Dielectric Behavior and Resistivities of Polyacrylonitrile and Some Pyrolyzates

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Synopsis

Dielectric losses in polyacrylonitrile (PAN) and three pyrolyzates were studied between 1 Hz. and 300 kHz. Pure PAN has at 20°C. a very broad loss region with a maximum at 70 Hz. which is ascribed to CN groups. Powdered PAN was pyrolyzed in a nitrogen atmosphere at 170, 220, and 300°C. PAN-170 has the same loss maximum as the unpyrolyzed polymer, but the maximum had disappeared in PAN-220. This is attributed to formation of conjugated chains by linking of CN groups above 200°C. However, this does not enhance the conductivity until hydrogen is eliminated above 350°C.

Introduction

Pyrolyzed polyacrylonitrile has received considerable attention, especially when Russian investigators reported on semiconductor properties.[1] A review of their results was given by Becher and Mark.[2] The formation of conjugated chain molecules by linking of nitrile groups was thought to enhance the conductivity. More recent work[3] confirmed increased conductivities at pyrolysis temperatures above 400°C. No data appear to be available to indicate at which pyrolysis temperature the nitrile groups begin to form conjugated chains. Therefore, dielectric measurements were undertaken in order to observe the occurrence of chain formation in low temperature pyrolyzates. The dielectric behavior of polyacrylonitrile (PAN) at room temperature was determined by Mead and Fuoss[4] between 60 Hz. and 100 kHz. The availability of a bridge for very low frequencies in our laboratory made it possible now to report the complete loss curve of pure PAN. Its dielectric loss is obviously caused by coordinated motions of nitrile groups. Fixation of CN groups in conjugated chains would restrict their orientation in an electric field and consequently show as a decrease of the loss maximum. Such effects were indeed observed and are described in the present paper.

Experimental

Very pure polyacrylonitriles were prepared as follows. In the fisst experiment a mixture of 160 g. of butanone, 80 g. of acrylonitrile, and 8 g. of azobisisobutyronitrile was added slowly to 1360 g. of boiling butanone in the course of 1½ hr. The precipitate was dried in vacuum at 60°C.

for 1 hr., boiled in methanol for 2 hr., and dried again in vacuum at 60°C. for 8 hr. The product was slightly yellow. In the second experiment 100 g. of acrylonitrile were boiled in 2 liters of water to which a solution of 2 g. of $K_2S_2O_8$ in 50 ml. of water was added. The boiling mixture was stirred for 1 hr. The precipitate was washed in boiling distilled water. After drying in vacuum at 75°C. for 1 hr., the white product was washed in methanol and dried in vacuum at 110°C. for 2 hr.

The two products were undistinguishable in their electrical properties. Most of the measurements reported were carried out with PAN prepared in butanone.

PAN was compressed to pellets (about 0.15 cm. in thickness, 1.5 cm. diameter) or to larger samples (diameter 5 cm.) under a pressure of 120 MN./m.² (1 MN./m.² = 10 kgf./cm.²). For dielectric measurements the faces of a sample were provided with silverpaint electrodes.

Pyrolysis was carried out in an oven in a stream of dry nitrogen. In the beginning compressed pellets were pyrolyzed, but the resulting products often cracked and were found to be heterogeneous. Therefore, PAN was pyrolyzed as powder for about 5 hr. and afterwards compressed. This method worked very well for samples pyrolyzed below 350°C., but pyrolyzates obtained above 350°C. did not form lasting pellets without a binder. In order to avoid this difficulty our experiments were restricted to samples pyrolyzed at 170, 220, and 300°C. After compression the samples were dried at 100°C. in an oven and stored in a vacuum desiccator.

Dielectric measurements at 20°C. between 60 Hz. and 300 kHz. were carried out with a Schering bridge (Rohde and Schwarz). Measurements in the range of 0.1–10 Hz. were performed with a low frequency bridge based on the design by Nakajima and Kondo.[5] Sample holders and adaptors were also constructed in our laboratory. The equipment was tested by measuring a very pure sample of poly(methyl methacrylate). Our results were the same as those recently reported by Scheiber.[6]

Direct current resistivities were determined at 500 v. with a precision megohmmeter (Megatrometer, model 710, Mid-Eastern Electronics).

