

Influence of Coupling Agent on Heat Build-up and Blowout Failure of Silica Filled Vulcanised Natural Rubber

AZEMI SAMSURI*# AND CHE MOHD SOM SAID*

The influence of coupling agent (Si69) on heat build-up (HBU) and the resistance to blowout temperature was investigated on vulcanised natural rubber (NR) containing 50 p.p.h.r. of precipitated silica. The amount of Si69 was varied from 1 to 6 parts per hundred of rubber (p.p.h.r.). The HBU increased as the amount of Si69 was increased. The increase in HBU was consistent with increase in hysteresis as the amount of Si69 was increased. Increase in hysteresis with increasing Si69 might be attributed to the breaking of rubber-filler interaction via coupling agent as reflected by the Young's modulus measurement. Young's modulus decreased progressively as the applied static loading was increased which might be associated with breaking of the rubber-filler interaction. Concomitantly, the volume fraction of rubber (v_r) in the swollen gel also decreased with increasing applied static loading. The v_r , in swollen gel increased as the amount of Si69 was increased for both cases before and after subjection to cyclic loading at 10 MPa for 10 cycles, thus indicating the enhancement of rubber-filler interaction with increasing Si69. The blowout temperature measured in the interior of the test piece was about a factor of 2 higher than that recorded at the base of the test piece. The blowout temperature increased as the amount of Si69 was increased due to enhancement of the rubber-filler interaction via coupling agent Si69 as indicated by the increase in v_r with increasing Si69 both before and after blowout failure.

Keywords: heat build-up; blowout temperature; blowout failure; volume fraction; rubber; swollen gel; hysteresis

Blowout failure can occur in thick rubber blocks such as truck and bus tyres, solid tyres, tank track pads and even rubber engine mounts. Blowout failure is associated with high heat generation in the interior of the thick rubber block due to various dissipative processes under dynamic deformations. Since rubber is a poor heat conductor, the heat generated in the interior of the rubber block

is not cooled rapidly, but accumulated to an extent that the temperature is sufficiently high to cause degradation associated with thermal decomposition of the rubber compound¹. As a consequence of this thermal decomposition, volatile products are produced which in turn exert internal pressure sufficiently large to tear open a path to the exterior.

* Department of Polymer Technology, Faculty of Applied Sciences, Universiti Teknologi MARA, 40450, Shah Alam Selangor.

Corresponding author (e-mail: azemi@salam.uitm.edu.my)



Figure 1. Cross section of a truck tyre that failed by blowout at the thick shoulder region.

A big hole around the thick shoulder region of the tyre is clear evidence of the explosive rupture in the interior of the rubber as shown in Figure 1.

Blowout failure does not occur in a passenger car tyre since the tread and the shoulder region of the tyre is relatively thinner than those of bus and truck tyres. A thin rubber section will have a smaller volume of material at decomposition temperatures than thicker ones and generate a correspondingly smaller amount of volatiles. Apart from that, a thin rubber section does not provide sufficient volume to permit high heat accumulation. Consequently, the accumulated heat does not reach the necessary temperature to cause blowout failure.

At a high loading capacity and fast speed, temperature in the shoulder region of a truck and bus tyre can reach 150°C or higher². Modern truck tyre tread formulations usually incorporate a small quantity of precipitated silica. Apart from reducing rolling resistance, the addition of a small quantity (10 – 15 p.p.h.r.) of silica in a conventional carbon black filled (35 – 45 p.p.h.r.) tread compound formulation is to reduce heat build-up while maintaining other properties such as tear resistance³. Evans

*et al.*⁴ found that incorporation of 9 p.p.h.r. of silica in black filled (42 p.p.h.r N330 HAF black) NR/BR (50:50) sidewall compound, reduced the hysteresis (G'' at 30°C) by about 27 percent. In view of the fact that silica fillers are being used in tyre tread formulations to reduce rolling resistance, it is very important that information on heat generation and blowout associated with silica fillers is made available.

Silica has a different surface activity from carbon black. It requires a coupling agent to enhance the rubber-filler interaction as silica is polar in nature while natural rubber is non-polar. The use of silica in this investigation enables us to investigate the effect of rubber-filler interaction on heat generation and blowout failure. The effect of silica on heat generation and blowout failure has not been investigated by previous researchers. The level of rubber-filler interaction was varied by varying the amount of coupling agent (Si69).

Formulations

The compound formulations are given in Table 1. The amount of precipitated silica was fixed at 50 p.p.h.r., but the amount of coupling

agent Si69, (bis[3-triethoxysilylpropyl]-tetrasulphide) abbreviated as TESPT was varied so that the effect of the extent of rubber-silica filler interaction on blowout failure can be investigated. A black filled NR compound was also included for the purpose of comparison with the silica filled compounds. Process oil was omitted in the formulation.

EXPERIMENTAL

Mixing

All rubber compounds were prepared by mixing rubber with the compounding ingredients given in each formulation using internal mixer BR1600. The fill factor used was 0.7. The mixing conditions and sequence of mixing were as follows:

Starting temperature = 70°C
 Rotor speed = 110 r.p.m.

Sequence of mixing

- 0' - Rubbers
- ½' - Powders

- 1' - Silica + Si69 / carbon black
- 2 ½' Sweep
- 3 ½' Dump

The recorded dump temperature for the mixes ranged from 120 – 130°C. Curatives were added on a two-roll mill. The mixing time on the two-roll mill was five minutes with frequent cutting and folding of the rubber band to ensure uniformity and homogeneity of the mix.

The optimum cure t_{95} of each compound was determined from a curometer MDR 2000 at 150°C.

Moulding

The test pieces for heat build-up, hardness, resilience and vulcanised rubber sheets for the preparation of dumbbell and tensile strip test pieces were prepared by compression moulding heated in an electrical press at 150°C.

They were cured to t_{95} in accord with the rheometer trace. Heat build-up test pieces were cured to $t_{95} + 5$ minutes. This additional

TABLE 1. COMPOUND FORMULATIONS FOR SILICA FILLED NR

Mix number	Gum	1	2	3	4	5	6	7	8
NR(SMR L)	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2
Santoflex 13	3	3	3	3	3	3	3	3	3
Carbon black (N220)	-	50	-	-	-	-	-	-	-
Ppt silica (Ultrasil)	-	-	50	50	50	50	50	50	50
*Si69	-	-	-	1	2	3	4	5	6
Diethylene glycol (DEG)	-	-	-	2	2	2	2	2	2
Sulphur	1.5	2.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

*Coupling agent Si69 - Bis[3-triethoxysilylpropyl]-tetrasulphide

5 min was necessary to allow the interior of the test piece to reach its vulcanisation temperature and fully cured since the test pieces were relatively thick.

