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# EXPERIMENTAL STUDY ON UPPER AND LOWER YIELD POINTS OF POLYMER SOLIDS

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## I. Introduction

Most amorphous high polymer materials which are so-called "hard" at room temperature, show very abnormal yield phenomena near room temperature. For example, the three-dimensional networks of phenol resin, epoxy resin, diallyl-phthalate homopolymer (DAP) and polyester resin under compressive load, and the ductile chain structures such as celluloid, polycarbonate under both tensile and compressive loads, show tardy yield phenomena with upper and lower yield points at room temperature.

Such a yield phenomenon is, however, very singular and can be observed in metals, only on mild steel near room temperature. Kuroda<sup>1)</sup> and others have proved that this is due to its characteristic crystalline structure.

While there are many works<sup>2-5)</sup> on such phenomena as "Melt Fracture", almost all the high polymer investigators<sup>6)</sup> have no interest in a very remarkable phenomenon that so-called "hard" amorphous high polymer materials almost have distinct upper and lower yield points near room temperature. The present study has its principal object to examine various conditions concerning the generation of upper and lower yield points in high polymer materials and to consider its generation mechanism in connection with its inner molecular structure.

## II. Material and Method for Experiment

Celluloid, an amorphous chain polymer, and cast epoxy resin, an amorphous three-dimensional network polymer were employed. Epoxy resin, shows remarkable tensile brittle fracture at room temperature; it leaves little permanent strain yet has distinct upper and lower yield points for compression, as can be seen from Fig. II-1. Celluloid, whose tensile "Fließkurve" is shown in Fig. II-2, behaves similarly under compression.

It is doubtful whether a true stress-strain curve from the upper yield point to the lower one can be obtained with a pendulum-type instrument because of the influence of inertia; consequently, the author devised a special dynamometer in which an electric resistance wire is utilized<sup>7)</sup> to measure the stress-strain curves. As this special dynamometer is designed so as to work always on compressive load only, a specimen and the dynamometer connected with a tension

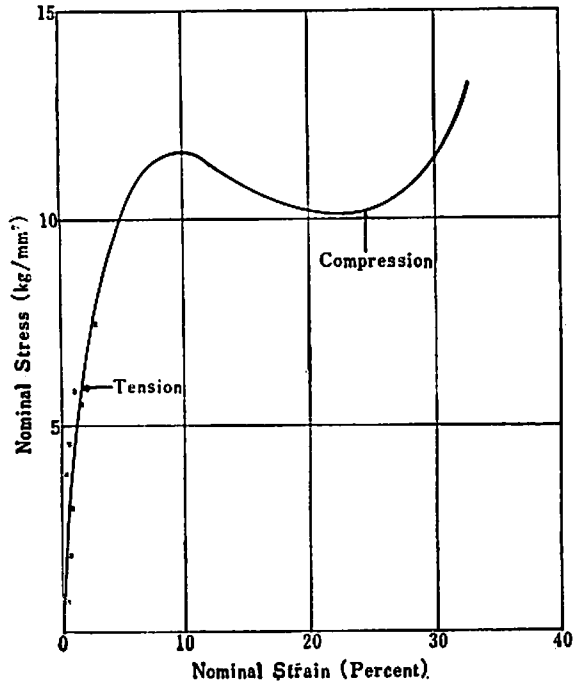


Fig. II-1. Nominal stress-strain curves for epoxy cast resins at room temperature.

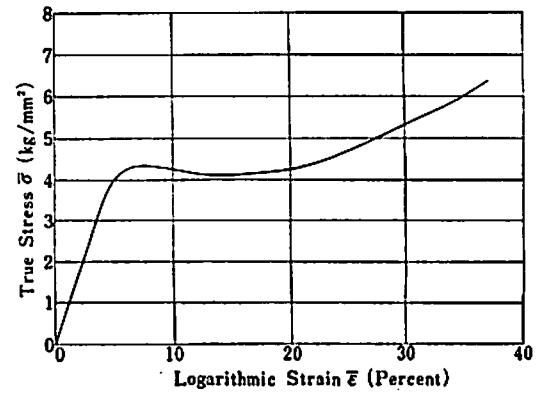


Fig. II-2. Tensile "Fließ-kurve" for celluloid at room temperature.

bar was used for tensile test. Although a thin teflon film (thickness 2 mil) between a cylindrical compressive specimen and the upper and lower pressure surfaces of a compression jig was used for antifricition, a slight drum-like deformation of the specimen was unavoidable in the range of large compressive strain.

### III. Form Effect of Cylindrical Compressive Specimen

As a form effect of a cylindrical compressive specimen,  $k_0 = d_0/h_0$  ( $d_0$ : the initial diameter of the cylindrical specimen,  $h_0$ : the initial height of the cylindri-

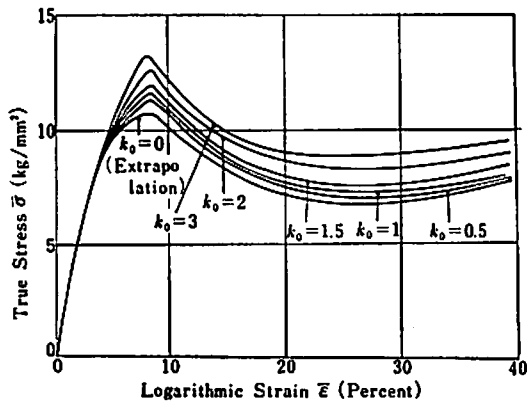


Fig. III-1. Compressive "Fließ-kurve" for epoxy cast resins with various values of  $k_0$ .

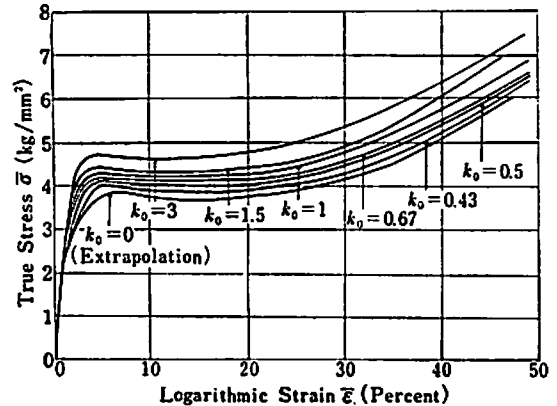


Fig. III-2. Compressive "Fließ-kurve" for celluloids with various  $k_0$ .

cal specimen) is taken. It is needless to say that any compression test cannot be carried out because of buckling in the case of a too small  $k_0$ , but it is supposed on the other hand that the appearance or disappearance of upper and lower yield points is influenced by  $k_0$  because of the increased friction resistance of pressure surface in the case of cylindrical compression specimen having large  $k_0$ . The effect of  $k_0$  on compressive stress-strain curve at room temperature are shown in Fig. III-1 and III-2. "Fließ-kurve" obtained by extrapolation of  $k_0 \rightarrow 0$  according to the Sachs' method<sup>8)</sup> are shown in these figures. Distinct upper and lower yield phenomena appear both for a disc-like specimen of  $k_0=3$  and for a cylindrical specimen of  $k_0=0.43$  or  $k_0=0.75$  to show that the form effect (value of  $k_0$ ) of cylindrical compression specimen does not influence the generation of the upper and lower yield points. Consequently, cylindrical compression specimens of  $k_0=1$  are used if not otherwise specified.

