



## Crack Growth and Wear Properties of Silica-reinforced Styrene-butadiene Rubber Compounds: Effect of Processing Oil Type

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### 실리카충전 스티렌-부타디엔 고무컴파운드의 균열성장 및 마모특성: 공정오일 종류의 영향

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**ABSTRACT** : Commercial grades of solution styrene-butadiene rubbers extended with high aromatic oils having high polycyclic aromatic compounds (PCA) and low PCA oils were used to study the effect of the processing oil particularly on the crack propagation resistance and frictional wear resistance of the vulcanizates. The aromatic oil based vulcanizates exhibited superior fracture behavior over the low PCA oil extended vulcanizates based on tensile and trouser tear tests. Compounds with aromatic oil showed superior crack propagation resistance compared with those containing low PCA oil, especially at the lower ranges of tearing energy. In terms of frictional wear resistance, the aromatic oil extended compounds showed superior performance particularly in the lower frictional work ( $W_f$ ) range but in the higher  $W_f$  range the low PCA oil extended vulcanizates performed better.

**요약** : 용액중합 스티렌-부타디엔 고무 컴파운드 가교체의 균열저항성 및 마모특성에 미치는 공정오일의 영향을 조사하기 위해 방향족 고리화합물(PCA) 성분을 다량 함유하고 있는 방향족 오일과 저 PCA 오일을 선택하였다. 인장강도 및 인열강도 결과에 의하면 방향족 오일함유 컴파운드가 저 PCA 오일함유 컴파운드에 비해 우수한 물성을 나타내었다. 또한 방향족 오일함유 컴파운드가 균열저항성이 월등히 우수하였고, 특히 인열에너지가 낮은 범위에서 더 우수한 결과를 나타내었다. 마모저항특성은 마찰에너지가 낮은 범위에서는 방향족 오일함유 컴파운드가 우수한 결과를 나타낸 반면, 높은 마찰에너지 범위에서는 저 PCA 오일 함유 컴파운드가 오히려 높은 저항성을 나타내었다.

**Keywords** : high aromatic oil, polycyclic aromatic compounds (PCA), fatigue crack propagation, frictional wear

## I. Introduction

Environmental problems like global warming are a cause of concern for everyone. One of the primary reasons of global warming is the rapid industrialization leading to greater greenhouse gas emissions. The burning of fossil fuels is significantly responsible for increased carbon dioxide concentrations, a major greenhouse gas. Most governments and organizations are complying with the Kyoto Protocol to reduce greenhouse gas emission. The tire and rubber industries are also proactive in this regard through research and development to substitute car-

bon black (manufactured primarily by the partial combustion of oils and thus causing global warming) partly and / or substantially with silica. Systematic research by Rhone Poulenc<sup>1</sup> and Michelin<sup>2</sup> paved the way for the introduction of highly dispersible precipitated silica in conjunction with silane coupling agents in elastomers. The introduction of silica as a reinforcing agent along with the carbon black in tires improved the rolling resistance of the tires but the tire tread wear increased significantly by the partial replacement of carbon black with silica.<sup>3</sup> However, modification of the silica surface by a silane coupling agent decreased tread wear significantly while allowing the rolling resistance improvement.<sup>4</sup>

