Kinetics of Peroxide Vulcanization of Natural Rubber

Rejitha Rajan, Siby Varghese[#] and K.E. George[a]

Rubber Research Institute of India, Rubber Board P.O, Kottayam 686 009
[a]Cochin University of Science and Technology, Cochin University P.O, Cochin 682 022

SUMMARY

This study was undertaken to optimize the vulcanization conditions and explore the effect of residual peroxide in the peroxide vulcanization of natural rubber. The study was followed through the kinetics of the vulcanization reaction at various temperatures viz. 150,155,160 and 165ºC. Dicumyl peroxide (DCP) was used as the crosslinking agent. The Monsanto Rheometer was used to investigate the different crosslinking stages and vulcanization kinetics. The thermal decomposition of peroxide followed a first order free radical decomposition reaction. Half-lives at various temperatures were determined. The percentage of residual peroxide was calculated from the cure kinetic data. The effect of residual peroxide on mechanical properties was studied at various peroxide levels and also by extending the cure time (from t_{90} to t_{95} and then to t_{100}). Mechanical properties such as tensile strength, elongation at break, modulus and compression set (70 and 100ºC) were measured. Excess peroxide was found to cause a high compression set at elevated temperature and the cure time was selected to achieve minimum residual peroxide in the product. Results indicate that peroxide concentration is the dominant factor controlling the crosslink density and hence the properties of the vulcanizates.

Keywords: Dicumyl peroxide, Half–life, Kinetics, Natural rubber, Organic peroxide, Residual peroxide

INTRODUCTION

The crosslinking of elastomers with peroxide has been known for more than 90 years [1]. Peroxide curing was introduced to overcome the deficiencies of sulphur vulcanization [2]. The peroxide crosslinked vulcanizates exhibit very good heat resistance and hence the technique is important in automotive applications. Emerging trends for improved performance and longer service

---

[#] corresponding author (e-mail: sibyvarghese100@yahoo.com) life, particularly in the transportation industry, have prompted a renewed interest and acceptance of peroxide vulcanization. Selection of a curing system for a particular application requires a better understanding of crosslinking mechanism and the factors controlling reaction rates (kinetics). Organic peroxides can be used for the vulcanization of natural rubber (NR) and for most synthetic rubbers, but the chemistry of crosslinking and properties provided are different.

Peroxide vulcanization and the resulting crosslink structure of various rubbers have been studied by a number of researchers [3-10]. Hummel [11] studied the decomposition of dicumyl peroxide in natural rubber. The compression set (high temperature) and the vulcanization time of the natural rubber - peroxide cure system, were investigated by Bristow [12, 13]. Ogunniyi [14] studied the generalized mechanism of the crosslinking reaction and elastomers where only a peroxide system is suitable. Dluzneski [15] reviewed the competing chemical reactions, polymer selection, cure temperature and the effect of other compounding additives in the peroxide vulcanizates.

Though peroxide vulcanization of natural rubber has been widely explored, details of parameters such as the optimum peroxide required, the effect of other ingredients and the elucidation of vulcanization time etc. still remain unanswered. Due to the marching cure behaviour of peroxide, the reported cure time for a particular system is often inconsistent. This deviation of cure time from actual values results in either over-cure or excess residual peroxide (under-cure) in the vulcanizates; both causing a reduction in mechanical properties. The physical properties of peroxide cured natural rubber have been previously investigated [16], however the influence of residual peroxide on mechanical properties has not been reported to date. Hence this study was proposed to optimize the vulcanization conditions and explore the effect of residual peroxide in the peroxide vulcanization of natural rubber. The study followed through the kinetics of peroxide vulcanization at different temperatures. Assessment of mechanical properties was also performed to evaluate the cure level in the vulcanizates.

EXPERIMENTAL

Materials Used

Natural rubber used for the study was ISNR 5 grade, obtained from the Pilot Crumb Rubber Factory, Rubber Board, Kottayam, Kerala, India. Dicumyl peroxide (DCP) was supplied by Arkema Peroxides India Private Limited, Cuddalore, Tamil Nadu, India. This industrial grade DCP has an activity of 40%.

Cure Characteristics

The Monsanto Rheometer (ODR) was used for studying the cure characteristics of the rubber compound. Three important parameters that an ODR curve provides are delta torque (M_H-M_L), scorch time (ts_2) and the time required to reach a given percentage of delta torque. The cure kinetic data were collected in the temperature range 150 to 165°C.

Vulcanization Kinetics

The kinetic order of the decomposition was determined by curing compounds for various levels and then analysing the unreacted or residual peroxide. The general equation for the kinetics of a first order chemical reaction is:

$$\ln(a - x) = -kt + \ln a \tag{1}$$

Where, a - initial peroxide concentration, x - reacted quantity at time ‘t’, k - first order reaction rate constant. The half-life $t_{1/2}$ is obtained as:

$$t_{1/2} = \frac{0.693}{k} \tag{2}$$

Preparation of Compounds

The formulation used is given in **Table 1**. The compounds were prepared in a two-roll mixing mill as per ASTM D 3182-07. The compounds were moulded to their respective t_{90}, t_{95} and t_{100} values as obtained from the rheometer.

Table 1. Formulation of mixes

Ingredients	A	B	C	D	E	F
NR, phr	100	100	100	100	100	100
*DCP, phr	2.35	3.40	5.00	6.00	7.00	8.50
** dicumyl peroxide with 40% active ingredient*						

Measurement of Mechanical Properties

Tensile specimens were cut from the cured sheets and the measurements were carried out according to ASTM D 412 using a universal testing machine (UTM) Zwick model 1474 with a crosshead speed of 50 cm/min at room temperature.

