

An Analysis of the Plasticity Retention Index of the Standard Malaysian Rubber Scheme

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Molecular degradation is the main process occurring during the Plasticity Retention Index (PRI) test of commercial grades of raw natural rubber. The relationship between Wallace plasticities and number-average degrees of polymerisation allows one to express the PRI in terms of number-average degrees of polymerisation.

The degradation data, for a number of commercial grades of natural rubber, can be represented by typical first-order type of kinetic equations. For such rubbers, the dependence of PRI on the initial Wallace plasticity and the chain scission rate constant is determined. A generalised treatment of the factors that influence the PRI value is presented and some of the empirical observations made with regard to the PRI are rationalised. The effectiveness of the PRI, as a measure of the susceptibility of raw natural rubber, is gauged.

The Plasticity Retention Index (PRI) of the Standard Malaysian Rubber (SMR) Scheme has been designed to provide a rapid assessment of the susceptibility of raw natural rubber (NR) to thermal oxidative degradation^{1,2}. High PRI values are generally associated with rubbers that possess good resistance to thermal oxidation breakdown^{2,3}. The PRI values are also useful in that they can be correlated with certain performance aspects of the rubbers during mastication and compounding and with the ageing performance of the derived vulcanisates^{1,2,3}.

For the majority of commercial grades of NR samples studied, the degradation as measured in terms of Wallace plasticities, can be satisfactorily represented by typical first-order type of kinetic equations, particularly for the early stages of degradation^{4,5}. It was therefore considered that PRI reflects a genuine thermal oxidative characteristic of NR and is independent of the progress of oxidation and the initial Wallace plasticity of the rubber.

A recent study⁶ has shown that NR degradation data can be satisfactorily represented by first-order type of kinetic equations if chain

scission of NR starts off with zero-order or pseudo-zero-order kinetics and becomes auto-catalytic in due course of time. However, deviations are bound to occur as chain scission of NR can follow varying kinetic paths.

Experimental evidence for the independence of PRI on P_o was obtained from mastication experiments^{3,5}. However, a more critical examination of the mastication data reveals that in some instances the differences in PRI values are significantly greater than the normal $\pm 3.5\%$ error associated with PRI measurements⁴. A recent mastication experiment conducted showed that PRI of a SMR CV rubber decreased as P_o of the rubber was progressively lowered *via* mastication at room temperature⁷. It has been reported⁸ that rubbers with low P_o values tend to have high PRI values and PRI values in excess of the maximum theoretical value of 100 have been quoted^{2,8}.

It seems necessary now to quantify some of the observations related to PRI and obtain a satisfactory understanding of the factors that can influence PRI values. The effectiveness of PRI as a measure of thermal oxidative degradation of NR is gauged.

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EXPERIMENTAL

The ageing of NR samples and PRI determinations were done according to the procedure laid out for the PRI test⁹. PRI is given by the expression

$$\text{PRI} = P_{30}/P_o \times 100 \quad \dots 1$$

where P_o is the initial plasticity and P_{30} is the plasticity after ageing for 30 min at $140^\circ\text{C} \pm 0.5^\circ\text{C}$.

The intrinsic viscosities $[\eta]$ of NR solutions of toluene were determined at $30^\circ\text{C} \pm 0.01^\circ\text{C}$. The number-average molecular weights (\bar{M}_n) were calculated from the expression

$$[\eta] = K\bar{M}_n^a \quad \dots 2$$

(where $K = 1.288 \times 10^{-3} \text{ dl g}^{-1}$ and $a = 0.66$) obtained from data pertaining to a set of unfractionated commercial NR samples¹⁰.

RESULTS AND DISCUSSION

The Wallace plasticity of an NR sample which has been subjected to thermal oxidative ageing for a time t is satisfactorily given by the expression⁵

$$P_t = P_o - P_d + P_{hg} + P_{hr} \quad \dots 3$$

where P_t is the aged plasticity

P_o is the initial plasticity

P_d is the decrease in plasticity due to thermal oxidative degradation

P_{hg} is the increase in plasticity due to the hardening of the rubber arising from crosslinking reactions of functional groups present in the NR system^{11,12} (of possible importance in the early stages of the ageing process)

P_{hr} is the increase in plasticity due to crosslinking of radical intermediates produced during the oxidative process¹³.

