DENATURATION OF HORN KERATIN OBSERVED BY PIEZOELECTRIC MEASUREMENTS*

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SUMMARY: Simultaneous measurements of the piezoelectric strain constant d_{14} and of the thermal depolarization current of bovine horn keratin are made as the temperature is increased from 20°- 200°C. The denaturation of the natural eletret occurs in two stages and contributes two current peaks of opposite polarity showing the presence of two independently oriented and bound dipole systems. Piezoelectricity appears to originate from these oriented dipole systems.

INTRODUCTION: A peak for depolarization current has been observed at the denaturation temperature of keratin (1). The thermally simulated current in the axial direction of porcupine quill shows maxima at 210°C and 235°C, where the helixcoil transformation in molecular conformation of keratin successively takes place. Since the current flows from the tip to the root in an external short circuit, the direction of dipole of peptide groups (CO-NH) in helix is such that oxygen atoms direct towards the tip and the hydrogen atoms towards the root.

The uniaxial orientation of peptide dipoles is also suggested by the observation of the piezoelectric and pyroelectric effects in keratin (2,3). The temperature dependence of the piezoelectric

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constants for keratin has not been investigated in detail. We wish to report in this communication that the denaturation of keratin is also observed by the measurement of piezoelectric constant. Also for the first time, a simultaneous measurement of temperature dependence of piezoelectric and electret depolarization was accomplished.

METHOD: The samples were prepared from bovine horn. The z-axis was assigned to the direction of the horn axis. In order to observe the piezoelectric constant, d_{14}, rectangular specimens with length of 20 mm, width of 8 mm and thickness of 1 mm were cut so that the direction of horn axis lies in the plane of the surface and makes an angle of 45 degrees to the direction of length. Silver paste was painted onto two surfaces of the sample as electrodes. Sinusoidal vibration at 20 Hz was given in the length direction. The real and imaginary components of $d_{14} = d'_{14} = id''_{14}$ were determined with increasing temperature. For experimental details on the piezoelectric measurements the reader is referred to previous papers (4).

RESULTS: Figure 1 shows an example of the observations. Both d'_{14} and d''_{14} increases with rising temperature and shows a maximum at about 175°C. Some relaxation of piezoelectric constants is also seen around 100°C. The rate of heating was about 2°C/min. The initial decrease of d' is due to the influence of water originally present in the sample. The gradual increase of d' can be ascribed to the increasing flexibility of keratin molecules. The sharp decrease of d' at about 175°C is due to the denaturation of keratin. Once the helical keratin molecules are uncoiled to the random state, the non-centrosymmetric structure required to give piezoelectricity disappears. The appearance of the sample also changed after heating to this temperature range, and the weight of the sample decreased by about 10%, which may be due to the loss of water content. Repeated measurements of the denatured sample showed that the piezoelectric constant became zero for all temperatures.

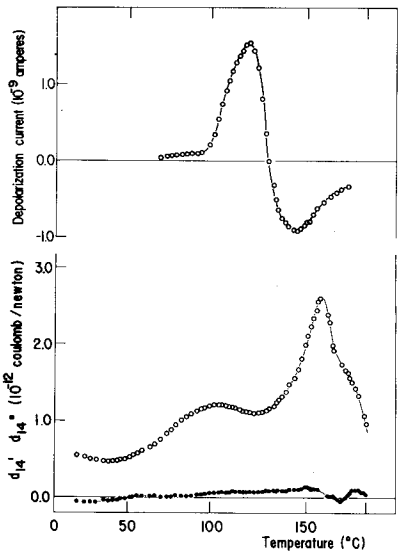

Fig. 1: The complex piezoelectric strain constant d_{14} (lower curves) and the depolarization current (upper curve) for bovine horn keratin during a uniform rate of heating (2°C/min). This thermal denaturation indicates the presence of two independently oriented and bound natural eletrets.

The piezoelectric constant, d_{33} , was also measured using a sample cut perpendicularly to the axis of horn. A maximum for d_{33} was also observed at about 180°C.

The temperature dependence of the depolarization current was measured simultaneously during the piezoelectricity measurements. Both are shown in Figure 1. The depolarization current reverses sign at about 130°C, both for measurements perpendicular and parallel to the growth axis. The sense of current flow below 130°C is axially toward the root and radially outward, and above 130°C both components reverse direction. A sample which is thermally re-cycled below 130°C, and reheated gives current only above 130°C and in one direction only, showing a step-wise denaturation process. All indications are that bovine horn keratin has two independently oriented dipole systems, one that denatures below 130°C and another that denatures above 130°C. These, according to a previous interpretation by Menefee for porcupine

quill keratin, would correspond to differently hydrogen-bonded dipolar residues.

The general agreement of the peak temperatures for the thermal depolarization current and piezoelectric constants supports the concept that the piezoelectric effect in keratin originates in the orientation of peptide dipoles in the helical molecules. This is also consistent with the conclusions drawn by Menefee to interpret the keratin natural electret.

References:

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