

The Dielectric Behavior of Natural Resin Shellac

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Synopsis

The Cole-Cole method has been applied for an analysis of the dielectric relaxation data of the natural resin shellac, obtained by Bhattacharya in the temperature range 20–110°C. Three relaxation processes were observed for temperatures 20–60°C. At 70°C, two relaxation processes were noticed, whereas only one was observed by Bhattacharya between 20 and 110°C. The relaxations at 80°C and above represented typical Cole-Cole type. The variation of the static dielectric constant with temperature revealed three distinct slopes, which indicated different phases of the resin during its thermal transition from solid to liquid state. Two “transformation points,” around 40 and 70°C were noted, i.e., the glass transition temperature and melting point of the resin, respectively. Significant changes in static dielectric constant, dielectric increment, relaxation time, and Cole-Cole distribution parameter were observed during a rise of temperature from 80 to 110°C. The results of the present study indicate that some rearrangement in the tertiary disposition of the resin molecules takes place during the rise of temperature from 20 to 110°C.

INTRODUCTION

The dielectric properties of the natural resin shellac were investigated by Bhattacharya¹ in the frequency range 50 Hz–500 kHz at temperatures between 20 and 110°C. In that study the dielectric dispersion curves of the resin at different temperatures indicated only one relaxation process in the above frequency range. Lakshminarayanan and Gupta² subsequently reported the dielectric relaxation of shellac modified with amino resins in the frequency range 100 Hz–100 kHz at temperatures between 20 and 120°C, in which two relaxation processes were obtained for the modified resins. The dielectric data of both native and modified shellac compositions^{1,2} and other resins^{3,4} were ascribed to the relaxation of the hydroxyl groups present in the resin molecules.^{1,2}

An analysis of the dielectric data of the natural resin Manila copal by the Cole-Cole⁵ method at different temperatures between 30 and 150°C in the frequency range 50 Hz–500 kHz has been reported earlier.⁶ The application of the Cole-Cole method was found more effective in obtaining information regarding the different relaxation processes and the conformational changes occurring in the resin molecules with the rise of temperature from 30 to 150°C. The present paper reports an analysis of the dielectric data of the natural resin shellac, obtained earlier by Bhattacharya,¹ by the same Cole-Cole method in the frequency range 50 Hz–500 kHz and at temperatures 20 to 110°C. The advantage of the Cole-Cole method, which was not applied previously by Bhattacharya,¹ is that it is more informative regarding the different relaxation processes involved and also of the changes in the tertiary disposition of the resin molecules during their transition from the solid to the liquid state.

Theoretical

The Cole-Cole expression for the complex dielectric constant (ϵ^*) at any frequency ω for molecules having distribution in relaxation times is given by

$$\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/[1 + (i\omega\tau)^{1-\alpha}] \quad (1)$$

The real (ϵ') and imaginary (ϵ'') parts are given by

$$\epsilon' - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty)[1 + (\omega\tau)^{1-\alpha} \sin \alpha\pi/2]/[1 + 2(\omega\tau)^{1-\alpha} \sin \alpha\pi/2 + (\omega\tau)^{2(1-\alpha)}] \quad (2)$$

and

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)(\omega\tau)^{1-\alpha} \cos \alpha\pi/2/[1 + 2(\omega\tau)^{1-\alpha} \sin \alpha\pi/2 + (\omega\tau)^{2(1-\alpha)}] \quad (3)$$

where ϵ_0 and ϵ_∞ are the low- and the high-frequency dielectric constants, τ is the relaxation time, and α is the distribution parameter. The Debye⁷ expressions for complex dielectric constant and the real and imaginary parts of the complex dielectric constant can be obtained by putting $\alpha = 0$ in the Eqs. (1)–(3), respectively.

In the present paper, the low- and high-frequency dielectric constants (ϵ_0 and ϵ_∞) have been determined from the intersections of plots of ϵ'' versus ϵ' with the abscissa. The relaxation times at different temperatures have been determined from the relation

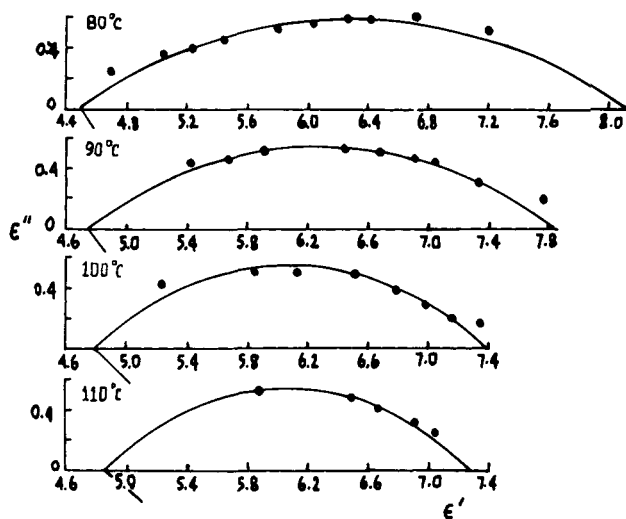
$$(\omega\tau)^{1-\alpha} = v/u \quad (4)$$

where v and u are the distances from ϵ_0 and ϵ_∞ , respectively, from a point on the semicircle corresponding to the frequency ω .

