

PEROXIDE CROSSLINKING REACTIONS OF POLYMERS

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ABSTRACT

The current status of our understanding of the chemical mechanism of peroxide vulcanization is reviewed.

INTRODUCTION

The subject of peroxide curing has always been of interest to chemists and physicists working in the elastomer field. The reasons for this interest stem mainly from the relatively simple chemistry involved and the simple resulting network structure. The more widely used vulcanization systems based upon sulphur or sulphur compounds are very much more complex in mechanism and produce more varied crosslinks together with other chain modifications¹. Indeed until recently both this mechanism and the resultant network structure were unknown.

The introduction of newer saturated rubbers gave the study of peroxide curing reactions some impetus and a large number of rubbers were studied. Much of this work was reviewed by the author in 1967².

Up to that time substantially all of the work had been performed using one of two or three peroxides in simple combination with the rubber of interest, the influence of co-vulcanizing agents having received little attention. Since then further work has been performed with perhaps a somewhat different emphasis. The importance of coagents such as polyfunctional monomers has been recognized and investigated and a substantial increase in the number of suitable peroxides has been exploited.

There is now, perhaps, one further factor which makes the study of peroxide vulcanization systems very timely. The continuous production of vulcanized extruded articles is of practical importance and the limitations on such processes often result from difficulties in vulcanization. The current development of radiation technology suggests that electron irradiation crosslinking may soon be economically desirable and indeed some suggest that it is so already³. Crosslinking during electron irradiation occurs by a free radical process and utilizes the same types of coagents as are, at present, used for peroxide curing. Its mechanism is probably very similar to that of peroxide crosslinking and thus information obtained on this latter process may be useful in what may be the technology of the future.

The aim of this presentation is to summarize briefly the material previously reviewed and devote more attention to the more recent developments.

UNSATURATED RUBBERS

It is now well established that two types of reaction occur with unsaturated rubbers. The first of these is typified by natural rubber in which the simple reaction listed in textbooks really occurs⁴. This consists of hydrogen abstraction by the alkoxy radical derived from the peroxide followed by pairwise combination of the resultant polymer radicals to give crosslinks. The process is shown in general terms in *Figure 1*. Such a mechanism results in a unit crosslinking efficiency as measured by the ratio crosslink density: peroxide and has been shown to be operative with two peroxides, cumyl⁵ and *t*-butyl⁴. There are complications of a minor degree in so far as some alkoxy radicals break down to give a ketone and a methyl radical before abstracting hydrogen. This does not, however, interfere with the general picture of one crosslink per molecule of peroxide decomposed.

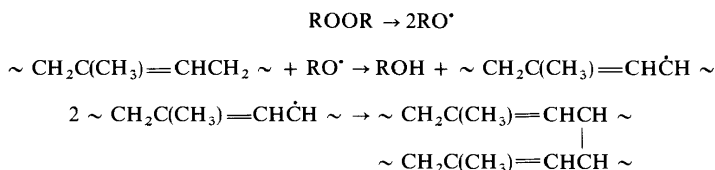


Figure 1. Peroxide crosslinking in natural rubber

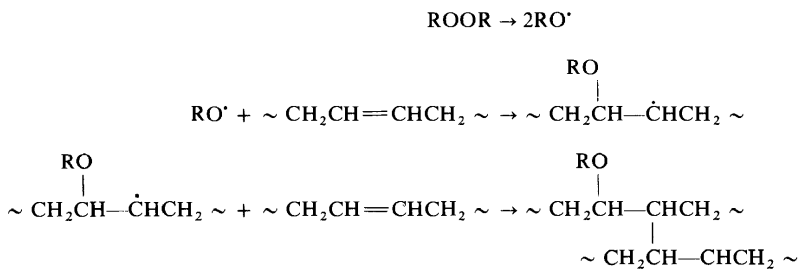


Figure 2. Peroxide crosslinking in *cis*-polybutadiene

The second type of reaction which can occur between peroxides and unsaturated rubbers is what we might call a polymerization reaction. Here the alkoxy radicals derived from the peroxide initiate a 'polymerization' of the double bonds in the polymer. The polymerization chain is quite short but is sufficient to give crosslinking efficiencies well above unity and values of around ten have been reported for *cis*-polybutadiene and styrene-butadiene rubber (SBR). This type of reaction is shown again in an idealized way in *Figure 2*. Of course, this simple reaction sequence is incomplete, hydrogen abstraction does occur as shown by the presence of alcohol in the reaction products, but some cumyloxy residues (in the case where cumyl peroxide was used) are unrecoverable, presumably due to their permanent attachment to the network⁶. This highly efficient reaction is, as might be

expected, inhibited by the presence of radical traps in the shape of antioxidants; similarly any centres easily attacked by free radicals may interfere. As an example of this latter possibility the acrylonitrile groups present in nitrile rubber limit the crosslinking efficiency to unity⁶.

