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Assessing Ageing Resistance of Chlorinated Natural Rubber Gloves by Thermoanalytical Technique

A. H. ENG*#, Y. SYAHIDAH* AND P. F. LAI*

Ageing resistance of chlorinated natural rubber gloves was evaluated by measuring its activation energy of oxidation, using differential scanning calorimetry technique. All the samples examined were found to conform to the Kissinger's equation. A linear correlation with the corresponding tensile retention data was found. However, the correlation with crosslink density ratio data was less linear. The significance of these observations was discussed.

The estimation of service life span is an important performance indicator for a rubber product. It is usually estimated by measuring relative degradation of properties at an elevated temperature as compared to that of the control specimen. The measurements are mostly single-point determinations which do not accurately indicate the effect of degradation of different rubbers in different environments at extended exposure times, temperature, and stress. If the same procedure is used at a number of elevated temperatures and stresses, more meaningful data should be obtained.

There are several thermal analytical techniques, which have been used to study rubber ageing and evaluate the performance of antioxidants in the rubber, of which differential scanning calorimetry (DSC) is the most popular technique. These techniques usually involve the determination of various parameters such as enthalpy, onset temperature, isothermal induction time, energy of activation, and oxidation peak temperature[1].

Activation energy of oxidation has been used to study the effectiveness of antioxidant in protecting raw natural rubber from thermal oxidation, using DSC technique[2]. However, this study was only carried out on raw rubbers, whereas, natural rubber products are normally cured rubbers. Therefore, the possibility of using this technique to assess the ageing resistance of natural rubber gloves and cured rubber products, was explored in the present study.

EXPERIMENTAL

Commercial chlorinated natural rubber gloves were used directly without any pre-treatment. Ageing of the latex films was carried out at 70°C for 7 days. Tensile measurements were performed on the dumbbell-shaped specimen with an Instron Tensiometer, operating at 500 mm per min. Tensile retention was calculated from the following equation:

* Rubber Research Institute of Malaysia, P.O. Box 10150. 50908 Kuala Lumpur, Malaysia
# Corresponding author (e-mail: aheng@lgm.gov.my)

$$\text{Tensile retention} = \frac{\text{Tensile strength after ageing}}{\text{Tensile strength before ageing}} \times 100\%$$

DSC measurements were carried out according to the method reported by Goh[2]. Approximately 1 mg of each rubber sample was placed in an aluminum sample pan and scanned with a Perkin-Elmer DSC 7 from 50°C to 450°C at the rates of 2°C, 4°C, 6°C, 8°C, 16°C, 32°C and 64°C per min by using oxygen as the purging gas, flowing at a rate of 20 ml/min. The activation energy of oxidation was calculated according to Kissinger's equation[3]:

$$\frac{d \log(r/T_p^2)}{d\,(1/T_p)} = \frac{-E}{2.303R} \quad \ldots 1$$

where r is the heating rate; T_p the exothermic peak temperature; E the activation energy and R the gas constant. A plot of log (r/T_p^2) *versus* $1/T_p$ thus yields a straight line where the activation energy could be calculated from the gradient. The DSC was calibrated against indium and zinc. Crosslink density of the rubber sample was determined by solvent swelling method described elsewhere, by using toluene as solvent[4]. Crosslink density ratio value, was obtained from the crosslink density of the rubber sample after ageing, divided by the crosslink density of the rubber sample before ageing.

RESULTS AND DISCUSSION

The validity of using Kissinger's equation in the determination of activation energy of raw natural rubber has been reported[2]. In the case of cured rubber, besides the polymer, it normally contains small quantities of additives such as sulphur, antioxidants, activators, and accelerators. The influence of these additives on the rubber oxidation at elevated temperature and subsequently the activation energy was investigated.

Figure 1 shows the overlaid DSC curves of a natural rubber glove sample scanned at different heating rates. The broadness of the exothermic peak was found to increase with scanning rate. Besides the main exothermic peak of rubber oxidation, several other minor peaks, possibly due to oxidation of the compounding chemicals were also observed. As expected, the temperature of exothermic peak increased with increasing heating rate of the sample. The Kissinger plots of the rubber samples are shown in *Figure 2*. The results indicate that the experimental data conform to the Kissinger's equation and that the non-rubber minor components did not appear to significantly interfere with the exothermic peak temperature of the rubber.

