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Time–temperature dependence of the thermo-oxidative aging of polychloroprene rubber
The time–temperature-transformation (TTT) superposition method and the lifetime prediction

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Abstract

The time–temperature dependence of the thermo-oxidative aging of polychloroprene rubber (CR) was studied using the time–temperature-transformation (TTT) superposition method and the IEC-216 norm. Aging of the material was performed inside temperature-controlled oven under circulated air temperature. The samples were characterized by gravimetry (G), thermogravimetric analysis (TG) and Shore A hardness before and after aging. It was demonstrated that the basic idea of Wisanrrakkit and Gilham for the TTT treatment of DSC thermal analysis data can be applied in the studies of CR aging processes. A quantitative relation between aging temperature, aging time, Shore A hardness and mass loss variation was demonstrated, which permits the prediction of lifetime under thermo-oxidative condition of CR.
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Keywords: Aging; Superposition; Thermogravimetry; Polychloroprene rubber

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1. Introduction

Aging of polymers is usually related to the material degradation, which depends upon the specific function, environmental conditions, the temperature and the time [1]. The presence of chemical agents, humidity, dry air or chemical inert atmosphere are parameters, which affect the aging process [2]. The dry air atmosphere is considered oxidative and its activity in combination with thermal conditions defines the thermo-oxidative degradation process. The methods of investigating polymer degradation are as numerous as the processes themselves. Thermal analysis methods are generally used in the studies of polymer stability.

This paper presents results obtained in the investigation of the thermo-oxidative degradation of polychloroprene rubber (CR) during an accelerated aging inside temperature-controlled oven under circulated air atmosphere.

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The thermo-oxidative aging process can be approximated by the general reaction (1) [3]

$$\sum A_i \rightarrow \sum B_j * F(\alpha(x)) \tag{1}$$

which considers that the overall degradation process is the result of N subprocesses. A_i and B_j are the chemical specimens, reactants and products, of the degradation processes, $F(\alpha(x))$ is a function of the conversion factor α which is related with the observable (x) and the operator $*$ defines the relation between concentration of chemical specimens and the function $F(\alpha(x))$.

A reaction rate can be defined as the time derivative of the conversion factor α. For thermogravimetric analysis (TG), the conversion factor is defined as the ratio of actual mass loss to total mass loss corresponding to a given stage of the degradation process:

$$\alpha = \frac{m_0 - m_{t,T}}{m_0 - m_\mathrm{f}} = \frac{\Delta m_{t,T}}{\Delta m_\mathrm{tot}} \tag{2}$$

where $m_{t,T}$, m_0 and m_f are the actual, initial and final mass of the sample, respectively. The rate of conversion in a dynamic TG experiment at a constant heating rate can be expressed as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \phi \frac{\mathrm{d}\alpha}{\mathrm{d}T} = k(T) f(\alpha) \tag{3}$$

where ϕ is the heating rate, $\phi = \mathrm{d}T/\mathrm{d}t$, $k(T)$ the rate constant and $f(\alpha)$ the conversion function. For polymers showing decomposition, it may be assumed that the rate of conversion is proportional to the concentration of non-degraded or unreacted material. The temperature dependence of the rate constant $k(T)$ may be described by Arrhenius expression

$$k(T) = A \exp\left(-\frac{E_\mathrm{a}}{RT}\right) \tag{4}$$

where A is the frequency pre-exponential factor, E_a the activation energy, R the gas constant (8.314 J K^{-1} mol^{-1}) and T the absolute temperature.

We suppose that the basic idea of Wisanrrakkit and Gilham [4,5] for the treatment of the DSC thermal analysis data [6] can be applied in the TG too. Starting with Eq. (3), integrating at constant temperature and taking the natural logarithm, Eq. (5) is obtained

$$\ln \int \frac{\mathrm{d}\alpha}{f(\alpha)} = \ln k(T) + \ln(t) \tag{5}$$

The left-hand side of the above equation is a function of the conversion factor (α) only. Considering that α is a unique function of Δm (Eq. (2)) a new function $F(\Delta m)$ can be introduced as follows:

$$F(\Delta m) = \ln k(T) + \ln(t) \tag{6}$$

Analysis of this equation indicates that the same value of $F(\Delta m)$ can be carried out for different pairs of aging temperatures and aging times as indicated in Eq. (6)