#### IV. Effect of Strain Rate

If the above cylindrical compression specimen is connected in series with the special dynamometer and the upper and lower pressure surfaces approach each other under a constant velocity, a compression experiment at a constant compressive rate  $r_c$  can be carried out. As this constant compressive rate can be changed, it is possible to examine the influence of compressive strain rate  $r_c$  on the upper and lower yield points. Fig. IV-1 and IV-2 show nominal stress-strain curves for epoxy cast resin and for celluloid under various strain rates  $r_c$ . It can be seen from these results that  $r_c$  is not so deeply connected with the appearance or disappearance of the upper and lower yield points, although it is

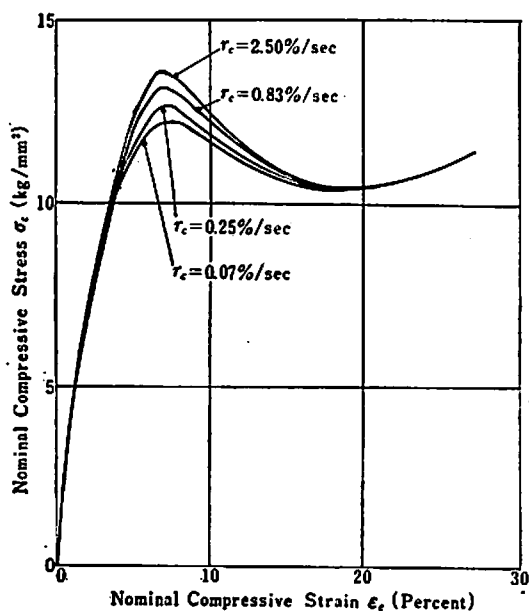


Fig. IV-1. Compressive stress-strain curves for epoxy cast resin under various strain rates  $r_c$ .

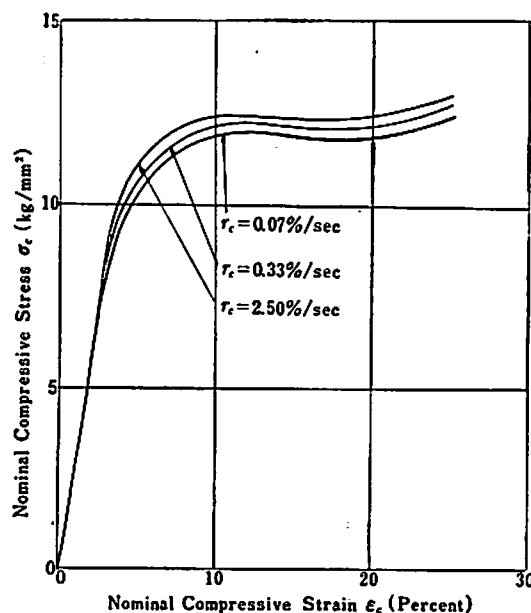


Fig. IV-2. Compressive stress-strain curves for cast resin of diallylphthalate homopolymer under various strain rates  $r_c$ .

sure that  $r_c$  has influence on the stress-strain curve to some degree. Consequently, both of tension and compression tests are, if not otherwise specified, carried out at about 0.07%/sec of mean strain rate for which the experiment is easily done.

### V. Effect of Temperature

As the yield point of mild steel becomes indistinct at a higher temperature, it is an interesting problem how the yield phenomena of high polymer materials at room temperature change with the increase of temperature. In particular, as the so-called secondary bonding force in a three-dimensional network polymer is easily dissociated to transit into rubber elasticity, it is natural that changes occur in the yield point and consequently in the "Fließ-kurve". The compressive "Fließ-kurve" for epoxy cast resin and for cast resin of diallylphthalate homopolymer (DAP cast resin) are shown in Fig. V-1 and V-2, while the temperature dependence of mechanical properties of each resin is shown in Fig. V-3 and V-4. As can be seen from these drawings, the yield points of both the resins ultimately disappear with the increase of temperature, although the transition into rubber slasticity is sharper for epoxy resin than for DAP resin because of the very narrow thermal dissociation temperature range for the former, for its type of secondary bonding force is different from that of DAP resin, hydrogen bonding force being the main constituent for the former, which is comparatively simple.

On the other hand, the compressive "Fließ-kurve" at elevated temperature for the chain polymer, celluloid, is as shown in Fig. V-5. This experiment could

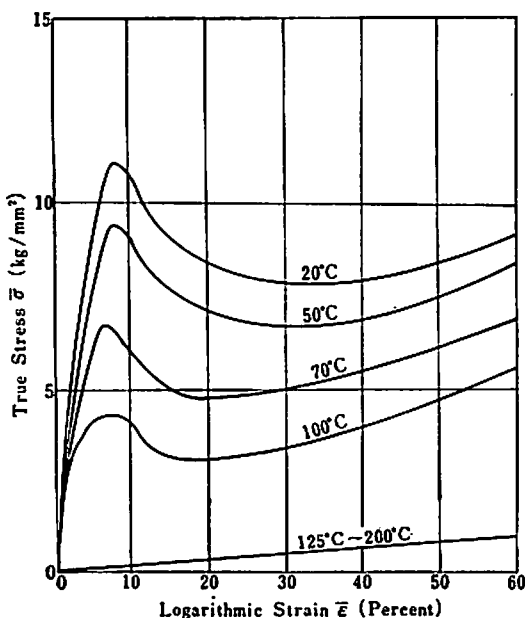


Fig. V-1. Compressive "Fließ-kurve" for epoxy cast resin at elevated temperatures.

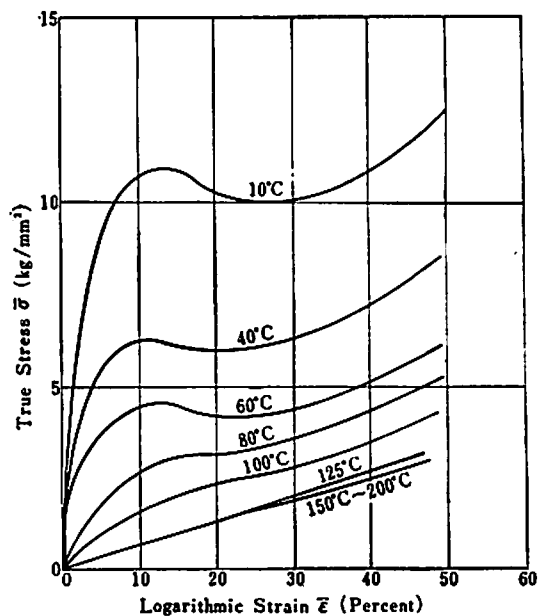


Fig. V-2. Compressive "Fließ-kurve" for cast resin of diallylphthalate homopolymer at elevated temperatures.

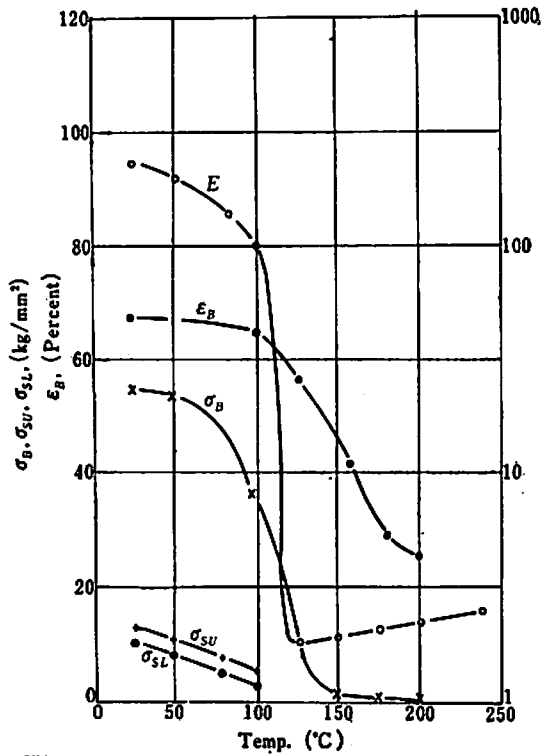


Fig. V-3. Temperature dependence of mechanical properties for epoxy cast resin.

$E$ : Modulus of elasticity,  
 $\sigma_B$ : Ultimate Compressive Strength,  
 $\epsilon_B$ : Compressive Strain at Fracture,  
 $\sigma_{su}$ : Upper Yield Point,  
 $\sigma_{sl}$ : Lower Yield Point.

