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Dielectric relaxation processes in vacuum dried rhinoceros horn

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With 7 figures and 1 table

Introduction

In a previous paper (1) the dielectric properties of rhinoceros horn dried over magnesium perchlorate were reported.

It has since been found (2) that the horn sample under those conditions was not perfectly dry and in fact contained ~2.6% water. The absorption band labelled β in that paper (1) and thought due to motion of side chains is clearly due to the absorbed water. This paper presents dielectric data on rhinoceros horn dried under constant evacuation; the temperature range of 200 °C to — 188 °C is larger than that of the previous paper and further absorption bands due to side chain and possibly end group motions have been observed.

Fig. 1. Sample Capacitor

Experimental

The experimental procedure was as outlined previously (1) with the additional feature that gold electrodes were evaporated directly onto the rhinoceros horn discs and the sample capacitor was mounted in a sealed container which was continuously evacuated. It was found in the present experiments that some absorbed water was not removed by evacuation at 20 °C and a small absorption band due to this water was observed. Experiments on the drying of wool by *Watt* et al. (3) has shown that wool still contains approximately 0.3% water after drying under vacuum at 35 °C. The dielectric results at 20 °C indicate however a water content of = 0.6% ± 0.1% (4). This small quantity of water was desorbed at higher temperatures.

The results were analysed in terms of *Cole* and *Cole* (5) equations as outlined previously (6).

The sample thickness could be measured by measuring the capacity of three small auxiliary electrodes which were arranged at 120° intervals around the outside of the keratin disc. They had a vacuum as a dielectric and their capacity was thus a measure of the spacing between the main electrodes and hence was inversely proportional to the thickness of the rhinoceros horn disc (see fig. 1).

The conductance of the disc was measured after the voltage of 45 volts had been applied for 20 h, i.e. just prior to the measurement of the discharge current which was used to provide the low frequency dielectric loss factors (10^{-5} hz to 10^{-2} hz).
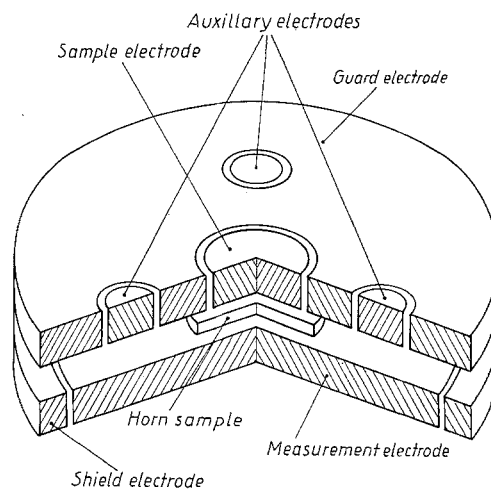
Results

The results are presented on transition maps (figs. 2, 3), with each point being labelled with the magnitude of the maximum dielectric loss for that peak.

Fig. 4 shows the usual log dielectric ε'' versus log frequency plot for a temperature of 132 °C to show the component absorption peaks. Fig. 5 is a similar plot for a temperature of — 168 °C. Table 1 lists information on the *Cole* and *Cole* parameters and the activation enthalpies of the various peaks.

Table 1. Dielectric data

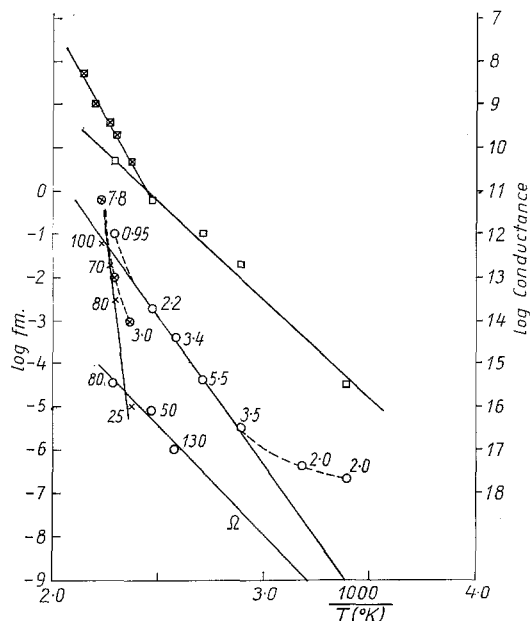| Relaxation Process	Activation Enthalpy	Cole-Cole Parameter	Amplitude ε_m''
Ω	26 kcal/g mole	0.73	~ 100
α'	32	0.38	~ 3
α''	28	0.84	~ 0.7
β	10	0.18	~ 0.05
γ'	6	0.36	~ 0.015
γ''	0.9	0.38	~ 0.01
δ	0.6	1.0	~ 0.3

