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X-ray diffraction study on carnauba wax thermoelectrets prepared with different cooling rates

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Orientation parameters of carnauba wax thermoelectrets prepared with 3·3 kv/cm field strength with two different cooling rates have been determined by X-ray diffraction technique. It has been concluded that the orientations are not solely responsible for the dipole-field interactions

1 INTRODUCTION

X-ray diffraction studies on electrets show preferred orientation in them (Ewing 1930, Chandy 1973, Puri 1968, Pan 1976) but howfar the orientation of crystallites in thermoelectret forming materials shapes the electric behaviour of an electret state is yet to be established The present study has been undertaken to investigate the nature of orientation and how it varies for different regions of a thermoelectret with different cooling conditions.

2 EXPERIMENTAL DETAILS

Thermoelectrets from molten purified prime yellow carnauba wax have been prepared in the following manner A cylindrical brass dish of inner radius 1·5 cm and height 2 cm with tin foil lining inside has a 3 mm annular ebonite ring whose inside and outside diameters are 1·8 cm and 2·6 cms respectively. The dish with the ebonite ring is filled up with the moten wax upto a height of about 5 mm when a brass disc of 2 cm diameter wrapped with tin foil and a thin brass ring of 2·4 cm diameter is suitably placed upon the ebonite ring The brass dish, the disc and the ring has arrangements for electrical connections so that they forms a condensor with a guard ring The condensor with wax is placed inside an oven whose temperature can be controlled. The oven temperature is raised to 82±0·5°C and kept at that temperature for about half an hour when a field of 3·3 kv/cm is applied At this stage the oven temperature is allowed to fall at a desired rate. The electric field is switched off when the wax temperature fell to about 6°C above the room temperature The disc shaped electret is then taken out, wrapped with tin foil and placed inside a dessicator Subsequently a section measuring 1·8 cm 0·3 cm 0·05 cm from the central region of the electret disc is cut out for X-ray diffraction study The sample is mounted on a carrier in front of the collimator of a flat plate camera so that the forming electric field direction lying along the vertical is perpendicular to the incident X-rays. Diffraction photographs for different sample regions along a line centrally situated and perpendicular to the field direction has been taken by sliding the carrier horizontally.

3. Results and Interpretations

An examination of the diffraction photographs from samples reveals the following characteristic features.

(a) The number of maxima on (110) ring is four while that for (200) the number is two (figure 1).

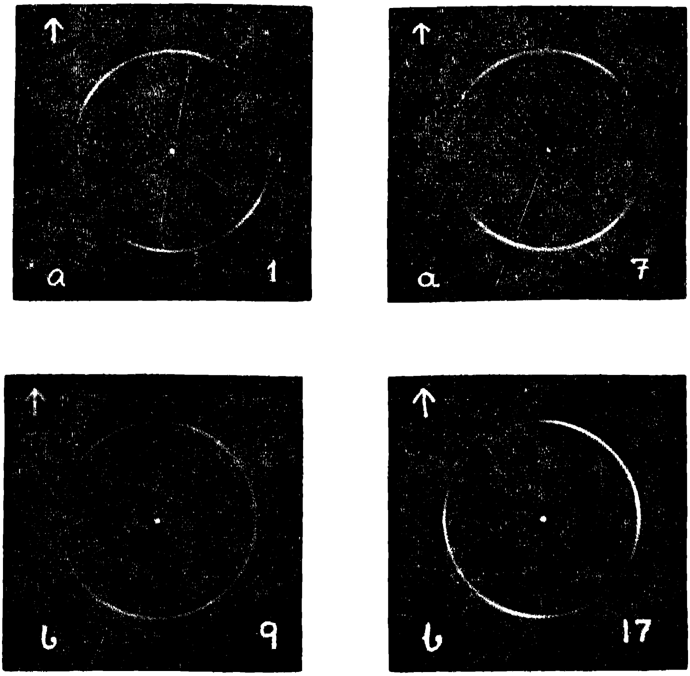

Fig. 1. X-ray diffraction photographs of carnauba wax thermoelectrets prepared with 3·3 Kv/Cm and with cooling rates 0·8°C/min (Photos marked *a*) and 0·27°C/min (marked *b*), X-rays are perpendicular to electret forming field direction (arrows), Integers denote distances in mm from one edge of the sample under investigation, C_uK_α radiation sample to film distance - 4·25 cms, Radial lines show positions of maxima on (110) and (200) and (200) rings,

