

Some Dielectric Properties of Nanosilylated Cellulose

I.M. El-Anwar¹, S. A. El-Henawii², and A. H. Salama¹

¹Physical Chemistry Department, NRC, Dokki, Egypt

²Physics department, Faculty of science, Helwan University, Egypt

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ABSTRACT: The effect of silylation of cellulose on electrical properties is investigated by tracing the changes occurred in the dielectric constant, dielectric loss and the activation energy of dielectric relaxation. The test samples are activated cellulose with ethylene diamine, with sodium hydroxide and unactivated cellulose before and after silylation. The measurements are carried out within the frequency band 10^5 to 10^7 Hz and the temperature range from 10 to 50 °C using multi-deka-meter. Cellulose molecules are more activated by treatment with ethylene diamine than with sodium hydroxide. Generally, silylation causes a marked decrease of the dielectric constant and dielectric loss, meanwhile the silylation samples are affected with the pretreatment of linters with sodium hydroxide and ethylene diamine.

KEYWORDS: Dielectric Properties, Nanosilylated Cellulose.

1 INTRODUCTION

One of the most important natural products with an abundance of free hydroxyl groups which significantly determine its physical properties is cellulose. Replacement of some or all of the hydroxyl protons of cellulose by silyl groups can be expected to alter radically the properties of this polymer, just as esterification or alkyl ether formation can drastically modify the parent cellulose.

Electric field alignment of nanofibrilled cellulose (NFC) in silicone oil impact on electric properties was studied ⁽¹⁾. Dielectric properties have shown that the dielectric constant of the medium increases in comparison to the randomly dispersed NFC (when no electric field is applied). The optimal parameters of alignment were found to be 5000 V_{pp}/mm and 10 KHz for duration of 20 min for both kinds of NFC. The highest increase in dielectric constant was achieved with NFC oxidized for 5 min (NFC-C-5 min) at optimum conditions mentioned above.

The influence of natural and stimulated oxidation on luminescent properties of silicon – cellulose nanocomposites were investigated ⁽²⁾. A composite has been developed on the basis of nano-crystalline cellulose and silicon nanoparticles which exhibited more intense photoluminescence in the visible range of the spectrum than did nanoporous silicon. The effect of temperature and gas –phase oxidation on the luminescent properties of the material indicates a high stability of the luminescent properties of the composite. Investigation of the charging effect of the nanocomposite allows silicon nanoparticles to be considered as centers of accumulation of the bulk electricity charge.

The behavior of cellulose whiskers (CWs) in silicone oil was examined ⁽³⁾ under the influence of an Ac electric field. The whiskers first rotate in the direction of the electric field, and then the ends of the whiskers interact with each other to form chains. Alignment and chain formation were found to be functions of electric field magnitude, frequency and duration. The driving force for chain formation is thought to be dielectrophoresis. The optimal alignment with chain formation was achieved at 300 V_{pp} mm⁻¹ and 500 mHz for a duration of 20 min. the dielectric constant of the solutions was studied as a function of microstructure. In general, the dielectric constant for the aligned samples increased as compared to the random case. The highest increase was achieved at the optimum conditions mentioned above. It was also found that the thickness

and length of formed CW chains impact the effective properties resulting in an almost three –fold increase in dielectric constant.

The relation between the properties of poly-ampholytes in aqueous solution and their adsorption behaviors on silica and cellulose surfaces was investigated ⁽⁴⁾. Four poly-ampholytes carrying different charge densities but with the same nominal ratio of positive to negative segments and two structurally similar poly-electrolytes were investigated by using quartz crystal microgravimetry using silica – coated and cellulose – coated quartz resonators. Time resolved mass and rigidity (or viscoelasticity) of the adsorbed layer was determined from the shifts in frequency (Δf) and energy dissipation (ΔD) of the respective resonator.

Deposition of nanosized latex particles onto silica and cellulose surfaces was studied by optical refractometry ⁽⁵⁾. The major conclusion of this work was that the nature of the substrates played an important role in a saturated layer of deposited colloidal.

