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A Theory of Pseudo Cross-Link

5. Rupture

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Summary

The rupture of the polymer solid is classified into three categories: 1. A brittle fracture takes place at very rapid or low temperature extension due to the break-down of the pseudo cross-link. Craze or crack occurs. 2. An elastic rupture occurs at ultimate elongation of the chain due to the break-down of the primary bond. 3. A plastic rupture occurs at elevated temperature when the resistance due to viscous flow predominates over the elastic force. For cases 1 and 2 the elongation at break decreases while the strength increases as the rate of extension increases. For the case 3 both the elongation and strength increases. Failure envelope, optimum cure, effect of filler, segmented rubber and rupture energy are discussed theoretically.

Introduction

The rupture of polymers is a very complicated problem, because the rupture is much affected by the condition such as the rate of deformation and the temperature. There are various modes of rupture; very rapid deformation gives rise to the fracture whereas the deformation at very slow or very high temperature results in other type of rupture or the plastic rupture. For vulcanized rubber rupture occurs at the point near the ultimate extension also affected by the rate of extension and temperature. T.L. Smith[1] proposed failure spectra giving relations of the strength and the elongation at break with the rate of extension and also a failure envelope between the strength and the extension at break.

There may be various causes of rupture. In addition to the abscission of the primary bond the cohesion of the molecule may play an important role. The author proposes a theory of rupture based on a pseudo cross-link concept which is to be available for various types of rupture

Theory

As pointed out by T.L. Smith[1] the dependency of strength on the extension rate or temperature is similar to the relaxation spectrum, and this fact suggests that the mode of rupture is closely associated with the state of the polymeric material: the brittle, viscoelastic and plastic ruptures seem to correlate with the glassy, viscoelastic and viscous states of the polymer solids, respectively.

On the other hand, the pseudo cross-link theory suggests two types of bond rupture as a cause of failure: One is the abscission of the primary bond and the other is rupture of pseudo cross-link. The latter induces the flow of chain at slow extension due to the regeneration of the link, but the break-down of the pseudo cross-link remains as the craze in the glassy state, which grows up to the crack or failure. As the result, three types of rupture are proposed. 1. The brittle fracture occuring at the very rapid or low temperature extension or impact, at which the rupture of pseudo cross-link is a main mechanism. 2. The elastic rupture occuring at a moderate rate extension and temperature at which the abscission of the primary bond of the molecular chain occurs. 3. The plastic rupture for non- or semi-vulcanized rubber occuring at elevated temperature and/or at very slow extension, at which the chain flow is a predominant process and the rupture occurs when the plastic force predominates over the elastic force.

1. Brittle fracture

It is assumed that the abscission of the primary or secondary bond occurs at the ultimate elongation. In the very rapid deformation and/or at very low temperature, the polymer solid behaves as glassy and at this state a large number of pseudo cross-link exists, whose break-down is a cause of failure. The ultimate elongation of the chain, λ, is given as a square of the chain length n, and as a function of the remaining pseudo cross-link as

$$\lambda = n^{1/2} = (N/\nu_0 e^{-k't})^{1/2} \qquad (1)$$

where ν_0 is the initial number of the pseudo cross-link and k' is its rate of break-down. The chain extension λ also correlates with the extension of the specimen α as

$$\lambda = \alpha e^{-k't/6} \qquad (2)$$

Combining equations (1) and (2), it follows that

$$\alpha = (N/\nu_0)^{1/2} \exp[(2/3)\{k'(\alpha - 1)/\dot{\alpha}\}]$$

or

$$\alpha = (N/\nu_0)^{1/2} \frac{1 - (2/3)(k'/\dot{\alpha})}{1 - (N/\nu_0)^{1/2}(2/3)(k'/\dot{\alpha})}$$

$$\alpha \cong (N/\nu_0)^{1/2}[1 + \{(N/\nu_0)^{1/2} - 1\}(2/3)(k'/\dot{\alpha})] \qquad (3)$$

