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EFFECT OF PROCESS AIDS ON ENGINEERING PROPERTIES OF NATURAL RUBBER

K. T. Thomas, Baby Kuriakose and N. M. Mathew

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Six different process aids — naphthenic oil, paraffinic oil, aromatic oil, pine tar, white factice and CI resin — in natural rubber were evaluated for their effect on physical properties of vulcanizates, with special reference to those relevant to engineering application. Creep, stress relaxaton, set, hysteresis, heat build-up and resilience were studied. It was found that naphthenic oil showed the optimum properties, where as CI resin gave the least desirable set of properties. These two process aids were further evaluated to study the effect of their concentrations on properties. It was found that the engineering properties were improved by the addition of naphthenic oil upto 10 phr. However, CI resin showed abnormal behaviour. A rating of process aids was made as far as general engineering properties were concerned.

Key words – Process aid, Creep, Stress relaxation, Hysteresis, Heat build-up, Set, Resilience.

K. T. Thomas (for correspondence), Baby Kuriakose, and N. M. Mathew, Rubber Research Institute of India, Kottayam – 686 009, India.

INTRODUCTION

Elastomers are being used in many engineering applications and the design parameters for such applications have been described by several authors (Freakley and Payne, 1978; Turner *et al*, 1979). Viscoelastic behaviour, stress-strain relations, creep, stress relaxation, set, dynamic-mechanical behaviour etc., are some of the properties of rubber vulcanizates which are of prime importance in engineering applications.

Much work has been done on the effect of environmental factors, compounding ingredients and type of crosslinks on creep and related properties (Thrion and Chasset, 1963; Puydak, 1970). The effects of carbon black and other fillers on the dynamic properties of natural rubber (NR) and other rubber vulcanizates have also been reported (Medalia, 1978; Isono and John, 1984). Similar studies have also been made to evaluate the effect of antioxidant on creep and stress relaxation (Scheele and Hillmer, 1969). The effect of curatives on these properties was studied by Tamura and Murakami (1973). Though the influence of process aids on physical properties of rubber vulcanizates has been studied (Zverev and Zubov, 1959; Rechuite and Dimellar, 1982), the effect of the same on creep and related properties has not been reported.

Natural rubber is one of the polymers used in many engineering applications. Since these products contain considerable amount of fillers, incorporation of process aids becomes essential. This study is intended to evaluate the effect of different process aids on the properties of NR vulcanizates, particularly creep, stress relaxation, set, hysteresis, heat build-up and resilience.

EXPERIMENTAL

Natural rubber used in this study was ISNR-5. The petroleum oils *viz.* naphthenic, paraffinic and aromatic, were obtained from M/s Indian Oil Corporation. The basic properties of these oils are given in Table 1.

Table 1. **General characteristics of process oils**

Characteristics	Aromatic	Naphthenic	Paraffinic
Pour point (°C)	-1 to 21	-40 to -12	0
Aniline point (°C)	47	78	101
Viscosity gravity constant (VGC)	0.90 & above	0.85 to 0.90	0.79 to 0.85
Aromaticity as C%	35 to 50	10 to 30	0 to 10

Table 2. **Characteristics of white factice**

Characteristics	Average value (%)
Acetone extract	10 ± 2
Free sulphur (sulphite)	0.5 ± 0.1
Ash content	10 ± 2
Specific gravity	1.10 ± 0.05

Pine tar having a specific gravity of 1.1 and Saybolts viscosity range 700–1000 at 50°C was supplied by M/s Camphor & Allied Products, Bareilly. The white factice used in this study was obtained from M/s Rishiroop Polymers, Bombay. The characteristics of the same are given in Table 2.

Commercial grade Coumarone Indene (CI) resin, having a specific gravity of 1.09 and softening point in the range of 78-81°C, was used. Semi-reinforcing black (SRF, N-762) was supplied by M/s Phillips Carbon Black Ltd., Durgapur.

