Determination of epoxy groups in natural rubber by degradation methods

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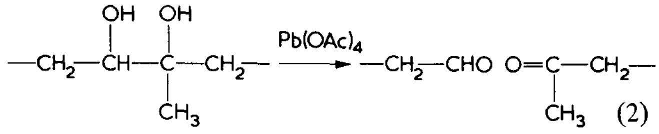
The degradation of acid hydrolysed natural and epoxidized synthetic rubbers with lead tetraacetate and periodic acid have been studied, viscometrically. The epoxy content calculated from the degradation experiments is very much lower than that determined by a direct titration method. The discrepany is attributed mainly to incomplete hydrolysis of the rubber epoxides. The results demonstrate that the epoxy content of natural rubber is predominantly located on the rubber backbone.

INTRODUCTION

In a preliminary communication[1] the degradation of acid hydrolysed natural rubber with $Pb(OAc)_4$ has formed the basis of the proposal that epoxide groups (I) are present in the backbone of the polymer. Hydrolysis of the epoxide groups:

(I) (1)

and subsequent degradation of the resulting diols with $Pb(OAc)_4$:



$$-CH_2-CH(OH)-C(OH)(CH_3)-CH_2- \xrightarrow{Pb(OAc)_4} -CH_2-CHO \quad O{=}C(CH_3)-CH_2- \qquad (2)$$

permit estimation of the number of such groups by measurement of the reduction in molecular weight.

This paper describes a more comprehensive investigation of the hydrolysis and degradation of natural and epoxidized synthetic rubbers, and a comparison with epoxide determination by a direct titration method[2].

EXPERIMENTAL

Isolation of rubber

Natural rubber was isolated from freshly tapped rubber latices of clones specified in text. For control experiments, fresh latex was diluted to twice its volume with distilled water and the rubber coagulated by addition of 2% acetic acid. The soft coagulum was extensively washed with water, pressed into thin sheets and dried under vacuum at room temperature.

Epoxidation of synthetic rubber

Synthetic polyisoprene of 97% *cis*-1,4 content was epoxidized by a method described earlier[2].

Acid hydrolysis of rubber with sulphuric acid

For natural rubber, 1.5 ml of fresh field latex was diluted with 98 ml of water and 2 ml of 2 M H_2SO_4, and was subsequently refluxed under a nitrogen atmosphere for 6 h. The rubber, which had coagulated out after about 4 h, was then isolated, washed with water and dried under high vacuum at room temperature.

For epoxidized synthetic rubber, a solution containing 0.7 g of rubber in 20 ml of benzene was mixed with 80 ml of water and 2 ml of 2 M H_2SO_4 and refluxed under nitrogen for 6 h. The rubber was recovered by methanol precipitation.

Acid hydrolysis of rubber with perchloric acid

Epoxidized synthetic rubber was hydrolysed by the addition of 0.25 ml of 20% $HClO_4$ to 50 ml of a 2% solution of rubber in THF. The reaction mixture was stirred overnight at about 26°C in the dark. The rubber was subsequently recovered by methanol precipitation.

Viscosity measurement

Viscosity measurements were made on approximately 0.1% w/v solutions of rubber in benzene at 30.00° ± 0.01°C. Addition of Pb $(OAc)_4$ was found to slightly reduce the solvent flow time and consequently the reduced value was used for computing the viscosities of the degraded rubber. On the other hand, periodic acid had no detectable effect.

Lead tetraacetate degradation

0.5 ml of 0.04 M solution of $Pb(OAc)_4$ in glacial acetic acid was added to 20 ml of the rubber solution in the viscometer. After mixing, the flow time of the solution was measured at intervals from the time of addition of the Pb $(OAc)_4$. The reaction time was computed from the following relationship:

Reaction time = time interval + ½(solution flow time)

Periodic acid degradation

0.2 g of solid periodic acid was added to 10 ml of the rubber solution in a viscometer equipped with a sinter filter, so as to prevent solid particles entering the capillary. The experiment was continued as described above.

