

Role of Fatty Acids in Autoxidation of Deproteinised Natural Rubber

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The effects of stearic, oleic and linoleic acids and their methyl esters on the autoxidation of deproteinised natural rubber (DPNR) have been investigated. The carboxyl group of the free acids was found to be of primary importance in increasing the rate of oxidation and enhancing chain scission. Oleic and linoleic acids exhibited synergistic pro-oxidant activity as a result of their co-oxidation. Chain breaking antioxidants such as butylated hydroxytoluene (BHT) helped protect polyisoprene from fatty acid promoted autoxidation.

The autoxidation of natural rubber (NR) has been studied extensively over the past fifty years due to the realisation that oxidation of the polyisoprene chain leads to a dramatic loss in the physical properties of a vulcanisate^{1,2}. It is therefore important to identify factors which may accelerate the process so that their detrimental effects may be reduced or eliminated. In raw rubber, autoxidation is accelerated by numerous variables such as heat, light and transition metal ions³⁻⁶. Although non-rubbers such as tocotrienols may impart stability to the rubber due to their known antioxidant activity, the role of other non-rubbers such as proteins is less clear⁷. In technological sulphur vulcanisates, autoxidation becomes increasingly more complex due to the presence of different types of sulphur crosslinks, fillers and curative residues such as accelerators, sulphur and zinc oxide^{8,9}.

Recent research by Boon¹⁰ proposed that the acid catalysed decomposition of allylic hydroperoxides (Hock Cleavage) is partly responsible for main-chain scission in NR sulphur vulcanisates. In this study, sodium carbonate and proton sponge were found to reduce the loss in tensile properties of a semi-efficient vulcanisate and to a lesser extent a conventional vulcanisate. In contrast, base was found to have no effect on the tensile properties of a peroxide vulcanisate suggesting that sulphur acids were the source of catalysis for

Hock Cleavage. It was also suggested that Hock Cleavage explains the discrepancies in the classical scission mechanism derived from peroxy radical cyclisation.

There have been other investigations on the role of acidic substances in polymer degradation¹¹⁻¹⁴. Cooray and Scott¹¹ demonstrated the dual action of hydrogen chloride in the degradation of PVC. They found evidence for homolytic and heterolytic decomposition mechanisms. At low ratios of hydroperoxide to hydrogen chloride, a free-radical mechanism predominated but at high ratios, the ionic process was prominent. It has similarly been shown that sulphur dioxide and derived acids, which are thought to be important in the activity of sulphur-containing antioxidants, act through both homolytic and heterolytic mechanisms¹².

Keller *et al.*¹⁵ have examined the oxidative role of fatty acids in Guayule resin. They proposed that the unsaturated acids such as linoleic and linolenic acids were highly susceptible to autoxidation and their oxidation products (hydroperoxides) acted as initiators in polyisoprene oxidation. As NR contains a variety of saturated and unsaturated fatty acids, it was of interest to investigate the effect of these acids in terms of the rate of autoxidation and the amount of chain scission that occurs during oxidation.

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This paper reports the role of stearic, oleic and linoleic acids and their methyl esters in the autoxidation of DPNR.

EXPERIMENTAL

Gas Liquid Chromatography

Fatty acid methyl esters (FAME) were prepared using methanolic boron trifluoride and analysed by GLC using heptadecanoic acid as the internal standard. Experimental procedures were essentially the same as those of Crafts *et al.*¹⁶

Gel Permeation Chromatography

Analyses were carried out on two 60 cm mixed bed columns (Polymer Laboratories Ltd) with THF as the solvent and a flow-rate of 0.5 ml/min at 40°C. UV detection was carried out at 215 nm and the instrument calibrated with polystyrene standards (Polymer Laboratories Ltd).

Purification of Natural Rubber

HA latex was deproteinised according to the procedure of Chong¹⁷ and the DPNR recovered by precipitation in methanol. The rubber was subsequently extracted with cold acetone and the soluble rubber extracted with

re-distilled petroleum ether (bp 30°C – 40°C). The soluble rubber was re-precipitated in methanol, dried, re-dissolved in petrol and precipitated once more. This purification procedure resulted in a soluble rubber with a nitrogen content of less than 0.01 wt%.