Measurement of Heat Build-up and Blowout Failure

Heat build-up test pieces, cylindrical in shape, with a diameter of 17.8 ± 0.15 mm and a height of 25 ± 0.25 mm were used. Two test pieces were tested and average of two results reported. In the case of temperature rise measurements, the test pieces were subjected to repeated compression at a frequency of 30 Hz using a compression flexometer, as described in *ISO 466/3-1982*. The load applied on the beam was 11 kg, the stroke applied was 5.71 mm and the chamber temperature was 100°C . The temperature rise after 25 min was noted.

For determination of fatigue properties or blowout failure, more severe test conditions were used. In this case, the load applied on the beam was 22 kg, the stroke was 6.35 mm and the chamber temperature was 100°C . The blowout temperature measured at the base of the test piece and the interior of the test piece was recorded. Temperature rise in the interior of the test piece was monitored continuously until the occurrence of blowout failure. This was done by inserting a thermocouple wire in the interior of the test piece during moulding as shown in *Figure 2*. During the test, the temperature profile was recorded simultaneously by a computer system attached to the control unit as shown in *Figure 3*. The control unit is fitted with an Amcell S-type load cell, simple datalogger (Model L320) and LCD display counter all computerised to monitor the temperature rise at the bottom plate and interior of the test piece. The test was terminated when the test piece blew out.

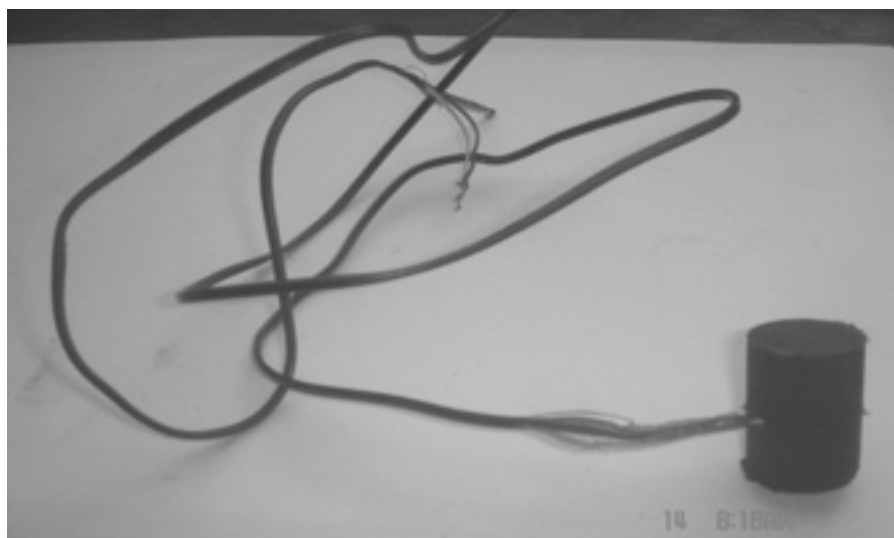


Figure 2. Shows the molded HBU test piece carrying a thermocouple wire at the centre of its interior.

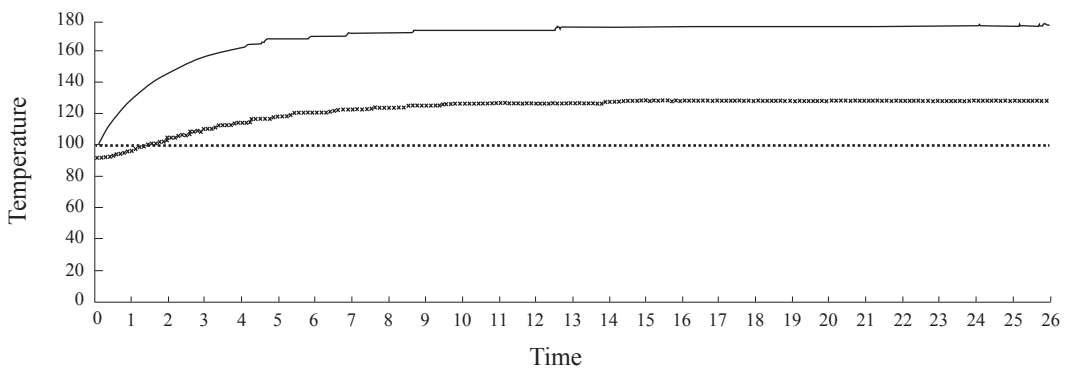


Figure 3. Data of heat build-up generated during the test. Dotted line indicates the oven temperature, crosses indicates the temperature profile at the base of the test-piece, and full line indicates the temperature profile of the interior of the test-piece. The test-piece was vulcanized NR filled with 50 p.p.h.r. of ISAF (N220) black.

Measurement of Volume Fraction of Rubber in the Swollen Gel

In this investigation, the volume fraction of rubber in the swollen gel, v_r , was determined by the equilibrium swelling measurement. The differences in v_r between blowout samples and virgin samples provide a relative measure of the damage caused by blowout. High v_r indicates that the crosslink concentration is relatively high and low v_r indicates the crosslink concentration is relatively low.

Heat build-up test pieces were cut and samples from the centre region of the test piece were taken and referred to as virgin samples. It is necessary to take samples from the interior region of the test piece to minimise error associated with the variations of crosslink concentration within the thick test piece. In the case of blowout test pieces, samples were taken from the interior region where blowout had occurred as shown in *Figure 4*. No samples were taken outside the blowout region. This blowout region is very distinct from regions surrounding it.

The volume fraction of the rubber in the swollen specimen, v_r , was calculated and

corrected for the volume occupied by the filler and zinc oxide particles⁵, using the relationship in *Equation 1*.

$$v_r = V_{RN} / (V_{RN} + V_s) \quad \dots 1$$

where V_s is the volume of solvent absorbed and V_{RN} is volume of rubber network. The rubber network (RN) refers to the network formed from the rubber hydrocarbon and the curative by the vulcanisation process, including any atoms or groups introduced in crosslinks or as modifications of the main rubber chains⁶. V_{RN} was calculated from the initial weight of samples and mix compositions, using the relationship⁶ in *Equation 2*.

$$V_{RN} = (M_{RN})(M_o) / (M_m)(\rho_{RH}) \quad \dots 2$$

where M_{RN} is the weight of rubber network, *i.e.*, the weight of rubber hydrocarbon (RH) and sulphur combined, M_m is the total weight of mix composition, M_o is the initial weight of the sample and ρ_{RH} is the density of rubber hydrocarbon. The calculation was based on the assumption that all the acetone insoluble material present in the raw rubber was present in the network, *i.e.*, that there was no sol rubber⁶.

