

# Dielectric Behavior of the Constituents of the Natural Resin Shellac

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## Synopsis

The dielectric relaxation data of the constituents of natural resin shellac have been analyzed by the Cole–Cole method at temperatures between 10° and 90°C in the frequency range of 50 Hz to 500 kHz. The functional groups present in hard and soft lac appeared to be responsible for the dielectric properties exhibited by shellac below and above its glass transition and melting temperature, respectively. A combination of 70% hard lac and 30% soft lac was found to exhibit the dielectric properties of shellac satisfactorily.

## Introduction

It has been observed recently that the natural resin shellac exhibits multirelaxation processes (below its melting temperature<sup>1</sup>) like various polymers.<sup>2–8</sup> It has been shown that different relaxation processes of shellac could not be explained by the relaxation of hydroxyl groups only, as suggested by previous investigators.<sup>9,10</sup>

It is known that pure lac resin or simply hard lac, soft lac, and lac wax are the three constituents of shellac. Hard lac is the main fraction of shellac comprising about 70 wt % of the whole lac (shellac). Soft lac contributes 25–30 wt % when lac wax does not comprise more than 5% of the whole lac.<sup>11</sup> It is of interest, therefore, to study the dielectric behavior of these constituents for a better understanding of the dielectric properties exhibited by shellac. The application of the Cole–Cole<sup>14</sup> method has been found to be very effective to solve a few anomalies in the dielectric properties of the natural resins Manila Copal<sup>15</sup> and shellac.<sup>1</sup> In the present work, the same Cole–Cole method has been employed to analyze the dielectric relaxation data of the constituents of shellac obtained by Bhattacharya.<sup>12</sup> The analysis has thrown some light on the contribution of hard and soft lac resins toward the dielectric relaxation of shellac. The relaxation data of different combinations of hard and soft lac obtained by Bhattacharya<sup>13</sup> has also been analyzed to confirm whether the dielectric properties of shellac could be explained by the mixture of its constituents.

## THEORETICAL

The method of analysis of the data was as described previously for the natural resins Manila Copal<sup>15</sup> and shellac.<sup>1</sup>

## Results

The Cole–Cole patterns<sup>1,14,15</sup> for soft and hard lac resins at different temperatures were drawn using the data obtained by Bhattacharya<sup>12</sup> and are illustrated in Figures 1 and 2, respectively. For all temperatures between 10° and 40°C, the  $\epsilon''$ -versus- $\epsilon'$  ( $\epsilon'$  and  $\epsilon''$  are the real and imaginary parts of the complex dielectric constant<sup>1,15</sup>) plots for soft lac can be represented by two overlapping Cole–Cole arcs (marked I and II in Fig. 1). At 50°C and above, single typical Cole–Cole semicircles were obtained. The Cole–Cole curves for the hard resin at temperatures 30° to 60°C and at 70°C consisted of three and two overlapping relaxation processes, respectively (marked I, II, and III in Fig. 2). At 80° and 90°, single semicircular typical Cole–Cole patterns were observed. It may be noted from the figure that process III occurred in the frequency range of 25 to 500 kHz for all temperatures between 30° and 70°C.

Different dielectric parameters evaluated from the Cole–Cole diagrams at different temperatures for soft and hard lac resins are shown in Tables I and II, respectively. The variation of  $\epsilon_0$  with temperature for both soft and hard resins is illustrated in Figure 3. The corresponding variation for shellac has been incorporated in the same figure for comparison. Two transition points (marked

