

## The Dielectric Behavior of The Natural Resin Manila Copal

DIPENDRA N. GOSWAMI and PROMODE R. BHATTACHARYA,  
*Division of Chemistry, Indian Lac Research Institute NAMKUM, Ranchi,  
Bihar, India*

### Synopsis

The dielectric relaxation data of the natural resin Manila copal, obtained by Bhattacharya,<sup>1</sup> has been analyzed by the Cole-Cole method at temperatures from 30° to 150°C. Two distinct relaxation processes were found for temperatures of 70°, 80°, and 90°C as opposed to only one as observed by Bhattacharya.<sup>1</sup> The relaxation at 100°C and at higher temperatures could be represented by the typical Cole-Cole patterns. The variation by temperature of the static dielectric constant ( $\epsilon_0$ ) exhibited three distinct slopes, which indicated the different phases of the resin during thermal transformation. Two "transformation points," around 70° and 100°C, were found instead of only one at 105°C as observed by Bhattacharya.<sup>1</sup> The static dielectric constant, the dielectric increment, the Cole-Cole distribution parameter, and the relaxation time decreased markedly owing to the increase of temperature from 100° to 150°C. These indicated some changes in conformation of the resin molecules during transition from the solid to the liquid state.

### INTRODUCTION

Dielectric behavior studies provide information about the electric polarization and the relaxation time of molecules. The former is related to the dipole moment, and the latter is essentially a function of the molecular dimensions. An analysis of the data on these two parameters provides information about the molecular structure.<sup>2</sup> An investigation on the variation of different dielectric parameters with the temperature and frequency of polymers offers a suitable device to detect molecular motions. This includes whole molecule rotation and motion in the backbone or of side chain movements.<sup>3,4</sup> The relaxations arising from different modes have been assigned  $\alpha$ ,  $\beta$ ,  $\gamma$ , etc.<sup>3,4</sup> Dielectric behavior studies of resins have also revealed such multirelaxation processes.<sup>5,6</sup> The data available on the dielectric properties of natural resins are few and require more detailed study.

The dielectric dispersion of the natural resin Manila copal was studied by Bhattacharya<sup>1</sup> in the frequency range of 50 Hz to 500 kHz at temperatures ranging from 30° to 150°C. Both the frequency profiles of the dielectric constant and the dielectric loss exhibited single dispersion in the observed frequency range for all temperatures. The existence of one "transformation point" around 105°C was reported.<sup>1</sup> The dielectric dispersion of the resin was attributed to the relaxation of a rotator of radius 3.8 Å in the alternating field.

The Cole–Cole<sup>7</sup> diagram is helpful in understanding the relaxation process of a dielectric substance in an alternating electric field. This was not applied in Bhattacharya's work. The present paper consists of a critical analysis of the dielectric dispersion data obtained by Bhattacharya<sup>1</sup> for the resin Manila copal in light of the Cole–Cole<sup>7</sup> method.

The study revealed the existence of two clear "transformation points" instead of only one as reported by Bhattacharya<sup>1</sup>—one in the low-temperature region and the other in the high-temperature region. The different dielectric parameters evaluated by the present method appeared to throw further light on the relaxation processes and on the conformational changes undergone by the resin molecules due to the increase in temperature from 30° to 150°C.

### THEORETICAL

The Debye<sup>8</sup> expression for the complex dielectric constant is given by

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

when the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the complex dielectric constant ( $\epsilon^*$ ) at any frequency  $\omega$  are given by

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

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)\omega\tau/(1 + \omega^2\tau^2) \quad (3)$$

where  $\epsilon_0$  and  $\epsilon_\infty$  are the low- and the high-frequency dielectric constants, respectively, and  $\tau$  is the relaxation time. Equations (2) and (3) can be put in the following form:

$$[\epsilon' - (\epsilon_0 + \epsilon_\infty)/2]^2 + \epsilon''^2 = [(\epsilon_0 - \epsilon_\infty)/2]^2 \quad (4)$$

