

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Filler Physical Properties

The physical properties of the seven fillers studied are summarized in Table 4.1.

Table 4.1 Physical properties of fillers.

Filler	Grade	Surface Area (m ² /g) (N ₂ BET)	Mean Agglomerate Particle Size (μm)	Pore Volume (cm ³ /g)
Carbon black	N330	84	19.00	0.0306
	N220	121	18.11	0.0456
	N110	144	16.21	0.0564
Precipitated silica	Ultrasil VN2	120	18.43	0.0455
	Hi-Sil 255	136	17.19	0.0525
	Hi-Sil 927	159	15.11	0.0603
Gypsum	75	10	30.07	0.0034

From Table 4.1, the data showed that each filler type affected a variety of the physical characteristics of fillers, including, surface area, mean agglomerate particle size, and pore volume. The high nitrogen BET surface area of a filler is the low mean agglomerate particle size and high pore volume. For precipitated silica, Hi-Sil 927 is the highest nitrogen BET

surface area relating to the lowest mean agglomerate particle size. On the other hand, gypsum shows opposite results to precipitated silica. Moreover carbon black, N220 and precipitated silica, Ultrasil VN2 are similar to nitrogen BET surface area. Therefore these fillers were selected for study according to their differences in surface area which relating to particle size. (Donnet, J-B., 1998)

4.2 Cure Properties of Rubber Compound

The effects of the various fillers types and filler loading on the rubber compound cure properties were investigated. The completed datas of all fillers studied in the rubber compound formulations are summarized in Table 4.2.

Table 4.2 Cure properties of rubber compound.

Rubber compound	Max. Torque (dNm)	Min. Torque (dNm)	Scorch time (t_{s2}) (min)	Cure time (t_{90}) (min)
Mix 1	50.5	4.3	5.0	9.5
Mix 2	41.8	3.3	5.0	10.0
Mix 3	48.3	12.0	2.2	2.2
Mix 4	81.3	14.1	2.2	8.1
Mix 5	85.1	13.2	1.8	7.5
Mix 6	72.2	22.1	5.5	16.2
Mix 7	63.5	35.7	5.2	22.3
Mix 8	62.3	32.2	5.4	25.0
Mix 9	68.2	8.3	2.4	6.4
Mix 10	61.1	6.2	2.4	6.5
Mix 11	62.4	10.8	2.4	7.4
Mix 12	57.2	9.8	2.5	8.3

The data showed that for the same filler type, e.g. carbon black (Mix 3-Mix 5) and precipitated silica (Mix 6-Mix 8), in rubber compounds, the increasing surface area and smaller particle size of filled NR demonstrate shorter cure time and higher minimum and maximum torque. It can be seen that the addition of N110 in NR compound (Mix 5) has the lowest cure time for carbon black-filled NR. Conversely, the addition of Hi-Sil927 in NR compound (Mix 8) has the highest cure time for precipitated silica-filled NR because its surface is acidic activity which retards sulfur vulcanisation. For the same surface area of filler, the carbon black-filled NR compound (Mix 4) showed shorter cure time than that of precipitated silica-filled NR compound (Mix 6). Since sulfur vulcanisation is accelerated by alkaline materials but it is retarded by acids. This is explained by the acidic surface

of silica which is capable to retard sulfur vulcanisation while the surface of carbon black is well suited to hydrocarbon elastomers or is more compatible with NR. (Wagner, M. P.,1976 and Donnet, J-B.,1998). The cure time of gypsum-filled NR compound is quite high when it is compared to carbon black-filled NR compound due to the low nitrogen BET surface area.

Compounds no. 9-12 (Mix 9-12) contain the partial replacement of carbon black with gypsum and silica-filled NR compounds. These compound performances are compared to that of (only) carbon black-filled NR (Mix 5). Their minimum and maximum torques become lower and cure time becomes shorter especially the compound no. 12 (Mix 12) because of the increasing amount of precipitated silica. However, the change in cure properties is acceptable since there is only small replacement of loading of gypsum and precipitated silica.

4.3 Mechanical Properties of Rubber Compound

4.3.1 Effect of Filler Type

The effect of filler type on the mechanical properties of filled NR compounds were shown in Table 4.3.

Table 4.3 Mechanical properties of filled rubber compound.