(b) Two (200) maxima always lie diametrically opposite to each other. However the angle between the external field direction on the photographic plate with the diameter of the (200) ring joining the two maxima are different for different regions of the samples under investigations.

(c) With reasonable accuracy a single axis of symmetry can always be drawn (through the common centre of the rings) about which each pair of (110) maxima and (200) maxima are symmetrically situated. However in general the angle between the axis of symmetry and one pair of (110) maxima slightly differ from that for the other pair. This indicates that it is a fibre pattern orientation about a single axis tilted by an angle not equal to 90 degrees with the incident X-ray beam.

(d) Assuming the orienting crystallites to be orthorhombic (Muller 1928, Pan 1976) whose axial length c is much larger than the other two axial lengths a and b, the normal to the (200) planes (a axis) makes an angle $\chi = \tan^{-1} a/b$ with the normal to (110) planes The value of χ can easily be computed from Bragg angles and it has been found that χ is nearly equal to the angle between (110) and (200) maxima subtended at the centre of the rings (table 1a & b, column 2, 3 & 9) The difference between the Bragg angles for (110) and (200) planes is about one degree for Cu K_α

(e) The angle between the symmetry axis and the observed (200) maxima is $\pi/2$ in all the cases and each maxima is associated with appreciable angular dispersion. Therefore we conclude that each maxima observed on (200) ring is a superimposition of two very close maxima.

The incident X-ray beam direction is always normal to the thickness of the sample i.e. X-rays are normal to the direction of the applied electric field Let us choose a coordinate system in which the point at which the incident X-ray beam impinges upon the sample as the origin, the negative direction of the incident X-rays is the X-axis, a line passing through the origin and parallel to the axis of symmetry on the diffraction pattern is the E-axis (the plate being normal to the incident X-rays) Therefore for obvious reasons the orientation axis lies in the XZ plane and let us suppose tht it makes an angle ψ with the Z axis lying towards positive X-axis The normals to (110) and (200) planes of the orienting crystallites will be the generating lines of two right circular coaxial cones about the orientation axis These comes have their semiappex angle ρ_{110} and ρ_{200} respectively The normals to (110) and (200) planes which are responsible for producing (110) and (200) rings will also constitute two co-axial right circular cones about X-axis with semiapex angle $\pi/2-\theta_{110}$ and $\pi/2-\theta_{200}$ respectively where θ_{110} and θ_{200} are their respective Bragg angles.. If δ_1 and δ'_1 be the angular positions of each pair of (110) maxima on the plate with respect to the line of symmetry and δ_2 be the same for (200) maxima, the normals to the

(110) planes producing maxima in the upper half of the plate will have direction cosines

$$l_1 = \text{Sin}\, \theta_{110}$$
$$m_1 = \pm \text{Cos}\, \theta_{110}\, \text{Sin}\, \delta_1 \quad \dots (1)$$
$$n_1 = \text{Cos}\, \theta_{110}\, \text{Cos}\, \delta_1$$

where + and − sign indicates for the maxima lying in the first or second quadrant of the photographic plate For two (110) maxima lying in the lower half we have the direction cosines

$$l'_1 = \text{Sin}\, \theta_{110},\ m'_1 = \pm \text{Cos}\, \theta_{110}\, \text{Sin}\, \delta'_1,\ n'_1 = -\text{Cos}\, \theta_{110}\, \text{Cos}\, \delta'_1.$$

