Thermochimica Acta, 218 (1993) 435–443
Elsevier Science Publishers B.V., Amsterdam

STUDIES ON THE DIELECTRIC PROPERTIES OF SOME NATURAL (PLANT) AND SYNTHETIC FIBRES IN AUDIO FREQUENCY RANGE AND THEIR DC CONDUCTIVITY AT ELEVATED TEMPERATURE

Bora M. N., Baruah G. C. and Talukdar C. L.

Department of Physics, Gauhati University, Guwahati 781014, Assam, INDIA

KEYWORDS : capacitance, dielectric constant, conductivity, dehydration, decomposition, activation energy, glass transition, hydroscopicity.

ABSTRACT

The capacitance (C_p) and dielectric constant (ε) of locally available natural (plant) and synthetic fibres—Ramie, Jute, Cotton and Polyester have been studied in the audio frequency range from 1 kHz to 20 kHz under thermo-chemical conditions. The DC conductivity of the samples at the elevated temperature has been investigated. The experiments have been carried out in the temperature range between 296 K and 580 K.

The values of dielectric constant are 5.18 for Ramie, 4.46 for Jute, 4.23 for Cotton and 4.22 for Polyester at moderate temperature. This value of the fibres decreases with increase in frequency. The hygroscopicity of plant fibres plays a role for variation of dielectric properties. The DC conductivity of the samples is almost constant upto about 320 K and then it increases with rise of temperature. At the room temperature, this value is 0.33×10^{-13} mho/cm for Ramie, 0.19×10^{-12} mho/cm for Jute, 0.84×10^{-13} mho/ cm for Cotton and 0.86×10^{-13} mho/ cm for Polyester.

The causes for variation of these dielectric properties and DC conductivity in fibrous polymers under thermo-chemical conditions have been analysed.

INTRODUCTION

Natural (plant) fibres : Ramie, Jute and Cotton are organic polymers. These electrical insulating fibres are semi-crystalline in nature.The characteristic electrical properties of these polymeric fibrous insulators make them important in electric and electronic industries. Therefore, in recent years much attention has been made to study the electrical behaviours of natural and synthetic fibres.

0040-6031/93/$06.00 © 1993 Elsevier Science Publishers B.V. All rights reserved

The dielectric properties of various kinds of polymers have been studied by some investigators (Mc Cubbin, 1970; Wada, 1977; Lewis and Bowen, 1984). Reports have been published on electrical conduction studies of some textile fibres (Slazas, 1978; Ieda and Hikita, 1983; Ieda, 1984). Investigation on electro-chemical behaviours of fibres have also been reported (Kitamara, 1970). However, these kinds of studies on natural plant fibres are scarce (Gupta, et al., 1986. Abdel Moteleb, et al., 1982).

The action of absorbed water on crystalline orientation of some plant fibres has been reported (Ray, 1967; Ray, 1973). The influence of gum on crystalline structure of some plant fibres have been investigated (Ray, 1975). However, the study about the role of absorbed water and gum on electrical behaviour of plant fibres has not been reported. Therefore, it will be worthwhile to investigate how the absorbed water and gum play role on capacitance and conductance attributed in the plant fibres under thermo-chemical conditions.

In view of these facts, attempts have been made to study the dielectric properties in audio frequency range and the DC conductivity of natural (plant) fibres— Ramie, Jute and Cotton, and locally produced synthetic Polyester fibre under various thermal and chemical conditions.

EXPERIMENTAL

Materials and Sample Preparation :

The bust fibres free from bark— Ramie and Jute and the seed fibres— Cotton were collected from different parts of the North Eastern Region of India. The Polyester fibre synthesised locally from DMT and Ethylene Glycol was collected from Bongaigaon Refinery and Petro-Chemical Laboratory, Assam. The DMT used for this purpose is produced from para ethylene, which is derived from Assam crude oil.

One portion of plant fibres was delignified with alcohol-Benzene (1:1) for 6 hours and then bleached with NaOH and KOH solutions at various concentrations (5 to 9%). These treated samples were then washed with distilled water and dried at 330K. The treatment was confined to the concentrations upto 9%, since crystalline structure was found to remain unaltered upto this concentration from earlier investigation. (Baruah and Bora, 1988).

To study the effects of annealing and quenching, dielectric and DC conductivity studies were made by heating some samples at 373K, some at 473K and some at 523K for 6 hours and then rapidly or slowly cooling to room temperature (296K).

