

Thermal Aging of Polyethylene-*co*-methyl Acrylate Elastomer Activation Energies of Physical and Physicochemical Mechanisms

P. DOLE, J. CHAUCHARD

Laboratoire d'Etudes des Matériaux Plastiques et des Biomatériaux, UMR CNRS 5627, Université Claude Bernard Lyon I 69622 Villeurbanne Cedex, France

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ABSTRACT: This article deals with the thermal aging of a polyethylene-*co*-methyl acrylate elastomer. Six different activation energies have been determined corresponding to the following different mechanisms: surface oxidation, whole bulk oxidation in the case of heterogeneous oxidation, consumption of antioxidant, creep, and relaxation (compression set). Relaxation mechanism has been found to have the lowest activation energy (45 kJ/mol). Dominant chemical modification has been found to have the highest activation energy (119 kJ/mol). The case of heterogeneous oxidation is considered in details: a variation of the activation energy is obtained. The activation energy varies from a constant upper value related to homogeneous oxidation, to a lower value related to the so-called "total heterogeneous oxidation." © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2507–2515, 1997

Key words: poly(ethylene-*co*-methyl acrylate); aging; activation energy; total heterogeneous oxidation; creep; relaxation

INTRODUCTION

An important application of elastomers is the fabrication of seals. The durability of equipment containing seals is often directly connected to the lifetime of the basic elastomer. The calculation of the lifetime value of this type of material is often obtained directly by a calculation based on the Arrhenius law. Application of the Arrhenius equation leads to the determination of the activation energy, which is often given by the raw material supplier. In the case of a sealing function, two types of properties have to be considered, and also a minimum of two values should be given: (a) properties connected to the chemical composition, the microstructure of the matrix (if the elastomer is semicrystalline), and/or the formulation of the blend; (b) strain properties (creep or relaxation),

which are only connected to the mobility of macromolecules under stress. The difficulty is in this case to determine the pure variations of irreversible strain without the influence of chemical or physicochemical mechanisms.

This article deals with the determination of all activation energies of the thermal aging of a polyethylene-*co*-methyl acrylate elastomer. The oxidation mechanism of the basic pure rubber has been proposed previously.¹ The anomalous evolution of the glass transition temperature (which tends to increase in the presence of oxygen) is explained by the formation of ester links and/or hydrogen bonds between alcohols obtained from oxidation of polyethylene sequences, and methyl acrylate groups (Fig. 1). Due to the importance of oxygen in the degradation of ethylene-*co*-methyl acrylate copolymers (no significant variation of properties under nitrogen at temperatures lower than 200°C) there occurs a problem of heterogeneous degradation in the case of thick samples. In previous articles^{2–4} the problem of the model-

Correspondence to: P Dole.

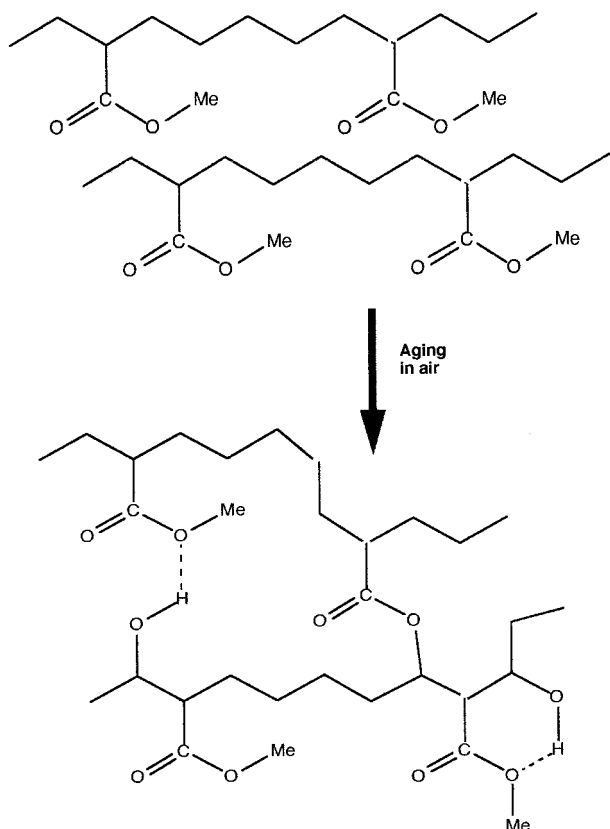


Figure 1 Oxidative crosslinking mechanism of poly(ethylene-*co*-methyl acrylate).

zation of oxidation profile shapes and the correlation with the macroscopic properties has been discussed. The object of this article will be to observe the consequence of heterogeneous degradation on the apparent variation of the apparent activation energy.

