Table 1 Effect of temperature on the translational diffusion coefficient and hydrodynamic radius of the micelles

T/°C	$(\bar{D}_0)_z/10^{-8}$ cm^2 s^{-1}	$(\bar{R}^{-1})_z^{-1}$/nm
50	0.17	74
75	0.38	79
100	0.68	89
120	1.00	96

where η is the viscosity of the oil and k the Boltzmann constant. The results suggest that as the temperature is raised, the micelles swell somewhat due to an increase in the solvent power of the oil.

Other Studies. Conventional light scattering measurements made over the temperature range 20°–80°C confirmed the presence of compact globular micelles. They also indicated that, up to 80°C, the micelle/free-chain equilibrium was overwhelmingly in favour of the micelles. Light-ultramicroscopy studies enabled the movement of the micelles to be observed directly and supported the electron microscopy result that the size distribution of the micelles was narrow.

A full account of the work recorded in this communication together with a study of the effect of micelles on solution viscosity will be presented later.

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Network changes in natural rubber vulcanizate subjected to different physical tests

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Introduction

During service, rubber products are exposed to tension, compression, cyclic deformation and a variety of other factors leading to, in many cases, a rise in temperature inside the product. It is very likely, therefore, that the rubber vulcanizate may undergo structural changes due to mechanical and thermal effects during use. Cunneen and Russell[1] reported changes in chemical structure of natural rubber tyre tread vulcanizates during service. The changes include a marked reduction in the concentration of polysulphidic crosslinks and an increase in the amount of monosulphidic crosslinks and main-chain modifications. Howard and Wilder[2] observed that tyre treads undergo structural changes, i.e. increase of crosslink density during service. The extent of increase of crosslinking depends on the curative system and nature of the base polymer. Podkolzina, Petrova and Fedorova[7] studied the structural changes in *cis*-1,4-polyisoprene vulcanizate during heat ageing and fatigue at elevated temperatures. They showed that the structural changes in the vulcanizate network in heat ageing and fatigue are similar. With fatigue, however, there was a marked increase in the degree of modification of the polymer chains by cyclically-bound sulphur and by residues of combined sulphur. This is stated to be one of the causes of the reduced vulcanizate life under dynamic load conditions.

In the present work, we have studied changes in the network structure of both gum and filled natural rubber vulcanizate subjected to tensile, compression, Goodrich heat build-up, de Mattia flexing, and other tests, in the hope that these tests singly or in combination, will simulate at least a few service conditions. Knowledge of such structural changes will help in predicting the behaviour of rubber during prolonged use. We have chosen a conventional vulcanization system.

Experimental

Formulation of the mixes is shown in *Table 1*. Samples for tensile and de Mattia tests were cured at optimum cure times, while thicker samples (for Goodrich flexometer, compression set and abrasion tests) were overcured in order to prevent undercure in the core of the sample. Different curing times are summarized in *Table 2*. The physical tests were carried out according to ASTM methods[3].

Original vulcanizate samples from before and after completion of the physical tests were used for chemical analyses. For tensile (2.0–2.5 mm thickness), abrasion and flexing tests (1.0 mm thickness), samples for analyses were collected from the fracture surfaces, while for heat build-up and compression set tests, middle sections (1.0 mm thickness) were used. Methods of estimation of chemical crosslink density, $[2M_{c,chem}]^{-1}$, of gum and filled natural rubber vulcanizate have been described earlier[4,5]. The method of determination of network combined sulphur (S_c) is as recently described[6].

Table 1 Composition of the mixes

	Conventional system	
Ingredients	Gum	Filled
Natural rubber[a]	100	100
Zinc oxide	5	5
Stearic acid	2	2
MOR[b]	0.5	0.5
Sulphur	2.5	2.5
HAF-black	0	40
Process oil	0	5

[a] Crumb grade, obtained from the Rubber Research Institute of India, Kerala, India
[b] Benzothiazyl-2-sulphene morpholide

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The ratio $[S_c]/[2M_{c,chem}]^{-1}$ is defined as the sulphur inefficiency parameter (E); the higher the value of E, the less complete is sulphur utilization in crosslinking.

Results and discussion

Physical properties of the different gum and filled vulcanizates (*Table 2*) show expected behaviour: filled vulcanizates show higher tensile strength, higher heat build-up, less abrasion, higher compression set and better flex-crack resistance than the gum vulcanizates. These properties assist characterization of the vulcanizate.

Tables 3, 4 and *5* summarize the results of chemical characterization of the vulcanizates. The chemical crosslink density in filled vulcanizates is higher than in gum vulcanizates. Since the network combined sulphur remains almost constant, E in filled vulcanizates is lower than in gum vulcanizates. Mukhopadhyay and De[5] made a similar observation for ISAF and HAF–black filled, efficiently vulcanized, natural rubber systems.