The interaction of cellulose layers with colloidal silica particles was investigated ⁽⁶⁾ by direct force measurements with the atomic force microscope (AFM). Radtchenko, I.L. et al summarized that adsorption of cellulose to probe surfaces was dominated by nonelectrostatic forces, probably originated from hydrogen bonding.

The effect of polymer modification by silylation had been demonstrated in at least three cases ⁽⁷⁻⁹⁾, the increased solubility of silylated polymers in non-polar solvents was particularly noteworthy ⁽⁷⁾. Klebe ⁽⁸⁾ measured some electrical properties of silylated cellulose. The measurements showed a low dielectric loss from 0.001 to 0.1 within the frequency range 60 to 10^5 Hz. The dielectric constant calculated in the same range of frequency was 2.8 for trimethyl silyl cellulose and ranged from 14.5 to 12.7 for dimethyl (γ - cyanopropyl) silyl cellulose. The high corona resistance was noteworthy, it was characteristic of polymers with relatively high silicon content.

2 EXPERIMENTAL

2.1 PREPARATION OF TESTED MATERIALS

The tested materials including unactivated cellulose, cellulose activated with sodium hydroxide and with ethylene diamine were prepared and silylated as described in a previous work ⁽⁹⁾.

2.2 DIELECTRIC MEASUREMENTS

The equipment used in the dielectric measurements consists of the multi-deka-meter, the working cell and the vacuum system.

(1) The multi-deka-meter having a frequency band from 0.1 to 12 MHz the measured dielectric constant was obtained from a calibration curve. The standard materials used were trolitul ($\epsilon' = 2.45$), glass ($\epsilon' = 7.0$) and air ($\epsilon' = 1$) at 20 °C.

The dielectric loss ϵ'' was measured by the same apparatus using the same cell and following the difference substitution method. The following formula was applied:

$$\epsilon'' = \frac{\epsilon'}{2\pi f R_x \Delta C}$$

Where, ϵ' is the dielectric constant of the material, f is the measuring frequency in MHz, R_x is the cathodic resistance in mega-ohms and ΔC is the capacitance of the sample in $\mu\mu\text{F}$. The accuracy of the apparatus from ± 0.3 to 0.5 %.

(2) The working cell:

The type of the measuring cell ⁽¹⁰⁾ used for determining the dielectric constant ϵ' and the dielectric loss ϵ'' was primarily designed for measurements under atmospheric conditions. Owing to the hygroscopic nature of the investigated materials, the cell was modified to render its applicability for dielectric measurements of tested samples under vacuum.

A circular hole was made in a stainless steel disc. This hole was of such diameter that the cell could be held firmly by the disc. Also, four other small holes each having a diameter of 1 cm was drilled in the disc for thermosetting and evacuating purposes. The upper surface of the disc was optically polished and the cell was then fitted and sealed tightly to the disc at a position about 1 cm below the measuring chamber. The upper part of the cell as the four holes was covered with a brass bell jar with its optically polished edge resting on the metal disc.

3 RESULTS AND DISCUSSIONS

It can be seen from Fig. 1, which represents the variation of the dielectric constant ϵ' of cellulose samples with frequency that the dielectric dispersion occurs specially at high frequencies. This decrease of ϵ' with increasing frequency can be explained by the lag of the molecules behind the alternations of the applied electric field. Also, it can be noticed that ϵ' increases with the increase of temperature. This can be attributed to the decrease in the effect of dipole – dipole interactions due to the increased mobility of playable and flexible portions in the cellulose chains. This decrease enhances the ease of rotation and polarization of the side groups and other flexible portions of cellulose. On the other hand the increase of ϵ' signifies increase in the contribution of the orientation polarization to the dielectric constant. This may be attributed to secondary transitions resulting in smaller bulkiness of side groups so that the orientation freedom of these groups or the chance of the amorphous chains to achieve random disorder is more facilitated and requires smaller volume. The effect of temperature on dielectric properties is almost equivalent to that of frequency. The observed shifts of maxima of the dielectric loss towards higher frequencies as the temperature is increased (Fig. 2 and Fig. 3) may be attributed to the increased mobility of polar groups (OH groups) with temperature. The loss broadening with increasing temperature indicates an increment in the number of mobile dipoles.