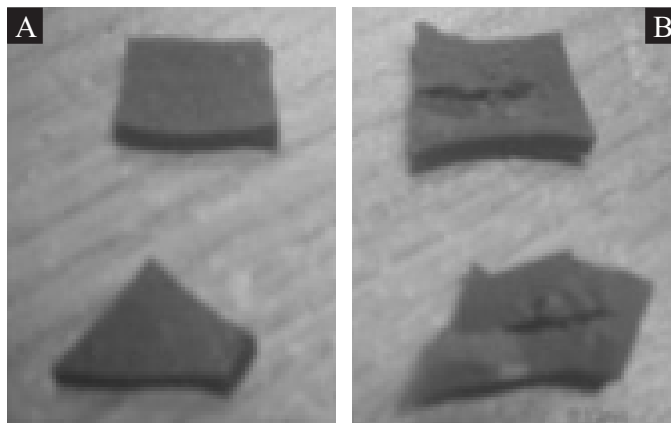


Figure 4. Photographs showing virgin samples (A) and blowout samples (B) used in equilibrium swelling measurement to determine the volume fraction of rubber in the swollen gel.

Measurement of Hysteresis

The test pieces $75 \text{ mm} \times 10 \text{ mm} \times 1 \pm 0.2 \text{ mm}$ were prepared by stamping a die on a flat vulcanised rubber sheet of uniform thickness. A tensile machine was used to conduct the experiment on hysteresis. The speed of the tensile machine was set to 500 mm per minute. The test was conducted at $23 \pm 2^\circ\text{C}$. The test piece was clamped between the two grips and the gauge length (40 mm) between the grips was noted. The test piece was stretched to a 300% strain level and then brought down to zero strain. This process was repeated six times. The hysteresis was determined from the area of the hysteresis loop (area bound by the extension and retraction curves as shown by a schematic diagram in *Figure 5*) of the first cycle and the sixth cycle.

Measurement of Young's Modulus

Simple extension measurement at low strain (below 50%) was done on a parallel strip of vulcanised rubber having dimensions of

$150 \text{ mm} \times 3 \text{ mm} \times 0.5 \text{ mm}$. The cross sectional area of the test piece was determined from a density measurement. Young's modulus of the vulcanisate was estimated from the slope of the straight line of the stress-strain plot as shown in *Figure 6*. The stress here refers to engineering stress. The mean value from two measurements was reported. Simple extension measurements were also done on test pieces subject to pre-stressing at different stresses by hanging dead loads on the test piece for 3 min, after which time the load was removed. This was done to assess strength of the rubber-filler interaction as a function of coupling agent. Simple extension measurement was done immediately after unloading.

RESULTS AND DISCUSSION

Effects of Si69 on Physical Properties of Silica Filled NR Vulcanisates

The physical properties of the vulcanisates are shown in *Table 2*. The hardness of gum (unfilled) vulcanised NR is 40.1 IRHD for this

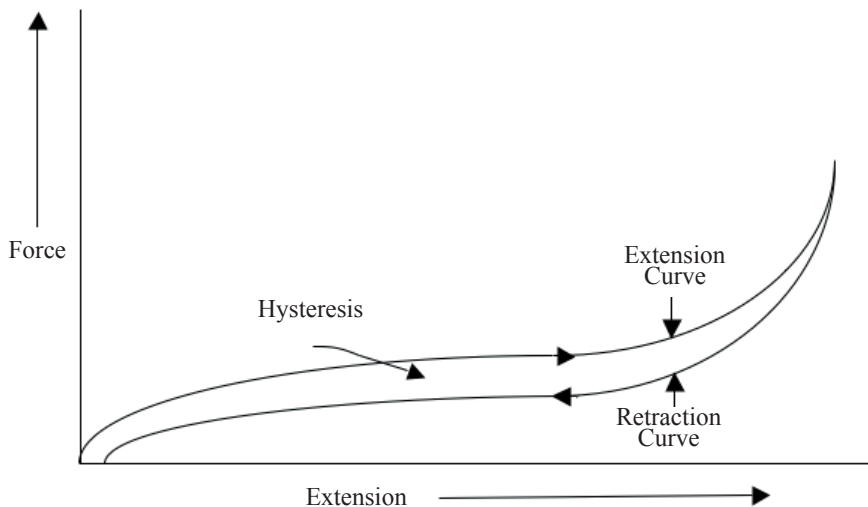


Figure 5. Schematic diagram showing the force-extension and retraction curves. The area bound by the extension and retraction curves is known as hysteresis.

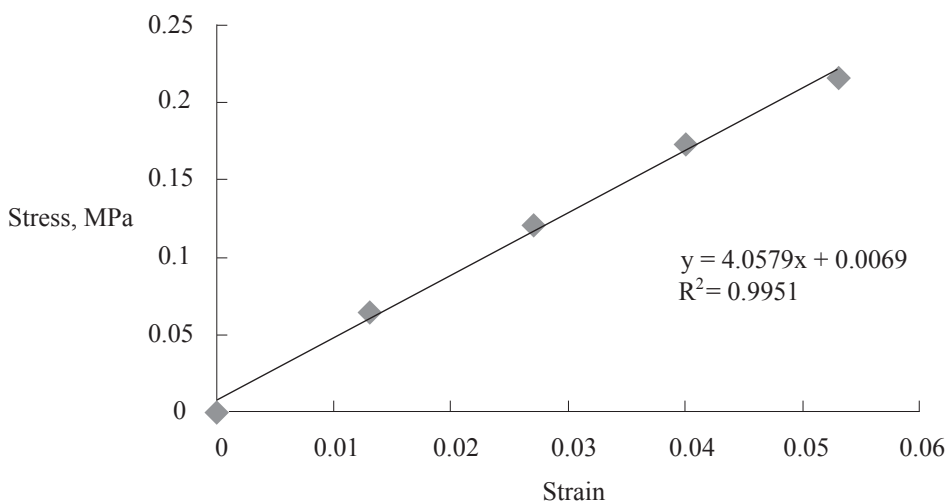


Figure 6. Stress-strain plot of pre-stressed silica filled vulcanised NR containing 3 p.p.h.r. of silane coupling agent.