From eq. (4) it is clear that a plot of  $\epsilon''$  versus  $\epsilon'$  will give a semicircle with its center on the abscissa  $[0, (\epsilon_0 + \epsilon_\infty)/2]$  and radius  $(\epsilon_0 - \epsilon_\infty)/2$ . For some materials, Cole and Cole<sup>7</sup> obtained a plot of depressed arc with the center lying below the  $\epsilon'$ -axis. They introduced a distribution parameter  $\alpha$  in the original Debye eq. (1) after which the modified equation is written as follows<sup>7</sup>:

$$\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/[1 + (i\omega\tau)^{1-\alpha}] \quad (5)$$

The real and the imaginary parts are given by

$$\epsilon' - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty)[1 + (\omega\tau)^{1-\alpha} \sin(\alpha\pi/2)] / [1 + 2(\omega\tau)^{1-\alpha} \sin(\alpha\pi/2) + (\omega\tau)^{2(1-\alpha)}] \quad (6)$$

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)(\omega\tau)^{1-\alpha} \cos(\alpha\pi/2) / [1 + 2(\omega\tau)^{1-\alpha} \sin(\alpha\pi/2) + (\omega\tau)^{2(1-\alpha)}] \quad (7)$$

Thus, it is concluded that if the dielectric relaxation is characterized by a single relaxation time, the  $\epsilon''$  versus  $\epsilon'$  plot will be a semicircle with its center on the abscissa. If there is a distribution of relaxation times, the center will lie below the abscissa and a depressed arc is obtained. The correct low- and high-frequency dielectric constants ( $\epsilon_0$  and  $\epsilon_\infty$ ) are obtained from the intersections of the circle with the abscissa. The angle between the abscissa and the line joining the center with the  $\epsilon_\infty$  point is expressed by  $\alpha\pi/2$ ,  $\alpha$  being the distribution parameter appearing in the Cole–Cole eq. (5).

In the present paper, the Cole–Cole plot has been used for the determination of  $\epsilon_0$  and  $\epsilon_\infty$ , and relaxation times have been calculated from the following equation:

$$(\omega\tau)^{1-\alpha} = v/u \quad (8)$$

where  $v$  and  $u$  are the distances from  $\epsilon_0$  and  $\epsilon_\infty$ , respectively, from a point on the semicircle corresponding to the frequency  $\omega$ .<sup>7</sup>

## RESULTS

The Cole–Cole plots ( $\epsilon''$  versus  $\epsilon'$ ) for the resin Manila copal at different temperatures were drawn from the data of Bhattacharya<sup>1</sup> (Fig. 1).

The dielectric constant and the dielectric loss were reported constant throughout the observed frequency range (50 Hz to 500 kHz), and no dielectric dispersion was observed for temperatures from 30° to 60°C.<sup>1</sup> The  $\epsilon''$ -versus- $\epsilon'$  plot at 60°C [Fig. 1(a)] also revealed the same information. The plots for temperatures 30°, 40°, and 50°C were found to be similar.

The Cole–Cole patterns for temperatures 70°, 80°, and 90°C differed from those at other temperatures. All the points in the  $\epsilon''$ -versus- $\epsilon'$  plots were not contained in a single Cole–Cole arc. It appeared from the patterns that the dielectric dispersions of the copal resin for these temperatures were the result of two relaxation processes (I and II); each process could be represented by a Cole–Cole semicircle. The  $\epsilon''$ -versus- $\epsilon'$  patterns for 100° to 150°C were, however, perfect semicircular Cole–Cole types.

The different dielectric parameters evaluated from the Cole–Cole diagrams at various temperatures are given in Table I. The  $\epsilon_0$  and  $\epsilon_\infty$  values obtained from the same plots for 100° to 150°C are shown in columns 2 and 3, respectively. The values of  $\epsilon_0$  and  $\epsilon_\infty$  determined experimentally by Bhattacharya<sup>1</sup> are also included for comparison. It is found that the  $\epsilon_0$  and  $\epsilon_\infty$  values obtained from the Cole–Cole plots differ from the values observed experimentally.