Results

The dielectric loss factor x'' of pure PAN as a function of frequency is given in Figure 1. It is advantageous to use a double-logarithmic plot, especially when the loss curve is very broad. The slopes of the peak become straight lines beyond the maximum, which makes it easier to determine the extent of broadening and the critical frequency. Very broad loss curves are most conveniently characterized[7] by the semiemperical equation of Fuoss and Kirkwood:

$$x'' = x_m''/\cosh[\beta \ln(\nu/\nu_m)] \tag{1}$$

where ν_m is the frequency of maximum loss and β is the Fuoss-Kirkwood parameter. Equation (1) becomes the simple Debye equation when
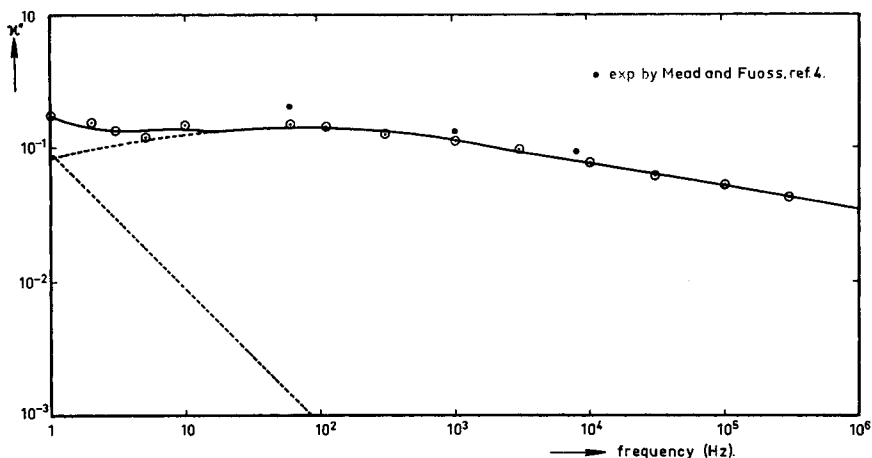
Fig. 1. Dependence of loss factor of polyacrylonitrile upon frequency. The dotted
straight line represents conductivity loss.

$\beta = 1$. For broader curves, $0 < \beta < 1$, which means that the dielectric
dispersion can no longer be described by one relaxation time. Poley has
demonstrated[7] that eq. (1) is equivalent with the Cole-Cole equation and
that a simple relation exists between β and the Cole-Cole parameter
α. The loss curve in Figure 1 is characterized by $\beta = 0.25$, which corre-
sponds to $\alpha = 0.66$. The maximum loss factor is given by

$$x_m{''} = \beta(x_s - x_\infty)/2 \qquad (2)$$

where x_s and x_∞ are the limiting dielectric constants at frequencies very
much lower and higher than ν_m, respectively.

The three points in Figure 1 at 60 Hz. and at 1 and 8 kHz. are values at
10°C. reported by Mead and Fuoss.[4] The density of their samples was
higher, namely, 1.19 g./cm.[3], compared with 1.03 g./cm.[3] in the present
case.

The experimental loss curve in Figure 1 begins to deviate at low fre-
quencies. The deviation can be explained as caused by a d.c. resistivity of
2×10^{11} ohm.-m. which is in good agreement with the value $\rho = 2.5 \times$
10^{11} ohm-m. measured at 500 v. The d.c. conductivity is known to produce
dielectric loss $x_\sigma{''}$ following

$$x_\sigma{''} = \sigma/2\pi\nu\epsilon_0 \qquad (3)$$

where $\epsilon_0 = 8.85$ pF./m. is the dielectric constant of the vacuum. Another
advantage of double logarithmic plots is that eq. (3) appears as a straight
line. The solid curve at low frequencies in Figure 1 is the sum of the two
dotted lines representing conductivity loss and the loss curve calculated
from eq. (1).

