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Effect of Leaching on the Physical Characteristics of Cast NR Latex Films[†]

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Under ambient humidity conditions, leaching increases tensile strength and modulus of vulcanised natural rubber (NR) latex films. The increase in modulus of NR vulcanisates is generally analogous to an increase of the apparent physical crosslinks in the vulcanisates. However, in vulcanised NR latex films, changes in modulus brought about by leaching the films in water may not be due to the crosslink formation or rearrangement. These results are very unlikely to happen in the mild conditions adjusted for leaching the films. Some insights into the leaching mechanism in vulcanised NR latex films are discussed. Leached latex films generally gave higher tensile strength and modulus values than unleached films. Equilibrium swelling results showed that leached NR latex films inclined to swell more than their unleached counterpart. The discrepancy between the leached and the unleached is more apparent in swollen films with low sulphur content. The changes seen in the equilibrium swelling could be the result of changes in the polymer mobility of these films, whereby swelling was affected by the polymer mobility, upon removal of some of the non-rubbers of films. Nuclear Magnetic Resonance (NMR) and Differential Scanning Colorimeter (DSC) techniques were used to detect polymer mobility. When these techniques were applied to vulcanised NR latex films, the polymer mobility of leached samples were found relatively greater than that of the unleached samples. The equilibrium swelling, NMR and DSC results agreed with the theory of an increase of free volume in the latex films after the removal of leachable materials.

Key words: leaching, physical characteristics, cast NR, latex film, crosslinks, vulcanisate, polymer mobility

The mechanism of sulphur vulcanisation in NR latex is thought to be similar to dry rubber vulcanisation[1], however, the course in which the vulcanisation commences may be somewhat different. In the case of latex, chemicals are mixed into the latex emulsion, whereas in dry rubber these chemicals are milled into the rubber in dry state. The widely accepted theory on sulphur vulcanisation in latex has been summarised by Loh[2] and Porter[3]. During the latex stage, vulcanisation occurs within each rubber particles before the particles agglomerate to form the dry products. Non-rubber materials that are trapped within

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the particles may influence the properties of the final latex films. Leaching of the films may wash off some of these non-rubbers and may affect the properties of the films. Aqueous leaching of films deposited from vulcanised NR latex usually causes an increase in the modulus and tensile strength of films[3–5]. Leaching was shown to have an effect on the Mooney-Rivlin elastic constant (C_1) parameter of vulcanised NR latex films, but with essentially no change in the swelling behaviour of films[4]. The changes in modulus and C_1 values are normally associated with an increase in the degree of crosslinking, but it is very unlikely that the mild leaching conditions can enhance further crosslinks in the latex films. Based on the modulus and the swelling results, these observed changes are attributed to the improved degree of integration in the films, upon removal of leachable non-rubber materials[4]. The complications introduced by these non-rubbers confuse the interpretation of the leaching effect if based on the results of physical properties. Furthermore, hydrophilic non-rubbers in NR latex films can induce moisture uptake, affecting the physical properties of films[5].

The traditional method to estimate crosslink density in rubber, other than the stress-strain method *via* Mooney-Rivlin relationship, is to do a relatively simple technique of equilibrium swelling of the rubber in an organic solvent[6]. However, swelling may disintegrate latex films of low crosslinks because of the lack of strength in these low crosslinked structures to endure the swelling[2,7]. Thus, other techniques such as using Nuclear Magnetic Resonance (NMR) and Differential Scanning Colorimeter (DSC) can qualitatively estimate the course of crosslinking in rubber vulcanisates[8,9]. Increase in crosslinking is known to inhibit the movement of polymer either as a whole or as the polymer backbone. Changes in the mobility of polymer affect the two parameters in NMR *i.e.* spin lattice relaxation (T_1) and spin-spin relaxation (T_2). The width of the peaks resulted from any compound is partly affected by the T_2. The peak width at half-height is indirectly related to the H% which is defined as the ratio of the height of the chosen side of a peak and its height. The position of the side of the peak which is chosen gives the best sigmoidal shape. Loadman and Tinker[8] introduced the H% method to measure the T_2 effect by means different from the peak width at half-height and was found to give more meaningful results.

