

Beta Dielectric Dispersion in Natural Rubber Latex

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Synopsis

The dielectric dispersion of natural rubber latex has been investigated over a frequency range of 0.1–100 MHz and at six temperatures from 20° to 70°C. A computer analysis of the dispersion data showed that the Cole–Cole structural equation gave a better fit than the Debye. The large values of the Cole–Cole α spread parameter suggest heterogeneity of structure in rubber latex. The latex viscosity and the relaxation time were both found to be influenced by changes in temperature. Application of the Arrhenius temperature equation to the data yielded a mean activation enthalpy of 32.6 ± 2.8 kJ/mol for the relaxation process.

INTRODUCTION

The propagation of electromagnetic waves in biological materials is determined by their dielectric properties. These properties give information about the mechanism of interaction of electromagnetic fields with various systems such as heterogeneous materials, biopolymers, and colloidal suspensions. The dielectric properties of usual interest are the relative permittivity or dielectric constant ϵ' , the dielectric loss factor ϵ'' and also the conductivity σ . These properties are known to depend on the material in question and vary with frequency and temperature.^{1–4}

Latex is generally defined as a stable dispersion of a polymeric substance in an essentially aqueous medium and it may be classified as natural, synthetic, or artificial according to whether it occurs naturally as a product of metabolism of a plant, or is produced by the process of emulsion polymerization or by dispersion of the bulk polymer in an aqueous medium.⁵ Natural rubber latex which has been investigated in this study is a complex biological colloid known to undergo coagulation within a few hours of tapping from the tree, resulting in a separation into clots of rubber and a clear serum.^{5–8} It is however often necessary to preserve it in the liquid form for transportation to factories where it is processed into various forms of industrial dry rubber. Preservation prevents coagulation and subsequent putrefaction of the latex. One of the popular methods of natural rubber latex preservation, which is also used on a commercial basis is by application of around 0.3% ammonia which acts as a bactericide, an alkali, and also as an ion stabilizer.

The purpose of this study is to investigate the dielectric dispersion characteristics of the ammoniated natural rubber latex over a frequency range of 0.1–100 MHz, and at six temperatures from 20° to 70°C. This would establish the β -dispersion parameters for the latex and add to the existing knowledge about its structural properties.

EXPERIMENTAL

Each sample of the natural rubber latex investigated was collected in 100 mL conical flasks from freshly tapped rubber trees (*Hevea brasiliensis*) which are cultivated for commercial production of rubber. Ammonia was immediately added to each sample at a level of around 0.3% and shaken to prevent coagulation. Latex concentrate was then prepared by centrifuging at 4000 rpm for 20 min using a Minor (MSE) table centrifuge. All dielectric and other subsequent measurements on the sample were made within 5 hours of preparation. Measurements were repeated for latex samples collected on five different occasions. The dry rubber content of each sample was estimated by the method of precipitation with acetic acid and it was found to vary between 54.2 and 59.4% with a mean of $56.8 \pm 2.3\%$.

Dielectric measurements were carried out using a resonance technique. This method involved use of a commercially available magnification meter (made by Marconi Instruments Co., U.K.) and includes a Q meter TF1245 working in conjunction with two oscillators TF1246 (for the frequency range 0.04–50 MHz) and TF 1247, for the range 20–300 MHz. The effective capacitance C and conductivity σ of the samples were determined by resonating the test circuit with and without the specimen connected and obtaining the respective tuning capacitances and Q values at resonance. The sample cell used in the experiment contained two circular brass electrodes each having a diameter of approximately 0.6 cm with an interelectrode distance of 6 cm. Full details of measurement technique and correction for electrode polarization effects have been reported elsewhere.⁹

With a specimen introduced in the cell, the effective capacitance of the system at a particular frequency and temperature may be written as

$$C = \epsilon' \epsilon_0 k + C_o \quad (1)$$

and the conductance:

$$G = \sigma k = 2\pi f \epsilon_0 \epsilon'' k \quad (2)$$

where ϵ' is the relative permittivity of the sample in the cell, ϵ'' is its dielectric loss, σ is the conductivity, and f is frequency. Also ϵ_0 is the permittivity of free space, k is the cell constant, and C_o is the residual capacitance. The values of k and C_o for the dielectric cell used were determined from measurements on air and distilled water and were checked by using glycerol and ethanol. Specimen temperature was controlled using a Grant water bath (Grant Instr. Ltd., U.K.) permitting a variation between 20° and 70°C.

