

Where α is a parameter in the Cole-Cole law which is zero in the Debye theory, ϵ_0 is dielectric constant in d.c. and ϵ_∞ is in infinite frequencies.

From the theory of rate process of Eyring, the free energy ΔF^\ddagger , heat ΔE^\ddagger and entropy ΔS^\ddagger of activation in the dielectric relaxation process are evaluated as follows.

$$\begin{aligned}\Delta F^\ddagger &= 9.09 \text{ K cal/mol}, & \Delta E^\ddagger &= 59.2 \text{ K cal/mol} \\ \Delta S^\ddagger &= 660 \text{ cal/}^\circ\text{C/mol}, & \tau &= \frac{1}{\pi} \times 10^{-6} \text{ sec}\end{aligned}$$

where τ is a relaxation time.

These results show that silicone resin is polymer and the rotations of the dipolar molecules accompany with a considerable increase of entropy.

11. Studies on Silicone Resins. (VIII)

On the X-Ray Diffraction Pattern

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The X-ray diffraction patterns of poly-condensated silicone resin taken by the powder method have been studied.

The anti-cathod of our X-ray apparatus is copper and its wave length is 1.54\AA .

We used two kinds of samples: the one is gelatinized silicone resin and the other is normally poly-condensated one.

The X-ray pattern of the former shows only one ring and the latter shows four rings.

According to these rings the distance between lattices which diffract the X-ray is evaluated as follows. The value of the former is 4.22\AA and the latter is 4.22\AA , 3.14\AA , 2.525\AA and 2.25\AA .

Comparing these results with the X-ray diffraction pattern of silica which is already well-known, the remarkable resemblance is found. That is, the X-ray pattern of the vitreous silica assembles as the gelatinized silicone resin and that of α -cristobalite assembles as the normally poly-condensated silicone resin. The position of the band obtained from vitreous silica indicated a spacing of diffraction centers (4.33\AA) close to that in the α -cristobalite (4.11\AA). As above-mentioned, our X-ray diffraction pattern of the gelatinized silicone resin and the longest spacing of the pattern of crystallized silicone resin shows 4.22\AA . The spacing of 2.525\AA and 2.14\AA of crystalline silicone resin may well be understood from their siloxane bond, but the existence of 2.25\AA can not be explained yet.

It can be seen from the above that the difference of the structure between

gelatinized silicone resin and normally poly-condensated silicone resin is the same as the difference of vitreous and crystalline silica.

12. Studies on Silicone Resins. (IX)

On the Glass Cloth Laminates

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We reported on the molding products in the preceding reports. (This Bulletin, 22, 87 (1950)). After that, the silicone-bonded glass cloth laminates have been produced on trial and their electrical and mechanical properties have been measured.

By the silicone resin, glass cloths are stucked at 200–250°C under about 500kg/cm² pressure.

We found that our laminates had far stronger tensile strength than that of molding products and considerable heat resistance and good electrical properties as much as the molding products. And likewise they are able to drill and file.

(1) The insulating resistance is near to the value of non-alkali-glass and 10¹³ Ω-cm at 200°C.

(2) The arc resistance according to A.S.T.M. Standard shows 420sec, while molding products show 360sec and bakelite only 15sec.

(3) The dielectric strength measured in transformer oil is 12kv/mm at 60 cycles and 18kv/mm at d.c.

(4) The dielectric loss angle decreases as frequency becomes higher. At 1MC its values is 0.0070. By heating after ordinary preparation process it becomes smaller. The effect of catalysers—ethyl-borate, benzoic-peroxide and etc.—for the dielectric properties are little.

(5) The tensile strength is 700–800kg/cm².

(6) The relations between mechanical strain and temperature under a constant load were measured. These results showed that the curing temperature and time affected on these relation. The allowable temperature of these products are 250–300°C.

These properties promise the wide use of these products as the molding ones.

Above three reports—(VII), (VIII) and (IX)—are on the methyl-ethyl and methyl-ethyl-phenyl silicone resins which are being prepared on trial at the Laboratory of Shimadzu Mfg. Co., Kyoto.