The variation of the static dielectric constant ( $\epsilon_0$ ) with temperature has been illustrated in Figure 2. The  $\epsilon_0$ -versus-temperature curve indicates three distinct slopes (marked 1, 2, and 3 in Fig. 2). From the same figure, it may be seen that  $\epsilon_0$  is almost constant up to 60°C; it increases sharply and reaches a maximum at 100°C.  $\epsilon_0$  then decreases with further increase in temperature. The  $\epsilon_\infty$ , on the other hand, increases with temperature.

The values of the dielectric increments  $\Delta\epsilon (= \epsilon_0 - \epsilon_\infty)$ , which are related to the dipole moments, are given in column 4 of Table I. The  $\Delta\epsilon$  for temperatures 100°C to 150°C were evaluated using  $\epsilon_0$  and  $\epsilon_\infty$  obtained from the Cole–Cole diagrams. The  $\Delta\epsilon$  values for temperatures 70° to 90°C were obtained from the experimental values of  $\epsilon_0$  and  $\epsilon_\infty$ . As there was no dielectric dispersion for temperatures from 30° to 60°C, the  $\epsilon_\infty$  values could not be ascertained and, therefore,  $\Delta\epsilon$  values were not determined. The  $\Delta\epsilon$  value increases from 0.22 at 70°C to 1.93 at 100°C (about an 8.8 times increase) and then decreases to 0.91 at 150°C (52.8% decrease).

The relaxation time for the resin molecules for temperatures 100°C to 150°C was calculated using eq. (8) and is given in column 5 of Table I. The relaxation time  $\tau$  decreases markedly from a value of  $1.18 \times 10^{-4}$  sec at 100°C to  $1.75 \times 10^{-7}$  sec at 150°C (a 99.8% decrease). This suggests increased compactness of the molecules at high temperatures.