For measurements of capacitance and conductance, the cylindrical cells with the fibre sample were used as described elsewhere (Baruah, et al., 1990).

Measurements :

The experimental arrangement for dielectric measurements consisted of a Beat Frequency Oscillator (Agronic), an Isolating Transformer of type TM 7120 (Marconi) and an Universal Bridge of type TF 2700 (Marconi). The experimental arrangements for DC conductivity measurements consisted of an ECIL Bridge Electrometer type EA 815 with an accuracy of 3% in 10^6—10^{10} ohm input resistance range. The cell with the thermo-couple arrangement was put vertically inside the Muffle Furnace fitted with a temperature controlling device. The specimen temperature was recorded with the calibration data of the Copper-Constantan Thermocouple. Low capacity co-axial cables were used to connect the cell to the bridge and shieldings of the cables were grounded.

The values of the capacitance (C_P) were directly read from the Bridge. From these values of cell dimensions, the values of dielectric constant (ε) were computed. From the observed values of resistance in the electrometer, the values of DC conductivity (δ) were evaluated.

RESULTS AND DISCUSSION

The untreated plant fibres— Ramie, Jute and Cotton are white in colour. The delignified fibres become brighter and slightly stiff.

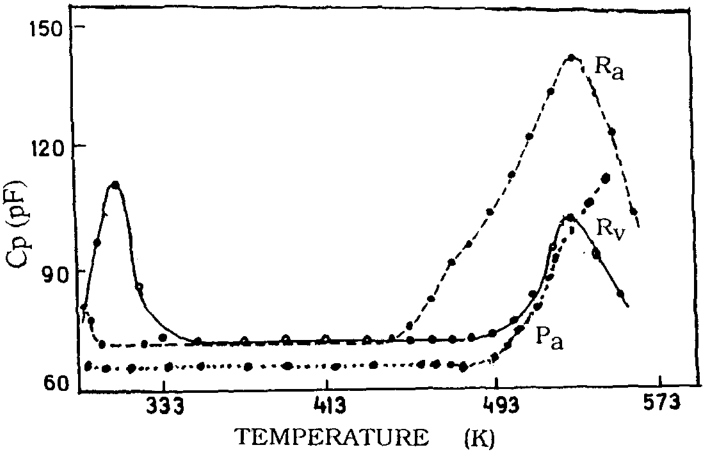

Fig. 1. Plot of capacitance (Cp) Versus temperature at frequency 1 kHZ.
R_a — Ramie in air, R_v — Ramie in vacuum, P_a — Polyester in air.

The results (Figure 1) show the remarkable variation of capacitance value of ramie fibre in the temperature ranges 303—333 K and 473—560 K in air atmosphere at the frequency 1 kHz. No first step variation of dielectric curves is attributed in the samples kept in vacuum (about 10^{-3} torr) for 24 hours. But a slight decrease in capacitance value is observed initially in the sample kept in vacuum for 6 hours. The Polyester fibre in air shows only one step increase in capacitance value in the temperature range 480—560 K.

The variation of the dielectric constant values with temperature in Ramie, Jute and Cotton fibres in air atmosphere at the frequency 1 kHz are displayed in Figure 2. After keeping each of the samples in vacuum for about 6 hours, the records were made in the same vacuum state. The variation of the values of dielectric constant (ε) with temperature under vacuum are shown in Figure 3.

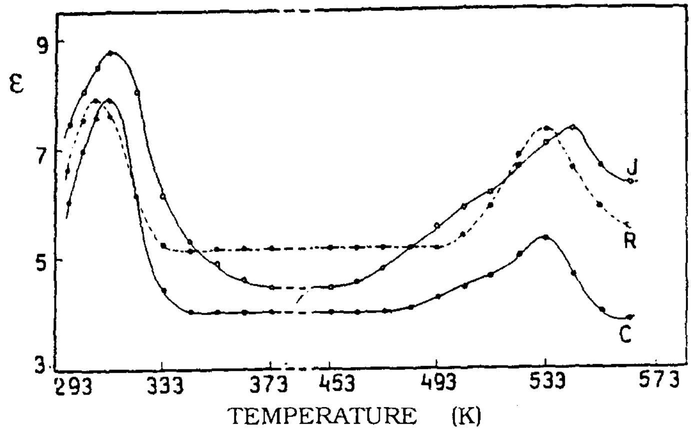

Fig. 2. Variation of dielectric constant (ε) with temperature at 1 kHz in air.
Sample : R — Ramie, J — Jute, C — Cotton.

