Kinetics of Decomposition of Tert-butyl Peroxyisobutyrate During Vulcanisation of Natural Rubber Latex

MA'ZAM MD. SAID*, T.D. PENDLE** AND D.C. BLACKLEY***

The development of a modified iodometric method of estimating the concentration of tert-butyl peroxyisobutyrate (tBPIB) in natural rubber (NR) latex is described. The decomposition of tBPIB in NR latex, in the presence or absence of fructose was found to be a first-order reaction with respect to tBPIB concentration. The initial rate of tBPIB decomposition, however, was found to be half order with respect to initial tBPIB concentration. The effect of reaction variables on the rate of tBPIB decomposition is discussed. The activation parameters are calculated from the rate measurements. The significance of the kinetics of tBPIB decomposition in relation to tBPIB reaction and the kinetics of crosslinking is discussed.

In an earlier paper[1], the tert-butyl peroxyisobutyrate/fructose system was shown to be an effective prevulcanising system for NR latex. In this paper, the investigation on the kinetics of tBPIB decomposition during vulcanisation of NR latex is reported. No work has been published so far on the kinetics of peroxide reaction during vulcanisation of NR latex. This paper also describes a modified iodometric method developed to determine tBPIB concentration in NR latex. Development of the modified iodometric method requires the establishment of a suitable reaction medium and conditions for dispersing NR latex and fast peroxide-iodide and iodine-thiosulphate reactions. In addition, factors influencing blank titration volume need to be studied since the 'actual' blank titration volume of samples taken during the course of prevulcanisation cannot be determined.

EXPERIMENTAL

The material and the procedure for prevulcanisation of NR latex were the same as described earlier[1]. The materials, apparatus and procedure used for development of the modified iodometric method for determination of peroxide in latex were generally the same as described in the standard method[2]. Analar toluene was added in the reaction mixture to help disperse NR latex. Potassium iodide was replaced with saturated sodium iodide. Sodium iodide was found to be more soluble in a reaction mixture of isopropyl-acetic acid-autoxidised olefin than was potassium iodide[3]. This allows for a higher concentration of sodium iodide to be used, resulting in an increase in the rate of reaction and a decrease in the possible addition of iodine to unsaturated

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substances[3,4]. Copper chloride was used as a catalyst for the peroxide-iodide reaction. The liberated iodine was titrated with a standard thiosulphate to a colourless end-point. In the standard method, water (50 ml) is added before titration to speed up the iodine-thiosulphate reaction[3].

Development of a Modified Iodometric Method

Using the standard iodometric method of determination of peroxyester content[2], it was found that the blank titre is not affected by the levels of fructose, toluene, isopropanol and acetic acid. The result of the effect of fructose on blank titre *is significant since the concentration of* fructose would decrease during prevulcanisation. In the presence of acetic acid, fructose does not appear to react with the liberated iodine. It has been found that reducing sugars react with iodine under alkaline condition[5]. The blank titre increases proportionately with the amount of copper chloride, that is 6 ml of $0.01N$ sodium thiosulphate per 1 ml of 1% copper chloride solution. Texofor FP170 is a non-ionic surfactant used for preparing the peroxide emulsion. The blank titre increases with increasing amounts of Texofor FP170 and standing time *(Figure 1)*. However, the effect of Texofor FP170 on determination of tBPIB in latex would not be important since the amount used was small[1]. When determining the contribution of latex to blank titre or determining the tBPIB concentration in latex, a known amount of latex was injected into the reaction medium using a graduated syringe. The reaction medium was stirred using a magnetic stirrer during the addition of latex. A solvent mixture of toluene (70 ml)/isopropanol (30 ml) dispersed latex (2 ml at 50% d.r.c.) very satisfactorily. In the presence of acetic acid (5 – 15 ml), a mixture of toluene (60 ml)/isopropanol (40 ml) produced a satisfactory medium for dispersing latex. The acetic acid, however must be added slowly after the latex has been dispersed in toluene/isopropanol mixture to avoid coagulation of latex. In the absence of acetic acid in the reaction mixture, the blank titre was found to decrease with increasing amounts of latex *(Figure 2)*. This is probably as a result of the addition of iodine to polyisoprene. In the presence of acetic acid in the reaction mixture, the blank titre increases very slightly with increasing amounts of latex. This is probably due to the increasing inhomogeneity of the reaction mixture with increasing amounts of latex, which tends to lead to over-stepping of the end point. Further evaluation of the method was carried out using latex containing a known concentration of tBPIB. Accurate determination of tBPIB in latex (2 ml at 50% d.r.c.) was made using reaction mixture containing toluene (60 ml), isopropanol (40 ml), acetic acid (15 ml), 1% copper chloride solution (1 ml) and saturated sodium iodide (4 ml). However, water must not be added into the reaction mixture and the normality of thiosulphate should be adjusted to avoid excessive dilution. The formation of an inhomogenous reaction mixture which tended to produce higher results, would then be avoided. The above modified iodometric procedure was used to determine the concentration of tBPIB remaining in latex during prevulcanisation. The concentration of peroxide was calculated using,

Peroxide concentration (g mol/g rubber)

$$= \frac{(a-b) \times N \times 8 \times M \times 100}{c \times \varrho \times D} \frac{M \times 100}{16}$$

where a is the volume of thiosulphate (ml) required to titrate the sample

b is the blank titre (ml)

N is the normality of sodium thiosulphate

M is the molecular weight of peroxide

c is the volume of latex (μl)

