

Effect of Acetone Extraction on Elastic Constants and Mechanical Strengths

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Vulcanised unfilled natural rubbers containing different quantities of oil were prepared. The amount of oil was varied from 5, 10, 25, 35 and 40 p.p.h.r. The oil was later extracted by means of hot-acetone extraction. Simple extension tests were conducted to determine the elastic constants C_1 and C_2 before and after acetone extraction. The elastic constant C_1 decreased with increasing amounts of oil due to the dilution effect. After the oil had been fully extracted, the elastic constant C_1 also decreased in the order of increasing oil initially present in the rubber. Statistical theory of rubber elasticity was referred to explain the phenomenon. It was found that the T_g of the rubber was not affected very much by aromatic oil but was affected significantly by paraffinic oil. The T_g decreased with increasing amounts of paraffinic oil present in the rubber. After acetone extraction, the T_g s of the vulcanisates were the same. Tensile strength of unfilled NR did not show much difference before and after acetone extraction. In contrast, tearing energy of vulcanised black-filled NR was significantly affected by oil extraction. This work has important practical issues since the loss of oil through slow evaporation may affect the stiffness of the rubber component. In rubber engineering applications, consistency in stiffness is very important in service performance.

Keywords: elastic constants C_1 and C_2 ; acetone extraction; glass-transition temperature, T_g ; tensile strength; tearing energy

Process oil is one of the processing additives commonly used to facilitate the mixing process, especially when high filler loading is involved. When the oil is incorporated into the rubber, it softens the rubber through its swelling action. When the rubber is soft, it facilitates the incorporation of compounding ingredients, thus shortening the overall mixing time. Consequently, output rate increases and saves production cost. Besides that, process oil also reduces viscosity of the rubber compound and thus improves flow that is very important

in the shaping processes such as extrusion, calendaring and moulding. Process oil also provides internal lubrication to reduce heat generation during the mixing and fabrication processes. Apart from its application in processing, oil can also be used to modify hardness and low temperature flexibility of vulcanised rubber. Oils reduce hardness or increase low temperature flexibility through their plasticising effect by creating spaces or free volume due to their rapid molecular mobility. Oils or any low molecular weight

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liquids compatible with rubber are known as plasticisers. A plasticiser reduces the glass-transition (T_g) of the polymer, while process oil may not necessarily reduce T_g of the polymer.

The amount of oil used to facilitate mixing typically varies from 5 to 10 parts per hundred of rubber (p.p.h.r.). However, there are cases where high amounts of oil (20 – 30 p.p.h.r.) is desired, for instance in the design of high damping rubber for vibration isolations, earthquake protection and also in the production of oil extended rubber. This unvulcanised rubber is in fact diluted with the oil. A supercoiled network is formed when unvulcanised rubber diluted with oil or solvent is crosslinked in the diluted state and the diluent is then removed by extraction (or by evaporation)^{1,2}. As the rubber chains are unconstrained when being crosslinked, it is assumed that the chains are then in their random configuration. When the diluent (solvent) is removed the crosslinks move towards each other, and so the end-to-end distance between the chain ends (at crosslinks) is less than it would be for the rubber crosslinked to the same extent in the dry state in the usual way³. According to the statistical theory, as the free energy of a single chain varies as the square of the end-to-end distance, the modulus will vary similarly as the initial end-to-end distance³. This distance is assumed to be proportional

to the linear swelling ratio, so the change in modulus can be calculated for the degree of dilution³.

In practice, oils present in the rubber components may be lost by slow evaporation if exposed at elevated temperatures. Equally true, the oil may be lost if immersed in a liquid or solvent that can extract the oil. A rubber seal that is in contact with the oil may encounter this problem. This paper discusses preliminary work to investigate the effect of acetone extraction on the elastic constant C_1 and dynamic modulus of unfilled vulcanised natural rubber (NR) since the work is both of fundamental and practical interest. Apart from gum (unfilled) vulcanisate, this paper also discusses the effect of acetone extraction on tearing energy of black-filled NR vulcanisates.

EXPERIMENTAL

Formulations

Tables 1 and 2 show the compounding formulations for unfilled NR compounds containing aromatic and paraffinic oils respectively. These formulations differ only in the quantity of oil, otherwise all compounding ingredients are the same. The quantity of oil

TABLE 1. FORMULATIONS AND CURE TIME FOR UNFILLED COMPOUND CONTAINING AROMATIC OIL

Mix No.	1	2	3	4	5	6
SMR CV 60	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Santoflex 13	3	3	3	3	3	3
Aromatic oil	-	5	10	25	35	40
CBS	0.75	0.75	0.75	0.75	0.75	0.75
Sulphur	1.50	1.50	1.50	1.50	1.50	1.50
t_{95} at 150°C (min)	13.0	13.5	13.8	13.5	13.5	14.0

was varied from 0 to 40 parts per hundred of rubber (p.p.h.r.) in order to get a wide range of modulus. Two types of oil used were aromatic and paraffinic oil which differ in terms of its aromatic content and viscosity. The difference in aromatic content and viscosity of the oil affects the extent of plasticisation in the vulcanised rubber. The viscosity gravity constant (VGC) can be used to classify the types of petroleum oil⁴. Oils with VGC value around 0.8 are classified as paraffinic, and those having VGC values above 1.0 are classified as aromatic oils.

Table 3 shows the formulations for black-filled NR compound containing aromatic

oil for the work to investigate the effect of acetone extraction on the tearing energy of the vulcanisate.

Mixing

Rubber mixing was carried out in a laboratory Banbury mixer (1600 cm³) with the following mixing conditions and mixing sequence:

Starting mixing temperature 50°C
Rotor speed 80 r.p.m.

Cooling water was turned on during mixing.

TABLE 2. FORMULATIONS AND CURE TIME FOR UNFILLED COMPOUND CONTAINING PARAFFINIC OIL

Mix No.	7	8	9	10	11
SMR CV 60	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Santoflex 13	3	3	3	3	3
Paraffinic oil	5	10	25	35	40
CBS	0.75	0.75	0.75	0.75	0.75
Sulphur	1.50	1.50	1.50	1.50	1.50
t ₉₅ at 150°C (min)	14	14	14	14	14

TABLE 3. FORMULATIONS AND CURE TIME FOR BLACK-FILLED COMPOUND

Mix No.	12	13	14	15
SMR CV 60	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Santoflex 13	3	3	3	3
Aromatic oil	-	5	25	35
CBS	0.75	0.75	0.75	0.75
Sulphur	1.50	1.50	1.50	1.50
HAF (N330)	50	50	50	50
t ₉₅ at 150°C (min)	9.8	10.5	11.5	12.8

Sequence of mixing

- 0 min - add rubber
 1 min - Add all chemicals and*
 (add ½ black)
 2 min - Add oil and*
 (add remaining black)
 4 min - sweep
 5 min - discharge

* only for black-filled compound.