Equation (3) indicates that the extension at break decreases as the rate of extension increases or the temperature or k' is lowered. There is a critical value given by

$$k'/\dot{\alpha} < (3/2)(\nu_0/N)^{1/2} \qquad (4)$$

The strength at break may be given by the elastic force at the ultimate extension, but the force at this point is steeply increased to infinitive. On the contrary, if the strength at break is determined by the breaking force of the pseudo cross-link, it can be demonstrated by a product of the following factors. The number of pseudo cross-link remaining after the extension is given by

$$\nu = \nu_0 e^{-k't} \qquad (5)$$

The bond force of the pseudo cross-link is given as

$$d(-\Delta H)/N_0 \ell^2 d\ell \simeq -\Delta H/V \qquad (6)$$

where ΔH is the molar heat of formation of pseudo cross-link whose diameter and molar volume are ℓ and V, respectively, N_0 being the Avogadro's number. $-\Delta H$ is almost 1360 cal and V is 28 cm^3 for the $(CH_2)_2$-unit of polyethylene. The fraction of pseudo cross-link breaking is given by a probability of bearing the energy larger than the bond energy $-\Delta H$ when the total energy is $\lambda^2 RT$. And λ^2 is equal to N/ν at the ultimate extension. As a result, the fraction is

$$\exp\{-(-\Delta H/\lambda^2 RT)\} = \exp\{(\nu/N)(\Delta H/RT)\} \qquad (7)$$

and the force of breaking of the specimen f is

$$\begin{aligned} f &= (RT/V)(-\Delta H/\lambda^2 RT)\exp(\Delta H/\lambda^2 RT) \\ &= (RT/V)(\nu/N)(-\Delta H/RT)\exp\{(\nu/N)(\Delta H/RT)\} \qquad (8) \end{aligned}$$

Equation (8) indicates that f is increasing with increasing λ to some extent and attains a maximum f_{max}

$$f_{max} = RT/eV \qquad (9)$$

at

$$\lambda^2 = N/\nu = -\Delta H/RT \qquad (10)$$

For a $(CH_2)_2$-unit, $-\Delta H$ is 1.36 Kcal, λ becomes 1.5 and ν/N becomes 0.66. The brittle fracture induces craze or void at the first stage which gives rise to crack or failure. However, craze is healed at elevated temperature. The high impact strength of the block polymer is ascribed to prevent the growth of craze to crack which is healed.

2. Viscoelastic and elastic rupture

In the extension of modelate rate a significant fraction of pseudo cross-link is released or flowed and the ultimate extension λ is given as a function of the remaining pseudo cross-link as equation (11) instead of equation (2)

$$\lambda = \alpha \exp(-k't/6 - k'\phi t) \qquad (11)$$

where $\exp(-k'\phi t)$ is a factor due to the flow of chains, and ϕ is a fraction of flowing chain given as

$$\phi = \nu_B/\{\nu_e + (\nu_0 - \nu_e)\exp(-k't)\} = \nu_B/\nu_2$$

Here, ν_2 is the remaining pseudo cross-link and ν_B is the flowing chain or cross-link. The remaining pseudo cross-link is given by equation (12) instead of equation (1)

$$\nu_2 = \nu_e + (\nu_0 - \nu_e)\, e^{-k't} \qquad (12)$$

However, the regenerated pseudo cross-link corresponding to ν_e does not form at the same position as that broken but at the position after flow and therefore the actual value is given not by equation (12) but by equation (1). As a result, equation (3) is rewritten as

$$\alpha = (N/\nu_0)^{1/2}[1 + \{(N/\nu_0)^{1/2} - 1\}(2/3 + \phi)(k'/\dot{\alpha})] \qquad (13)$$

On the other hand, the size of pseudo cross-link b to be broken increases and if the bond energy of the b-size pseudo cross-link, i.e. b($-\Delta H$) is larger than the primary bond energy, i.e. D, the primary bond is broken. However, the number of remaining chain is very small at this stage and the break-down of the primary bond is to be considered. In the case of vulcanized rubber, the remaining chain or cross-link is the sum of primary and pseudo cross-link, and the following equation holds.