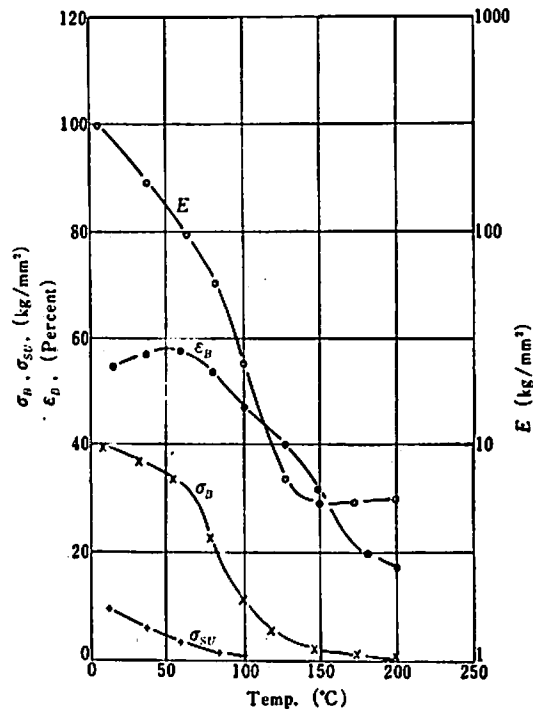


Fig. V-4. Temperature dependence of mechanical properties for cast resin of diallylphthalate homopolymer.

$E$ : Modulus of elasticity,  
 $\sigma_B$ : Ultimate Compressive Strength,  
 $\epsilon_B$ : Compressive Strain at Fracture,  
 $\sigma_{su}$ : Upper Yield Point.

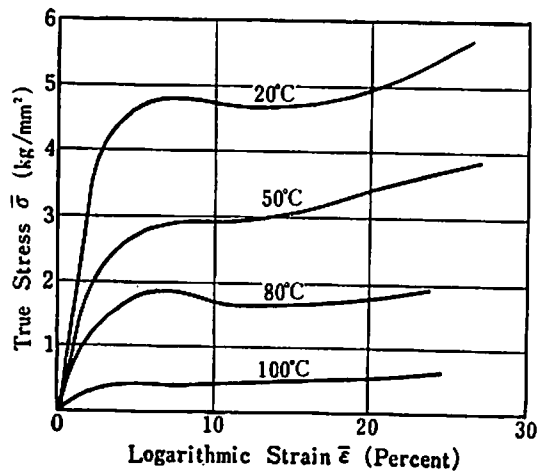


Fig.V-5 . Compressive "Fließ-kurve" for celluloid at elevated temperatures.

be carried out only until 100°C due to the inflammability of celluloid, but as can be seen from Fig. V-5, its yield points become indistinct with the increase of temperature. In this manner, the upper and lower yield points of solid polymer disappear if its secondary bonding force is dissociated thermally, so it can be understood that the existence of secondary bonding force is necessary for the appearance of upper and lower yield points.

## VI. Effect of Working Strain

Of course, the above-mentioned stress-strain curves are experimental results concerning such specimens as one having stable molecular structure, that is amorphous and non-oriented polymers. It is evident that the stress-strain curve, especially the appearance or disappearance of yield points is affected by the molecular orientation with working strain given to the specimen beyond its upper yield point. The effect of this kind of working strain on yield phenomena will be examined in the following.

Fig. VI-1 shows nominal tensile stress-strain curves for celluloid at room temperature. Whether or not the load was removed and immediately reapplied, as indicated by the arrows at 10%, 20%, 30% and 50% strain, the locus of maximum stress points attained during a cycle coincided exactly with the basic "Fließ-kurve". The same situation prevailed with compressive curves for epoxy resin, as shown in Fig. VI-2. The strain recovery slopes were approximately parallel to the original loading portion of the curve indeed, if one averaged the

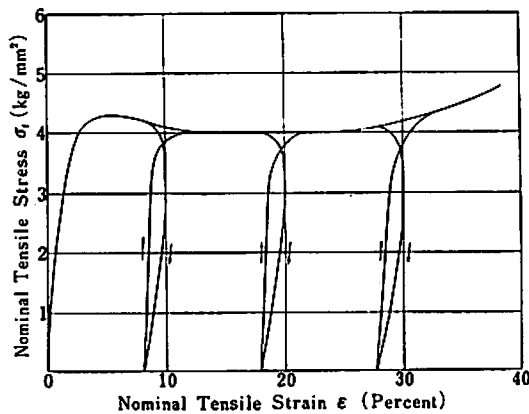


Fig. VI-1. Nominal tensile stress-strain curves for celluloid with the removal of load.

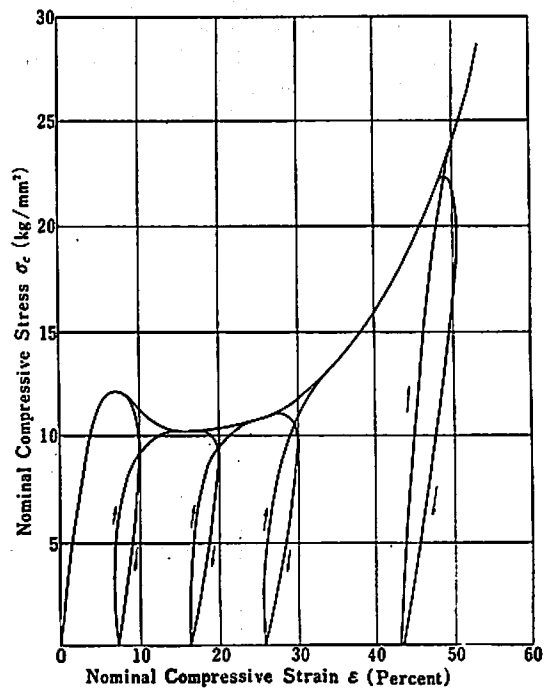


Fig. VI-2. Nominal compressive stress-strain curves for epoxy cast resin with the removal of load.

recovery and reloading curve values, the parallelism would be nearly perfect. Consequently, the maximum working strain  $\epsilon_m$  at the time of load removal exceeds the residual strain  $\epsilon_r$ . In this case, the celluloid shows little local contraction up to tensile breaking, and also anisotropy appears only to a slight degree. As the strains in the direction of plate thickness and width are consequently almost equal also in tensile test, the specimen removed of tensile load can be used in the following tension test as a specimen given with the maximum tensile working strain  $t\epsilon_m$ . On the contrary, because the drum-like deformation of cylindrical specimen ( $k_0=1$ ) is unavoidable in compression test and the form effect (value of  $k_0$ ) in cylindrical compression test effect the "Fließ-kurve", specimen given with the maximum compressive working strain  $c\epsilon_m$  is prepared by machining cylindrical compression specimen of  $k_0=1$  from the middle part of a specimen given with compressive working strain. At this time, there are following two cases according to whether a specimen for reloading is taken in the same direction as that of the initial load or opposite to it:

- (1) Appearance or disappearance of yield points by reloading in the same direction as that of working.

In order to investigate the behavior of Fließ-kurve, in particular yield points, when a specimen given with working strain is again given with strain in the same direction as before, tensile test is carried out on celluloid plate, while compressive test is done on epoxy resin. As can be seen from these results shown in Fig. VI-2 and Fig. VI-3, the upper yield point of unworked specimen, which lies near 7-9%, disappear if it receives such slight working strain as 10% of the maximum working strains  $\epsilon_m$ . That is, a specimen given with working strain over the upper yield point does not appear any upper or lower yield point under stress in the same direction. This disappearance of upper and lower yield points seems to be due to the fact that the orientation of molecules is further promoted under stress in the same direction if it is realized over the upper yield point.

