Chemistry of Epoxide Resins.   XVII.*   Influence of Structure and Curing Conditions on the Density, Degree of Cure, and Glass Transition Temperature During the Curing of Epoxide Resins†

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Synopsis

During an investigation of various epoxide resin systems, some cases were found in which the room temperature density decreased with increasing curing temperature and increasing degree of cure.   In other systems the density was found to be independent of the curing temperature.   In these cases it is possible by deliberately stopping the reaction to measure density values which also decrease as the curing progresses.   This unexpected behavior can be explained in a purely physical manner from the pattern of the density changes during an entire curing cycle.   The density decrease of the noncured mixture, which is due to the increased curing temperature, outweighs all contraction effects consisting of isothermal chemical and cooling shrinkage, whereby the latter is dependent to a great extent on the glass temperature.   In those cases where the glass temperature exceeds the curing temperature, the chemical reactions come to a standstill, when the temperature difference reaches a certain value, i.e. it "freezes chemically".   By means of values that can be measured readily at low temperatures, it is possible to construct diagrams from which the variation of the density at higher temperatures of the curing cycle can be estimated.

In a reactive system the density increase often serves to measure the course of a chemical conversion.   Particularly in the field of macromolecular chemistry, this method is frequently used.   In many studies on polymerization, the increase in amount of polymer formed is followed only by the change in density.

While investigating the curing of epoxide resins, a case was found in which the density measured at room temperature decreased with increasing curing temperature.[1]

In the present paper, nine different curing systems (A–J) have been investigated.   It was found that the dependence of the room temperature density and the glass temperature on the curing temperature showed marked variations.

* For Part XVI, see Reference 1.

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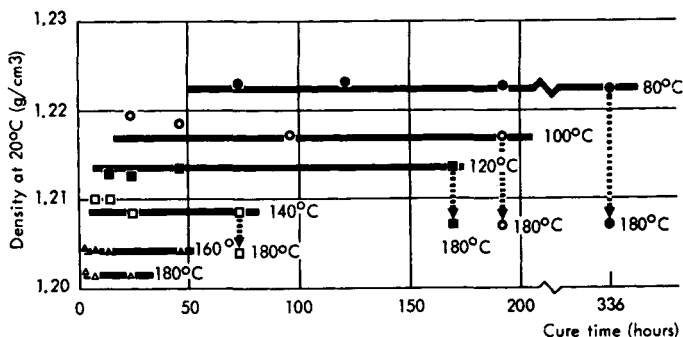
Fig. 1. Density at 20°C as a function of the duration of curing and curing temperature for system A.

Curing System A

Curing system A had the following composition: 100 parts by weight Araldite CY 175 (CIBA) [epoxidized acetal from tetrahydrobenzaldehyde and 1,1-bis(hydroxymethyl)cyclohexene-3], 95 parts Hardener HT 907 (hexahydrophthalic anhydride), and 12 parts Accelerator DY 065 (basic accelerator).

Figure 1 shows the density of a cycloaliphatic epoxy resin measured at room temperature as a function of the duration and temperature of curing. For every single reaction temperature, the density tended towards a constant value with increasing curing time. Increasing curing temperature reduces the density overall by about 2%. Even subsequent treatment of a sample cured at a lower temperature, for 6 hr at 180°C, reduces the density considerably (broken line), without, however, reaching the value obtained by the direct curing at 180°C. Related to room temperature, this corresponds to the effect of a negative shrinkage.
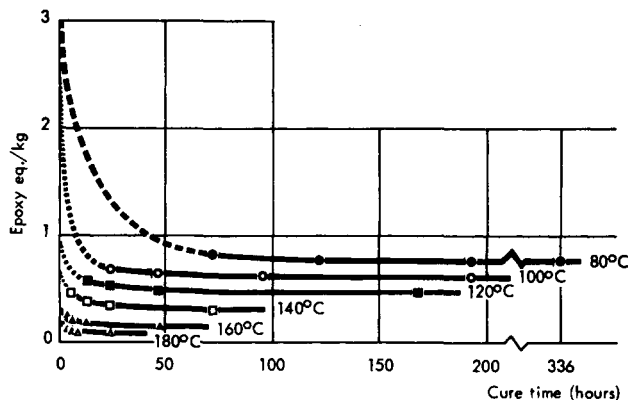

