$$

where $x = \ln(f/f_m)$.

The corresponding expression of dielectric loss ϵ'' as a function of frequency is

$$\epsilon'' = \frac{1}{2} (\epsilon_0' - \epsilon_{\infty}') \frac{\sin(\beta\pi/2)}{\cosh(\beta x) + \sin(\beta\pi/2)}. \quad (7)$$

In Figure 6 is shown the calculated curve (dashed line) of the dielectric constant ϵ' as a function of frequency. The curve was calculated using eq. (6). Constants β , ϵ_0' , and ϵ_{∞}' were obtained from the Cole-Cole analysis for the slightly hydrated film. Drawn with full line is the experimental curve for the same film measured at 20°C. The agreement between the two curves is good. The discrepancies are partially due to inaccuracy in determining the Cole-Cole parameters and to ionic conduction occurring at low frequencies.

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