The effect of working strain by reloading on mechanical properties is, however, different according to whether the reloading is tensile or compressive. As can be seen from Fig. VI-3, clear work hardening occurs in the same direction as that of the initial working strain for the tension of

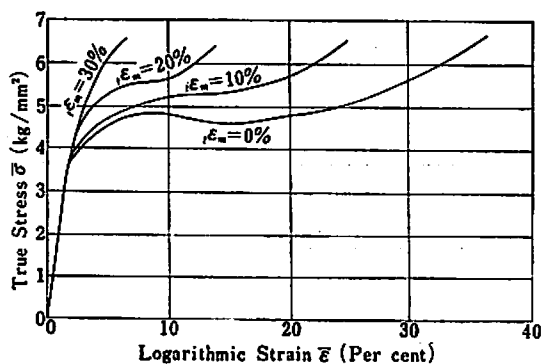


Fig. VI-3. Effect of initial tensile working strain  $t\epsilon_m$  on the tensile stress-strain curves for celluloid in the same direction.



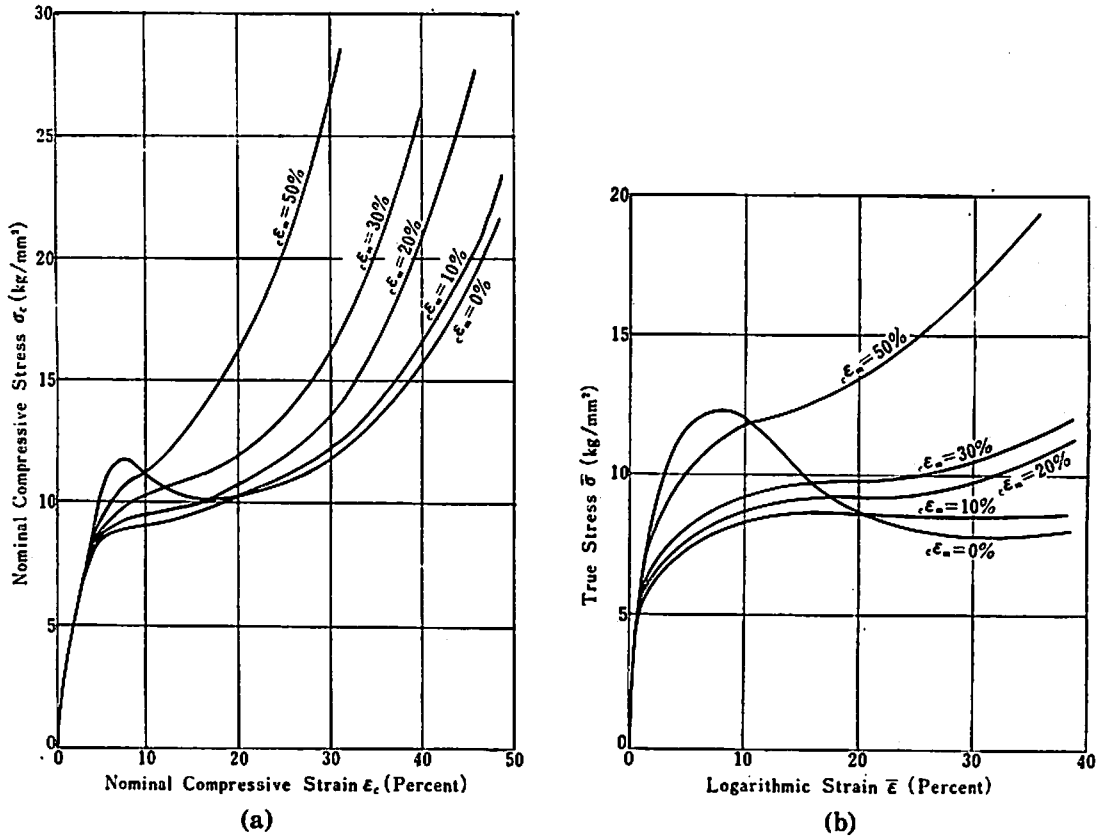


Fig. VI-4. Effect of initial compressive working strain  $c\epsilon_m$  on the compressive stress strain curves and "Fließ-kurve" for epoxy cast resin in the same direction.

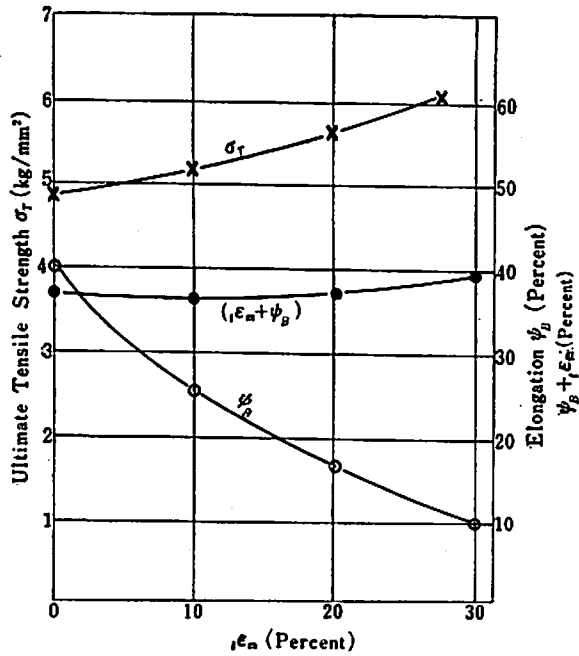


Fig. VI-5. The relation between initial tensile working strain  $i\epsilon_m$  and the mechanical properties of celluloid.

celluloid. In Fig. VI-5, of which abscissa is the maximum tensile working strain  $t\epsilon_m$ , various mechanical properties are shown. While the elongation percentage at fracture  $\phi_B$  is decreased with the increase of  $t\epsilon_m$ ,  $t\epsilon_m + \phi_B$  that is, the total elongation percentage calculated from the unworked specimen remains approximately constant regardless of the value of  $t\epsilon_m$ .

In the case of epoxy resin, on the other hand, the circumstances are considerably complicated as shown in Fig. VI-4. The upper yield point perfectly disappears by the initial maximum compressive working strain  $c\epsilon_m$ . And although the specimen given with  $c\epsilon_m$  suffers work hardening in a range of large strain, it does on the contrary work softening, this being clearly shown in a range of small strain of the stress-strain curve or Fließkurve in Fig. VI-4.

Although this tendency of work softening is gradually decreased by increasing  $c\epsilon_m$ , the work softening still appears in a range of small strain even in the case of the maximum value,  $c\epsilon_m = 50\%$  in this experiment. In order to demonstrate the effect of the maximum compressive working strain  $c\epsilon_m$  of epoxy resin on, its mechanical properties, the relation of  $c\epsilon_m$  and hardness is shown in Fig. VI-6. While the Shore hardness remains constant regardless of the maximum compressive working strain  $c\epsilon_m$  because the

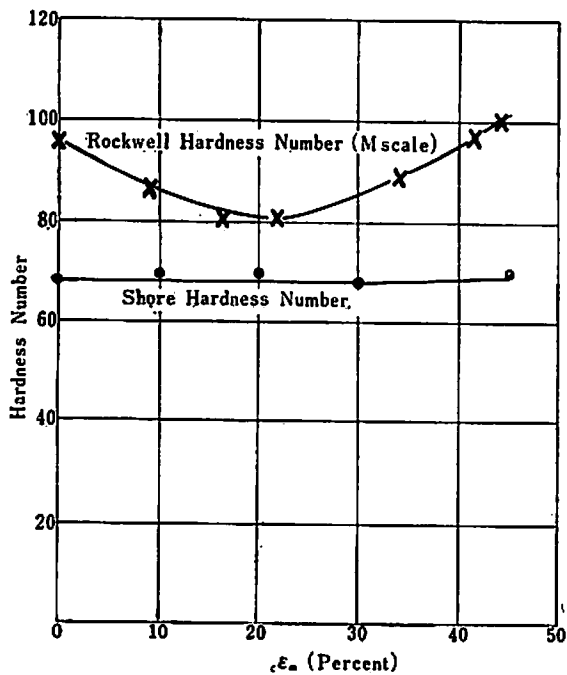


Fig. VI-6. The relation between initial compressive working strain  $c\epsilon_m$  and the hardness numbers of compressed epoxy cast resin.