ϱ is the density of latex

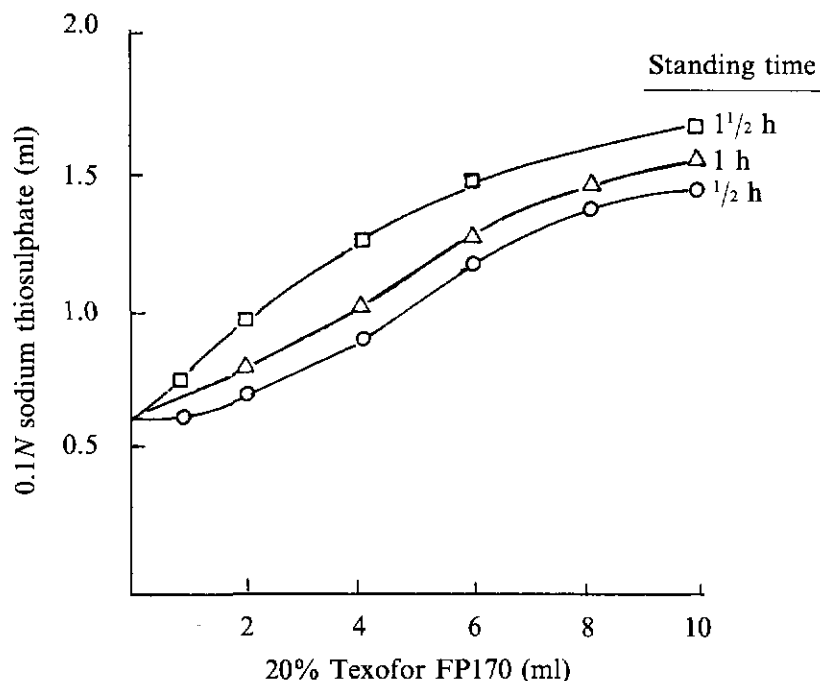D is the dry rubber content of latex

Figure 1. Effect of Texofor FP170 and standing time on titration volume of thiosulphate using the Akzo Chemie method of iodometric analysis.
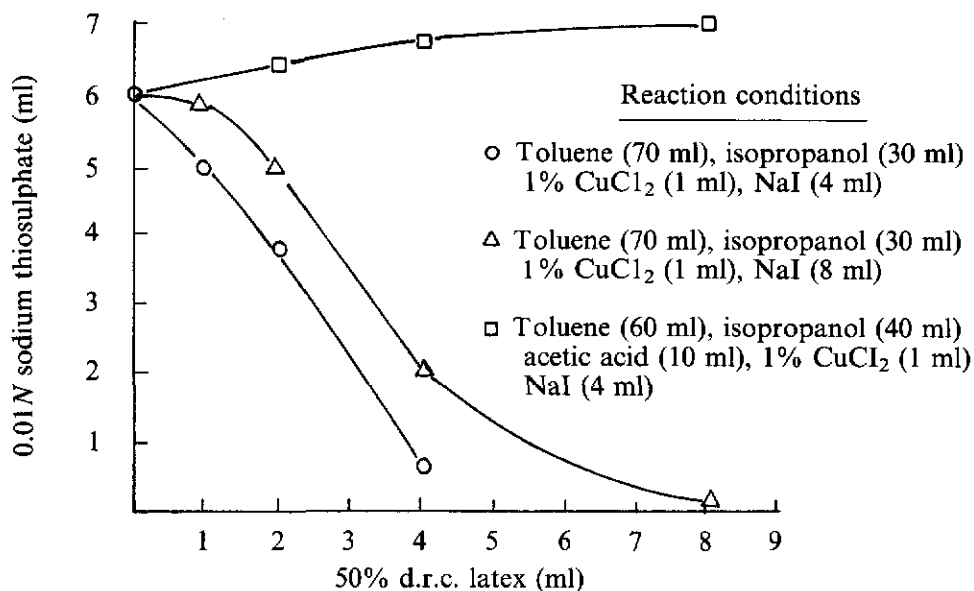

Figure 2. Effect of NR latex and reaction conditions upon titration volume of thiosulphate. Standing time was 1 h at room temperature.

The blank titre of a reaction mixture containing prevulcanised latex was assumed to be the same as that of a reaction mixture containing unvulcanised latex.

RESULTS AND DISCUSSION

Rate of Reaction

Figures 3, 4 and *5* show straight line plots of $-\ln$ [tBPIB] *versus* prevulcanisation time, where [tBPIB] is the concentration of the undecomposed tBPIB in latex. The results suggest that the decomposition of tBPIB in NR latex is a first-order reaction satisfying the following first-order rate equation:

$$-\ln \text{[tBPIB]} = k' t - \ln \text{[tBPIB]}_o$$

where k' is the rate of coefficient for tBPIB decomposition

t is the prevulcanisation time [tBPIB]$_o$ is the initial concentration of tBPIB.

The slopes of the lines in *Figures 3, 4* and *5* give the various values of k'. First-order decomposition of tBPIB in NR latex was also observed when using other reaction conditions, both for fructose-activated and non-activated tBPIB systems.

The value of k' remains fairly constant over a range of initial tBPIB concentration for systems containing equimolar initial concentrations of tBPIB and fructose at 60°C *(Figure 6)*. At constant initial tBPIB concentration and at constant temperature, the value of k' increases with increasing initial fructose concentrations *(Figure 7)*. The value of k' increases with temperature, more rapidly for fructose-activated systems than for non-activated systems *(Figure 8)*. *Figures 7* and *8* also show the effect of reaction variables on the value of k'', the rate coefficient for crosslink formation[1]. Although the patterns in which k' and k''