There exists no simple expression for the dielectric constants x' corre-
sponding with eq. (1), except at ν_m, where $x_m{'} = (x_s + x_\infty)/2$. Mac-
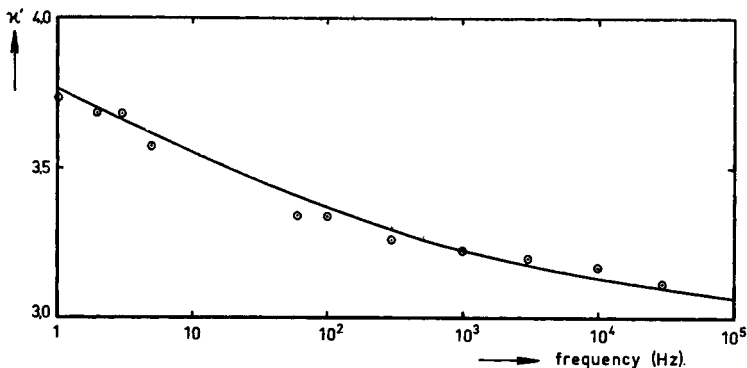
Fig. 2. Dependence of dielectric constant of polyacrylonitrile upon the logarithm of frequency. The curve is the theoretical one corresponding with the loss curve of Fig. 1.
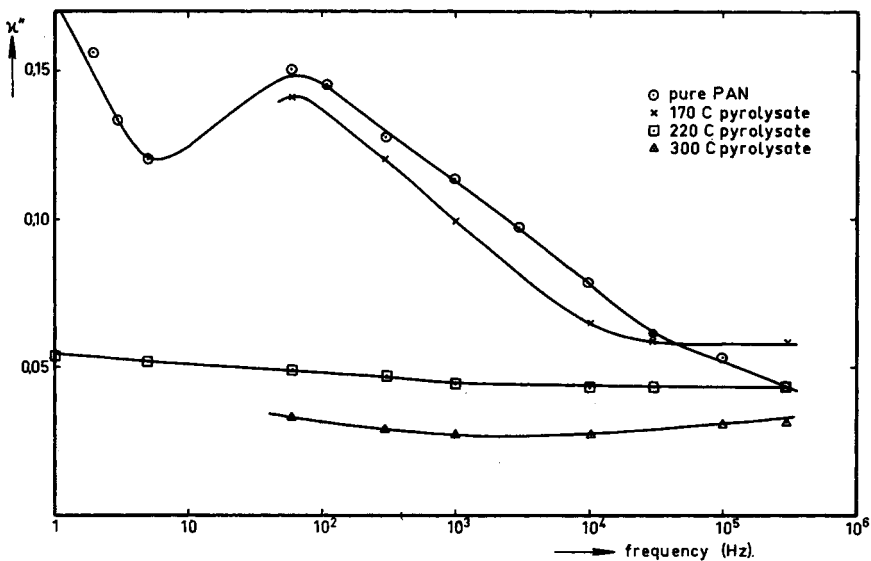

Fig. 3. Dependence of loss factor of PAN and some low temperature pyrolyzates upon the logarithm of frequency.

donald[8] has analyzed the mathematical problem and computed a number of curves from which x' can be determined at different values of β and (ν/ν_m). The dispersion curve in Figure 2 was derived in this way, and good agreement with experiment is found. The dielectric data are summarized in Table I.

The dielectric loss in PAN is compared with that in some pyrolyzates in Figure 3. The loss factor x'' is now plotted against the logarithmic frequency. A sample pyrolyzed at 170°C. has about the same loss curve as the unpyrolyzed sample. Significantly the loss peak has completely disappeared in PAN-220. A further decrease was found in PAN-300, which had losses too low to be detected.

TABLE I

Maximum Loss Factor x_m'', Critical Frequency ν_m, Limiting Dielectric Constants x_s and x_∞, Fuoss-Kirkwood Parameter β, and Resistivity ρ of Compressed PAN at 20°C.

Density, g./cm.³	1.03
x_m''	0.14
ν_m, Hz.	70
β (for $\alpha = 0.66$)	0.25
ρ, ohm-m.	
From dielectric data, eq. (3)	2×10^{11}
From d.c. measurement at 500 v.	2.5×10^{11}
x_s	4.15
x_∞	3.03

TABLE II

Chemical Compositions and Resistivities of PAN and some Pyrolyzates
(Densities about 1 g./cm.³)

Pyrolysis temp., °C.	Color	D.c. resistivity, ohm-m.	Composition		
			C, %	N, %	H, %
—	White	2.5×10^{11}	67.1	25.9	5.7
170	Light brown	4.0×10^{11}	66.6	25.5	5.6
220	Dark brown	1.2×10^{12}	61.7	23.0	5.5
300	Brown to black	4.0×10^{12}	63.1	22.1	5.0

The d.c. resistivities measured at 500 v. are given in Table II, together with the results of chemical analysis. From the formula $(C_3H_3N)_n$ one would expect 68% C, 26.4% N, and 5.7% H.

Discussion

The broad dispersion found around 70 Hz. is probably caused by nitrile groups. It is very unlikely that polar impurities are responsible for the loss observed, because the same loss was found in both polymers prepared in butanone and water, respectively. Extensive drying in vacuum or at 110°C. did not change the dielectric properties. An interesting effect was observed when the thickness of a sample was reduced by chiseling in a lathe. The slope of the loss peak was found to have decreased, and the Fuoss-Kirkwood parameter β had become 0.12. This may indicate that broadening in this case reflects polydispersity, assuming chiseling would tend to break polymer molecules in the sample.