Fig. 2. Transition Map for high temperatures. ○ α' and Ω for 1st temperature run; ⊗ α' for 2nd temperature run; × Ω for 2nd temperature run; □ Conductance for 1st temperature run; ⊠ Conductance for 2nd temperature run.

Fig. 4. Log Dielectric loss factor versus log frequency for vacuum dry rhinoceros horn at 132 °C
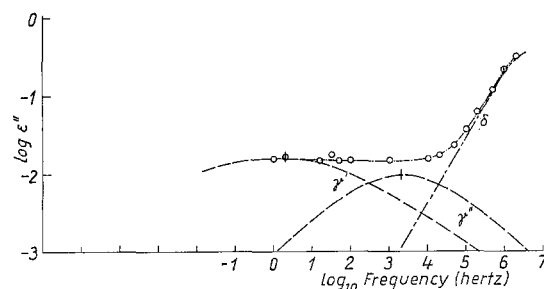
Fig. 5. Log Dielectric loss factor versus log frequency for vacuum dry rhinoceros horn at − 168 °C

The respective absorption peaks have been labelled Ω, α'', α', β, γ', γ'' and δ in order of increasing frequency at 20 °C. This departure from the usual practice with mechanical data (7) is due to the fact that the Ω absorption is most likely purely electrical in origin and probably due to a *Maxwell-Wagner* interfacial polarisation and furthermore there are two absorptions α', α'' which may arise from different amorphous regions within the horn and two γ absorptions whose origin is uncertain.

Discussion

The most important difference between these present results and the earlier data (1) is that the absorption peak called β in that paper appears to be due to the reorientation of absorbed water itself (4). The peak called β in the present paper has the characteristics associated with the β absorption found in many polymers (8), i.e. it is very broad ~ 10 decades wide at $1/2$ peak amplitude and has an activation enthalpy of ~ 10 kcal/g mole.

Other differences between the present results and those of Ref. (1) is that two α
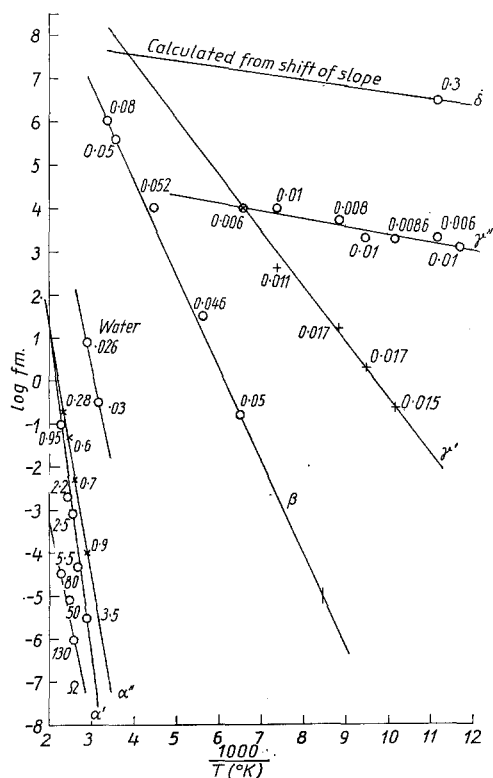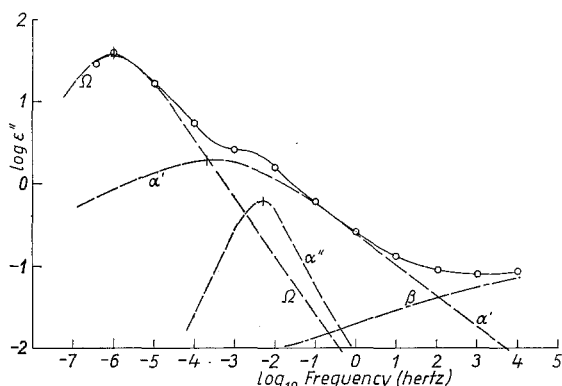