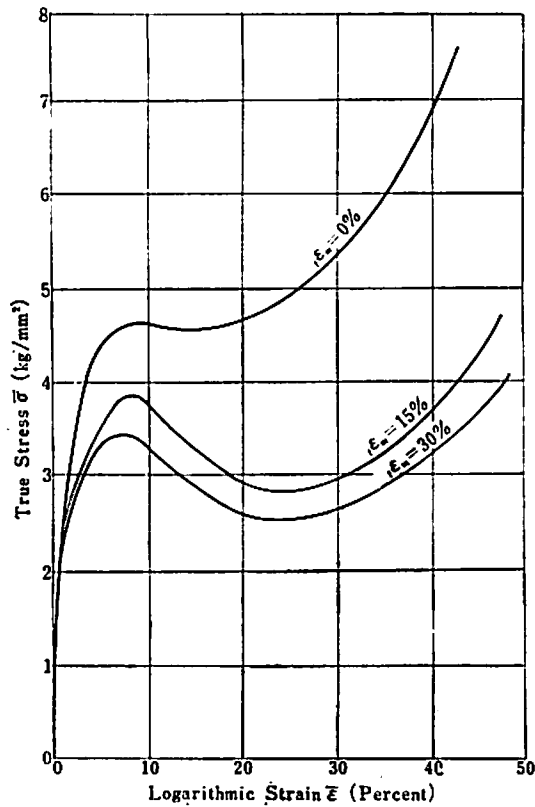


Fig. VI-7. Effect of initial tensile working strain  $t\epsilon_m$  on the compressive "Fließkurve" for celluloid.

elastic properties are not altered by  $c\varepsilon_m$ , the Rockwell hardness show a tendency of work softening in a range of the small maximum compressive working strain  $c\varepsilon_m$  and further that of work hardening with the increase of  $c\varepsilon_m$  by more than 40%. As can be seen also from the stress-strain curve or Fließ-kurve, such result as shown in Fig. VI-6 seems due to the comprehensive effects of complicated strains in which there are two cases of work softened and work hardened in each strain range dependent upon the various values of  $c\varepsilon_m$ , for Rockwell hardness test is affected by these effects. It is easy to understand that work softening shall occur especially at about 10% or 20% of the maximum compressive working strain  $c\varepsilon_m$  and at the same time the Rockwell hardness numbers are also decreased.

(2) Appearance or disappearance of yield points by reloading in the direction opposite or perpendicular to that of working.

The behavior of the specimens, in which molecular orientation appears due to working strain, will be investigated when loaded in the direction opposite or perpendicular to that of the working. As for celluloid plate, the results of experiment under compressive load on the cylindrical specimen machined of  $k_0=1$  obtained from the plate given with the maximum tensile working strain  $t\varepsilon_m$ , are shown in Fig. VI-7. As can be seen from this figure, the Bauschinger's effect appears, in which the elastic moduli, etc. are not altered in comparison with an unworked specimen, but the Fließ-kurve is lowered with the maximum tensile working strain  $t\varepsilon_m$  as observed in metal. And in comparison with unworked specimen, the upper and lower yield points are remarkably generated.

As epoxy resin suffers remarkable brittle fracture in tension, as shown in Fig. II-1, so it is impossible to investigate both the effect

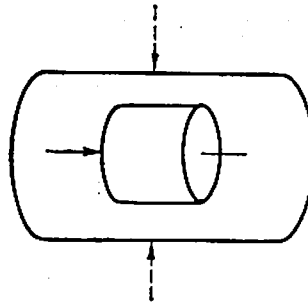


Fig. VI-8. Test specimen obtained in the transverse direction from large specimen initially compressed.

of tension and compression in the similar way as celluloid. Consequently, cylindrical compressive specimen is taken in the direction perpendicular to that of the initial working from drum-like specimen given with the maximum compressive working strain. That is, the cylindrical compressive specimen is machined, as shown in Fig. VI-8, so that it can be compressed in the direction perpendicular to that of the initial working strain. Stress-strain curves of the specimen given in this manner with the various maximum compressive working strain  $c\varepsilon_m$  are shown in Fig. VI-9. As can be seen from the results shown in Fig. VI-9 on epoxy resin

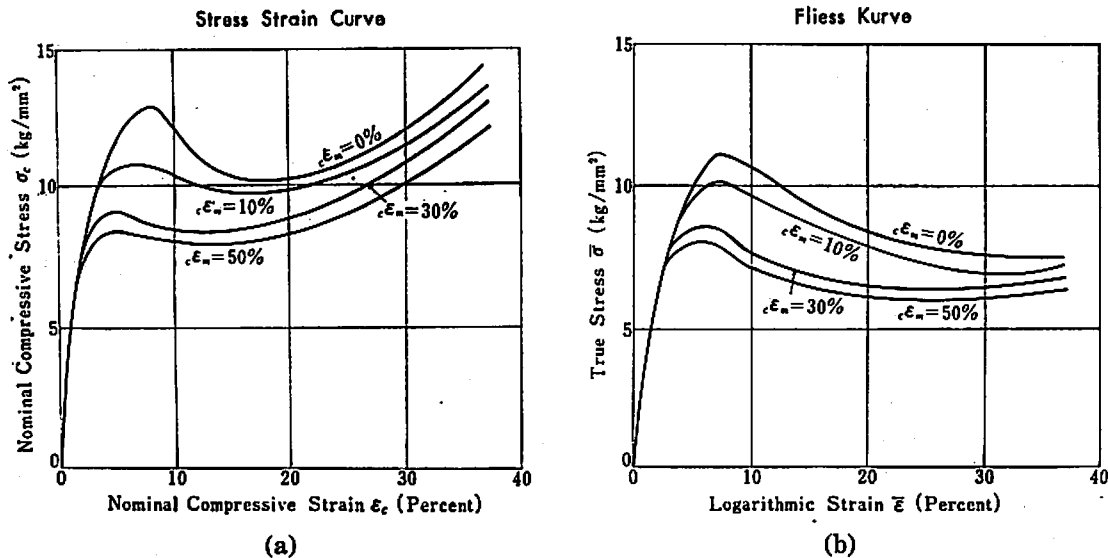


Fig. VI-9. Effect of initial compressive working strain  $\epsilon_m$  on the compressive stress strain curves and "Fließ-kurve" for epoxy cast resin in the transverse direction.

as well as that in Fig. VI-7 on celluloid plate, the Bauschinger's effect appears and the upper and lower yield points also clearly do, under the stress in such direction as to restore to the original stable orientation the specimen having molecular orientation by disturbing it.

As can be seen from these experimental results, no upper or lower yield point can be generated for polymer material having molecular orientation in the direction which promotes it. For the generation of upper and lower yield points in amorphous polymer, it is necessary that the material presents its original stable molecular structure or load is applied in such direction as to convert its molecular orientation, if any, into the original stable one by disturbing it.

## VII. Effect of Free Annealing of Worked Specimen

Cast epoxy resin compressed under the working strain of  $\epsilon_m = 50\%$  at room temperature is freely annealed at various temperatures for 48 hours. The compressive stress-strain curve and Fließ-kurve on compressive specimen of  $k_0=1$  machined in the same direction, obtained from the specimen strain-relieved to some degree by annealing, are shown in Fig. VII-1. From the figure, it can be seen that the stress-strain curve of compression-worked specimen are restored to respective original one with the increase of annealing temperature  $\theta_a$ . If it is annealed near the glass transition temperature of epoxy resin, the strain-recovery in the form of specimen is almost perfect and distinct upper and lower yield points generate again. These circumstances can be easily understood from the three-dimensional network polymer structure of epoxy resin which has no flow strain<sup>9</sup>).

