PEROXIDE PREVULCANIZATION OF NATURAL RUBBER LATEX

BY

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PROGRAMME OF RELATED STUDIES

The author has attended the lecture courses and tutorials on surface chemistry, colloid science and emulsion polymerization, in partial fulfilment of the requirements of the degree of Doctor of Philosophy. He has undertaken a guided study on aspects of rubber vulcanization chemistry. He has also attended several research colloquia at MRPRA, attended International Polymer Latex II Conference, and has made presentations of his own research results at a colloquim at MRPRA and at a seminar at MRPRA Golden Jubilee Celebration.

ABSTRACT

The peroxide prevulcanization of NR latex using a range of commercially-available organic peroxides and an inorganic peroxide (potassium peroxydisulphate), in both activated and non-activated systems, has been investigated. A range of reducing agents and compounds that are known to promote peroxide-initiated emulsion polymerization and peroxide curing of polyesters have been evaluated as promoters for the peroxide prevulcanization of NR latex. A few reactive peroxyesters have been found to be effective as prevulcanizing agents at temperatures in the range 80 °C-100 °C. the effectiveness of the prevulcanization systems was characterized by the rate and efficiency of crosslinking achieved by these systems. Fructose-activated peroxyester and fructose-activated hydroperoxide systems were found to effect prevulcanization at temperatures in the range 50 °C-80 °C. There is no clear correlation between the structure/reactivity of peroxyesters and the effectiveness of fructose-activated prevulcanization systems. The relative reactivity of the alkoxy radicals generated by the commercial hydroperoxides partly explains the differences in the effectiveness of various fructose-activated hydroperoxide prevulcanization systems.

The prevulcanization kinetics for the fructose-activated t-butyl peroxyisobutyrate (tBPIB) system have been investigated. The overal rate of tBPIB decomposition in NR latex, in both non-activated and fructose-activated systems was found to be first-order reaction with respect to tBPIB concentration. However, investigation of initial rate of tBPIB decomposition in NR latex indicates that the initial rate of tBPIB decomposition in NR latex is half order with respect to initial tBPIB concentration. This is probably a consequence of induced decomposition of tBPIB by certain non-rubber substances, and termination by recombination of radicals derived from tBPIB. But, the reason for the difference in the reaction order with respect to tBPIB concentration, at the initial stage of the reaction and during the run is not clear. The prevulcanization kinetics also exhibit a number of other peculiar characteristics. Thus at temperatures greater than 70 °C, and using a high fructose concentration, the rate coefficient for crosslink formation tends to be greater than that for peroxide decomposition. This is probably attributed to the differences in the temperature-coefficients of the various competing reactions during peroxide prevulcanization of NR latex. The instantaneous crosslinking efficiency was found to increase linearly with prevulcanization time. At temperatures greater than 70 °C, the instantaneous crosslinking efficiency can attain values greater than 50%, indicating the involvement of alkyl radicals as well as the alkoxy radicals in the crosslinking reaction. The experimental activation energies for peroxide decomposition and crosslink formation were found to decrease to apparently constant values with increasing fructose/peroxide concentration ratio. The rate of tBPIB decomposition was found to be significantly determined by activation free energy and not just activation energy for the decomposition.

The factors which influence the physical properties of films from peroxide-prevulcanized NR latex have been investigated. The crosslink concentration was found to be the most important factor in determining the physical properties of films from peroxide-prevulcanized NR latex. Factors that account for the differences in the physical properties of films from peroxide- and sulphur-prevulcanized latices, and peroxide gum NR vulcanizates have been discussed.

Attempts to improve the ageing properties of films from peroxide-prevulcanized NR latex indicate that a preventive antioxidant is an essential component for an effective antioxidant system for these films.

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LIST OF ABBREVIATIONS AND SYMBOLS

DRC	Dry rubber content
HA	High-ammonia (latex)
NR	Natural rubber
TSC	Total solids content

DCP	Dicumyl peroxide
CHP	Cumene hydroperoxide
dIBMHP	Diisopropyl benzene monohydroperoxide
dMHDHP	Dimethylhexane dihydroperoxide
tBP	Di-t-butyl peroxide
tBHP	t-Butyl hydroperoxide
tBPAC	t-Butyl peroxyacetate
tBPBO	t-Butyl peroxybenzoate
tBPEH	t-Butyl peroxy-2-ethylhexanoate
tBPIB	t-Butyl peroxyisobutyrate
tBPND	t-Butyl peroxyneodecanoate
tBPPV	t-Butyl peroxypivalate
ZDEC	Zinc diethyldithiocarbamate
ZnO	Zinc oxide

E_a, E_{exp}	Arrhenius activation energy or experimental activation energy E_{exp}
E'	Experimental activation energy for peroxide (tBPIB) decomposition
E''	Experimental activation energy for crosslink formation using tBPIB prevulcanizing system
f_∞	Overall crosslinking efficiency for peroxide prevulcanizing system
F_t	Instantaneous crosslinking efficiency for peroxide prevulcanizing system
h	Planck constant
$\Delta H^\ddagger$	Activation energy
$\Delta G^\ddagger$	Activation free energy
k_B	Boltzmann constant
k'	Rate coefficient for peroxide (tBPIB) decomposition
k''	Rate coefficient for crosslink formation
Q	Solvent swelling index, a measure of crosslink concentration
R	Gas constant
$\Delta S^\ddagger$	Activation entropy
$t_{\frac{1}{2}}$	Half-life time
$[X]_{chem}$	Concentration of chemical crosslink
$[X]_{phys}$	Concentration of physically-effective crosslink
χ	Rubber-solvent interaction parameter
v	Volume fraction of rubber
Z	Arrhenius frequency factor

CONTENTS

CHAPTER 1 INTRODUCTION AND REVIEWS OF PREVIOUS WORK

CHAPTER 2 VULCANIZATION OF NR USING ORGANIC PEROXIDES: PROPERTIES AND REACTIONS OF ORGANIC PEROXIDES

CHAPTER 3 CROSSLINK CONCENTRATION OF PEROXIDE VULCANIZATE, PEROXIDE CONCENTRATION IN LATEX AND ANALYSIS OF PREVULCANIZATION KINETICS

CHAPTER 4 MATERIALS AND EXPERIMENTAL METHODS

CHAPTER 5 INVESTIGATIONS OF PEROXIDE PREVULCANIZATION OF NR LATEX

CHAPTER 6 KINETICS OF NR LATEX PREVULCANIZATION USING tBPIB-FRUCTOSE SYSTEM

CHAPTER 7 PROPERTIES OF FILMS FROM PEROXIDE-PREVULCANIZED NR LATEX

CHAPTER 8 CONCLUSION AND SUGGESTIONS FOR FURTHER WORK

CHAPTER 1

INTRODUCTION AND REVIEWS OF PREVIOUS WORK

1.1. Introduction

A prevulcanized latex is defined as one in which the rubber particles are chemically crosslinked so that on drying it gives a vulcanized film. The crosslinking of the rubber in latex can be effected by reaction with sulphur (1-3), sulphur-donors(3), peroxides(4,5) or by radiation treatment(6,7). All commercially produced prevulcanized natural rubber (NR) latex is prepared by reacting with sulphur and one or more accelerators of the dithiocarbamate type, usually zinc diethyl dithiocarbamate (ZDEC). Prevulcanization is carried out by heating the latex containing the vulcanizing agents for typically 3-5 hours at 50-60 C°. In recent years there has been great concern about the possibility of carcinogenic nitrosamines being present in products from conventional sulphur-vulcanized latex(8), and also in the possible presence of secondary amines capable of nitrosation when in contact with traces of nitrous acids or nitrites. The nitrosamine problem is particularly significant for latex products such as baby teats and soothers. Competing silicone rubbers provide a commercial threat to the NR latex products because they are reputed to be free of nitrosamines and nitrosatable amines.

Gorton *et al*(9) have reported some sulphur-accelerator vulcanizing systems for NR latex that meet nitrosamine regulatory limits. However, these vulcanizing systems are generally slower than sulphur-dithiocarbamate systems. In the present investigation, the prevulcanization of NR latex using various commercially-available peroxides is studied. Peroxide-prevulcanized latex films have been found to be free of nitrosamines and nitrosatable amines(9).

1.2 Preliminary considerations concerning selection of peroxides for prevulcanization of NR latex

Braden *et al*.(10) have outlined the characteristics of an ideal peroxide for vulcanizing rubber. The requirements of the ideal peroxide prevulcanizing agent for NR latex are probably less severe than those identified by Braden *et al*. For instance, the problems of scorch and interferences of acidic filler materials and added antioxidants with the crosslinking are generally unimportant. Fillers or antioxidants may be added after the latex has been prevulcanized. The following are the preliminary requirements of an ideal peroxide prevulcanizing agent for NR latex:

1) It must produce reactive free radicals which are able to effect crosslinking.
2) It should not combine with rubber in side reactions and should not tend to react with the non-rubber constituents of the latex.
3) It should be compatible with the latex and preferably be in liquid form at processing temperature. It should not cause latex instability. It must have a great tendency to associate with the latex particles, so that the radicals are not wasted in the aqueous phase.
4) Its ultimate decomposition products should be harmless and preferably water-soluble, so that they can be easily leached out of the prevulcanized latex films.
5) It must be stable and safe to handle at processing temperatures, and be non-toxic and non-irritant.
6) It should be cheap and readily available.

When a peroxide activator or coagent is used, most of the above characteristics of an ideal peroxide vulcanizing agent for NR latex are also required for an ideal activator or coagent. The activator should be effective in promoting peroxide prevulcanization, whilst the coagent should be effective in enhancing crosslinking efficiency. Groot and

Bollen(11) have discussed the major safety aspects of the various processes involved in the crosslinking of polymers by organic peroxides.In the peroxide prevulcanization of NR latex, the possibility of using less thermally-stable peroxides or those that are sensitive to decomposition by contaminants, requires appropriate safety considerations. The structure, composition, temperature reactivity, safety characteristics and toxicological data of the various organic peroxides used in this investigation will be given in Chapter 4. The non-promoted reactivity of peroxide is expressed by its half-life time ($t_{\frac{1}{2}}$), i.e., the time it takes one-half of any quantity of peroxide present to decompose thermally at a given temperature. It can also be expressed as the temperature which gives a particular half-life time value.

1.3 Theory of strength of prevulcanized latex films

The strength properties of dry rubber vulcanizates and their relationship to structure have been described by various authors(12-15). Prevulcanized latex film is formed when the latex particles are brought into contact and immobilized. This process occurs by evaporation of water and gelation of the latex. Gelation is a uniform destabilization of the latex which results in the formation of a three-dimensional aggregate of rubber particles termed a 'gel'. Gelation can be effected by using acids, salts and heat-sensitizing agents(16). For NR latex, it is probably that gelation also occurs even in film-forming processes which appear to involve only drying(17). The strength and coherence of prevulcanized latex films are governed by the forces that hold the rubber particles together. Loh(18) has reviewed various theories that account for the strength of prevulcanized latex films. These theories have been developed based on data generated from sulphur-prevulcanized latices and latex films. In this investigation, attempts will be made to ascertain if the strength properties of peroxide-prevulcanized latex films accord with these theories.

The theories in which the strength of prevulcanized latex films is attributed to the formation of inter-particle primary valence bonds(19), or to the adsorbed layer of proteins and other non-rubbers on the particles functioning as a cement holding the particles together(20), have been disproved by Humphreys and Wake(21). The theory formulated by van Dalfsen(22) that the strength and coherence of prevulcanized latex films are a consequences of secondary valence bonds between the rubber molecules has been widely accepted. The secondary valence bonds are also known as van der Waals forces. Although these forces between two molecules are known to be weak, the sum of the van der Waals forces between two rubber particles can be appreciable because of high number of rubber molecules in a rubber particle. For a rubber particle of diameter 1μm which contains rubber of number-average molecular weight 300,000, the number of rubber molecules in the particle is approximately 10^6.

Blackley(23) has given a diagramatic illustration of the secondary-valence-bond theory for a pair of latex particles as shown in Figure 1.1 for latex particles from unvulcanized and vulcanized latices. When the latex is dried down, the rubber particles cohere together to give regions of overlap between the particles. In these regions of overlap, secondary valence bonds between the rubber molecules of different particles are formed. Merrill(24) has interpreted the stress-strain behaviour of unvulcanized and prevulcanized latex films, as shown in Figure 1.2, in terms of this theory. The initial flat region is associated with rearrangement of the rubber molecules independently of each other. The steep rise in stress on further extension of the prevulcanized latex film is due to the molecules in any given particle being no longer able to move independently of each other because they are attached to a large number of other molecules by means of crosslinks. Merrill(24) argued that the tensile strength of prevulcanized latex film will be the stress per unit area necessary to overcome at the same time the secondary valence bonds which have formed

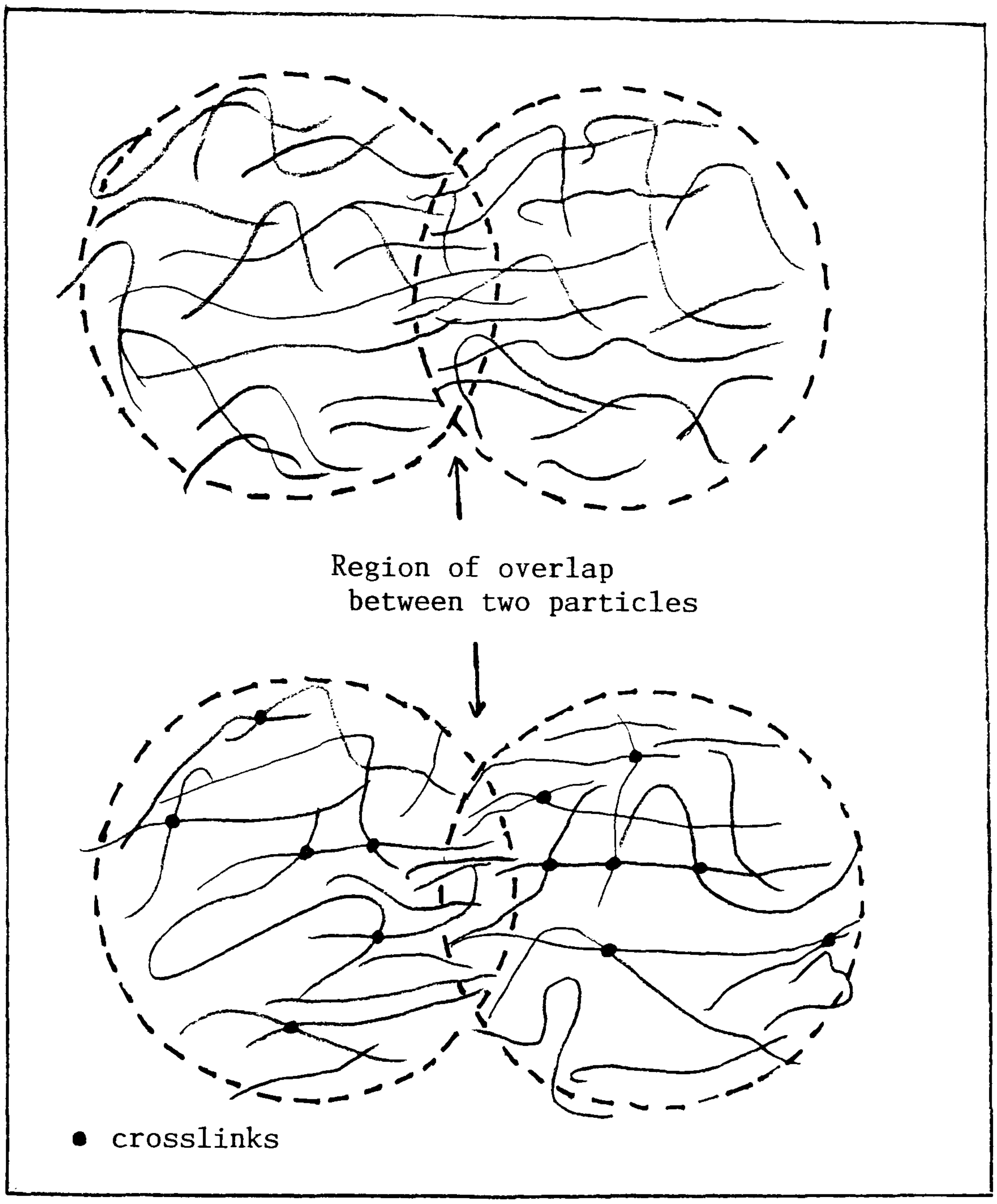


Figure 1.1. Schematic representation of the secondary valence bond theory showing rubber particles in films obtained from unvulcanized and prevulcanized latices (23).

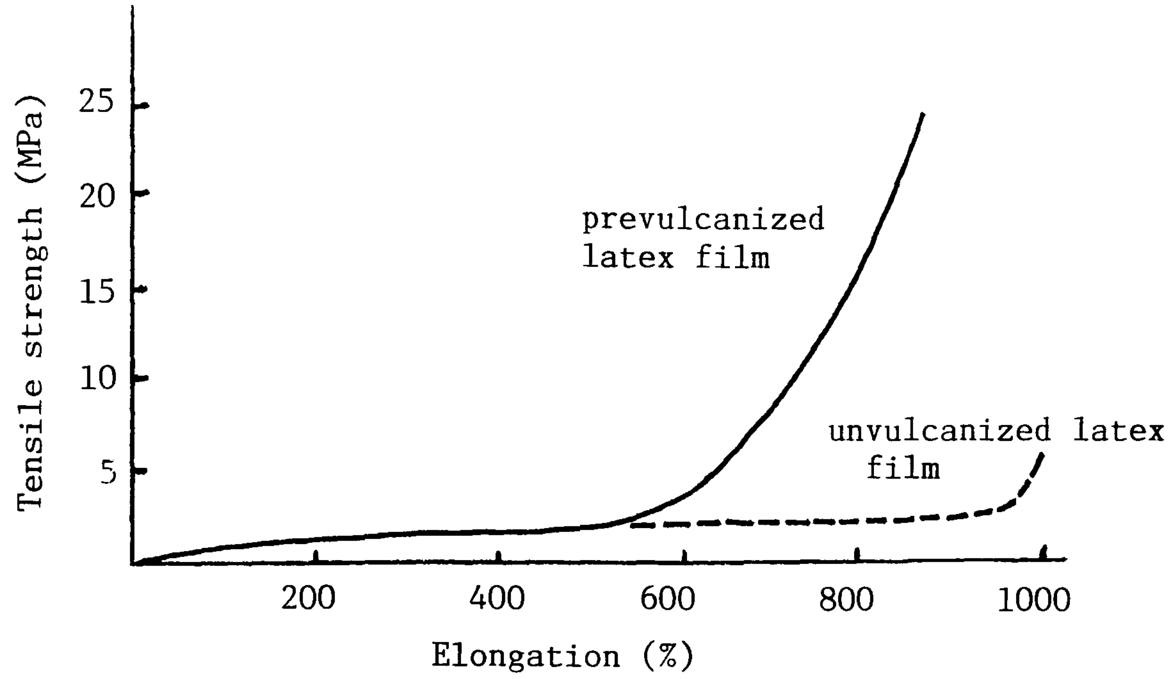


Figure 1.2. Stress-strain behaviour of unvulcanized and sulphur-prevulcanized latex films (24).

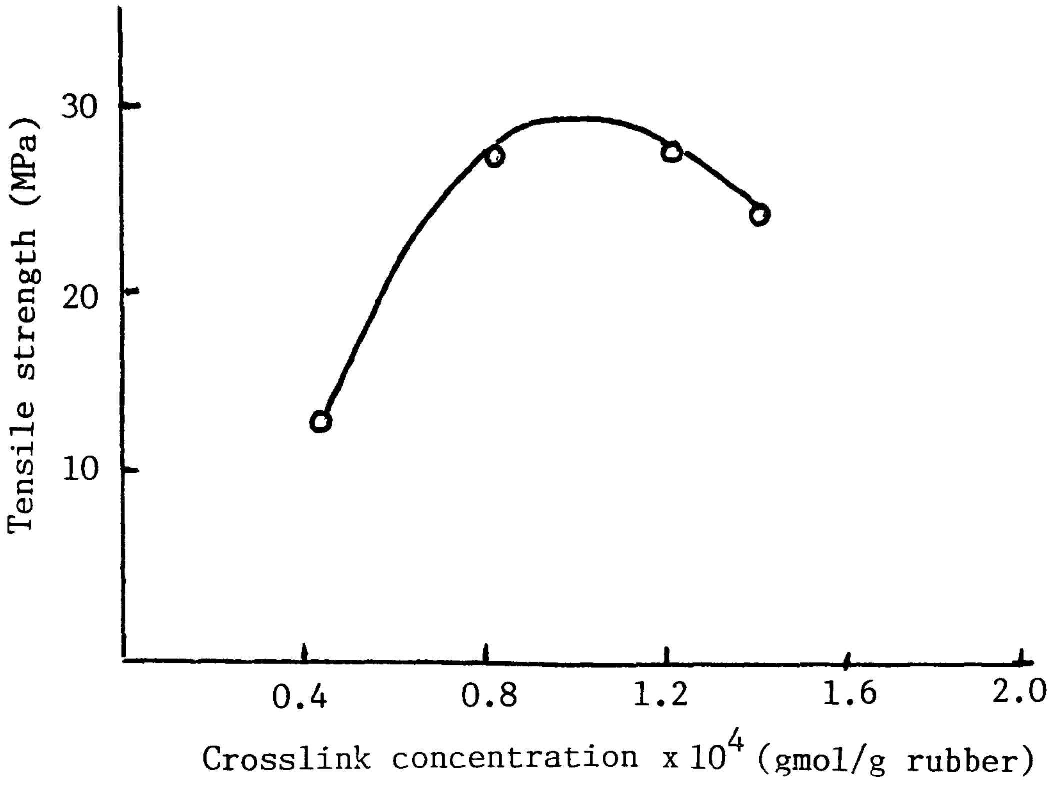


Figure 1.3. Relationship between tensile strength and crosslink concentration of sulphur-prevulcanized latex film (24).

between a large number of molecules. But the presence of crosslinks will also favour strain-crystalization of the rubber, which additionally contributes to its stiffness.

The variation of tensile strength of prevulcanized latex film with crosslink concentration, as shown in Figure 1.3, can also be explained in term of the secondary valence theory. The initial increase of tensile strength is due to crosslink insertion. Further increase of crosslink concentration will restrict the mobility of the chains and hence reduce the number of chain-ends which contribute to the secondary valence forces between neighbouring particles, and consequently the tensile strength is reduced.

According to Hu *et al*(25), the strength of prevulcanized latex film is attributed to van der Walls forces between rubber particles as well as to the formation of a crosslinked structure between the particles. The crosslinked structure is formed by the redistribution of crosslinked structures already existing within the particles, during film or gel formation. However, it can be argued that such a crosslinked structure could also be formed by post-vulcanization involving residual curatives. Hu *et al*. claimed that the redistribution of the crosslinked structure is possible because of the mobility of the molecular chain segments in the prevulcanized latex particles; this deduction was made from NMR half-line width data for prevulcanized latex(26). The NMR half-line width data also indicate that the level of molecular motion in radiation-prevulcanized latex is significantly lower than in sulphur-prevulcanized latex. This is because the carbon-carbon crosslinks in radiation-prevulcanized latex are less flexible than are the polysulphidic crosslinks in sulphur-prevulcanized latex. There are other observations that support the theory of Hu *et al*. on the strength of prevulcanized latex films. If the strength of prevulcanized latex film is solely a consequence of van der Waals forces between rubber particles, then the tensile strength of the film should be independent of factors such as combined sulphur and crosslink concentration. This is generally the case, as is demonstrated by the results of Humphreys and Wake(21) shown in Figure 1.4. However the results of Hu at el.(25) shown in Figure 1.5 indicate a definite relationship between the properties of dried film and the combined sulphur and crosslink concentration. Hu et al.(25) also found that the stress-relaxation behaviour of prevulcanized and post-vulcanized latex films is similar, thus indicating similarity in the structure of these films. The tensile strength maximum for sulphur-prevulcanized latex film obtained by these workers occurs at a much higher crosslink concentration than that obtained by Merril(24), i.e., at a crosslink concentration similar to that for post-vulcanized latex films or for dry rubber sulphur-vulcanizates(13). The redistribution of crosslinked structure between rubber particles is illustrated in Figure 1.6.

1.4 NR latex and latex concentrates

NR latex is obtained from the Hevea brasiliensis tree by tapping. It comprises a dispersion of particles of a hydrocarbon polymer, cis-1:4-polyisoprene, in an aqueous medium which contains various non-rubber substances. This latex is normally called 'field latex'; it contains on average 33 per cent by weight of rubber. The non-rubber substances may have an effect on prevulcanization using peroxides. They have been found to affect prevulcanization using the sulphur-dithiocarbamate vulcanizing systems(18,27). Preservation of NR latex is necessary in order to avoid coagulation and putrefaction as a result of bacterial attack. Bacterial attack on carbohydrates and sugars present in NR latex leads to the formation of volatile fatty acids that tend to destabilixe the latex. Ammonia is an effective(28) and widely-used preservative for NR latex. The composition of ammonia-preserved NR latex changes after storage. The lutoids, Frey-Wyssling particles and other particulate phase dissolve in the serum. The latex becomes a two-phase system, comprising rubber particles and serum

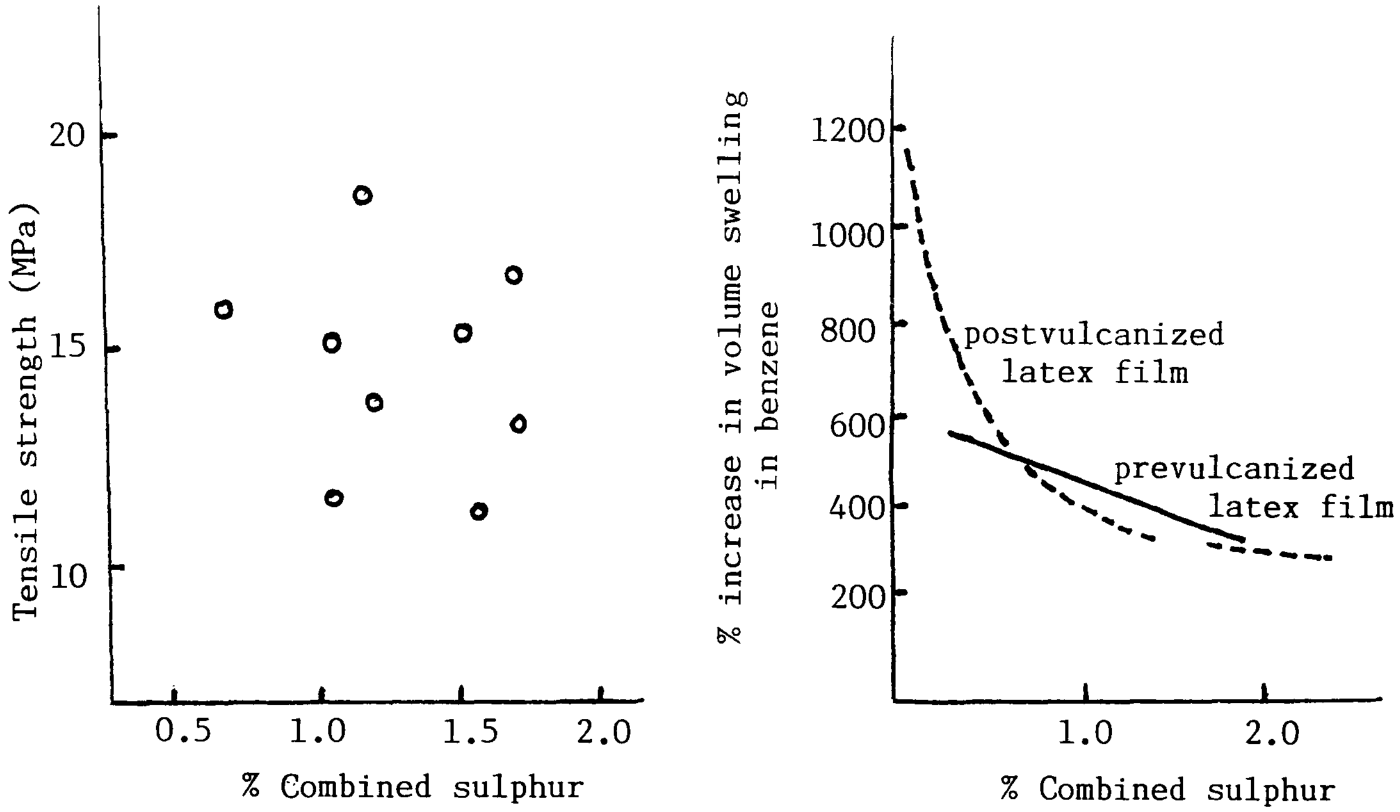


Figure 1.4. Results showing that tensile strength and crosslink density of sulphur-prevulcanized latex film are independent of combined sulphur concentration (21).

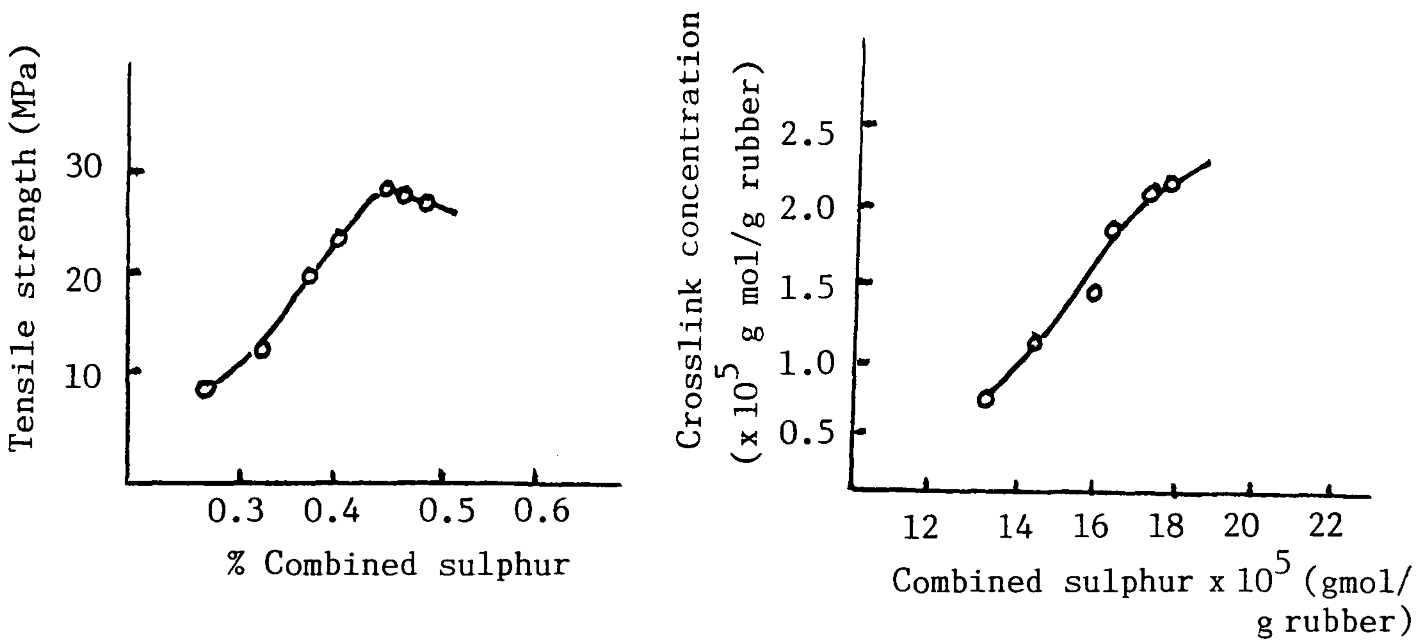
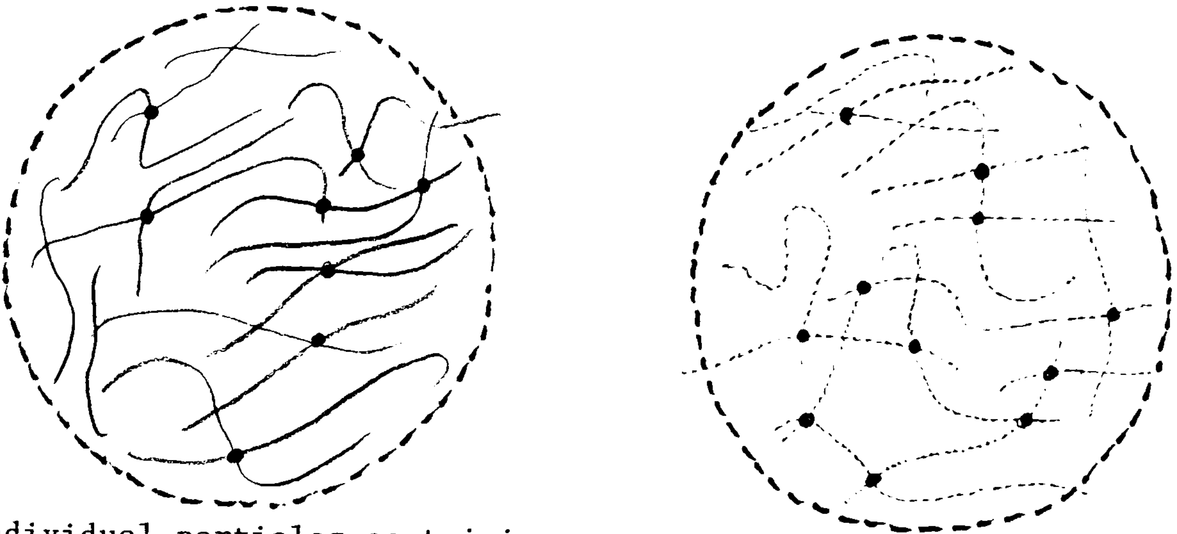
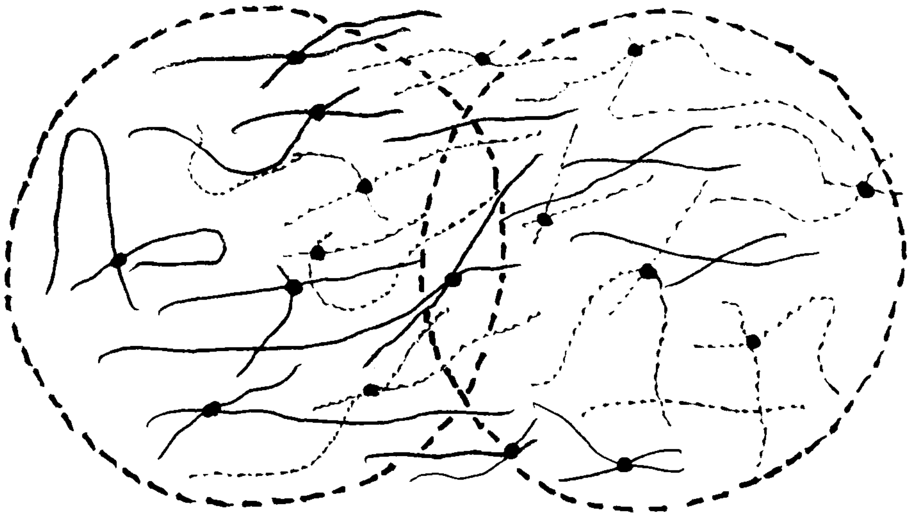


Figure 1.5. Results of Hu et al. (25) showing the relationship between tensile strength and crosslink concentration, and combined sulphur concentration of prevulcanized latex film.



Individual particles containing crosslinked structures in prevulcanized latex



Redistribution of crosslinked structure between particles during film or gel formation

Figure 1.6. Schematic representation (18) of the theory of redistribution of crosslinked structure between particles during film formation.

only. The concentrations of some of the non-rubber substances tend to fall; ammonia promotes hydrolysis of proteins to polypeptides and amino acids, and hydrolysis of phospholipids to glycerol, fatty acid anions, phosphate anions and organic bases. Table 1.1 summarises the composition of freshly-tapped and ammoniated NR latex(29).

It is necessary to concentrate field latex because of the economic advantage of transporting latex concentrates rather than field latices. Most important processes for the fabrication of latex articles utilize high-solid latex concentrate of 60 per cent minimum rubber content. Latex concentrates tend to be more uniform in quality than do field latices. NR latex concentrate is prepared by centrifugation, evaporation and creaming. The centrifugation method is used for some 95 per cent of the total production of NR latex concentrate(17). Different types of preservatives are used to preserve NR latex concentrates(30). Table 1.2 shows the various types of latex concentrates and their preservative systems. Centrifuged HA latex concentrate accounts for some 66 per cent of the total market share for NR latex concentrate(17). In the present investigation, centrifuged HA latex concentrate was used in order to minimize complications from possible effects of secondary preservatives or other preservative systems upon the peroxide prevulcanization of NR latex.

The composition of HA latex concentrate is likely to be different from that of ammoniated field latex. The precise composition of NR latex concentrates has not been established yet. Table 1.3 shows the overall composition and properties of a typical commercial HA latex concentrate (31,32). Some of the properties of latex concentrate are directly related to the nature of the non-rubber substances. For instance, the potassium hydroxide (KOH) number gives the total anions concentration in the latex.

The average diameter of the rubber particle in NR latex varies between 0.25μm and 0.8μm. The molecular weight

Table 1.1. The constituents of hevea latex (29)

- **FRESH LATEX**
  D.R.C. 37%
  T.S. 40·5%
  - **RUBBER PHASE**
    - Protein
      N × 6·3 = 0·5
    - Lipids
      0·9
      - Fats & waxes
      - Phospholipids
        0·6
        - Lecithins
          0·48
        - Kephalins
          0·02
        - Metal phosphatidates
          0·10
      - Sterols & sterol esters
    - Metals
      - Ca
      - Mg
      - Cu
  - **FREY WYSSLING PARTICLES**
    - Lipids
    - Carotenoids
  - **SERUM**
    - Inositols
      - Meso-inositol
      - Quebrachitol
        1·0–1·9
    - Carbohydrates
      - Glucose
      - Galactose
      - Fructose
    - Proteins
      0·5
      - Basic protein
      - Hevein
      - α-Globulin
      - Enzymes
    - Glutathione
      0·01
    - Free amino acids
      0·08
      - Alanine, Tyrosine
      - Glutamic acid, Glycine
      - Leucines, Cysteine
      - Phenylalanine, Valine
      - Cystine
      - Proline
    - Organic acids
    - Nitrogenous bases
      0·04
      - Methylamine
      - Stachydrine
      - Trigonelline
      - Tetramethylenediamine
      - Pentamethylenediamine
      - Alkaloids
    - Nucleic acids
      0·004
    - Pyrophosphate nucleosides 0·0003
      - Adenosine pyrophosphates
      - Cytidine pyrophosphates
      - Uridine pyrophosphates
    - Inorganic anions
      - CO_3
      - PO_4
    - Metals
      - K
      - Mg
      - Cu
      - Fe
      - Na
      - Ca
      - Rb
  - **BOTTOM FRACTION**
    - Soluble protein
      0·2
      - Basic protein
      - Hevein
      - Other proteins
      - Enzymes
    - Phospholipids
    - Miscellaneous nitrogen compounds
      0·2
      - Nucleic acid
      - Nucleotides
      - Insoluble protein
      - Other N compounds
    - Rubber
    - Metals
      - K
      - Mg
      - Rb
      - Cu
    - Carotenoids

Compounds existing only in combination as more complex substances

- Reducing sugar
- Inositol
- Glycerol
- Phosphoric acid
- Choline
- Ethanolamine
- Fatty acids
  - Palmitic
  - Stearic
  - Arachidic
  - Linoleic
  - Oleic
- Potassium

(From Nucleic acid and Nucleotides:)

- Guanine
- Adenine
- Cytosine
- Uracil
- Ribose
- Phosphate

- **NORMAL AMMONIATED LATEX**
  0·7% NH_3
  - **RUBBER**
    - Protein
      0·25
    - Lipids
      - Fats & waxes
        0.17
      - Phospholipids
      - Sterols & sterol esters
    - Higher fatty acids
      0·36
    - Nitrogenous bases
    - Metals
    - Carotenoids
  - **SERUM**
    - Choline
      0·06
    - Quebrachitol
    - Free phosphate
      0·01
    - Glycerophosphate
      0·04
    - Fatty acids
      0·4
      - Higher fatty acids
        0·4
        - Palmitic
        - Stearic
        - Arachidic
        - Linoleic
        - Oleic
      - Volatile fatty acids
        0·02
        - Acetic
        - Formic
        - Propionic
    - Nitrogenous bases
      0·04
    - Other organic acids
      - Oxalic
      - Tartaric
      - Citric
      - Malic
      - Malonic
      - Succinic
      - Fumaric
      - Oxaloacetic
      - Glyoxylic
      - Pyruvic
      - α-Ketoglutaric
    - Proteins
      0·25
      - Basic protein
      - α-Globulin
    - Free amino acids
      0·14
      - Alanine, Aspartic acid
      - Arginine, Histidine
      - Cystine, Glutamic acid
      - Dihydroxyphenylalanine
      - Glycine, Hydroxyproline
      - Leucines, Methionine
      - Lysine, Phenylalanine
      - Ornithine, Proline
      - Tryptophan, Valine
      - Tyrosine, Cysteine
    - Polypeptides
    - Metals
  - **SLUDGE**
    - $MgNH_4PO_4$
    - Sterol glycosides

The figures under a component indicate its approximate concentration in gm/100 gm latex.

Table 1.2. Types of NR latex concentrates (30)

Type of latex concentrate	Preservatives*
centrifuged & creamed concentrate min. 60% d.r.c.	
high ammonia (HA)	0.7% ammonia
low ammonia-tetramethylthiuram disulphide/zinc oxide (LA-TZ)	0.2% ammonia + 0.013% TMTD + 0.013% ZnO + 0.05% lauric acid
low ammonia-Santobrite (LA-SPP)	0.2% ammonia + 0.2% sodium pentachlorophenate
low ammonia-boric acid (LA-BA)	0.2% ammonia + 0.24% boric acid + 0.05% lauric acid
low ammonia-zinc diethyl dithiocarbamate (LA-ZDC)	0.2% ammonia + 0.1% ZDC + 0.05% lauric acid
evaporated concentrate	
high solids (min. 72% TSC)	250 m-equiv. KOH + soap
low solids (about 68% TSC)	250 m-equiv. KOH + soap
high ammonia (about 62% TSC)	0.7% ammonia

*Preservatives are added based on weight/weight of latex.

Table 1.3. Overall composition and typical properties of centrifuged HA latex concentrate (32)

composition (% by weight on latex)	
rubber	59.67
protein, etc[a]	1.06
soaps[b]	0.23
salts	0.40
ammonia	0.68
water	37.96
properties	
total solids content (%)	61.31
dry rubber content (%)	59.69
alkalinity, as NH_3 (%)[c]	0.68
pH	10.65
volatile fatty acid number, VFA	0.07
potassium hydroxide number, KOH	0.63
mechanical stability time, MST (s)	1,168
zinc oxide-mechanical stability test, ZST (s)	223
viscosity (MPa.s)[d]	77
nitrogen (% of total solids)	0.29
potassium (% of total solids)	0.19
phosphorous (ppm of total solids)	394
magnesium (ppm of total solids)	38

a Includes carbohydrates, amino acids and sugars .

b Calculated as ammonium stearate .

c Per cent by weight on latex.

d Brookfield LVT Viscometer, 60rpm, 25° C.

of the rubber is in the region of one million. The rubber contains an insoluble (gel) fraction, the content of which increases steadily to a maximum value as the latex is stored. The increase of gel content with storage time is presumably caused by a process similar to the 'storage hardening' which occurs in dry rubber(33). However, it occurs more rapidly in latex than in dry rubber. The particle of ammonia-preserved latex concentrate possesses an adsorbed layer of proteins, lipids and fatty-acid soaps. The fatty-acid soaps are formed by the hydrolysis of lipids. The hydrolysis of lipids is often assumed to be complete in mature latex concentrate, but some indirect evidence suggests that neutral lipids(34) and phospholipids(33,36) may still be present. The surface proteins have never been identified, and they are often presumed to be similar to those which have been identified in the serum(29,37). The cation present in HA latex concentrate is predominantly ammonium ions, and about 10-20 per cent of the ammonium ions are associated with the adsorbed anions(32).

The major constituents of the non-rubber substances in the serum from latex concentrates are proteins and their decomposition products, fatty-acid soaps, and a range of organic and inorganic salts. The proteins in mature latex concentrate serum have not been identified specifically, but are presumed to be the same as those which have been identified in fresh latex serum. The amounts of fatty-acid soaps in the serum are presumed to be small, since they are surface-active and would be expected to be adsorbed at the particle surface. The salts in HA latex concentrate serum have been analysed(32) and 13 anions have been identified as shown in Table 1.4. The concentration of the specific anion may vary from batch to batch of latex concentrate, but the total anion concentration was found to be relatively constant. The predominant cation present in the serum is ammonium, although the serum also contains significant amounts of potassium. Potassium and other trace metals, such as magnesium and copper, are associated with both the rubber particles and the serum. The serum of fresh field

Table 1.4. Average anion concentrations found in mature HA latex concentrate sera (32)

anion	concentration (m moles/100g rubber)
carbonate	22.25
acetate	12.81
malate	9.28
succinate	5.45
citrate	5.04
formate	4.67
α- glycerophosphate	2.81
glucose-phosphate	2.24
phosphate	2.01
oxalate	1.16
chloride	1.10
sulphate	0.58
hydroxide	0.51

latex contains a significant concentrations of carbohydrate and sugars. The compositions of the various carbohydrates and sugars in HA latex concentrate serum have not been established.

1.5 Reviews of previous work on peroxide-prevulcanization of NR latex

There is a dearth of information concerning the use of organic peroxides for the prevulcanization of NR latex, despite the commercial availability of several organic peroxides for over 60 years. In 1927, dibenzoyl peroxide was commercially produced. Before the end of World War II, dilauryl peroxide, t-butyl peroxybenzoate, acetyl peroxide and cyclohexanone peroxides were available commercially(38). There are now about 40 organic peroxides that are commercially available. The publications of Kunisawa and Okikura(39), Philpott(40,41) and Gazeley(5,42) in the early 1960s describe the last-known investigations of the peroxide-prevulcanization of NR latex. There were probably a number of reasons for the apparent lack of interest in the investigation of the peroxide-prevulcanization of NR latex:

1) the high-temperature prevulcanizations used in earlier work appeared to be technically unsatisfactory, e.g., because of formation of a high coagulum content and the poor physical properties of the prevulcanized latex films obtained;
2) inferior physical properties of peroxide-prevulcanized latex films compared to sulphur-prevulcanized latex films;
3) lack of awareness of the nitrosamine problem associated with latex products vulcanized using conventional sulphur systems, which would have encouraged teh development of other prevulcanizing systems; and
4) intensive and sustained research effort since the 1960s in the field of radiation prevulcanization

of NR latex as an alternative process to other non-sulphur prevulcanization processes.

In the earlier period (1930-1960) of peroxide-prevulcanization studies, prevulcanization was carried out using non-activated peroxide-prevulcanizing systems at temperatures mostly above 100 °C. However, the information given in the various patents generally does not contain the essential details pertaining to the prevulcanization process and the physical/performance characteristics of the final product. The earliest reported work on the peroxide prevulcanization of NR latex was by Stevens(4) using benzoyl peroxide at 95 °C. The physical properties of the products from this prevulcanized latex were apparently poorer than those of products obtained from latex prevulcanized with sym-trinitrobenzene(4). Films from the latter latex have tensile strengths of about 13 MPa. Hercules Powder Company (43) used a range of aryl and alkyl peroxides and hydroperoxides to vulcanize NR latex. The latex was vulcanized at temperatures above 100 °C under superatmospheric pressure. High-temperature prevulcanization of NR latex using hydroperoxides and dialkyl peroxide has also been carried out by other workers(44-46). The following examples illustrate some of the best results for the properties of films from prevulcanized latex obtained using different peroxide prevulcanizing systems.

1)(44) NR latex concentrate was prevulcanized using 1 pphr t-butyl hydroperoxide at 150 °C for 1 hour. The hydroperoxide was employed as an emulsion, prepared <u>in situ</u> using potassium hydroxide and oleic acid. The physical properties of the prevulcanized latex film were:

	modulus at 300% (MPa)	tensile strength (MPa)	elongation at break (%)
unvulcanized	0.48	13.0	1270
prevulcanized	0.90	19.1	970

2)(30) NR latex concentrate was prevulcanized as in the previous example, but using 0.75 pphr bis (α,α- dimethyl-benzyl) peroxide. The physical properties of the prevulcanized latex film were:

modulus at 300% (MPa)	0.89
tensile strength (MPa)	16.3
elongation at break (%)	865

3)(46) NR latex concentrate was diluted to 50% DRC and prevulcanized using 1 pphr di-t-butyl peroxide in a sealed vessel at 170 °C for 6 minutes. The physical properties of the prevulcanized latex film before and after ageing in a Geer oven at 70 °C were:

	elongation at break (%)	tensile strength (MPa)
unaged film	745	16.5
aged 14 days	757	19.6
aged 29 days	756	18.7

The results show that the physical properties of the films were unaffected by heat ageing in air.

Bloomfield(47) used a hydroperoxide-tetraethylene pentamine initiator system to polymerize vinyl monomers in NR latex at temperatures below 80 °C. This above initiator system was found to cause hardening of the rubber in the absence of the monomers. Kunisawa and Okikura(39), of the Foundation of NR Development (FNRD), Japan, utilized the hydroperoxide-tetraethylene pentamine system to vulcanize NR latex. The effects of certain reaction variables (surfactant concentration, prevulcanization time and temperature, hydroperoxide and tetraethylene pentamine concentration) upon the properties of prevulcanized latex (viscosity, mechanical stability, wet-gel strength), the degree of crosslinking and the physical properties of the prevulcanized latex film were studied(48). Figure 1.7 shows that the mechanical stability and wet-gel strength of peroxide-prevulcanized latex decrease, whilst its viscosity increases, with increasing amount of nonionic surfactant. The surfactant is used to disperse the peroxide in the latex. Figure 1.8 shows that, for maximum tensile strength and modulus of the prevulcanized latex films, the optimum amount of nonionic surfactant to be used is 10-25 per cent of the hydroperoxide. Figure 1.9 shows that the rate of crosslinking increases with increasing temperature. Figure 1.10 shows that the tensile strength of prevulcanized latex film is enhanced after the film is heated for 2 hours at 90 °C. The properties of film obtained from latex prevulcanized using 0.5 pphr t-butyl hydroperoxide and 0.5 pphr tetraethylene pentamine at 60 °C for 8 hours, before and after ageing, were(49):

	modulus at 300% (MPa)	tensile strength (MPa)	elongation at break (%)
unaged film	1.47	24.0	1040
aged, 100 °C for 48 hrs in air	1.18	12.0	905

Modification of peroxide-prevulcanized latex by compounding, graft polymerizing or blending with another polymer latex produce NR latex adhesives which are suitable for the treatment of fabrics(50). The modified latices were generally found to have higher bonding strength than sulphur-compounded NR latex or carboxylated styrene-butadiene latices(50). Philpott(40,41) and Gazeley(5,42) have investigated various activated peroxide prevulcanizing systems using hydroperoxides, peroxyesters and ketone peroxides, and activators such as fructose, tetraethylene pentamine, hydroxylamine hydrochloride and hydrazing hydrate, were found to be relatively effective (fast and efficient crosslinking) systems at 50-60 °C. Hydroxylamine hydrochloride was found to be an effective activator for room-temperature

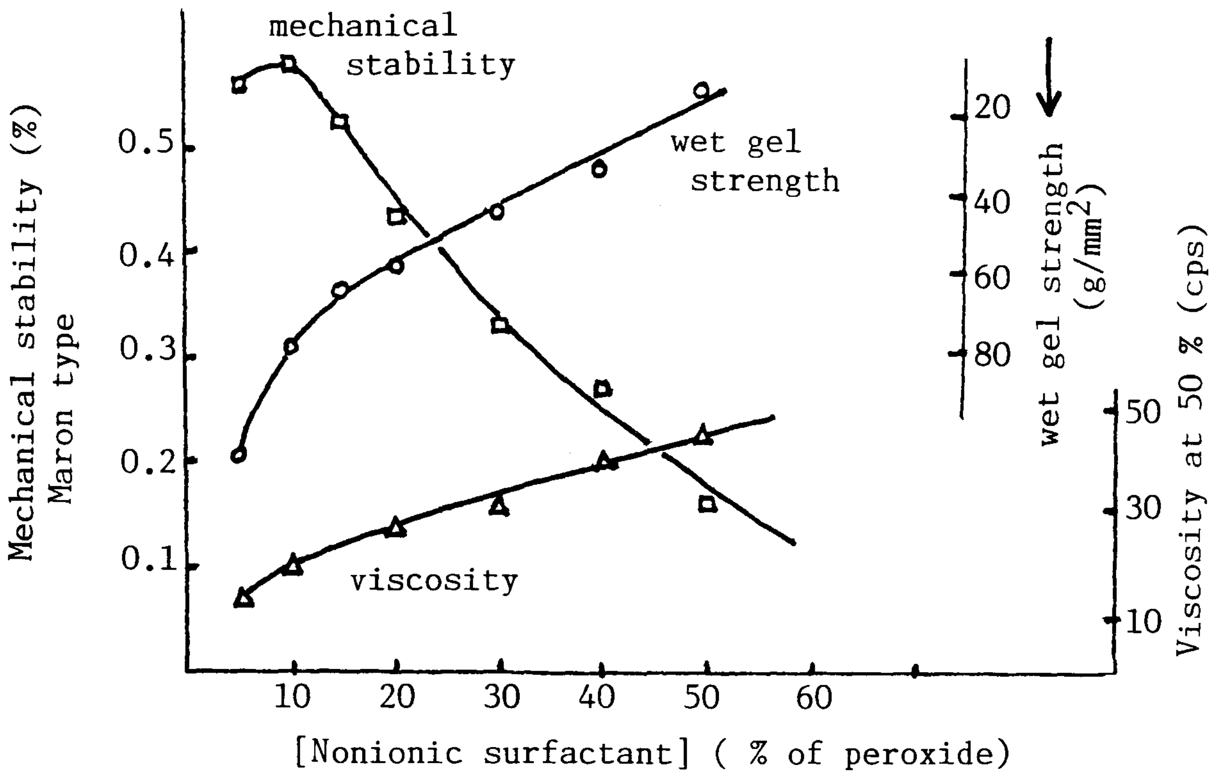


Figure 1.7. Effect of nonionic surfactant concentration on properties of peroxide prevulcanized latex (48).
Prevulcanization using 0.5 phr t-butyl hydroperoxide (tBHP) and 0.5 phr tetraethylene pentamine (TEP) for 18 hr at 60°C.

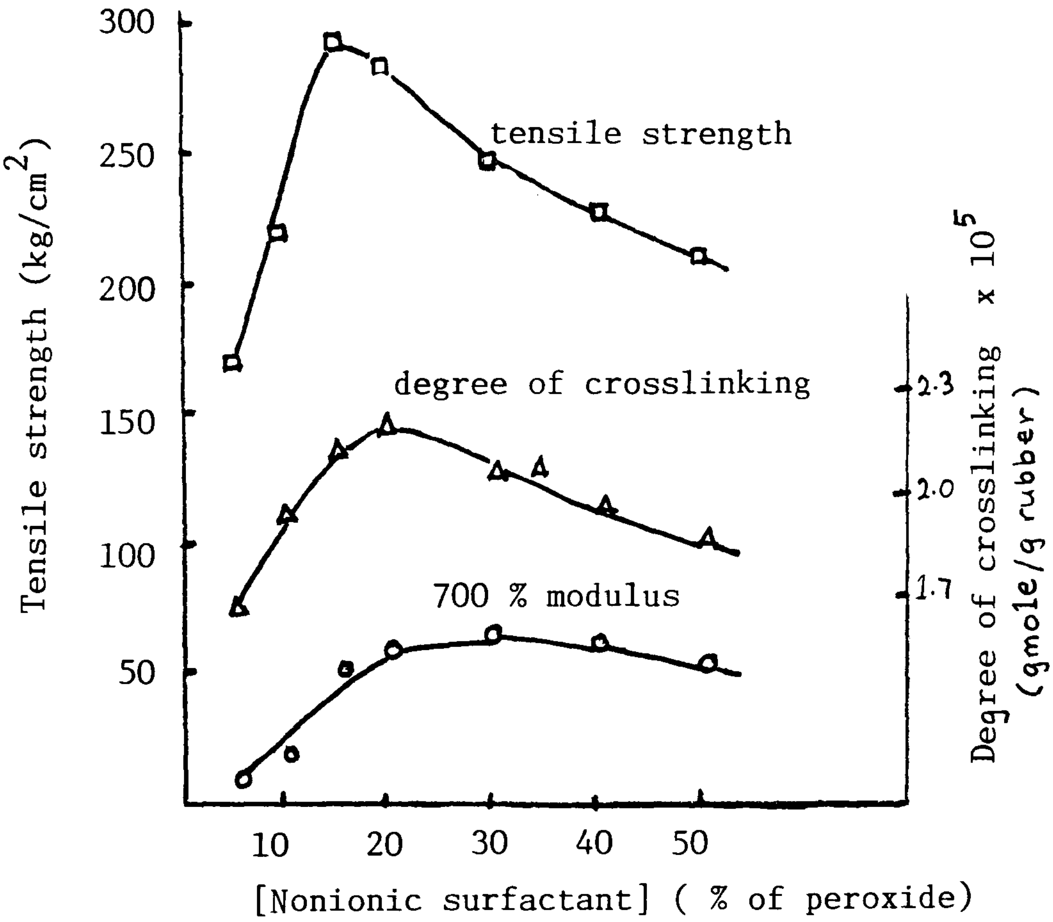


Figure 1.8. Effect of nonionic surfactant concentration on properties of prevulcanized latex film (48).
Prevulcanization using 0.5 phr tBHP and 0.5 phr TEP for 18 hr at 60 °C, dried film heated for 2 hr at 90 °C.