The mix was discharged on a 2-roll mill where curatives were added immediately. Cutting and folding were done for about 3 min to ensure proper dispersions and distribution of curatives during mixing. The finalised mix was then sheeted out to about 3 mm thick, cooled and stored for 24 h before moulding.

Moulding of Test-pieces

Thin vulcanised rubber sheets of uniform thickness were moulded by means of compression moulding in an electrically heated press at 150°C. They were all cured to their optimum cure time (t_{95}). In the case of unfilled compounds, the quantity of oil did not appear to affect the cure time very much, except for black-filled compounds where t_{95} varied from about 10 to 13 minutes.

Acetone Extraction

All the test-pieces were immersed in boiling acetone (b.p. 56°C) using a hot Soxhlet acetone apparatus for 48 hours. After 48 h, the test-pieces were dried under vacuum at room temperature until their dried weight was constant. The dried acetone extracted test-pieces were again immersed in a hot acetone for a further 24 h to ensure complete extraction

of oil or any soluble material remaining in the test-piece. It was found that the dried weight of the test-pieces after the second acetone extraction was the same as that after 48 h of acetone extraction. Thus, this indicates that the oil and other acetone soluble materials were extracted from the test-pieces within 48 h of acetone extraction.

Determination of C_1

The C_1 test-pieces in the form of parallel strips having dimensions of 100 mm long and 3 mm wide were prepared from vulcanised sheets of uniform thickness (about 2 mm). Simple extension test was done using Greensmith's apparatus. By means of a rack arrangement, the rubber strip was extended through a series of predetermined extensions. The load required to balance the force of extension was then measured. Test was conducted at 23°C. The cross-sectional area, A_0 , measured in the unstrained state was calculated from density, weight and length of the test-piece. The Mooney-Rivlin plot (Load/ ($\lambda - 1/\lambda^2$)) was plotted against λ^{-1} , where λ is the extension ratio.

The straight line portion of the plot was extrapolated to cut the y-axis. The value of the intercept was used to calculate C_1 and the slope of the straight line gives C_2 which is a measure of chain entanglements. Thus, C_1 was calculated using Equation 1.

$$C_1 = (\text{Intercept} \times 9.81 \text{ ms}^{-2} \times 298K) / 2 A_0 (273 + 23^\circ\text{C}) \quad \dots 1$$

The temperature was standardised to 25°C to account for the small changes in thermal expansion. The load in gram (g) was converted to kilogram (kg) and multiplied with the acceleration due to gravity to convert to force, F in Newton (N).

Tensile Test

Tensile test was done in accordance with the *ISO 37* where a dumbbell shaped test-piece (75mm long with a central neck 25 mm long and 3.6 mm wide) was pulled at a constant rate (500 mm per min) by a tensile machine until broken. The tensile stress at every 100% elongation, elongation at break and tensile strength (force to break / unstrained cross-sectional area) were recorded. Test temperature was 23°C.

Tear Test

Tear tests were conducted at various speeds by separating the legs of the trouser test-piece at a uniform rate by using an Instron tensile machine. The temperature of the test was at 23°C unless stated otherwise. The tearing energy^{2,5} was computed using *Equation 2*.

$$T = F(\lambda + 1)/h \quad \dots 2$$

where T is the tearing energy, F is the force to propagate tearing, h is the average nominal thickness and λ is the average extension ratio in the legs of the test-piece. The relation is valid provided λ is not much greater than unity and the stress-strain curve is approximately linear. However, in practice, the equation still holds even if $\lambda > 2$, and the error⁵ introduced is less than 4%.

Determination of Glass-transition Temperature

A differential scanning calorimeter (DSC) was used to determine the glass-transition temperature. The sample was heated from -100°C to 0°C at 20°C per min. Calibration was done by using cyclohexane. In addition,

standard raw NR T_g s were measured before and after the sample series. The sample T_g s were then corrected.

RESULTS AND DISCUSSION

Mooney-Rivlin Plot and Determination of Elastic Constants

Figure 1 shows a Mooney-Rivlin plot of unfilled NR containing different quantities of aromatic oil. The Mooney-Rivlin equation^{3,7} for a simple extension is given by *Equation 3*.

$$F = 2A_o (\lambda - 1/\lambda^2) [C_1 + C_2\lambda^{-1}] \quad \dots 3$$

where F is the force to extend the strip of rubber in simple extension, A_o is the cross-sectional area measured in the unstrained state, C_1 is the elastic constant given by *Equation 4* below⁷.

$$C_1 = \rho RT[X]_{phys} \quad \dots 4$$

where ρ is density of rubber, R is the molar gas constant, T is the test temperature in Kelvin and $[X]_{phys}$ is the physically manifested crosslink concentration. C_2 is a measure of chain entanglements which can be determined from the slope of the straight line portion of the plot. The plot in *Figure 1* gives a straight line for all the unfilled vulcanisates. The elastic constant C_1 for each vulcanisate will be discussed in the next section. *Figure 2* shows the Mooney-Rivlin plot after the aromatic oil in the unfilled vulcanisate was extracted by acetone extraction. It is interesting to observe that the plot follows the same pattern as shown in *Figure 1* although the oil has been extracted. The elastic constants C_1 with different subscript abbreviations are shown in *Tables 3* and *4* for unfilled NR vulcanisates before and after acetone extraction respectively. All those terminologies and the method of calculations were based on reference 1.

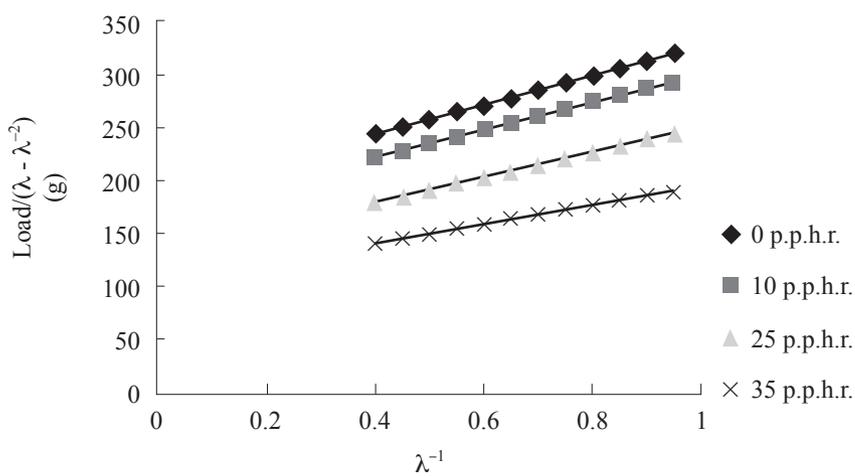


Figure 1. $Load/(\lambda - \lambda^{-2})$ vs λ^{-1} of NR gum vulcanisate containing aromatic oil before acetone extraction.

