Dielectric Analysis of Cellulose and Its Vinylic Copolymers

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SYNOPSIS

The real and imaginary parts of the complex dielectric permittivity, ϵ' and ϵ'', for some vinylic copolymers of cellulose [prepared with vinyl acetate (VA) and methyl acrylate (MA) and Ce(IV) ions as initiator] and for cellulose were measured over a frequency band of 0.1–10^2 kHz and a temperature range from -40 to $100°C$. In vinylic copolymers of cellulose, we observed one dielectric relaxation attributed to the α-relaxation of the vinylic side chain grafted on cellulose. In cellulose dielectric spectra, this relaxation did not appear, but we detected one relaxation that may correspond to the β-relaxation. For these vinylic copolymers of cellulose, the ϵ'' against ϵ' plot gives a skewed arc that closely resembles that of the Davidson–Cole model, with a broader distribution for high frequencies that shows the overlap of several relaxations in the process considered. Some differences observed between the vinylic copolymers of cellulose may be due to the composition and the length of the vinylic side chains and to the frequency of grafting on the cellulose.

INTRODUCTION

It is known that the electrical properties of small molecules differ markedly from those in which the dipoles are on large molecules. The Debye's theory in which the fundamental assumption is a finite time of relaxation provides a satisfactory explanation of the dielectrical properties of small molecules, but does not explain the behavior of polymeric systems. In these polymeric systems, it is assumed that many times of relaxation rather than a single one are involved. Of course, it is plausible for a macromolecular system containing polar groups to exhibit a distribution of relaxation times, because the motion of any dipole affects the motion of its neighbors, and this is reflected by the distribution function for the relaxation times. Although the single relaxation time model cannot be used for polymeric materials, their real relaxations can be understood in terms of deviations from the ideal relaxation, that is, a relaxation with a single relaxation time.

Polyvinyl acetate (PVA) and polymethyl acrylate (PMA) are linear polymers with the $-OCOCH_3$ and $-COOCH_3$, respectively, as polar inductor groups. Their main dielectric relaxations have been characterized by other authors,[1,2] showing the differences in the temperature and intensity of the relaxation peaks. Moreover, cellulose has a polar nature because of the presence of $-OH$ groups. As cellulose has two phases, crystalline and amorphous, its dielectric spectrum is complex because it may have different orientation processes in both crystalline and amorphous regions and in the border between them.

In the present work, the application of dynamic dielectric analysis allowed us to detect a dielectric relaxation in the vinylic copolymers of cellulose, which may be the α-relaxation of the vinylic side chains grafted on cellulose. The data of dielectric loss ϵ'' and dielectric constant ϵ' are given, and the plots of ϵ'' vs. ϵ' show that there is not a Gaussian distribution of relaxation times but that it closely resembles instead those of the empirical skewed-arc function.

EXPERIMENTAL

The vinylic copolymers of cellulose were prepared by grafting polymerization of VA and MA on cotton

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cellulose initiated by the Ce(IV) ion method, as we described in a previous work.[3] Different cellulosic substrates prepared from cotton cellulose purified and treated with NaOH solutions of different concentrations (mercerized cotton), using different volumetric ratios of monomers, V_{VA}/V_{MA}, allowed us to achieve different graft percentages, $\%G$, different grafting frequencies, GF, and different viscosimetric average molecular weights of the grafted chains, M_v. The composition PVA/PMA of the vinylic side chains was also different.

The following samples were selected for the present work:

1. Purified cotton cellulose.
2. The vinylic copolymers of cellulose as shown in Table I.

As was shown in our previous paper,[3] the GF of the copolymers increases as follows:

$$CD2 < CD1 < CB1$$

and the viscosimetric average molecular weight and, therefore, the chain length increases as follows:

$$CB1 < CD2 < CD1$$

The samples were pressed to achieve better uniformity, cut into a disc shape of 3–4 cm diameter and about 0.5 mm thickness, and then dried at 40°C in vacuum for 24 h. Then, both sides were metallized with aluminum.

The dielectric loss measurements were made with a capacitor bridge GENRAD 1615 A and a GENRAD 1310 B oscillator over a frequency band of 0.1–10^2 kHz and a temperature range from -40 to $100°C$.