The flexibility of an amorphous polymer such as NR decreases drastically when the polymer is cooled below a characteristic transition temperature called the glass transition temperature (T_g). There is no segmental motion at temperatures below T_g. On the other hand, at T_g, motion due to segmental molecular chains increases. This causes the specific volume of the polymer to increase, affecting properties such as modulus, refractive index, dielectric properties, gas permeability, X-ray absorption and size of the accompanying change of the heat capacity (ΔC_p). Thus, changes in DSC parameters such T_g and ΔC_p should reflect molecular mobility of the polymer. ΔC_p is the difference in heat capacity before and after the glass transition temperature due to the increase in heat flow of the sample. This change in heat capacity occurring at the glass transition enables the measurement of T_g.

In this study, the effect of leaching on cast NR latex films prepared from zinc dibutyl dithiocarbamate (ZDBC) accelerated NR latex mixes, was deduced from the techniques mentioned above. It was noted that ZDBC was a very active accelerator under ambient conditions of 28°C to 30°C[7,10]. Thus, sulphur crosslinking was expected to occur immediately and throughout the drying stage of these cast films, and the amount of sulphur added into each compound governed the sulphur crosslink densities of the films.

EXPERIMENTAL

Materials

Commercial concentrated high ammoniated NR latex from the same batch of latex was used throughout the study. This was done to minimise variation between different latex batches. The vulcanising ingredients that were used to prepare the latex mixtures are of commercial-grades. Water insoluble ingredients were prepared by dispersing it in water with the aid of a dispersing aid (commercial grade).

METHODS

The formulation for the preparation of NR latex mixes are shown in *Table 1*.

A 30-min stirring time was observed after the addition of the chemical ingredients to the latex. A volume of latex that produced a film of 0.2 mm thickness was drawn from each latex mixture and poured onto a levelled glass mould of known dimension. The latex was left to cast under ambient condition (26°C ± 3°C) for at least two days. The dried cast films were peeled off the plate and each film was cut into two portions. One portion was leached in about 1 L distilled water for 24 h at room temperature. The leached latex films were then air dried at room temperature. The leached and unleached films were stored in the dark.

The tensile strength, modulus and elongation at break were determined according to *ISO 37:1998*. The relaxed modulus (MR100) values were determined at 100% extension[11]. For swelling measurements, test pieces of about 0.2 g each were cut from the cast samples. The test piece was weighed and then immersed in pure toluene (Analar grade) to swell to equilibrium at 40°C ± 3°C. After reaching equilibrium swelling, the test piece was removed and excess toluene on the test piece was blotted off with filter paper. The swollen test piece was placed in a weighing bottle and weighed, then placed under vacuum and de-swollen to constant weight. The swelling ratio is the difference between the swollen weight and the initial weight compared to the initial weight.

For NMR and DSC experiments, latex films were cut to several 0.5 cm x 5 cm pieces and acetone-extracted in the dark for 24 h. The samples were dried in the oven at 40°C ± 3°C until the weight stabilised.

TABLE 1. FORMULATION FOR NR LATEX VULCANISATION MIXES (PART PER HUNDRED RUBBER)

	1	2	3	4	5	6	7	8	9	10	11[b]
NR Latex	100	100	100	100	100	100	100	100	100	100	100
Sulphur	0.2	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.6	3.0
ZBDC[a]	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Zinc oxide	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2

[a] Zinc dibutyldithiocarbamate

[b] Test results for NMR, DSC and T_g plots only.

NMR spectroscopy was performed on a Bruker AMX400 WB NMR spectrometer (^1H, 400.1 MHz). The acquisition parameters were set at pulse angle of ~ 50°, pulse delay of 20 s. The samples were thinned from 0.5 cm to about 0.1 cm before being soaked in about 2 mL of deuteriated chloroform ($CDCl_3$) and stored in the dark for 24 h. The resultant swollen rubber was then transferred to NMR tube. The amount of $CDCl_3$ were topped up with fresh $CDCl_3$. H% is calculated as the percentage of the ratio of reference height (OR) divided by peak height (OP). The position for OR was chosen to give the best expected curve. While ^1H T_2 values are multivalued, reflecting the number of phases occurring in the polymer[9], a more general observation of utilising H% method is used[8].

DSC experiments were performed on a Mettler Toledo (DSC821e) instrument. The samples were weighed to about 5 mg – 10 mg in aluminium crucibles. A hole was made on the lid before sealing the crucible to prevent pressure built-up. The calibration of the instrument was done daily by carrying out the measurement of temperature and heat flow of single indium. The temperature of the analyses ranged between –100°C to 40°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The tensile strength and modulus values determined from the NR latex films are given in *Table 2.*

As expected under the experimental condition, the general observation of increased tensile and modulus values due to leaching was comfirmed. Nevertheless, the improvement of these properties is small in some of the films and could be attributed to experimental error.

