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Study of the Ultimate Properties of Rubbers

(Report 1, Dependence of the Ultimate Properties of an SBR on Strain Rate and Temperature)*

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The time and temperature-dependent ultimate properties of an unfilled SBR was investigated at several strain rates and at ten temperatures between 40 and -57°C . The results obtained are as follows:

- 1) The time and temperature superposition of the ultimate strain of an unfilled SBR is almost the same as given by W. L. F.'s equation.
- 2) For the tensile stress at break, the superposition could not be admitted without consideration of the effect of the testing strain rate in respect to the local disproportion of deformation of the cold drawing, especially at low temperatures.
- 3) The time and temperature-independent failure envelope of unfilled SBR seems to suggest two different types of fracture mechanism. One will be predominant for the fracture of SBR when the material behaves rubber-like at high temperature and another when the material behaves viscoelastically at low temperature. And the substitution of predominance occurs at a particular condition of strain rate and temperature.

1. Introduction

Many rubbers have been made available for use in recent industrial fields as elastic, viscoelastic materials, etc. And it is known that these materials are often used under severe conditions such as at an extremely low temperature or a high strain rate, and under vibrational load. Thus, there have been several theoretical and experimental studies on the mechanical behaviors, the fracture mechanisms and phenomena of these materials by many investigators. Especially for amorphous polymers, like gum vulcanizates, at temperatures above the glass transition temperature T_g , the viscoelastic properties in small strains have been studied rather extensively and several molecular theories have been known. Among molecular theories, for example, there are Flory's⁽¹⁾ theory which treated the tensile strength of polymeric material depending on the number of the available network chains, Taylor-Darin's⁽²⁾ theory based on the chain orientation, and F. Bueche's⁽³⁾ study paying attention to uneven length of network chains, and so on. Moreover, Tobolsky and Eyring⁽⁴⁾

induced the theory of rate processes to fracture of polymeric materials, M. L. Williams⁽⁵⁾ extended the fracture theory for brittle material to viscoelastic one, and recently W. G. Knauss⁽⁷⁾ proposed a defect growth theory on viscoelastic material. But few systematic studies have been made of the dependence of ultimate properties of such materials on time and temperature. We are only able to know that the tensile strength and ultimate strain of polymeric or viscoelastic materials depend on both the temperature and strain rate.

Recent studies by T. L. Smith⁽⁶⁾ treat the time and temperature dependence of tensile strength and ultimate strain; moreover, they propose a unique failure envelope which does not depend upon either temperature or strain rate.

In this paper, the authors would like to treat phenomenologically the fracture mechanisms of viscoelastic materials on the basis of their temperature and strain rate dependency.

2. Experimental

2.1 Tensile specimen

The tensile specimen used in the experiment is shown in Fig. 1; it is a ring cut out from the sheet of unfilled SBR with a special cutter mounted in a press. These ring specimens have a rectangular

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cross section and an average value of the inside diameter 19 mm, an outside diameter 25 mm, thickness 3 mm.

Although JIS (Japan Industrial Standards) specifies dumbbell specimens for usual tensile tests on rubber-like or viscoelastic materials, the authors used the ring specimens mentioned above, for the following two reasons.

1) The ring specimen gives the constant strain rate tensile test easier than the dumbbell one. Since the dumbbell specimen has not a uniform cross section over the whole length of the specimen, it is very difficult to get a constant strain rate even if the cross-head is moved at constant speed.

2) For mounting the specimen to a chuck, the dumbbell one has to be pressed strongly on both sides of the specimen in order to protect the specimen from falling off by the friction between surfaces of chuck and specimen. At relatively low temperatures (but above T_g), these materials behave as if apparent plastic ones, the frictional force decreases and the specimen is easy to take off the chuck.

Specimen was extended with two pins covered by Teflon tubes which were provided to avoid the frictional force between specimen and pin, at constant speed, as shown in Fig. 2. If the diameter of pin were too small, the specimen would be broken by the contact face pressure between specimen and pin. And if it were too large, stress or strain concentration caused by frictional force between specimen and pin would rupture the specimen. The diameter of pin was chosen from the results of pre-experiments and the effect of the contact face pressure and stress concentration was ascertained to be almost negligible.