$$F(\Delta m) = \ln k(T_1) + \ln(t_1) = \ln k(T_2) + \ln(t_2) \tag{7}$$

Consequently

$$\ln(t_1) - \ln(t_2) = \ln k(T_2) - \ln k(T_1) \tag{8}$$

In other words, for any two isothermal processes $[\ln k(T_2) - \ln k(T_1)]$ is a constant. Therefore, for a kinetically controlled reaction, considering the curves for two different degradation temperatures (T_1 and T_2), the argument $\Delta m(t)$ of the function $F(\Delta m)$ as a function of ln(aging time) will have the same functional form, however the curve for the temperature T_2 will be displaced from that of the temperature T_1 by a constant factor $a_T = \Delta(\ln t)$. That means, all curves of $\Delta m(t_\mathrm{f})$ versus ln(aging time) at different aging temperatures can be superposed by simply shifting each curve along the ln(time) axis relative to a curve at an arbitrary reference temperature by a shift factor $a_T = [\ln(t_{T_\mathrm{ref}}) - \ln(t_T)]$, where t_{T_ref} is the time in the reference temperature (T_ref) and t_T is the time in the temperature T. Considering a kinetically controlled reaction mechanism, the temperature dependence of the rate constant is expected to be the Arrhenius relationship (Eq. (4)). Eq. (9) provides the relationship between the time factors and the rate constants

$$a_T = \ln(t_{T_\mathrm{ref}}) - \ln(t_T) = \ln k(T) - \ln k(T_\mathrm{ref}) \tag{9}$$

Consequently the Eq. (10) can be used in order to obtain the Arrhenius activation energy (E_a) of the aging process.

$$a_T = -\frac{E_\mathrm{a}}{RT} + \frac{E_\mathrm{a}}{RT_\mathrm{ref}} \tag{10}$$

Wise et al. [7] has studied the Arrhenius extrapolation assumption for thermally aged elastomers. They employed time–temperature-transformation (TTT) superposition method to analyze the data of the aged elastomers obtained by different techniques.

2. Experimental

The aim of this work was to perform a comparison of the aging characteristics of the polymer material,

Table 1
Time and temperature aging conditions

Temperature (°C)	Aging time (h)
80	100, 200, 400, 800, 1600, 3200
110	10, 50, 100, 200, 800, 1600, 3200
140	4, 9, 24, 28, 32, 120, 536
160	0.25, 1, 2.5, 12, 24
180	0.12, 0.25, 0.42, 1, 2.5

using the TTT superposition method and the International Electrotechnical Commission IEC-216 norm [8]. The observables used in the TTT method were the mass loss during the aging in oven and the mass loss obtained by thermogravimetry in the samples after aging. The study according to IEC-216 norm was performed using Shore A hardness measurements of the samples before and after aging according to ASTM D 2240-97 norm using a durometer Microtest 7206-SB [9]. The Shore A hardness to non-aged material was 63 ± 1.

The material studied was commercially available vulcanized CR (CR-4716-ORION). The accelerated material aging was carried out at different temperatures between 80 and 180 °C and during different times between 7.5 min and 3200 h, inside temperature-controlled oven under circulated air atmosphere. Table 1 summarizes the thermo-oxidative aging conditions used in this experiment.

The TG analysis for the aged material was performed in the temperature range 20–550 °C with a heating rate $\phi = 2\ ^\circ\mathrm{C\,min^{-1}}$. The samples with mass between 8 and 15 mg were studied using Netzsch Thermobalance Model TG 209 coupled to TASC 414/3 controller. The measurements were performed under nitrogen (N_2) atmosphere continuos flow (15 ml $\mathrm{min^{-1}}$).

3. Results and discussion

The mass loss obtained by gravimetry (G) during the thermo-oxidative aging in oven as function of aging time at different temperatures is shown in Fig. 1. The curves in Fig. 1A for 110, 140, 160 and 180 °C were shifted in order to obtain superposition in the range 2–4% mass loss, by the shift factors a_T relative to reference temperature curve $T_{\mathrm{ref}} = 110\ ^\circ\mathrm{C}$. The obtained superposition curve is shown in Fig. 1B. This curve demonstrates a relatively good superposition of the analyzed data. The a_T values are given in Table 2 as a_T G column.