Fig. 3. Transition Map for 1st temperature series from − 188 to + 161 °C. Lines are for the absorption peaks as shown. The numbers on the graph are the magnitude of ε''_m

absorption peaks α', α'' can be observed whereas it was only possible to observe one α peak in Ref. (1).

The γ peak in Ref. (1) is in fact a β peak and can be compared with the β peak in the present results. Due to the much lower temperatures used in obtaining the present data further absorption peaks have been observed. These are γ', γ'' and δ. The two peaks due to degradation in Ref. (1) (ψ and φ) have not been observed in the present results although a single degradation peak was observed at 20 °C after the sample had been heated above 161 °C. This peak was not studied in detail.

Ω absorption

Baird et al. (9) have suggested that one of the absorption bands in keratin could be due to interfacial polarisation and this would appear to be the case for the Ω absorption for the following reasons. From fig. 2, the activation enthalpy of the Ω absorption band is the same as that of the conductance (24 kcal) below 150 °C and both show a transition at approximately 150 °C.

α' absorption

This band is probably due to chain motion in the amorphous regions of the keratin and it also shows an increase in activation

Fig. 6. Thickness of rhinoceros horn disc for 2nd series
of high temperatures

enthalpy (32 kcal/g mole to 138 kcal/g mole) at approximately 150 °C. This indicates a transition of some kind. *Menefee* and *Yee* (10) suggested that a transition which they observed at ~ 170 °C by torsional experiments on wool fibres, could be due to a type of glass to rubber transition. The marked increase in mobility of the chains above 150 °C would agree with that concept although the process is irreversible, degradation occurs, volatile material is given off (3) and fig. 6 shows that the rhinoceros horn shrank in thickness by $\sim 3.4\%$.

The thermal history of that sample was 149 °C for 3 days, 174 °C for 2 days, then 3 days at 161, 168, 174, 146, 145, 157, 182, 194°C, then 1 day at 200 °C and finally 20 °C. In another sample, degradation (as indicated by a new dielectric absorption band at ~ 10 K hertz at 20 °C) was not observed until the sample had been held for 3 days at 161 °C which is just above the transition temperature. When rhinoceros horn has $\sim 2.6\%$ H_2O present however degradation products were observed (1) after the sample was heated to only ~ 130 °C showing the marked effect of water in facilitating breakdown, probably into peptides and dipeptides.

The deviation of the data from a straight line at low temperatures in fig. 2 is probably partly due to the plasticising effect of the 0.6% H_2O but mainly due to the fact that the sample was not "aged" (11) or "annealed" at a high temperature before making the low temperature measurements. The sample had been dried from a water-swollen state and thus would have internal stresses.

α'' absorption

This α'' absorption band is small in comparison with the α' band, the peak dielectric loss $\varepsilon_m'' \sim 0.9$ for α'' and ~ 3.4 for the α'. The peaks occur at very close frequencies and the α'' peak was difficult to isolate when analysing the data. Nevertheless it was clearly present as a distinctly separate peak at some temperatures and fig. 2 shows that the data for various temperatures are a reasonable fit to a straight line. The cause of this absorption is not known although it could be due to amorphous chains in a different region to that responsible for the α' absorption.