are affected by the ratio of initial fructose concentration to initial tBPIB concentration, and temperature are generally similar, under certain reaction conditions, the values of k' and k'' are not equal. Thus, for instance, for non-activated systems, k' is greater than k'' over a wide temperature range. The value of k'' becomes significantly greater than k' at temperatures greater than 80°C, particularly when using a high ratio of initial fructose to initial tBPIB concentration. According to the simple mechanism of peroxide vulcanisation, it ought to be impossible for k'' to exceed k'. Hummel and Scheele[6] stated two conditions for k'' to be equal to k'. Firstly, the intermediate reactions during vulcanisation must be fast so that the concentrations of their products are very small. This condition is likely to be satisfied by a peroxide vulcanising system. The second condition is that the instantaneous crosslinking efficiency (F_t) must be constant throughout the vulcanisation reaction. The value of F_t can be obtained by plotting the concentration of crosslinks formed against the concentration of tBPIB decomposed. The slope taken at a point corresponding to time t gives the F_t value. It is found that F_t increases with prevulcanisation time, for various systems regardless of whether k'' is equal or not equal to k' as shown by the examples in *Figures 9, 10* and *11*. Thus, the variation of F_t with prevulcanisation time only partly explains the inequality of k'' and k'. Perhaps, differences in the temperature coefficients for the various competing reactions that occur during peroxide prevulcanisation of NR also influence the relationship between k'' and k' and the variation of F_t with prevulcanisation time. The increase of F_t with prevulcanisation time is probably also a result of depletion of free radical scavengers as prevulcanisation progresses. The results in *Figure 11* show that the value of F_t exceeds 50% towards the end of the reaction. This probably suggests that at high temperatures, both alkyl and butoxy radicals generated from the decomposition of tBPIB participated in the crosslinking reaction.
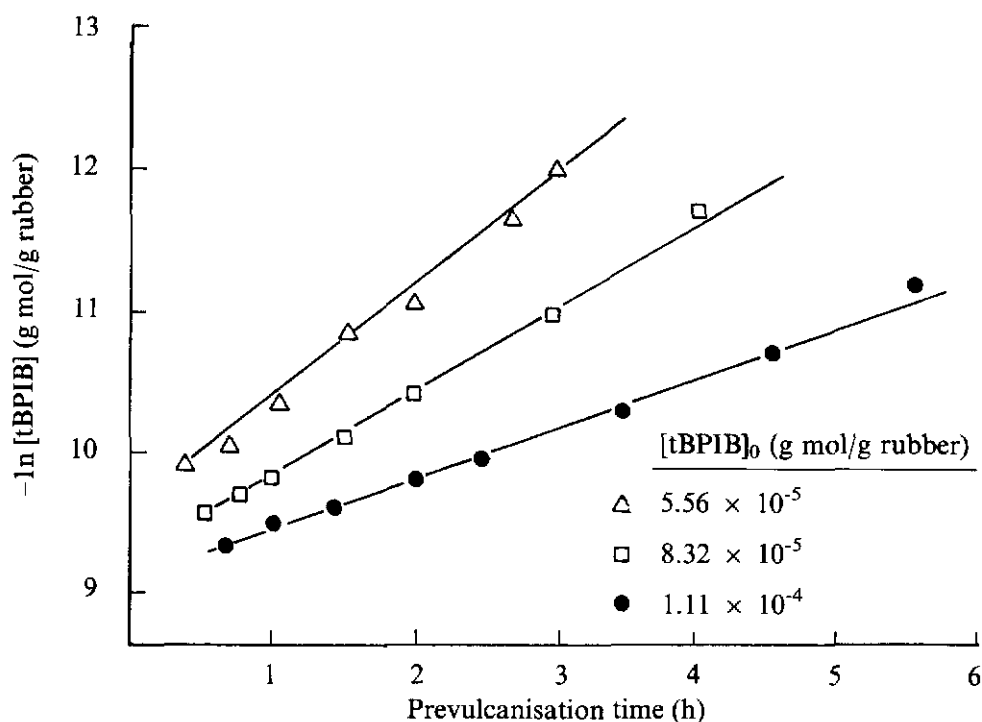
Figure 3. First-order plots for tBPIB decomposition in NR latex at 60°C for systems which initially contained 1 p.h.r. fructose and different concentrations of tBPIB.

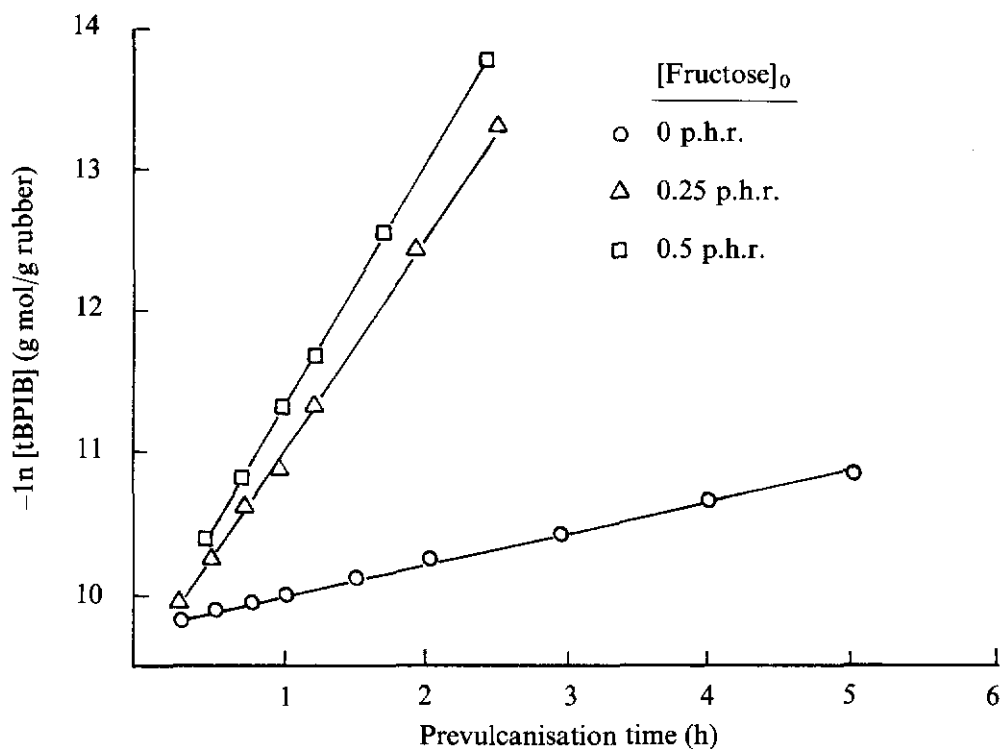*Figure 4. First-order plots for tBPIB decomposition in NR latex at 80°C for systems which initially contained 5.56 × 10^{-5} g mol/g rubber tBPIB and different concentrations of fructose.*
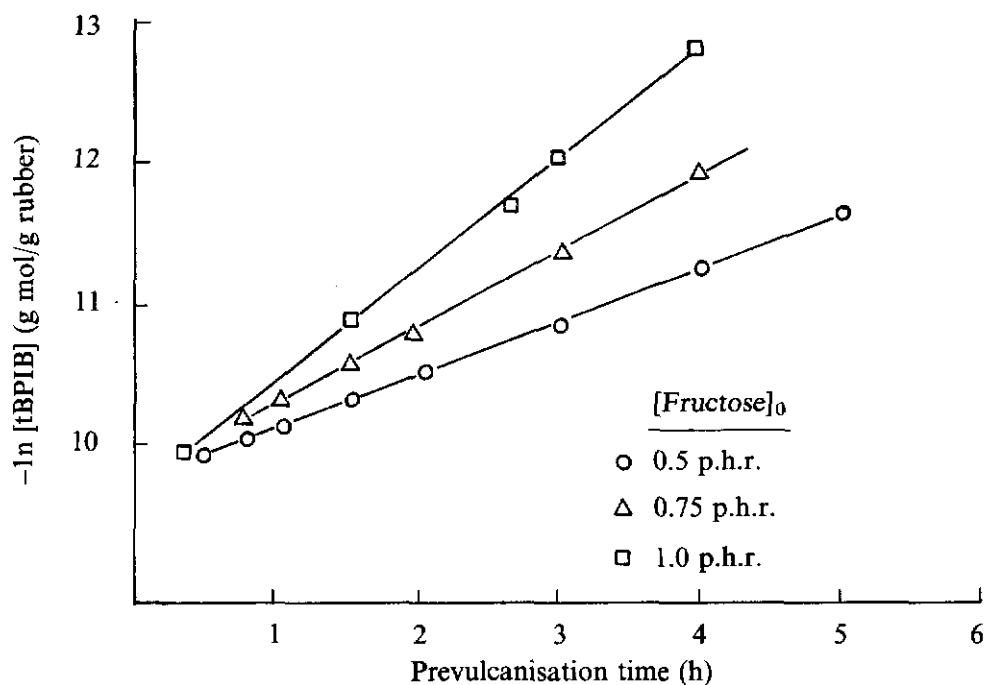
Figure 5. First-order plots for tBPIB decomposition in NR latex at 60°C for systems which initially contained 5.56 × 10⁻⁵ g mol/g rubber tBPIB and different concentrations of fructose.