If l_0, m_0, n_0 be the direction cosines of the orientation axis we have

$$l_0 = \text{Sin}\, \psi, \quad m_0 = 0, \quad n_0 = \text{Cos}\, \psi. \quad \dots (2)$$

And following Glocker (1936) one obtains

$$\text{Cos}\, \rho_{110} = \text{Sin}\, \theta\, \text{Sin}\, \psi + \text{Cos}\, \theta_{110}\, \text{Cos}\, \psi\, \text{Cos}\, \delta_1$$
$$= -\text{Sin}\, \theta_{110}\, \text{Sin}\, \psi + \text{Cos}\, \theta_{110}\, \text{Cos}\, \psi\, \text{Cos}\, \delta'_1. \quad \dots (3)$$

Hence

$$\tan \psi = \frac{\text{Cos}\, \delta'_1 - \text{Cos}\, \delta_1}{2 \tan \theta_{110}} \quad \dots (4)$$

and

$$\text{Cos}\, \rho_{200} = \text{Sin}\, \theta_{200}\, \text{Sin}\, \psi + \text{Cos}\, \theta_{200}\, \text{Cos}\, \psi\, \text{Cos}\, \delta_2. \quad \dots (5)$$

To corelate the orientation parameters with the crystal axes and the external electric field direction an analytical method has been developed as described here. If l_E, m_E and n_E be the direction cosines of the electric field we have

$$l_E = 0, \quad m_E = \text{Sin}\, \epsilon \quad \text{and} \quad n_E = \text{Cos}\, \epsilon \quad \dots (6)$$

which ϵ is the angle between the symmetry axis and the field direction on photographic plate. The angle between the orientation axis and the external field direction ϕ is obtained from eqs. (2) and (6) as

$$\text{Cos}\, \phi = \text{Cos}\, \psi\, \text{Cos}\, \epsilon. \quad \dots (7)$$

If the orientation axis lie along the b axis of the crystallites and X-rays are incident normal to the same axis, the normals to the (200) planes of the oriented crystallites would produce maxima diagonally opposite to each other while the maxima on (110) ring would be shifted through an angle $\chi = \tan^{-1} a/b$ provided θ_{110} and θ_{200} are small and same. In this hypothetical case the crystallites whose (110) normals would be responsible for producing maxima are also responsible for (200) maxima. Hence the angle between (110) and (200) normals producing maxima is $\chi = \tan^{-1} a/b$ A departure from tris value is due to (i) the orientation axis being slightly shifted from the b axis, (ii) the orientation axis being not exactly normal to the incident X-ray beam and (iii) the difference between θ_{110} and θ_{200} which is about one degree If however these departures are small, the (200) normals of the crystallites whose (110) normals produce maxima lie nearly along the (200) normals of the crystallites producing maxima on the (200) ring. Under such condition considering the direction cosines of maxima producing normals we have

$$\begin{aligned}\cos\chi &= \cos\tan^{-1} a/b \\ &\simeq \sin\theta_{110}\sin\theta_{200}+\cos\theta_{110}\cos\theta_{200}\cos(\delta_2-\delta_1) \\ &\simeq \sin\theta_{110}\sin\theta_{200}+\cos\theta_{110}\cos\theta_{200}\cos(\delta'_2-\delta'_1)\end{aligned} \quad \ldots \quad (8)$$

where δ_2 and δ'_2 are the two resolved angular positions of (200) maxima which when superimposed given rise to

$$\delta_2\,(\text{observed}) = \frac{\delta_2+\delta'_2}{2}$$

Therefore

$$\delta_2-\delta_1 = \delta'_2-\delta'_1 - 2\Delta\delta\ (\text{say})$$

Hence

$$\begin{aligned}\delta_2 &= \delta_2\,(\text{obs})+\Delta\delta \\ \delta'_2 &= \delta_2\,(\text{obs})-\Delta\delta \\ \delta_1 &= \delta_1\,(\text{Av})+\Delta\delta, \\ \delta'_1 &- \delta_1\,(\text{Av})-\Delta\delta. \\ \therefore\ \delta_2-\delta_1 &= \delta_2\,(\text{obs})-\delta_1\,(\text{Av})\end{aligned}$$

