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The effect of silane coupling agent (Si-69) on thermoxidative stability of butyl rubber compounds

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Thermal analysis and the ageing studies of butyl rubber (IIR) compounds have been carried out in order to assess the effect of a silane coupling agent, *Bis*-(3-triethoxysilylpropyl)tetra sulphide (Si-69) on thermal and thermoxidative stability of IIR. The thermal stability of the raw rubber remained uneffected on adding Si-69, whereas the thermoxidative stability was enhanced. Similar behaviour, though to a lesser extent, has been observed for compounded rubber. The ageing properties and service life are also improved with Si-69. A suitable mechanism has been proposed.

1. Introduction

The effect of EPDM rubber on the enhancement of the heat-resistance properties of butyl rubber (IIR) and thus, the achievement of better service life of automobile tubes, have been reported earlier [1, 2]. *Bis*-(3-triethoxysilylpropyl)tetra sulphide, a silane coupling agent (Si-69), is commonly employed as a reversion resistance additive for general-purpose rubber, using a sulphur accelerator curing system [3]. However, no systematic information is available for rubbers with low unsaturation in its backbone. In this paper, the effect of Si-69 on IIR compounds is reported.

2. Experimental procedure

The procedures used in this study are listed in Table I.

3. Results and discussion

3.1. Filled stock (C1 and C2)

On addition of Si-69, scorch time, t_2, and optimum cure time, t_{90}, increase along with reversion time (Table III). The retardation effect of Si-69 on sulphur accelerator (MBT) curing of IIR, may be due to the reaction between Si-69 and MBT during vulcanization.

The addition of Si-69 has little effect on physical properties. However, after ageing, a pronounced effect is observed. The retention of modulus and hardness shows substantial improvement on addition of Si-69. This indicates that Si-69 can be used as an additive for increasing heat and air ageing properties in filled butyl compounds.

3.2. Gum stock (B1 and B2)

As in the filled stock, Si-69 has a retarding effect on curing (Table III). The retention of modulus and hardness was found to be better for compounds with Si-69. The V_r values (volume fraction of insoluble rubber, a representative of cross-link density measured under equilibrium swollen condition in cyclohexane at room temperature) [4] indicates that the retention of cross-links after ageing is more for compounds with Si-69 which directly reflects on the retention of physical properties during ageing.

3.3. Thermal analysis

Thermogravimetric (TG) analysis and oxidative differential scanning calorimetry (DSC) of raw and gum compounds have been carried out to understand the mechanistic aspects of IIR degradation. The results are shown in Table IV and Figs 1–3. The DSC peak for gelation [5] is shifted to higher temperature on addition of Si-69; however, ΔH remains almost constant (Fig. 1). This indicates that Si-69 retards the gelation of IIR, prior to oxidative degradation. Thermal stability of IIR (raw) is decreased marginally on adding Si-69, whereas thermoxidative stability is enhanced (as is evident from the T_{max} value, the temperature at which maximum degradation occurs in TG analysis, shown in Table IV and Fig. 2). Both ΔE and $t_{1/2}$ at 120 °C show an incremental trend with Si-69 in both atmospheres. However, this effect is more prominent in oxygen. For gum compounds, a similar effect but to a lesser extent, is observed (Fig. 3). This indicates that IIR undergoes degradation through chain scission in which double bonds in the backbone are acting as “weak links” [1, 6]. In oxygen, Si-69 hinders the gelation of IIR which occurs prior to oxidative chain scission, resulting in an increase of the thermoxidative stability and consequently the retention of properties after oxidative ageing.

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TABLE I Experimental procedures

Parameters studied	Method followed/equipment used	Remarks
Mixing of IIR gum compounds	Brabender Plasticorder PL 2000-3 with N50 mixer head	30 r.p.m., 100 °C; mix formulation in Table II
Mixing of black-filled IIR compounds	Stewart Bolling lab. banbury (model 000)	30 r.p.m., 90 °C; mix formulation in Table II
Rheometric study	MDR-2000	At 175 and 191 °C
Tensile properties	ASTM D412-80	Using die C.
Hardness (Shore A)	ASTM D2240-78	–
Ageing study	–	In air at 120 °C for 1 and 7 days
Thermal and thermoxidative behaviour	Perkin-Elmer 7-Series thermal analyser	With TGA 7 and DSC 7 module in N_2 and O_2.
Kinetics of oxidation	Kissenger method [1]	Following the respective TG curve.

