# Degradation and Life Prediction of a Natural Rubber Engine Mount Compound

**Frederick E. Ngolemasango,[1,2] Martyn Bennett,[3] Jane Clarke[1]**

[1]*Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough, Leicestershire LE11 3TU, United Kingdom*
[2]*Department of Chemistry, Faculty of Science, University of Buea, P.O. Box 63, Buea, Cameroon*
[3]*Avon Materials Development Centre, Brook Lane Industrial Estate, Westbury, Wiltshire BA13 4EP, United Kingdom*

**ABSTRACT:** To assess and predict the functional life of a natural rubber engine mount compound, the mechanical property changes were determined under accelerated aging conditions. The rubber was aged at temperatures ranging from 70 to 110°C for times ranging from 1 h to 5 weeks. Tensile and fatigue measurements were used to characterize the aging trends and mechanisms of the engine mount compound. With the time–temperature superposition approach, the activation energy was found to be about 98 kJ/mol for the elongation at break, 93 kJ/mol for the tensile strength, and 60 kJ/mol for the fatigue life. The tensile strength after aging for 13 weeks at 50°C was predicted to be 18.73 MPa, which was very close to the experimental value of 19.04 $\pm$ 2.25 MPa. With a 50% reduction in the tensile strength used as the failure criterion, it was predicted that the tensile strength of the engine mount compound would take 80 days to decrease by 50% at 70°C. At 23°C, it would last approximately 140 times (31 years) its lifetime at 70°C. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 348–355, 2008

**Key words:** activation energy; fatigue analysis; kinetics (polym.); mechanical properties; rubber

## INTRODUCTION

Rubbery materials are usually subjected to physical and chemical property changes due to aging, whether they are in service or in storage.[1–5] In the rubber industry, it is usually necessary to evaluate the aging resistance of automobile components such as the engine mount, tires, and seals, but this might take several years for a complete process to be observed in real service. Moreover, because of considerable variations in the conditions in terms of location and seasonal variations, it is very difficult to evaluate changes due to degradation in a natural rubber compound in absolute terms. Under real service conditions, engine mounts are exposed to a combination of factors including oxygen, heat, various liquids, and dynamic motion. Aging, therefore, is a composite of all these factors.[6]

In recent years, studies on the mechanisms and types of degradation in natural rubber have attracted wider attention because of the changes in the service conditions of this polymer, especially in the automobile industry.[1,7,8] With the fast changing environmental conditions, many of the components that use natural rubber as one of the base polymers, such as tires and engine mounts, fail before their anticipated life span. This has necessitated new approaches to describing the mechanisms and service life predictions of these engineering parts because some standard models do not consider all aspects of the service environment.

Baldwin et al.,[3] researching tires in different areas of the United States, found out that despite the differences in the environmental conditions in the sampled states, the degradation mechanisms were almost the same, no matter what the make of the tires was. Furthermore, Baldwin et al. studied the degradation kinetics of skim rubber when tires were subjected to a treatment in an air-circulating oven. The time–temperature superposition (TTS) approach, developed by Gillen et al.,[9] was applied to swelling measurements and peel strength. They found that when the tires were inflated with 100% air or a 50/50 blend of $N_2/O_2$, the apparent activation energies for the effect of degradation were the same for the peel strength (101 kJ/mol) and swelling ratio (109 kJ/mol). However, Bauer et al.[10] found that the rate of oxidation increased by a factor of 1.4 when a 50/50 blend of oxygen and nitrogen was used as the fill gas.

The life prediction of polymeric materials has been one of the most sought after objectives in the polymer industry. Reproducible methods and reliable predictive models must be obtained if premature

failure is to be reduced to a minimum. The methods so derived could be useful for the development of new or modified compound formulations. The Arrhenius methodology is the most common and widely used for the calculation of the activation energy for degradation at high temperatures and functional life predictions. If the Arrhenius relationship holds, this is extrapolated to lower temperatures to make predictions. Many problems have been encountered when the Arrhenius model is used for the prediction of the life of certain commercial polymers. Some of these problems, as explained by Gillen et al.,[9] are dependent on physical effects such as extrapolation across a polymer transition. Other factors include diffusion-limited oxidation, antioxidant behavior involving its redistribution by internal diffusion, and evaporation/blooming at the surface. Changes in the effective activation energy can also be brought about by such things as a switch in the dominant mechanism as the temperature is changed or a slow temperature-dependent change due to the complex form of the effective activation energy. This has resulted in non-Arrhenius behavior, especially at low temperatures.[11] Gugumus[12] attributed this non-Arrhenius behavior in some polymers to the activity of transition-metal impurities, such as trace metal iron from processing equipment.