Ishide⁽¹¹⁾ and other authors found that in high polymers in the solid state there were two loss regions. The first was due to α -relaxation characterized by a loss peak located at temperature above glass transition point and the second was due to β -relaxation which was characterized by a flat loss maximum extending over a wide temperature range below the transition point. The primary α -relaxation characterized by high apparent activation energy (about 209 KJ/mole) has been attributed to large scale conformational rearrangement of the main chains. The secondary or β -relaxation whose activation energy is of the order 62.7 KJ/mole has been the object of many studies regarding the assignment to a particular mechanism. It was suggested that β -relaxation is local in nature and is attributed to the motion of polar side groups in the amorphous phase. Assuming that the crystalline phase contains various kinds of imperfections, the motion associated with the β -relaxation would be possible even in such crystalline defects. In certain cases the β -relaxation due to crystalline defects can be distinguished from β -relaxation due to amorphous phase, the former is a low temperature process and the latter is a high temperature process.

In view of the temperature and frequencies at which dielectric loss maxima appears (Figs. 2 and 4) that is reasonable to consider these relaxations as secondary or β -relaxation originated mainly in the amorphous phase as associated with the orientation of polar –OH side groups. The apparent times of treated and untreated cellulose samples are calculated from the relation:

$$2\pi f_m \tau = 1 \quad (1)$$

Where, τ is the apparent relaxation time and f_m is the critical frequency corresponding to maximum energy loss. The values obtained are listed in table 1.

Table 1. The apparent relaxation times and activation enthalpies of cellulose and silylated cellulose

t °C	Relaxation time $\tau \times 10^3$ /s	
	For cellulose	For silylated cellulose
10	12.65	33.37
20	8.00	15.92
30	3.15	8.00
40	-----	3.15
ΔH /(KJ/mole)	31.8	51.4

Eyring⁽¹²⁾ applied the theory of absolute reaction rates to dielectric relaxation. Kauzmann⁽¹³⁾ gave an extensive analysis of this phenomenon. It is assumed that molecular dipole orientation involves passage over a potential energy barrier with a certain probability of jumping from one equilibrium position to another so that the dipole needs certain free energy of activation to make its passage possible. The dipole relaxation K_0 is related to the probability that a dipole molecule with move from one orientation (θ, ϕ) into a new position (θ', ϕ') with a solid angle Ω in an interval of time dt given by the relation:

$$(\theta, \phi \rightarrow \theta', \phi') = \frac{1}{4\pi} K_0 (\theta, \phi \rightarrow \theta', \phi') dt d\Omega \quad (2)$$

K_0 is the rate constant or jump rate for unimolecular reaction giving the number of times a molecule leaves its equilibrium position per second. The intrinsic relaxation time τ_e is the reverse of the jump rate K_0 .

$$\text{i.e.,} \quad \tau_e = \frac{1}{K_0} \quad (3)$$

This theory leads to the expression

$$\tau_e = \frac{1}{K_0} = \frac{h}{KT} e^{-\frac{\Delta G}{RT}} \quad (4)$$

Where, ΔG is the molar free energy of activation for dipole relaxation, h Plank's constant and K Boltzmann constant.

Substitution by $\Delta G = \Delta H - T\Delta S$, then by taking the logarithm and differentiating we have:

$$\text{Ln} \left(\frac{T\tau_e K}{h} \right) = \frac{1}{T} \frac{\Delta H_\epsilon}{R} - \frac{\Delta S_\epsilon}{R} \quad (5)$$

Here ΔH_ϵ and ΔS_ϵ are the enthalpy of activation and the entropy change per mole for dipole relaxation.