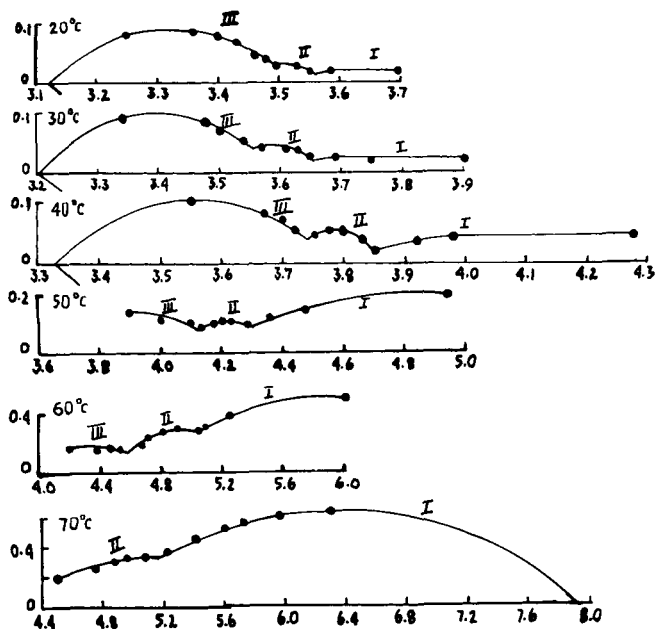
RESULTS

The Cole-Cole patterns (ϵ'' versus ϵ' plots) for the natural resin shellac at different temperatures were derived from the data reported by Bhattacharya¹ and are shown in Figure 1. All the observed points in the ϵ'' versus ϵ' plots for temperatures 20–60°C, however, were not contained in a single semicircular arc. The dielectric relaxation of shellac for these temperatures are reported by three relaxation processes (I, II, and III in the figure). It may be noticed that, at 20, 30, and 40°C, process I is not so prominent, and the dispersions have occurred at frequencies greater than 1–2 kHz (processes II and III). At temperatures 50 and 60°C, the contribution resulting from the process III is almost insignificant. The dielectric relaxation of the resin at 70°C afforded two dispersion processes. At temperatures 80°C and above, however, the ϵ'' versus ϵ' plots represented perfect semicircular Cole-Cole patterns.

The various dielectric parameters determined from the Cole-Cole diagrams at different temperatures, along with the experimentally obtained values,¹ are given in the Table I, where the ϵ_0 and ϵ_∞ values of shellac are shown in columns 1 and 2, respectively. At temperatures for which complete Cole-Cole arcs could not be obtained, the ϵ_0 and ϵ_∞ values shown in the table are the experimental values obtained by Bhattacharya.¹ The static dielectric constant (ϵ_0) of shellac increased from 3.7 at 20°C to 8.13 at 80°C and then decreased to a value of 7.26 when the temperature increased from 80 to 110°C. The variation of the ϵ_0 of shellac with temperature has been plotted in Figure 2. Three distinct slopes (1–3 in the figure) are shown.



(a)



(b)

Fig. 1. Cole-Cole patterns of shellac at different temperatures.

The values of the dielectric increments ($\Delta\epsilon = \epsilon_0 - \epsilon_\infty$), which are related to the dipole moments, have been given in Table I, column 3. It may be seen that the value of the $\Delta\epsilon$ of shellac increased from 0.61 at 20°C to 3.65 at 80°C (an approximately sixfold increase), followed by a decrease of about 36% during the further rise of temperature from 80 to 110°C.