The determination of the activation energy of the dominant mechanism of degradation (under accelerated aging conditions) of the pure material is not sufficient: (a) antioxidant additives often lead to the existence of an induction period during which time the oxidation of the matrix is inhibited: the step of antioxidant consumption.^{5,6} In some cases, when the oxidative degradation of the matrix is rapid, the lifetime of the material is only approximated by the induction period. Under these conditions, the activation energy does not depend on the nature of the matrix, or only indirectly (mobility of the additive); (b) the third problem concerning physicochemical and chemical aging is to look for secondary mechanisms that might be dominant under real aging conditions. In the case of crosslinking mechanisms, chain scissions have to be studied carefully.

MATERIALS

The present study concerns the thermal degradation of a VAMAC (registered trademark of Du Pont de Nemours)-based industrial rubber. The formulation used contains 41.5% of black filler, 56% of ethylene-*co*-methyl acrylate copolymer (vulcanized by hexamethylene diamine), and 2.5% of additives (antioxidant: substituted diphenylamine, lubricant: aliphatic phosphate, accelerator: diorthotolylguanidine). The stoichiometric composition of the basic rubber is given in Figure 2.

Thermal aging has been made at 220, 200, 180, 152, 125, 120, 97, $90 \pm 1^\circ\text{C}$ in ventilated ovens, in air at atmospheric pressure.

METHODS

Surface Resistance

Measurements have been made using a four-point resistivity probe, using the imposed intensity mode (10^{-4} A). This value has been chosen in a range where the Ohm law was verified.

UV Measurements

Samples have been extracted by diethyl ether using three different methods: (a) soxhlet extraction (1 day); (b) extraction simply by immersion (2 h) at 23°C ; (c) extraction simply by immersion (5 min) at 23°C .

In the first two cases, a complex UV spectra is obtained: a convolution of peaks occurs at 212, 220, 227, and 291 nm. The spectra of extractable species is quite similar to the UV spectra of the antioxidant (substituted diphenylamine).

In the third case, if the analysis is made immediately after extraction, only peaks at 212 and 291 nm are observed. After a 1-h storage time of the extractable solution, an evolution of the spectra is observed, becoming increasingly more important with time: appearance of absorption peaks at 220 and 227 nm. The same result is obtained when solutions of increasing concentration of antioxidant are analyzed immediately after dissolution. These phenomena may also be connected to superposition of antioxidant molecules (dimers, trimers) leading to the formation of highly absorbent species, which become more and more numerous with storage time and concentration.

To help interpret the spectra, samples ($5 \times 5 \times 2$ mm) were extracted for 5 min (in 20 mL of diethyl ether) and analyzed immediately.

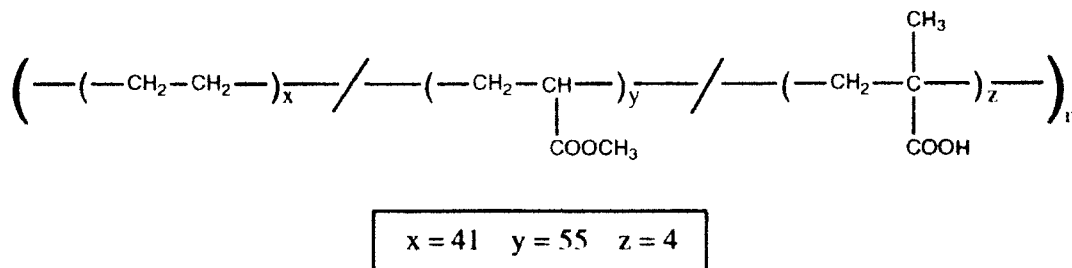


Figure 2 Basic rubber of the material studied.

The partial fraction extracted should be constant because no significant modifications of the chemical network occurs during the induction period (period of antioxidant consumption) and also no variation of diffusion properties occurs.

Compression Set

The most frequently used test to evaluate the lifetime of seals is the compression set (French normalization: NFT46-011). Plots (diameter 28 mm, thickness: 12.6 mm) are compressed at constant strain 18%. After aging, the stress is suppressed, and the measure of the "irreversible" strain is made after 30 min. The compression set is given by eq. (1):

$$\text{compression set} = \frac{\text{Irreversible strain}}{\text{Imposed strain}} \quad (1)$$

Creep

Variation of strain as a function of time is calculated using a Perkin-Elmer DMA 7. Constant stress applied: 2 N/5 mm diameter.

Pinpoint DMA

This article uses pinpoint DMA results presented in refs. 2 and 3, where the principle of pinpoint DMA has been described in detail.

Swelling

Samples are immersed in CS₂ at 23°C until constant weight was reached.