Mixing and Vulcanization

The mixes were prepared on a laboratory size two-roll mixing mill (15 cm x 30 cm) at a friction ratio of 1:1.25. The formulations of the mixes are given in Table 3. A semi-EV system was selected. No antioxidant was incorporated in the mixes in order to study the effect of process aids on ageing. To study the effect of concentration of process aids on the engineering properties, naphthenic oil and CI resin at different loadings were used. The formulation and cure characteristics of the mixes are given in Table 4.

Table 3: **Formulation of mixes**

Mix	1	2	3	4	5	6
Natural rubber (ISNR-5)	100	100	100	100	100	100
Stearic acid	2	2	2	2	2	2
Zinc oxide	5	5	5	5	5	5
SRF black	50	50	50	50	50	50
Naphthenic oil	5	—	—	—	—	—
Paraffinic oil	—	5	—	—	—	—
Aromatic oil	—	—	5	—	—	—
Pine tar	—	—	—	5	—	—
White factice	—	—	—	—	5	—
CI resin	—	—	—	—	—	5
CBS[a]	1.5	1.5	1.5	1.5	1.5	1.5
TMTD[b]	0.5	0.5	0.5	0 5	0.5	0.5
Sulphur	1	1	1	1	1	1

a — N-Cyclohexyl – 2 – benzothiazole sulphenamide b — Tetramethylthiuram disulphide

Table 4. Formulation and cure characteristics of mixes

Mix	C	D	E	F	G	H	I	J	K	L
Natural rubber (ISNR-5)	100	100	100	100	100	100	100	100	100	100
Stearic acid	2	2	2	2	2	2	2	2	2	2
Zinc oxide	5	5	5	4	5	5	5	5	5	5
SRF black	50	50	50	50	50	50	50	50	50	50
CI resin	1	2	4	8	—	—	—	—	—	—
Naphthenic oil	—	—	—	—	—	1	2	4	8	10
CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TMTD	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulphur	1	1	1	1	1	1	1	1	1	1
Optimum cure time at 150°C (min)	5	5.5	5	6	5.5	5.5	5.5	5.5	5.5	5.5
Maximum torque (dN/m)	82	79	75	69	85	81	77	72	67	65
Cure rate index	66.6	66.6	50	50	50	50	50	50	50	50

Vulcanization was carried out in a 45 cm x 45 cm hydraulic press, having steam heated platens maintained at a temperature of 150°C and a pressure of 4.5 MPa on the mould, upto optimum cure times.

TESTING

Cure characteristics of the compounds were evaluated using a Monsanto Rheometer R-100 and a Scott Mooney viscometer. For evaluation of green strength, the compounds were hot pressed at 100°C, without pressure, into sheets of 2 mm thickness. Dumbbell specimens were cut using ASTM die D. The green strength of the compounds were measured using a Zwick Universal Testing Machine (Model 1474). The physical properties such as 300% modulus, tensile strength, elongation at break, hardness, rebound resilience, compression set, heat build-up and tension set were determined as per the relevant ASTM procedures. Creep was measured according to BS-903, Part A. Bench marks were made (L_o=4 cm) and the samples were clamped using specially designed grips. A constant load of 30 Newtons was applied on the lower grip. The extension of the specimen with respect to the bench marks (L_1) was noted one min after the application of the load. Thereafter extensions at different time intervals were also noted (L_t) and the observations were carried out upto 6 days (Fig. 1). The relative deformation at a particular period was calculated from the formula:

$$\text{Relative deformation}(\%) = \frac{L_t - L_1}{L_1 - L_o} \times 100$$

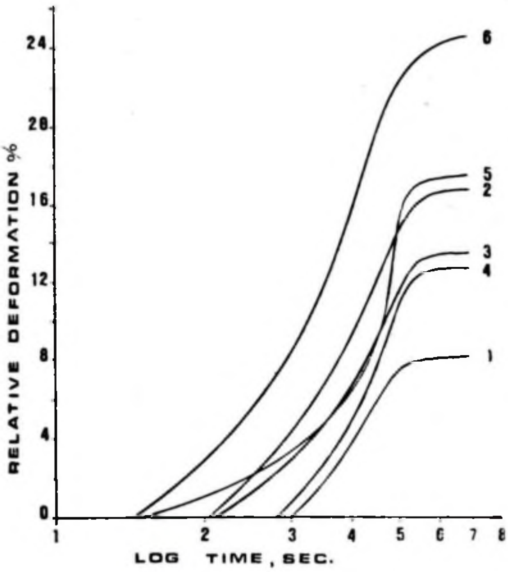

Fig. 1. Effect of different process aids on creep

Creep was also measured at 70°C for the samples containing different loadings of CI resin. The principle suggested by MacKenzie (1984) was made use of in determining stress relaxation under tension. Benchmarks were made 2.5 cm apart on the dumbbell sample. The sample was held in the jaws of a Zwick Universal Testing Machine(UTM), strained to 200 per cent elongation for 3 hrs. Initial stress and the stress at different intervals were noted. Coefficient of relaxation (f_t/f_0) was calculated for different periods (Fig. 2).

The hysteresis loops of the vulcanizates were obtained by straining the specimen to 200 per cent elongation and then retracting it to the normal position on the UTM. The hysteresis was calculated as the percentage of the area between the loading and unloading curves and the strain axis.

RESULTS AND DISCUSSION

The effect of six process aids on the engineering properties at a fixed concentration and the effects of incorporation of different loadings of two process aids, one showing the most desirable and the other, the most undesirable effect as far as creep and related properties are concerned, are presented and discussed separately.

I. Effect of Process Aids on the Engineering Properties

The optimum cure time, cure rate index, scorch time, green strength and minimum compound viscosity are given in Table 5.

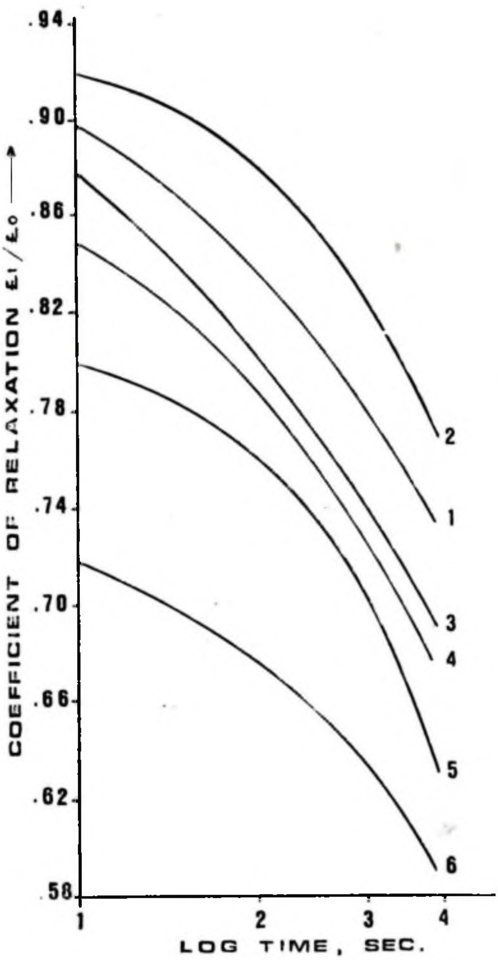

Fig. 2. Effect of different process aids on stress relaxation

The creep and stress relaxation curves of the vulcanizates are given in Fig. 1 and Fig. 2, respectively. It is seen from Table 5, that green strength, which is a measure of the ability of the compound to withstand shaping operations is the highest for white factice, followed by pine tar, aromatic oil and paraffinic oil in order. Among the petroleum oils, naphthenic oil is having the minimum green strength. CI resin shows the poorest strength among the process aids used in the study. The Mooney viscosity of the compounds containing these process aids also shows the same trend. The scorch time of all the compounds is comparable except for the one containing Cl resin which shows a slightly higher value.

The vulcanizate containing naphthenic oil gives the highest tensile strength and elongation at break (Table 6). The compound containing white factice shows the lowest strength followed by that containing CI resin. Pine tar behaves almost similar to aromatic oil. Tear strength of the vulcanizates also follows the same trend.