RESULTS AND DISCUSSION

Dielectrical Analysis of Cellulose

The dielectric loss ϵ'' and tan δ (δ is the dielectric loss angle and tan $\delta = \epsilon''/\epsilon'$) values obtained at different

Table I   Vinylic Copolymers of Cellulose

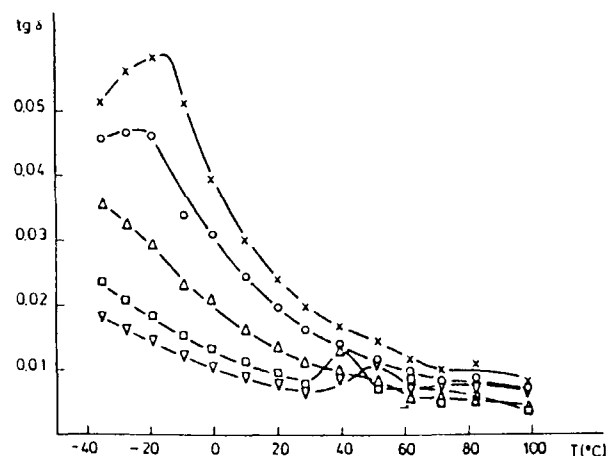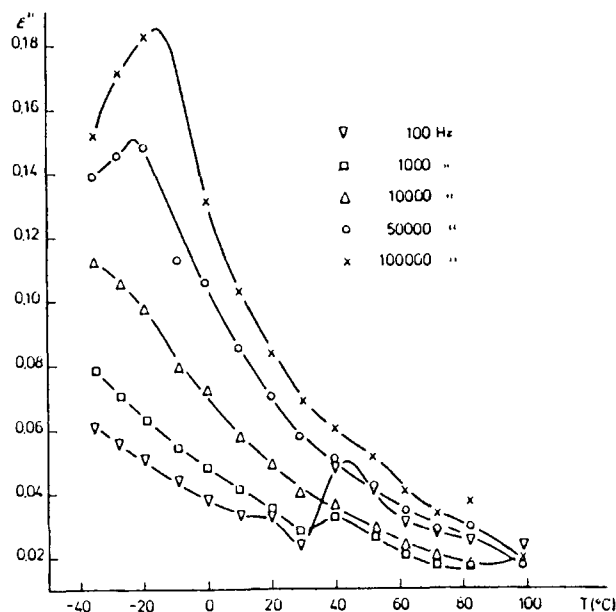| Copolymer	$\%G$	%NaOH in Mercerized	V_{AV}/V_{AM}
CD1	305	15	80/20
CD2	184	15	85/15
CB1	136	10	80/20

Figure 1   Cellulose dielectric loss ϵ'' and T_g δ vs. temperature at various frequencies.

ferent frequencies for cellulose against temperature are shown in Figure 1.

In Figure 1, two peaks can be observed: The first one is at $-15°C$ and a frequency of 100 kHz, which is shifted to $-23°C$ when the frequency is 50 kHz. The experimental conditions of the present work did not allow us to detect this peak at higher frequencies or lower temperatures. Nevertheless, the temperature of the maximum loss permittivity, the frequency at which it appears, and the apparent activation energy, calculated as in eq. (1) below, agree with the data given by other authors[4-8] as shown in Table II, for the β-relaxation of cellulose.

Table II Apparent Activation Energy (E_a) of Cellulose Dielectric Relaxation from Some Authors and That Found in the Present Work

Authors	Ref.	E_a (kcal/mol)
Seidman and Mason	4	9.3
Trapp and Pungs	5	11.8
Ishida et al.	6	13.0
Nanassy	7	8.0
Okumura et al.	8	11.9
Present work		11.2

The apparent activation energy, E_a, of this relaxation was calculated by an Arrhenius-type equation:

$$\ln f_m = \ln A - E_a/RT_m \qquad (1)$$

where f_m is the frequency at which the maximum ϵ'' appears, and T_m, its temperature. The E_a value was 11.2 kcal/mol.

We have plotted the $\log f_m$ against $1/T$ of the ϵ'' maximum values obtained in the present work and that from other authors who described this peak as corresponding to the β-relaxation of cellulose (Fig. 2). We also show the value that we found in the viscoelastic analysis of cellulose.[9] A good linear relationship is observed between them.