Table 2
Shift factor a_T obtained by gravimetry (a_T G column) and thermogravimetry (a_T TG column) using $T_{\mathrm{ref}} = 110\ ^\circ\mathrm{C}$

T_{aging} (°C)	a_T G[a]	a_T TG[a]
110	0.00 ± 0.00	0.00 ± 0.00
140	2.83 ± 0.18	0.43 ± 0.02
160	6.30 ± 0.60	3.90 ± 0.27
180	6.96 ± 0.31	4.94 ± 0.16
E_a (kJ $\mathrm{mol^{-1}}$)	153 ± 21	110 ± 33

[a] Average values obtained by superposition in the 2–4% range for mass loss through gravimetry and 5–8% by thermogravimetry.

The linear regression plotting of the shift factor a_T versus $1/T$ according to Eq. (10) yielded the activation energy of 153 ± 21 kJ $\mathrm{mol^{-1}}$, as shown in Fig. 4 (□: a_T TG). The same procedure used in the TTT superposition method for aged CR in oven was applied to the results obtained through TG technique for the samples previously aged in oven.

The mass loss (%) obtained through TG technique refers to the degradable material as demonstrated by "D" in Fig. 2. The values of the mass loss (%) obtained by TG analysis are not related to 100% of the mass of the unaged material but to the mass of the samples after aging in oven. Thermogravimetry studies with unaged CR material, demonstrated that the temperature of 550 °C corresponds to be degradation of 50%. In other words, we assume that the aging at lower temperatures, in that case 110, 140, 160 and 180 °C for different aging times, does not affect the processes in temperature higher than 550 °C, and consequently the undegradable 50% of the material. Under this assumption, the thermogram of the aged material permits to obtain the "real mass loss" of the sample after the aging procedure.

Fig. 2 shows a typical thermogravimetry curve of aged CR at 140 °C for 120 h. As example, in a thermogram of aged CR (Fig. 2), we obtained degradable $D = 48.81\%$, undegradable $U = 51.19\%$. Considering that the "U" value corresponds to the 50% of the unaged material, the value of 48.81% would correspond to 47.67% and the mass loss during the aging is 2.33%. The values of the mass "loss" obtained by TG technique are plotted in Fig. 3 which