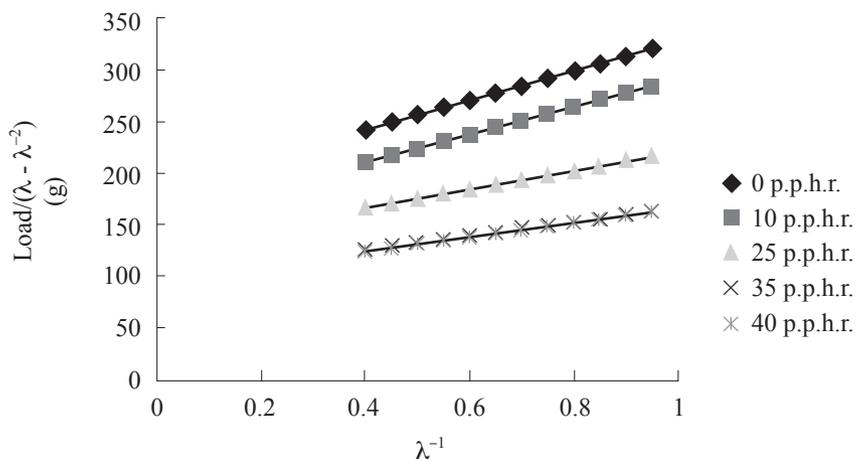


Figure 2. $Load/(\lambda - \lambda^{-2})$ vs λ^{-1} of NR gum vulcanisate containing aromatic oil after acetone extraction.

The elastic constant $C_{1,RH}$ decreases almost linearly with increasing amounts of aromatic oil as shown in *Figure 3*. The decrease is due to dilution effect associated with the oil. The expected $C_{1,RH}$ due to dilution effect can be estimated by multiplying the observed $C_{1,RH}$ with dilution factor as shown in the footnote of *Table 3*. However, the expected $C_{1,RH}$ value is higher than the observed value. The difference ranges from about 2% to 10%.

$$V_r = V_R / (V_R + V_o) \quad \dots 5$$

where V_R is the volume of rubber and V_o is the volume of oil.

#Correction for the stiffening effect of filler¹,

$$C_{1,RM} = C_{1,RV} (1 + 2.5v_f + 14.1v_f^2)^{-1} \quad \dots 6$$

** Correction on a simple volume basis for the presence of soluble extra network materials of network combined atoms introduced during crosslinking¹.

$$C_{1,RH} = C_{1,RM} (1 - v_f) / V_{RH} \quad \dots 7$$

where $V_{RH} = W_{RH} \rho_{RV} / (\rho_{RH} W_{RV})$. The symbols V , W and ρ refer to volume, weight and density

respectively¹. The subscripts RH, RM and RV refer to rubber hydrocarbon, rubber matrix and rubber vulcanisate as prepared respectively¹. The total volume fraction of fillers in the rubber vulcanisate $v_f = W_f \rho_{RV} / W_{RV} \rho_f$. According to Bristow and Porter¹, the term “filler” may include also any extra-network material present in the vulcanisate as solid particles. For gum sulphur NR vulcanisates, it generally comprises free elemental sulphur in excess of the equilibrium solubility concentration of about 1 wt % at room temperature, zinc oxide, zinc sulphide, *etc.*

The expected elastic constant $C_{1,RH, expected}$ is given by *Equation 8* below¹.

$$C_{1,RH, expected} = \text{Dilution factor} \times C_{1,undiluted} \quad \dots 8$$

($C_{1,undiluted} = 153$ kPa of mix 1 since there is no oil in the formulation).

The constant $C_{2,RV}$ which indicates the extent of chain entanglements also decreases with increasing amount of oil as shown in *Table 3*, indicating that the effect of dilution reduces the tendency of the chain molecules to get entangled.

TABLE 4. C_1 AND C_2 OF NR GUM VULCANISATE CONTAINING AROMATIC OIL BEFORE ACETONE EXTRACTION

Mix No.	1	2	3	4	5	6
Aromatic oil	-	5	10	25	35	40
v_f	0.0078	0.0075	0.0072	0.0063	0.0060	0.0058
*Dilution factor	1	0.95	0.92	0.81	0.76	0.73
V_{RH}	0.9167	0.8787	0.8437	0.7538	0.7037	0.6811
$C_{1,RV}$ (kPa)	144	122	120	92	78	70
$C_{2,RV}$ (kPa)	114	92	97	62	49	49
# $C_{1,RM}$ (kPa)	141	120	118	90	77	69
** $C_{1,RH,dil}$ (kPa)	153	136	139	119	109	101
*** $C_{1,RH,expected}$ (kPa)	153	145	141	124	116	112
$C_{1,RH} / C_{1,expected}$	1	0.94	0.98	0.96	0.94	0.90

*Dilution factor is actually the volume fraction V_r of the oil in the vulcanisate. The usual calculation of V_r is given by *Equation 5*.

TABLE 5. C_1 AND C_2 OF NR GUM VULCANISATE CONTAINING AROMATIC OIL AFTER ACETONE EXTRACTION

Mix No.	1	2	3	4	5	6
Aromatic oil	0	5	10	25	35	40
$C_{2,ERV}$ (kPa)	115	108	107	93	80	81
$C_{1,ERH,extracted}$ (kPa)	163	160	162	139	137	134
$C_{1,RH,dil} / C_{1,RH,extracted}$	0.9386	0.8500	0.8580	0.8561	0.7956	0.7537

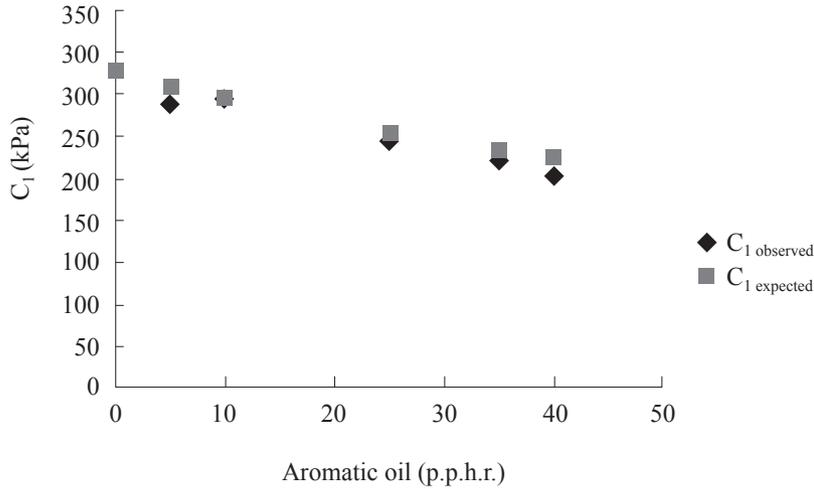


Figure 3. Comparison between observed $C_{1,RH}$ and expected $C_{1,RH}$ of NR gum vulcanisate containing aromatic oil.