Since tensile retention is a method commonly used in assessing the ageing resistance of natural rubber gloves, the activation energy of oxidation was compared with the tensile retention data. A fairly linear correlation between the two parameters was obtained as shown in *Figure 3* ($R^2 = 0.71$). Despite this, a good correlation is not expected for several reasons. The correlation demands that the degradation mechanism in both methods is the same despite the fact that they were carried out at different temperatures. In addition, the presence of a higher amount of antioxidant could increase the activation energy of oxidation but would not increase tensile retention value accordingly if the value approaches 100% because antioxidant does not increase the tensile retention of rubber film beyond 100%. Finally, during the ageing test at 70°C, crosslinking reactions might continue to take place if the sample contains residual unreacted compounding chemicals. This would increase tensile retention ratio of the sample but would have less impact on the activation energy

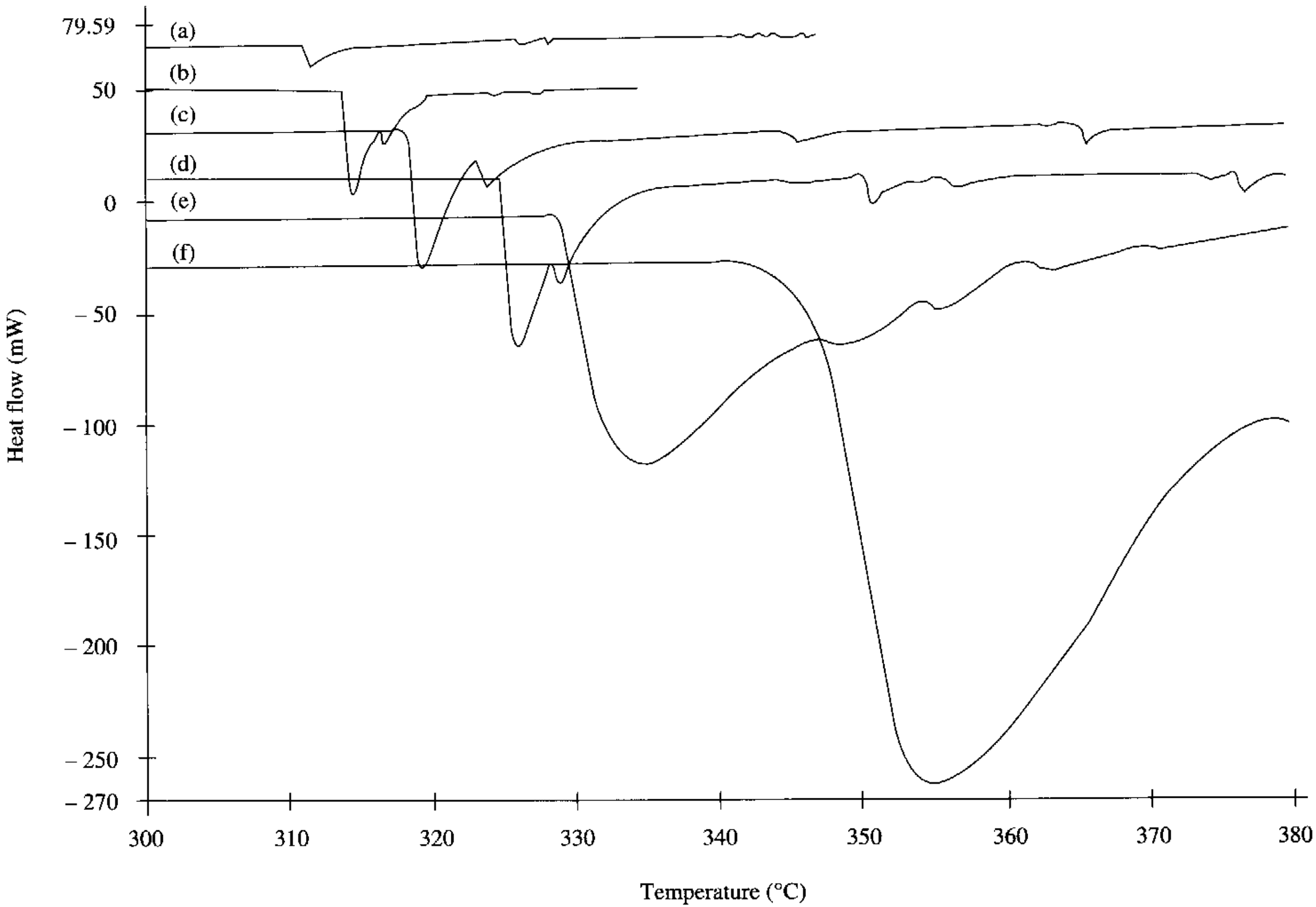

Figure 1. Overlaid DSC curves of a natural rubber gloves scanned at different heating temperatures: (a) 2°C/min; (b) 4°C/min; (c) 6°C/min; (d) 16°C/min; (e) 32°C/min and (f) 64°C/min.