The relaxation times (τ) of shellac for temperatures 80–110°C were calculated from the Cole-Cole diagrams using relation (4) and shown in Table I, column 4. A decrease in τ from 5.5×10^{-5} sec at 80°C to 2×10^{-7} sec at 110°C was observed. A plot of $\ln(T\tau)$ versus $1/T$ has been drawn as in the Figure 3. The activation

TABLE I
Different Dielectric Parameters of Shellac Derived from the Cole-Cole Diagrams at Different Temperatures

Temperature (°C)	Low-Frequency Dielectric Constant, ϵ_0		High-Frequency Dielectric Constant, ϵ_∞		Dielectric Increment, $\epsilon_0 - \epsilon_\infty$	Relaxation Time, τ (sec)	Cole-Cole Parameter, α
	Obsd Value	From Cole-Cole Diagram	Obsd Value	From Cole-Cole Diagram			
20	3.7		3.25	3.12			
30	3.91		3.34	3.20			
40	4.28		3.55	3.32			
50	4.95		3.90				
60	6.00		4.19				
70	7.12	7.9	4.49				
80	7.85	8.13	4.69	4.48	3.65	5.50×10^{-5}	0.61
90	7.78	7.85	4.90	4.74	3.11	8.74×10^{-6}	0.58
100	8.08	7.38	5.24	4.80	2.58	1.80×10^{-6}	0.51
110	8.23	7.26	5.90	4.91	2.35	2.00×10^{-7}	0.47

energy has been calculated from the slope (Fig. 3) using Eyring's equation and found to be 60 kCal/mol.

The Cole-Cole distribution parameters (α) for shellac at different temperatures have been shown in the last column of Table I. A decrease in the value of α was noted from 0.61 at 80°C to 0.47 at 110°C.

DISCUSSION

The different slopes in the ϵ_0 -temperature plot (Fig. 2) of shellac indicate three distinct phases during its thermal transition from the solid to the liquid state. The two transformation points around 40 and 70°C (T_i and T_{ii} in Fig. 2) are attributed to the glass transition temperature and the melting point of the resin, respectively. Bhattacharya¹ has also mentioned the existence of two transition temperatures, one around 35°C and the other in the range 60–110°C. If Cole-Cole diagrams in the present case are carefully examined, we may infer some rearrangement inside the molecules around 60–70°C as revealed from the transition from three relaxation processes to two. Dielectric studies on polyethyl methacrylate⁸ and on the natural resin Manila copal⁶ have shown an analogous transition from two relaxation processes to one with the rise of temperature as observed from their Cole-Cole diagrams.

The dielectric dispersion curves for shallac obtained by Bhattacharya¹ showed only one dispersion for the entire temperatures range between 20 and 110°C. An inspection of the frequency profiles of the dielectric loss of shellac obtained by Bhattacharya¹ for 50, 60, and 70°C, however, revealed the existence of another dispersion region at the high-frequency end. The present investigation indicates the existence of yet another, third, relaxation process for temperatures 20–60°C, which was not reported in the earlier paper by Bhattacharya.¹

From an inspection of the Cole-Cole patterns (Fig. 1) at different temperatures, it appears that process I between 20 and 70°C arises from the orientation of a segment. This process becomes prominent above the glass transition temperature ($\sim 40^\circ\text{C}$) due to decreased viscosity. In order to gain a qualitative insight

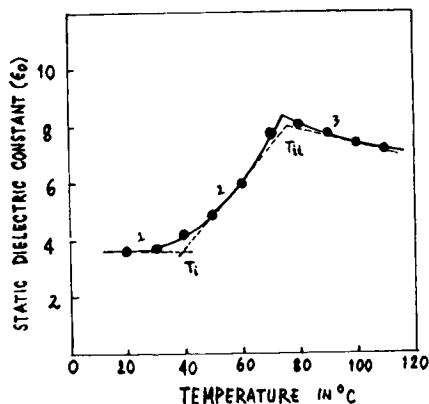


Fig. 2. Variation of static dielectric constant (ϵ_0) of shellac with temperature.

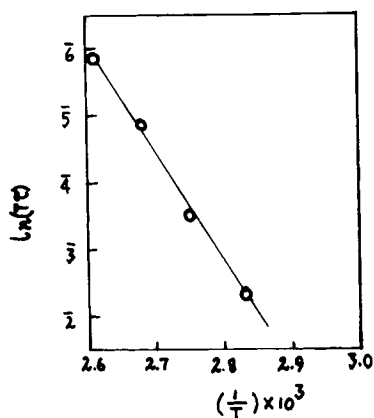


Fig. 3. Plot of $\ln(T\tau)$ vs $1/T$ plot for shellac.

into the different relaxation processes of shellac, we have separately analyzed process II at 30–60°C (Fig. 1) and process III at 20–40°C (Fig. 1) in the Cole-Cole diagrams of Figures 4 and 5, respectively. The various dielectric parameters evaluated from these diagrams are given in Tables II and III, respectively. It may be seen from Table II that both the dielectric increment and the relaxation time for process II increase with temperature. This suggests a progressive increase in the overall charge and size of the rotating unit under the conditions studied. Process II may thus be attributed to the orientation of any segment whose size increased with the temperature.