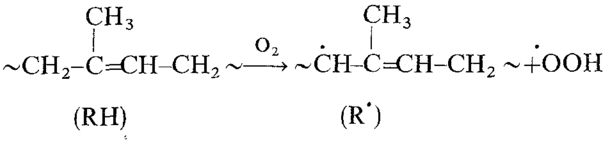
TABLE II Mix formulation (p.h.r.)

Mix	A1	A2	B1	B2	C1	C2
IIR	100	100	100	100	100	100
Carbon Black	–	–	–	–	60	60
Si-69	–	2	–	2	–	2

Note: Mixes B1, B2, C1 and C2 contain ZnO 5; St. Acid 1; MBT 0.5; TMTD 1.

3.4. Mechanism

The isoprene units in the IIR back-bone react with oxygen during ageing as in Reaction 1 with the formation of hydroperoxide. According to Wolff [7] Si-69 disproportionates in the presence of heat and oxygen as in Reaction 2. The S_x bonds ($x > 2$), due to low-energy requirement, may generate $R_1S^{\cdot}$ and $R_1S^{\cdot}_{(x-1)}$. Peroxide decomposition by sulphide takes place according to Reaction 4. These sulphoxides, on further oxidation, form sulphur acids which act as antioxidants [8]



$$\sim CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2\sim \xrightarrow{O_2} \sim\dot{C}H-\overset{\overset{CH_3}{|}}{C}=CH-CH_2\sim+\dot{O}OH$$

$$\text{(RH)} \qquad\qquad (R^{\cdot})$$

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$$

$$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \qquad (1)$$

$$(C_2H_5O)_3-Si-(CH_2)_3-S_4-(CH_2)_3-Si-(OC_2H_5)_3 \rightleftharpoons$$

$$(C_2H_5O)_3-Si-(CH_2)_3-S_x-(CH_2)_3-Si-(OC_2H_5)_3$$

$$(x = 2\text{–}8) \qquad (2)$$

$$(C_2H_5O)_3-Si-(CH_2)_3-S_x-(CH_2)_3-Si-(OC_2H_5)_3 \xrightarrow[\text{heat}]{O_2}$$

$$(C_2H_5O)_3-Si-(CH_2)_3-S^{\cdot} + {}^{\cdot}S_{x-1}-(CH_2)_3-Si-(OC_2H_5)_3$$

$$(R_1S^{\cdot}) \qquad\qquad (R_1S^{\cdot}_{x-1})$$

$$(3)$$

$$R^{\cdot} + R_1S^{\cdot} \rightarrow R-S-R_1$$

$$R-S-R_1 + ROOH \rightarrow (RR_1)S{=}O \qquad (4)$$

$$(RR_1)S{=}O \rightarrow \text{sulphur acids (antioxidants)}$$

TABLE III Rheometric and physical properties of IIR compounds

	B1	B2	C1	C2
Rheometric data				
at 175 °C: scorch time (t_2 min)	2.40	2.54	2.40	2.60
Optimum cure time (t_{90} min)	7.44	8.61	9.60	9.80
Reversion time (at 191 °C, t_r min)	–	–	14.40	16.20
Physical properties:				
Tensile strength	1.65	2.21	11.30	10.60
(MPa)	(106) (65)	(85) (64)	(81) (67)	(85) (75)
Modulus (M-300)	1.49	1.50	5.30	5.20
(MPa)	(82) (45)	(98) (48)	(102) (90)	(120) (128)
Elongation	350	400	575	575
at break (%)	(121) (> 250)	(88) (> 225)	(69) (90)	(85) (78)
Hardness	31	29	52	52
	(– 1) (–)	(+ 3) (–)	(+ 1) (– 1)	(+ 3) (+ 5)
V_r	0.185	0.184	–	–
	(89) (22)	(96) (30)		

Note: Figures in parenthesis are percentage retention after ageing in air at 120 °C for 1 and 3 days, respectively.