RESULTS AND DISCUSSION

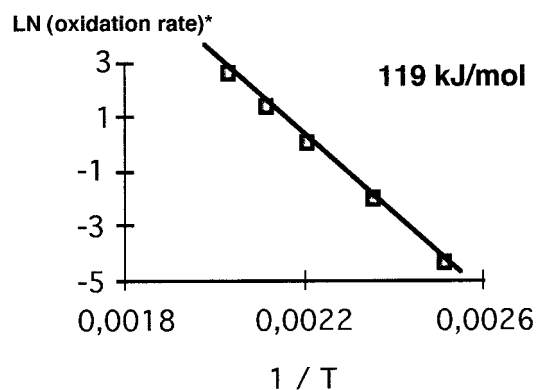
Two types of mechanisms are presented in this section: modifications directly or indirectly connected to the variation of the hardness of the elas-

tomer, and the variation of the irreversible strain of the samples. Concerning physico-chemical and chemical modifications, four different mechanisms have been studied: the oxidation at the surface; the heterogeneous oxidation, the variation of the antioxidant concentration, and chain scission mechanisms. Concerning physical mechanisms, creep and relaxation have been studied.

Oxidation at the Surface

When heterogeneous oxidation occurs, the pure mechanism of degradation (not influenced by oxygen diffusion) must be characterized by a surface analysis. In a previous article, it has been shown that the $\tan \gamma T_g$ profiles ($\tan \gamma T_g$: height of the damping peak associated with the glass transition) could be extrapolated to obtain the variation of the damping peak at the surface. The variation of this response with time at different temperatures leads to a first activation energy (Fig. 3) as presented in previous article.⁴

Oxidation at the surface



* Oxidation rate estimated by viscoelastic measurements [4]

Figure 3 Arrhenius plot of oxidation rate at the surface (see ref. 4).

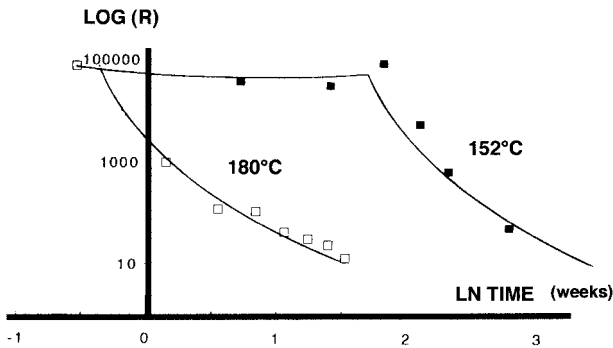


Figure 4 Variation of surface resistance versus aging time.

The second approach, which enables the activation energy of the pure degradation phenomena to be determined, is to make an analysis directly at the surface. As the elastomer contains black filler, ATR IR spectroscopy is not possible. The variation of the surface resistance as a function of aging time at 180 and 152°C is shown in Figure 4. It can be observed that the resistance decreases by four orders of magnitude. This large decrease corresponds to the crossing the percolation threshold. This result can be interpreted in two different ways (Fig. 5): (a) either the conductivity

is made by the formation of dipoles between the filler particles; (b) and/or the conductivity is made directly by the percolation of the filler particles. The connection of the fillers should be either the consequence of the densification of the matrix (as a consequence of the crosslinking modification), or the consequence of the decrease of the [polymer]/[filler] yield (as a consequence of the degradation of the matrix); (c) in the first case, a delay time of stabilization of the tension should be observed, connected to the relaxation time of the dipoles. In the second case, conduction is instantaneous. The second case has been observed.

If Arrhenius equation is arbitrarily applied between 180 and 152°C (only two points) an activation energy equal to 120 kJ/mol is obtained. This result is close to the value obtained by pinpoint DMA approach. The densification at the surface is also directly connected to the crosslinking reaction, and is not influenced by the weight loss mechanisms (even if both reactions are initiated by oxidation processes), which has a different activation energy (see further on).

Heterogeneous Oxidation

When heterogeneous oxidation occurs, a deviation from the Arrhenius equation is observed. This de-