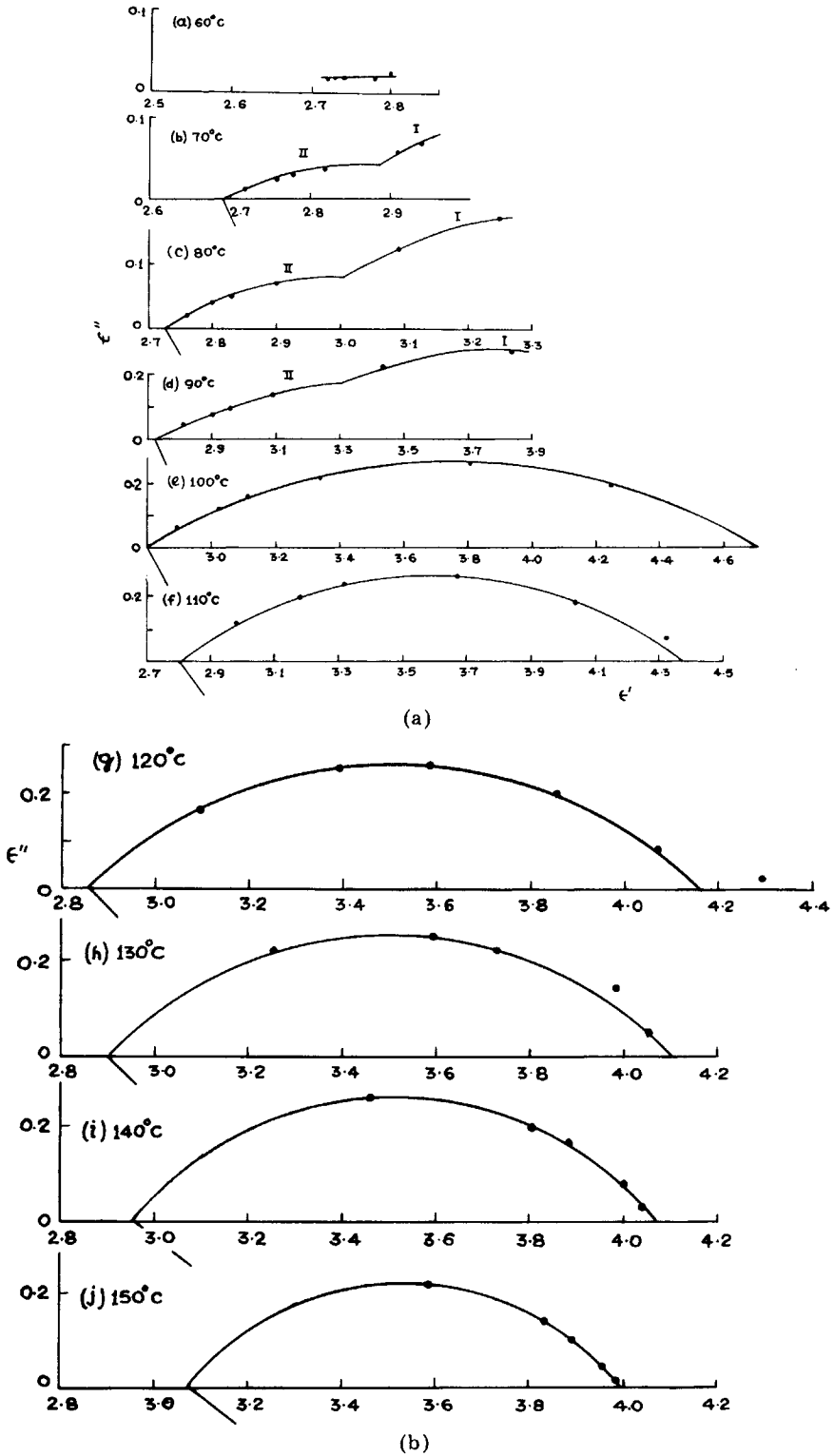


Fig. 1. (a) and (b) Cole-Cole diagrams of the resin at different temperatures.

TABLE I  
Different Dielectric Parameters of Manila Copal at Different Temperatures,  
Obtained from Cole-Cole Diagrams

Temperature, °C	$\epsilon_0$		$\epsilon_\infty$		Dielectric increment	$\tau$ , sec	$\alpha$
	Obtained from diagram	Observed value <sup>a</sup>	Obtained from diagram	Observed value <sup>a</sup>			
30		2.70					
40		2.72					
50		2.75					
60		2.80					
70		2.94	2.69	2.72	0.22		
80		3.25	2.73	2.76	0.49		
90		3.88	2.72	2.81	1.07		
100	4.73	4.25	2.80	2.89	1.93	$1.18 \times 10^{-4}$	0.66
110	4.38	4.33	2.80	2.98	1.58	$1.04 \times 10^{-4}$	0.59
120	4.17	4.30	2.85	3.09	1.32	$2.09 \times 10^{-6}$	0.51
130	4.10	4.22	2.90	3.26	1.20	$8.09 \times 10^{-7}$	0.49
140	4.08	4.12	2.96	3.46	1.12	$3.03 \times 10^{-7}$	0.44
150	3.99	4.02	3.08	3.58	0.91	$1.75 \times 10^{-7}$	0.43

<sup>a</sup> Bhattacharya.<sup>1</sup>

The variation of  $\ln(T\tau)$  with  $(1/T)$  is represented in Figure 3. The linear plot suggests no change in the state of the resin between 100° and 150°C. The activation energy calculated from the slope of Figure 3 (on the basis of the Arrhenius equation) was 30 kcal/mole. This value is in good agreement with the value earlier reported by Bhattacharya<sup>1</sup> from the slopes of dc conductivity, resistivity, and viscosity-versus- $1/T$  plots above the melting point.

The Cole-Cole distribution parameter  $\alpha$  for temperatures of 100° to 150°C of the resin are given in the last column of Table I. There is a decrease in  $\alpha$  from a value of 0.66 at 100°C to 0.43 at 150°C (a 34.8% decrease).