Each latex sample was introduced into the cell and the relative permittivity ϵ' and a.c. conductivity σ measured over a frequency range 0.1–100 MHz at six temperatures 20, 30, 40, 50, 60, and 70°C, respectively. The estimated uncertainty using the resonance technique is around 6% for the dielectric quantities measured. Viscosity measurements were also carried out on the samples with an Ostwald capillary viscometer. The average water content in the samples was $62.9 \pm 5.2\%$ as determined by using an oven (Griffin 300 FC) maintained at a temperature of around 50°C.

RESULTS AND ANALYSIS

The values of the relative permittivity of natural rubber latex as a function of frequency and at six temperatures are shown in Figure 1. The a.c. conductivity σ calculated from the dielectric loss ϵ'' are also plotted against frequency in Figure 2. Both the relative permittivity and conductivity data represent an average of six different measurements and Table I gives the mean values and standard deviations showing the spread of ϵ' and σ at selected frequencies within the β -dispersion range covered in the experiment.

A computer analysis of the data was used to obtain the β -dispersion parameters of the rubber latex. This involves using a curve-fitting routine¹⁰ to fit the measured dielectric data to two different structural models in accordance with the Debye¹¹ and Cole-Cole¹² equations, both being corrected for ionic conductivity σ_o . Using the Debye equation, the complex permittivity ϵ^* of the latex sample is of the form

$$\epsilon^* = \epsilon' - j\epsilon'' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + jff_R} - j \frac{\epsilon_o}{2\pi f\epsilon_o} \quad (3)$$

while the Cole-Cole equation gives

$$\epsilon^* = \epsilon' - j\epsilon'' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (jff_R)^{1-\alpha}} - j \frac{\sigma_o}{2\pi f\epsilon_o} \quad (4)$$