Effect of Acetone Extraction on Elastic Constant, $C_{1,RH}$ of Unfilled Vulcanisate Containing Aromatic Oil

It is interesting to observe that the $C_{1,RH}$ value after the oil has been removed from the vulcanisate by acetone extraction decreases almost linearly with the amount of oil initially present in the vulcanisate. This phenomenon can be explained with reference to statistical theory of rubber elasticity. According to the statistical theory of rubber elasticity^{3,6,7}, the mean square distance between chain ends (denoted as \bar{r}^2) for a single chain is given by

$$\bar{r}^2 = 3/2 \beta^2 \quad \dots 9$$

$$\beta^2 = 3/2nl^2 \quad \dots 10$$

where n is the number of freely jointed links, each of length l . The free energy w of a single chain varies as the square of the end-to-end distance r as shown by Equation 11.

$$w = -kT \ln P = kT \beta^2 r^2 = 3kTr^2/2nl^2 \quad \dots 11$$

k is Boltzmann's constant and P is a Gaussian probability function. The total change in strain energy, W is given by the mathematical relationship below:

$$W = 1/3 NkT\beta^2 \bar{r}^2 (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \quad \dots 12$$

$$W = C_1(I_1 - 3) + C_2(I_2 - 3) \quad \dots 13$$

where I_1 and I_2 are strain invariants⁷. The mean square end-to-end distance \bar{r}^2 in the undeformed state is likely to be the same as that of free chains ($3/2 \beta^2$), because crosslinks are likely to form at points where the molecular strands are randomly arranged when crosslinking is done on an unoriented polymer melt³. However, serious departures from this condition would be for a network that is prestrained, for example, by swelling with a compatible liquid after crosslinking^{3,9}. In cases like this, \bar{r}^2 would be significantly different from $3/2 \beta^2$. Since the modulus will vary similarly as the initial end-to-end distance, this distance is assumed to be proportional to the linear swelling ratio, so that the change in modulus can be calculated for the degree of dilution. *Table 4* shows that $C_{1,ERH}$ (elastic constant after acetone extraction) is not the same for all the six vulcanisates even after the oil has been extracted. This is because W is a function of $\beta^2 \bar{r}^2$ in accord with *Equation 12* above. Since \bar{r}^2 after oil extraction is significantly different from $3/2 \beta^2$ of the vulcanisate without any oil initially, thus $C_{1,ERH}$ will not be the same since W is dependent on $\beta^2 \bar{r}^2$. The results show that $C_{1,ERH}$ decreases in the ratio of $C_{1,RH,dil} / C_{1,RH,extracted}$ in accord with the dilution factor.

Effect of Acetone Extraction on Elastic Constant, $C_{1,RH}$ of Unfilled Vulcanisate Containing Paraffinic Oil

Apart from differences in aromatic content and viscosity, aromatic oil and paraffinic oil also differ in their solubility parameter. The solubility parameter of elastomers and liquids determines the extent of compatibility and swelling resistance. Indeed, the greater the thermodynamic compatibility between liquid and elastomer, the greater the absorption of liquid occurring when both have similar solubility parameters. The solubility parameter

δ is related to a parameter to measure the specific interaction between molecules known as cohesive energy density (CED) by the following mathematical relationship^{11,12}.

$$\delta = (CED)^{1/2} \quad \dots 14$$

$$CED = (\Delta H - RT)/M/\rho \quad \dots 15$$

where ΔH is the latent heat of vapourisation, T is the absolute temperature, M is the molecular weight of the polymer, ρ is the density of the polymer and R is the molar gas constant. For example, natural rubber has a solubility parameter value¹² of 16.7 MPa^{1/2}. Most of the petroleum oils have a solubility parameter¹² of 16.3 MPa^{1/2}. The extent of aromatic oil-rubber interaction is lower than that of paraffinic oil as a consequence of the former being aromatic in nature. Aromatic oil has a solubility parameter of 17.5-19.2 MPa^{1/2} and paraffinic oil has a solubility parameter of 1.4-17.5 MPa^{1/2}. It is of interest to see whether the differences in the solubility parameter would affect the elasticity and other physical properties.

The elastic constants of unfilled NR vulcanisate containing different concentrations of paraffinic oil before and after acetone extraction are shown in *Tables 6* and *7* respectively.

Figure 5 shows the effects of paraffinic oil concentration on the elastic constant $C_{1,RH}$ before and after acetone extraction. The results show a similar trend as that of aromatic oil, where $C_{1,RH}$ decreased progressively as the paraffinic oil concentration was increased. Before acetone extraction, the decrease in $C_{1,RH}$ was attributed to dilution effect. After acetone extraction, the decrease in $C_{1,RH}$ is associated with the value of \bar{r}^2 after oil extraction^{3,6,7,9} that is significantly different from $3/2 \beta^2$ of vulcanisate without any oil as explained in the section above.

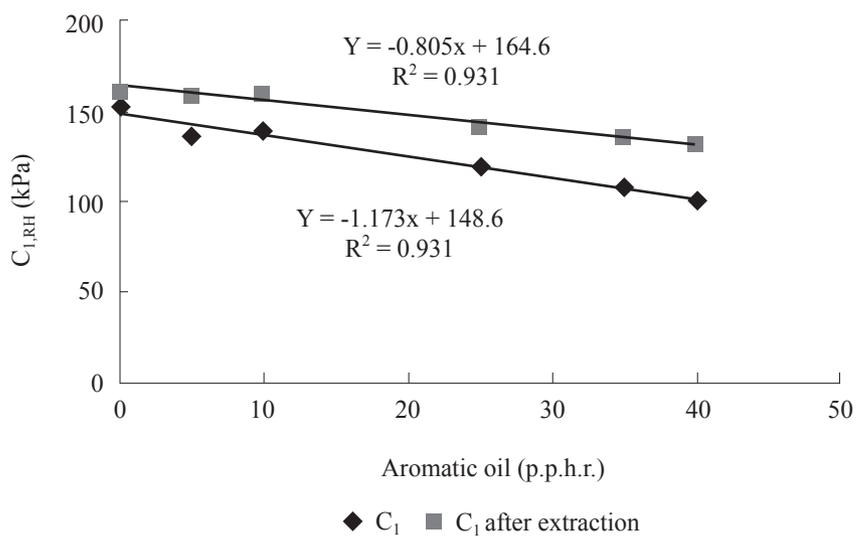


Figure 4. Comparison of $C_{1,RH}$ of NR gum vulcanisate containing aromatic oil before and after acetone extraction.