Oxygen Uptake Measurements

The purified rubber was cast as a thin film (approx. 0.03 mm) on the inside of a test-tube using a rotary film evaporator. The sample tube was placed in a thermostated oil bath at 80°C and oxidation carried out in oxygen at atmospheric pressure. The apparatus consisted of the sample tube connected *via* capillary tubing to a graduated pipette with glass side-arm (containing low viscosity silicone oil). A number of taps allowed the apparatus to be evacuated and the introduction of oxygen or nitrogen. Errors in following oxygen uptake could be minimised by making allowances for changes in atmospheric temperature and pressure.

RESULTS AND DISCUSSION

Fatty Acid Composition of Bale Rubbers

The free fatty acid compositions of a number of SMR grades are presented in Table 1. All

TABLE 1. FATTY ACID COMPOSITION OF VARIOUS SMR GRADES
(RESULTS PRESENTED AS WT% FATTY ACID WRT RUBBER)

Fatty acid	SMR L	SMR 5	SMR 10	SMR 20	SMR CV	Skim
12:0	Trace	Trace	Trace	Trace	Trace	0.08
14:0	Trace	0.01	0.01	0.01	Trace	0.02
16:0	0.06	0.08	0.10	0.10	0.05	0.24
16:1 (n-9)	0.01	0.01	0.01	0.01	0.01	0.04
18:0	0.14	0.22	0.18	0.16	0.12	0.44
18:1 (n-9)	0.14	0.11	0.13	0.12	0.10	0.84
18:2 (n-6)	0.30	0.33	0.30	0.23	0.28	0.97
18:3 (n-3)	0.02	0.03	0.03	0.02	0.03	0.07
Furanoic	0.10	0.14	0.08	0.10	0.04	0.07
Total	0.77	0.93	0.84	0.76	0.63	2.77

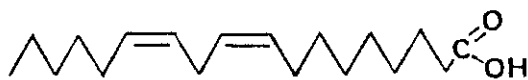
rubbers had fatty acid level of between 0.5 wt% and 1.0 wt% with the exception of skim rubber which contained 2.68 wt%. The major fatty acids were found to be stearic, oleic and linoleic acids (1, 2 and 3)



1. 18:0



2. 18:1 (n-9)



3. 18:2 (n-6)

which accounted for nearly 70% of the total. A furanoid fatty acid which is reported to be a major constituent of field latex was present at relatively low levels¹⁸.

Effects of Fatty Acids on Rate Profile

Soluble deproteinised natural rubber (sol DPNR) was used in all autoxidation experiments to avoid interpretational difficulties from non-

rubbers and to simplify the molecular weight analysis. Measurements were made in the absence of added radical initiators such as AIBN to avoid the possibility of masking subtle effects of the fatty acids on the rate profile. This procedure had the disadvantage of increasing the variability of oxidation rate between nominally identical samples. All comparisons were therefore made between sets of samples prepared together from the same rubber solution.

Effects of Stearic Acid on Rate

The effects of varying concentrations of stearic acid on the oxygen uptake of purified sol DPNR are presented in *Figure 1*. The results showed that as the concentration of stearic acid was increased, an enhancement in the rate of NR autoxidation occurred. This may have resulted from an increase in the number of radicals participating in chain propagation. A heterolytic mechanism such as Hock Cleavage does not produce free radicals and would therefore not have been expected to contribute to the enhanced rate. However, the oxidation of stearic acid itself is recognised as a slow process and is unlikely to have contributed to the observed results. One possible explanation which we are currently investigating is the formation of hydrogen bonded complexes between the fatty acids and rubber-bound hydroperoxides. Privalova and Maizus¹⁹ demonstrated that homolysis of such dimers is a more facile process than unimolecular decomposition of the free hydroperoxide.

