Study on the life expectancy of storage and ageing for rubber vulcanizates

4. The method of ultimate fracture under constant rate strain

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Summary

In this paper the relationship of the ageing time to the tensile strength and the ultimate elongation of rubber vulcanizates was derived from the combination of ageing kinetics with the molecular theory of ultimate tensile strength of elastic networks, basing on the micro-structure model of rubber vulcanizates. According to this relation, a new simple method for determining the coefficients (α_4) of ageing time and the ageing rate constants (k_4) of rubber vulcanizates from the data of the extension tests was proposed. The accelarated ageing experiments of Butadiene-acrylonitrile Rubber (BAR) vulcanizates were carried out at the range of temperature 70-110°C in a given period of 1-100 days, and the molecular parameters were determined by using this new method. It is shown that the experimental results are consistent to the theory.

Introduction

It is of practical and theoritical significance to study the relationship between the storage and ageing life of polymer materials, such as rubber vulcanizates, with their mechanical properties. The relationship between the ageing time with the compressed stress and the compressed strain of rubber vulcanizates and between the ageing time with the compressed permanent deformation of rubber vulcanizates have been established, respectively.[1,2] According to these relations, the methods for determining the coefficients of the ageing time and the ageing rate constants by measurements of the stress relaxation and the permanent deformation were proposed.[1,2] But the two methods

show a limitation, that is, they are only suitable to evaluate the parameters of the rubber materials with small compressed deformations. Besides, if the two methods are used, the plastical deformations of the samples have to be removed previously. And so, it will make the experimental procedures complicated. In order to overcome these defects, in this paper, the method of ultimate fracture at constant rate strain was proposed. It is basing on the relationship between the ageing time with the tensile strength and the ultimate elongation, that is derived from the combination of the ageing kinetics with the fracture equation of state for elastic networks.[3] It provides a theoritical foundation, as well as a method for the expectancy of storage and ageing time of rubber vulcanizates. The coefficients of the ageing time and the ageing rate constants can be determined from the data of the extension tests by this method.

Theory
1. Equation of state for ultimate fracture
    In previous paper a new model theory of tensile strength for polymeric networks was proposed.[3] And an equation of state for ultimate fracture was derived from the theory.
    Owing to the characteristics of nonuniform network structure and unhomoheneous deformation, the failure of polymeric networks consists of three factors: 1. the time dependence of the bulk stress to strain relation; 2. the time dependence of failure initiation mechanism—— the formation of overstressed polymeric chains in the local deformation region; And 3. the kinetics of the bond rupture of overstressed polymeric chains. In fact, both three factors occur together and it is difficult to separate them. Basing on the above idea of failure phenomena, the theory of Eyring reaction rate and the theory of rubber elasticity at large deformations, the coefficient of overstressed polymeric chains was derived by combining the factors 1 and 2 as an united event for failure of polymeric networks. A kinetic equation for bond rupture of overstressed chains is established by using the coefficient of overstressed polymeric chains as a variable. After integration and simplication, a general relation between the tensile strength and ultimate el-

ongation with temperature and the parameters of network struc-
tures was obtained, it is given by equation (1):

$$\frac{\sigma_b(\lambda_b-1)}{\lambda_b-\lambda_b^{-2}} = \frac{k_\lambda}{K_0} e^{U_0/kT} \cdot \beta \left[A + 2B(\lambda_b^2 + 2/\lambda_b) \right] \cdot \sum_{i,j=1}^{4} \frac{\nu_{iob} + \nu_{job}}{\nu_{ib} + \nu_{jb}} \qquad (1)$$

Where σ_b is tensile strength; λ_b is ultimate elongation; k_λ is
the rate constant of strain; K_0 is a constant depending on the
kind of polymer; U_0 is activation energy of bond rupture; T is
the test temperature; k is Boltzmann constant; β is active
volume; ν_i and ν_j is the number of elastically active long and
short molecular chains in an unit volume of the networks
(crosslinked, tied, carbon-polymer absorped and carbon-polymer
conjected), respectively; the subscript "ob" represents the
start time of the extension and "b" the time to failure;
$A = \sum_{i,j=1}^{4} \nu_{ib}/(\nu_{iob} + \nu_{job})$; $B = \sum_{i,j=1}^{4} \nu_{ib}/(\nu_{iob} + \nu_{job})$.