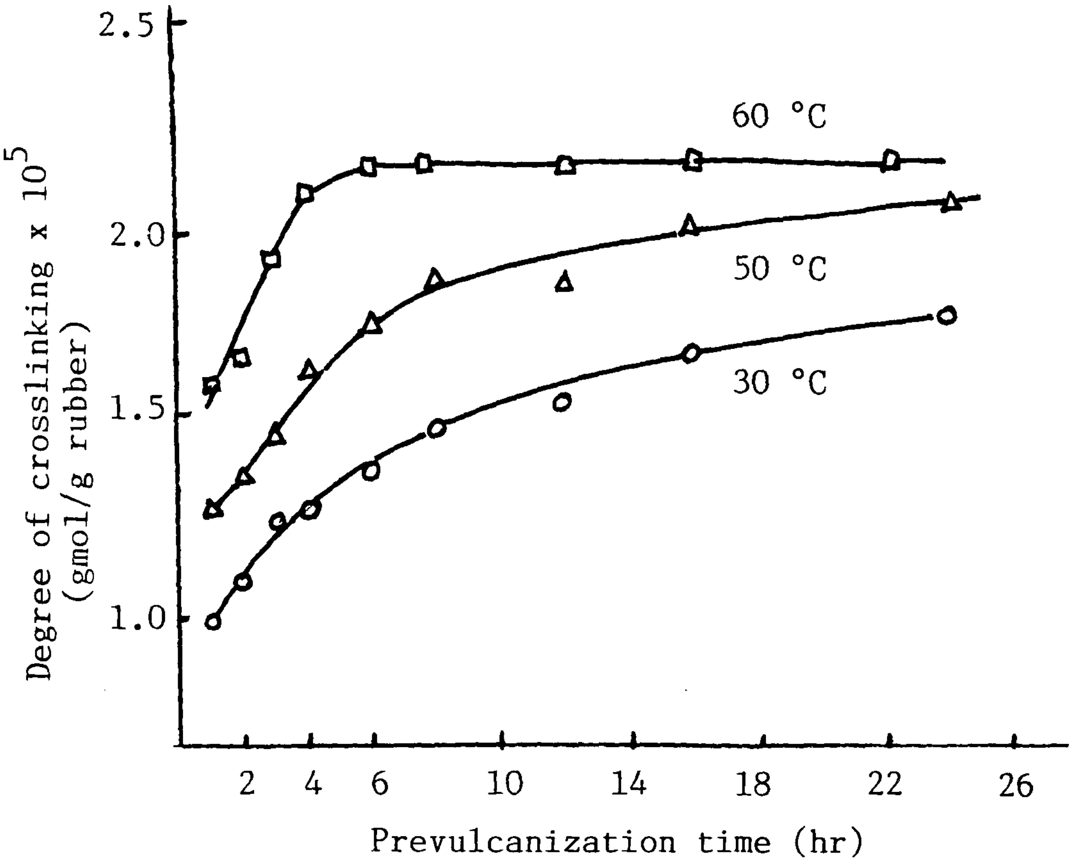


Figure 1.9. Effect of temperature on prevulcanization (48).
Prevulcanization using 0.5 phr tBHP and 0.5 phr TEP, and nonionic surfactant at 15 % of peroxide.

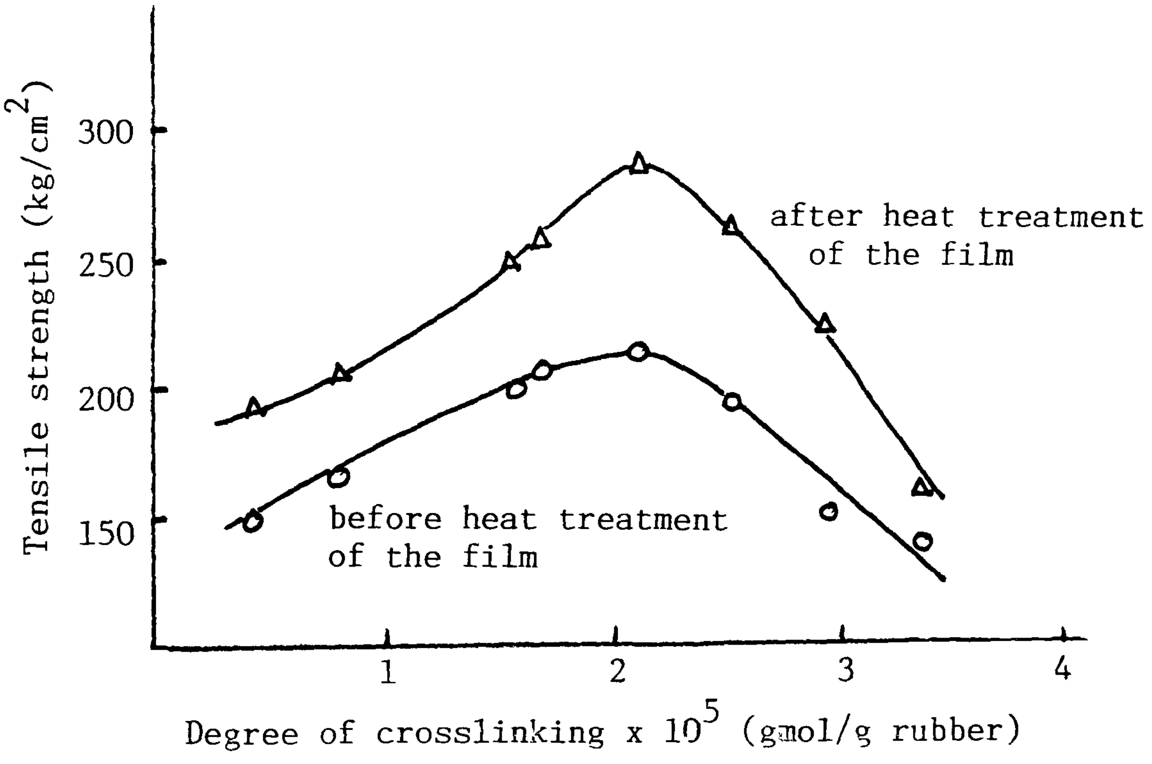


Figure 1.10. Effect of heating (for 2 hours at 90 °C) of peroxide prevulcanized latex films on tensile strength properties (48).

prevulcanization using hydroperoxides. However, the use of hydroxylamine hydrochloride badly affects the colloid stability of prevulcanized latex. Prevulcanization of synthetic cis-1:4-polyisoprene latex using hydroperoxide/hydroxylamine system was found to be less efficient than that of NR latex(28). This is presumably because of the difference in the non-rubber substances present in these two types of latices. Philpott(40) prevulcanized NR latex using the t-butyl hydroperoxide/tetraethylene pentamine system in the presence of polyfunctional monomers such as diallylphthalate, diallylsebacate, triallylphosphate, triallylcitrate and triallylcyanurate(40). However, the presence of these monomers did not result in increase in crosslink concentration or improvement in the physical properties of the prevulcanized latex film. Gazeley(5,42) found that the physical properties of peroxide-prevulcanized latex films are improved by leaching the films. This is presumably a consequence of removal of extractable non-rubber substances which enhances the cohesion of latex particles. The oven-ageing properties of peroxide-prevulcanized latex films were found to be poor, whilst the sterilization resistance was found to be quite good. The results of a sterilization test(5) (heating in steam at 120 °C for 6 periods of twenty minutes each with a 20-minute interval between each sterilization) on peroxide-prevulcanized latex film are shown below:

	modulus at 300% (MPa)	tensile strength (MPa)
before test	1.57	24.2 (21*)
after test	1.18	17.9 (14*)

* B.S. 1803 requirements for surgeons gloves

Rodaway and Calvert(51) claim a patent in which latex is prevulcanized using a system comprising hydrogen peroxide and an organic compound which yields a per-acid or per-salt by reaction with hydrogen peroxide. Such a system is currently being used to epoxidize NR latex(52,53). However the epoxide groups can be utilized for crosslinking by reaction with dithiols, dibasic acid, diamines and acid anhydrides(54). Calvert(55) used di-t-butyl peroxide to vulcanize NR latex films and foams. The vulcanized foam rubber was claimed to exhibit an outstanding retention of tensile strength upon ageing. The vulcanized rubber films were found to be more transparent, both before and after ageing, than are conventional sulphur-vulcanized rubber films.

The vulcanization of dry NR using a peroxide (benzoyl peroxide) was first reported by Ostromislensky(56). Braden *et al*.(10,57) have investigated various peroxide crosslinking agents for NR. The mechanical strength of peroxide gum vulcanizate is poor, but this can be improved by incorporating reinforcing carbon black in the unvulcanized mix. Dicumyl peroxide is the most widely-used peroxide for crosslinking NR, because of its high crosslinking efficiency. Furthermore, its efficiency is generally unaffected by reinforcing carbon blacks(57).

1.6 Aims of present investigation

In the previous published work on the peroxide prevulcanization of NR latex, the investigations were limited to a few organic peroxides that were commercially available at that time. An increased number of reactive peroxides is now commercially available. New peroxide prevulcanizing systems that are more efficient, and that can yield prevulcanized latex films having better properties than those previously obtained, could possibly be obtained. Previous workers have been generally aimed at producing peroxide-prevulcanized latex and determining the physical-technical properties of vulcanizates obtained from it. No detailed investigations have been carried out on the kinetics of peroxide prevulcanization and the effects of reaction variables upon either the prevulcanization reaction or the properties of films obtained from the prevulcanized latex.

CHAPTER 2

VULCANIZATION OF NR USING ORGANIC PEROXIDES: PROPERTIES AND REACTIONS OF ORGANIC PEROXIDES

2.1 Introduction

The mechanism of peroxide prevulcanization of NR latex is not understood. However it is likely that the actual crosslinking of the polyisoprene molecules within the rubber particles occurs by reactions which are similar to those by which the peroxide vulcanization of dry rubber occurs(58,59). This chapter briefly describes the chemistry and kinetics of peroxide vulcanization of dry NR. The peroxide prevulcanization of NR latex also involves the diffusion of peroxide molecules or radicals from the aqueous phase to the rubber phase. When an activated peroxide prevulcanizing system is used, there are also the possibility of peroxide-activator interactions in both the aqueous and the rubber phases. The diffusion rates of peroxide-activator complex and of the peroxide molecule may differ. The non-rubber substances in NR latex may affect the vulcanization of NR latex by peroxides.

Although there are some 40 organic peroxides available commercially, only the 10 most stable - those that also yield the most active free radicals - are being used for crosslinking of polymers(60). These are; 2,5-dimethyl-2,5-di(t-butyl peroxy) hexyne-3, di-t-butyl peroxide, 2,5-dimethyl-2,5-di(t-butyl peroxy) hexane, bis(t-butyl peroxy isopropyl) benzene, t-butyl cumyl peroxide, dicumyl peroxide, 4,4-di-t-butyl peroxy n-butyl valerate, 1,1-di-t-butyl peroxy-3,3,5-trimethyl cyclohexane, dibenzoyl peroxide, t-butyl peroxy benzoate and bis(2,4-dichloro benzoyl) peroxide. Dicumyl peroxide is generally used for crosslinking of dry NR and blends of NR and synthetic polymers.

There are a great number of reactions that could be effected by peroxides and the free radicals derived from them.

The aims of the present investigation were therefore:

1) to evaluate the effectiveness of a range of commercially available organic peroxides and an inorganic peroxide (potassium peroxydisulphate) in vulcanizing NR latex;
2) to evaluate the effectiveness of activators in promoting the decomposition of peroxide in NR latex;
3) to evaluate the effectiveness of activated peroxide prevulcanizing systems;
4) to study the effect of reaction variables (peroxide and activator concentrations, prevulcanization time and temperature, peroxide coagents, non-rubber substances) on the rate and efficiency of prevulcanization;
5) to seek correlations between the effectiveness of peroxide prevulcanizing systems and the structures of peroxides and activators;
6) to investigate in greater detail the kinetics of the peroxide prevulcanization of NR latex using the most efficient of the prevulcanizing system obtained;
7) to evaluate the properties of peroxide-prevulcanized latex films, and to ascertain some of the factors which influence these properties.

The potassium peroxydisulphate system provided an example of a water-soluble inorganic peroxidic prevulcanization system. Kinetics study would yield information on the rate of crosslinking, the rate of disappearance of peroxide, reaction orders, activation parameters and crosslinking efficiency. An attempt has been made to interpret the results of the investigation in the light of relevant current theories, particularly those pertaining to colloid science and to the peroxide vulcanization of NR.

The nature of these reactions depends upon the nature of the peroxides and free radicals, the substrates, reaction environments and reaction conditions. In the peroxide prevulcanization of NR latex, reactions of peroxides and free radicals with the constituents of NR latex may occur to varying degrees. The efficiency of prevulcanization will depend upon the efficiencies of free radical generation and of utilization of these radicals in crosslinking reactions. The efficiency of free radical generation will depend upon factors that influence homolytic or heterolytic reactions of peroxides. The efficiency of free radical utilization will depend upon:

1) factors that determine the tendency for peroxide decomposition to occur in the rubber phase or aqueous phase; and
2) the nature of the free radicals, is determining the tendency for the radical to abstract hydrogen from polyisoprene and to participate in other reactions.

Reactions of peroxides are difficult to classify mechanistically. Some may start as polar reactions but end as free radical ones. The treatise cited in Reference 61-63 gives detailed information concerning the various reactions of peroxides and free radicals. This chapter briefly describes the structure-reactivity relationships of peroxides, the decomposition mechanism and products. The reactions and properties of some free radicals will also be described.

2.2 Chemistry of vulcanization of NR by organic peroxides

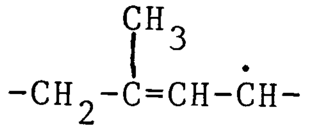
Alkoxy radicals, RO·, are produced by O-O cleavage of a peroxide molecule, ROOR (Reaction 2.1). Such a process can be brought about by thermal or assisted-thermal decomposition of the peroxide. Reactive alkoxy radicals or other reactive free radicals that could be formed by subsequent rearrangement or decomposition of the alkoxy radicals can abstract hydrogen from polymer molecules, PH, yielding polymeric radicals, P· (Reaction 2.2). A crosslink is formed when two polymeric radicals combine (Reaction 2.3).

$$RO\vdots OR \xrightarrow{\text{heat}} 2RO\cdot \qquad (2.1)$$

$$PH + RO\cdot \xrightarrow[\text{fast}]{} P\cdot + ROH \qquad (2.2)$$

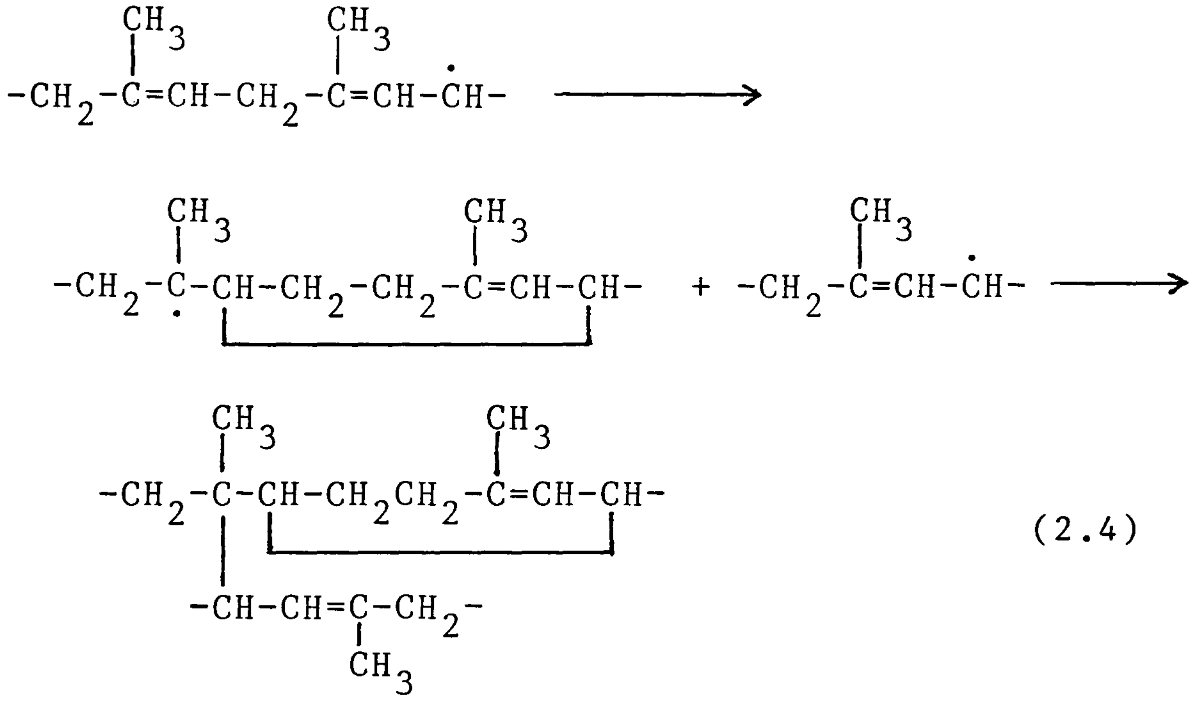
$$2P\cdot \xrightarrow[\text{fast}]{} P\text{-}P \qquad (2.3)$$

In the case of NR, the α-methylenic hydrogen atom is the most easily abstracted. Consequently the following polyisoprenyl radical should be the most abundant of those produced by Reaction 2.2.



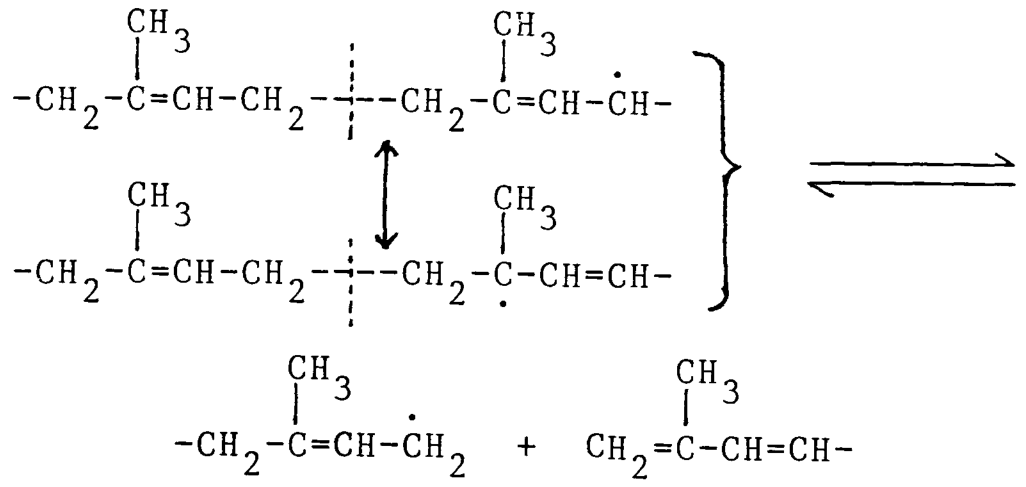
$$-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\dot{C}H-$$

Polyisoprenyl radicals tend to cyclize (Reaction 2.4). However the predominant fate of these radicals is combination(59):



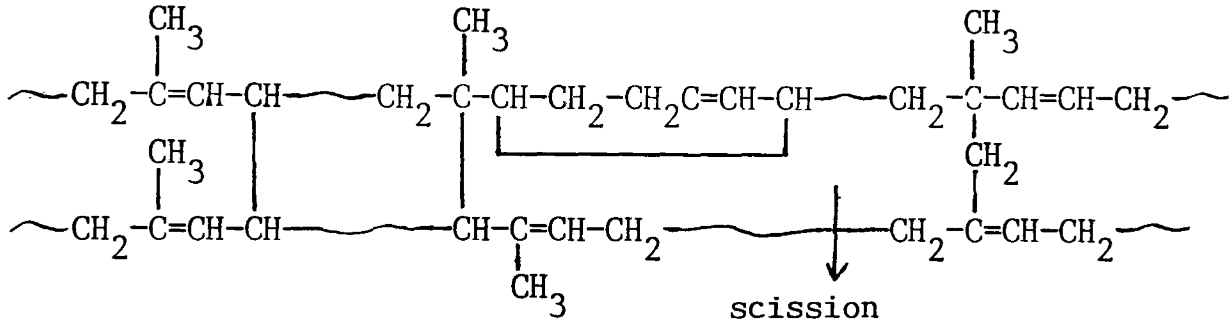
(2.4)

Scission of the polyisoprene backnone (Reaction 2.5) occurs to a small extent during the peroxide vulcanization of NR(46):

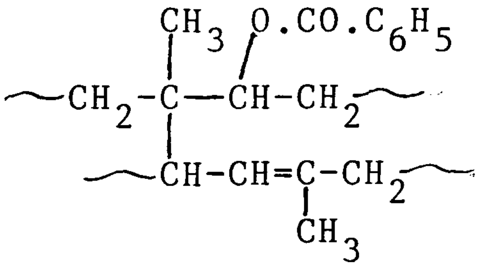


(2.5)

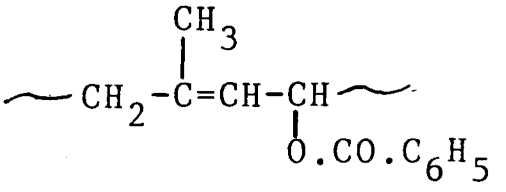
The overall NR network resulting from vulcanization by peroxides such as di-t-butyl peroxide and dicumyl peroxide can be represented as:



The use of dibenzoyl peroxide or an alkyl peroxybenzoate produces a different type of NR network as a result of the benzoyloxy group becoming attached to the main chain(46) either at the site of the crosslink;



or at isolated points in the chain;



$$\sim CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-\underset{\displaystyle O.CO.C_6H_5}{\underset{|}{CH}}\sim$$

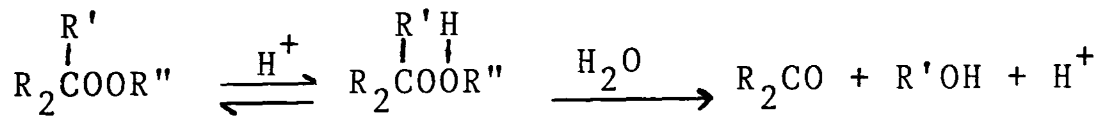
Farmer and Moore(64) deduced, that in the reactions between t-butyl hydroperoxide and simple olefins, some part of the hydrogen abstraction is accomplished by the hydroxyl radicals. However, most of the dehydrogenation is attributed to the t-butoxy radicals. Most of the hydroxyl radicals are apparently used in oxygenation of the olefin, principally in converting olefin radicals into olefinic alcohols:

$$R\cdot + \cdot OH \longrightarrow ROH \qquad (2.6)$$

NR vulcanization by t-butyl hydroperoxide has not been investigated, partly because the volatility of this hydroperoxide results in losses during mixing, and partly because this hydroperoxide is less compatible with the rubber than peroxides such as dicumyl peroxide.

The amount of extra-network material in peroxide vulcanizates is very small. When di-t-butyl and dicumyl peroxides are used, the extra-network material comprises mainly the undecomposed peroxide and the derived alcohol, and minor amount of acetone or acetophenone derived from the decomposition of t-butoxy or cumyloxy radicals respectively. When dibenzoyl peroxide is used, the extra-network material is mainly benzoic acid.

Besides cyclization of polymeric radicals and chain scission of polymer back-bone, there are also other possible side reactions which may occur during the peroxide vulcanization of NR. The presence of acid may catalyze ionic decomposition of peroxide by a mechanism such as



$$R_2\overset{R'}{\overset{|}{C}}OOR'' \overset{H^+}{\rightleftharpoons} R_2\overset{R'}{\overset{|}{C}}\overset{H}{\overset{|}{O}}OR'' \xrightarrow{H_2O} R_2CO + R'OH + H^+$$

(2.7)

This occurs quite readily in the case of hydroperoxides and diacyl peroxides. In the presence of oxygen, the generated polymer radicals may react with molecular oxygen to yield hydroperoxides, which in turn may lead to oxidative degradation (see Chapter 7). Free radical inhibitors, such as natural antioxidants or added antioxidants, interfere with the crosslinking reaction.

2.3 Peroxide coagents

Coagents are multifunctionally unsaturated molecules that can be added to a rubber compound in order to increase the crosslinking efficiency of the peroxide(65). Their usage also enhances some of the vulcanizate properties(62). The coagents are built into the polymer network by copolymerization, and although, their mode of action is not fully understood, they lead to the formation of C-C crosslinks(65). The following are commonly used as coagents for the peroxide crosslinking of rubbers(65): triallyl cyanurate, triallyl isocyanurate, trimethylolpropane trimethacrylate, ethyleneglycol dimethacrylate, and diallyl terepthalate. In NR vulcanization, it has been found that the incorporation of trimethylolpropane trimethacrylate necessitates a decrease in peroxide concentration if vulcanizates of constant modulus are to be obtained(67).

2.4 Kinetics of peroxide vulcanization of NR

As indicated by the Reactions 2.1-2.3, the slowest, and therefore the rate-determining, of the whole crosslinking reaction sequence is the peroxide-decomposition step. All subsequent steps are much faster. The decomposition of peroxide is kinetically a first-order reaction, i.e., the rate of decomposition at a given temperature is directly proportional to the first power of peroxide concentration. Since the decomposition step is the rate-determining step, the rate of crosslink formation will apparently be first-order in peroxide concentration. Lorenz and Scheele(68) found that, in the vulcanization of NR by benzoyl peroxide, the peroxide concentration decreases according to a reaction of the first-order, but with higher initial peroxide concentration (above the solubility limit of the peroxide in NR), the reaction is of zero-order. Hummel et al.(69) observed that, in the vulcanization of NR by dicumyl peroxide, the rate of decrease of peroxide concentration and the rate of crosslink formation are of first-order reactions. Under certain reaction conditions, particularly at higher temperatures, the rate coefficients for peroxide decomposition and crosslink formation are not equal, as shown in Table 2.1. Hummel and Scheele(70) put foward two conditions under whch these two rate coefficients will be equal: the crosslinking efficiency must be constant throughout the entire reaction, and the intermediate reactions must be so fast that the concentration of their products is very small.

In the kinetic studies of the vulcanization of NR by sulphur/accelerator systems, several workers(71-73) recognized the importance of taking degradation or reversion reaction into account when determining the rate coefficient for crosslink formation. An accurate determination of the maximum degree of crosslinking in cases, where reversion absent is important, because it can decide not only the value of the rate coefficient for crosslink formation but also the reaction order(73). Thomas(74) found that the crosslinking efficiency (number of crosslinks formed per peroxide molecule decomposed) for dicumyl peroxide in purified NR is about 100% and is generally independent of vulcanization temperature and time, as shown in Table 2.2. Van Der Hoff(75,76) found that the crosslinking efficiency of dicumyl peroxide in purified NR and synthetic cis-1:4-polyisoprene is greater than 100%. Van Der Hoff attributed the slightly lower crosslinking efficiency obtained by Thomas(74) to the effect of oxygen when the samples were vulcanized in the press. Crosslinking efficiencies of greater than 100% can be explained by higher values (greater than zero)(75) of the kinetic chain length, the latter being defined as the number of propagation or transfer steps per radical from its generation to its termination. However no reaction mechanism was put foward by Van Der Hoff to account for the kinetic chain length of about 0.5 in the peroxide

Table 2.1. Rate constants of dicumyl peroxide decomposition (k') and crosslink formation (k") in peroxide vulcanization of NR (69)

Vulcanization temp. (°C)	$k' \times 10^3$ (min^{-1})	$k'' \times 10^3$ (min^{-1})
120	1.16	1.14
125	1.75	1.96
130	3.32	4.01
135	6.30	7.04
140	10.6	11.8
145	17.4	20.0
150	30.2	31.5

Table 2.2. Variation of crosslinking efficiency with vulcanization temperature and time of dicumyl peroxide in purified NR (74)

Temperature (°C)	Crosslinking efficiency (%)	Vulcanization time (min) at 140 °C	Crosslinking efficiency (%)
110	95	50	96
120	95	65	102
125	92	98	94
130	102	120	98
135	98	144	97

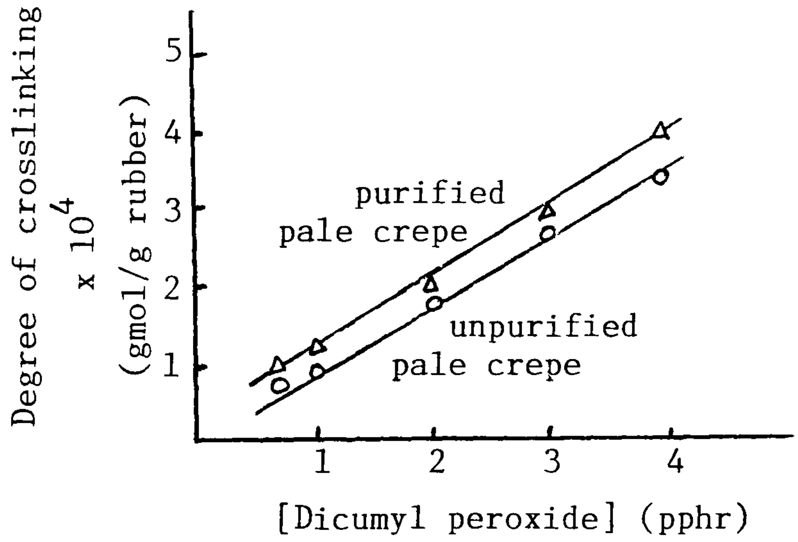


Figure 2.1. Dicumyl peroxide vulcanization of NR(75). NR cured for 8 hours at 145 °C, and NR purified by acetone extraction for 48 hours.

crosslinking of NR. Van Der Hoff(75) found that the use of unpurified NR resulted in a lower degree of crosslinking than when purified NR was used, as shown in Figure 2.1. This difference was attributed to reaction between impurities, such as the natural antioxidants, and polymeric radicals or peroxyradicals. The difference in crosslink concentration between purified and unpurified NR is independent of the peroxide concentration. This implies that a constant amount of peroxide,equivalent to the amount of impurities, is unavailable for crosslinking reactions.

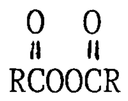
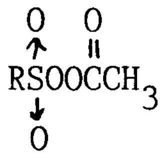
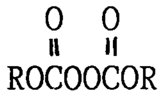
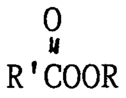
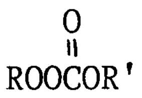
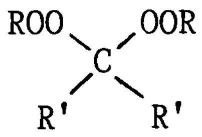
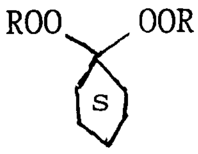
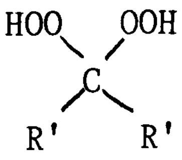
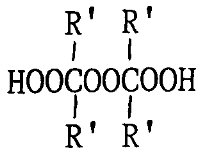
2.5 Organic peroxides: their structures, activities and non-promoted decomposition

There are nine major different organic peroxide types which are produced commercially for the polymer and resin industries. The chemical structures of the different types of peroxides, and the ranges over which they have useful activity when decomposition is not promoted are shown in Table 2.3. Certain types of organic peroxides, such as the diacyl peroxides and peroxyesters, show a wide variation in temperature activity depending upon the structure of the R groups. Other peroxide types, such as the peroxydicarbonates, monoperoxycarbonates, diperoxyketals and dialkyl peroxides, show a moderate variation. The sulfonyl peroxides are low-temperature peroxides used exclusively as initiators for polymerizing vinyl chloride. They were not used inthe present investigation, and therefore will not be discussed further. The hydroperoxides generally show the highest temperature ranges for useful non-promoted decomposition.

Structural differences that affect the activity of peroxides fall under three main headings:

a) relative stability of the radicals formed; the more stable the radical(s) formed, the less stable is the peroxide;
b) steric factors, e.g., highly strained peroxides

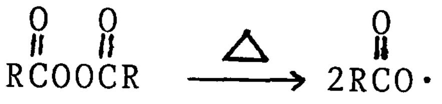
Table 2.3. Commercial peroxide classification

Peroxide type	Structural formula	10 hour $t_{\frac{1}{2}}$ range, °C
diacyl peroxides	 $R\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}R$	20-75
acetyl alkyl-sulfonyl peroxides	 $R\overset{O}{\overset{\uparrow}{\underset{\underset{O}{\downarrow}}{S}}}OO\overset{O}{\overset{\|}{C}}CH_3$	32-42
dialkyl peroxy dicarbonates	 $RO\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}OR$	49-51
tert-alkyl peroxyesters	 $R'\overset{O}{\overset{\|}{C}}OOR$	49-107
tert-alkyl peroxy monocarbonates	 $ROO\overset{O}{\overset{\|}{C}}OR'$	90-100
di-(tert-alkyl) peroxyketals	 cyclic structure such as; 	92-115
di-tert-alkyl peroxides	ROOR	117-133
tert-alkyl hydroperoxides	ROOH	113-172
ketone peroxides	 +  $HOO\overset{R'}{\overset{\mid}{\underset{\underset{R'}{\mid}}{C}}}OO\overset{R'}{\overset{\mid}{\underset{\underset{R'}{\mid}}{C}}}OOH$ + other structures	-

will be less stable, since decomposition relieves steric strain; and

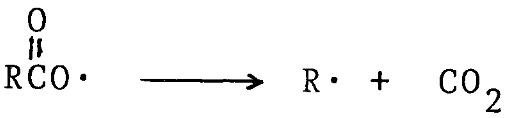
c) electronic effects where electon donating functions destabilize and electron withdrawing functions stabilize peroxides.

The activity of diacyl peroxides can be best correlated with the relative stability of the radicals generated. The O-O bond breaking of diacyl peroxide would produce two acyloxy radicals:



$$R\overset{O}{\overset{\|}{C}}O O\overset{O}{\overset{\|}{C}}R \xrightarrow{\Delta} 2R\overset{O}{\overset{\|}{C}}O\cdot \qquad (2.8)$$

Acyloxy radicals can undergo decarboxylation:



$$R\overset{O}{\overset{\|}{C}}O\cdot \longrightarrow R\cdot + CO_2 \qquad (2.9)$$

The decarboxylation rate depends primarily upon three factors:

a) temperature,
b) pressure and
c) the relative stability of the R· radical formed.

Higher temperature, lower pressure and higher stability of the radical R· promote fast decarboxylation. The relative stability of the R· radicals can be correlated to the hydrogen bond dissociation energies of the parent compounds, as shown in Table 2.4. The higher the bond dissociation energy, the less stable (more reactive) is the corresponding radical formed by removing the hydrogen atom. With the exception of acetoxy and benzoyloxy radicals, the decarboxylation of acyloxy radicals is extremely fast at all temperatures, and may occur simultaneously with the breaking of the peroxy bond. However, a relatively fast decarboxylation of acetoxy and benzoyloxy radicals would occur if they are not quickly scavenged.

Table 2.4. Hydrogen bond dissociation energies of various types of hydrocarbon (77)

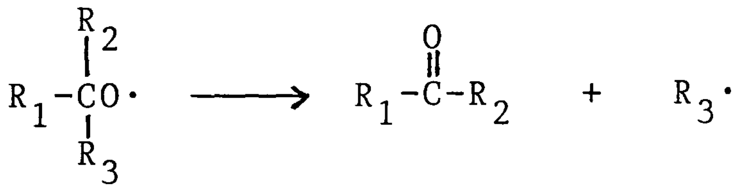
Hydrocarbon	Bond energy (kcal/mole)
$(R)_3C$ —H	91
$(R)_2CH$—H	95
RCH_2—H	98
CH_3—H	104
C_6H_5—H	112

Peroxyesters are another class of peroxides that can form acyloxy radicals upon cleavage of the peroxy bond:

$$R\overset{\overset{O}{\|}}{C}OOR' \longrightarrow R\overset{\overset{O}{\|}}{C}O\cdot \quad + \quad \cdot OR' \tag{2.10}$$

For the same R' group, the stability of the radical formed on decarboxylation of the acyloxy radical correlates with the activity of the peroxyester. The more stable the radical R•, the less stable is the peroxyester. Electronic effects are important for peroxyesters and also for diacyl peroxides. Electron-donating substituents, e.g., CH_3-, CH_3O, destabilize, and electron-withdrawing substituents, e.g., CF_3, NO_2, F, stabilize these peroxides.

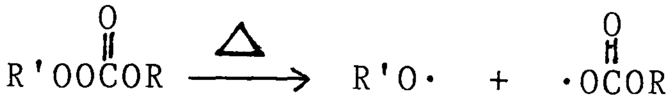
Peroxyesters also generate an alkoxy radical (R'O•) upon cleavage of the peroxy bond. All commercial peroxyesters generate tertiary-alkoxy radicals. The nature of the tertiary R' group plays an important role in determining the activity of the peroxyesters, and also the reactivity of the alkoxy radical. The tertiary-butyl peroxyesters are the most stable, followed by the tertiary-amyl, tertiary-octyl and tertiary-cumyl peroxyesters that are derived from the same carboxylic acid. Alkoxy radicals may undergo a subsequent reaction known as β-scission.



$$R_1-\underset{\underset{R_3}{|}}{\overset{\overset{R_2}{|}}{C}}O\cdot \longrightarrow R_1-\overset{\overset{O}{\|}}{C}-R_2 \quad + \quad R_3\cdot \tag{2.11}$$

In this reaction, the R_3 group that splits off is the group that forms the most stable radical. β-scission is temperature-dependent, i.e., more scission occurs if the alkoxy radical is generated at higher temperatures.

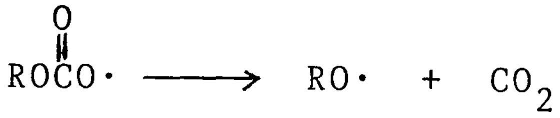
Peroxymonocarbonates are another class of peroxides that generate alkoxy radicals:



$$\mathrm{R'OO\overset{O}{\overset{\|}{C}}OR} \xrightarrow{\Delta} \mathrm{R'O\cdot} + \mathrm{\cdot O\overset{O}{\overset{\|}{C}}OR}$$

(2.12)

The other radical generated is an alkoxycarbonyloxy radical which can undergo decarboxylation to form another alkoxy radical:



$$\mathrm{RO\overset{O}{\overset{\|}{C}}O\cdot} \longrightarrow \mathrm{RO\cdot} + \mathrm{CO_2}$$

(2.13)

It is the nature of the R' group, and not that of the R group which determine the activity of the monoperoxycarbonates. The relationship between R' and peroxide activity follows the same pattern discussed above for peroxyesters.

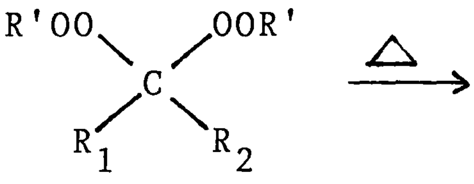
Peroxydicarbonates also generate alkoxycarbonyloxy radicals:

$$\mathrm{RO\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}OR} \xrightarrow{\Delta} \mathrm{2RO\overset{O}{\overset{\|}{C}}O\cdot}$$

(2.14)

In the commercial peroxymonocarbonate and peroxydicarbonates, the R groups are secondary alkyl groups. The decomposition of the alkoxycarbonyloxy radicals will generate secondary alkoxy radicals.

Diperoxyketals also generate alkoxy radicals:



$\xrightarrow{\Delta}$ 2R'O· plus other fragments including $R_1\cdot$, $R_2\cdot$, and CO_2

(2.15)

The nature of R' and also R_1 and R_2 play a role in the activity of diperoxyketals. With the same R_1 and R_2 groups, the effect of the R' group on non-cyclic diperoxyketals follows the same pattern as discussed for peroxyesters.

Cyclic diperoxyketals have higher thermal stabilities than do non-cyclic ones. With diperoxyketals, the stability of the radicals generated does not correlate too well with activity.

Dialkyl peroxides generate two alkoxy radicals upon cleavage of the peroxy bond:

$$ROOR' \xrightarrow{\Delta} RO\cdot + \cdot OR' \qquad (2.16)$$

The activity of dialkyl peroxide is affected by the nature of the R and R' groups and correlates to some extent with their electron-donating or withdrawing ability, i.e., electron-donating groups tend to decrease the stability of these peroxides.

Hydroperoxides generate alkoxy and hydroxyl radicals upon cleavage of the peroxy bond:

$$ROOH \xrightarrow{\Delta} RO\cdot + \cdot OH \qquad (2.17)$$

The activity of hydroperoxides depends upon the nature of R, which follows the same pattern as that of dialkyl peroxides.

Potassium peroxydisulphate is an inorganic peroxide which was used in the present investigation. It is a powerful oxidizing agent in aqueous solution. The aqueous decomposition of peroxydisulphate may proceed by radical-forming process which is independent of pH, and a polar reaction which is acid-catalyzed(78). The radical-forming reaction produces sulphate-ion radicals:

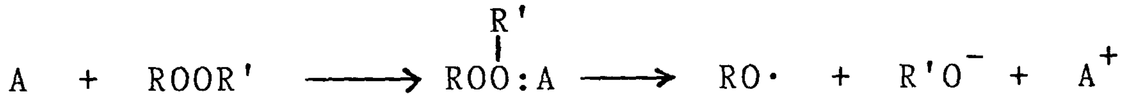
$$S_2O_8^{-2} \xrightarrow{\Delta} 2SO_4\cdot \qquad (2.18)$$

2.6 Induced homolytic decomposition of peroxides

The decomposition of peroxides described in the previous section is by unimolecular homolysis. Homolytic decomposition of peroxides can be induced by substances, A, which transfer one electron to the peroxide. The substance A is a reducing agent. This type of reaction is called assisted homolytic. It is also known as a redox reaction. Hydroperoxides have greater tendency to undergo assisted homolysis than do dialkyl peroxides and diacyl peroxides. Assisted homolytic reaction of peroxide yields a radical and a negative ion:

$$A + ROOR' \longrightarrow A^{+} + RO\cdot + R'O^{-} \qquad (2.19)$$

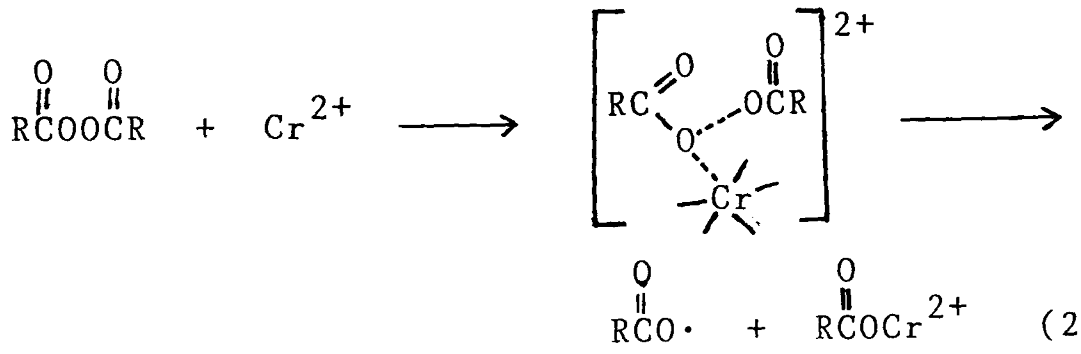
Tbe above reaction probably occurs via the formation of a peroxide-activator complex:



$$A + ROOR' \longrightarrow RO\overset{R'}{\overset{|}{O}}{:}A \longrightarrow RO\cdot + R'O^{-} + A^{+}$$

(2.20)

For example, a complex of diacyl peroxide and chromous ion(79) is involved in the following reaction:



(2.21)

The reactions of transition-metal ions of variable valency with hydroperoxides are slightly more complex than with diacyl peroxides or peroxyesters(80,81). The decomposition of hydroperoxides by millimolar amounts of transition-metal ions, M^{n+}, in unreactive solvents generally occurs as follows(82):

$$ROOH + M^{n+} \longrightarrow RO\cdot + M^{(n+1)+}(OH^{-}) \qquad (2.22)$$

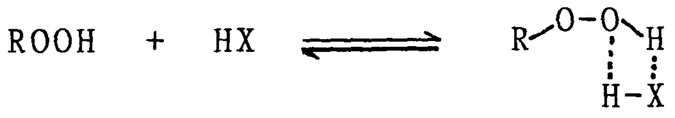
$$ROOH + M^{(n+1)+} \longrightarrow ROO\cdot + M^{n+}(H^{+}) \qquad (2.23)$$

Metal ions in large excess, however, compete effectively for RO•, resulting in reduction to ROH and H_2O:

$$RO\cdot + M^{n+} \longrightarrow RO^- + M^{(n+1)+} \qquad (2.24)$$

The ability of metal ions to participate in Reactions 2.22, 2.23 and 2.24 can be influenced by the gegen-ion or by complexing ligands(82,83). However, the correlation between the activity of these ions in the above reaction and their oxidation-reduction potentials is not clear(83).

Complexes involving hydroperoxides and organic activators such as amines and ketones are formed by hydrogen-bonded association(84):



$$ROOH + HX \rightleftharpoons R{-}O{-}O{-}H \cdots H{-}X \qquad (2.25)$$

(X = O- or N<)

The 'complex' of hydroperoxide with aldehyde is not usually hydrogen bonded, but results from addition to the C=O bond:

$$ROOH + {>}C{=}O \longrightarrow ROO{-}\overset{|}{\underset{|}{C}}{-}OH \qquad (2.26)$$

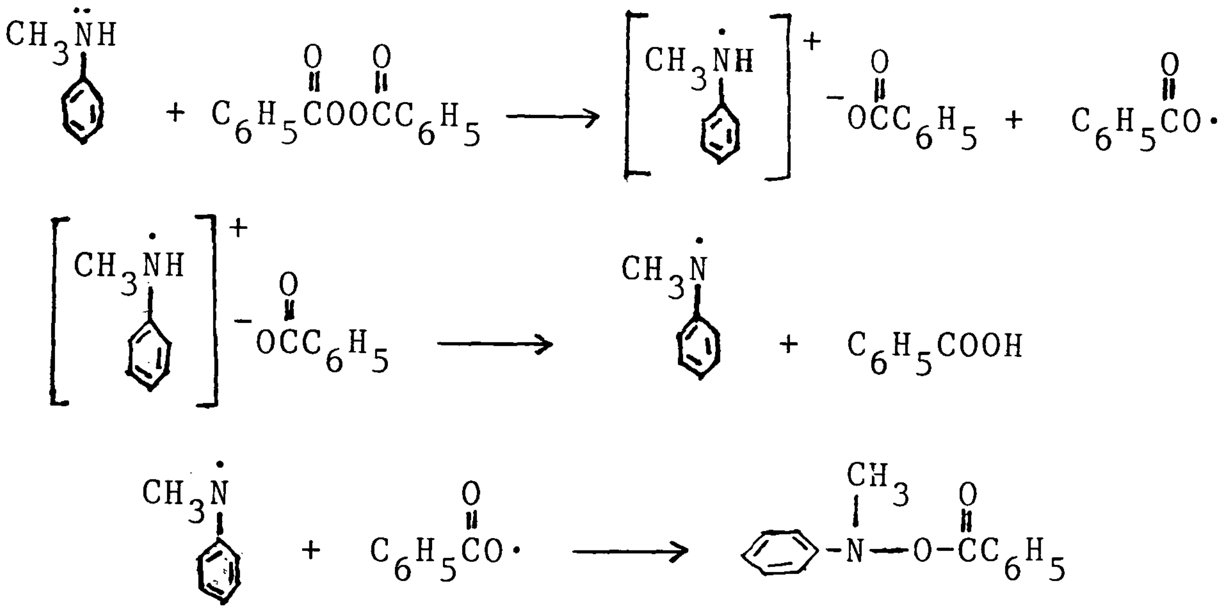
The homolytic decomposition of peroxides can also be induced by free-radicals. Radical-induced decomposition is more important with diacyl peroxides than with peroxyesters or hydroperoxides. This type of decomposition may reduce the efficiency of free-radical generation. Radical-induced decomposition occurs by free-radical displacement on O-O:

$$RO{-}OR'' + R'\cdot \begin{cases} \longrightarrow ROR' + \cdot OR'' \\ \longrightarrow R'OR'' + RO\cdot \end{cases} \qquad (2.27)$$

In the case of hydroperoxides, decomposition can also occur by free radical abstraction, yielding alkylperoxy radical:

$$ROO\text{-}H + R'\cdot \longrightarrow ROO\cdot + R'H \qquad (2.28)$$

The decomposition of peroxides activated by organic molecules is generally more complicated than that activated by metal ions. For instance, the reaction between benzoyl peroxide and amines(85,86) is suggested to occur by a bimolecular reaction involving one-electron transfer and also by free radical induced decomposition by amino-type radicals. Horner and Schlenk(87) have proposed a set of mechanisms which could explain the reaction products of benzoyl peroxide with amines. As an example, the reaction of benzoyl peroxide with methylaniline is shown below:



The primary step in the above reactions is an electron transfer from unshared pair of the N atom to one of the peroxidic oxygen, resulting in the breaking of the O-O bond.

2.7 Heterolytic decomposition of peroxides

Peroxide decomposition can also occur by unimolecular heterolytic cleavage of the O-O bond, yielding ions of unlike charges:

$$ROOR' \longrightarrow RO^{+} + OR'^{-} \quad (\text{or } RO^{-} + OR'^{+}) \qquad (2.29)$$

The possible occurrence of heterolytic decomposition of peroxides during prevulcanization will obviously affect the efficiency of prevulcanization. Peroxy acids exhibit a pronounced tendency for heterolytic decomposition. However, under certain conditions other types of peroxides may tend to undergo unimolecular heterolytic decomposition. The tendency for heterolytic cleavage of peroxides is increased in solvents having high dielectric constants. This type of solvent play a very important role in solvating the ions or ion pairs, thus enhancing the heterolytic cleavage tendency of peroxide:

$$\mathrm{ROOR'} + (x + y)S^{*} \longrightarrow [\mathrm{RO}^{-}][S^{*}]x \quad + \quad [\mathrm{R'O}^{+}][S^{*}]y \qquad (2.30)$$

where S^{*} is solvent, x and y are whole numbers.

The heterolytic cleavage of peroxide can also occur by reaction with a generalized Lewis acid A or a generalized base B:

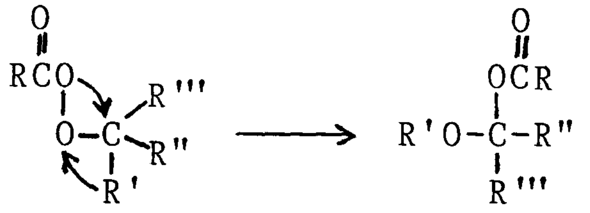
$$\mathrm{ROOR'} + \mathrm{A} \rightleftharpoons (\mathrm{ROOR'})(\mathrm{A}) \longrightarrow [\mathrm{AOR}]^{-} + \mathrm{R'O}^{+} \qquad (2.31)$$

$$\mathrm{ROOR'} + \mathrm{B} \rightleftharpoons (\mathrm{ROOR'})(\mathrm{B}) \longrightarrow \mathrm{RO}^{-} + [\mathrm{R'OB}]^{+} \qquad (2.32)$$

This type of reactions are in practice generally more important than unimolecular heterolytic reactions of peroxides, particularly with peroxy acids, diacyl peroxides and hydroperoxides. The base B is a nucleophile, e.g., halides, phosphines, phosphites, metal hydrides and sulphites. Under some conditions, decompositions by sulphur compounds, amines as well as other strongly-basic nucleophiles may also yield free radical intermediates. Many reducing agents are nucleophiles. Thus it appears that the basicity of these reducing agents and the nature of the peroxide reaction conditions determine the tendency towards free radical of polar reactions. The rate of nucleophilic substitution in a peroxide increases as the basicity of the nucleophile increases and as the basicity of the leaving anion RO^{-} decreases.

2.8 Other reactions of peroxides

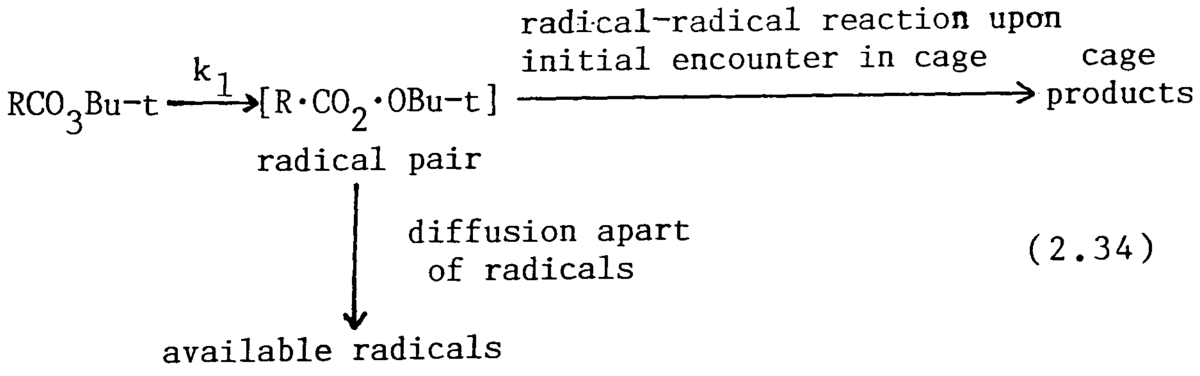
Peroxyesters may undergo the Criegee rearrangement(88), which competes with homolytic decomposition:



(2.33)

The above process is facilitated by i) strong electron-withdrawing group in R, ii) groups of high migratory ability and carbonium stabilization features in the alkyl portion, and iii) polar media. From the consideration of structural features described in (i) and (ii), it appears that the Criegee rearrangement is probably not important in commercial peroxyesters.

The reactions of peroxides and free radicals are affected by solvents(89). One of the effects is the "solvent cage" effect, where the fragments from the cleavage of peroxide molecule cannot immediately separate because they are surrounded by a 'cage' of solvent molecules. The following reaction illustrates the cage effect in peroxyester decomposition(90):



(2.34)

Cage reactions of radical pairs generated from the decomposition of peroxyesters reduce the number of radicals which are available for subsequent reactions. Table 2.5 shows the effects of R group, temperature and solvent upon the cage effect in the decomposition of peroxyesters(90).

The cage effect in Table 2.5 was determined by using galvinoxyl which reacts with the fraction of radicals that escape the cage. This fraction is

$$F = \left(-\frac{d[\text{galvinoxyl}]}{dt} \times \frac{1}{2k_1[P]} \right)$$

where [P] is the average concentration of the peroxyester during the run. The cage effect is defined as the quantity 1-F.

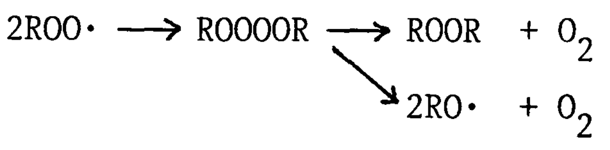
2.9 Reactions and properties of oxy radicals

Radical reactions can be classified into four types:

1) Radical-forming reactions: These reactions have already been described in Sections 2.5 and 2.6.

2) Radical transformations: The decomposition of tertiary-alkoxy radical in Reaction 2.11 and acycloxy radical in Reaction 2.13 illustrates one type of radical transformation. Alkylperoxy radicals may undergo unimolecular or bimolecular decompositions(91):

$$RR'CHOO\cdot \longrightarrow RR'\dot{C}OOH \longrightarrow RR'C{=}O + \cdot OH \qquad (2.35)$$



$$\begin{tikzcd}2ROO\cdot \arrow[r] & ROOOOR \arrow[r] \arrow[dr] & ROOR + O_2 \\ & & 2RO\cdot + O_2\end{tikzcd} \qquad (2.36)$$

Free radicals can also rearrange to form a more stable radical. The first step in Reaction 2.35 illustrates the rearrangement of alkylperoxy radical by intramolecular hydrogen transfer. Radical transformations generally produce less reactive free radicals and this may affect the prevulcanization efficiency of the peroxides from which these radicals are derived.

3) Radical attack on substrates: A discussion on this subject will be given in Section 2.8.1.

4) Radical-destroying processes: Radical combinations

Table 2.5. Cage effects in peroxyester decomposition (90)

R in RCO_3Bu-t	Temperature (°C)	Cage effect (%)[a]
$(CH_3)_3C$	49	25-50[b]
p-$CH_3OC_6H_4CH_2$	49	28.9 ± 1.0[b]
$C_6H_5C(CH_3)_2$	34	44.0 ± 1.0[b]
	40	56.5 ± 3.5
$(C_6H_5)_2CCH_3$	34	43[b]
$(C_6H_5)_2CH$	40	28.2 ± 1.2
$(C_6H_5)_3C$	14	10

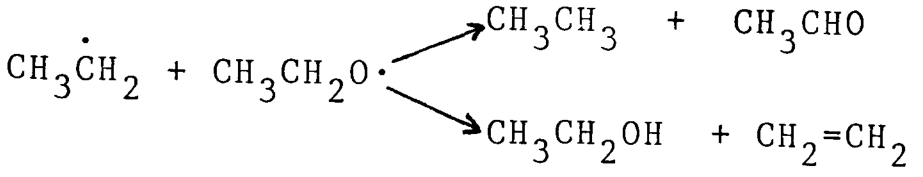
[a] Cage effect in cumene by galvinoxyl method.
[b] In chlorobenzene.

Table 2.6. Reactivity (average) of C-H bonds to alkoxy radicals at 40 °C (93)

	Paraffinic		Benzylic	Allylic[a]
	$(CH_3)_3CO\cdot$	$CH_3O\cdot$	$(CH_3)_3CO\cdot$	$(CH_3)_3CO\cdot$
Primary	1.0	1.0	10	12 (p) 20 (s)
Secondary	12.2	14	32	61 (p) 93 (s)
Tertiary	44	46	69	375 (cyclic) 176 (p)

[a] Letter in parentheses indicates substitution on 3-carbon center.

or couplings in solution occur at rates which depend upon the reactivities of the radicals(91,92). The coefficient for the combination rate of radical X· and Y· can be correlated with the bond strength of X-Y, i.e., the higher the bond strength, the higher the rate coefficient for combination. Radical disproportionation is another radical-destroying processes, but is generally less important than radical combination. The following reaction illustrates radical disproportionation:



$$CH_3\dot{C}H_2 + CH_3CH_2O\cdot \begin{cases} \rightarrow CH_3CH_3 + CH_3CHO \\ \rightarrow CH_3CH_2OH + CH_2{=}CH_2 \end{cases} \qquad (2.37)$$

Oxidation-reduction reactions illustrated by Reaction 2.24 between oxy radicals and metal ions are radical-destroying processes which may be important in the prevulcanization of NR latex using peroxide.

2.9.1 Reactions of oxy radicals with substrates

In the peroxide prevulcanization of NR latex, the reaction of free radicals derived from the peroxide with the components of NR latex may be a much more important sequence of radical reactions than the radical transformations or radical-destroying reactions described in the preceding sections. This is because of the presence in large excess of a variety of substrates with which different types of free radicals can react. The natures of the substrates and free radicals determine the relative importances of different competing reactions. Reactions of free radicals with substrates that are relevant for the present investigation will now be discussed.

a) Hydrogen abstraction by radicals. Hydrogen abstraction from organic substrates is the most common reaction of alkoxy radicals. Table 2.6(93) shows the reactivity of various types of hydrogens to alkoxy radicals. The data indicate that allylic hydrogen tends to be more easily abstracted by alkoxy radicals than does benzylic or paraffinic hydrogen. Also, tertiary-hydrogens are more easily abstracted by alkoxy radicals than secondary and primary hydrogens. The tendency for alkoxy radicals to react by hydrogen abstraction(94) is approximately in the order $CH_3O\cdot > CH_3CH_2O\cdot > (CH_3)_3CO\cdot$. The relative rates of hydrogen abstraction from a series of hydrocarbon listed in Table 2.6 are virtually independent of the nature of alkoxy radical, whether the reaction is carried out in solution or in the gas phase. However, other types of radicals show different rates, as indicated in Table 2.7(95).