β absorption

As stated previously this absorption is probably due to the localised motion of polymer chains in the amorphous regions. It
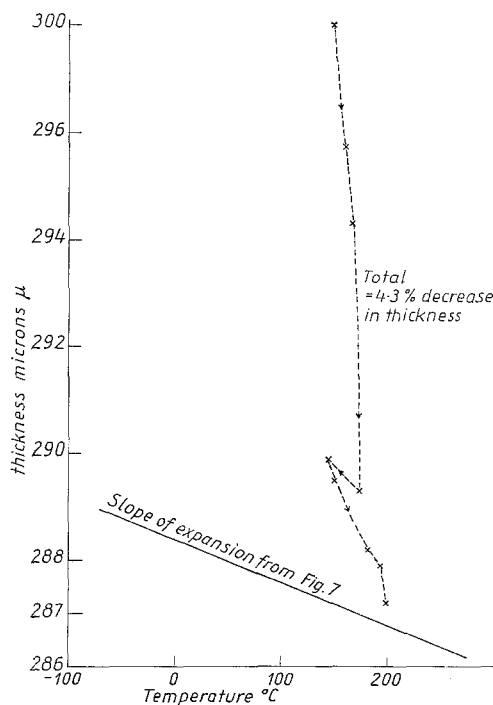
20*

is unlikely to be due to side chains, as keratin contains 19 amino acids each with a different side chain group and yet the β absorption is similar to that in much simpler polymers such as polyvinyl chloride and polyethylene-terephthalate (8).

A transition associated with the β absorption occurs at ~ -150 °C. The expansion coefficient in the thickness of the sample fig. 7 shows a marked change in slope at -150 °C when the sample originally at -200 °C was heated at $^3/_4$ °C/min up to room temperature.
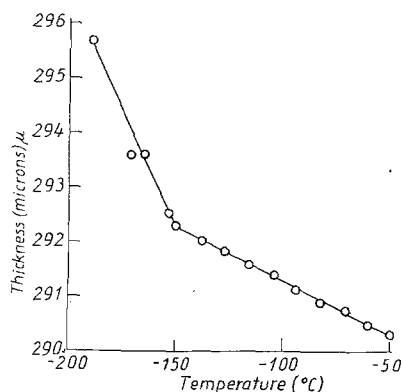

Fig. 7. Thickness of rhinoceros horn disc as a function of temperature at low temperatures

Note: The expansion coefficient for the thickness (i.e. across the fibril direction) is negative.

2.6% of H_2O does not affect this β absorption band other than to change the amplitude ε_m'' from ~ 0.05 to ~ 0.03.

γ absorptions

The two γ absorptions are probably due to the motion of polar groups associated with the side chains in either crystalline or amorphous regions (12).

δ absorption

The δ peak has the characteristics of the δ peak observed in polymers containing side chains -- (12) i.e. a low activation enthalpy (0.6 kcal/g mole) and an extrapolated temperature for 1 hertz near absolute zero (~ 20 °K). It is unusual in comparison with the other peaks in that its shape is such that it can be described by a single relaxation time.

Water peak

The water peak shifts downwards in frequency as the horn becomes drier but shifts upwards due to an increase in temperature so that an activation enthalpy cannot be deduced from the slope in fig. 3. This water peak has been described in a previous paper (4).

General

The fact that there are two α and two γ absorptions and that the temperature for the transition of the amorphous material (150 °C) is high in relation to the melting temperature (220 °C) (13) of the crystalline regions implies that the amorphous regions must be stabilised by side chain cross linking, in particular by cystine. Keratin can be chemically isolated into two fractions, one of which contains a small quantity of cystine and the chains of which are largely helical, whilst the other is non-crystalline and contains a much greater quantity of cystine (14). The dielectric results also indicate that keratin is a mixed polymer of two different polymers one which is crystalline and one which is amorphous and strongly cross linked.

Summary

The complex dielectric constant of vacuum dried rhinoceros horn has been measured over the frequency range of 10^{-6} to 10^6 hertz and the temperature range -188 to 200 °C.

The results have been analysed into 7 absorption regions and the properties of these absorptions including their activation enthalpies, have been derived and discussed.

Zusammenfassung

Die komplexe Dielektrizitätskonstante von trockenem Rhinozeroshorn wurde über ein Frequenzintervall von 10^{-6} bis 10^6 hertz und im Temperaturintervall von -188 bis 200 °C gemessen. Die Resultate lassen sich auf Grund der 7 gefundenen Absorptionsgebiete, ihres Verhaltens und der Aktivierungsenthalpie erklären.

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