Table 1 Verification of single point determination

Sample	Concentration (g/dl)	$\frac{\eta_{sp}}{c}$	$[\eta]$ From single point equation	$[\eta]$ By least squares fit of equation (3)
A	0.113	11.53	8.05	$[\eta] = 8.41$
	0.0485	10.91	8.20	$r = 0.992$
	0.0563	9.82	8.29	
	0.0432	9.66	8.50	
	0.0338	9.38	8.48	
B	0.1171	9.98	7.18	$[\eta] = 7.15$
	0.0753	8.95	7.30	$r = 0.999$
	0.0555	8.50	7.34	
	0.0437	8.20	7.30	
C	0.0646	7.73	6.62	$[\eta] = 6.64$
	0.0430	7.36	6.65	$r = 0.997$
	0.0323	7.12	6.64	
	0.0215	6.98	6.64	
D	0.128	8.32	6.14	$[\eta] = 6.12$
	0.104	7.96	6.24	$r = 0.998$
	0.0765	7.42	6.24	
	0.0604	7.17	6.27	
E	0.126	4.79	3.99	$[\eta] = 4.12$
	0.0755	4.53	4.07	$r = 0.999$
	0.0503	4.39	4.09	
	0.0377	4.32	4.09	

r is the correlation coefficient

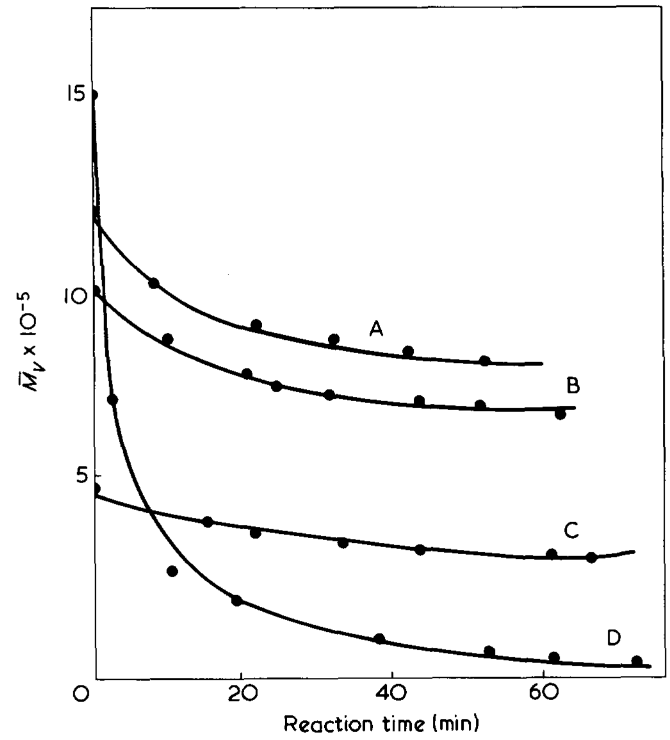


Figure 1 Lead tetraacetate degradation of natural and synthetic rubbers. A, untreated natural rubber, clone Tj 1; B, untreated natural rubber, clone RRIM 600; C, synthetic rubber, control; D, sulphuric acid hydrolysed natural rubber, clone PR107

RESULTS AND DISCUSSION

Molecular weight determination

For dilute polymer solutions the dependence of the specific viscosity on concentration is given by the Huggins' equation:

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \qquad (3)$$

Generally, the intrinsic viscosity $[\eta]$ is obtained by extrapolation of the plot of η_{sp}/c *versus* c to infinite dilution. However, to follow the change in molecular weight during the degradation of rubber, it is necessary to detemine $[\eta]$ from a single measurement of viscosity. The following equation has been employed in this study[4]:

$$[\eta] = \frac{\eta_{sp}/c}{1 + 0.333\eta_{sp}} \qquad (4)$$

To establish the validity of this equation for dilute solutions of rubber in benzene the intrinsic viscosities of a series of rubbers were determined by both the extrapolation and single point calculations. The values obtained by the two methods (*Table 1*) show good correlation, particularly at lower values of $[\eta]$, and hence confirm the applicability of equation (4) to this system.

