Reprint from Kautschuk + Gummi · Kunststoffe, Vol. 42. (1989), No. 8, pages 674–676, Dr. Alfred Hüthig Verlag, Heidelberg

Effect of Silane Coupling Agent on Mechanical Properties and Polymer-Filler Interaction in Silica-filled Epoxidised Natural Rubber

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The effect of a silane coupling agent on polymer-filler interaction and physical properties of silica-filled ENR has been evaluated. It was found that silane coupling agent improved the polymer-filler interaction and imparted better physical properties.

Der Einfluß des Silan-Kupplungsmittels auf die mechanischen Eigenschaften und die Polymer/Füllstoff-Wechselwirkung in Kieselsäure-gefüllten epoxidierten Naturkautschukmischungen

Der Einfluß des Silan-Kupplungsmittels auf die Polymer-Füllstoff-Wechselwirkung und die physikalischen Eigenschaften von Kieselsäure-gefüllten ENR wurde untersucht. Es wurde gefunden, daß das Silan-Kupplungsmittel die Polymer/Füllstoff-Wechselwirkung und die physikalischen Eigenschaften verbessert.

1 Introduction

Epoxidised NR (ENR) is prepared by the partial epoxidation of NR latex with a peracid. The preparation and properties of this modified form of NR have been reported earlier [1, 2]. ENR with 50 mol % epoxidation (ENR-50) has oil resistance and air permeability comparable to that of medium acrylonitrile NBR and butyl rubber respectively. It has also been reported that ENR can undergo strain crystallisation [3] and has the unique ability to be highly reinforced with silica fillers in the absence of coupling agents [4]. In the present paper, we report the results of our studies on the effect of silane coupling agent on vulcanization, polymer-filler interaction and physical properties of silica-filled ENR with 25 mol % epoxidation. Earlier *Pal* and *De* have reported similar studies with EPDM and NR [5, 6].

2 Experimental

The formulations of the mixes are given in *Table 1* and their curing characteristics, as obtained from Monsanto Rheometer R-100, in *Table 2*. The mixes were prepared on a laboratory mixing mill and moulded to optimum cure at 150 °C in a steam heated hydraulic press. ENR of 25 mol % epoxidation, obtained from the *Malaysian Rubber Producers' Research Association (MRPRA)*, was used for the study. Physical properties of the vulcanizates (*Table 3*) were tested as per the following standards:

Stress-strain	ASTM D 412-87
Tear	ASTM D 624-86
Hardness	ASTM D 2240-86
Resilience	BS : 903 : Part A8 : 1963 (Method A)
Compression set	ASTM D 395-85 (Method B)
Flex cracking	BS : 903 : Part A10 : 1956 (Method A)
Heat build-up	ASTM D 623-78
Abrasion resistance	BS : 903 : Part A9 : 1957 (Method A)
Ageing resistance	ISO 188-1982 (E)

Table 1. **Formulation of mixes**

	1	2	3	4	5	6	7	8	9	10	11
ENR-25	100	100	100	100	100	100	100	100	100	100	100
Na_2CO_3	0,25	0,25	0,25	0,25	0,25	0,25	0,25	0,25	0,25	0,25	0,25
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2
Ultrasil VN3	–	5	10	20	30	40	5	10	20	30	40
Si-69[a]	–	–	–	–	–	–	0,25	0,5	1,0	1,5	2,0
Naphthenic oil	–	0,5	1	2	3	4	0,5	1	2	3	4
TMTD[b]	1,6	1,6	1,6	1,6	1,6	1,6	1,6	1,6	1,6	1,6	1,6
MOR[c]	2,4	2,4	2,4	2,4	2,4	2,4	2,4	2,4	2,4	2,4	2,4
Sulphur	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,3

[a]Bis(triethoxysilylpropyl)tetrasulphide – [b]Tetramethylthiuram disulphide – [c]N-oxydiethylenebenzothiazole-2-sulphenamide