Fig. 2. Epoxide content as a function of the duration of curing and curing temperature for system A.
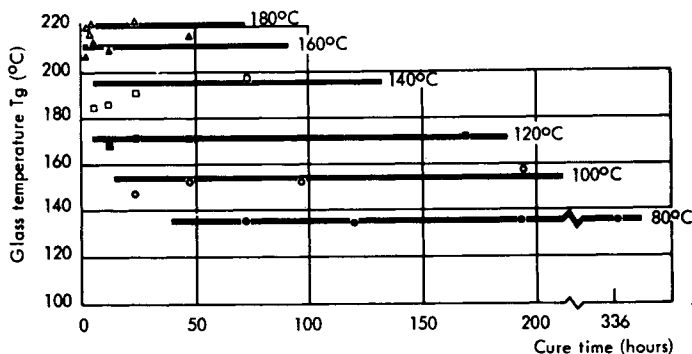
Fig. 3. Glass temperature as a function of the duration of curing and curing temperature for system A.

To clarify this behavior, a chemical analytical method was used. As explained in an earlier paper, the chemical structure of epoxide resins cured with dicarboxylic acid anhydrides[2,3] can be analyzed completely by using the swollen state. Figure 2 shows the results of this method as applied to the determination of the epoxide content of all the samples shown in Figure 1. Here too, the measured results for each curing temperature tend to a constant value which decreases with increasing curing temperature. As is to be expected, the extent of the curing reaction as measured by chemical analysis increases with increasing reaction temperature.

Another question arises: why does the reaction come to such a premature standstill at 80°C, for example after the conversion of only $^3/_4$ of the original epoxide groups despite the large amount of accelerator?

Here the glass temperature as an additional measure of the extent of crosslinking, can give some information. This value was determined by means of thermoanalysis, i.e., with a differential scanning calorimeter.

The results are shown in Figure 3 and Table I. The same behavior can

TABLE I

Final Value of T_g and $T_g - T_c$ as a Function of the Curing Temperature for System A

Cure temperature T_c, °C	Glass temperature T_g, °C	$T_g - T_c$, °C
80	136	56
100	154	54
120	171	51
140	195	55
160	211	51
180	221	41

be observed. For each curing temperature T_c, the glass temperature T_g approaches a constant value which is always considerably higher than the

temperature at which the curing was carried out. Further, the differences between these temperatures $(T_g - T_c)$ are roughly the same.

From this result we can draw the following conclusions. As soon as the glass temperature, which increases throughout curing, exceeds the curing temperature by a certain value, the chemical conversion comes to a standstill, irrespective of the continuation of the isothermal treatment. The system "freezes chemically". Curing at 180°C leaves a residual amount of epoxide groups that exceed the standard error of measurement. Even at this temperature, it is not possible to achieve complete curing.

The Martens heat distortion method was also used to determine the degree of curing. Curing temperatures of 80°C and 100°C give Martens temperatures that also lead to a constant value with prolonged curing. The results obtained are about 20°C lower than the glass temperatures found by differential thermoanalysis. A wider scatter in the measured values is shown by the products obtained at the higher curing temperature. This is plausible because the test temperature must of necessity exceed the curing temperature leading to an uncontrolled post-curing during the evaluation. This effect is much more pronounced with the Martens method (temperature increase 0.8°C/min) than with differential thermoanalysis. Due to the small sample quantities required by the latter method it can be carried out at a heating rate that is roughly twenty times higher and therefore gives a more reliable insight into the real state of incomplete curing.

Curing System B

In curing system B, the epoxidized cyclic olefin compound is replaced by a polyglycidyl ether based on bisphenol–epichlorhydrin. The composition is 100 parts Araldite F (epoxy equivalent 190), 80 parts Hardener HY 906 (methylnadic anhydride), 1 part Accelerator HY 960 (compound with tertiary amino groups).
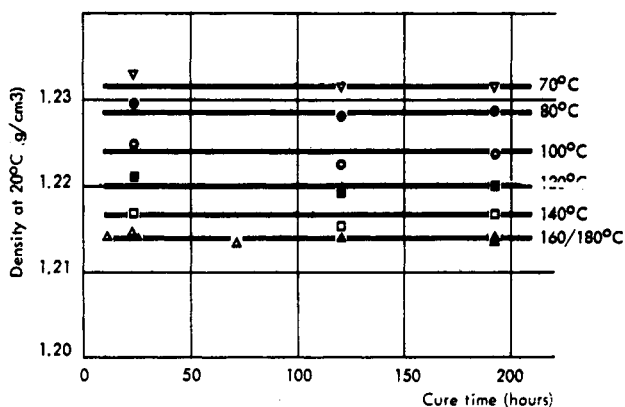

