New Theory on the Physical Properties of Polymers from Cured Resins to Linear Polymers: Melting Temperature, Glass-Transition Temperature, and Strength

Yahachiro Matsushita

2-37 Ikeda 5 Chome Niiza-Shi, Saitama-Ken, 352-0015, Japan

ABSTRACT: Here it is shown how a property is acquired with a new segment. This means that when a polymer is produced without a melting temperature by heating (T_m) or solvent and mechanical stress, new physical properties will not occur. A new segment starts from crosslinking, which takes the three steps of initiation, propagation, and termination, such as the polymerization of a vinyl monomer. An excess of crosslinking causes a crack in the resin. The boiling water absorption expresses the magnitude, which consists of a closed and open cell. The limit of the thermal elongation of the C—C-bond-composed main chain is 1% from 0°C, which is a common value making possible a comparison for the general polymer, extending the C—C bond of the organic compound. An equation of the glass-transition temperature (T_g) is obtained from summation inversely to the linear coefficient of thermal expansion of each molecular unit. DNA is given as a perfect form composed of all new segments without waste; the molecular unit responds to an individual function as a condition of a living thing. T_g is a signal to change direction to the thermal elongation of the main chain for T_m; $T_m - T_g$ indicates a similar process in the original direction of T_g. There is no T_m without T_g. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1467–1475, 2005

Key words: resins; glass transition; strength

INTRODUCTION

Polymer and *resin* are popular names for macromolecular materials. The difference between a cured resin and a linear polymer is the existence of crosslinking. A linear polymer has a melting temperature by heating (T_m) and dissolves in a solvent, but this does not happen for a cured resin. The segment is defined as a special group unit of 20–40 molecules composed mainly of C—C bonds. A new segment is formed by part of two arrays having the direction of the main chain between two main chains. The segment of a cured resin is formed by a crosslinking chain; one of a linear polymer is formed by connecting points based on the van der Waals force. The thermal properties include the glass-transition temperature (T_g), the heat distortion temperature (HDT), and the linear coefficient of thermal expansion (α). T_g is shown by a changes from rigidity to softness. It used to be thought that T_g is caused by agitation freeing portions of the resin chains to rotate around the bonds.[1] A comparison of an epoxy resin with respect to the physical properties used to include T_g. If the temperatures of

curing and postcuring reactions disagree, the resultant data are meaningless because T_g changes with the reaction temperature. T_g does not make clear what a substance is, so there are three typical theories for its origin.[2] In particular, T_g of a linear polymer involves complicated phenomena recurring with annealing or stretching.[3] Approaches to T_g can be classified into two types. One is based on a theory of a change in the volume or viscosity or enthalpy, and another is based on a segment from the thermal movement of the main chain at T_g. However, the approaches have widely and vaguely been handled because of the nature of polymers. For example, the origin of T_g, when the temperature goes down from T_m to T_g, can be explained as the time of a fixed free volume or viscosity; this is based on a theory of an isofree-volume state or isoviscous and configurational entropy. However, there are questions, in the case of reverse changes, of how a solid polymer can be perceived at the time of T_g just like a living thing. For a segment, there is a question of how the segment can be in the direction of the main chain and form a unit group with some molecules. Ready-made test pieces with latent faults have been given with respect to the nature when the chemical reaction is finished. Even if this is important until then, why they occur and what the substance in back is will be disregarded. The same matter is taken up concerning the degree of polymerization (P). This has also been accepted as a factor, given the influence on T_g of a

linear polymer. This indicates an important fact but cannot be examined further because of the nature of polymers. It is more important to know why and how it is applicable. When T_g becomes high, a crack often occurs in a resin. The problem of cracking is a newly discovered phenomenon; it occurs in all cured resins with high T_g's and may be explained only with new information.

EXPERIMENTAL

The measurements were performed with the JIS K 6911 method (general measurement for thermosetting plastics). Both T_g and HDT changed as the temperature increased, and their differences depended on whether a load was given or not. HDT is the elongation by bending with a required load, and T_g is elongation by the stretching direction without a load. HDT is handled in the same way as T_g in this article, as assumed by Koike.[4] The mixing ratio of the resin was 1 g equiv of epoxide to an equivalent weight of the hardening reagent (equivalent weight of the hardening reagent = molecular weight of hardening reagent/ number of hydrogens at amine or phenol).

RESULTS AND DISCUSSION

New viewpoint for T_g of cured resins

Epoxy resins are hardened with curing reagents such as amines, novolac, acids, and acid anhydrides. A postcure is a well-known way of improving properties through the transaction of heat at a higher temperature after resin hardening. Until the present, postcuring has been thought to finish the chemical reaction of hardening. As described in this article, postcuring only half-completes hardening. Whether the hardening is finished or not, a higher T_g should not happen after a postcure at a higher temperature.