Losses observed by Mead and Fuoss were a little higher ($x'' = 0.27$ at 60 Hz. and 20°C.) but very similar to our observations. When the temperature is raised, one would expect the maximum to move to higher frequencies. Surprisingly, the peak was not found by Mead and Fuoss when they measured x'' at 60 Hz. as a function of temperature; perhaps it was erased by conductivity loss. Instead, another maximum was reported at 110°C. At room temperature this second loss should shift to

very low frequencies, apparently outside our frequency range. Evidently, at 60 Hz. the α-transition occurs at 110°C. and the β-transition owing to CN groups at 20°C.

Pyrolysis is supposed to cause linking of CN groups so that chains of conjugated double bonds are formed, as shown in eq. 4. However, the chemical composition does not remain constant, even on heat treatment at low temperatures, as seen in Table II. Below 300°C. the hydrogen content decreases very slowly. This was also found by Shindo,[9] who reported a very strong decrease above 350°C. The changes below 300°C. chiefly involve loss of C and N, especially above 170°C. Since it is not known how this loss, perhaps in the form of $(CN)_2$, changes the chemical structure of the polymer, the interpretation of electrical properties becomes even more complicated. The increased conductivity in samples heat-treated above 400°C. is attributed to

$$ \text{(4)} $$
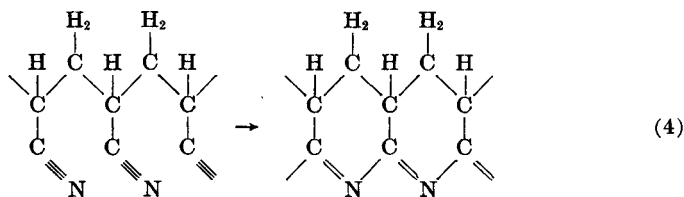
CN chain formation. However, the dielectric results shown in Figure 3 suggest that this chain formation occurs at much lower pyrolysis temperatures. Linking of CN groups would exclude them from dipolar polarization and lower dielectric loss. This appears to happen already in samples heat treated at 220°C., in which the loss factor at the critical frequency decreased by 60%. At the same time, the resistivity even increased, as Table II shows, although chain formation appears to take place. Of course, linking of CN groups may be partial at the lower temperatures, so that conjugated chain segments are interrupted by single nitrile groups. Even so it is interesting that the existence of such segments does not at all enhance the conductivity.

Higher heat treatment temperatures are needed to reduce the resistivity. Brennan, Brophy, and Schonhorn[3] reported $\rho = 7.7 \times 10^7$ ohm-m. for PAN-400 and 1.5×10^4 ohm-m. for PAN-500. Although these authors pyrolyzed compressed samples, which we found to be heterogeneous, their results indicate that a change in electrical properties occurs between 300 and 400°C. This was also observed by Shindo,[9] who concluded from x-ray diffraction studies that above 350°C. polynuclear aromatic chains are formed, while the hydrogen content goes down very steeply. This second conjugation by elimination of one H_2 molecule per monomer unit seems to be the process which really lowers the resistivity.

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Résumé

Les pertes diélectriques du polyacrylonitrile (PAN) et trois charbons ont été étudiées aux fréquences de 1 Hz à 300 kHz. PAN pure avait une courbe experimentale très aplatie autour d'une fréquence critique de 70 Hz attribuée aux groupes CN. PAN était pyrolysé sous forme de poudre dans un courant d'azote sec aux températures de 170, 220 et 300°C. PAN-170 avait les mêmes pertes diélectriques que le polymère pure, mais le maximum avait disparu au cas de PAN-220. Ce phénomène est attribué, à la formation des chaînes conjugées par liaison des groupes CN au-dessus de 200°C. Il n'y avait pas d'effet de la conjugation sur la conductivité jusqu'à 350°C. quand hydrogène se dégage.

Zusammenfassung

Dielektrische Verluste des Polyacrylnitrils (PAN) und drei Pyrolysaten wurden studiert zwischen 1 Hz und 300 kHz. PAN selbst hat bei 20°C ein sehr breites Verlustgebiet mit einem Maximum bei 70 Hz, das CN-gruppen zugeschrieben wird. PAN wurde pyrolysiert als Pulver in einer Stickstoff-Atmosphäre bei 170, 220 und 300°C. PAN-170 hat dieselben dielektrische Verluste wie das unbehandelte Polymer, aber das Maximum ist verschwunden für PAN-220. Die Erzeugung konjugierter Doppelbindungen durch Ketten-Bildung der CN-Gruppen bei über 200°C kann die Abnahme der Verluste erklären. Die Leitfähigkeit nimmt aber nicht zu bis Wasserstoff-Abspaltung bei etwa 350°C anfängt.