

Kinetics of the Effect of Ageing on Tensile Properties of a Natural Rubber Compound

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ABSTRACT: Natural rubber (NR) undergoes chemical changes on heat and air ageing. These changes affect its physical properties and as such, affect the service life of the rubber compound. In this study, a vulcanized NR compound of a typical engine mount composition was subjected to thermo-oxidative ageing at temperatures from 70 to 110°C, to assess the effect on the tensile properties. The kinetics of degradation of the rubber compound, in terms of changes in these properties, was investigated. A fractional rate law was used to describe the kinetics of ageing in terms of its effect on modulus. Rates of ageing, in terms of effect on modulus, passed through a minimum at about 80°C, indicating the danger of trying to extrapolate in-service ageing behavior from high

temperature ageing data. The activation energy of ageing in terms of its effect on modulus, determined for temperatures of 90–110°C, was 151 kJ mol⁻¹. A second order rate law was used to describe the kinetics of ageing in terms of its effect on tensile strength and elongation at break, with activation energies of 88.32 and 74.3 kJ mol⁻¹, respectively. According to Ahagon's (Ahagon et al., *Rubber Chem Technol*, 1990, 63, 683) classification of ageing mechanisms, Type I and Type III ageing mechanisms were predominant. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3732–3740, 2006

Key words: natural rubber; degradation; tensile properties; kinetics; activation energy

INTRODUCTION

The use of natural rubber (NR) components for under-hood applications requires them to withstand high temperatures with minimal deterioration. One such NR component used in under-hood applications is the engine mount. This component during its service life is subjected to various temperature conditions, amplitudes, and frequencies of vibration, which result in changes in the material's properties over time. These changes are usually traced to physical and chemical changes in the molecular structure, which may adversely affect the mechanical behavior of the engine mount and shorten its service life.^{1,2}

Ageing of NR and other polymers, which can be thermal, photodegradative, or thermo-oxidative has been widely investigated.^{3–10} Most of these studies employ destructive techniques such as the thermogravimetric methods at elevated temperatures, to determine the kinetics of degradation and so, predict the

service life of the material. Such predictions are usually misleading in that they either overestimate the service life of the material or underestimate it.¹¹ Another method is the solution method, which is based on the changes in the average molecular weight of the material.¹² Because of the complexity of NR compounds, few studies of the degradation kinetics of NR vulcanizates have been undertaken using nondestructive methods, which mimic service conditions.^{1,13,14}

Natural rubber [poly(*cis*-1,4-isoprene)] contains double bonds, which renders it particularly sensitive to oxidation in the presence of molecular oxygen.¹⁵ The oxidation of NR, in the solid state, is complex, with two competitive processes; scission and crosslinking taking place almost simultaneously. These two mechanisms change the physical properties of the material. Chain scission will result in the loss of stiffness and elasticity, whereas crosslinking will result in increased stiffness and a consequent increase in brittleness. As a general rule, the more predominant effect of the oxidation process is chain scission. However, in the case of polybutadiene, for example, it has been shown that crosslinking overrides chain scission.¹⁶ For poly(isoprene), whether a scission or crosslinking, mechanism predominates depends strongly on the quantity of oxygen that diffuses into the material.^{17,18}

Using a nondestructive method, we attempt to derive the kinetics of thermo-oxidative ageing of a NR

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TABLE I
Formulation for the Natural Rubber Compound

Material	Composition (phr)
NRCV60	100
Carbon black (N772)	49
Zinc oxide	5
Stearic acid	2
Antiozonant wax	2
6PPD	1.5
TMQ	1
TBBS	0.7
TMTD	0.5
Sulfur	1.7

compound, by monitoring changes in physical properties over a range of time and temperature conditions.

EXPERIMENTAL

Materials

Natural rubber (SMRCV60) was supplied by the Tun Abdul Razak Research Centre, UK; carbon black (N772) was supplied by Columbian Chemicals, UK; tetramethylthiuram disulfide (TMTD), *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (6PPD), 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), *N*-*tert*-butyl-2-benzothiazolesulphenamide (TBBS) were supplied by FLEXSYS Belgium; antiozonant wax was supplied by Richard Baker Harrison Ltd., (UK). Sulfur, zinc oxide, and stearic acid were also used.

Compounding

The formulation used for the compound is given in Table I, representing a typical engine mount compound.