Therefore, the dielectric peak found in this work may be due to the β-relaxation of cellulose. It is generally assumed that this relaxation is related to movements of —OH primary groups in the amorphous region of cellulose.[2,4,10–13] The second peak at about 43°C hardly moves with the frequency. The peak intensity decreases when the frequency in-

creases. We have not found a plausible explanation for this peak. It could be due to some impurity.[14]

Dielectrical Analysis of Vinylic Copolymers of Cellulose

Dielectric spectra of vinylic copolymers of cellulose do not show the peak of the β-relaxation of cellulose, which may be due to both the low ratio of cellulose in the material and the decrease in the number of OH groups in the amorphous region of cellulose because of the existence of grafted vinylic chains.[3] In the viscoelastic analysis of these materials, we observed the same fact: The β-relaxation of cellulose does not appear in its vinylic copolymers.[9]

Only higher %G vinylic copolymers of cellulose clearly show one relaxation peak (about 40°C at 100 Hz). Therefore, we have selected those of 305, 184, and 136 %G. The dielectric data of these copolymers, ϵ'' and ϵ' for different frequencies, are shown against temperature in Figure 3.

In Figure 4, we plotted the ϵ' and ϵ'' values against the logarithm of frequency at different temperatures for the copolymers considered.

Figure 3 shows a maximum for the ϵ'', which shifts to a higher temperature when the frequency increases. In addition, Figure 4 shows complementary information about this relaxation.

The numerical data of peak temperature at some of the experimental frequencies are shown in Table III. At the same frequency, the maximum ϵ'' tends to shift to a lower temperature when the %G decreases, although the differences in temperatures do not seem significant (Table III).

The experimental data show a linear relationship between the $\log f_m$ and the inverse of temperature (Fig. 5). The slope of the graph is nearly the same
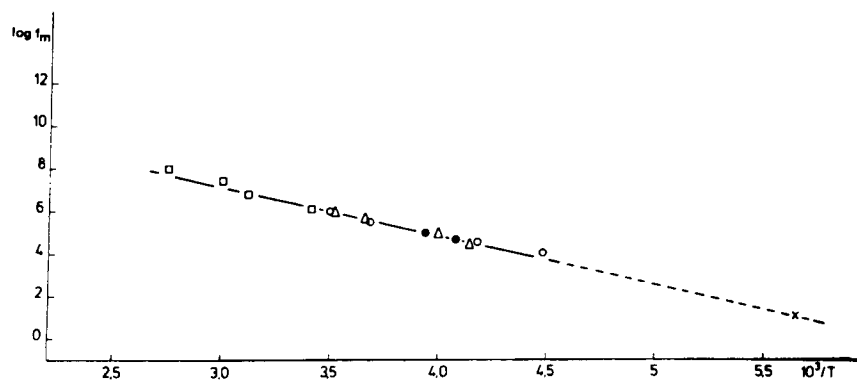