Hence

$$\cos\chi = \sin\theta_{110}\sin\theta_{220}+\cos\theta_{110}\cos\theta_{200}\cos[\delta_2(\text{obs})-\delta_1(\text{Av.})] \quad (9)$$

Again from the measurement of the Bragg angles we have

$$\frac{a}{b} = \left\{\left(\frac{2\sin\theta_{110}}{\sin\theta_{200}}\right)^2-1\right\}^{\frac{1}{2}} \quad (10)$$

where

$$\frac{a}{b} = \tan\chi.$$

We can compare the two values of χ obtained from eqs. (9) and (10). If they are nearly equal to each other we may conclude that the orientation axis is very near to the plane containing the a and b axes of the orienting crystallites and is very close to the b axis of the crystals

The experimentally determined values of different parameters mentioned above are given in tables 1a & b.

Table 1a. Cooling rate 0·27°C/min. δ_2(obs) = 90°

Dist. from one edge n mm	ρ_{110} in deg. (Eqn 3)	ρ_{200} in deg. (Eqn 5)	ψ in deg (Eqn 4)	ϵ* in deg.	ϕ in deg (Eqn 7)	a/b (Eqn 10)	a/b (Eqn 9)	$\pi/2-\chi$ in deg from Col (7)	δ_1 (AV) in deg.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
1	34 41	89 10	5 19	24 6	25 12	1 50	1 50	33·65	32 44
2	33·97	89 79	1·23	8 3	8·39	1·50	1·51	33 65	32 37
3	33·34	89 91	0 44	2 8	2·83	1 45	1·54	34·68	31 72
4	34 59	89 67	1 63	3·1	3 50	1·54	1·47	33 01	33·01
5	33 13	89·66	1·66	2·2	2·76	1·52	1·56	33·43	31 45
6	31 93	89·23	3·69	1 9	4 15	1 51	1 65	33 58	30 00
7	33·70	89 69	1·47	6·5	6 70	1 48	1 52	34·12	32 07
8	29 38	89·15	1 10	7 3	8 37	1 51	1·83	36 55	27 27
9	31 19	88 77	5 97	4·9	7 72	1·51	1 73	33·48	28·79
10	32 04	88 71	6 20	0·0	6 20	1 50	1·67	33 73	29 68
12	32·96	88 55	7 04	4 1	8·14	1·50	1 61	33 62	30 53
14	29 10	89·36	3 10	1·9	3 64	1 49	1 83	33·85	27 35
16	30·98	89 80	0·96	20·6	20 62	1·50	1 70	33·78	29·21

* ϵ is the angle between symmetry axis and field directio

Table 1b Cooling rate 0·80°C/min, δ_2 (obs) -- 90°

Dist. from one edge in mm.	ρ_{110} in deg. (Eqn 3)	ρ_{200} in deg. (Eqn 5)	ψ in deg (Eqn.4)	ϵ* in deg.	ϕ in deg. (Eqn.7)	a/b (Eqn 10)	a/b (Eqn 9)	$\pi/2-\chi$ in deg. from Col (7)	δ_1 (AV) in deg.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
2	35 32	88 87	5·40	27 8	28 28	1 48	1·45	34 05	33 40
4	31·89	89·08	4·38	0·6	7 94	1·49	1 65	33·83	29 84
5	36 19	88 20	8 69	10 7	13·79	1·48	1·44	33 97	33·68
6	34·59	89 85	0 74	7·8	7 99	1·49	1 53	33 81	32·00
7	31·85	90·00	0 00	5 6	5 62	1·48	1 64	33 99	30·18
8	33·07	89·56	2 11	4 6	5 06	1·49	1·56	33 87	31·37
9	34·44	89 86	3·76	4·6	5 94	1·50	1 49	33·78	32 70
10	33 22	88 53	7 08	4·6	8·44	1 49	1·60	33·81	30·80
12	34 25	89 52	3·89	4·6	6 02	1·48	1·50	33·99	32·48
14	34 38	89 21	3 79	9·6	10·31	1·49	1·49	33·88	32 62
16	33 36	88·63	6 61	27·1	27·87	1 50	1 50	33 78	32·45
17	34 18	88·73	6·16	52·8	53 04	1·48	1·52	33·99	32·08

ϵ is the angle between symmetry axis and field direction.