Fig. 4. Density at 20°C as a function of the duration of curing and curing temperature for system B.
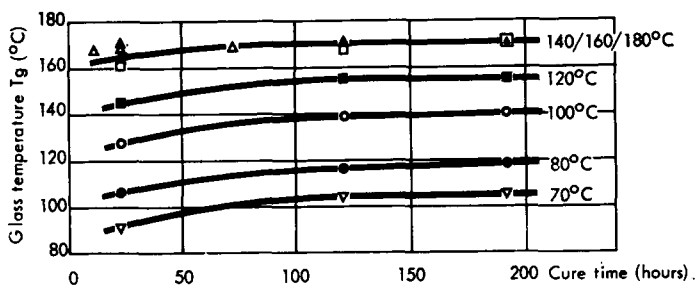
Fig. 5. Glass temperature as a function of the duration of curing and of the curing temperature for system B.

Here again, the room temperature density decreases with increasing curing temperature, except in the case of the two highest temperatures 160 and 180°C (Fig. 4). However, the differences are less marked, and the final evaluation is less precise. A similar picture is given for the glass temperature.

For each curing temperature the glass temperature (Fig. 5) tends to a constant value.

Obviously, complete curing is achieved at 140°C. Higher curing temperatures cannot greatly change the final state. Beyond 140°C the glass temperature and to a great extent the density, become practically independent of the curing temperature (Table II).

TABLE II

Final Value of T_g and $T_g - T_c$ as a Function of the Curing Temperature for System B.

Cure temperature, T_c, °C	Glass temperature T_g, °C	$T_g - T_c$, °C
70	101	31
80	120	40
100	140	40
120	155	35
140	171	31
160	171	11
180	171	-9

Curing System C

Curing system C had the composition: 100 parts Araldite F (CY 205) (cf. system B), 27 parts Hardener HT 972 (methylene dianiline).

Curing system C is based on the reaction of a liquid bisphenol epoxide resin with an aromatic amine. In this case, too, the values approach a constant with increasing duration of curing; in order to simplify the diagrams, Figure 6 and all subsequent figures show only the constant final values which are practically independent of the duration of curing.
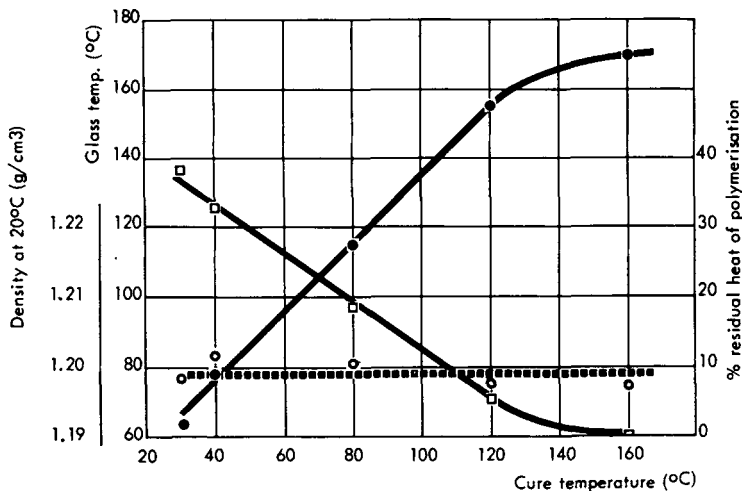
Fig. 6. Density, glass temperature, and residual heat of reaction as a function of the curing temperature for system C: (O) density; (●) glass temperature; (□) residual heat of polymerization.

As can be seen from Figure 6, the density is approximately constant for all curing temperatures, but the glass temperature increases rapidly and levels off at a cure temperature of about 140°C.

This unexpected behavior made the precise determination of the extent of curing particularly interesting. Unlike the anhydride-cured resin systems, there is no known chemical analytical method to determine the epoxy content of epoxide resins crosslinked with amines. According to Dannenberg,[4] the precision of the infra-red method is not quite adequate. An attempt was made to determine quantitatively the extent of conversion with the aid of the differential scanning calorimeter. The residual heat evolution of the isothermal reaction was determined by measuring the areas of the energy versus time curves. Curing system C gives reproducible values for the residual reaction heat. Figure 6 shows them as percentages of the total heat evolved during cure starting from noncured system and finishing with almost complete curing.