Caproic acid was found to increase the rate of oxidation of n-decane and the rate of hydroperoxide decomposition at 140°C. In addition, caproic acid was found to act catalytically and could be recovered quantitatively from the reaction:



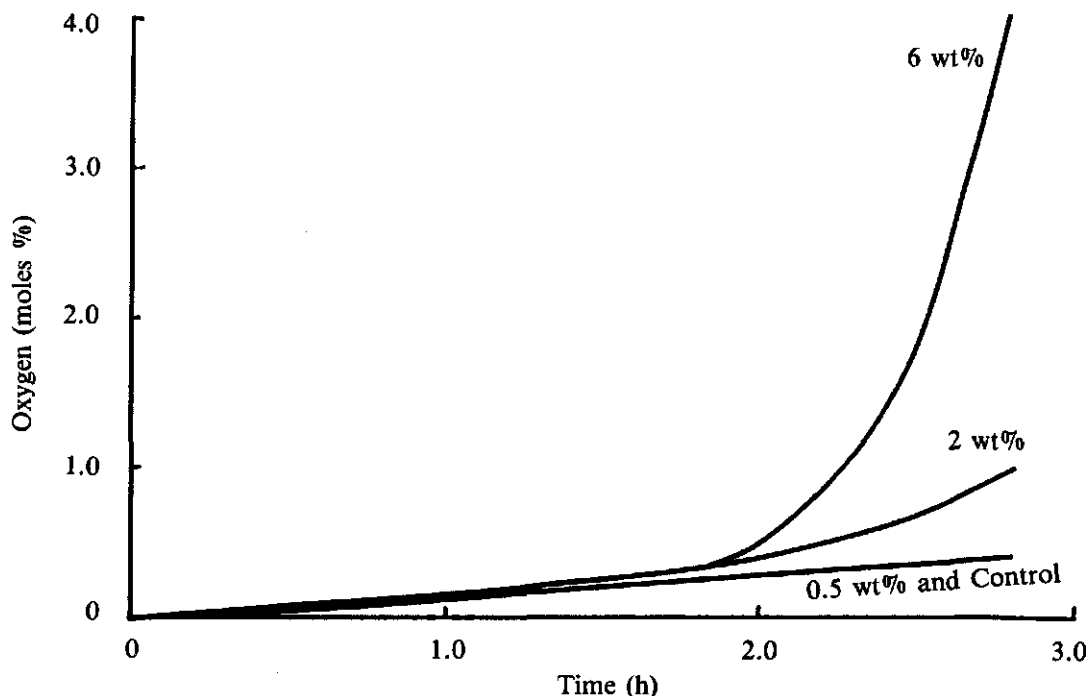


Figure 1. Effect of varying levels of stearic acid on autoxidation of sol DPNR at 80°C.

Although carboxylic acids are susceptible to attack by peroxy radicals, leading to decarboxylation, hydrogen-bonding has been reported to prevent this occurring²⁰. In non-polar solvents, carboxylic acids and hydroperoxides are believed to exist almost entirely as hydrogen-bonded dimers. In NR, added carboxylic acids would be expected to have greater mobility than rubber-bound hydroperoxides which may have resulted in carboxylic acid-hydroperoxide complexes having formed in preference to hydroperoxide dimers. Further research is obviously required to identify the formation of such complexes in NR and on how readily they decompose.

Another possible explanation for the catalytic activity of stearic acid is the reaction of pro-oxidant metals such as copper, cobalt, iron and manganese with fatty acids to produce metal carboxylates. This could have increased the solubility of the metal and imparted a more favourable redox potential. The role of metal

carboxylates and chelating groups in the oxidation of cyclohexane has been extensively studied by Chalk and Smith^{21,22}. They found that metal ion solubility, the presence of chelating groups and concentration were all important factors in predicting the metal's pro-oxidant activity. The actual state of metal ions in DPNR is not known but they might be expected to be co-ordinated to functional groups such as epoxides and carbonyls in addition to residual protein. Addition of a fatty acid may disrupt this association, although it would be extremely difficult to predict the effect on activity of the metals.

Butylated hydroxytoluene (BHT) was found to reduce the catalytic activity of stearic acid (Figure 2) and provide further evidence that rate enhancement did not occur *via* Hock Cleavage. These results suggest that antioxidants indigenous to NR may help protect it from fatty acid promoted oxidation.