These radical reactions are generally outweighed by scission reactions and can only assume importance during the advanced stages of oxidation¹³.

Since PRI has been designed to denote the susceptibilities of NR to thermal oxidative breakdown, then naturally erroneous estimations of the susceptibilities are obtained if crosslinking reactions leading to the hardening of the rubber can occur concurrently with degradation during the PRI test. The aged Wallace plasticity after 30 min then needs to be written as

$$P_{30} = P_o - P_d + P_{hg} \quad \dots 4$$

and

$$\text{PRI} = 100(P_{30}/P_o) = 100(1 - P_d/P_o + P_{hg}/P_o) \quad \dots 5$$

Ideally P_{hg}/P_o should be negligible compared to P_d/P_o so that PRI is a reflection only of the degradative behaviour of the rubbers. While the contribution of P_{hg}/P_o may be significant for freshly prepared samples in laboratory experiments^{5,8}, its contribution to commercial grades of SMR is probably not significant⁵. We will therefore assume, in our subsequent discussions, that degradation is the dominant process occurring during the PRI test.

The thermal oxidative degradation of NR can follow varying kinetic paths⁶. However, for a number of commercial grades of NR studied, the degradation, could be represented by typical first-order kinetic equations of the type^{4,5},

$$P_t = P_o \exp - k_d t \quad \dots 6$$

where k_d is a rate constant of degradation expressed in unit of min^{-1} . PRI for such rubbers can be expressed as

$$\text{PRI} = 100 \exp - 30 k_d \quad \dots 7$$

While PRI becomes independent of the progress of oxidation on the basis of Equations 6 and 7, yet, one cannot infer that PRI is independent of P_o , unless one can show that k_d is independent of P_o .

For aged NR samples, $[\eta]$ of NR solutions of toluene are linearly related to Wallace plasticities (P) of the rubbers by a simple relationship of the type^{5,6,14}

$$[\eta] = bP + c \quad \dots 8$$

In view of *Equations 2 and 8*, one can write⁶

$$P_t = \bar{X}_t^a / \alpha - \beta / \alpha \quad \dots 9$$

where P_t is the Wallace plasticity at ageing time t

\bar{X}_t is the number-average degree of polymerisation at ageing time t

$$\alpha = b / KM_r^a$$

$$\beta = c / KM_r^a$$

M_r is the molecular weight of the repeating unit of NR.

Equation 9 allows us to discuss PRI either in terms of number-average degrees of polymerisation or Wallace plasticities.

Equation 6 can also be expressed on terms of number-average degrees of polymerisation according to the expression^{5,6}

$$\ln[1 - (\bar{X}_{P=0} / \bar{X}_o)^a] - \ln[1 - (\bar{X}_{P=0} / \bar{X}_o)^a (1 + s)]^a + a \ln(1 + s) = k_d t \quad \dots 10$$

where \bar{X}_o is the initial number-average degree of polymerisation

$\bar{X}_{P=0}$ is the number-average degree of polymerisation calculated from the intrinsic viscosity value $[\eta]_{P=0}$ corresponding to the zero reading on the plastimeter scale

s is the average number of chain scission events experienced by an initial NR molecule up to an ageing time t .

It has been shown⁶ that when *Equations 6 and 10* are operative,

$$k_d = ak_s / 1 - (\bar{X}_{P=0} / \bar{X}_o)^a \quad \dots 11$$

where $s = k_s t$, $k_s = k_o / N(O) = k_o M_r \bar{X}_o / \rho L$ or $k_1 \bar{X}_o$ for zero-order or pseudo-zero-order chain scission process respectively

k_o and k_1 are the zero-order and first-order rate constants of chain scission respectively

$N(O)$ is the initial concentration of NR molecules expressed usually in terms of molecule per cubic centimetre

ρ is the NR bulk density

L is the Avogadro constant.

The use of kinetic expressions that do not incorporate the diffusion parameter is justified as it has been shown that homogeneous degradation of NR pellets will occur during the PRI test⁶.