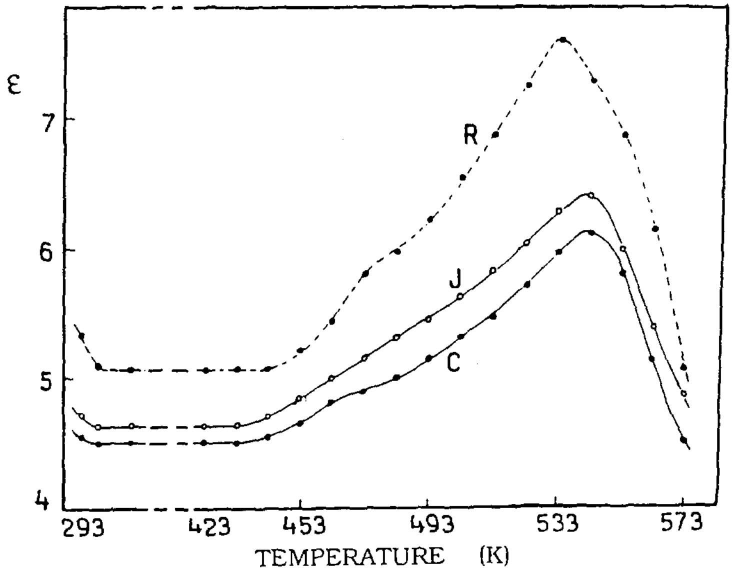

Fig. 3. Variation of dielectric constant (ε) with temperature at 1 kHz in vacuum.
Sample : R — Ramie. J — Jute, C — Cotton.

It is evident from the results (Figures 2 and 3) that the plant fibres—Ramie, Jute and Cotton show almost similar dielectric behaviour with change in temperature at constant frequency. This indicates that the fibres possess identical molecular setup. This is supported by our earlier X-ray crystallographic investigation (Baruah and Bora, 1988).

The results (Figure 2) show that the values of dielectric constant increase from room temperature to about 313 K for Ramie, 320 K for Jute and 318 K for Cotton in air atmosphere. It is also evident (Figure 4-R_1) that the dielectric constant decreases with increasing frequency even at room temperature (296 K) forRamie fibre kept in a humid atmosphere. This indicates that lower the frequency of the alternating field applied to the fibrous dielectric medium, is greater the increase in capacitance due to moisture absorption (Tareev, 1979). From the results, it may be inferred that the plant fibres are hydrophillic and synthetic Polyester fibre is hydrophobic in nature. Because of considerable dipole moment and smaller molecular size, water molecules give high value of dielectric constant which increases rapidly with increasing temperature. This is in agreement with earlier study made for proteins (Neurath and Bailey, 1966). It may be inferred that dehydration of surface water molecules from the hygroscopic plant fibres causes for rapid decrease in dielectric constant with rise in temperature. The decrease in ε values in the temperature range 296—303 K (Figure 3) indicates that surface water molecules are not completely evaporated at room temperature under vacuum condition for 6 hours. They attain the anhydrous state even at room temperature when made vacuum for about 24 hours.

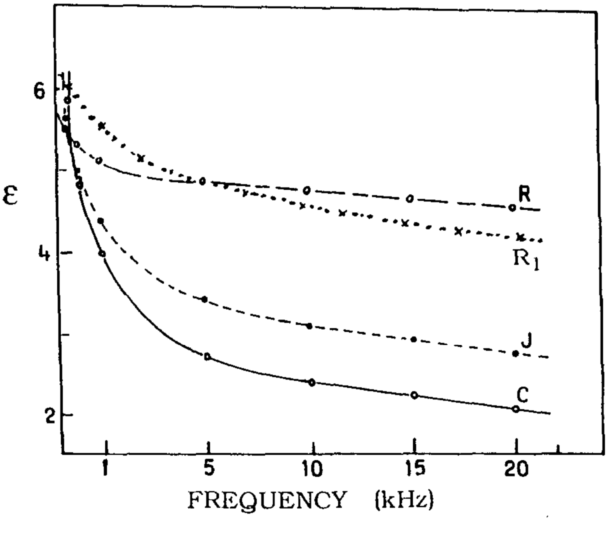

Fig. 4. Plot of dielectric constant Vs frequency. Samples : R— Ramie at 373 K, R_1— Ramie at 296 K, J— Jute at 373 K, C— Cotton at 373 K.