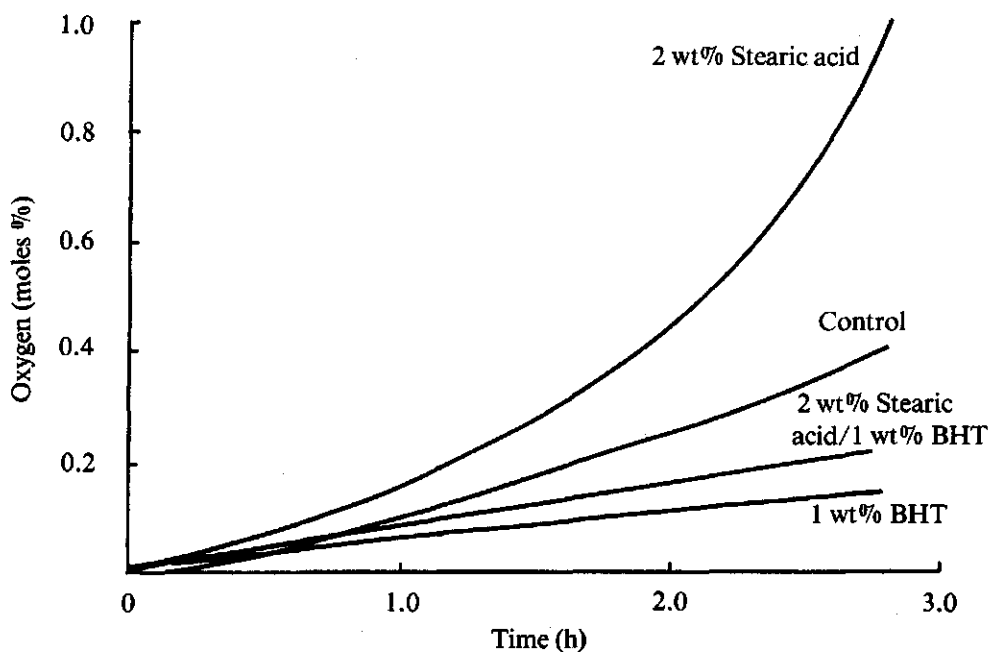


Figure 2. Effect of stearic acid and BHT on autoxidation of sol DPNR at 80°C.

Effect of Oleic and Linoleic Acids on Rate

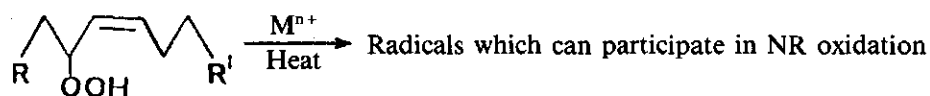
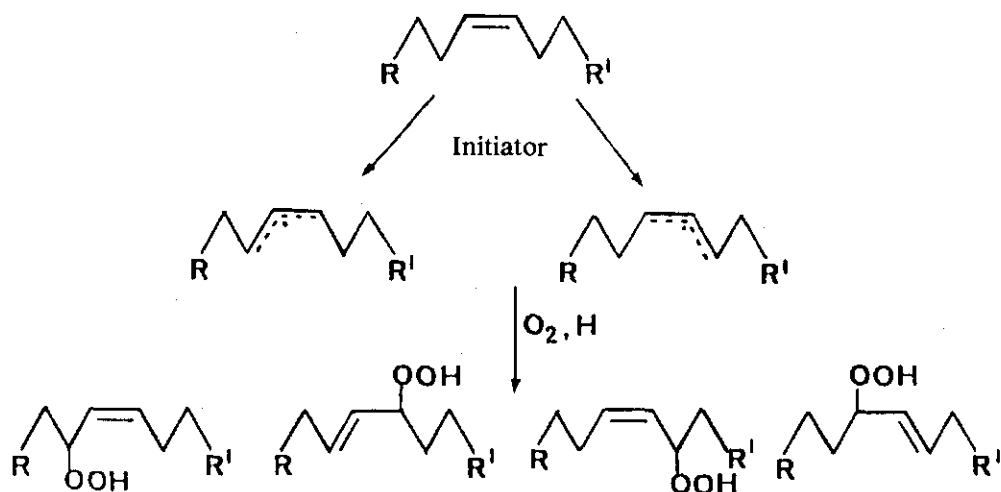
The role of oleic and linoleic acids in promoting NR oxidation was also studied. In addition to the carboxylic group, these acids may themselves oxidise and their oxidation products act as initiators in polyisoprene oxidation. Autoxidation of oleic acid involves hydrogen abstraction from *Position 9* or *12* producing a simple allylic radical that reacts rapidly with oxygen giving a peroxy radical which, after hydrogen abstraction, yields one of four possible allylic hydroperoxides (*Scheme 1*). In linoleic acid, hydrogen abstraction from the doubly allylic CH_2 produces a pentadienyl radical which leads to one of four possible allylic hydroperoxides (*Scheme 2*)²³. The additional delocalisation energy of the pentadienyl radical is proposed to explain the high reactivity of linoleic acid compared to oleic acid. These hydroperoxides would be vulnerable to metal ion catalysed decomposition producing radicals capable of promoting polyisoprene oxidation. A comparison of the differences between stearic, oleic and linoleic