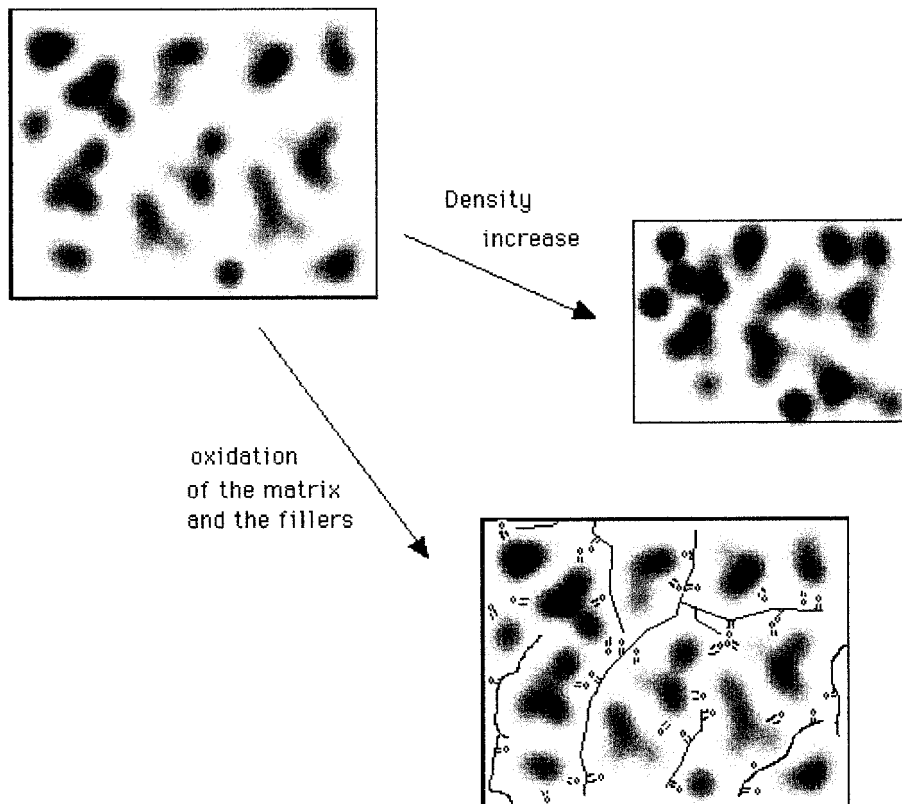


Figure 5 Two different interpretations of resistivity decrease.

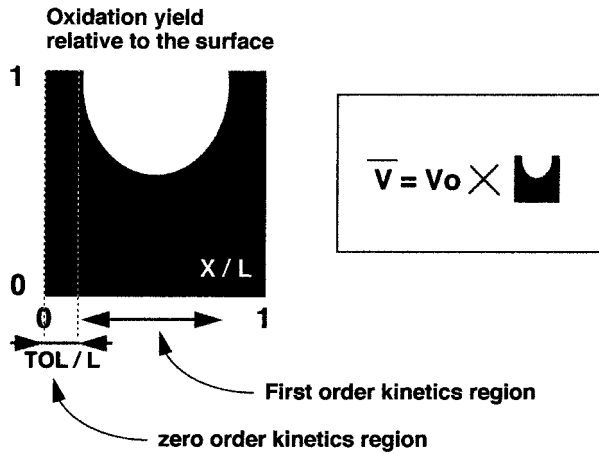


Figure 6 Principle of calculation of the whole oxidation rate.

viation becomes more important when aging temperature increases. It has been shown in a previous article⁴ that the modified oxidation rate \bar{V} could be approximated by eq. (2) (the principle of the calculation is shown in Fig. 6):

$$\bar{V} = V_o \left(\frac{TOL}{L/2} (1 - \bar{\tau}) + \bar{\tau} \right) \quad (2)$$

where

$$\bar{\tau} = \frac{\tanh(\phi L/2)}{\phi L/2}$$

= Whole oxidation yield relative to the surface in the first order kinetics region

L = Thickness of the sample

TOL = Thickness of homogeneous oxidized layer (zone of zero order kinetics)

V_o = oxidation rate at the surface (zero order kinetics)

$\phi = \sqrt{\alpha/D}$ where α is the rate constant of first order kinetics and D is the diffusion coefficient of oxygen

It is interesting to calculate the consequence on the apparent activation energy, which can be obtained using this type of modelization.

The variation of the bulk whole rate is a function of the thickness of the sample. the variation of \bar{V} is presented in an Arrhenius plot in Figure 7. At low temperature one master curve is observed. The thicker the sample, the more important is the deviation from the Arrhenius equation at high temperature. The derivative of the

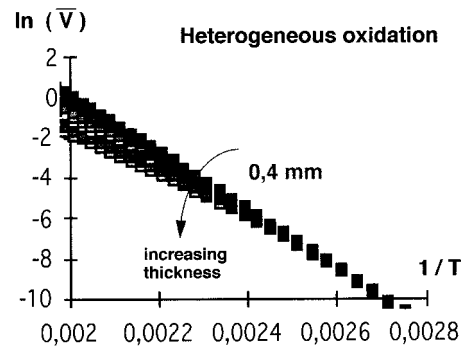


Figure 7 Arrhenius plot of the whole oxidation rate.

last plot vs. $1/T$ leads to the variation of apparent activation energy as a function of aging temperature. It can be observed in Figure 8 that for high temperatures and/or large thicknesses of samples, the apparent activation energy tends towards a constant value of 82 kJ/mol. This result can be explained by the study of the limits of eq. (2), when L tends to an infinite value.

$$\text{As } x \xrightarrow{\text{lim}} \infty \tanh(x) = 1; L \xrightarrow{\text{lim}} \infty \bar{V} = r_o/\phi \frac{L}{2}$$