The NR compound was prepared in a water cooled Francis-Shaw K1 intermix having a volume of 5.5 L. A fill factor of 0.55 was used and the mixing was done at

TABLE II
Cure Properties of the Fresh Compound

Maximum torque, M_H (dN/m)	87.72
Minimum torque, M_L (dN/m)	19.16
Scorch time, ts_2 (min)	2.62
Cure rate index, CRI	8.64
tc_{95} (min)	14.2

a speed of 40 rpm, with a circulating water temperature of 40°C. The rubber was first masticated in the internal mixer for 2 min together with the activators (zinc oxide and stearic acid), the antiozonant wax and the antioxidants (TMQ and 6PPD). Carbon black was then added and the compound was mixed for a further 4 min before introducing the accelerators (TMTD and TBBS) and the crosslinking agent (sulfur). The mixing was then carried out for a further 1 min before dumping. The compound was then sheeted out on a two-roll mill to a thickness of about 3.2 mm.

Cure parameters were determined using a Monsanto R100S Rheometer operating at a strain amplitude of 3° and at a temperature of 150°C. From the rheographs obtained, the scorch time, cure rate index, minimum and maximum torque were determined. Test samples were then compression molded to 95% cure at a temperature of 150°C for 15 min.

Accelerated thermo-oxidative ageing

Thermo-oxidative ageing was carried out in a circulating air environmental chamber at temperatures of 70, 80, 90, 100, and 110°C for times ranging from 1 to 4 weeks depending on the ageing temperature.

Tensile testing

Tensile properties were measured in accordance with the BS903-A2¹⁹ on Type II dumbbell test pieces, which

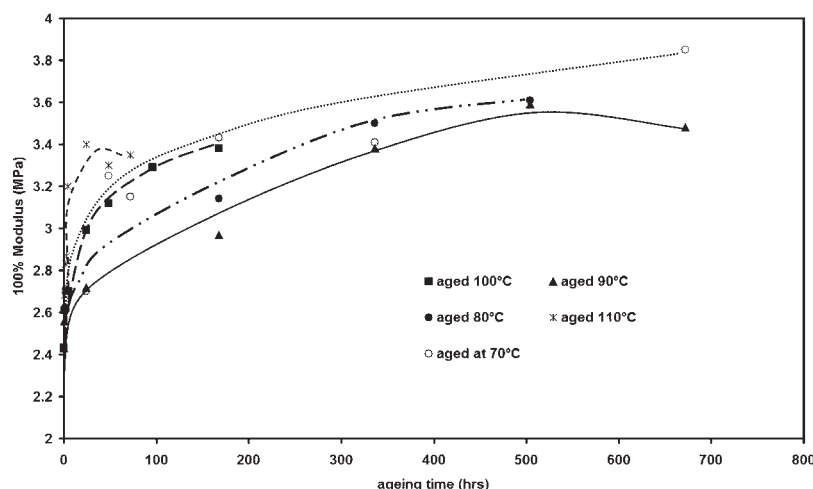


Figure 1 Effect of ageing temperature on 100% modulus.

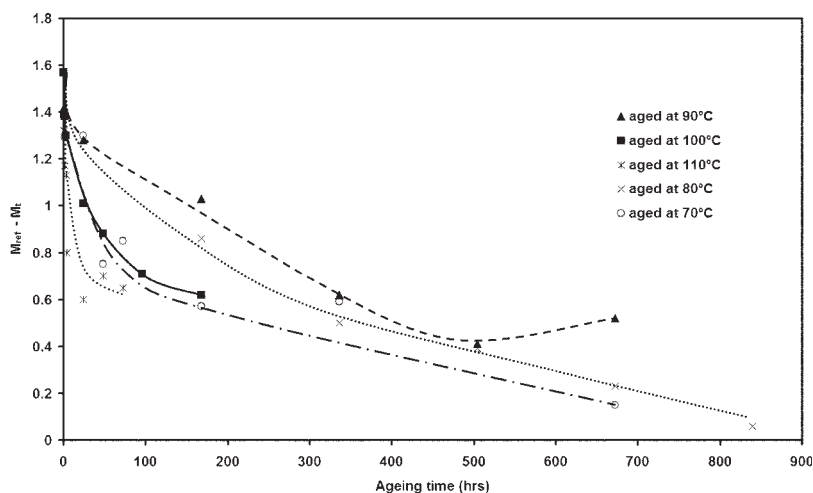


Figure 2 Relationship between ageing time and reduced modulus at the different ageing temperatures.

were die stamped from the 2 mm thick vulcanized sheets along the milling direction. A Hounsfield tensile testing machine was used, operating at a cross head speed of 500 mm/min, with a Hounsfield 500L laser control apparatus attached to measure the extension. The tensile strength, elongation at break, and modulus were acquired using QMAT-Dongle: 2003 computer software. A minimum of eight specimens were tested from each molded sheet.