Table 5. **Cure and process characteristics of mixes**

Mix	Control*	1	2	3	4	5	6
Optimum cure time min at 150°C	5.5	6	5	5	4.5	5.5	5
Maximum torque (dN/m)	85	67	70	72	67	80	70
Cure rate index	50	50	50	50	66.6	40	50
Green strength (MPa)	0.7	0.6	0.6	0.7	0.7	0.8	0.3
Minimum compound viscosity at 120°C	34	20	33	37	37	40	18
Scorch time (min) at 120°C	21.5	20	19.5	21	19	21	24.5

(* Without process aid)

Table 6. **Effect of different process aids on properties**

Mix	1	2	3	4	5	6
300% modulus (MPa)	9.0	9.0	9.6	7.1	9.1	7.3
Tensile strength (MPa)	25.5	23.5	24.6	25.2	20.7	22.2
Elongation at break (%)	717	643	665	712	553	680
Retention in properties after ageing at 70°C for 10 days (%)						
300% Modulus	162	167	142	171	158	141
Tensile strength	78	88	73	82	78	71
Elongation at break	59	63	57	58	61	61
Tear resistance (kN/m)	84	87	80	71	67	79
Hardness (Shore A)	54	54	56	53	58	59
Compression set at 25% compression at 70°C, for 22 hr (%)	23.4	21.3	28.4	23.0	20.9	32.0
Compression set at 25% compression at room temperature for 72 hr (%)	6.5	6.2	9.6	7.6	6.8	17.1
Heat buildup (△T) at 50°C (°C)	17	17	19	20	19	26
Resilience (%)	68.5	69.4	64.8	64.2	68.1	62.9
Hysteresis (%)	42	49	42	48	47	50

The effects of petroleum oils on the ageing characteristics agree well with the studies reported earlier (Zverev and Zubov, 1959). It is seen that the compound containing paraffinic oil shows the highest retention of tensile properties, whereas that containing aromatic oil has the minimum retention. Among the process aids studied, CI resin gives the minimum ageing characteristics followed by white factice.

Regarding the general engineering properties, the lowest set characteristics are shown by naphthenic oil. Vulcanizates containing aromatic oil show marked differences in properties compared to those containing naphthenic oil. The highest set values are obtained for CI resin. Results of compression set tests at 70°C and at room temperature show the same trend.

Set characteristics can effectively be used to predict the creep and stress relaxation of rubber vulcanizates. The compression set values, especially those at room temperature, show good correlation with stress relaxation and creep behaviour.

Table 7 shows the slope of the stress relaxation curves at three periods. As the slope increases, the stress decay becomes faster. It is seen from the table that paraffinic oil shows the least stress relaxation characteristics. In the case of aromatic oil, white factice and CI resin, the rate of decay is higher even after long periods, showing indefinite stress relaxation characteristics.

From the creep curves (Fig. 1) for the above vulcanizates it can be seen that naphthenic oil shows the least creep followed by pine tar and aromatic oil. Paraffinic oil shows high creep characteristics contrary to its behaviour with respect to stress relaxation. This unusual behaviour of paraffinic oil can be attributed to its bleeding tendency due to incompatibility with the polymer. As the relaxation experiments were done for a limited period of 3 hr only, this phenomenon may not be prominent. But in the case of creep testing the duration is longer and the chances for bleeding are higher. The loss of process aid may lead to reduced mobility of the polymer chains, which enables them to reorient for accommodating the applied stress. As the effective load distribution among the polymer chains becomes difficult, there will be more stress concentration on the polymer-filler interphase which results in higher creep.

The resilience and hysteresis test results show that CI resin has the lowest and the highest values, respectively. It also shows comparatively higher heat build-up.

Therefore, for the second part of this study, naphthenic oil and CI resin were selected for further evaluation.