What factors in the structure of the rubber determine which of these reactions occurs? Leaving aside the more obvious factors such as the presence of new reactive groups in nitrile rubber, the detailed structure around the double bond and the peroxide structure may conceivably be important. We also shall leave aside the latter factor to be dealt with in a later section and consider here only the polymer structure.

The presence of adventitious antioxidants in the natural rubber does not explain the magnitude of the difference between the two types of behaviour. Experiments using synthetic *cis*-1,4-polyisoprene show a crosslinking efficiency close to unity where natural antioxidants cannot be present. Likewise the presence of vinyl groups in the polybutadiene (resulting from some 1.2 addition) do not explain the high crosslinking efficiency with this polymer⁷. The choice between hydrogen abstraction or polymerization appears to be determined by the degree of substitution of the double bond. This seems quite reasonable when one recalls that 1,2 substituted olefins do not polymerize in the normally accepted sense of the word and trisubstituted olefins (with substituents on both double bonded carbons) would obviously be less likely to react in this way.

One exception to the above two alternative crosslinking reactions should also be mentioned: butyl rubber. This has long been known to degrade when heated with peroxide⁸⁻¹⁰ and the mechanism of its degradation and of the closely related polyisobutylene by cumyl peroxide have been studied by Thomas⁹ and by Loan¹⁰. The latter author showed that degradation depended very sensitively on the amount of unsaturation present, the reactivities of isobutylene and isoprene units differing by some one hundredfold. More recently a peroxide curable butyl has been made which in addition to isoprene as a comonomer also includes divinyl benzene; this leads to some gel during the polymerization reaction.

SATURATED RUBBERS

The situation portrayed above for unsaturated polymers is paralleled here in so far as two main reactions occur. The first of these results in scission and the second in crosslinking. Mechanisms for these reactions are shown in *Figure 3* using polypropylene and polyethylene as examples.

The type of reaction observed in a given polymer obviously depends upon two major factors, the nature of the hydrogen atom most easily abstracted and the polymer structure around this radical. In the case of linear polyethylene and poly(ethylene oxide) only one type of hydrogen atom exists and the polymer radicals formed can most easily react by combination to give crosslinks. With nonlinear polyethylene, polypropylene and polypropylene oxide the possibility for scission arises and, indeed, in the latter two polymers proves to be the predominant reaction.

A much more interesting situation exists where both types of unit are present

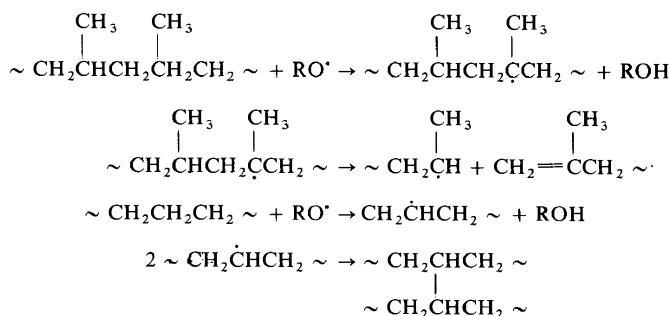


Figure 3. Scission and crosslinking in saturated polymers

in a single polymer chain. This, of course, occurs in ethylene-propylene rubbers and as might be expected a mixture of crosslinking and scission reactions occur^{11, 12}. The most labile hydrogen atom, towards radical attack, is the tertiary hydrogen¹³ of the propylene unit. Abstraction of this hydrogen gives rise to a tertiary radical which, unlike the similar radical from polypropylene, cannot easily lead to scission. As shown in *Figure 4* the simple reaction leading to scission produces a primary radical from the original tertiary one and thus seems unfavourable. Abstraction of secondary hydrogen β to the methyl group, however, leads to an easy scission reaction as shown in *Figure 4*. This specific abstraction occurs quite simply where two propylene units occur together when the reaction shown for polypropylene occurs.

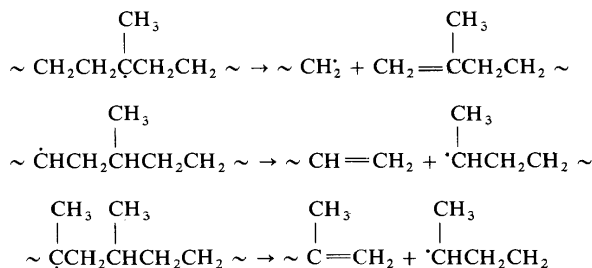


Figure 4. Possible scission reactions in ethylene-propylene rubbers

Thus although the propylene groups in ethylene-propylene rubbers have been shown to be the really important groups in providing scission sites, their exact part in the reaction is not yet clear. A study of the dependence of scission upon propylene content and sequence distribution would do much to eliminate this uncertainty but with the narrow band of compositions available until recently this has not been possible.