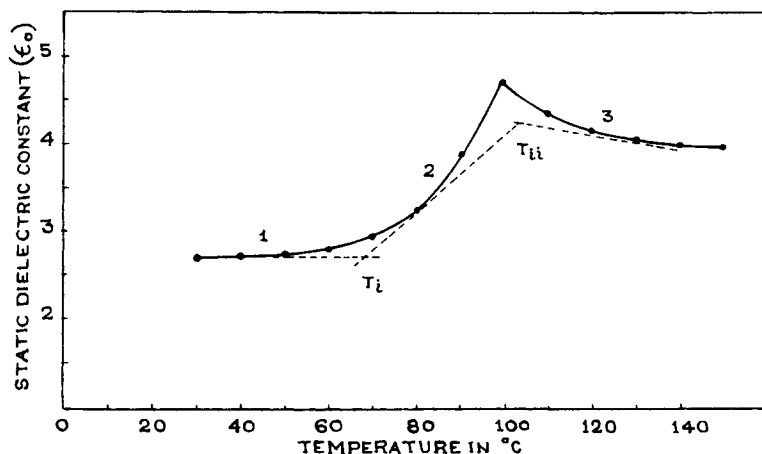


Fig. 2. Variation of the static dielectric constant ( $\epsilon_0$ ) with temperature.

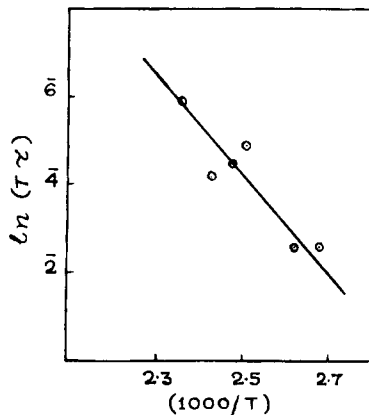


Fig. 3. Plot of  $\ln(T\tau)$  vs  $(1/T)$ .

## DISCUSSION

The assembly of the electrodes for investigation of the dielectric properties was so designed that during the experiment, the physical state of the resin, changing from solid to liquid, could be maintained at any temperature between 30° and 150°C.<sup>1,9</sup> Thus, the dielectric behavior exhibited was a true reflection of the changes in the physical state of the resin with temperature. An inspection of the Cole-Cole diagrams of the Manila copal resin revealed that distinct variations in the relaxation processes developed with the increase in temperature. The changes in the different dielectric parameters obtained from the Cole-Cole patterns indicated that some molecular transformations had occurred as the temperature increased from 30° to 150°C.

Bhattacharya<sup>1</sup> reported only one relaxation process in the whole frequency region for all temperatures between 70° and 150°C. The present investigation, however, indicates the existence of two distinct relaxation processes for temperatures 70°, 80°, and 90°C (Fig. 1). For temperatures beyond 90°C, the resin molecules follow the typical Cole-Cole type of behavior. The present investigation confirms the early study:<sup>1</sup> below 70°C no dielectric dispersion was observed in the frequency range of 50 Hz to 500 kHz.

The different slopes in the  $\epsilon_0$ -versus-temperature plot indicates three distinct phases of the resin during thermal transformation and the possibility of the existence of two "transformation points" around 70° and 100°C, respectively (marked  $T_i$  and  $T_{ii}$  in Fig. 2). The transition points  $T_i$  and  $T_{ii}$  are attributed to the glass transition temperature and the melting point of the resin, respectively. Bhattacharya<sup>1</sup> also had postulated the existence of such a transformation point at about the same temperature of 105–106°C, which is the melting point of the copal resin. He indicated the possible existence of another transformation point around 50°C, which actually was found in the present study (around 70°C). An inspection of the Cole-Cole diagrams (Fig. 1) at different temperatures also supports the above phenomenon.