2.2 Chemical composition of material

The chemical composition of the material used in the experiment, which was indicated by weight ratio, and the condition of mixing and vulcanization are shown in Table 1. The rubber sheets contained 28 parts of Styrene and 72 parts of Butadiene by weight, and cured for 50 minutes at 153 °C (and

called Polysar Krylene NS).

2.3 Experiments

The ultimate tensile data were collected using a uniaxial tensile tester which could extend the ring specimen at constant rate of elongation in a range of rates 0.5~150 mm/min, and had the maximum load capacity 300 kg and the maximum stroke 400 mm. The temperature was controlled to an accuracy of 0.3 °C. Rate of elongation was measured by photo-transistor to record the rotation of the end axis of gear box. And the ultimate tensile data were collected at ten temperatures between 40 and -57 °C, and at five strain rates between 1.87×10^{-2} and 4.90 min^{-1} . These test temperatures were chosen with the consideration of viscoelastic behavior of the material which would be observed above the glass transition temperature, while the measurement of T_g using a dilatometer with silicone oil as the confining liquid gave an average value of -58 °C.

2.4 Calculation of ultimate strain and strain rate, and the actual stress at break

The calculations of ultimate strain and strain rate were carried out using equations

$$\epsilon_b = 2l/\pi d_i \quad (1)$$

$$R = 2s/\pi d_i \quad (2)$$

where ϵ_b is ultimate strain, R is strain rate min^{-1} , l is ultimate elongation mm, s is cross head speed mm/min, d_i is the inside diameter of the ring specimen mm. For measurement of ultimate strain, the inside diameter was used instead of the average diameter since as the ring was extended the inside was stretched more than the outside, and most ruptures were considered to occur from the inside of the ring.

The ultimate tensile strength was expressed by the actual stress at break. Assuming that there is no volume change in such rubber-like materials during the test, the actual stress at break would be given by the equation

$$\sigma_b = F_b(1 + \epsilon_b)/A_0 \quad (3)$$

where σ_b is rupture stress, kg/mm^2 ; F_b is the force at break, kg; A_0 is the undeformed sectional area of a ring specimen, mm^2 .

In the theory of rubber elasticity, the stress in rubber-like materials is caused by the increase of

Fig. 1 A ring specimen cut out from SBR sheet

Fig. 2 A ring specimen under loading

Table 1 Chemical composition of 28/72 SBR

28/72 SBR	Parts
Polysar Krylene NS	100.0
Kormolex No. 2 (Plasticizer)	5.0
Stearic acid	1.0
Zinc oxide	3.0
2-mercaptobenzothiazole (Accelerator)	1.1
Sulfur	2.1

Cured 50 min at 153 °C.

entropy which is due to intensity of the micro Brownian motion of the chain molecules. That is to say, the stress is proportional to the absolute test temperature. So, to make comparison of those stresses measured at different temperatures T_i , we have to multiply the stresses by T_0/T_i and standardize them according to the stress at a certain reference temperature T_0 (Standard Temperature).

In this paper, the standard temperature T_0 was chosen at 0°C , and the whole stress data were standardized. Moreover, since the data of the ultimate strength of strain were considerably scattered by the structural unevenness of the material, several tensile data from the same test condition were collected and treated with Kase's equation⁽⁸⁾ which was given by the statistical study on the fracture of rubber-like materials. When at the same test condition, the data of the ultimate strength were taken four times, the reliable average tensile strength was given by the equation

$$\bar{s} = 0.5s_1 + 0.3s_2 + 0.1(s_3 + s_4) \quad s_1 \geq s_2 \geq s_3 \geq s_4 \quad \dots\dots\dots(4)$$