Figure 1 indicates the elongation rate ($\Delta l / l$) versus temperature t (°C). α is given by

$$\alpha = (\Delta l / l) / t, \tag{1}$$

where Δl is the expanded length from 0°C to length l of the test piece and α is given as a gradient of BC. Although T_g is used to explain BCE in Figure 1 so that point C is T_g with a change from rigidity to softness, a new point D occurs upon the extension of the original straight line from the successive postcure. A hardening of the resin happens, from a liquid to a solid, which is composed of three kinds of chains: a main chain, a crosslinking chain, and a preliminary chain for crosslinking. A change in T_g with the postcure reacts to a transfer from precrosslinking to crosslinking; this occurs when both functional groups combine because of the thermal elongation of the molecular
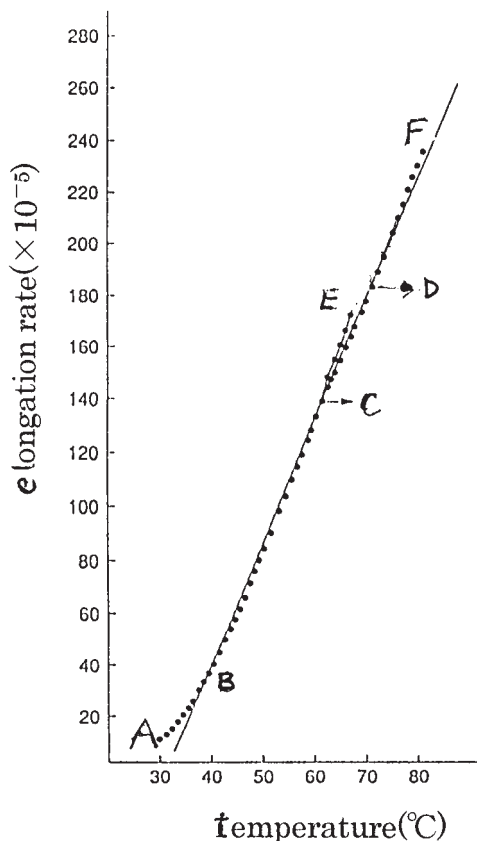

Figure 1 Elongation rate versus temperature [resin = bisphenol A of diglycidyl ether (190 equiv); hardener = modified aliphatic amine (26 equiv)]: (A–C,E) 20°C for 24 h and 60°C for 3 h and (A,B,D,F) postcure at 70°C and 3 days at 20°C above the test piece.

unit composing the precrosslinking. The segment in the hard part and the crosslinking in the soft part are reversible with up-and-down changes in the temperature. Figure 1 gives an estimate for the formation of each segment with three steps: initiation, propagation, and termination. When a cured resin is left for 2–3 h at a predetermined temperature for postcuring, T_g increases to nearly that temperature.[5] Therefore, eq. (1) can be changed from t (°C) to T_g (°C) by

$$\alpha T_g = \Delta l / l \tag{2}$$

A hardening of an epoxy resin is performed via heating or at room temperature. T_g of the latter will be less than and greater than 50°C, for it changes according to the magnitude of the exotherm.

Limit of thermal elongation ($\alpha T_g = 1\%$ from 0°C)

Figure 2 shows the relation between α and T_g according to data reported by Morita.[6] The line numbers in Figure 2 are the means of the elongation ratios; they
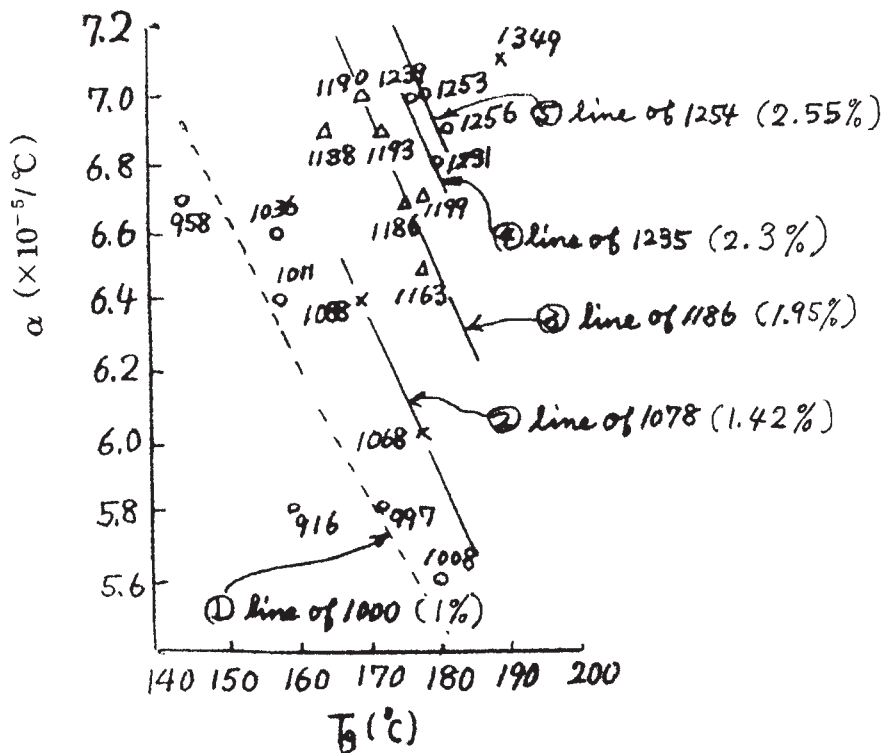
Figure 2 α versus T_g with changing αT_g [resin = polyfunctional phenol epoxy resin; hardener = phenol novolac resin; accelerator = 2-methyl imidazole (1 phr)].