RESULTS AND DISCUSSION

Various kinetic models have been employed to study the degradation of polymers.²⁰ Using the Kissinger, Ozawa, Van Krevelen, Horowitz–Metzger, Coats–Redfern, and MacCallum–Tanner methods, Regnier and Guibe⁵ found that the activation energy for the multistage degradation of polyimide polymer was between 143 and 206 kJ mol⁻¹. It is worthwhile noting that all these methods apply high temperature weight

loss thermal analysis techniques and not direct physical property measurements, as in our case.

The cure properties of the fresh compound are shown in Table II. The effect of ageing time and temperature on tensile modulus were qualitatively different from the effects on tensile strength and elongation at break. The two effects are discussed separately in the following two sections.

Modulus

The stress at 100% strain, referred to as the 100% modulus, (M_{100}) was used to follow the changes in stiffness of the compound during ageing. As the ageing time increased, the modulus (M_{100}) also increased until a point where it either leveled off, at the lower temperatures, or decreased at the higher ageing temperatures (Fig. 1). Ahagon et al.¹ and Baldwin et al.,¹⁴ in their studies of accelerated ageing of tire compounds, also observed a modulus increase and subse-

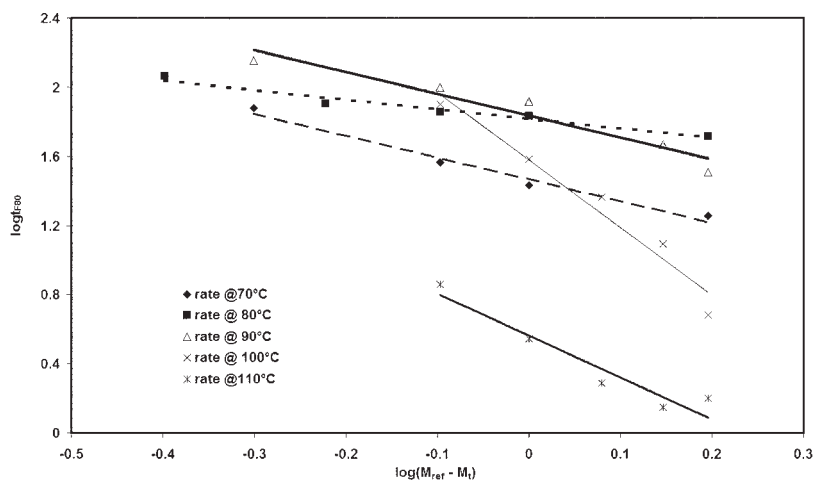


Figure 3 Fractional rate law plot for ageing reactions as they affect modulus.

TABLE III
Order and Rate Constants for Ageing of NR,
in Terms of Effect on Modulus

Ageing temperature (°C)	n	k (10^{-3})	r^2	E_a (kJ mol^{-1})
70	2.26	8.1	0.9806	151.92
80	1.55	3.56	0.9601	
90	2.26	4.5	0.9316	
100	4.91	12.8	0.9571	
110	3.43	62.7	0.9214	

quent reduction, depending on the ageing mechanism. From 90 to 110°C, the rate of modulus increase decreases with increasing temperature, as would be expected. However, between 70 and 90°C the rate of modulus increase increases with decrease in temperature. Particularly striking is the fact that ageing at 70 and 100°C has a similar effect on modulus, at least up to 200 h. The apparently anomalous effect of ageing temperature on modulus is likely to be due to the complexity of the reactions taking place in the rubber. During ageing there are both crosslinking and scission reactions occurring at the same time, which have opposing effects on modulus. Since the crosslinking and scission reactions are likely to have different activation energies from each other, the relative contribution of each reaction to overall ageing is likely to vary with temperature.

The fractional life equation²¹ shown below was used to describe the kinetics of degradation of the NR vulcanizate in terms the modulus (M_{100}).

$$t_F = \frac{(0.8)^{1-n} - 1}{k(n-1)} (M_{\text{ref}} - M_t)^{1-n} \quad (1)$$

where $M_{\text{ref}} - M_t$ is the reduced modulus; t_F is the time taken for the reduced modulus at time t to fall to 80%

of its value; n is the order of the reaction; k is the rate constant.

Using this method, reduced modulus ($M_{\text{ref}} - M_t$) was plotted against ageing time t (Fig. 2) and values of t_F were determined. A value for the reference modulus M_{ref} of 4 MPa was chosen as the asymptotic value approached, at very long ageing times at low temperatures.