In this study, we used Gillen et al.'s[9] approach to determine the activation energy of the thermooxidation of natural rubber by following the changes in the mechanical properties over time at different temperatures. The aim was to contribute to the development of a model that could predict the functional life of a natural rubber engine mount.

## EXPERIMENTAL

### Materials

Natural rubber (SMRCV60) was supplied by the Tun Abdul Razak Research Centre (Hertford, UK), and carbon black (N772) was supplied by Columbian Chemicals (Avon Mouth, UK); tetramethylthiuram disulfide (TMTD), N-(1,3-dimethylbutyl)-N″-phenyl-p-phenylenediamine (6-PPD), 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), and N-tert-butyl-2-benzothiazolesulfenamide (TBBS) were supplied by Flexsys (Brussels, Belgium). Sulfur, zinc oxide, antiozonant wax, and stearic acid were used as supplied.

### Methods

#### Compounding

A typical engine mount formulation, shown in Table I, was used for the compounding.

The natural rubber compound was prepared in a Francis–Shaw K1 water-cooled intermixer (Farrel

**TABLE I**
**Formulation for the Natural Rubber Engine Mount Compound**

| Material | Composition (phr) |
| --- | --- |
| SMRCV60 | 100 |
| Carbon black (N772) | 49 |
| Zinc oxide | 5 |
| Stearic acid | 2 |
| Antiozonant wax | 2 |
| 6-PPD | 1.5 |
| TMQ | 1 |
| TBBS | 0.7 |
| TMTD | 0.5 |
| Sulfur | 1.7 |

Ltd., Rochdale, UK) with a volume of 5.5 L. A fill factor of 0.55 was used, and the mixing was performed at a speed of 40 rpm; the rotors and mixing chambers were cooled with circulating water at 40°C. The rubber was first masticated in the internal mixer for 2 min together with the activators (zinc oxide and stearic acid) and the antiozonant wax. Carbon black was then added, and the compound was mixed for another 4 min before the antioxidants (TMQ and 6-PPD), accelerators (TMTD and TBBS), and crosslinking agent (sulfur) were introduced. The mixing was then carried out for another minute before dumping. The compound was then sheeted out on a two-roll mill to a thickness of about 3.2 mm.

#### Cure measurements and vulcanization

Cure parameters were determined with a Monsanto R100S rheometer (Prescott Instruments Ltd., Tewkesbury, UK) operating at a strain amplitude of 3° and at a cure temperature of 140°C. From the rheographs obtained, the scorch time, cure rate index, and minimum and maximum torque were obtained. Test sheets were then compression-molded with a hydraulic press with electrically heated platens to 95% cure at 140°C for 24 min.

#### Accelerated thermal/thermooxidative aging

Thermooxidative ageing was carried out in an air-circulating environmental chamber at temperatures of 70, 80, 90, 100, and 110°C for times ranging from 1 h to 5 weeks. At the end of each aging time, samples were removed and kept at room temperature before testing within 48 h of removal from the aging chamber.

#### Tensile testing

Tensile properties were measured in accordance with BS903-A2[13] with type II dumbbell test pieces,
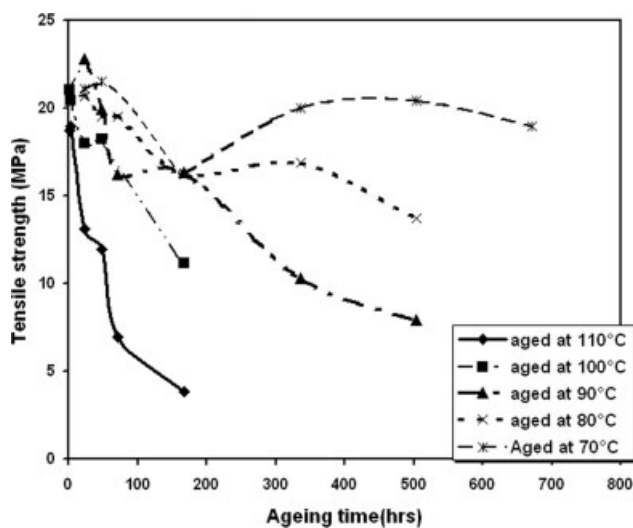
**Figure 1** Effect of aging on the tensile strength.

which were die-stamped from 2-mm-thick vulcanized sheets along the milling direction. A Hounsfield tensile testing machine (Tinius Olsen Ltd., Redhill, UK) operating at a crosshead speed of 500 mm/min was used with a Hounsfield 500L laser control apparatus attached to it to measure the extension. Benchmarks were placed at a distance of 2 cm from each other. The tensile strength, elongation at break, and modulus were acquired with QMAT-Dongle 2003 computer software (Tinius Olsen Ltd., Redhill, UK). At least eight specimens were tested from each molded sheet.