4 Conclusion

The electret behaviour of an electret depends upon the forming field strength, the forming temperature, rate of cooling, the age of the electret and the depth of the sample along the direction of the forming field (Gutman 1948, Good & Stranathan 1939, Frekin & Zheludev 1960). In the present work the forming field, temperature, age of the electret and the depth of the sample along the direction of the external electric field are kept unaltered while two different rates have been employed X-ray investigations have been made at different points in the specimen along a line normal to the thickness of the electret

The inclination of the orientation axis (ψ) with the Z axis (axis of symmetry) in general decreases from the periphery to tre central region of the sample (Table 1a & b, Column 4) This general trend remains unaltered when the rate of cooling is varied The angle between the axis of symmetry and the electric field (along the thickness of the electret) also changes attaining smaller values at the central region (Table 1a & b, column 5) The variation of ψ with distance is however small But the angle between orientation axis and the external field (Table 1a & b, column 6) changes appreciably for different rate of cooling, specially at the edges. Near the middle region it attains a minimum value but for no region the orientation axis coincides with the electric efield direction For a cooling rate of 0·80°C per minute it attains larger values at the two ends of the electret when compared to those for 0·27°C per minute cooling rate Near the middle region the angle does not depend much upon the cooling rate Or in other words, the quicker the carnauba wax is solidified the departure of the orientation axis with respect to the field is much more pronounced For the middle region a longer time is necessary to solidify from the liquid state causing the orientation axis to deviate little from the field direction

The angle ρ_{200} remains practically constant being nearly equal to 90 degrees irrespective of the region of investigation and the cooling rate (Table 1, column 3) Or in words the a axis is always alligned along a direction very nearly normal to orientation axis But the orientation of (110) normals fluctuates reasonably with cooling rate as well as with the region of investigation (Table 1, column 2) Therefore the orientation axis is not a fixed direction with respect to the crystal axes. Carnauba wax is a polar substance and hence the resultant dipole moment has a fixed direction within the crystal. Hence the orientation axis is not the dipole axis of the crystals.

The axial ratio a/b measured from Bragg angles agrees within 10 per cent with those obtained from eq (9) for most of the cases (Table 1, column 7 & 8) This indicates that the orientation axis is very near to the b axis and lies close to the plane containing a and b If the conditions of coincidences of the orientation axis with b axis as described before are satisfied then $\rho_{200} \simeq \pi/2$ and

$\rho_{100} = \pi/2-\chi$. Though in our results the first condition is nearly satisfied, ρ_{110} deviates from $\pi/2-\chi$ (Tables 1a & b, column 9 & 10). Therefore the exact coincidence is never observed.

From the analysis of our experimental observations we are of opinion that at the forming temperature when the carnauba wax is in the molten state cybotactic groups (Frenkel 1946) are formed They allign themselves in a preferred direction due to dipole-field interaction caused by the external field. However there must be another process responsible for allignment which arises due to preferrential orientation of the long chain molecules (Frenkel 1946). A competition between these two separate processes ultimately shapes the final orientation. The latter strongly depends upon the dimension of the cybotatic groups in the liquid state. The size of the groups in their turn depends upon the forming temperature, the rate of cooling and also upon the external field (Frenkel 1946) The groups orient themselves in the presence of a liquid environment and the process is slow. Therefore the orientation is far from complete if the molten wax solidifies quickly This may explain the large deviation of the axis of orientation with the direction of the forming field at the peripherial region as well as when the rate of cooling is increased

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