Taking logarithms on both sides of eq. (1), we have

$$\log t_F = \log \left(\frac{0.8^{1-n} - 1}{k(n-1)} \right) + (1-n) \log(M_{\text{ref}} - M_t) \quad (2)$$

From eq. (2), it can be seen that a plot of $\log t_F$ against $\log(M_{\text{ref}} - M_t)$ should give a straight line. Using this plot, the order of the reaction can be obtained from the slope and the rate constant from the intercept. Figure 3 shows the fractional rate law plots for the various ageing temperatures. It is notable that the slope and therefore, the order of the ageing reaction varies with ageing temperature. The orders of reaction and reaction rate constants were obtained from the plots and are shown in Table III. There is a general increase in order of reaction with increase in ageing temperature and this is perhaps a reflection of the increased complexity of the reactions affecting modulus at higher temperatures. The correlation coefficient r^2 from linear regression analysis was found to be in the range $0.9214 \leq r^2 \leq 0.9806$, supporting the validity of using this approach to describe the kinetics of ageing.

It is usual to make use of the Arrhenius relationship below, to obtain activation energies of reactions.

$$k = A e^{(-E_a/RT)} \quad (3)$$

where A is the pre-exponential constant; E_a , the activation energy; R , the gas constant; T , the absolute temperature; k , the rate constant at temperature T .

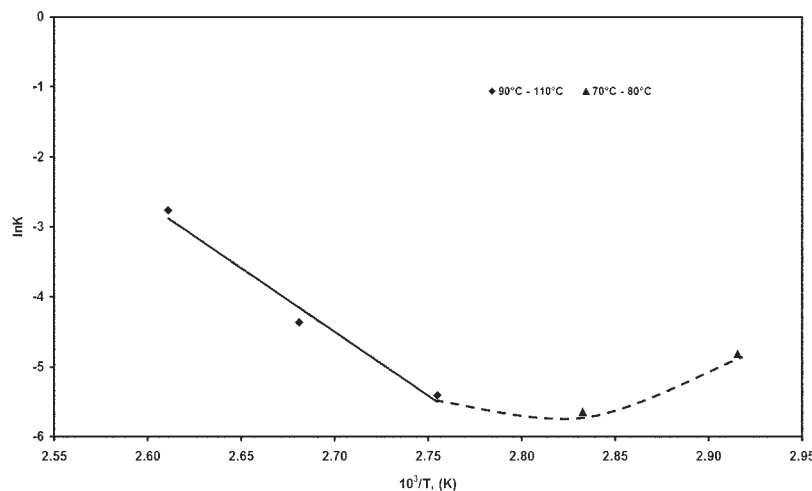


Figure 4 Arrhenius plot for ageing in terms of its effect on modulus.

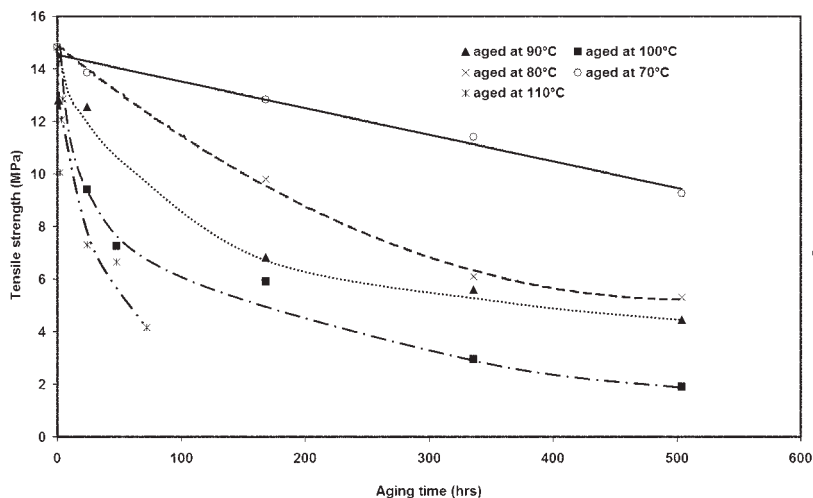


Figure 5 Effect of ageing temperature on tensile strength.

From eq. (3) one obtains

$$\ln k = \ln A - \frac{E_a}{RT} \quad (4)$$

Thus, when $\ln k$ is plotted against $1/T$ the slope of the resulting straight line can be used to give the activation energy.

Figure 4 shows an Arrhenius plot for the ageing reaction in terms of modulus. The points clearly do not lie on a straight line but lie on a curve that passes through a minimum. Using only the higher ageing temperature results (90–110°C), an activation energy of 151 kJ mol⁻¹ can be obtained. However, if these high temperature data were extrapolated to lower temperatures, to predict the changes in modulus during the service life of the rubber material, then completely incorrect values would be obtained. The results illustrate the dangers of using accelerated ageing data to build predictive models. The curved shape of the Arrhenius plot indicates

that there are two processes, which affect modulus in opposite ways and that each process has a different activation energy. It is known that ageing causes both crosslinking reactions, which result in an increase in modulus and scission reactions, which result in a decrease in modulus as has been explained elsewhere.^{14,22} Both of these reactions will increase in rate with increase in temperature. However, the results indicate that the scission reactions have a higher activation energy than the crosslinking reactions. Hence, with decrease in temperature, the rate of scission reactions decrease more rapidly than the rate of crosslinking, giving the appearance, over a particular temperature range (70–80°C) that rate of crosslinking actually increases as temperature decreases. Extrapolating this effect to lower temperatures would suggest that the lower the temperature, the more rapid the increase in modulus would become. Clearly, this will not happen and so, at lower ageing temperatures it is expected that a negative slope for the Arrhenius plot would be