The 82 kJ/mol corresponds to the difference of activation energies of r_o (119 kJ/mol^{3,4}) and ϕ (37 kJ/mol^{3,4}). This limit is obtained when the two oxidations profiles of the two surfaces of a sample are not cumulative at the center of the sample, i.e., when oxidation does not occur in the bulk material. This case should be called the “total heterogeneous oxidation.” The total heterogeneous oxidation is studied in bibliography using simply the parameter “TOL” (thickness of oxidized layer).^{7,8} The problem is that TOL can be easily used only in the case of zero-order oxidation reactions. The transition domain between homogeneous oxidation and total heterogeneous oxida-

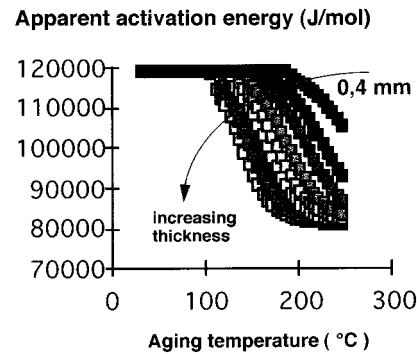


Figure 8 Variation of activation energy versus aging temperature.

tion is relatively large (ΔT between 50 and 100°C). The complexity of this study made on 2-mm thick samples is due to the fact that accelerated aging conditions were in this transition domain. A simpler study should have been made using samples 0.4 and 20 mm thick in order to characterize the two different model behaviors.

Antioxidant Consumption

Figure 9 shows the variation of swelling in CS₂ during aging at various temperatures. Three steps are observed in the degradation mechanisms. During the first step the swelling value quickly decreases to a stable value (from 192 to 185%, in mass). This first stage should be related to the desorption of low mass species and or the postvulcanization of the material. During the second step no significant variations of swelling (and other properties) are observed. This step is connected to the period of antioxidant consumption, which inhibits other oxidation mechanisms. At the third step oxidation of the matrix occurs. This third step has been correlated to the whole degradation rate obtained by integration of $\tan \gamma T_g$ profiles: the same variation of the activation energy (from 119 to 82 kJ/mol) is obtained.⁴

The kinetics of antioxidant consumption has been studied as a function of aging temperature. Results are presented in Figure 10. An apparent activation energy equal to 115 kJ is obtained (Fig. 11).

The period of antioxidant consumption is closely connected to the induction period observed in Figure 9, but no direct relation has been established between the two time constants. In fact, it must be considered that induction period presents two different phenomena: (a) the antioxidant con-

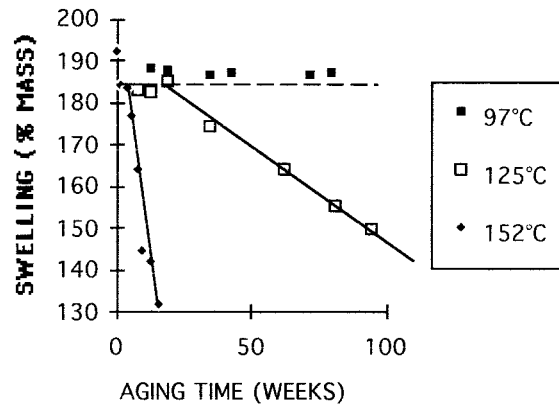


Figure 9 Variation of swelling in CS₂ at 23°C.

sumption more important at the beginning of the induction period; (b) and the real "induction period," during which hydroperoxides are accumulated (the flowing stage, the degradation, corresponding to the decomposition of these species). The antioxidant consumption also does not control alone the induction time, and the other mechanism does not present the same activation energy.

Chain Scissions

Mass loss can be associated to two types of mechanisms: (a) mass loss due to the oxidation of the networks; (b) mass loss due to the desorption and/or degradation of additives.

The whole mass loss can be evaluated by gravimetry. The mass loss due to additive elimination is assumed to occur at the first stages of the aging mechanism (step during which oxidation of the network does not occur because of the presence of antioxidant), and it is assumed to lead to a maximum mass loss of 2.5% (cf. Material