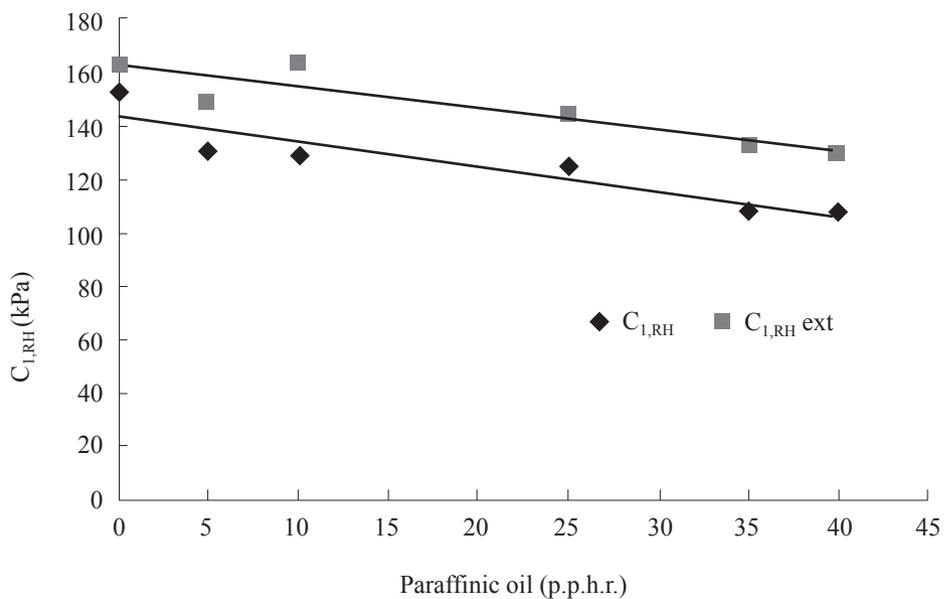


Figure 5. Effect of concentration of paraffinic oil on elastic constant $C_{1,RH}$ (before acetone extraction) and $C_{1,RH}$ ext (after acetone extraction).

TABLE 6. EFFECT OF CONCENTRATION OF PARAFFINIC OIL ON ELASTIC CONSTANT C_1 OF UNFILLED NR VULCANISATE BEFORE ACETONE EXTRACTION

Mix No.	7	8	9	10	11
Paraffinic oil	5	10	25	35	40
v_f	0.0075	0.0072	0.0063	0.0060	0.0058
$C_{1,RV}$ (kPa)	118	108	96.4	77.7	75.4
$\#C_{1,RM}$ (kPa)	116	109.7	95.0	76.5	74.3
$**C_{1,RH,dil}$ (kPa)	131	129	125	108	108

TABLE 7. EFFECT OF ACETONE EXTRACTION ON ELASTIC CONSTANT C_1 OF UNFILLED NR VULCANISATE CONTAINING DIFFERENT CONCENTRATION OF PARAFFINIC OIL

Mix No.	7	8	9	10	11
Paraffinic oil	5	10	25	35	40
v_f	0.0075	0.0072	0.0063	0.0060	0.0058
$C_{1,RV}$ (kPa)	140	150	123	108	103
$\#C_{1,RM}$ (kPa)	137	147	120	106	101
$**C_{1,RH,dil}$ (kPa)	149	164	145	133	130

The effects of types of oil on the elastic constant $C_{1,RH}$ before and after acetone extraction are shown in *Figures 6* and *7* respectively. Generally aromatic oil gave marginally higher $C_{1,RH}$ (by about 2% - 4%) than that given by paraffinic oil. The reasons are not entirely clear, but might be attributed to the solubility parameter and viscosity of the oil. Paraffinic oil has lower viscosity than aromatic oil, and its solubility parameter is closer to the solubility parameter of NR compared to the solubility parameter of aromatic oil to that of NR. Consequently, paraffinic oil is more compatible with NR than aromatic oil is with NR. Thus, paraffinic oil has a higher plasticising effect than aromatic oil. This plasticising effect might be responsible for the lower $C_{1,RH}$ in paraffinic oil than that produced by aromatic oil.

The elastic constants for the case of filled vulcanisates are not discussed here since the author has already published the work elsewhere².

Glass-transition Temperature Before and After Acetone Extraction

Glass-transition temperature affects mechanical strengths and physical properties, for this reason the effect of acetone extraction on T_g was investigated. The results are tabulated in *Tables 8* and *9* for swollen (containing oil) and solvent extracted (deswollen) samples respectively. In *Table 8*, the T_g of unfilled NR containing aromatic oil was apparently not affected by its varying quantities. This result indicates that aromatic oil is not a plasticiser but more of a softener. In contrast, paraffinic oil reduced the T_g of the rubber as the quantity of the oil was increased. Thus, paraffinic oil can be considered as a plasticiser as suggested and discussed earlier. As seen in *Table 9*, it is interesting to note that after extraction the T_g of all vulcanisates initially containing different types of oil is similar indicating that all the oil initially present were fully extracted. This is reflected in *Figure 7* where the elastic constants before acetone extraction ($C_{1,RH}$) and