are also presented as αT_g [eq. (2)] with the omission of the term $\times 10^{-5}$. The postcure is 8 h at 180°C after hardening for 2 h at 160°C. Each mean of αT_g increases from 1000 up to 1254 because the crosslinking number is greater than the normal value, as described later. When the elongation ratio is higher, α is higher. When T_g is high, α, shown in Figure 2, is also high, remarkably and unreasonably. By normalization, α is able to transfer reasonably so that the unusual α values (shown as circles) appear lower than the 1000 baseline (shown as multiplication symbols) upon their extension, as shown in Figure 3. A normalized α value (α_0) can be obtained as follows:

$$\alpha_0 = \alpha(1000 \text{ by } \alpha T_g / \alpha T_g \text{ of above } 1000) \quad (3)$$

The limit of elongation (shortened as the limit) is shown as $\alpha T_g = 1000 \times 10^{-5} = 1\%$ from 0°C. α consists of α_G up to T_g and α_R by an elastomatic state above T_g. For a middle temperature (ca. 100°C), the elongation of αT_g will be $(500-600) \times 10^{-5}$, usually without 1% of the standard. When T_g is high (e.g., >150°C), the inference of α_R does not appear because the proportion of α_G is great. When T_g is low, just as for the middle temperature, the inference of α_R becomes great. Equation (4) indicates that eq. (3) can be applied up to but below some extent:

$$\alpha_G / \alpha_0 = \alpha_G T_g / 1000 \quad (4)$$

The elongation of a lower T_g value, given as αT_g, is shown as a proportion (%) of α_G with respect to α_0; this provides a useful graph. We can also easily deter-
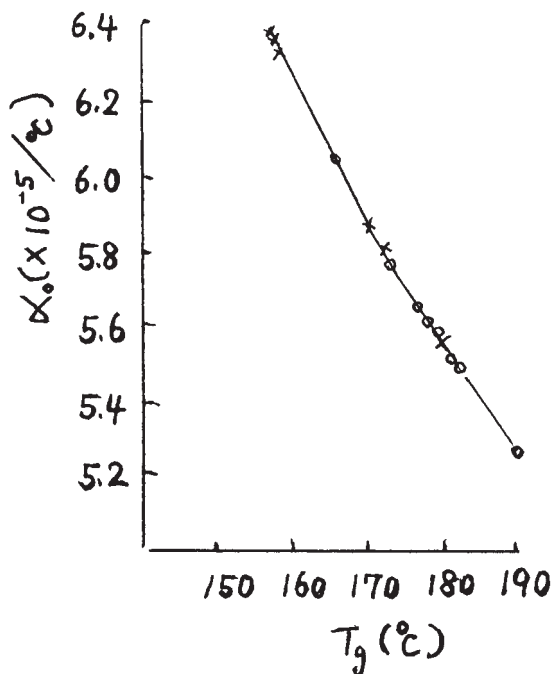
Figure 3 Normalization of α_0: ($\times$) from the 1000 baseline and ($\bigcirc$) from above the 1000 baseline.
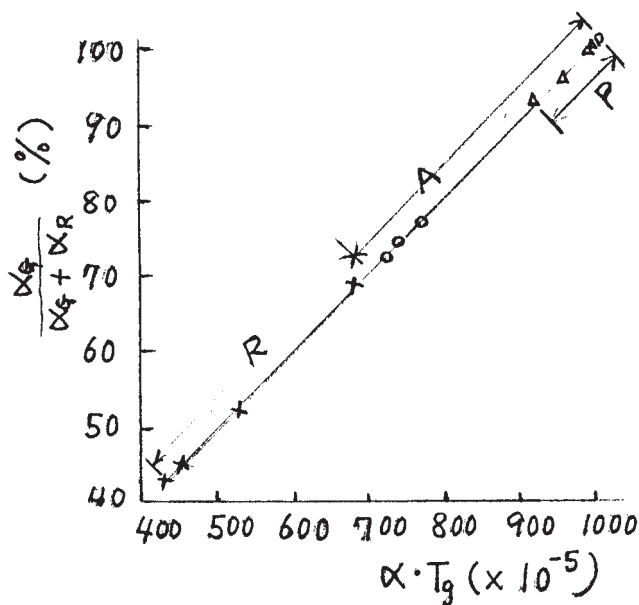
Figure 4 Lower αT_g versus the proportion of α_G (%) with respect to α_0: ($\triangle$) P is a polyfunctional phenol epoxy resin cured with a novolac reagent, ($\bigcirc$) A is a bisphenol A epoxy resin cured with an amine reagent, and ($\times$) R is a resorcinol epoxy resin cured with an amine reagent.