The shift towards "green" (in other words environment-

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friendly) material and technologies are also observed in other areas of the tire industry like the usage of safer process oils as mandated by the European Union (EU) environmental regulations which require tire manufacturers to eliminate polycyclic aromatic compounds (PAHs) from all tires sold in Europe by January 1<sup>st</sup>, 2010.<sup>5</sup> Process and extender oils are extensively used in various tire components like tread, sub-tread and shoulder. Till now, high aromatic oils, also known as distillate aromatic extracts (DAE), have been traditionally used as extender oils for such applications. However, the report by the Swedish Chemicals Agency (KemI) in 1994 showing the presence of a high content of polycyclic aromatic compounds (PCA) in high aromatic oils was of great environmental concern since the polycyclic aromatics were not chemically bound into the elastomer matrix and was responsible for the release of PAHs as a result of tire wear.<sup>6,7</sup> Several of these PAHs are known to be carcinogenic, mutagenic and teratogenic and this is why the EU is seeking to reduce the release of these compounds into the environment.<sup>8</sup> Even though, the legislation applies to the EU, the impact is expected to be global and so the tire industry was forced to look out for suitable alternatives for the high aromatic process oils and these substitute oils, usually naphthenic, treated distillate aromatic extract (TDAE) and medium extracted solvate (MES), have low PCA content. Null compared the properties of emulsion styrene-butadiene rubber (E-SBR) extended with high aromatic oil and low PCA oils in a typical tire tread formulation and concluded that although only minor differences existed in terms of the vulcanizate properties, extensive compounding and evaluation was still needed by the tire manufacturers to optimize their proprietary formulations with the low PCA oils.<sup>9</sup>

Nowadays, solution-polymerized styrene-butadiene rubber (S-SBR) are used extensively for high-performance tires such as "green" tires, anti-skid tires and super light-weight tires due to their superior performance characteristics with respect to low rolling resistance, high grip and durability. In this paper, we have used S-SBRs extended with high aromatic oils and low PCA oils and compared the vulcanizate properties especially in terms of fatigue fracture and wear resistance. The suitability of replacement of the aromatic oil extended vulcanizates with the low PCA oil vulcanizates is also discussed.

## II. Experimental

### 1. Materials

Two grades of high aromatic oil extended S-SBR, viz., T 3335 (Asahi, Japan) and SOL 6450S (Kumho Petrochemical, Korea) and two grades of low PCA oil extended S-SBR, viz., VSL 5025-2 HM (Lanxess, Germany) and SOL 6270SL (Kumho Petrochemical, Korea) were used as the oil extended

polymers in this study. Polybutadiene rubber (BR01, Kumho Petrochemical, Korea) was blended with these oil extended rubbers. The other compounding ingredients used are as follows: N330 type carbon black, highly dispersible silica of Zeosil 115GR from Rhodia, silane coupling agent of bis-(3-triethoxysilylpropyl) tetrasulfane (Si-69) from Degussa, Germany, wax, *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (IPPD, Kumanox 3C from Kumho Petrochemical Co., Korea. Sulfur from Dongyang Chemical Co., Korea, cure accelerator of *N*-cyclohexylbenzothiazyl sulfonamide (CBS) from Shandong Co., China. The diphenylguanidine (DPG), zinc oxide (ZnO) and stearic acid (StA) were supplied from domestic chemical companies.

### 2. Compound mixing and preparation of samples

The compound formulations in phr (parts by weight per hundred parts of rubber) are given in Table 1 along with the sample designations. S-SBR and BR were blended in a Banbury mixer for 30 s at a chamber temperature of 130 °C. The silica and silane coupling agent were then compounded into the rubber mix for 30 s. Next the carbon black and other ingredients except the curatives were mixed for 300 s and the mix was dumped onto a two-roll mill below 100 °C where the curatives were added and incorporated into the mix to get the final batch. The final batch was then sheeted out from the two-roll mill.

**Table 1. Compound Formulations**

Ingredient	(unit: phr)			
	Aro1	Aro2	Low1	Low2
BR	30.0	30.0	30.0	30.0
T 3335	70.0	-	-	-
SOL 6450S	-	70.0	-	-
VSL5025-2 HM	-	-	70.0	-
SOL 6270SL	-	-	-	70.0
N330	40.0	40.0	40.0	40.0
Silica	40.0	40.0	40.0	40.0
Si-69	2.6	2.6	2.6	2.6
ZnO	3.0	3.0	3.0	3.0
StA	2.0	2.0	2.0	2.0
IPPD	3.0	3.0	3.0	3.0
Wax	2.0	2.0	2.0	2.0
CBS	2.0	2.0	2.0	2.0
DPG	0.6	0.6	0.6	0.6
S	1.7	1.7	1.7	1.7

### 3. Physical properties

Cure characteristics were obtained using oscillating disc rheometer (ODR 2000, Alpha Technologies, USA) at 150 °C. Vulcanizates were prepared by compression molding at 150 °C for ~ 10 min. The cured sheets thus obtained were kept at room temperature for 24 h maturation before testing.