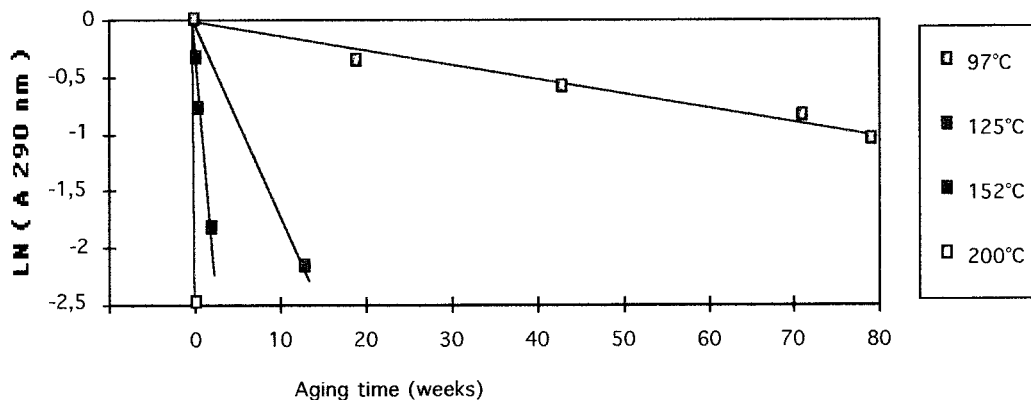
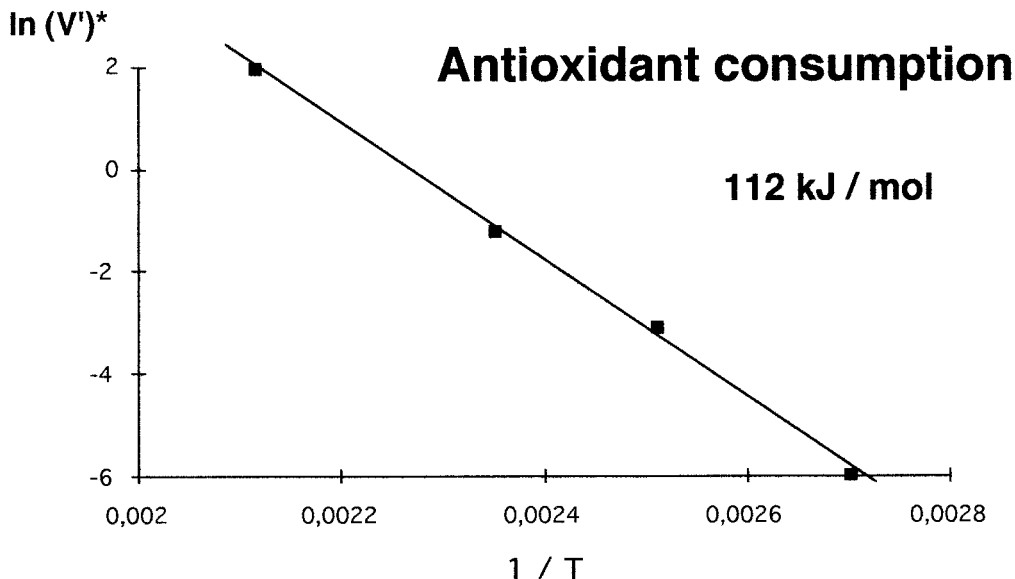


Figure 10 Variation of UV absorbance at 290 nm of extractible fraction in diethyl ether.



* V' = Antioxidant consumption rate = d (ln A₂₉₀) / dt (days)

Figure 11 Arrhenius plot of antioxidant consumption rate.

section). The shift factor becomes constant between two curves of aging, for mass loss more than 3%. It can be also assumed that this shift factor is only related to mass loss due to network degradation, also being connected to chain scission reactions. The Arrhenius plot is shown in Figure 12. The activation energy is equal to 92 kJ/mol.

Creep

The strain evolution of sample submitted to constant stress at from 170 to 250°C allows measuring of the variation shift factor a_T connected to the creep mechanism in the considered temperature

range. The Arrhenius plot of the shift factor is shown in Figure 13. The apparent activation energy is equal to 64 kJ/mol.

Compression Set (Relaxation)

The compression set leads to two major problems: first, the problem of the separation of physical and chemical aging. Even if the two mechanisms should be mathematically separated (see ref. 9 for the case of creep test) a second problem is the heterogeneous degradation (Fig. 14). To illustrate this, Figure 15 shows the variation of the lifetime taken for a value of compression set equal to 90% (a typical value for this test). It can be

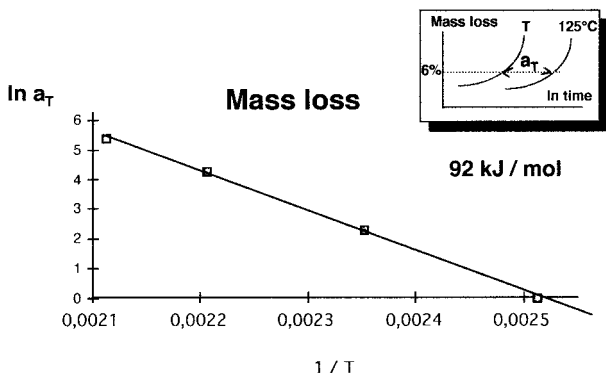


Figure 12 Arrhenius plot of mass loss rate.