The intrinsic viscosity is related to the viscosity-average molecular weight by the Mark–Houwink equation:

$$[\eta] = K\bar{M}_v{}^{\alpha} \qquad (5)$$

which allows the molecular weight to be determined if K and α are known. Values of $K = 5.02 \times 10^{-4}$ and $\alpha = 0.67$, reported by Carter *et al.*[5], have been used in this study since Bloomfield[6] has shown that the molecular weight calculated from these values gives good correlation with the $\bar{M}_n$ from osmotic data, for fractionated samples of fresh rubber.

$Pb(OAc)_4$ degradation of natural and synthetic rubbers

The changes in $\bar{M}_v$ during the degradation of various rubbers by $Pb(OAc)_4$ are shown in *Figure 1*. Evidently $Pb(OAc)_4$ is able slowly to degrade the synthetic polyisoprene sample which presumably contains no 1,2-diols. This is not altogether surprising since decomposition of $Pb(OAc)_4$ can generate radical species which will promote oxidative degradation, favoured by contact with atmospheric oxygen[7]. That radical scission reactions commence almost immediately after addition of $Pb(OAc)_4$ is consistent with the opinion that chain scission occurs mainly in the propagation step rather than after the peroxide concentration is built up[8,9]. The radical nature of this degradation reaction appears to be confirmed by the inhibiting effect of 2,6-di-tertbutyl-*p*-cresol on the chain scission (*Table 2*).

Table 2 Effect of antioxidant during degradation

Natural rubber (clone RRIM600)		Synthetic rubber	
Reaction time (min)	Solution flow time (sec)	Reaction time (min)	Solution flow time (sec)
0	288.5	0	273.3
10.2	278.1	9.8	268.6
20.9	266.0	22.2	263.5
32.8	257.3	31.2	260.8
44.7	253.0	43.6	258.4
57.3	249.5	55.3	256.5
67.5	247.2	60.8	255.8
84.3*	244.1	72.0	254.3
90.9	244.1	76.3*	253.5
101.3	244.2	83.9	253.0
113.8	244.0	89.6	253.0
126.0	243.8	93.9	252.8

* 2,6-di-tert-butyl-*p*-cresol added at this point

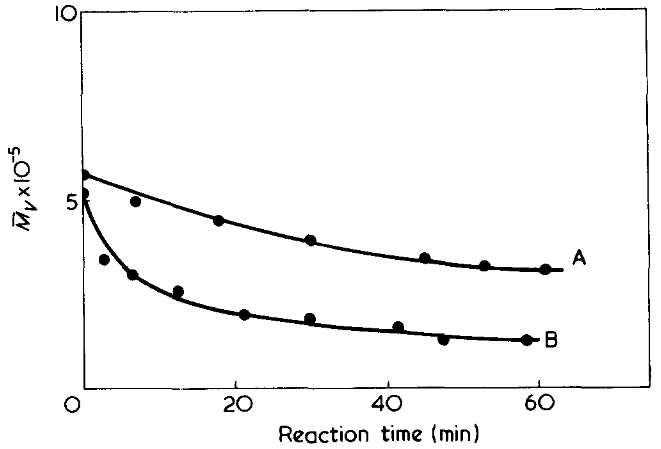


Figure 2 Lead tetraacetate degradation of epoxidized, and hydrolysed epoxidized synthetic rubbers. A, epoxidized synthetic rubber; B, hydrolysed epoxidized synthetic rubber

Table 3 Effect of hydrolysis and epoxidation on intrinsic viscosity

	Intrinsic viscosity		
	Untreated	Epoxidized	Acid hydrolysed
Natural rubber (clone PR107)	7.35	–	7.02
Synthetic rubber	3.82	3.77	3.31

Whereas the degradation of the control rubber is slow, acid hydrolysed natural rubber shows a sharp drop in molecular weight during the first 10 min (*Figure 1*), the rate of degradation being significantly faster than the control. Subsequently, the rate of scission slows down and gradually approaches a rate similar to that of the control. The initial rapid degradation is attributable to glycol scission which has been shown to be rapid[10], whereas the continuing slow degradation is probably due to accompanying oxidative chain scission. The pattern of natural rubber samples, which have not undergone acid hydrolysis (*Figure 1*), is similar to that of the control, although there is some evidence of a slightly faster initial drop in the molecular weight. This could be due to the presence of a few 1,2-diols in natural rubber, which could be formed by the amino-acid catalysed hydrolysis of rubber epoxides at the latex stage. (Amylene glycol has been isolated as one of the products in the reaction of glycine with amylene oxide, in aqueous media, at ambient temperatures[11].)