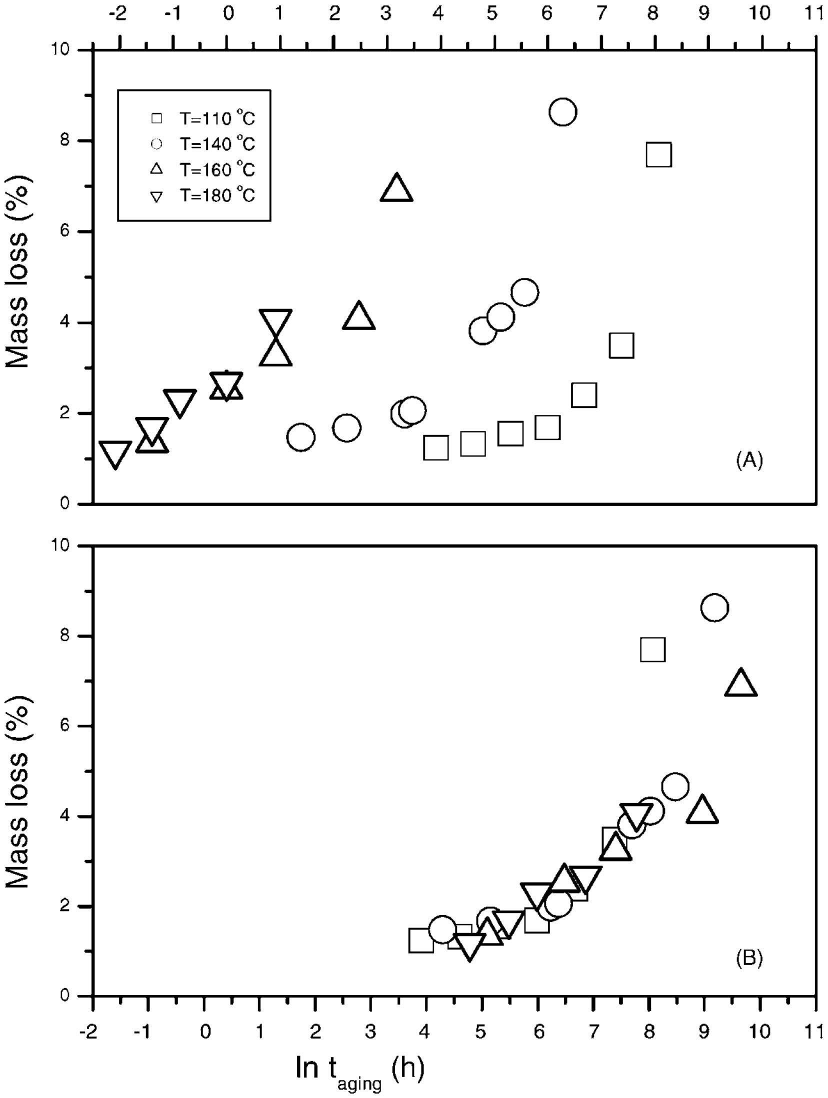

Fig. 1. (A) Mass loss (%) obtained by gravimetry of polychloroprene during aging in oven at different temperatures. (B) Master curve according to the TTT superposition with $T_{ref} = 110$ °C.

show the mass loss (%) of the CR versus time at different temperatures.

According to the TTT procedure, the curves have been shifted in order to obtain superposition in the range 5–8%. Using reference temperature $T = 110$ °C the "master curve" shown in Fig. 3B was obtained. The a_T TG values used to shift the curves are given in Table 2. Again, using Eq. (10) and plotting the shift factor a_T versus $1/T$, as shown in Fig. 4 (○: a_T G), the activation energy of 110 ± 33 kJ mol^{-1} was obtained.

The difference of the obtained activation energies can be related with the obtained mass loss (%) according to the gravimetry (Fig. 1) and thermogravimetry (Fig. 3) techniques. It can be observed that the gravimetry indicates mass loss (%) values from 1 to 9% while the thermogravimetry indicates values in the range from 1 to 17%. The gravimetry indicates values lower than the thermogravimetry. The comparison with literature data demonstrates that the activation energy of 110 kJ mol^{-1} obtained by thermogravimetry lies

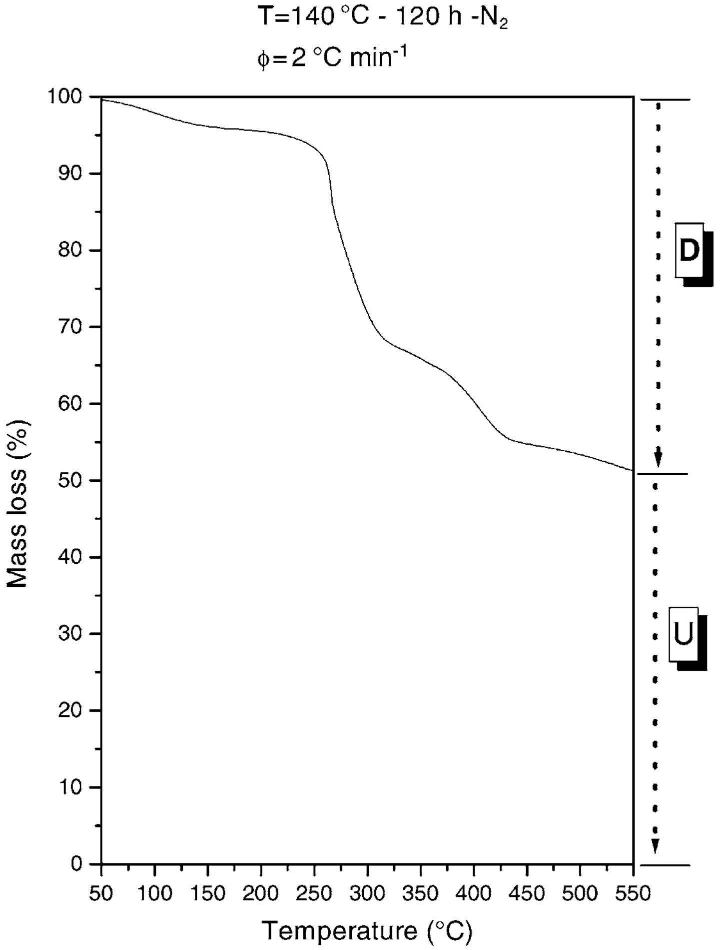

Fig. 2. Typical thermogravimetric curve of aged CR at 140 °C for 120 h in N_2 atmosphere. Heating rate: 2 °C min^{-1}, *D*: degradable, *U*: undegradable.

very near to the value obtained by Wise et al. [7]. It can be understand that during the thermo-oxidative aging process additionally to the mass loss, an oxygen incorporation process takes play which causes the obtained differences between gravimetry and thermogravimetry mass loss values. This way, the two techniques here presented (gravimetry and thermogravimetry) are not equivalent and consequently the obtained activation energies are not expected to be equal.