Compression Set

Compression set was determined by pressing the specimen to 25% of the original thickness for 22 h at 70 and 100°C. The specimen was then removed and the permanent set was measured as a percentage of the original thickness (ASTM D-395). Set is calculated using the equation:

$$C_B = \left[\frac{(t_0 - t_i)}{(t_0 - t_n)}\right] x100\% \tag{3}$$

where, C_B - compression set expressed as percentage of original deflection, t_0 -original thickness of the specimen, t_i- final thickness of the specimen, t_n - thickness of the spacer bar used.

Swelling Measurement

Cured test pieces were swollen in toluene for equilibrium swelling. The crosslink density is measured using the Flory–Rehner equation [17].

Degree of crosslinking is given by [18]:

$$\upsilon = \frac{1}{2}Mc \tag{4}$$

Where, M_C is the molar mass between crosslinks, which can be calculated using the equation [19]:

$$Mc = \frac{-\rho_r V(\varphi)^{1/3}}{\ln(1-\varphi)+\varphi+\chi\varphi^2} \tag{5}$$

Where, ρ_r - density of rubber (ρ_r = 0.92 for NR), V- molar volume of the solvent (toluene), ϕ - volume fraction of rubber in the solvent swollen sample, χ - rubber solvent interaction parameter (χ = 0.3 for NR- toluene system).

Volume fraction of rubber in the swollen gel:

$$\varphi = \frac{Dw/\rho_r}{\left(Dw/\rho_r\right) + \left(Sw - Dw\right)/\rho_s} \qquad (6)$$

Where, *S*w - swollen weight, *D*w - deswollen weight, ρ_s - density of solvent.

RESULTS AND DISCUSSION

The purpose of this study is to understand the effect of temperature on the crosslinking reaction of peroxide with natural rubber. Since the optimum amount of peroxide required for natural rubber based formulation is 5 phr (40% DCP), mix C (**Table 1**) was selected for the kinetic study. Accordingly, different temperatures viz. 150, 155, 160 and 165°C were selected and the rheographs recorded at these temperatures are given in **Figure 1**. It can be seen that as temperature increases there is a marginal increase in torque due to the crosslinking of rubber with DCP and hence the maximum torque

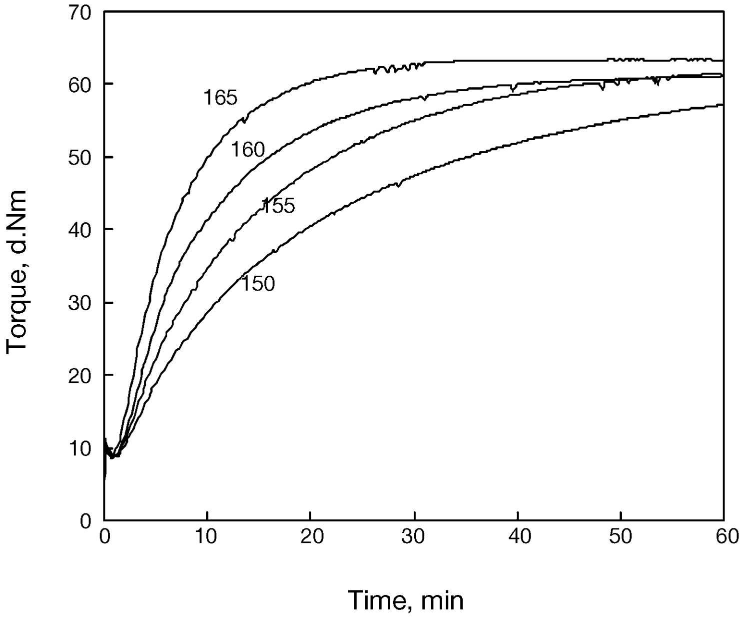

***Figure 1**. Rheometric curves of DCP cured NR at 150, 155, 160 and 165°C of mix C (ref. Table 1)*

is temperature dependent, i.e. as the temperature increases the rate of cure increases which leads to a high torque [9]. The cure parameters drawn from the rheographs are given in **Table 2**. At 150°C, optimum cure is not reached and it would take a minimum of 2 h for complete consumption of the DCP in the vulcanizate. The curves (at 155 and 160°C) converge to a point and at 150, 155 and 160°C, t_{100} remains almost constant. At 165°C, the rate of decomposition of the peroxides is high and it is consumed in a limited time, hence the lower t_{100} value.

Table 2. Rheometric properties of the vulcanizates (mix C, 5 phr DCP loading)

Temperature, °C	M_H, d.Nm	M_H -M_L, d.Nm	t_{90}, min	t_{95}, min	t_{100}, min	ts_2, min
150	57.18	46.71	41.65	49.32	59.96	2.76
155	61.47	52.72	32.82	40.95	59.33	1.92
160	61.12	52.61	24.14	31.55	59.82	1.72
165	63.39	52.96	16.53	21.18	50	1.72

Optimum Cure Time (t_{90})

The optimum cure time is calculated using the equation:

$$t_{90} = 0.9\left(M_H - M_L\right) + M_L \qquad (7)$$

where M_H is the maximum torque and M_L is the minimum torque. The variation of t_{90} and t_{95} at different temperatures is given in **Figure 2**. It is observed that with an increase of cure temperature there is a decrease in t_{90} and t_{95}. An empirical relationship exists between cure temperatures and cure time. For every 5°C increase in temperature, the optimum cure time t_{90} decreases by 8 minutes and the t_{95} decreases by 10 minutes. The scorch time ts_2 remains more or less constant except at 150°C.

