

Mechanism of the Dielectric and Mechanical β -Dispersion in the Thermosetting Phenolic Resins

To explain the mechanism of the dielectric and mechanical β -dispersion for phenolic resin reported by the author,^{1,2} a further study was made on the dielectric as well as the mechanical behavior of the substance.

The samples were an ammoniac resol type of phenol-*o*-cresol-formaldehyde resin (sample A)^{1,2} and butylated sample A (sample B).³ The thickness of both sample films was 0.2 to 0.3 mm.; they had been dried almost completely. The dielectric measuring devices were a mutual inductance bridge and a modified resistive-ratio arm bridge.¹ The frequency dependence of the dielectric constant ϵ' and the loss ϵ'' was measured for the samples over the frequency range of 0.3 to 10^6 cycles/sec. and the temperature range of about -60 to 35°C . Dynamic modulus E' and mechanical loss $\tan \delta$ were measured by means of the vibrating reed method at $50 (\pm 5)$ cycles/sec.

The results are given in Figure 1 which shows $T \times (\epsilon_0 - \epsilon_\infty)$ versus temperature. The value of the total dispersion ($\epsilon_0 - \epsilon_\infty$) corresponds to the length of the chord of the Cole-Cole arc, and is a parameter relating to the magnitude of dipole orientation.⁴ The magnitude of ($\epsilon_0 - \epsilon_\infty$) of sample A treated by acetone extraction with Soxhlet's apparatus for about 50 hr. is somewhat smaller than that of the untreated one cured under the same conditions but the dispersion cannot be eliminated by the acetone extraction. The magnitude of the mechanical dispersion shown in Figure 2 also agrees in trend with the dielectric dispersion.

The magnitude of ($\epsilon_0 - \epsilon_\infty$) for sample A cured at 200°C is somewhat smaller than that of the one cured at 170°C . This result seems to suggest that more amount of the polar

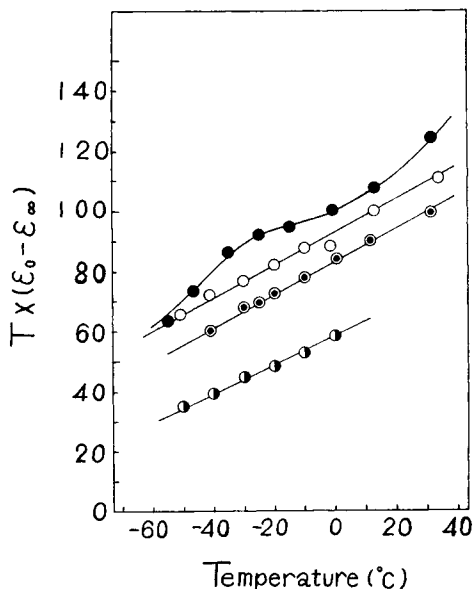


Fig. 1. Temperature dependence of $T \times (\epsilon_0 - \epsilon_\infty)$ for sample A and sample B: (O) cure 30 min. at 200°C , sample A; (●) 30 min. at 170°C , sample A; (⊙) 30 min. at 170°C , sample A; acetone extraction; (◐) 30 min. at 170°C , sample B.

functional groups such as the methylol group and amino group, introduced by the ammoniac catalyst, are consumed for the formation of the network structure of this resin when the curing reaction proceeds at higher temperature.² It is apparent from Figures 1 and 2 that the magnitudes of the dielectric and mechanical dispersions of sample B having less methylol content³ are considerably smaller than those of sample A cured at 170°C .

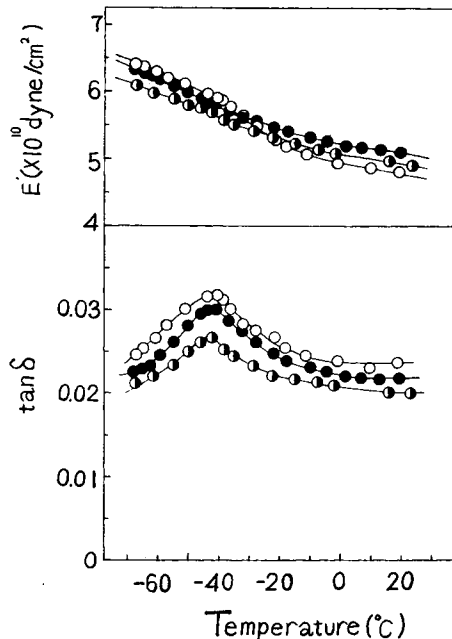


Fig. 2. Dynamic modulus and loss $\tan \delta$ vs. temperature for sample A and sample B cured at 170°C . for 30 min.: (O) sample A; (●) sample B; (⊙) sample A, acetone extraction.

The apparent activation energy for this dielectric β -dispersion was 17 kcal./mole and is in the same order as the activation energies reported for the orientation of local parts, such as side groups, in many polymers.⁵ It seems, from all the results mentioned above, that the β -dispersion might be caused by the movement of unreacted methylol and amino groups in the phenolic resin molecules. A detailed report will be published in the near future.

References

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Received March 22, 1961
Revised June 13, 1961