$$\alpha \exp\{-(k'/6 + k'\phi/2)t\} = \{N/(\nu_1 + \nu_0 e^{-k't})\}^{1/2}$$

It is approximated to equation(14) when ν_1 is larger than ν_2

$$\alpha = (N/\nu_1)^{1/2} e^{\bar{k}t}\{1 - (1/2)(\nu_0/\nu_1)\, e^{-k't}\} \qquad (14)$$

$$\cong (N/\nu_1)^{1/2}(1 + \bar{k}\alpha/\dot{\alpha})\{1 - (1/2)(\nu_0/\nu_1) + (1/2)(\nu_0/\nu_1)(k'\alpha/\dot{\alpha})\}$$

$$\alpha \cong (N/\nu_1)^{1/2}\{1 - (1/2)(\nu_0/\nu_1)/(1 - \bar{k}'/\dot{\alpha})\} \qquad (15)$$

where $\bar{k}'$ is $(k'/6 + k'\phi/2)$. The strength at break depends mainly on the primary bond and is represented as

$$f = (RT/V)(D/\lambda^2 RT)\exp(-D/\lambda^2 RT)$$

$$= (RT/V)\{(\nu_1 + \nu_2)/N\}(D/RT)\exp[\{-(\nu_1 + \nu_2)/N\}(D/RT)] \qquad (16)$$

Equation (16) attains a maximum value, i.e., RT/eV at $\lambda = (D/RT)^{1/2}$. Taking D and RT to be 80 Kcal and 0.6 Kcal λ becomes about 10 and the remaining cross-links close to ν_1/N becomes 0.01. The latter implys that an optimum cure is about 1 %.

3. Plastic rupture

At elevated temperature non- or semi-vulcanized rubber is elongated accompanied by the flow of chain. The elastic force f_{el} is much decreased with increasing viscous flow due to the decrease of the chain extension and cross-sectional area and is expressed as

$$f_{el} \cong (\nu_1 + \nu_2)\, kT\, (A/A_0)(\lambda/\alpha)\alpha = (\nu_1 + \nu_2)\, kT\, e^{-k'\phi t}\alpha \qquad (17)$$

On the other hand, the viscous flow resistance f_v is given by

$$f_V = \eta \dot{\alpha} \alpha = (\nu_B kT\dot{\alpha}/k')\alpha \qquad (18)$$

It is postulated that f_{el} is larger than f_V for the continuous deformation and at the condition that f_V attains f_{el} the plastic rupture occurs. In other words, the equation for the plastic rupture is

$$(\phi\dot{\alpha}/k')\, e^{-k'\phi t} = 1 \qquad (19)$$

where ϕ is a fraction of flowing chain, i.e. $\nu_B/(\nu_1 + \nu_2)$. Since the rate of break-down of pseudo cross-link k', is much enhanced by extension as

$$k' = k_0 \exp\{f(n^{1/2}\ell)^2 \delta\ell b N_0/RT\} = k_0 \exp\{F(\lambda)\}$$

equation (19) is transformed to

$$\ln\alpha + \delta b F(\lambda) = \rho\alpha = \ln(\dot{\alpha}/k_0'\phi) + \ln\ln(k'/\phi\dot{\alpha}) \qquad (20)$$

where ρ is a constant factor. Equation (20) indicates that α is increasing with increasing the logarithmic function of $\dot{\alpha}/k_0'\phi$. On the other hand, the strength at break f is equal to f_V,

$$f = f_V = (\nu_B kT/k')\dot{\alpha}(\alpha - \lambda) \cong (\nu_B kT/k')\dot{\alpha}\alpha(1 - e^{-k't}) \cong \nu_B kT\alpha^2 \qquad (21)$$

and f_V increases with increasing rate of extension.