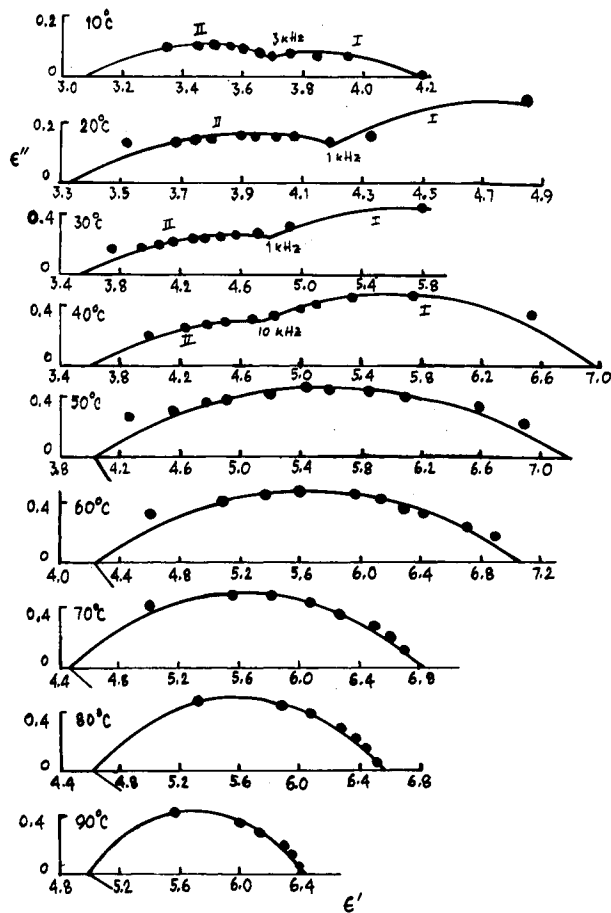


Fig. 1. Cole–Cole diagrams of soft lac at different temperatures.

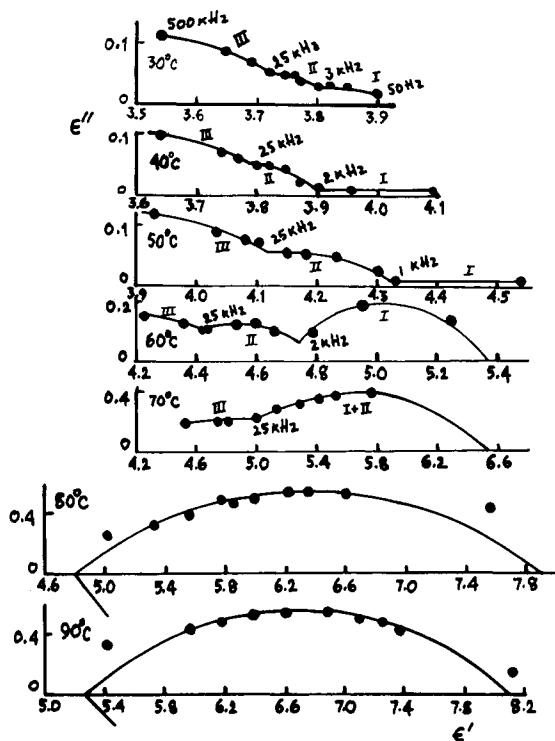


Fig. 2. Cole-Cole diagrams of hard lac at different temperatures.

$T_g$  and  $T_m$ ) may be noted for shellac around 40° and 70°C which were attributed to glass transition and melting temperatures of shellac<sup>1</sup> (which can be considered as semicrystalline material), respectively. A transition point ( $T_{ms}$ ) around 40°C was noted for soft lac, which may be termed the melting point of the resin. It appears from the figure that the glass transition temperature ( $T_{gs}$ ) of the soft resin is around 10°C. The abrupt change in relaxation process I due to the rise of temperature from 10° to 20°C (Fig. 1) also supports this phenomenon. For

Table I  
Different Dielectric Parameters of Soft Lac Evaluated from Cole-Cole Diagrams at Different Temperatures

Temperature, °C	$\epsilon_0$		$\epsilon_\infty$		Dielectric Increment $\Delta\epsilon$	Relaxation time $\tau$ , sec	Distribution parameter $\alpha$
	Observed value	Obtained from Cole-Cole diagram	Observed value	Obtained from Cole-Cole diagram			
10	4.2	4.2	3.35	3.08	1.12		
20	4.33	—	3.52	3.32	1.01		
30	5.8	—	3.74	3.54	2.26		
40	6.54	6.98	4.0	3.62	3.36		
50	6.92	7.18	4.22	4.02	3.16	$2.93 \times 10^{-5}$	0.63
60	6.9	7.08	4.6	4.24	2.84	$6.9 \times 10^{-6}$	0.58
70	6.72	6.82	5.0	4.48	2.34	$1.77 \times 10^{-6}$	0.49
80	6.51	6.57	5.33	4.62	1.95	$7.16 \times 10^{-7}$	0.41
90	6.4	6.44	5.56	4.99	1.45	$6.38 \times 10^{-7}$	0.32