The TTT superposition method using two different observables was shown to be valid in the study of the thermo-oxidative aging of the CR. The question to be treated in the next step is "how we can relate the TTT superposition results to the International Electrotechnical Commission IEC-216 norm which uses the ASTM D 2240-97 method in order to realize a lifetime prediction of CR and other rubbers artifacts in use"?

3.1. Lifetime prediction of the CR

In order to obtain information about lifetime of polymeric materials, accelerated aging methods can be used to simulate in a short time the aging under normal application conditions. The results obtained can be extrapolated to longer times. It is possible, through techniques of measurement of easy execution and low cost equipment to obtain results that permit

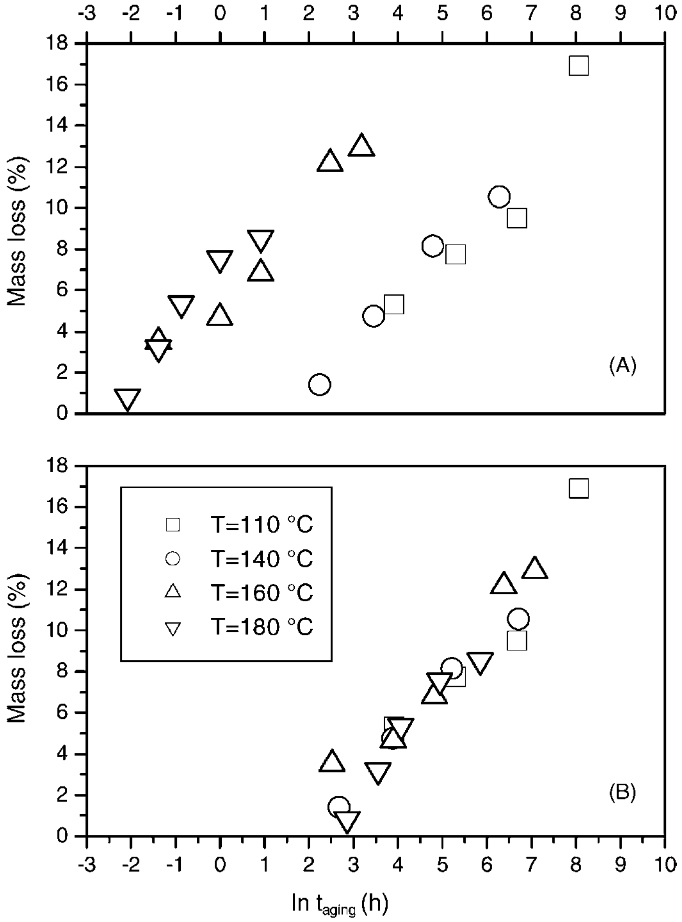

Fig. 3. (A) Mass loss (%) of aged polychloroprene obtained by thermogravimetry analysis. (B) Master curve according to the TTT superposition with $T_{\mathrm{ref}} = 110\,^{\circ}\mathrm{C}$.

the estimation of the lifetime of a polymeric material. The result can help to estimate expenses, piece reposition, comparison between materials, etc.

Some empirical methods have been proposed, for example the Weibull distribution, lognormal distribution, non-parametric model [10], etc. Bruning and Campbell [11] have studied the effect of aging on dielectric cables with their lifetime predicted. Arrhenius method relating the reaction rate versus temperature, has been used in the aging study.

Determining the criterion more adequate to fix the lifetime of the materials can be a big problem. Usually, the main criterion, in the aging test, is to define the adequate value for the lifetime. Some norms suggest that the value correspond to a variation of 50% of the start value of the property. This limit, in the specific case of Shore A hardness in the CR study, seems to be very high. Other norms admit a hardness variation until 10%. However, Shore A hardness norm recommends the use of values in the scale of the equipment between 10 and 90, where the variation percentage must be calculated.