particular semi-EV system. The addition of 50 p.p.h.r. of carbon black and silica has increased the hardness markedly. The mechanism by which filler enhances the hardness and modulus is reasonably well understood, at least in qualitative terms. The stiffening is in part attributed to the absence of deformation within the rigid filler particles and partially with immobilisation of rubber at the interface between the rubber matrix and the filler particles, as well as the hydrodynamic effect^{7,8}. As a rule of thumb⁹, the approximate loading of reinforcing black and silica to give a ten point increase in hardness on the IRHD scale is about 20 p.p.h.r. At 50 p.p.h.r. of silica, the hardness would increase by 25 IRHD and the expected hardness of filled silica would be 65.1 IRHD. However, the hardness of silica filled NR was substantially higher than expected, even without a coupling agent. With 1 p.p.h.r. of Si69 (mix 3), the hardness increases by 4 IRHD compared with silica filled without

a coupling agent (mix 2). The hardness of silica filled vulcanisate is also higher than that of the black filled vulcanisate. In this case it is not very clear whether the difference in hardness between the silica filled and black filled vulcanisate is associated with the filler or crosslink concentration as the amount of curatives were not the same. However, it was reported by Luginsland *et al.*⁷ that silica filled vulcanised rubber exhibited a higher degree of immobilisation than that of carbon black filled vulcanised rubber. They explained that the increase in immobilisation in silica filled vulcanised rubber was attributed to chemical bonding that formed two network structures during vulcanisation, *viz*; (i) the silica-rubber network resulting in the “in-rubber structure” and (ii) the matrix network by sulphur crosslinking of the polymer chains. This two network formation is believed to be associated with the presence of a coupling agent to enhance the rubber-silica surface interaction.

According to Vilgis *et al.*⁸ coupling agents such as TESPT have triethoxysilyl functions which can react with the silanol groups on the silica surface. This chemical reaction is known as the “silanisation reaction”. During the reaction, one ethoxy group of each Si-unit reacts with an accessible silanol group on the silica surface and therefore, links chemically to the filler⁸. The increase in hardness might be attributed to these chemical links. However, the hardness of silica filled vulcanisates does not increase significantly as the amount of coupling agent was increased to more than 1 p.p.h.r. It is not entirely clear if the short mixing time in the Banbury mixer and low dump temperature might have a direct influence on the efficiency of chemical linkages of the rubber to the filler *via* a coupling agent.

The effect of coupling agent on Young’s modulus is shown in *Figure 7* where it increases progressively as the amount of Si69 was increased from 1 p.p.h.r to 3 p.p.h.r. At 4 – 6 p.p.h.r., the influence of Si69 on Young’s modulus appears to level off. Since the measurement of Young’s modulus was done at a very low strain level, it might be that the measurement was not sensitive enough to be detected when the vulcanisate was too stiff. The effect of TESPT on M300 is slightly more discriminative than hardness

and Young’s modulus. Here, the M300 increases progressively in a linear manner with increasing amounts of TESPT as shown in *Figure 8*. Since the amount of precipitated silica is the same (50 p.p.h.r.) and amount of curatives is also the same for each vulcanisate, the difference in M300 might be attributed to the chemical linkages that formed at the filler surface between one ethoxy group of TESPT and silanol group on the silica surface as as postulated by Vilgis *et al.*⁸

The tensile strength results shown in *Table 2* are for the purpose of quality control to check the quality of the compound. The tensile strength of gum (unfilled) vulcanised NR is relatively high because of its ability to strain crystallise during stretching. Indeed the tensile strength of gum vulcanisate is higher than silica filled NR without coupling agent (mix 2). At first sight, it is unthinkable that silica filled vulcanised NR gives a lower tensile strength than unfilled vulcanised NR. This is a very good example of the complex nature of the mechanism of reinforcement of particulate fillers in vulcanised rubber. Silica has very fine particle size, but in the absence of efficient bonding or interaction at the rubber-filler interface, the expected reinforcement will not be achieved. In the presence of a coupling agent, silica filled vulcanised

TABLE 2. PHYSICAL PROPERTIES OF VULCANISED SILICA FILLED NR

Mix number	Gum	1	2	3	4	5	6	7	8
t_{95} (minutes) at 150°C	18	12.5	22.0	14.7	14.6	16.6	18.4	19.8	20.7
Si69 (p.p.h.r)		-	0	1	2	3	5	5	6
Hardness (IRHD)	40.1	70	74.6	78.3	79.3	79.5	79.7	78	79.3
Resilience (%)	89	61	57	62	60	60	62	64	64
M300 (MPa)	1.6	14.1	14.9	15.5	15.8	16.3	16.6	16.8	17.1
Tensile Strength (MPa)	22.0	26.5	11.2	23.6	25.8	27.4	27.4	27.0	27.3

NR gives markedly higher tensile strength than that without a coupling agent. This indicates significant influence of the coupling agent to enhance rubber-filler interaction.

The high tensile strength of silica filled vulcanised NR gives an indication of the good quality of the mix in spite of the short mixing cycle.

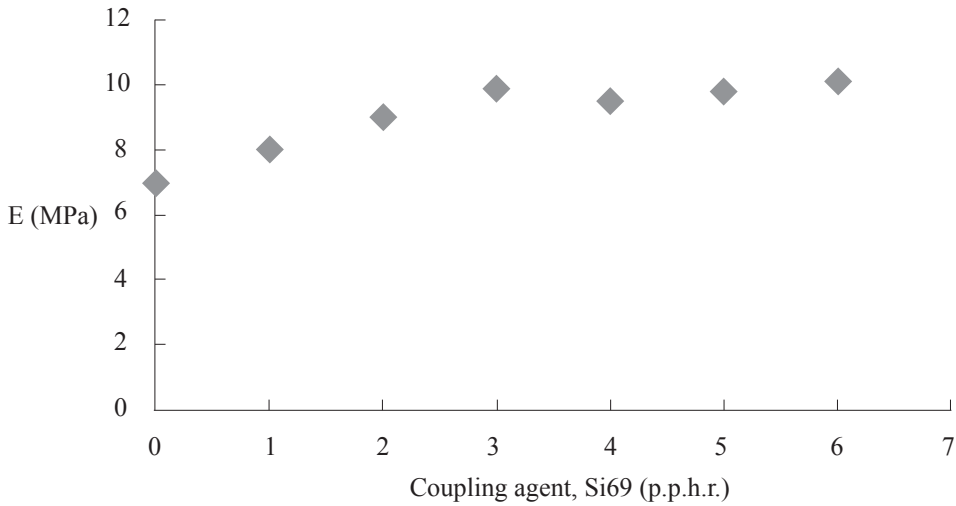


Figure 7. Effect of coupling agent TESPT (Si69) on Young's modulus, E of silica filled NR vulcanisate.