Table II  
Different Dielectric Parameters of Hard Lac Evaluated from Cole-Cole Diagrams at Different Temperatures

Temperature, °C	$\epsilon_0$		$\epsilon_\infty$		Dielectric increment $\Delta\epsilon$	Relaxation time $\tau$ , sec	Distribution parameter $\alpha$
	Observed value	Obtained from Cole-Cole diagram	Observed value	Obtained from Cole-Cole diagram			
30	3.9	—	3.54	—	0.36		
40	4.1	—	3.64	—	0.46		
50	4.54	—	3.93	—	0.61		
60	5.24	5.37	4.23	—	1.14		
70	5.75	6.58	4.52	—	2.06		
80	7.56	7.9	5.0	4.8	3.1	$8.0 \times 10^{-5}$	0.57
90	8.13	8.1	5.41	5.28	2.82	$2.0 \times 10^{-5}$	0.52

hard resin the existence of a transition point around 50°C was noted, which is termed the glass transition temperature ( $T_{gh}$ ). The transition from two relaxation processes to one due to the rise of temperature from 70° to 80°C observed for hard lac (Fig. 2) suggested that its melting temperature is around 80°C (similar to what was observed for soft lac, shellac<sup>1</sup>, and Manila Copal<sup>15</sup>). Thus, the glass transition and melting temperature of soft lac are found to be about 30°C lower than those of shellac, while the corresponding temperatures for hard lac are found to be greater than those of shellac by 10°C. The transition temperatures of the resins reported here were verified from index of refraction and specific heat measurements. At temperatures below 40°C, the  $\epsilon_0$  values for hard lac were very much close to those for shellac. The static dielectric constant of lac wax was found to be almost constant in the temperature range of 10° to 100°C (Fig. 3).

Dielectric increment  $\Delta\epsilon$  ( $= \epsilon_0 - \epsilon_\infty$ ) of soft lac increased by three times as the temperature changed from 10° to 40°C, which accompanied a decrease (56.8%) in  $\Delta\epsilon$  with further rise of temperature up to 90°C. An approximately ninefold increase in  $\Delta\epsilon$  was observed for hard resin owing to the change of temperature from 30° to 80°C, followed by a decrease of 9% when temperature increased from

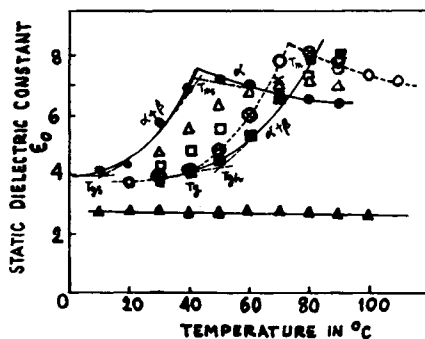


Fig. 3. Variation of static dielectric constant with temperature of soft lac, hard lac, and their mixtures: (●) soft lac; (■) hard lac; (○) shellac; (▲) lac wax; hard-soft lac mixture: (Δ) 20%–80%; (□) 50%–50%; (×) 70%–30%.

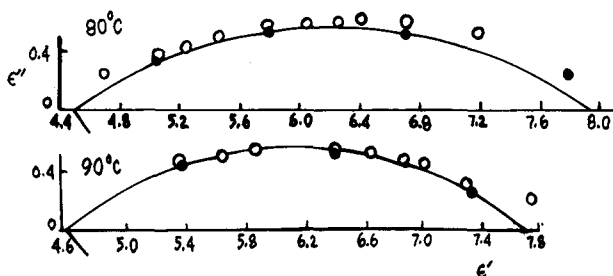


Fig. 4. Cole-Cole diagrams of 70%-30% mixture of hard lac and soft lac at 80° and 90°C.