2. Kinetic equation of ageing

During storage and ageing, the bond rupture of polymer
chains will be occured in rubber vulcanizates, that results in
the reduction of the numbers of elastic molecular chains and
then makes the chemical stress relaxation. So, it is reasonable
to consider that the main elements which affect on the rate of
the bond rupture of polymer chains are: 1. the numbers of elas-
tically active chains remained in the networks; 2. the ageing
temperature. 3. the ageing activation energy; 4. the ageing
time. The distribution of the number of long chains ($\sum_{i=1}^{4} \nu_i$) and
short chains ($\sum_{j=1}^{4} \nu_j$) in the networks and the dependence of the
distribution on the ageing atmosphere (air, dark, light etc.)
all change with the ageing time. The resultant effects are
determined by both concentration of atmosphere (n) in the net-
works and ageing time (t). Therefore we assume that it may be
expressed by the relation of $n = D \cdot t^{\alpha_4 - 1}$ or $n = d \cdot t^{\alpha_4 - 1}$ (without
light) through the expansion constant (D) and diffusion con-
stant (d). Combining these factors with the storage and ageing
kinetic equation, the rate of change of elastically active
chains can be expressed by eq.(2):[1,2]

$$- \frac{d\sum_{i,j=1}^{4}(\nu_i + \nu_j)}{dt} = m \cdot \sum_{i,j=1}^{4} (\nu_i + \nu_j) \cdot t^{\alpha_4 - 1} \cdot e^{-\Delta E/kT} \qquad (2)$$

Where $m = P \cdot D$ (or $m = P \cdot d$); P is the degree of polymerization; D
and d are the expansion constant and diffusion constant, resp.

m depends on the kind of polymers and ageing conditions (temperature and strength of light); α_4 is the coefficient of ageing time; t is ageing time; ΔE is thermo-ageing activation energy; T is ageing temperature. After integration, we have:

$$\sum_{ij=1}^{4}(\nu_{it}+\nu_{jt})=\sum_{ij=1}^{4}(\nu_{i0}+\nu_{j0})\exp\left\{-\frac{m}{\alpha_4}\cdot e^{-\Delta E/kT}\cdot t^{\alpha_4}\right\}$$ (3)

3. Reduced equation of state for ultimate fracture

Introducing eq.(3) and the condition of $A/2B(\lambda_b^2+2/\lambda_b)\ll 1$ into eq.(3), we have:

$$\frac{\sigma_{bt}(\lambda_{bt}-1)}{\lambda_{bt}-\lambda_{bt}^{-2}}=\frac{k_\lambda}{k_0}\cdot e^{U_0/kT}\cdot\beta\cdot 2B_t\left(\lambda_{bt}^2+2/\lambda_{bt}\right)\cdot\sum_{ij=1}^{4}\frac{\nu_{iob}+\nu_{job}}{\nu_{ib}+\nu_{jb}}\exp\left\{-\frac{m}{\alpha_4}\cdot e^{-\Delta E/kT}\cdot t^{\alpha_4}\right\}$$ (4)

when t=0, the eq.(4) reduces to eq.(5):

$$\frac{\sigma_{bo}(\lambda_{bo}-1)}{\lambda_{bo}-\lambda_{bo}^{-2}}=\frac{k_\lambda}{k_0}\cdot e^{U_0/kT}\cdot\beta\cdot 2B_o\left(\lambda_{bo}^2+2/\lambda_{bo}\right)\cdot\sum_{ij=1}^{4}\frac{\nu_{iob}+\nu_{job}}{\nu_{ib}+\nu_{jb}}$$ (5)

Deviding eq.(4) by eq.(5) and introducing the condition of $\lambda^{-3}\ll 1$, the relationship of the ageing time to the tensile strength and the ultimate elongation was obtained and given by eq.(6):

$$\frac{\sigma_{bt}(\lambda_{bt}-1)}{\sigma_{bo}(\lambda_{bo}-1)}\left(\frac{\lambda_{bo}}{\lambda_{bt}}\right)^3=\frac{B_t}{B_o}\cdot\exp\left\{-\frac{m}{\alpha_4}\cdot e^{-\Delta E/kT}\cdot t^{\alpha_4}\right\}$$ (6)