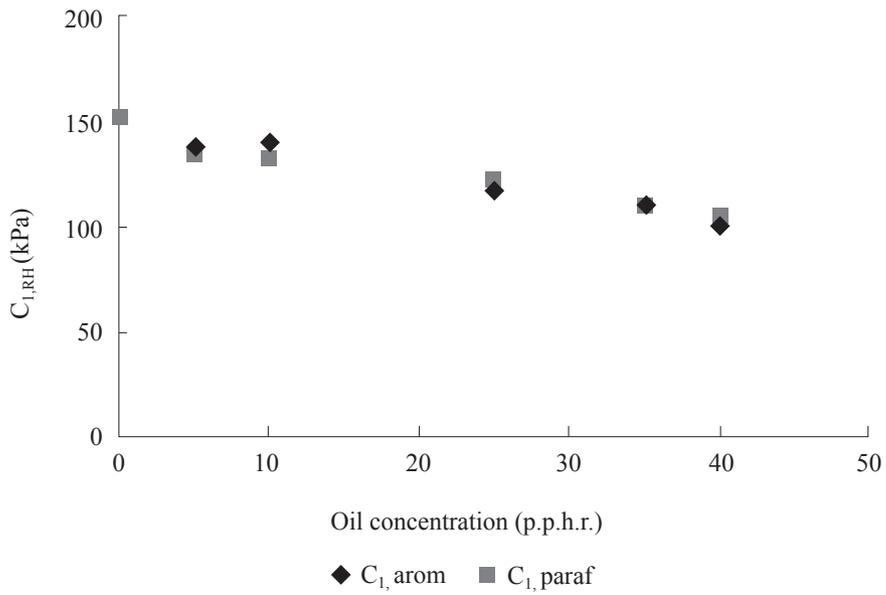


Figure 6. Effects of types of oil on the elastic constant $C_{1,RH}$ before acetone extraction (arom = aromatic oil ; paraf = paraffinic oil).

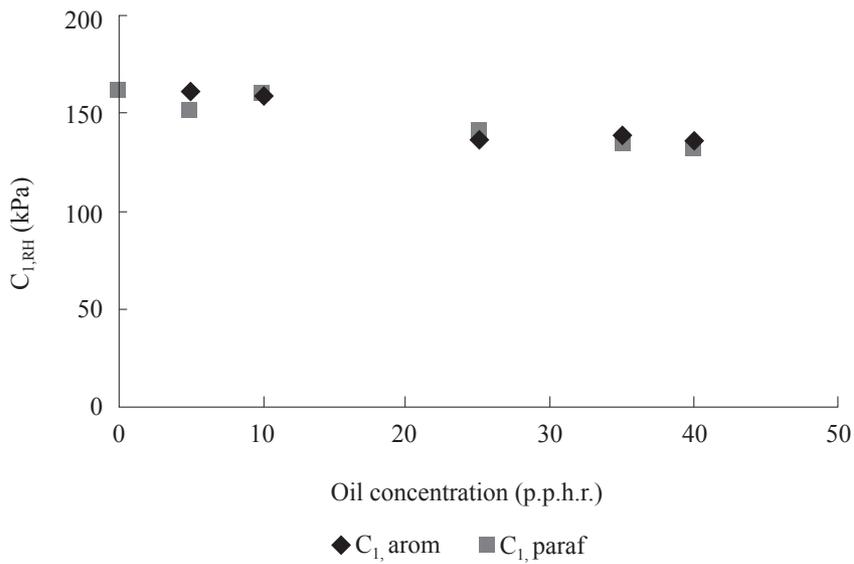


Figure 7. Effects of types of oil on the elastic constant $C_{1,RH}$ after acetone extraction (arom = aromatic oil ; paraf = paraffinic oil).

TABLE 8. EFFECTS OF OIL CONCENTRATION ON THE GLASS TRANSITION TEMPERATURE OF UNFILLED NR VULCANISATE

Oil (p.p.h.r.)	0	5	10	25	35	40
T _g °C (Aromatic)	-69.3	-68.9	-69.3	-69.3	-69.1	-69.6
T _g °C (Paraffinic)	-69.3	-71.3	-72.3	-77.3	-78.0	-78.6

TABLE 9. EFFECTS OF OIL CONCENTRATION GLASS TRANSITION TEMPERATURE OF EXTRACTED UNFILLED NR VULCANISATE

Oil (p.p.h.r.)	0	5	10	25	35	40
T _g °C (Aromatic)	-69.5	-69.7	-69.2	-69.0	-69.0	-69.4
T _g °C (Paraffinic)	-69.5	-69.0	-69.7	-69.7	-70.4	-69.7

after acetone extraction ($C_{I,RH,ext}$) appear to overlap each other since their T_g s were similar.

Tensile Properties of Unfilled NR Vulcanisate

Figure 8 above shows a plot of modulus (strictly speaking tensile stress at 100% elongation) for unfilled vulcanised NR containing paraffinic oil before and after acetone extraction. The results follow the same trend as that shown in *Figure 4* discussed earlier. The same explanation is applicable here.

Figure 9 shows tensile strength of unfilled NR vulcanisate treated with aromatic oil before and after acetone extraction. The tensile strength was not much different before and after extraction since the T_g values were more or less the same. As pointed out earlier, T_g affects mechanical strength and it is well established that polymers with high T_g value enhances mechanical strength because of the high energy dissipation¹⁰. The difference seen in *Figure 9* is associated with the scale of the plot. Generally, tensile strength decreases with increasing oil level initially present in the rubber.

Figure 10 shows the tensile strength of unfilled NR containing paraffinic oil before and after acetone extraction. There is not much difference between the tensile strength before and after acetone extraction in spite of the significant difference in T_g before and after acetone extraction.

Tearing Energy of Black-filled NR Vulcanisate

The effect of oil on tearing energy before and after acetone extraction is more pronounced than that of tensile strength of unfilled vulcanisates as shown in *Figure 11*. Extracted samples gave higher tearing energy than swollen samples. The results here are consistent with work reported earlier².

Tearing energy of swollen and extracted black-filled NR vulcanisates containing paraffinic oil is shown in *Figure 12* below. The results follow the same trend as that shown in *Figure 11* where tearing energy of extracted samples are higher than swollen samples since the former dissipates higher energy than the latter.

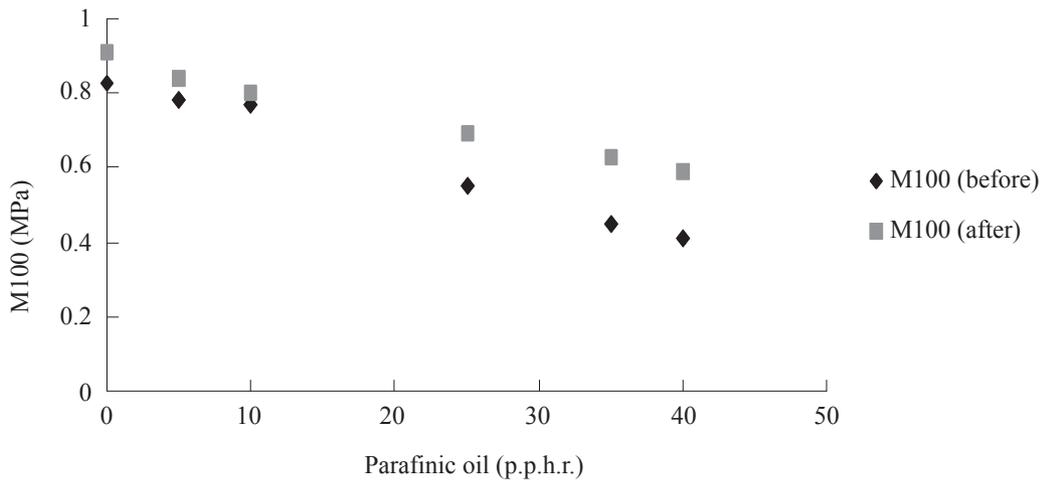


Figure 8. Comparison of M100 of NR gum vulcanisate containing paraffinic oil before and after oil extraction.