The hydroxyl radical is capable of abstracting hydrogen from most organic substrates, and in this respect it is more reactive than alkoxy radicals such as the t-butoxy radical. The relative reactivity of oxy radicals can be estimated from the O-O bond-dissociation energy, i.e., the higher the bond-dissociation energy, the more reactive are the radicals produced by the cleavage of this bond. Table 2.8(96) shows the bond-dissociation energies of several polyoxides. The data indicate that hydroxyl radical is the most reactive, followed by alkoxy, acyloxy and peroxy radicals. Also, t-butoxy radical appear to be slightly more reactive than ethoxy and methoxy radicals. Thus it appears that, whilst the reactivity of alkoxy radicals increases, their tendency for hydrogen abstraction decreases. Although the hydroxyl radical is apparently more capable of abstracting hydrogen from organic substrates than alkoxy radicals, Farmer and Moore(64) found that abstraction of olefinic hydrogen by hydroxyl radicals is insignificant compared to hydrogen abstraction by t-butoxy radicals. This is because the ease of hydrogen abstraction by hydroxyl radicals (Reaction 2.38) depends upon the structure of R, and is generally slower when electron-withdrawing groups are present in the molecule RH(91):

$$RH + \cdot OH \longrightarrow H_2O + R\cdot \qquad (2.38)$$

Table 2.7. Abstraction of alkyl hydrogen by alkoxy and other radicals* (95)

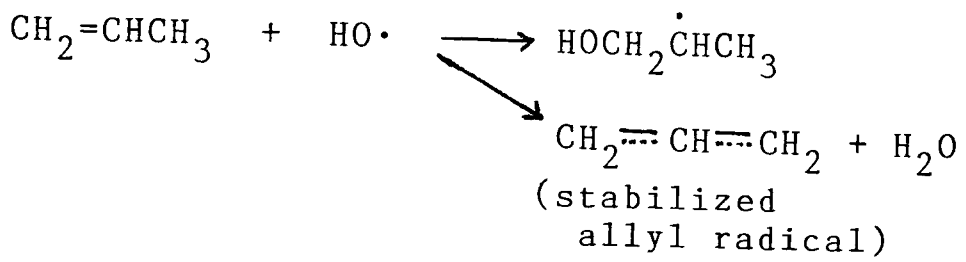
	$CH_3\cdot$		$CH_3O\cdot$		$Cl\cdot$	
R-H	log k	E_a	log k	E_a	log k	E_a
CH_4	1.9	12.8	3.5	11.0	8.9	3.8
CH_3CH_3	3.1	10.4	5.0	7.1	10.5	1.0
$c\text{-}C_3H_6$	2.8	10.3	4.5	9.7	8.7	4.1
$CH_3CH_2CH_3$	3.5	10.1	5.7	5.2	10.9	0.7
$CH_3(CH_2)_2CH_3$	3.8	8.3	6.0	2.9	11.1	0.3
$(CH_3)_2CHCH_3$	4.1	7.5	5.9	4.1	10.0	0
$(CH_3)_4C$	3.3	10.2	5.2	7.3	10.8	0.9

* k in $M^{-1}sec^{-1}$, E_a in kcal/mole. The bond energies are $CH_3\text{-}H$ = 104, $CH_3O\text{-}H$ = 104 and H-Cl = 103 kcal/mole.

Table 2.8. Bond-dissociation energies of polyoxides (96)

Oxide (R= CH_3 ··· t-Bu)	D (kcal/mole)
HO-OH	51
$HO_2\text{-}OH$	20
$R\underset{O}{\underset{\|}{C}}O\text{-}O\underset{O}{\underset{\|}{C}}R$	30
RO-OR	38
$RO_2\text{-}OR$	21
$RO_2\text{-}O_2R$	8
$RH\overline{CO_2\text{-}OC}RH$	17
$CF_3O_2\text{-}OCF_3$	30
RO-H	104
$RO_2\text{-}H$	90

The hydroxyl radical, owing to its electrophilic properties tends to react with unsaturated linkages(97):



$$CH_2{=}CHCH_3 + HO\cdot \longrightarrow HOCH_2\dot{C}HCH_3$$

$$CH_2{=}CHCH_3 + HO\cdot \longrightarrow CH_2 \cdots CH \cdots CH_2 + H_2O \qquad (2.39)$$

(stabilized allyl radical)

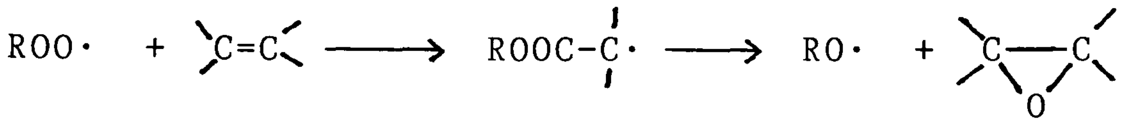
The hydroxyl radical, being a powerful one-electron oxidant can undergo various redox reactions with substrates. The reactions of hydroxyl radicals with substrates are less selective than are those of alkoxy radicals.

The sulphate ion-radical, $SO_4^{\cdot -}$, is also capable of abstracting hydrogen from organic substrates. However, sulphate ion-radicals have a great tendency to effect electron-transfer oxidation, and they oxidize hydroxide ions to hydroxyl radical(98):

$$SO_4^{\cdot -} + H_2O \longrightarrow HSO_4^- + \cdot OH \qquad (2.40)$$

$$2HO\cdot \longrightarrow H_2O + \tfrac{1}{2}O_2 \qquad (2.41)$$

Alkylperoxy radicals are considerable less reactive than are alkoxy radicals in hydrogen-abstraction reactions(99). Alkylperoxy radicals tend to rearrange(100) and add to unsaturated substances:



(2.42)

The reactivity of alkylperoxy radicals decreases with alkyl rubstitution on the α-carbon in the same way that alkoxy radicals do (see Table 2.6).

b) Addition of radicals to C=C bonds. Addition reactions of hydroxyl and alkylperoxy radicals to C=C bonds have already been described in the preceding paragraph. Hydrogen abstractions and additions are usually competitive in the reaction of alkenes with alkoxy radicals. Table 2.9 (102) shows that addition of t-butoxy radicals from t-butyl hypochlorite to alkenes is favoured by cis configuration and asymmetrical substitution about the double bond. However, the addition reaction is less significant than hydrogen abstraction in the reaction of these alkenes with t-butoxy radical. The t-butoxy radical has the unique property of showing an unusual preference for allylic attack compared to other radicals, as indicated in Table 2.10(103). The relatively stable acyloxy radicals such as benzoyloxy radical also tend to add to double bonds (see Section 2.5).

2.10 Reactions and properties of alkyl radicals

Aliphatic acyloxy radicals derived from diacyl peroxides or peroxyesters will undergo rapid decarboxylation to yield alkyl radicals. The reactivity of alkyl radicals is in the order $CH_3\cdot > (R)_2CH\cdot > (R)_3C\cdot$ (see Section 2.5). The bond dissociation energies of CH_3-H, CH_3O-H and $(CH_3)_3O$-H are all equal, i.e., 104 kcal/mole. Thus it appears that the reactivities of methyl radical and alkoxy radicals are similar. Methyl radicals derived from the decomposition of t-butoxy radicals were found to be as effective as t-butoxy radicals in abstracting hydrogen from polyisoprene(59). However Table 2.11(99) shows that different hydrocarbons exhibit different relative reactivities towards alkyl and alkoxy radicals. Table 2.7 indicates that the methyl radical shows a lower rate and higher activation energy of hydrogen abstraction than the methoxy radical. Table 2.9 indicates that the methyl radical has a relatively higher rate of addition to double bonds than an alkoxy radical. Table 2.12(95) shows that the rate coefficient for the combination of alkyl radicals is considerably higher than those for alkoxy radicals. All this information seems to suggest that the contribution of alkyl radicals derived from peroxyesters used in this investigation towards the crosslinking of NR latex would be less important than the contribution of alkoxy radicals.

Table 2.9. Addition and hydrogen abstraction with t-butoxy radicals from t-butyl hypochlorite (102)

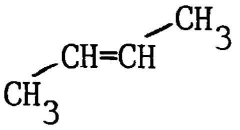
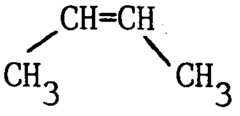
Alkene	Temperature (°C)	Addition (%)	Abstraction (%)
	-78	trace	100
	40	3-4	95
	-78	16	84
	40	17	83
$CH_3CH_2CH{=}CH_2$	-78	trace	100
	40	3	97
$(CH_3)_2C{=}CH_2$	-78	12	88
	40	17	83

Table 2.10. Rates of allylic attack relative to addition of X· on $RCH_2CH{=}CH_2$ (103)

X·	Source	Temperature (°C)	k_a/k_{add}
$(CH_3)_3CO\cdot$	$(CH_3)_3COCl$	40	30
ROO·	autoxidation	100	1.0
$CH_3\cdot$	$(CH_3CO)_2$	100	0.3
$PhCO_2\cdot$	$(PhCO_2)_2$	70	0.2
Cl·	Cl_2	-9	0.13
$CCl_3\cdot$	$BrCCl_3$	78	0.02
$CF_3\cdot$	$CF_3N{=}NCF_3$	50	0.02
RS·	RSH	-	very small

Table 2.11. Relative reactivities of various types of hydrocarbon C–H bonds toward common radicals (99)

Radical	$C_6H_5\cdot$	$CH_3\cdot$	$(CH_3)_3CO\cdot$	$(CH_3)_3COO\cdot$	$Cl\cdot$
D[R–H] (kcal/mole)	112	104	104	90	103
Temperature (°C)	60	65	40	30	40
C–H bond:					
primary aliphatic	0.12	0.4	0.1	~ 0.0006	0.8
secondary aliphatic	1.0	4.0	~ 1.2	0.025	~3
tertiary aliphatic	4.8	9.4	4.4	0.25	3.6
primary allylic	1.6	0.6	~ 1.6	1.25	-
secondary allylic	3.3	6.4	~7	8.3	-
tertiary allylic	13	26	18	10	-
toluene (α)*	1	1	1	1	1
ethyl benzene (α)	4.6	4.1	3.2	17	2.5
cumene (α)	9.7	13	6.9	8.3	5.5

* Reference.

Table 2.12. Rate constants for association of alkyl and alkoxy radicals (95)

Association reaction	Bond energy (kcal/mole)	Rate constant ($M^{-1}sec^{-1}$)
$R\cdot + R\cdot$ $R\cdot + RO\cdot$	80-90	$10^{10} - 10^{11}$
$RO\cdot + RO\cdot$	35-40	$10^{7} - 10^{9}$

CHAPTER 3

CROSSLINK CONCENTRATION OF PEROXIDE VULCANIZATE, PEROXIDE CONCENTRATION IN LATEX AND ANALYSIS OF PREVULCANIZATION KINETICS

3.1 Characterization of the rubber network of films from peroxide-prevulcanized NR latex

The network in peroxide-vulcanized NR comprises polyisoprene chains linked by C-C crosslinks. There is little other chemical modification of the rubber molecule(59). In an ideal crosslink network which is free from chain ends and permanent chain entanglements, the concentration of chemical crosslinks can be calculated from a knowledge of functionality of the crosslinks, i.e., the number of network chains which are terminated by each crosslink, and $\overline{M}_c$, the number-average molecular weight of network chains between crosslinks. In the case of a network which contains tetrafunctional crosslinks, each crosslink is associated on average with $2\overline{M}_c/N$ grams of rubber, where N is the Avogadro constant. One gram of rubber will therefore contain $N/2\overline{M}_c$ crosslinks, i.e., one gram of rubber will contain $1/2\overline{M}_c$ g moles of crosslinks. This latter quantity is a convenient measure of the degree of crosslinking.

3.1.1 Determination of $\overline{M}_c$

$\overline{M}_c$ can be determined experimentally from stress-strain measurements using a method which depends upon the statistical theories of rubber elasticity(104-106). For small extensions of a rubber network, the elementary theory gives the following relationship:

$$f = 2A_oC(\lambda - \lambda^{-2}) \qquad (3.1)$$

where f is the equilibrium force required to extend the rubber to an extension ratio λ, A_o is the cross-sectional area of the unstretched rubber, and C is an elastic constant which is directly proportional to the degree of crosslinking of the network. Rivlin and Saunders(107,108) have shown that better accord between f and λ for extensions up to approximately $\lambda = 2$ is given by the empirical equation,

$$f = 2A_o(C_1 + \lambda^{-1}C_2)(\lambda - \lambda^{-2}) \tag{3.2}$$

where C_1 and C_2 are constants for the rubber. The value of C_1 has been shown(109,110) to be related to the chemically-determined degree of crosslinking to a fair approximation by the equation

$$C_1 = \rho RT/2\overline{M}_c \tag{3.3}$$

after correction for network chain ends, where ρ is the density of the rubber network, R is the gas constant, and T is the absolute temperature. The C_2 term is regarded as making correction for the over-simplification of the model (111) used in the simple theory of rubber elasticity. It has been shown(112) that for NR vulcanizates, the C_2 term becomes insignificant for highly swollen vulcanizates.

$\overline{M}_c$ can also be determined from swollen compression stress-strain measurements. The compressive stress, f', is related to λ', the ratio of the thickness of the stressed swollen test-piece to the thickness of the unstressed swollen test-piece, by the following empirical equation (113,114)

$$f' = A'v^{\frac{1}{3}}G_{cs}(\lambda'^{-2} - \lambda') \tag{3.4}$$

where A' is the unstrained area of the swollen test-piece, v is volume fraction of rubber in the swollen network, and G_{cs} is the compression modulus. It has been shown(113,114) that G_{cs} is approximately equal to $2C_1$ for highly swollen networks.

In the present investigation, $\overline{M}_c$ was determined from equilibrium swelling measurements. The modified Flory-Rehner equation(115) relating the changes in the chemical potential of the solvent when it enters the network from the surrounding liquid and the volume fraction v of rubber in the swollen network is

$$RT\left\{\ln(1-v) + v + \chi v^2 + \frac{\varrho V_o}{\overline{M}_c}(v^{\frac{1}{3}} - \tfrac{1}{2}v)\right\} = \mu_1 - \mu_1^{\,o} \tag{3.5}$$

where R is the gas constant, T is the absolute temperature, χ is the rubber-solvent interaction parameter, ϱ is the density of the rubber network, V_o is the molar volume of the solvent, μ_1 is the chemical potential of the solvent in the swollen network and $\mu_1^{\,o}$ is the chemical potential of the solvent in pure solvent at the same temperature and pressure. The value of v will have reached its equilibrium value when $\mu_1 = \mu_1^{\,o}$, i.e., $\mu_1 - \mu_1^{\,o} = 0$, i.e., when there is no tendency for further solvent to enter the network or for the solvent to be expelled from the network. Setting the above expression equal to zero gives

$$1/\overline{M}_c = -\frac{\ln(1-v) + v + \chi v^2}{\varrho V_o\,(v^{\frac{1}{3}} - \frac{1}{2}v)} \tag{3.6}$$

The value of χ must be determined by using $\overline{M}_c$ values ontained from vulcanizates of the same type by an independent method. For instance, using the C_1 value obtained from Equation 3.2 or Equation 3.4, and assuming that C_1 is given by Equation 3.3, χ can be calculated using the equation

$$-\left[\ln(1-v) + v + \chi v^2\right] = \frac{2C_1V_o}{RT}(v^{\frac{1}{3}} - \tfrac{1}{2}v) \tag{3.7}$$

In the present investigation, toluene was used as the solvent. The χ-value used was 0.391, this being the value reported by Bristow and Watson(110) for toluene and NR vulcanized by dicumyl peroxide. This value of χ was considered appropriate, as the present work is also concerned with NR networks crosslinked by reaction with peroxides. Additionally, for a good solvent such as toluene, the value of χ has been found not to vary significantly with crosslink concentration over a range of v values corresponding to those encountered in this work(110).

The concentration of crosslinks obtained by any of the above methods is taken as the concentration of physically-effective crosslinks, $[X]_{phys}$. The value of $[X]_{phys}$ has been found to exceed considerably the concentration of actual chemical crosslinks, $[X]_{chem}$, particularly at lower degrees of crosslinking(116). This discrepancy is attributed to the effects of permanent chain entanglements. In the present investigation, the empirical relationship between $[X]_{phys}$ and $[X]_{chem}$ reported by Mullins(116) for NR vulcanizate networks produced by vulcanization with di-t-butyl peroxide or dicumyl peroxide was used to calculate $[X]_{chem}$ from $[X]_{phys}$. The Mullins relationship is as follows:

$$C_1 = \rho RT[X]_{phys} = (\rho RT[X]_{chem} + 7.8 \times 10^5)\left(1 - \frac{2.3}{2[X]_{chem}\overline{M}_n}\right) \text{N/m}^2 \qquad (3.8)$$

where $\overline{M}_n$ is the number-average molecular weight of the rubber molecules before vulcanization. The number 7.8×10^5 is a correction factor which includes the maximum contribution from entanglements. The value of 1×10^6 was assumed for $\overline{M}_n$. This is a reasonable assumption, as the value of $\overline{M}_n$ for the sol fraction of fresh NR latex varies from 2×10^5 to 5.2×10^5(33). Multiplying the terms in Equation 3.8 by $[X]^2_{chem}$ and rearranging them gives

$$[X]^2_{chem} + \left(\frac{7.8 \times 10^5}{\rho RT} - \frac{2.3}{2\bar{M}_n} - [X]_{phys}\right)[X]_{chem} - \frac{2.3 \times 7.8 \times 10^5}{\rho RT\bar{M}_n} = 0 \tag{3.9}$$

Equation 3.9 is of the form

$$aX^2 + bX + c = 0 \tag{3.10}$$

where a,b and c are known, and X is an unknown quantity. The solution for X is

$$X = \frac{-b \pm (b^2 - 4ac)^{\frac{1}{2}}}{2a} \tag{3.11}$$

The value of $[X]_{chem}$ in Equation 3.9 can be solved using the above formula. This formula gives two solutions for $[X]_{chem}$. Only the positive value of $[X]_{chem}$ is to be taken.

From equilibrium swelling measurements, the "equilibrium swelling index", Q, can be calculated as

$$Q = \frac{W_1 - W_2}{W_2} = \frac{\text{weight of solvent}}{\text{weight of vulcanizate after deswelling}} \tag{3.12}$$

where W_1 is the weight of the swollen rubber network and W_2 is the weight of the deswollen rubber network. This equation is equivalent to

$$Q = \frac{\rho_s}{\rho}(1/v - 1) \tag{3.13}$$

where ρ_s is the density of solvent, ρ is the density of the rubber network, and v is the volume fraction of rubber in the swollen network. The equilibrium swelling index is a convenient measure of the degree of crosslinking of the network.

3.2 Determination of peroxide concentration

References 117 and 118 describe various methods for the determination of organic peroxides. The applicability and accuracy of the different methods depend upon the reactivities of the peroxides and the presence of materials that may interfere with the determination. Some of the important methods are as follows:

> Volumetric methods: iodometric, stannous ion reduction, arsenious oxide reduction, and cerric ammonium sulphate oxidation methods.
>
> Colorimetric methods: ferrous ion reduction, leuco-base of methylene blue, phenolphthalin, and iodometric methods.
>
> Physical and instrumental methods: polarographic, infra-red absorption, and gas chromatographic methods.

The volumetric method of peroxide determination is generally based upon the titration of a product formed from the oxidation of a reducing agent, or the titration of excess reducing agent (excess oxidizing agent in the case of the cerric ammonium sulphate oxidation method). These titrations give the equivalent amount of peroxide present in a given sample. The colorimetric methods are based upon the colour changes which accompany the oxidation of reducing agents by peroxides. After the reaction is completed, the absorbance of the sample in a cell at an appropriate wave-length is determined. A calibration curve is prepared from data for peroxides of known purity, or by adding known amounts of product formed from the oxidation of the reducing agent. The infrared spectroscopic method is based upon measurements of infrared absorptions assigned to the stretching vibration of O-O or OO-H bonds. The polarographic technique is based upon the reduction of peroxide by a 2-electron reaction when potential is applied across a sample which contains peroxide in a polarographic cell:

$$ROOR' + 2H^+ + 2e \longrightarrow ROH + ROH' \qquad (3.14)$$

The reduction results in a flow of current (diffusion current) in the external circuit of the polarographic cell. This current is directly proportional to the concentrations of peroxide and to other factors associated with the polarographic cell. Gas chromatography is useful for separating volatile and stable peroxides in a mixture. A sample is injected at the entrance of a chromatographic column which is heated to an appropriate temperature, and gas is fed to the column at a controlled pressure. The effluent is then analyzed for the components of the mixture that is separated. By the use of known reference substances, it is possible to identify the components of the mixture. The known components that are separated can be determined quantitatively by using appropriate analytical methods.

There are several recommended iodide-reduction methods for determining a range of peroxides, from peroxides which are easy to reduce to those which are difficult to reduce(118). The sodium arsenite reduction method is recommended for determining traces of peroxide in petroleum products, since this method avoids the interference from sulphur compounds present in petroleum products. Ferrous thiocyanate methods are recommended for the colorimetric determination of traces of hydroperoxides in lipids, whilst the colorimetric iodide procedure is recommended for estimating traces of hydroperoxide in organic solvents. Polarographic methods are useful for virtually all organic peroxides when there is no interference from reducible non-peroxides; but such interferences can be eliminated by appropriate preliminary separations by thin-layer or column chromatography. Gas chromatography is used where applicable for organic peroxides having sufficient volatility and thermal stability.

3.2.1 Determination of peroxide concentration in rubber

Determinations of peroxides in uncrosslinked rubbers(119-121) generally involve the preparation of a dilute solution of the rubber in a solvent such as benzene, toluene or chloroform, or a mixture of solvents such as methanol/benzene(120) and ethanol/chloroform(121). The peroxide in the rubber solution could be determined by volumetric, colorimetric or infrared spectroscopic methods. For vulumetric or colorimetric method, a solvent mixture in which the rubber and inorganic reagents are soluble is required. The method developed by Nozaki(122) for tthe determination of benzoyl peroxide in dry rubber vulcanizate involves the extraction of the vulcanizate with acetic anhydride and then reduction of the peroxide in the extract by potassium iodide. The liberated iodine is titrated with sodium thiosulphate. Lorenz and Scheele(68) used acetone to effect a faster extraction of benzoyl peroxide in highly-crosslinked vulcanizate. Campbell(123) determined hydrogen peroxide in NR latex by potassium iodide reduction of the peroxide, catalyzed by ammonium molybdate, in a toluene-isopropanol-acetic acid-water medium. The liberated iodine was titrated with sodium thiosulphate. The titration was carried out using a Radiometer Autotitrator, and the end-point was determined by electrochemical detection of free iodine with two platinum electrodes. In a series of experiments, 19.1% DRC latex containing about 12 x 10^{-3} to 5 x 10^{-3} gmol/g rubber of hydrogen peroxide (0.1 ml) was reacted in a mixture of toluene (10 ml) and a 50% v/v solution of isopropanol in water containing 5% v/v acetic acid (20 ml)

3.3 Analysis of prevulcanization kinetics

In the kinetic studies of the peroxide prevulcanization of NR latex, the following matters pertaining to rate processes were investigated: rate of disappearance of peroxide, rate of appearance of crosslinks, temperature-dependence of rate of disappearance of peroxide, and depencence of rate of disappearance of peroxide upon concentration of reactant(s). Thermodynamic quantities were derived from kinetic data using the transition-state theory of chemical reactions. A brief discussion is given here concerning the scope of chemical kinetics and thermodynamics in interpreting rate processes. Kinetics is concerned with the effects of reaction variables upon the rate of the rate process whereby a system gets from one state to another. Kinetics will provide information, perhaps crudely, concerning the rate of reaction. Thermodynamics is concerned only with the initial and final states of a system, and is particularly concerned with the state of equilibrium. Thermodynamics will predict with precision the ultimate equilibrium extent of reaction.

3.3.1 Treatment of data for reaction rates

For reaction which is of order n with respect to a single component, the concentration-dependence of the rate can be expressed by the equation

$$dx/dt = k[A]^n = k(a - x)^n \qquad (3.15)$$

where, a is the initial concentration of reactant A, x is the reacted quantity of the reactant, t is the time and k is the rate coefficient for the reaction. For first-order reaction, the intergrated form of the rate expression is

$$\ln (a - x) = -kt + \ln a \qquad (3.16)$$

For $n \neq 1$, the intergrated rate expression is

$$\left(\frac{1}{(1 - n)}\right)(a - x)^{1-n} = -kt + \left(\frac{1}{(1 - n)}\right)a^{1-n} \qquad (3.17)$$

The vulcanization of NR using peroxides has been found to exhibit first-order reaction kinetics with respect to peroxide concentration. In this case, a plot of ln [peroxide] against time will produce a straight line of slope equal to the rate coefficient for peroxide decomposition. Since the decomposition of peroxide is a first-order reaction, the crosslink formation should also be a first-order reaction. Thus a plot of the logarithm of a variable that is directly or inversely proportional to the concentration of crosslinks against time should produce a straight line of slope equal to the rate coefficient for crosslink insertion. One such variable is $[X]_t/[X]_\infty$, where $[X]_t$ is the concentration of chemical crosslinks form after time t and $[X]_\infty$ is the maximum concentration of chemical crosslinks obtained by the vulcaniziig system.

Suppose that the empirical rate expression for a reaction involving two components is

$$dx/dt = k[A]^{n_a}[B]^{n_b} \qquad (3.18)$$

where [A] and [B] are the concentrations of substances A and B respectively. The values of k, n_a and n_b can be evaluated by fitting rate data into the various intergrated rate equations(122,123). If only the concentration of A is effectively changing, the reaction is said to be of the pseudo-n_ath order. This assumes that the character of the reaction is not changed by having B in large excess. In this case, the rate expression can be written as

$$dx/dt = k^*[A]^{n_a} \qquad (3.19)$$

where k^* is a new effective rate coefficient, and is equal to $k[B]^{n_b}$. For a complex reaction, the values of k, n_a and n_b in Equation 3.15 can be conveniently evaluated by direct comparison between the initial rate, $(dx/dt)_o$, and initial concentrations of the reactants, $[A]_o$ and $[B]_o$. If $[A]_o$ is varied whilst $[B]_o$ is kept effectively constant by having $[B]_o \gg [A]_o$ at a fixed temperature, and the corresponding $(dx/dt)_o$ measured, then a plot of $\ln(dx/dt)_o$ against $\ln[A]_o$

will give a straight line of slope equal to n_a. The value of n_b can be similarly obtained by varying $[B]_o$ whilst $[A]_o$ is kept effectively constant by having $[A]_o \gg [B]_o$. The value of $(dx/dt)_o$ can be obtained from the slope of a curve of x versus time at the beginning of the reaction, or, alternatively, by extrapolating a curve of dx/dt versus time to zero time.

3.3.2 Temperature-dependence of rate of reaction; activation parameters

Observed rates and rate coefficients may vary with temperature in various ways(122). The most typical form is called the Arrhenius temperature-dependence. It is expressed by the equation

$$k = Ze^{-E_a/RT} \tag{3.20}$$

where T is the absolute temperature, Z is a constant called Arrhenius frequency factor and E_a is Arrhenius activation energy or apparent activation energy. The relationship between k and T predicted by this equation is illustrated schematically in Figure 3.1. E_a is commonly regarded as being independent of temperature. Strictly speaking E_a is more correctly defined as the experimental activation energy, E_{exp}, because it is obtained in practice from the slope of plots of the observed values of ln k against 1/T. In many reactions, the Arrhenius equation only holds approximately because of the temperature dependence of Z and E_a. A more accurate equation is

$$k = AT^m e^{-E/RT} \tag{3.21}$$

where A is a constant, AT^m is a frequency factor which gives a measure of the frequency of collisions between the reactants, m is a number the value of which depends upon the kind of theory used to describe reaction rate and the nature of reaction being considered(125), and E is the

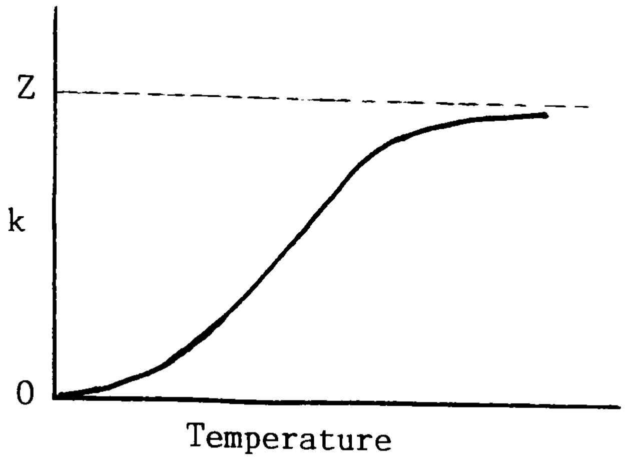


Figure 3.1. Arrhenius temperature dependence of a rate coefficient (k)

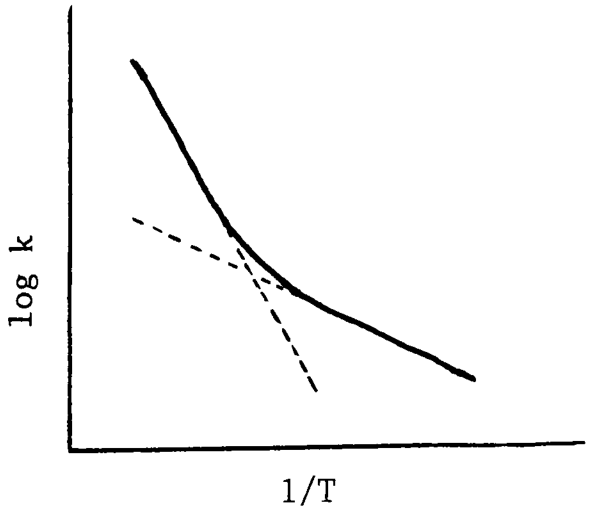


Figure 3.2. Pronounced curvature of log k against 1/T plot – suggesting two competing reactions with different activation energies.

activation energy. In simple collision theory, the value of m is equal to $\frac{1}{2}$, whilst in transition-state theory m is equal to 1. The relationship between E and E_a is given by the following equation(122)

$$E = E_a - mRT \qquad (3.22)$$

If the temperature range is not great, the frequency factor and experimental activation energy can be taken as constant. If the temperature range is wide and Equation 3.21 is correct with $m \neq 0$, then a plot of $\ln k$ against 1/T will show a slight curvature. There are cases where pronounced curvature is observed. The curve may sometimes be resolved into two parts, each of which is approximately linear as indicated in Figure 3.2. This can result if there are two competing reactions which have different activation energies.

The transition-state theory of reaction rates(125), sometimes refered to as the "theory of absolute reaction rates", relates reaction rate to energy of activation and entropy of activation. The theory takes account of all the internal motions of the reacting molecules. The potential energy of the interacting molecules at the time of collision is a function of the relative positions of the various nuclei. There will be a configuration of nuclei which has minimum potential energy, this minimum potential energy being related to the activation energy. The attainment of this configuration ensures a high probability that the system will pass from reactants to products. This configuration is called the transition state. A system in the transition state is called an "activated complex". In this theory, the reaction rate is related to the relevant thermodynamic quantities of the transition state by the equation(122):

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT} \qquad (3.23)$$

i.e.,

$$k = \frac{k_BT}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R} \qquad (3.24)$$

where $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ denote respectively standard activation free energy, activation energy and activation entropy accompanying the activation process with reactants and activated complex, k_B is the Boltzmann constant, and h is Planck constant. $\Delta G^{\ddagger}$ is defined by the equation:

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad (3.25)$$

$\Delta G^{\ddagger}$ is equal to $-RT\ln K^{\ddagger}$, where $K^{\ddagger}$ is the equilibrium constant between the reactants and the activated complex. For reactions in solution, the value of $\Delta H^{\ddagger}$ is related to E_a by the equation(122):

$$\Delta H^{\ddagger} = E_a - RT \qquad (3.26)$$

Equation 3.24 can then be written as

$$k = \frac{ek_BT}{h} e^{-E_a/RT} e^{\Delta S^{\ddagger}/R} \qquad (3.27)$$

Comparing Equation 3.27 and Equation 3.20, the following relationship between $\Delta S^{\ddagger}$ and Z is obtained:

$$Z = \frac{ek_BT}{h} e^{\Delta S^{\ddagger}/R} \qquad (3.28)$$

i.e.,

$$\Delta S^{\ddagger} = R\ln\left(\frac{Zh}{ek_BT}\right) \qquad (3.29)$$

According to the collision theory(125), for bimolecular reactions, $e^{\Delta S^{\ddagger}/R}$ represents the fraction of collisions for which the colliding molecules have the proper orientation to react. The value of $\Delta S^{\ddagger}$ decreases as the molecular weight and complexity of the reagents increase. For unimolecular reaction, $e^{\Delta S^{\ddagger}/R}$ is a factor which determines whether the reaction goes faster or slower than the "normal" rate. The latter is taken as being equal to $\frac{k_B T}{h} e^{-E_0/RT}$, where E_0 the activation energy at absolute zero temperature. If $\Delta S^{\ddagger}$ is positive, then the reaction is faster than normal. If $\Delta S^{\ddagger}$ is negative, the rate is slower than normal. The participation of solvent molecules, particularly reactive polar solvents such as water, in the transition state affects the reaction rate and the thermodynamic quantities. The energy of activation due to solvation increases with the entropy of activation due to solvation. An unusually low activation energy is often associated with an unusually low activation entropy. When the activation energy is lowered by a number of factors acting together, the concerted action is reflected in a more complex, more rigid transition state, and hence in a lower activation entropy.

3.3.4 Rate expression and empirical formula of transition-state

Chemical reactions consist of a number of elementary steps. The slowest of which is the rate-determining step. For each of the elementary steps, the reaction rate is given by the law of mass action. Although the rate expression for the overall reaction may have the same form as that for an elementary step, the overall reaction may be complex. From the rate expression for the overall reaction, it is possible to derive the empirical formula of the transition state complex for the rate-determining step. For reactions involving substances A,B,C,...., the general rule for deriving empirical formula for the transition-state complex is

Rate expression: rate = $k[A]^a[B]^b[C]^c....$

Empirical formula of transition-state complex: $aA.bB.cC......yY$

where Y represent the formula of the solvent or other substances of constant concentration, a,b,c,····y are intergers or rational fractions. For complicated reactions, there may be no single step that can be identified as the rate-determining step. The rate therefore depends upon more than one transition state, and there is no simple way of deducing the empirical formula of any one of these transition-state complexes from the rate expression.

CHAPTER 4

MATERIALS AND EXPERIMENTAL METHODS

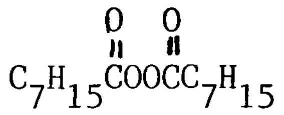
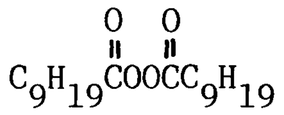
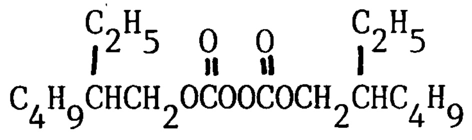
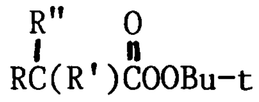
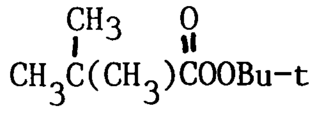
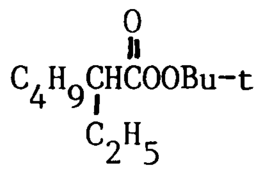
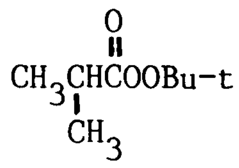
4.1 Materials

High quality HA-latex concentrates of Malaysian origin which met the requirements of Specification ISO 2002 for NR latex concentrates were used. Three batches of HA-latex were used throughout the course of this work. The latex was transferred from a drum into 1-gallon plastic containers in order to minimize loss and variation of ammonia content if the latex were to be kept in a partially filled drum. Where appropriate, the ammonia level of the latex was adjusted to 0.7% weight/weight (w/w) on the whole latex. In order to avoid batch-to-batch variations, the same batch of latex was used throughout a particular series of experiments. Texofor FP170 was used as the peroxide emulsifier when attempting to vulcanize the latex at temperatures below 90 °C. Texofor FP 170 is a non-ionic surfactant comprising an adduct of an alkyl phenol and ethylene oxide. Its aqueous solutions have a cloud point of about 97 °C. Potassium oleate was used as the emulsifier when attempting to vulcanize the latex at 100 °C. The amount of surfactant used was generally in the range of 15-30% w/w on peroxide. Activators and surfactants were usually employed as 10-20% aqueous solutions. Ferric ion complex (0.25% w/w solution) to be used as a co-activator was prepared by mixing the following reagents:

	Weight (g)
$Fe(NO_3)_3.9H_2O$	1.00
$Na_4P_2O_7.10H_2O$	5.55
water	39.74

The organic peroxides were supplied by Akzo Chemie Limited and Laporte Chemical Limited. Table 4.1a and 4.1b show some of the information on the composition, reactivity, handling

Table 4.1a Organic peroxides used in the investigation; composition

Trade name	Peroxide	Structural formula	Peroxide conctent	Active oxygen content (%)
Perkadox SE 8	di-octanoyl peroxide	 $C_7H_{15}\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}C_7H_{15}$	98% (in the form of flakes)	5.59-5.48
Perkadox SE 10	di-decanoyl peroxide	 $C_9H_{19}\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}C_9H_{19}$	98% (in the form of flakes)	4.67-4.58
Trigonox EHP-C 65	bis(2-ethylhexyl) peroxydicarbonate	 $C_4H_9\overset{\overset{C_2H_5}{\vert}}{C}HCH_2O\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}OCH_2\overset{\overset{C_2H_5}{\vert}}{C}HC_4H_9$	65% solution in arom. free mineral spirit	3.0 min.
Trigonox 23-C 75	t-butyl peroxy neodecanoate*	 $R\overset{\overset{R''}{\vert}}{C}(R')\overset{\overset{O}{\|}}{C}OOBu\text{-}t$	75% solution in aliphatics	4.85-4.99
Trigonox 25-C75	t-butyl peroxy pivalate	 $CH_3\overset{\overset{CH_3}{\vert}}{C}(CH_3)\overset{\overset{O}{\|}}{C}OOBu\text{-}t$	75% solution in arom. free mineral spirit	6.81-6.99
Trigonox 21 S	t-butyl peroxy 2-ethylhexanoate	 $C_4H_9\underset{\underset{C_2H_5}{\vert}}{C}H\overset{\overset{O}{\|}}{C}OOBu\text{-}t$	97% min.	7.18 min.
Trigonox 41-C 75	t-butyl peroxy isobutyrate	 $CH_3\underset{\underset{CH_3}{\vert}}{C}H\overset{\overset{O}{\|}}{C}OOBu\text{-}t$	75% solution in aliphatics	7.30-7.70

* R = C_4H_9, C_5H_{11} or C_6H_{13}, R' = CH_3 or C_2H_5, R" = CH_3 or C_2H_5, R+R'+R" = 9C

Table 4.1a (continued)

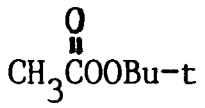
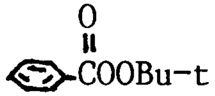
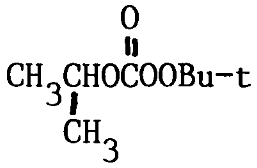
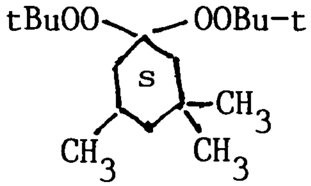
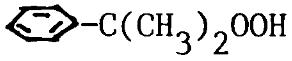
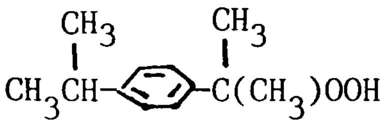
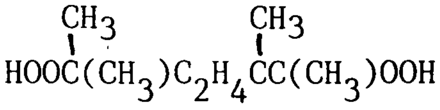
Trigonox F-C 50	t-butyl peroxy acetate	 $CH_3\overset{\overset{O}{\|}}{C}OOBu\text{-}t$	50% solution in aliphatics	5.93-6.17
Trigonox C-M 50	t-butyl peroxy benzoate		50% solution in dimethyl phthalate	4.13
Trigonox BPIC-C 75	t-butyl peroxy isopropyl carbonate	 $\underset{CH_3}{CH_3\underset{\|}{C}H}O\overset{\overset{O}{\|}}{C}OOBu\text{-}t$	75% solution in aliphatics	6.72-6.90
Trigonox 29-B 50	1,1-di-t-butyl peroxy-3,3,5-trimethylcyclohexane		50% in dibutyl phtlalate	5.19-5.41
Trigonox B	di-t-butyl peroxide	t-BuOOBu-t	99% (liquid)	10.94-10.83
-	t-butyl hydroperoxide	t-BuOOH	72% liquid in di-t-butyl peroxide	12.8
Trigonox K-80	cumene hydroperoxide		81% solution in solvent mixture	8.51
Trigonox M-50	diisopropyl benzene monohydroperoxide		50% solution in solvent mixture	4.12
-	2,5-dimethylhexane 2,5-dihydroperoxide	 $HOO\overset{\overset{CH_3}{\|}}{C}(CH_3)C_2H_4\overset{\overset{CH_3}{\|}}{C}C(CH_3)OOH$	75% water damped	13.5

Table 4.1b Organic peroxides used in the investigation; reactivity, handling and toxicological data

Peroxide	Temp.(°C) to give $t_{\frac{1}{2}}$ of:		SADT^a & CT^b (°C)	Max. storage tempt. (°C)	Acute oral toxicity (rats) (LD$_{50}$: mg/kg body wt.)	Primary skin irritation (rabbits)
	1 hr	10 hr				
di-ocatanoyl peroxide	79	61	60^b	10	-	-
di-decanoyl peroxide	79	60	45^a	15	> 5000	moderate
bis(2-ethylhexyl peroxydicarbonate	61	44	10^a	-15	1020 (75% in Soltrol 130)	slight
t-blutl peroxy-neodecanoate	62	42	20^a	-10	> 12 (ml/kg body weight)	severe
t-butyl peroxy pivalate	71	51	20^a	-5	4300 (75% in OMS)	severe
t-butyl peroxy 2-ethylhexanoate	90	70	35^a	10	10000	non-irritant
t-butyl peroxy isobutyrate	95	75	35^a	10	> 4000	moderate
t-butyl peroxy acetate	117	95	70^a	10	632 (mice)	moderate
t-butyl peroxy benzoate	122	101	90^b	20	-	-
t-butyl peroxy isopropyl carbonate	114	94	70^a	25	~ 5 (mice: ml/kg body wt.)	no severe reaction (mice)

a Self-accelerating Decomposition Temperature, the lowest temperature at which the decomposition become uncontrollable.

b Critical Temperature, the temperature at which the peroxide starts forming free-radicals. SADT is generally slightly lower than CT.

Table 4.1b (continued)

1,1-di(t-butyl) peroxy-3,3,5-trimethyl cyclohexane	105	83	55[a]	25	>12918	non-irritant
di-t-butyl peroxide	136	113	80[a]	30	-	-
t-butyl hydroperoxide	199	171	110[b]	30	-	-
cumene hydroperoxide	193	159	110[b]	30	328	moderate
diisopropyl benzene monohydroperoxide	182	150	110[b]	30	-	moderate

instructions and toxicological data of the various organic peroxides used in this investigation. The peroxides were generally used as supplied, without further dilution or purification. Most peroxyesters and hydroperoxides were used on the basis of peroxide contents assayed by iodometric analysis. Others were used on the basis of the peroxide contents indicated by the suppliers. Precautions were taken to store the peroxides under appropriate conditions; contamination during handling was avoided in order to maintain high peroxide content for a long time. With these precautions, a reduction in peroxide content of less than 3 percent w/w over a period of 6 months was noted for the peroxyesters. The hydroperoxides were found to be much more stable than the peroxyesters. The materials for the iodometric analysis of peroxides will be shown in the appropriate section of this chapter. For the sulphur prevulcanization of NR latex, 50% dispersions of sulhur, zinc diethyl dithiocarbamate (ZDEC) and zinc oxide (ZnO), prepared by vibro-milling, were used. The disodium salt of methylene dinapthalene sulphonic acid was used as the dispersing agent, at concentrations of 4,1 and 1 percent w/w for sulphur, ZDEC and ZnO respectively. For ageing experiments, 10% dispersions or emulsions of antioxidants were prepared using an ultra-high speed mixer. A combination of 0.3 percent w/w each of disodium methylene dinapthalene sulphonic acid and ethylene oxide adduct (Vulcastab LW) were used as dispersing or emulsifying agents. General-purpose toluene (low in sulphur) was used for determining crosslink concentrations by solvent-swelling measurements

4.2 Procedure for vulcanization of NR latex

The formulations for the peroxide prevulcanizations cannot be presented in a general form because of the different types of peroxides, activators, co-activators and coagents used, variation in the concentration of the ingredients used, and changes in the peroxide content during storage. Table 4.2 illustrates an example of a formulation using t-butyl peroxyisobutyrate (tBPIB). Table 4.2 indicates that the concentration of tBPIB is expressed as parts per hundred rubber (pphr). However, to facilitate comparisons between the various peroxide prevulcanizing systems (Chapters 5-7), the effective peroxide concentration will be expressed in gmol/g rubber.

Table 4.2. A typical peroxide prevulcanization formulation

Ingredient	Parts by weight wet
60% DRC latex	167
75% tBPIB	1.185[a]
20% Texofor FP170	1.0[b]
20% fructose	5.0[a]
water	25.8[c]

[a] Equivalent to 5.55×10^{-5} gmol/g rubber

[b] About 17 percent w/w of neat tBPIB or 0.2 pphr

[c] Amount required to adjust dry rubber content (DRC) to 50%

Prevulcanizations at 40-90 °C were carried out in a beaker immersed in a water bath. All formulations were adjusted to 50% dry rubber content. The amounts in grams of latex and ingredients used for prevulcanization were usually four times the amounts shown in Table 4.2. These quantities required the prevulcanizations to be carried out in 1-litre reaction vessel. Peroxide emulsions were prepared by mixing the peroxide, surfactant and about half the water in a 100-ml beaker using an ultrasonic mixer and aided by manual stirring with a glass rod for about 1-2 minutes. The peroxide emulsion was slowly added to the latex at room temperature contained in a 1-litre beaker, the latex being continuously stirred. The remaining portion of the water was used to wash residual peroxide emulsion from the beaker into the latex. The stirrer was angled for efficient mixing, and the stirring speed was adjusted such that aeration of the latex was minimal. Where appropriate, the other ingredients were added to the latex in the following order: acitivator, co-activator, and coagent. Each ingredients was allowed to mix in the latex for 2-5 minutes before the addition of the next ingredients. The beaker containing the latex was kept at constant temperature. The beaker was covered with polythene to minimize the loss of water from the latex by evaporation. A small hole was made in the polythene to allow the stirrer shaft to pass through. The latex was then continously stirred. The time when the reaction vessel was immersed in the water-bath was taken as the commencement of prevulcanization. The peroxide-NR latex reactions were found to be slightly exothermic. It was observed that the temperature of the latex increased by 1 to 2 °C after 15 minutes to $1\frac{1}{2}$ hours of heating, depending upon the prevulcanizing system and the prevulcanization temperature. The temperature-rise generally occurred for a short period, after which the temperature of the latex became approximately that of the bath temperature.

Prevulcanizations at 100 °C were carried out under reflux in a round flask heated by a heating mantle. The latex mix was diluted to 40% dry rubber content. The mixing of the vulcanizing ingredients was, however, carried out in a beaker at room temperature. The temperature of the latex was quickly raised until the latex began to simmer, by heating at a high rate. The rate of heating was then reduced to prevent frothing. It took about 10-15 minutes to raise the latex temperature from about 20 °C to 100 °C. The commencement of prevulcanization was taken as the time when the reaction vessel was placed in the heating mantle.

For prevulcanizations at room temperature (about 20 °C), the latex mix was left standing for several days with occasional stirring.

A conventional sulphur-prevulcanized latex was prepared using the formulation shown in Table 4.3. The addition of the vulcanizing ingredients was in the order shown in Table 4.3. The prevulcanization was carried out in a 1-litre beaker immersed in a heated (60 °C) water bath. The conditions of stirring were essentially similar to those described when prevulcanizing latex at 40-90 °C using peroxides.

Table 4.3. Formulation for sulphur prevulcanization

Ingredients	Parts by weight wet
60% DRC latex	167
20% potassium hydroxide	1.3
10% potassium caprylate	2.5
50% sulphur dispersion	2.0
50% ZDEC dispersion	1.0
50% ZnO dispersion	0.4
water (to bring down the TSC of the compound to 55%)	7.6

4.3 Sampling of prevulcanized latex and film preparation

Prevulcanized latex was sampled at the requisite time intervals to provide latices for the preparation of films, or for the determination of the concentration of undecomposed peroxide. The prevulcanized latex was quickly chilled by immersing a beaker containing the latex in iced water in order to prevent further vulcanization. The chilled latex was either used the same day to make cast films or stored overnight in a refrigerator at about 5 °C before being used to prepare films. For ageing experiment, a requisite amount of antioxidant dispersion was added to the chilled prevulcanized latex.

sufficient film was cast for the determination of the various film properties. The latex was filtered through two layers of muslin cloth whilst casting the films, in order to remove coagulum and eliminate air bubbles. Cast films about 0.5-1.0 mm thick were prepared for tensile strength determinations, and about 2 mm thick for determinations of tension set and tear strength. Cast films were dried at room temperature for 1-3 days, depending upon the thickness of the films. The films were considered to be dry when they had become transparent. Dried cast films were lightly dusted with talc, and then leached in distilled water at room temperature for 24 hours. Leaching removed water-soluble non-rubber substances, so that high strength properties could be obtained. The leached films were then dried at room temperature. The dried films were kept at ambient conditions prior to physical testings and determination of crosslink concentration. The determinations of crosslink concentration and physical properties of the films were usually carried out within 5 and 10 days, respectively, after the leached films had become dried.

4.4 Determination of physical properties of cast films

Modulus, tensile strength and elongation at break were determined according to ISO 37. The test-pieces for tensile testing were cut from latex films using T_2 or T_3 dumb-bell cutters. T_3 dumb-bell test-pieces with large tabs were used in cases where breakage tended to occur at the grips. The median of three test results was taken. Tear strength and tension set (100% strained for 22 hours, relaxed for 30 minutes) were determined according to ISO 34 and ISO 2285 respectively. 'Trouser' test pieces were used for determination of tear strength. For ageing tests, dumb-bell test-pieces were aged in a circulating hot-air oven at 70 °C for 7 days. Test-pieces from different films were aged in separate containers. The aged test-pieces were conditioned for 24 hours at 23 °C before determining tensile properties.

4.5 Determination of crosslink concentration and molecular weight between crosslinks, $\overline{M}_c$

Determination of the number average molecular weight of network chains between crosslinks, $\overline{M}_c$, by equilibrium solvent swelling measurements involves the determination of equilibrium volume fraction (v) of the vulcanizate in the swollen sample. The volume fraction is given by

$$v = \frac{W_1}{W_1 + \frac{\rho}{\rho_s}(W_2 - W_1)} \tag{4.1}$$

where W_1 is the weight of the vulcanizate after deswelling, W_2 is the weight of swollen vulcanizate, ρ is the density of rubber and ρ_s is the density of solvent. The average density of the rubber at 23 °C as determined by the ISO 2781 method was found to be 0.915 g/cc. The density of toluene at 25 °C was taken as 0.86 g/cc (111).

In the present work, about 0.5 g of vulcanized latex film was immersed in 20-30 cc of toluene in a stoppered bottle. The bottle was immersed in a water-bath. The temperature of the water-bath was maintained at 25 °C. A change of solvent after one day of immersion was made in order to remove the soluble fraction of the rubber. Figure 3.1 shows that immersion of the sample in toluene for two days was sufficient to reach equilibrium swelling. The swollen vulcanizate was lightly blotted with filter paper in order to remove excess solvent. The weight, W_2 , of the swollen vulcanizate was determined by difference, using a stoppered weighing bottle. The vulcanizate was then immersed in acetone for 30 minutes in order to extract the toluene, and then dried at room temperature to a constant weight, W_2. The extraction of toluene by acetone quickened the drying of the vulcanizate. It took about 1-1½ days for the vulcanizate to dry at room temperature. For lightly-crosslinked latex film, the excess toluene from the swollen vulcanizate was blotted using vegetable paper. Using the measured v value and a rubber-toluene interaction parameter, χ , which was taken as 0.391 (110), the value of $\overline{M}_c$ was calculated using Equation 3.6. From this $\overline{M}_c$ value, the physically-effective crosslink concentration, $[X]_{phys}$, and the chemically-effective crosslink concentration, $[X]_{chem}$, were calculated. The value of $[X]_{phys}$ is equal to $1/(2\bar{M}_c)$. The value of $[X]_{chem}$ was obtained by solving the quadratic Equation 3.8. For lightly-crosslinked vulcanizates, the swelling index, Q , was found to discriminate better than $[X]_{chem}$ between vulcanizates having different crosslinking. The swelling index Q is the ratio of the weight of solvent to the weight of rubber (Equation 3.12). Figure 4.2 shows the relationships between $[X]_{phys}$ and Q, and between $[X]_{chem}$ and Q.

4.6 Determination of efficiency of peroxides in prevulcanization reactions

Using [X] to represent the concentration of chemical crosslinks in the rubber and [P] to represent the concentration of peroxide in the rubber, assuming that none was dissolved in the aqueous phase, two types of crosslinking efficiency will be defined. The crosslinking efficiency f_∞ of a peroxide prevulcanizing system is

$$f_\infty = \frac{[X]_\infty}{[P]_0} \qquad (4.2)$$

where $[X]_\infty$ is the maximum concentration of chemical crosslinks obtained by the system and $[P]_0$ is the initial peroxide concentration. This defination assumed the peroxide to have completely decomposed when $[X]_\infty$ is obtained. The crosslinking efficiency F_t at any time t is

$$F_t = \frac{d[X]_t}{d[P_d]_t} \qquad (4.3)$$

where $[X]_t$ and $[P_d]_t$ are concentrations of chemical crosslinks and peroxide decomposed after time t, respectively. $d[X]_t/d[P_d]_t$ was obtained graphically by plotting $[X]_t$ against $[P_d]_t$ and taking the slope at the point corresponds

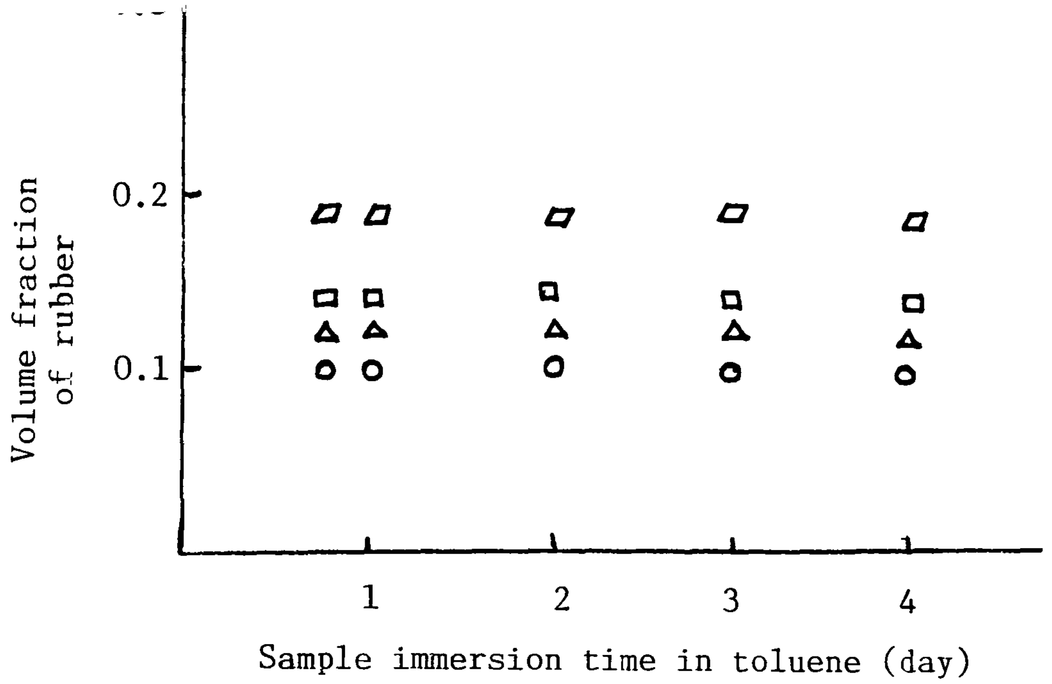


Figure 4.1. Volume fraction of rubber (v) versus immersion time at 25 °C for peroxide prevulcanized latex films with different degree of crosslinking.