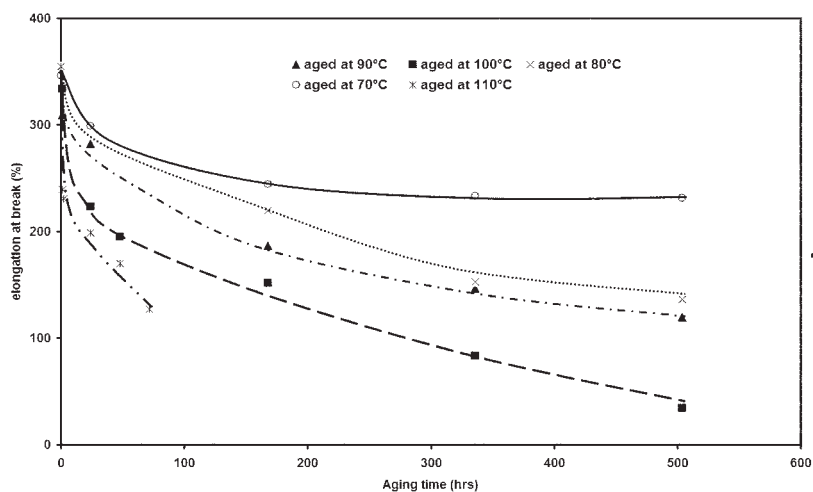


Figure 6 Effect of ageing temperature on elongation at break.

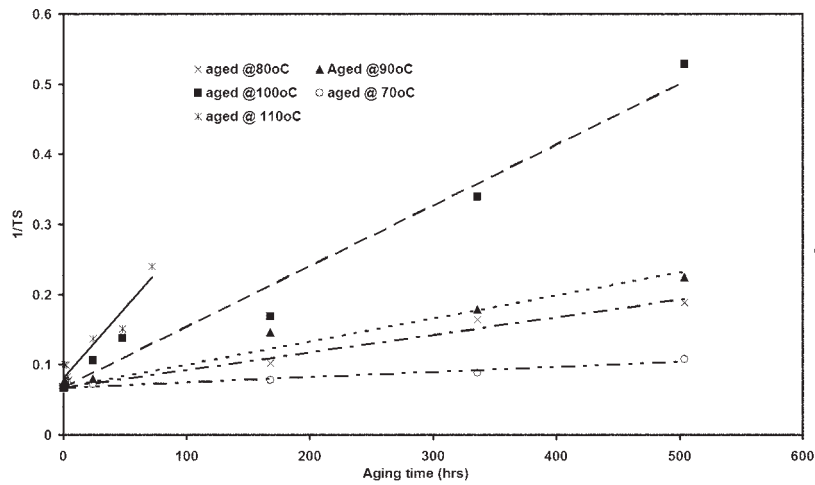


Figure 7 Second order rate plot of ageing in terms of its effect on tensile strength.

re-established. It is likely that the slope in the low temperature region will be lower than that in the high temperature region, corresponding to the lower activation energy required for crosslinking reactions.

Tensile strength and elongation at break

The tensile strength and elongation at break decreased with increase in ageing time (Figs. 5 and 6). The rate of decrease in these properties increased with increase in ageing temperature. The results are more straight forward than those for modulus, presumably because both crosslinking and scission reactions result in a decrease in strength. It is to be expected that scission reactions would cause a decrease in strength, because the tensile stress would be carried on fewer chains. Elongation at break would be expected to decrease with increase in ageing due to both crosslinking and scission reactions. However, crosslinking should not necessarily have a negative effect on tensile strength.

For example, increasing the level of cure of a rubber compound can increase strength, until a maximum is reached, after which embrittlement can lead to a decrease in strength.

The effect of ageing on tensile strength and elongation at break was found to follow second order kinetics.

$$\frac{1}{\xi_t} = kt + \frac{1}{\xi_0} \quad (5)$$

where ξ_t is the property at time t of ageing and ξ_0 is the initial value before ageing.