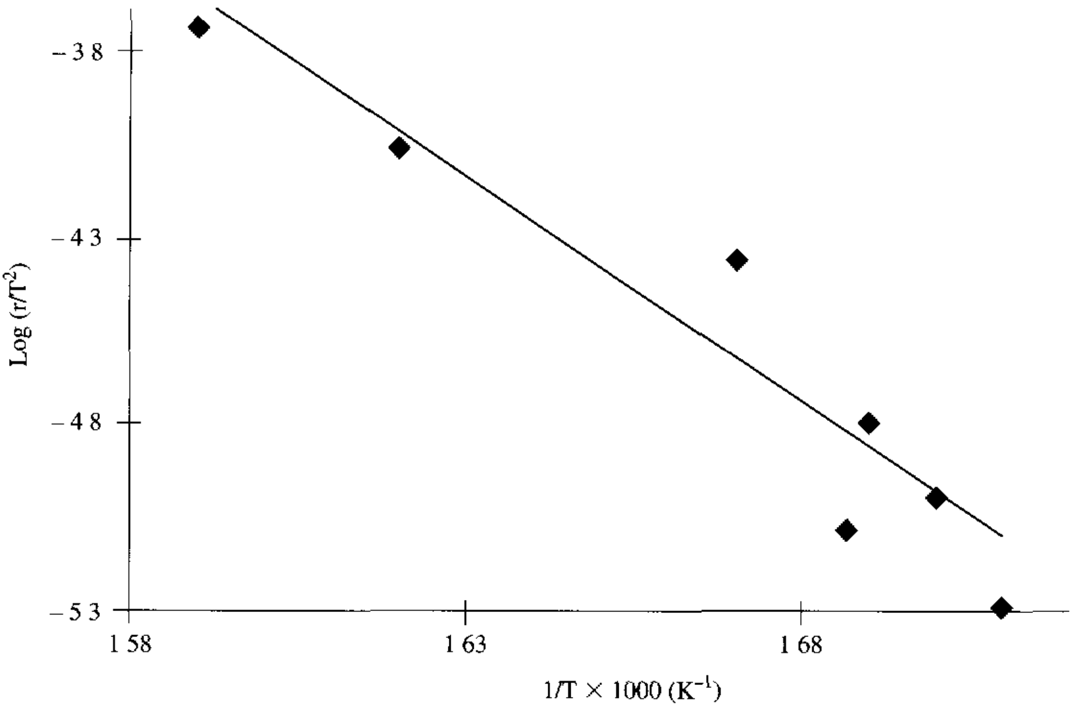

Figure 2 Kissinger s plot of a chlorinated rubber glove sample

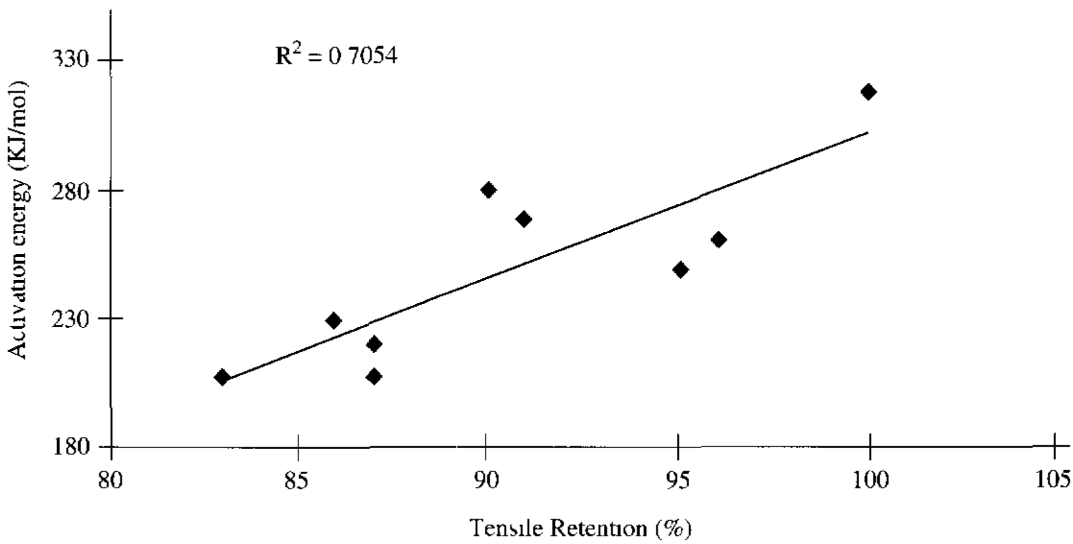

Figure 3 Activation energy of oxidation versus *tensile retention*

of oxidation By taking these factors into consideration it is therefore conceivable that the correlation is fortuitous

These data were further compared with the crosslink density ratio of the aged to unaged samples, determined by using solvent swelling technique The results are shown in *Figures 4* and *5* Surprisingly, the correlation between crosslink density ratio and tensile retention was found to be very poor (R^2 = 0 17), considering that both experiments used the same sample treated under the same conditions This was also observed in the plot of crosslink density *versus* activation energy of oxidation (R^2 = 0 02) Besides the possible factors indicated earlier, other factors such as higher error in the technique used in the determination of crosslink density, small range of crosslink density ratio examined might also have contributed to the scattering pattern of the plot

There are several problems related to tensile retention as a method to assess ageing resistance of a rubber glove The accuracy of tensile strength data is influenced by the film's thickness Unevenness on the rubber films would cause significant error in the thickness measurement The unevenness of glove may arise from the flow of coagulant before dipping, the flow of latex after dipping and the presence of excessive powder For gloves with textured surface, the accurate measurement of the glove's thickness is even more difficult The continuous crosslinking reaction during ageing test in oven may also contribute to the