The tensile properties of dumbbell specimens were measured using a universal tensile tester (LRX Plus, Lloyd Instruments, UK). All tests were performed in accordance with ASTM D 412 at room temperature using a crosshead speed of 500 mm/min.

Trouser tear specimens 95 mm long, 35 mm wide, ~ 0.85 mm thick and having a precut of 20 mm at the center were used for measurement of the tear energy (fracture energy or strain energy release rate) of the vulcanizates. The specimens were tested at a speed of 50 mm/min. Reinforcing cotton cloth 10 mm wide was placed along each leg of the test specimens and thus the unreinforced width was 15 mm. For trouser test geometry, the tear energy is given by the relation:<sup>10,11</sup>

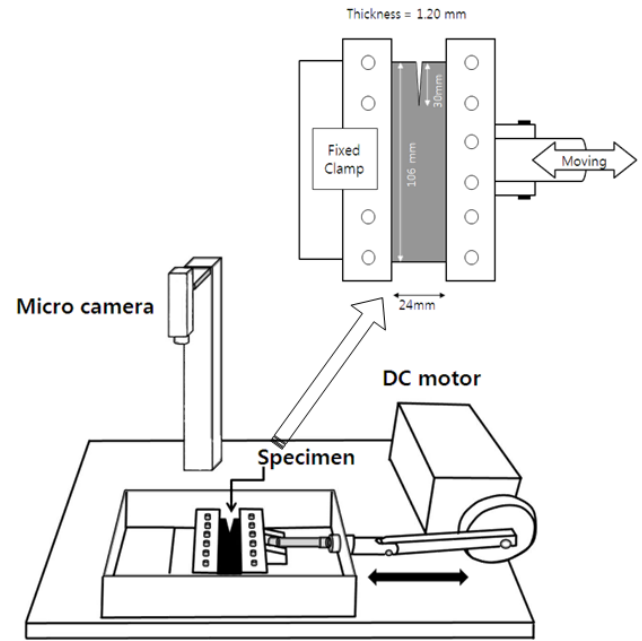
$$G_T = \frac{2F\lambda}{t} - wU \quad (1)$$

where  $F$  is the force applied to the ends of the test piece,  $\lambda$  is the extension ratio,  $t$  is the specimen thickness,  $w$  is the total width of the test piece and  $U$  is the strain energy density in the legs of the test specimen. If  $w \gg t$ , then  $\lambda$  approaches unity and  $U$  is essentially zero, so the " $wU$ " term in Equation (1) becomes negligible and thus Equation (1) reduces to

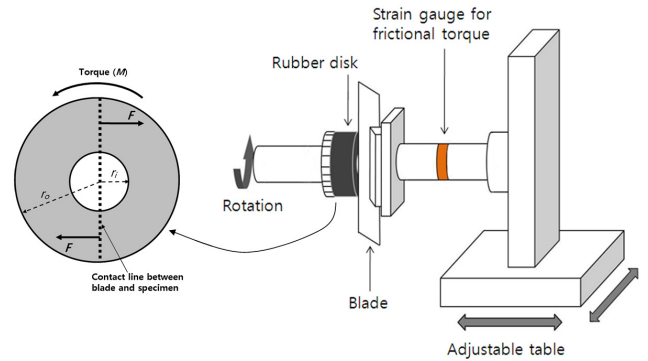
$$G_T = \frac{2F}{t} \quad (2)$$

The glass transition temperature ( $T_g$ ),  $\tan \delta$  at 0 °C and at 70 °C for the four types of vulcanizates were measured using a dynamic mechanical property tester (EPLEXOR<sup>®</sup> 150 N, GABO QUALIMETER Testanlagen GmbH, Germany).