Vulcanization Kinetics

First order reactions are characterized by an exponential decay of reactant concentration with time. The larger the value of the first order rate constant k, the faster the reaction. A first order reaction is identified by the linearity in the plot of log (a-x) against time. **Figure 3** reveals that thermal decomposition of peroxide follows first order kinetics at all temperatures. The advantage of first order kinetics is that the value of the rate constant can be derived

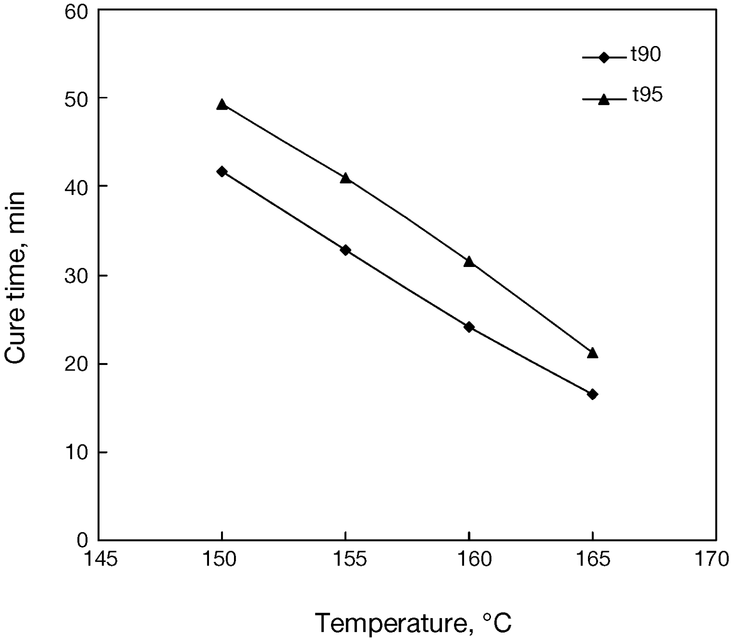

***Figure 2**. Variation of optimum cure time t_{90} and t_{95} with temperature of mix C (ref. Table 2)*

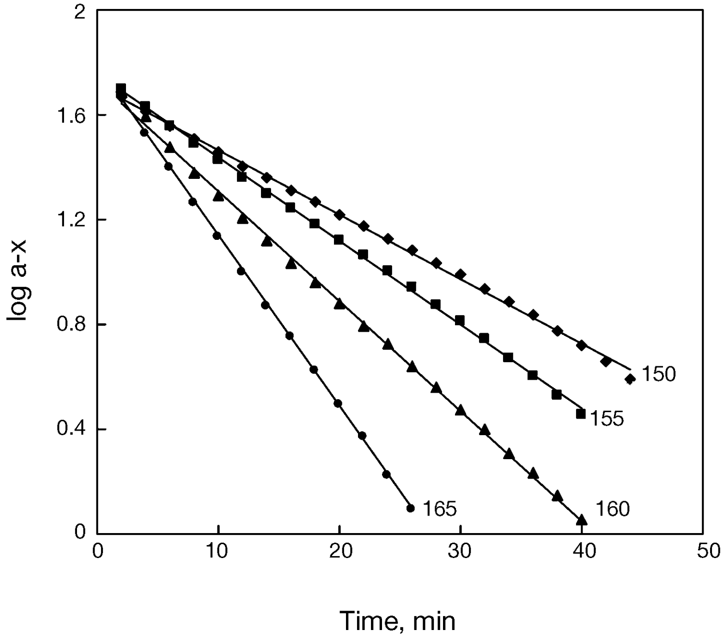

***Figure 3**. Variation of log (a-x) with time for DCP cured NR at 150, 155,160 and 165°C of mix C (ref. Table 1)*

from a relative measure of the reactant concentration with time; the absolute concentration of reactant is not required.

Temperature Dependence of the Rate Constant

The rate constant for a particular reaction has a constant value at a particular temperature. The temperature dependence of the rate constant is described by the Arrhenius equation:

$$\ln k = \ln A - {}^{Ea}\!/_{RT} \qquad (8)$$

Where, *A* - is the pre-exponential factor or Arrhenius frequency factor and *Ea* - is the activation energy. The two parameters, *A* and *Ea*, are together known as the Arrhenius parameters and are characteristics of each reaction. A plot of ln *k* against 1/T is a straight line with slope *–Ea/R* and intercept ln *A*.

The activation energy of the reaction was calculated (**Figure 4**) and found to be positive; when the *Ea* is positive, the reaction rate increases with an increase in temperature. The larger the activation energy, the greater is the sensitivity of the reaction to temperature changes. For every 10K rise in temperature the rate constant doubles as shown in **Table 3**. The half-life, the time required for

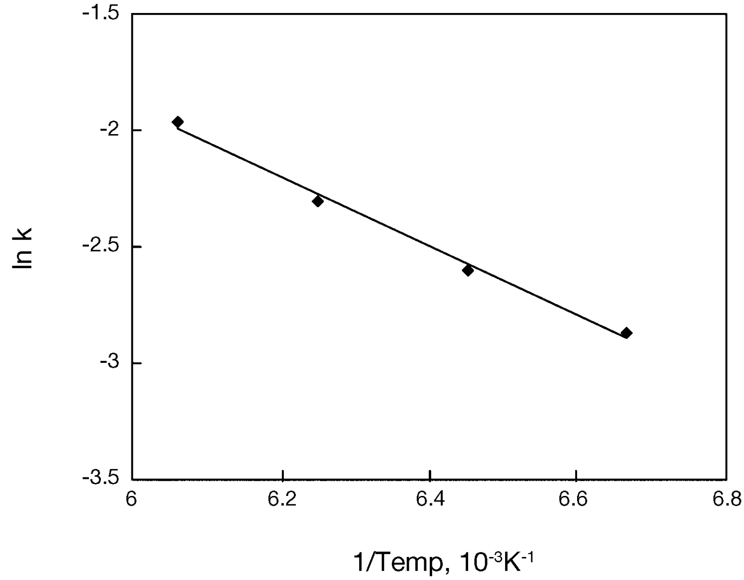

***Figure 4**. Variation of ln k with 1/T of mix C*

Table 3. Variation of rate constant and $t_{1/2}$ competed half-life with temperature