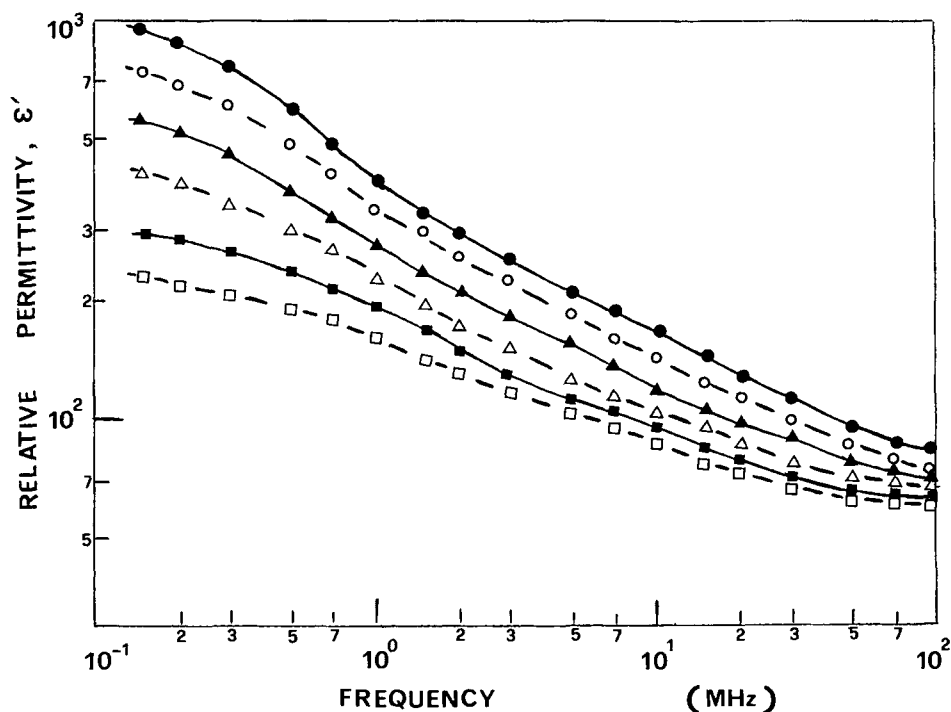


Fig. 1. Relative permittivity of natural rubber latex as a function of frequency at six temperatures. ●, 20°; ○, 30°; ▲, 40°; △, 50°; ■, 60°; and □, 70°C.

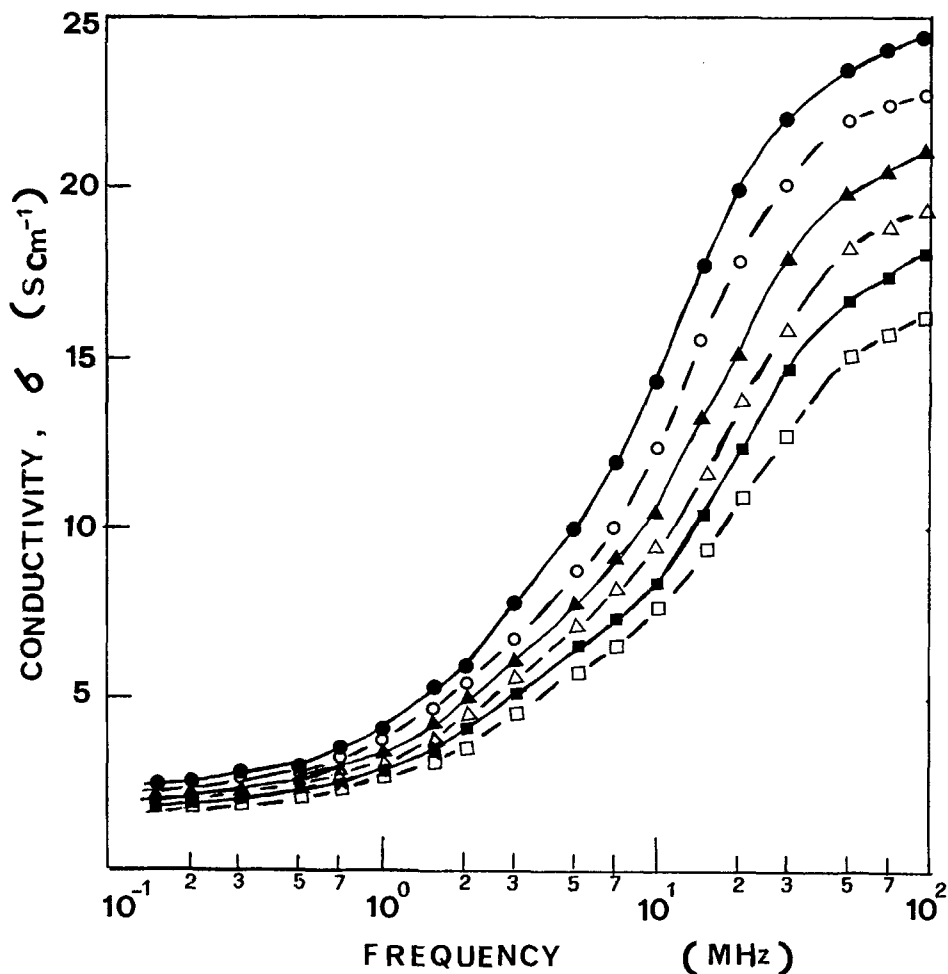


Fig. 2 Variation of a.c. conductivity of rubber latex with frequency at six temperatures. ●, 20°; ○, 30°; ▲, 40°; △, 50°; ■, 60°; and □, 70°C.

where ϵ_s and ϵ_∞ are the static and high frequency permittivities, respectively, f_R is the relaxation frequency, ϵ_o the ionic conductivity, α is the spread of the relaxation frequencies, and ϵ_o is the permittivity of free space.