The fatigue crack propagation behaviors of the vulcanizates were studied using a dynamic fatigue tester as shown in Figure 1. The dynamic fatigue strain was varied from 0.15 to 0.70 and was applied at a speed of 1.1 Hz. A pure shear test geometry (shown in Figure 1) was selected to determine the rate of crack propagation and was effectively clamped to prevent the strip from decreasing in width during testing.<sup>12</sup> The pure shear specimen had the dimensions 24 mm (height,  $h_0$ ) x 106 mm (width) x ~ 1.2 mm (thickness,  $t$ ). An initial precut of length 30 mm was made at one end of the specimen and the tip was sharpened using a sharp razor blade. The length of the crack propagated,  $c$ , was observed by a camera attached



**Figure 1.** A sketch of the dynamic fatigue tester along with a specimen dimension.



**Figure 2.** A schematic diagram of a blade-type wear apparatus.

to the fatigue tester. The rate of crack propagation ( $dc/dn$ ) was obtained from the slope of the graph between the crack length ( $c$ ) and the number of cycles ( $n$ ) at each strain level. Most rubbery materials obey a power law dependency between the crack growth rate and the tearing energy ( $G$ ) on the assumption that the crack growth is mainly due to the mechanical factor as follows:

$$\frac{dc}{dn} = AG^\alpha \quad (3)$$

where  $A$  and  $\alpha$  are constants. For the pure shear geometry, the tearing energy is obtained from the relation:<sup>10</sup>

$$G = Uh_0 \quad (4)$$

where  $U$  is the strain energy density per unit volume at the instant of tearing and  $h_0$  is the unstrained height of the test piece.  $U$  was obtained from the area under the retraction stress strain graph using the same shear test geometry as the dynamic fatigue experiment but without any precut.

The wear tester used for measuring the rate of wear and frictional energy was based on a knife wear tester designed by us and described elsewhere.<sup>13,14</sup> Figure 2 gives the schematic of the wear tester along with wear specimen. The specimen has a hole in the center to prevent the stress concentrating and also to aid in the dissipation of heat due to frictional work. The rate of wear ( $W_R$ ) in g/rev is related to the weight loss ( $T$ ) by friction (measured in g) and the number of revolutions ( $n_R$ ) by the following formula:

$$W_R = \frac{T}{n_R} \quad (5)$$

The frictional work,  $W_f$  ( $\text{Jm}^{-2}$ ) is related to the frictional torque,  $M$  (Nm) by the relation:

$$W_f = \frac{M}{(r_o^2 - r_i^2)} \quad (6)$$

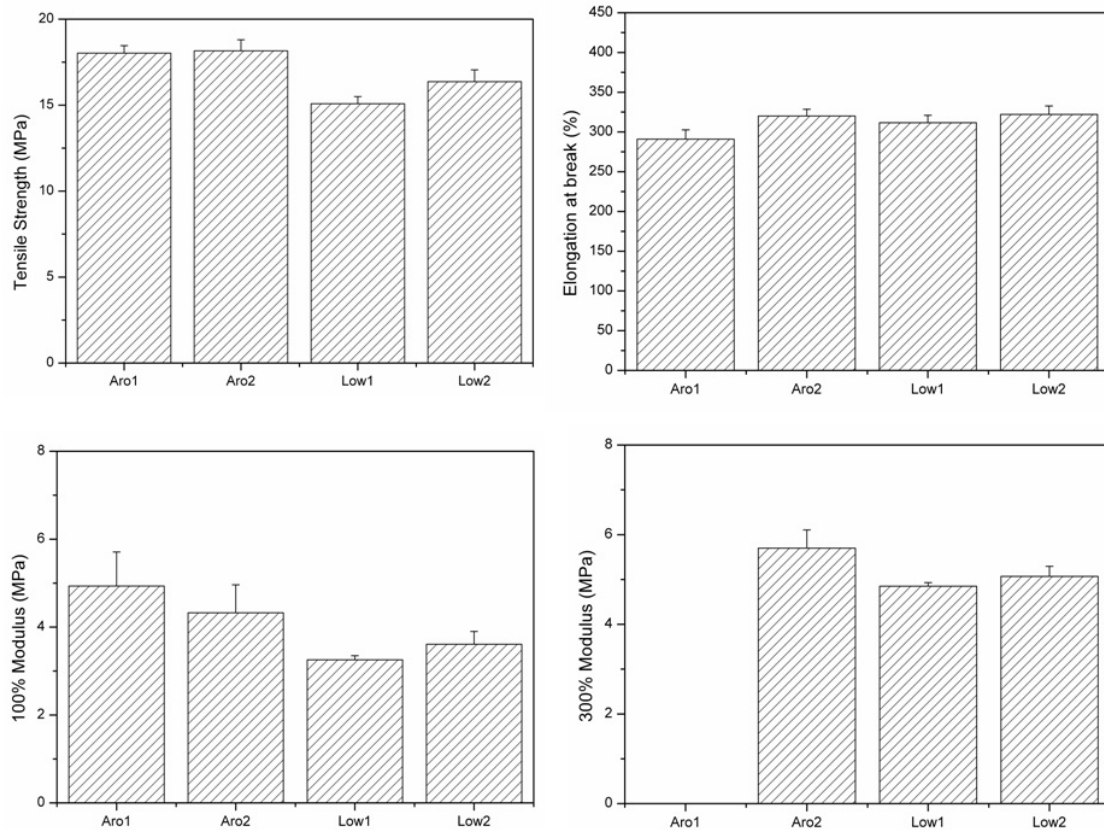
where  $r_o$  is the external diameter of the specimen (in this case 18.6 mm),  $r_i$  is the radius of the inside hole of the specimen (5.6 mm).

### III. Results and Discussion

The vulcanization characteristics, viz., maximum torque ( $M_H$ ), minimum torque ( $M_L$ ), difference in the maximum and minimum torque,  $\Delta M$ , i.e. ( $M_H - M_L$ ), scorch time ( $t_{s2}$ ) and optimum curing time ( $t_{90}$ ) for the compounds are compared in Table 2. It is evident from Table 2 that the vulcanizates containing aromatic oil (Aro1 and Aro2) have slightly higher maximum torque values than the vulcanizates containing low

**Table 2. Cure Characteristics of Rubber Compounds**

Compound	$M_H$ (dNm)	$M_L$ (dNm)	$\Delta M$ (dNm)	$t_{s2}$ (min)	$t_{90}$ (min)
Aro1	40.64	8.15	32.5	5.22	8.48
Aro2	41.71	10.49	31.2	5.14	8.49
Low1	35.53	8.12	27.4	5.03	8.53
Low2	35.48	8.76	26.7	5.01	8.68