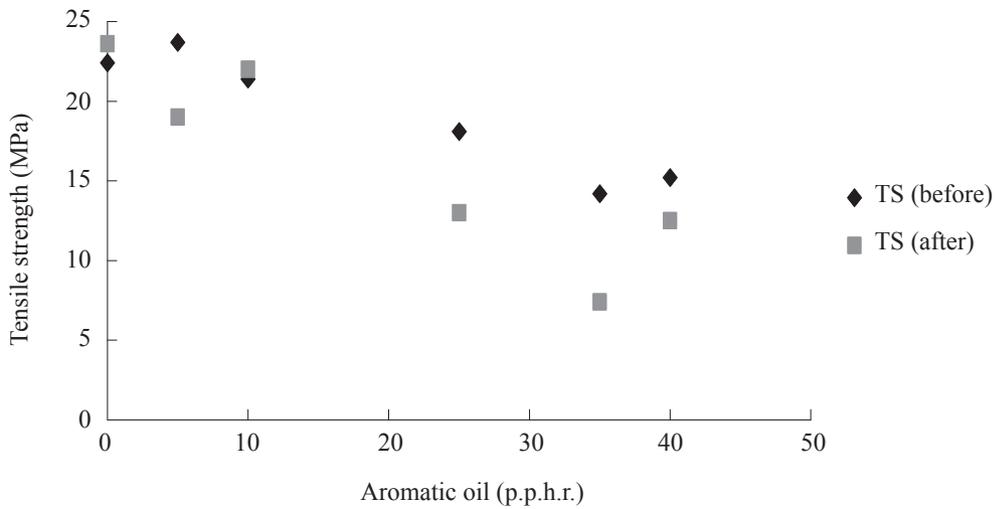


Figure 9. Effects of aromatic oil on tensile strength of unfilled NR before and after acetone extraction.

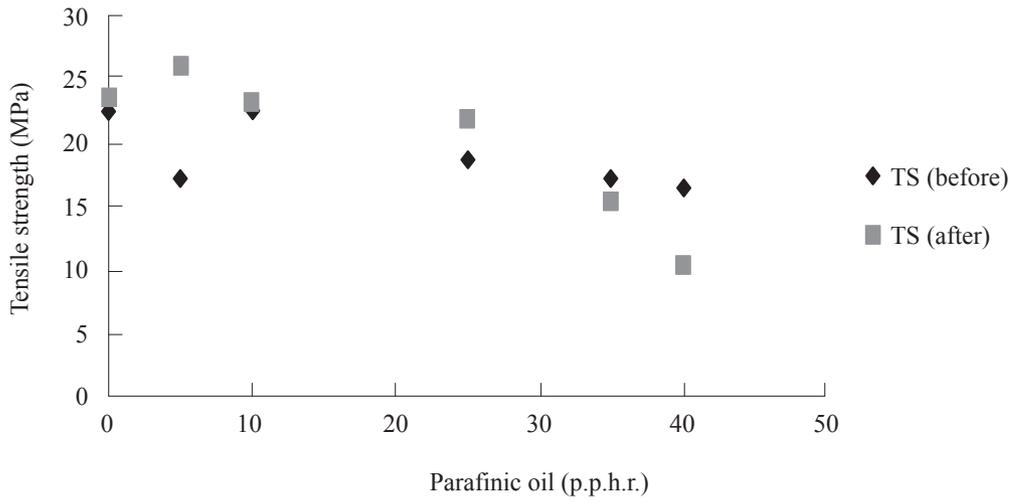


Figure 10. Effects of paraffinic oil on tensile strength of unfilled NR before and after acetone extraction.

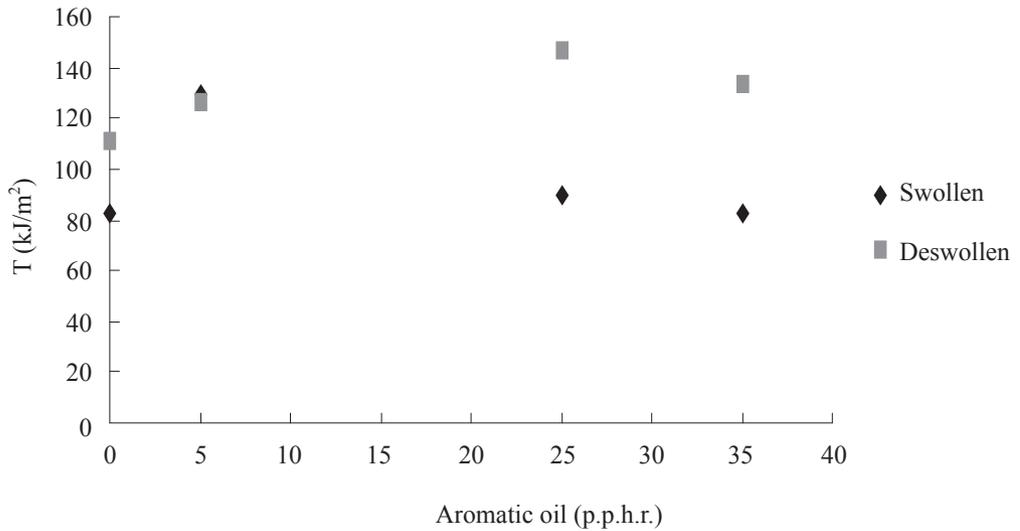


Figure 11. Tearing energy vs aromatic oil loading. Effect of concentration of aromatic oil on tearing energy of black-filled NR before and after acetone extraction.