II. Effect of Concentration of Process Aids on the Engineering Properties

Table 8 shows the physical properties of the vulcanizates containing different loadings of naphthenic oil. It can be seen that modulus and tensile strength decrease with increase in the proportion of naphthenic oil. However, elongation is found to increase. Ageing properties do not show any marked difference. Hardness decreases as may be expected. Resilience first decreases and then increases. Hysteresis also shows the same trend.

Creep and stress relaxation curves for the above vulcanizates are given in Fig. 3 and Fig. 4, respectively. It is found that as the process aid loading is increased, the creep decreases. As the process aid loading increases, uniform stress distribution in the matrix is made easier as it facilitates the mobility of polymer chains more effectively.

Table 7. **Stress relaxation characteristics**

Time (sec)	Slope of the stress relaxation curves for mixes					
	1	2	3	4	5	6
30	1.7	1.2	2.0	1.6	1.1	1.0
600	2.5	1.6	2.5	2.2	2.5	2.0
5400	3.0	2.5	3.3	2.6	3.3	3.3

Table 8. **Effect of concentration of naphthenic oil on properties**

Mix	G	H	I	J	K	L
300% modulus (MPa)	12.4	11.1	10.5	9.2	8.6	8.1
Tensile strength (MPa)	24.3	23.7	23.2	23.6	23.3	22.5
Elongation at break (%)	596	598	635	659	682	689
Retention in properties after ageing at 70°C for 10 days (%)						
300% modulus	144	150	146	147	142	144
Tensile strength	73	76	75	81	79	77
Elongation at break	60	62	63	61	57	58
Tear strength (kN/m)	79	81	81	78	74	69
Hardness (Shore A)	59	58	58	59	55	55
Compression set at 25% compression at 70°C, for 22 hr (%)	24.5	24.6	26.1	25.8	26.6	26.9
Compression set at 25% compression at room temperature for 72 hr (%)	6.7	6.7	7.1	6.3	5.8	6.0
Heat build up (△T) at 50°C (°C)	18	19	18	17	17	17
Resilience (%)	71.8	71.8	70.4	71.1	71.8	72.3
Hysteresis (%)	34.2	35.5	38.4	34.6	33.2	31.4

Table 9 shows the physical properties of compounds containing different loadings of CI resin. The compression set values, both at room temperature and at 70°C, increase as the resin loading is increased. The same effect is shown by the creep curves (Fig. 5). This trend is contrary to the behaviour shown by the naphthenic oil, in which case creep is reduced with increase in the process aid content. Stress relaxation curves (Fig. 6) also show the same trend. CI resin softens as the temperature is raised and hence shows more plasticising effect at a higher temperature. Hence creep tests were conducted at 70°C, results of which are given in Table 10. The results show the same trend as that of the creep tests done at room temperature. Hence it is assumed that the CI resin acts only as a process aid and does not impart

Table 9. Effect of concentration of CI resin on properties

Mix	C	D	E	F
300% modulus (MPa)	11.4	10.3	8.5	7.8
Tensile strength (MPa)	23.5	24.3	23.9	22.6
Elongation at break (%)	592	638	644	635
Retention in properties after ageing at 70°C for 10 days (%)				
300% modulus	148	145	140	130
Tensile strength	72	73	67	64
Elongation at break	60	63	61	59
Tear resistance (kN/m)	79	76	76	74
Hardness (Shore A)	58	58	58	58
Compression set at 25% compression at 70°C, 22 hr (%)	25.8	25.7	28.9	30.2
Compression set at 25% compression, room temperature, 72 hr (%)	10.9	13.5	15.0	18.0
Heat buildup (△T) at 50°C (°C)	18	19	24	27
Resilience (%)	66.2	65.9	60.7	58.3
Hysteresis (%)	45	47	49	54

Table 10. Effect of concentration of CI resin on creep at 70°C

Mix	DEFORMATION (%)		
	2 hr	28 hr	70 hr
Control*	3.3	26.7	40.0
C	6.3	34.7	45.5
D	9.3	34.3	50.0
E	18.4	35.7	50.0
F	19.0	38.7	58.0

* Without process aid.