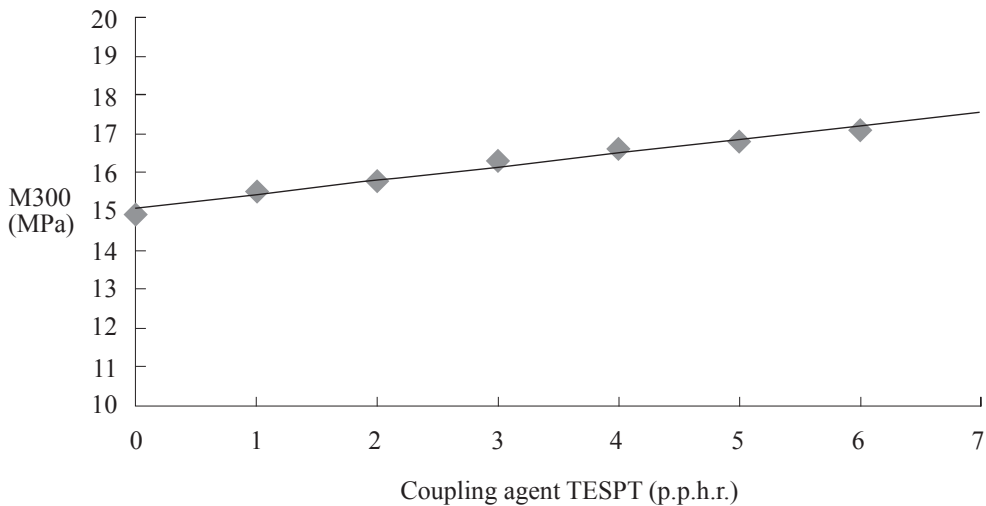


Figure 8. Effect of coupling agent TESPT (Si 69) on tensile stress at 300% strain (M300) of silica-filled NR vulcanisate.

Effect of Coupling Agent TESPT (Si69) on Heat Build-up

The plot of heat build-up (HBU) versus coupling agent (Si69) shown in *Figure 9* indicates that HBU increased as the quantity of coupling agent was increased. The increase in HBU with increasing Si69 might be associated with the enhancement of rubber-filler interaction. Enhancement in rubber-filler interaction is reflected by the increase in hardness and tensile strength as the amount of Si69 was increased (refer to *Table 2* above). At the same filler loading, silica filled vulcanised NR gave higher heat generation (HBU) than that of carbon black filled vulcanised NR (mix 1) since Medalia¹³ reported that the former was more hysteretic than the latter. Medalia¹³ suggested that silica filled rubber compounds might give higher hysteresis than carbon black filled rubber owing to this strong interaggregate interaction when the

compounds were adjusted to be comparable in other aspects.

Influence of TESPT (Si69) on Hysteresis

Figure 10 is a plot of hysteresis against coupling agent (Si69). It is very clear that the hysteresis increases with increasing amounts of Si69.

Reasons for increase in hysteresis as the amount of Si69 was increased can be explained as follows: Addition of Si69 enhances rubber-filler interaction. However, strength of the chemical link formed at the rubber-filler interface would affect the magnitude of energy dissipation. When silica filled vulcanised rubber is deformed, it is believed that these chemical linkages are broken at a low stress level resulting in energy dissipation. Thus, to provide experimental

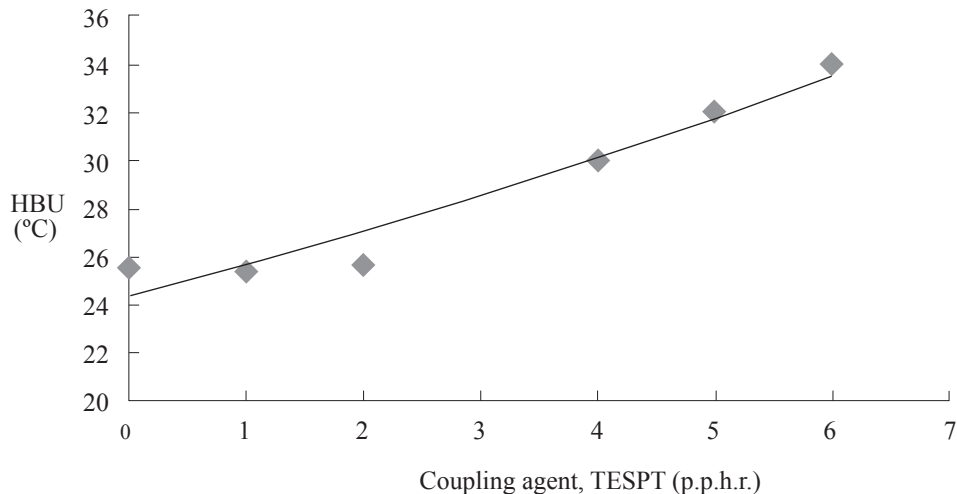


Figure 9. Heat build-up (HBU) vs TESPT. Effect of rubber-filler interaction on HBU.

evidence to support this possibility, experiments were conducted to determine the Young's modulus as well as equilibrium swelling before and after the samples were pre-stressed. If the chemical linkages were strong, the Young's modulus and volume fraction of rubber in the swollen gel would not differ significantly after pre-stressing.

Effects of Static Loading on Young's Modulus, E

Figure 11 shows that Young's modulus E decreased progressively with increasing levels of pre-stressing, which might be associated with the breaking of chemical bond at the rubber-filler interface, as well as the effect of stress-softening, since the simple extension measurement was done immediately after unloading. To verify that

chemical links adjoining the silica surface to rubber chains *via* coupling agent were broken during pre-stressing, a separate experiment was done where the pre-stressed samples were swollen in toluene in a glass bottle until equilibrium swelling was attained. Generally, the volume fraction of rubber in the swollen gel v_r decreased progressively with increasing levels of pre-stressing as shown in Figure 12. The decrease in v_r with increasing stress levels indicates the high number of chemical linkages adjoining silica filler to rubber molecules was broken during pre-stressing. Consequently more solvent was diffused into the rubber network as the number of broken chemical linkages increased. This result provides experimental evidence that chemical linkages adjoining silica filler to rubber molecules were relatively weak since they were broken at moderately low stresses (5–10 MPa).