acids in promoting NR oxidation is presented in *Figure 3*. The higher rate of oxidation of NR in the presence of linoleic acid relative to oleic acid is likely in part to have been a consequence of the higher oxidisability of linoleic acid. The horizontal line (*Figure 3*) indicates oxygen uptake to a level equivalent to the concentration of the fatty acid and indicates that oxygen uptake was not just a result of fatty acid oxidation. To differentiate between catalysis by the carboxyl group and that originating from oxidation of the unsaturated centres, the pro-oxidant activity of the free acids was compared with that of their methyl esters. The results (*Figures 4* and *5*) indicate that the carboxyl group was of key importance in promoting oxidation. However, the greater differences in the catalytic activity of the free acids compared with their methyl esters indicated synergism between the two modes of rate enhancement.

Keller *et al.*¹⁵ demonstrated that the unsaturated fatty acids of Guayule resin enhanced the oxidative deterioration of NR. However, they proposed that the fatty acid

R - Fatty alkyl chain

R' - Fatty acyl chain



Scheme 1

Autoxidation of oleic acid and methyl oleate - the primary products and their decomposition

oxidation products (hydroperoxides) acted as radical chain initiators and were wholly responsible for the enhancement in rate. The results presented here clearly show that the carboxyl group is of primary importance in catalysing NR autoxidation.

Effect on Chain Scission

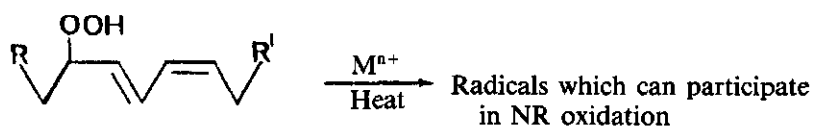
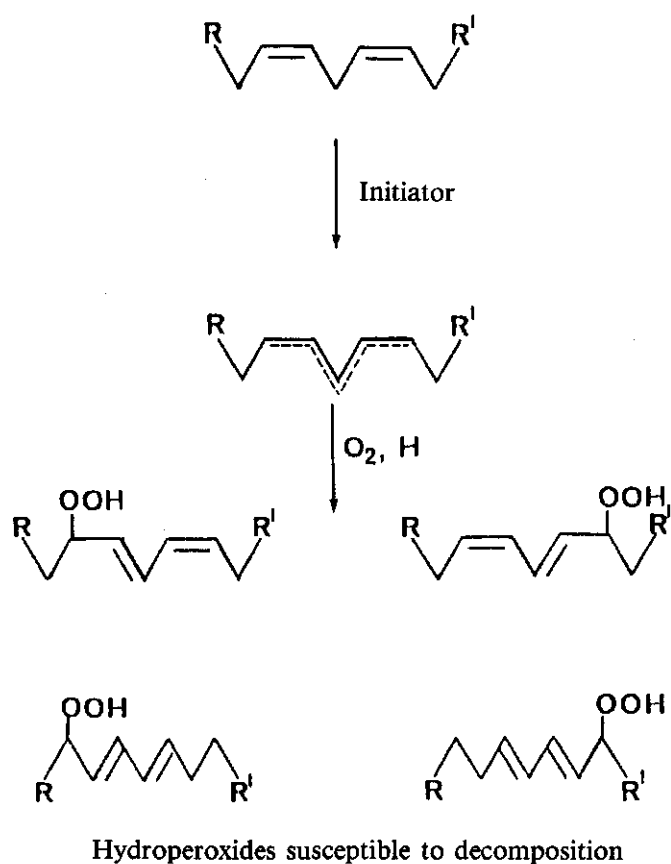
An important consequence of autoxidation is that chain scission of the polymer backbone occurs which ultimately leads to a loss in the

useful elastomeric properties of a vulcanisate. We have studied chain scission by following changes in the molecular weight distribution as determined by GPC. The results are presented as a scission efficiency number (ϵ) which is defined as the number of molecules of oxygen causing one scission event:

$$\epsilon = \frac{O_2 \text{ uptake mole\%} \cdot Mn}{\left(\frac{M_{no} - Mn}{Mn} \right) \cdot 6800}$$