Figure 2 Representation of $\log f_m$ vs. $1/T$ of ϵ'' maximum for cellulose dielectric relaxation. Present work (●) and other studies: (△) Ref. 4; (○) Ref. 5; (□) Ref. 7. (✕) viscoelastic relaxation.[9]
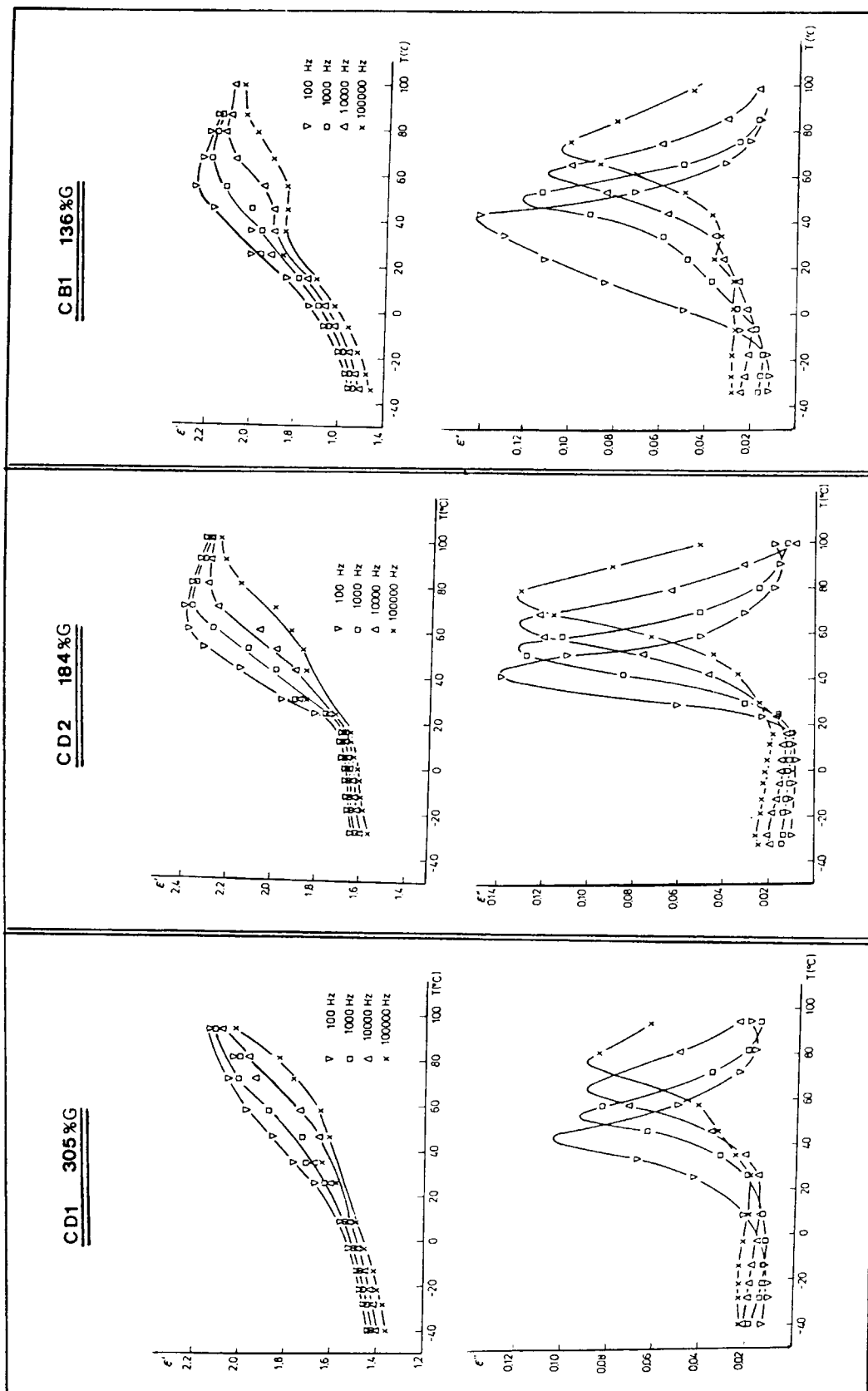
Figure 3 Dielectric constant ϵ' and loss factor ϵ'' of vinylic copolymers of cellulose vs. temperature at various frequencies.
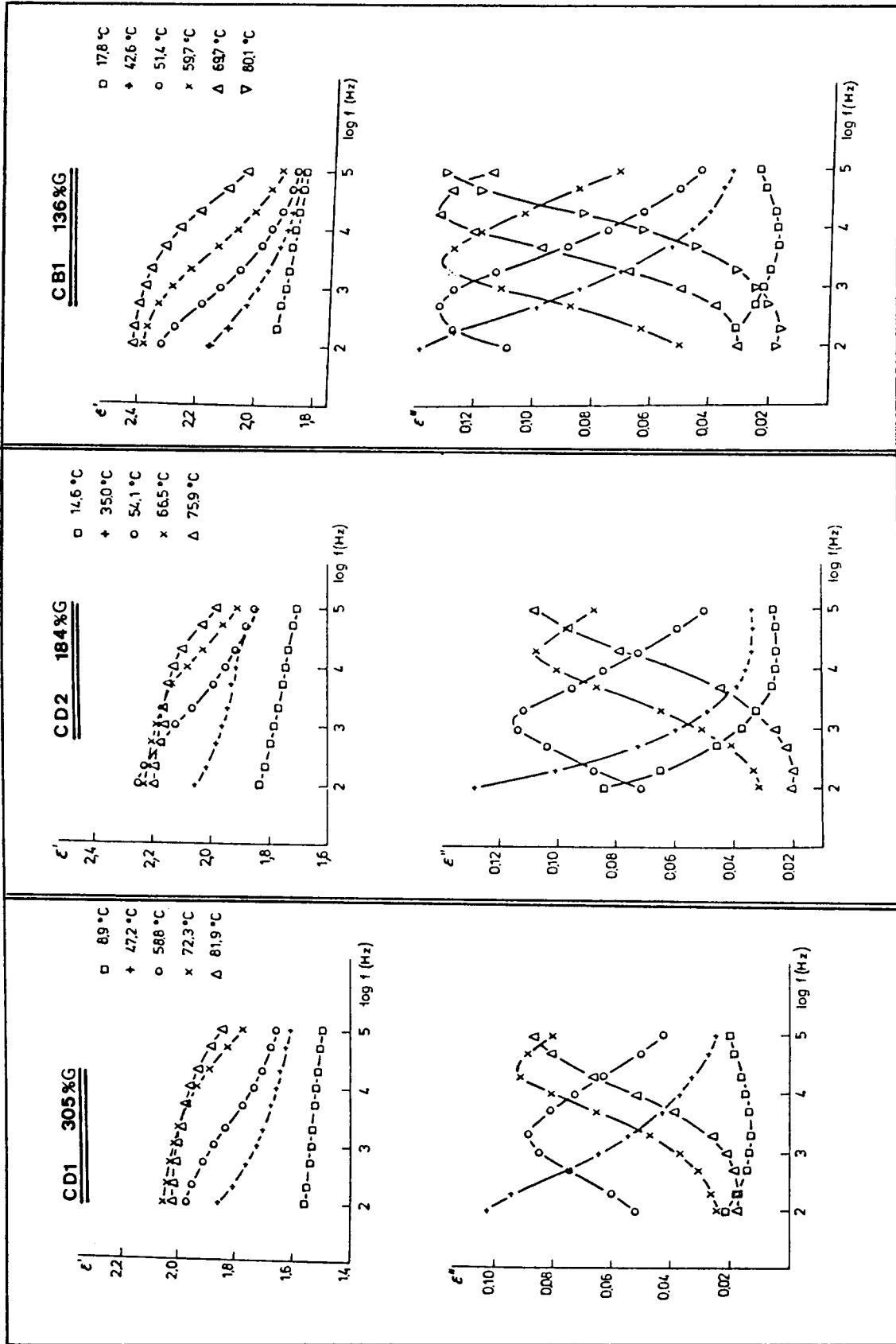
Figure 4 Dielectric constant ϵ' and loss factor ϵ'' of vinylic copolymers of cellulose vs. the logarithm of frequency at various temperatures.