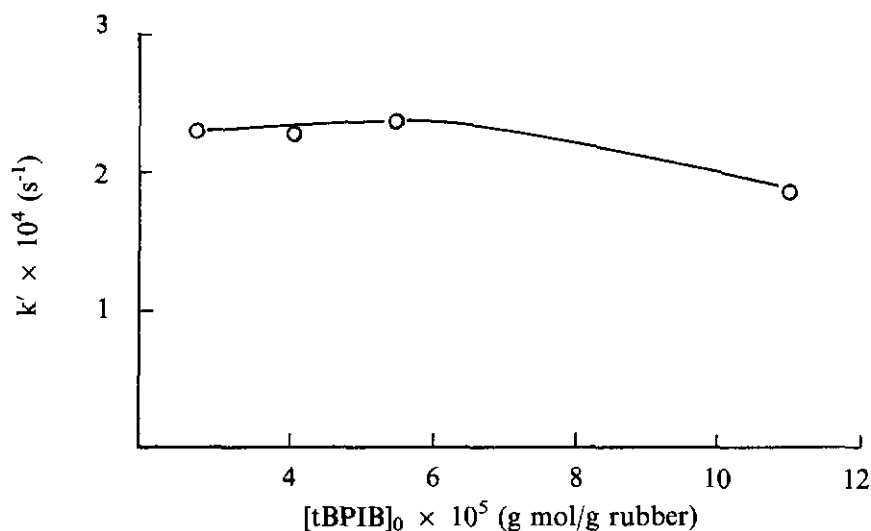*Figure 6. Effect of initial tBPIB concentration on rate coefficient k' for decomposition of tBPIB in NR latex at 60°C using equimolar tBPIB and fructose concentrations.*
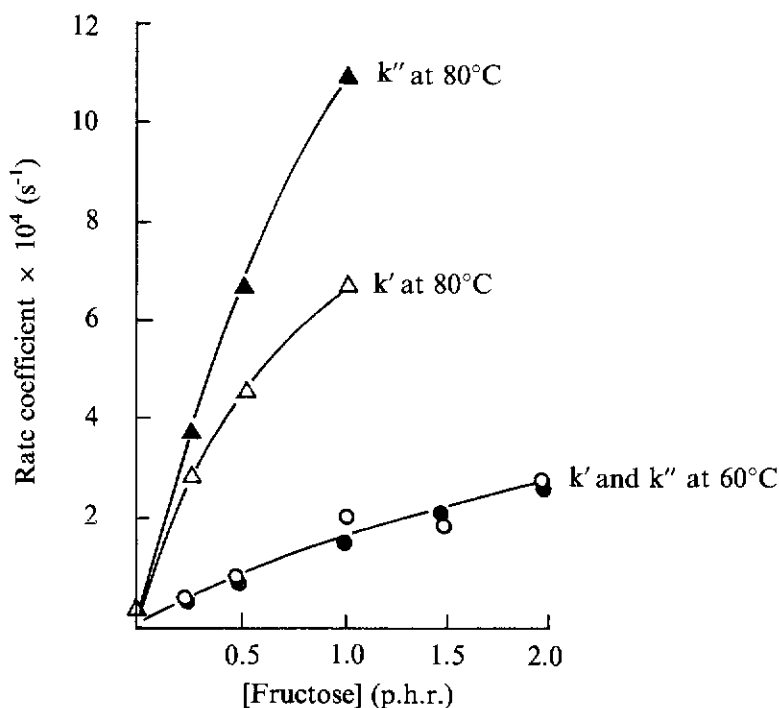
Figure 7. Effect of fructose concentration and prevulcanisation temperature on rate coefficients for tBPIB decomposition (k') and crosslink formation (k'') at 60°C and 80°C using 5.56×10^{-5} g mol/g rubber tBPIB.
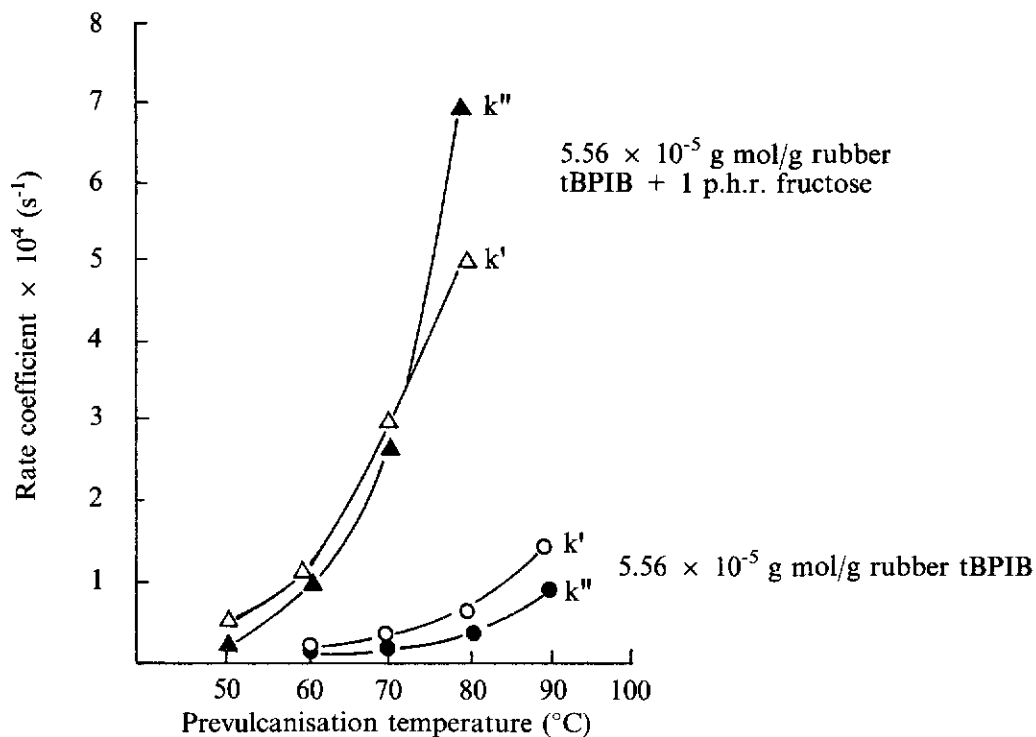

