

9.9 and 10.0 Hildebrands, the amount of solvent taken up by the surface layer of polymer would be similar and the 'surface tension' of the polymer would be reduced by a similar amount in both instances. A minimum would still be expected at the point where δ_p and δ_L have the same value.

The average experimental value for the solubility parameter of *o*-hydroxypropyl cellulose, in strong and moderate hydrogen bonding solvents, is 10.7 Hildebrands. The calculated value is 10.2 and the value in poor hydrogen bonding solvents would be expected to be less than 10.7. This is lower than might be anticipated for a water-soluble polymer. However a structure for the polymer has been proposed by Samuels⁵ in which the hydroxyl groups of the anhydroglucose

units and of the propylene glycol chains are predominantly intramolecularly hydrogen bonded. This would reduce the interchain forces of attraction and give a relatively low solubility parameter. The aqueous solubility and the extremely wide solubility spectrum in strong hydrogen bonding liquids is due to the numerous sites on the polymer chain available for bonding with these solvents. As the hydrogen bonding power of the solvents decreases the width of the solubility spectrum decreases. Thus it is the aqueous solubility, not the organosolubility, that must be regarded as anomalous. This agrees with the fact that *o*-hydroxypropyl cellulose is thermoplastic and can be readily melt processed³, making it unique among water-soluble cellulose derivatives.

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Effect of accelerator system and addition of lignin on the network structure of natural rubber vulcanizate

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Kumaran and De¹⁻³ showed that lignosulphonate (hereafter referred to as lignin) lowered the tensile strength, modulus, hardness and resilience and increased the abrasion resistance and flex resistance of natural rubber vulcanizates. While studying different accelerator systems in lignin-containing vulcanizate³ it was observed that increase in compression set⁴ due to addition of lignin was less in the MBT system than that in other systems (CBS/CBS-TMTD/CBS-DPG/MBT-DPG). In order to understand the pos-

sible correlation between the vulcanizate structure and properties of the vulcanizates, we have studied the effect of different accelerator systems on the vulcanizate network structure in the absence and in the presence of lignin.

EXPERIMENTAL

Details of materials, mixing, vulcanization and testing procedures have been published earlier^{1-3,5}. The compositions of the mixes used in the present study are shown in *Table 1*. Vulcanizates

were prepared by curing the compounded stock at 140°C for the respective optimum cure times, determined by using a viscurometer³. The \bar{M}_n values of the rubber in the mixes were in the range of 1.4×10^5 to 1.5×10^5 , as determined by the determination of the limiting viscosity number^{5,6}. Chemical crosslink density was determined by the swelling method^{5,7-10} and the crosslink type (mono-, di-, polysulphidic) by using thiol-amine chemical probes^{11,12}. The total sulphur was determined by the combustion of the vulcanizate, followed by absorption of the sulphur dioxide in hydrogen peroxide and quantitative titration of the resulting sulphate ions⁹. Sulphide sulphur was determined iodometrically from the formation of cadmium sulphide¹⁴. *F* values were calculated as the number of g ions of sulphide sulphur present in the network per chemical crosslink¹⁸.

The crosslink efficiencies, *E* and *E'* were calculated as the number of atoms of sulphur combined in the vulcanizate network per chemical crosslink before and after treatment with triphenyl phosphine⁹. The *E* value is interpreted as a measure of overall structural complexity of a sulphur vulcanized network, while *E'* is a direct measure of sulphur combined in the main chain modification such as cyclic sulphidic groups and pendant sulphidic groups.

Table 1 Composition of the mixes

Mix No.	1	1A	2	2A	3	3A	4	4A
Natural rubber	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	3	3	3	3	3	3	3	3
<i>N</i> -cyclohexyl-2-benzothiazyl sulphenamide (CBS)	0.6	0.6	0.6	0.6	—	—	—	—
Diphenyl guanidine (DPG)	0.1	0.1	—	—	0.2	0.2	—	—
Tetramethyl thiuram disulphide (TMTD)	—	—	0.1	0.1	—	—	—	—
Mercapto benzothiazole (MBT)	—	—	—	—	0.8	0.8	1.0	1.0
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Lignin	0	10	0	10	0	10	0	10

Notes to the Editor

Table 2 Distribution of different types of crosslinks in different accelerator systems in presence and in absence of lignin