Fatigue testing

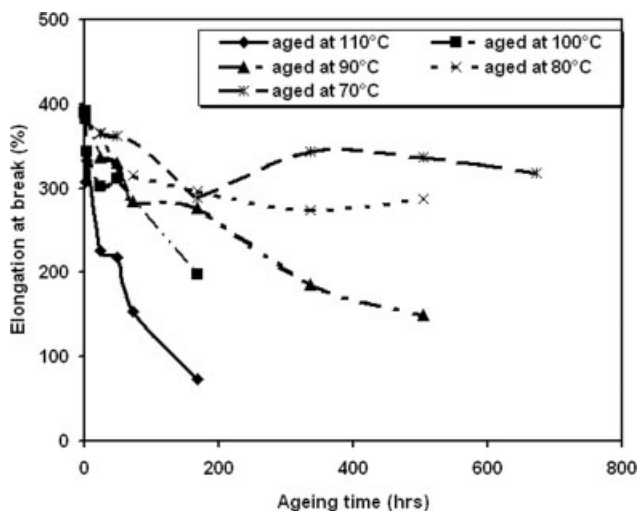Type II dumbbell samples cut from aged rubber sheets were fatigue-tested in uniaxial tension with a Hampden dynamic testing machine (Hampden Test Equipment Ltd., Kettering, UK) to determine the fatigue life of the rubber compound. A frequency of 2 Hz and a strain amplitude of 100%, with the strain on each test piece relaxed to zero after each fatigue cycle, was applied. At least 14 test pieces were tested for each aging time and temperature. The number of cycles to failure was then recorded. All the measurements were carried out at the ambient temperature.

## RESULTS AND DISCUSSION

### Tensile strength and elongation at break

The tensile strength and elongation at break of the natural rubber compound decrease with the aging time (Figs. 1 and 2), but the rate of decrease of the tensile strength and elongation at break decreases with a decrease in the aging temperature. It is well established that both crosslinking and scission reactions result in a decrease in the elongation at break and tensile strength.[14,15]

### Modulus

Figure 3 shows the effect of the aging temperature on the stress at 100% elongation (100% modulus). The modulus generally increases with an increase in the aging time, the rate of increase generally increasing with the aging temperature. This was the same trend observed by Ahagon et al.[1] and Baldwin et al.[2,3] in their studies on the accelerated aging of tire compounds. However, the change in the modulus with the aging time is quite complex; for many temperatures, a peak in the modulus is observed at relatively short aging times of less than 100 h. Hamed and Zhao[15] explained that in the early stages of aging, additional network chains can result from crosslinking by residual curatives, rearrangement of crosslinked sulfur, and/or oxidative coupling. A
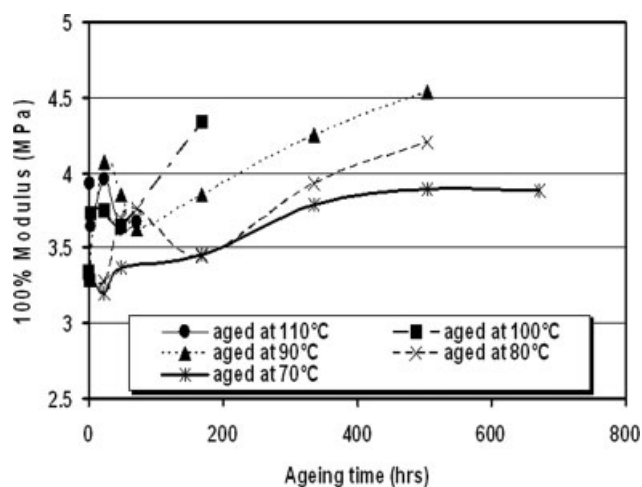


**Figure 2** Effect of aging on the elongation at break.



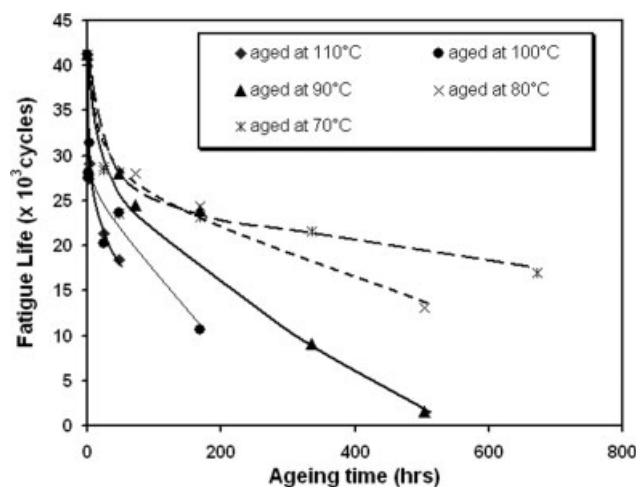**Figure 3** Effect of aging on the 100% modulus.