The residual heat evolution diminishes linearly with respect to the curing temperature from 38% at 30°C to about 6% at 120°C. At a curing temperature of 160°C the residual heat evolved was only 0.2%. Complete curing is therefore practically achieved at 160°C in agreement with the course of the glass temperature curve.

It should be mentioned that with the reaction system A the above method leads to values that are not readily reproducible. This difference might be explained by the fact that amine curing is based on irreversible chemical conversions. In the case of anhydride curing, however, according to earlier experiments,[5] the reaction of the anhydride with the hydroxyl groups leads to a half-ester by a reversible reaction. At high temperatures, in particular

when the anhydride can evaporate, the reaction moves towards the starting products. In this case, the heat of evaporation disturbs the determination of the heat evolution.

Other Curing Systems

Apart from the three systems described, six other reactive mixtures were examined with regard to density at room temperature and some of them also with regard to the glass temperature.

The chemical composition of all resin systems and other characteristic data, are summarized in Table III.

TABLE III
Compositions and Some Properties of Curing Systems

System	A	B	C	D	E	F	G	Hᵃ	J
Resin									
Araldite CY 175	100								
Araldite F		100	100			100	100	100	
Araldite B				100	100				100
Hardener									
HT 901ᶜ					30				
HT 906		80							
HT 907	95				34.2	80			
HT 972			27						
MHHPAᵈ							85		103
IPDᵉ								22.5	
Accelerator									
DY 062ᶠ						1			
DY 065	12								12
HY 960		1							
Properties									
$-\Delta d/\Delta T_c \times 10^5$	21	20	0	0	0	16	15	7	25
Transition $\Delta d/\Delta T_c =$									
0, °C	>180	150	—	—	—	130	140	>160	>180
$\Delta T_g/\Delta T_c$	0.93	1.0						1.0	
Transition $\Delta T_g/\Delta T_c$									
= 0, °C	>180	140	140					140	
$-\Delta d/\Delta T_g \times 10^5$	23	20	0					7	

  ᵃ With regard to the exothermic reaction, all samples cured at temperatures above 40°C were precured for 24 hr at 40°C.

  ᵇ Solid bisphenol epichlorhydrin resin. Epoxy equivalent ca. 380.

  ᶜ Phthalic acid anhydride.

  ᵈ Methylhexahydrophthalic acid anhydride.

  ᵉ Isophorondiamine.

  ᶠ Basic accelerator.

The density changes (extrapolated end values) as a function of the curing temperature for all nine systems are shown graphically in Figure 7.

One can differentiate three types of systems.

TABLE IV

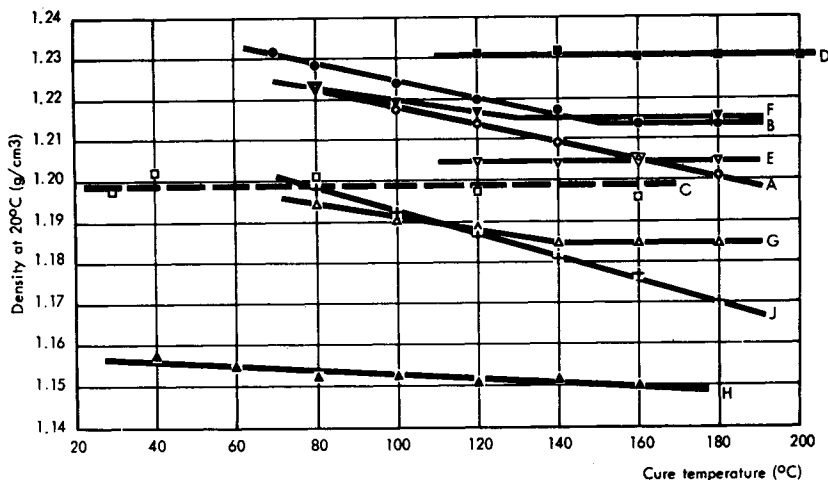| Cure temperature T_c, °C	System A (Araldite CY 175, Hardener HT 907, Accel. DY 065)		System B (Araldite F, Hardener HY 906, Accel. HY 960)		System C (Araldite F, Hardener HT 972)		System D (Araldite B, Hardener HT 901)		System H (Araldite F, IPD)	
	T_g, °C	$T_g - T_c$	T_g, °C	$T_g - T_c$	T_g, °C	$T_g - T_c$	T_g, °C	$T_g - T_c$	T_g, °C	$T_g - T_c$
30					63	33				
40					78	38			71	31
60									95	35
70			101	31						
80	136	56	120	40	115	35			120	40
100	154	54	140	40					140	40
120	171	51	155	35	155	35	115	—5	155	35
140	195	55	171	31			116	—24	166	26
160	211	51	171	11	170	10	116	—44	164	4
180	221	41	171	—9			116	—64		