Figure 8. Effects of prevulcanisation temperature and fructose/tBPIB concentrations on the values of k' and k''.
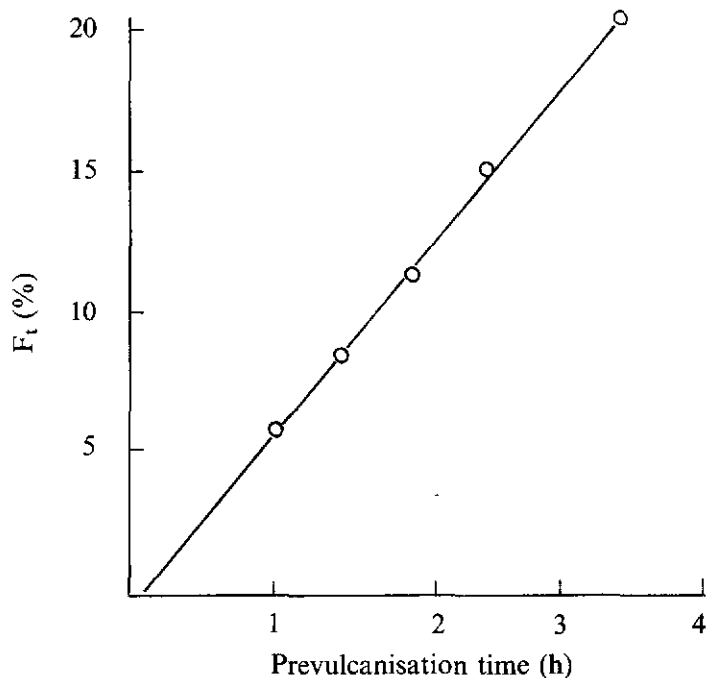
Figure 9. Variation of crosslinking efficiency F_t with prevulcanisation time at 60°C for a system which initially contained 1.11 × 10⁻⁴ g mol/g rubber tBPIB and 1 p.h.r. fructose.
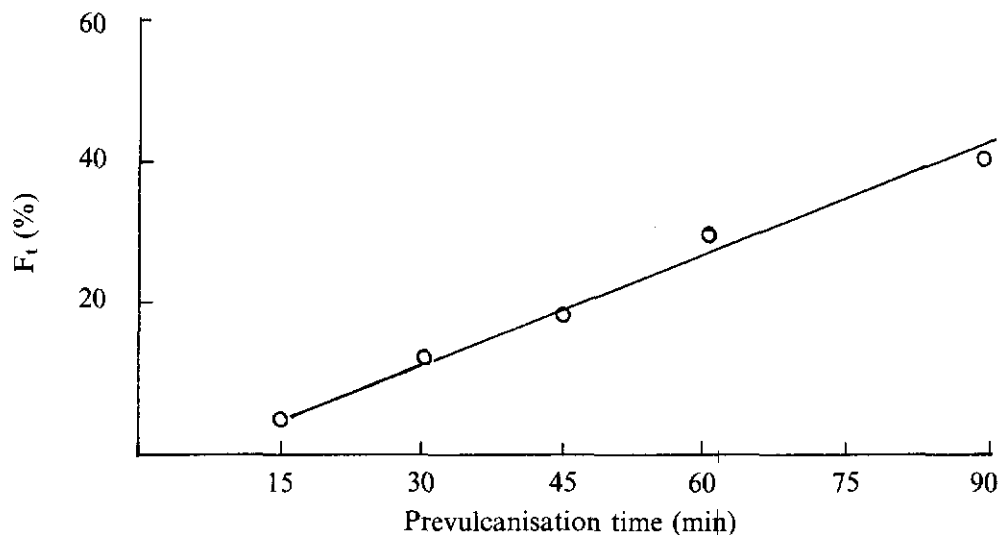

Figure 10. Variation of crosslinking efficiency F_t with prevulcanisation time at 60°C for a system which initially contained 5.56 × 10⁻⁵ g mol/g rubber tBPIB and 2 p.h.r. fructose.
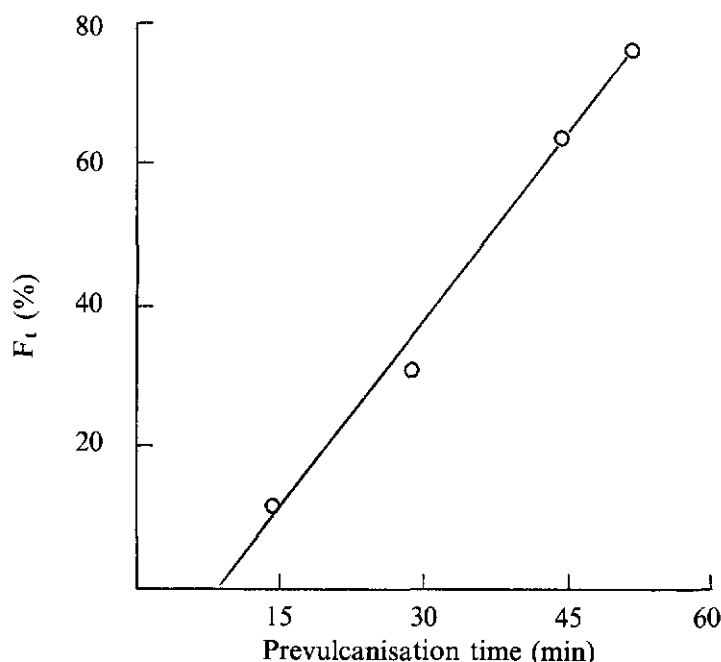
Figure 11. Variation of crosslinking efficiency F_t with prevulcanisation time at 80°C for a system which initially contained 1.11×10^{-4} g mol/g rubber tBPIB and 1 p.h.r. fructose.