**Figure 4** Effect of aging on the fatigue life.

reduction in the rank of sulfur and some additional crosslinking as a result of maturation of the sulfur crosslinks will result in an increase in the modulus. With increasing aging time, the modulus drops and then starts increasing again. The drop in modulus may be due to scission of bonds taking place. The increase in the modulus after this slight decrease can be attributed to chain cleavage resulting in the formation of free radicals, which then bond to form new crosslinks, hence leading to an overall increase in the crosslink density. Overall, the reason for the general increase in the modulus can be attributed to the crosslinking reactions outweighing the scission reactions during the thermooxidative aging process. Further aging results in scission events becoming predominant.

## Fatigue life

As the aging temperature and aging time increase, the fatigue life decreases significantly (Fig. 4). Several reasons may be advanced for the observed trend. It is well known that natural rubber strain-crystallizes and that strain crystallization inhibits crack growth. This effect is usually observed at low temperatures. The strain crystallization is reduced as a result of oxidative aging; once a crack is initiated, the fatigue crack growth rate significantly increases, and this results in a decrease in the fatigue life.[16] Another reason is that during aging, antioxidants are consumed, and oxygen diffuses into the rubber, bringing about chain cleavage, but at higher temperatures, there is diffusion-limited oxidation, resulting in a hard skin forming at the surface of the rubber, which can easily crack during the fatigue process. These cracks, once initiated, propagate easily, resulting in failure of the compound. Diffusion-limited oxidation can happen only at lower aging temperatures

at longer aging times. Generally, oxidative aging causes embrittlement of the rubber and affects the fatigue life.[17] Furthermore, the dominant types of crosslinks formed during aging also affect the fatigue life. Polysulfide crosslinks are said to be superior to monosulfide crosslinks or carbon–carbon crosslinks. This is because the polysulfide networks have the ability to break before the rubber network chains and subsequently reform. This leads to increased crack tip blunting and to increased heat dissipation due to hysteresis.[17]

## Kinetics and functional life prediction

The Arrhenius model has mostly been used as a predictive tool for the lifetime of polymers aged at low temperatures with extrapolation from high-temperature measurements. One of the shortcomings of this method is that measurements from individual aging temperatures are used to calculate the rate constant $k$, which is then used in the plot to calculate the activation energy of degradation and subsequently used for the prediction of the functional life of the material.[18] The use of this approach may lead to overestimation/underestimation of the service life of the natural rubber component if data are extrapolated to lower temperatures.

Using the TTS method, in which all the individual data at all aging temperatures (70–110°C) are used to construct a master curve, may give reliable results. The method, however, does not remove the extrapolation problem also encountered when the Arrhenius approach is directly used; it is just a different way of averaging results that may be less prone to error because there are fewer stages in the manipulation of the data.

Gillen and coworkers[9,19] developed a TTS method that can conveniently be used to predict the service life of a material that is subjected to aging. In this method, the lowest aging temperature is used as the reference temperature. Then, for each set of data at a higher temperature, the experimental times at this temperature are multiplied by a constant empirically determined shift factor, such that the data at this temperature best superpose the reference temperature data. The Arrhenius type model is then used to explain the relationship between the empirically determined shift factors and the temperature:

$$a_T = \exp \frac{E_a}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right) \tag{1}$$