Temperature, °C	k, min^{-1}	$t_{1/2}$, min	t_{90}, min	t_{95}, min	t_{100}, min
150	0.056757	12.20	3.41	4.04	4.91
155	0.074249	9.33	3.51	4.38	6.34
160	0.096562	7.17	3.37	4.40	8.34
165	0.150188	4.61	3.59	4.59	10.00

half of the peroxide in the formulation to thermally decompose, decreases with increased temperature. The half-life and the number of half-lives completed at t_{90}, t_{95} and t_{100} are also given in **Table 3**.

Decomposition of Peroxide with Cure Time

The characteristic of the peroxide crosslinking of rubber is its decomposition rate which is expressed as a half-life (**Table 3**). In the first half-life, 50% of the peroxide decomposes as shown in **Table 4**. The process continues and theoretically never reaches 100% decomposition/consumption. The following table shows the relationship between the number of completed half-lives and the portion of peroxide decomposed.

Table 4. Variation of percentage of peroxide with half-lives

Half-lives	Amount of peroxide decomposed, %
1	50
2	75
3	87.5
4	93.75
5	96.9
6	98.4
7	99.2
8	99.6
9	99.8
10	99.9

Essentially for maximum decomposition of peroxide during vulcanization requires the cure time to be at least five half-lives at the cure temperature, giving 96.9% decomposition, or preferably 10 half-lives, which accounts for 99.9% decomposition. It is to be noted that t_{90}, accounts for an average of three half-lives (**Table 3**) leaving 12.5% residual peroxide in the product. At t_{95} this is four half-lives and at t_{100} it varies between 6 and 10 half-lives according to the temperature. As excess peroxide causes higher compression set, the cure temperature should be selected so as to leave minimum residual peroxide in the product.

Residual Peroxide

The amount of residual peroxide at four different temperatures, 150, 155, 160 and 165°C, is calculated theoretically from the equation ((a-x)/a) x 100, where, 'a' is the initial concentration of peroxide (M_H-M_L) and 'x' is the reacted quantity of peroxide at time 't' (Mt-M_L). The results are given in **Figure 5**. It is to be noted that at all temperatures, the percentage of residual peroxide after the first half-life is approximately 50%, except at the high temperature (165°C) where the percentage remaining is around 41%.

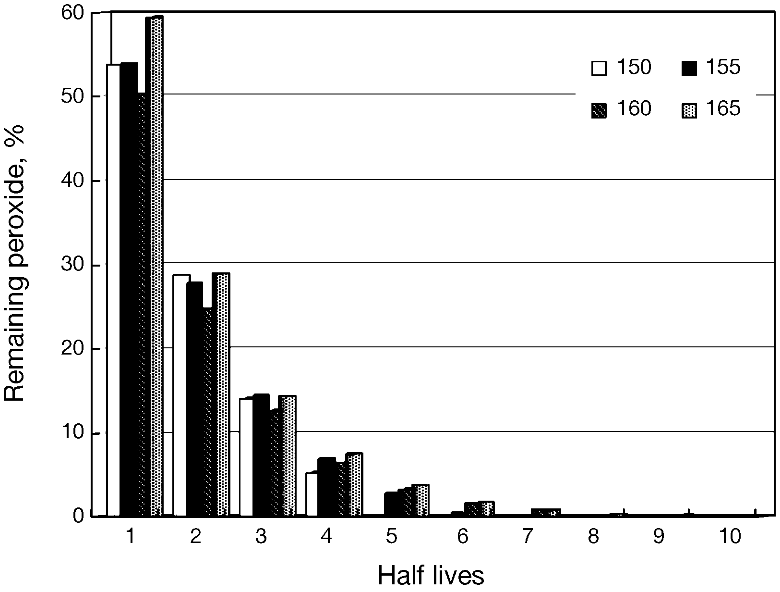

***Figure 5**. Variation of residual peroxide with half-lives at respective temperatures*

Table 3 shows that at the optimum cure time, t_{90}, peroxide decomposition accommodated three half-lives and the percentage of residual peroxide is approximately 12%. At t_{95}, vulcanizates contain approximately 6%

residual peroxide since it includes more than four half-lives. At 150°C, t_{100} accommodated 4.9 half-lives and about 97% of the peroxide is expected to have reacted at this temperature. At 155°C, the half-life is 9.33 minutes with 6.34 completed half-lives for t_{100} and 98.4% peroxide has been consumed. At 160°C for t_{100}, 99.6% decomposition occurs as the cure time is equal to 8.34 half-lives. At 165°C, the completed half-lives and peroxide consumption are 10 and 99.9% respectively. Hence the cure temperature (t_{90}, t_{95} or t_{100}) should be calculated from a fully decomposed peroxide cure curve. In order to achieve this, the peroxide vulcanization reaction (rheographs) should be run for a minimum of 60 minutes.

Effect of Varying Concentration of Peroxide on Cure Time

Since the cure time and residual peroxide influences the mechanical properties, the study was extended to include vulcanizates with different loadings of DCP. **Figure 6** shows the variation of rheometric torque with different concentrations of peroxide at 160°C. Rheometric properties of the vulcanizates are given in **Table 5**.