R - Fatty alkyl chain

R' - Fatty acyl chain



Scheme 2

Autoxidation of linoleic acid and methyl linoleate - the primary products and their decomposition

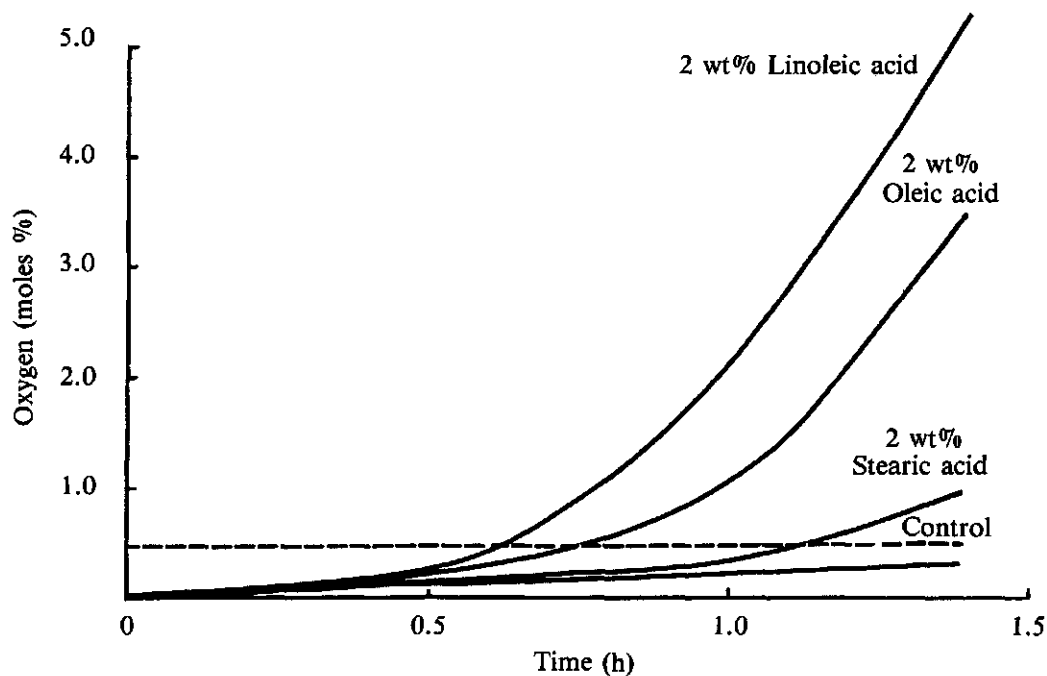


Figure 3. Effect of stearic, oleic and linoleic acids on autoxidation of sol DPNR at 80°C.