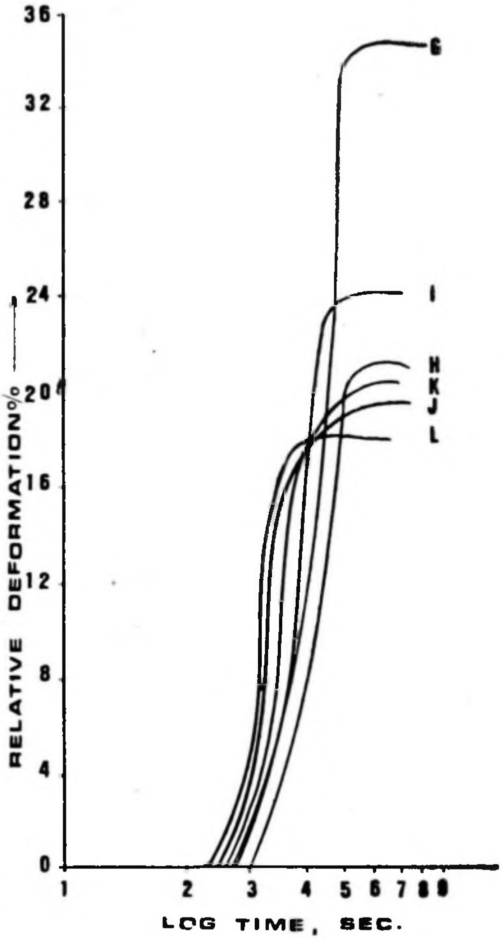

Fig. 3. Effect of concentration of naphthenic oil on creep

any mobility to the polymer chains. Another interesting point noted is that hardness of the vulcanizates prepared by incorporating different loadings of CI resin are virtually the same. This behaviour is different from that of normal process aids, as they reduce the hardness, on increasing the concentration.

SUMMARY AND CONCLUSIONS

The results of the study enable to draw the following conclusions:

1. A rating of process aids can be made in the order, naphthenic oil > paraffinic oil > pine tar > aromatic oil > white factice > CI resin, as far as engineering properties of the vulcanizates are concerned.