Fig. 7. Density as a function of the curing temperature for systems A–J.

In the type 1 system the decrease of density is constant over the whole temperature range.   This is the cycloaliphatic epoxy resin cured with hexahydrophthalic (A) and methyl hexahydrophthalic anhydride (J), of which the latter shows the highest slope.   The liquid epoxy resins based on bisphenol A cured with isophorone diamine (H) also belong to this system, but show, however, smaller slopes.

In the type 2 systems, the density first decreases and then becomes constant; examples are the liquid bisphenol A resin cured with methylnadic (B), hexahydrophthalic (F), and methylhexahydrophthalic (G) anhydrides.

For the type 3 systems, the density is independent of the curing temperature.   This effect is shown by the solid bisphenol A casting resin cured with phthalic anhydride (D) and with hexahydrophthalic anhydride (E), and also by the previously described liquid bisphenol A epoxy resins cured with methylene dianiline (C).

Numerically, the dependence of the density on the curing temperature T_c is given by the expression $-\Delta d/\Delta T_c$ (where Δd denotes the change in density), which becomes zero for constant density values.   This is shown in Table III.   In cases where the density becomes independent of the curing temperature, the corresponding temperature is given, too.

A similar classification can be seen when the glass temperature is considered (Fig. 8 and Table IV).

Type 1 shows an approximately constant increase (system A).

In type 2 systems, the glass temperature increases at first and then at approximately 140°C reaches a constant value as shown with liquid bisphenol resin cured with methylnadic anhydride (B), methylene dianiline (C), and isophorone diamine (H).

In type 3 systems the glass temperature is independent of the curing temperature.   This is the case with solid bisphenol A resin and phthalic anhydride (D), a system which will be discussed further on.
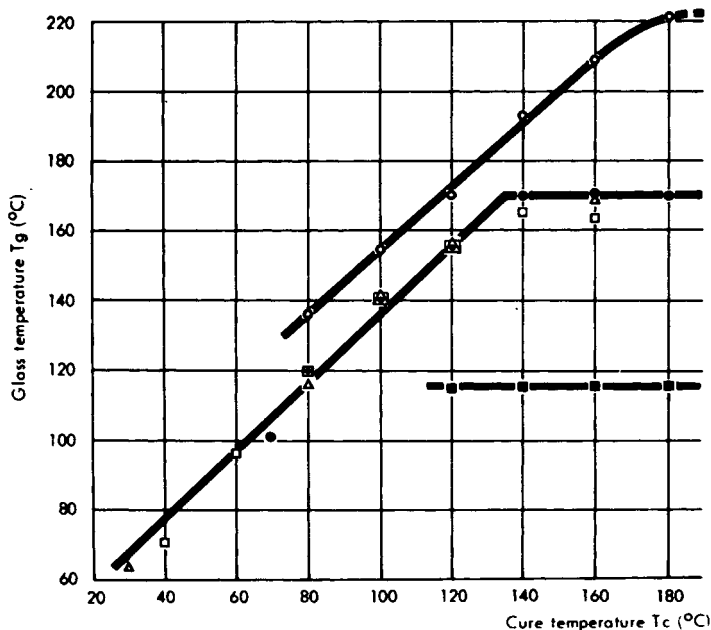
Fig. 8. Glass temperature as a function of the curing temperature for systems A–D and H: (O) system A; (●) system B; (△) system C; (■) system D; (□) system H.

In addition, the dependence of the glass temperature T_g on the curing temperature T_c which is numerically given by $\Delta T_g/\Delta T_c$ and the temperatures at which the glass temperature becomes constant, are also given in Table III. The equation:

$$-\frac{\Delta d}{\Delta T_c} : \frac{\Delta T_g}{\Delta T_c} = -\frac{\Delta d}{\Delta T_g}$$

shows that for the linear ranges the glass temperature also is a linear function of the density.