mine the magnitude of the thermal elongation for a chemical structure so that the aliphatic is high and the aromatic is low. For example, the difference between

resorcinol and a bisphenol A epoxy resin cured with the same amine,[7] as shown Figure 4, can be shown with a detailed ranking that cannot be obtained from a comparison by T_g. The next equation is obtained from each thermal elongation at T_g:

$$\alpha_0 = \alpha_G + \alpha_R \qquad (5)$$

The magnitude of α_R is usually shown as the α_R/α_G ratio from Figure 1, which is inversely proportionate to αT_g from eqs. (4) and (5). Then, when T_g is low, the ratio is an inclination for a great change, but when T_g is high, the ratio is low.

Strength (σ) of the cured resins

σ of a cured epoxy resin filled Fe powder is shown (tensile and bending) in Figure 5 as a nearly straight line. When σ is σ_0 at $T_g = 0°C$

$$\sigma - \sigma_0 = kT_g(\text{or HDT}) \qquad (6)$$

where k is a proportional coefficient. This is just like starting from 0°C. The relation between T_g and the crosslinking density (ρ) has been published as an equation improved to apply a wide extent for Loeshack's equation, which is obtained from a reduction of the free volume by crosslinking:[8]
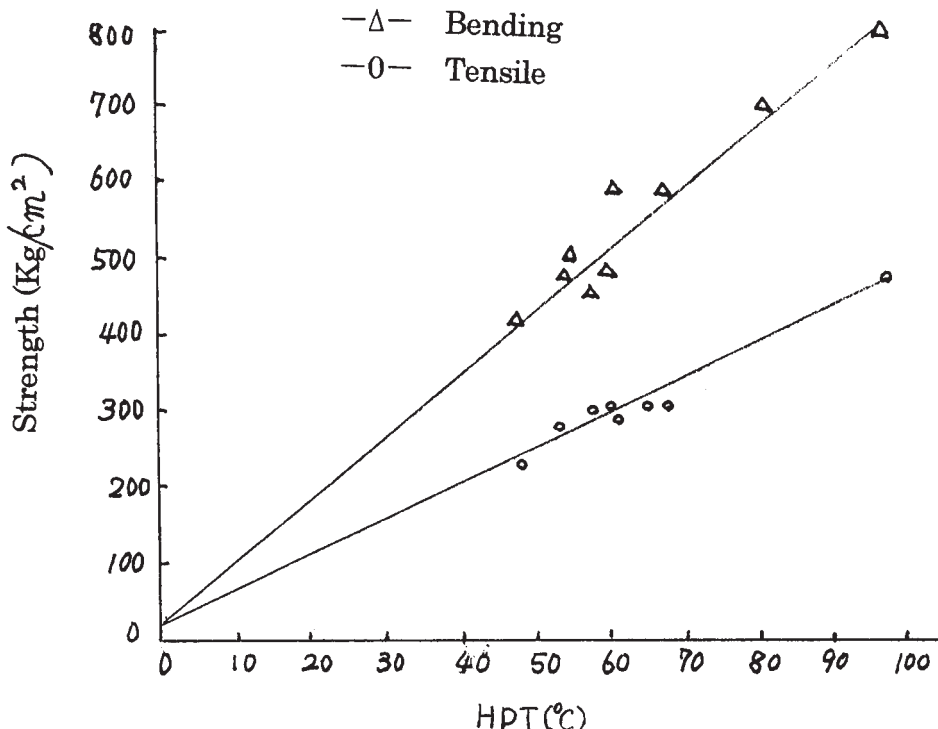

Figure 5 HDT versus σ [resin = bisphenol A of diglycidyl ether (Devcon A, Nihon Devcon Co.); hardener = mainly DTA]. A test piece for HDT and σ was prepared and left for 2 h at the free temperature of the postcure; the test was performed after 24 h at 25°C. The original was prepared with 7 days of resin hardening at 25°C.

TABLE I
Change in the Strength with the Postcure

Curing condition (23°C)	Room temperature	Postcure at 120°C
HDT (°C)	52	122
Tensile strength (kg/cm²)	470	690
Tensile elongation rate (%)	3.4	5.9
Young modulus by (kg/mm²) bending	342	360

A mixing ratio of an epoxy resin and a curing reagent was applied with the same equivalent. The epoxy resin was bisphenol A of glycidyl ether, and the curing reagent was TTA. A test piece cured at room temperature was prepared in 7 days at 23°C and postcured in 5 h at 120°C after room curing for 4 h at 23°C.

$$Tg = m_1 \log m_2\rho \qquad (7)$$

where ρ (mol/g) expresses the number of crosslinks per unit of weight and m_1 and m_2 are constants. ρ of the new theory is given as the number of segments in the repeat unit of the main chain, although they are not actually different. σ is also able to take the same treatment as T_g from a linear function. Equation (8) is derived from eqs. (6) and (7) as follows:

$$\sigma - \sigma_0 = km_1 \log m_2\rho \text{ or } \sigma \div km_1 \log m_2\rho \qquad (8)$$