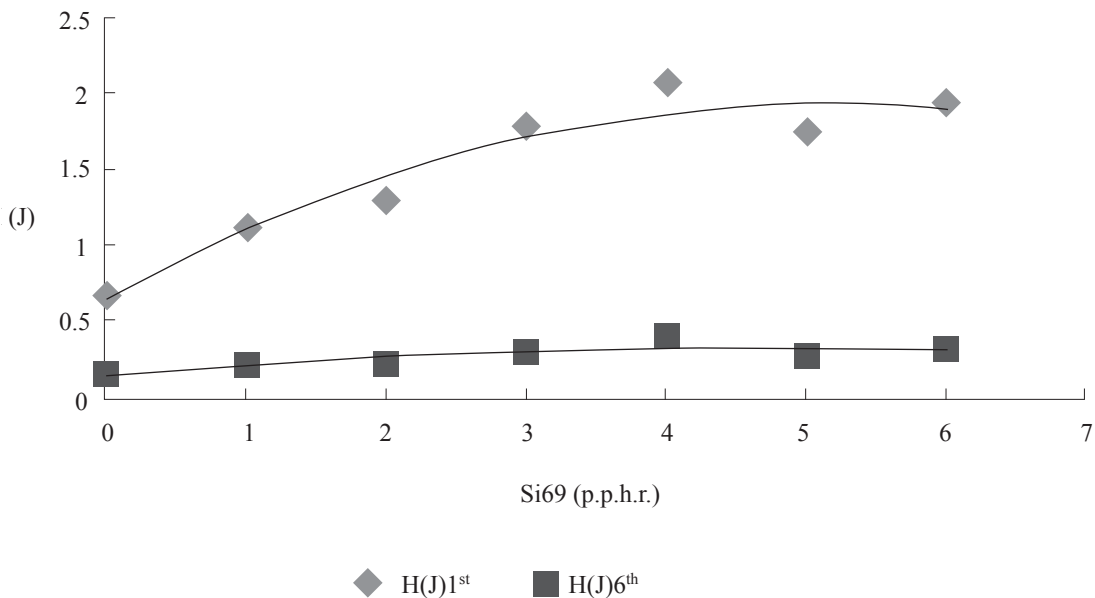


Figure 10. Influence of coupling agent (Si69) on hysteresis cycles to 300% strain after first (1th) cycle and sixth (6th) cycle.

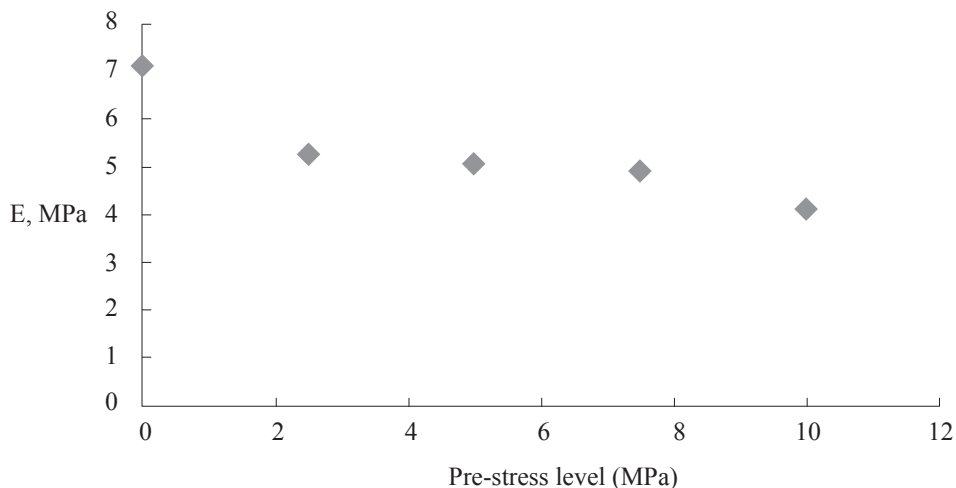


Figure 11. Effect of pre-stressing on the Young's modulus of silica filled vulcanised NR containing 4 p.p.h.r. Si69.

Effect of Cyclic Loading on Volume Fraction of Rubber, v_r , in the Swollen Gel

In this experiment, cyclic pre-stressing was applied to a thin strip of vulcanised silica filled NR containing different amounts of Si69. The samples were pre-stressed to ten cycles before the equilibrium swelling measurement. The stress applied was 10 MPa. The samples were swollen in toluene until equilibrium swelling was attained before and after pre-stressing. The results are shown in Figure 13. The effect of coupling agent Si69 on v_r was very marked, where before applying cyclic loading v_r increased as the quantity of Si69 was increased. This might be associated with development of chemical linkages at the rubber-filler interface *via* Si69 which might restrict the diffusion of the solvent into the rubber matrix. But when the sample was pre-stressed dynamically to ten cycles, v_r decreased markedly at each level of Si69 loading indicating that the quantity of solvent absorbed was more than the

unstressed sample. The chemical linkages at the rubber-filler interface might be broken to some extent during cyclic pre-stressing which consequently provided an easy passage for the solvent to diffuse into the rubber. The results in Figure 13 compliment those in Figure 12.

Effect of Coupling Agent (Si69) on Blowout Failure

Figure 14 shows the blowout failure of silica filled vulcanised NR and that of black filled vulcanised NR. The silica sample did not produce complete failure across the test piece, in contrast to the complete failure across the test piece observed for the black filled vulcanised NR. The exact reason is not entirely clear, but in the author's opinion it might be attributed to the differences in the stiffness between silica filled and black filled vulcanisates. The former is stiffer than the latter as indicated by the hardness results shown in Table 2.

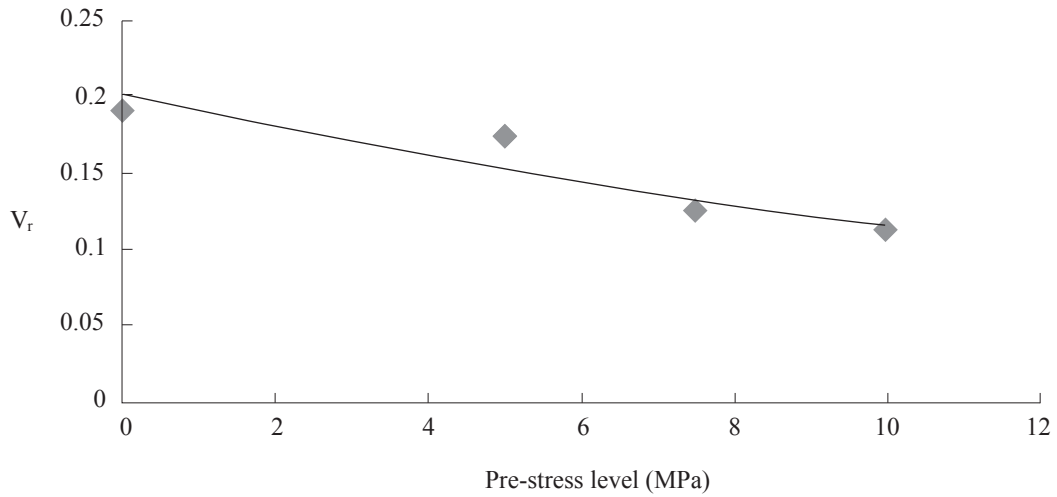


Figure 12. Effect of pre-stressing (static loading) on the volume fraction of rubber in the swollen gel of silica filled vulcanised NR containing 4 p.p.h.r. Si69.