The low values of both the dielectric constant and the loss at 60°C and below were attributed by Bhattacharya<sup>1</sup> to the limited orientational freedom of the dipoles due to high viscosity. According to Yano and Wada,<sup>10</sup> below the glass transition temperature where the segmental motion is frozen, the relaxation may

arise from local motion in the form of rotation or rotational oscillation.<sup>10,11</sup> It may be mentioned, however, that segmental motion has been reported for poly(dimethylsiloxane) even below the temperature at which the fluid solidified.<sup>12</sup> In the present experiment, as the temperature of the resin reached the glass transition temperature ( $T_i$ ), the viscosity decreased rapidly and the orientation of the dipoles resulted in a higher value of  $\epsilon_0$ . The 8.8 times increase in the dielectric increment (and hence in the dipole moment) due to an increase in temperature from 70° to 100°C lends support to this phenomenon. A similar increase in  $\epsilon_0$  with temperature was noted in the transition phase for many polymers such as polyamides,<sup>13</sup> styrene-acrylonitrile copolymers,<sup>14</sup> and poly(vinylidene fluoride).<sup>15</sup>

When the temperature changed from 60° to 70°C, two dispersion regions appeared suddenly, suggesting an abrupt change in phase of the resin in this region [Figs. 1(b)–1(d)]. The reason for the occurrence of two relaxation processes is not clearly known. Between the glass transition temperature and the melting point, the different segments of the resin molecules experience various hindering forces depending on the internal viscosity. This renders different degrees of segmental orientation producing the two relaxation processes. The segmental orientation ( $\beta$  process) in the transition phase has been reported in polymers, viz., polymaleimide,<sup>4</sup> ethylene-methacrylic acid copolymers,<sup>16</sup> polystyrene,<sup>10</sup> poly(invylidene fluoride),<sup>15</sup> styrene-acrylonitrile copolymers.<sup>14</sup>

Between 100° and 150°C, only one relaxation process was observed with distribution in relaxation times. The process exhibited to some extent the characteristics of a dipole orientation polarization. In a study on the dielectric properties of phenol-formaldehyde resin in paper laminates, the relaxation process above  $10^4$  Hz was reported to be due to rotational movements of the hydroxyl groups present in the resin and cellulose.<sup>6</sup> A similar conclusion was reached from dielectric studies of natural resin shellac<sup>9</sup> and shellac-melamine-formaldehyde compositions.<sup>5</sup> For other polymers such as poly(vinylidene fluoride)<sup>15</sup> poly(chlorotrifluoroethylene),<sup>17</sup> and styrene-acrylonitrile copolymers,<sup>14</sup> the relaxation at high temperature was attributed to molecular motions ( $\alpha$  process). The dielectric data were explained from the viewpoint of intermolecular interaction and molecular motions.<sup>15,17</sup> In the present experiment, the symmetrical Cole-Cole patterns of the resin, the 52.8% decrease in  $\Delta\epsilon$ , the 99.8% decrease in  $\tau$ , and the 35% reduction in  $\alpha$  due to the rise in temperature from 100° to 150°C also indicated some changes in the conformational rearrangement of the resin molecules in the liquid state. This is presumably due to the formation of crosslinks as reported in the case of natural resin shellac and its composites.<sup>18,5</sup>

It may be mentioned that two kinds of relaxation processes, one at high temperature and the other at low temperature, were also reported for various amorphous polymers: (i) with flexible polar side groups, viz., poly(acrylic esters)<sup>19</sup> and poly(vinyl esters)<sup>20</sup>, and (ii) of molecules without flexible side groups, viz., amorphous polyesters,<sup>21</sup> poly(vinyl chloride)<sup>22</sup> and polychloroprene.<sup>23</sup> The molecular mechanism of high-temperature relaxation was attributed to large-scale conformational rearrangement of the main chains, while the low-temperature relaxation resulted from the local twisting modes of the main chain or from the motion of the side groups.<sup>19–23</sup> In semicrystalline polymers, such as polyester, polycarbonates, dry polyamides, and polyethers, two kinds of relaxation processes were also observed.<sup>3</sup>

TABLE II  
Comparison of Calculated and Observed  $\epsilon_M''$  Values

Temperature, °C	Calculated $\epsilon_M''$	Experimentally observed <sup>a</sup> $\epsilon_M''$
100	0.263	0.26
110	0.26	0.26
120	0.266	0.27
130	0.255	0.26
140	0.26	0.26
150	0.22	0.22