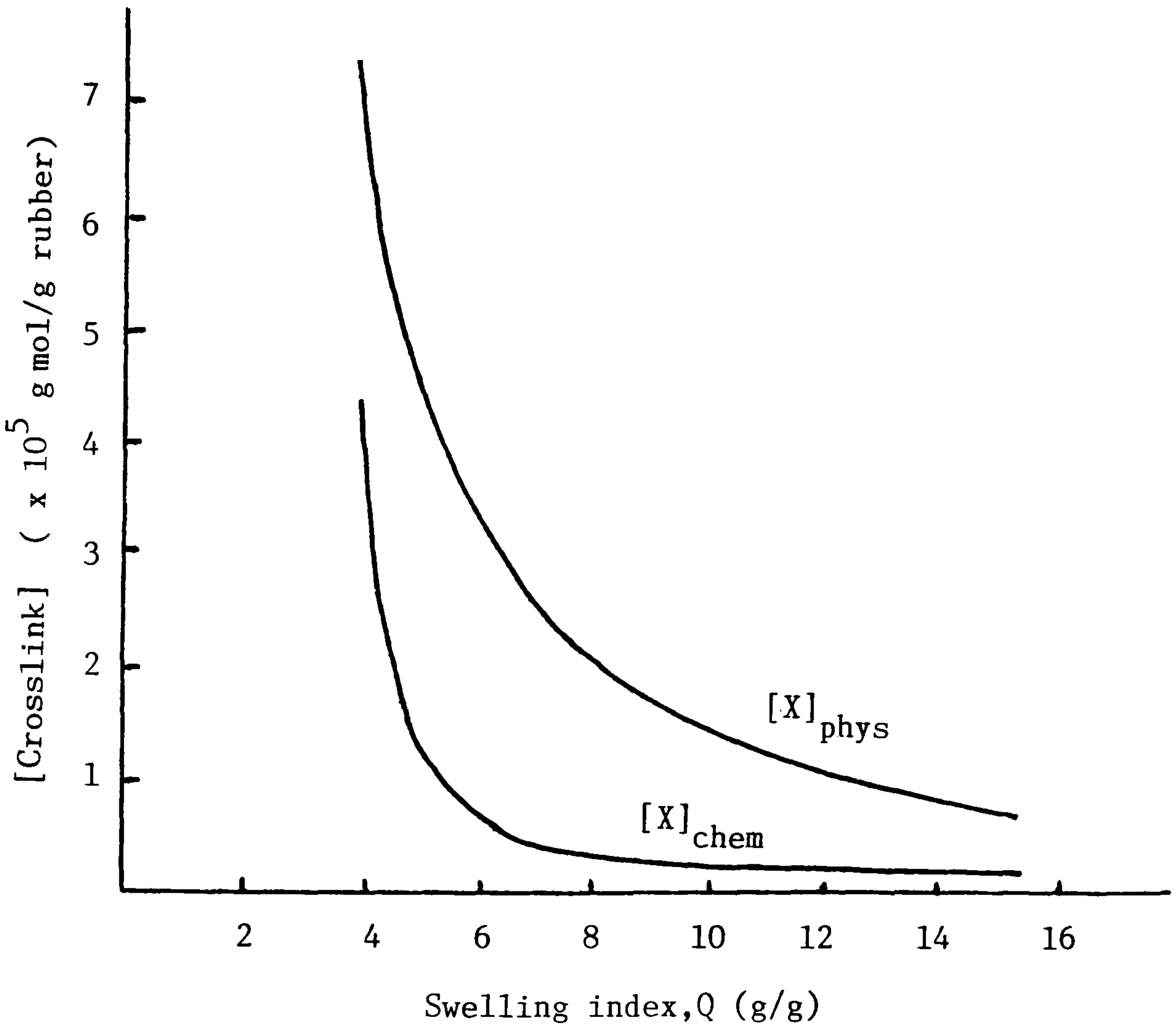


Figure 4.2. Relationship between crosslink concentration and Q value. χ was taken as 0.391 for rubber and toluene at 25 °C, and $[X]_{phys}$ and $[X]_{chem}$ assumed to be related by the Mullins equation(116).

to time t to give F_t. The crosslinking efficiencies have been expressed as percentages.

4.7 Determination of hydroperoxide content

The materials for the determination of hydroperoxide content by iodometric method, together with the appropriate reagent solutions to be prepared for the determination, are as follows:

Reagent	
acetic acid	- glacial Analar
chloroform	- Analar
ferric chloride hexahydrate	- 0.0005% solution in glacial acetic acid
sodium iodide	- saturated aqueous solution
sodium thiosulphate	- approximately 0.1N
nitrogen	

The hydroperoxides were assayed by reacting them with iodide in a chloroform-acetic acid medium, thereby liberating an equivalent amount of iodine which was titrated with a standard thiosulphate solution. Ferric chloride was used as catalyst.

The procedure was as follows: Chloroform (10 ml) was placed in a 250-ml conical flask with stopper. Nitrogen was passed over the liquid, the flow rate being adjusted so that it caused a slight dimple on the surface of the liquid. The flow was maintained during further additions. Nitrogen was fed in for at least 2 minutes before adding the sample. The sample (containing about 15 mg of available active oxygen) was weighed to the nearest 0.1 mg into a weighing cap. The cap was transferred into the flask and swirled to dissolve the sample. Ferric chloride solution (30 ml) was added, and the solution swirled to mix. Sodium iodide solution (5 ml) was then added to the flask. The flask was stoppered, swirled and allowed to stand for at least 10 minutes in the dark at room temperature. Water (100 ml) was added, and the mixture titrated with sodium thiosulphate solution to a colourless end point. No indicator was used, because the thiosulphate and iodine reacted rapidly, and the danger of overstepping the end point was slight. A blank determination was carried out for each determination. The hydroperoxide content was calculated using equation

$$\text{hydroperoxide content } (\%w/w) = \frac{(a-b) \times N \times 8}{w} \times \frac{M}{16} \times 100 \qquad (4.4)$$

where a is the volume of sodium thiosulphate solution (ml) required to titrate sample, b is the volume of sodium thiosulphate solution (ml) required to titrate blank, w is the weight of sample (mg), N is the normality of sodium thiosulphate solution and M is the molecular weight of peroxide. For dihydroperoxide content, the right-handside of equation 4.4 should be divided by a factor 2. The term $\frac{(a-b) \times N \times 8}{w}$ in Equation 4.4 represents the weight fraction of active oxygen in the sample.

4.8 Determination of peroxyester content

The materials for determination of peroxyester content by iodometric method, and the appropriate reagent solutions to be prepared for the determination, are as follows:

Reagent

acetic acid - glacial Analar
isopropanol - Analar
copper (2) chloride - 1% $CuCl_2$ solution in water
potassium iodide - 50% KI in water
sodium thiosulphate - approximately 0.1N
nitrogen or carbon dioxide

The peroxyesters were assayed by reacting them with iodide in an isopropanol-acetic acid medium, thereby liberating an equivalent amount of iodine which was titrated with standard thiosulphate solution. Copper (2) chloride was used as catalyst.

The procedure was as follows: Isopropanol (40 ml) was placed in a 250-ml conical flask with stopper. Acetic acid (15 ml) and copper (2) chloride solution (exactly 1.0 ml) were added. Nitrogen was passed over the liquid, the flow rate being adjusted so that it caused a slight dimple on the surface of the liquid. The flow was maintained during further additions. Nitrogen was fed in for at least 2 minutes before adding the sample. The sample (containing about 15 mg of available active oxygen) was weighed to the nearest 0.1 mg into a weighing cap. The cap was transferred into the flask and swirled to dissolve the sample. Potassium iodide solution (4 ml) was then added to the flask. The flask was stoppered, swirled and allowed to stand for at least 30 minutes in the dark at room temperature. Water (50 ml) was added, and the mixture titrated with sodium thiosulphate to a colourless end point. No indicator was used. A blank determination was carried out for each measurement. The peroxyester content was calculated according to Equation 4.4.

4.9 Determination of partition coefficients for distribution of organic peroxides between n-decane and water

Differences in the physico-chemical nature of peroxides may affect their partitioning between the rubber particles and the aqueous phase in NR latex, and hence also their prevulcanization behaviour. The partitioning behaviour of several peroxyesters in n-decane/water, a mixture which simulates the rubber and aqueous phases of NR latex, was therefore investigated.

The procedure was as follows: A known amount of peroxyester (about 1 x 10^{-4} mol/g n-decane) was poured into a 100-ml glass bottle containing water (25 ml) and n-decane (25 g). This composition corresponds approximately to a typical composition of peroxide prevulcanizing system, if n-decane is considered equivalent to the rubber hydrocarbon of the latex. The mixture was stirred using a magnetic stirrer for 2 hours at 5 °C under nitrogen, and stored overnight in a refrigerator (about 5 °C) to allow the phases to separate. The low temperature of mixing and standing was necessary in order to ensure that the peroxide did not decompose significantly during the experiment. The peroxide concentrations in both the water and n-decane phases were determined by the procedure described in Section 4.8. A long standing period was apparently necessary if the sum of the amounts of peroxide determined in the n-decane and water phases was to approximate to the amount which had been added. The above mixture was further stirred for another hour at 5 °C, allowed to stand overnight in a refrigerator, and the peroxide concentrations in both the water and n-decane fractions determined. The process was repeated until two consecutive determinations produced similar results. The partition coefficient for the peroxide ($C_{d/w}$) between n-decane and water was calculated from the ratio of the peroxide concentration in n-decane to that in water.

4.10 Determination of t-butyl peroxyisobutyrate (tBPIB) concentration in NR latex

Investigation of the kinetics of prevulcanization using the tBPIB-fructose system requires the determination of the concentration of tBPIB in the latex as prevulcanization proceeds. In the present investigation, a modified iodometric method, based upon the method(128) described in Section 4.8 was developed for the determination of tBPIB in prevulcanized NR latex. Under ideal conditions, the iodometric methods are considered to the the most convenient, precise and accurate methods for analyzing easily-reduced peroxides(117). The modified iodometric method developed in this investigation used toluene-isopropanol-acetic acid mixture as the reaction medium. Latex was dispersed in the medium, so that the crosslinked latex particles were swollen by toluene and the soluble rubber fraction was dissolved. Peroxide molecules were distributed in two phases. Isopropanol-acetic acid mixture provides a good medium for the inorganic reagents. The peroxide is reduced by iodide, and the liberated iodine titrated with standard thiosulphate solution. The development of the modified iodometric method required an investigation of the effect of various reaction conditions upon the accuracy and precision of the determination. In the kinetic studies of the peroxide prevulcanization of NR latex, a much lower range of peroxide concentrations than that encountered by Campbell (123) was used. It was therefore possible that a sample of larger size might be required for greater accuracy, but this might create problems of dispersing the latex. Changes in the concentration and nature of fructose and some of the non-rubber substances will occur during the peroxide prevulcanization of NR latex. Such changes may affect the blank titre value for the prevulcanized latex samples. The "actual" blank titre value of the prevulcanized latex is that of the prevulcanized latex minus the remaining undecomposed peroxide. Since it is not possible to determine the above blank titre, an investigation was made to estimate the variation of the actual blank titre value with the level of prevulcanization.

4.10.1 Development and discussion of the method

The materials, apparatus and procedure used for the development of the modified iodometric method for peroxide determination in latex were generally the same as those described in Section 4.8 for the Akzo Chemie method(128) of determining peroxyester content. Analar toluene was used as the reaction medium. Potassium iodide was replaced with saturated sodium iodide. Sodium iodide was found to be more soluble in the reaction mixture of isopropyl alcohol-acetic acid-autoxidized olefin(130) than was potassium iodide. A higher concentration of sodium iodide can be used, tending to increase the reaction rate(130) and decrease the possible addition of iodine to unsaturated substances(130, 131). Other changes in the procedure and the amount of reagents used in the determination will be stated.

a) Determination of blanks; effect of Texofor FP170, fructose, latex and reagents for iodometric analysis

Preliminary experiments were carried out to ascertain the effect of these substances upon the titration vulume of thiosulphate. The effects of Texofor FP170 and fructose were examined using isopropanol (40 ml)-acetic acid (15 ml) as reaction medium. Figure 4.3 shows that the titration volume of thiosulphate increases with increasing amount of Texofor FP170 and standing (or reaction) time. But it appears that the effect of Texofor FP170 concentration in the actual determination of peroxide in prevulcanized NR latex is insignificant, particularly when the titration volume for the sample is large. In latex prevulcanization, the amount of (20% w/w) Texofor FP170 used was in the range 0.5-1.0 ml per 100 ml of 50% DRC latex. Thus if, say, 2 ml of the latex were used for the peroxide determination, it contains 0.01-0.02 ml of 20% w/w Texofor FP170. Figure 4.3 indicates that this will not contribute significantly to the blank titre value.

Table 4.2 shows that the titration volume of thiosulphate is not affected by the variation in the amount of fructose and the standing time. This is a very significant set of results, as the changes in in the concentration of fructose in latex during prevulcanization and the actual blank titre values of the prevulcanized latex (minus the peroxide) were not or could not be determined. The concentration of fructose used in latex prevulcanization was as high as 20 ml of 20% w/w fructose per 100 ml of 50% DRC latex. Thus if, say, 2 ml of the latex were used for the peroxide determination, it contains 0.4 ml of 20% w/w fructose. Caldwell et al.(129) determined reducing sugars by oxidation of the sugars by iodine under alkaline pH of

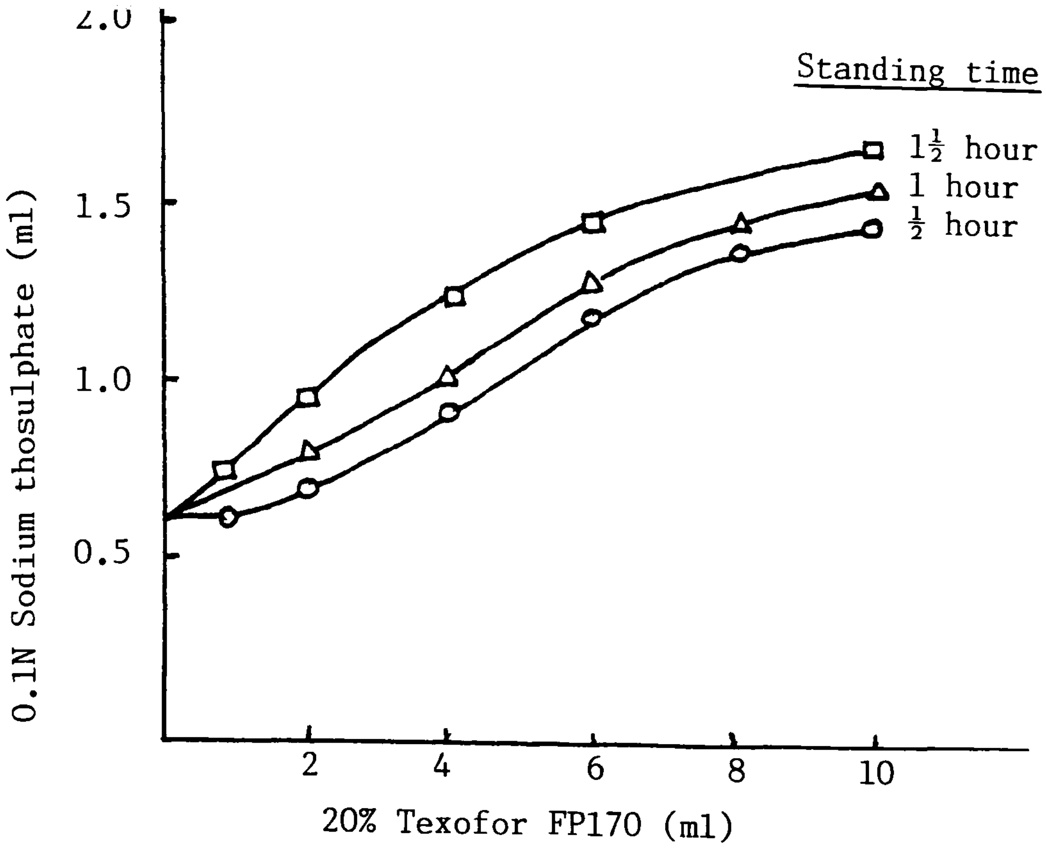


Figure 4.3. Effect of Texofor FP170 and standing time on titration volume of thiosulphate using Akzo Chemie method of iodometric analysis .

Table 4.2. Effect of fructose and standing time on titration volume of thiosulphate

20 % Fructose (ml)	2	2	2	3	4	5
Standing time (hr)	½	1	1½	½	½	½
0.1N Sodium thiosulphate (ml)	0.6	0.6	0.6	0.6	0.6	0.6

approximately 9.9. In the present experiments, fructose appeared not to react with the liberated iodine, probably because the reaction was carried out at acidic pH. In the determination of peroxide in NR latex, the presence of ammonia in the latex would not likely to affect the pH of the reaction medium if acetic acid were used and present in large amount. Table 4.3 shows that, when a known amount of peroxide in the presence of varying amount of fructose was determined by the Akzo Chemie method at room temperature, almost 100 percent of the active peroxide was analyzed. Thus, under the prescribed reaction conditions, fructose was found not to interfere with the peroxide determination by iodometric method. The results obtained in the present series of experiments, and those of Caldwell et al.(129), seem to suggest that, for fructose to be effective as activator for peroxide prevulcanization, the prevulcanization should be carried out under alkaline pH, and this condition pertains in HA latex.

Table 4.4 shows that variations in the amounts of toluene, isopropanol and acetic acid do not affect the blank determinations. Table 4.4 also indicates that the titre value of the reagents increases linearly with the amount of copper (2) chloride used. The results indicate that the titration volume of the reagents is mainly determined by the amount of copper (2) chloride used. Thus it is necessary to use an exact amount of copper (2) chloride for the blank determinations and for the peroxide determinations.

In order to determine the contribution of NR latex to the titre value, the latex had to be dispersed in a suitable medium, and the medium had be favourable for iodide-peroxide and iodine-thiosulphate reactions to take place. A variable amount of 50% DRC latex (to which peroxide, surfactant and fructose had not been added) was dispersed in 100 ml of toluene-isopopanol mixture. The latex was injected into this mixture using a graduated syringe whilst the solution was stirred using a magnetic stirrer under a

Table 4.3. Effect of fructose upon determination[a] of tBPIB content using Akzo Chemie method

20% Fructose (ml)	1	2	3
76.15% tBPIB[b] (g)	0.7738	0.8384	0.8194
Active tBPIB recovered by the analysis (%)	99.4	101.0	99.7

[a] Peroxide was added after the addition of fructose into the reaction mixture, 1 hour standing time at room temperature.

[b] Peroxide content was determined using Akzo Chemie method.

Table 4.4. Effect of reaction media and conditions upon titration volume of thiosulphate

Toluene/isopropyl alcohol/acetic acid (ml)	1% $CuCl_2$ (ml)	Saturated NaI (ml)	0.01N Sodium thiosulphate (ml)
70/30	1	4	6
70/30	1	8	6
60/40/10	1	4	6
60/40/5	1	4	5.9
60/40/10	1	4	6
60/40/15	1	4	6
60/40	0.5	4	3
60/40	1.0	4	6
60/40	1.5	4	9
60/40	2.0	4	12

Note: Standing time was 1 hour at room temperature.

nitrogen atmosphere. The speed of mixing during the injection of the latex sample should be high, so that the latex droplets break up to smaller droplets on impact with the surface of the solvent mixture, and are dispersed. The speed of mixing was then lowered sufficiently to keep the polymer uniformly dispersed in the solution. It was found that 100 ml of toluene-isopropanol mixture, containing 20-50 percent by volume of isopropanol could disperse up to 10 ml of 50% DRC latex. Latex droplets tend not to break up to finer droplets and to produce a homogenous solution in a toluene-rich mixture, presumably because the latex particles are initially rapidly swollen by the solvent and then fused together. On the other hand, latex dispersed in an isopropanol-rich mixture tends to form small pieces of coagulum. A solvent mixture of toluene (70 ml)-isopropanol (30 ml) was found to have the optimum composition for producing a fine dispersion anad a fairly homogenous solution. When toluene-isopropanol-acetic acid medium was used, the latex tended to coagulate when introduced into the mixture. A satisfactory dispersion could be made by first dispersing the latex in the toluene-isopropanol mixture, and then adding the acetic acid to the mixture slowly with stirring. However, agglomeration of the dispersed latex tended to occur during the addition of the acid when using a large sample and an incorrect ratio of toluene-isopropanol mixture. It was observed that, when a mixture of toluene (60 ml)-isopropanol (40 ml) was used, 1-2 ml of dispersed latex remained fairly dispersed after the addition of 5-15 ml acetic acid. The problem of polymer agglomeration would appear when this ratio was varied.

Figure 4.4 shows that when toluene (70 ml)-isopropanol (30 ml) mixture was used, the titration volume of thiosulphate decreased when the amount of latex was increased. The decreased of the titre value with increasing amount of latex probably indicates the addition of the liberated iodine to the double bonds of the polymer. When a higher amount of saturated sodium iodide (8 ml) was employed, the extent of the addition of iodine to the

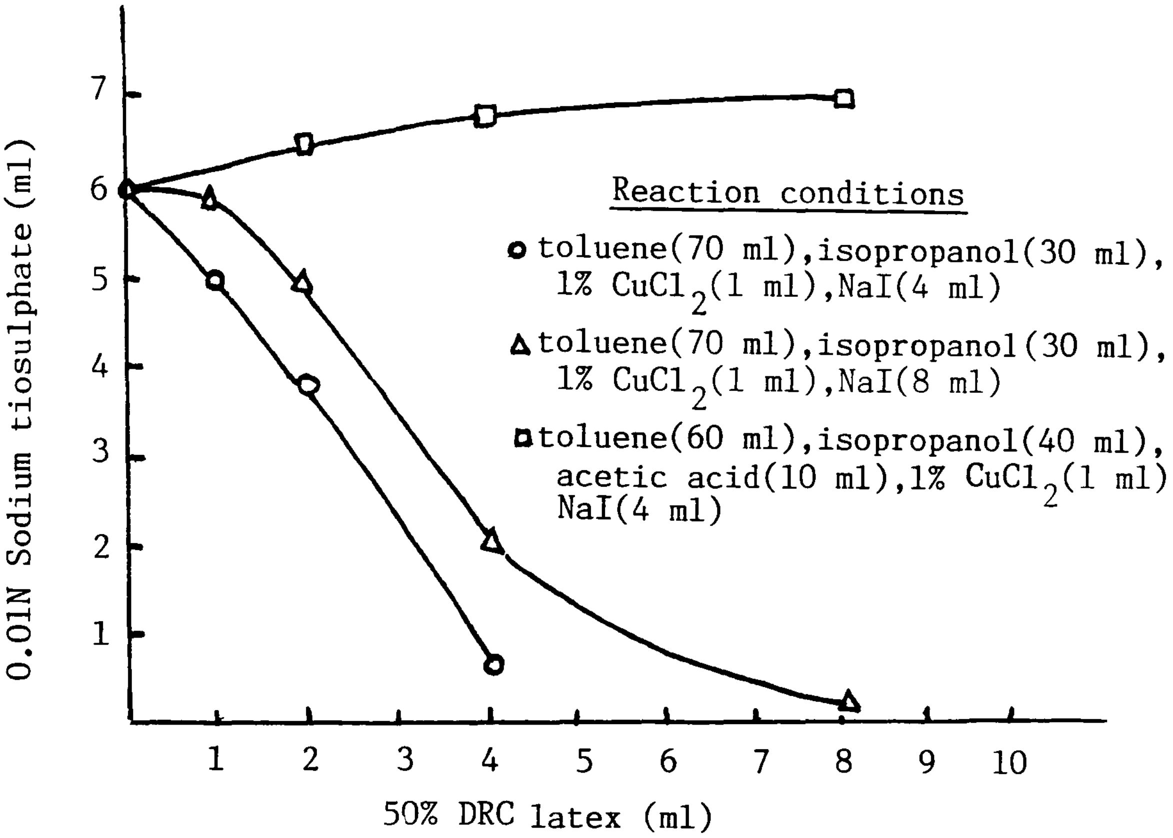


Figure 4.4. Effect of NR latex and reaction conditions upon titration volume of thiosulphate. Standing time was 1 hour at room temperature.

double bonds was apparently decreased. In the presence of acid, i.e., when using toluene (60 ml)-isopropanol (40 ml)-acetic acid (10 ml), the titration volume of thiosulphate increased only very slightly with increasing amount of latex. In this case, the slight increase of the titre value with increasing sample size is perhaps nothing to do with side reactions, but is possible a consequence of the increasing inhomogeneity of the reaction mixture, this tending to lead to over-stepping of the end-point. The results obtained so far suggest that the blank titre value for peroxide prevulcanized latex is probably the same as the titre value of unvulcanized latex when the reaction medium for the iodometric analysis contains acetic acid.

b) Determination of peroxide content in the absence of acetic acid

Determinations of peroxide in NR latex using a toluene-isopropanol-acetic acid medium and water added before titration tended to yield higher peroxide contents than expected. This problem was initially considered to be due to factors associated with the use of acetic acid. Attempts were made to find out if accurate and fast determinations of peroxide content could be made without using acetic acid. However, in the absence of acetic acid, the peroxide contents were found to be significantly lower than expected. Increasing the concentration of copper (2) chloride, the reaction temperature and the standing time did not result in any significant increase in the peroxide content as determined by this method. Thus acetic acid is apparently essential in the iodometric determination of peroxide content.

c) Determination of peroxide in HA latex and prevulcanized latex

In some of the previous and subsequent experiments, a solution of copper (2) chloride in acetic acid was used as catalyst. This was for convenience, reducing the number of steps in the procedure and increasing the accuracy of the addition of copper (2) chloride to the reaction mixture. The solution was prepared by mixing 1 ml of 1% w/w copper (2) chloride in water in 14 ml of acetic acid. A larger magnetic follower bar (45 mm instead of 35 mm) was used to effect a good mixing of the reaction mixture.

In the evaluation of the modified iodometric method for the determination of peroxide in latex, a known amount of active peroxide was added to the latex. For accurate introduction of the peroxide, the peroxide was diluted with water plus about 0.25% w/w of Texofor FP170 on active peroxide, to typically 3% active peroxide. Determination of peroxide in latex using toluene (60 ml)-isopropanol (40 ml)-acetic acid (5ml-15ml) media and water (50 ml) added before titration tended to produce higher results (by about 10 percent) than expected. Wagner _et al_. (130) found that appreciable amounts of water (5-10% in the reaction mixture) must be present at the titration end-point in order to avoid high results due to the slowness of the reaction between iodine and thiosulphate. In the present determination, the amount of water (50 ml) added in the reaction mixture was more than the minimum requirement observed by Wagner _et al_.(130). Nevertheles, experiments using higher levels of water were carried out. However, a higher level of water resulted in the formation of a viscious, inhomogenous solution during mixing, affecting the rapidity of the iodine-thiosulphate reaction. A higher level of water lightened the colour of the reaction mixture near the end-point, thus tended to reduce precision in judging the end-point. When the determination was carried out without the addition of water before titration, the amount of peroxide found was close to 100 percent, as indicated in Table 4.5. However, the problem of the formation of viscious, inhomogenous solutions appeared when high amounts of thiosulphate and latex were used.

Table 4.5. Determination[a] of tBPIB concentration in latex using toluene-isopropanol-acetic acid medium and without the addition of water before titration

Toluene/isopropanol/ acetic acid[a] (ml)	60/40/15	50/50/15	60/40/15	60/40/25[b]	60/40/25[b]
50% DRC latex[c] (ml)	1	1	1	½	2
tBPIB added in the latex (10^5 g mol/g rubber)	14.50	14.50	4.08	4.08	4.08
tBPIB recovered by the analysis (%)	99.82	97.10	100.03	100.01	103.33

[a] Determination using 0.0666% w/v of $CuCl_2$ in acetic acid, NaI (4 ml), 1 hour standing time, 0.01N sodium thiosulphate.

[b] Determination using 0.04% $CuCl_2$ in acetic acid.

[c] Latex contained 0.24 pphr Texofor FP170

d) Recommended procedure for determination of peroxide in prevulcanized latex

It is recommended that 50% DRC latex (2 ml) be dispersed in a toluene (60 ml)-isopropanol (40 ml) medium, followed by addition of 0.0666% w/v copper (2) chloride in acetic acid (15 ml) and saturated sodium iodide (4 ml). The reaction time should be about 30-60 minutes, and should not be prolonged. No water is to be added before titration with thiosulphate. The amount of thiosulphate solution should preferably be less than 25 ml. This means that a suitable sample size and standard thiosulphate solution should be used. Higher levels of latex, besides causing the problems described earlier, also tend to affect judgement of the end-point. This is due to the appearance of brownish specks of non-rubber substances which could obscure the end-point. With latex prevulcanized for more than 15 minutes, the brownish specks would appear even when a small amount of latex was used. The end-point could be ascertained by comparing with the colour of a reaction mixture where a slight excess of thiosulphate has been added. The speed of mixing towards the end should not be high or the solution would appear to be homogenously brownish, which could be misinterpreted as indicating the presence of an appreciable amount of iodine. In the calculation of peroxide concentration based on dry rubber, knowledge of latex DRC is required. The DRC of the prevulcanized latex was assumed to be constant throughout the prevulcanization reaction.

4.11 Miscellaneous tests

Films from latex prevulcanized using t-butyl peroxy 2-ethylhexanoate (tBPEH) were found to have comparatively low tensile strength and high modulus, at higher crosslink concentrations. This could be due to modification of the rubber, such as cis-trans isomerization and addition of acyloxy groups to the rubber. The films were examined by infra-red spectroscopy, but the spectra obtained were essentially similar to that of raw NR film. The films were also examined by DSC, heating from -110 °C at 20 °C per minute. The T_g of the films occurred around -73 ± 1 °C and this is considered to be an insignificant shift from the T_g of raw NR of -72 °C. The films were also examined by NMR for trans isomer content. The samples (0.5 g) were thermally degraded (to render the sample soluble in benzene) by heating at about 200 °C for 10 minutes in an oil-bath, allowed to cool at room temperature, and then benzene (1 ml) added. The samples were left overnight in benzene and then examined by NMR. The spectra indicated that no significant trans isomerization had occured in the films. Elemental analysis of several HA latices was carried out in order to find out the effect of variation of these elements on peroxide prevulcanization. Copper, iron, manganese, zinc, magnesium and calcium were determined by atomic adsorption spectroscopy, phosphorous by the phosphomolybdate colorimetric method, nitrogen by the Kjeldahl method, and soap content, calculated as ammonium stearate, was determined by potassium hydroxide titration.

CHAPTER 5

INVESTIGATIONS OF PEROXIDE PREVULCANIZATION OF NR LATEX

5.1 Evaluation of peroxide prevulcanizing systems

The effectiveness of a prevulcanizing system can be characterized by the rate of crosslink formation and the efficiency of crosslinking (f_∞). The crosslinking of rubber in NR latex using the various peroxide prevulcanizing systems was found to be a first-order reaction with respect to peroxide concentration (Chapter 6). The rate of crosslink formation can thus be represented by the first-order rate coefficient k" described in Chapter 3. The effectiveness of prevulcanizing systems that use similar concentration of peroxide can be compared by the number of crosslinks formed or the swelling index (Q) obtained after a specific prevulcanization time. The effect of reaction variables on the effectiveness of a few selected prevulcanizing systems will be studied. The peroxide prevulcanizing systems will be generally grouped according to the type of peroxides used or the type of free radicals they generate.

5.1.1 Peroxydisulphate systems

Ostromislensky(56) observed that ammonium peroxydisulphate can vulcanize rubber. However the product obtained was porous, brownish in colour, and of little value. Table 5.1 shows that unactivated peroxydisulphate and the peroxydisulphate-thiosulphate redox system did not result in any significant prevulcanization. This is probably because of the tendency of the sulphate ion-radicals to partition in aqueous phase. A system comprising peroxydisulphate and lauryl mercaptan can generate thiyl radical, RS·, which probably tend to partition in the rubber.

$$SO_4^{\cdot -} + RSH \longrightarrow HSO_4^{-} + RS\cdot \qquad (5.1)$$

The effect of the above reaction in NR latex upon the properties of the product was investigated. However, it is known that thiyl radicals tend to add to NR (132,133).

Table 5.1. Results of latex prevulcanization experiments using peroxydisulphate systems

$K_2S_2O_8$ (phr)	Additive or monomer (phr)	Reaction		Q (g/g)
		tempt. (°C)	time (hr)	
control 1	-	(unvulcanized latex film)		56
control 2	-	100	24	60
0.8	-	100	24	60
0.8	$Na_2S_2O_5$ (0.2)	60	24	55
1.5	LSH (2.3)	60	6	49
1.5	MA (1.0)	60	6	49
1.5	BA (1.8)	60	6	45
1.5	BMA (2.0)	60	6	45
1.5	HEMA (1.8)	60	6	45
1.5	VPD (1.3)	60	6	40

LSH - lauryl mercaptan, MA - methacrylic acid, BA - butyl acrylate, BMA - butyl methacrylate, HEMA - hydroxyethyl methacrylate, VPD - N-vinyl-2-pyrollidone.

Table 5.2. Results of latex prevulcanization experiments[a] using diacyl peroxides and a peroxydicarbonate

Peroxide[b]	Q (g/g)
unvulcanized latex film	56
dioctanoyl peroxide	44
didecanoyl peroxide	58
bis-2-ethylhexyl peroxydicarbonate	61

a Prevulcanization was carried out at 70 °C for 6 hours .

b Using 5.55 x 10^{-5} gmol/g rubber of peroxide. Ferric ions (0.1 pphr) was added as catalyst for diacyl peroxide systems.

The results in Table 5.1 shows that there was no significant prevulcanization with the peroxydisulphate-lauryl mercaptan system. Several combinations of vinyl monomers and peroxydisulphate were investigated, in order to ascertain if there was any advantage in transferring the sulphate ion-radical to a vinyl monomer and any consequent propagating polymer chain. Some of these systems showed a reduction in the Q-value. Attempts have also been made to prevulcanize NR latex using combinations of peroxydisulphate and polyfunctional monomers, e.g., ethylene glycol dimethacrylate and tetraethylene glycol dimethacrylate. These monomers can be used as coagents for peroxides in the vulcanization of polymers(65,134). The use of the above polyfunctional monomers with peroxydisulphate resulted in rapid gelation of the latex after about 15 minutes heating at 60 °C. This is probably a consequence of rapid homopolymerization of the monomers and graft-copolymerization of the monomers with the rubber. The homopolymers probably compete for the latex stabilizers and cause mechanical entrapment of the latex in the latex-homopolymer network. The graft-copolymers that are probably distributed near the latex particle surface would directly promote coalescence of latex particles or the graft-copolymerization could bridge two or more latex particles together. Neither increasing the level of latex stabilizer nor using other stabilizing systems (Emulvin W, potassium oleate and caprylate) prevented gelation.

5.1.2 Diacyl peroxide and peroxydicarbonate systems

Prevulcanization studies using dioctanoyl and didecanoyl peroxide, and bis-(2-ethylhexyl) peroxydicarbonate were carried out at 70 °C. At least 50% of these peroxides should have decomposed after 6 hours of heating at 70 °C. This is because the half-life times for the unpromoted decomposition of these peroxides are less than 3 hours at 70 °C. However, there was no significant prevulcanization achieved using these peroxides, as indicated in Table 5.2.

5.1.3 Dialkyl peroxide and peroxyketal systems

Table 5.3 shows that the Q-value was reduced from about 60 to 12.8 when di-t-butyl peroxide was used to prevulcanize NR latex at 100 °C for 24 hours. Calculation using the rate coefficient for the unpromoted decomposition of di-t-butyl peroxide (9.17×10^{-7} sec^{-1} at 100 °C) shows that about 7.6% of the peroxide had decomposed after 24 hours at 100 °C, giving a crosslinking efficiency of about 20%. Quaternary ammonium chloride, tetraethylene pentamine and fructose have been used with 1,1-di-t-butyl peroxy-3,3,5-trimethyl cyclohexane to prevulcanize NR latex at 80 °C. Certain quaternary ammonium chlorides have been found to activate the decomposition of peroxyketals in polyester curing(135). The results in Table 5.3 show that there was no significant prevulcanization with the above peroxyketal system at 80 °C for 6 hours.

5.1.4 Hydroperoxide and peroxyester systems

Table 5.4 shows the value of $[X]_{chem}$ obtained after 24 hours of prevulcanization at 100 °C using t-butyl hydroperoxide (tBHP) and several peroxyesters. The peroxyesters are tabulated in order of increasing half-life time for their unpromoted decomposition, i.e., from 25 minutes at 100 °C for t-butyl peroxy 2-ethylhexanoate (tBPEH) to 10 hours at 100 °C for t-butyl peroxybenzoate (tBPBO). tBPEH and t-butyl peroxyisobutyrate (tBPIB) are more effective vulcanizing agents for NR latex than are tBHP and other peroxyesters studied. A significantly lower crosslink concentration was obtained when purified NR latex was prevulcanized using tBHP. This indicates that some of the non-rubber substances that are present in the unpurified NR latex promote the decomposition of tBHP.

5.1.5 Discussion

The peroxydisulphate ion is one of the strongest oxidizing agents known in aqueous solution(78). The

Table 5.3. Results of latex prevulcanization experiments using a dialkyl peroxide and peroxyketal

Peroxide[a]	Activator[b] (pphr)	Reaction tempt. (°C)	Reaction time (hr)	Q (g/g)
tBP	-	100	24	12.8
tBPTCH	TEP (1.05)	80	6	68
tBPTCH	BZTAC (1.03)	80	6	63
tBPTCH	fructose (1.0)	80	6	42

a tBP is ditertiary butyl peroxide, employed at 6.84 x 10^{-5} gmol/g rubber. tBPTCH is 1,1-ditertiary butyl peroxy-3,3,5-trimethyl cyclohexane, employed at 2.77 x 10^{-5} gmol/g rubber.

b TEP is tetraethylene pentamine and BZTAC is benzyltrimethyl ammonium chloride.

Table 5.4. Results of latex prevulcanization experiments using a hydroperoxide and peroxyesters

Peroxide	[Peroxide] x 10^5 (gmol/g rubber)	$[X]_{chem}$[a] x 10^6 (gmol/g rubber)
tBHP	11.1	0.45
tBHP	11.1	0.30[b]
tBPEH	11.3	35.5
tBPIB	11.2	28.8
tBPIC	11.1	13.9
tBPAC	11.0	9.6
tBPBO	10.6	0.55

a For films from latex prevulcanized for 24 hours at 100 °C.

b Using purified NR latex prepared by enzymolysis and centrifugation treatments.

decomposition of the peroxydisulphate ion generates reactive sulphate ion-radical which are capable of abstracting hydrogen from olefins(56,91). The high reactivity of the sulphate ion-radical is also indicated by the high activation energy (140 kjoule/mole) for the homolytic cleavage of the peroxydisulphate anion(136). However, in a latex system peroxydisulphate is ineffective as a vulcanizing agent. This is probably because of the propensity of the sulphate ion-radical to react with the non-rubber substances and with water molecules by electron-transfer oxidation(98). These reactions are probably further favoured by the strong tendency of the sulphate ion-radical to partition in the aqueous phase. But some of the hydroxyl radicals produced by the reaction of sulphate ion-radicals and water molecules (Reaction 2.40) may partition in the rubber phase, and could initiate the crosslinking of the rubber. Burfield _et_ _al_.(137) also postulated that it is the hydroxyl radical rather than the sulphate ion-radical that initiates the graft-copolymerization of vinyl monomers in NR latex when peroxydisulphate is used as the initiator. This is because the negatively charged latex particle surface poses a high potential energy barrier for the sulphate ion-radical penetrating the latex particle. In the present case, the hydroxyl radical seems to be also ineffective in crosslinking the rubber. This is probably because only a very small fraction of the hydroxyl radicals is partitioned in the rubber phase, the rest may undergo various redox reactions with the non-rubber substances in the aqueous phase anad in the adsorbed layer of the latex particle. Although an hydroxyl radical can abstract hydrogen from the polymer, it may tend to add to the polymeric radical (see Chapter 2).

The thiyl radical produced by the reaction of sulphate ion-radical and mercaptan, and the monomeric or polymeric radicals produced by the reaction of sulphate ion-radical and vinyl monomers, probably have a great tendency to partition in the rubber phase. However, these radical did not appear to effect crosslinking of the rubber. In the case of the peroxydisulphate-lauryl mercaptan systems a polyisoprenyl radical may be formed, probably by the addition of a thiyl radical to the C=C bond rather than by hydrogen abstraction(133,138). Hydrogen abstraction by a thyil radical only occurs in the presence of reactive hydrogen donors(138). However, the polyisoprenyl radical probably abstracts hydrogen from mercaptan in preference to combining with another polyisoprenyl radical to form a crosslink. The reaction of hydrogen transfer from mercaptan to free radical is a facile one(138).

In the case of peroxydisulphate-vinyl monomer systems, polyisoprenyl radicals may be formed by the reaction of sulphate ion-radicals(139) or hydroxyl radicals(137) with the rubber. In the presence of vinyl monomer, the polyisoprenyl radical is probably utilized to form a graft-copolymer in preference to combining with another polyisoprenyl radical to form a crosslink. The grafting efficiency for the peroxydisulphate-initiated graft-copolymerization of methyl methacrylate(140) was found to be low. This is presumably because of the effectiveness of peroxydisulphate to initiate aqueous homopolymerization of the monomers. It also means that the number of polyisoprenyl radicals formed by the reaction of sulphate ion-radicals or hydroxyl radicals with the rubber is low, the reasons for this have been discussed earlier. The reduction of Q-value in the presence of vinyl monomers may have been a consequence of the formation of a graft-copolymer rather than the formation of crosslinks.

The ineffectiveness of diacyl peroxide and peroxydicarbonates in vulcanizing NR latex is probably due to the generation of alkyl radicals of low reactivity. Additionally, diacyl peroxides are susceptible to acid-catalyzed ionic decomposition. Prevulcanization using di-t-butyl peroxide (tBP) at 100 °C proceeds at a slow rate. The decomposition of tBP could not be easily activated, and hence it would be effective only at temperatures much higher than 100 °C(10,45,60). The crosslinking efficiency of tBP appears to be significantly lower in latex than in dry rubber(141). This is probably because some of the tBP decomposition occurs in the aqueous phase of the latex, or heterolytic cleavage of the peroxide occurs by reaction with acids or some of the anions present in the latex. Evidence from graft-copolymerization studies of NR latex suggests that sulphate ion-radicals and hydroxyl radicals generated in the aqueous phase of the latex can diffuse into the latex particles and initiate the appropriate reactions. This should be true also for butoxy radicals generated by the decomposition of tBP. However, it can be envisaged that numerous competing reactions can occur between butoxy radicals and the non-rubber substances.

The peroxyketal is more reactive than tBP. The presence of activators in the peroxyketal systems did not results in any prevulcanization, although the fructose-peroxyketal system showed a very slight increase in crosslink concentration after 6 hours at 80 °C. Thus a peroxyketal would probably be effective as a vulcanizing for NR latex or rubber at elevated temperatures(45,141). The results also indicate that the effectiveness of peroxide activators depends upon the reaction systems and conditions.

Prevulcanization using tBHP at 100 °C resulted in a small degree of crosslinking only. However, since the half-life time for the non-promoted decomposition of tBHP at 100 °C is very long (more than 1500 hours), it is probable that there is some promoted decomposition of tBHP by the non-rubber substances present in NR latex. The promotion of the decomposition of tBHP by the non-rubber substances is also evidenced by the slightly lower degree of crosslinking obtained when purified NR latex was used. The purified NR latex contained considerably lesser amounts of non-rubber substances than did the untreated latex. The effectiveness of peroxyesters as vulcanizing agents for NR latex appears to increase with increasing reactivity of the peroxyesters. This probably suggests that the non-promoted thermal decomposition of peroxyesters in NR latex at 100 °C is more significant than decomposition activated by the non-rubber substances. Table 5.5 shows the partition coefficients of t-butyl peroxyesters, RC(O)OOBu-t, between n-decane and water at 5 °C. The partition coefficient, $C_{d/w}$, generally increases with increasing size of the R group. However, the reactivity of t-butyl peroxyester generally also increases with increasing size of the R group. Thus, the significance of the partition coefficients of these peroxyesters on the effectiveness of prevulcanization of NR latex at 100 °C is not clear.

5.2 Evaluation of activated peroxide prevulcanizing systems of NR latex

The results in Section 5.1.4, and those of other workers(5,39-42), indicate that the decomposition of hydroperoxides and peroxyesters in NR latex can be promoted by using suitable activators. The use of suitable activators should allow the peroxide prevulcanization of NR latex to be carried out effectively at lower temperatures. In the present investigation, the performance of a number of activators for the peroxide prevulcanization of NR latex was investigated. An activator which was found to be effective and not to cause poor latex stability and ageing properties was then used to evaluate a number of activated hydroperoxide and peroxyester prevulcanizing systems for NR latex.

5.2.1 Evaluation of activators

Various reducing agents and chemical agents that are known to promote peroxide decomposition in latex prevulcanization(5,39-42), in polyester curing(142) and in emulsion polymerization(143-147) have been evaluated. The effectiveness of these activators was assessed from the degree of crosslinking obtained after 6 hours of prevulcanization at 60 °C using tBHP and activators.

Table 5.5. Partition coefficients of peroxyesters between n-decane and water mixture at 5 °C

Peroxide	Partition coefficient ($C_{d/w}$)
tBPAC	1.8
tBPBO	35.6
tBPIB	35.8
tBPPV	73.6
tBPEH	89.7

Table 5.6. Effectiveness of activators in promoting tBHP prevulcanization[a] of NR latex at 60 °C

Activator	Q (g/g) after 6 hours
fructose	5.9
tetraethylene pentamine(TEP)[b]	12.9
maltose, lactose, catechol	> 10 > 20
ascorbic acid, quinol, p-hydroxyethoxy benzaldehyde, 1,3-dibutyl-2-thiourea + n-dodecyl mercaptan[c]	> 20 > 30
phenyl phosphinic acid, NN-dimethyl p-toluidene, anisaldehyde, 2,6-dimethyl phenol, p-hydroxy & o-hydroxy diphenols, 8-hydroxy quinoline	> 30

[a] Using 11.1 x 10^{-5} gmol/g rubber each of tBHP and activator.

[b] Q value obtained after 24 hours using 7.89 x 10^{-5} gmol/g rubber of tBHP and 0.22 pphr of TEP

[c] Using 0.49 pphr of the thiourea and 1.12 pphr of mercaptan.

Table 5.6 shows that fructose is an effective activator for tBHP in NR latex prevulcanization. Some of the activators studied are stronger reducing agents than fructose but were found to be less effective than fructose as activators. Others, whilst being effective in some systems, were found to be ineffective in the latex system.

5.2.2 Hydroperoxide-fructose redox systems

tBHP, cumene hydroperoxide (CHP), diisopropyl benzene monohydroperoxide (dIBMHP) and 2,5-dimethylhexane-2,5-dihydroperoxide (dMHDHP) have been studied in fructose-activated peroxide prevulcanizing systems at 60 °C and 80 °C.

5.2.2.1 Effects of nature of hydroperoxide on prevulcanization rate and crosslinking efficiency

Figure 5.1 shows the changes in the crosslink concentrations with time of prevulcanization for hydroperoxide-fructose systems at 60 °C. It should be noted that the curves shown in Figure 5.1 would not converge at zero. Calculation of crosslink concentration shows that the unvulcanized latex film had a chemical crosslink concentration of 1.15×10^{-6} gmol/g rubber. This value is significant for lightly crosslilked latex film, and must accordingly be substracted when calculating the crosslinking efficiency of a prevulcanizing system. In this investigation, dMHDHP was employed at half the concentration of the other hydroperoxides, but the total number of alkoxy or alkylhydroperoxy radicals that could be generated is the same for all the hydroperoxide systems. The slope of the curve in Figure 5.1 indicates the rate of crosslink insertion, and the maximum number of chemical crosslinks obtained indicates the crosslinking efficiency for the system. The rate of crosslink insertion and the crosslinking efficiency of hydroperoxide-fructose redox systems is in this order: tBHP > CHP > dIBHP and dMHDHP. The dMHDHP-fructose system was found to exhibit a long induction period before prevulcanization commenced at 60 °C. Latex which had been heated for one hour had about the same

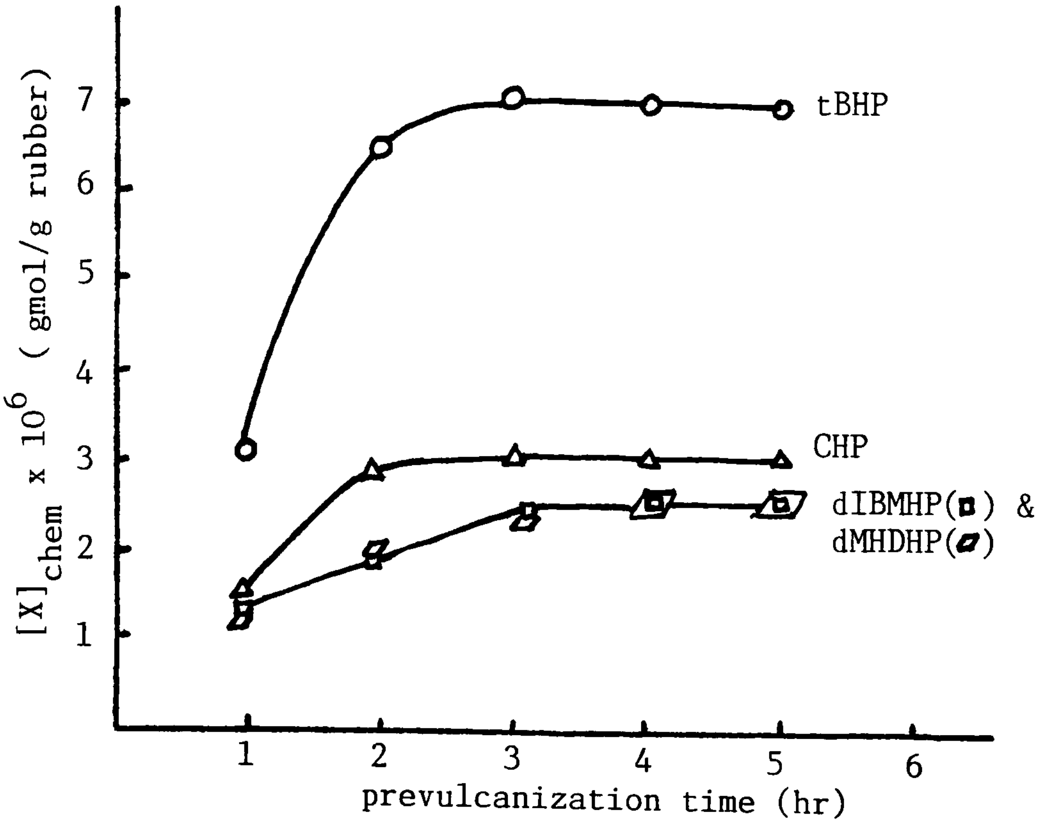


Figure 5.1. $[X]_{chem}$ versus prevulcanization time for hydroperoxide-fructose systems at 60 °C; tBHP, CHP & dIBMHP was employed at 1.11×10^{-4} gmol/g rubber, dMHDHP at 5.55×10^{-5} gmol/g rubber.

Table 5.7. Effects of reaction variables upon crosslinking efficiency (f_∞) and rate coefficient for crosslink formation for tBHP-fructose system

$[tBHP] \times 10^5$ (gmol/g rubber)	[Fructose] (phr)	Tempt. (°C)	f_∞ (%)	$k'' \times 10^4$ (sec^{-1})
5.55	1	60	4	1.18
11.1	1	60	4	4.45
11.1	2	60	4	1.52
11.1	3	60	5	1.95
16.6	2	60	5	5.89
22.2	2	60	6	2.47
22.2	3	60	6	6.43
5.55	1	80	7	-
11.1	1	80	11	-

Q-value as that of unvulcanized latex film. The same prevulcanization characteristic was observed with dMHDHP-fructose-ferric ions redox system at 20 °C (Section 5.3).

5.2.2.2 Effects of reaction variables upon prevulcanization rate and crosslinking efficiency (f_∞)

Table 5.7 shows the effect of certain reaction variables upon the rate coefficient for the crosslink formation, k'', and crosslinking efficiency, f_∞, of tBHP-fructose redox system. Some of the rate coefficients for crosslink formation were calculated from a few data because prevulcanization stopped in a short time. Changes in the tBHP and fructose concentrations significantly affect the rate of crosslinking but not the efficiency of crosslinking. The relationship between fructose/peroxide concentrations and the rate of crosslinking is not clear, although it seems that there is an optimum fructose/peroxide concentration ratio for maximum rate of crosslinking. The crosslinking efficiency increases slightly when the temperature was increased from 60 °C to 80 °C. Apparently there was a significant increase in crosslinking rate when the prevulcanization temperature was increased, but the rate coefficient for crosslink formation could not be determined as the prevulcanization was completed in too short a time.

5.2.3 Peroxyester-fructose redox systems

tBPBO, tBPIB, tBPEH, t-butyl peroxyacetate (tBPAC), t-butyl peroxypivalate (tBPPV) and t-butyl peroxyneodecanoate (tBPND) were used in conjunction with fructose to prevulcanize NR latex.

5.2.3.1 Effects of nature of peroxyesters on prevulcanization rate and crosslinking efficiency (f_∞)

Table 5.8 shows that the rate coefficient for crosslink formation and efficiency of crosslinking of

Table 5.8. Crosslinking efficiency and rate coefficient for crosslink formation of peroxyester-fructose systems* at 60 °C

Peroxyester	f_∞ (%)	k" x 10^5 (sec^{-1})
tBPND	5	10.1
tBPPV	6	6.6
tBPEH	15	11.5
tBPIB	13	23.1
tBPAC	6	16.1
tBPBO	8	7.4

* Using 5.55 x 10^{-5} gmol/g rubber of peroxyester and 2 pphr fructose.

Table 5.9. Effects of reaction variables upon crosslinking efficiency and rate coefficient for crosslink formation of tBPPV-fructose system

[tBPPV] x 10^5 (gmol/g rubber)	[Fructose] (phr)	Tempt. (°C)	f_∞ (%)	k" x 10^5 (sec^{-1})
5.55	0.5	60	4	8.0
5.55	1	60	5	10.1
7.77	1	60	11	10.4
11.1	0.5	60	4	5.9
11.1	1	60	9	10.3
5.55	0.25	80	10	-
11.1	0.25	80	17	-

Table 5.10. Effectiveness of maltose and ascorbic acid as activators for tBHP* in prevulcanization of NR latex at 60 °C

Prevulcanization time (hr)	Q (g/g)	
	Maltose	Ascorbic acid
2	29.2	26.6
3	20.6	26.8
4	16.6	26.2
5	13.0	26.2
6	12.5	26.0
7	12.2	

* tBHP and activators were used at 1.11 x 10^{-4} gmol/g rubber.

peroxyester-fructose system generally increased and then decreased with increasing reactivity of the peroxyester. The peroxyester-fructose prevulcanizing systems were found to be more effective than the hydroperoxide-fructose systems.

5.2.3.2 Effects of reaction variables upon prevulcanization rate and crosslinking efficiency (f_∞)

Table 5.9 shows the effects of certain reaction variables upon the rate coefficient for crosslink formation and efficiency of crosslinking for the tBPPV-fructose system. A more detailed investigation of the effects of reaction variables upon the prevulcanization kinetics of the tBPIB-fructose system will be presented in the next chapter. Changes in the tBPPV and fructose concentrations affect both the rate of crosslinking and the efficiency of crosslinking. The rate of crosslinking and the efficiency of crosslinking generally increase with icreasing fructose/tBPPV concentration ratio and were significantly increased when the prevulcanization temperature was increased from 60 °C to 80 °C. The tBPPV-fructose system shows a lower rate of crosslinking but higher efficiency of crosslinking when compared with the tBHP-fructose system.

5.2.4 Discussion

Fructose was found to be an effective activator for hydroperoxides and peroxyesters. It also has other advantageous properties compared with other activators. It is non-toxic, non-irritant, does not affect latex stability like certain amines(42), and does not impart poor ageing properties to the prevulcanized latex films like metal salts(40). It is apparently compatible with latex colloidal system, and fructose and its acidic oxidation products(23) can be easily leached out from latex films.

It appears that activators which are easily oxidized, i.e., strong reducing agents, tend to be less effective in promoting peroxide prevulcanization of NR latex than are those which are less easily oxidized. This is probably because they are easily oxidized by the oxidizing agents present in NR latex. The strong reducing agent may behave as a nucleophile which promotes heterolytic cleavage of the peroxide (see Chapter 2). Thus fructose, which has a keto group, is more effective than maltose which has at least one free aldehyde group. Aldehydes are more easily oxidized than are ketones; ketones are generally resistant to oxidation, except α-hydroxy and polyhydroxy ketones(148). Ascorbic acid is apparently more easily oxidized than is maltose. Thus prevulcanization using tBHP-ascorbic acid stops at a lower degree of crosslinking after a short heating time compared to that for the tBHP-maltose system, as indicated by Table 5.10. Ascorbic acid also undergoes reversible oxidation(149). The nature of peroxide-activator association complexes may also affect the effectiveness of peroxide prevulcanizing systems. Thus fructose and tetraethylene pentamine are more effective activators than, say, maltose, probably because the association of hydroperoxide with ketone and amine is by hydrogen bonding(84). Such a bonding reduces the probablity of the formation of the relatively less reactive alkylperoxy radicals, which could initiate autoxidation of rubber(150). Catechol and quinol are diphenols, and they are powerful reducing agents(151). However, catechol was found to be more effective activator for tBHP than was quinol. Various phenolic compounds can be classified as antioxidants. Although they may promote peroxide decomposition, they also reduce to varying extents the efficiency of crosslinking(152). p-benzoquinone, the oxidation product of quinol, is more stable than is o-benzoquinone, the oxidation product of catechol(153). The reaction of p-benzoquinone with a free radical leads to the formation of a more stable radical(154). This probably explains the differences in the effectiveness of catechol and quinol as peroxide activators. Phenyl phosphinic acid promotes the decomposition of most peroxides (142). However, it tends to destabilize NR latex, and, as a result, probably renders itself ineffective as a peroxide activator.

The rate of crosslinking and the efficiency of crosslinking, f_{∞}, for the hydroperoxide-fructose redox systems appear to increase with increasing reactivity of the tertiary alkoxy radicals generated by the hydroperoxides. However, the difference in the efficiency of crosslinking between tBHP-fructose and CHP-fructose system is too great to be solely attributable to the difference in the reactivity of butoxy and cumyloxy radicals. Additionally, the difference in the efficiency of crosslinking could be due to tBHP being more resistant to acid-catalysed heterolysis than is CHP(61). Hydroperoxides with aryl groups, such as CHP and dIBMHP, are relatively less stable to acids compared to tBHP. The hydroperoxide-fructose systems are considerably less efficient than the peroxyester-fructose systems. This is probably because of differences in the extent of unimolecular homolytic and assisted-homolytic decompositions between hydroperoxides and peroxyesters. Besides, hydroperoxides are usually not efficient free-radical initiators, as a substantial fraction of the radicals produced is wasted by induced free-radical chain decomposition (155) yielding relatively less reactive alkylperoxy radicals. The extent of heterolytic reactions of hydroperoxides and peroxyesters with the non-rubber substances in NR latex may also be different. The reason for the induction period exhibited by the dMHDHP-fructose system is not clear. From the structure of dMHDHP, the information on cyclization of alkylperoxy radicals(156), the postulate that some of the hydroperoxide-activator associations are in the form of coordinated ring complexes(155), and that the association complexes formed by hydrogen bonding could be formed via the carbonyl or the hydroxyl groups, could possibly favour the formation of a cyclic dMHDHP-fructose complex. The induction period may possibly be the consequence of the time required for the opening of the ring complex and the rearrangement of the association bond from a hydroperoxide-hydroxyl to a hydroperoxide-carbonyl bond, resulting in the formation of a more active complex.