Let: $B_t/B_0=K_4$, K_4 is a constant; $-me^{-\Delta E/kT}=k_4$, k_4 is the ageing rate constant; $\sigma_{bt}(\lambda_{bt}-1)\lambda_{bo}^3/\sigma_{bo}(\lambda_{bo}-1)\lambda_{bt}^3=y_4$; then the eq.(6) can be written in the form:

$$y_4=K_4\cdot\exp\left\{k_4\cdot t^{\alpha_4}/\alpha_4\right\}$$ (7)

The eq.(7) can also be written by eq.(8):

$$\ln y_4=\ln K_4+(k_4/\alpha_4)\cdot e^{\alpha_4\ln t}$$ (8)

It is shown that $d\ln y_4/d\ln t$ exists, and then we have:

$$\ln\left(\frac{d\ln y_4}{d\ln t}\right)=\ln k_4+\alpha_4\ln t$$ (9)

The eq.(9) shows that $\ln(d\ln y_4/d\ln t)$ is a linear function of the values of $\ln t$. So, the values of α_4 and k_4 can be determined by the method of linear regression.

The eq.(7) can also be written in another form

$$\ln y_4=\ln K_4+k_4\cdot t^{\alpha_4}/\alpha_4$$ (10)

The eq.(10) means that there is a linear relationship between

lny_4 and t^{α_4}/α_4, and the values of K_4 can be determined from the intercept of the line.

According to the relation of $-me^{-\Delta E/kT}=k_4$, the value of ageing activation energy can be determined from the slope of the line by plotting the lnK_4 vs. $1/T$.

Experiments

(1) The formulation of BAR vulcanizates is given in Table 1. And the accelarated ageing experiments of the BAR vulcanizates with dimension of 200×200×2 (mm) were carried out at the temperature of 70, 80, 90, 100 and 110°C, in a given limited air air for the period of 1-100 days.

(2) The tensile strength and the ultimate elongation of the BAR vulcanizates were determined by Instron at the extension rate of 500 mm/min. And the results are given in Fig.1a and 2, resp.

Table 1. Compound formulations(parts by weight)[*]

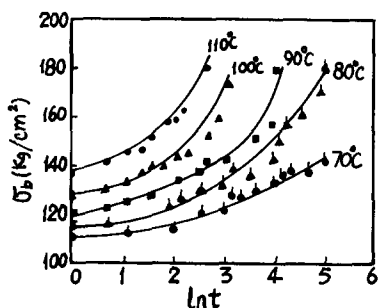| Nitrile rubber	Sulfur	accelarator D		Stearic acid	DM
100	2	0.25		1	1.25
Zinic Oxide	Calcium carbonate		Carbon black	Dibutyl sebacate	
5	45		75	20	

* To be cured at 151±1°C for 20 min.

Fig.1 The experimental results for the dependence of tensile strength on the ageing time at five different temperatures
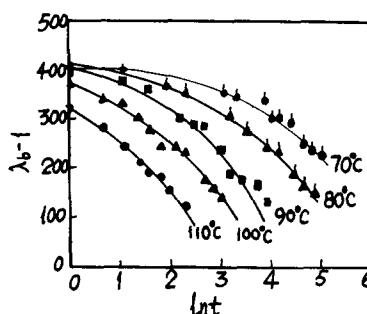

Fig.2 The experimental results for the dependence of elongation on the ageing time at five different temperatures

Results and Discussions

The values of $\ln y_4$ at different temperatures were calculated according to the equation $y_4 = \sigma_{bt}(\lambda_{bt}-1)\lambda_{bo}^3 / \sigma_{bo}(\lambda_{bo}-1)\lambda_{bt}^3$
Plots of $\ln y_4$ vs. $\ln t$ are given by Fig.3.

According to the results of Fig.3, the differential $(d\ln y_4/d\ln t)$ of every experimental point was determined by the numerical values analysis method with the "middle point rule". It is obviously that there are expected linear relationships between $\ln(d\ln y_4/d\ln t)$ and $\ln t$ at the experimental ageing temperatures, and the results at 80 and 110°C are shown in Fig.4.