where $a_T$ is the shift factor, $E_a$ is the activation energy (kJ/mol), $R$ is the gas constant, $T$ is the absolute temperature, and $T_{ref}$ is the reference temperature. If the Arrhenius expression is valid, then a plot of log $a_T$ against $1/T$ (K) should show linear be-
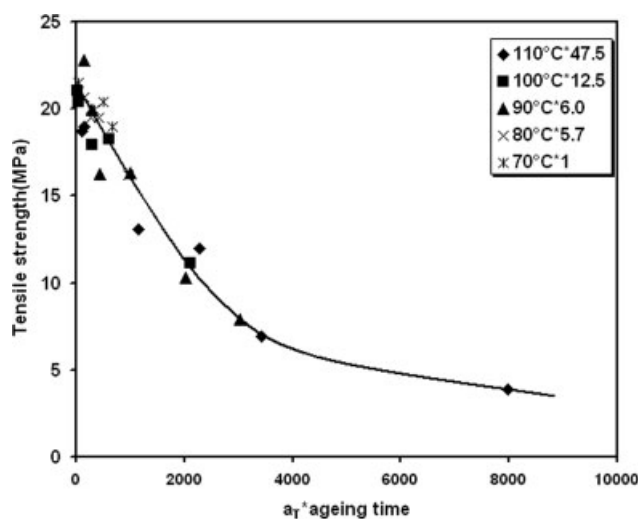
**Figure 5** TTS plot for the tensile strength for the aging of natural rubber at a reference temperature of 70°C.



**Figure 7** Arrhenius plot of log $a_T$ versus $1/T$ for the tensile strength.

havior. This method was also used by Baldwin et al.[2,3] to predict the service life of some polymer compounds.

### Tensile strength and elongation at break

Figures 5 and 6 present shifted plots for the tensile strength and elongation at break. The line plot is a model describing the fitness of the shifted data. Correlation coefficients of 0.9211 and 0.9065 were obtained for tensile strength shifted data and elongation at break shifted data, respectively.

A plot of the logarithm of the shifted factors against the inverse absolute temperature was constructed for both the tensile strength and elongation at break to determine the activation energy. Apply-
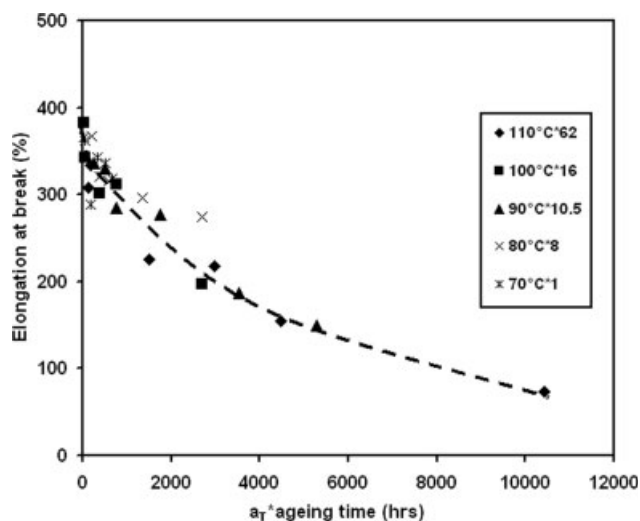
ing eq. (1), we obtained a straight line for the plots of the tensile strength and elongation at break with correlation coefficients of 0.9223 for the tensile strength (Fig. 7) and 0.9065 for the elongation at break (Fig. 8). From these plots, the activation energy was calculated to be ~93 kJ/mol for the tensile strength and ~98 kJ/mol for the elongation at break (Table II). As explained by Gillen et al.,[19] the activation energy for oxidation processes is normally in the range of 80–120 kJ/mol.

### Fatigue life prediction

Figures 9 and 10 present shifted plots for the fatigue life and Arrhenius-type plots for the shifted data, respectively. The model describing the fitness of the plot had a regression coefficient of 0.9327. Points



**Figure 6** TTS plot for the elongation at break for the aging of natural rubber at a reference temperature of 70°C.
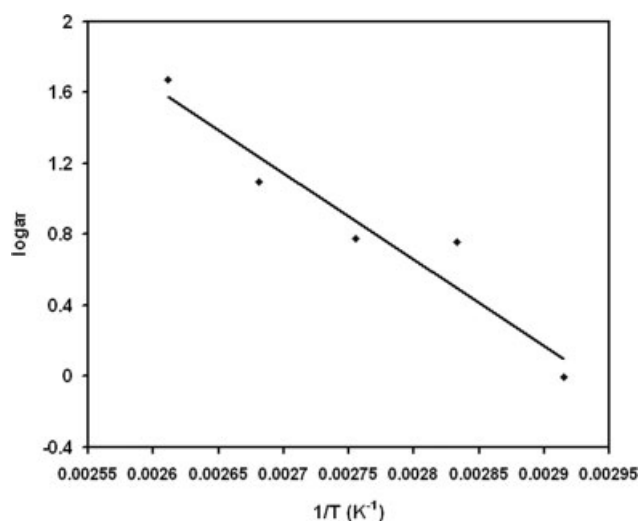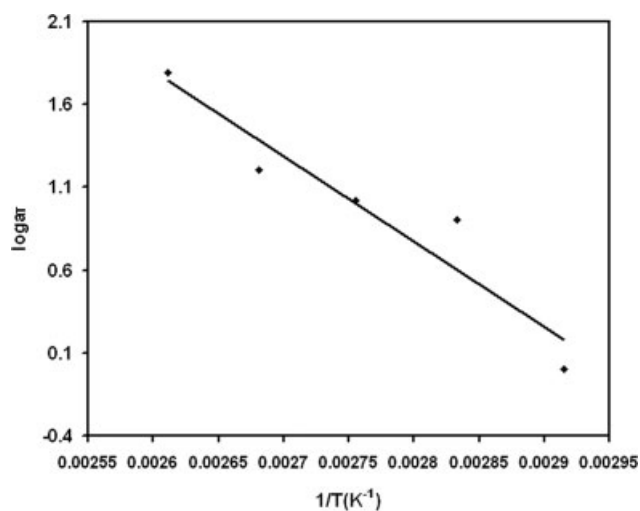


