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THE EFFECT OF OVERCURE ON THE PROPERTIES OF BUTYL RUBBER

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ABSTRACT

The rates of a network formation and degradation during vulcanization of butyl rubbers have been investigated. It has been concluded that in the both overmentioned reactions the unsaturated isoprene units are involved. The effect of overcure on the mechanical properties of vulcanizates has been demonstrated and discussed.

INTRODUCTION

If the optimal values of vulcanization parameters, time or temperature are exceeded /an overcure/ the mechanical properties of vulcanizates drop. The extent of these changes, called "reversion" depends on a kind of rubber, crosslinking substance, accelerator and perhaps other factors also [1-4]. The goal of this work was to investigate an effect of an elastomer backbone unsaturation on its ability to reversion.

EXPERIMENTAL

Three butyl rubbers of the ESSO Chem Co.with various molecular weights and isoprene units content were the subjects of our studies [5]. The formulation of rubber mix was as follows, w.p.: butyl rubber 100.0, stearic acid 1.0, zinc oxide 5.0, phenyl-β-naphtylamine 1.0, tetramethylthiuramdisulphide 1.25, dibenzothiazyl disulphide 0.50, sulphur 2.00. The samples of vulcanizates were prepared at the temperature 160, 170,180 and 190°C. The periods of heating were so choosen that the relative rheometric crosslinking degree C_D started at value 0.7, passed through a maximum and reached, in the region of overcure, again the value 0.7. The C_D value was calculated according to the formula:

$$C_D = \frac{M_x - M_{min}}{M_{max} - M_{min}} \qquad /1/$$

The symbols M_{max}, M_{min} and M_x denote the rheometer torque moment, maximal, minimal and a time x, respectively. The mechanical properties of vulcanizates were measured using dumbell specimens at the

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rate of elongation 500 mm/min.

RESULTS AND DISCUSSION

The isobutylene units in butyl rubbers are practically unreactive toward sulphur under the conditions of vulcanization therefore in crosslinking only isoprene units are involved. A decrease of C_D value, as a result of overcure, probably is connected mainly with the thermal free radical cleavage of di- and polysulphide crosslinks primarily formed, because the backbone of the butyl rubber is very thermostable. The rates of crosslinking and degradation increase with temperature. An effect of rubber unsaturation depends on a kind of reaction. In the case of crosslinking it is positive and manifests itself distinctly in the lower region of vulcanization temperature /Fig.1/.

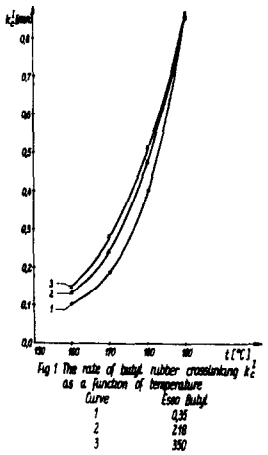

Fig.1 The rate of butyl rubber crosslinking k_2^1 as a function of temperature

Curve	Esso Butyl
1	0,35
2	2,18
3	3,50

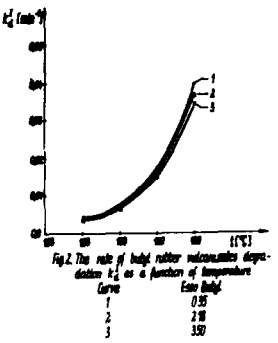

Fig.2 The rate of butyl rubber vulcanizates degradation k_2^1 as a function of temperature

Curve	Esso Butyl
1	0,35
2	2,18
3	3,50

In contrary to that the rate of degradation diminishes a little with the unsaturation of butyl rubber. However in this case the differences between three rubbers investigated could be clearly recognised only at high temperature, above 170°C /Fig.2/. Both reactions follow the first order kinetic equation. The constants of degradation are approximately of the order minor as compared to adequate values of crosslinking rate constants. Undoubtedly the effect of the accelerator added, which operate almost exclusively during the period of cure the reason of this difference. On the basis of

Arrhenius equation in form proposed by Scheele and coworkers [6,7] the activation energies E_a of the both overmentioned reactions were calculated /Table 1/. The activation energy of a given vulcanizate degradation is close to that of di- and polysulphide crosslinks

Table 1. The activation energy of crosslinking and degradation.

Rubber	Activation energy, kJ/mol	
	crosslink.	degrad.
ESSO BUTYL 035	116.4	128.6
ESSO BUTYL 218	106.0	113.6
ESSO BUTYL 325	100.9	110.8

cleavage [8] and higher in comparison to the activation energy of adequate rubber crosslinking. The activation energies of both reaction decrease as the concentration of the isoprene units increases. Therefore these units take part not only in the crosslinking process but also facilitate a cleavage of crosslinks. Probably they act as the scavengers of thiyl radicals formed during thermal dissociation of di- and polysulphide crosslinks. The properties of vulcanizates depend on a degree of crosslinking, C_D. Usually the rubbers are vulcanized at so called optimal vulcanization time, at which C_D=0.9. It seemed interesting to compare the mechanical properties of rubbers vulcanized at t_{90} and t'_{90}, i.e. at the times of optimal cure and the adequate overcure. The stress at 300% elongation or modulus M_{300}, the tensile strength f_s and the elongation at break ε were measured on the samples vulcanized at t_{09} and t'_{09} and the ratios of the appropriate values were calculated, i.e.:

$$R_{/M,T,\varepsilon/} = \frac{\text{a value at } t'_{09}}{\text{a value at } t_{09}} \qquad /2/$$

The results are collected in table 2. As was expected the overcure of butyl rubbers as a result of additional heating from t_{09} to t'_{09} does not change essentially their crosslink density, the values of $R_M \cong 1$. However the R_T and R_ε values decrease with the temperature and unsaturation of rubber. It should be emphasized that the overcure to t'_{90} is not equivalent for rubbers with different unsaturation. In the period of overcure, i.e. between t_{09} and t'_{09} an

Table 2.

Rubber	T °C	t_{09} min	t'_{09} min	$t_{09}-t'_{09}$ min	R_M	R_T	R_ε
ESSO BUTYL 035	160	27.0	120.0	93.0	0.93	0.74	1.06
	170	15.8	58.5	42.7	0.91	0.73	0.93
	180	10.2	32.0	21.8	-	-	-
	190	5.3	17.4	12.1	0.97	0.62	0.82
ESSO BUTYL 218	160	21.0	120.0	99.0	1.08	0.62	0.75
	170	11.4	46.5	35.1	1.26	0.23	0.54
	180	7.0	26.0	19.0	1.36	0.15	0.43
	190	4.2	14.0	9.8	-	-	-
ESSO BUTYL 325	160	17.0	90.0	73.0	1.01 [1]	0.52	0.69
	170	12.1	58.5	46.4	1.00 [1]	0.45	0.52
	180	7.6	29.6	22.0	1.15 [1]	0.53	0.53
	190	5.1	15.7	10.6	0.82	0.61	0.80

[1] Moduli measured at ε = 200%

additional amount of crosslinks is first formed and then destroyed. The difference between moduli values, $M_{max} - M_{09}$ could be taken as the measure of that maturing of a network. From our investigations it follows that an extent of a network structure transformations increases with a rubber unsaturation. This statement probably is of general validity and could be adopted for analysis of different rubbers overcure.

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