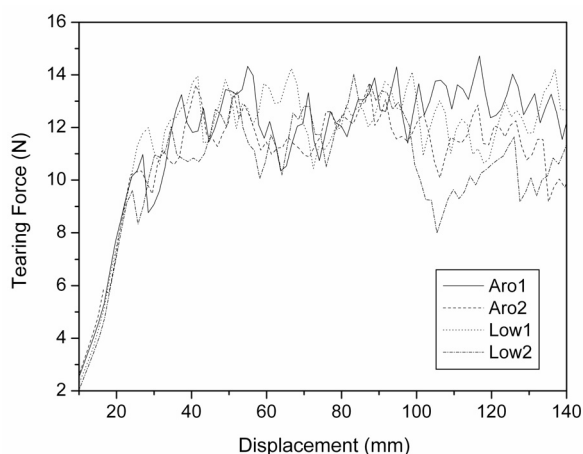


**Figure 3.** Tensile properties of rubber vulcanizates.

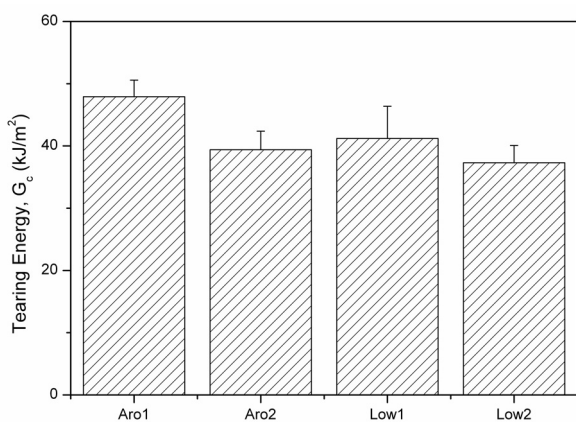
PCA oil, possibly due to the higher aromatic component. However, there is not much perceptible difference among the vulcanizates as regards the optimum curing time or the scorch time.

The tensile properties of the vulcanizates are compared in Figure 3. The aromatic oil loaded vulcanizates show higher tensile strength than the low PCA oil based vulcanizates. The increase in the 100% and 300% modulus values showed a similar trend (however, the Aro1 compound ruptured before the 300% modulus level was reached), thereby proving that the aromatic oil based compounds are stiffer than the low PCA oil based compounds. However, the elongation at break of the compounds (excepting Aro1 compound) are more or less similar. The results may be ascribed due to the better dispersion of the reinforcing agents (like carbon black) in high aromatic oils due to their good rubber compatibility.<sup>15,16</sup>

The tear force versus displacement ( $d$ ) curves for the four different vulcanizates are given in Figure 4. The average value



**Figure 4.** Tearing force,  $F$  vs. tearing distance,  $d$  of rubber vulcanizates.



**Figure 5.** Tearing energy,  $G_c$ , of rubber vulcanizates.

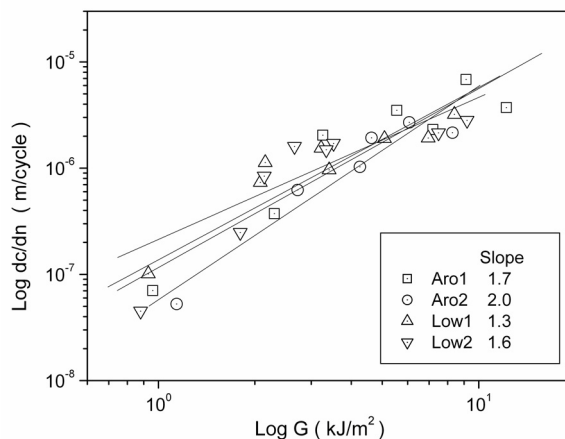
**Table 3.** Dynamic Mechanical Properties of Vulcanizates

Compound	$T_g$ ( $^{\circ}\text{C}$ )	$\tan\delta$ at $0^{\circ}\text{C}$	$\tan\delta$ at $70^{\circ}\text{C}$
Aro1	-21.9	0.338	0.094
Aro2	-22.0	0.372	0.096
Low1	-19.9	0.395	0.107
Low2	-21.9	0.369	0.090

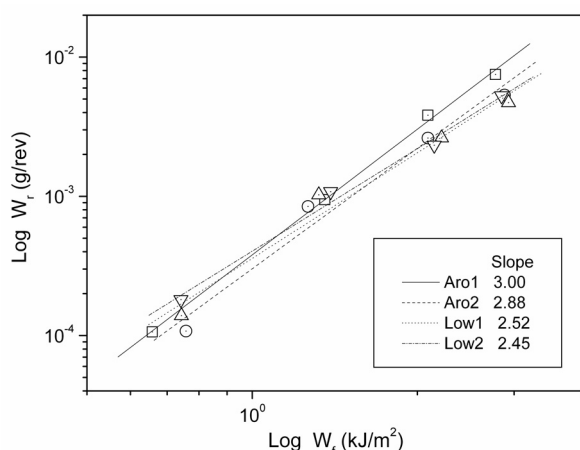
of tear force was used to calculate the trouser tear energy for each of the vulcanizates and compared in Figure 5. Aro1 vulcanizate had the highest tear strength. The low PCA based Kumho S-SBR (Low2) showed only slightly lower tear strength than its corresponding high aromatic oil extended vulcanizate.