Next, the tensile specimens of celluloid given at room temperature with the maximum tensile working strain  $\epsilon_m=30\%$  were freely annealed at  $50^\circ\text{C}$ ,  $75^\circ\text{C}$  and  $100^\circ\text{C}$ . The tensile Fließ-kurve and the effect on mechanical properties of such specimens reloaded in the same direction are shown in Fig. VII-2 and VII-3, respectively. In Fig. VII-3,  $\epsilon_r'$  means the strain-recovering rate by free annealing of tensile working strain, as shown in the following:

$$\epsilon_r' = \frac{al_i - al_f}{al_i - l_0} \times 100 (\%) \quad (\text{VII-1})$$

where

- $l_0$ : Initial gauge length in tensile specimen;
- $al_i$ : Gauge length in tensile specimen before annealing;
- $al_f$ : Gauge length in tensile specimen after annealing.

While  $\epsilon_r'$  becomes 100% at annealing temperature of about  $100^\circ\text{C}$  to complete apparently the strain recovery as can be seen from Fig. VII-3, the tensile Fließ-kurve does not completely restore to the original condition. This is shown in Fig. VII-2. This seems to some degree due to the insufficient annealing at  $100^\circ\text{C}$  because of the inflammability, but the main reason is believed to be that its molecular orientation cannot be perfectly removed by such degree of annealing as experimented, because of the existence of flow-strain even during the working at room temperature due to chain molecular structure. The upper yield point in question can, however, be satisfactorily observed in Fig. VII-2, in which the tensile specimen is softened by annealing and the elonga-

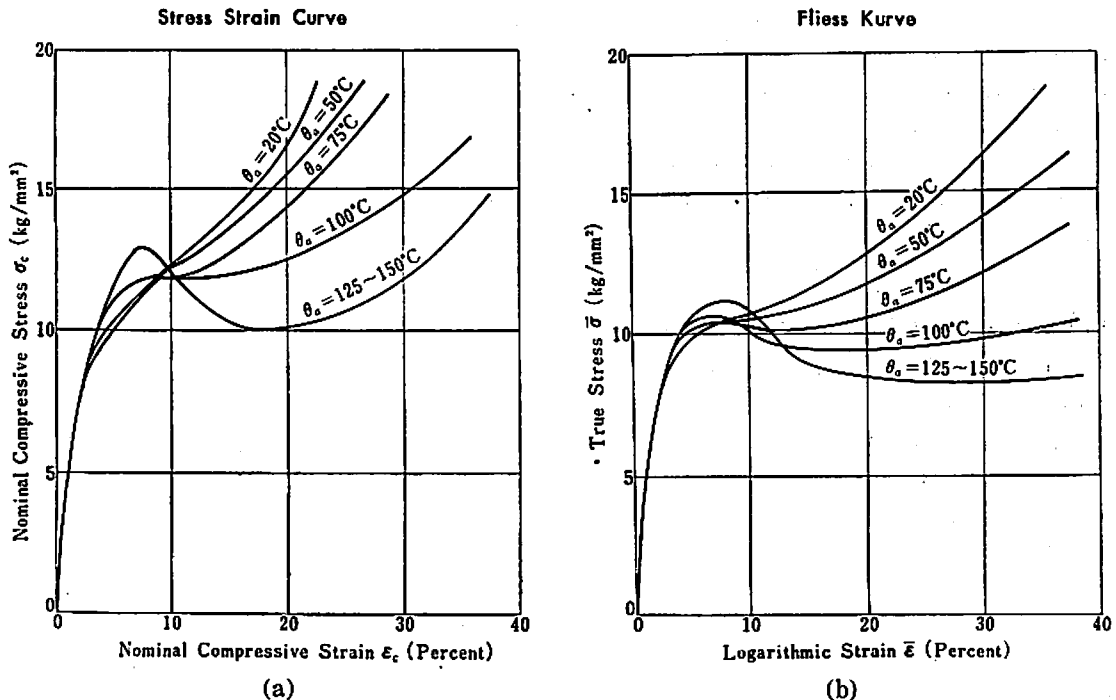


Fig. VII-1. Effect of free annealing on the stress strain curve and "Fließ-kurve" for epoxy cast resin compressed in the amount of  $\epsilon_m=50\%$ .

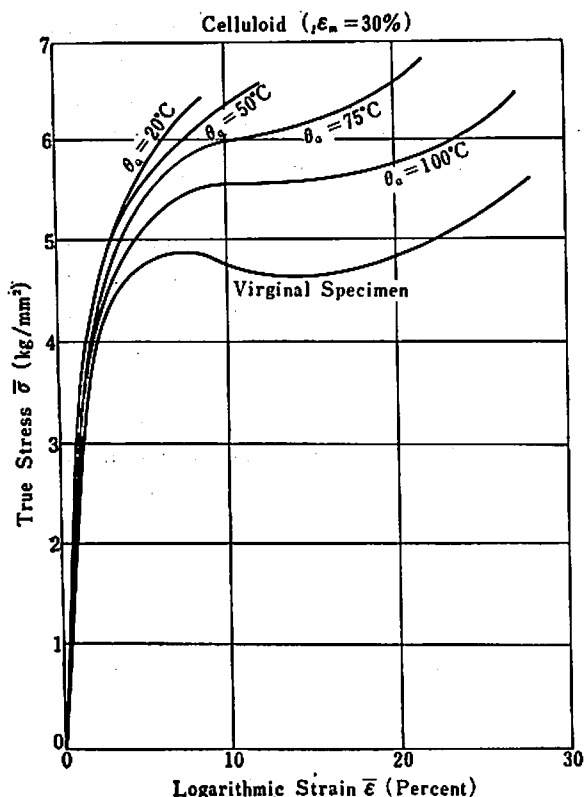


Fig. VII-2. Effect of free annealing on the tensile "Fließ-kurve" for celluloid pulluloid pulled in the amount of  $\epsilon_m = 30\%$ .

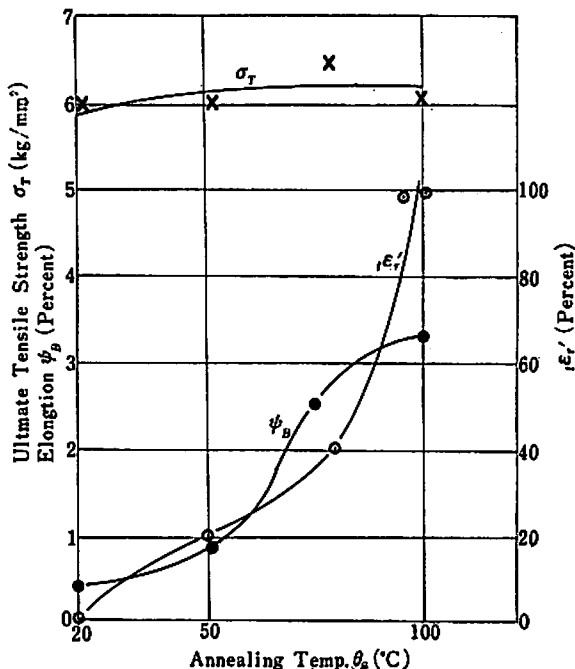


Fig. VII-3. Effect of annealing temperature  $\theta_a$  on the mechanical properties of pulled celluloid.

tion percentage  $\psi_B$  is increased with the increase of annealing temperature  $\theta_a$ . The fact that the tensile strength  $\sigma_T$  does not so change with the annealing temperature  $\theta_a$  has perhaps resulted from the concurrence of the specimen's softening and the increase of elongation percentage  $\psi_B$ .