The dielectric increment in process III, on the other hand, remained almost constant (Table III), and the relaxation time is found to decrease by 38% during the temperature rise from 20 to 40°C. It appears that the process III phenomenon is due to the relaxation of a polar group, the rotating unit may be either the carboxyl or hydroxyl groups of the shellac molecule as suggested by Bhattacharya¹ and later on by Lakshminarayanan and Gupta.² The effect of process III became insignificant with increased temperature when the decreased viscosity favored orientation of larger segments.

We find that between 20 and 70°C the molecules experienced limited orientational freedom due to the presence of various internal forces owing to high viscosity as reflected by the low values of both the dielectric constant and the

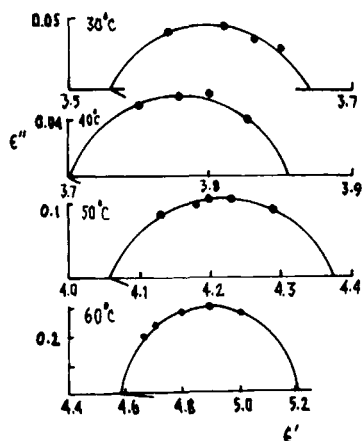


Fig. 4. Cole-Cole plots for process II at different temperatures.

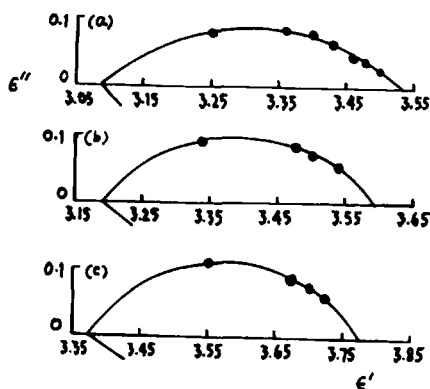


Fig. 5. Cole-Cole arcs for process III at different temperatures: (a) 20°C, (b) 30°C, (c) 40°C.

TABLE II
Different Dielectric Parameters of Relaxation Process II at Different Temperatures

Temperature (°C)	Dielectric Increment, $\epsilon_0 - \epsilon_\infty$	Relaxation Time, τ (sec)	Distribution Parameter, α
30	0.14	2.13×10^{-5}	0.28
40	0.15	3.36×10^{-5}	0.21
50	0.32	4.4×10^{-5}	0.24
60	0.63	7.78×10^{-5}	0.04

dielectric loss.^{1,2} Yano and Wada⁹ attributed the relaxation process below the glass transition temperature to local motion in the form of oscillation or rotational oscillation. On the other hand, segmental motion has been reported for polydimethyl siloxane molecules even below the temperature at which the fluid solidified.¹⁰ Segmental orientation (β -process) in the transition phase has also been reported in many polymers i.e., polystyrene,⁹ ethylene methacrylic acid copolymers,¹¹ poly(vinylidene fluoride),¹² and styrene-acrylonitrile copolymers.¹³

The single Cole-Cole arcs, the marked decline in dielectric increment, the

TABLE III
Dielectric Parameters of Relaxation Process III at Different Temperatures

Temperature (°C)	Dielectric Increment, $\epsilon_0 - \epsilon_\infty$	Relaxation Time, τ (sec)	Distribution Parameter, α
20	0.44	6.85×10^{-7}	0.53
30	0.41	4.54×10^{-7}	0.41
40	0.40	4.25×10^{-7}	0.36

relaxation time, and the distribution parameter at temperatures greater than 80°C observed in the present experiment all suggest that the relaxation at high temperature resulted from molecular motions. The relaxation behavior at high temperatures of a few polymers, i.e., poly(vinylidene fluoride),¹² polychlorotrifluoroethylene,¹⁴ styrene-acrylonitrile copolymers,¹³ and methacrylate homopolymers and copolymers¹⁵ was ascribed to α -process molecular motions. Dielectric studies on phenolformaldehyde resins and paper laminates have suggested that the relaxation process above 10^4 Hz is due to the rotational movements of the hydroxyl groups present in the resin and cellulose.⁴ Similar conclusions were drawn from studied on shellac-melamine-formaldehyde compositions.²