Activation Parameters

The experimental activation energy E' of tBPIB decomposition is obtained using the Arrhenius equation:

$$k' = A_e{}^{-E'/RT}$$

where A is a constant

R is the gas constant (8.313 J/K)

T is the temperature.

E' is obtained by multiplying R by the negative slope of the line obtained from the plot of ln k' *versus* $1/T$ *(Figure 12)*. The experimental activation energy E'' of crosslink formation is obtained in a similar way *(Figure 13)*. Other activation parameters of tBPIB decomposition are obtained from the value of E' using the following equations:

$$\triangle H^+ = E' - RT$$

$$\triangle S^+ = R\{ \ln\frac{k'\,h}{k\,t} + \frac{\triangle H^+}{RT} \}$$

$$\triangle G^+ = \triangle H^+ - T\triangle S^+$$

where, $\triangle H^+$ is the activation energy

$\triangle S^+$ is the activation entropy

$\triangle G^+$ is the activation free energy

h is Planck constant

k is Boltzman constant.

The relationship between ln k' and $1/T$ apparently shows a strong departure from linearity at temperatures greater than 70°C for systems containing more than 1 p.h.r. fructose *(Figure 12)*. This departure is partly due to the temperature dependence of the experimental activation energy, but the major factor is probably the occurrence
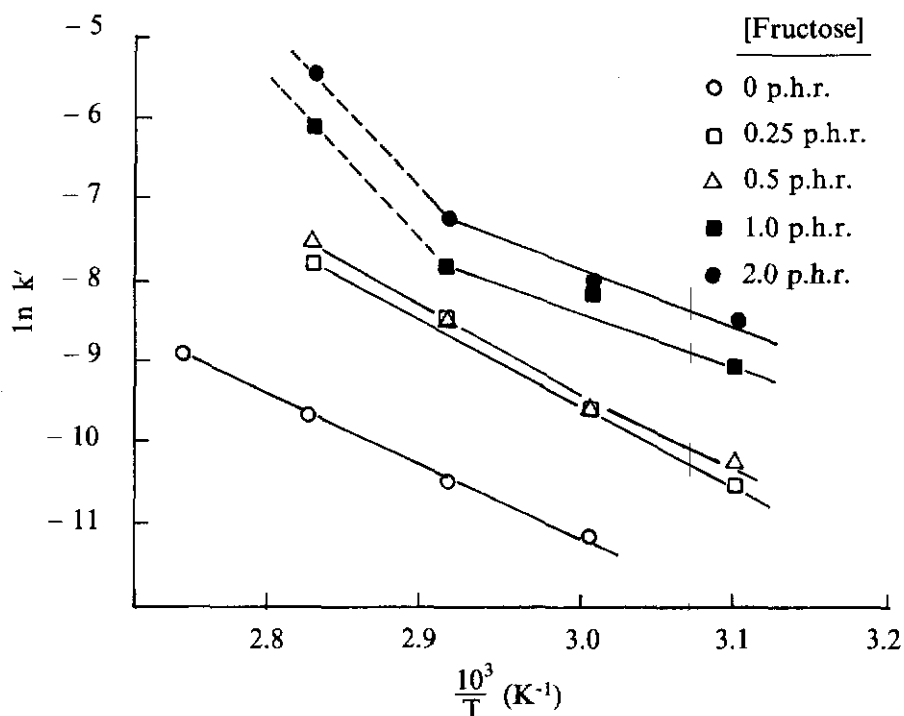
Figure 12. Plots of 1n k' against T^{-1} for prevulcanisation using 5.56×10^{-5} g mol/g rubber tBPIB and various fructose concentrations.
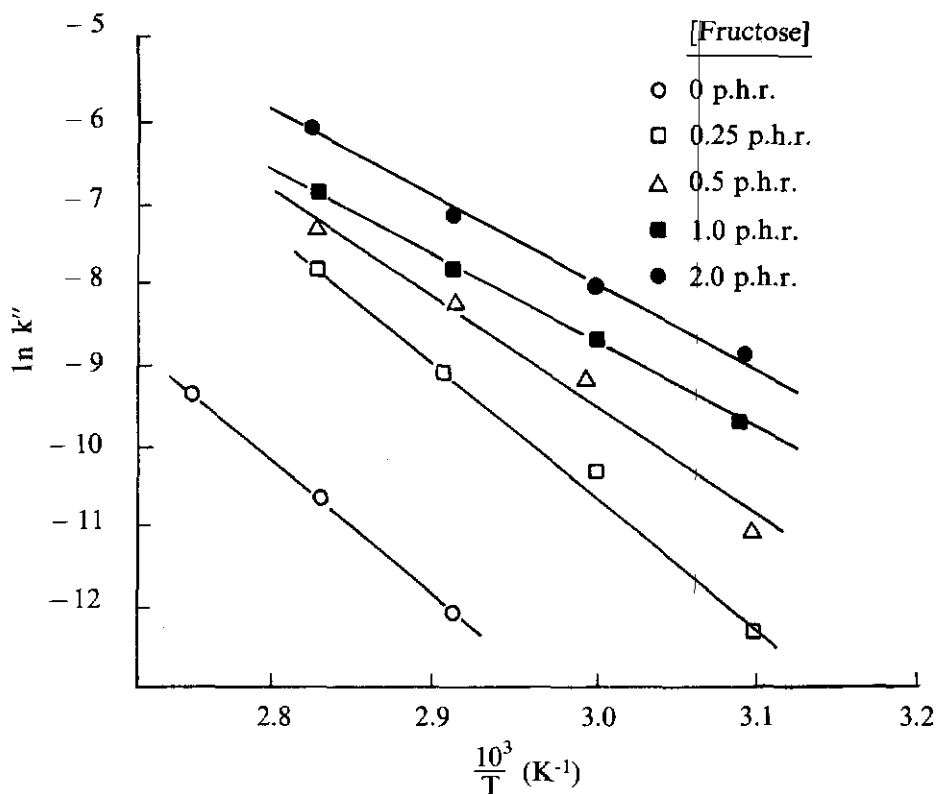