80° to 90°C (Table II). At temperatures for which single Cole-Cole patterns were obtained for both soft and hard resins, the relaxation times ( $\tau$ ) were determined following Cole and Cole.<sup>1,14,15</sup> The relaxation time for soft lac was found to decrease from  $2.93 \times 10^{-5}$  sec at 50°C to  $6.38 \times 10^{-7}$  sec at 90°C (Table I).  $\tau$  for hard resin also decreased from  $8 \times 10^{-5}$  sec at 80°C to  $2 \times 10^{-5}$  sec at 90°C (Table II). An about 50% decrease in  $\alpha$  (Cole-Cole parameter<sup>1,15</sup>) for soft resin was observed due to the change of temperature from 50° to 90°C (Table I). For hard resin only a 9% decrease in  $\alpha$  was obtained when the temperature increased from 80° to 90°C (Table II).

The variation of static dielectric constant with temperature for different combinations of hard and soft lac resins, viz., 70-30, 50-50, and 20-80 wt % have been drawn using the data obtained by Bhattacharya<sup>13</sup> and are shown in Figure 3 together with those of soft and hard lac resins (100%) as described earlier. The profile for soft lac (100%) gradually approaches to that of hard resin with increased addition of the latter in the hard-soft lac resin mixture. It may be seen from the figure that the experimental points for 70-30% hard-soft lac mixture fitted well with those of shellac (Fig. 3).

The  $\epsilon''$ -versus- $\epsilon'$  plots for the 70-30% hard-soft lac mixture at 80° and 90°C are shown in Figure 4. These were single Cole-Cole patterns like shellac at these temperatures.<sup>1</sup> The experimental points obtained for shellac (shown in the same figure for comparison) fitted well with the curves for hard-soft lac combinations. The curves for temperatures lower than 80°C and for other combinations could not be drawn because of fewer observed points.<sup>13</sup>

Different dielectric parameters derived from the Cole-Cole diagrams of 70-30% combinations of hard and soft lac for temperatures of 80° and 90°C are shown in Table III together with those of shellac for comparison. The data obtained for 70-30% mixtures are found to be in good agreement with those of shellac.

Table III  
Comparison of Different Dielectric Parameters of Shellac and Hard-Soft Lac (70-30%) Mixture at Two Temperatures Evaluated from Cole-Cole Diagrams

Temperature, °C	Sample	$\epsilon_0$	$\epsilon_\infty$	$\Delta\epsilon$	$\epsilon_m'$	$\tau$ , sec	$\alpha$
80	shellac	8.13	4.48	3.65	0.58	$5.5 \times 10^{-5}$	0.61
	hard-soft lac mixture	7.98	4.5	3.48	0.55	$4.39 \times 10^{-5}$	0.61
90	shellac	7.85	4.74	3.11	0.54	$8.74 \times 10^{-6}$	0.58
	hard-soft lac mixture	7.72	4.64	3.08	0.54	$8.26 \times 10^{-6}$	0.57

### Discussion

The observed greater  $\epsilon_0$  and  $\Delta\epsilon$  values of soft lac between 10° and 70°C compared to those of hard lac and shellac (Fig. 3, Tables I and II) indicate that for soft lac the effective dipole moment per motional unit is greater than those of others.<sup>16</sup> For temperatures below 40°C, the nearly equal  $\epsilon_0$  values for both hard lac and shellac suggest that the number of dipoles present in both of the resins are the same.<sup>17</sup>

The  $T_g/T_m$  ratios for soft and hard lac were found to be 0.90 and 0.91, respectively. The ratio for shellac has been observed to be 0.92. These values are somewhat greater compared to those obtained by Beaman<sup>18</sup> and Boyer<sup>19</sup> for polymers and other materials. The  $T_g/T_m$  ratios of 14 other natural resins have been studied by the author and were found to be within the limit  $0.88 < T_g/T_m < 0.95$ , with an average of 0.92.<sup>20</sup> It appears that the natural resins form a different class of materials.