**Figure 8** Arrhenius plot of log $a_T$ versus $1/T$ for the elongation at break.

**TABLE II**
**Activation Energies and Service Life Predictions of a
Natural Rubber Engine Mount Compound**

| Property | Activation energy (kJ/mol) | Prediction with the TTS model | |
|---|---|---|---|
| | | Experimental value at 50°C | Predicted value at 50°C |
| Tensile strength | 92.9 | 19.04 ± 2.3 | 18.73 |
| Elongation at break | 98.1 | 321.04 ± 33.8 | 327.12 |
| Modulus | 79.5 | 4.17 ± 0.09 | 3.66 |

Service life prediction (failure criteria: 50% property reduction)

| | Temperature | | | |
|---|---|---|---|---|
| | 70°C | 50°C | 40°C | 23°C |
| Tensile strength | ~ 80 days | ~ 1.3 years | ~ 4 years | ~ 31 years |



**Figure 10** Arrhenius plot of log $a_T$ versus $1/T$ for the fatigue life.

were close to the linear model fit. The plot of the logarithm of the shift factor against the inverse absolute temperature for fatigue data, with the application of eq. (1), had a linear correlation coefficient of 0.9685. That activation energy was calculated to be about 60 kJ/mol. This low activation energy of the fatigue life of the aged rubber might be a result of the fact that fatigue measurements are not temperature-sensitive as the equilibrium temperature is easily attained during measurements, and any other effect on fatigue life might be as a result of aging that has already taken place, affecting the chemical structure and hence the crack growth rate.

To use the TTS model for the prediction of the functional life of our material, the rubber was aged
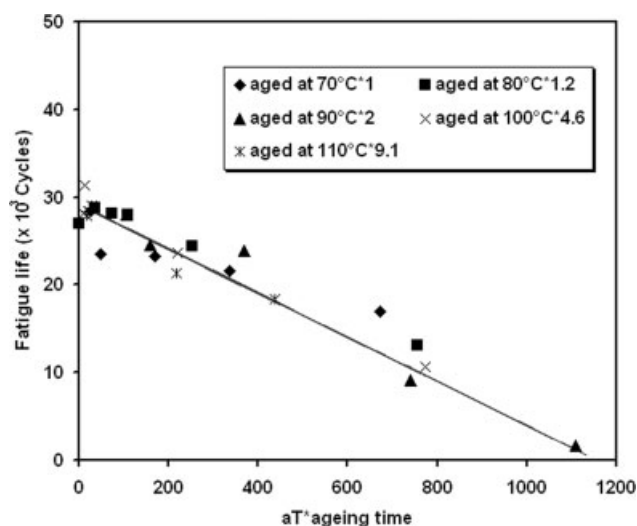


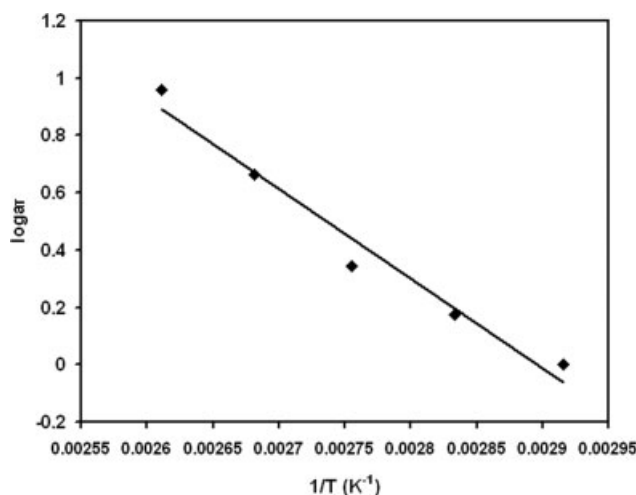**Figure 9** TTS plot for the fatigue life of aged natural rubber at a reference temperature of 70°C.