Figure 13. Plots of 1n k'' against T^{-1} for prevulcanisation using 5.56×10^{-5} g mol/g rubber tBPIB and various fructose concentrations.

of two competing reactions[7]. In the present case, these reactions may be those of activated and non-activated decomposition of tBPIB and the latter reaction probably predominates at the higher temperatures. Calculation of the E' value in the temperature range, 70°C to 80°C for the system containing 2 p.h.r. fructose produced an E' value of 135 kJ/mol, which is approximately equal to the activation energy of non-promoted decomposition of tBPIB in chlorobenzene[8].

The value of E' for the decomposition of tBPIB in NR latex without the addition of fructose was found to be 79 kJ/mol *(Table 1)*. The lower activation energy for the decomposition of tBPIB in NR latex compared to that in chlorobenzene probably suggests that some of the non-rubber substances activate the decomposition of tBPIB. The E' and $\triangle H^{+}$ values increase and then decrease with increasing fructose concentrations. However k' was shown to increase with increasing fructose concentrations *(Figure 7)*. Thus, the rate of tBPIB decomposition appears to be influenced by both the activation energy and activation entropy of decomposition, that is the activation free energy which decreases with increasing fructose concentrations *(Figure 14)*. A higher value of $-\triangle S^{+}$ for the decomposition of tBPIB in NR latex compared to the decomposition in chlorobenzene[8] suggests the formation of a more rigid tBPIB-activator(s) complex in

NR latex. The activation energy for crosslink formation decreases and then becomes constant with increasing fructose concentrations (0 to 2 p.h.r.) The activation energy for crosslink formation is higher than that for tBPIB decomposition, for all the systems studied. For comparison, the activation energy[9] for the decomposition of dicumyl peroxide in *cis*-1,4-polyisoprene and the activation energy for the crosslink formation are both the same, 150 kJ/mol.

Initial Rate of tBPIB Decomposition

The dependence of the initial rate of tBPIB decomposition, $(d[P]/dt)_o$, on the initial concentrations of tBPIB, $[P]_o$, was analysed. The value of $(d[P]/dt)_o$, was obtained from the slope of the concentration of residual peroxide, $[P]$, *versus* time curve at the initial stage of the reaction. Plotting $\ln (-d[P]/dt)_o$ against $\ln [P]_o$ for reaction systems for which $[F]_o$ is kept constant, a straight line with slope n is obtained *(Figure 15)*. Plotting $\ln (-d[P]/dt)_o$ against $\ln [F]_o$ for reaction systems for which $[P]_o$ is kept constant, a straight line with slope m is obtained at the higher range of initial fructose concentrations *(Figure 16)*. The value of n is approximately equal to 1/2 for both the systems shown in *Figure 15*. The value of m shows a temperature-dependence, being equal to approximately 1.0, 0.7 and 0.6 at 50°C, 60°C and 80°C respectively.

TABLE 1. ACTIVATION PARAMETERS OF tBPIB DECOMPOSITION AND CROSSLINK FORMATION FOR PREVULCANISATION USING 5.56 × 10⁻⁵ G MOL/G RUBBER OF tBPIB AND VARIOUS CONCENTRATIONS OF FRUCTOSE

[Fructose] (p.h.r.)	E' (kJ/mol)	$\triangle H^{+}$ (kJ/mol)	$\triangle G^{+}$ ((kJ/mol)	$-\triangle S^{+}$ (J/mol/K)	E'' (kJ/mol)
0	79	76	110	102	142
0.25	93	90	106	48	139
0.5	87	84	105	64	112
1.0	62	59	103	131	92
2.0	65	62	101	118	92

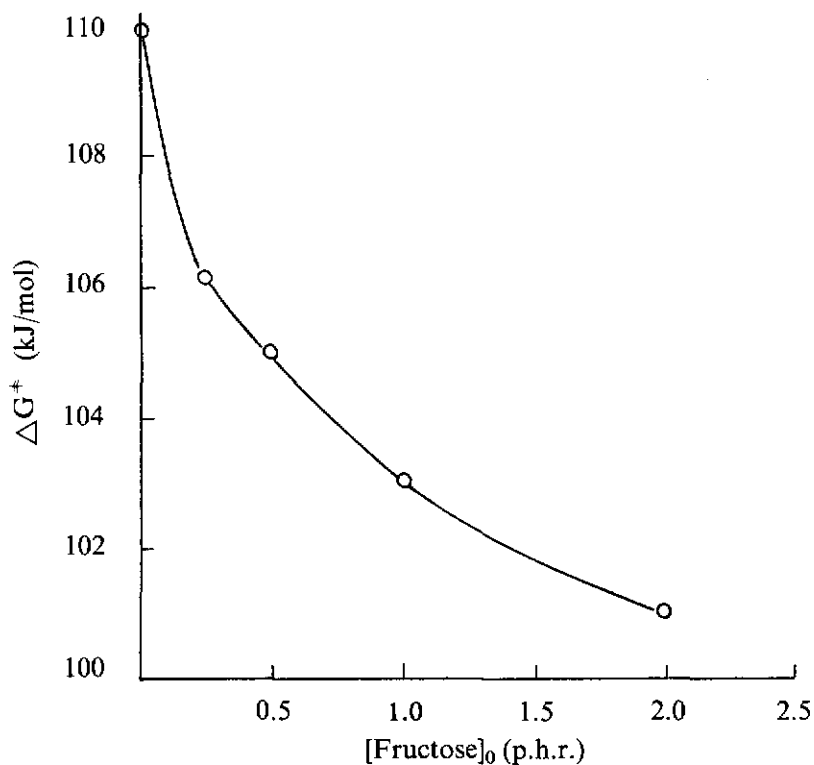Figure 14. Effect of initial fructose concentrations at constant tBPIB concentration of 5.56×10^{-5} g mol/g rubber on $\triangle G^{+}$.
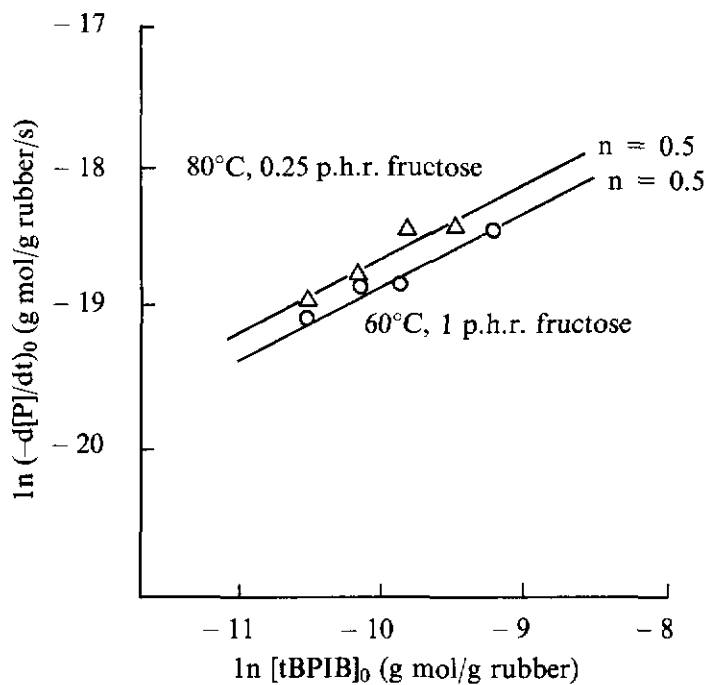