The introduction of unsaturation into ethylene-propylene rubbers has a marked effect on the crosslinking efficiency. Whereas the saturated copolymers have been shown to have crosslinking efficiencies in the range 0.4 to 0.7 typical unsaturated terpolymers may show efficiencies greater than unity^{12, 14}. It seems reasonable to suppose that the lability of hydrogen atoms in the

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different structures will be different and thus give rise to different rates of reaction and this effect has been recently studied¹².

Using a variety of unsaturated monomers in an ethylene-propylene copolymer the effect of the unsaturated unit on crosslinking efficiency was measured. The summarized results are shown in *Table 1*. The results quoted

Table 1. Crosslinking efficiencies in EPDMs

	Crosslinking efficiency
5-Methylene-2-norbornene	1.78
5-Ethylidene-2-norbornene	0.61
5-Vinyl-2-norbornene	1.55
5-Propenyl-2-norbornene	0.61
5-Isopropenyl-2-norbornene	1.06
5-Crotyl-2-norbornene	0.51
5-(2-buten-2-yl)-norbornene	0.62
5-Methallyl norbornene	0.79
5-Methyl-5-vinyl norbornene	0.61
None*	0.28

* Cumyl peroxide concentration 7.54 pphr.

in this table are those observed at the highest cumyl peroxide concentrations (1.9–2.0 pphr) as measured by compression modulus. The monomers giving the highest efficiencies are those with unsubstituted terminal double bonds and since the efficiencies observed are greater than one some 'polymerization' must be occurring. A somewhat lower efficiency is found where the residual unsaturation is terminal but substituted as in the case of the polymer made with the isopropenyl substituted norbornene. The monomers with internal double bonds show the lowest efficiencies. One surprising exception to these conclusions is the polymer containing 5-methyl-5-vinyl norbornene. A somewhat higher efficiency might have been expected in this case and indeed is observed at lower peroxide concentrations. All of the terminal unsaturation polymers show a similar dependence of crosslinking efficiency on peroxide concentration. The remaining polymers have efficiencies showing no dependence upon peroxide concentration. This variation in efficiency may be explained by analogy with polymerization reactions where the chain length increases as the initiation rate is decreased.

The variation of crosslinking efficiency in EPDMs has also been studied as a function of temperature¹⁴. In the temperature range 150° to 180°C the efficiency decreases with increasing temperature for a polymer having a dicyclopentadiene unsaturated unit.

A much more complex dependence was observed in the SBR cumyl peroxide system. As the curing temperature is increased from 140° to 180°C the efficiency first increases and then decreases¹⁴. This type of dependence may be connected with a change from a polymerization to a hydrogen abstraction mechanism but an insufficient number of systems have so far been investigated. As in so many aspects of peroxide curing more work is necessary.

PEROXIDES AND THEIR EFFICIENCIES

Perhaps the first matter to be raised under this heading should concern the decomposition of the peroxide. It would be reasonable to say that until recently everyone took shelter behind the concept of a unimolecular decomposition unaffected, at least to any substantial extent, by the environment. It is strange that it took so long to reveal this gross over-simplification for what it is; recent data from Hercules Inc.¹⁵ show that the decomposition rates of both cumyl peroxide and *p*-bis[2-(2-*t*-butylperoxy)propyl]benzene may vary by as much as a factor of three in different media. The slowest rates were observed in polyethylene and the fastest in SBR and natural rubber.

The majority of the work referred to above had been done prior to the last review. Since that time some effort has been directed towards the study of a variety of different peroxides. Until 1960 the only peroxides widely considered in rubber vulcanization were cumyl and *t*-butyl peroxides. Since that time a variety of peresters, alkyl and aryl peroxides have been used. The primary incentive has been perhaps the elimination of the unpleasant odour of dicumyl peroxide cures, the volatility of *t*-butyl peroxide making it undesirable for industrial use. Work with these different peroxides has, however, revealed some interesting effects which will be discussed.