The chemical freezing effects described here are effective beyond the range of the usual conditions (temperature and time). Further conversion cannot be ruled out completely when the postcuring is prolonged over months and years. In any case, the point of chemical "freezing" is characterized by the fact that the curing rate is reduced by several orders of magnitude.

Density Changes During a Full Curing Cycle

All density values given so far in this study refer to measurements taken at room temperature; the range of application for such individual values is very limited. One should take the density pattern of one whole curing cycle for evaluation. Such an evaluation of the test results was reported earlier[2,3] with regard to reaction system D, the solid bisphenol resin (Fig. 9).

The cycle consists of: (a) the density of the noncured mixture at room temperature as starting point A; (b) the expansion AB of the noncured mixture during heating to the curing temperature; (c) the isothermal
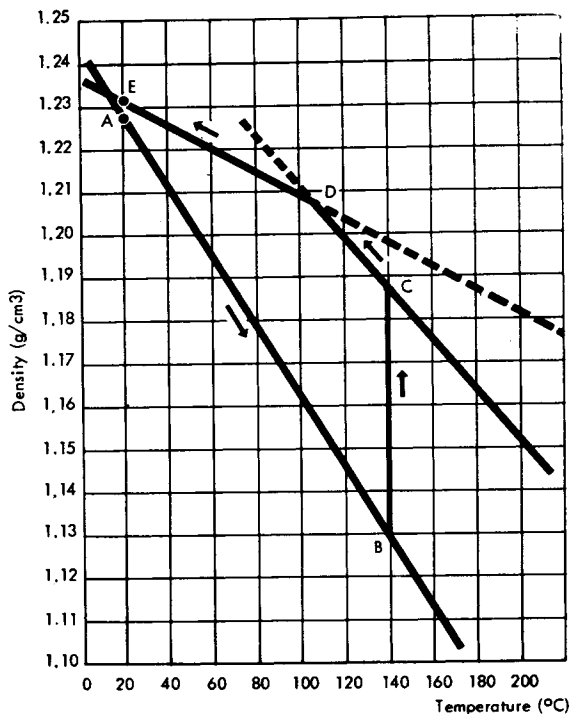
Fig. 9. Density changes during the curing cycle for system D.

chemical shrinkage BC during curing; (d) contraction during cooling, CD, above and (e) DE below the glass temperature.

The explanation suggested in the earlier paper that this diagram describes the density changes and chemical shrinkage for all curing temperatures is confirmed by this study. Both the density at room temperature as well as the glass temperatures prove to be independent of the curing temperature for system D. These two fixed points, the density of the noncured mixture, and the three expansion coefficients, determine the curing cycle for all temperatures.

Figure 9 is no longer applicable as soon as the density measured at room temperature becomes dependent on the curing temperature. This is the case with most of the systems described here.

Figure 10 shows the results for curing cycles at various curing temperatures for a cycloaliphatic epoxide resin (system A). For the noncured mixture, the temperature dependence of the density is by coincidence the same as that in system D (the solid bisphenol resin and phthalic acid anhydride), namely $83 \times 10^{-5} \, g \, cm^{-3} \, °C^{-1}$. The density change of the cured resin during cooling depends considerably on the curing temperature used; cured at 80°C it is 32×10^{-5}; at 160°C, $20 \times 10^{-5} \, g \, cm^{-3} \, °C^{-1}$. For comparison, system D has the value $60 \times 10^{-5} \, g \, cm^{-3} \, °C^{-1}$ for temperatures above the glass temperature and $18 \times 10^{-5} \, g \, cm^{-3} \, °C^{-1}$ for those below it.