A plot of $\frac{1}{\xi_t}$ versus t using eq. (5) gives straight lines (Figs. 7 and 8), for rubber aged at 70, 80, 90, 100, and 110°C. The significance of these plots are $0.878 \leq r^2 \leq 0.97673$ (Table IV), indicating a good correlation.

The rate constants, determined from the slopes of the lines, were then plotted on Arrhenius coordinates (Figs. 9 and 10). The activation energy was calculated to be about $88.32 \text{ kJ mol}^{-1}$ for the tensile strength and

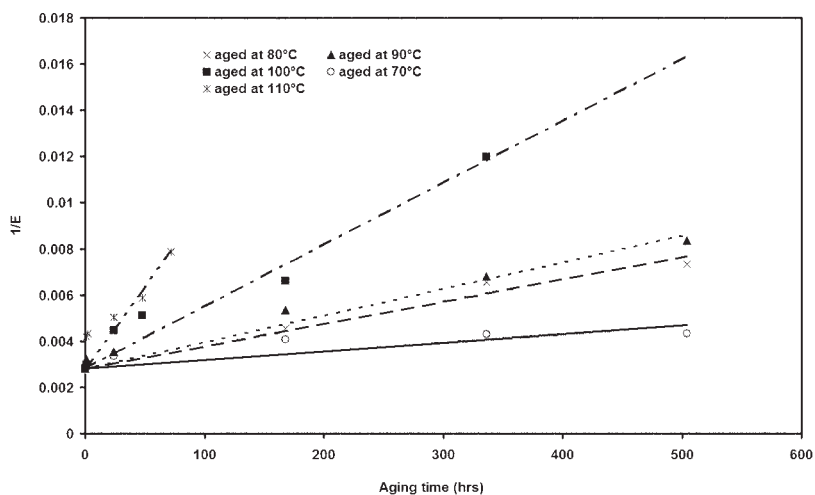


Figure 8 Second order rate plot of ageing in terms of its effect on elongation at break.

TABLE IV
Rate Constants for Ageing of NR, in Terms of Effect on Tensile Strength and Elongation at Break

Ageing temperature (K)	Tensile strength			Elongation at break		
	k	r^2	E_a (kJ mol ⁻¹)	k	r^2	E_a (kJ mol ⁻¹)
343	7.0×10^{-5}	0.9571	88.32	4.0×10^{-6}		74.3
353	3.0×10^{-4}	0.9749		1.0×10^{-5}	0.9712	
363	3.0×10^{-4}	0.9629		1.0×10^{-5}	0.9666	
373	9.0×10^{-4}	0.9767		3.0×10^{-5}	0.9544	
383	23×10^{-4}	0.8780		7.0×10^{-5}		

74.3 kJ mol⁻¹ for the elongation at break. However, the activation energy calculated from modulus data at high temperatures (151 kJ mol⁻¹) is significantly greater than the values calculated from tensile strength and elongation at break data. This is probably because data from lower temperatures were included in the calculation using tensile strength data. At lower temperatures, crosslinking reactions predominate and so it is likely that their lower activation energy contributes more to the apparent overall activation energy of the ageing process. Other investigators found that the activation energy for the oxidation of sulfur-vulcanized NR was 102 kJ mol⁻¹.²³ For accelerated ageing of tires, Baldwin et al.¹⁴ found that when the tire was inflated with air and a 50/50 blend of N₂/O₂, and aged at temperatures of between 40 and 70°C for one set of experiments and between 70 and 110°C for another, the wedge rubber had an activation energy of 107 kJ mol⁻¹. These two temperature ranges were selected to study the mechanism of degradation under these two conditions of air and a 50/50 blend of N₂/O₂.

Straus and Madorsky²⁴ studied the effect of various additives to NR with or without subsequent vulcanization on the degradation process during pyrolysis in a vacuum. They found that pyrolysis was completed at 390°C and carried all subsequent experiments at this pyrolysis temperature. The rates and activation energies of the thermal degradation in vacuum of vulcan-

ized and unvulcanized NR was also studied.²⁴ They found the activation energy value for the thermal degradation of vulcanized NR to be between 234.42 and 272.09 kJ mol⁻¹ for the different formulations. Using swelling measurements and peel strength and applying the same technique from their previous study,¹⁴ Baldwin et al.²² found that the activation energy for skim rubber in the tested tires was 101 kJ mol⁻¹ for the swelling ratio and 109 kJ mol⁻¹ for the peel strength. Meanwhile Mott and Roland²⁵ found the activation energy for the ageing of NR in air and seawater at temperature ranges of 60–120°C in both cases, to be around 94 and 66 kJ mol⁻¹, respectively. The results obtained at low temperatures by these authors are close to what we obtained in our study (temperature range 70–110°C), for tensile strength and elongation at break. From our results and those reported in the literature, it appears that there is a general increase in activation energy of ageing with increase in ageing temperature. However, it is also clear that the activation energy is dependent on the compound composition, precise ageing conditions, and the method used to detect the extent of ageing.