Thus, from the slope of the plot of $\text{Ln} \left(\frac{T\tau_e K}{h} \right)$ against $\frac{1}{T}$, ΔH_ϵ can be obtained. The value obtained (31.8 KJ/mol.) is in good agreement with literature values⁽¹³⁾.

It can also be observed from Fig.1 that the treatment of cellulose with NaOH and ethylene diamine results in an increase of the dielectric constant values as compared with the corresponding values of untreated cellulose.

This increase can be attributed to the increased activity of the side polar OH groups which contribute to the increase of the orientation polarization and hence the dielectric constant. The apparent increase in ϵ' in the case of cellulose activated with ethylene diamine is greater than that in the case of cellulose treated with sodium hydroxide. The effect of activation on the dielectric loss is equivalent to that occurring in the dielectric constant (Fig. 2). Also, the values of dielectric loss increase while the critical frequencies of dielectric relaxations are not affected. The results of activation of cellulose molecules when treated with ethylene diamine and sodium hydroxide from the chemical point of view are in good agreement with the above mentioned results.

Figures 3 and 4 represent the variation of the dielectric constant and the dielectric loss of silylated cellulose samples with frequency. From Fig.3 it is noticed that the silylation decreases the values of ϵ' very sharply to a value near that of non-polar materials. These results indicate that the possible mechanism of silylation is the condensation of the silylation agent with cellulose molecules through cross linkage. The probability of the ring formation through the reaction of the dichlorodisilyoxane and the hydroxyl groups of the same glucose chain and also the graft polymerization are improbable, since these formations would increase the polarization of the molecules. This result is also reached through the study of the mass spectrum analysis of the silylated samples⁽¹⁴⁾.

It is also noticed that the values of ϵ' of silylated cellulose pretreated with ethylene diamine are greater than that pretreated with sodium hydroxide which themselves are greater than that of silylated untreated cellulose. This result seems to contradict the fact that the first sample mentioned above contains higher silicon percentages⁽⁷⁾ and hence the number of the residual polar -OH groups should be lower as compared with the second samples or the third sample. This contradiction can be argued if we take into consideration the effect of pretreatment of cellulose. Thus, it can be seen that the pretreatment enhance the ease of rotation and orientation of the side -OH groups which leads to an increase in the total polarization and hence the dielectric constant. This conclusion can be reinforced by the results obtained for the water retention values of these samples as well as the degree of silylation^(7&15).

From Fig.4 it can be seen that the silylation results in a shift of ϵ''_m towards lower frequencies as compared with the unsilylated samples. Also, the values of the dielectric loss become much lower due to condensed form of silylated cellulose and the effective decrease in the polar -OH side groups. The apparent relaxation times and the activation enthalpy of dielectric relaxation are calculated as mentioned above and are given on table 1. The values obtained show that the silylation leads to more condensed structure with longer relaxation time and higher activation enthalpy.