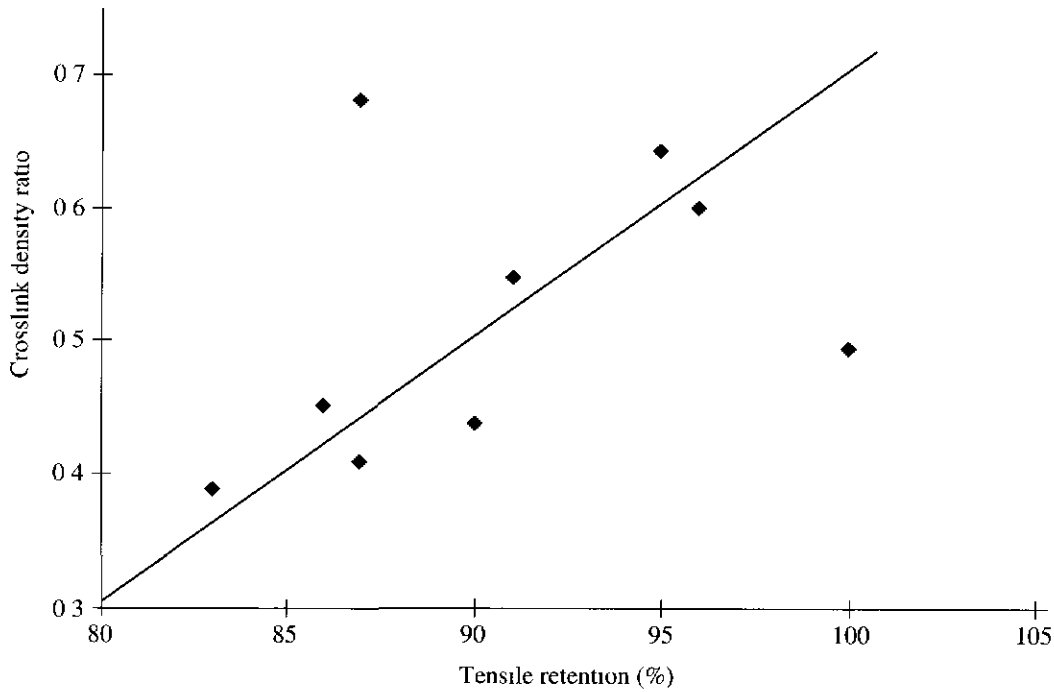

Figure 4 Crosslink density ratio versus *tensile retention*

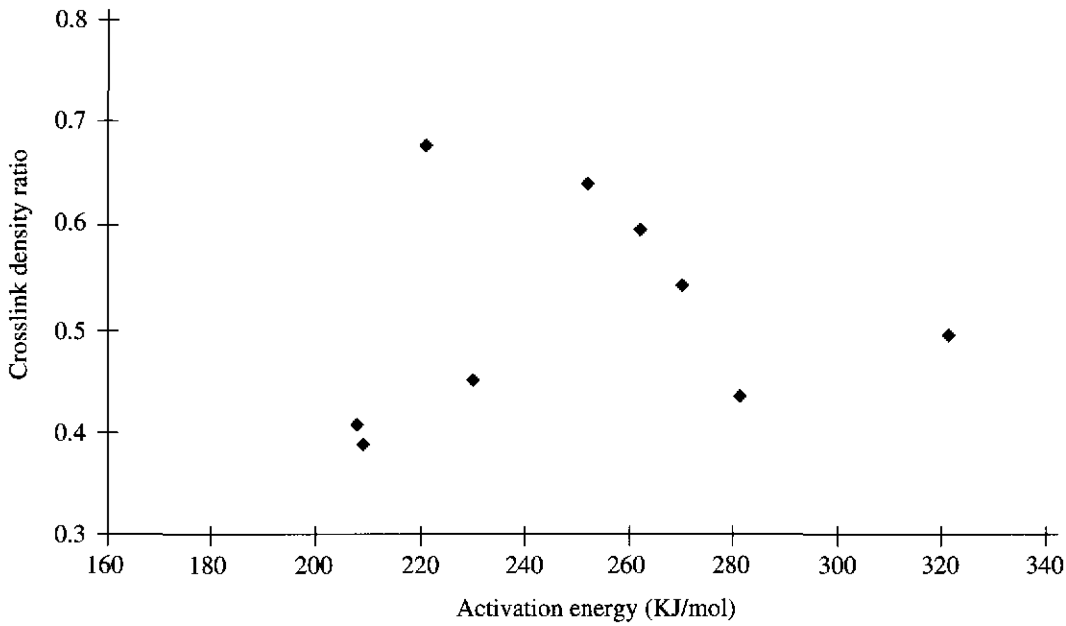

Figure 5. Crosslink density versus *activation energy of oxidation.*

error in assessing the ageing resistance of a rubber glove.

Although activation energy provides more information on the ageing properties of rubber glove, heating the rubber sample at high temperature might have changed its physical and rheological properties which could affect the degradation mechanism in the extrapolated range. It was suggested that such data should be verified with other measurements such as failure data from service life and long term ageing data under controlled conditions[1].

CONCLUSION

The exothermic peak temperatures of chlorinated natural rubber gloves scanned with a DSC at different heating rates were observed to conform to the Kissinger's equation. Activation energy of oxidation obtained from the plot could provide more information on the ageing resistance of natural rubber glove samples whose tensile strength value is near to 100%, than the tensile retention test.

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