Figure 15. Plots of ln $(-d[P]/dt)_0$ against ln $[tBPIB]_0$ using two different initial fructose concentrations and temperatures.
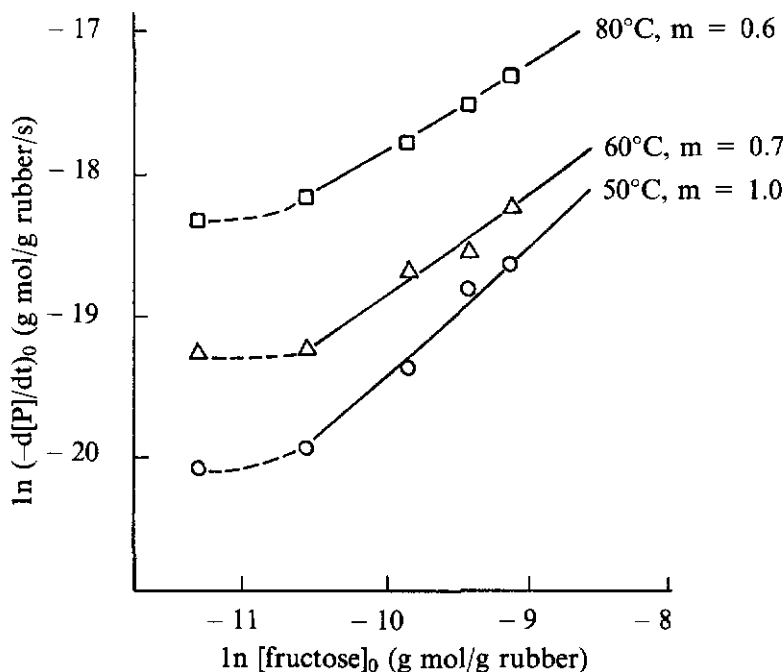
Figure 16. Plots of ln $(-d[P]/dt)_0$ against ln $[fructose]_0$ using initial tBPIB concentration of 5.56 × 10^{-5} g mol/g rubber at various temperatures.

The values of m obtained for reactions carried out at 60°C and 80°C are kinetically not rational numbers. The results probably suggest that the initial rate of tBPIB decomposition comprises more than one term containing the fructose concentration:

$$(-d\,[P]/dt)_o = [P]_o^{\frac{1}{2}}\,(k_1\,+\,K_2\,[F]_o^{\frac{1}{2}} + K_3\,[F]_o\,+\,......)$$

where k_1, k_2, k_3.... are the rate coefficients for tBPIB decomposition, associated with the appropriate terms.

The decomposition of peroxide has seldom been found to be half order with respect to peroxide concentration. The decomposition of peroxide can be half order with respect to peroxide concentration if the decomposition is induced by solvent radicals and the termination reactions involve recombination of radicals derived from the peroxide[10]. Such reactions, however, are perhaps not important for the reaction systems investigated in this report. However, under certain conditions, induced decomposition of tBPIB may be significant[10,11]. It was shown earlier that the overall rate of tBPIB decomposition is first order with respect to peroxide concentration. It is not clear why the reaction orders with respect to peroxide concentration at the initial stage of reaction and during the course of the run are different. The results suggest that the initial rate of decomposition is faster than the subsequent rate of decomposition. Perhaps the concentration of agents that accelerate the initial rate of tBPIB decomposition depletes rapidly so that the subsequent reaction would be first order with respect ot tBPIB concentration.

CONCLUSION

Decomposition of tBPIB in NR latex was found to be first order with respect to peroxide concentration. However, an investigation of the initial rate of tBPIB decomposition in NR latex revealed a more complex rate expression than a simple first-order formulation. The rate coefficients for tBPIB decomposition and crosslink formation were generally found to increase with increasing fructose concentrations and temperatures. It is the activation free energy rather than just the activation energy that determines the rate coefficient of tBPIB decomposition. At high prevulcanisation temperatures, the rate coefficient of crosslink formation tends to be significantly greater than the rate coefficient of tBPIB decomposition. The instantaneous crosslinking efficiency of tBPIB systems was found to increase with prevulcanisation time, suggesting that the concentration of free-radical scavengers decreases with prevulcanisation time. In some reaction systems, the instantaneous crosslinking efficiency tends to be greater than 50%, suggesting that both the alkyl and alkoxy radicals generated from the decomposition of tBPIB participate in the crosslinking reaction.

ACKNOWLEDGEMENT

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