at 50°C for more than 3 months. The tensile strength after aging for 13 weeks at 50°C was determined to be 19.04 ± 2.25 MPa, and the predicted value at 50°C was 18.73 MPa (Table II). When a 50% reduction in the tensile strength and elongation at break was selected as a failure criterion, it was predicted that the tensile strength of the engine mount compound would take approximately 80 days to decrease by 50% at a temperature of 70°C. At 23°C, it would take approximately 31 years to attain the same level versus its lifetime at 70°C (Table II).

**Mechanisms of the aging process**

The aging mechanism is a function of temperature. For natural rubbers, lower temperature aging leads to increases in the modulus, whereas high-temperature aging leads to a decrease in the modulus. Thus, with the aging time, during low-temperature aging, an increase in the crosslink density is observed, whereas a decrease in the crosslink density is observed at higher aging temperatures.[6] The degra-
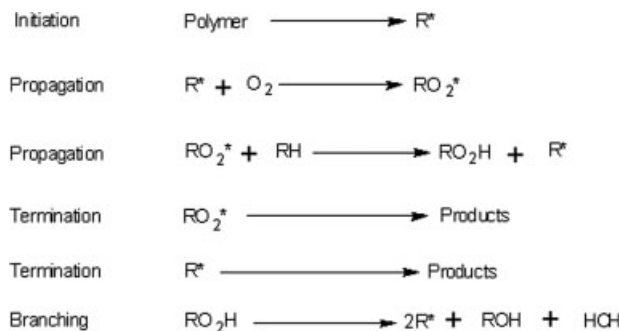


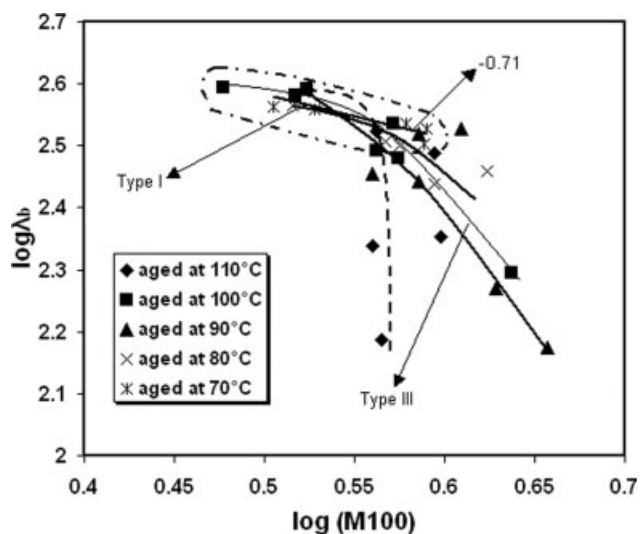**Figure 11** Scheme of a typical autoxidation reaction of natural rubber.

**Figure 12** Ahagon plot for the aging mechanisms of a natural rubber compound ($\lambda_b$ = elongation at break; $M_{100}$ = 100% modulus).

dation mechanism of natural rubber compounds and most polymers has long been established. Various schemes have been proposed for the aging of rubber and other polymers,[7,19,20] but all of them point to the fact that crosslinking and scission take place almost simultaneously. One such mechanism proposed by Gillen et al.[19] to derive the oxygen consumption rate is shown in Figure 11. To follow the degradation mechanism during the thermooxidative aging of the natural rubber engine mount compound, we used the method described by Ahagon et al.[1,3] Two types of aging mechanisms were observed when a plot of the logarithm of the elongation at break against the logarithm of the modulus was made (Fig. 12). Type I is predominantly a crosslinking mechanism with a characteristic slope of $-0.71$. The points enclosed within the ellipse lie on lines with a slope close to $-0.71$. At the lowest aging temperature of 70°C, all the data lie on this line, indicating the predominance of crosslinking reactions. For the other aging temperatures, apart from 110°C, data from the early stages of aging fall within the type I category, showing that crosslinking reactions were predominant in the early stages of aging. The remaining data lie on lines with steeper slopes, corresponding to the type III mechanism, which is characterized by mostly scission reactions. It has been proposed by many authors[20–22] that the degradation of natural rubber follows mostly a free-radical mechanism. They explain that in the presence of sufficient oxygen, a hydroperoxide is generated that breaks down to form two radicals, which then trigger a series of chain reactions. The presence of antioxidants in the compound slows down the reaction by consuming some of the free radicals, but as the antioxidants are depleted, the

free radicals that are generated with the aging time and temperature continue to enhance chain scission reactions. The results indicate that at high temperatures and in later stages of the aging process, scission processes predominate.