A change in σ for a cured resin with increasing temperature can be handled with the same crosslinking number for T_g. The increase in σ during the postcure is confirmed by increasing elongation,[9] as shown in Table I. An increase in the tensile elongation rate causes the increase in the strength. The relationship between σ, the elongation, and the crosslinking number is shown as follows:

$$\sigma = ER = E_1\Delta R_1 + \cdots E_i\Delta R_i + \cdots = \Sigma E_i\Delta R_i \qquad (9)$$

where E is Young's modulus, R is the elongation rate of the resin, and ΔR_i is R by the i number segment from the first in gradation. Equation (9) can explain why σ rises. E is supposed to be nearly constant without an influence on changes in T_g, which has been given for 16 different cured epoxy resins,[6] and so double the standard deviation is 12% of the mean E value of 303 kg/mm². The resultant is put as a constant:

$$\sigma = E\Sigma\Delta R_i \qquad (10)$$

$\Sigma\Delta R$(post) is expressed by $\Sigma\Delta R$(room) + $\Sigma[\Delta R$(post) − ΔR(room)] ∴ $\Sigma\Delta R$(post) > $\Sigma\Delta R$(room) ∴ σ(post) > σ(room).This indicates through the segment that thinking about the component T_g by the molecular unit can also be applied to σ as it is. The impact strength is important for determining the toughness of materials. It once was thought that the postcure crosslinking of a cured resin made it brittle and harder. However, this was a mistake for the following result. The Izod impact of a bisphenol A epoxy resin cured by a modified aliphatic polyamide was 1.1 kg/cm cm at room temperature (25°C for 7 days) and changed by 9.3–9.8 kg/cm cm after treatment for 1–6 h at 80°C. Thus, it was improved by almost 9 times, for a general cured epoxy resin has a value of 1–3 kg/cm cm. The toughness is shown by the enclosed area of a stress–strain curve. That indicates Σstress $\times$ R ė ½σR = ½ER^2. Accordingly, an increase in R improves the toughness, including the impact strength.

Equation of T_g by the segment

For a linear polymer, T_m comes from a single main chain with the disappearance of two arrays. Because the limit of 1% is common to cured resins and linear polymers, a comparison of both can basically be applied. However, T_g of a cured resin increases with a gradual change in the thermal elongation. This indicates a relation between the formation of the segment and T_g given as a magnitude. Meanwhile, each segment in a linear polymer is the same, and each is independent. It does not involve a change of T_g up to termination, except for P. $T_g = \Sigma Q_i T_{gi}$ has been used as a base for the mathematical machinery of a method of additive properties in the United States of America.[10] T_{gi} is T_g for component i, Q_i is the weighting function for component i or the volume of component atoms in the main chain (f_i) divided by the total volume of main-chain atoms (Σf_i) in the repeat unit:

$$T_g = \Sigma f_i T_{gi}/\Sigma f_i \qquad (11)$$

The various equations of combination have been introduced with linear, reciprocal, and logarithmic types. They are applied to the summation of components by the molecular unit at the limit:

$$\alpha_0 T_g = \Sigma \alpha_i T_{gi} = 1\% \qquad (12)$$

The equation of T_g obtained from α can be expressed as follows:

$$T_g = 10^{-2}\Sigma f_i(1/\alpha_i)/\Sigma f_i \qquad (13)$$

When a functional group of precrosslinking (shown as a circle in Fig. 6), such as a component of a bifunctional epoxy resin, expands with increasing temperature, it encounters another functional group (shown as a multiplication symbol) of the main chain; for example, one of a polyamine curing reagent, T_{gi}, with each
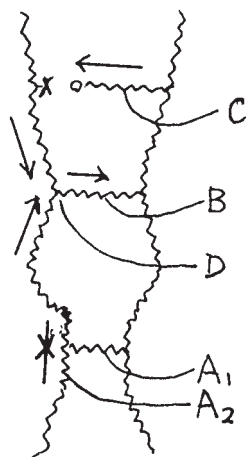
Figure 6 Forms of crosslinking and segments: (A$_1$) component of the epoxy resin, (A$_2$) component of the polyamine segment, (B) crosslinking, (C) precrosslinking, ($\bigcirc$,$\times$) functional groups, and (D) connection point.