3. Result and discussion

3.1 Dependence of ultimate strain on temperature and strain rate

At first, the strain rate dependence of ultimate strain ϵ_b at ten temperatures is shown in Fig. 3. It is seen that ϵ_b increases with an increasing strain rate and a decreasing temperature at temperatures above -20°C , and especially at -20°C , the maximum ultimate strain of the material (unfilled SBR) was shown. But at temperatures below -30°C , ϵ_b decreases gradually with an increasing strain rate and a decreasing temperature, and the curves of ϵ_b for strain rate look parallel except at -50 and -57°C where glass transition occurred especially at

Fig. 3 The variation of ultimate strain with strain rate R at ten temperatures between 40 and -58°C

high strain rate. Especially at -50 and -57°C , the data of ultimate strain show extremely low values and the specimen is broken without large deformation. Before glass transition occurs, cold drawing takes place during the tensile test especially at low temperatures below -40°C . When cold-drawing occurred, the stress-strain curves passed through a peak point at small strains, and then the stress either remained relatively constant or varied erratically until the whole material was cold-drawn. As the ultimate properties under such conditions appeared fairly erratic, we have to control temperature more precisely to discuss the properties of the material at the temperature near glass transition temperature T_g .

According to the studies on mechanical behavior of viscoelastic materials at small strains, it is usually known that the mechanical behavior at a high temperature and a high strain rate corresponds to that at a low temperature and a low strain rate, i.e. the time and temperature superposition will be recognized at least in the linear viscoelastic range. It is fairly questionable, however, whether the same time and temperature superposition as at small strains is able to happen at ultimate properties after large deformation of such materials. When, for ultimate strain data, the same or a certain superposition can be seen, we will be able to discuss generally the fracture processes over a wide strain rate range. Moreover, a recent Bueche's theory predicts that ultimate tensile data can be superposed by using the same shift factor a_T which is used to superpose viscoelastic data measured in small strains. So, we shifted along the abscissa which indicates the axis of strain rate, the curves shown in Fig. 3, which were the ultimate strains at different temperatures, and combined to yield composite plots. And then, we could get a smooth master curve of ultimate strain over a wide range of reduced strain rates as shown in Fig. 4.

The dependence of the shift factor a_T on temperature is shown in Fig. 5, which is reduced to a

Fig. 4 The master curve of ultimate strain with reduced strain rate Ra_T

reference temperature $T_0 = -8^\circ\text{C}$. A physical mean of the time and temperature shift factor a_T is roughly given by the next equation.

$$a_T(T) = t_T/t_{T_0} = R_{T_0}/R_T \dots \dots \dots (5)$$

where t_T and R_T are time and strain rate for the observation of mechanical behavior at temperature $T^\circ\text{K}$, t_{T_0} and R_{T_0} are time and strain rate for the observation of the same mechanical behavior at $T_0^\circ\text{K}$, i.e. the reduced time and strain rate.

The studies on the time and temperature superposition of viscoelastic materials have been made extensively and there are two typical theories of time and temperature superposition. One is W.L.F.'s equation⁽⁹⁾ and another is Arrhenius's equation. The former is expressed as follows

$$\log_{10} a_T(T) = -\frac{K_1(T - T_R)}{K_2 + T - T_R} \dots \dots \dots (6)$$

where $T_R^\circ\text{K}$ is the reference temperature which is usually chosen to be above glass transition temperature T_g by 50°K ; and K_1 , K_2 are the general material constants for amorphous polymers, $K_1 = 8.86$, $K_2 = 101.6$.

The latter is written as follows

$$\log_{10} a_T(T) = \frac{\Delta H}{2.303 R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \dots \dots \dots (7)$$

where ΔH is the activation energy of the relaxation process of the material in viscoelastic temperature range. R is the gas constant, and $T_0^\circ\text{K}$ is a reference temperature. The broken line and the solid line in Fig. 5 show respectively W.L.F.'s and Arrhenius's equation, which were calculated from Eqs. (6), (7) with T_s or $T_0 = 265^\circ\text{K}$. And the experi-

Fig. 5 Experimental values of the time and temperature shift factor $\log a_T$ of ultimate strain, compared with W.L.F.'s and Arrhenius's equation

mental values of a_T give -58°C for T_g which is in good agreement with -58°C obtained dilatometrically. Especially at low temperature which is near T_g , the time and temperature shift factor seems not to depend upon temperature, and to be constant.