$Pb(OAc)_4$ degradation of epoxidized synthetic rubber

It seems unlikely that $Pb(OAc)_4$ can cleave epoxide groups directly since epoxidized synthetic rubber and the control sample show the same behaviour towards $Pb(OAc)_4$ (*Figure 2*). However, degradation of acid hydrolysed epoxidized synthetic rubber (*Figure 2*) shows a sharp drop in $\bar{M}_v$ during the first 10 min, which is analogous to the behaviour of hydrolysed natural rubber, although admittedly less extensive. This observation supports the proposal that the initial rapid degradation in the case of acid hydrolysed natural rubber is due to glycol cleavage.

It is worthy of note that acid hydrolysis by sulphuric acid, and the epoxidation reactions, do not significantly affect the molecular weight of natural or synthetic rubber (*Table 3*).

Periodic acid catalysed degradation of rubber

The results of the degradation of synthetic rubber and acid hydrolysed natural rubber are summarized in *Figure 3*. In contrast to the behaviour of lead tetraacetate, periodic acid does not appear to degrade the control rubber. However, with the acid hydrolysed natural rubber an immediate drop in viscosity is observed, although the reaction appears to be slower than the analogous reaction with $Pb(OAc)_4$.

Addition of periodic acid to untreated natural rubber results in a slow but significant degradation (*Table 4*). This could again be explained by the presence of a few 1,2-diol groups in the rubber macromolecule.

A more extensive examination of the effect of periodic acid on the degradation of natural and synthetic rubbers (*Table 4*) reveals that in fact periodic acid does catalyse oxidative chain scission reactions, albeit far more slowly than $Pb(OAc)_4$. Thus the molecular weights of the natural and synthetic rubbers decrease by a factor of 12 and 11 respectively over the reaction period from 4 h to 6 days. If it is assumed that glycol cleavage is complete within the first 4 h this suggests that the radical chain scission reactions are of similar importance for both rubbers.

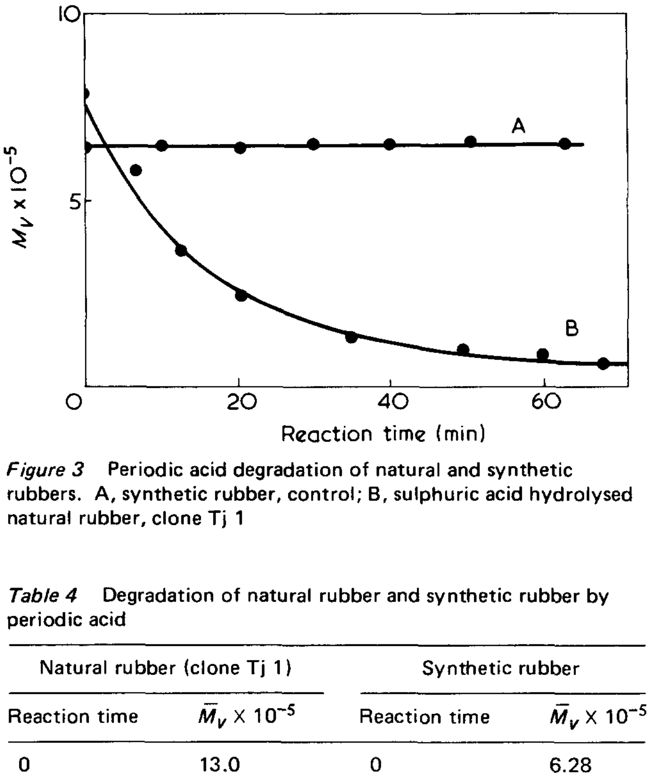


Figure 3 Periodic acid degradation of natural and synthetic rubbers. A, synthetic rubber, control; B, sulphuric acid hydrolysed natural rubber, clone Tj 1