The root mean square errors (RMSEs) of the fitted data were found to be smaller for Eq. (4) than for Eq. (3) as shown in Table II. The values of α were also significantly different from zero suggesting that the rubber latex does not exhibit a Debye behavior. The fitted parameters have therefore been presented on the basis of the Cole-Cole model. Table III shows the computer-fitted parameters and their respective 95% confidence intervals. Table IV gives the variation of the latex viscosity η and the relaxation time τ with temperature. This table shows that the higher the temperature, the smaller the latex viscosity and also its dielectric relaxation time. The relaxation time (τ) for the dispersion obtained at each temperature is plotted against the inverse of temperature ($1/T$) and shown in Figure 3.

TABLE I
Mean Values with Standard Deviations Showing Spread of ϵ' and σ at Selected Frequencies

Frequencies (MHz)	Frequencies						
	0.5	1.0	5.0	10.0	50.0	100.0	
Relative permittivity of latex							
20°C	567.1 ± 18.4	398.7 ± 15.9	225.1 ± 11.3	182.0 ± 5.5	93.3 ± 4.7	78.1 ± 3.4	
30°C	496.0 ± 17.6	350.3 ± 14.0	196.2 ± 7.8	155.1 ± 6.2	86.1 ± 4.9	74.3 ± 3.6	
40°C	385.3 ± 17.1	275.0 ± 10.7	161.1 ± 6.7	127.2 ± 5.4	76.3 ± 4.2	71.2 ± 4.0	
50°C	304.1 ± 12.2	228.1 ± 11.4	132.9 ± 7.0	108.6 ± 4.9	69.9 ± 3.5	67.5 ± 2.9	
60°C	240.3 ± 10.6	188.1 ± 8.6	111.5 ± 4.8	95.1 ± 4.7	65.2 ± 2.9	62.8 ± 3.1	
70°C	198.0 ± 8.9	161.1 ± 7.2	102.6 ± 4.6	85.5 ± 3.4	61.1 ± 3.1	59.3 ± 3.2	
a.c. conductivity of latex $\sigma \pm$ SD (S/cm)							
20°C	3.2 ± 0.2	4.3 ± 0.2	10.1 ± 0.5	14.3 ± 0.8	23.6 ± 1.1	24.3 ± 1.0	
30°C	3.2 ± 0.3	3.8 ± 0.2	8.8 ± 0.4	12.4 ± 0.6	22.0 ± 1.0	22.8 ± 1.2	
40°C	2.8 ± 0.2	3.4 ± 0.2	7.8 ± 0.4	10.6 ± 0.5	19.9 ± 0.8	21.0 ± 1.0	
50°C	2.4 ± 0.2	3.1 ± 0.3	7.2 ± 0.3	9.4 ± 0.6	18.3 ± 0.9	19.4 ± 0.9	
60°C	2.4 ± 0.2	3.0 ± 0.2	6.5 ± 0.3	8.6 ± 0.5	16.8 ± 0.8	18.2 ± 0.8	
70°C	2.2 ± 0.1	2.8 ± 0.1	5.8 ± 0.2	7.7 ± 0.4	15.2 ± 0.7	16.2 ± 0.8	

TABLE II
Root Mean Square Errors for Debye and Cole-Cole Models

Latex temperature (°C)	RMSE	
	Debye	Cole-Cole
20	2.15	1.18
30	2.65	1.20
40	1.85	0.64
50	1.36	0.83
60	1.69	0.63
70	1.52	0.71