The condition at 80°C and above, represented by the typical single Cole-Cole diagrams, indicate one relaxation process with distribution. The Cole-Cole patterns for these temperatures closely resemble those obtained previously for the natural resin Manila copal at temperatures 100°C and above.⁶ It has been reported that the shellac at high temperatures forms a three-dimensional network structure either by the association or crosslinking of linear polymers by an intramolecular interaction.^{16,17} The observed reduction in ϵ_0 at temperatures above 80°C may be due to the decreased orientational freedom of the polar groups resulting from the crosslinkages. The 36% decrease in the dielectric increment (and hence in the dipole moment) due to rise of temperature from 80 to 110°C also lends support to the above conclusion. The phenomenon of a decrease in the dielectric constant with increasing degree of crosslinking has been reported in literature for unsaturated polyester resins and was also attributed to the immobilization of the polar groups in few cases.¹⁸

The marked fall in the relaxation time from a value of 5.5×10^{-5} sec at 80°C to a value of 5.0×10^{-7} sec at 110°C signifies some change in the tertiary disposition of the resin molecules in the liquid state. The state of compactness of the molecules resulting from the crosslinkages may explain the observed decrease in τ for the resin molecules, as suggested earlier. Dielectric behavior similar in nature has been reported previously for the natural resin Manila copal.⁶

The 23% decrease in the value of α obtained in the present experiment indicates that the resin molecules become dielectrically more symmetric, undergoing conformational rearrangement in course of the rise of temperature. Studies on the dielectric behavior of a few biopolymers have shown that the variation of the distribution parameter was associated with a structural change in the molecules.^{19,20} Also, in some ethylene-carbon copolymers²¹ and poly(vinylidene fluoride)²² a narrowing of the distribution parameter with temperature was reported together with the decrease of α , which was suggested to arise from chain folds and the chain torsion mechanisms.²¹ It may be noted that a similar 35%

decline in α was observed for the natural resin Manila Copal upon increasing the temperature from 100 to 150°C.⁶

The experimentally observed maximum ϵ'' value (ϵ''_m) of shellac¹ was reported to be somewhat less than one-third of the value obtained from the Debye equation $\epsilon''_m = (\epsilon_0 - \epsilon_\infty)/2$ [obtained by putting $\alpha = 0$ in Eq. 3], as also obtained in other plastic materials²³; this discrepancy was explained by the existence of a distribution in the relation time.^{1,23} The maximum values of ϵ'' for the molecules obeying a Cole-Cole type of distribution are obtained by putting $\omega\tau = 1$ in eq. (3):

$$\epsilon''_m = (\epsilon_0 - \epsilon_\infty) \cos \alpha\pi/2 / 2(1 + \sin \alpha\pi/2) \quad (5)$$

The ϵ''_m values calculated using relation (5) for temperatures 80–110°C are shown in Table IV along with the ϵ''_m values obtained experimentally by Bhattacharya¹ for comparison. It is found that the ϵ''_m values obtained by calculation and experiment are in close agreement. The data in Table IV, therefore, further justify the application of the Cole-Cole method to the understanding of the different processes involved in the dielectric dispersion of resins. It is considered that the hydroxyl groups present in the shellac and other resins provide the mechanism of dielectric loss.^{1,2,4} It was also noted that for both linear and branched poly(propylene oxide) ϵ_0 was an almost linear function of hydroxyl content.^{24,25} The observed decrease in the ϵ_0 and ϵ''_m values between 80 and 110°C, therefore, suggests that the number of hydroxyl groups participating in the relaxation process decrease for temperatures greater than 80°C. In Manila copal, however, no noticeable change occurred in the ϵ''_m values in the temperature range 100–150°C.⁶ The dielectric behavior exhibited by the natural resin shellac, as observed in the present work, has been found to be quite similar to the natural resin Manila copal reported earlier.⁶

Bhattacharya¹ used the relation $\tau = 4\pi\eta a^3/kT$ for obtaining some information about the size of the rotating unit in an applied alternating field. It has been discussed earlier⁶ that the above relation is of limited value and is inadequate for obtaining such information. From the present investigation it appears that the dielectric relaxation of shellac cannot be explained by the orientation of only hydroxyl groups, as suggested by Bhattacharya.¹ The data can be explained on the basis of relaxations of different segments and polar groups present in the resin. One of the three relaxation processes observed below the melting temperature in this study was interpreted to be due to the orientation of a polar group (which may be the hydroxyl group). The other processes (I and II) were attributed to segmental β -relaxation. At temperatures greater than melting point,

TABLE IV
Experimental and Calculated Values of ϵ''_m

Temperature (°C)	ϵ''_m	
	Experimental	Calculated ^a
80	0.62	0.58
90	0.54	0.54
100	0.5	0.52
110	0.52	0.51

^a From eq. (5).

the single relaxation process arose from molecular motions (α -process) resulting from molecular rearrangements in the liquid state.

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