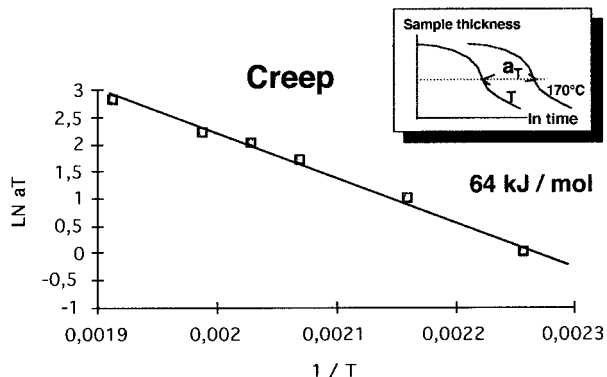


Figure 13 Arrhenius plot of creep rate.

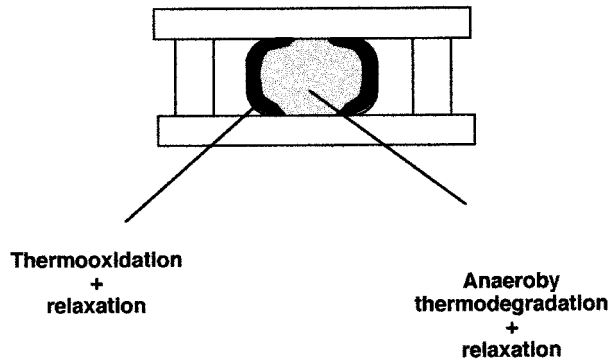


Figure 14 Problem of heterogeneous chemical modification for compression set.

seen that the Arrhenius law is not verified with the lifetime obtained in this way, chemical and physical aging not being activated by the temperature with the same activation energy. The solution is to change the end life criteria. At the first stage of the degradation of the elastomer (during the period of antioxidant consumption) oxidation of the matrix does not occur. Consequently, no chemical changes are observed and also no modification in relaxation properties occur during this period. Figure 16 shows the variation of the shift factor taken at compression set equal to 20%: the Arrhenius law is confirmed between 90 and 120°C: activation energy = 49 kJ/mol. The difference between the result obtained for relaxation and creep must be considered. In a first approximation, both mechanisms concern large movements of macromolecular chains. The difference is that relaxation is connected to very large local stress (at $t = 0$) very far from the only equilibrium imposed

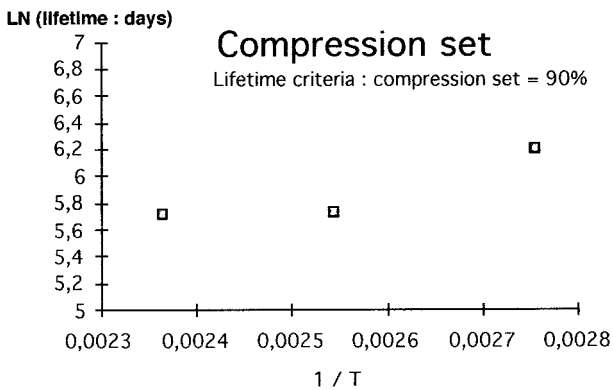


Figure 15 Arrhenius plot of lifetime determined by the criteria: compression set = 90%.

state; and creep is connected to smaller movements closer to the equilibrium state, which varies with time. Moreover, in this study it must be underlined that the temperature range was different in the two cases.

CONCLUSION

Figure 17 shows the different activation energies determined and the different temperature ranges studied. Some aspects must be underlined.

In the case of heterogeneous oxidation (large transition region between homogeneous oxidation and total heterogeneous oxidation) the activation energy is a function of the thickness of the samples.

All mechanisms that not directly concern cross-linking reaction present an activation energy lower than the dominant mechanism. These secondary phenomena could be dominant at low aging temperatures. This is particularly the case in physical modifications of the network (strain mechanism), which present a very low activation energy. The present study was relatively straight forward because all mechanisms have been studied separately. Under real aging conditions, chemical modifications largely influence physical strain behavior. Under such conditions, it becomes very difficult to model the bulk physical strain properties, because of the dependence on two different factors: chemical aging, which is largely activated by temperature, and physical strain modification, which generally has a quite low activation energy.

The aim of this work was not to make a list of six activation energies. Authors would like to underline that the classic methods like ultimate mechanical properties have not been used to follow the degradation of the studied material. Dif-

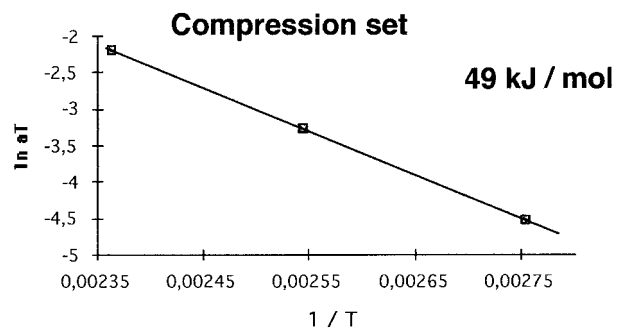


Figure 16 Arrhenius of the shift factor for compression set = 20%.