Table 2. **Cure characteristics**

	1	2	3	4	5	6	7	8	9	10	11
Minimum torque at 150 °C in dN · m	5,0	5,0	5,0	8,0	11,0	12,0	5,0	5,5	8,5	10,8	12,3
Maximum torque at 150 °C in dN · m	49	56	59	72	76	81	56	64	76	88	98
Scorch time at 150 °C in min	5,75	6,0	6,0	5,5	5,0	4,45	6,0	5,0	5,5	4,25	3,5
Optimum cure time at 150 °C in min	13,25	14,0	14,75	13,0	9,5	8,5	15,25	13,0	12,25	12,5	15,0
Mooney scorch at 120 °C in min	40,0	38,0	41,0	35,5	28,5	25,75	38,0	28,5	27,5	24,5	21,0

Table 3. **Physical properties of the vulcanizates**

	1	2	3	4	5	6	7	8	9	10	11
Modulus 300 % in MPa	1,52	1,96	2,60	4,03	5,10	7,70	2,82	3,60	5,36	7,73	10,58
Tensile strength in MPa	9,47	10,10	13,20	16,60	17,60	19,50	10,00	12,30	17,40	15,00	16,40
Elongation at break in %	700	657	650	690	550	520	550	525	550	420	415
Tear strength in kN/m	20,8	26,4	32,0	48,0	50,0	58,0	29,4	39,0	49,0	55,0	57,0
Hardness in Shore A	30	35	39	48	54	60	38	42	50	57	63
Rebound resilience at 40 °C in %	80	74	74	71	65	60	74	73	72	70	67
Compression set in %	13	14	14	17	20	22	13	13	16	17	18
Abrasion loss in cm^3/h	16,20	15,50	13,30	2,80	2,80	2,30	16,00	11,39	2,78	2,56	1,88
Flex cracking resistance, time for failure in min (no. of cycles per min = 300)	462	293	181	176	175	40	232	165	82	70	40
Heat build-up at 50 °C, ΔT in °C	9	12	13	15	21	27	9	14	15	17	20
Dynamic set (after 25 min) in %	1,10	1,60	1,73	2,48	3,46	4,80	0,95	1,10	1,37	1,38	1,72

2.1 Polymer filler interaction

The extent of polymer-filler interaction was assessed using Cunneen-Russel equation [7]

$$\frac{v_{ro}}{v_{rf}} = ae^{-z} + b \quad (1)$$

where v_{ro} and v_{rf} are the volume fractions of rubber in the unfilled and filled vulcanizates respectively, z is the weight fraction of filler in the vulcanizate and a and b are constants characteristic of the system. By plotting v_{ro}/v_{rf} against e^{-z}, a and b were determined from the slope and intercept respectively. The higher the value of a, the higher is the polymer-filler interaction and hence the higher the reinforcement [8].

2.2 Determination of volume fraction of rubber (v_r)

The volume fraction of rubber, v_r, was calculated from the equilibrium swelling data by the method reported by *Ellis* and *Welding* [9], which takes into account the correction of swelling increment with duration of immersion after the equilibrium has been attained.

$$v_r = \frac{(D\text{-}FT) \cdot \varrho_r^{-1}}{(D\text{-}FT) \cdot \varrho_r^{-1} + A_0 \cdot \varrho_s^{-1}} \quad (2)$$

where T is the weight of the specimen, D its deswollen weight, F the weight fractions of insoluble components and A_0 the weight of the absorbed solvent, corrected for the swelling increment; ϱ_r and ϱ_s are the densities of the rubber and the solvent respectively. Chloroform was used as solvent in the present study.

3 Results and discussion

3.1 Cure characteristics

It has already been reported that a conventional sulphur curing system for ENR results in vulcanizates with poor ageing characteristics [4]. Therefore, an EV formulation suggested by *Baker* et al. [2] was used in this study. The cure characteristics of the various mixes are given in Table 2. It is found that the addition of precipitated silica increases both the minimum and maximum torque. The increase in maximum torque is more prominent in the presence of the coupling agent (*Figure 1*). This can be attributed to the formation of strong coupling bonds as discussed later. Scorch time progressively decreases with the addition of silica, but coupling agent is found to decrease it further, indicating early onset of curing reactions. The optimum cure time is also found to decrease with the addition of filler. However, the coupling agent is found to increase it in mixes containing high proportions of the filler.