4, Failure envelope

In this way, the relations of the strength or strain at break with the rate of extension or temperature are obtained as failure spectra as shown in figure 1. The relation between the strength and strain at break is given as a failure envelope as shown in figure 2. The point A i.e., the transition from the brittle fracture to the elastic rupture is given by equation (4). The point B i.e., the transition from the elastic rupture to the plastic one is given at

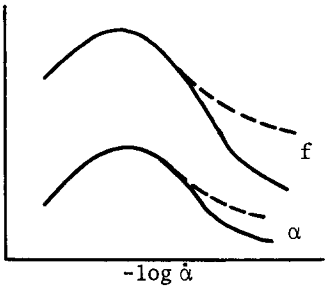

Fig.1 Failure spectra ; dotted curves refer to the biaxial extension

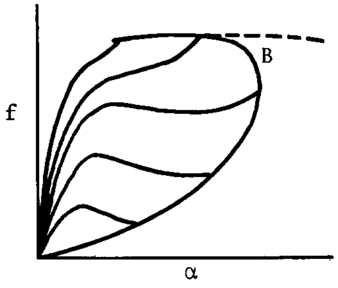

Fig.2 Stress-strain relation and failure envelope denoted by broken line curve

$$k'\phi t = 1 \qquad (22)$$

Combining equations (19) and (22), it follows that

$$\phi\dot{\alpha}/k' = 1/e \qquad (23)$$

or

$$\phi\alpha/k't = \phi^2\alpha = 1/e \qquad (24)$$

Equation (24) gives a relation between ϕ and α. Taking the maximum α to be 7, ϕ becomes

$$\phi = (1/e\alpha)^{1/2} = 1/4.3 \qquad (25)$$

or

$$\nu_1 + \nu_2 = 4.3\ \nu_B$$

At the optimum cure giving the maximum extension at break, the sum of the primary and secondary bond is 4.3 times larger than the ν_B, i.e., the critical flow point. Equation (23) also gives the temperature T_B giving the maximum elongation at break, as

$$\ln \phi\dot{\alpha} + 1 = \ln k' = (1/2) \ln (kT/h\ n_B^3) - E^*/RT_B$$

or

$$T_B = (E_B^*/R)/\{(1/2) \ln (kT/h) - \ln\phi\dot{\alpha} - 1\} \qquad (26)$$

T_B increases with increasing rate of extension $\dot{\alpha}$ and decreasing degree of vulcanization as known in the literature[2]. For the rubber capable of strain-induced crystallization T_B is enhanced by the entropy of crystallization ΔS^* as

$$T_B = (E_B^*/R)/\{(1/2) \ln (kT/h\ n_B^3) - \ln \phi\alpha - 1 - \Delta S^*\} \qquad (27)$$

5. Biaxial extension

For the equibiaxial extension equation (20) is modified as

$$\ln \alpha + 2\,\delta\, bF(\lambda) \simeq 2\,\rho\,\alpha = \ln(\dot{\alpha}/k_0'\phi) + \ln \ln (k'/\phi\dot{\alpha}) \qquad (28)$$

Equation (28) suggests that the slope of the failure spectra becomes more flat than that for the uniaxial extension as pointed out by T.L. Smith.

6. Filled rubber

For filled rubber the chain extension λ is smaller than the extension of the specimen α by a volume effect of filler as

$$\alpha = x^{1/3} + \lambda(1 - x)^{1/3}$$

where x is a volume fraction of the filler. Accordingly, the slope of the failure spectra become flat. In the same sense as equation (28)

$$\rho\alpha/(1 - x)^{1/3} = \ln (\dot{\alpha}/k_0'\phi) + \ln \ln (k'/\phi\dot{\alpha}) \qquad (29)$$

Moreover, for the active filler the additional pseudo cross-link forming on the filler surface participates in the viscous flow and equation (21) becomes

$$f_V/kT = (\nu_B/k' + x\nu_f/k_f')\dot{\alpha}\alpha \qquad (30)$$

where the suffix f refers to the filler and ν_f is the number of pseudo cross-link on the surface of the unit fraction of the filler. In other words the filler decreases the elongation but enhances the strength at break for the plastic rupture. For the elastic rupture the viscous flow resistance participates in the rupture force as

$$f_{max} = (RT/eV)(\nu_B/k' + x\nu_f/k_f')\dot{\alpha}(\alpha - \lambda)kT \qquad (31)$$