The glass transition temperature ( $T_g$ ),  $\tan\delta$  at  $0^{\circ}\text{C}$  and at  $70^{\circ}\text{C}$  for the four types of vulcanizates are shown in Table 3. The  $T_g$  of the low PCA oil vulcanizates are almost same or slightly lower than the high aromatic oil vulcanizates. Higher  $\tan\delta$  value at  $0^{\circ}\text{C}$  indicates better wet grip properties of the rubber vulcanizate.<sup>10</sup> Low2 vulcanizate showed higher hysteresis than Aro1 vulcanizate and was only marginally lower than Aro2 compound. The  $\tan\delta$  at  $70^{\circ}\text{C}$  signifies the rolling resistance of a tire compound and the lower the  $\tan\delta$  values at this temperature, the lower is the rolling resistance. Low2 (low PCA oil vulcanizate) showed lower rolling resistance than the other vulcanizates.

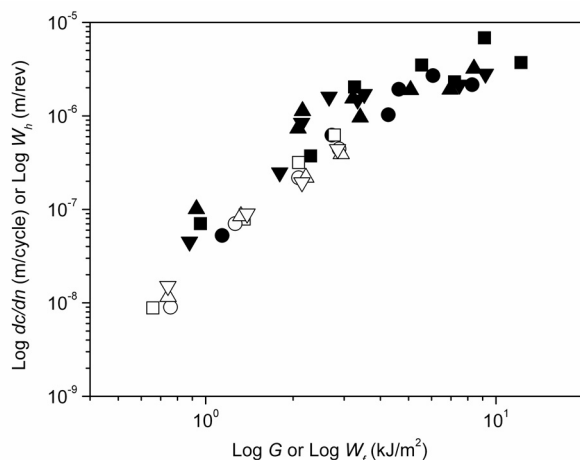
The log-log plot of crack growth rate ( $dc/dn$ ) as a function of the fracture energy ( $G$ ) is shown in Figure 6 and the experimental results obey the Power Law dependency as indicated in Equation (3). The exponents  $\alpha$  (slope values) for the vulcanizates are shown in Figure 6. The lower value of the exponent for the low PCA oil loaded vulcanizates compared to the aromatic oil loaded vulcanizates implies that the low PCA oil loaded vulcanizates have more resistance to crack



**Figure 6.** Crack propagation rate,  $dc/dn$  vs. tearing energy,  $G$  of rubber vulcanizates.



**Figure 7.** Wear rate,  $W_f$ , as a function of frictional work input of rubber vulcanizates.



**Figure 8.** Correlation between crack propagation,  $dc/dn$  and wear rate,  $W_f$ , as a function of input energy,  $G$  and  $W_f$ , respectively: Open symbols represent wear rate and closed symbols represent crack propagation.

growth. It was known that the more elastic compounds tend to show higher exponents.<sup>10</sup> When comparing the value of  $\tan \delta$  the aromatic oils had lower value than the low PCA oil materials.

The frictional work ( $W_f$ ) versus rate of wear is given in Figure 7. All the data show a linear relationship suggesting the wear rate also follows the power-law, as observed for crack propagation. The slopes of high aromatic oil vulcanizates are higher than low PCA oil ones. In case of small frictional work ranges, the wear rates are lower for the aromatic oils, while in case of high frictional work ranges, low PCA oil has lower wear rate.