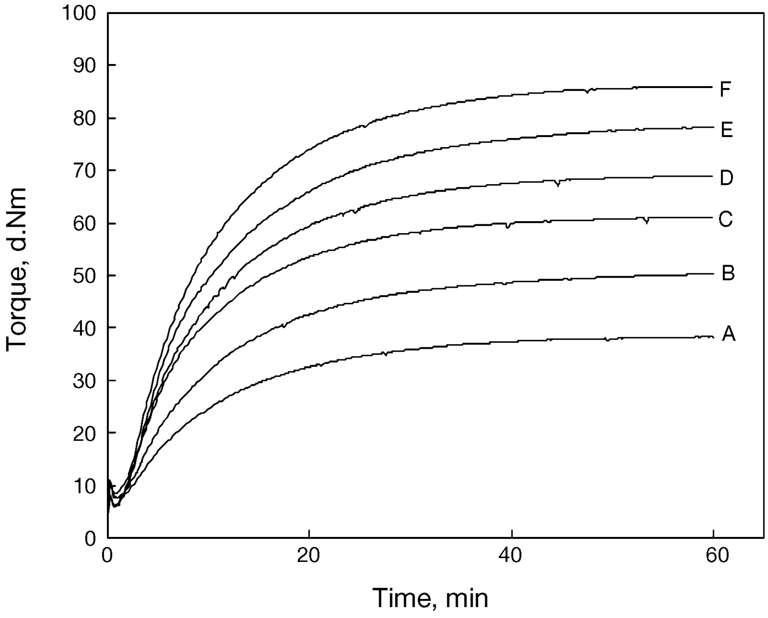

Figure 6. Variation of rheometer torque with concentration of peroxide vulcanized at 160°C

Table 5. Rheometric properties of the vulcanizates at 160ºC

Sample	Peroxide loading, phr	M_H, d.Nm	M_H-M_L, d.Nm	t_{90}, min	t_{95}, min	t_{100}, min	ts_2, min
A	2.35	38.33	30.58	27.73	34.8	59.77	2.38
B	3.40	51.08	43.51	28.95	36.79	59.37	2.24
C	5.00	61.12	52.61	24.14	31.55	59.82	1.72
D	6.00	69.06	60.92	25.16	32.58	59.69	1.67
E	7.00	78.18	70.56	26.28	34.67	59.76	1.59
F	8.50	86	77.86	24.72	32.23	59.82	1.47

As the concentration of peroxide increases, the torque increases regularly. This is due to the fact that as the concentration of peroxide increases, more radicals are formed and thus crosslinking efficiency will be higher. It is also evident from the crosslink density measurement which will be discussed later (**Table 6**). It is to be noted that as the concentration of peroxide increases, M_H value increases, whereas the minimum torque M_L remains almost the same.

Mechanical Properties

The mechanical properties of the vulcanizates were measured at different cure times, t_{90}, t_{95} and t_{100}, to study the influence of cure time and residual peroxide content on the mechanical properties such as tensile strength, elongation, modulus etc. and after ageing (set) properties. At a higher peroxide level there is an increase in the amount of residual peroxide, as well as the possibility of the formation of clusters due to the non-homogeneous distribution of crosslinks [8, 10, 20].

The variation of tensile strength with concentration of peroxide and cure time is shown in **Figure 7**. At t_{90} and t_{95}, the tensile strength increased, with an increase in concentration of peroxide, up to an optimum level (5 phr) and then decreased. This order is slightly different at t_{100} as there is an increase in tensile strength with concentration of peroxide up to 3.4 phr and thereafter it decreased. At low peroxide levels (2.35 and 3.4 phr), increasing cure time (t_{90} to t_{100}) has very little effect on tensile strength. When the cure temperature is high, the peroxide decomposes at a faster rate and hence the crosslink density also increases, as a result an increase in tensile strength is expected. Increasing the cure time (decrease in residual peroxide content) has no significant effect on the tensile strength at very high (8.5 phr) peroxide loading. At or above 5 phr, as the cure time increases from t_{90} to t_{100}, the amount of residual peroxide decreased and there is a significant decrease

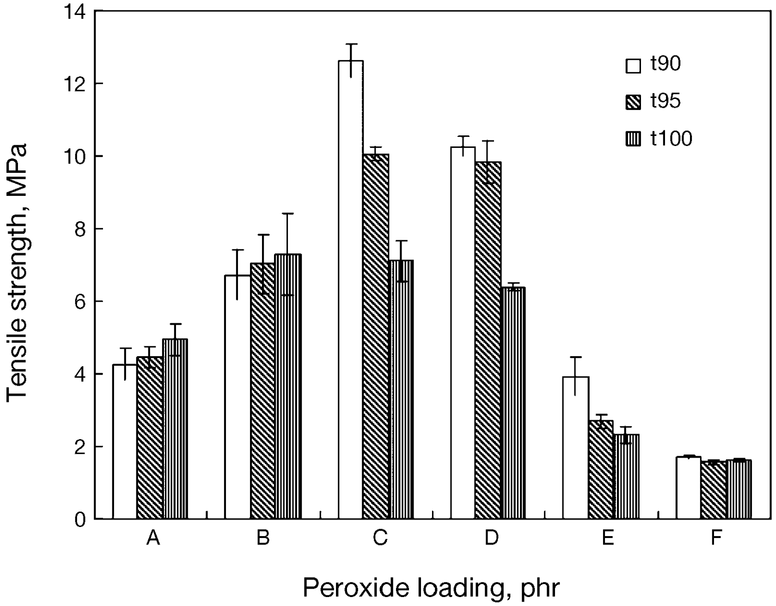

Figure 7. Variation of tensile strength as a function of the concentration of peroxide vulcanized at 160°C

in tensile strength at a particular loading of peroxide (C, D, and E) as shown in **Figure 7**. Furthermore, as the number of crosslinks increases, the shorter C-C crosslinks restrict the orientation of the macromolecular chains of the NR (strain crystallization) producing stiffer vulcanizates with lower mechanical properties. This has been further confirmed by the stress-strain curves of mixes C, E and F as shown in **Figure 8**.