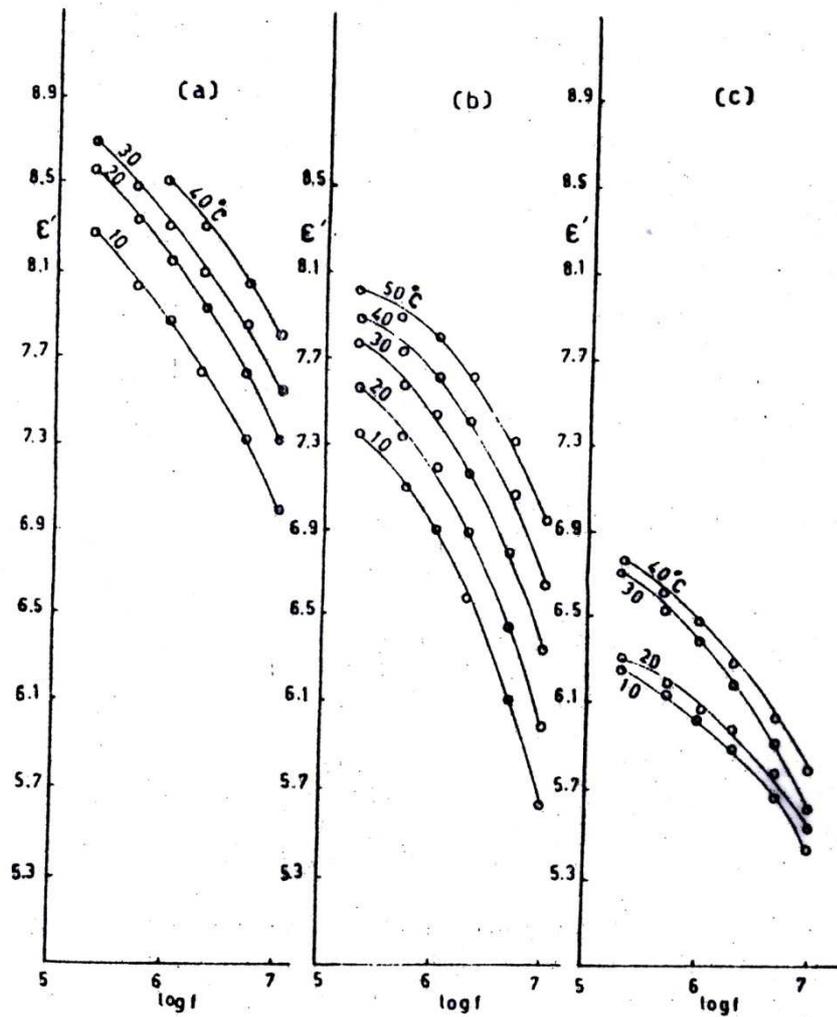


Figure 1. Variation of the dielectric constant, ϵ' with frequency for cellulose (a) treated with ethylene diamine, (b) treated with sodium hydroxide, (c) untreated at different temperatures.