Figure 10 explains on a purely physical basis why this surprising effect of
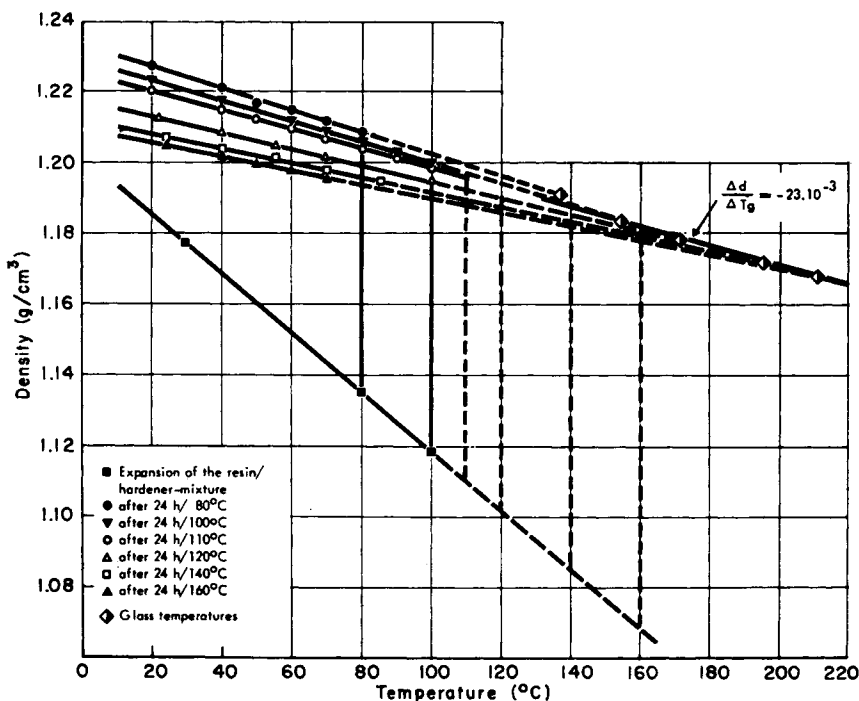
Fig. 10. Density changes in the curing cycle at various curing temperatures for system A.

the decreasing room temperature density with increasing curing temperature occurs.

The following points are of importance: (1) As stated earlier, the glass temperature is always higher than the curing temperature; therefore, on cooling only the smaller contraction coefficient needs to be taken into account. (2) This contraction coefficient is dependent on the curing temperature. It decreases with increasing curing temperature and increasing degree of curing in a remarkable way. (3) Under the influence of these two factors, the decrease in the density of the uncured mixture on heating, outweighs in every case all increases of density, i.e., all contraction effects consisting of isothermal shrinkage and contraction on cooling. (4) Therefore, the density of the end-product at room temperature must decrease with increase of the curing temperature.

The effect, the decrease in density of the end-product at room temperature with increasing curing temperature, tends to lower the internal stresses in the system and is, therefore, of considerable technical importance.

By extrapolation of the density versus temperature curves of the cured products at various curing temperatures to the measured glass transition temperature, density values were obtained which fall approximately on a straight line.   The slope of -23×10^{-5} g cm^{-3} °C^{-1} is identical with the calculated value for $\Delta d / \Delta T_g$ given in Table III.
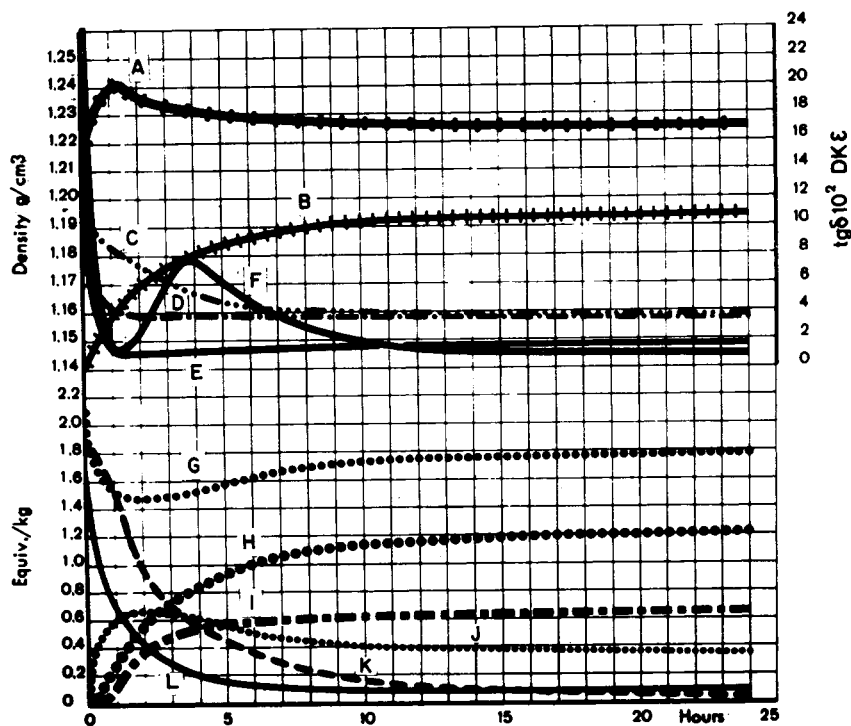
Fig. 11. Values for chemical and physical properties during the curing of system D at 125°C. (A) Density at 25°C; (B) Density at 125°C; (C) DK at 125°C (100KC); (D) DK at 25°C (100 kc); (E) tg δ at 25°C (100 kc); (F) tg δ at 125°C (100 kc); (G) Hydroxyl; (H) Diester; (I) Ether; (J) Monester; (K) Epoxy; (L) Anhydride.