For zero-order chain scission process, *Equation 11* takes the form

$$k_d = a k_o M_r \bar{X}_o / \rho L (1 - \bar{X}_{P=0} / \bar{X}_o)^a \quad \dots 12$$

For pseudo-zero-order chain process, *Equation 11* takes the form

$$k_d = a k_1 \bar{X}_o / 1 - (\bar{X}_{P=0} / \bar{X}_o)^a \quad \dots 13$$

Equations 12 and 13 show that k_d values are dependent upon \bar{X}_o (or P_o) values and PRI cannot be considered as independent of P_o values on the basis of the observed first-order kinetics of degradation as given by *Equations 6 and 7*. The dependence of PRI on \bar{X}_o (or P_o), when *Equations 6 and 7* are obeyed, can be determined in the following manner.

For a set of rubbers differing only in \bar{X}_o (or P_o) values, one can write from *Equation 12* the following expression

$$dk_d / d\bar{X}_o = a k_o M_r / \rho L \left\{ [1 - (\bar{X}_{P=0} / \bar{X}_o)^a - a (\bar{X}_{P=0} / \bar{X}_o)^a] / [1 - (\bar{X}_{P=0} / \bar{X}_o)^a]^2 \right\} \quad \dots 14$$

for zero-order chain scission, and from *Equation 13*

$$dk_d / d\bar{X}_o = a k_1 \left\{ [1 - (\bar{X}_{P=0} / \bar{X}_o)^a - a (\bar{X}_{P=0} / \bar{X}_o)^a] / [1 - (\bar{X}_{P=0} / \bar{X}_o)^a]^2 \right\} \quad \dots 15$$

for pseudo-zero chain scission process. From *Equations 14 and 15*, one can obtain the conditions that

$$dk_d / d\bar{X}_o \text{ is } + \text{ for } (\bar{X}_{P=0} / \bar{X}_o) < 0.46 \quad \dots 16$$

and

$$dk_d / d\bar{X}_o \text{ is } - \text{ for } (\bar{X}_{P=0} / \bar{X}_o) > 0.46 \quad \dots 17$$

In the experiments conducted with commercial grades of NR so far, $(\bar{X}_{P=0}/\bar{X}_o)$ value has seldom exceeded 0.3. In view of this, Equation 16 is applicable to the degradation data. Thus, according to Equations 6 and 7, PRI decreases as \bar{X}_o (or P_o) increases. This is in consonance with the empirical observation that rubbers with high P_o values tend to have low PRI values⁸.

For a set of rubbers differing only in k_o or k_1 values, Equations 6, 7, 12 and 13 allow us to draw the inference that PRI will decrease with increasing magnitude of the chain scission rate constant. In view of the fact that it may not always be possible to represent the degradation data according to Equations 6 and 10, it is now necessary to present a generalised treatment of the factors that influence PRI and rationalisation of some of the empirical observations made with regard to PRI.

The use of Equations 8 and 9 allow PRI of NR to be expressed as⁵

$$PRI = 100 (\bar{X}_{30}^a - \bar{X}_{P=0}^a) / (\bar{X}_o^a - \bar{X}_{P=0}^a) \quad \dots 18$$

where \bar{X}_{30} is the number-average degree of polymerisation after ageing for 30 min at $140^\circ\text{C} \pm 0.5^\circ\text{C}$. The ageing period for the PRI test is 30 min and it is likely that, for the majority of NR samples, the zero-order or pseudo-zero-order chain scission kinetic model is operative^{6,15,16}. For the 30 min ageing period one can write

$$s = \bar{X}_o / \bar{X}_{30} - 1 \quad \dots 19$$

and taking into account the expressions for the zero-order and pseudo-zero-order chain scission processes, PRI can be written as

$$PRI = 100 [(\bar{X}_o/1 + k_c \bar{X}_o 30)^a - \bar{X}_{P=0}^a] / (\bar{X}_o^a - \bar{X}_{P=0}^a) \quad \dots 20$$

where $k_c = k_1 (\text{min}^{-1})$ for pseudo-zero-order chain process and $k_c = k_o M_r / \rho L$ (molecules $\text{cm}^{-3} \text{min}^{-1}$) for zero-order chain scission process.