Table III Temperatures in °C for the Maximum ϵ'' at Different Frequencies of Vinylic Copolymers of Cellulose

Copolymer	%G	0.1 kHz	1 kHz	10 kHz	100 kHz
CD1	305	45	55	66	78
CD2	184	44	55	65	77
CB1	136	42	52	63	74

for all the copolymers. This slope gave the apparent activation energy of the relaxation, whose values were 46.97, 47.03, and 46.79 kcal/mol for the CD1, CD2, and CB1, respectively. This similarity may indicate that it could be the same relaxation process. As this relaxation did not appear in cellulose, it must be attributed to the vinylic side chains, which are PVA with small quantities of PMA. The dielectrical data for the α-relaxation of PVA and PMA given in the literature[2] allow us to suppose that the relaxation observed in the copolymers may be the α-relaxation of the vinylic chains, although the peak temperatures for the copolymers are situated between those for PVA and PMA and the apparent activation energy is lower than that of PVA and PMA.[2] As there is no significant difference in the temperature of the maximum ϵ'' (Table III) or in the E_a values among the copolymers considered, it may be thought that the influence of the cellulose on the relaxation of the vinylic chains is independent of the percentage of cellulose in the copolymer.

Arc Diagrams

We considered some phenomenological models to study the possible influences of the PVA/PMA composition of the vinylic chains and the cellulosic substrate on the dielectric relaxation observed in the vinylic copolymers of cellulose.

Figure 6 shows the experimental arc of ϵ'' against ϵ' for the vinylic copolymers of cellulose and also those of Debye, Cole–Cole, and Davidson–Cole.

Model of Debye

The plot of ϵ'' vs. ϵ' values for a given temperature may be a semicircle if the relaxation follows Debye's model (single relaxation time approximation). The radius and center of the semicircle are calculated by formulae (2) and (3):

$$r = \frac{\epsilon_0 - \epsilon_\infty}{2} \qquad (2)$$

$$\text{Center:} \left(\frac{\epsilon_0 + \epsilon_\infty}{2}, 0 \right) \qquad (3)$$

ϵ_0 is the dielectric constant when the frequency is 0, and ϵ_∞, when the frequency is infinite. These values are determined on the ϵ'' against ϵ' graph and/or on the ϵ' against the logarithm of frequency by extrapolation. The ϵ_∞, the ϵ_0, the oscillator strength (amplitude) $\Delta\epsilon = \epsilon_\infty - \epsilon_0$, and the radius and center of Debye's semicircle at two temperatures for the vinylic copolymers of cellulose are shown in Table IV.