When the peroxide level was 5 phr (optimum) the tensile strength was at a maximum as the strain induced crystallization came into effect (strain induced crystallization usually occurs in NR above 400% elongation). At high peroxide concentrations (mixes E and F) the tensile strength was low as there is no strain induced crystallization due to the over crosslinking and hence the lower elongation.

Figure 9 shows the elongation at break as a function of concentration of DCP. It is clear that elongation is high for sample A and decreased with increasing concentration of peroxide. The higher the level of peroxide the greater the crosslink density, resulting in a lower elongation at break (**Table 6**). Increasing the cure time from t_{90} to t_{100} (decreasing residual peroxide content) has no significant effect on elongation, as shown in **Figure 9**.

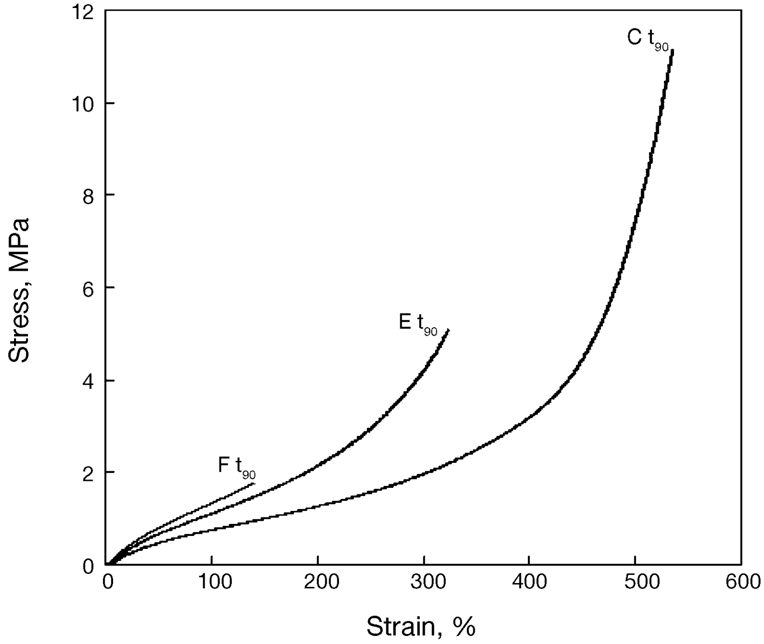

***Figure 8**. Stress- strain curves of mixes C, E and F vulcanized at 160°C*

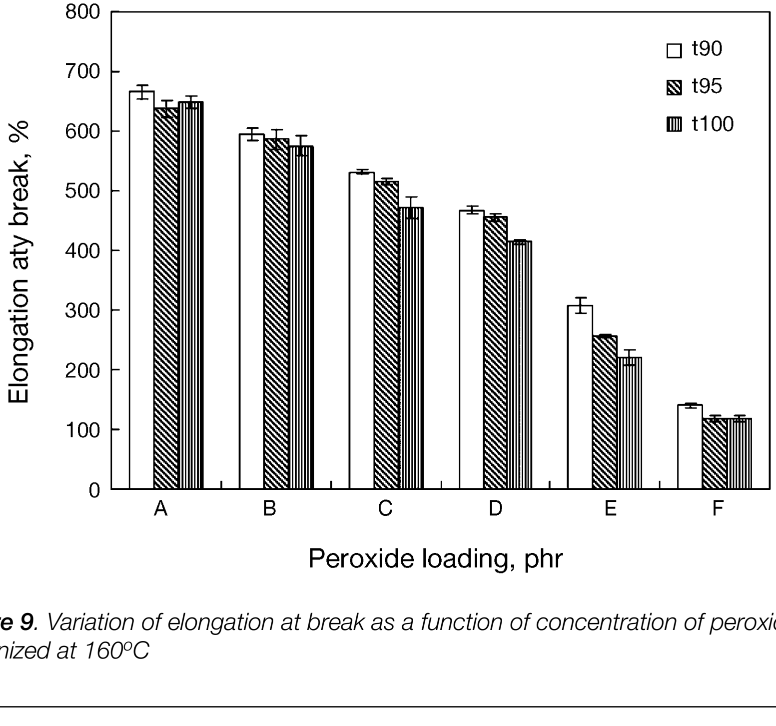

***Figure 9**. Variation of elongation at break as a function of concentration of peroxide vulcanized at 160°C*

The variation of modulus for 100% elongation with peroxide loading and cure time (t_{90}, t_{95} and t_{100}) is shown in **Figure 10**. At t_{90} the modulus increases with an increase in concentration of peroxide and showed a slight increase at higher cure intervals (t_{95} and t_{100}). The modulus depends upon the extent of crosslinking.