Accelerator system	Lignin content (phr)	Total crosslink density $\times 10^5$ (g mol/g RH)	Polysulphidic crosslinks $\times 10^5$ (g mol/g RH)	Disulphidic crosslinks $\times 10^5$ (g mol/g RH)
CBS-DPG (Mix no. 1, 1A)	0	6.51	5.40	1.11
	10	3.06	2.08	0.98
CBS-TMTD (Mix no. 2, 2A)	0	6.27	4.97	1.30
	10	3.73	2.55	1.18
MBT-DPG (Mix no. 3, 3A)	0	6.90	5.58	1.32
	10	2.77	1.72	1.05
MBT (Mix no. 4, 4A)	0	3.38	2.14	1.24
	10	2.19	1.07	1.12

RESULTS AND DISCUSSION

Results of total chemical crosslink density, the relative proportion of disulphidic and polysulphidic crosslink are shown in Table 2. Monosulphidic crosslinks were found to be in negligible proportions in all mixes and were not included in the results. Table 3 shows the results of crosslinking efficiencies (E and E') and F values. The MBT system was found to have the least crosslink density. Addition of lignin caused significant reduction in the crosslink density in all systems and the reduction was minimum in the case of the MBT system. The ratio of polysulphidic crosslink to disulphidic crosslink is about 4:1 in all systems except in the MBT system where the ratio is 1.7:1. This indicates that the MBT system contributes least towards polysulphidic crosslinks in the total chemical crosslinks. The reduction of overall crosslink density

in the lignin-containing vulcanizate is mostly due to reduction of the proportions of polysulphidic crosslinks. It is apparent, therefore, that the MBT system shows better than expected compression set due to preponderance of disulphidic crosslinks which helps in preventing crosslink slippage under the conditions of compression set testing.

E , E' and F values were found to attain maximum in the MBT system. This indicates that vulcanizate of the MBT system has maximum structural complexity, inefficient utilization of sulphur in crosslink formation and main chain modifications. The low values of modulus, tensile strength, hardness and resilience in the MBT-accelerated vulcanizate³ is due to these factors. Addition of lignin caused an increase in these values in all accelerator systems indicating that lignin increases the structural complexity of the vulcanizate and causes less efficient utilization of sulphur and higher modifications of the

main chain, which inhibits strain-induced crystallization. The increased flex crack resistance is possibly due to stress relaxation caused by the lower state of crosslinking and the improved crack growth resistance is possibly due to higher percentage of disulphidic crosslinks in the lignin-filled vulcanizate. Several workers have reported earlier that fatigue life of networks consisting of a major proportion of mono- and disulphidic crosslinks and a highly modified main chain structure equals that of a network consisting of a high proportion of polysulphidic crosslinks (about 70%) and some degree of main chain modification ($E' = 7$) as encountered in the conventional sulphenamido-accelerated system¹⁶⁻¹⁸. It is interesting to note that lignin-filled vulcanizate has a network consisting of a major proportion of disulphidic crosslinks and extensively modified main chain structure.

Although addition of lignin caused a reduction of polysulphidic crosslinks, the disulphidic crosslinks remain almost unaffected. It is assumed that lignin masks portions of the vulcanization sites of the polymer chains² thereby increasing the ratio of curing agents to actually available crosslinking sites. With increasing proportions of curing agents (in lignin-filled vulcanizates), the ratio of polysulphidic to disulphidic crosslinks decreases and the structural complexity increases. Studebaker¹⁵ also reported that a decrease in the ratio of polysulphidic to disulphidic crosslinks occurred with increasing quantity of curing agents at a fixed sulphur to accelerator ratio. In the lignin-filled vulcanizate, we can assume that at the same sulphur to accelerator ratio the quantity of curing agents has

Table 3 Chemical characterization of vulcanizates with different accelerator systems in absence and in presence of lignin

Accelerator system	Lignin content (phr)	Network combined sulphur $\times 10^4$ (g atom/g RH)		Sulphur efficiencies (atoms/chemical crosslink)		Sulphide sulphur $[S^{2-}] \times 10^4$ (g ion/g RH)	F (Sulphide ions/chemical crosslink)
		$[S_C]$, before Ph_3P treatment	$[S'_C]$, after Ph_3P treatment	E , before Ph_3P treatment	E' , after Ph_3P treatment		
CBS-DPG	0	6.75	2.81	10.4	4.4	0.44	6.74
	10	7.63	3.47	25.0	11.4	0.66	21.56
CBS-TMTD	0	6.25	2.84	10.0	4.6	1.00	15.94
	10	7.69	4.34	20.6	11.6	0.69	18.48
MBT-DPG	0	6.63	3.44	9.6	5.0	0.50	7.24
	10	7.00	2.94	25.2	10.6	0.47	16.98
MBT	0	5.78	1.78	17.0	5.2	0.56	16.56
	10	7.44	2.72	34.0	12.4	0.78	35.60

effectively increased (in comparison to the vulcanizate without lignin) because portions of the crosslinking sites become non-available to the curing agents due to the masking effect of lignin.