The difference in the relaxation observed for soft and hard resins (Figs. 1 and 2) arises from their constitutional difference and difference in spatial arrangement of the free polar groups and/or segments. Many relaxation processes, as observed in the present study below  $T_m$ , suggest that the dielectric properties of both hard and soft lac cannot be explained by the relaxation of only hydroxyl groups, as suggested earlier by Bhattacharya.<sup>12</sup> The relaxation for both the resins below their melting temperatures may be ascribed to the combined  $\alpha$  and  $\beta$  processes as suggested by Ishida and co-workers for certain polymers. Overlapping Cole-Cole patterns, analogous to those obtained in this study, also have been reported for natural resin Manila Copal,<sup>15</sup> poly(ethyl methyl acrylate),<sup>21</sup> and mixtures of isoamyl bromide and 1-propanol<sup>22</sup> and polyethylene isophthalamide.<sup>23</sup>

Process III of hard lac, which occurs always beyond 25 kHz (Fig. 1) for all temperatures between 30° and 70°C, is attributed to the relaxation of a polar group probably due to the free OH groups. An inspection of the dispersion data obtained by Bhattacharya<sup>9</sup> and the Cole-Cole diagrams of shellac<sup>1</sup> between 30° and 70°C reveals that the relaxation process III of shellac also always occurred beyond 25 kHz.

The marked changes in the dielectric parameters obtained for both the soft and hard resins above  $T_m$  and the transition from two processes to single Cole-Cole arcs above the melting temperature suggest some rearrangement in the tertiary disposition of different polar groups and/or segments of the resin molecules.<sup>1,15</sup> The relaxation above the melting temperature of hard and soft lac resins arises from  $\alpha$ -process molecular orientations, as has been said to be the case for shellac<sup>1</sup> and Manila Copal.<sup>15</sup> The high-temperature relaxation ( $\alpha$  relaxation) was interpreted to arise from molecular motions for many polymers such as poly(trichlorotrifluoroethylene),<sup>24</sup> poly(vinylidene fluoride),<sup>25</sup> styrene acrylonitrile copolymers,<sup>26</sup> methacrylate homopolymers,<sup>27</sup> etc.

The relaxation times of shellac when compared with those of its constituents at 80° and 90°C (for which complete Cole-Cole arcs were obtained) are found in the order soft lac < shellac < hard lac. The molecular weights of the resins were found to be also in the same order,<sup>11</sup> thus explaining the above phenomenon. The decrease in Cole-Cole distribution parameter ( $\alpha$ ) noted for soft lac and for hard lac above their melting temperatures suggests increased symmetry of the resin molecules undergoing conformational rearrangement, analogous to those

reported for the natural resins Manila Copal<sup>15</sup> and shellac<sup>1</sup>. Similar decrease in the distribution parameter observed for some biopolymers<sup>28,29</sup> and other polymers<sup>6,30</sup> was attributed to arise from structural changes in the molecules. The distribution in relaxation time for some stereoregular polymers has been attributed to changes in the conformation of the main chain.<sup>31</sup>

Dielectric loss in shellac and other resins is considered to arise from the relaxation of the hydroxyl groups present.<sup>9,10,13,32</sup> The decrease in  $\epsilon_m''$  (14%)<sup>1,15</sup> from a value of 0.50 at 70° to 0.43 at 90°C as observed for soft lac resin (Fig. 1) suggests a decrease in the number of free hydroxyl groups participating in the relaxation. For hard lac no such decrease has been found. For shellac an approximately 12% decrease in  $\epsilon_m''$  was noted above its melting temperature.<sup>1</sup> It appears that the hydroxyl groups present in the soft lac probably take part in the conformational rearrangement of shellac above its melting temperature.

It may be concluded from the present study that the functional groups present in hard and soft lacs are responsible for the dielectric properties of shellac below its glass transition and above its melting temperature, respectively. The close fitting of the temperature profile of  $\epsilon_0$ , the Cole–Cole diagram, and the close agreement of different dielectric parameters of both shellac and hard–soft lac mixtures (70–30 wt %) confirmed the proposition that shellac is a physical mixture of its soft and hard fractions. A molecular assignment of the observed relaxations is difficult, due to their being natural products. The importance of the work lies in its ability to use mixture data to reproduce the shellac data.

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