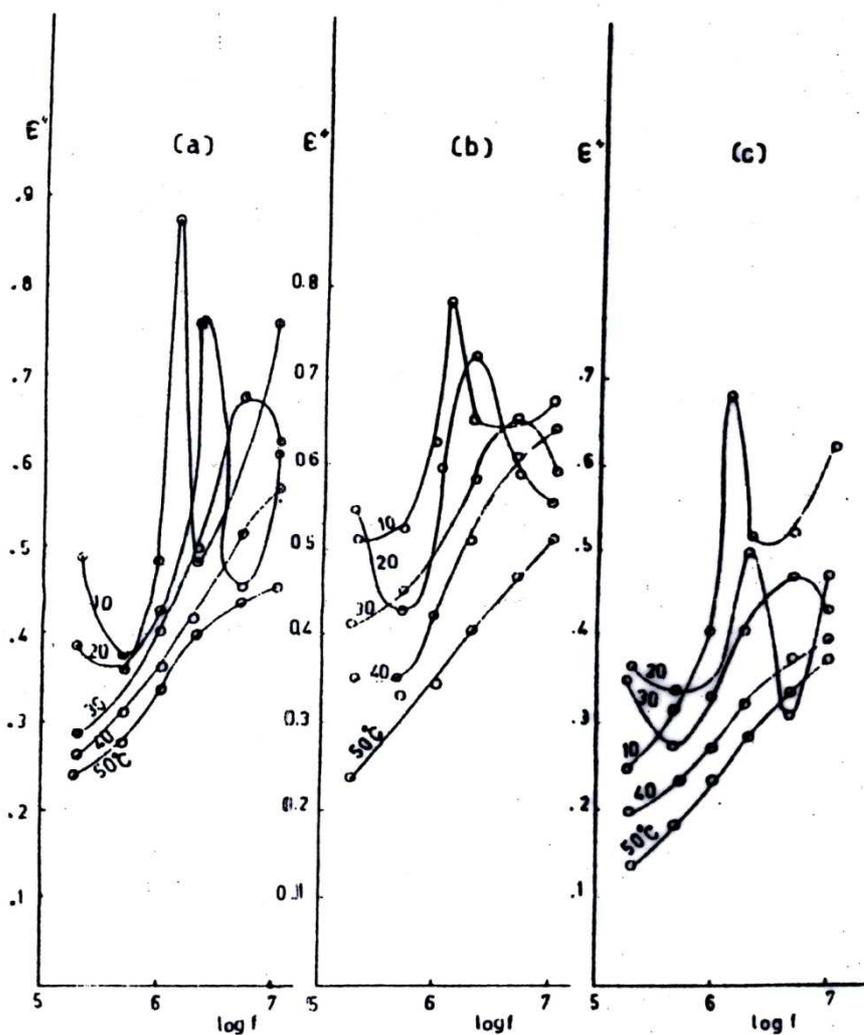


Figure 2. Variation of the dielectric loss, ϵ'' , with frequency for cellulose (a) treated with ethylene diamine, (b) treated with sodium hydroxide, (c) untreated at different temperatures.

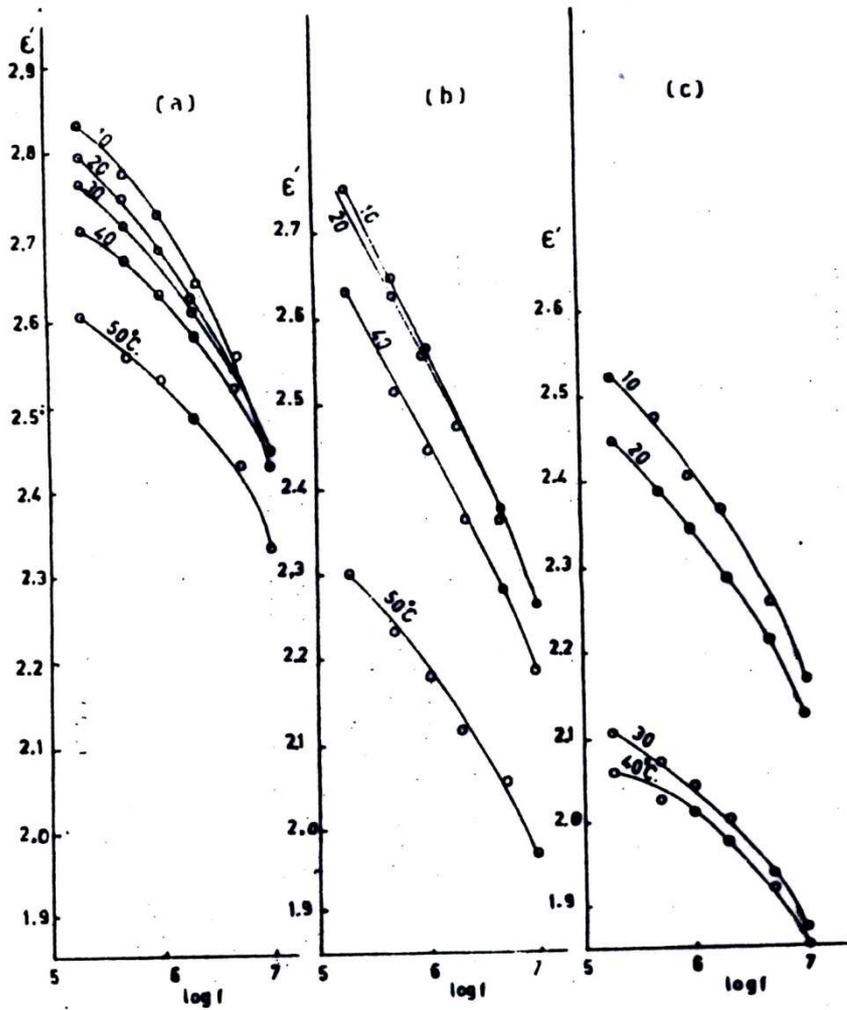


Figure 3. Variation of the dielectric constant with frequency for silylated cellulose (a) pretreated with ethylene diamines, (b) pretreated with sodium hydroxide, (c) untreated at different temperatures.