TABLE III
Computer-fitted Dielectric Parameters for Natural Rubber Latex

Latex temperature (°C)	Δ ($\epsilon_s - \epsilon_\infty$)	ϵ_∞	f_p (MHz)	α	σ_o S/cm
20	1647 ± 41	100.8 ± 11.5	0.173 ± 0.011	0.36 ± 0.02	2.2 ± 0.2
30	1165 ± 35	70.9 ± 9.2	0.224 ± 0.016	0.41 ± 0.03	2.0 ± 0.2
40	856 ± 31	59.8 ± 7.5	0.258 ± 0.019	0.42 ± 0.03	2.1 ± 0.1
50	494 ± 23	60.8 ± 6.6	0.469 ± 0.029	0.37 ± 0.04	1.6 ± 0.1
60	310 ± 16	58.0 ± 6.3	0.701 ± 0.034	0.36 ± 0.02	1.9 ± 0.2
70	211 ± 11	53.7 ± 5.9	1.109 ± 0.072	0.34 ± 0.02	1.8 ± 0.1

TABLE IV
Variation of Viscosity and Relaxation Time with Latex Temperature

Latex temperature (°C)	Viscosity, η (mNs m ⁻²)	Relaxation time, τ (μ s)
20	6.88 ± 0.28	0.92 ± 0.06
30	4.89 ± 0.22	0.71 ± 0.05
40	3.36 ± 0.19	0.62 ± 0.05
50	2.38 ± 0.14	0.34 ± 0.02
60	1.81 ± 0.10	0.23 ± 0.01
70	1.40 ± 0.08	0.14 ± 0.01

DISCUSSION

In this study, natural rubber latex measured at six temperatures from 20° to 70°C was found to exhibit a β -dielectric dispersion in the frequency range 0.1–100 MHz. Some of the phenomena giving rise to such dispersion have been associated with the Maxwell-Wagner polarization effects and also the rotation of polar molecules.^{3,13} It is believed that in this relaxation region, molecules are no longer able to rotate with the applied electric field without the occurrence of a phase lag which causes an absorption of energy from the field, with a consequent fall in the relative permittivity ϵ' and an accompanying rise in conductivity σ with frequency. This trend was generally observed in the latex samples investigated. Also, in line with previous

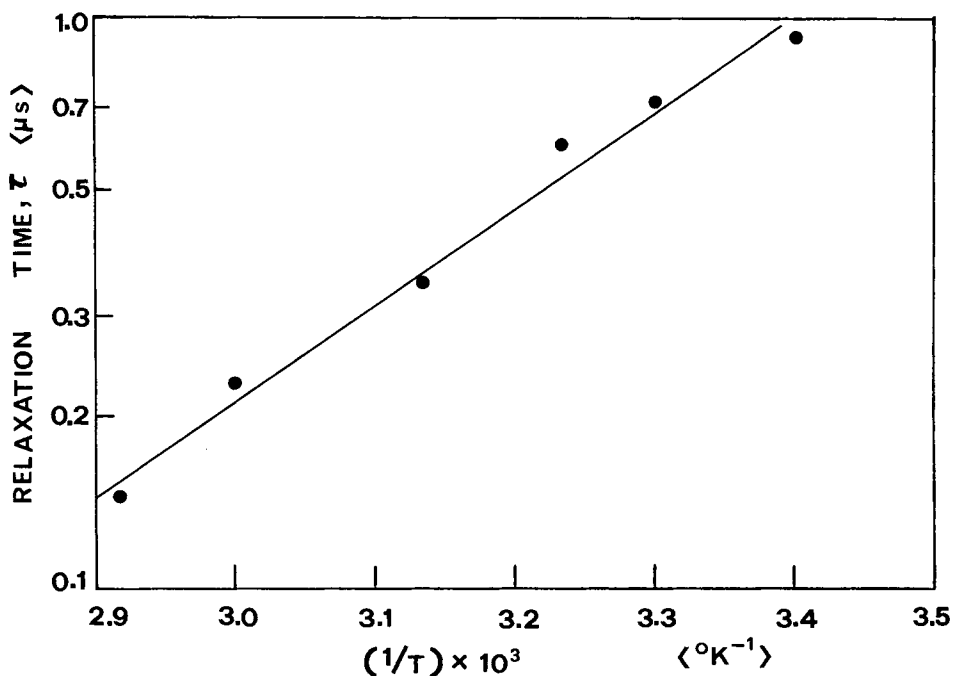


Fig. 3. Relationship between relaxation time and temperature of natural rubber latex.

reports on the dielectric properties of biological fluids,^{1,3} the dispersion in the latex was found to be temperature dependent.