<sup>a</sup> Bhattacharya.<sup>1</sup>

From an extensive study on the dielectric behavior of biopolymers of different molecular weights, Takashima<sup>24</sup> suggested that the distribution in the relaxation time arises either from asymmetry in the shape of the molecules or from the distribution in molecular weights. It was suggested later that changes in the shape of the molecules were the most important contributing factor,<sup>25</sup> and the increase in  $\alpha$  was attributed to the increased asymmetry of the molecules.<sup>26</sup> The 35% decrease in the value of  $\alpha$  observed in the present experiment indicates that the resin molecules become dielectrically more symmetrical with increase in temperature from 100° to 150°C. The Cole–Cole plots of some ethylene–carbon copolymers also revealed narrowing of distribution of relaxation times with temperature.<sup>27</sup> The decrease of  $\alpha$  was attributed to chain folds and chain torsion mechanisms. A similar decrease in the distribution parameter was reported for poly(vinylidene fluoride).<sup>28</sup>

Bhattacharya<sup>1</sup> calculated the relaxation time  $\tau$  from the relation

$$\omega\tau = (\epsilon_\infty' + 2)/(\epsilon_0' + 2)$$

at a temperature corresponding to the peak of the dielectric loss–temperature curve at a fixed frequency. The dielectric relaxation of the resin Manila copal is explained in the present study in light of the Cole–Cole theory, and correct values of the relaxation times are given in Table I.

The observed maximum  $\epsilon''$  value ( $\epsilon_M''$ ) of the resin was reported<sup>1</sup> to be somewhat less than one third of the value obtained from Debye's eq. (3),  $\epsilon_M'' = (\epsilon_0 - \epsilon_\infty)/2$ . A similar result was obtained from the dielectric study of other plastic materials.<sup>29</sup> The discrepancy was attributed to the existence of a distribution in the relaxation time.<sup>1,29</sup> In eq. (7),  $\epsilon''$  signifies the molecules obeying a Cole–Cole type of distribution. The maximum value of  $\epsilon''$ , in eq. (7), is obtained by using  $\omega\tau = 1$ . Then

$$\epsilon_M'' = \frac{(\epsilon_0 - \epsilon_\infty) \cos(\alpha\pi/2)}{2[1 + \sin(\alpha\pi/2)]} \quad (9)$$

The  $\epsilon_M''$  value calculated using relation (9) for temperatures 100° to 150°C are shown in Table II. The corresponding values for  $\epsilon_M''$  obtained experimentally are given in the last column for comparison. It was found that the values of  $\epsilon_M''$  obtained by calculation were in close agreement with those obtained by experiment. The data in Table II, therefore, justify the application of the Cole–Cole method to understand the different processes involved in the dielectric dispersion of copal resin.



Bhattacharya<sup>1</sup> used the Debye equation relating relaxation time ( $\tau$ ), radius of the molecule ( $a$ ), coefficient of viscosity ( $\eta$ ) of the medium, Boltzmann constant ( $K$ ), and temperature ( $T$ ):

$$\tau = 4\pi\eta a^3/kT \quad (10)$$

and calculated a value of 3.8Å as the radius of the Manila copal rotator. The dielectric behavior of the copal resin was interpreted by him as due to the relaxation of the rotator (3.8Å) in the alternating electric field.

A comparatively larger value of the relaxation time, e.g.,  $1.18 \times 10^{-4}$  sec at 100°C, was observed in the present case; the marked decrease in  $\tau$  due to the increase in temperature from 100° to 150 °C and the transition from two relaxation processes to one with the rise in temperature cannot be explained by the relaxation of the rotator of size 3.8 Å as suggested by Bhattacharya.<sup>1</sup> Moreover, eq. (10) was derived on the basis of molecules of spherical shape and moving in a continuous viscous fluid having an internal coefficient of viscosity  $\eta$ .<sup>30,31</sup> The resin molecules are not spherical, and since each molecule is surrounded by other similar molecules, the molecular environment was very different from a homogeneous fluid. Later, it was shown that eq. (10) does not represent adequately the relation between the relaxation time, molecular radius, and the macroscopic viscosity.<sup>30,31</sup>

It appears from the present study, that below the glass transition temperature, the orientation of the polar groups was due less to high viscosity, thus yielding one relaxation time distribution. Between the glass transition and the melting point, segmental orientation occurred giving rise to two relaxation processes. For temperatures above the melting point, different degrees of molecular orientation, resulting from conformational rearrangements of the resin molecules in the liquid state, yielded the Cole–Cole-type single relaxation process.