The relationship between the chemical structure of peroxyester and the effectiveness of peroxyester-fructose prevulcanizing systems is obscure. The inefficiency of the highly reactive peroxyesters, such as tBPPV and tBPND, is probably a consequence of their rapid decomposition in the aqueous phase. The inefficiency of the less reactive peroxyesters such as tBPAC and tBPBO, is probably a consequence of the formation of relatively stable acyloxy radicals(90) or the formation of carboxylate anions in the metal-ion catalysed reaction(157) that add to the polymer radical and hence compete with the crosslinking reactions. The tendency for tBPAC and tBPBO to undergo a rearrangement reaction(88,90) with the formation of inert products, or for the radicals to undergo 'cage' reactions(90) that could lead to the formation of ethers and alcohols(158), may also be responsible for their inefficiency as vulcanizing agents. The efficiency of crosslinking of peroxyester-fructose systems shows no correlation with the peroxyester partition coefficients between n-decane and water at 5 °C. The reaction kinetics of these systems is probably influenced not only by the partition coefficients of the peroxyesters, but also by that of the peroxyester-fructose complexes. Redox systems comprising peroxyesters and organic activators have not been studied as extensively as diacyl peroxides and hydroperoxides redox systems. An attempt will be made in Chapter 6 to explain the reaction mechanism of a peroxyester-fructose system in NR latex.

In comparison with the tBPPV-fructose system, prevulcanization using the tBHP-fructose system shows a relatively high rate of crosslinking but low efficiency of crosslinking. This is probably a manifestation of rapid tBHP decomposition, radical transfer and termination reactions. Accordingly, the extent of radical transfer reactions by abstracting hydrogen from the rubber is relatively small. The fact that the efficiency of crosslinking of the tBHP-fructose system is poor, and that the variation of tBHP/fructose concentrations does not significantly alter the efficiency of crosslinking, probably suggests that a large proportion of the tBHP is partitioned in the aqueous phase of the latex. The effect of temperature upon the rate of crosslinking and the efficiency of crosslinking of the tBPPV-fructose system is much greater than in the case of the tBHP-fructose system. This is probably because the relatively higher increase of thermally-assisted unimolecular homolytic decomposition in the case of tBPPV than in the case of tBHP.

5.3 Hydroperoxide-fructose-ferric ion and peroxyester-fructose-ferric ion redox systems

Table 5.11 shows that prevulcanization at 40 °C using the tBPEH-fructose system proceeds at a very slow rate. However, a significant increase in the rate of prevulcanization was observed when a trace amount of ferric ion was added to the system. The peroxyester-fructose-ferric ion and hydroperoxide-fructose-ferric ion redox systems were also used to prevulcanize NR latex at ca 20 °C. Tables 5.12a and 5.12b show that NR latex could be prevulcanized at 20 °C using fructose/ferric ion-activated hydroperoxide or peroxyester systems. However the rate of prevulcanization is lower at 20 °C than at 40 °C. The two most reactive peroxyesters, tBPPV and tBPND, were found to be the most effective prevulcanizing agents at 20 °C when used in conjunction with fructose and ferric ion.

5.3.1 Discussion

Transition-metal ions are present in NR latex(29). However, the peroxyester-fructose and hydroperoxide-fructose systems became reasonably activated at 20 °C - 40 °C when a ferric ion complex was added. This is probably because metal ions differ in their ability to perform catalysed reactions of peroxide(154). The reactivity of a metal ion also depends upon its form. For instance, the cobaltic EDTA complex is not reduced by hydroperoxides(159), whilst cobaltic carboxylates are reduced by hydroperoxides (160). Most ferric salts do not reduce hydroperoxide readily, whilst the iron phthalocyanine complex does(160). In this

Table 5.11. Effects of ferric ions on the prevulcanization of NR latex using tBPEH-fructose system at 40 °C

Prevulcanizing system	Prevulcanization time (hr)	Q (g/g)
1.09×10^{-5} gmol/g rubber of tBPEH + 2 pphr fructose	1	61
	2	46
	3	42
	4	35
	5	32
	6	26
1.09×10^{-5} gmol/g rubber of tBPEH + 2 pphr fructose + 0.02 pphr ferric ion	1	16.6
	2	9.3
	3	7.6
	4	6.1
	5	5.3
	6	4.8

Table 5.12a. Results of latex prevulcanization experiments using hydroperoxide-fructose/ferric ion systems* at *ca* 20 °C

Hydroperoxide	Prevulcanization time (day)	Q (g/g)
tBHP	1	16.7
	2	12.1
	3	11.9
	4	11.9
CHP	1	18.5
	2	11.1
	3	10.5
	4	10.5
DMHDHP	1	60
	2	11.4
	3	9.3
	4	8.8

* Using 5.55×10^{-5} gmol/g rubber of hydroperoxide, 1 pphr fructose and 0.02 pphr ferric ion.

Table 5.12b. Results of latex prevulcanization experiments using peroxyester-fructose/ferric ion systems* at ca 20 °C

Peroxyester	Prevulcanization time (day)	Q (g/g)
tBPND	1	16.8
	2	9.1
	3	8.0
	4	7.8
tBPPV	1	15.5
	2	8.9
	3	7.6
	4	7.5
tBPEH	1	22.3
	2	12.4
tBPIB	1	18.5
	2	11.4
	3	11.2
tBPAC	1	16.3
	2	10.5
	3	8.7
	4	8.7
tBPBO	1	23.5
	2	12.1
	3	11.5

* Using 5.55 x 10^{-5} gmol/g rubber of peroxyester, 1 pphr fructose and 0.02 pphr ferric ion.

investigation, the use of ferric ion in the form of an iron pyrophosphate complex probably enhances the reactivity of peroxyester-fructose-ferric ion and hydroperoxide-fructose-ferric ion systems. The function of pyrophosphate is to retain the ferric ion in a soluble or sequestered state(146). The activity of a metal complex depends upon its structure, stability constant and oxidation-reduction potential(161). However, the relationship between the properties of the ferric ion complex, the nature of the peroxide and the effectiveness of the various fructose/ferric ion-activated peroxide prevulcanizing systems at 20 °C is not clear. For instance, CHP is more effective than tBHP although tBHP yields a more reactive tertiary alkoxy radical than CHP. With peroxyesters, tBPBO is more effective than tBPEH although tBPBO is much less reactive than tBPEH. Perhaps the effectiveness of these systems ought to also be discussed in term of the physico-chemical properties of peroxide-fructose-metal ion complexes in NR latex, although this aspect is far from being understood. Since fructose did not appear to be an effective peroxide activator at 20 °C, then the effectiveness of fructose-ferric ion activating system is probably due to the role of fructose in converting ferric to ferrous ion, which is in a more appropriate oxidation state to activate decomposition of peroxides. A redox system consisting of peroxide, a reducing sugar and ferrous pyrophosphate has been used to initiate emulsion polymerization(143-146). Fryling et al.(144) found that in the absence of reducing sugars, ferrous pyrophosphate activated emulsion polymerization by cumene hydroperoxide, but ferric pyrophosphate did not activate the reaction. However, ferrous ion tends to be easily oxidized by atmospheric oxygen(144,146). The oxidation of ferrous ion in NR latex may be more rapid than that encountered in emulsion polymerization system. Fryling et al. (144) recommended that if ferrous salt is to be used on a large scale for emulsion polymerization, the ferrous ion must be stabilized, and this can be achieved by inclusion of a reducing sugar in the solution. Thus, it appears that, fructose is an essential component for peroxide-fructose-iron complex prevulcanizing system at 20 °C. In the presence of fructose, the iron complex can be employed either in the form of ferrous or ferric ion complex. The results of this investigation also indicate that the activation energy for metal ion-activated decompositions of hydroperoxides or peroxyesters in NR latex is lower than that of the corresponding fructose-activated decomposition of these peroxides.

5.4 Miscellaneous investigation

The effects of factors besides temperature and peroxide/activator concentrations upon the efficiency of prevulcanization were also investigated.

5.4.1 Effect of non-rubber substances upon prevulcanization

Several HA-latices from different sources were prevulcanized using tBHP withoud added activator. Elemental analysis of the unvulcanized latex was carried out. Table 5.13 shows the levels of various non-rubber substances in the initial latex, together with the degree of crosslinking obtained after 24 hours of prevulcanization with tBHP at 100 °C. The phosphorous content gives a measure of phospholipids and phosphates. The nitrogen content gives a measure of proteins, polypeptides, amino acids and nitrogenous bases. There is no significant correlation between the effectiveness of tBHP as a prevulcanizing agent and the amounts of non-rubber substances in NR latex, notwithstanding the marked variation in the concentrations of some of the non-rubber substances. Perhaps the effects of the non-rubber substances would be more pronounced with more reactive peroxides such as peroxyesters. The contributions of the non-rubber substances to prevulcanization using tBHP appear to be very small as indicated by the low degree of crosslinking obtained. This is probably partly because the metal elements present in NR latex are not in the form of an appropriate complex, nor are they present in the form of soluble and ionized metallic salts or soaps(16,29), nor are they present in appropriate oxidation states. There is no

Table 5.13. Levels of various non-rubber substances in HA latex from different sources, together with prevulcanization behaviour of latex using tBHP at 100 °C

HA-latex	Non-rubber contents[a]									Q[b]
	Cu	Fe	Mn	Zn	Mg	Ca	P	N	soap	(g/g)
A	2.9	6.4	0.3	280	34	11	465	0.37	1.7	11.3
B	0.9	3.2	0.2	44	0.9	6	620	0.30	1.3	10.7
C	4.0	3.3	0.3	130	57	11	490	0.37	3.2	11.4
D	2.3	2.9	0.2	70	26	13	385	0.31	1.4	11.8
E	2.5	2.4	0.2	98	40	22	410	0.30	1.4	10.9

a Cu, Fe, Mg, Mn, Ca is in 10^{-6} g/g total solids; N and soap (expressed as stearic acid) is in percent of total solids.

b Q value obtained after 24 hours of prevulcanization using 1.11×10^{-4} gmol/g rubber of tBHP.

Table 5.14. Effects of coagents on the prevulcanization of NR latex using tBPIB-fructose system at 60 °C

Prevulcanizing system and the coagent	Prevulcanization time(hr)	Q (g/g)
5.55×10^{-5} gmol/g rubber of tBPIB + 1pphr fructose	1 2 3 4	7.4 6.1 5.9 5.8
1.10×10^{-4} gmol/g rubber of tBPIB + 1 pphr fructose + 2 pphr sulphur	1 2 3 4	12.0 9.4 9.3 9.2
5.55×10^{-5} gmol/g rubber of tBPIB + 1 pphr fructose + 1.9 pphr trimethylol propane trimethacrylate	1 2 3 4	5.5 5.0 5.0 5.0
5.55×10^{-5} gmol/g rubber of tBPIB + 1 pphr fructose + 0.3 pphr glutaric dialdehyde	1 3 4	6.3 5.4 5.4

information to suggest the phosphate and ester groups in phospholipids can assist decomposition of hydroperoxides into radicals. The amine groups in proteins, amino acids and polypeptides could probably assist the radical decomposition of tBHP. If this is correct, then it appears that they are considerably less effective than tetraethylene pentamine (TEP). Whitby et al.(162) found that the effectiveness of polyalkylene polyamines in activating the initiation of emulsion polymerization by cumene hydroperoxide reaches a mazimum in TEP and pentaethylene hexamine and then gradually decreases for the higher members of the polyamine series. Perhaps the chain-length of protein and polypeptides, and whether they are present in the serum or rubber phase, influence their performance in promoting peroxide decomposition. Heterolytic reactions of peroxide with the non-rubber substances, nucleophilic substitutions by anions, acid-catalyzed heterolysis and acid-catalyzed addition of peroxide due to the presence of fatty acids and other organic acids would greatly reduce the efficiency of the peroxide prevulcanization of NR latex.

5.4.2 Effect of coagents upon prevulcanization

The use of coagents is intended to increase the crosslinking efficiency of peroxide vulcanizing systems. Table 5.14 shows the effect of sulphur, trimethylpropane trimethacrylate (TMPTM) and glutaric dialdehyde (GDA) on prevulcanization of NR latex using fructose-activated tBPIB system. Tetraethylene glycol dimethacrylate (TEGMA) was also tried but latex became unstable after a short period of heating. This is probably due to rapid homopolymerization of TEGMA. Acrylate and methacrylate esters have a tendency to homopolymerize, thereby reducing their effectiveness as peroxide coagents(163). The presence of sulphur lowered the efficiency of prevulcanization of the tBPIB-fructose system. This is probably due to peroxide free radicals being scavenged by the sulphur(164). Peroxide prevulcanization in the presence of sulphur causes a bad odour possibly due to the formation of alkyl sulphide or mercaptan. The use of TMPTM as a coagent increases the rate of prevulcanization and the efficiency of prevulcanization. A slight increase of rate of prevulcanization is also shown by GDA.

5.4.3 Effect of ammonia concentration upon prevulcanization

Table 5.15 shows the effect of ammonia concentration upon the prevulcanization behaviour of the fructose-activated tBPEH system at 60 °C. The results show that, when the ammonia level increased from 0.7% to 2.1% w/w on latex, the rate of prevulcanization was slightly increased , whereas the efficiency of prevulcanization was slightly decreased. These effects may not be directly due to the increased ammonia content, but to the possible formation of a more active reaction product of fructose and ammonia. In the presence of alkali, fructose can undergo interconversion to glucose and manose(165). Reaction of glucose and ammonia could produce an aldehyde-ammonia addition product(165). Nevertheles, the effect of ammonia upon the prevulcanization behaviour of the fructose-activated peroxyester system is for practical purposes insignificant.

5.4.4 Effect of surfactants upon prevulcanization

Texofor FP170 is a polyethylene oxide-alkyl phenol adduct. Texofor FP170 appears to be a good and efficient emulsifier for peroxyesters and hydroperoxides, whereas potassium caprylate and laurate were rather poor emulsifiers for hydroperoxides, notably tBHP. The emulsifying propensities of the surfactants was compared by observing the tendency for peroxide-surfactant-water mixtures to separate into two phases.

Table 5.16 shows the effects of using different surfactants, Texofor FP170, and potassium caprylate, upon the prevulcanization characteristics of the fructose-activated tBPEH system. The differences between the two surfactants appears to be insignificant in this respect.

Table 5.15. Effect of ammonia on the prevulcanization of NR latex using tBPEH-fructose system* at 60 °C

[Ammonia] (pphl)	Prevulcanization time (hr)	Q (g/g)
0.7	1	15.0
	2	8.5
	3	7.7
	4	6.3
	5	5.8
2.1	1	9.6
	2	7.2
	3	6.3
	4	6.3
	5	6.2

* Using 5.45 x 10^{-5} gmol/g rubber of tBPEH and 1 pphr fructose.

Table 5.16. Effect of surfactants on the prevulcanization of NR latex using tBPEH-fructose systems[a] at 60 °C

Surfactant[b]	Prevulcanization time (hr)	Q (g/g)
Texofor FP170	4	5.6
	6	5.0
potassium caprylate	4	5.8
	6	4.8

a Using 1.09 x 10^{-4} gmol/g rubber of tBPEH and 2 pphr fructose

b Used at 10 % w/w on peroxide .

5.4.5 Effect of storage of latex compound

Storing an unvulcanized latex compound for a period of time, and under conditions such that no decomposition of the peroxide occurred would permit a large fraction of the vulcanizing agents to be imbibed to equilibrium by the latex particles prior to prevulcanization. It will be shown in Chapter 7 that the storage of latex compound prior to prevulcanization has an effect upon the physical properties of films obtained from peroxide-prevulcanized latices. Storage also affects the kinetics of peroxide prevulcanization, as is evident from the results given in Table 5.17. These results show that the storage of unvulcanized latex compound does not appear to affect the ultimate efficiency of prevulcanization of the tBPEH-fructose system, but does significantly slow down the rate of crosslink insertion. This is probably a consequence of the tendency for peroxide to partition in the rubber phase whilst that of fructose in the aqueous phase. Thus, in the case of the stored latex compound, when the partition equilibrium was reached, a fraction of the added peroxide was in the rubber phase, and probably all of the added fructose is in the aqueous phase. In the initial period of prevulcanization (may be the first 2 hours), prevulcanization may be largely attributable to homolytic decomposition of peroxide present in the rubber phase plus some fructose-activated decomposition of peroxide in the aqueous phase. This probably resulted in a lower overall rate of crosslink insertion compared to prevulcanization using latex compound which was not subjected to storage. In the latter case, prevulcanization may be largely attributable to fructose-activated decomposition of the peroxide in the aqueous phase of the latex, over the entire period of prevulcanization. This requires that the alkoxy or also alkyl radicals generated in the aqueous phase must partition in the rubber phase in order to effect crosslinking. Alkoxy and alkyl radicals probably have a greater tendency to partition in the rubber phase than sulphate ion-radical or hydroxyl radical. It has been mentioned earlier that sulphate ion-radical and hydroxyl radical generated in the

Table 5.17. Effect of 'maturation' of latex compound on the prevulcanization of NR latex using tBPEH-fructose system[a] at 60 °C

Mixing procedure	Prevulcn. time (hr)	Q (g/g)
A) emulsified peroxide and fructose were mixed into latex at *ca* 20 °C for 5-10 minutes, and the latex was then prevulcanized	0[b]	56.0
	1	9.7
	2	7.1
	3	6.2
	4	5.5
	5	5.1
	6	4.8
B) emulsified peroxide and fructose were mixed into latex at 3 °C for 2 hours, the latex was then stored at 5 °C for 20 hours before it was prevulcanized	0[c]	55.3
	1	17.7
	2	12.4
	3	8.0
	4	6.9
	5	6.6
	6	5.6
	7	5.1
	8	4.8

[a] Using 1.09 x 10^{-4} gmol/g rubber of tBPEH and 2 pphr fructose.

[b] Unvulcanized latex film.

[c] Sample taken at the end of storage period.

Table 5.18. Post-vulcanization of NR latex cast films using tBPPV-fructose system*

Post-vulcanization		Q
temperature (°C)	time (hr)	(g/g)
70	0*	11.7
	1	12.4
	2	12.3
	3	12.1
	4	11.9
100	0*	11.7
	1	16.3
	2	16.6
	3	15.8

* Cast films were prepared from latex which has been prevulcanized for 1 hour at 60 °C using 5.45 x 10^{-5} gmol/g rubber of tBPPV and 1 pphr fructose.

aqueous phase of NR Latex can initiate polymerization and graft-copolymerization of vinyl monomers in NR latex.

5.4.6 Post-vulcanization using peroxyester-fructose system

The work of Calvert(55) on the post-vulcanization of NR latx films and foams using tBP appears to be the only published reference to the peroxide post-vulcanization of NR latex. However, the state of cure obtained and the properties of the products are not reported by Calvert. Table 5.18 shows that no significant further crosslinking occurs when a latex film containing tBPPV and fructose was post-vulcanized at 70 °C. This is probably attributable to the difficulty in forming an activated peroxyester-fructose complex and to the occurrence of peroxyester 'cage' reactions, in dry latex films. There are probably other secondary reasons, e.g., loss of peroxide by evaporation during drying and heating, thermal oxidative degradation of fructose (indicated by the darkening of the latex films on heating), and oxidation of the rubber as indicated by the high Q-value obtained when latex film was heated at a higher temperature, 100 °C. Oxygen may promote thermal degradation of rubber during peroxide prevulcanization of NR latex. But it appears that the effect of oxygen in the degradation of rubber during post-vulcanization of latex film using peroxide in air-circulating oven is much more significant than that during peroxide prevulcanization of NR latex.

5.4.7 Comparison between peroxide prevulcanization and sulphur prevulcanization of NR latex

Figure 5.2 shows the change in crosslink concentration with prevulcanization time at 60 °C during the prevulcanization of NR latex using (a) the fructose-activated tBPIB system, (b) the ZDEC/ZnO-accelerated sulphur system, and (c) the fructose-activated tBHP system. The concentration of sulphur used in gatom/g rubber is about three times the concentration of tBPIB in gmol/g rubber. The rate of prevulcanization and

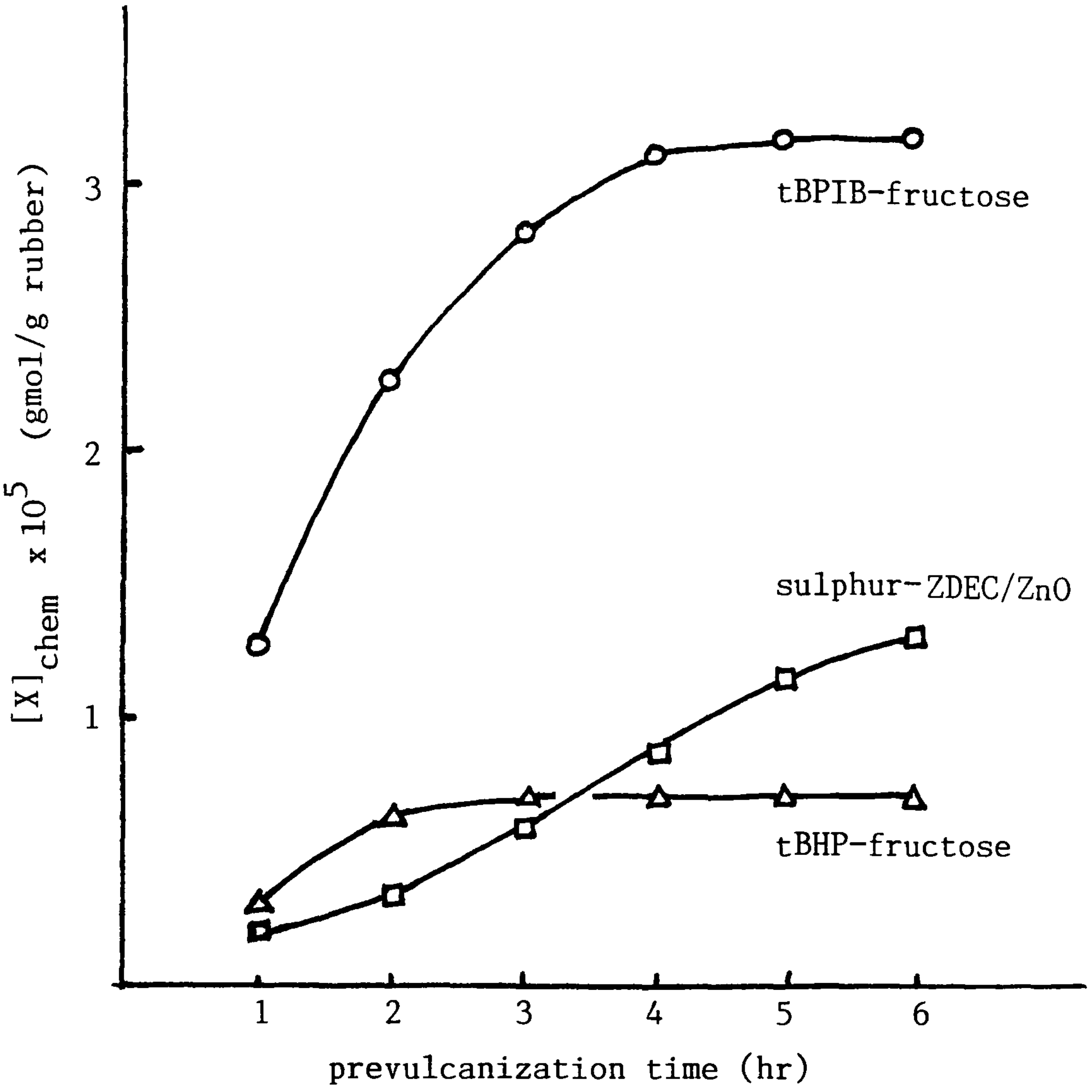


Figure 5.2. $[X]_{chem}$ versus prevulcanization time for peroxide and sulphur prevulcanizing systems at 60 °C; tBPIB & and tBHP were used at 1.11 x 10^{-4} gmol/g rubber, fructose, sulphur, ZDEC and ZnO were used at 2 pphr, 1 pphr, 0.5 pphr and 0.2 pphr respectively.

the efficiency of prevulcanization of the fructose-activated tBPIB system is higher than that of ZDEC/ZnO-accelerated sulphur system. The maximum crosslink concentration obtained by the fructose-activated tBHP system is lower than the ZDEC/ZnO-accelerated sulphur system. The overall rate of crosslink insertion of these two systems appears not to be significantly different. Factors which may contribute to the inefficiency of peroxide prevulcanizing systems have been discussed in the preceding sections. For the ZDEC/ZnO-accelerated sulphur prevulcanizing system, the inefficiency of crosslinking is attributed to the amount of uncombined sulphur(18,21), the limitation of the amount of sulphur that can combine with rubber network(21), and the formation of di-sulphidic and poly-sulphidic crosslinks. In peroxide prevulcanization, crosslinking reactions presumably stop when all the peroxide molecules added initially have decomposed. In ZDEC/ZnO-accelerated sulphur prevulcanization, prevulcanization still proceeds with prolonged heating, though at a slower rate. This is due to the increase in the combined sulphur if the maximum network-combined sulphur is not yet attained, and also to the rearrangement of poly-sulphidic crosslinks to form di-sulphidic and mono-sulphidic crosslinks(18).

5.4.8 Comparison between peroxide prevulcanization of NR latex and peroxide vulcanization of dry NR

Dicumyl peroxide (DCP) is the most widely used peroxide for the vulcanization of dry NR. A detailed comparison between the kinetics of NR latex prevulcanization using fructose-activated tBPIB system and NR vulcanization using DCP will be given in the next chapter. The shapes of crosslink concentration-time curves for the peroxide prevulcanization of NR latex and peroxide vulcanization of NR(69) are generally similar. Peroxide prevulcanization of NR latex using peroxyester or hydroperoxide systems is considerably less efficient than is the peroxide vulcanization of dry NR using DCP. This is probably attributable to the differences in the amounts and types of non-rubber substances in NR latex and in dry NR, differences in the vulcanization kinetics between NR latex and dry NR, and differences in the reaction chemistry of the two peroxides.

5.5 Summary

The effectiveness of a peroxide prevulcanizing systems was found to depend significantly upon the nature of the peroxide and activator used. Fructose-activated peroxyester prevulcanizing systems were found to be generally more effective than other activated peroxide systems. Some of the experimental results seem to indicate that for the fructose-activated peroxide system, the activation of peroxide decomposition tends to occur in the aqueous phase, and the free radicals generated partition in the rubber phase to effect crosslinking. Schematic diagrams of the partition of compounding ingredients in NR latex during prevulcanization, for activated and non-activated peroxide prevulcanizing systems, will be shown in the next chapter. Amongst the peroxide prevulcanizing systems investigated, fructose-activated tBPIB system was found to be the most effective at 60 °C - 80 °C. The tensile strength property of films obtained from the prevulcanized latex is generally better than that of films obtained from other peroxide-prevulcanized latices. A detailed kinetic study of the prevulcanization of NR latex using fructose-activated tBPIB system was made, and the results of the investigation will be reported in Chapter 6.

CHAPTER 6

KINETICS OF NR LATEX PREVULCANIZATION USING tBPIB-FRUCTOSE SYSTEM

6.1 Introduction

The fructose-activated tBPIB system was selected for a detailed kinetic study of peroxide prevulcanization of NR latex. This is because the system was found to be an effective prevulcanizing system, and it yielded prevulcanized latex films which had good physical properties. The effects of selected reaction variables upon the decomposition kinetics of tBPIB and the formation of crosslinks were investigated. The data from this investigation were used to obtain the rates and activation parameters for peroxide decomposition and crosslink formation. Additionally, the crosslinking efficiency for the prevulcanization reaction was obtained, as also was the rate equation for the decomposition of tBPIB in the presence of added fructose in NR latex.

The peroxide prevulcanization of NR latex involves the diffusion of peroxide molecules or radicals from the aqueous phase to the rubber phase. Figures 6.1a and 6.1b show schematic diagrams of partition of peroxide molecules and free-radicals in NR latex for a non-activated and an activated system respectively. Figure 6.1b shows that the activators (fructose, metal ion M^{++} and amines) are not partitioned in the rubber phase. Some of the experimental evidence obtained in Chapter 5 suggests that this is probably the case for fructose. Besides, fructose has a high miscibility in water, therefore probably has a great tendency to partition in the aqueous phase of the latex. Figure 6.1c shows that peroxide molecules may be adsorbed at the latex particle surface. The free radicals generated at the adsorbed layer of the latex particle probably tend to pass into the rubber. This manner of peroxide decomposition surely leads to a more efficient utilization of free radicals for crosslinking than if the

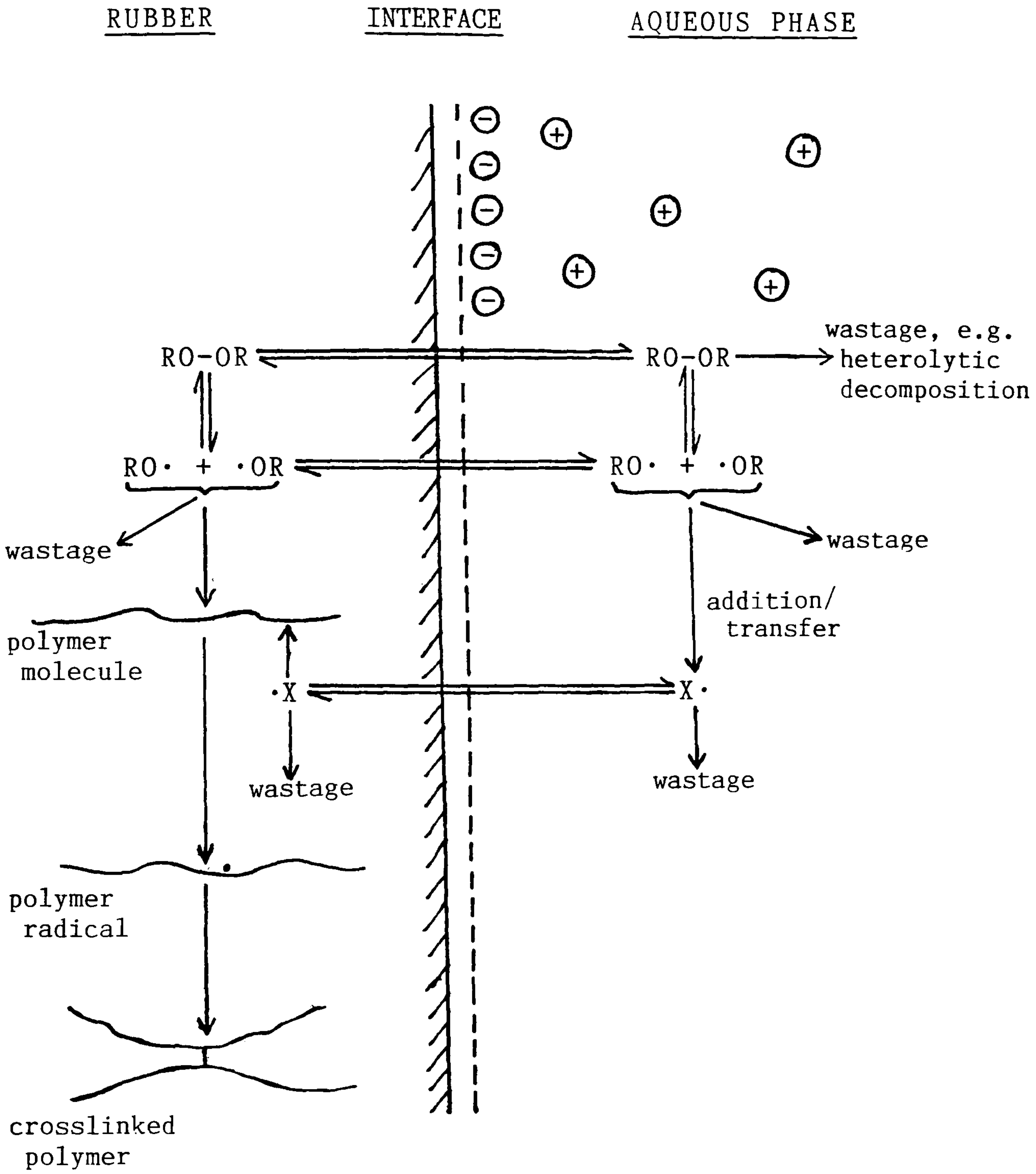


Figure 6.1a. Schematic diagram of partition of peroxide and free-radicals between the rubber phase of a latex particle and the aqueous phase, showing their reactions in latex when using a non-activated peroxide vulcanizing system.

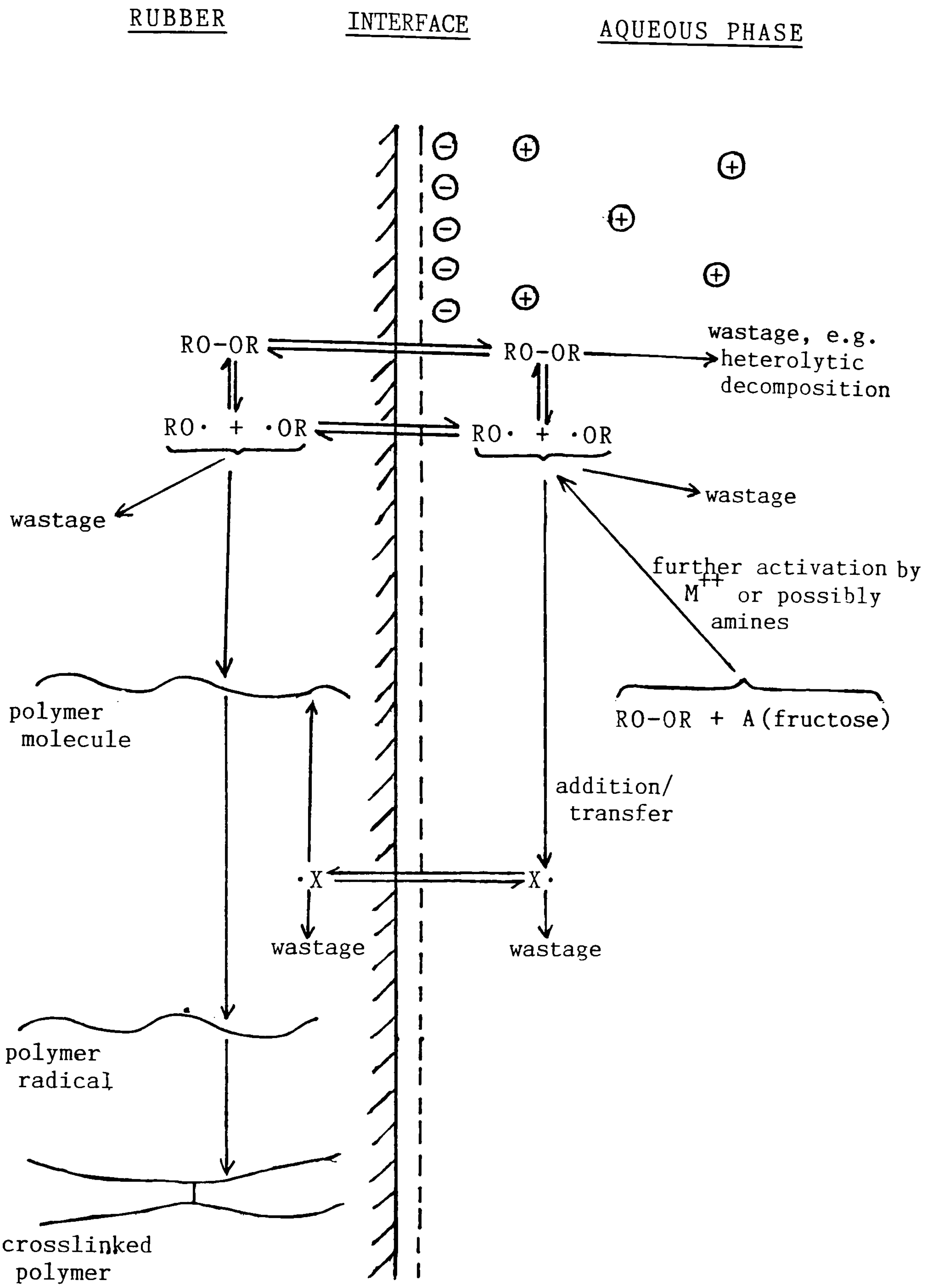


Figure 6.1b. Schematic diagram of partition of peroxide and free-radicals between the rubber phase of a latex particle and the aqueous phase, showing their reactions in latex when using an activated peroxide vulcanizing system.

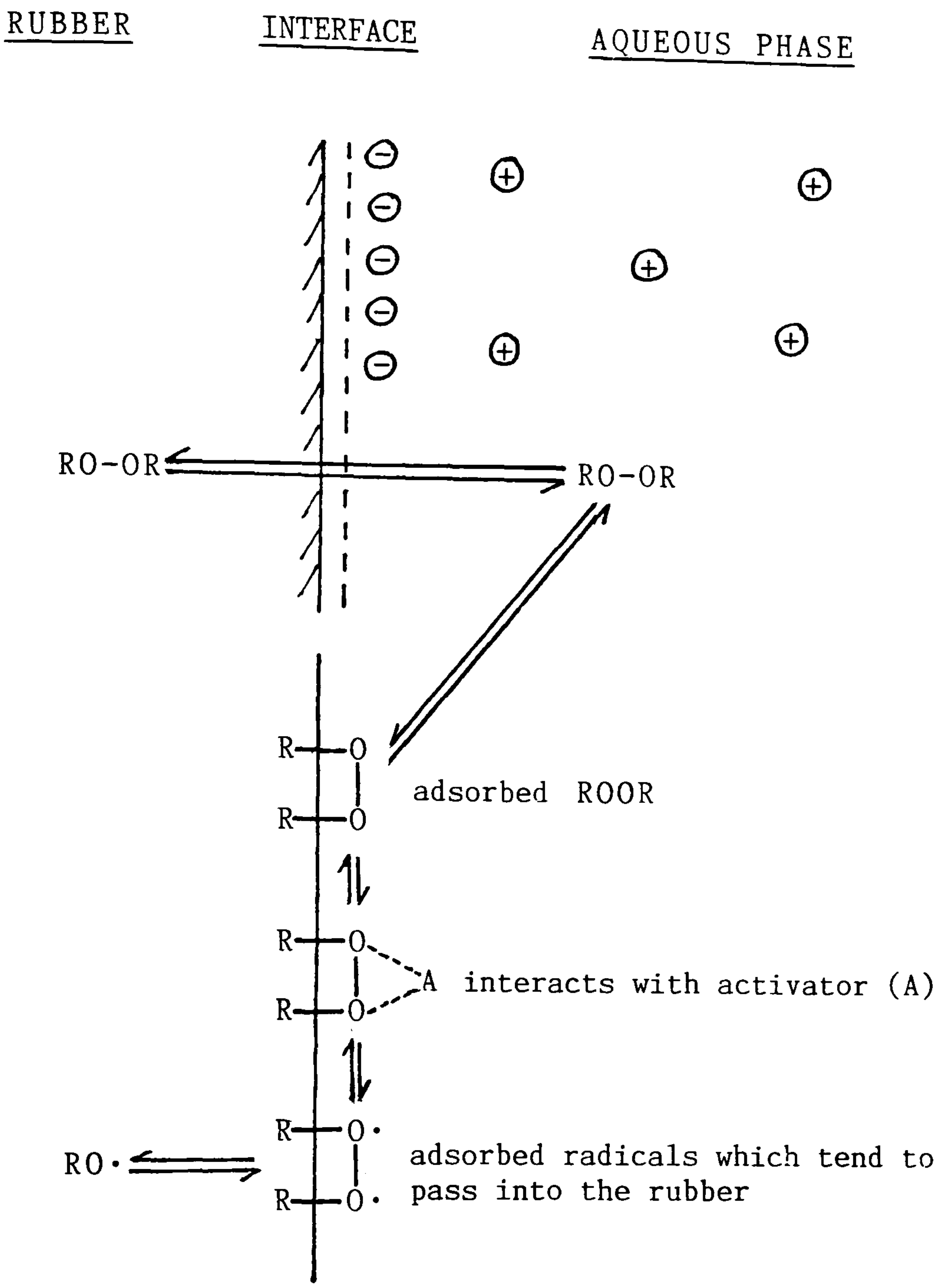


Figure 6.1c. Schematic diagram of partition of peroxide and free-radicals between the rubber phase of a latex particle and the aqueous phase, showing adsorbed peroxide and free-radicals at the latex particle surface.

decomposition occurs in the aqueous phase. FigureS 6.1a and 6.1b also show that, the free radicals generated from the decomposition of peroxide in the aqueous phase may transfer their activity to the non-rubber substances, forming another radicals (X·) which may participate in the crosslinking of the rubber.

6.2 Decomposition of tBPIB and reaction order

Figure 6.2 shows the decrease in the concentration of tBPIB with prevulcanization time at 60 °C for a system which initially contained 5.56×10^{-5} gmol/g rubber tBPIB and 1 pphr fructose. A plot of -ln [tBPIB] against prevulcanization time produced a straight line, as shown in Figure 6.3. The decomposition of tBPIB is therefore a first-order reaction. The slope of the line in Figure 6.3 gives k' equal to 2.31×10^{-4} sec^{-1}, the first-order rate coefficient for the decomposition. A second-order plot (Figure 6.4) and a half-order plot (Figure 6.5) for other tBPIB-fructose systems produced curvilinear lines. 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.

6.3 Crosslink formation and reaction order

Figure 6.6 shows the change of chemical crosslink concentration, $[X]_t$, with prevulcanization time at 60 °C for a system which initially contained 5.56×10^{-5} gmol/g rubber tBPIB and 1 pphr fructose. The suffix 'chem' which denotes chemical crosslink is ommited for simplicity, and the suffix t is to denote time. Figure 6.7 shows that a plot of $-\ln [X]_t/[X]_\infty$ against prevulcanization time, where $[X]_\infty$ is the maximum crosslink concentration achieved by the system is linear. Thus crosslink formation in the vulcanization of NR latex using the tBPIB-fructose system is a first-order reaction. The slope of the line in Figure 6.7 gives k" equal to 1.62×10^{-4} sec^{-1}, the first-order rate coefficient for crosslink formation. First-order crosslink

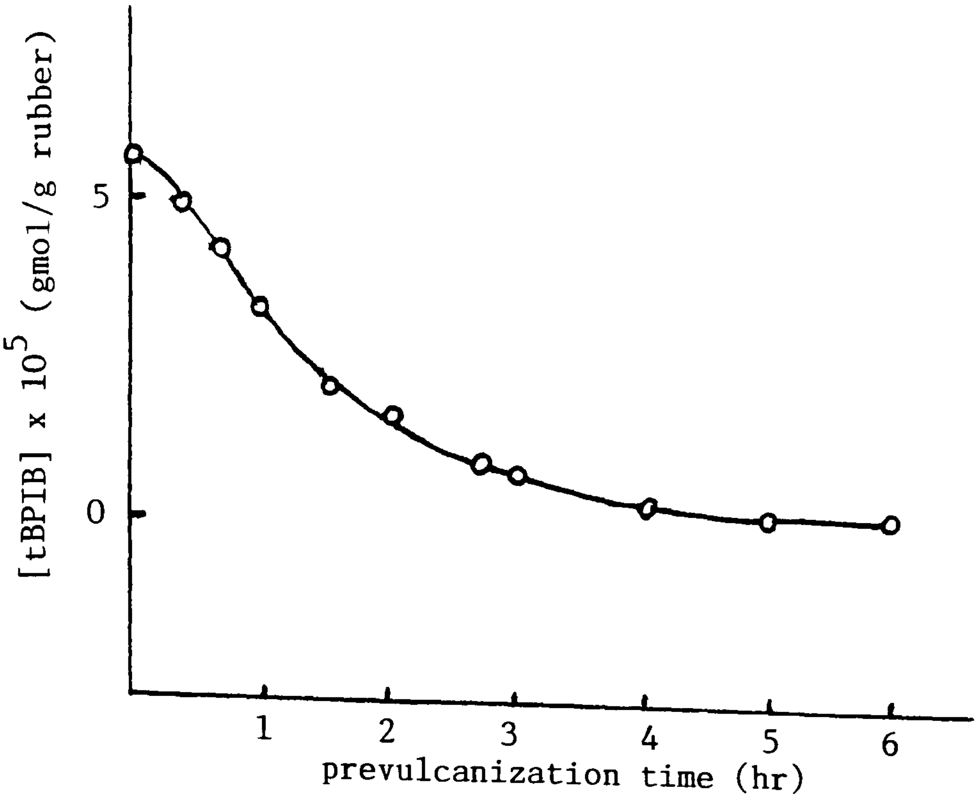


Figure 6.2. Decrease of [tBPIB] with prevulcanization time at 60 °C for a system which initially contained 5.56 x 10^{-5} gmol/g rubber tBPIB and 1 pphr fructose.

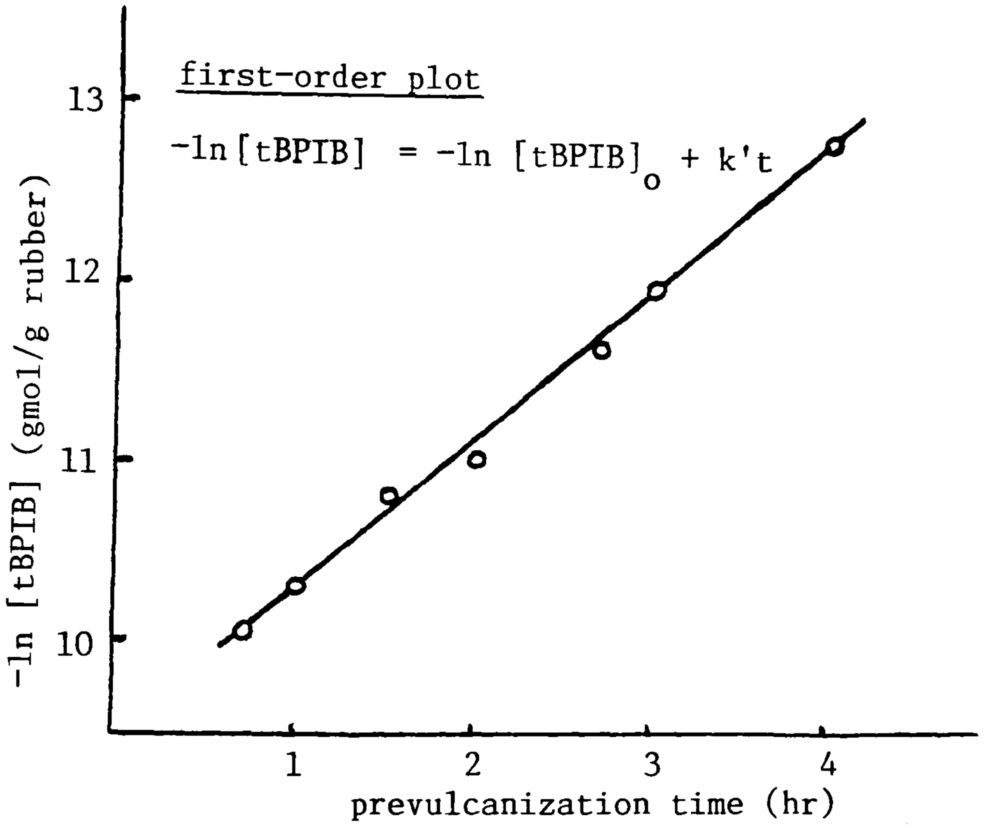


Figure 6.3. First-order plot for tBPIB decomposition in NR latex at 60 °C for a system which initially contained 5.56 x 10^{-5} gmol/g rubber tBPIB and 1 pphr fructose.

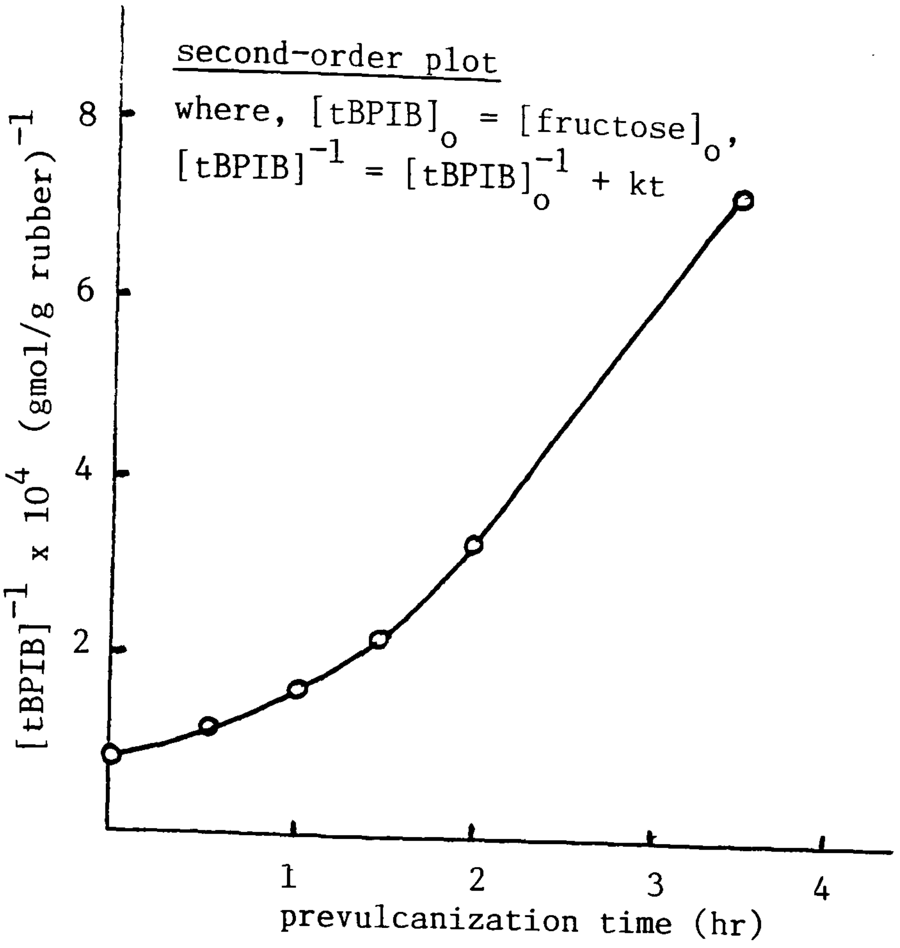


Figure 6.4. Second order plot for tBPIB decomposition in NR latex at 60 °C for a system which initially contained 1.11×10^{-4} gmol/g rubber each of tBPIB and fructose.

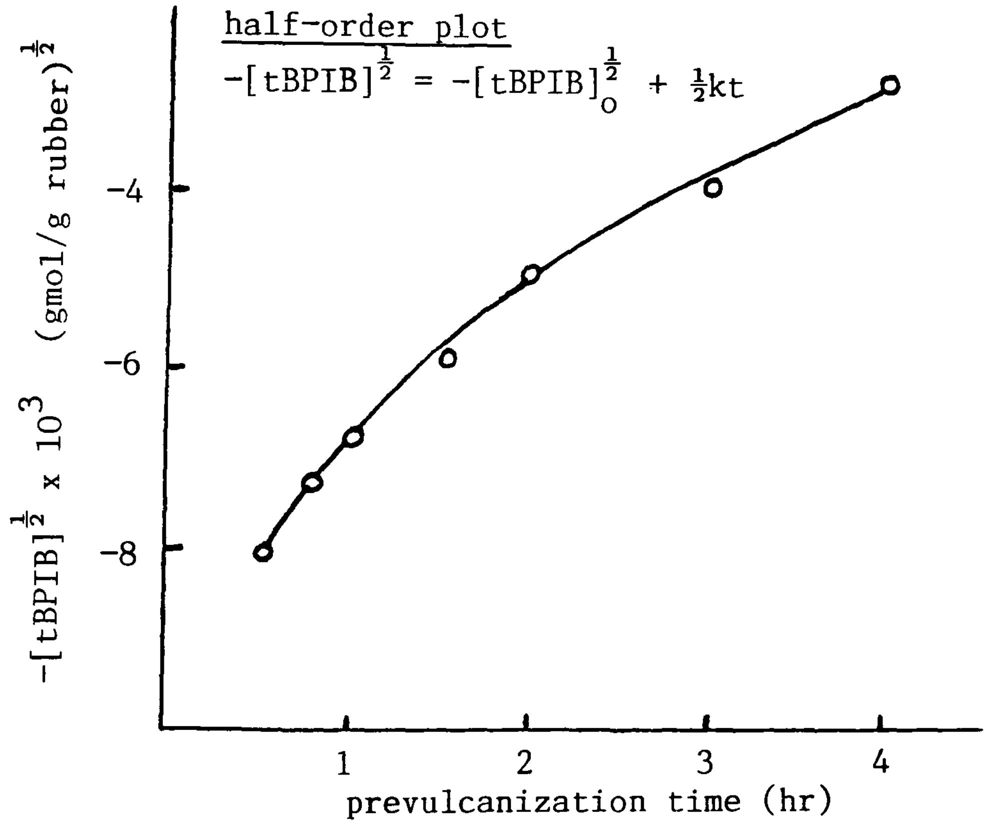


Figure 6.5. Half-order plot for tBPIB decomposition in NR latex at 60 °C for a system which initially contained 1.11×10^{-4} gmol/g rubber each of tBPIB and fructose

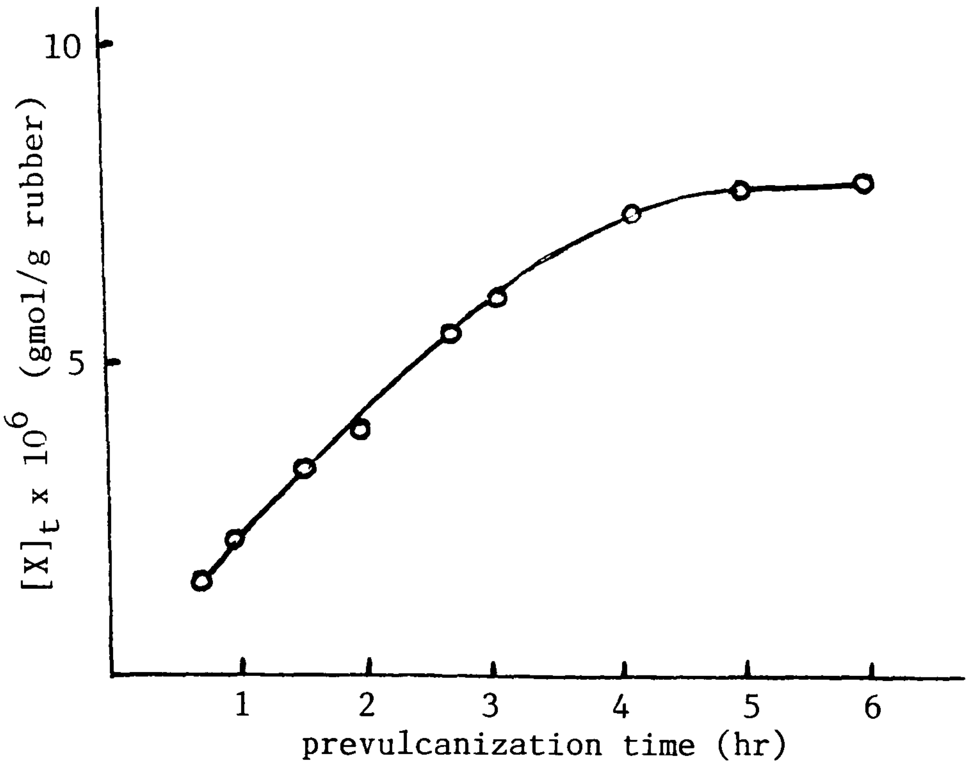


Figure 6.6. Change of concentration of chemical crosslinks with prevulcanization time at 60 °C for a system which initially contained 5.56 x 10^{-5} gmol/g rubber tBPIB and 1 pphr fructose.

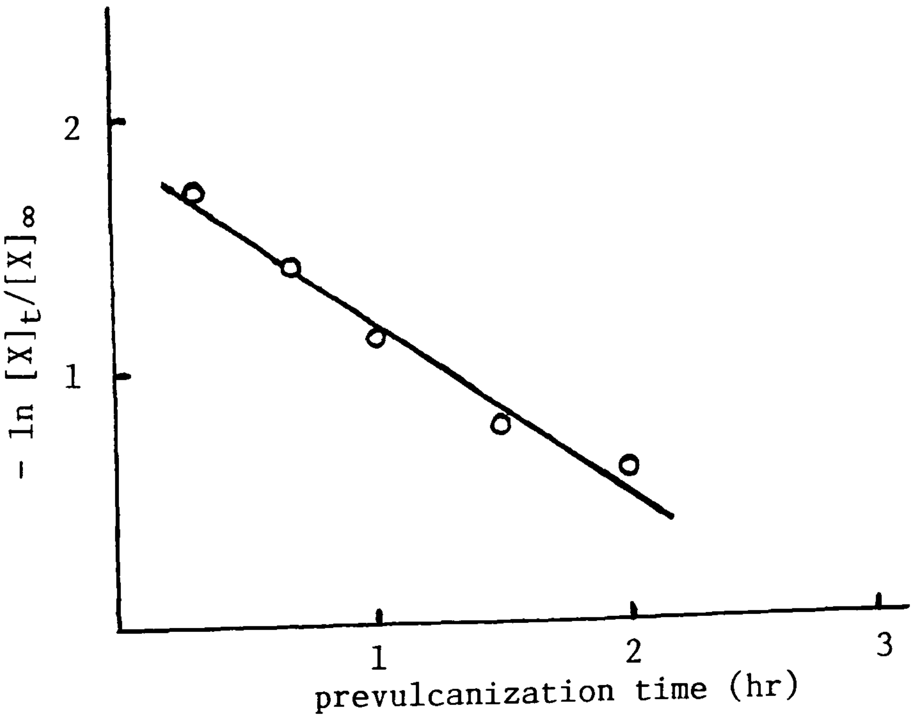


Figure 6.7. Plot of $-\ln [X]_t/[X]_\infty$ against prevulcanization time at 60 °C for a system which initially contained 5.56 x 10^{-5} gmol/g rubber tBPIB and 1 pphr fructose.

insertion was also observed when using other reaction conditions, both for fructose-activated and for non-activated tBPIB systems.