Table 4 Degradation of natural rubber and synthetic rubber by periodic acid

Natural rubber (clone Tj 1)		Synthetic rubber	
Reaction time	$\bar{M}_v \times 10^{-5}$	Reaction time	$\bar{M}_v \times 10^{-5}$
0	13.0	0	6.28
30 min	12.7	20 min	6.28
60 min	12.1	40 min	6.30
90 min	11.5	60 min	6.28
4 h	5.80	4 h	5.85
7 h	3.93	5 h	5.43
2 days	1.12	1 day	4.03
3 days	0.79	3 days	1.06
4 days	0.67	6 days	0.59
6 days	0.47		
*Control (clone Tj 1)		*Control (synthetic rubber)	
Reaction time	$\bar{M}_v \times 10^{-5}$	Reaction time	$\bar{M}_v \times 10^{-5}$
0	13.0	0	6.28
10 days	7.69	10 days	5.78

* Control samples were not treated with periodic acid

Table 5 Comparison of degradation and titration methods for estimating epoxide groups

Sample	$\bar{M}v_i$ (initial) $\times 10^{-6}$	$\bar{M}v_d$ (degraded) $\times 10^{-5}$	$\left(\frac{\bar{M}v_i}{\bar{M}v_d} - 1\right)$	Epoxide content (mmol/kg) Degradation method[c]	Epoxide content (mmol/kg) Titration method
Natural rubber clone PR107[a]	1.55	0.90	16	10	50 ± 1
Natural rubber clone Tj 1[b]	0.78	0.70	11	14	31 ± 1
Epoxidized synthetic rubber[a]	0.53	1.4	3	5	28 ± 1
Epoxidized synthetic rubber[a,d]	0.53	0.88	5	9	28 ± 1

[a] Degradation using $Pb(OAc)_4$, cleavage of 1,2-diols assumed complete in 40 min. [b] Degradation using periodic acid, cleavage of 1,2-diols assumed complete in 60 min. [c] The values in this column are obtained from equation (8). [d] Hydrolysed with perchloric acid

Table 4 also shows that the extent and rate of degradation in the presence of periodic acid are considerably greater than for control samples exposed only to atmospheric oxygen.

Estimation of epoxide group concentration

If it is assumed that the epoxide groups are randomly distributed over the whole molecular weight range then the average number of epoxide groups per chain (n) is given by the relationship:

$$n = \frac{\bar{M}_n \text{ (initial)}}{\bar{M}_n \text{ (degraded)}} - 1 \qquad (6)$$

If the approximation is made that $\bar{M}_v = k\bar{M}_n$ where the value of k remains constant* throughout the degradation, then equation (6) becomes:

$$n = \frac{\bar{M}_v \text{ (initial)}}{\bar{M}_v \text{ (degraded)}} - 1 \qquad (7)$$

and consequently the number of epoxide groups may be calculated from the degradation experiments. In order to compare n with the epoxide concentration in mmol/kg, it is necessary to use the relationship:

$$\text{Epoxide concentration (mmol/kg)} = n \times \frac{10^6}{\bar{M}_n} \qquad (8)$$

However, in these calculations the initial viscosity-average molecular weight ($\bar{M}_{vi}$) is substituted for $\bar{M}_n$, and consequently the epoxide concentration will be low by a factor $\bar{M}_v/\bar{M}_n$. In addition, for the purpose of computing the number of epoxide groups from the degradation data, the effect of concomitant oxidative chain scission is neglected; however, this does not lead to serious errors in the determination.

A comparison of the number of epoxide groups as determined by the degradation method and an independent direct titration technique[2] is made in *Table 5*. It is immediately apparent that correlation between the two methods is very poor. Since the direct titration method is believed to be accurate[2] it follows that the degradation method gives values which are too low. The discrepancy is almost certainly due to a breakdown in the assumptions implicit in the method. These may be summarized as follows:

(i) that hydrolysis of epoxide groups to 1,2-diols and the subsequent cleavage by $Pb(OAc)_4$ or periodic acid are quantitative;

(ii) that epoxide groups are present in the main-chain structure of rubber, and that the distribution of such groups is random;

(iii) that the relationship:

$$\frac{\bar{M}_v \text{ (initial)}}{\bar{M}_v \text{ (degraded)}} = \frac{\bar{M}_n \text{ (initial)}}{\bar{M}_n \text{ (degraded)}}$$

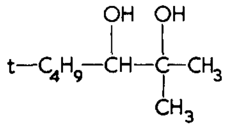
is a good approximation

It seems likely that the third assumption is reasonable provided that degradation is not too extensive, since good correlation has been observed between viscosity and osmometry data for fractionated rubbers.