From Equation 20, PRI is a function of \bar{X}_o , k_c and $\bar{X}_{P=0}$ and one can write

$$\begin{aligned} dPRI &= (\partial PRI / \partial \bar{X}_o) d\bar{X}_o \\ &+ (\partial PRI / \partial k_c) dk_c \\ &+ \left(\frac{\partial PRI}{\partial \bar{X}_{P=0}} \right) d\bar{X}_{P=0} \end{aligned} \quad \dots 21$$

It is now of interest to explore the changes in PRI resulting from changes in \bar{X}_o , k_c and $\bar{X}_{P=0}$.

The dependence of PRI on \bar{X}_o (or P_o) is given by the expression

$$\begin{aligned} (\partial PRI / \partial \bar{X}_o)_{k_c, \bar{X}_{P=0}} &= 100 a \bar{X}_o^a / (1 + k_c \bar{X}_o 30)^a \\ &(\bar{X}_o^a - \bar{X}_{P=0}^a) [1 / \bar{X}_o \\ &+ \bar{X}_{P=0}^a (1 + k_c \bar{X}_o 30)^a / \\ &\bar{X}_o (\bar{X}_o^a - \bar{X}_{P=0}^a) \\ &- 30 k_c / (1 + k_c \bar{X}_o 30) \\ &- \bar{X}_o^{a-1} / (\bar{X}_o^a - \bar{X}_{P=0}^a)] \end{aligned} \quad \dots 22$$

An examination of Equation 22 reveals that $(\partial PRI / \partial \bar{X}_o)_{k_c, \bar{X}_{P=0}}$ can take up values which can be positive or negative or zero. This is confirmed by Plots A, B and C of Figure 1.

The significance of the plots of Figure 1 can best be ascertained if PRI is firstly correlated with a fundamental parameter of degradation. The fundamental parameter that reflects the ability of a macromolecule to resist breakdown is \bar{X}_{30}/\bar{X}_o of Equation 19. The effectiveness of PRI can be gauged by determining how well it correlates with $100 (\bar{X}_{30}/\bar{X}_o)$.

Figure 2 gives the plot of PRI versus $100 (\bar{X}_{30}/\bar{X}_o)$ based on data pertaining to Plot A of Figure 1. A positive relationship exists between PRI and $100 (\bar{X}_{30}/\bar{X}_o)$ up to the maximum point of the plot. Beyond the maximum point, PRI in fact decreases rapidly as $100 (\bar{X}_{30}/\bar{X}_o)$ increases. If one accepts the established practice that high PRI values denote high resistance of NR to thermal oxidative breakdown, then PRI values beyond the maximum point would give misleading estimations of the susceptibilities of the rubbers to degradation. In view of this, the useful regions for PRI