The relationship between fatigue fracture properties and frictional wear properties are compared in Figure 8. A fairly good

correlation can be observed between crack propagation and wear properties as they are compared as a function of input tearing and frictional energy, respectively. This strongly indicates that the frictional wear for highly silica-loaded rubber compounds in this study is dominated by the mechanical fatigue crack propagation mechanism as proposed by Thomas et al.<sup>17,18</sup> based on the assumption of fully-developed Schallamach wear pattern.<sup>19</sup> Thus the wear performance can be expected from the values of fatigue crack propagation tests.

## IV. Conclusions

The vulcanizate characteristics, viz. the maximum torque of the high aromatic oil materials was slightly higher than the low PCA oils, the scorch safety time and optimum curing time was more or less equal. The high aromatic oil-extended vulcanizates showed superior physical properties.

The rates of both crack growth and wear were proportional to the input tearing energy and frictional energy, respectively, in a power law. At lower energy ranges, the resistance to crack and wear was better for high aromatic oil-extended rubber compounds. A reverse trend was found at higher energy ranges.

A fairly good correlation can be observed between crack propagation and wear properties as they are compared as a function of input tearing and frictional energy, respectively.

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## References

1. Rhone Poulenc (J. C. Morawski), European Patent EP 0157703 (1985).
2. Ets Michelin, European Patent EP 0501 227 A1 (1992).
3. S. Wolff, U. Gorl, M. J. Wang, and W. Wolff, "Silica-based tread compounds", *Eur. Rubber J.*, **176**, 16 (1994).
4. S. Wolff and E. H. Tan, *Am. Chem. Soc.: Rubber Division* (Paper #66), New York, April 8-11 (1986).
5. Joon M, "Non-carcinogenic tire extender oils providing good dynamic performance", *Rubber World*, **235**, 15 (2007).
6. S. Dasgupta, S. L. Agrawal, S. Bandyopadhyay, S. Chakraborty, R. Mukhopadhyay, R. K. Malkani, S. C. Ameta, "Characterization of eco-friendly processing aids for rubber compound", *Polym. Test.*, **26**, 489 (2007).
7. S. Dasgupta, S. L. Agrawal, S. Bandyopadhyay, S. Chakraborty, R. Mukhopadhyay, R. K. Malkani, S. C. Ameta, "Characteri-

- zation of eco-friendly processing aids for rubber compound: Part II”, *Polym. Test.*, **27**, 277 (2008).
8. A. Luch, “The Carcinogenic Effects of Polycyclic Aromatic Hydrocarbons”, Imperial College Press, London, 2005 (Chapter 1).
  9. V. Null, “Rubber tests with safer extender oils”, *Tire Technol. Int.*, 21 (1999).
  10. A. N. Gent, “Engineering with rubber: how to design rubber components”, Hanser, Munich, Hanser, 2001 (Chapter 6).
  11. Rivlin RS, Thomas AG, *J Polymer Science* 1953;10:291-318.
  12. S. Kaang and C. Nah, “Fatigue crack growth property of double-networked natural rubber”, *Polymer*, **39**, 2209 (1998).
  13. A. N. Gent and C. Nah, “Abrasion of rubber by a blade abrader: effect of blade sharpness and test temperature for selected compounds”, *Rubber Chem. Technol.*, **69**, 819 (1996).
  14. C. Nah, J. Cho, and S. Kaang, “An improved test method of abrasion of rubber in blade abrader”, *Polym. Test.*, **17**, 11 (1998).
  15. J. E. Pocklington, “A safer alternative to aromatic process oils”, *Tire Technol. Int.*, 43 (1998).
  16. Mobil Europe Lubricants Ltd, “Oils without labels”, *Tire Technol. Int.*, 10 (1999).
  17. E. Southern and A. G. Thomas, “Study of rubber abrasion”, *Plast. Rubber: Mat. Appl.*, November (1978).
  18. D. H. Champ, E. Southern, and A. G. Thomas, “Fracture mechanics applied to rubber abrasion”, *American Chemical Society, Division of Organic Coatings and Plastics Chemistry*, **34**, April (1974).
  19. A. Schallamach, “Abrasion of rubber by a needle”, *J. Polym. Sci.*, **9**, 385 (1952).