α_i forms to combine with them. All α_i values appear at the termination of T_g's increase. When the temperature goes down from T_g, a connection point D between the crosslinking and main chain is dragged into the shrinkage of crosslinking. Upon this dragging, some molecular units of the main chain on both sides of a connection point start orienting to the main chain, matching one of shrinkage (as shown by an arrow). The array part thus produced participates in the formation of T_g with a fixed direction. α_i of eq. (13) at termination is shown as all molecular units of a component-joined reaction of crosslinking. The segment with two array parts has a component of an epoxy resin (A$_1$) and one of a polyamine (A$_2$; Fig. 6). DNA is the specific form of a cured resin segment, and the β sheet of the protein is equivalent to the segment of a linear polymer with two arrays. If a portion of DNA is made by a synthetic method, such as the reaction between the deoxyribose in the main chain and the amine of precrosslinking, crosslinking on the way to termination must be removed, for the molecular units do not respond to individual functions perfectly. The synthetic DNA, which is the segment at termination with a fixed direction of a spiral form, can only function as condition of a living thing. Thinking about the limit of elongation provides a theoretical base for the sum equation of T_g. In other words, their approval gives a proper reason for the existence of the limit. The last component of the molecular unit reaches a fundamental C—C-bond-composed organic compound. It seems to be important in terms of the melting of an organic compound. The cured resin is different from the linear polymer because of crosslinking. Becker[10] reported the following equation: $T_g = (\Sigma f_i T_{gi} + kq)/\Sigma f_i$, where q is the number of network points and k is a constant equal to 890 K. There are two exceptional

occasions when this does not apply for $\alpha T_g = 1\%$. One case is oxidation with long handling times above 200°C; T_g is higher than it usually is. Another is a specific compound formed only of main chains, such as an aliphatic cyclic epoxy compound cured by cationic polymerization with ethylene glycol.

Equation of T_g and strength by P

T_g and strength was presented to change through degree of polymerization (P) in a linear polymer as follows. P versus T_g is given by the Fox–Flory equation:[3]

$$T_g = A - (B/P) \quad (14)$$

where A is equal to $T_{g\infty}$ and B is a constant. Meanwhile, Kanamaru[11] presented an improved equation of strength which de Beer calculated with an idealized model in which the van der Waals force worked only to break fiber. The equation is shown as the next general form as follows:
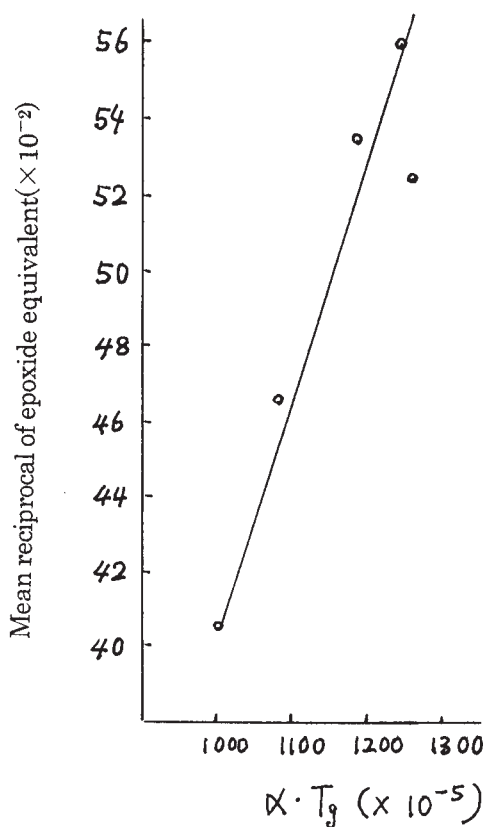
$$\sigma = a - (b/P) \quad (15)$$

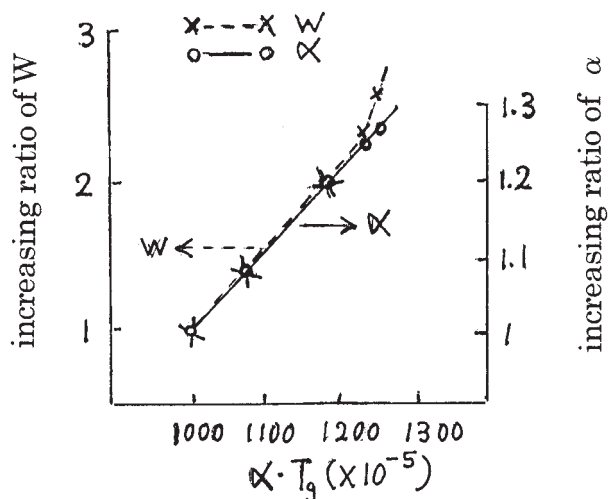
Figure 7 Reciprocal of the epoxide equivalent versus αT_g.

Figure 8 Increasing ratio of α and W versus αT_g. Each ratio is taken from the base of $\alpha T_g = 1000$.

where a and b are constants. Both equations of T_g and strength through P indicate the same form. This provides an important result, that the same object causes them. However, P is an inherent value of a polymer. It meaning is equal to T_g and so forth because it is a result of a chemical reaction without a process. Accordingly, P cannot be used to clarify why and how they change. In other words, P can be replaced with the total segment in the polymer because it is proportional to P. It signifies a change in the number of segments. For T_g, separating two main chains from the segment, from hard up to soft, happens easily with lower P. A $m_2\rho$ of eqs. (7) and (8) is applied so that m_2 is variable and ρ is constant.