The values of dielectric constant remain almost constant in the temperature range 338—490 K for Ramie, 360—450 K for Jute and 343—470 K for Cotton, in air atmosphere (Figure 2). The temperature upto which these values remain constant corresponds to the glass transition (T_g) of the plant fibres. This is in agreement with the results obtained earlier for some polymers (Stetsovskii and Tarasova, 1978). Beyond this temperature, degradation of the fibrous molecules starts. Due to this void of the fibres, intrinsic defects are formed. These defects contribute to the interfacial polarization between the samples and gases evolved out of the structure during decomposition stage. As a result, increase in dielectric constant is attributed in the fibres during decomposition stage. This is supported by the results of variation ε with frequency in isothermal condition (Figure 4). The decrease in the values of dielectric constant with increasing frequency at higher temperature occurs due to influence of interfacial polarization during decomposition stage. This is in agreement with the results obtained earlier for some silk fibres (Kitamara, 1970). The peak temperature at which dielectric constant reaches maximum value is 533 K for Ramie, 540 K for Jute and 544 K for Cotton. Beyond this temperature, the rapid decrease in dielectric values may represent the dielectric relaxation process caused in the residual fibres which remained as ashes.

The observed values of dielectric constant of the samples— untreated (raw), delignified, annealed from 373 K and quenched from 373 K are listed in the Table I.

Table I

Dielectric constants (ε) for treated and untreated samples at different frequencies and temperatures in air (Samples : a— untreated, b— delignified, c— annealed, d— quenched)

Frequency	Temperature	Ramie (ε)				Jute (ε)				Cotton (ε)			
kHz	K	a	b	c	d	a	b	c	d	a	b	c	d
	373	5.18	4.89	4.92	4.91	4.46	4.16	4.24	4.20	4.03	3.71	3.99	3.88
1	473	5.78	5.22	5.51	5.51	4.89	4.52	4.70	4.69	4.43	4.12	4.25	4.21
	523	6.84	6.18	6.70	6.68	6.62	6.33	6.42	6.31	5.01	4.72	4.93	4.89
	373	4.75	4.25	4.51	4.49	3.17	2.86	2.96	2.89	2.41	2.18	2.22	2.15
10	473	4.86	4.41	4.66	4.62	3.61	3.25	3.41	3.40	2.89	2.51	2.62	2.61
	523	6.48	5.97	6.27	6.21	5.33	5.01	5.17	5.10	3.45	3.16	3.28	3.19
	373	4.61	3.98	4.22	4.18	2.81	2.53	2.62	2.47	2.08	1.97	1.92	1.89
20	473	4.95	4.48	4.62	4.61	3.16	2.83	3.06	3.01	3.06	2.52	2.71	2.69
	523	6.34	5.82	6.11	6.00	4.97	4.66	4.78	4.68	3.12	2.85	2.92	2.79

The results of variation of DC conductivity with temperature under vacuum are displayed in the Figure 5. The observed conductivity data at three specific temperatures—the room temperature (296 K), and the temperatures 373 K and 473 K from which samples were annealed and quenched are listed in the Table II.

The values of DC conductivity (δ) remain almost constant from room temperature (296 K) to about 315 K for Ramie, 323 K for Jute, 330 K for Cotton and 333 K for Polyester due to relative weak temperature dependence of carrier mobility. Beyond this temperature, it increases with temperature for all samples. It is evident from the results (Figure 5) that the electrical conductivity in plant fibres is ionic in nature as observed for some polymers (Saito, et al., 1968). Therefore, it is inferred that the increase in δ values with temperature may occur due to faster carrier mobility. The Polyester fibre shows anomalous behaviour with increase in temperature probably due to thermo-chemical instability occured in the chemical constituents of the synthetic fibre. The noticeable anomaly in δ variation shown in and arround its melting point is due to thermal degradation attributed during phase change.