2. Creep and stress relaxation characteristics improve on addition of process aids, except CI resin.

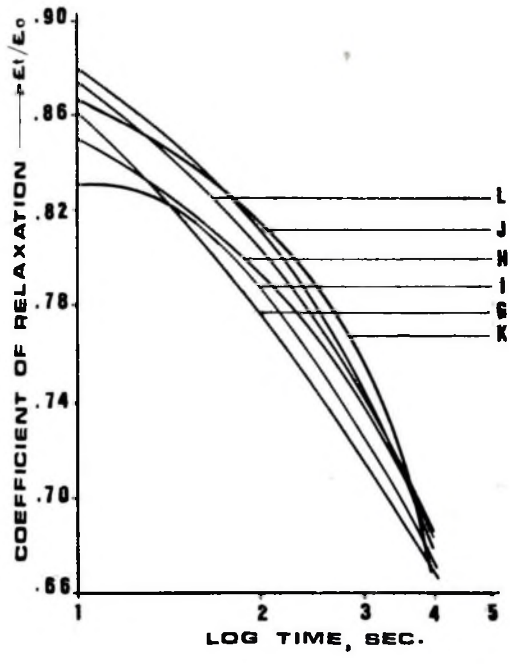

Fig. 4. Effect of concentration of naphthenic oil on stress relaxation

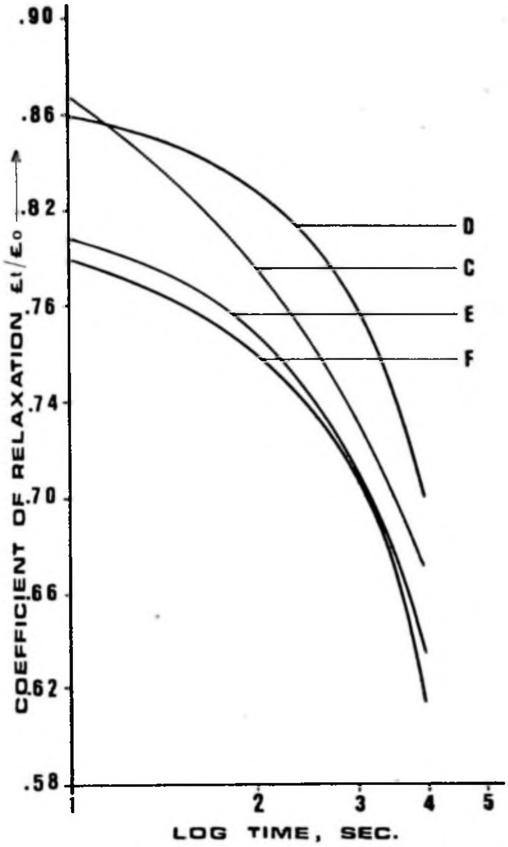

Fig. 5. Effect of concentration of CI resin on creep

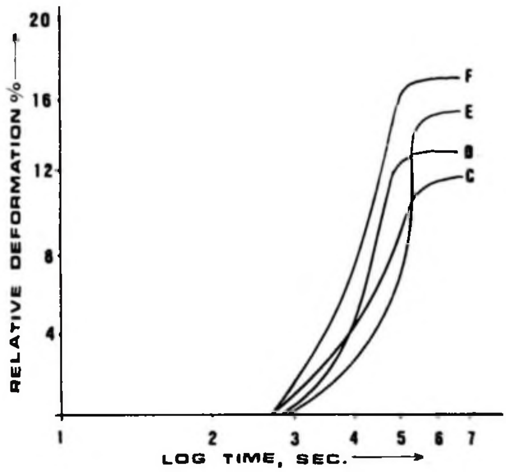

Fig. 6. Effect of concentration of CI resin on stress relaxation

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REFERENCES

Freakley, P. K. & Payne, A. R. (1978). *Theory and Practice of Engineering with Rubber*, 24–110, Applied Science Publishers, London.

Isono, Y. & John, D. F. (1984). Stress relaxation and differential dynamic modulus of carbon black-filled styrene-butadiene rubber in large shearing deformations. *Rubber Chemistry and Technology*; **57**: 925–943.

MacKenzie, C. I. (1984). Stress relaxation in carbon-black filled rubber vulcanizates at moderate strains. *Polymer*, **25**, 559–568.

Medalia, A. I. (1978). Effect of carbon black on dynamic properties of rubber vulcanizates. *Rubber Chemistry and Technology*, **51**: 437–521.

Puydak, R. C. (1970). *Compounding Exxon Butyl Rubber for optimum dynamic and mechanical properties*. Exxon Chemical Company, Texas, U. S. A.

Rechuite, A. D. & Dimellar, G. R. (1982). The Effect of petroleum extender oil types on the properties of a compounded radial styrene block thermoplastic. *Rubber Chemistry and Technology*, **55**: 1437–1446.

Scheele, W & Hillmer, K. H. (1969). Degradation of highly elastic polymers. *Kautschuk and Gummi*, Kunstoffe, **22:** 93–108.

Tamura, S. & Murukami, R. (1973). Stress relaxation mechanisms for various curing systems in natural rubber at high temperature. *Polymer* **14:** 569–591.

Thrion, P & Chasset, R. (1963). Relative contributions of visco elasticity and ageing to the relaxation of rubber vulcanizates. *Rubber Chemistry and Technology*, **36**: 50–58.

Turner, D. M., Moore, M. D. & Smith, R. A. (1979). Rubbers relevant to the engineering of their processes. In: *Elastomers: Criteria for Engineering Design*. (eds.) Hepburn C. and Reynolds, R. J. W. Applied Science Publishers, London. pp. 35–46.

Zverev, M. & Zubov, P. I. (1959). Effect of plasticisers on the physical properties of styrene-butadiene rubber. *Rubber Chemistry and Technology*, **32**: 536–538.