In principle it is therefore possible to establish by means of values that are readily accessible at low temperatures a scheme valid for all temperatures which will allow one to estimate the density pattern in that curing cycle at higher temperatures.

By analogous considerations one can also answer another question. As reported earlier,[2,3] the curing system of the solid bisphenol resin cured with phthalic anhydride could be explained completely by chemical analysis up to the cured state, whereby all functional and all end groups have been determined.

In addition some physical data were measured (Fig. 11). For the present discussion we shall only consider the density. At a given curing temperature it increases steadily during curing, whereas the value determined at room temperature first increases, attains a maximum around the gel point, and then decreases steadily on continued curing (Fig. 11).

By measuring the density during a complete curing cycle of system D at different stages of curing (Fig. 12), where incomplete curing is obtained by deliberately stopping the reaction, an explanation is given for the effect.

If the uncured mixture is heated, the density decreases to about 1.14 g/cm³. After curing for 45 min at 125°C, the density increases to about
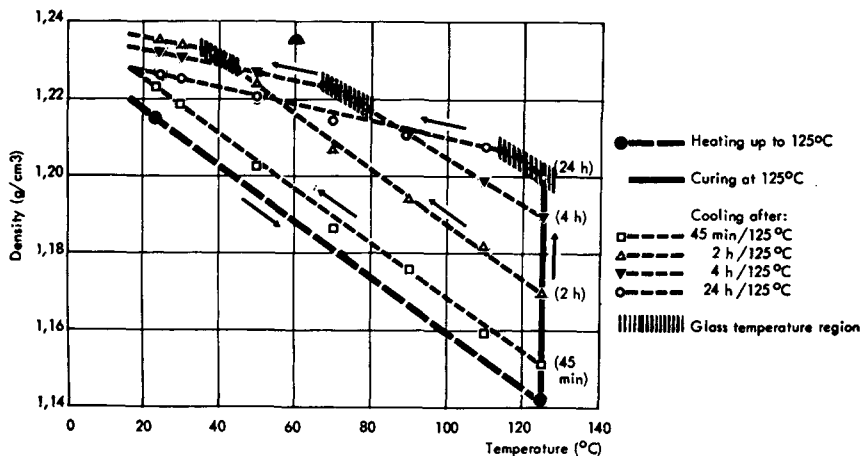
Fig. 12. Effect of the duration of curing on density, expansion coefficient, and transition temperature for system D.

1.15 g/cm³ due to chemical shrinkage. On cooling, the contraction coefficient is almost unchanged. The glass temperature still lies under the room temperature. The increase in density is therefore, at 20°C approximately the same. After curing for 2 hr, the chemical shrinkage is increased further and leads to a density of 1.17 g/cm³. The glass temperature is now at 40°C. The determining factor for the contraction is still the larger coefficient above this temperature, so that at 20°C, one can still measure a further increase in density. After 4 hr curing, the density is 1.19 g/cm³. The glass temperature has now reached 75°C, so that the smaller cooling coefficient below the glass temperature becomes important. The density of the end-product at 20°C, unlike that in the earlier experiment, is decreased. After 24 hr curing, the influence of the smaller cooling coefficient below the glass temperature is still larger. The end-product, therefore, again shows a decrease in density.

Through these measurements it is possible to explain clearly why the room temperature density goes through a maximum with increasing curing. Here, it is the large change in glass temperature which is mainly responsible for this effect. For the cycloaliphatic resin, however, it is the small and diminishing contraction coefficient below the glass temperature which causes the decrease in room temperature density.

References

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