Table 2 Technical properties of the vulcanizates

Property	Conventional system Gum	 Filled
1 Cure time (min)		
(a) Tensile and de Mattia flexing sample	16.0	15.0
(b) Goodrich heat build-up sample	26.0	25.0
(c) Compression set and abrasion test sample	21.0	20.0
2 Tensile strength (MPa)	14.9	16.0
3 Goodrich heat build-up after 20 min at 50°C, ΔT(°C)	8.1	27.0
4 Goodrich heat build-up after 20 min at 100°C, ΔT(°C)	5.0	42.0
5 de Mattia flex cracking, kilocycles to failure	590	700
6 Akron–Croydon abrasion loss, (cm^3 1000 revolutions^{-1})	2.31	0.78
7 Compression set, ASTM Method B (%)	71.7	93.5

Table 3 Chemical characterization of the original and tested samples

	Heat build-up at 50°C				Heat build-up at 100°C			
	Gum		Filled		Gum		Filled	
Parameter	Before testing	After testing	Before testing	After testing	Before testing	After testing	Before testing	After testing
1 $[2M_{c,chem.}]^{-1} \times 10^5$ mol g^{-1} (RH)	2.34	2.57	2.74	2.77	2.34	2.57	2.74	2.99
2 Polysulphidic linkages[a] (%)	59.5	62.4	64.4	44.5	59.5	62.0	64.4	41.0
3 Network-combined S × 10^4 mol S g^{-1} (RH) (S_c)	7.39	7.26	7.18	7.04	7.39	7.45	7.18	6.61
4 Sulphur inefficiency, atoms/chem. crosslink (E)	31.5	28.1	26.2	25.3	31.5	29.0	26.2	22.1

[a] the rest are disulphidic linkages. The proportion of monosulphidic linkages is negligible, as determined by the thiol-amine chemical probes[10]

Table 4 Chemical characterization of the original and tested samples

	Tensile test				Flex cracking			
	Gum		Filled		Gum		Filled	
Parameter	Before testing	After testing	Before testing	After testing	Before testing	After testing	Before testing	After testing
1 $[2M_{c,}\ chem.]^{-1} \times 10^5$, mol g^{-1} RH	2.18	2.35	2.39	2.53	2.04	2.49	2.40	2.82
2 Polysulphidic linkages[a] (%)	53.2	61.9	55.2	39.7	55.7	63.2	58.9	47.5
3 Network combined S × 10^4, mol Sg^{-1} (RH) (S_c)	7.30	7.60	7.55	7.28	7.29	7.63	7.51	7.36
4 Sulphur inefficiency, atoms/chem. crosslink (E)	33.0	32.3	31.5	28.7	35.7	30.6	31.3	26.0

[a] the rest are disulphidic linkages. The proportion of monosulphidic linkages is negligible, as determined by the thiol-amine chemical probes[10]

Table 5 Chemical characterisation of the original and tested samples

	Compression set				Abrasion			
	Gum		Filled		Gum		Filled	
Parameter	Before testing	After testing	Before testing	After testing	Before testing	After testing	Before testing	After testing
1 $[2M_{c,}\ chem.]^{-1} \times 10^5$, mol g^{-1} (RH)	2.18	3.51	2.27	4.24	2.13	2.26	2.44	2.66
2 Polysulphidic linkages[a], (%)	58.7	69.9	53.9	61.3	58.4	60.3	61.8	42.6
3 Network combined S × 10^4, mol Sg^{-1} (RH) (S_c)	7.51	7.37	7.29	7.01	7.34	7.53	7.42	7.12
4 Sulphur inefficiency, atoms/chem. crosslink (E)	34.3	20.9	32.1	16.5	34.4	33.2	30.3	26.7

[a] the rest are disulphidic linkages. The proportion of monosulphidic linkages is negligible, as determined by the thiol-amine chemical probes[10]

With the exception of the compression set, the tested samples do not undergo significant structural changes. Changes in crosslink density of both gum and filled vulcanizates after tensile, heat build-up, abrasion and flex cracking tests are within experimental error. However, the compression set tested samples show an increase in crosslink density. It is evident that testing conditions (30% strain, 70°C and 22 h) are responsible for maturation or post-vulcanization reactions during the compression set test. Other testing conditions (tensile, heat build-up, abrasion and flex-cracking) do not cause such post-vulcanization reactions, nor do they cause breakage of sulphur–sulphur crosslinks. Since the network combined sulphur (S_c) in all cases does not change after testing, E decreases after compression set testing and remains almost constant after tensile, heat build-up, abrasion and flex-cracking tests.

One remarkable observation is that the proportion of polysulphide linkages in the tested gum vulcanizates does not change significantly and definitely decreases in the tested filled vulcanizates. Although we are unable to explain this phenomenon, the result shows that filler-reinforced vulcanizates produce crosslinks of lower sulphur content under service conditions. We are of the opinion that under service conditions morphological changes of the polymer matrix become more important than changes in the network structure. Recent studies[8,9] of failure surfaces by scanning electron microscopy (*SEM*) have revealed that the failure of rubber occurs either by viscous flow and cavitation or by stretching and rupture.

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