Mechanism of thermo-oxidative ageing

The rate of thermo-oxidative degradation is affected by the rate of oxygen diffusion into the NR compound. It

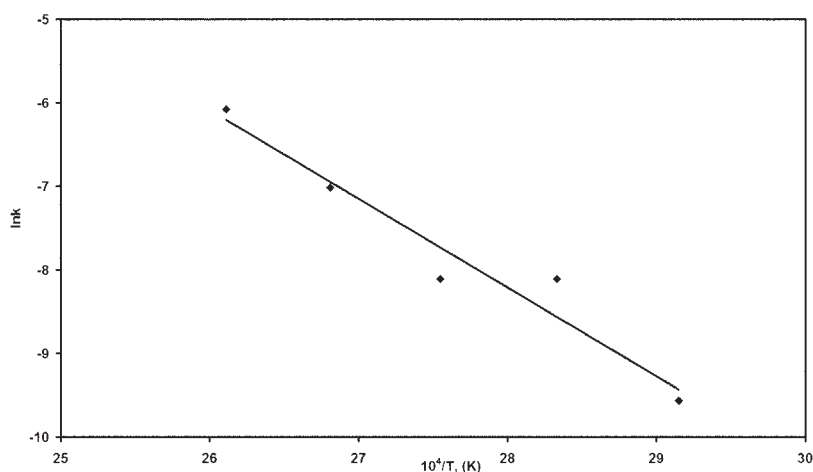


Figure 9 Arrhenius plot for ageing in terms of its effect on tensile strength.

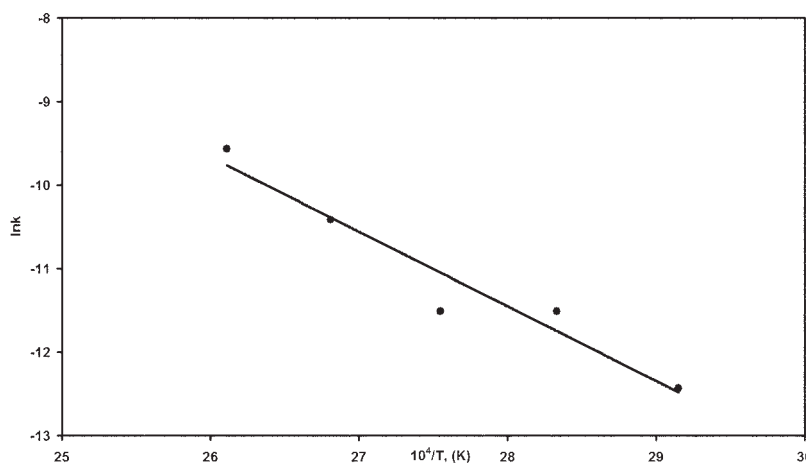


Figure 10 Arrhenius plot for ageing in terms of its effect on elongation at break.

has been postulated that if the temperature is relatively low, for an unprotected NR vulcanizate, diffusion occurs more quickly than oxidation and therefore there is oxidation throughout the product. However, as the temperature rises, the rate of oxidation increases much more than the rate of diffusion, so substantial oxidation occurs on the surface and an oxidized (hard skin) surface is formed.²⁶ For rubber containing antioxidants, the same effects are observed but the rate of diffusion of oxygen into the rubber is slowed down, because the antioxidant present in the rubber is being consumed at the surface. Surface oxidation that results in a brittle surface layer causes cracks to form on the surface of the rubber as it is being stretched. These cracks act as stress concentrators thereby reducing both the tensile strength and elongation at break. As ageing time is increased, more and more antioxidants are being consumed resulting in an increase in oxygen diffusion into the rubber and an increase in thickness of the oxidized layer accompanied by a further decrease in tensile strength. According to Bell et al.,²⁶ as ageing increases the thickness of the hard layer and hence, the size of the cracks increases. At a particular level of ageing the cracks become greater than the critical value for crack propagation, and test pieces tear rather than fracture, resulting in low tensile strengths. Upon tensile testing of rubber samples used in the current study, after ageing at 90°C for 72 h, cracks could be seen emanating from the surface in all directions (Fig. 11). The presence of cracks indicates that surface hardening has taken place and that oxidation is occurring more rapidly than oxygen diffusion.