In order to apply the norm, the empirically defined limit of 7.5 and 10% Shore A hardness variation at the aging temperatures was used, with the aim to obtain the time values necessary for this variation. The Shore A hardness behavior of the material after aging at 80, 110 and 140 °C is shown in Fig. 5. The results

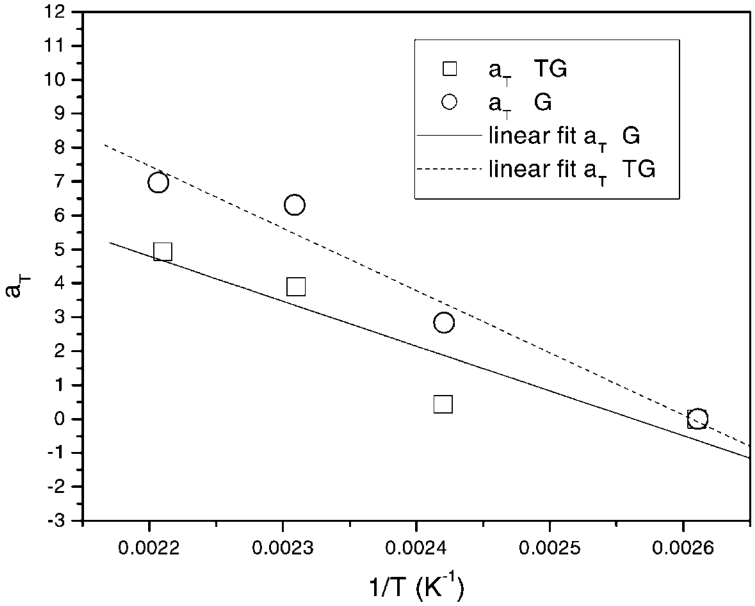

Fig. 4. Shift factor a_T versus $1/T$ obtained by TTT method using as observables mass loss through aging in oven obtained by thermogravimetry (□: a_T TG) and gravimetry (○: a_T G).

obtained for 7.5 and 10% deterioration are shown in Table 3.

The values showed in Table 3 are used in order to obtain the lifetime of the material according to the norm for the 50 and 70 °C temperatures. The respective values are given in Table 4. The method permits the comparison between different samples.

The TTT superposition method can be used in order to obtain the polymeric material lifetime. According to Eqs. (9) and (10), in order to obtain the lifetime at the desired temperature ($\ln(t_T)$) we need the corresponding shift factor a_T which is obtained from Fig. 4 and the $\ln t_{T_{\text{ref}}}$ values for the corresponding mass loss which is obtained by the master curve is shown in Fig. 1B. Using criterion of 7.5 and 10% mass loss the predicted lifetimes are shown in Table 5. In this case the aging temperatures are 50 and 70 °C.

Table 3
Aging time necessary to obtain a Shore A hardness variation of 7.5 and 10% at different temperatures

Temperature (°C)	Time per month for 7.5% variation	Time per month for 10% variation
80	2.23	3.78
110	0.27	0.34
140	0.07	0.08

Table 4
Values of time–temperature relation at Shore A hardness variation for CR

Variation of the Shore A hardness (%)	Aging temperature (°C)[a]	Aging temperature (°C)[b]	Aging time per month[c]	Aging time per month[d]
7.5	30.6	55.5	9.2	3.1
10	45.0	67.3	20.5	5.8

[a] Temperature necessary to obtain the indicated Shore A hardness variation in 20,000 h (27.8 months).
[b] Temperature necessary to obtain the indicated Shore A hardness variation in 5000 h (6.94 months).
[c] Time necessary to obtain the indicated Shore A hardness variation if the aging temperature had been 50 °C.
[d] Time necessary to obtain the indicated Shore A hardness variation if the aging temperature had been 70 °C.