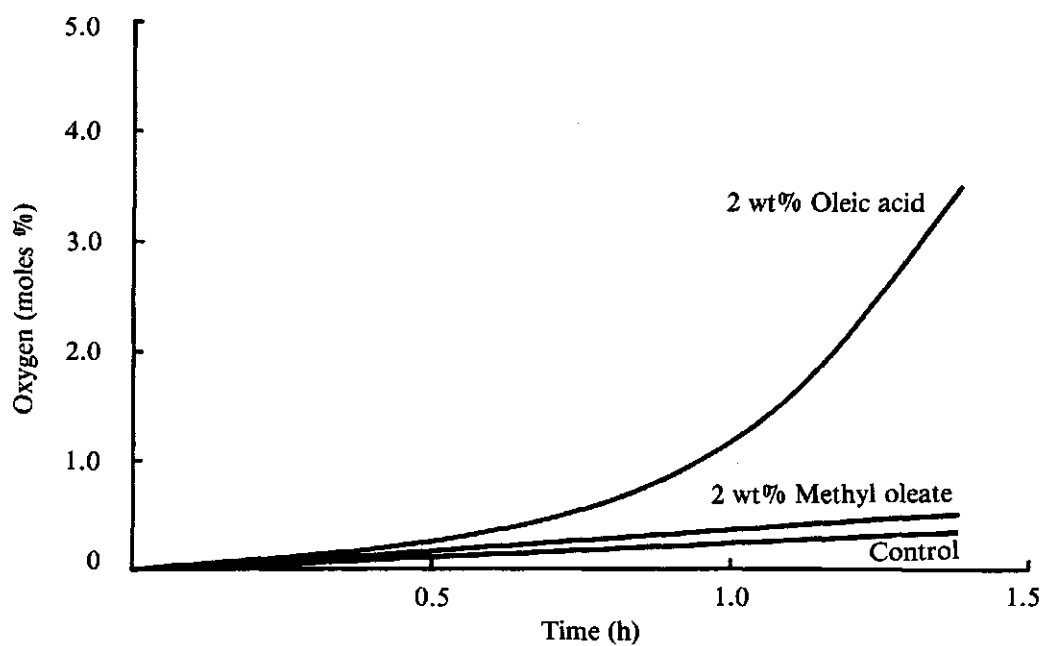


Figure 4. Effect of oleic acid and methyl oleate on autoxidation of sol DPNR at 80°C.

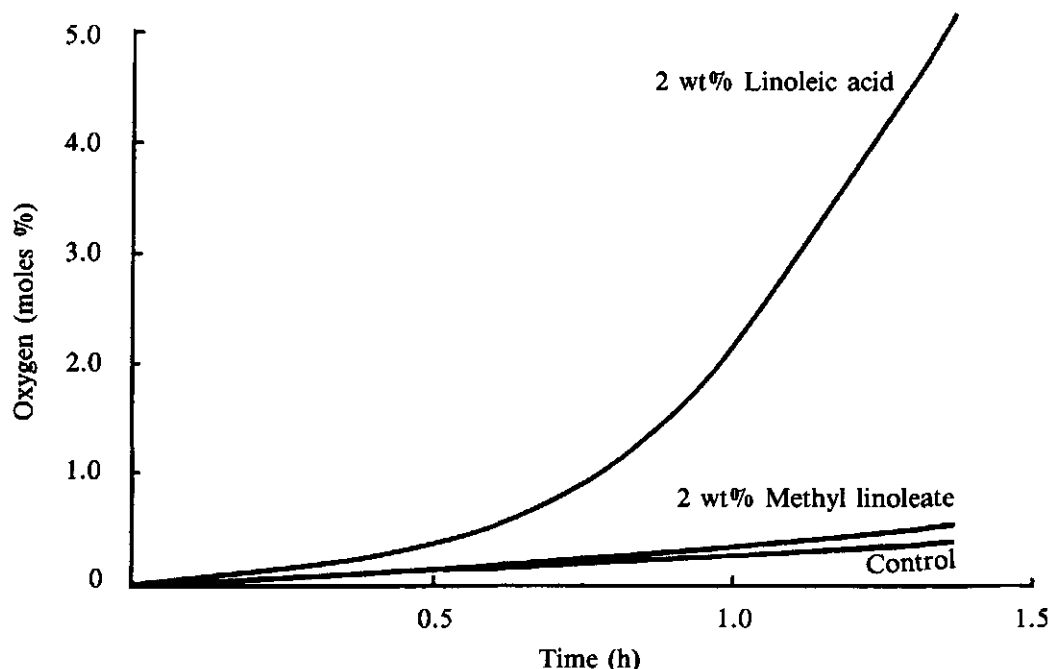


Figure 5. Effect of linoleic acid and methyl linoleate on autoxidation of sol DPNR at 80°C.