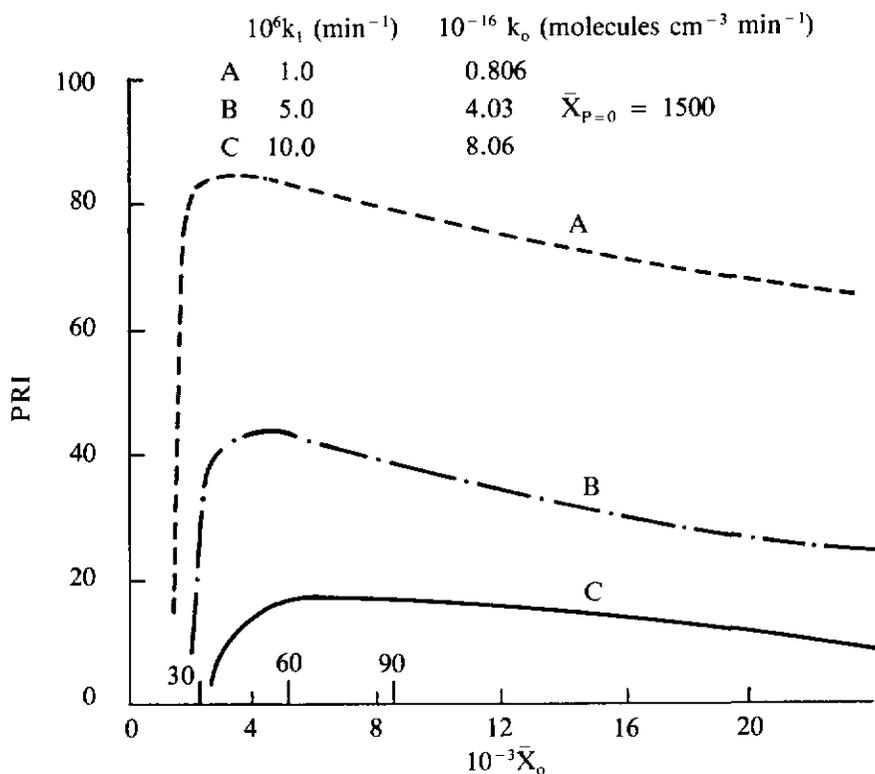


Figure 1. Plots of PRI versus \bar{X}_o (average $P = 30, 60$ and 90 are indicated).

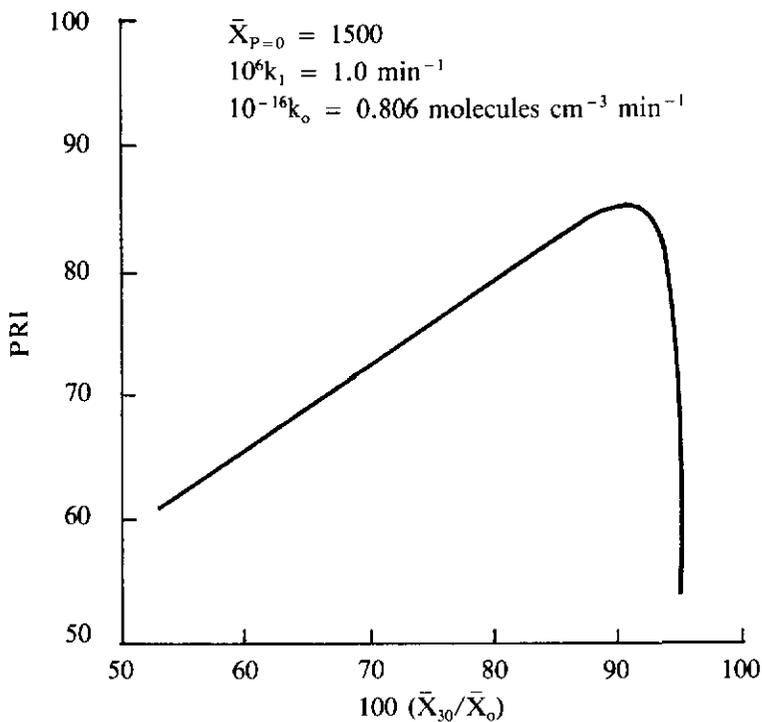


Figure 2. PRI versus $100 (\bar{X}_{30} / \bar{X}_o)$ based upon theoretical data.

are beyond the maxima of *Plots A, B* and *C* of *Figure 1*. This imposes the condition that below a certain P_o value of the rubber, PRI values can become misleading. The maximum points of *Plots A, B* and *C* of *Figure 1* occur at \bar{X}_o of 3500, 4000 and 6000 respectively. Molecular weight studies of clonal and SMR grades of rubbers^{8,10} show that \bar{X}_o varies from about 3000 to 9000 and only in a few instances is \bar{X}_o below 3500. Thus, it is likely that, in the majority of cases, quoted PRI values would provide an index of thermal oxidative degradation.