## CONCLUSIONS

Thermooxidative aging of the natural engine mount compound resulted in a decrease in the tensile strength, elongation at break, and fatigue life with an increase in the modulus when the rubber was aged at temperatures between 70 and 110°C. The TTS method was used to describe the kinetics of aging. The activation energies for the effect of aging on the tensile strength and elongation at break were found to be about 93 and 98 kJ/mol, respectively. The activation energy for the fatigue life was determined to be ~60 kJ/mol.

From the Arrhenius plots, the tensile strength after aging for 13 weeks at 50°C was predicted to be 18.73 MPa, which was very close to the experimental value of 19.04 ± 2.25 MPa. For life prediction, a 50% reduction in the tensile strength was selected as a failure criterion. It was predicted that the tensile strength of the engine mount compound would take approximately 80 days to decrease by 50% at a temperature of 70°C. At 23°C, it would last approximately 140 times longer (31 years) versus its lifetime at 70°C. When fatigue life was considered, it would last approximately 4 times longer at 50°C versus its lifetime at 70°C and 33 times longer at 23°C.

Two types of aging mechanisms (type I and III) were predominant. Type I aging is characterized by crosslinking being the dominant event, resulting in an increase in the modulus and lowering of the elongation at break. Type III is characterized by both crosslinking and chain scission due to oxidation at high temperatures.

## References

1. Ahagon, A.; Kida, M.; Kaidou, H. Rubber Chem Technol 1990, 63, 683.
2. Baldwin, J. M.; Bauer, D. R.; Ellwood, K. R. Rubber Chem Technol 2005, 78, 336.
3. Baldwin, J. M.; Bauer, D. R.; Ellwood, K. R. Rubber Chem Technol 2005, 78, 767.
4. Brown, R. P.; Butler, T.; Hawley, S. W. Ageing of Rubber - Accelerated Heat Ageing Test Results; Rapra Technology Ltd.: Shawbury, 2001; p 37.
5. Ngolemasango, F.; Ehabe, E.; Ayrmard, C.; Sainte-Beuve, J.; Nkouonkam, B.; Gobina, S.; Bonfils, F. Polym Int 2003, 52, 1365.
6. Deng Huang, B. J. L.; Castro, J. M.; Ignatz-Hoover, F. Polym Degrad Stab 2001, 74, 353.
7. Bevilacqua, E. M. In Thermal and Oxidative Degradation of Natural Rubber and Allied Substances; Conley, R. T., Ed.;

Thermal Stability of Polymers; Marcel Dekker: New York, 1970; Vol. 1, p 189.

8. Boon, A. J. J Nat Rubber Res 1988, 3, 90.

9. Gillen, K. T.; Celina, M.; Keenan, M. R. Rubber Chem Technol 2000, 73, 265.

10. Bauer, R. D.; Baldwin, J. M.; Ellwood, R. K. Rubber Chem Technol 2005, 78, 777.

11. Gillen, K. T.; Bernstein, R.; Derzon, D. K. Polym Degrad Stab 2005, 87, 57.

12. Gugumus, F. Polym Degrad Stab 1999, 63, 41.

13. Method for Determination of Tensile Stress–Strain Properties: Physical Testing of Rubber; British Standard Association: London, UK, 1995; Vol. A2.

14. Gent, A. N.; Hartwell, J. A.; Lee, G. Rubber Chem Technol 2003, 76, 517.

15. Hamed, G. R.; Zhao, J. Rubber Chem Technol 1999, 72, 721.

16. Young, D. G. Axel Phys Test Services Rep 2001, 6, 1.

17. Mars, V. M.; Fatemi, A. Rubber Chem Technol 2004, 77, 391.

18. Ngolemasango, E. F.; Bennett, M.; Clarke, J. J Appl Polym Sci 2006, 102, 3732.

19. Gillen, K. T.; Celina, M.; Bernstein, R. Polym Degrad Stab 2003, 82, 25.

20. Howard, J. Rubber Chem Technol 1974, 74, 975.

21. Shelton, J. R. Rubber Chem Technol 1972, 45, 359.

22. Dunn, J. R. Rubber Chem Technol 1974, 47, 960.