6.4 Crosslink efficiency of tBPIB systems

The crosslinking efficiency f_∞ is the ratio of $[X]_\infty$ to initial tBPIB concentration. The crosslinking efficiency F_t is obtained from the slope of $[X]_t$ versus $[tBPIB_d]_t$ curve, as shown in Figure 6.8. $[tBPIB_d]_t$ represents the concentration of tBPIB which has decomposed after time t. The relationship between F_t and prevulcanization time is shown in Figure 6.9. Figures 6.8 and 6.9 indicate that there is a short induction period before the crosslinking reaction begins. This is a consequence of an induction period for the decomposition of tBPIB (Section 6.5) which probably arises from the need to establish equilibrium as regards the temperature of the latex and distribution of vulcanizing agents in the latex. Also, a small fraction of free radicals derived from the tBPIB could have been wasted by reaction with the non-rubber substances, such as natural antioxidants, during the establishment of equilibrium conditions. The results also indicate that F_t increases linearly with prevulcanization time. This is in contrast to the prevulcanization of NR by DCP(74), where F_t remains constant throughout the reaction time and is equal to approximately 100%. The increase in F_t with prevulcanization time is possibly a consequence of decrease in the concentration of free-radical scavengers from the non-rubber substances as prevulcanization proceeds. With this hypothesis, the linear relationship between F_t and the concentration of free-radical scavengers, $[X^*]$, can be written:

$$F_t = F_\infty - k_1[X^*] \qquad (6.1)$$

where F_∞ is the maximum value of F_t and k_1 is a proportionality constant. Because dF_t/dt is constant, the rate of decrease of the concentration of X* is also constant. The intergrated rate equation for [X*] can be written:

$$[X^*] = -k_2t + c \qquad (6.2)$$

where k_2 is the rate coefficient for the decrease of the

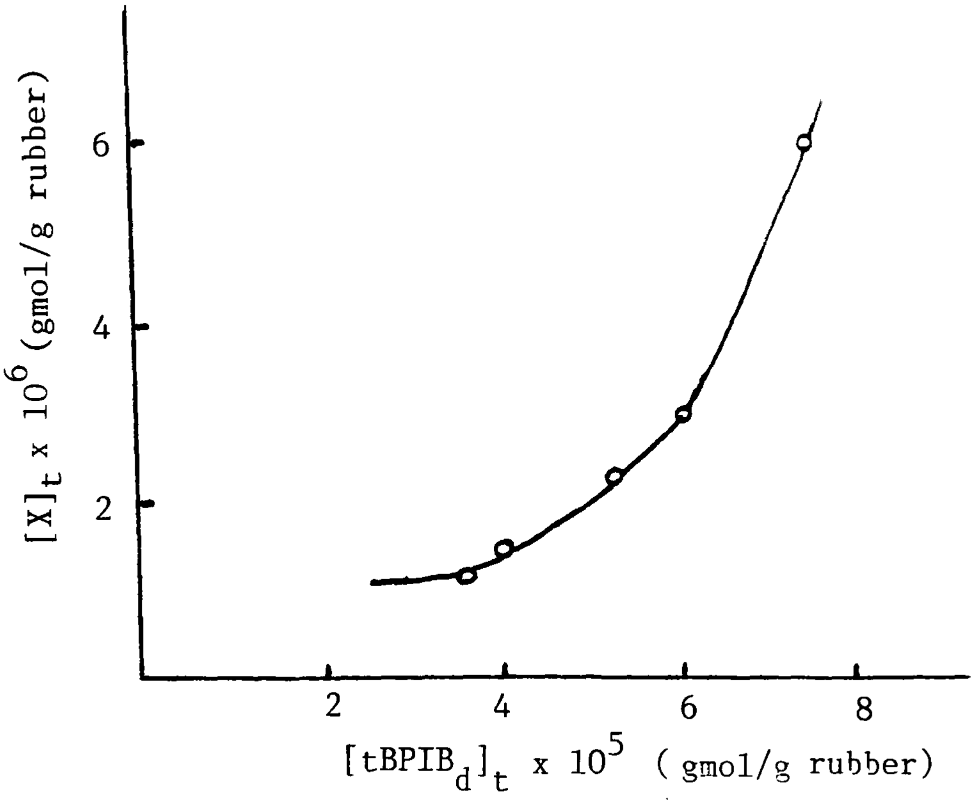


Figure 6.8. Relationship between concentration of chemical crosslinks and concentration of tBPIB decomposed at 60 °C for a system which initially contained 1.11×10^{-4} gmol/g rubber tBPIB and 1 pphr fructose.

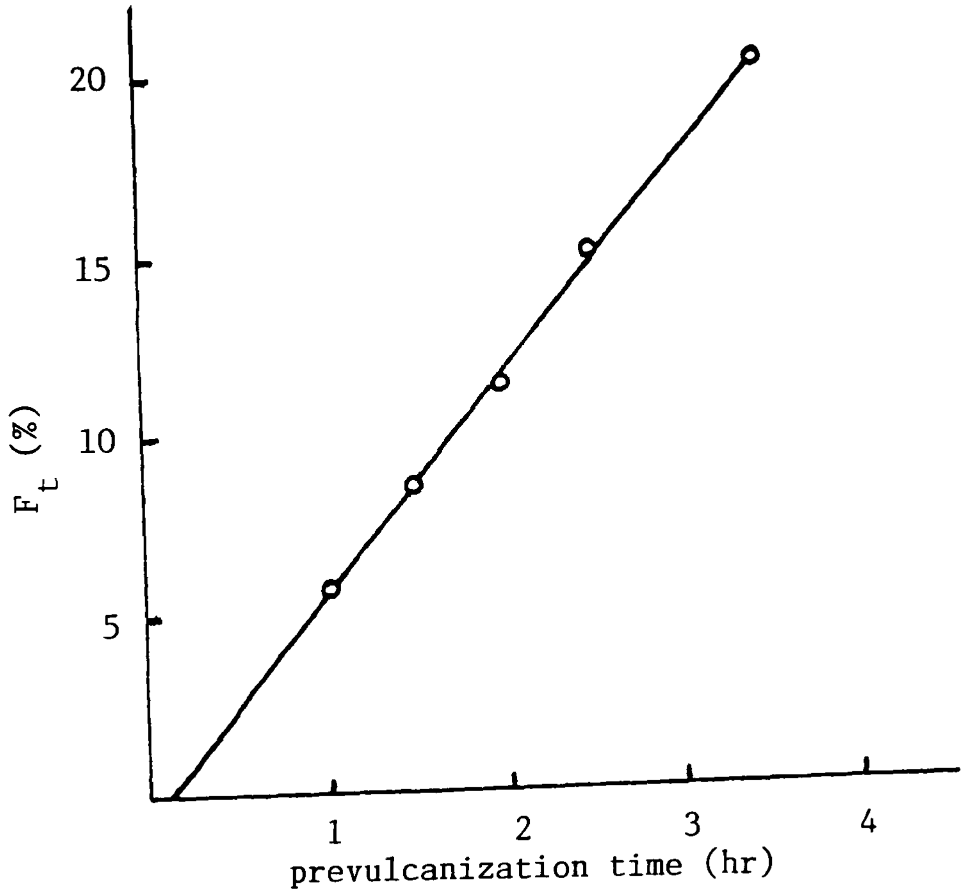


Figure 6.9. Variation of crosslinking efficiency F_t with prevulcanization time at 60 °C for a system which initially contained 1.11×10^{-4} gmol/g rubber tBPIB and 1 pphr fructose.

concentration of free-radical scavengers and c is a constant. When t=0, c is equal to $[X^*]_o$, the initial concentration of free-radical scavengers. Putting the value of $c=[X^*]_o$ into Equation 6.2, and then substituting the resultant value of $[X^*]$ into Equation 6.1, gives

$$F_t = F_\infty - k_1[X^*]_o + k_1k_2t \qquad (6.3)$$

Equation 6.4 indicates that F_t increases in direct proportion to t. The results in Figure 6.9 can also be expressed by

$$F_t = F_o + k_3t \qquad (6.4)$$

where F_o is the value of F_t at t=0, and k_3 is the slope of the line obtained from the plot of F_t against t. Equation 6.4 is equivalent to that of Equation 6.3.

The results in Figures 6.9 and 6.10 indicate that F_o and k_3 are constants only for a given set of reaction conditions. It appears that the values of F_o and k_3 increases with increasing temperature. The increase of the value of F_o with increasing temperature is a consequence of the increase in the value of F_∞. The reason for the increase of the value of F_∞ with increasing temperature will be explained in the next section. The increase of the value of k_3 with increasing temperature is a consequence of the increase in the rate coefficient k_2 for the decrease of $[X^*]$ as a result of the increase in the rate of generation of free-radicals. The value of F_o tends to be negative for many reaction systems. This implies that the value of $k_1[X^*]_o$ is greater than F_∞ for these systems.

The effects of the non-rubber substances probably also account for the increase in the crosslinking efficiency f_∞ with increasing initial tBPIB concentration, which is shown in Figure 6.11. In this case the relative fraction of free radicals wasted by the non-rubber substances probably decreases with increasing

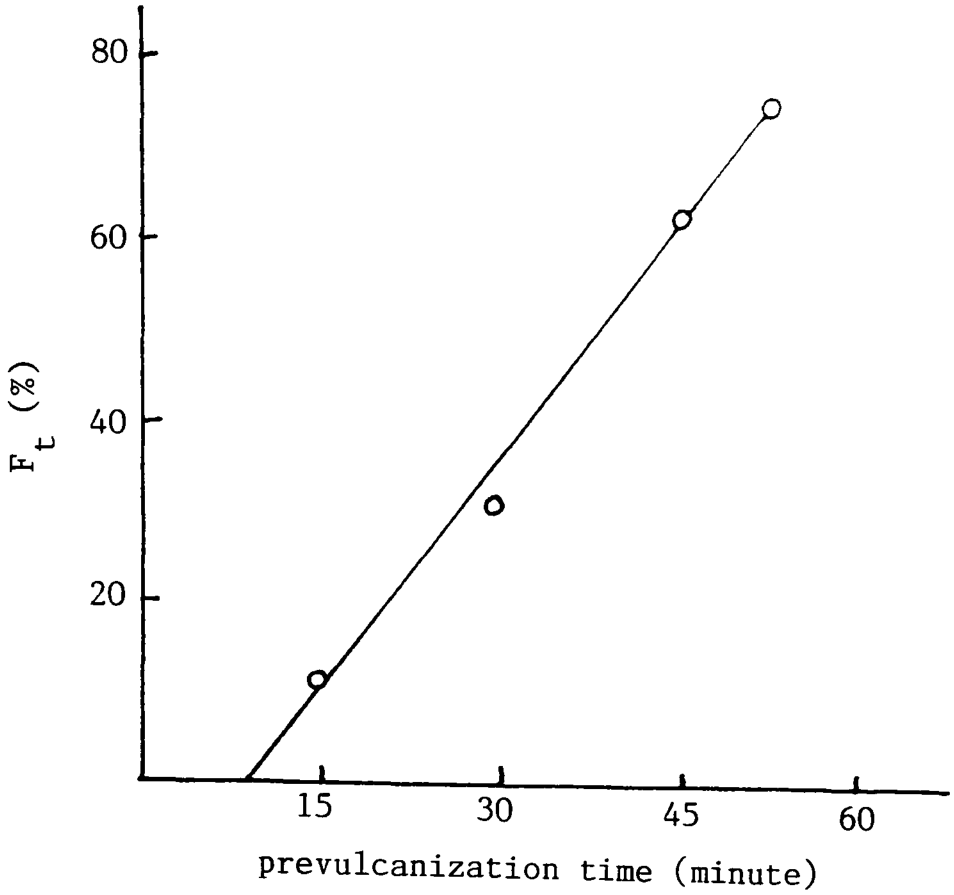


Figure 6.10. Variation of crosslinking efficiency F_t with prevulcanization time at 80 °C for a system which initially contained 1.11 x 10^{-4} gmol/g rubber tBPIB and 1 pphr fructose.

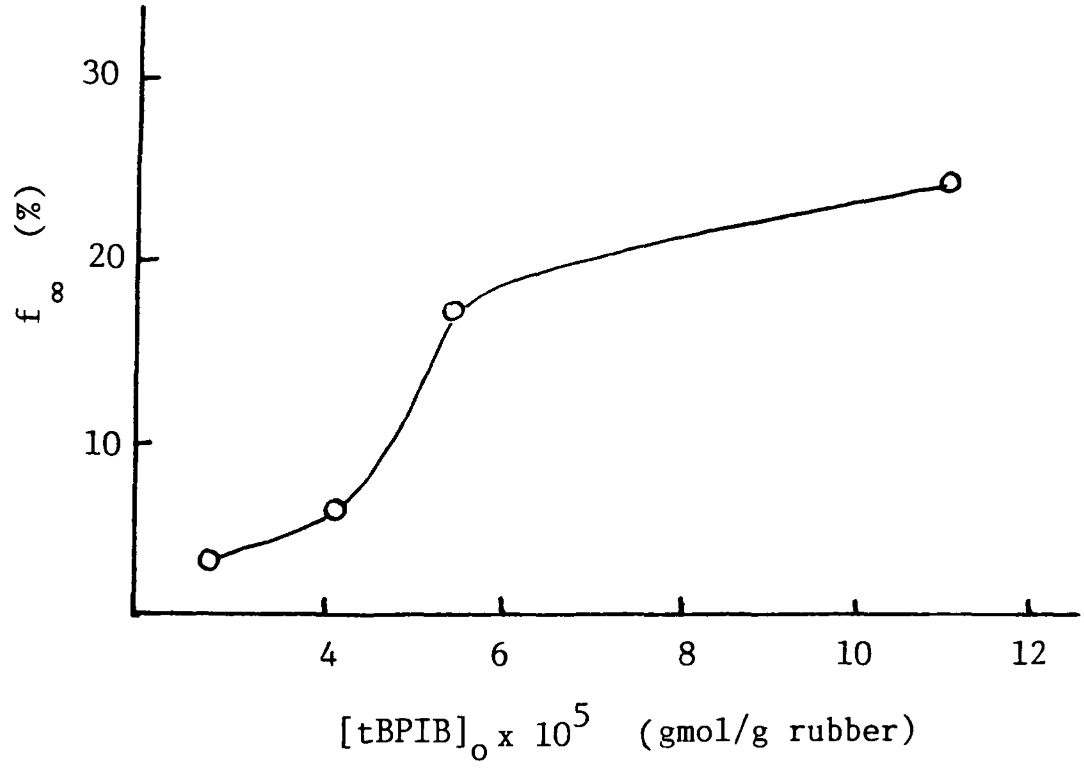


Figure 6.11. Effect of initial tBPIB concentration upon crosslinking efficiency f_∞ at 60 °C using equimolar tBPIB and fructose concentrations.

initial tBPIB concentration. However, the value of f_∞ never exceeds ca. 25% with further increase of $[tBPIB]_o$. This is possibly because the ratio of the concentration of peroxide and free-radicals partitioned in the aqueous phase to that partitioned in the rubber is not significantly affected by the increase in $[tBPIB]_o$. The low value of f_∞ is consequences of many wastages of the peroxide and the radicals generated as depicted in Figure 6.1b. Additionally, activated decomposition of peroxide yields a radical and a negative ion. Theoretically, with this type of peroxide decomposition, the maximum value of f_∞ that can be achieved by a system is 50%.

6.5 Effects of reaction variables upon k', k'', f_∞ and F_t

Figures 6.12-6.14 show plots of -ln [tBPIB] against prevulcanization time at various temperatures for systems which initially contained different concentrations of tBPIB and fructose. The slopes of the lines in Figures 6.12-6.15 give the rate coefficients (k') for the decomposition of tBPIB. In general, if other conditions are kept constant, the value of k' increases with increasing initial fructose concentration and increasing temperature. Further discussion as regards the effects of certain reaction variables upon k' will be given later. The lines produced from the plots of -ln [tBPIB] against prevulcanization time should intersect the ordinate-axis at points which correspond to the concentrations of tBPIB initially added. However, the results shown in Figures 6.12-6.15 indicate that these lines tend to intersect the ordinate-axis at points which correspond to higher tBPIB concentrations than that initially added. This is a consequence of a short induction period for the decomposition of tBPIB. Factors that increase the rate of crosslink insertion appear to shorten the induction period for tBPIB decomposition. Figure 6.15 indicates the induction period for tBPIB decomposition for a tBPIB-fructose system at 50 °C.

Figures 6.16-6.18 show plots of $-\ln [X]_t/[X]_\infty$

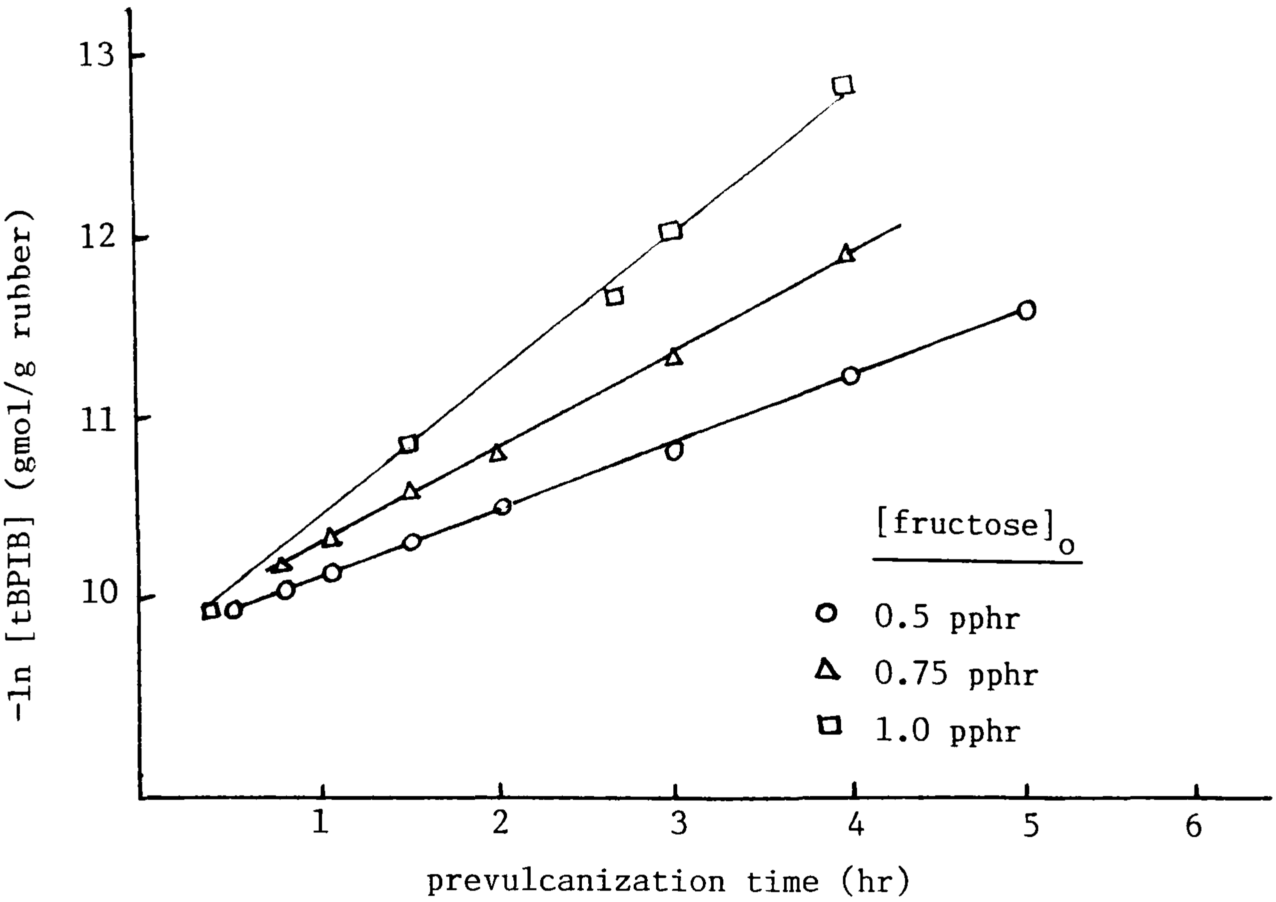


Figure 6.12. First-order plots for tBPIB decomposition in NR latex at 60 °C for systems which initially contained 5.56 x 10^{-5} gmol/g rubber tBPIB and different concentrations of fructose.

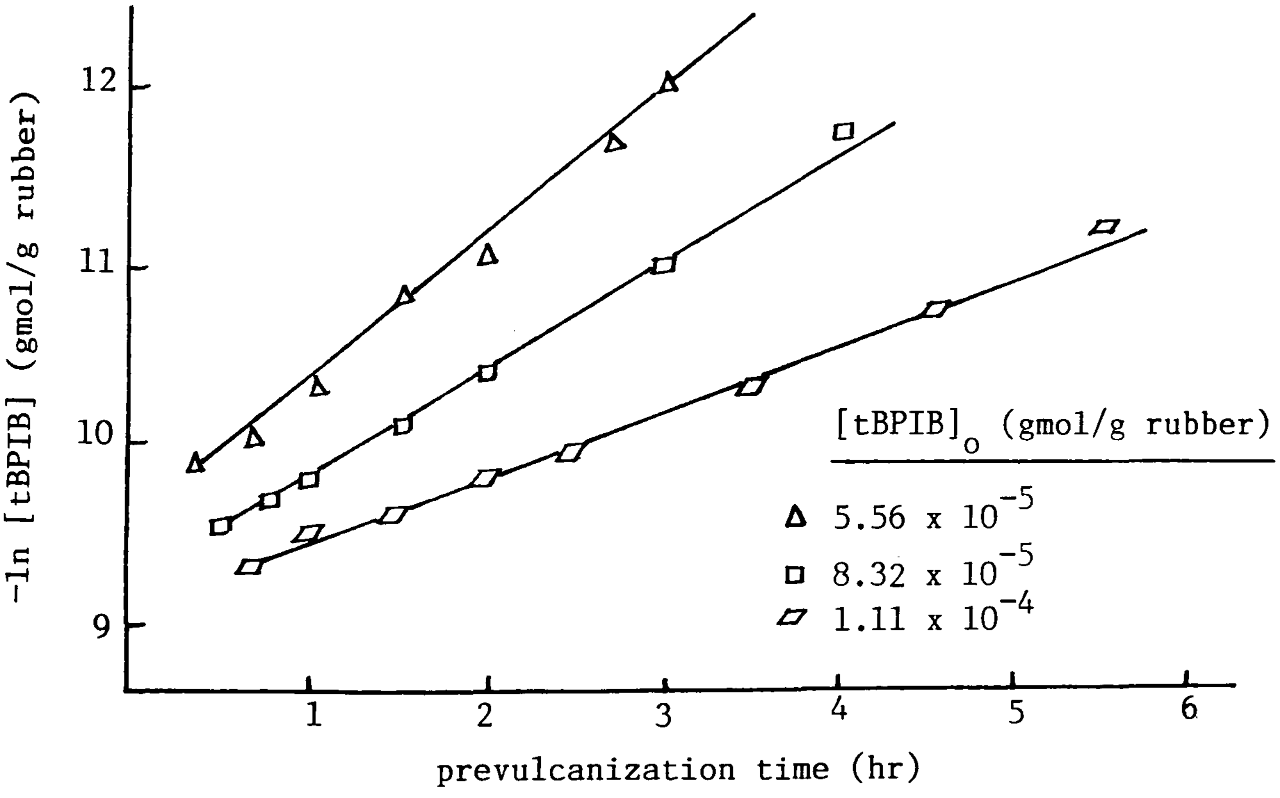


Figure 6.13. First-order plots for tBPIB decomposition in NR latex at 60 °C for systems which initially contained 1 pphr fructose and different concentrations of tBPIB.

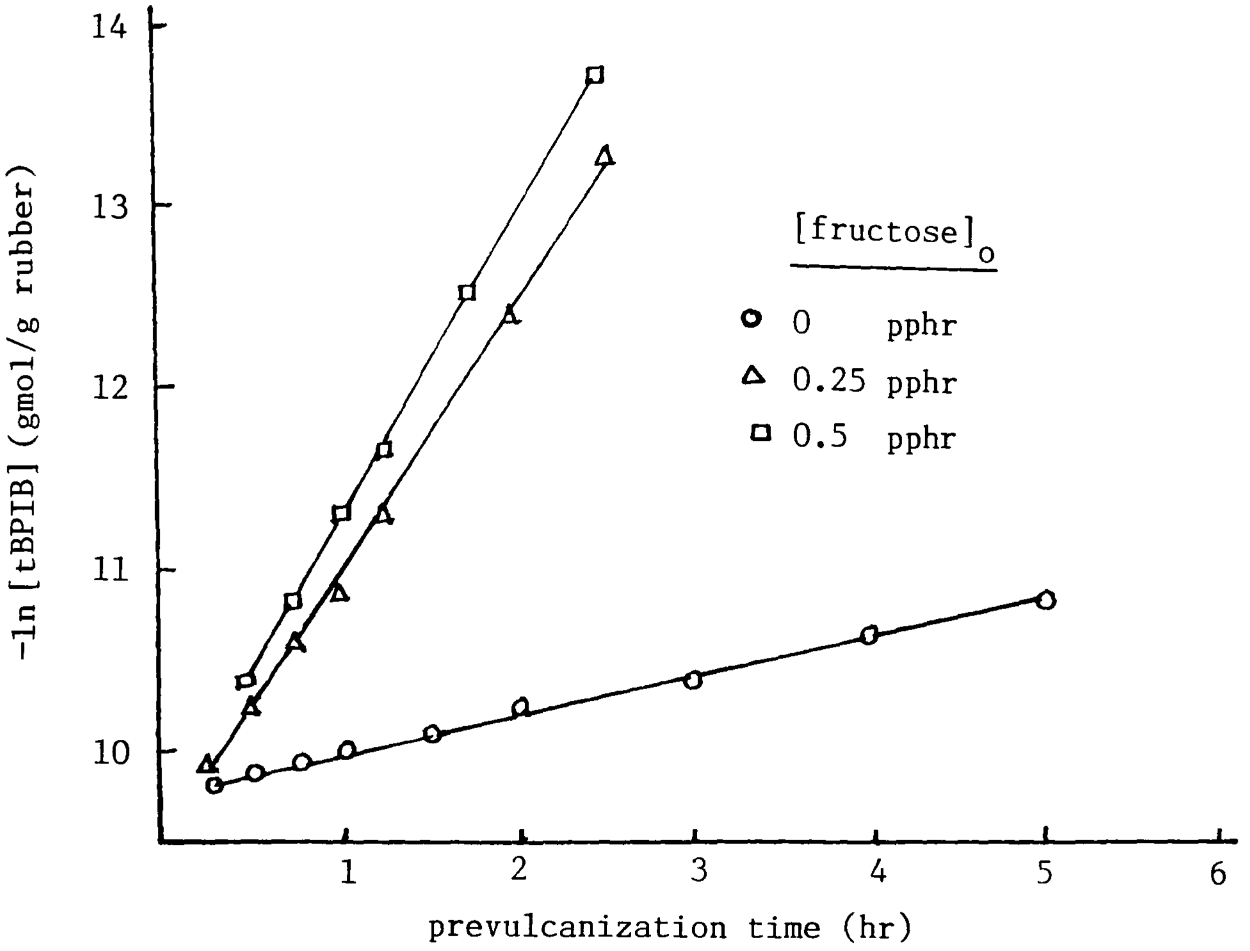


Figure 6.14. First-order plots for tBPIB decomposition in NR latex at 80 °C for systems which initially contained 5.56 x 10^{-5} gmol/g rubber tBPIB and different concentrations of fructtose.

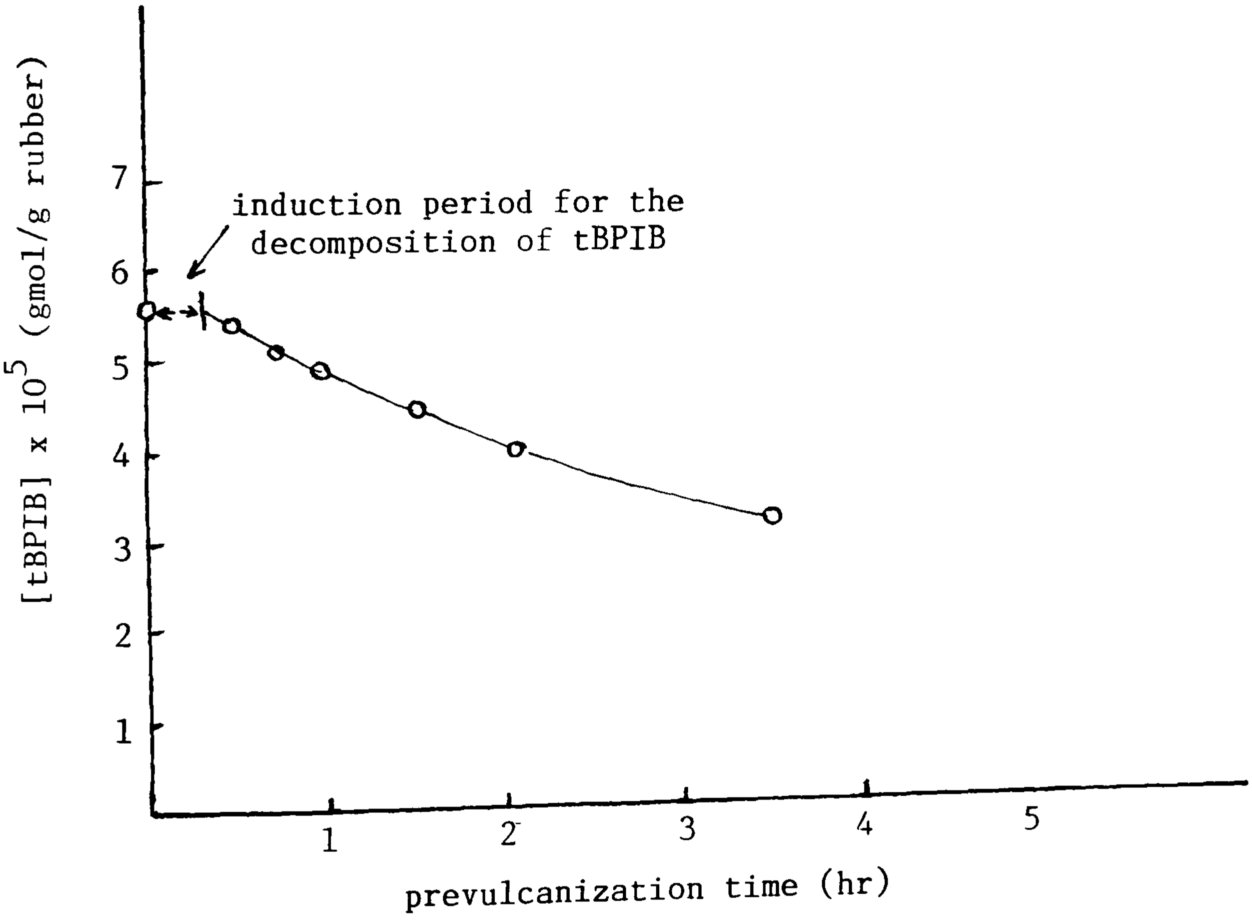


Figure 6.15. Decrease of [tBPIB] with prevulcanization time at 50 °C for a system which initially contained 5.56 x 10^{-5} gmol/g rubber tBPIB and 1 pphr fructose.

against prevulcanization time at various temperatures for systems which initially contained different concentrations of tBPIB and fructose. The minus slopes of the lines in Figures 6.16-6.18 give the rate coefficients (k") for the crosslink formation. In general, if other conditions are kept constant, the value of k" increases with increasing initial fructose concentration and increasing temperature. Figure 6.17 indicates that, the value of k" at 60 °C increases and then decreases with increasing initial tBPIB concentration in the range $2.78 \times 10^{-5} - 1.11 \times 10^{-4}$ gmol/g rubber, at a constant initial fructose concentration of 1 pphr. The initial increase of k" with increasing initial tBPIB concentration is probably because of the relative increase in the ratio of the number of radicals available for crosslinking to that wasted by reactions with non-rubber substances. The decrease of k" at a higher initial tBPIB concentration is a consequence of the decrease in the $[\text{fructose}]_o/[\text{tBPIB}]_o$ ratio . The results in Figure 6.16 show that k" decreases with decreasing $[\text{fructose}]_o/[\text{tBPIB}]_o$ ratio. Most of the lines shown in Figures 6.16-6.18 intersect at different points on the ordinate-axis. This is consequences of the variation of the induction period for crosslink formation and the variation of $[X]_\infty$ from one system to another, and that the value of $[X]_t$ being not equal to zero at the zeroth hour, i.e., it is equal to the crosslink concentration of unvulcanized latex films.

Figure 6.19 shows the effect of $[\text{tBPIB}]_o$ upon k' for tBPIB in NR latex at 60 °C for systems containing equimolar initial concentration of tBPIB and fructose. The value of k' remains constant within experimental error over a range of initial tBPIB concentration, but is slightly reduced at a higher initial tBPIB concentration. Figure 6.20 shows that k' and k" increase with increasing initial fructose concentration and temperature at constant initial tBPIB concentration. Figure 6.21 shows that the values of k' and k" for both the non-activated and fructose-activated systems increase significantly with increasing temperature.

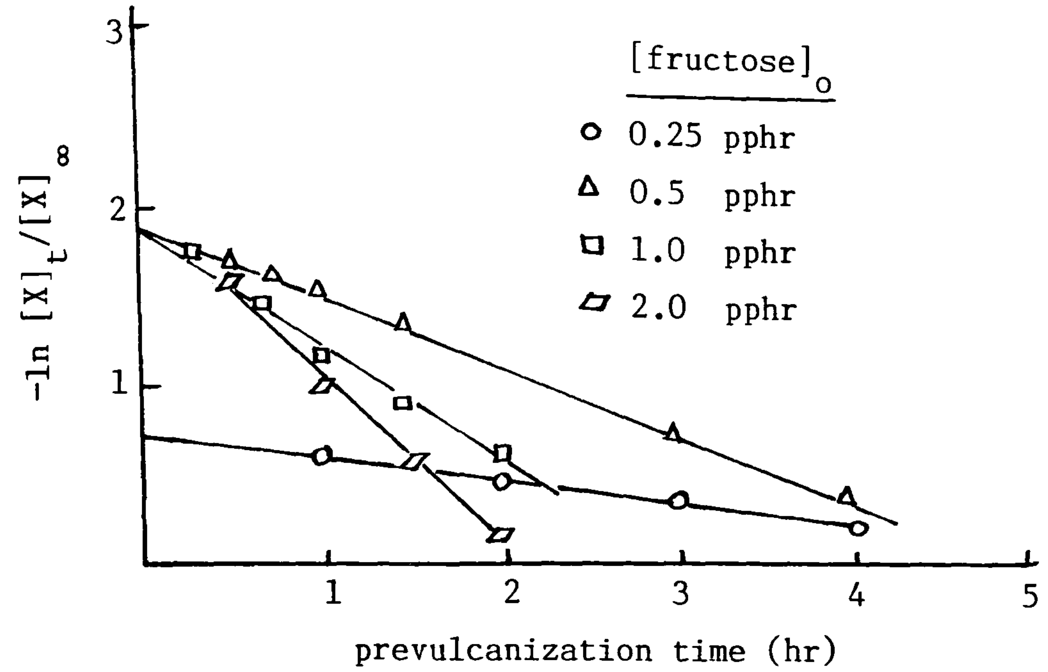


Figure 6.16. Plots of -ln $[X]_t/[X]_\infty$ against prevulcanization time at 60 °C for systems which initially contained 5.56×10^{-5} gmol/g rubber tBPIB and different concentrations of fructose.

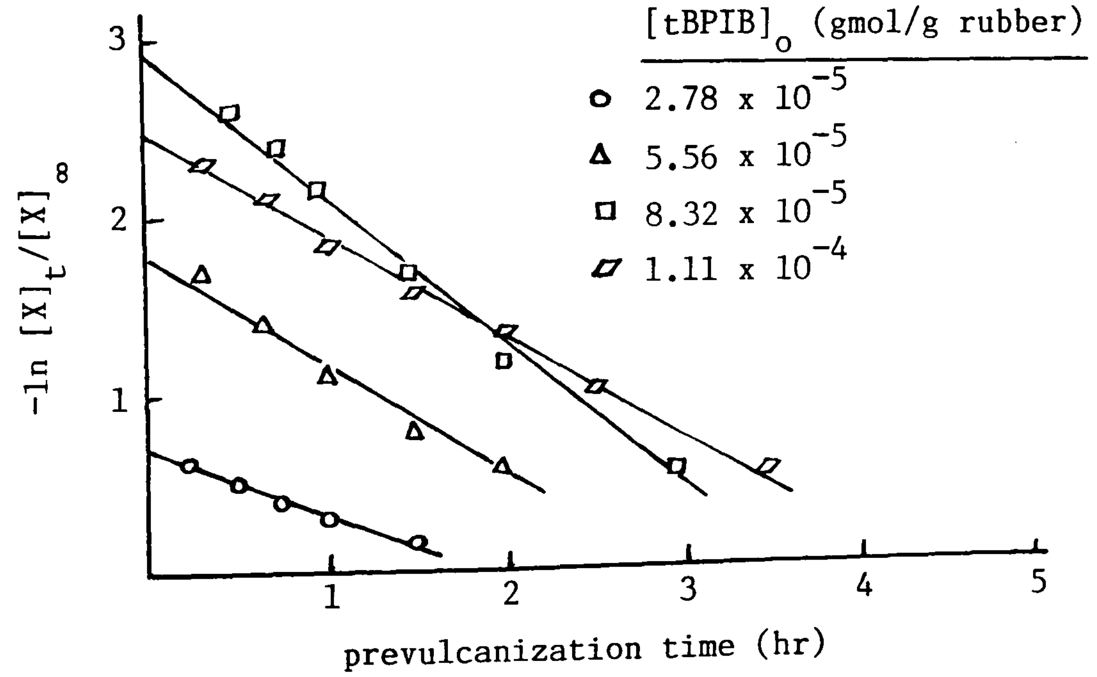


Figure 6.17. Plots of -ln $[X]_t/[X]_\infty$ against prevulcanization time at 60 °C for systems which initially contained 1.0 pphr fructose and different concentrations of tBPIB.

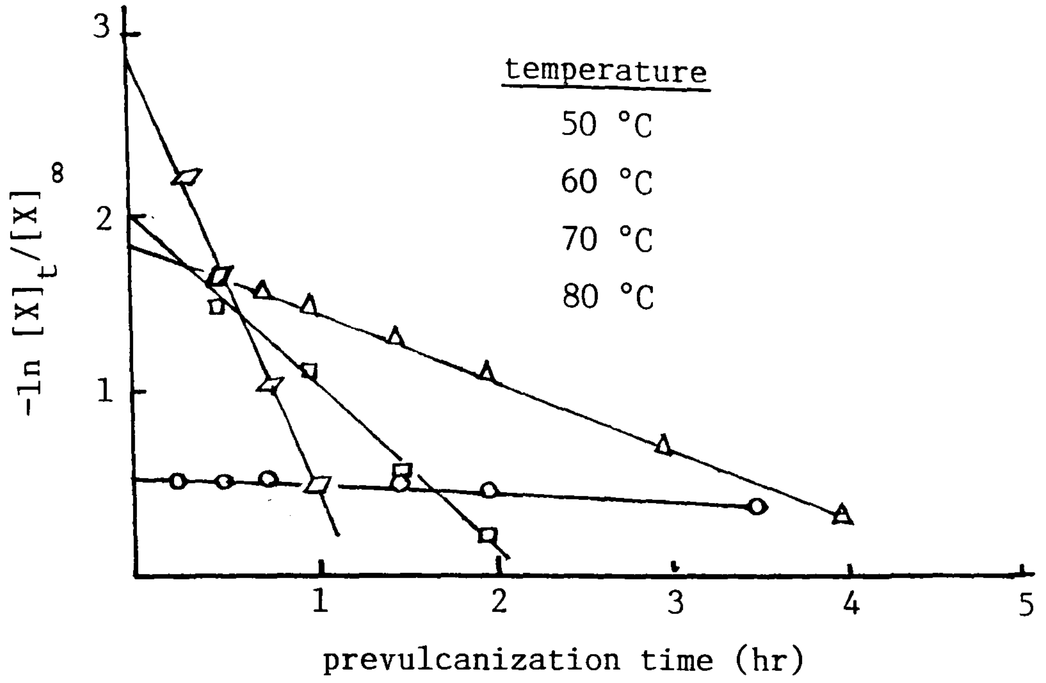


Figure 6.18. Plots of $-\ln [X]_t/[X]_\infty$ against prevulcanization time at various temperatures for systems which initially contained 5.56×10^{-5} gmol/g rubber tBPIB and 0.5 pphr fructose.

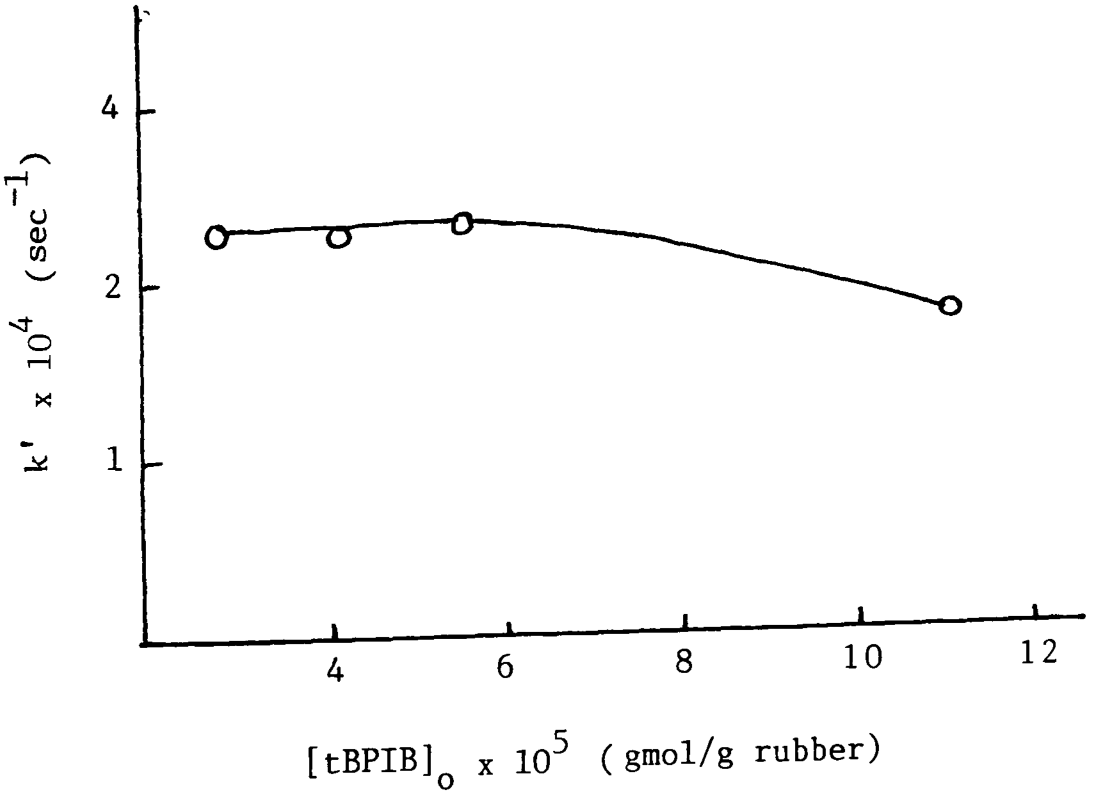


Figure 6.19. Effect of initial tBPIB concentration upon rate coefficient k' for decomposition of tBPIB in NR latex at 60 °C using equimolar tBPIB and fructose concentrations.

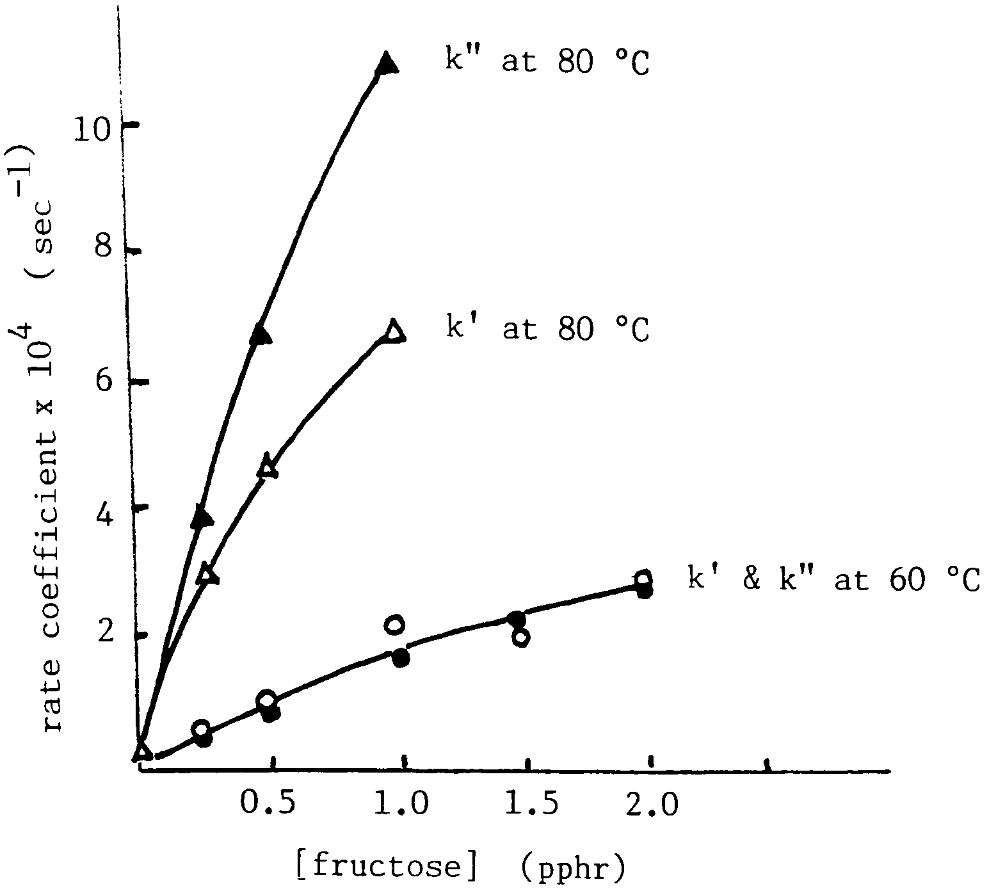


Figure 6.20. Effect of fructose concentration and prevulcanization temperature upon rate coefficients for tBPIB decomposition (k') and crosslink formation (k") at 60 °C and 80 °C using 5.56 x 10^{-5} gmol/g rubber tBPIB.

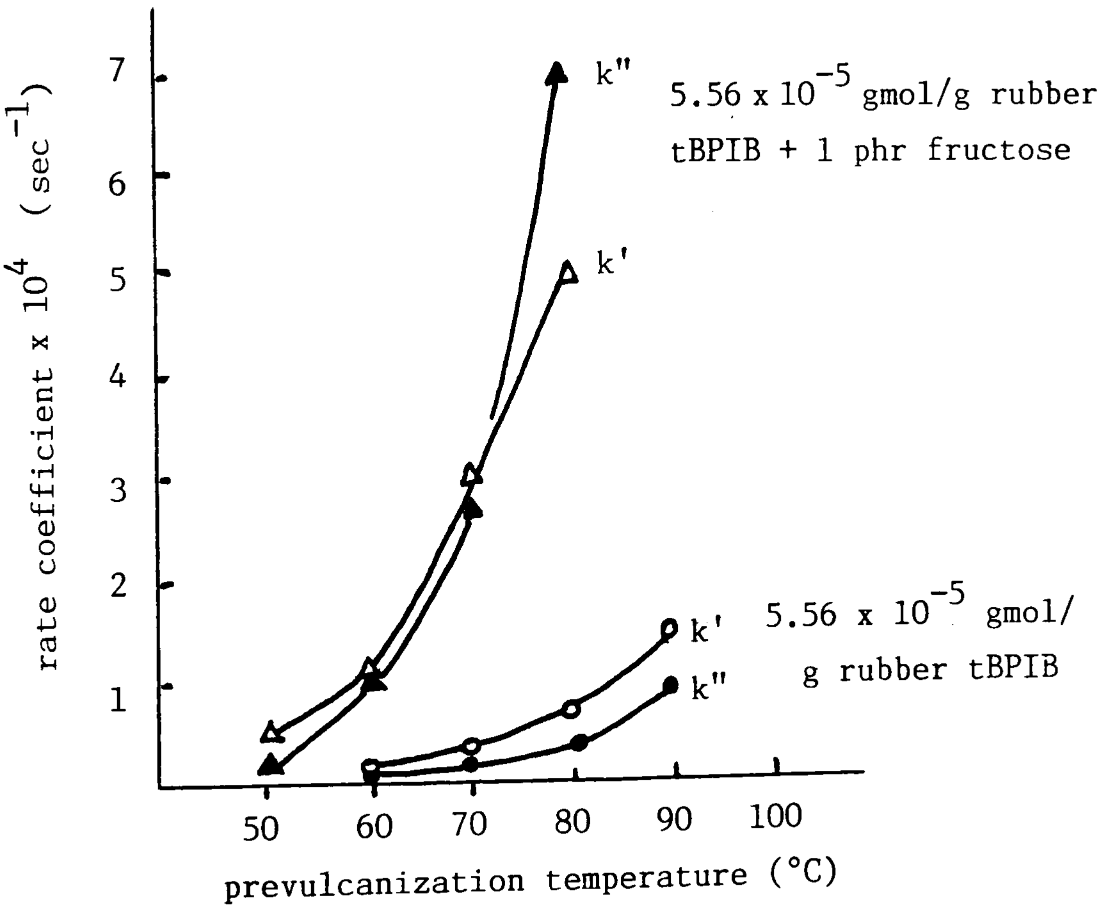


Figure 6.21. Effects of prevulcanization temperature and fructose/tBPIB concentrations on the values of k' and k".

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. This is again in contrast to the vulcanization of dry NR using DCP, where k' is generally equal to k". From the results shown in Figures 6.20 and 6.21, it appears that, for non-activated systems, k' is greater than k" for a wide range of temperatures. However, the value of k" becomes significantly greater than k' at temperatures greater than 80 °C, particularly when using high a ratio of initial fructose concentration to initial tBPIB concentration. According to the simple mechanism of peroxide vulcanization, it ought to be impossible for k" to exceed k'. Hummel and Scheele(70) proposed two conditions for k" to be equal to k'. Firstly, the intermediate reactions during vulcanization must be so fast that the concentration of their products are very small. This condition may be applicable to sulphur or accelerated-sulphur systems(72), but is probably not applicable to peroxide systems. The second condition for k" to be equal to k' is that F_t must be constant throughout the vulcanization reaction. The results shown in Figure 6.20 for the fructose-activated system at 60 °C indicate that the values of k" and k' are about the same notwithstanding that the F_t values are not constant throughout the prevulcanization time (Figure 6.9). Thus there are apparently other factors that contribute to the difference between k" and k' (see Section 6.7 and Section 6.8). Figure 6.10 shows rather unexpectedly that the F_t values for a fructose-activated system at 80 °C significantly exceed 50% towards the end of prevulcanization reaction. This probably implies that the less reactive alkyl radical (isobutryl) generated by tBPIB also participates in the crosslinking reaction. It is probably that the contribution of the relatively stable alkyl radicals to crosslinking increases towards the end of the reaction time, because the concentration of free-radical scavengers is reduced. Besides, the non-activated decomposition of tBPIB probably becomes much more significant than the activated decomposition when the concentration of activators is reduced towards the end of the reaction, and when the reaction is carried out at a high temperature. These reaction conditions promote an efficient generation of alkyl radicals which can be utilized for crosslinking of rubber. Prior to this investigation, it has always been concluded that only butoxy radicals were involved in the crosslinking of NR latex by t-butyl peroxyesters. This conclusion was drawn because of the ineffectiveness of diacyl peroxides in vulcanizing NR latex and the value of f_∞ obtained in this investigation for peroxyester systems has never been found to exceed 50%. The differences in the values of f_∞ of the various peroxyesters investigated in Chapter 5 are probably also consequences of difference in the contribution of alkyl radicals towards crosslinking, these differences arising from the differences in their reactivities. The variation in the relationship between k' and k", and the variation of F_t and f_∞ with temperature, are probably consequences of differences in the temperature-coefficients for the various competing reactions that occur during peroxide prevulcanization of NR latex. These competing reactions are:

a) reactions between free radicals generated from the decomposition of peroxide with the rubber hydrocarbon leading to the formation of crosslinks, and reactions between these above radicals with non-rubber substances and atmospheric oxygen leading to the reduction of crosslinking efficiency; and
b) recombination of polymeric radicals to form crosslinks, and combination of polymeric radicals with non-polymeric radicals resulting in the reduction of crosslinking efficiency.

Figure 6.22 shows the relationship between k" and k' for tBPIB prevulcanization systems. A relatively large amount of data has been generated for systems initially containing 5.56×10^{-5} gmol/g rubber tBPIB. This is because these systems generally tend to produce prevulcanized latex films

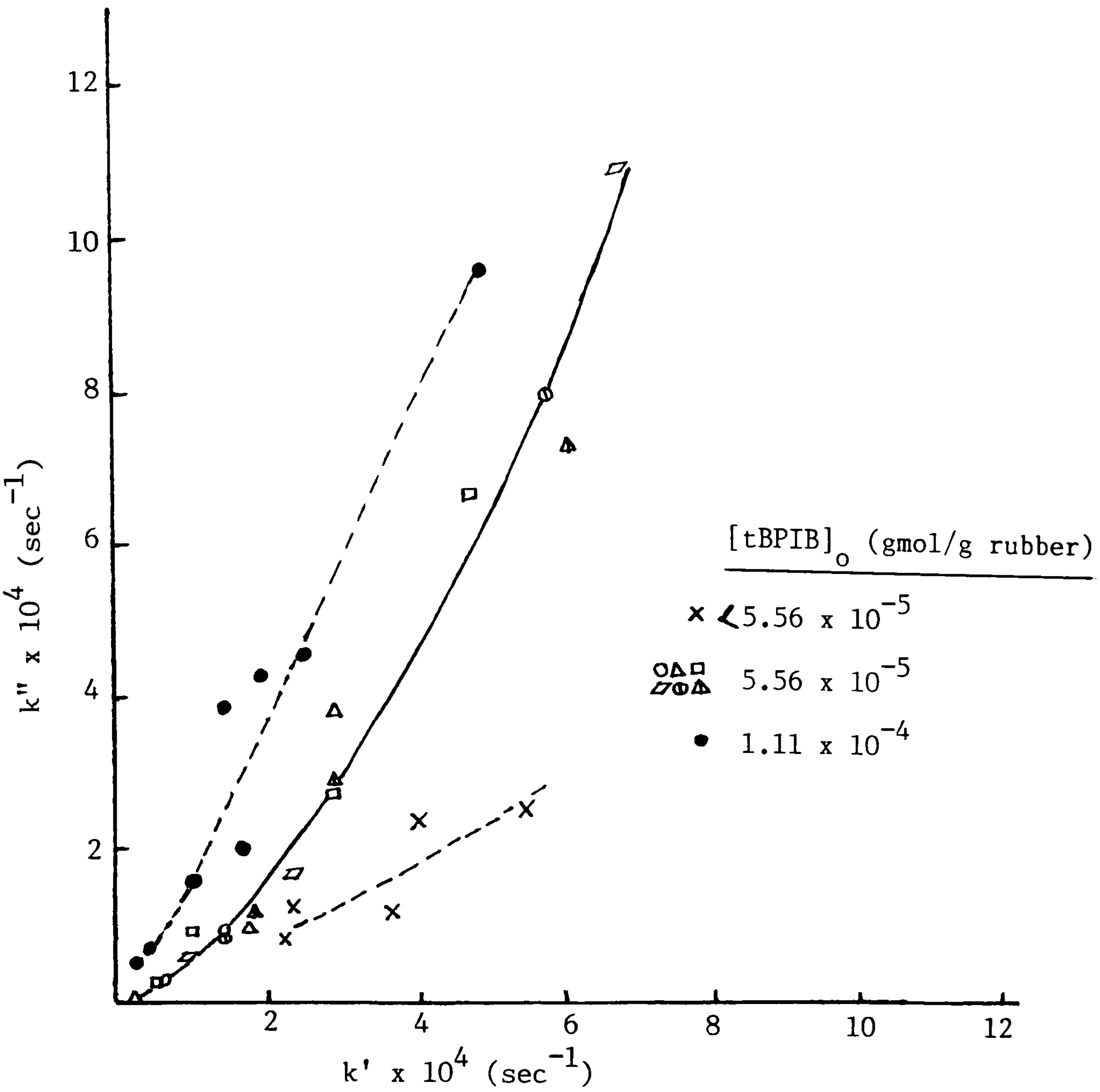


Figure 6.22. Relationship between k' and k" for tBPIB prevulcanization systems.

with values of $[X]_\infty$ correspond to high tensile strength properties. The results in Figure 6.22 indicate that, for systems initially containing 5.56×10^{-5} gmol/g rubber tBPIB, the values for k' and the corresponding values for k" tend to fall on a master-curve, notwithstanding the variation in temperature and initial fructose concentration. It also appears that, systems containing different initial tBPIB concentrations tend to have different curves for the relationship between k' and k". The curve tends to shift towards the ordinate-axis as the initial tBPIB concentration is increased. This implies that the value of k" becomes increasingly higher than k' as the initial tBPIB concentration is increased. Thus it appears that the values of k' and k" are affected by initial tBPIB concentration and also other factors which have been discussed earlier.