Crack by crosslinking and (W) versus α

An epoxy resin cured with a novolac curing reagent has been used for the packaging of semiconductors. It has been used as a cured resin 150°C above T_g to apply molten solder. When T_g becomes high, W rises up often;[6] the measurement of W (%) is performed by the

weighing of a test piece after dipping in 100°C water for 24 h. For a cured resin with a higher W value, wire is often broken by water to an Al base. It has been thought in Japan that the yielding cracks in a resin are caused by abrupt gasification of holding water in resin during operating of solder process.[12] However, W of a cured resin seems to be related to the magnitude of the crack. This means that it is not the cause of cracking but the result of cracking. Figure 2 presents α versus W (in parentheses). W is the mean of each value on the line. When αT_g increases, α and W increase together. Figure 7 presents αT_g as a nearly straight line for the reciprocal of the epoxide equivalent. The reciprocal values are obtained from the mean of each value on the line in Figure 2. They are proportionate to the total segment per unit of length of the main chain because of the same curing reagent, and σ for each can be stated. This means that the increase in αT_g over 1% causes a crack by shear among segments for inside stress happening from an excess of crosslinking density. Figure 8 indicates an increasing ratio of α and W; as shown in Table II, a base of 1% αT_g, though different magnitudes are given, provides an equivalent change. The W values show differences for α from over 1235 of αT_g. The apparent α value of a cured resin seems to change with an increase in the closed cells. Meanwhile, W consists of both closed and open cells. W of closed cells is caused by the diffusion of boiling water for a long time; the crack keep boiling water flowing through the passage of open cells in the resin. Figure 8 shows that W of open cells increases to have a chance of connecting among the closed cells when the closed cells are many. The following calculation can confirm the apparent α base of closed cells. α with two components is given as $\alpha = f_1\alpha_1 + \alpha_2 f_2$, where α_1 is α of a virgin resin and α_2 is α of the substance generated by the ascent to α. If α_2 is caused by closed cells, the volume ratio of W is f_2. Because W is by water, the weight ratio is equal to the volume ratio, the specific gravity of which is 1 g/mL. From numbers 1 and 3 in Table II, $\alpha_1 \fallingdotseq 4.69 \times 10^{-5}/°C$ and $\alpha_2 \fallingdotseq 1.24 \times 10^{-3}/°C$ are obtained by the solution of simulta-

TABLE II
Data of the W Line and α Line

	Line no.				
	1	2	3	4	5
Average αT_g ($\times 10^{-5}$)	1000	1078	1186	1235	1254
Increasing rate for $\alpha T_g = 1000$	1	1.08	1.19	1.24	1.25
α of $T_g = 170°C$	5.88	6.34	7.02	7.25	7.38
Increasing rate for α of $T_g = 170$ °C	1	1.09	1.20	1.25	1.27
Average of the W line (%)	1.00	1.42	1.95	2.30	2.55
α_2 ($\times 10^{-3}/°C$)	1.24	1.21	1.24	1.16	1.10

A polyfunctional epoxy resin was cured with a phenol novolac resin hardening took 2 h at 160°C, and posting cure took 8 h at 180°C.
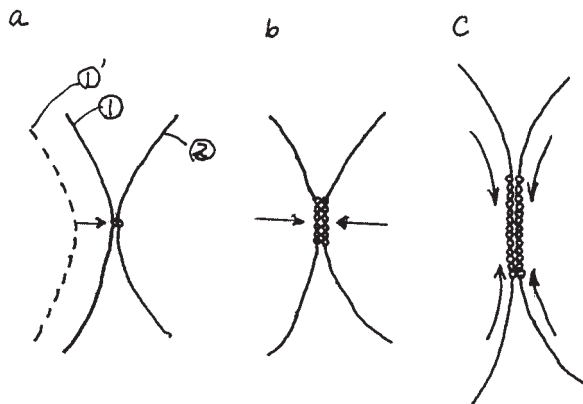
Figure 9   From the genesis of T_m to T_g.

neous equations. The resultant substance can be confirmed to be air, for which α is $1.22 \times 10^{-3}/°C$ according to the Boyle–Charles law; the cubic coefficient of expansion (β) of air is introduced by $\beta = \Delta V/V \times 1/t$ (°C) $= 1/273$ °C, where V is the volume and ΔV is the increase in V from 0°C to t (°C). $\alpha = 1/3 \times 1/273$ °C $= 1.22 \times 10^{-3}/°C$ is obtained from this equation with the next condition. α is 1/3 to β, and Kelvins can be transformed into degrees Celsius because the temperature of the equation is applied as the difference without each value.