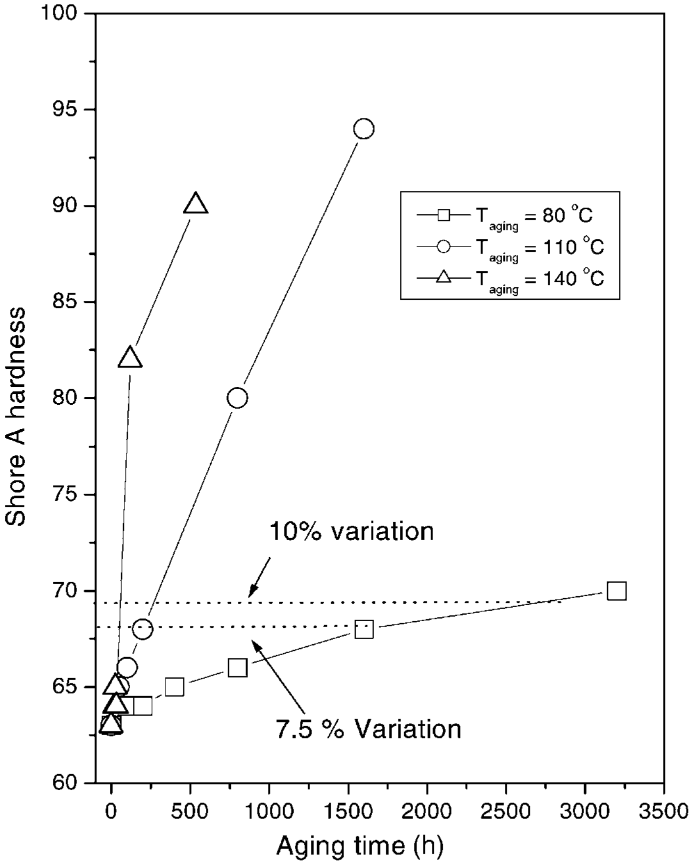

Fig. 5. Shore A hardness of CR versus aging time for different aging temperatures.

It can be seen that there is no correlation between the data in Tables 5 and 6 for aging temperatures at 50 or 70 °C for the same percentage variation of the observables.

Tables 5 and 6 show that for 10% variation of Shore A hardness at 50 °C aging the time necessary is approximately 20.5 months, whereas for 10% variation of mass loss the time necessary is approximately 53143 months of aging. This difference in the observed values indicate the necessity of stipulating the correct criterion for lifetime evaluation using different methods and techniques. In order to obtain the equivalence between Shore A hardness variation and the respective mass loss (%) we used the aging times in Table 4 for 7.5 and 10% Shore A variation at temperatures of 50 and 70 °C and applied the TTT

Table 5
Lifetime for CR using the TTT superposition method

Mass loss (%)	t_{50} (months)	t_{70} (months)
7.5	33886	1275
10	53143	2000

Table 6
Equivalence values between Shore A hardness and mass loss (%) at 50 and 70 °C

	Aging temperature (°C)			
	50		70	
IEC-216—Shore A hardness variation (%)	7.5	10	7.5	10
TTT superposition—mass loss in oven (%)	0.28	0.31	0.34	0.38
Corresponding aging time per month	9.2	20.5	3.1	5.8

superposition method. The equivalence values between Shore A hardness variation and mass loss in oven for 50 and 70 °C of the aging temperature are shown in Table 6.

The results demonstrate clearly that the choice of criteria for lifetime prediction cannot be an arbitrary matter. In the case of TTT method and IEC-216 norm was possible to establish a quantitative relation is given in Table 6.

4. Conclusion

It is concluded that the thermo-oxidative aging process of CR can be studied according to the TTT superposition method. The study demonstrated that the basic idea of Wisanrrakkit and Gilham for the treatment of DSC thermal analysis data can be applied in the studies of CR aging processes. The observables used in this first part of the study were the mass loss in oven during aging obtained by gravimetry and TG of the aged samples.

The analysis of the results obtained through the TTT method indicates similar activation energy values namely, $110 \pm 33\,\mathrm{kJ\,mol^{-1}}$ for TG analysis and $153 \pm 21\,\mathrm{kJ\,mol^{-1}}$ for gravimetry, however the two techniques are not physically equivalent.

The study of polychloroprene thermo-oxidative aging according to the well established IEC-216-ASTM D 2240-97 norm, was used in comparison to the TTT method in order to introduce the correct criteria for the lifetime prediction. The quantitative relation between aging temperature, aging time, Shore A hardness variation and mass loss variation in oven is given in Table 6 indicates that both techniques are capable of predicting the lifetime of CR under thermo-oxidative conditions. However, the IEC-216 method is more sensitive than the TTT superposition one used in this study.

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