TABLE 2. PHYSICAL PROPERTIES OF NR LATEX FILMS OF VARYING SULPHUR CONTENT

Sulphur content (p.p.h.r.)	Tensile strength (MPa)		Modulus at 300% (MPa)		Elongation at break (%)		Relaxed modulus MR 100 (MPa)	
	UL	L	UL	L	UL	L	UL	L
0.2	3.6	4.8	0.4	0.4	1030	1100	0.30	0.28
0.6	24.7	23.4	0.7	0.6	1150	1100	0.45	0.47
0.8	21.3	31.4	0.8	1.0	1000	1040	0.52	0.55
1.0	21.5	28.5	0.9	1.0	1000	900	0.54	0.64
1.2	20.9	30.7	0.9	1.5	1000	950	0.56	0.62
1.4	22.5	21.6	1.0	1.0	1100	950	0.65	0.51
1.6	24.5	26.5	1.0	1.1	1000	970	0.64	0.67
1.8	26.2	26.2	1.0	1.1	990	950	0.64	0.67
2.2	24.8	28.0	1.0	1.2	980	980	0.63	0.68
2.6	24.3	25.5	1.0	1.3	1000	940	0.63	0.69

UL = Unleached samples; L = leached samples; MR100 = an average value of 2 test pieces; TS, EB and M300 values are median values of five test pieces.

The plots of tensile strength and MR100 values against sulphur content are shown in *Figures 1* and *2*. The improvement in physical property due to leaching was more apparent in the modulus results (MR100) than in the tensile strength. The modulus of sulphur vulcanised NR is expected to increase with the increase in the degree of crosslinking[12]. In this study, the expected increase of sulphur crosslinks, reflected by the increase of the modulus values was observed in films with low sulphur level. As the sulphur level approached 1 p.p.h.r., the modulus values began to level-off (*Figure 2*). In other words, the modulus values of these cast films indicate that minimal crosslinking activities were taking place in the films formulated to contain sulphur dosage above the 1 p.p.h.r. level.

Without considering other crosslink characterising techniques, under the experimental conditions of the study, the action of leaching appeared to improve the tensile properties of NR latex films. One way to investigate whether the discrepancy could be related to the crosslinks was to perform equilibrium organic solvent swelling on the latex films. Work by Porter and Wong[13] on NR latex films shows that leaching does not essentially affect the swelling behaviour. However, in their study, the effect due to different levels of sulphur was not considered.

The equilibrium swelling results of cast NR latex films of varying sulphur content are shown in *Figure 3*. The results are in accordance with the modulus results, whereby the increase in

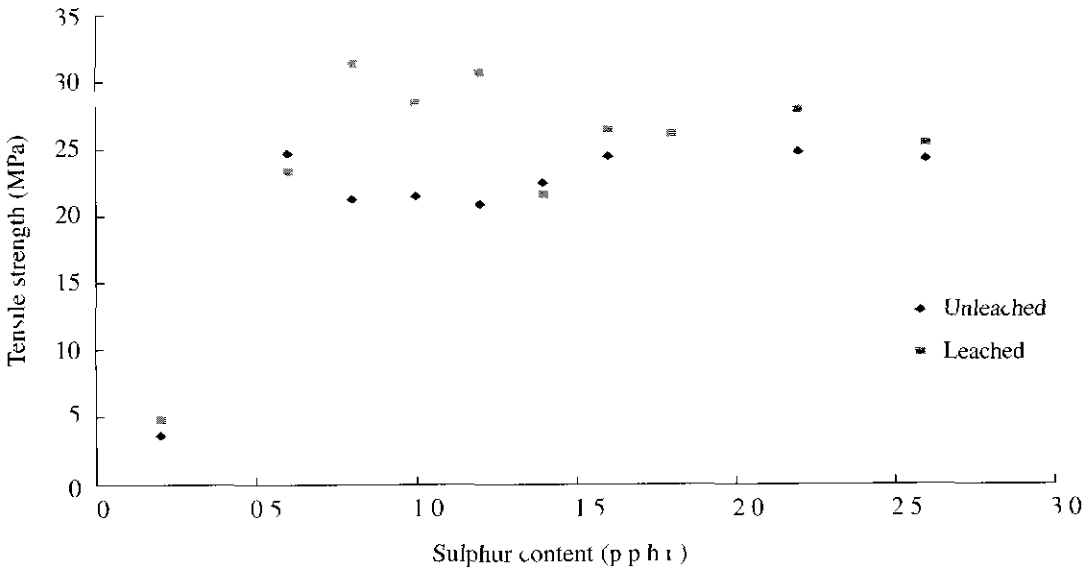

Figure 1. Tensile strength values for unleached and leached samples.