The composition of natural rubber latex includes rubber hydrocarbon, carbohydrates, proteins, mineral salts, and a large proportion of water. The latex also contains a variety of enzymes of which invertase has been identified the most important, particularly from the viewpoint of substrate breakdown.¹⁴ Invertase hydrolyses sucrose into glucose and fructose both of which are often utilized by latex bacteria to produce volatile fatty acids.¹⁵ The presence of invertase and sucrose has therefore been recognized as a general cause of latex instability. Thus, a small quantity of ammonia ($\sim 0.3\%$) was added to the latex samples as an anticoagulant and preservative. It acts as a bactericide, an enzyme poison which can complex with the nonrubber substrates in latex to give a material not readily broken down by bacteria. However this proportion of ammonia in the samples is too low to contribute significantly to the dielectric dispersion observed in the latex.

The computer analysis of the dielectric data showed that in agreement with previous findings in some other biological materials,^{3,4,16,17} the Cole-Cole structural model is more appropriate than the Debye in describing the β -dispersion observed in the natural rubber latex. The large values of the Cole-Cole α -spread parameter obtained at different temperatures are in support of heterogeneity of structure in latex. The latex viscosity (η) and the relaxation time (τ) decrease with increasing temperature resulting in a shift in the relaxation frequency toward the high frequency region of the dispersion.

The linearity of the graph of $\ell n \tau$ against the reciprocal of the absolute temperature in Figure 3 shows that a mean activation enthalpy (ΔH) can be defined for the relaxation process and calculated using the Arrhenius temperature equation given by:^{4,18}

$$\Delta H = R \cdot \frac{\partial(\ell n \tau)}{\partial(1/T)} - RT \quad (5)$$

where T is absolute temperature, τ is the relaxation time, and R is 8.3 J/mol K⁻¹. The slope of the graph in Figure 3 gave for the relaxation process in the latex an activation enthalpy of 32.6 ± 2.8 kJ/mol which is about two hydrogen bond energies.

The mechanism of the dielectric dispersion phenomenon in natural rubber latex may be generally associated with molecular rotation largely due to the presence of rubber hydrocarbon molecules. Also, since some amount of oxygen may be present possibly in the form of the carbonyl groups, such molecular groups in addition to the protein molecules in the rubber latex may contribute to the observed dispersions. As pointed out earlier, the results of this investigation are for latex concentrates with 54.2–59.4% dry rubber content and the average age of the trees from which the samples were obtained was around 16 years. While the concentration of a biological material is generally believed to have a marked influence on the dielectric dispersion characteristics, the contribution of age is not well known, and it is not within the coverage of the present investigation. Also, it is unlikely that the type of stabilizer used in the latex will affect the dielectric dispersion results provided its concentration in the latex sample is low (e.g., $\sim 0.3\%$ as for ammonia). It is known⁵ that many important latex processes often require as raw material a high latex concentrate with a minimum of around 60% dry rubber content. The results obtained in this study are valid for latex concentrates with an average of 56.8% dry rubber content and may thus be of general importance.

In conclusion, the significance of this work lies in the dielectric parameters established for the fresh natural rubber latex as they are related to the structural properties of the latex. The technique may be found useful for routine monitoring of the quality of rubber latex preserved for industrial processing.

The author acknowledges with thanks the kindness of Professor E. H. Grant and Dr. R. J. Sheppard for the use of their curve-fitting programs in this study.

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Received October 21, 1985

Accepted February 1, 1986