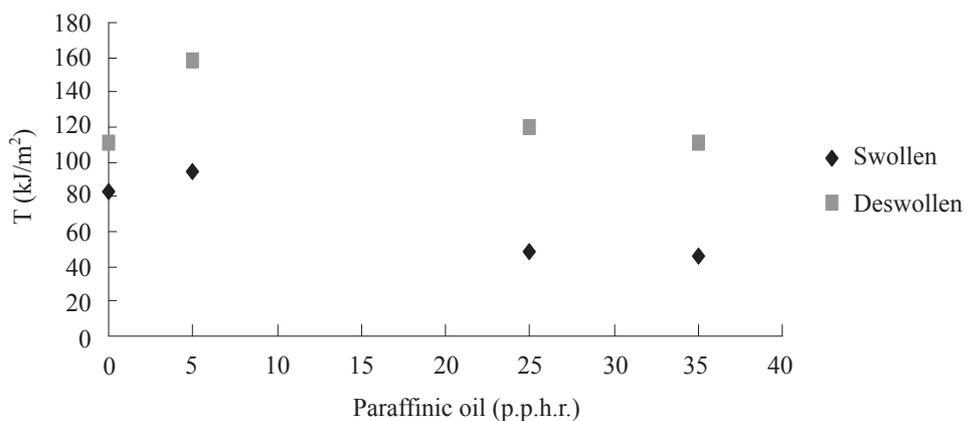


Figure 12. Tearing energy vs paraffinic oil loading. Effect of concentration of paraffinic oil on tearing energy of black-filled NR before and after acetone extraction.

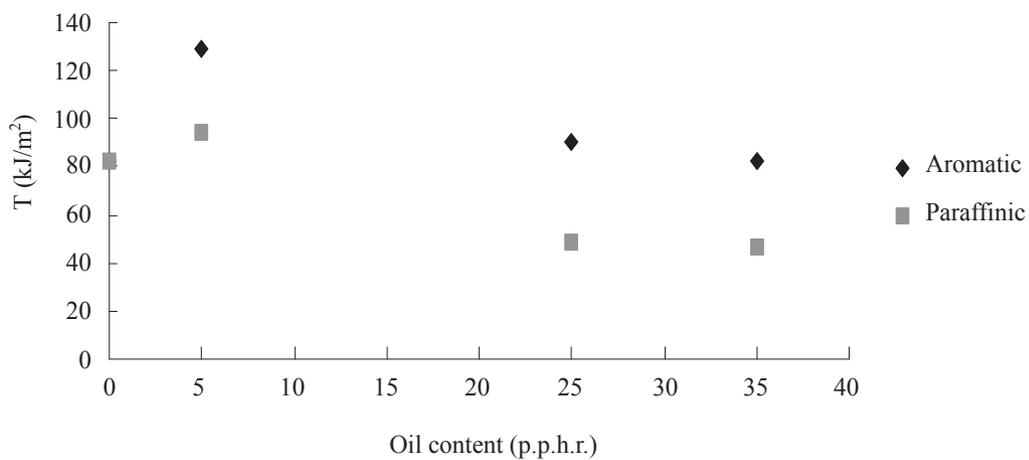


Figure 13. Comparison between aromatic and paraffinic oil – swollen samples of black-filled NR vulcanisates.

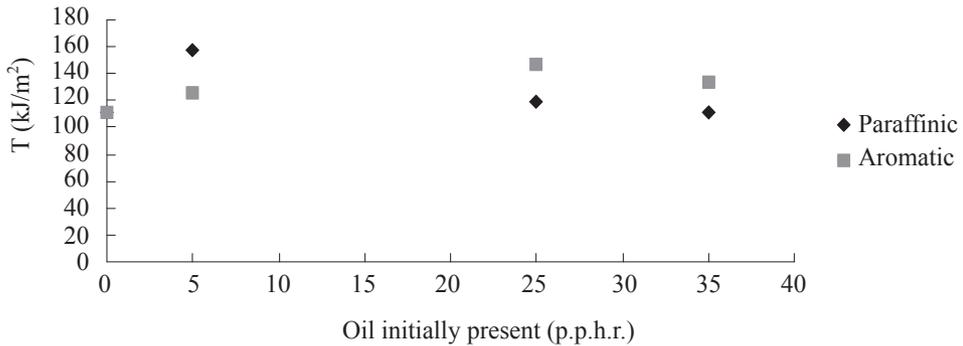


Figure 14. Comparison between aromatic and paraffinic oil – extracted samples of black-filled NR vulcanisates.

Samples swollen in aromatic oil gave higher tearing energy than those swollen paraffinic oil as shown in *Figure 13*. This might be attributed to viscosity of the oil. Aromatic oil has higher viscosity than paraffinic oil. This is also reflected in the T_g results where vulcanisates swollen in aromatic oil gave higher T_g than vulcanisates swollen in paraffinic oil. Thus, paraffinic oil has a higher plasticising effect than aromatic oil. One would also expect vulcanisates swollen in aromatic oil to give higher tearing energy than paraffinic oil because the former would dissipate higher energy than the latter (since the former had a higher T_g than the latter).

It is interesting to see that extracted aromatic oil samples showed higher tearing energy than those of extracted paraffinic oil although the T_g s of these extracted samples were very much similar as shown in *Table 9* above. The reasons for this are not entirely clear at this moment. All samples produced knotty tearing with high tearing energy.

CONCLUSIONS

The elastic constant $C_{1,RH}$ decreases with increasing quantity of oil present in the

vulcanised rubber associated with the dilution effect. The trend is still the same even after the oil initially present in the rubber is totally extracted. In this case, the decrease in $C_{1,RH}$ is associated with the value of \bar{r}^2 after oil extraction that is significantly different from $3/2 \beta^2$ of vulcanisate without any oil initially. $C_{1,ERH}$ decreases in the ratio of $C_{1,RH,dil} / C_{1,RH,extracted}$ in accord with the dilution factor.

This finding has an important practical implication in situations where rubber products have high quantity of oil for high damping applications such as in seismic bearings. If the oil in the vulcanisate is loss either due to an elevated temperature, leaching due to long exposure to water *etc*; the stiffness will change and perhaps the damping properties as well. Thus, this matter needs further investigation.

ACKNOWLEDGEMENTS

Most of the work published here was conducted at the Tun Abdul Razak Research Centre, Hertford, United Kingdom when the author was on a short attachment. The author would like to express his thanks to Dr. C.S.L.

Baker, who was then the Director of Research for permission to use the laboratories facilities to conduct C_1 measurements using the Greensmith's machine, and Mr. C. Hull to conduct DSC measurement on the samples. The author also would like to express his sincere thanks to Prof. A.G. Thomas for some useful discussions.

Date of receipt: April 2011

Date of acceptance: October 2011

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