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Evidence for a high molecular weight tail in the Dow S-102 polystyrene

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INTRODUCTION

Polystyrene (Dow S-102) is one of a series of polystyrenes prepared in benzene using n-butyllithium as the initiator¹. As a result, the members of this series should possess a near-monodisperse distribution of molecular weights. As a consequence of the near-monodisperse molecular weight distributions of these polymers, the Dow polystyrenes have long been used as 'standard' polystyrenes in a variety of physical measurements.

However, several recent papers^{2,3} have reported anomalous behaviour for several members of this polystyrene series. Penwell and Graessley² discussed the differences in the zero-shear melt viscosities between the S-109 polystyrene and other polystyrenes of comparable weight-average molecular weights. The S-109 material had the lower viscosity, by a factor of about 2, and this difference was maintained over a temperature range of 142° to 227°C. A recent examination⁴ of the S-109 by gel permeation chromatography (g.p.c.) revealed that the low melt viscosity values for this polystyrene cannot be accounted for by the presence of a low molecular weight tail in the molecular weight distribution. In addition, the S-102 polystyrene has been reported³ to exhibit an anomalously low (by 3° to 4°C) glass transition temperature when compared to a series of near-monodisperse polystyrenes from Pressure Chemicals Co.

Hence, it was thought to be of interest

to examine the S-102 polystyrene by g.p.c. in order to elucidate in greater detail some previously reported⁴ anomalies (an unusual *high* molecular weight tail) present in the molecular weight distribution of this polymer. Thus, fractions of the S-102 were examined in order to identify the nature of the high molecular weight components.

EXPERIMENTAL

The Waters Ana-Prep instrument was used with seven 4 ft Styragel columns. The porosity range of these columns was from 2×10^3 to 5×10^6 Å. The carrier solvent was tetrahydrofuran at 40°C. The detector was the Waters differential refractometer and solution concentrations of 1/4% (w/v) were used. The measurements were conducted at a flow rate of 1/3 ml/min. Full loop (2 ml) injections were made. The instrument was equipped with a 5 ml syphon. This syphon was covered and the syphon chamber saturated with solvent vapour in order to minimize solvent evaporation.

The calibration of this 7 column set was carried out using commercial polystyrene standards and polystyrenes synthesized and characterized in these laboratories. The column set had a plate count of 900 ppf at the 1/3 ml/min flow rate.

The S-102 polystyrene was fractionated at 30°C using methyl ethyl ketone and isopropanol. A total of 23

fractions were collected. The tacticity of the whole polymer and one of the high molecular weight fractions was examined by ¹³C n.m.r. Perdeuteriochloroform was the solvent used for the n.m.r. measurements.

RESULTS AND DISCUSSION

S-102 polystyrene has been characterized with regard to molecular weights by various groups^{1,5-10}. Ratios for \bar{M}_w/\bar{M}_n ranging from 1.05 to 1.11 were reported. These results seemingly indicate that the S-102 sample can be classified as having a narrowly dispersed molecular weight. However, an inspection of the fractionation data of Breitenbach and Streichsbier¹¹ reveals that their fraction 1 (out of a total of 7) had an intrinsic viscosity of 0.55 dl/g in toluene, a value which corresponds to a molecular weight of approximately 1.2×10^5 g/mol. The existence of some high molecular weight species

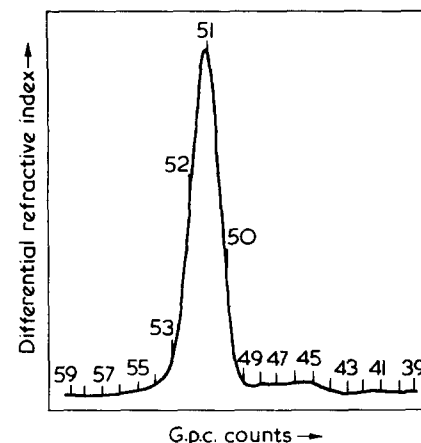


Figure 1 Chromatogram of the unfractionated Dow S-102 polystyrene. $\bar{M}_w = 8.1 \times 10^4$ g/mol; $\bar{M}_n = 7.4 \times 10^4$ g/mol