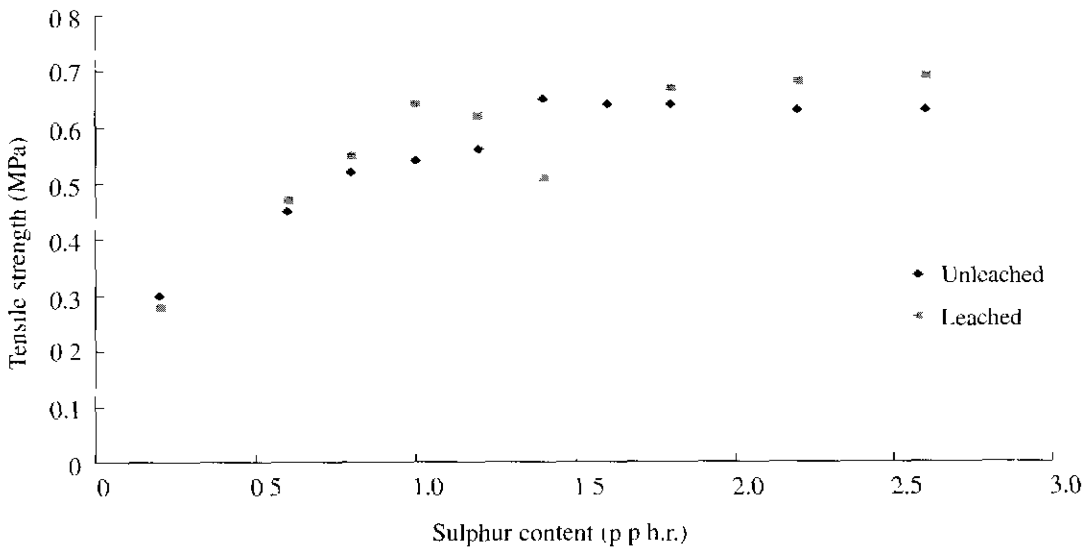

Figure 2 Relaxed modulus values (MR100) for unleached and leached samples.