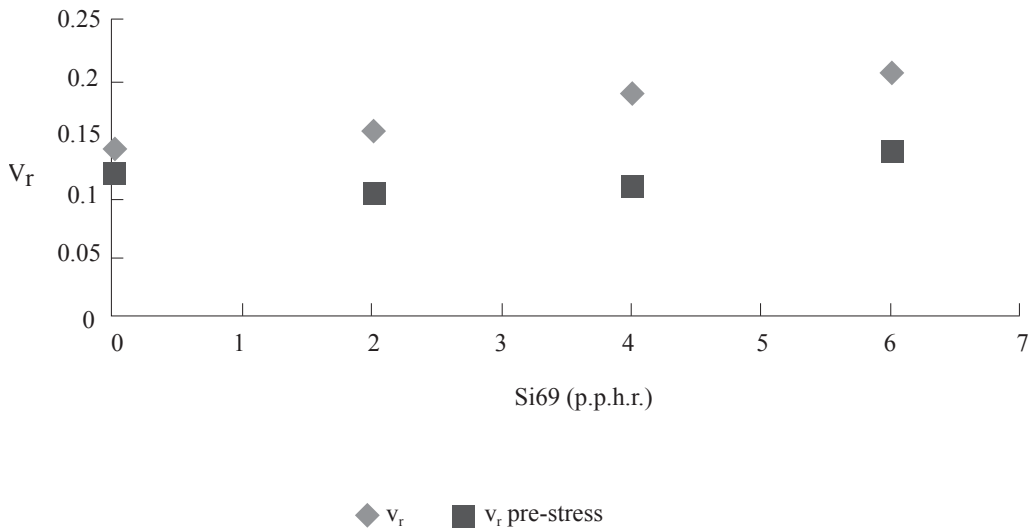


Figure 13. Effect of cyclic pre-stressing (10 cycles at 10MPa) on volume fraction of rubber in the swollen gel of silica filled vulcanised NR containing different amounts of coupling agent, Si69.

Figure 15 shows the actual blowout temperature in the interior of the test piece. The actual blowout temperatures were much higher than the temperature recorded at the base of the test piece. This result is in accord with Gent's hypothesis which stated that blowout occurs once the interior of the rubber reaches a critical temperature of about 200°C, similar to the polymer decomposition temperature. These actual blowout temperatures are in good agreement with those reported independently by Gent and Hindi¹, and that of Choi and Kim¹². This good agreement bears two important points. Firstly, it proves that the temperature profile recorded during the test was reliable and accurate since the results are consistent with those reported by Gent and Hindi¹ as well as Choi and Kim¹². Secondly, it indicates that the heat in the interior of the test piece was not lost immediately since rubber is a poor heat conductor. Thus measuring the temperature in the interior of the test piece immediately after blowout failure as reported by Gent and Hindi¹ as well as by Choi and Kim¹² is still reliable.

The blowout temperature was also affected by the quantity of Si69. The blowout temperature increased by 10°C – 20°C as the amount of Si69 was increased, probably due to enhancement of the rubber-filler interaction.

The blowout temperature of silica filled NR was higher than black filled NR even in the absence of a coupling agent indicating that the former is more resistant to blowout failure than the latter.

Comparison of Volume Fraction of Rubber in Swollen Gel, v_r , between Virgin and Blowout Samples

The volume fraction of rubber in swollen gel, v_r is plotted against coupling agent as shown in Figure 16. The trend is the same for both virgin and blowout samples where v_r increased with increasing amount of Si69 indicating the presence of a “network” that reduced the amount of solvent diffused into the rubber network. However, at any given amount of Si69, the v_r of blowout samples was lower than v_r of virgin samples, indicating that the extent of rubber-filler interaction or the “network” of the former was lower than the latter. It might be attributed to the breaking of parts of the “network” during blowout failure. It should be noted that the virgin samples here were taken from the HBU test pieces in contrast to the virgin samples (refer to Figure 13) taken from vulcanised tensile sheets.

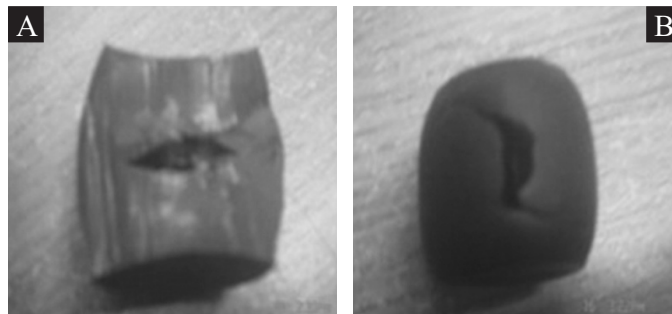


Figure 14. Blowout samples indicating the opening of the interior of the test piece. (A) silica filled NR (mix 7). (B) black filled NR (mix 1).

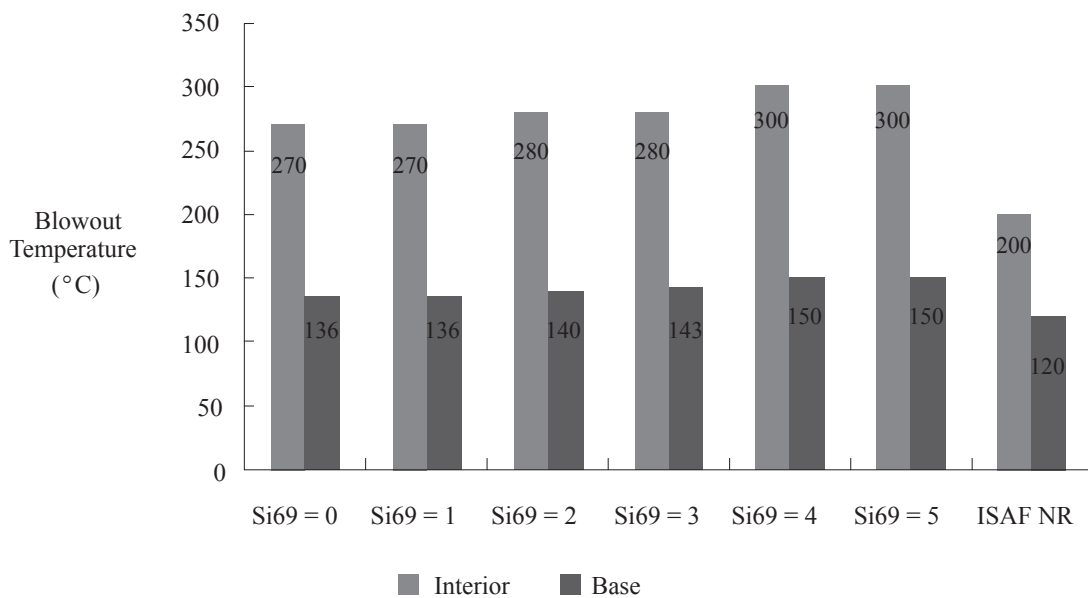


Figure 15. Effect of coupling agent (Si69) on blowout temperature of the interior of the test piece.