3.2 Dependence of the stress at break on temperature and strain rate

Now, the dependence of the actual stress at break on strain rate is shown in Fig. 6. Figure 6 shows plots of $\log (T_0/T)\sigma_b$ vs. $\log R$, where T_0 is the standard reference temperature 265°K , T the temperature of measurement in $^\circ\text{K}$, and R the strain rate in min^{-1} . As mentioned previously, the stresses at break are multiplied by the factor T_0/T , since the elastic forces in polymeric chains are proportional to the absolute temperature according to the statistical theory of rubber-like elasticity. And this factor T_0/T should be included before tensile strengths at different temperatures are compared.

It is seen that $(T_0/T)\sigma_b$ increases generally with an increasing strain rate and a decreasing temperature except at relatively low temperatures where cold drawing occurs. According to another experiment on cold drawing, which was carried out more precisely by authors, the stresses at break and ultimate strains after cold drawing happened seem to decrease with an increasing strain rate and a decreasing temperature. Then, as the curves for dependence of the stress at break on strain rate at relatively low temperatures have respectively maximum values, they can not be superposed to combine uniquely into a smooth composite master curve. In this range of temperatures, it is easily supposed that we must

Fig. 6 The variation of actual stress at break with strain rate R at ten temperatures between 40 and -58°C

consider the difference of mechanical behaviors between at small strain and at large deformation. But there is a little knowledge of the mechanisms in the processes of polymeric chains at large deformation. Then we define the available stress at break by next equation.

$$\sigma_R = \sigma_b \times f(R); f(R) = \exp(\alpha R^\beta) \dots \dots \dots (8)$$

where α and β are material constants and $f(R)$ is a function which indicates the effect of tested tensile strain rate. For unfilled 28/72 SBR, α and β are given inductively from Fig. 7, the values being $\alpha = 0.4$, $\beta = 0.45$. Fig. 8 shows plots of $\log(T_0/T)\sigma_R$ vs. $\log R$. The available stress at break σ_R is shifted to yield a composite master curve, and then we can find the time and temperature superposition for tensile strength of polymeric materials. The time and temperature shift factor plotted against temperature is shown in Fig. 9, and it looks to be almost the same as the shift factor which was obtained in the case of ultimate strain. Now, we are able to have a discussion on the dependence of ultimate strength of viscoelastic materials on strain rate and temperature generally. But the authors, unfortunately, have too little knowledge of the mechanical or molecular behaviors of polymeric chains at large deformation to give a clear explanation for the available stress at break or the effect

Fig. 7 The master curve of stress at break with reduced strain rate Ra_T . The branches at each temperatures are observed

Fig. 8 The master curve of the available stress at break with reduced strain rate R

of actual strain rate. And it is fairly interesting that the reduced strain rate where the maximum ultimate strain occurs was almost identical with that where the branches of the curves of stress at break begin to be observed.

3.3 Failure envelope of 28/72 SBR

Plots of the tensile stresses at break against the associated ultimate strain which were measured at several temperatures and strain rates are shown in Fig. 10. According to a recent T. L. Smith's study,

Fig. 9 Experimental values of the time and temperature shift factor $\log a_T$ of stress at break, compared with W. L. F.'s and Arrhenius's equation

Fig. 10 Failure envelope for 28/72 SBR from the data determined at various strain rates and temperatures

the ultimate properties of amorphous polymers are characterized by a "failure envelope," which is independent of time and temperature effects and also appears to be independent of the type of test used to determine the ultimate properties, though as mentioned previously, the tensile stress at break and the ultimate strain of a polymeric material signify individually a remarkable dependence on the test conditions such as temperature or strain rate. In conclusion, the failure envelope is defined only by the tensile stress at break and the associated ultimate strain, and the equilibrium stress-strain curves at glass-like and rubber-like states of the material.