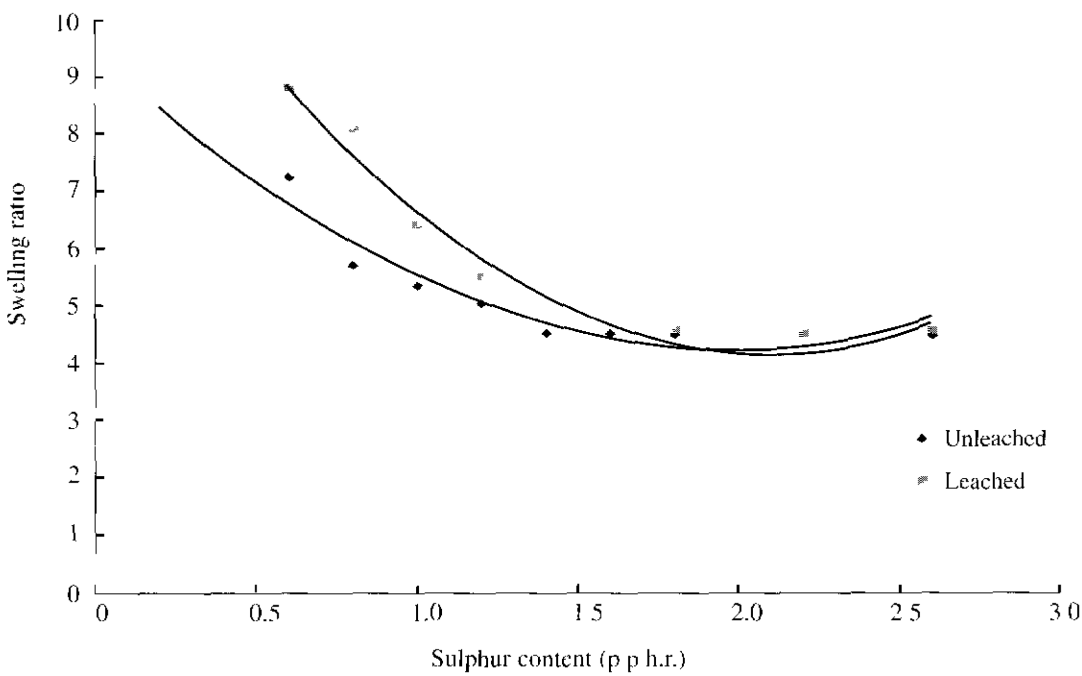

Figure 3. Equilibrium swelling in toluene of unleached and leached samples

crosslinking implied by the reduction in swelling was more evident in films with low sulphur levels. The increase in crosslinks appeared to minimise upon approaching 1 p.p.h.r. sulphur level.

The effect of leaching was more marked in the swelling behaviour of cast films with low sulphur level. The differences in the swelling ratio between leached and unleached films were quite large for low sulphur samples (*Figure 3*). The magnitude in which leaching induced the swelling behaviour of low sulphur samples could be related to the removal of materials that restricted swelling. At high sulphur content, the dense crosslinks formed in both leached and unleached latex films seemed to minimise the swelling variance between these films.

To further investigate these phenomena, NMR and DSC techniques were considered. Removal of leachable materials from the rubber might affect the mobility of the polymer structure and the changes in the polymer mobility if any could be detected by NMR and DSC techniques. The spin-spin relaxation in NMR is sensitive to the motion of polymer and DSC detects polymer mobility due to their behaviour at the heat capacity of the polymer at the glass transition point (T_g). The increase in H% in NMR results typically relates to the decrease of sample mobility. Expectedly, the increase of mobility due to polymer structure with increasing sulphur content was observed in the NMR results (*Figure 4*). Consistent with the swelling and modulus results, the optimised level was achieved after more than 1 p.p.h.r. of sulphur. It was interesting to note that although the samples were from the same NR latex films, unleached samples showed relatively higher H% plateau in the NMR plot (*Figure 4*) indicating restricted polymer mobility compared to that of the leached samples.

The DSC parameters that can provide a sensitive measure for polymer mobility are the T_g and ΔC_p. Increased crosslinking would restrict the freedom of movement in the

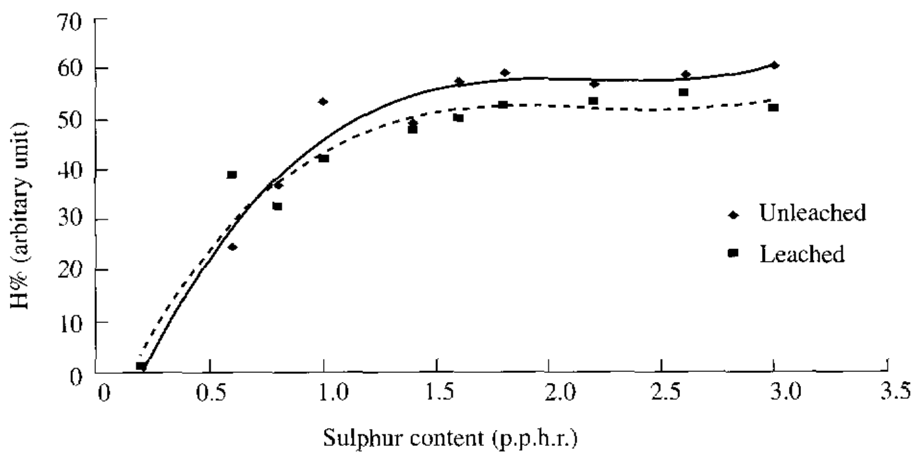

Figure 4. The NMR H% values for leached and unleached NR latex films of varying sulphur contents.