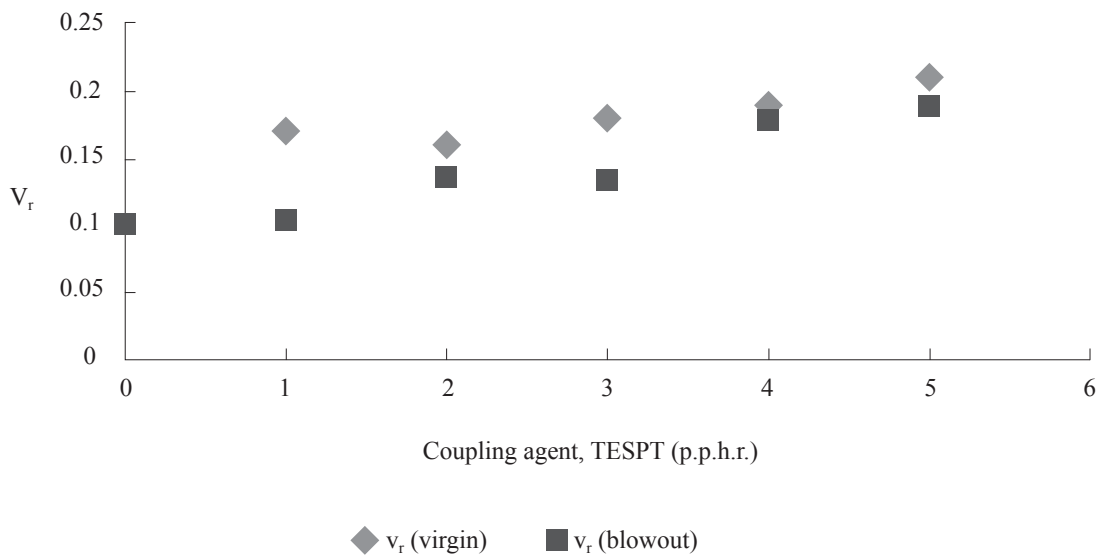


Figure 16. Volume fraction of rubber in swollen gel, v_r , vs coupling agent TESPT.

CONCLUSIONS

The coupling agent TESPT (Si69) in silica filled NR influenced heat generation and the resistance to blowout failure. The heat build-up (HBU) and temperature to cause blowout failure increased as the amount of Si69 was increased. The hysteresis increased as the quantity of Si69 was increased which might be responsible for the increase in HBU. The rubber-filler interaction increased as the quantity of Si69 was increased as indicated by the increase in volume fraction of rubber, v_r , in the swollen gel. Application of static load and cyclic loading breaks the rubber-filler interaction as indicated by the decrease in volume fraction of rubber, v_r , in the swollen gel. The blowout temperature measured in the interior of the test piece was markedly higher than the temperature measured at the base of the test piece. Thus, the former gave a more accurate blowout temperature than the latter.

ACKNOWLEDGEMENTS

We would like to express our thanks to Prof. Dr. Ri Hanum Yahaya Subban for giving the permission to publish this work. One of the authors (Prof. Dr. Azemi Samsuri) would like to express his sincere thanks to the late Prof. Dr. A.N. Gent for his advice and suggestions.

Date of receipt: August 2012

Date of acceptance: January 2013

REFERENCES

- GENT, A. N. AND HINDI, M. (1988) Heat Build-up and Blowout of Rubber Blocks. *Rubb. Chem. Technol.*, **61**, 892–905.
- WILLIAMS, A. R. (1997) Tyres – The Continuous Invention, *Proc. Int. Rubb. Conf. 97*, Kuala Lumpur, October 1997, 3–25.
- LEE, K.W. (1988) Evaluation of Copelletized Carbon Black/Silica in Tire Tread Formulations, *Am. Chem. Soc.*, Paper No. 13, Spring 1988.
- EVANS, L.R., HOPE, J.C. AND WADDLE, W.H. (1994) Use of Reinforcing Silica in Model Sidewall Compounds: Effects of Carbon Black Type, Polymer Type and Filler Level, 145th Meeting of the Rubber Division, *Am. Chem. Soc.*, Chicago, Illinois, April 21.1994.
- PORTER, M. (1967) Structural Characterisation of Filled Vulcanisates High Abrasion Containing Furnace Black. *Rubb. Chem. Technol.*, **40** (3), 882.
- BRISTOW, G.M. AND PORTER, M. (1967) Structural Characterization of Vulcanisates. Determination of Degree of Chemical Crosslinking of NR Gum Vulcanisate Networks. *J. Appl. Polym. Sci.*, **11**, 2215.
- LUGINSLAND, H.D., FROHLICH, J. AND A. WEHMEIER (2001) Influence of Different Silanes on the Reinforcement of Silica-filled Rubber Compounds, paper No. 59 presented at the ACS Meeting, Rhode Island/USA, April 24–27.
- VILGIS, T.A., HEINRICH, G. AND KLUPPEL, M. (2009) Reinforcement of Polymer Nano-Composites, Theory, Experiments and Applications, **Vol. Ch. 1.**, Cambridge, UK: Cambridge University Press.
- Natural Rubber Formulary. (1984) The Malaysian Rubber Producers' Research Association, ISBN 0–9504401-3-2, p 23.
- PARK, D. M., HONG, W.H., KIM, S.G. AND KIM, H.J. (2000) Heat Generation of Filled Rubber Vulcanizates and its Relationship with Vulcanizate Network Structures. *Eur. Polym. J.*, **36**, 2429–2436.
- SCHURING, D.J. (1980) The Rolling Loss of Pneumatic Tires. *Rubb. Chem. Technol.*, **53**, 1–3.
- CHOI, S.S. AND KIM, I.S. (1998) Blowout of Rubber Vulcanizates: Influences of Cure Systems, Content of Carbon Black, and Organic Additives. *Bull. Korean Chem. Soc.*, **19**(2), 174–178.
- MEDALIA, A.I. (1991) Heat Generation in Elastomer Compounds: Causes and Effects. *Rubb. Chem. Technol.*, **64**, 481.