### VIII. Effect of Restricted Annealing of Worked Specimen

The yield phenomena of specimens given with working strain were investigated after the specimens were restrictedly annealed so as not to permit freely the recovery of the initial working strain. That is to say, this corresponds to a case, in which a specimen is kept under working strain by hot working for a sufficient time and then slowly cooled. From the drum-like compressive specimens of epoxy resin slowly cooled from  $50^\circ$ ,  $75^\circ$  and  $125^\circ\text{C}$  of restricted annealing temperature, that is, hot working temperature  $\theta_w$ , under 50% of residual compressive working strain  $c\epsilon_{res}$ , cylindrical compressive specimens of  $k_0=1$  are prepared by machining. The stress-strain curves or Fließ-kurve on these worked specimens in the same direction of compression, which are shown in Fig. VIII-1 (a) and (b), do not show any upper and lower yield points. The specimen, which was sufficiently annealed at a temperature higher than the

transition temperature into rubber elasticity such as the hot working temperature  $125^{\circ}\text{C}$ , is considered to be that its secondary bonding force is perfectly dissociated to occupy the most stable configuration. Since neither upper nor lower yield points appear nevertheless as shown in Fig. VIII-1 (a) and (b), it can be seen that neither upper nor lower yield points can appear, if, beside secondary bonding force having sufficiently stable morphology, the primary bonding forces related to the secondary one have such high degree of orientation as residual compressive working strain  $c\epsilon_{\text{res}}$  of 50%, on the application of stress in the same direction as to promote the orientation. As shown in Fig. VIII-1(a) (b), stress-strain curve and Fließ-kurve on the specimen worked in the amount of  $c\epsilon_m = 50\%$  at room temperature are in a location lower than those on the specimen of  $c\epsilon_{\text{res}} = 50\%$  at hot-working temperature (restricted annealing temperature) of  $50^{\circ}\text{C}$ . This fact is of course due to the difference between the residual compressive working strain  $c\epsilon_{\text{res}}$  and the maximum working strain  $c\epsilon_m$ .

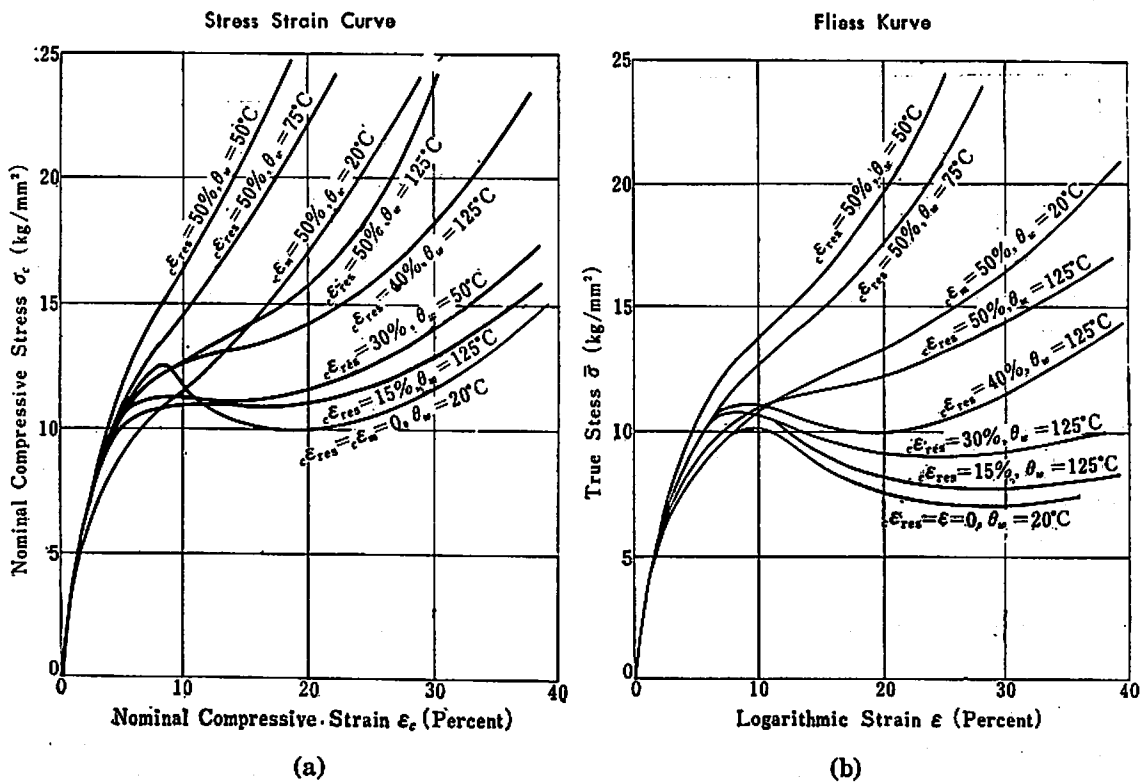


Fig. VIII-1. Effect of restricted annealing i.e. hot working on the compressive stress strain curve and "Fließ-kurve" for epoxy cast resin compressed.

Accordingly, at what degree of residual working strain, that is, of working strain to the primary bonding force in the range of smaller than 50%, may the upper and lower yield points appear when the secondary bonding force has sufficiently stable structure after the specimen is restrictedly annealed while being hot worked at such temperature higher than transition temperature to

rubber elasticity? On cylindrical compressive specimens of epoxy resin worked at hot working temperature (restricted annealing temperature) of 125°C and in the amount of  $\epsilon_{\text{res}} = 50\%$ , 40%, 30% and 15%, their Fließ-kurve under compression in the same direction are experimented at room temperature. As can be seen from these results which are also shown in Fig. VIII-1, the smaller the residual compressive working strain  $\epsilon_{\text{res}}$  is, the more the stress-strain curve is naturally lowered and the Fließ-kurve considerably changes with the orientation of the primary bonding force, although the secondary bonding force is stable. The upper yield point begins to appear when the residual compressive working strain  $\epsilon_{\text{res}}$  reaches near 40% and the distinct upper and lower yield points are generated at  $\epsilon_{\text{res}}$  smaller than 30%. Therefore, upper and lower yield points appear or disappear dependent on the degree of orientation of the primary bonding force, even if the secondary bonding force is sufficiently stable. Thus, it is necessary for the appearance of upper and lower yield points that beside the stable secondary bonding force, the molecular orientation of which principal constituent is such primary bonding force as to follow in the direction of stress is not so large.

### IX. Discussion on Yielding Mechanism

For the appearance of upper and lower yield points in solid polymer which is so-called "hard" near room temperature, it is necessary that both of the stable secondary bonding force and the primary bonding force, of which orientation degree is not so high, exist; or, if there is orientation, it is to be stressed in such direction as to make the polymer return to the original amorphous and stable molecular structure.

While the yield phenomenon of mild steel at room temperature is so sharp that it is called as landing, those of solid polymer are, as shown in the preceding sections in detail, always very slow and tardy. While the latter appears in connection with the primary bonding of heterogeneous polymer, it is mainly due to the mutual action of the secondary bonding which plays an important role in its behavior as material. This is, there are various lengths of molecular chain, which follow the molecular weight distribution in a chain structure polymer, while various dimensions of molecular group exist also in a network structure polymer, and these orient in the direction of stress suffered<sup>10)</sup>. In this case, fracture does not appear up to higher range of strain for the secondary bonding which accompanies the long molecular chain or the large molecular group. That is, as the molecular chain or group is long, even if the external strain  $\bar{\epsilon}$  is large, the strain per a secondary bond is so small as to make its fracture difficult. The secondary bond, which accompanies the short molecular chain or the small molecular group, fractures even under small strain. It is concluded that polymer shows tardy yield phenomena, because in correspondence with the molecular chain or group continuously distributed, the fracture of secondary bonds continuously occur with the increase of strain  $\bar{\epsilon}$ .

And while the stress which corresponds to the upper yield point is widely different dependent upon the various kinds of high polymer, the strain which corresponds to the point is approximately constant, 7-9% regardless of the differ-



ence in polymer. Among the fractures of various secondary bonds considered from the above-mentioned for the generation of the upper yield point, such secondary bond as to appear to exist usually in common with any polymer which is considerably hard from a mechanical point of view at room temperature and is considerably simple from a standpoint of molecular structure, for example, hydrogen bond, seems to fracture as described before.