As must be expected in polymeric materials, none of the experimental arcs of the copolymers correspond to Debye's semicircle (Fig. 6). This means that the dielectric distribution is broader and the ϵ'' maximum is lower than those for a single relaxation time model (Debye's model). As the single relaxation time approximation is not valid for vinylic copolymers of cellulose, we have determined the empirical correction parameters introduced by Cole and Cole[15] and Davidson and Cole.[16]

Cole–Cole Equation

The Cole–Cole equation gives a depressed semicircle. It introduces the parameters $\bar\beta(0 > \bar\beta > 1)$ and τ_0, called the generalized relaxation time. From this equation, we obtain a circumference whose radius and center are given below:

$$r = \frac{\epsilon_0 - \epsilon_\infty}{2} \cdot \csc \frac{\bar\beta\pi}{2} \qquad (4)$$

$$\text{Center:} \left[\frac{(\epsilon_0 + \epsilon_\infty)}{2}, -\frac{\epsilon_0 - \epsilon_\infty}{2} \cot \frac{\bar\beta\pi}{2} \right] \qquad (5)$$

The Cole–Cole equation relates the dispersion and absorption curves that are symmetrical around the position
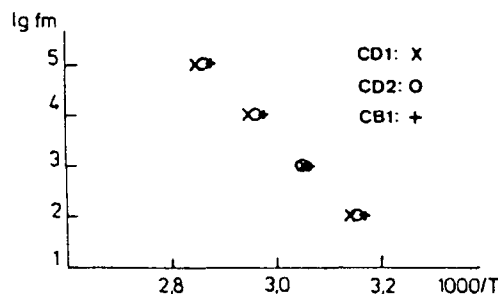
$$\omega_{max} \cdot \tau_0 = 1 \qquad (6)$$

Figure 5 Relationship between the logarithm of the frequency of ϵ'' maximum and the inverse of temperature.
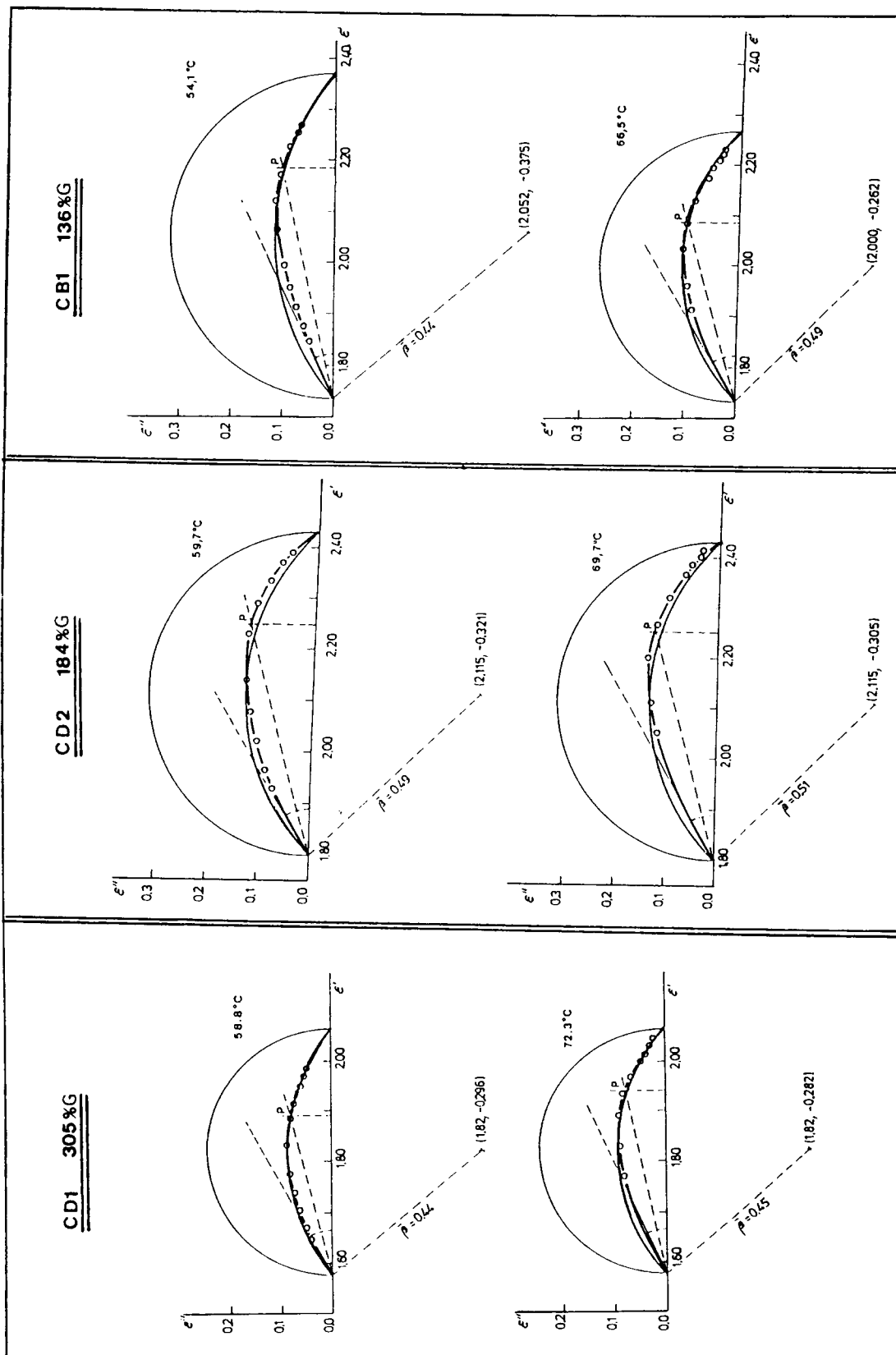
Figure 6   Arc diagrams for vinylic copolymers of cellulose: (———) Debye; (▬▬▬) Cole–Cole; (–O–O–O–) experimental.