Some of the published data are summarized in Table 2. This shows

Table 2. Crosslinking efficiencies for various peroxide-polymer combinations

	EPDM		SBR	PE
	(a)	(b)	(b)	
Cumyl peroxide	1.5	1.5	13	1.0 ^c
<i>p</i> -Bis[2-(2- <i>t</i> -butylperoxy)propyl]benzene	1.5			1.0 ^d
2,5-Dimethyl-2,5-di- <i>t</i> -butylperoxyhexane	0.44			
2,5-Dimethyl-2,5-di- <i>t</i> -butylperoxyhexyne-3	0.62			
<i>t</i> -Butyl peroxide		0.87		
<i>t</i> -Butylperbenzoate			2.5	
<i>t</i> -Butylperoxyisopropylate			0.4	
Benzoyl peroxide			0.37	

^a Hercules data¹⁶. The EPDM value of 1.5 was assigned for easy comparison with b. Values obtained from peroxide concentration necessary to produce given modulus in a black vulcanizate.

^b Data of ref.¹⁴.

^c Data of ref.¹⁷.

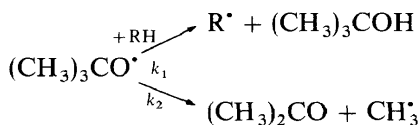
^d Data of ref.¹⁸.

that all peroxides do not behave similarly and such a conclusion was foreshadowed by some earlier work. Viohl, Little and Stiteler¹⁹ found that, while polyisobutylene could be crosslinked by a combination of sulphur and *t*-butyl peroxide, sulphur and cumyl peroxide were ineffective. The present author has found that the scission efficiencies of these two peroxides in polyisobutylene differ by a factor of two² and Lenas also has noted a variation of efficiency with peroxide²⁰.

The reasons for the difference in effectiveness are not at this stage clear. A number of the peroxides used contain more than one peroxy link and hence

questions about the effectiveness and indeed the formation of the potential diradical have been raised. However, the simple possibility of diradical formation need not diminish the efficiency of crosslinking as evidenced by the high efficiency of *p*-bis[2-(2-*t*-butylperoxy)propyl] benzene. In this material the radical sites are separated by a rigid structure and it has been suggested that where the structure is more flexible (e.g. in 2,5-dimethyl-2,5-di-*t*-butylperoxyhexane) cyclization may occur with a resulting loss of radicals. No definite evidence seems to be available on this point and further investigations would appear to be desirable.

As is now well known the tertiary alkoxy radicals formed by decomposition of some peroxides decompose easily to a methyl ketone and a methyl radical. This decomposition provides a useful way of measuring the ease of hydrogen abstraction as this is quite simply obtained from the alcohol/ketone ratio



$$\frac{k_1}{k_2} = \frac{[(\text{CH}_3)_3\text{COH}]}{[(\text{CH}_3)_2\text{CO}][\text{RH}]}$$

This type of measurement thus allows the measurement of the rate of one of the basic processes in peroxide vulcanization. Two recent papers have used this measurement^{13, 18}. In studies with five different elastomers¹³ it was found that the presence of sulphur in the reaction mixture hardly affected the alcohol:ketone ratio for cumyl peroxide thus suggesting only a minimum influence at the hydrogen abstraction stage. Other measurements showed qualitative agreement between abstraction rate ratios for different types of hydrogen for cumyloxy and *t*-butoxy²¹ radicals. A similar agreement was also found with the rates for methyl radicals. This agreement was not exact, however, and further comparisons between the relative reactivities of different alkoxy radicals would be interesting.

COAGENTS

The use of coagents in peroxide cures started to receive serious attention upon the introduction of ethylene-propylene rubbers. It was quickly discovered that the efficiency of crosslinking using peroxide alone was low and that the introduction of sulphur improved some vulcanizate properties. Sulphur did not, however, increase the state of cure in a gum vulcanizate and also resulted in a very objectionable odour. Other additives were therefore sought.

Most of the additives now used are multi-functional monomers such as ethylene glycol dimethacrylate and triallyl cyanurate. Such monomers are now used in the peroxide curing of a variety of rubbers not only to increase the efficiency of curing but to give high hardness vulcanizates.

Until recently little work had been done on the mechanism of the peroxide coagent cure and a recent paper by Cornell, Winters and Halterman²² makes the first detailed investigation of this mechanism. Using a model system it was found that in a simulated crosslinking reaction using *n*-decane, cumyl peroxide and methyl methacrylate that the main high boiling point product was an addition compound of decane and methyl methacrylate. A lesser but significant product was probably a similar compound in which a short chain of methyl methacrylate units were present. When the methyl methacrylate was replaced in the reactants by ethylene glycol dimethacrylate a much greater tendency towards polymerization was observed leading to insoluble products.

In some related experiments involving radiation crosslinking Salmon and Loan²³ have found that the multifunctional coagent does indeed polymerize and appears to form a network into which the base polymer is subsequently bound.

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