It has been shown in Figure 6.11 that the value of f_∞ for systems initially containing equimolar concentration of tBPIB and fructose, tends to increase with increasing initial tBPIB concentration. Figure 6.23 shows that the value of f_∞ for systems which initially contained 5.56×10^{-5} gmol/g rubber tBPIB is generally unaffected by the changes in the initial fructose concentration, but is significantly affected by the prevulcanization temperature. Figure 6.24 shows that the value of f_∞ increases linearly with increasing temperature. By contrast, it is noted that the value of f_∞ for the vulcanization of dry NR using DCP is independent of temperature(74). Figure 6.24 also indicates that the fructose-activated tBPIB prevulcanization system would become ineffective at temperatures lower than 40 °C, and this has been experimentally observed (Chapter 5). Figures 6.25 and 6.26 show that the value of f_∞ increases with increasing values of k' and k". From these relationships, it would be expected that the value of f_∞ ought to increase with increasing temperature and also initial fructose concentration. However, only the temperature appears to affect significantly the value of f_∞. There are probably several reasons for the increase in the value of f_∞ with increasing temperature. It was noted earlier that the

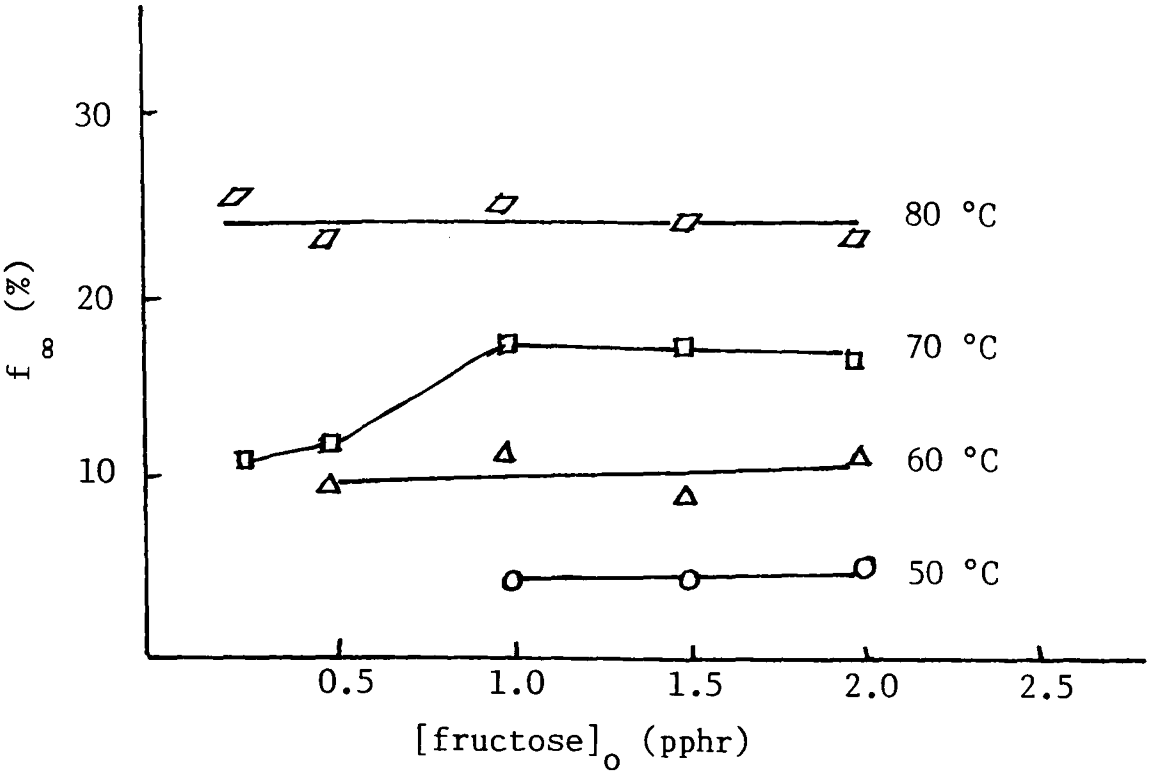


Figure 6.23. Effect of initial fructose concentration upon the value of f_∞ at various temperature for systems which initially contained 5.56 x 10^{-5} gmol/g rubber tBPIB.

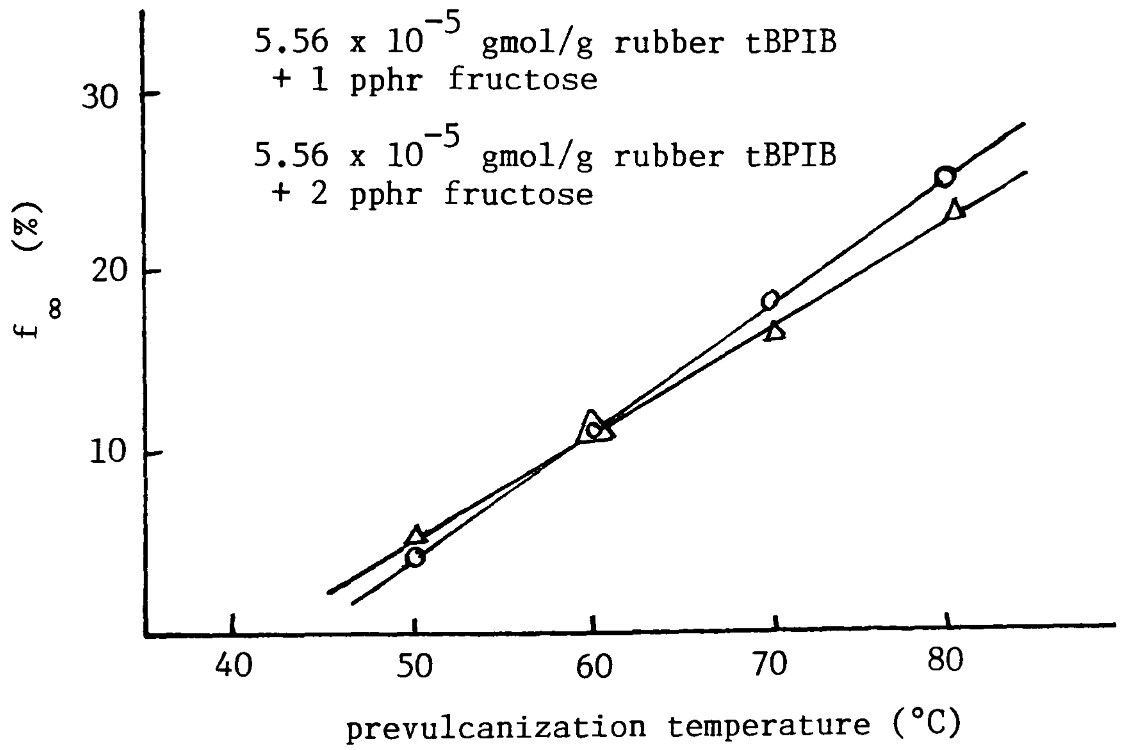


Figure 6.24. Effects of prevulcanization temperature and initial fructose concentration at constant initial tBPIB concentration upon the value of f_∞.

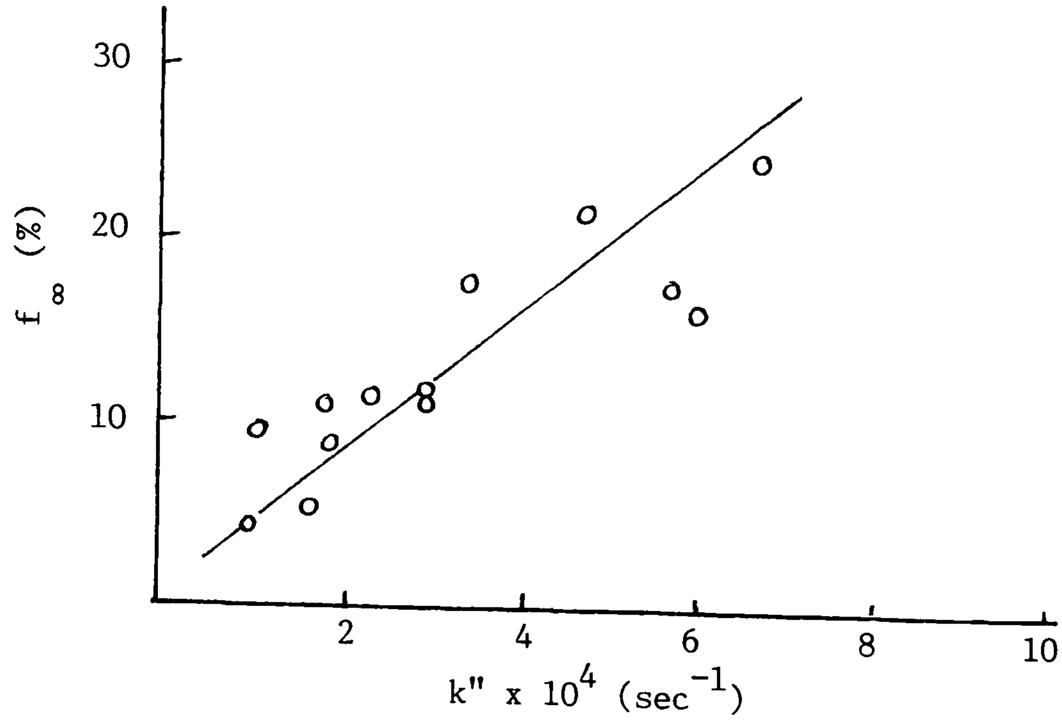


Figure 6.25. Relationship between the value of f_∞ and the value of k" for tBPIB prevulcanization systems.

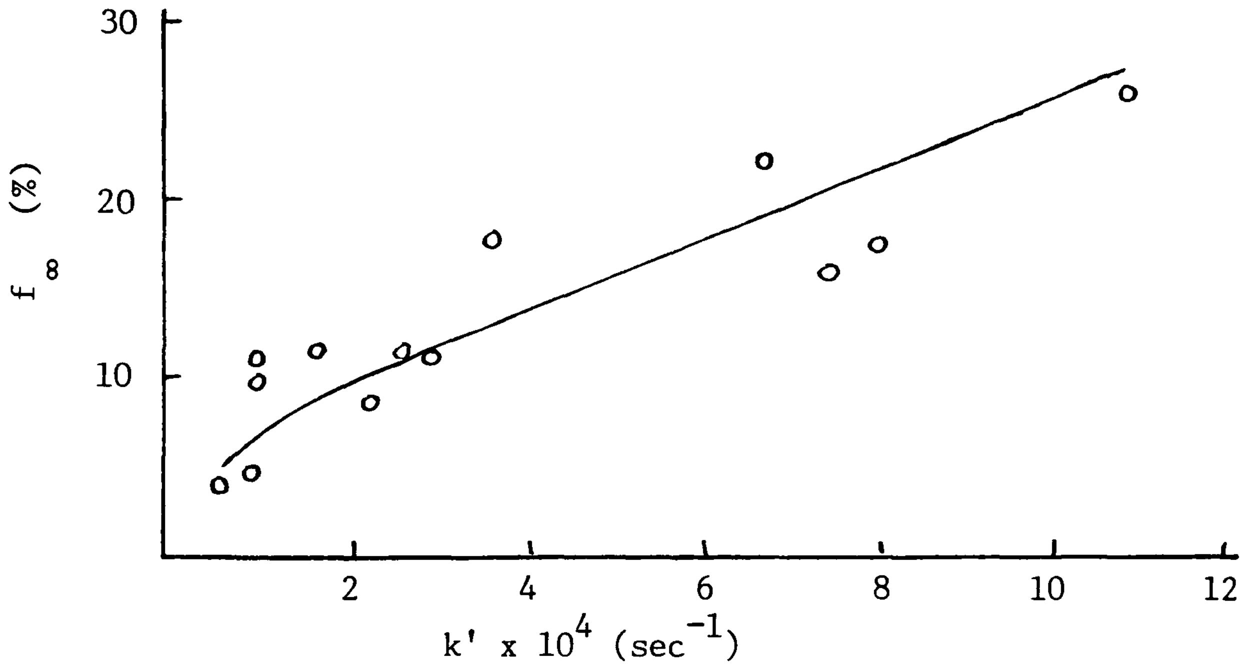


Figure 6.26. Relationship between the value of f_∞ and the value of k' for tBPIB prevulcanization systems.

contribution of alkyl radical derived from tBPIB towards crosslinking is enhanced by increasing the temperature. Increasing the temperature would increase the rate of diffusion of vulcanizing agents and free-radicals into the latex particles. Also, the increase in the mobility of the rubber molecules would enhance the rate of polymer radical recombination relative to the rate of them being scavenged by non-polymeric radicals(75). Fructose probably interacts with peroxide in the aqueous phase to produce free-radicals. Increasing the concentration of fructose was found to increase the values of k' and k", but the value of f_∞ remains constant. This probably implies that, the ratio of the concentration of free-radicals partitioned in the rubber, and are utilized for crosslinking, to that partitioned in the aqueous phase is constant throughout the reaction, and is independent of the rate of production of free-radicals in the aqueous phase.

6.6 Activation parameters of tBPIB decomposition and crosslink formation

The activation energy E' of tBPIB decomposition is obtained by multiplying R (8.313 JK^{-1}) by minus the slope of the line obtained when ln k' is plotted against T^{-1}. The activation energy E" of crosslink formation is obtained in a similar way from the slope of the line of ln k" versus T^{-1}. The activation energy $\Delta H^{\ddagger}$ for tBPIB decomposition is

$$\Delta H^{\ddagger} = E' - RT \qquad (6.5)$$

The values of $\Delta H^{\ddagger}$ reported in this chapter are those calculated using T equal to 333 °K. The activation entropy $\Delta S^{\ddagger}$ for tBPIB decomposition is obtained using equation:

$$\Delta S^{\ddagger} = R\left\{\ln \frac{k'h}{k_B T} + \frac{\Delta H^{\ddagger}}{RT}\right\} \qquad (6.6)$$

The value of k' in Equation 6.9 is that determined at temperature T equal to 333 °K. The activation free energy

$\Delta G^{\ddagger}$ for tBPIB decomposition is

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad (6.7)$$

The value of $\Delta G^{\ddagger}$ is calculated using T equal to 333 °K.

Figure 6.27 shows that, for prevulcanization systems using fructose to tBPIB concentration ratio of less than one on a molar basis, a good linear relationships between ln k' and T^{-1} are obtained over a temperature range 50 °C - 80 °C. For the systems in Figure 6.27 which contain more than 1 pphr fructose, the relationships between ln k' and T^{-1} apparently show a strong departure from linearity at temperatures greater than 70 °C. For these systems, the relationships between ln k' and T^{-1} were similar to that shown in Figure 3.2 in Chapter 3. These departures from the simple Arrhenius relationship are partly a consequence of the slight temperature dependence of the Arrhenius frequency factor Z and the experimental activation energy. But the major factor that contributes for the apparent departures is probably the occurence of two transition states, each of which predominates at different temperature ranges. Calculation of E' and $-\Delta S^{\ddagger}$ values in the temperature range 70 °C - 80 °C for the system containing 2 pphr fructose, produced an E' value of 135 kJ/mol and $-\Delta S^{\ddagger}$ value of -70 J/mol/K. This value of E' is approximately equal to the activation energy for the non-promoted decomposition of tBPIB in chlorobenzene, which is 134 kJ/mol(166). The value of $-\Delta S^{\ddagger}$ is lower than that for the decomposition of tBPIB in chlorobenzene, which is -39 J/mol/K(166). In the preceding sections, it has been deduced that for fructose-activated tBPIB system, the non-activated decomposition of tBPIB becomes significantly important at temperatures greater than 70 °C. This may explain for the departure from linearity of the relationships between ln k' and T^{-1} at temperatures greater than 70 °C for the systems containing more than 1 pphr fructose. However, it could not explain why the other systems containing less than 1 pphr fructose were not

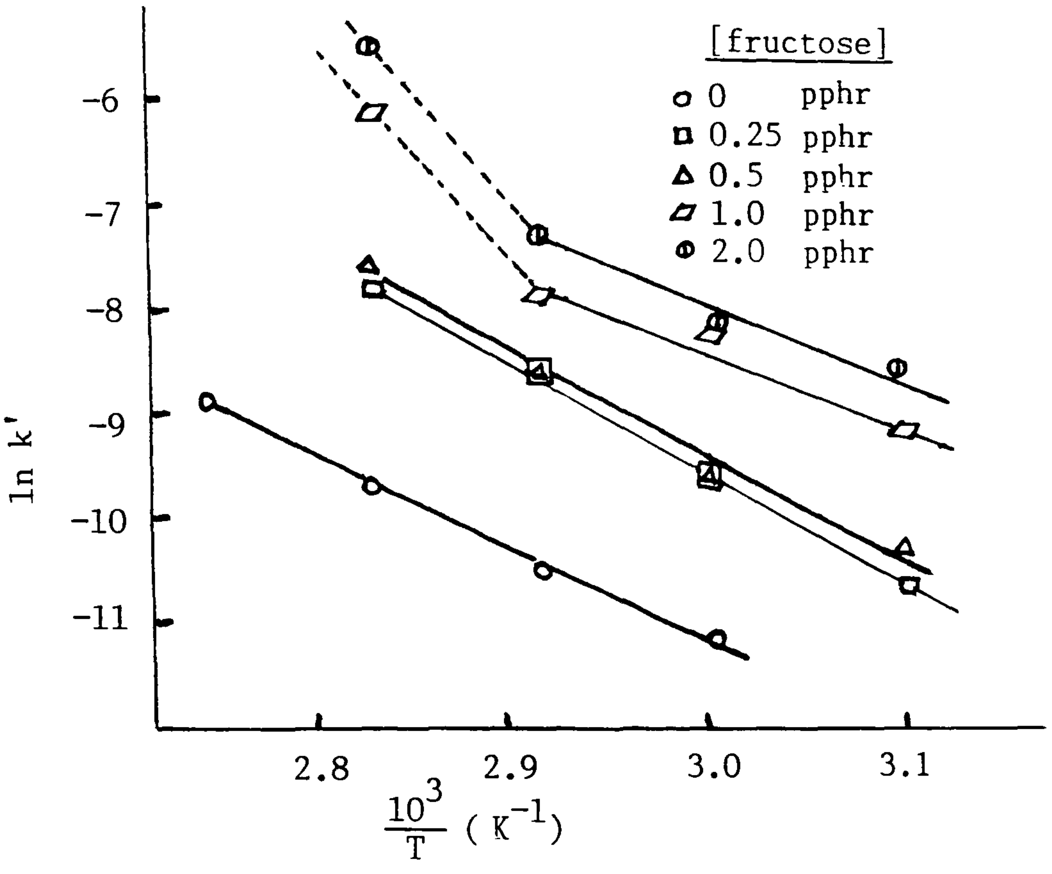


Figure 6.27. Plots of ln k' against T^{-1} for preculcanizations using 5.56×10^{-5} gmol/g rubber tBPIB and various fructose concentrations.

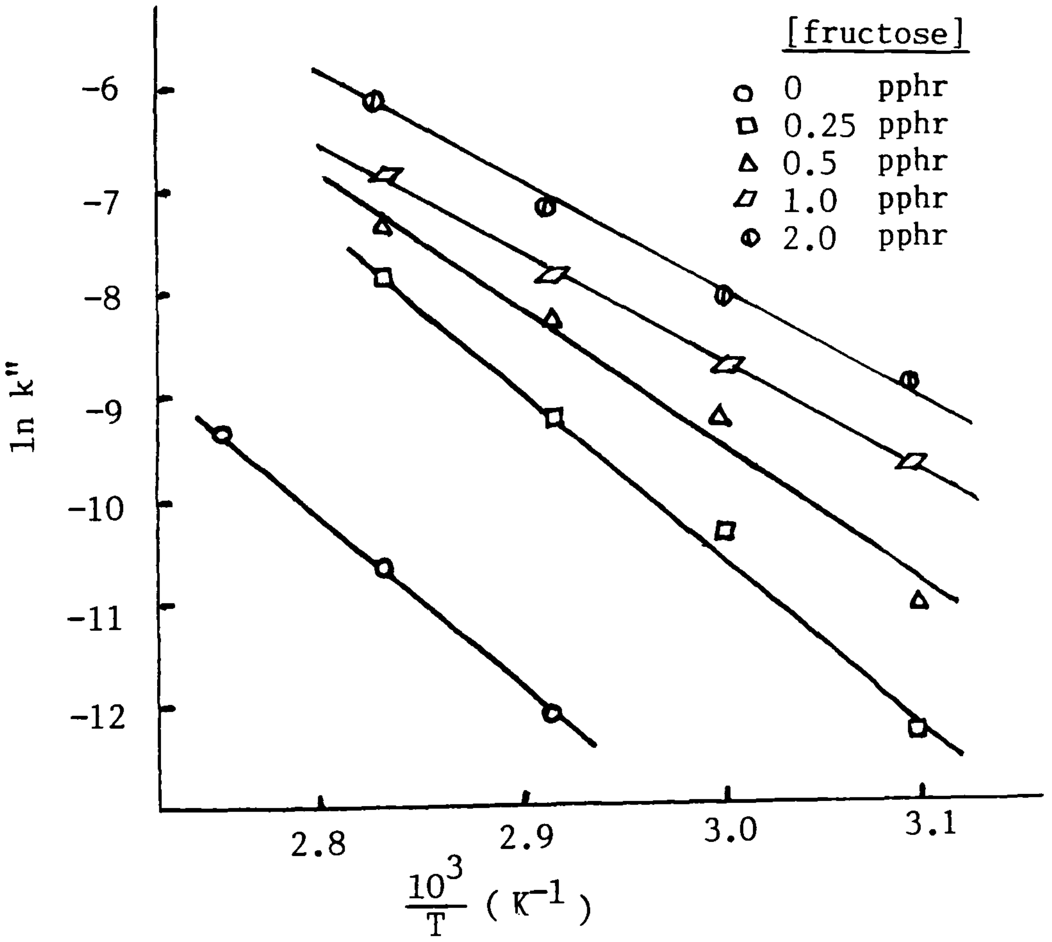


Figure 6.28. Plots of ln k" against T^{-1} for prevulcanizations using 5.56×10^{-5} gmol/g rubber tBPIB and various fructose concentrations.

similarly affected. Figure 6.28 shows that the relationships between ln k" and T^{-1} for various fructose-activated tBPIB systems are linear over a temperature range 50 °C - 80 °C. Table 6.1 shows the activation parameters for tBPIB decomposition and crosslink formation for the various systems. For the systems containing 1 pphr and 2 pphr fructose, the values of activation parameters for tBPIB decomposition shown in Table 6.1 are those determined over a temperature range 50 °C - 70 °C.

The value of E' for the decomposition of tBPIB in NR latex without an added activator was found to be 79 kJ/mol. Thus there is a significant reduction of the E' value for tBPIB decomposition, from 134 kJ/mol in chlorobenzene(167) to 79 kJ/mol in NR latex. Polymers and solvents can affect the activation energy for peroxide decomposition. However, their effect upon the activation energy for the decomposition of peroxides is generally not great(74,75). The lower activation energy for the decomposition of tBPIB in NR latex, as compared with the decomposition in chlorobenzene, could be a consequence of the decomposition being activated by non-rubber substances. When a small amount of fructose (0.25 pphr) was added to a system initially containing 5.56 x 10^{-5} gmol/g rubber tBPIB, the E' value increased from 79 kJ/mol to 93 kJ/mol, but the observed k' values at various temperatures were also increased. The entropy term contributed significantly to the higher k' values for this system, as is evidenced by the relatively lower $-\Delta S^{\ddagger}$ value in the results shown in Table 6.1. For all the systems, the lowering of the E' value is accompanied by an increase of the $-\Delta S^{\ddagger}$ value. These effects oppose each other in their effects upon the decomposition rate. This type of relationship between E' and $\Delta S^{\ddagger}$ has been observed in the decomposition of a series of peroxyesters(168). The relationship between E' and $\Delta S^{\ddagger}$ for the decomposition of tBPIB in NR latex is shown in Figure 6.29.

The variations of E' with fructose concentration (Figure 6.30), and of $\Delta S^{\ddagger}$ with fructose concentration (Figure 6.31) do not exhibit clear-cut relationships. But, $\Delta G^{\ddagger}$ is found to gradually decrease with increasing fructose

Table 6.1. Activation parameters of tBPIB decomposition and crosslink formation for prevulcanizations using 5.56 x 10^{-5} gmol/g rubber of tBPIB and various concentrations of fructose

[fructose] (pphr)	E' (kJ/mol)	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta G^{\ddagger}$ (kJ/mol)	$-\Delta S^{\ddagger}$ (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

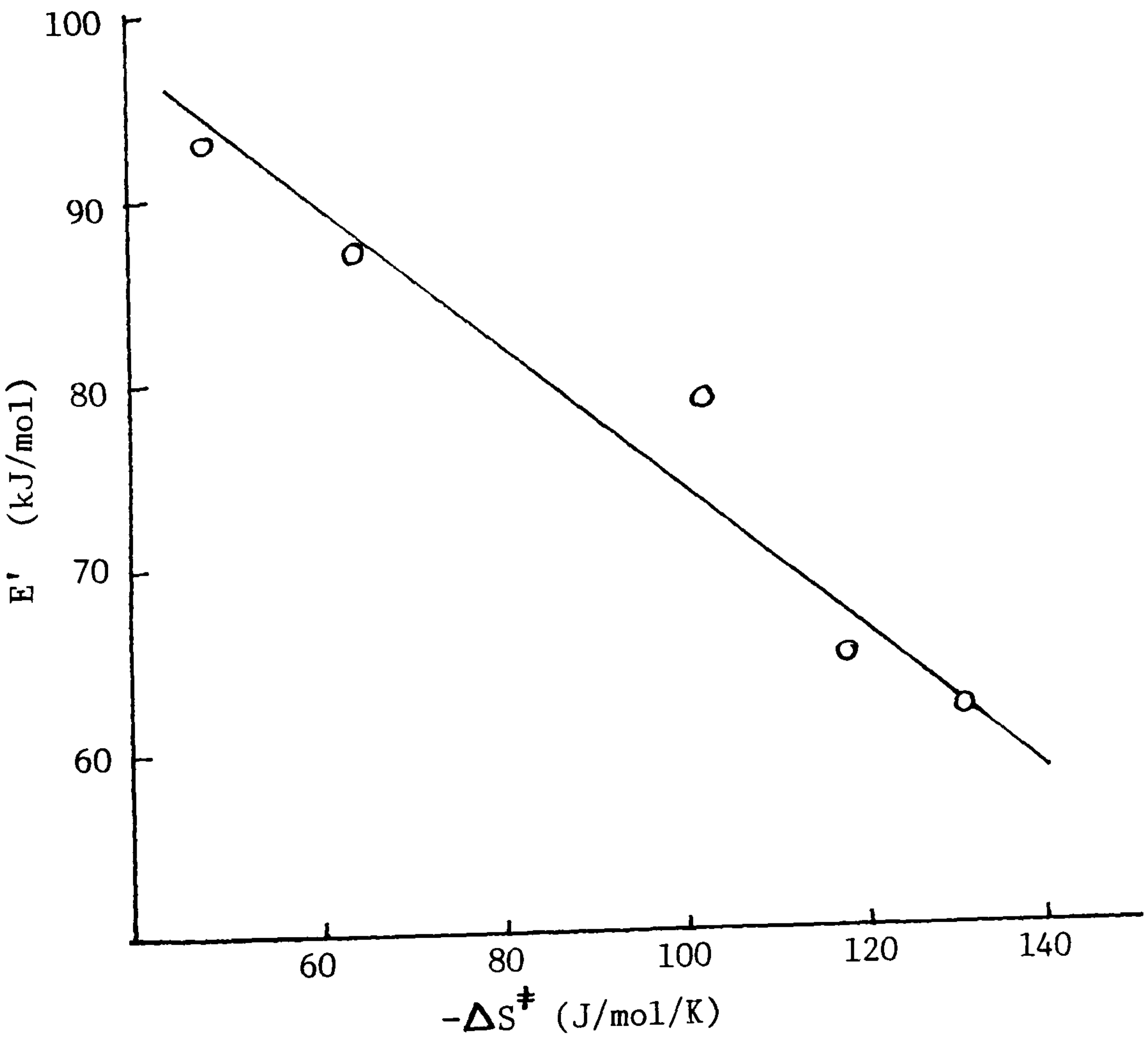


Figure 6.29. Relationship between E' and $-\Delta S^{\ddagger}$ for tBPIB decomposition in NR latex.

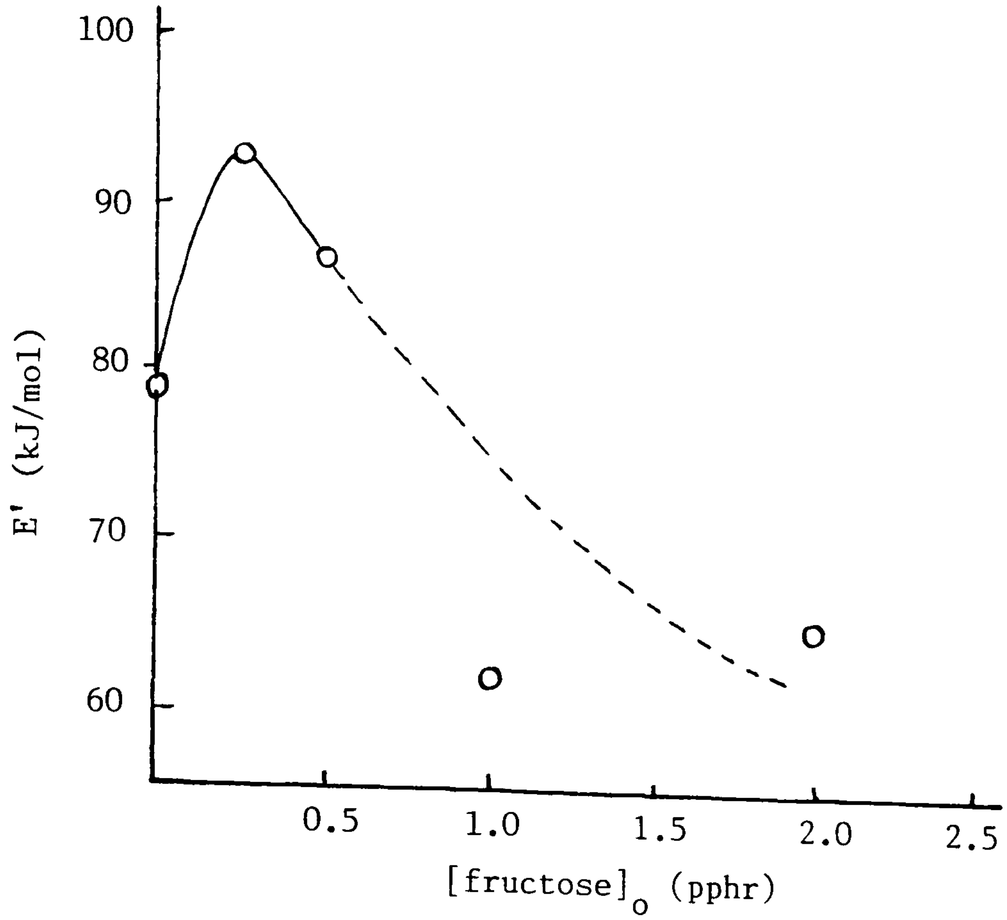


Figure 6.30. Effect of initial fructose concentration at constant tBPIB concentration of 5.56 x 10^{-5} gmol/g rubber upon E'

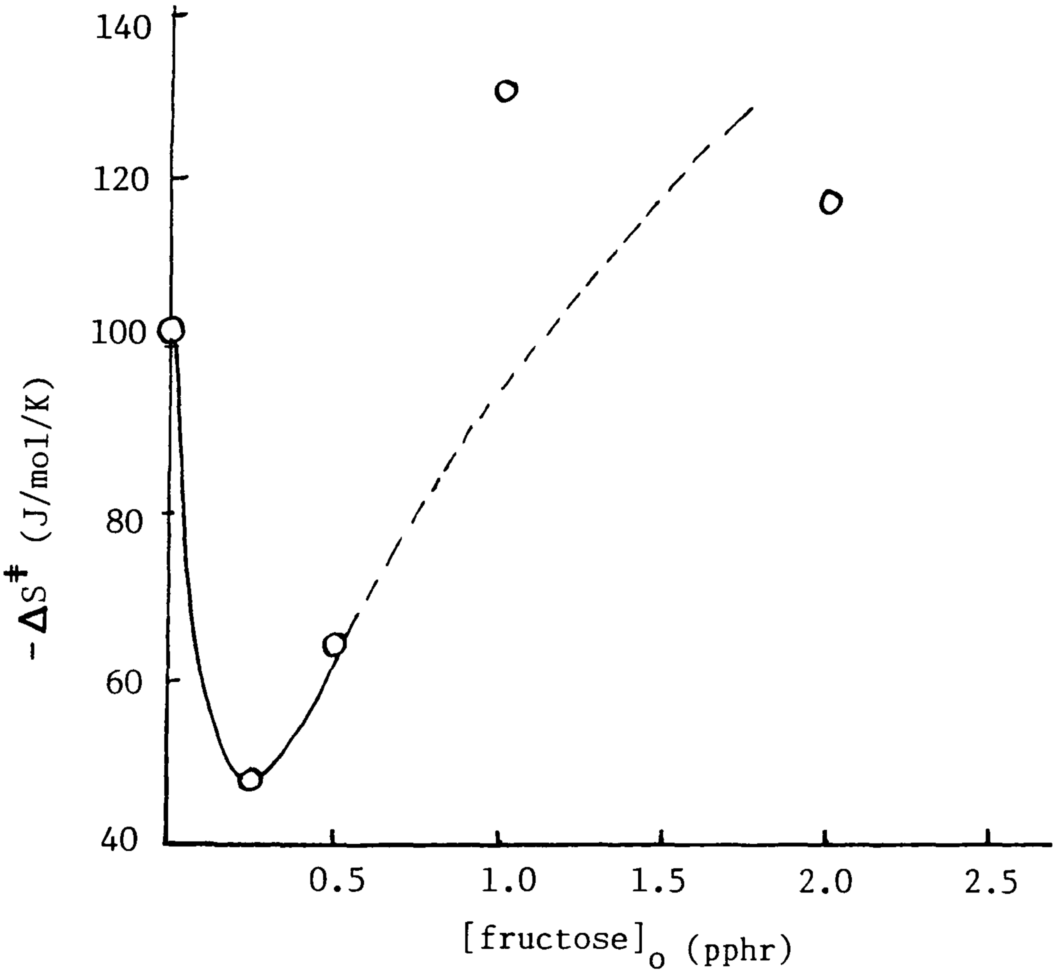


Figure 6.31. Effect of initial fructose concentration at constant tBPIB concentration of 5.56 x 10^{-5} gmol/g rubber upon $-\Delta S^{\ddagger}$.

concentration, as is indicated in Figure 6.32. The values of k' at a particular temperature were found to increase with increasing fructose concentration. The variation of $\Delta G^{\ddagger}$ and k' with fructose concentration is as a consequence of the combined effects of the variation of E' and $\Delta S^{\ddagger}$ with fructose concentration. Thus, it is actually the activation free energy that determines the rate of the decomposition of tBPIB in NR latex, as is predicted by the transition state theory for all chemical reactions. The effects of $\Delta H^{\ddagger}$ on the values of k', $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ follow the same pattern as that of E', and therefore will not be discussed further.

The variations of E' and $\Delta S^{\ddagger}$ with the ratio of $[\text{fructose}]_0$ to $[\text{tBPIB}]_0$ probably reflect the effects of fructose and tBPIB concentrations upon the nature of the activated complex and the rate process. The activated complex may also involve non-rubber substances, particularly the transition-metal ions. One possiblity is that the presence of fructose enhances metal-ion-catalyzed peroxide decomposition. The mechanism of the enhancement by fructose for the decomposition of peroxide activated by metal-ions has been discussed in Chapter 5. The values of $-\Delta S^{\ddagger}$ for the decomposition of tBPIB in NR latex, in the presence or in the absence of fructose, are relatively large. For comparison, the value of $-\Delta S^{\ddagger}$ for tBPIB decomposition in chlorobenzene is -39 J/mol/K(166). A higher value of $-\Delta S^{\ddagger}$ for the decomposition of tBPIB in NR latex as compared to that in chlorobenzene probably indicates the formation of a more rigid tBPIB-activator(s) complex in NR latex. The decomposition of tBPIB involves the breaking of more than one bond in a single step and this leads to rotational restrictions around the bonds of the activated molecule(90). An increase in the level of restricted rotation around the bonds of an activated molecule will show up by an increase in the value of $-\Delta S^{\ddagger}$. The following structure of a tBPIB molecule indicates the bonds that may undergo restricted rotation and the bonds that can break simultaneously:

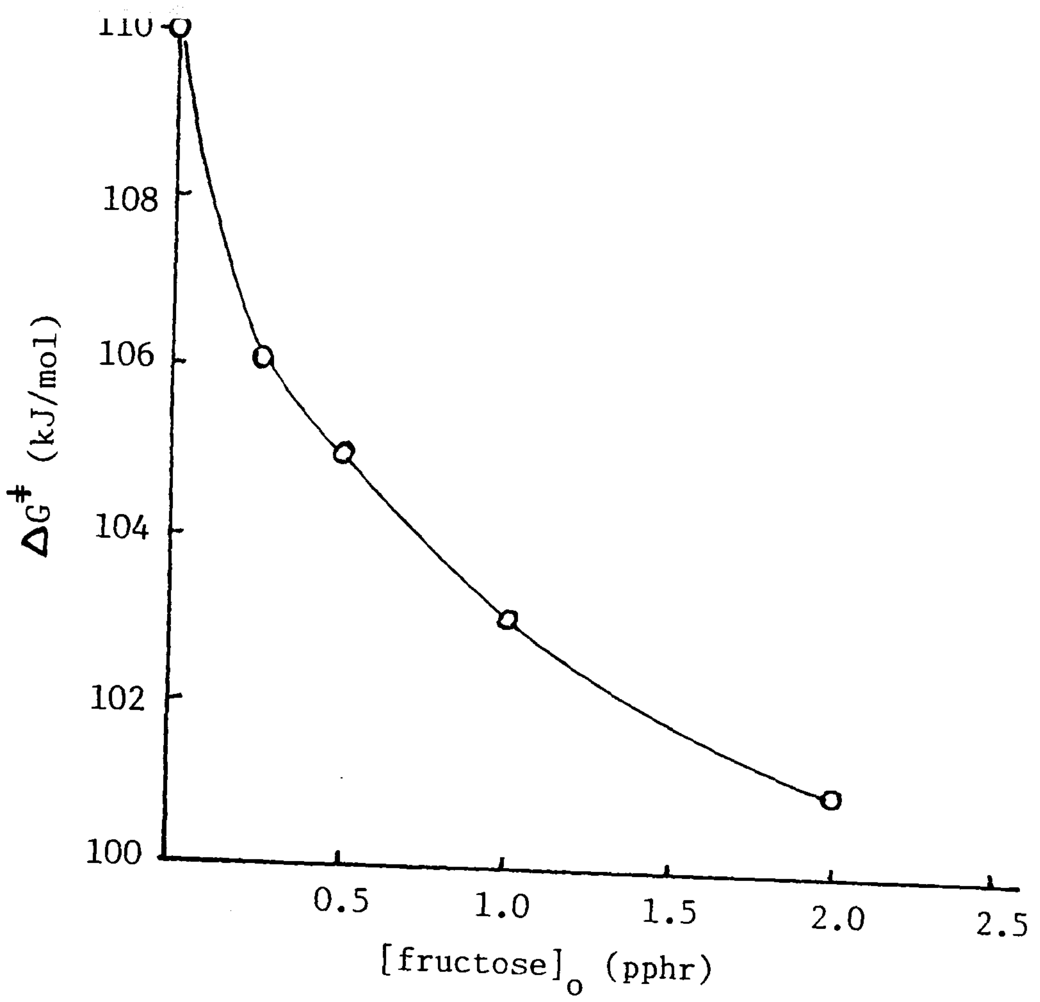


Figure 6.32. Effect of initial fructose concentration at constant tBPIB concentration of 5.56 x 10^{-5} gmol/g rubber upon $\Delta G^{\ddagger}$.

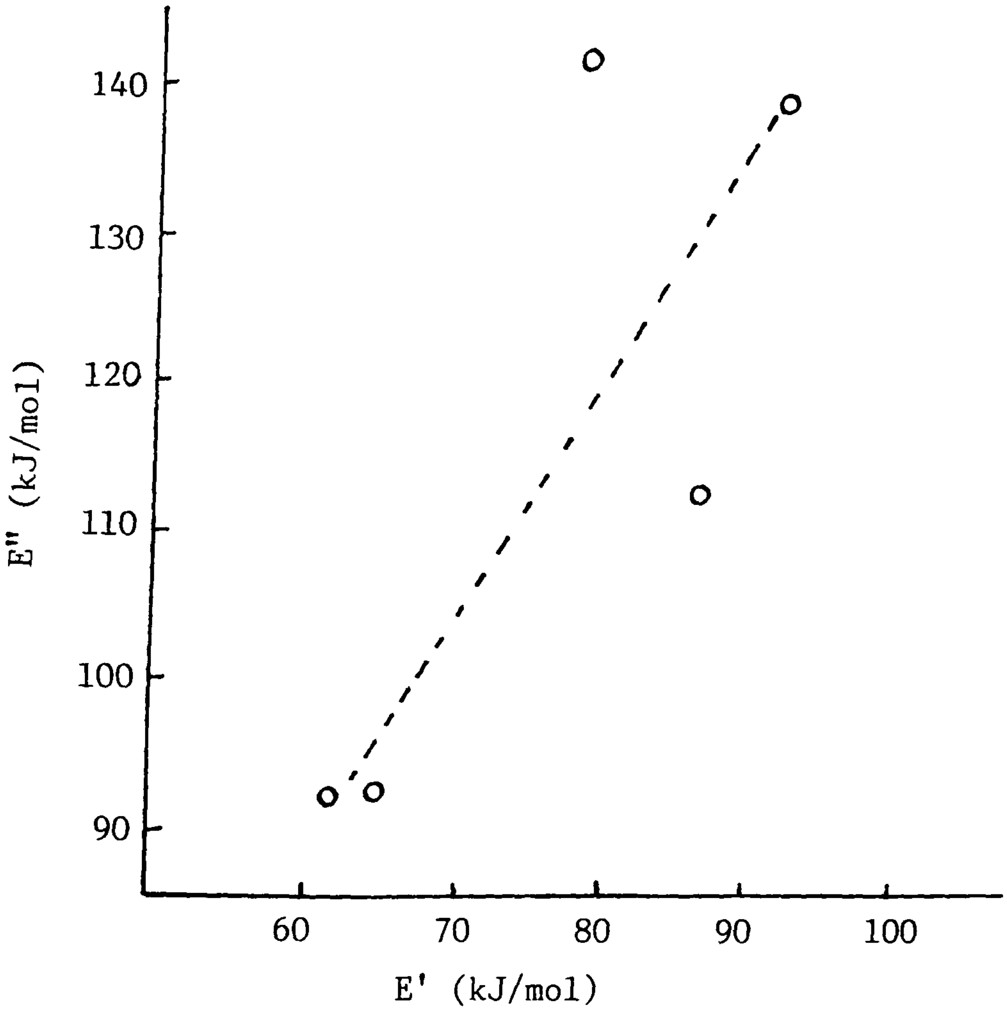
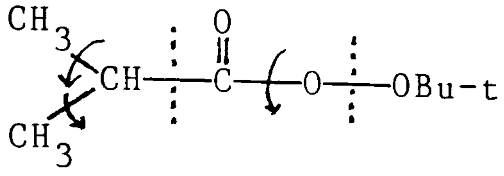


Figure 6.33. Relationship between E" and E' for tBPIB-fructose prevulcanization systems.



where, the arrow indicates restricted rotation around the bond and the dotted-line indicates breaking of the bond. The formation of a tBPIB-fructose or other type of peroxide-activator complex probably increase the extent of restricted rotation around some of the bonds in a tBPIB molecule.

The activation energy E" for crosslink formation for the fructose-activated tBPIB system is higher than the activation energy for tBPIB decomposition. For comparison, Hummel et al.(69) found that in the vulcanization of dry NR by DCP, the activation energy for crosslink formation equal to the activation energy for DCP decomposition. Figure 6.33 shows a general tendency for E" to increase with E', however, there is no clear-cut relationship between the two activation energies. Since the value of E" is lower than the value of E' for a particular tBPIB-fructose system, then k" ought to be lower than k' at any particular temperature. This is generally true for all cases, except at temperatures greater than 70 °C, and particularly when using high a fructose concentration.

6.7 Initial rate of tBPIB decomposition in NR latex in the present of fructose

The procedure described in Section 3.3.3 in Chapter 3 was used to obtain initial rate of tBPIB decomposition, $(-d[P]/dt)_0$, as a function of initial tBPIB concentration, $[P]_0$, and initial fructose concentration, $[F]_0$. The value of $(-d[P]/dt)_0$ was obtained from the slope of the concentration of residual peroxide versus time curve at the initial stage of the reaction. Accurate measurement of the initial rate of tBPIB decomposition was facilitated by the close intervals which the concentration of residual peroxide was monitored during the early period of prevulcanization. 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 as shown in Figure 6.34 is obtained. 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 concentration, as shown in Figure 6.35. The value of n is approximately equal to $\frac{1}{2}$ for the system at 60 °C which initially contained 1 pphr fructose, and also for the system at 80 °C which initially contained 0.25 pphr fructose. The value of m shows a temperature-dependent, being equal to approximately 1.0, 0.7 and 0.6 at 50 °C. 60 °C and 80 °C respectively.

6.7.1 Discussion

The results indicate that the initial rate of tBPIB decomposition is half order with respect to initial tBPIB concentration. The initial rate of the decomposition can be written:

$$(-d[P]/dt)_o = [P]_o^{\frac{1}{2}} \left\{ f(k, [F]_o) \right\} \qquad (6.8)$$

where f denotes function, and k is the rate coefficient for tBPIB decomposition. From the results in Figure 6.35, extrapolation of the lines to zero initial fructose concentration, i.e., at ln $[\text{fructose}]_o$ of approximately equal to -14, would produce intercepts on the ordinate axis. The intercept represents the initial rate of tBPIB decomposition at zero initial fructose concentration. The value of the intercept is higher at the higher temperature. Thus the initial rate of tBPIB decomposition contains a term which is independent of fructose concentration. The lines in Figure 6.35 deviate from linearity at the lower fructose concentration. The value of m is temperature-dependent, and the values of m obtained for reaction systems at 60 °C and 80 °C are kinetically not rational numbers. These observations probably suggest that the initial rate of tBPIB decomposition comprises more than one terms containing fructose concentration:

$$(-d[P]/dt)_o = [P]_o^{\frac{1}{2}} (k_1 + k_2[F]_o^{\frac{1}{2}} + k_3[F]_o + \cdots) \qquad (6.9)$$

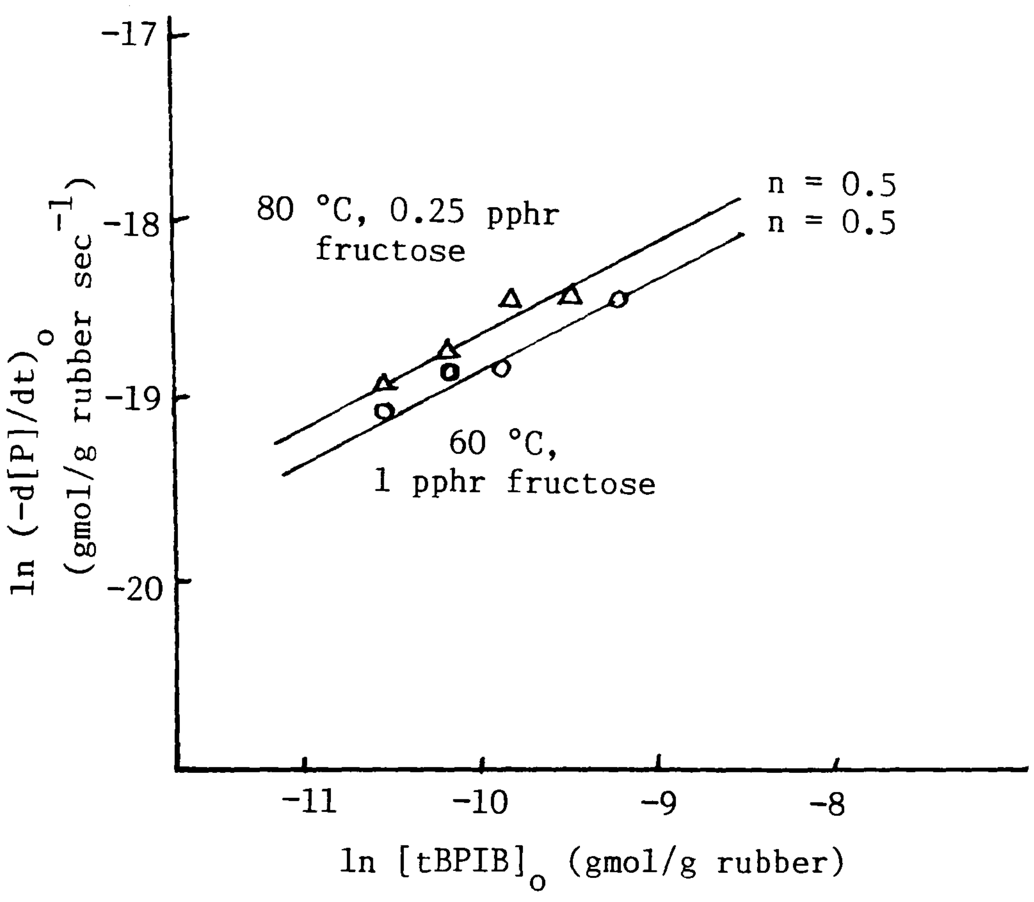


Figure 6.34. Plots of ln (-d[P]/dt)$_o$ against ln [tBPIB]$_o$ using two different initial fructose concentrations and temperatures.

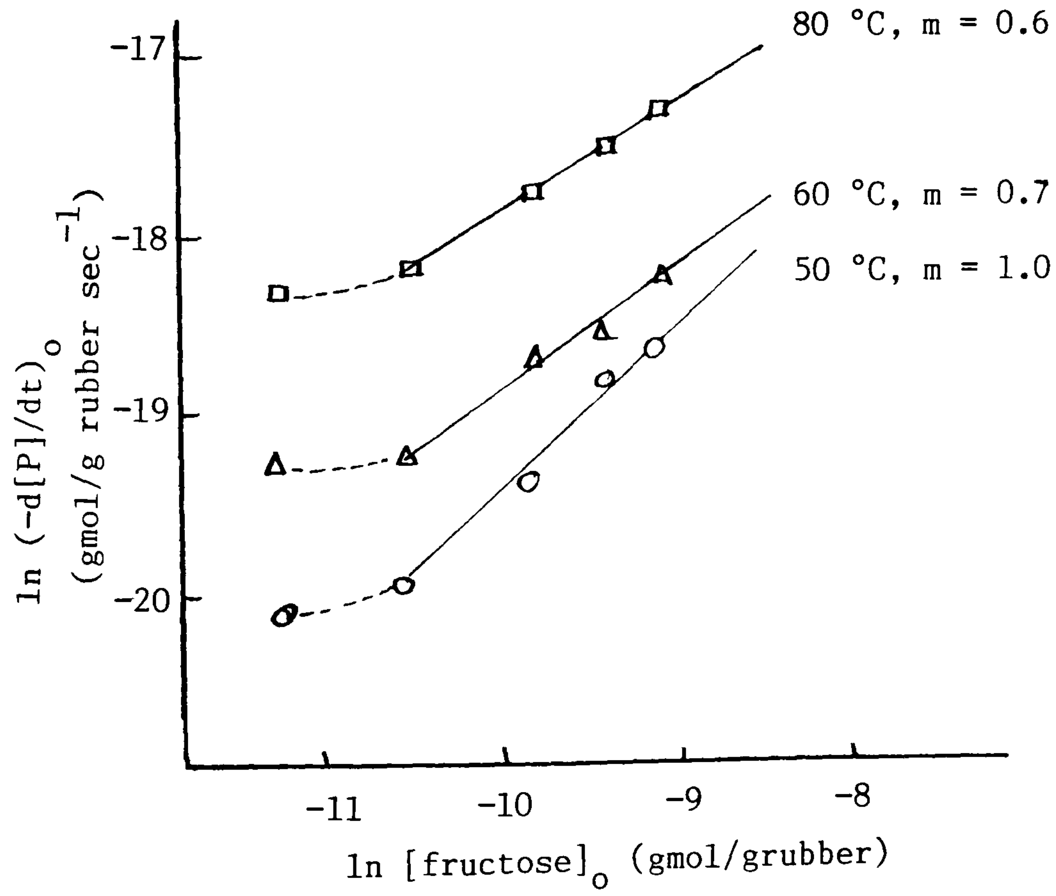


Figure 6.35. Plots of ln (-d[P]/dt)$_o$ against ln [fructose]$_o$ using initial tBPIB concentration of 5.56 x 10^{-5} gmol/g rubber at various temperatures.

where, k_1, k_2, k_3···· are the rate coefficients for tBPIB decomposition, associated with the appropriate terms. The possible activation of tBPIB decomposition by non-rubber substances, such as amines and metal ions, would lead to a more complex expression for the initial rate of tBPIB decomposition.

The decomposition of peroxide is rarely found to be half order with respect to peroxide concentration. No detailed studies of the decomposition of peroxyesters promoted by organic activators have been reported. However, it is appropriate to make reference to some relevant kinetic studies of peroxide decomposition. Bartlett and Nozaki(85) found that the triphenylamine-activated decomposition of benzoyl peroxide is first order with respect to amine concentration. Imoto and Choe(169) found that the dimethylaniline-activated decomposition of benzoyl peroxide is first order with respect to both peroxide and amine concentrations. Walling and Zavitsas(81) found that, at higher copper concentration, the copper-catalyzed peroxyester reaction with hydrocarbons is first order with respect to both peroxide and cuprous ion concentrations, or half order with respect to cupric ion concentration. Bartlett and Nozaki(170) postulated that, the kinetic order for 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. Induced decomposition is significant in t-butyl peroxyesters containing α-hydrogens, such as tBPIB, and particularly in solvents of poor hydrogen atoms transferring ability and at high substrate concentration (90,171). Bloomquist and Ferries(172) found that, the decomposition of peroxyesters in aromatic solvents is first order with respect to peroxide concentration, with slight induced decomposition. Rapid induced decomposition of peroxyesters was observed in alcohols and ethers(172).

In this investigation, the initial rate of tBPIB decomposition was found to be half order with respect to initial peroxide concentration. This probably implies that the decomposition is induced by certain non-rubber substances, and the termination by recombination of the radicals derived from tBPIB. However, the overal rate of tBPIB decomposition was found to be first order with respect to tBPIB concentration (Section 6.2). It is not understood how the reaction order with respect to peroxide concentration at the initial stage of the reaction and during the course of the run to be different. Perhaps the concentration of the inducing agents depletes rapidly at the initial stage of the reaction, so that the subsequent reaction would be first order with respect to peroxide concentration. If termination reaction is by recombination of radicals derived from tBPIB, then one of the procucts will be di-t-butyl peroxide, which is a relatively stable peroxide. This may have a bad consequences upon ageing properties of films from peroxide-prevulcanized latex.

6.8 Summary

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 coefficient for tBPIB decomposition and the rate coefficient for crosslink formation were generally found to increase with increasing fructose concentration and increasing temperature. The rate coefficient for tBPIB decomposition was found to be determined by activation free energy and not just by activation energy for the decomposition.

The instantaneous crosslinking efficiency of tBPIB systems was found to increase with increasing prevulcanization time. In some reaction systems, the instantaneous crosslinking efficiency tend to be greater than 50%. This indicates that both the alkoxy and alkyl radicals generated from the decomposition of tBPIB participate in the crosslinking reaction. The overall crosslinking efficiency of tBPIB systems was found to increase with increasing temperature. This is consequences of the effects of temperature upon efficiency of free-radical generation and efficiency of free-radical utilization for crosslinking.

CHAPTER 7

PROPERTIES OF FILMS FROM PEROXIDE-PREVULCANIZED NR LATEX

7.1 Introduction

In this chapter the properties of films dried down from peroxide- and sulphur-prevulcanized latices are compared. The sulphur-prevulcanized latex was prepared by heating HA latex with 1 pphr sulphur, 0.5 pphr ZDEC and 0.2 pphr ZnO for 2-6 hours at 60 °C. This formulation has been shown to yield a medium-modulus prevulcanized latex films(3). The peroxide-prevulcanized latices were mostly prepared from fructose-activated peroxide systems. The physical property tests were carried out on leached films, or as otherwise described. The factors which affect the physical properties of films from peroxide-prevulcanized NR latex are discussed. The effects of various antioxidants upon the ageing properties of films from peroxide-prevulcanized NR latex were investigated. Attempts will be made to explain the strength and coherence of films from peroxide-prevulcanized NR latex in terms of two popular theories which have been developed for films from prevulcanized NR latices in general, and for films from sulphur-prevulcanized NR latex in particular. These theories are:

1) that the strength and coherence of films from prevulcanized latex are a consequence of the formation of secondary valence bonds (van der Waals forces) between molecules at the regions of overlap between neighbouring latex particles (21-24), and
2) that the strength and coherence of films from prevulcanized latex are a consequence of distribution of crosslinks between latex particles during film or gel formation(25,26).

7.2 Formation of films from peroxide-prevulcanized NR latex

Films appear to form from peroxide-prevulcanized NR latices in a generally similar manner to that in which they form from sulphur-prevulcanized NR latices. The tendency for fissures or cracks to develop during film formation from prevulcanized latices depends upon the wet-gel strength of the film(173) and other associated factors, such as the level of prevulcanization, the homogeneity of prevulcanization, the thickness of film, and the drying conditions. Table 7.1 shows that the Q-value at which fissures begins to occur when films are dried from peroxide-prevulcanized latex apparently depends upon the type of peroxide and the prevulcanization conditions used. Factors which increase the rate of prevulcanization appear to increase the value of Q at which fissures first occur. Coherence films from tBPEH-prevulcanized latices formed less readily than did tBPIB-prevulcanized latex films.

7.3 Effects of leaching and addition of fructose upon physical properties of films from peroxide-prevulcanized NR latex

Table 7.2 shows that leaching in water significantly enhances the M500 and tensile strength of films from peroxide-prevulcanized latices. This is probably because the coherence of the film is improved by removal of water-soluble non-rubber substances, surfactant, unreacted fructose, and possibly also unreacted peroxide.

The results for the effects of adding extra fructose to the prevulcanized latex show that the presence of fructose badly affects the physical properties of films from peroxide-prevulcanized latex. Presumably the fructose discourages particle integration during drying. Consequently, the mutual forces of attraction (van der Waals forces) between the particles, on which the strength of the films depends, would be reduced. Van Dalfsen(22) explained that the difference in the strength behaviour of films from fresh and

Table 7.1. Effects of reaction variables upon crosslink concentration at which fissures tend to occur during film formation from peroxide-prevulcanized NR latex

Peroxide	[Peroxide] x 10^5 (gmol/g rubber)	[Fructose] (pphr)	Temp. (°C)	Q-value at which fissures occur
tBPIB	11.1	2	60	4.5
tBPIB	11.1	0.25	80	5.2
tBPEH	11.1	2	60	5.7
tBPEH	5.55	1	60	5.7
tBPEH	5.55	1	60	6.3[a]
tBPEH	11.1	2	40	4.6[b]

a The initial ammonia concentration used was 2.1% w/w on latex, and 0.7% for other systems.

b Prevulcanized in the presence of 0.02 pphr ferric ions.

Table 7.2. Effects of leaching[a] and addition of fructose into peroxide-prevulcanized NR latex[b] upon properties of latex films

Fructose added (pphr)	Film treatment	Q (g/g)	M500 (MPa)	TS (MPa)	EB (%)
0	unleached	6.3	1.29	20.5	903
0	leached	6.3	1.98	28.5	928
2	unleached	6.4	1.02	13.1	901
2	leached	6.4	2.42	27.0	929

a Leaching in distilled water for 24 hours at room temperature.

b Prevulcanized at 60 °C using tBPIB-fructose system.

purified NR latices is attributed to the differences in the thickness and the composition cf the adsorbed layers on the latex particles. A thick adsorbed layer on latex particles reduces the level of contact between rubber molecules from neighbouring particles, when the latex is dried down. Consequently the van der Waals forces between the particles would be reduced. The reduction of the van der Waals forces is particularly significant when the films are in a moist state, i.e., when the adsorbed layer is swollen.