Table IV   Dielectrical Constants of Vinylic Copolymers of Cellulose Relaxation and the Radius and Center of Debye's Semicircle

	%G	T (°C)	ϵ_∞	ϵ_0	$\Delta\epsilon$	r	Center
CD1	305	58.8	1.575	2.065	0.490	0.245	(1.82, 0)
		72.3	1.575	2.065	0.490	0.245	(1.82, 0)
CD2	184	59.7	1.800	2.430	0.630	0.315	(2.115, 0)
		69.7	1.800	2.430	0.630	0.315	(2.115, 0)
CB1	136	54.1	1.740	2.365	0.625	0.310	(2.05, 0)
		66.5	1.740	2.260	0.520	0.260	(2.00, 0)

where ω_{max} is the angular frequency at which ϵ'' is maximum.

The $\bar\beta$ parameter value was determined from the maximum ϵ'' by eq. (6):

$$\bar\beta = \frac{4}{\pi} \tan^{-1} \frac{2\epsilon''_{max}}{\epsilon_0 - \epsilon_\infty} \qquad (7)$$

As indicated above, the temperature of the maximum ϵ'' and the $\epsilon_0 - \epsilon_\infty$ values are shown in Tables III and IV, respectively.

Table V shows the parameters determined for this model and also the frequencies of the maximum, calculated on the log f_m vs. $1/T$ plot, and the τ_0 calculated from eq. (6).

Davidson–Cole Equation

It is seen in Figure 6 that there are some deviations from the Cole–Cole semicircle in the experimental loss curves, which have a high-frequency broadening, and the arcs are skewed. Therefore, we have determined the parameters of the Davidson and Cole equation, φ and γ, by the following equations:

$$\varphi = \gamma \frac{\pi}{2} \quad \text{and} \quad \tan \frac{\gamma}{2} = \frac{\epsilon''(\omega \cdot \tau = 1)}{\epsilon'(\omega \cdot \tau = 1) - \epsilon_\infty} \qquad (8)$$

The main relaxation time, τ, is determined from the experimental plot by using the relation

$$\omega \cdot \tau = 1 \qquad (9)$$

where ω is the angular frequency corresponding to the (ϵ', ϵ'') point, where the bisectrix of the angle $\varphi/2$ cuts the experimental arc (Fig. 7).

Table VI shows the results obtained for this model. From the arc diagrams and the parameters considered, it is possible to establish some differences between vinylic copolymers of cellulose:

- The experimental arcs are more similar to the Davidson–Cole model, and the process considered is therefore not a single relaxation time but a relaxation time distribution, which may mean that more than one relaxation takes place in the process considered.

- The calculated parameters of Davidson–Cole do not show significant differences among the copolymers considered. Therefore, the relaxation process may be very similar for all the materials considered and no important influence of the different percentage of cellulose is observed.