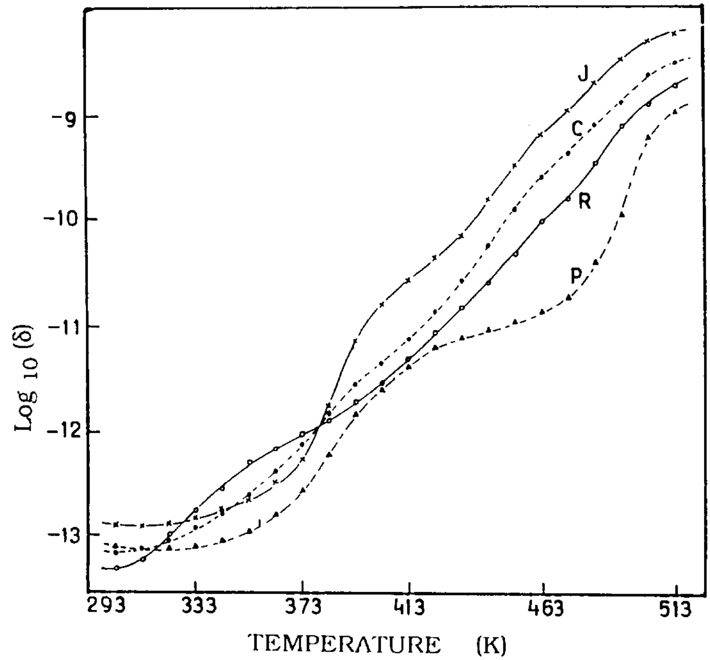

Fig. 5. Plot of $\log_{10}$ (Conductivity) Vs temperature in vacuum.
Sample : R— Ramie, J— Jute, C— Cotton, P— Polyester.

TABLE II

DC conductivity (δ) for treated and untreated fibres at different temperatures

Temperature (k)	Treatment	Ramie (mho/cm)	Jute (mho/cm)	Cotton (mho/cm)	Polyester (mho/cm)
296	Untreated	0.33×10^{-13}	0.19×10^{-12}	0.84×10^{-13}	0.86×10^{-13}
376	Untreated	0.10×10^{-11}	0.56×10^{-12}	0.78×10^{-12}	0.29×10^{-12}
	Delignified	0.31×10^{-10}	0.38×10^{-10}	0.68×10^{-10}	—
	Annealed	0.48×10^{-10}	0.69×10^{-11}	0.91×10^{-11}	—
	Quenched	0.49×10^{-10}	0.70×10^{-11}	0.98×10^{-11}	—
473	Untreated	0.17×10^{-9}	0.11×10^{-8}	0.46×10^{-9}	0.20×10^{-9}
	Delignified	0.08×10^{-8}	0.42×10^{-6}	0.02×10^{-8}	—
	Annealed	0.12×10^{-8}	0.92×10^{-7}	0.39×10^{-8}	—
	Quenched	0.14×10^{-8}	0.99×10^{-7}	0.47×10^{-8}	—

From the slopes obtained by plotting $\log_{10}$ (conductivity) versus temperature inversion, the activation energy (E) played a role for activation of the processes in dehydration and decomposition stages of plant fibres and in melting state of the synthetic Polyester fibre has been computed. The results are shown in the Table III.

TABLE III

Activation Energy (E) in electron volt (eV) of samples at different conditions.

Sample	Reaction	Temperature Range (K)	Untreated E(eV)	Delignified E(eV)	Annealed E(eV)	Quenched E(eV)
Ramie	Dehydration	313—383	0.22	0.11	0.20	0.20
	Decomposition	423—503	0.51	0.48	0.49	0.49
Jute	Dehydration	313—343	0.16	0.06	0.12	0.11
	Decomposition	393—483	0.47	0.40	0.42	0.41
Cotton	Dehydration	313—353	0.13	0.08	0.10	0.09
	Decomposition	393—493	0.47	0.42	0.43	0.43
Polyester	Melting step	463—520	1.36	—	—	—

The values of dielectric constants are reduced noticeably in delignified, annealed and quenched samples (Table I). These values are more in delignified samples than those of annealed and quenched samples. The values of DC conductivities are slightly increased in treated samples (Table II). The activation energy in the decomposition step is more than that in dehydration step. These values are more in Ramie and less in Cotton than those in Jute fibre (Table III). From the results, it is inferred that removal of gum resided in the amorphous region by delignification may cause for variation of ε and δ values in the samples. This agrees with the observation made earlier for influence of gum on crystallinity (Ray, et al., 1975). The samples annealed and quenched from the temperature quite below their decomposition stage show a little effect in capacitance and conductance behaviours. Of course, these values reduce noticeably when annealed and quenched from 473 K due to void in the fibres. It is evident from these results that the behaviour of DC conductivity in the semi-crystalline fibres is dependent on their amorphous regions also.