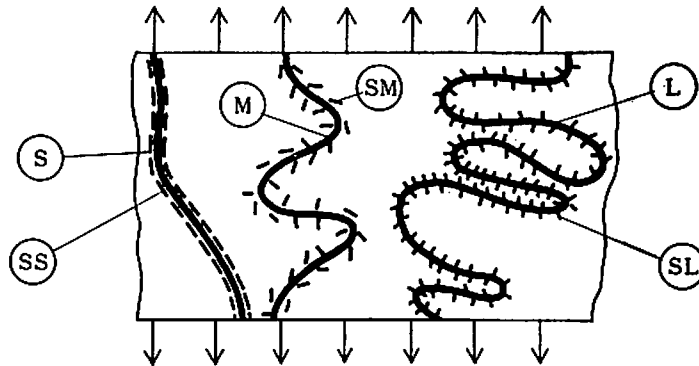


Fig. IX-1. Schematic representation on the fracture of secondary bonds associated with linear polymers of different molecular lengths.

- Ⓛ : Long molecular chain of primary bond.
- Ⓜ : Medium molecular chain of primary bond.
- Ⓢ : Short molecular chain of primary bound.
- ⓁⓁ : Secondary bounds associated with long molecular chain of primary bound.
- ⓈⓂ : Secondary bounds associated with medium molecular chain of primary bound and oriented more or less.
- ⓈⓈ : Highly oriented secondary bounds associated with short molecular chain of primary bound and just before their fracture.

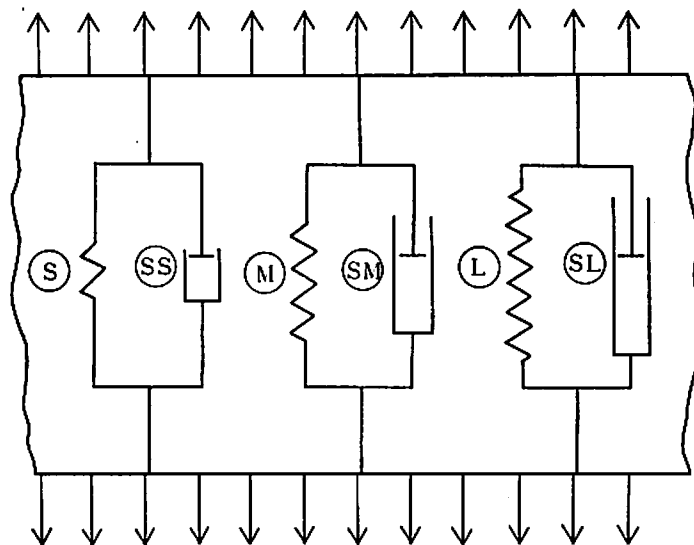


Fig. IX-2. Model Representation on yielding mechanism.

Next, this will be further explained on such a schematic figure as Fig. IX-1. When solid polymer exceeds a slight momentous elasticity of valence bond, the orientation of short molecular chain and consequently that of the secondary bonding which accompanies it appears. Let us take three molecular chains ③, ④ and ⑤ having different lengths as representatives, which are under elongated condition by strain  $\epsilon$ . As the molecular chains are initially amorphous, it is supposed that these are initially in the direction of  $45^\circ$  from that of tension. Fig. IX-1, in which three chain structures having different lengths and the corresponding secondary bonds under pulled condition are shown separately, represents that the shortest molecular chain ③ gradually orients in the direction of stress and its primary bonding molecular chain itself does not fracture but simple secondary bond which accompanies it orients is in such condition as just before fracture. At this time, the secondary bonds, which accompany the molecular chain ④, not to mention the longest molecular chain ⑤, gradually orient, but the external strain  $\bar{\epsilon}$  per a secondary bond is not so large as to cause fracture. With the increase of strain  $\bar{\epsilon}$ , however, the fracture of secondary bond begins from that which accompanies the molecular chain ④ and consecutively reaches at last to that which accompanies the long molecular chain ⑤. And when the most part of the secondary bonds which accompany the molecular chain near the length corresponding to the maximum value of molecular weight distribution fractures, the upper yield point appears. Thereafter the number of secondary bonds, which fracture, is gradually decreased. As the three-dimensional cross linking is not perfect also in a network polymer, there exist molecular groups of polymer having various dimensions so that its yield point generation mechanism is the same.

## X. Application

Next, let us consider some application. Fließ-kurve is schematically represented, as shown in Fig. X-1. This relation may be expressed in the following form:

$$\sigma = f(\epsilon) \quad (\text{X-1})$$

If it is hypothesized that the secondary bonding force has disappeared at room temperature, the above expression shows entropy elasticity. Consequently, the Fließ-kurve in this case can be expressed with the following relation of entropy elasticity, as shown with the dotted line in Fig. X-1:

$$\sigma_e = G\{(1+\epsilon) - (1+\epsilon)^{-2}\} \quad (\text{X-2})$$

where  $G$ : shear modulus. Thus, the stress difference  $\sigma_d$  between the formulas (X-1) and (X-2), that is, the hatched part in Fig. X-1, seems to correspond with the secondary bonding force:

$$\sigma_d = \sigma - \sigma_e = f(\epsilon) - G\{(1+\epsilon) - (1+\epsilon)^{-2}\} \quad (\text{X-3})$$

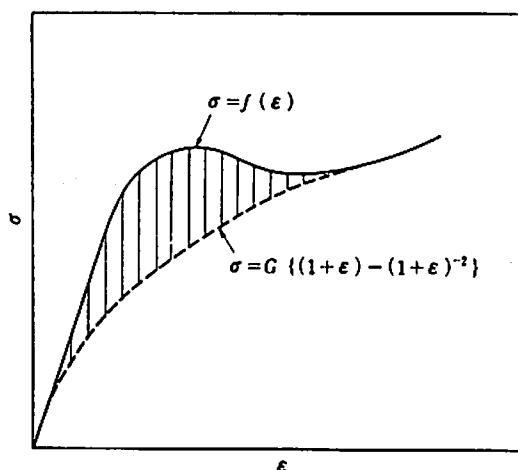


Fig X 1 Schematic "Fließ-kurve" for polymer solid at room temperature.

As the mechanical strength of high polymer at room temperature remarkably depends upon the secondary bonding force, it seems that the formula (X-3) shows a distribution of the mechanical strength of so-called "hard" solid polymer at room temperature. The mechanical properties of solid polymer at room temperature is never homogeneous in the similar way as the chemical non-homogeneity of its primary bond. The formula (X-3) shows the distribution of mechanical nonhomogeneity of polymer solid at room temperature.

As shown in Fig. IX-1, these resisting forces are proportional to the fracturing numbers of the secondary bonds at respective strain, which are, in a chain polymer, the product of the length  $W$  and the number  $F(W)$  of molecular chain, as expressed in the following.

$$\sigma_d = KWF(W) \quad (\text{X-4})$$

where  $W$ : Molecular weight,  $F(W)$ : distribution function of molecular weight, and  $K$ : constant.  $W$  is proportional to strain  $\epsilon$  in this yielding mechanism.

$$W = k\epsilon \quad (\text{X-5})$$

where  $k$ : constant. Hence  $F(W)$  may be analyzed from (X-4) using experimental data of  $\sigma_d$ . Since monomer and molecules of low molecular weight, which are often in a gas or liquid state at room temperature and normal pressure so as not to have solid strength, coexist in the polymer solid,  $K$  in (X-4) is not constant in reality. So, if mutual relation is studied to correct  $K$ , such a way to wide application would be developed that, from a stress-strain curve, both the distribution of mechanical properties and molecular weights in polymer solid may be predicted.

### Synopsis

An experimental research was carried out on the tardy but very distinct upper and lower yield points phenomena in amorphous polymer which is

so-called "hard" at room temperature. On epoxy cast resin as three-dimensional network polymer and on celluloid as linear polymer, the effects of temperature, strain rate, form of specimen, working, annealing, etc. on the appearance of upper and lower yield points were examined in detail. As the result, it was concluded that the most important factors in these effects are molecular orientation, the existence of secondary bonding force, etc. And the tardy but distinct upper and lower yield points of amorphous polymer appear due to the fact that the comparatively simple secondary bonding forces which accompany the heterogeneous primary bonding force suffer continuous but quantitatively non-uniform fracture with the increase of strain. It is consequently described that the microscopic distribution of mechanical strength of amorphous polymer at room temperature can be predicted from its Fließ-kurve.

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