The second term is transformed to

$$(\nu_B/k' + x\nu_f/k_f')\dot{\alpha}(\alpha - \lambda)kT = \{(\nu_B + x\nu_f)/NV\}\alpha^2 RT$$

$$= \{(\nu_B + x\nu_f)/\nu_1\}(\nu_1/N)\alpha^2(RT/V)$$

Since $(\nu_1/N)\alpha^2$ is almost unity, equation (31) becomes

$$f_{max} \cong (RT/eV)\{1 + (\nu_B + x\nu_f)/\nu_1\} \qquad (32)$$

The same equation can be derived: If the ultimate extension giving rise to rupture is taken to be $(N/\nu_1)^{1/2}$ although the strength is determined by the sum of the primary and secondary cross-link, equation (16) becomes

$$f = (\nu_1 + \nu_B + x\nu_f)(D/V)\exp(-D/\lambda^2 RT)$$

$$= (RT/V)(\nu_1/N)\{1 + (\nu_B + x\nu_f)/\nu_1\}\exp\{-(\nu_1/N)(D/RT)\} \qquad (33)$$

Equation (33) leads to equation (32) at a maximum. It is noticed that the chemical reactive filler loses the flowing nature and therefore equation (31) becomes

$$f_{max} = RT/eV$$

and equation (32) becomes

$$f_{max} = (RT/eV)\{1 + \nu_B/(\nu_1 + x\nu_f)\} \qquad (34)$$

In other words, the reactive filler acts as the vulcanizing agent to give a bound rubber and loses the reinforcing effect, although the stiffening effect remains. Equation (32) may be extended to the segmented polymer like the styrene-butadiene-styrene block copolymer. The strength is much enhanced by the reinforcement of the hard block domain, which acts as a filler, because the block copolymer gives a well-dispersed hard domain particle.

7. Crystallizable rubber

A rubber capable of strain-induced crystallization such as natural rubber exhibits very high tensile strength at break. In this case the Boltzmann's exponential factor in equation (33) is to be increased by the crystallization. At the degree of crystallization X, equation (33) becomes

$$f = (RT/V)(\nu_1/N)\exp\{-(\nu_1/N)(D/RT)(1 - X)\} \qquad (35)$$

It gives f_{max} as

$$f_{max} = (RT/eV)\{1/(1 - X)\} \qquad (36)$$

When X is 0.5, f_{max} is doubled. At X closes to unity f_{max} becomes infinitive and equation (36) is not available but instead, equation (37) can be used

$$f = (D/V)(1 - X) \qquad (37)$$

In this case equation (37) is not for rubber, but for fiber.

8. Rupture energy

The viscous flow resistance is important for reinforcement of vulcanized rubber. Grosch[3] proposed an important empirical equation that the rupture energy U absorbed in extension is proportional to the 2/3-power of the hysteresis H. This can be derived theoretically in terms of the pseudo cross-link concept as follows:

$$U = \int f\alpha d\alpha = \int(\nu_1 + \nu_2)(RT/V)\alpha d\alpha = (\nu_1 + \nu_2)(RT/V)(\alpha_B^2/2) \qquad (38)$$

and

$$H = \int (\nu_B \dot{\alpha}/k)\alpha(RT/V)d\alpha = (\nu_B \dot{\alpha}/k')(RT/V)(\alpha_B^2/2)$$

$$= \nu_B (RT/V)\phi(\alpha_B^3/2) \qquad (39)$$

where B is a turn-back point or the rupture point and $k'\phi t$ is unity at this point. Combining equations (38) and (39) the equation similar to the Grosch's equation is obtained as

$$U = (RT/V)^{1/3}(\nu_1 + \nu_2)/(\nu_B\phi)^{2/3}H^{2/3} \qquad (40)$$

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