CONCLUSION

From the present study, it has been concluded that the two-stage dielectric relaxation processes are attributed in plant fibres. The water molecules absorbed in the amorphous regions and adsorbed in the crystalline parts of the fibres have a role on dielectrical properties. The plant fibres— Ramie, Jute and Cotton have capacity to regain their initial physical properties even after delignified and annealed and quenched from elevated temperature. The observed steady values of dielectric constant in a wide range of temperature indicates their suitability to use as electrical appliances in the high temperature range upto 460 K. Similar DC conductivity and capacitance behaviours attributed in Polyester and plant fibres indicate the possibility of blending of plant fibres with the Polyester fibre, which may open a new scope in the textile and other industrial fields.

ACKNOWLEDGEMENT

The authors are thankful to the Staff members of the Department of Physics, Gauhati University for their kind co-operation and help in carrying out the experiments.

REFERENCES

Abdel Moteleb, M. M., Naoum, M. M., Shirouda, H. G. and Rizk, H. A., 1982. Some of the dielectric properties of Cotton cellulose and Rayons, J. Polym. Sci., 20 (3) : 765—772.

Baruah, G. C. and Bora, M. N., 1988. X-ray diffraction study of synthetic and plant fibres, The Journal of the Assam Science Society, 31(1): 66—72.

Baruah, G. C., Talukdar, C. and Bora, M. N., 1990.A study on dielectric properties of natural silk fibres endemic to N.E.R., Gauhati University Journal of Science, 30A : 45—52.

Gupta, N. P., Patri, P.C., Arora, R. K. and Chopra, S. K. 1986., Properties of alkali treated Jute, Ramie and Pine-apple leaf and yarns, Cellul. Chem. Technol., 20(5):575—582.

Ieda, M., 1984. Electrical conduction and carrier traps in Polymeric materials, IEEE Trans. Electr. Insul. EL., 19(3): 162—178.

Ieda, M. and Hikita, M., 1983. Recent studies on electrical break down in Polymers, Mem. Fac. Eng. Nagoya Univ., 35(2):205—253.

Kitamara, AIO., 1970. Interfacial electro-chemical properties of silk I, Nippon Sanshigaku Zasshi, 39(2): 119—125.

Lewis, T. J. and Bowen, P. J. 1984. Electronic processes in Biopolymer systems, IEEE Trans. Electr. Insul. EL., 19(3): 254—256.

Mc Cubbin, W. L., 1970. Conduction Processes of Jute and allied fibres, J. Appl Polym. Sci., 17:951—957.

Neurath, H. and Bailey, K., 1966. The Protiens, Academic Press Inc. Publ. NY., pp856.

Ray, P.K., 1967, On the crystelline orientation in Jute and Mesta fibres under different moisture conditions, J. Appl. Polym. Sci., 11:2021—2028.

Ray, P. K., 1973. The effect of methods of drying on the fine structure, density and some mechanical properties of Jute and allied fibres, J. Appl. Polym. Sci., 17:951—957.

Ray, P.K. and Montague, P. E., 1977, Crystallinity in Jute fibre as resolved by multipeak resolusion, J. Appl. Polym. Sci., 21: 1267—1272.

Ray, P. K., Bag, S. C. and Chakravarty, A. C., 1975. The influence of gum on the crystalline structure in Ramie fibre. J. appl. Polym. Sci., 19: 999—1004.

Saito, S., Sesabe, H., Nakajima, T. and Yada, K., 1968. Electrical conduction in Polymers, J. Polym. Sci. A, 2(6): 1297—1303.

Slazas, J., 1978. Evaluation of the electrical conductivity of textile filament, Izmer Tekh, 3: 68—71.

Stetsovskii, A. P. and Tarasova, L. V., 1978. Study of the dependence of the dielectric relaxation process in Polymers on their structure, Vysokomom Soedi Ser. A., 20(5): 1116—1123.

Tareev, B., 1979. Physics of dielectric Materials, MIR Publishers Moscow, (translated from Russian lang. by A. Troitsky), pp 105.

Wada, Y., 1977. Dielectric and related properties of Polymers in the solid state. Dielectric Related Molecular Processes, 3: 143—149.