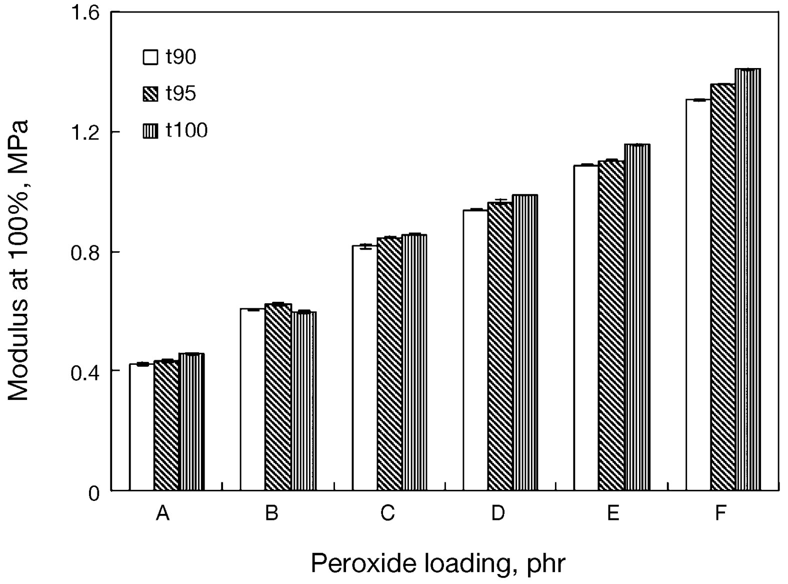

***Figure 10**. Variation of modulus for 100% elongation as a function of concentration of peroxide vulcanized at 160°C*

Compression Set

Theoretically, set is the deformation that remains after an imposed strain has been removed. Thus the set measures the ability of the elastomers to recover its original dimension after prolonged compressive stress at a given temperature and deflection. Variation of compression set at 70 and 100°C as a function of concentration of peroxide and cure temperature are shown in **Figures 11** and **12** respectively. Comparison of set values at t_{90}, t_{95} and t_{100} shows that, at 70°C, the set was not greatly influenced by the peroxide level. In all the cases, there is a slight improvement (decrease) in set values as the concentration of peroxide increases and it remains more or less constant at or above 5 phr. This is due to the fact that the rigid C-C bond has excellent thermal stability and does not undergo any cleavage or deformation in the compressed state.

At an elevated temperature (100°C) set values were mostly influenced by cure time as shown in **Figure 12**. Irrespective of the concentration of peroxide, maximum set values are observed at t_{90} with a minimum at t_{100}. At t_{90} and

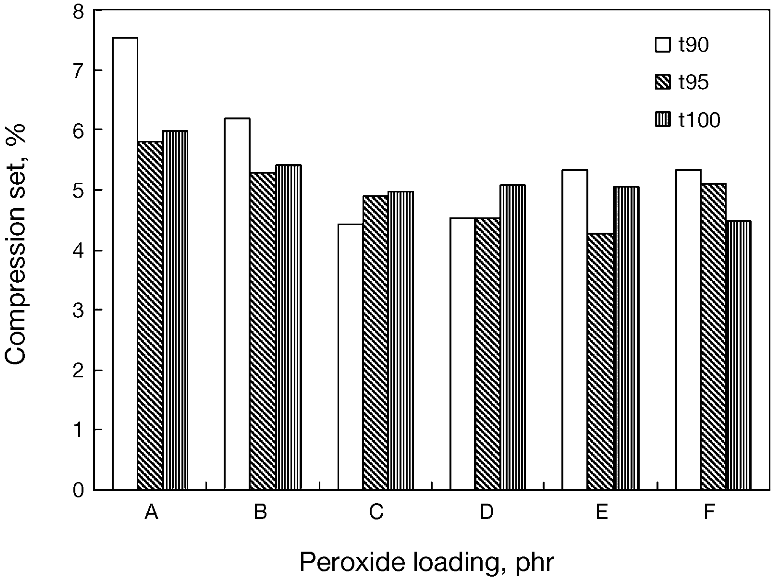

***Figure 11**. Variation of compression set as a function of concentration of peroxide after ageing at 70°C for 22 h*

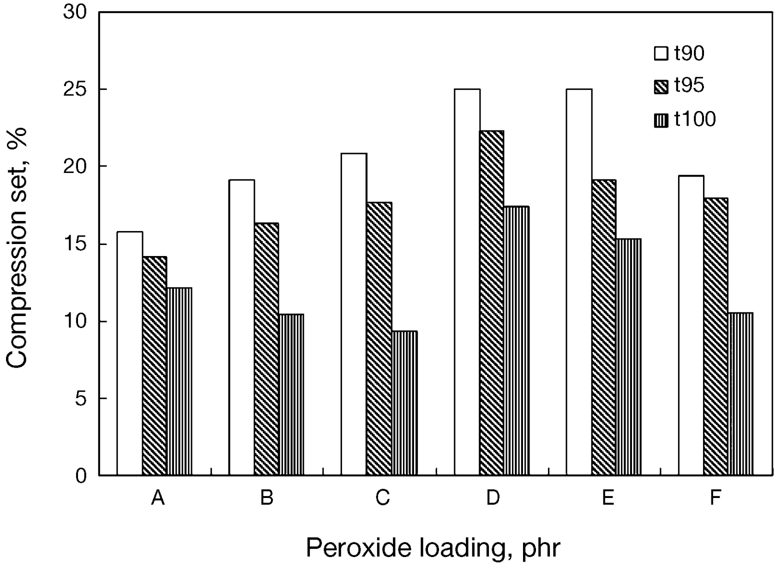

***Figure 12**. Variation of compression set as a function of concentration of peroxide after ageing at 100°C for 22 h*

t_{95}, as the peroxide loading increases, the set values increase (samples A and B), first reaches a maximum (sample D), and then increase. It is to be noted that mixes A and B have insufficient crosslinking, whereas for D, E and F the residual peroxide contributes to a high set. For t_{100} the lowest set values are obtained with optimum peroxide loading (mix C). Improved compression set with prolonged cure was related to network modifications as described by Ehabe [21]. Microcellular sheets were compression set, is an essential service parameter, it is advantageous to cure the material for longer times (t_{95} or t_{100}) in order to leave minimum residual peroxide content.