7.4 Colour and transparency of films from prevulcanized NR latex

Films from prevulcanized latex using peroxide-fructose systems are lighter coloured and more transparent than are films from sulphur-prevulcanized latex. The transparency of films from sulphur-prevulcanized latex depends upon the nature and quantity of accelerators used(3). An improvement in film clarity can be achieved by using zinc dibutyldithiocarbamate instead of zinc diethyldithiocarbamate, and by ommiting zinc oxide. Leaching should further enhance the transparency of films from peroxide-prevulcanized latices, whereas, the effect of leaching upon the transparency of films from sulphur-prevulcanized latices is insignificant. Unleached films from peroxide-prevulcanized latices tend to darken when dried at temperatures higher than 70 °C. Since the melting point of fructose is 102 °C, the darkening of the films at lower temperature is probably not just due to heat, but also to the products of the thermal oxidation of fructose. The problem of film darkening at high drying temperatures can be overcome, or at least mitigated, by leaching the film or by using a smaller amount of fructose. When the quantity of fructose is small, presumably most of it is oxidized to acids during prevulcanization. These acids would be more resistant to thermal-oxidative degradation than fructose itself.

7.5 Factors affecting physical properties of films from peroxide-prevulcanized NR latex

It will appear subsequently that crosslink concentration is the most important factors which determines the physical properties of films from peroxide-prevulcanized NR latex. Other factors, such as the type of peroxide prevulcanization systems used and prevulcanization temperature also have some influence upon tensile strength of the films. The levels of vulcanizing agents did not appear directly to affect the physical properties of films from peroxide-prevulcanized NR latex. In sulphur-prevulcanization, the levels of vulcanizing agents do affect the mechanical properties of the films(3). For films with comparable crosslink concentration, a formulation which contains high sulphur/ low accelerator ratio tends to produce film having slightly higher tensile strength and modulus, and poorer ageing properties, than does a formulation which contains high accelerator/low sulphur ratio.

7.5.1. Effects of crosslink concentration upon physical properties of films from prevulcanized NR latices

Figure 7.1 shows that the tensile strength of films from peroxide-prevulcanized NR latex increases and then decreases with increasing crosslink concentration. Figure 7.2 shows that the tensile strength of films from sulphur-prevulcanized latex obtained in the present investigation is unusually high, and does not show a similar tensile strength-crosslink concentration relationship as that obtained by earlier workers(24,27,174). This is presumably, partly because of the long time elapsed(about 5-10 days) between the measurement of $[X]_{chem}$ and tensile properties, and hence some post-vulcanization in the film could have occured during storage at ambient temperature. There is no time to investigate this matter further, therefore, the properties of films from peroxide-prevulcanized NR latex will be compared with those from sulphur-prevulcanized latex obtained by earlier workers. There is a significant variation in the shapes of tensile

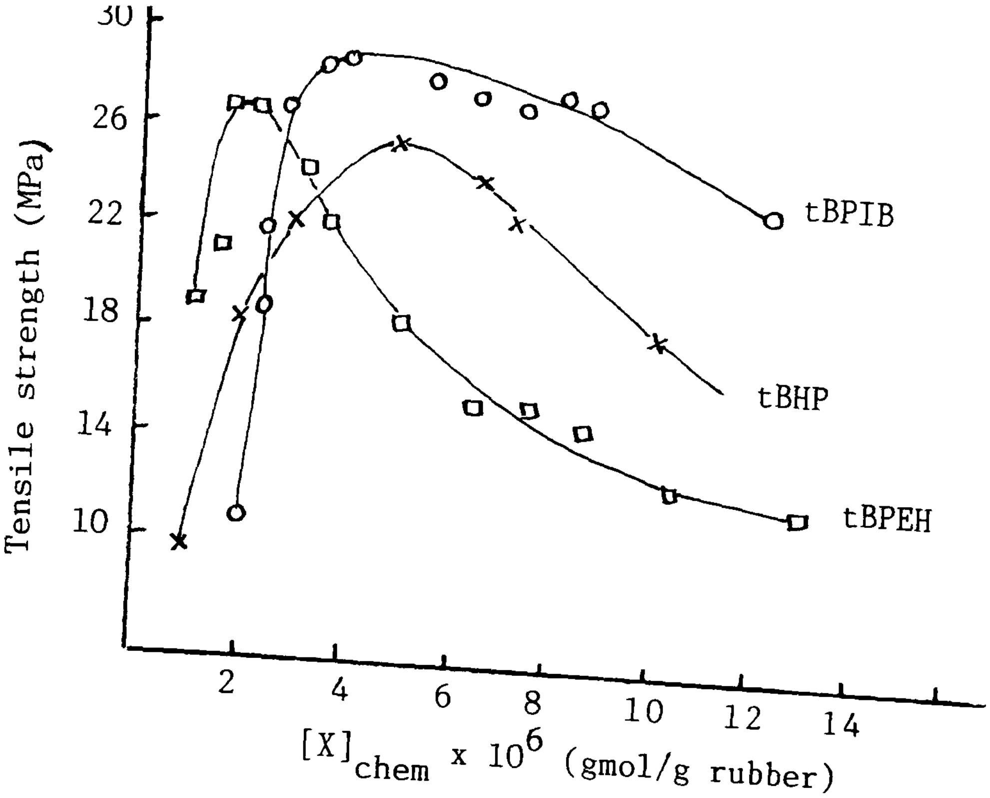


Figure 7.1. Tensile strength as a function of $[X]_{chem}$ for films from various peroxide-prevulcanized NR latices

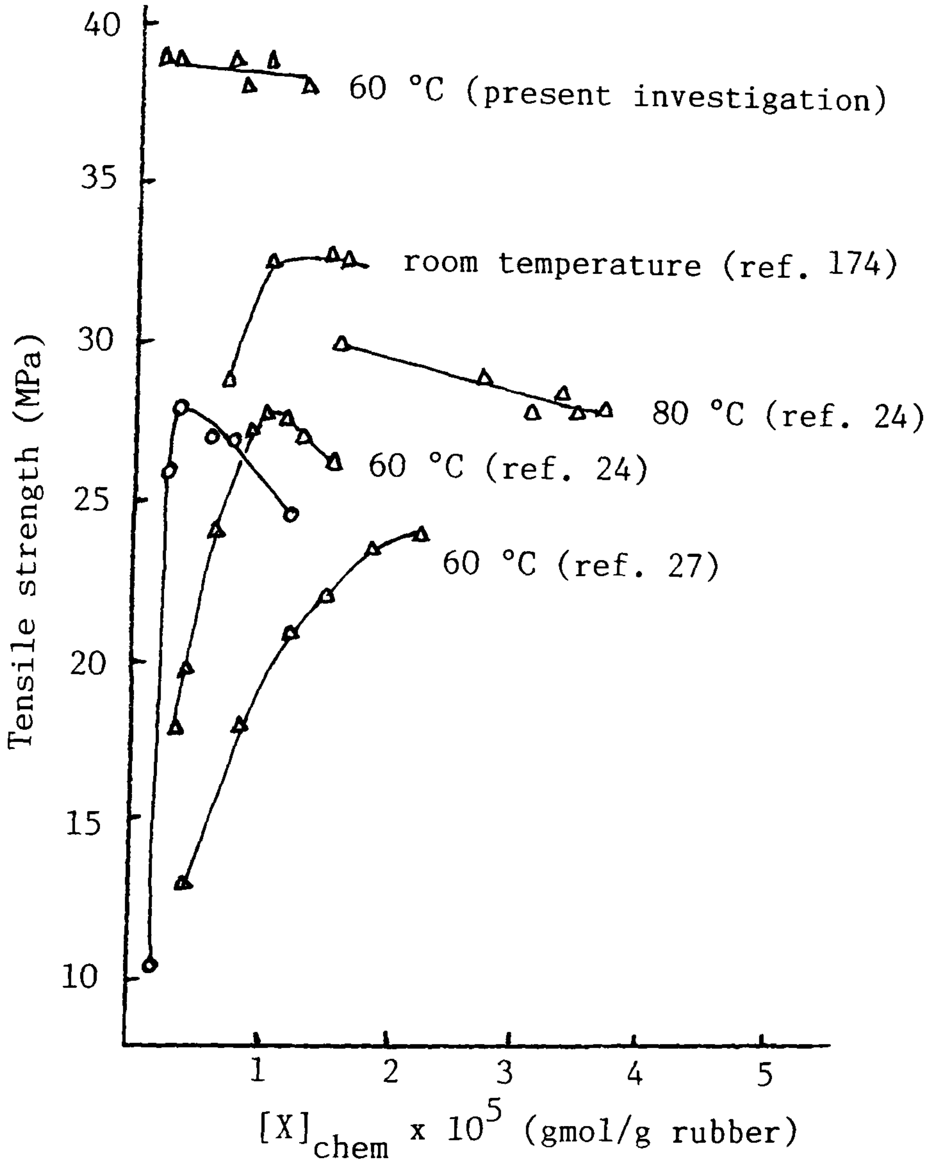


Figure 7.2. Tensile strength as a function of $[X]_{chem}$ for films from accelerated sulphur-prevulcanized NR latex (▵) obtained by various workers, and from tBPIB-prevulcanized NR latex (○).

strength-$[X]_{chem}$ curve for the sulphur-prevulcanized latex films obtained by the various workers (Figure 7.2). The tensile strength-$[X]_{chem}$ curve for peroxide-prevulcanized NR latex films is generally peakier, and the maximum tensile strength occurs at lower $[X]_{chem}$ than that for sulphur-prevulcanized latex films. Figure 7.3 shows that the shape of tear strength versus crosslink concentration curve for films from peroxide-prevulcanized latex is similar to the shape of the corresponding tensile strength versus crosslink concentration. Figures 7.4 and 7.5 shows the effect of crosslink concentration upon the modulus at 300% strain (M300) and the modulus at 500% strain (M500) respectively. Except for films from tBPEH-prevulcanized latex, the moduli of films from other peroxide-prevulcanized latices are generally similar. Figure 7.6 shows that the tension set of films from peroxide-prevulcanized latex decreases with increasing crosslink concentration.

7.5.1.1 <u>Discussion</u>

Merril(24) has attributed the initial increase in the tensile strength of films from sulphur-prevulcanized NR latex with increasing crosslink concentration to increase in the number of network chains available to bear the stress, and also to the enhancement of strain crystallization as the plastic flow of the chains is prevented. The decrease of tensile strength with further increase of crosslink concentration is attributed to reduction of van der Waals forces as a result of the reduction in the number of rubber-rubber contacts between particles as a consequence of the reduction in the mobility of the chains. The above discription should also hold for peroxide-prevulcanized latex, assuming for the moment that the strength of films from peroxide-prevulcanized latex films is primarily a consequence of van der Waals forces.

Because the maximum tensile strength for films from peroxide-prevulcanized NR latex occurs at much lower crosslink concentrations than in the case of peroxide gum dry NR

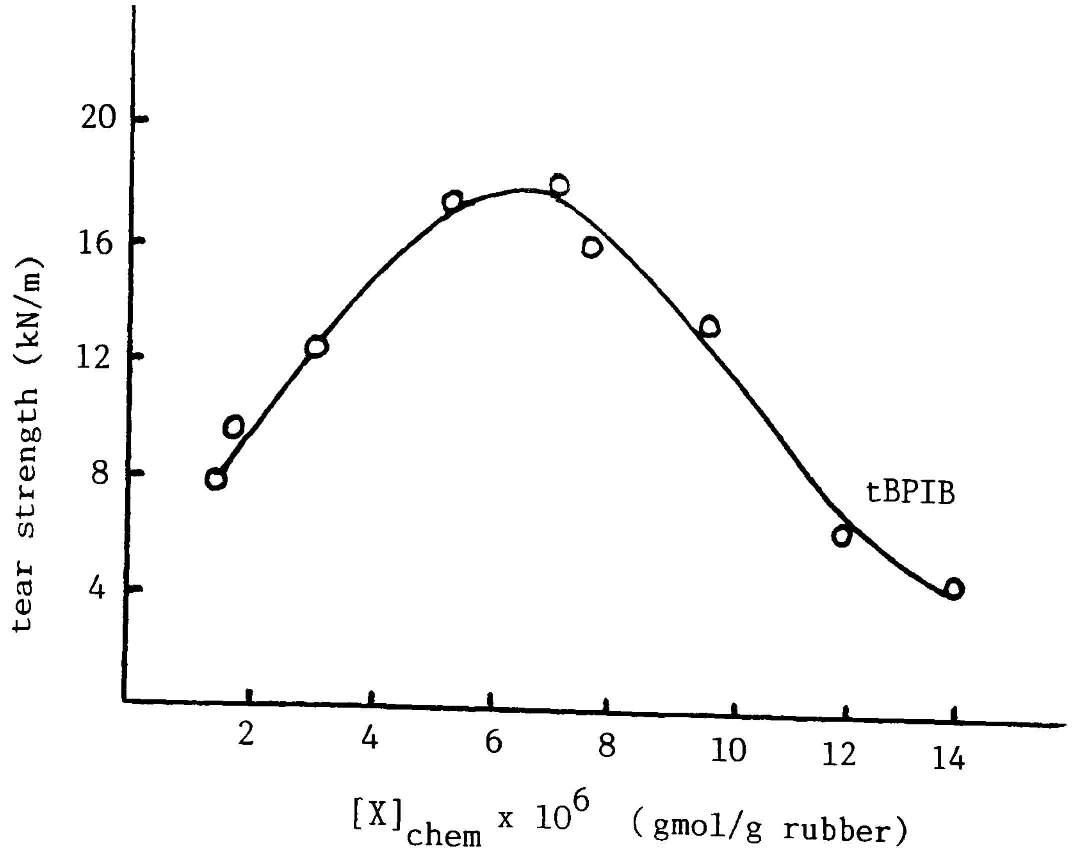


Figure 7.3. Tear strength as a function of $[X]_{chem}$ for films from tBPIB-prevulcanized NR latex.

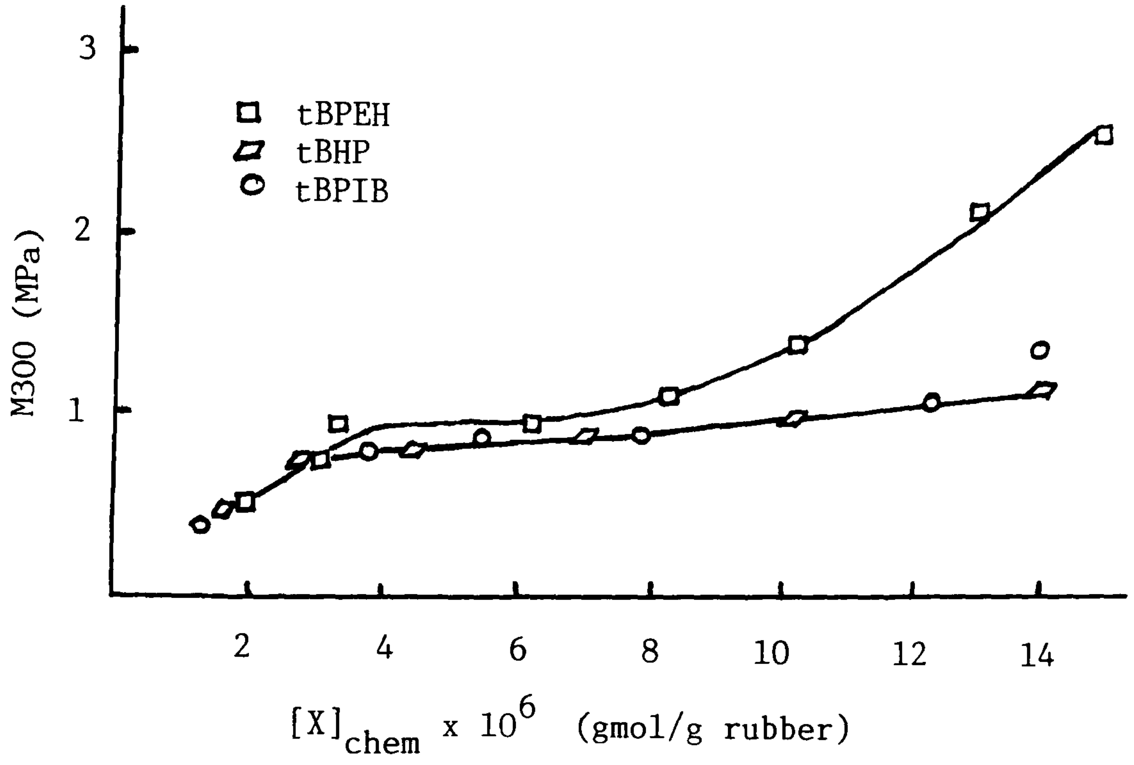


Figure 7.4. M300 as a function of $[X]_{chem}$ for films from various peroxide-prevulcanized NR latices.

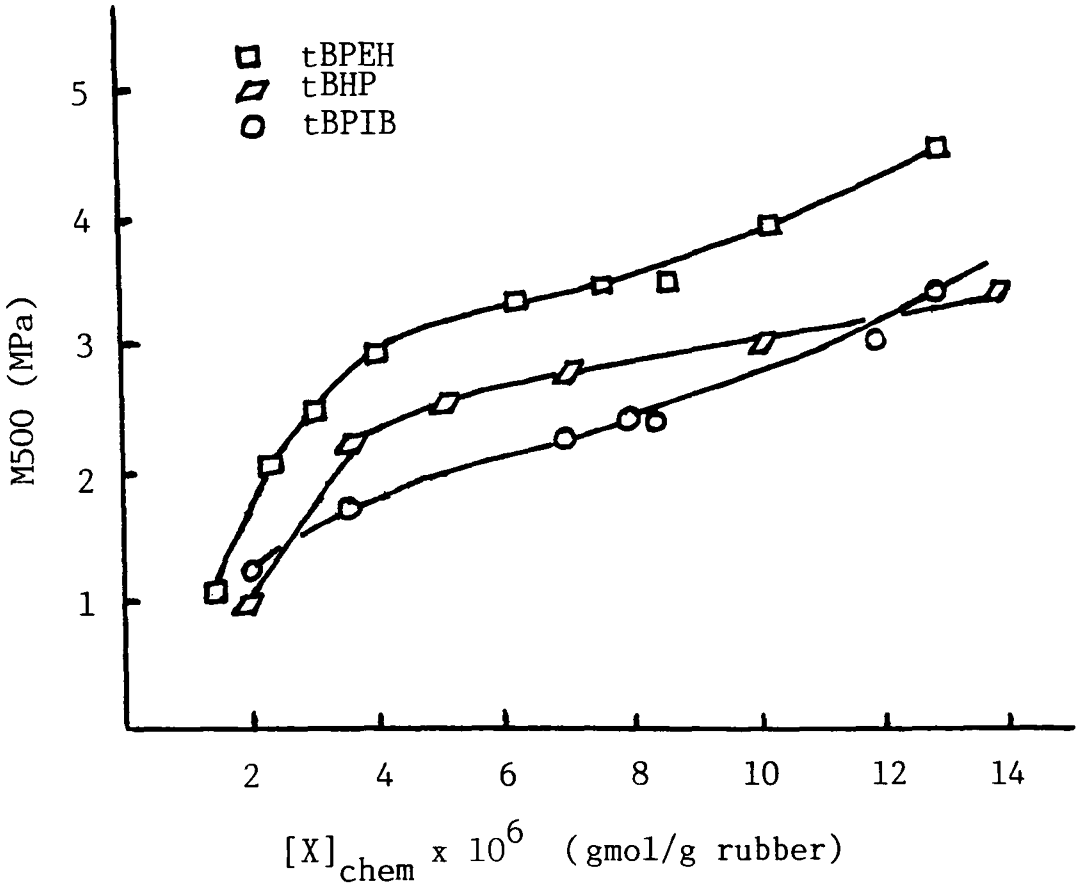


Figure 7.5. M500 as a function of $[X]_{chem}$ for films from various peroxide-prevulcanized NR latices.

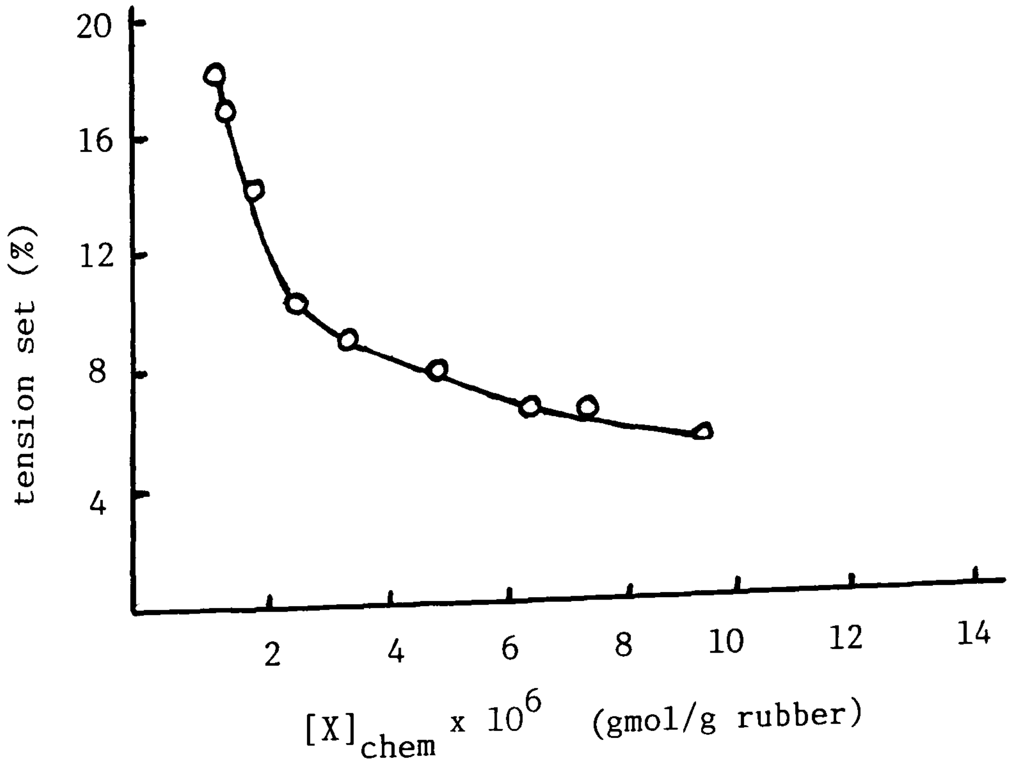


Figure 7.6. Tension set as a function of $[X]_{chem}$ for films from tBPIB-prevulcanized NR latex.

vulcanizate(13), the decrease of tensile strength, after reaching the maximum, with further increase of crosslink concentration cannot be attributed to shortening of the network chains making strain-induced crystallization unfavourable or causing the chains to be quickly brought to their rupture length. The results also suggest that the theory developed by Hu et al.(25,26) that the strength of prevulcanized latex films is due to the redistribution of crosslinks between latex particles cannot explain the strength behaviour of films from peroxide-prevulcanized latex. However, the theory of Hu et al. is reasonable for films from sulphur-prevulcanized latex, because S-S links are well-known to be labile, whereas C-C links are not labile under the same conditions, and so the theory is unreasonable for films from peroxide-prevulcanized latex. The decrease in the tensile strength of films from peroxide-prevulcanized latex with increasing crosslink concentration is probably primarily a consequence of reduction of van der Waals forces between the latex particles. The tensile strength maxima for films from sulphur-prevulcanized latex obtained by various workers(24,27,174) occured at higher crosslink concentration than those for films from peroxide-prevulcanized latices obtained in this investigation. It is possible that, in addition to the van der Waals forces, the formation of inter-particle crosslinks and/or the redistribution of crosslinked structures between particles during film formation could account for the higher crosslink concentrations at which the tensile strength maxima of films from sulphur-prevulcanized latex occured.

The tensile strength-crosslink concentration curve for films from peroxide-prevulcanized NR latex is peakier than that for films from sulphur-prevulcanized NR latex. This implies that the effect of increasing crosslink concentration upon the reduction of van der Waals forces is more profound in the films from peroxide-prevulcanized latex than in the films from sulphur-prevulcanized latex. Films from peroxide-prevulcanized NR latex show significantly higher tensile strengths than do peroxide gum dry NR vulcanizates(13).

This may be a consequence of differences in the molecular weight of the rubber. However, Subramaniam(33) found that the tensile strength of dry gum NR vulcanizates is not affected by the molecular weight if the number average molecular weight of the compounded rubber is greater than 1.5×10^5. The nature of the peroxide used to effect prevulcanization also influences the tensile strength-crosslink concentration relationships. Films from tBPEH-prevulcanized NR latex in particular show lower tensile strength at higher crosslink concentration compared with those of films from other peroxide-prevulcanized NR latices. It is not understood how the difference in the nature of peroxide used affect the tensile strength of these films. Chain modifications would stiffen the polymer backbone, and thus would affect the van der Waals forces, but such modifications were not detected in films from tBPEH-prevulcanized latex. Other possibilities are that these peroxides cause the breakdown of adsorbed materials to different extents or affect the distribution of crosslinks within the latex particles. High concentration of adsorbed materials and high concentrations of crosslinks distributed at the outer core of the latex particles would be expected to reduce the van der Waals forces between rubber molecules from neighbouring particles.

The tear strength of films from peroxide-prevulcanized latex is generally higher than that of peroxide gum dry NR vulcanizates(175,176). This is probably a consequence of the difference in the manner of tearing, i.e., knotty tear in films from peroxide-prevulcanized NR latex, and stick-slip tear in peroxide gum dry NR vulcanizates. Knotty tearing enhances the tear strength by increasing the effective tip diameter(177). According to Busse(178) the development of knotty tearing is associated with the strength anisotropy around the tip of the crack due to strain crystallization. Lake _et_ _al_.(175) postulated that the development of knotty tearing in prevulcanized NR latex is associated with the relatively weak zones between latex particles.

Modulus is the resistance of the network structure to deformation. Films from peroxide-prevulcanized NR latex generally show "medium" modulus. Films from tBPEH-prevulcanized NR latex show a relatively rapid increase of M300 value with increasing crosslink concentration, and also relatively higher M500 values compared with other films from other peroxide-prevulcanized latices. These results again indicate that possible modifications may hage occured in the films from tBPEH-prevulcanized latex.

Tension set is a measure of the residual, i.e., non-recovered, linear strain in a deformed sample after specified recovery conditions. Thus tension set represents partly permanent and partly subpermanent set. The decrease of tension set of films from peroxide-prevulcanized latex with increasing crosslink concentration is a consequence of the inhibition of permanent flow under deformation as the tangle of polymer molecules is converted into a network.

7.5.2. Effect of prevulcanization temperature upon tensile strength of films from peroxide-prevulcanized latex

Table 7.3 shows that, for films from peroxide-prevulcanized NR latex having comparable crosslink concentrations, prevulcanization at higher temperatures tends to produce films having lower tensile strength. Bristow(176) found that scission during peroxide vulcanization of dry NR at high temperatures is not a temperature-dependent process. Thus, if there is any possibilities for scission to occur during peroxide prevulcanization of NR latex, it is unlikely that it is a direct effect of temperature. The promotion of scission by oxygen might be temperature-dependent. Another possibility that accounts for the lower tensile strength at **higher** temperature is that, the rates of crosslink insertion is **higher** at higher temperatures, and this may not allow a uniform distribution of vulcanizing

Table 7.3. Effects of prevulcanization temperature upon tensile strength of films from peroxide-prevulcanized NR latex*

Prevulcanization temperature (°C)	Q (g/g)	TS (MPa)
40	8.1	20.7
20	8.1	28.8
40	7.6	19.5
20	7.6	27.3

* Prevulcanized using tBPEH-fructose-ferric ion system.

Table 7.4. Effects of coagents upon properties of films from peroxide-prevulcanized NR latex

Q (g/g)	Coagent	M500 (MPa)	TS (MPa)	EB (%)
9.2	without	0.69	21.1	1020
	with sulphur[b]	1.56	25.3	1088
5.0	without	3.80	17.8	778
	with TMPTM[c]	3.91	19.0	806
6.3	without	1.62	26.5	947
	with GDA[d]	2.06	27.3	991

a Prevulcanized using tBPIB-fructose system at 60 °C in the presence of coagent.
b Sulphur at 2 pphr.
c Trimethylol propane trimethacrylate, at 1.9 pphr.
d Glutaric dialdehyde, at 0.3 pphr.

agents to be attained. Hence the crosslink distribution within the particles is less uniform, thus reducing the van der Waals forces between the particles. Increasing the rate of prevulcanization may increase the degree of randomness in the crosslink insertions. Gehman(179) postulated that, the formation of short network chains increases with increasing degree of randomness in the crosslink insertions. Short network chains are elastically rather ineffective(180) and are detrimental for the development of high tensile strength(179).

7.5.3 Effects of coagents upon tensile properties of films from peroxide-prevulcanized latex

Table 7.4 shows that the use of peroxide coagents does not greatly affect the tensile strength of films from peroxide-prevulcanized NR latex. Perhaps the tensile strength would be affected if high concentrations of polyfunctional coagent are used, as the main chains might then be considerably modified by the coagent molecules being grafted on to the chains. However, the M500 value of the film with sulphur present is significantly higher than that without sulphur, although these films have the same crosslink concentration.

7.5.4 Effect of storage of latex compound upon tensile properties of films from peroxide-prevulcanized latex

Table 7.5 shows that the strength of films from tBPEH-prevulcanized latex was slightly increased when the compounded latex was stored for 20 hours at room temperature prior to use, a process which is commonly called maturation. maturation is claimed partly to affect the distribution and equilibration of the vulcanizing agents(181). In the present case, storage of the latex possibly leads to a more uniform distribution of crosslinks within the latex particles, and consequently to the enhancement of tensile strength. The results show that maturation appears to have little effect upon M500 values.

Table 7.5. Effects of 'storage' of latex compound upon properties of films from peroxide-prevulcanized NR latex[a]

Compound preparation before prevul.[a]	Prevul. time (hr)	Q (g/g)	M500 (MPa)	TS (MPa)	EB (%)
A	2	7.1	2.22	17.7	880
B	4	6.9	2.47	20.1	880
A	5	5.1	4.66	6.8	598
B	7	5.1	3.85	11.9	742
A	6	4.8	5.11	6.3	560
B	8	4.8	4.83	10.5	696

a Prevulcanized at 60 °C using 1.09 x 10^{-4} gmol/g rubber tBPEH and 2 pphr fructose.

b A) The latex compound was mixed for approximately 5 minutes at room temperature.

B) The latex compound was mixed for 2 hours at 3 °C, and then stored for 20 hours at 5 °C.

Table 7.6. Effects of film type and film treatments upon properties of films from peroxide-prevulcanized NR latex[a]

Type of film	Leaching[b]	Drying	Q (g/g)	M500 (MPa)	TS (MPa)	EB (%)
cast	A	at room temp.	6.7	2.72	21.6	993
coagulant[c] dipped	B	at room temp.	5.8	3.60	22.7	949
coagulant[c] dipped	B	at room temp.	6.1	3.60	22.7	1015

a Prevulcanized at 60 °C for 5 hours using 5.45 x 10^{-5} gmol/g rubber tBPIB and 2 pphr fructose.

b A) Leaching in water for 24 hours at room pemperature.

B) Wet-gel leaching in hot water (80 °C) for 15 minutes.

c 40% calcium nitrate in IMS.

7.5.5 Effect of type of films and film treatments upon properties of films from peroxide-prevulcanized NR latex

Table 7.6 shows that coagulant-dipped films exhibit slightly lower Q-values than did cast films from the same peroxide-prevulcanized NR latex. It is not clear how the coagulant dipping process could have affected the crosslink concentration of these films. The type of films, and the differences in the film treatments appear to have little effect upon tensile strength. Gazeley(42) found that heating of cast films from peroxide-prevulcanized NR latex for 45 minutes at 70 °C tends to increase the tensile strength of the films, whereas heating of the films for 40 minutes at 100 °C tends to decrease tensile strength. This is because, heating at 70 °C increases the coherence of the films by enhancing the intergration of rubber particles, whereas heating at 100 °C increases the coherence of the films and also increases the rage of degradation of the films. In the case of cast films from sulphur-prevulcanized NR latex, heating of the films for 45 minutes at 70 °C or 30 minutes at 100 °C, increases the crosslink concentration of the films and also tends to increase the tensile strength of the films. Heating of films from sulphur-prevulcanized latex would increase the coherence of the films by the formation of crosslinks between rubber molecules from neighbouring rubber particles. The ageing properties (Section 7.6) of unprotected films from peroxide-prevulcanized NR latices are poor. However, drying of the films for 3 hours at 80 °C does not appear to result in the deterioration of the physical properties of the films.

7.6 Ageing properties of films from peroxide-prevulcanized NR latex

Table 7.7 shows that the ageing properties of unprotected films from peroxide-prevulcanized NR latex are poor. This is because the natural antioxidants in NR latex have been oxidized during prevulcanization, and probably also the presence of pro-oxidants in the films. The addition

Table 7.7. Effects of antioxidants upon aged (70 °C for 7 days) properties of films from peroxide-prevulcanized NR latex[a]

Antioxidant	Percentage retention of property after ageing		
	M500	TS	EB
without antioxidant	36	5	60
ZDEC (1 pphr)	76	130	127
Antioxidant 2246[b] (1 pphr)	52	17	79
Irganox 1035 (1 pphr)	65	87	119
Irganox 1093 (1 pphr)	59	41	103
Irganox 1010 (1 pphr)	65	56	105
Irganox 1076 (1 pphr)	62	49	104
Irganox PS802 (1 pphr)	70	49	101
Irgafos TPP (1 pphr)	61	41	90
cadmium diisopropyl thiophosphate (1 pphr)	65	58	107
EDTA (1 pphr)	61	41	90
Antioxidant 2246 (0.5 pphr) +			
Irganox PS802 (0.5 pphr)	60	38	93
EDTA (0.5 pphr)	61	30	90
Irganox 1076 (1 pphr)	58	28	90
Irgafos TPP (0.5 pphr)	56	19	79
EDTA (0.5 pphr)	61	30	90
Antioxidant 2246 (0.5 pphr) +			
Irganox PS802 (0.5 pphr) +			
EDTA (0.5 pphr)	68	67	107
Irganox 1076 (0.5 pphr)	57	33	95
Irgafos TPP (0.5 pphr)	61	20	81

[a] Latex prevulcanized at 60 °C for 4 hours using 5×10^{-5} gmole/g rubber tBPIB and 1 pphr fructose. Unaged film properties; M500 = 3.03 MPa, TS = 21.1 MPa, EB = 849.

[b] Discoloration of all samples using Antioxidant 2246.

of certain antioxidants into peroxide-prevulcanized NR latex help improve the ageing properties of the films. Table 7.8 shows the structure of some of the antioxidants used in this investigation. Amongst the antioxidants studied, ZDEC was found to be the most effective. This is a pity, because one of the reasons for working to develop peroxide-prevulcanized NR latex is to avoid the use of dithiocarbamates. The second most effective antioxidant investigated is Irganox 1035. Some of the antioxidants are much more effective on their than when combined with other antioxidants.

7.6.1 Discussion

The autoxidation of polyolefins is believed to proceed as follows(150,182):

$$\begin{array}{lll} \text{Initiation} & nROOH \longrightarrow \text{production of } ROO\cdot, R\cdot & (7.1) \\ \text{Propagation} & ROO\cdot + RH \longrightarrow ROOH + R\cdot & (7.2) \\ & R\cdot + O_2 \longrightarrow ROO\cdot & (7.3) \\ \text{Termination} & \left.\begin{array}{l} R\cdot + R\cdot \longrightarrow \\ R\cdot + ROO\cdot \longrightarrow \\ 2ROO\cdot \longrightarrow \end{array}\right\} \text{non-radical products} & \begin{array}{l} (7.4) \\ (7.5) \\ (7.6) \end{array} \end{array}$$

where RH represents the polymer. The following reactions will also occur if antioxidant AH and hydroperoxide decomposer A* are present:

$$ROO\cdot + AH \longrightarrow ROOH + A\cdot \qquad (7.7)$$

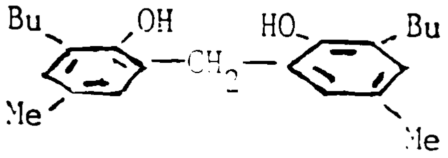
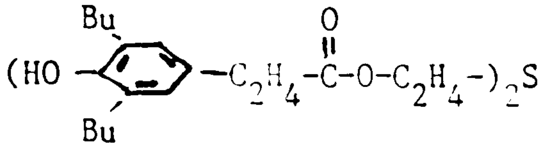
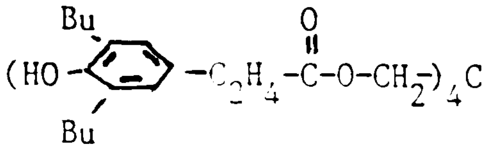
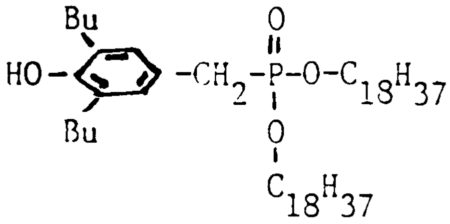
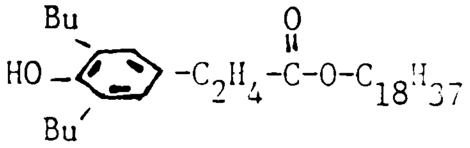
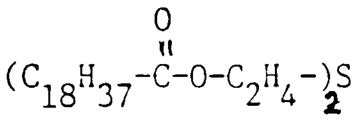
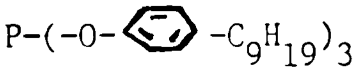
(scavenging peroxy radical)

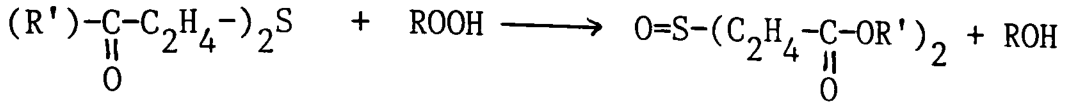
$$ROOH + A^{*} \longrightarrow ROH + A^{*}O\cdot \qquad (7.8)$$

(decomposing hydroperoxide)

Some of the antioxidants studied were chosen because of the specific antioxidation mechanism in which they are believed to participate. Irganox PS802 (thiodipropionate ester) and Irgafos TPP (aryl phosphite) are preventive antioxidants, reducing the rate of initiation of autoxidation by decomposing hydroperoxide(164, 183):

Table 7.8. Chemical structures of some antioxidants

Antioxidant	Structure
ZDEC	$[(C_2H_5)_2NCS_2]_2Zn$
Antioxidant 2246	
Irganox 1035, bis- (beta-(3,5-ditert-butyl-4-hydroxybenzyl)-methylcarboxyethyl) sulphide	
Irganox 1010, pentaerythrityl tetrakis (3,5-ditert-butyl-4-hydroxyphenyl) propionate	
Irganox 1093, distearyl-3,5-ditert-butyl-4-hydroxybenzyl-phosphonate	
Irganox 1076, stearyl-beta-(3,5-ditert-butyl-4-hydroxyphenyl) propionate	
Irganox PS802, distearyl thiodipropionate	 $(C_{18}H_{37}-\overset{O}{\overset{\parallel}{C}}-O-C_2H_4-)_2S$
Irgafos TPP, tris-(para-nonylphenyl) phosphite	

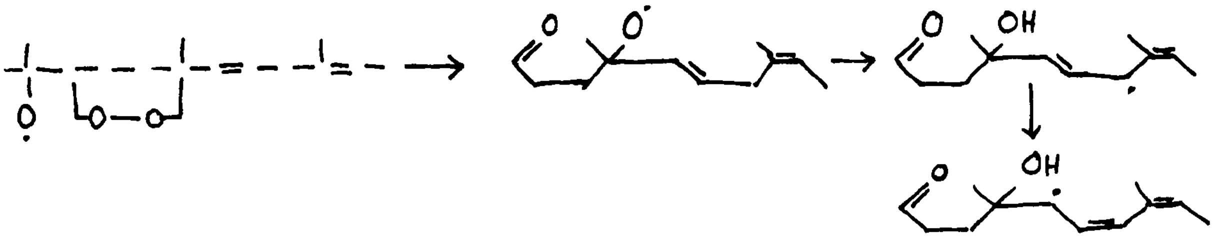


$$(R')-\underset{\overset{\|}{O}}{C}-C_2H_4-)_2S + ROOH \longrightarrow O{=}S-(C_2H_4-\underset{\overset{\|}{O}}{C}-OR')_2 + ROH \qquad (7.9)$$

$$P-(OR')_3 + ROOH \longrightarrow O{=}P-(OR')_3 + ROH \qquad (7.10)$$

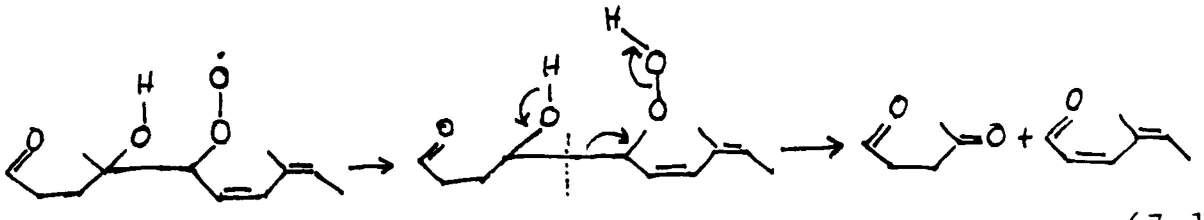
However, the sulphide shown in Equation 7.9 was found to be ineffective in dry NR at 75 °C and below(164,184). ZDEC probably functions by decomposing hydroperoxides(164) as well as sequestering heavy-metal ion(164,185). Blends of a non-volatile antioxidant, a zinc dithiocarbamate, zinc mercaptobenzimidazole and lime have been found to provide excellent protection for peroxide dry NR vulcanizate, particularly when all are included(186,187). Hindered phenolics and thiodipropionate esters have been found to exhibit synergistic effects in polymer stabilization(188). The synergistic mechanism involves several reaction steps including regeneration of the phenolic antioxidant. However, synergistic effects of antioxidants in NR have not been observed.

In the present investigation, the relative effectiveness of antioxidants was evaluated based on the percentage retention of tensile strength after ageing, as tensile strength is the property worst affected by oven ageing. The relatively poorer ageing properties of protected films from peroxide-prevulcanized NR latex compared to protected peroxide dry NR vulcanizates, and the effectiveness of ZDEC and Irganox PS802 as antioxidants for films from peroxide-prevulcanized NR latex suggest the presence of a pro-oxidant in the films. Irganox 1035 is considerably more effective than, say, Irganox 1010, notwithstanding that the differences in their chemical structures are minor. The presence of sulphide group in Irganox 1035 enhances its antioxidant potential, possibly by increasing its thermal stability or effecting a similar antioxidation mechanism to that effected by thiodipropionate ester. The antioxidant system comprising antioxidant 2246, Irganox PS 802 and EDTA was found to be fairly effective. This is probably a consequence of the combined effect of the different antioxidation mechanisms. EDTA is claimed to inhibit metal-catalyzed oxidation of rubber(185). This system could possibly be further improved if antioxidant 2246 were replaced by a more effective phenolic antioxidant, such as Irganox 1035. Antioxidant 2246 was found to be effective in reducing the rate of oxygen absorption and consequent extent of degradation of NR vulcanizates(189,190). However, antioxidant 2246 was found to increase the scission efficiency of oxygen(189). Barnard(191) reckoned that, if antioxidants could be found that do not increase scission efficiency, then protection of NR vulcanizates could be improved by a factor of five or more. The mechanism of scission of NR is not fully understood. Scission appears to take place in the propagation step of oxidation, and that scission in the termination step is dominant only in heavily inhibited systems(192,193). Various workers(192,194-196) have proposed different mechanisms for scission, and that proposed by Barnard <u>et al</u>.(192) is considered to be a more complete mechanisms for scission. The mechanisms of scission involve the formation of a cyclic peroxide , formation of a six membered ring system with the doubly-allylic hydrogen atom and extraction can occur to give an alcohol and a secondary radical:



(7.11)

The next step involves the addition of molecular oxygen to form a β-hydroxy peroxy radical. The peroxy radical could abstract a hydrogen atom intermolecularly to form a β-peroxy-hydroperoxide, leading to the formation of scission products:



(7.12)

7.7 Summary

Factors affecting physical properties of films from peroxide-prevulcanized latex have been investigated. The physical properties of films from peroxide-prevulcanized NR latex were found to be significantly affected by the concentration of crosslink. Differences in the strength of films from peroxide-prevulcanized NR latex, films from sulphur-prevulcanized NR latex and peroxide gum dry NR vulcanizates have been discussed. The strength of films from peroxide-prevulcanized NR latex appears to be determined, primarily by secondary valence forces. The ageing properties of unprotected films from peroxide-prevulcanized NR latex were found to be poor. This is probably due to the presence of a pro-oxidant in the films. Addition of certain antioxidants into the prevulcanized latex helps improve the ageing properties of the films.

CHAPTER 8

CONCLUSION AND SUGGESTIONS FOR FURTHER WORK

8.1 Introduction

The main findings of Chapters 5,6 and 7 are summarized in this chapter. Where appropriate suggestions for further work are made. Ther are minor differences in the effects of reaction variables upon the prevulcanization behaviour of various fructose activated peroxyester and fructose-activated hydroperoxide systems. However, the general effects of the reaction variables upon the prevulcanization behaviour will be summarized for the tBPIB-fructose system. Comparisons between the peroxide prevulcanization of NR latex and the peroxide vulcanization of dry NR and also between the peroxide and accelerated-sulphur prevulcanization of NR latex are made.

8.2 Effectiveness of non-activated peroxide prevulcanizing systems for NR latex

The effectiveness of a peroxide prevulcanizing system can be characterized by the crosslinking efficiency of the system (f_∞) and the rate coefficient for crosslink formation (k"). For most peroxide prevulcanizing systems, an increase in k" leads to a corresponding increase in f_∞. However, the relationship is not linear. The effectiveness of peroxide prevulcanizing systems was found to depend upon a number of factors, such as the type of peroxide and the nature of free radicals produced on decomposition, the presence of activators and coagents, the prevulcanization temperature, the concentration of peroxide and activator, and the non-rubber substances present in the latex.

For non-activated peroxide prevulcanization systems, the nature of the peroxide determines the temperature over which it is effective. Thus tBP was found to be ineffective at 100 °C; for the crosslinking of dry hydrocarbon polymers using tBP, a typical cure temperature is 190 °C(60). The peroxyesters were found to be generally effective prevulcanizing agents at 100 °C. In fact, tBPIB was found to be quite effective at 80 °C-90 °C. It is suggested that further prevulcanization studies using the more reactive peroxyesters, such as tBPEH, tBPPV and tBPND, could be carried out in the temperature range 70 °C-100 °C. A non-activated prevulcanizing system has the advantage of avoiding the use of an activator which incurs additional cost and possibly other technical problems associated with it. On the other hand, in principle, the use of an added activator should swamp any (variable) activating effects arising from the presence of non-rubber substances. There are a number of facts which suggest that the non-rubber substances present in NR latex do not significantly promote the free-radical decomposition of peroxyesters and hydroperoxides. It is suggested that the effects of the non-rubber substances in promoting peroxide prevulcanization, or in reducing the efficiency of prevulcanization, be systematically investigated. Such an investigation could be carried out by systematic addition of the non-rubber substances to a purified NR latex, or to a synthetic polyisoprene latex.

Diacyl peroxide and peroxydicarbonates were found to be ineffective in vulcanizing NR latex, probably because of the relatively less reactive alkyl radicals they generate. The ineffectiveness of peroxydisulphate systems is probably because of the tendency for the peroxydisulphate anions to partition in the aqueous phase. Burfield et al.(135) postulated that the negatively charge latex particles poses a high potential energy barrier for sulphate ion-radical to penetrate the latex particles. However, peroxydisulphate anion is so effective as an initiator for the emulsion polymerization of monomers of low water solubility, such as styrene. It would perhaps useful to study the effect of charge density on latex particles, and the effect of adsorbed layer upon the prevulcanization efficiency or graft-copolymerization efficiency of peroxydisulphate anions in NR latex.

8.3 Effectiveness of activated peroxide prevulcanizing systems for NR latex

It has been found that latex prevulcanization using hydroperoxides and peroxyesters can be accelerated by adding a suitable activator. Fructose was found to be very effective in promoting latex prevulcanization using hydroperoxides and peroxyesters. This is perhaps surprising, not only because it is one of the less oxidisable of the reducing agents tried, but also because it must partition almost entirely in the aqueous phase of the latex. Experimental results seem to indicate that reducing agents which are less readily oxidized tend to be more effective than those which are more readily oxidized. Prevulcanizations using the peroxyester-fructose or hydroperoxide-fructose systems can be effectively carried out at temperatures greater than 50 °C. It was found that the addition of a trace amount of a ferric ion-pyrophosphate complex to the above systems allows prevulcanization to be carried out quite effectively at a temperature within the range 20 °C-40 °C. It was mentioned earlier that the transition-metal ions in NR latex are not active in promoting peroxide decomposition in NR latex. One of the reasons for their ineffectiveness is probably that they are not in the form of metal-ion complexes. It is suggested that the effect of adding various complexing agents to latex on the peroxide prevulcanization of NR latex be investigated.

It was found that the effect of fructose upon the values of k'' and f_{∞} varies according the nature of the hydroperoxide or peroxyester. The fructose-activated tBHP system was found to be more effective than the fructose-activated CHP and dIBMHP systems, presumably because tBHP generates a more reactive alkoxy radicals than do the other hydroperoxides. Besides, tBHP is more resistance to acid-catalyzed reaction than are the other hydroperoxides. It was found that the effectiveness of fructose-activated peroxyester systems shows no correlation with the structures and reactivities of the peroxyesters. It was also found that there is no correlation between the effectiveness of a fructose-activated peroxyester system and the partition coefficient of the peroxyester between n-decane and water. Amongst the systems studied, the fructose-activated tBPEH and tBPIB systems were found to be the most effective prevulcanizing systems. It is suggested that the effect of peroxyester structures upon their fructose-activated decompositions in latex be investigated. This investigation could be carried out by using a synthetic polyisoprene latex, where interference by the naturally-occuring non-rubber substances in NR latex would be avoided. The contributions of unimolecular homolytic and fructose-activated homolytic decomposition of the peroxyester in the latex could then be ascertained. It was mentioned earlier that a ferric-ion complex enhances the effectiveness of peroxyester-fructose prevulcanizing systems. Theoretically, it is to be expected that it is the ferrous ion that reduces the peroxyester. In the present system, fructose can reduce ferric ion to ferrous ion. It is suggested that the effects of both ferric- and ferrous-ion complexes upon the decomposition rate of peroxyesters in NR latex be studied both in the absence and in the presence of fructose.

8.4 Kinetics of latex prevulcanization using tBPIB-fructose system

The kinetic studies of prevulcanization using the tBPIB-fructose system produced a number of unexpected results, some of which cannot be satisfactorily explained at present. It is suggested that the prevulcanization kinetics of other systems, particularly of the tBHP-fructose system, be investigated, so that comparisons can be made with the prevulcanization kinetics of tBPIB-fructose system.

The decomposition of tBPIB in NR latex and the formation of crosslinks in the rubber phase were both found to be first-order reactions with respect to peroxide concentration. The rate coefficients for the decomposition of tBPIB (k') and for the formation of crosslink (k") increase with increasing prevulcanization temperature and fructose/ tBPIB concentration ratio. k" tends to be greater than k' at temperatures higher than 70 °C and using a high fructose concentration. The instantaneous crosslinking efficiency (F_t) was found to increase with prevulcanization time and temperature. The variation of F_t, k' and k" with temperature, and the consequent effect of temperature upon the relationship between k' and k", are probably a consequence of the same effect, i.e., a consequence of several competing reactions each having different temperature coefficient. These competing reactions are: reactions of free radicals generated by the decomposition of peroxide with the rubber hydrocarbon and the non-rubber substances, recombination of polymeric radicals, and combination of polymeric radicals with non-polymeric radicals. It is suggested that prevulcanization studies using highly purified NR latex be carried out in order to ascertain the dependence of crosslinking efficiency with temperature.

For prevulcanizing systems using high levels of fructose, the experimental activation energy for the decomposition of tBPIB appeared to show strong temperature-dependence. This is probably because of the occurence of different tBPIB decomposition reactions having different activation energies. In the present case, there are at least three types of tBPIB-decomposition reactions: unimolecular homolytic decomposition, fructose-activated decomposition and metal-ion-catalyzed decomposition. Experimental results indicate that the activation energy for unimolecular homolytic decomposition of tBPIB is higher than that for fructose-activated decomposition, and the activation energy for metal-ion-catalyzed decomposition is lower than that for fructose-activated decomposition. It is suggested that a detailed investigation of the activation energy for the decomposition of tBPIB in purified NR latex using non-activated, fructose-activated, and metal-ion-catalyzed systems be carried out over a wide range of temperature, and a wide range of peroxide, fructose and metal ion concentrations.

Prevulcanization at temperatures greater than 80 °C using the tBPIB-fructose system can yield F_t values which are greater than 50%. This suggests that both the alkyl as well as the alkoxy radicals generated from tBPIB are involved in the crosslinking reaction. Diacyl peroxides generate alkyl radicals on decomposition. It is suggested that prevulcanization studies at high temperatures using different diacyl peroxides be investigated in order to find out the relative effectiveness of the various alkyl radicals in crosslinking of NR latex.

The initial rate of tBPIB decomposition in NR latex, and in the presence of fructose, was found to be half order with respect to initial peroxide concentration. This is probably a consequence of induced decomposition of tBPIB by certain non-rubber substances, and termination by recombination of the radicals derived from tBPIB. Experimental results apparently indicate that the initial rate expression for tBPIB decomposition in NR latex comprise more than one terms containing fructose concentration. The decomposition of tBPIB during the run was found to be first order with respect to peroxide concentration. The reason for the difference in the reaction-order with respect to peroxide concentration, at the initial stage of the reaction and during the run is not understood. Further research on this subject is needed. It is suggested that an investigation of the reaction products and kinetics of the reactions between tBPIB and fructose in aqueous solution, hydrocarbon and inert solvents be studied.

8.5 Comparison between fructose-activated tBPIB system and ZDEC-accelerated sulphur system for prevulcanization of NR latex

The rate of prevulcanization at a temperature range 50 °C-80 °C, using the tBPIB-fructose system is greater than that using the sulphur-ZDEC system. Peroxide prevulcanization ceases when all the added peroxide molecules have decomposed. In the case of the sulphur-ZDEC system, prevulcanization still proceeds after prolonged heating. The fructose-activated tBPIB system shows a higher degree of flexibility in respect of control of rate of prevulcanization and ultimate degree of crosslinking, as compared to the ZDEC-accelerated sulphur system. The crosslinking efficiency for the tBPIB-fructose system, expressed as the number of crosslinks formed per tBPIB molecule decomposed, is significantly higher than the crosslinking efficiency for the ZDEC-sulphur system expressed as the number of crosslinks formed per atom of sulphur combined. The decomposition of tBPIB and the dissappearance of sulphur in NR latex prevulcanization are both first order with respect to tBPIB concentration and sulphur concentration , respectively.

8.6 Properties of films from peroxide-prevulcanized NR latex; comparison with films from sulphur-prevulcanized NR latex and with gum NR vulcanizates

In this section, the properties of films from sulphur-prevulcanized NR latex prepared by other workers (3,24,25) are also considered. The physical properties of films from peroxide-prevulcanized NR latex were found to be considerably influenced by the degree of crosslinking of the rubber. The nature of the peroxide was also found to influence the properties of films from peroxide-prevulcanized NR latex to a small extent.

It was found that the tensile strength of films from peroxide-prevulcanized NR latex first increases and then decreases with increasing crosslink concentration. The tensile strength versus crosslink concentration curve for films from peroxide-prevulcanized NR latex is peakier than that for films from sulphur-prevulcanized NR latex. The tensile strength maximum for films from peroxide-prevulcanized NR latex was found to be lower than that for films from sulphur-prevulcanized NR latex. From these results, several conclusions have been drawn:

a) The strength and coherence of films from both peroxide- and sulphur-prevulcanized NR latices are governed mainly by the van der Waals forces between the polymer chains in the region of overlap between neighbouring latex particles;

b) The occurrence of a higher tensile strength maximum at a higher crosslink concentration for the films from sulphur-prevulcanized latex, relative to that for films from peroxide-prevulcanized latex, is attributed to the nature of crosslink, i.e., the type of crosslink that favours the development of higher tensile strength will also develop maximum tensile strength at a higher crosslink concentration; and

c) The sharper variation of tensile strength with crosslink concentration for films from peroxide-prevulcanized latex as compared with that for sulphur-prevulcanized latex, is a consequence of C-C bonds being more rigid than S-S bonds, and this affect the manner in which the van der Waals forces between neighbouring particles are affected by increasing the concentration of these bonds in the latex particles.

Films from peroxide-prevulcanized NR latex have higher tensile strength than does peroxide-cured dry NR. In the films from the prevulcanized latex, the particulate structure of the film helps to deflect the propagating crack, thus providing a mechanism whereby the strain energy near the tip of a propagating crack can be dissipated. It is suggested that further investigations be carried out to elucidate the mechanism(s) and factors that account for the strength and failure properties of films from prevulcanized NR latex. It is also suggested that the possibility of broadening the tensile strength versus crosslink concentration curve for films from peroxide-prevulcanized NR latex be investigated.

The modulus of films from peroxide-prevulcanized NR latex is comparable to that of films from a medium-modulus grade of sulphur-prevulcanized NR latex. The ageing properties of films from peroxide-prevulcanized NR latex were found to be poor. This is attributed to the absence of protection against oxidative ageing, and probably also due to the presence of a pro-oxidant in the film. It is suggested that films from peroxide-prevulcanized NR latex be extracted to remove the pro-oxidant. Antioxidants are then added by infusion to find out if the films then show the normal ageing properties of peroxide dry NR vulcanizates. This could lead to the identification of the pro-oxidant and then perhaps a simple way of removing it might be found.

8.7 Other suggestions for further work

It is suggested that the effect of variability in the properties of NR latex concentrates upon prevulcanization and processing behaviour using a peroxide-prevulcanizing system be investigated. The effect of storage upon the properties and the processability of peroxide-prevulcanized NR latex might also be investigated. The film-forming characteristics of the latex by straight, coagulant and heat-sensitized dipping process is another area which might be investigated. Finally, the nitrosamines, nitrosatable amines and other toxic materials that may be present in peroxide-prevulcanized latex and latex films should be determined, and the effect of film leaching upon the extraction of such substances and upon the properties of the film, should be investigated.

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