Segment of a linear polymer

The abstract segment of a linear polymer can be given through concrete crosslinking to T_g. However, σ of a linear polymer needs another way of treatment by the segment because it is an independent object with a different P value. The segment is formed by some connecting point between two main chains. The existence of the segment facilitates the generation of another segment to give a chance for access between the two main chains. It includes tension by mechanical action, except for T_g or thermal annealing. When the temperature descends from melting, a connecting point of Figure 9(a) yields at the place of the nearest C—C bond to confront the main chain by the van der Waals force. From the neighborhood of a connecting point, these increase quickly by still access [as shown by the arrowhead in Fig. 9(b)], forming T_g in a soft resin with some connecting point. A temperature a little higher than T_g is for a soft resin, but a temperature lower than T_g is for a hard resin. After T_g in a soft resin, more shrinkage quickly forms segments composed of sufficient connecting points with the direction fixed to the main chain [as shown by the arrowhead in Fig. 9(c)]; this changes to a hard resin and arrives at room temperature. The thermal expansion of the C—C bond by the segment in the hard resin is in the axial direction of the main chain as the longitude. The shortened segment in the soft resin at T_g changes the phenomenon by which the physical properties of the segment in the hard resin occur. Changing the hard weakens the restriction for thermal movement by a change in the segment length. The two arrays in the soft (expressed conveniently as the segment in the soft) have greater movement than a single
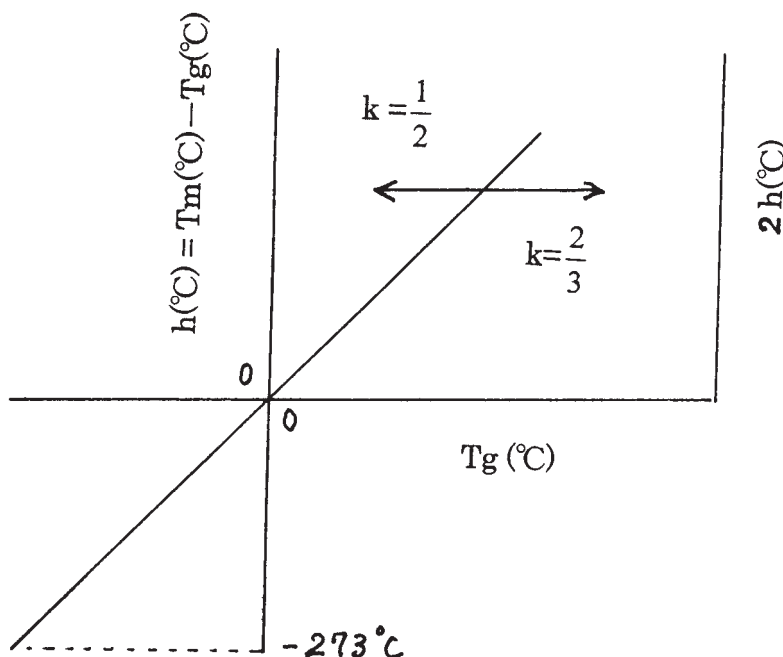

Figure 10 T_g (°C) versus h (°C) $= T_m$ (°C) $- T_g$ (°C). T_g of the main chain is the longitudinal direction, and h is the horizontal. The change from T_g to T_m indicates a similar change to T_g from 0°C. $k = \frac{1}{2}$ is a symmetrical structure, and $k = \frac{2}{3}$ is an unsymmetrical structure.

unit, so some C—C bonds act in a group. The movement of the oppositional direction by each main chain occurs to avoid mutual restrictions at connecting points, separating single main chains. The accumulating energy in the segment in the soft acts immediately after the separation as a motive power for Brownian movement of T_m with free movement by a single main chain. The segment in the soft is necessary for the growth of T_m

Relation between T_g and T_m

Without T_g, T_m does not happen because T_g is a signal for change in the direction of the thermal elongation of the C—C-bond-composed main chain. If the thermal expansion of the same direction is taken continuously without the limit, horizontal movement necessary for T_m cannot have a chance to occur because the arrangement of all main chains in the resin is unchangeable. When the heat of the increasing temperature is given, the movement of the C—C bond of the segment in the soft-composed T_g changes in the horizontal direction to stop thermal elongation. The next equation (K) is well known as an empirical law:

$$T_g / T_m = [T_g(°C) + 273\ K]/[T_m(°C) + 273\ K] = k \quad (16)$$

where k is ½ (symmetrical structure) and ⅔ (unsymmetrical). When $h = T_m - T_g$, a uniform equation is obtained:

$$h\ \text{or}\ 2h = T_g, \quad (17)$$

where $k = ⅔$ is $2h$ (°C) and $k = ½$ is h (°C). Figure 10 presents T_g versus h or $2h$. When T_g is higher, h is also higher. h is the increasing temperature required up to

T_m after T_g because of separation between main chains. The mechanism of h coincides with T_g basically, although there is the difference of magnitude by structure from eq. (17). The magnitude of the C—C bond component by the h side is handled in the same way as T_g, which is shown by inversely proportional α from the equation of the limit. An aliphatic group with a large α value indicates greater movement; an aromatic group with a small α indicates smaller movement. $T_g = 0°C$ is the base of calculation; for $T_g < 0°C$, it starts from $T_g = 0°C$ and reaches $-273°C$. From the relation between T_m and T_g, it is suggested that even below $T_g = 0°C$, with unchanged content, the straight line of thermal expansion extends to 0 K.

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