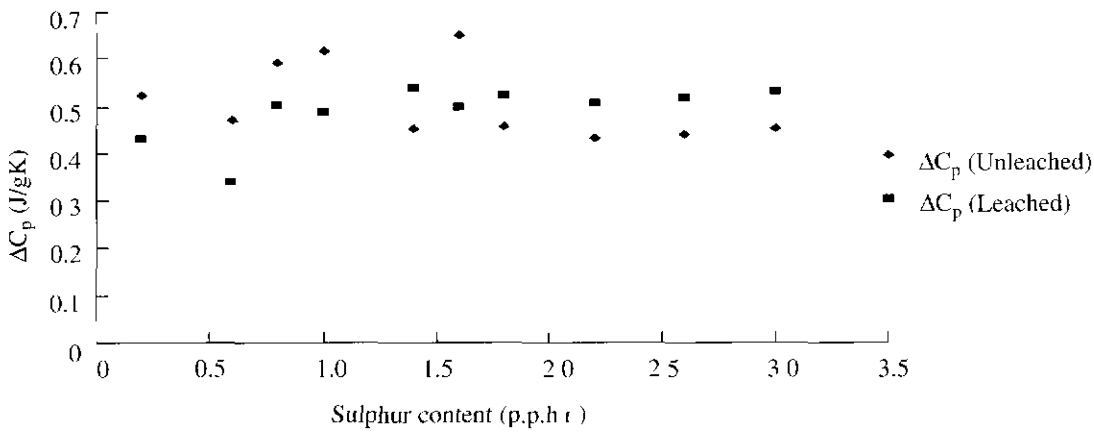

Figure 5. The ΔC_p values for leached and unleached NR latex films of varying sulphur contents

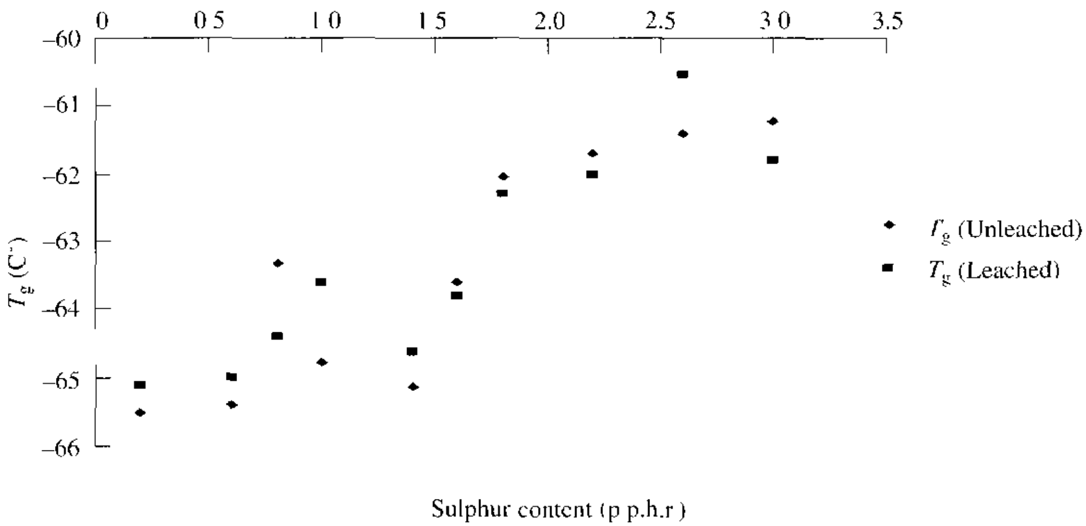

Figure 6. The T_g of values for leached and unleached NR latex films of varying sulphur content

polymer, resulting in a shift of T_g to a higher temperature and a decrease in ΔC_p

Differences in heat capacity results supported the NMR results as shown from 2 p p h r and above, whereby the unleached samples determined from ΔC_p were consistently lower than that of the leached samples (*Figure 5*) Due to the reduction in mobility and volume, the T_g of the samples increased with increasing sulphur content (*Figure 6*) However, its behaviour was sigmoidal and looked more like that of NMR

Shown in a consistent manner as NMR, ΔC_p and T_g the optimisation occurred around 2 p p h r of sulphur The difference between the unleached and leached was also observable in ΔC_p and T_g with minor anomaly of unleached samples of T_g which were higher at the higher plateau region There should not be any major difference in structure and morphology between leached and unleached films because they were prepared from the same latex mix The difference due to leaching seen in these results was attributed solely to the removal of mobility-hindered materials because room temperature leaching in distilled water was too mild a condition to bring about any structural changes in the polymer

CONCLUSIONS

Modulus, swelling and polymer mobility generally relates to the crosslink characteristics of vulcanised NR film The results from all of the techniques used in the study appeared to indicate that crosslinking activities seemed to be slowing when more than 1 p p h r sulphur was used at room temperature ZDBC accelerated sulphur vulcanised NR latex films The effects due to leaching could be deduced from the results of swelling, NMR and DSC techniques The swelling results, especially of the low-sulphur content films showed relatively clear differences in swelling characteristics after the films had been leached Leaching could have created more 'free volume by removing the hindering materials within the latex films hence increasing the mobility of the polymer structure

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