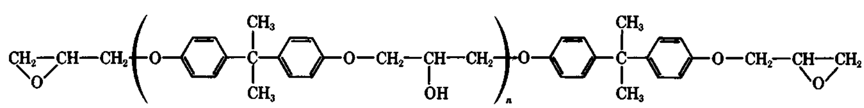
NOTES

Irregular Change in Specific Gravity for a Series of Epoxy Prepolymers

A series of the diepoxides of 4,4'-isopropylidene diphenol (bisphenol A) has been employed for its excellent adhesive and other mechanical properties and has wide commercial uses such as protective coatings, adhesives, electrical insulation, etc., with cross-links agents and other additives.

The epoxides are usually prepared by the reaction between bisphenol A (BPA) and epichlorohydrin in the presence of sodium hydroxide as dehydrochlorinating agent, which is known as conventional process.[1] The molecular weight of the epoxides is controlled by varying the ratio of bisphenol A to epichlorohydrin. Another process for preparing higher molecular weight homologs is to extend lower molecular weight epoxides by the reaction with bisphenol A in the presence of basic catalyst, which is called fusion process.[2] The methods of preparation can be distinguished by estimating molecular weight distribution by gel permeation chromatography.[3]

The generalized formula for the epoxides is usually written as follows, though a minor amount of branching has been recognized,[4]



where n ranges from 0 to 12 for commercial products.

The properties and the gel permeation chromatograms of the epoxides are presented in Table I and Figure 1, respectively. The products from the fusion process are characterized by the substantial absence of prepolymers with odd-numbered values for n. In

TABLE I
Properties of Epoxides

Code	Process of preparation	Epoxy equivalent weight[a]	Viscosity at 25°C, poises	Softening point, °C[b]	Specific gravity at 25°C[c]
Epoxide A	conventional	195	141	—	1.167
Epoxide B	conventional	254	>5000	—	1.167
Epoxide C	conventional	488	—	65	1.194
Epoxide D	fusion, A + BPA	490	—	70	1.190
Epoxide E	fusion, A + BPA	654	—	80	1.191
Epoxide F	conventional	955	—	97	1.187
Epoxide G	fusion, C + BPA	2070	—	120	1.187
Epoxide H	mixture 0.3A + 0.7G	1510	—	79	1.191

[a] HCl-dioxane method.
[b] Ring and Ball method, ASTM E28-51T.
[c] Flotation method.

Figure 2, the measured specific gravity and the softening point of the epoxides are plotted against the logarithmic scale of the epoxy equivalent weight ($\approx$ one half of the molecular weight). The specific gravity of the epoxides jumps from 1.167 for liquid prepolymers to ca. 1.19 for solid ones. The epoxides with epoxy equivalent weight 500 have

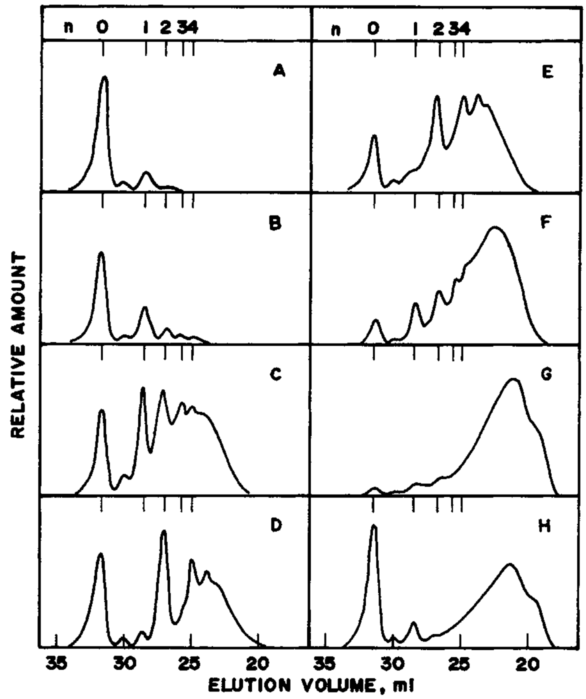


Fig. 1. Gel permeation chromatograms of epoxides.

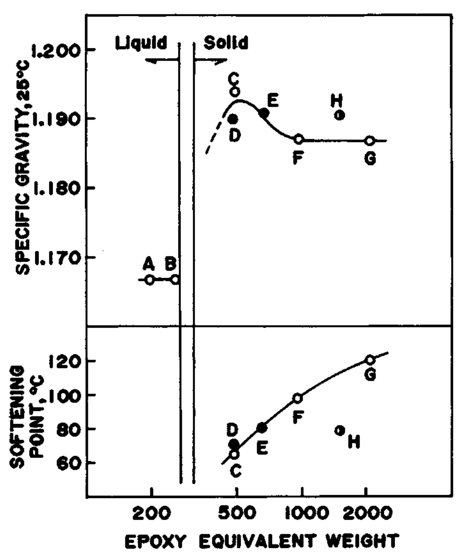


Fig. 2. Relation between properties and epoxy equivalent weight.

rather higher specific gravity than the other solid epoxides. This deviation in the specific gravity–epoxy equivalent weight curve seems quite irregular, though the relation between specific gravity and molecular weight of a series of homologous materials has not been clearly known.

The phenomena should be interpreted in terms of filling of free volume. The epoxides C, D, and E seem to be self-filled systems where low molecular weight epoxide behaves as fillers which pack the free volume of higher molecular weight ones. This high filling nature may be responsible for the higher specific gravity. This conclusion is confirmed by the results that the specific gravity of the mixture of epoxide A, 30 weight-% (SG 1.167), and epoxide G, 70 weight-% (SG 1.187), is found to be 1.191. Apparently, additivity in specific gravity does not hold for low molecular weight liquid epoxide and high molecular weight epoxide systems.

The contribution of the high filling nature of epoxy prepolymer to the mechanical behavior of crosslinked resins is not yet understood. However, the more advanced studies of the filling effect should give useful information for elucidating the behavior of free volume and the outstanding mechanical properties of the cured resins.

References

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NAOAKI HATA

Asahi Denka Kogyo K.K. (Asahi Electrochemical Co. Ltd.)
Arakawa-ku, Tokyo, Japan

JU KUMANOTANI

Engineering Research Institute
Faculty of Engineering
University of Tokyo
Tokyo, Japan

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