Crosslink Density

The chemical crosslinks prevent rubber molecules becoming completely surrounded by fluids, but cause swelling [22, 23]. The degree of equilibrium swelling provides additional information regarding the crosslink density of the vulcanized material. **Table 6** represents the variation of crosslink density with cure time and also with peroxide concentration. The increase in torque during rubber curing is a measure of the number of crosslinks formed per unit volume rubber. The maximum torque increases with temperature and also with the concentration of peroxide. It can be seen from the table that, as the concentration of peroxide increases, in all cases (t_{90}, t_{95} and t_{100}), crosslink density remains more or less same. Further heating will not result is a considerable decomposition of peroxide as indicated in **Table 4**. At higher peroxide levels there is also the possibility of the formation of clusters due to the non homogeneous distribution of crosslinks [10] which also results in a higher crosslink density.

Table 6. Variation of crosslink density with concentration of peroxide and cure time at 160°C

Sample	Crosslink density, x 10^{-5} mole/cm^3	Sample	Crosslink density, x 10^{-5} mole/cm^3	Sample	Crosslink density, x 10^{-5} mole/cm^3
A t_{90}	5.65	A t_{95}	5.85	A t_{100}	6.01
B t_{90}	8.36	B t_{95}	8.67	B t_{100}	8.69
C t_{90}	11.37	C t_{95}	11.79	C t_{100}	12.25
D t_{90}	13.33	D t_{95}	13.75	D t_{100}	14.27
E t_{90}	16.14	E t_{95}	16.06	E t_{100}	16.46
F t_{90}	18.60	F t_{95}	19.26	F t_{100}	19.77

CONCLUSIONS

The kinetics and cure characteristics of the peroxide vulcanization of natural rubber with dicumyl peroxide have been studied. The ideal temperature for the peroxide vulcanization of NR is 160ºC and the optimum level is 5 phr (40% DCP). When considering peroxide vulcanization, the cure time should be calculated from a fully crosslinked peroxide cure curve (i.e. the rheograph should be run for a minimum of 60 minutes). Residual peroxide has no significant effect on tensile strength, elongation at break, modulus or low temperature compression set. However, at high temperature, set increases with residual peroxide in the vulcanizate. For rubber products where set is a critical parameter, consumption of the entire peroxide must be ensured. The crosslinking efficiency of peroxide depends on the number of completed half-lives. The peroxide concentration is the dominant factor which controls the final crosslink density and properties of the vulcanizates.

REFERENCES

1. Ostromislensky I.I., *J. Russ. Phys. Chem.Soc.*, **47** (1915) 1885.
2. Annicelli R.A., 'Rubber Technology: Compounding and Testing for Performance' (Ed. J.S. Dick), Carl Hanser Verlag, Germany (2001) 434.
3. Thomas D.K., *J. Appl. Polym. Sci.*, **6** (1962) 613.
4. Scanlan J. and Thomas D.K., *J. Polym. Sci. Part A: General Papers*, **1** (1963), 1015.
5. Loan L.D., *Rubber Chem. Technol.*, **40** (1967) 149.
6. Loan L.D., *J. Appl. Polym. Sci.*, **7** (1963) 2259.
7. Brazier D.W. and Schwartz N.V., *Thermochim. Acta.*, **39**(1) (1980) 7.
8. Gonzalez L., Rodrigez A., Marcos A., and Chamorro C., *Rubber Chem. Technol.*, **69** (1996) 203.
9. Gonzalez L., Rodrigez A., Marcos A., and Chamorro C., *Kautsch. Gummi Kunstst.*, **51**(2) (1998) 83.
10. Valentin J.L., Posadas P., Fernandez-Torres A., Malmierca M.A., Gonzalez L., Chasse W., and Saalwachter K., *Macromolecules*, **43** (2010) 4210.
11. Hummel K., Scheele W., and Hilmer K.H., *Kautsch. Gummi Kunstst.*, **14**(6) (1961) 171.
12. Bristow G.M., *NR Technology*, **1**(1) (1970) 1.
13. Bristow G.M., *NR Technology*, **7**(3) (1976) 61.

14. Ogunniyi D.S., *Progress in Rubber and Plastics Technology*, **15**(2) (1999) 95.
15. Dluzneski P.R., *Rubber Chem. Technol*., **74** (2001) 451.
16. Braden M. and Fletcher W.P., *Trans. Inst. Rubber Ind*., **31** (1955) 155.
17. Flory P.J., *J. Chem. Phys*., **18** (1950) 108.
18. Morell S.H., ‘Rubber Technology and Manufacture’, (Ed. C.M. Blow), Butterworth, London, (1975) 162.
19. Khinnavar R.S. and Aminabhavi T.M., *J. Appl. Polym. Sci*., **42** (1991) 2321.
20. van der Hoff B.M.E., *Appl. Polym. Symp*., **n.7** (1968) 21.
21. Ehabe E.E. and Farid S.A., *European Polymer Journal*, **37** (2001) 329.
22. Sombatsompop N. and Christodoulou K.J., *Polym. Polym. Compos*., **5**(5) (1997) 377.
23. Progelhot R.C. and Throne J.L., ‘Polymer Engineering Principles: Properties, Processes, Tests for Design’, Hanser Publishers, New York, (1992).