According to Ahagon et al.¹ and Baldwin et al.,¹⁴ three types of ageing mechanisms are observed in NR; Types I, II, and III. Type I ageing is characterized by crosslinking being the dominant event resulting in an increase in modulus and lowering of the elongation at break. In Type II ageing the modulus either changes a little or is reduced, and the factors involved in Type II

ageing are main-chain modifications reducing the number of extensible units. Type III ageing is characterized by both crosslinking and chain scission due to oxidation at high temperatures. The Ahagon plot has also been used to describe the type of ageing process taking place in rubber tires.^{1,14} According to Ahagon et al.^{1,13} and Baldwin et al.,¹⁴ aerobic ageing of rubber is characterized by a straight line when log of the elongation at break is plotted against log of the stress at 100% strain. Type I ageing is characterized by a slope of about -0.75 . Type III high temperature aerobic ageing is characterized by an increase in the modulus (M_{100}) after ageing compared to the original, with the reduction in the elongation at break becoming larger with increasing ageing temperature. Type II anaerobic ageing of rubber gives data deviating from a straight line. It is worthwhile noting that the magnitude of the slope is a characteristic of the compound being studied.

From the Ahagon plot of data from the current study (Fig. 12), it was observed that ageing of the NR com-

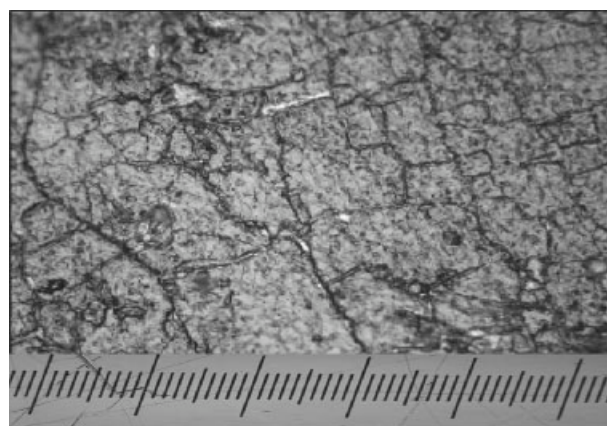


Figure 11 Light microscopic image showing crack surface of an aged rubber sample after tensile testing (each minor division is 10 μm).

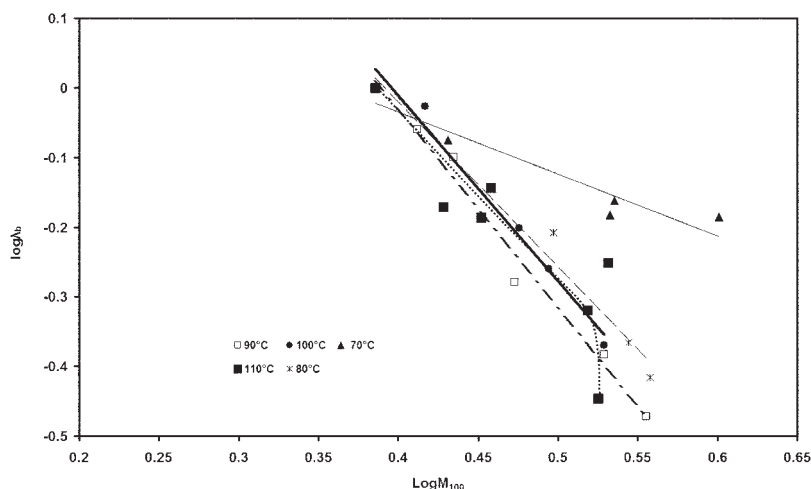


Figure 12 Ahagon plots for thermo-oxidative ageing.

pound at 70°C is Type I, with a slope of -0.89 , and was dominated by crosslinking events, which resulted in a steady increase in the modulus and lowering of the elongation at break. At all the other temperatures Type III ageing was observed.

CONCLUSIONS

Ageing in air at temperatures between 70 and 110°C resulted in increases in 100% modulus. The fractional rate law describes the kinetics of degradation of the NR compound in terms of the modulus. Rates of ageing, in terms of effect on modulus, passed through a minimum at about 80°C. The minimum in the Arrhenius plot indicates the danger in trying to extrapolate in-service ageing behavior from high temperature ageing conditions. It is assumed that the phenomenon is due to the balance of chain scission and crosslinking reactions varying with ageing temperature. The activation energy of ageing in terms of its effect on modulus determined for temperatures of 90–110°C was 151 kJ mol^{-1} .

Ageing in terms of the effect on tensile strength and elongation at break were found to follow second order kinetics, with activation energies of 88.32 and 74.3 kJ mol^{-1} , respectively. Results are consistent with the chain scission reactions having a higher activation energy than the crosslinking reactions.

From Ahagon plots, two types of ageing mechanisms were identified, Type I for ageing at 70°C, being dominated by crosslinking and Type III for 80–110°C, being affected by both crosslinking and scission reactions.

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