It has recently been shown[12] that the epoxide group content of natural rubber is predominantly associated with higher molecular weight fractions and this clearly invalidates the second assumption. However, this observation should lead to an increase rather than a decrease in the apparent number of epoxide groups.

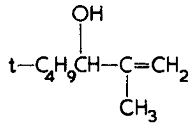
Since it is to be expected that the epoxy content of the epoxidized synthetic rubber will be present in the polymer main chain, and that the distribution of such groups will be random, and since the analysis of the epoxidized synthetic rubber is no more accurate than its natural rubber counterpart, it follows that the main experimental errors are derived from the first assumption. The cleavage of 1,2-diols is almost certainly complete since Criegee[13] has shown that 1,2-diols can be titrated quantitatively with $Pb(OAc)_4$ in acetic acid. Furthermore, the reaction is accelerated by replacement of acetic acid with benzene[14], the solvent employed in this study. In addition, Flory and Leutner[10] have shown that the cleavage of 1,2-diols in poly(vinyl alcohol) by both lead tetraacetate and periodic acid is very rapid.

It seems apparent that the discrepancy between the two methods is largely due either to incomplete hydrolysis of rubber epoxide groups or to side reactions occurring during hydrolysis. Thus hydrolysis of 2,3-epoxy-2, 4,4-trimethylpentane with 0.2 M sulphuric acid gives a product of predominantly the following components[15]:



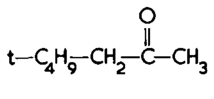
$t\text{—}C_4H_9\text{—}CH(OH)\text{—}C(OH)(CH_3)\text{—}CH_3$

(II)



$t\text{—}C_4H_9CH(OH)\text{—}C(CH_3){=}CH_2$

(III)



$t\text{—}C_4H_9\text{—}CH_2\text{—}C({=}O)\text{—}CH_3$

(IV)

Similar reactions would be expected with rubber epoxide groups. Since the alcohol (III) and the ketone (IV) should be resistant to cleavage by $Pb(OAc)_4$ and periodic acid, the apparent number of epoxide groups would be expected to be dramatically reduced, the actual value depending on the relative proportions of II, III and IV.

Elsewhere[16], perchloric acid in THF has been recommended as the reagent of choice for cleavage of epoxides with

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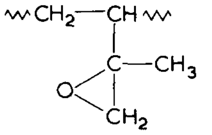
* Since the initial molecular weight distribution of natural rubber is very broad it is possible that degradation may lead to a narrowing of the distribution and hence a reduction in the value of k.

minimal side reactions. Degradation of perchloric acid hydrolysed epoxidized synthetic rubber (*Table 5*) is seen to give a slight improvement in the epoxide value compared to the sulphuric acid hydrolysed rubber. However, the use of perchloric acid is not without difficulty since it appears to induce crosslinking reactions which render the hydrolysed rubber incompletely soluble in benzene.

Thus the degradation method appears to founder mainly for lack of suitable reagents for the specific and quantitative hydrolysis of substituted epoxides. Although the method does not give quantitative estimates of the number of epoxide groups in rubber, it is important in that it clearly demonstrates that the epoxy content of natural rubber is mainly present in the backbone of natural rubber, e.g. (I) and not as side groups, e.g.



(V)

or as associated non-rubber impurities.

CONCLUSION

This study has shown that the degradation method is not reliable for the quantitative estimation of epoxide groups in rubber. Nevertheless, the results are significant in that they demonstrate that the epoxy content of natural rubber is predominantly situated on the backbone of the macromolecule and not as sidechains or associated non-rubber constituents.

ACKNOWLEDGEMENT

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