For a number of commercial grades of NR¹⁵, k_1 is in the region of $1.0 \times 10^{-6} \text{ min}^{-1}$ at $140^\circ\text{C} \pm 0.5^\circ\text{C}$ while the equivalent k_o value is $0.806 \times 10^{16} \text{ molecules cm}^{-3} \text{ min}^{-1}$. *Plot A* of *Figure 1* is based upon these values with $\bar{X}_{p=0} = 1500$. It will be shown later that the variation of PRI with the range of $\bar{X}_{p=0}$ found for rubbers is not large. In the useful region of PRI of *Plot A*, PRI decreases as \bar{X}_o (or P_o) increases. However, the decrease in $(\partial \text{PRI} / \partial \bar{X}_o)_{k_c, \bar{X}_{p=0}}$ is gradual and virtually linear. A two-fold increase in \bar{X}_o from $\bar{X}_o = 4000$ (average $P_o = 47.4$) to $\bar{X}_o = 8000$ (average $P_o = 84.4$) changes PRI from 84.9 to 80.2. This difference in PRI is not much greater than the 3.5% error involved in a single PRI determination⁴. If a rubber sample can be masticated without significantly changing the level of its hydroperoxide, then it is likely that one can observe that PRI does not significantly change as P_o decreases. For a set of rubbers from the same source material and prepared in a similar manner, magnitudes of the chain scission rate constants which reflect in the main, the levels of hydroperoxide, pro-oxidants and inhibitors present in the rubbers, are likely to be similar. If the variations in P_o are not extremely large, then PRI is likely to become independent of P_o . However, if small variations in k_1 or k_o values do occur, then the PRI values will cluster around a small range of values. This is in consonance with the observation that different grades of NR tend to have different ranges of PRI values^{2,3}.

The dependence of PRI on the chain scission rate constants k_1 and k_o is given by the expression

$$(\partial \text{PRI} / \partial k_c)_{\bar{X}_o, \bar{X}_{p=0}} = -3000 a \bar{X}_o^{a+1} / (1 + k_c \bar{X}_o 30)^{a+1} (\bar{X}_o^a - \bar{X}_{p=0}^a) \quad \dots 23$$

If chain scission of NR is a genuine first-order reaction, then at any particular temperature, PRI will be invariable as given by *Equation 23* since $k_c = k_1$. A recent kinetic study¹⁶ of degradation of NR advocates zero-order kinetics of chain scission. Chain scission is envisaged to occur between two peroxy radicals in the termination step of the oxidation mechanism. If the thermal oxidative degradation of NR is kept to the initial stages, then the overall hydroperoxide concentration of NR can be considered to remain constant during the degradation. Thus, the magnitude of the zero-order chain scission rate constant k_o will be linked to the concentration of the hydroperoxide present in the NR system. The zero-order chain scission mechanism seems plausible as there is significant variation in k_o and k_1 values¹⁵. This suggests that that chain scission rate-constant k_o is operative. Hence, according to *Equation 23*, PRI will decrease as k_o increases.

The magnitude of the chain scission rate constant k_o exerts a major influence on the PRI value. If the magnitudes of k_o for the rubbers (*Plots B* and *C* of *Figure 1*) are significantly greater than the value used for *Plot A* (*Figure 1*), then it is likely that SMR grades, derived from latex, sheet material and blend, will not be able to satisfy the PRI requirements¹⁷ of 60 and 50. However, SMR grades derived from field grade material, particularly SMR 20 and SMR 50 are likely to meet the PRI requirements of 40 and 30 respectively¹⁷. As mentioned before, the magnitude of the chain scission rate is mainly governed by the levels of hydroperoxide, pro-oxidants and inhibitors that are present in the NR system and it seems prudent to avoid situations that can enhance the levels of hydroperoxides and pro-oxidants in NR systems.

The dependence of PRI on $\bar{X}_{p=0}$ is given by the expression

$$\left(\frac{\partial \text{PRI}}{\partial \bar{X}_{p=0}} \right)_{\bar{X}_o, k_c} = -a \bar{X}_{p=0}^{a-1} [1 / (\bar{X}_o^a - \bar{X}_{p=0}^a) + (\bar{X}_{30}^a - \bar{X}_{p=0}^a) / (\bar{X}_o^a - \bar{X}_{p=0}^a)^2] \quad \dots 24$$

According to Equation 24, PRI decreases as $\bar{X}_{p=0}$ increases. Typical values of $\bar{X}_{p=0}$ lie in the region of 900 to 300⁶. For $\bar{X}_o = 5000$ and chain scission rate constants of Plot A (Figure 1), PRI has values of 87.0 and 89.5 when $\bar{X}_{p=0}$ changes from 900 to 300 respectively. The difference in PRI of 2.5 units is about the magnitude of the $\pm 3.5\%$ error involved in a single PRI determination⁴. Thus, it seems likely that variation of PRI with $\bar{X}_{p=0}$ may not be significant and possibly ignored for the majority of rubbers, unless one is dealing with an exceptional type of rubber.