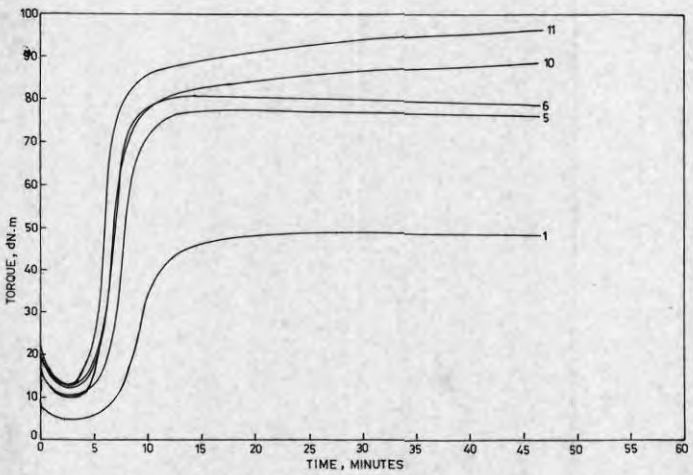

Figure 1. Rheographs of the mixes 1, 4, 5, 10 and 11

3.2 Reinforcement characteristics

The plots of v_{ro}/v_{rf} against e^{-z} according to the Cunneen-Russel equation are given in *Figure 2.* The curve for the mixes containing coupling agent (Si-69) shows a higher slope indicating a higher degree of polymer-filler interaction brought about by the coupling agent. All the silica-filled mixes obey the Cunneen-Russel equation (Figure 2).

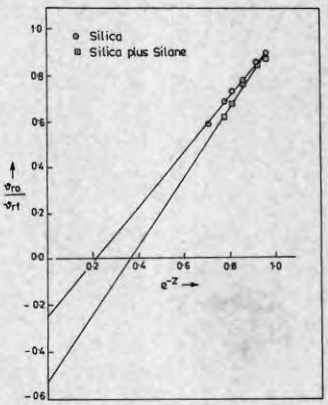

Figure 2. Plot of v_{ro}/v_{rf} versus e^{-z} according to Cunneen-Russel equation (eq. 1)

For mixes without Si-69:

$$\frac{v_{ro}}{v_{rf}} = 1{,}17\, e^{-z} - 0{,}25 \quad (3)$$

For mixes containing Si-69:

$$\frac{v_{ro}}{v_{rf}} = 1{,}5\, e^{-z} - 0{,}52 \quad (4)$$

3.3 Technical properties

That silica reinforces ENR-25 and additional coupling bonds are formed in the presence of the coupling agent is evident from the following observations. Addition of silica increases the tensile modulus and hardness of ENR and the increase is more significant in the presence of the coupling agent. Also elongation at break decreases more in the case of mixes containing the coupling agent. Tensile strength and tear strength increase on addition of silica, but the coupling agent does not have any appreciable effect on these properties. Earlier *Gelling* [10, 11] reported that the stereoregularity of NR is unaffected by epoxidation and he observed very high tensile strength for gum ENR vulcanizates. The strain-crystallising character of ENR was also confirmed by X-ray diffraction study [3, 4]. However, the results obtained in the present study do not fully support this view.

Abrasion resistance is found to increase progressively with the addition of silica and the coupling agent improves it further. Flex cracking resistance decreases as silica is added to ENR and the reduction is larger in the presence of the coupling agent as the vulcanizates become stiffer.

Expectedly, heat build-up progressively increases with silica loading but the presence of coupling agent is found to decrease it. This is believed to be due to the formation of covalent bonds between silica particles and rubber through the coupling agent. For similar reasons both dynamic set and compression set increase on the addition of silica but the addition of coupling agent improves the set behaviour remarkably.

3.4 Ageing resistance

The changes in tensile properties of the ENR vulcanizates after ageing at 70 °C for 96 h are given in *Table 4*. The results indicate that ageing resistance of silica-filled ENR vulcanizates is not influenced by the addition of coupling agents.

Table 4. **Ageing characteristics of vulcanizates**

	1	4	5	9	10
Change in modulus in %	7,18	11,6	12,0	8,8	10,5
Change in tensile strength in %	−1,7	−5,9	−5,8	−4,5	− 4,7
Change in elongation at break in %	−4,4	+3,6	−5,3	−2,8	−14,6

4 Conclusions

Addition of reinforcing silica filler to ENR causes improvement in physical properties due to polymer-filler interaction, which gets further strengthened in presence of silane coupling agent.

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