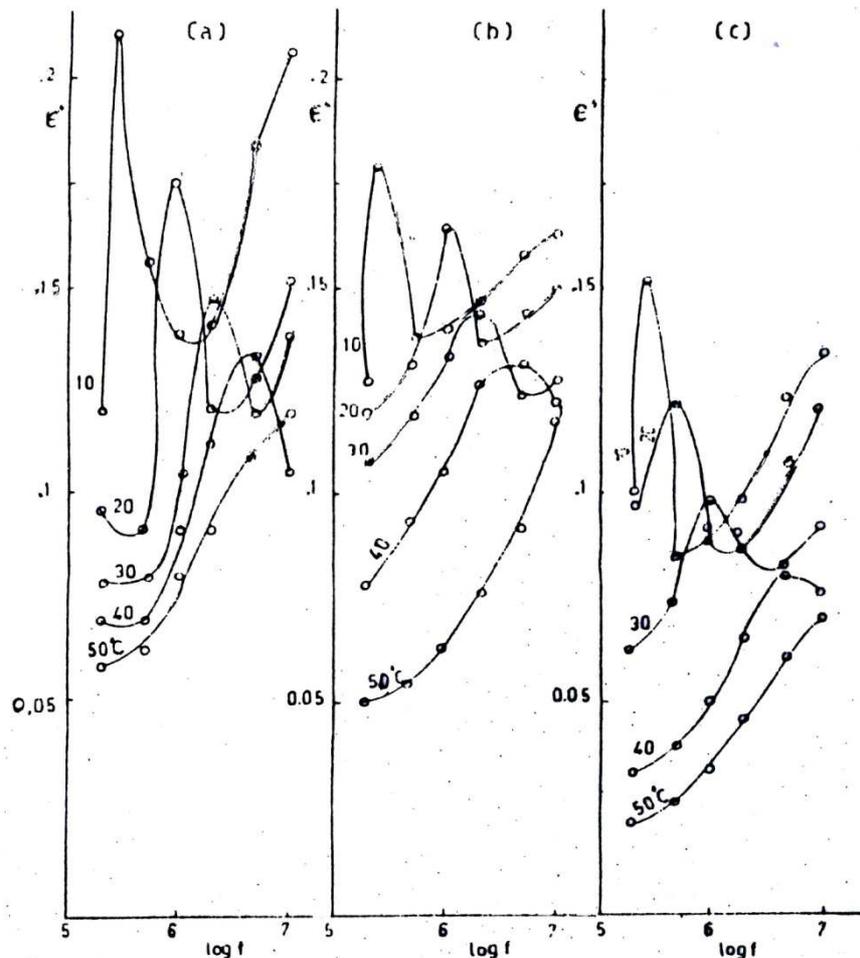


Figure 4. Variation of the dielectric loss with frequency for silylated cellulose (a) pretreated with ethylene diamine, (b) pretreated with sodium hydroxide, (c) untreated at different temperatures.

4 CONCLUSION

The analysis of the various results (i.e. dielectric constant ϵ' and dielectric loss ϵ'') indicates that the treatment of cellulose with NaOH and ethylene diamine results in an increase of the dielectric constant values as compared with the corresponding values of untreated cellulose. The increase in ϵ' in the case of cellulose activated with ethylene diamine is greater than that in the case of cellulose treated with sodium hydroxide. Additionally, the silylation of cellulose decreases the values of ϵ' very sharply to a value near to a value near that of non-polar materials. Silylation also results in a shift of ϵ'' towards lower frequencies as compared with the unsilylated samples. The values of the activation enthalpy of dielectric relaxation for cellulose and silylated cellulose are 31.8 and 51.4 (KJ/mole) respectively, these values show that the silylation leads to more condensed structure with longer relaxation time and higher activation enthalpies.

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