TABLIE IV Thermal analysis data for IIR compounds

	A1	A2	B1	B2
DSC (oxidative):				
Peak (°C)	252	269	275	277
Enthalpy (ΔH, kJ g^{-1})	5.30	5.24	5.19	4.87
TGA results				
T_{max} (°C)				
in nitrogen	382	377	378	375
in oxygen	273	288	307	308
Activation energy (ΔE, kJ m^{-1})				
in nitrogen	138	146	201	202
in oxygen	83	111	99	103
Half life ($t_{1/2}$, min)				
in nitrogen	2.9×10^8	8.0×10^8	1.9×10^{12}	3.7×10^{12}
in oxygen	5.9×10^4	1.7×10^6	4.3×10^5	7.5×10^5

Note: Heating rate 10 °C min^{-1}.

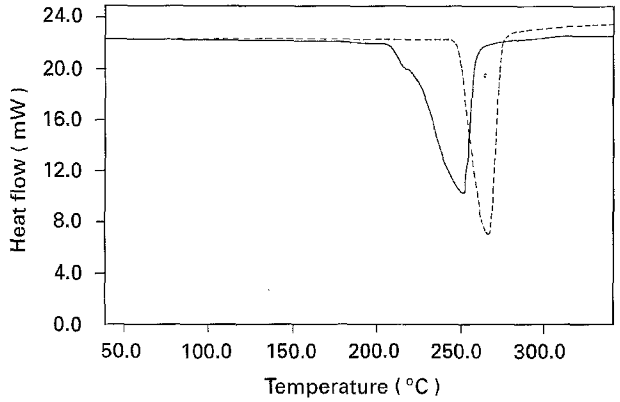


Figure 1 DSC curve of IIR (raw) in oxygen: (——) IIR, (– – –) IIR + Si-69 2 p.h.r.

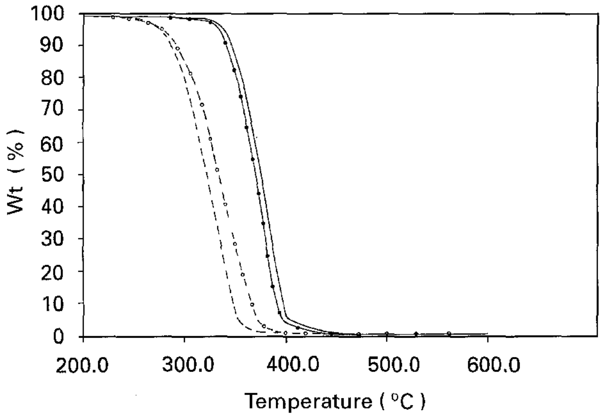


Figure 2 TG curves of IIR (raw). (——) IIR and (—●—) IIR + Si-69 (2 p.h.r.) in nitrogen; (– – –) IIR and (—○—) IIR + Si-69 (2 p.h.r.) in oxygen.

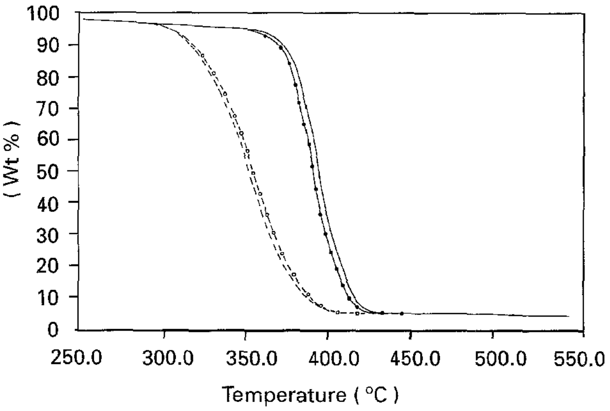


Figure 3 TG curves of IIR (gum vulcanizates). (——) IIR and (—●—) IIR + Si-69 (2 p.h.r.) in nitrogen; (– – –) IIR and (—○—) IIR + Si-69 (2 p.h.r.) in oxygen.

Hence, Si-69 is acting as stabilizer/antioxidant for IIR in thermoxidative ageing, resulting in enhancement of $t_{1/2}$ (service life).

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