The variations of PRI have been discussed in treating changes in \bar{X}_o , k_c and $\bar{X}_{p=0}$ separately. However, it is possible that for a set of rubbers, variations of all these parameters can exist and it is therefore possible for PRI to increase or decrease or become independent of \bar{X}_o (or P_o) according to the prevailing situation.

The effectiveness of PRI can be gauged by determining how well it correlates with the fundamental parameter of degradation \bar{X}_{30}/\bar{X}_o . A plot of PRI versus $100(\bar{X}_{30}/\bar{X}_o)$ for a number of NR samples is shown in Figure 3. It is encouraging to note that an increase in PRI corresponds to an increase in $100(\bar{X}_{30}/\bar{X}_o)$. PRI is a $f(\bar{X}_o, k_c, \bar{X}_{p=0})$, while $100(\bar{X}_{30}/\bar{X}_o)$ is a $f(\bar{X}_o, k_c)$ (see Equation 20). For the practical range of \bar{X}_o (or P_o) values, changes in $\bar{X}_{p=0}$ of the rubbers probably do not contribute significantly to changes in PRI values. If \bar{X}_o (or P_o) and k_c are independently varied, then one may or may not observe a positive relationship between PRI and $100(\bar{X}_{30}/\bar{X}_o)$.

For a set of rubbers, a positive relationship between PRI and $100(\bar{X}_{30}/\bar{X}_o)$ will definitely be observed if only one of the parameters \bar{X}_o or k_c is a variable. PRI is rather insensitive to \bar{X}_o (or P_o) and the chain scission rate constant k_c will exert a major influence in determining

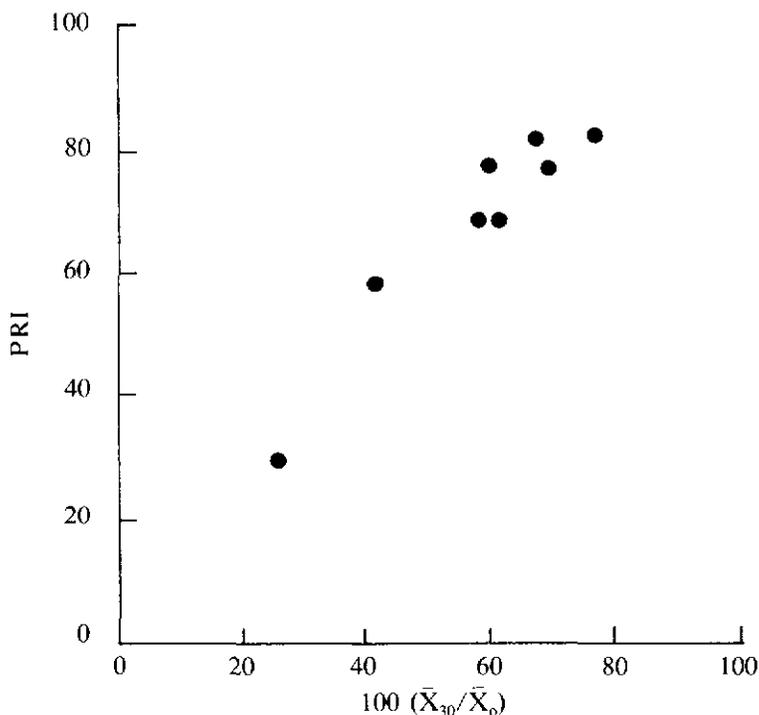


Figure 3. PRI versus $100(\bar{X}_{30}/\bar{X}_o)$ based upon experimental data.

the PRI value. In practical terms, this means that direct comparisons of PRI values are best restricted to within the individual grades of NR in order that PRI values reflect in an optimum manner the susceptibilities of the rubbers to thermal oxidative degradation.

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