Activation energy

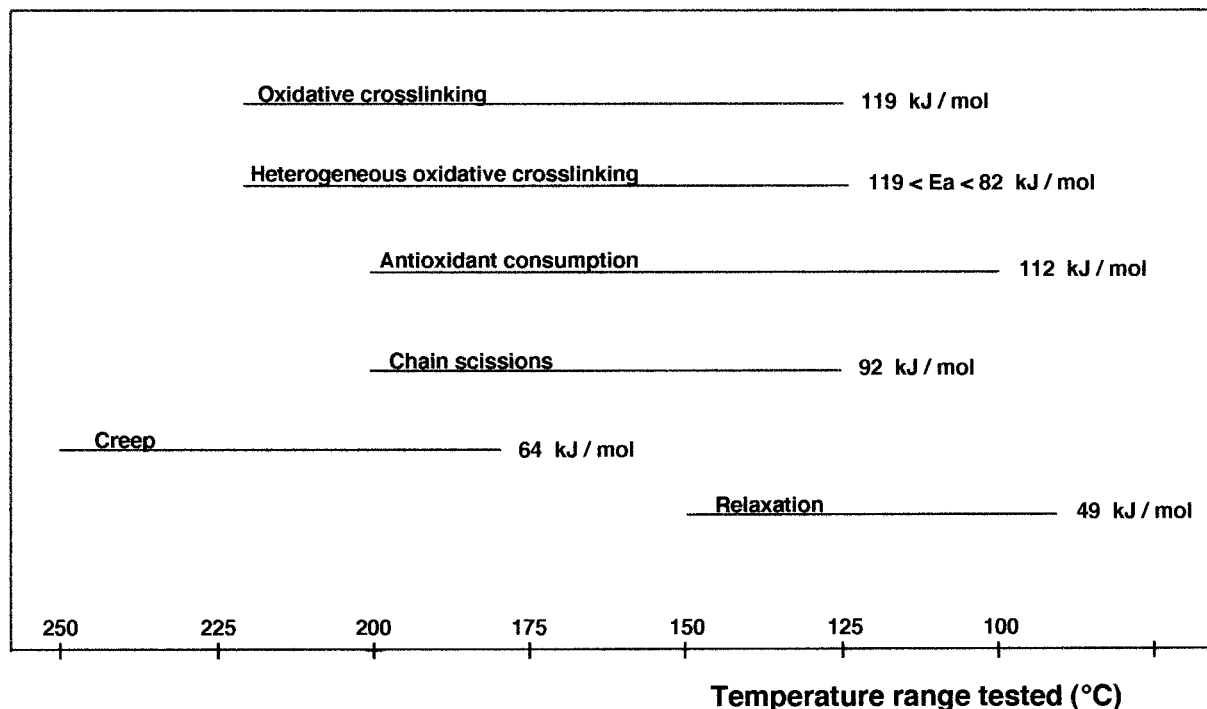


Figure 17 Temperature range of the different activation energies determined.

ferent properties that can be directly correlated to a physico-chemical or a chemical modification have been used. All the results should lead to different lifetimes of the material (if end-life criteria are used). The choice of the critical property will be, of course, a direct function of the real-life conditions. The apparent activation energy, which could be determined by mechanical properties, is a complex combination of the energies listed in this work. This combination depends, of course, on the temperature but also on the geometry of the samples. If mechanical properties are used, this should be the last stage for the study of the lifetime of a material, the "listing" of basic activation energies being the first stage for the understanding of such a complex mechanism.

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REFERENCES

1. P. Dole and J. Chauchard, *Polym. Degrad. Stabil.*, **53**, 63–72 (1996).
2. P. Dole and J. Chauchard, *Macromol. Chem. Phys.*, **195**, 3949–3961 (1994).
3. P. Dole and J. Chauchard, *Polymer Degrad. stabil.*, **47**, 441–448 (1995).
4. P. Dole and J. Chauchard, *Polym. Degrad. Stabil.*, **47**, 449–457 (1995).
5. V. Gueguen, L. Audouin, B. Pinel, G. Seytre, and I. Phellut, Proc. JICABLE 91, 24–28 June 1991, Versailles, France.
6. V. Gueguen, L. Audouin, B. Pinel, and J. Verdu, *Polym. Degrad. Stabil.*, **43**, 217 (1994).
7. L. Audoin, V. Langlois, and J. Verdu, *J. Mater. Sci.*, **29**, 569–583 (1994).
8. G. Papet, L. Audoin–Jirackova, and J. Verdu, *Radiat. Phys. Chem.*, **33**, 329–335 (1989).
9. M. Ito, *Polymer*, **23**, 1515–1518 (1982).