As shown in Fig. 10, the rupture points in the temperature and strain rate range used in the test, moved counterclockwise around the failure envelope either as strain rate is increased or as the test temperature is decreased. In Fig. 10, several rupture points at same temperature indicate the effect of strain rate. It seems to be likely, in view of the fact that the time and temperature superposition is recognized for the ultimate properties of tested material, that movements of the rupture points with an increasing strain rate and a decreasing temperature are qualitatively identical and, connected together, these points make a unique failure envelope.

At relatively high temperatures ($40^{\circ}\text{C} \sim -10^{\circ}\text{C}$), both the ultimate strain and the stress at break increased with an increasing strain rate and a decreasing temperature, but in low temperature range (below -20°C), the ultimate strain only decreased with an increasing strain rate and a decreasing temperature, in contrast with the fact that the stress at break increased. It may be concluded that one ultimate strain corresponds to two different stresses at break, which belong to high and low temperature ranges respectively. This seems to suggest that the fracture and large deformation processes of such materials are different from rubber-like state at high temperatures to partially plastic (viscoelastic) state at low temperatures, moreover in glass-like state. To show details of this phenomena, the stress strain curves elucidating the associated rupture point at a certain strain rate ($R=1.25 \text{ min}^{-1}$) are shown in Fig. 11, over a wide range of temperatures. In rubber like state at relatively high temperatures, the stress strain curves at certain constant strain rates seem to be almost the same and the rupture points merely move along the stress strain curve which reaches the maximum ultimate strain. But at low temperature range (below -10°C or -20°C), the stress strain curves extremely change their shapes all over the curves. In view of the tendency of rupture point movement and the changes of the

stress strain curve, there seems to be two different factors which affect the ultimate properties of such materials. One of them is predominant when the material is in rubber-like state at high temperature, and another is, when the polymeric chains which compose the material are restricted by its own viscosity, of course, though the internal viscosity of the material is caused by the micro Brownian motion which is proportional to the absolute temperature. And the two predominances change their place with each another at the temperature where the maximum strain is observed. If we confined the discussion of the definition of fracture to the ultimate strain only, it would be conceivable that a correlative retardation of the accumulation of microscopic defects to rupture at the actual strain rate draws the ultimate strain long with an increasing strain rate especially in high temperature range (and a decreasing temperature). By contrast, in low temperature range below the temperature at which the maximum ultimate strain is observed, stress or strain concentration around a small defect which would be caused by cold drawing and others, seems to shorten the ultimate strains. But there are many unsatisfactory explanations of the measured data, and many studies have to be made to investigate the fracture mechanisms of polymeric or viscoelastic materials.

4. Conclusion

It was not so difficult to conceive that the ultimate tensile properties of polymeric or viscoelastic materials, which were usually indicated by ultimate strain or tensile stress at break, would show the same remarkable time and temperature dependence as the mechanical behavior at small deformation. The results obtained in this experiment are as

Fig. 11 Stress-strain curves for 28/72 SBR with rupture points, from the data determined at various temperatures and at a certain strain rate $R=1.25 \text{ min}^{-1}$

follows:

1) Both the ultimate strain and the stress at break depend remarkably upon temperature and strain rate.

2) In respect to the ultimate strain, there is a remarkable interrelation between dependences of the ultimate strain on temperature and on strain rate. And the time and temperature shift factor which interrelates both dependences, is almost the same as the shift factor in W. L. F.'s or Arrhenius's equation which is used at small strains.

3) For the tensile stress at break, the time and temperature superposition could not be admitted simply, without consideration of the effect of the testing strain rate in respect to the local disproportion of deformation or the cold drawing, especially at low temperatures. Then the effect of testing strain rate $f(R)$ and the available stress at break σ_R were defined and a time and temperature shift factor which was almost same as the one of the ultimate strain was obtained.

4) The time and temperature-independent failure envelope of unfilled SBR seems to suggest two different types of fracture mechanism. One will be predominant for the fracture of SBR when the material behaves rubber-like at high temperature and another when the material behaves viscoelastically at low temperature. And the substitution of

predominance occurs at a particular condition of strain and temperature.

Particularly, the physical meaning of the available stress at break σ_R has not been explained clearly yet, and more precise investigation will be accomplished to discuss cold drawing or the disproportion of deformation in near future.

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