The authors wish to acknowledge with thanks the continuous encouragement of Dr. B. B. Khanna, Head of the Chemistry Division. They are also grateful to Dr. T. P. S. Teotia, Director of this Institute, for his kind interest in this work.

## References

1. G. N. Bhattacharya, *Indian J. Sci. Ind. Res.*, **4**, 713 (1946).
2. N. E. Hill, in *Dielectric Properties and Molecular Behavior*, N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, Eds., Van Nostrand-Reinhold, London, 1969.
3. N. G. McCrum, R. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solid*, Wiley, New York, 1967.
4. H. Block, R. Groves, and S. M. Walker, *Polymer*, **13**, 527 (1972).
5. T. R. Lakshminarayanan and M. P. Gupta, *J. Appl. Polym. Sci.*, **18**, 2047 (1974).
6. J. T. Jux, A. M. North, and R. Kay, *Polymer*, **15**, 799 (1974).
7. K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).
8. P. Debye, *Polar Molecules*, Chemical Catalogue Co., New York, 1929.
9. G. N. Bhattacharya, *Indian J. Phys.*, **18**, 1 (1944).
10. O. Yano and Y. Wada, *J. Polym. Sci. A2*, **9**, 669 (1971).
11. M. E. Baird and E. Houston, *Polymer*, **16**, 308 (1975).
12. M. E. Baird and C. R. Sengupta, *Polymer*, **12**, 802 (1971).
13. M. E. Baird, G. T. Goldsworthy, and C. J. Creasey, *Polymer*, **12**, 159 (1971).
14. M. Cook, G. Williams, and T. T. Jones, *Polymer*, **16**, 835 (1975).
15. K. Nakagawa and Y. Ishida, *J. Polym. Sci. A2*, **11**, 1503 (1973).
16. P. J. Phillips and W. J. MacKnight, *J. Polym. Sci. A2*, **8**, 72 (1970).
17. H. Sasabe, *J. Polym. Sci. A2*, **11**, 2413 (1973).

18. A. Kumar, *J. Appl. Polym. Sci.*, **8**, 1185 (1964).
19. Y. Ishida and K. Yamafuji, *Kolloid-Z.*, **177**, 97 (1961).
20. Y. Ishida, M. Matsuo, and K. Yamafuji, *Kolloid-Z.*, **180**, 108 (1962).
21. W. Reddish, *Trans. Faraday Soc.*, **46**, 459 (1950).
22. Y. Ishida, *Kolloid-Z.*, **168**, 29 (1960).
23. M. Matsuo, Y. Ishida, K. Yamafuji, M. Takayanagi, and F. Irie, *Kolloid-Z.*, **201**, 89 (1965).
24. S. Takashima, *J. Mol. Biol.*, **7**, 455 (1963).
25. D. N. Goswami and N. N. Das Gupta, *Biopolymers*, **13**, 391 (1974).
26. D. N. Goswami and N. N. das Gupta, *Biopolymers*, **13**, 1549 (1974).
27. P. J. Phillips, G. L. Wilkes, B. W. Delf, and R. S. Stein, *J. Polym. Sci. A2*, **9**, 499 (1971).
28. S. Yano, *J. Polym. Sci. A2*, **8**, 1057 (1970).
29. C. P. Smyth, *Dielectric Behavior and Structure*, McGraw Hill, New York, 1955, Chap. V, p. 188.
30. Reference 29, Chap. IV, p. 103.
31. C. P. Smyth, *Molecular Relaxation Processes*, Academic Press, New York, 1966.

Received March 12, 1976

Revised August 20, 1976