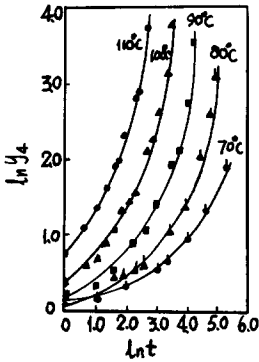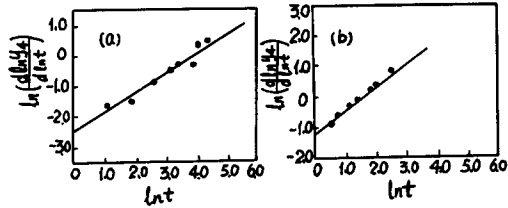Fig.3.The experimental results of $\ln y_4$ vs. $\ln t$ at the different ageing temperatures.

Fig.4 The plot of $\ln(d\ln y_4/d\ln t)$ vs. $\ln t$ at the different ageing temperatures.
(a) 80°C;   (b) 110°C.

Thus, the values of α_4 and k_4 were determined by linear regression and are shown in the Table.

When the values of α_4 and k_4 were determined, the plot of $\ln y_4$ vs. t^{α_4}/α_4 was drawn and given in Fig.5.

It is shown that there are linear relations between $\ln y_4$ and t^{α_4}/α_4 at the different ageing temperatures, just as the prediction by eq.(10). According to this equation, the values of K_4 and k_4 were determined from the intercept and the slop of the line, respectively. The values of K_4 are given in the Table, and the values of k_4 are pretty close to those obtained from the equation(9).

According to the relation of $-me^{-\Delta E/kT} = k_4$, the value of ageing activation energy (ΔE) was determined from the slop of
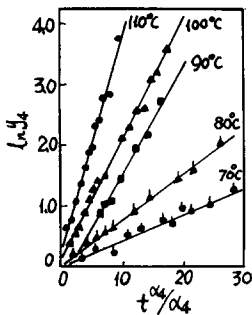
Fig.5 The relations of $\ln y_4$ to t^{α_4}/α_4 at different ageing temperatures
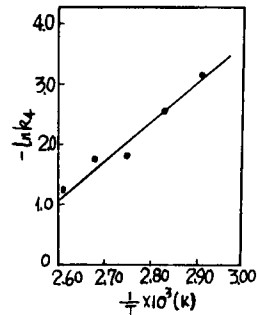

Fig.6 The plot of $\ln k_4$ vs. $1/T$.

the line of $\ln k_4$ vs. $1/T$, and the plot is given in Fig.6. The value of E is shown in the Table 2.

Table2 The molecular parameters of BAR vulcanizates

$T(^\circ C)$	α_4	k_4	K_4	$\Delta E(Kcal/mole)$
70	0.62	0.043	0.96	
80	0.64	0.078	1.01	
90	0.56	0.170	0.74	11.88
100	0.72	0.173	1.14	
110	0.76	0.322	1.40	

It can be seen from the Table1 that k_4 increases with the temperature increased, according to the eq.(5); K_4 increases with the temperature increases; α_4 is dependent slightly on the ageing temperature.

Conclusions

(1) A reduced equation of state for ultimate fracture at constant rate strain for polymer networks was derived from the combination of ageing kinetics with the equation of state for tensile fracture. According to the equation, a new simple method for determining the coefficients of ageing time and the ageing rate constants was proposed.

(2) The accelarated ageing of BAR vulcanizates were carried out, the coefficients of ageing time and the ageing rate constants at the different ageing temperatures and over a wide range of ageing time were determined by using this new method and it is shown that the experimental results are consistent to the theory.

References

(1) Song Mingshi, Hu Guixian et al. Symposium on Polymers, Preprints (1985)

(2) Hu Guixian et al., Computer and Applied Chemistry (China), 4(2), 94 (1987)

(3) Song Mingshi et al., Symposium on Polymers, Preprints part 3, 1047 (1987); J. Chem. Indu. and Eng. (China), (to be published)

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