Therefore, the lower the number, the more efficient the chain scission. Table 2 presents oxygen uptake and scission efficiency data for a series of rubber samples oxidised with varying levels of stearic acid and in the presence of

BHT. Samples were oxidised for fixed times which resulted in the comparison of rubbers with different oxygen uptake levels. For all samples oxidised with stearic acid, lower scission efficiency values were obtained. Bell²⁴

TABLE 2. EFFECT OF VARYING CONCENTRATIONS OF STEARIC ACID AND BHT ON SCISSION EFFICIENCY (ϵ). SAMPLES WERE OXIDISED FOR 160 MIN AT 80°C

Additive	O ₂ (mole %)	Mn	ϵ
Unoxidised Substrate		283 850	
Control ^a	0.41	174 350	27
0.5 wt% stearic acid	0.43	115 200	12
2.0 wt% stearic acid	1.01	57 900	11
6.0 wt% stearic acid	4.09	13 000	8
2.0 wt% stearic acid + 1.0 wt% BHT	0.33	234 200	45
1.0 wt% BHT	0.14	2 795 550	388

^aControl - sol DPNR only

TABLE 3. EFFECT OF STEARIC, OLEIC, LINOLEIC ACIDS, THEIR METHYL ESTERS AND ZINC STEARATE ON SCISSION EFFICIENCY (ϵ). ADDITIVES WERE PRESENT AT CONCENTRATION OF 2 WT% WRT RUBBER AND THE SAMPLES OXIDISED FOR 83 MIN AT 80°C

Additive	O ₂ (mole %)	Mn	ϵ
Unoxidised Substrate		200 500	
Control ^a	0.38	135 450	23
Stearic acid	1.00	46 050	9
Oleic acid	3.44	17 900	10
Linoleic acid	5.30	9 800	8
Methyl stearate	0.24	155 500	25
Methyl oleate	0.53	857 000	12
Methyl linoleate	0.52	84 350	12
Zinc stearate	0.42	85 750	9

^aControl - sol DPNR only

showed that when short kinetic chain lengths are observed (when a catalyst is present) enhanced chain scission occurs. This complication becomes important when considering an autocatalytic rate profile which does not exhibit steady-state kinetics in the early stages. Samples oxidised to varying degrees will have experienced different mean kinetic chain lengths.

Nevertheless, it is important to realise that although there was only a small difference in the level of oxygen uptake between the control and DPNR oxidised in the presence of 0.5% stearic acid, there was a significant difference in scission efficiency. This suggests that the enhanced scission in the presence of the acid cannot entirely be explained by the kinetic chain length effect. BHT appeared to inhibit stearic acid promoted chain scission of DPNR which suggests that scission occurred *via* a homolytic rather than heterolytic (Hock Cleavage) mechanism. This result is at variance with previously published results which found that the scission step is enhanced in the presence of a chain-breaking antioxidant²⁵.

In a separate experiment, the effect of stearic, oleic and linoleic acids, their methyl

esters and zinc stearate on chain scission were investigated (*Table 3*). The scission efficiency of samples oxidised with the free acids were all lower than of the control but very similar considering the large differences in oxygen uptake levels. DPNR oxidised in the presence of methyl stearate exhibited no enhanced chain scission in comparison to the control but both methyl oleate and linoleate caused a lowering in scission efficiency. The precise reason for the enhanced chain scission shown by the esters is difficult to explain. However, if the decomposition of H-bonded dimers (NR hydroperoxide-fatty acid hydroperoxide) was an important process, chain scission may have resulted from β -scission of these alkoxy radicals. Although zinc stearate did not exhibit significant pro-oxidant character, it did appear to reduce the molecular weight of the rubber. Zinc is not recognised as a powerful pro-oxidant due to an unfavourable redox potential but some catalytic activity has been observed previously²¹.

CONCLUSION

In conclusion, free fatty acids were found to be capable of promoting the autoxidation of

DPNR. The pro-oxidant activity of the acids was reduced in the presence of chain-breaking antioxidants such as BHT. It is likely to be diminished in the presence of natural antioxidants such as tocotrienols which are present in NR. Fatty acids esterified as lipids would be expected to show a lower pro-oxidant activity due to the absence of the free carboxyl group. The free fatty acids enhanced chain scission during autoxidation but the parallel effect on autoxidation rate suggests that this enhancement is associated with the free radical autoxidation process rather than Hock Cleavage that has been characterised for stronger acids. Zinc stearate also appeared to enhance chain scission but to a much smaller extent than the free acids.

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