Table V   Cole–Cole Parameters, Generalized Relaxation Time, and Frequency of the Loss Maximum for the Dielectric Relaxation of Vinylic Copolymers of Cellulose

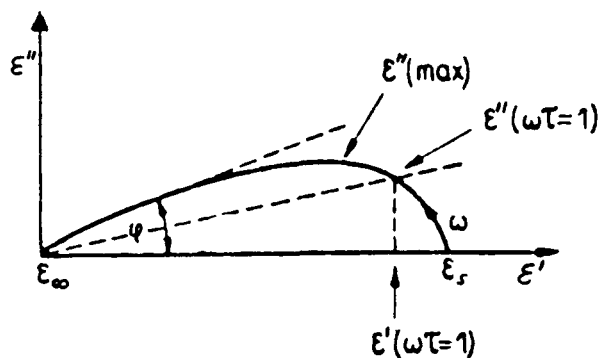|	%G	T (°C)	$\bar\beta$	r	Center	τ_0 (10⁵ s)	f_m (Hz)
CD1	305	58.8	0.44	0.384	(1.82, −0.296)	7.44	2138
		72.3	0.45	0.374	(1.82, −0.282)	0.45	35134
CD2	184	59.7	0.49	0.450	(2.115, −0.321)	4.82	3302
		69.7	0.51	0.439	(2.115, −0.305)	0.72	22083
CB1	136	54.1	0.44	0.488	(2.052, −0.375)	11.80	1349
		66.5	0.49	0.369	(2.000, −0.262)	0.89	17783

Figure 7 Arc and parameters of Davidson–Cole equation.

• The lower oscillator strength ($\Delta\epsilon$) observed in the copolymer CD1 of 305% G (Table IV) may show that the PMA percentage in the vinylic chain is higher than in the other materials considered, because, as it is known,[2] the α-relaxation intensity of PMA is lower than that of PVA. These data may be in agreement with the fact that this copolymer was prepared with a high ratio of MA in the monomeric mixture. Thus, the differences in $\Delta\epsilon$ may be due to the PVA–PMA composition of the vinylic chains.

• The $\Delta\epsilon$ values are affected only by temperature in the CB1 copolymer (136% G): They decrease when the temperature increases. This copolymer has a higher grafting frequency (GF) and its side chains are shorter than those of the other copolymers. As is known,[17] the oscillator strength may be related to the temperature by the following equation:

$$\epsilon_0 - \epsilon_\infty = \frac{C}{T} g_r \cdot \mu_{\text{ef}}^2(T) \tag{10}$$

where C is a factor that does not depend on temperature, μ_{ef} is the effective dipolar moment that

depends on the temperature only if the configuration of the molecule is changed, and g_r is the steric factor, which depends on the temperature because it is a measure of the intramolecular interactions. Therefore, when the molecular configuration and the intramolecular interactions are not changed in the range of temperature considered, the oscillator strength, $\epsilon_0 - \epsilon_\infty$, should decrease when the temperature increases. If $\epsilon_0 - \epsilon_\infty$ keeps constant or increases with the temperature, $\epsilon_0 - \epsilon_\infty$ may be governed mainly by the change in the intramolecular interactions. From the present results, it may be thought that the intramolecular interactions become less important when the chains of vinylic polymer are shorter and the grafting frequency higher as in the copolymer CB1.

CONCLUSIONS

1. The dielectric β-relaxation observed in cellulose does not appear in the copolymers, which was also observed in the viscoelastic experiments. Both dielectric and viscoelastic spectra fail to show this relaxation in the vinylic copolymers of cellulose, which may be due to graft and to the low ratio of cellulose in the sample.

2. In the copolymers we found one dielectric relaxation with the same apparent activation energy (E_a = 47 kcal/mol) and a maximum loss factor temperature that was very similar for all the copolymers considered (about 55°C at 1 kHz), attributed to the α-relation of the vinylic (PVA–PMA) side chains. Therefore, differences in cellulose percentage and in PAV/PMA ratio are not reflected in these results.

3. This α-relaxation seems to follow a Davidson–Cole model distribution of relaxation times, as the ϵ'' against ϵ' plot shows. The

Table VI   Parameters of Davidson–Cole, ϵ'' Frequency at Which $\omega \cdot \tau = 1$, Determined for the Vinylic Copolymers of Cellulose

	%G	T (°C)	ϵ' $\omega\tau = 1$	ϵ'' $\omega\tau = 1$	φ	γ	f_m	$\tau \cdot 10^5$ (s)
CD1	305	58.8	1.890	0.080	0.50	0.32	773	20.60
		72.3	1.941	0.080	0.43	0.27	9715	1.64
CD2	184	59.7	2.247	0.125	0.54	0.34	1781	8.94
		69.7	2.250	0.125	0.54	0.34	12820	1.24
CB1	136	54.1	2.182	0.102	0.45	0.29	470	33.90
		66.5	2.085	0.100	0.56	0.36	10278	1.55

Cole–Cole and Davidson–Cole parameters were determined.

4. The intramolecular interactions seem to become less significant for copolymers with high grafting frequency and with short vinylic side chains, judging from the temperature dependence of the oscillator strength of the relaxation.

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