Property	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7	Mix 8
Tensile strength (MPa)	19.33	20.57	26.58	27.78	28.96	13.36	12.75	11.79
Elongation at break (%)	763	617	560	546	524	551	557	577
300% Modulus (MPa)	3.45	4.17	11.39	14.92	16.54	5.00	5.02	4.23
Abrasion loss (mm ³)	81.01	78.13	48.31	43.6	43.0	65.91	75.97	84.03
Resilience (%)	80.5	77.0	47.0	48.31	47.89	49.9	48.1	46.3
Hardness, Shore A	39	49	69	69	71	68	70	70

A comparative study of the cured filled NR shows that fillers improve the mechanical properties. From Table 4.3, the results showed that the tensile strength of filled NR compounds increased with increasing nitrogen BET surface area exceptionally the precipitated silica-NR compounds (Mix 6-8). Compound no.5 (Mix 5) had the highest tensile strength in carbon black-filled NR compounds. Additionally, the interaction of strain crystallization and small particle size of filler in rubber are supported these results. Upon applying a stress, the small particle fillers are effectively taking up the slack in the crosslinked chains permitting a greater

degree of crystallization. In the similar nitrogen surface area of fillers of rubber compounds, compound no.4 (Mix 4) had higher modulus and tensile strength than that of compound no.6 (Mix 6) because the surface activity of carbon black is more compatibility with NR than that of silica surface. Precipitated silica-filled NR compounds exhibit similar elongation at break as that of carbon black-filled NR compounds. For these results, it can be summarized that, in case of carbon black-filled NR, tensile strength, modulus, hardness, and abrasion resistance data show a maximum value with highest surface area of carbon black filler since it seems to have better interaction and the highest pseudo-crosslink points density (Pal, P. K. *et al*, 1982). Hardness and elongation at break and resilience show the maximum value with highest surface area of silica in silica-filled NR (Bice, J-A. E. *et al*, 1997). Gypsum-filled NR shows the moderate increased in all properties but it shows the highest degree of resilience and elongation at break although its modulus and hardness are the lowest. These results can be explained considering that the physico-mechanical properties of vulcanisates depend on the filler characteristics as well as on polymer properties, chemical composition, operational condition and adhesion degree (Thammathadanukul, V.,1996). The most important filler characteristics are size, shape, specific surface area and combination of size distribution and shape. The filler used in this work presented very different primary characteristics, as can be seen in Table 4.1. High surface area, associated with the small diameter, and high-energy surface due to the functional groups, leads to a better interaction between filler and the polymer. Hence, better mechanical properties of the compound can be expected when the carbon black is used.

4.3.2 Effect of Mixed Filler and Filler Loading

Compound no. 9-12 (Mix 9-12) are the partial replacement of carbon black with gypsum and silica-filled NR compounds and their mechanical properties are displayed in the Table 4.4.

There was a former study about the effect of hysteresis from carbon black in rubber compounds done by Byers, J. T., and Patel, A. C., 1983. This work revealed that besides contributing the reinforcement necessary for good compound performance, adding carbon black also reduce the cost of compound. In recent years, the cost of the carbon black compound has increased dramatically due to its dependence on the petroleum sources for hydrocarbon feedstock and the energy that is consumed during its manufacture. Today, carbon black is no longer a low cost filler, but it is still a very important reinforcing agent that contributes the strength to polymer used in tire compounds. Unfortunately, adding carbon black also contributes to increased hysteresis-which make compromise a necessary. Therefore, the proper utilization of carbon black to obtained the maximum benefit is very important.

Table 4.4 Mechanical properties of filled rubber compound with only carbon black and with mixed filler.

Property	Mix 5	Mix 9	Mix 10	Mix 11	Mix 12
Tensile strength (MPa)	28.96	27.43	26.02	23.22	20.09
Elongation at break (%)	524	573	584	602	624
300% Modulus (MPa)	16.54	10.17	8.20	7.97	5.54
Abrasion loss (mm ³)	43	48.31	57.97	49.60	70.07
Resilience (%)	47.89	47.9	48.6	49.04	49.46
Hardness, Shore A	71	63	61	57	52
tan δ @ 60 °C	0.0927	0.0687	0.0290	0.0899	0.0582

From Table 4.4, these compound performances in all properties are compared to those of (only) carbon black-filled NR. It suggests that partial replacing carbon black with gypsum is relatively small enough to maintain high value of mechanical stress or slightly lower than that of pure carbon black-filled NR but too small to significantly bring up resilience. With gypsum, elongation at break is longer but abrasion loss increases. With increasing silica, tensile strength becomes poor and modulus reduces to half of that of carbon black-filled NR but elongation at break and resilience turn to increase. Silica causes increase in abrasion loss and reduces hardness due to poor adhesion to rubber. Therefore, the possibility to improve the mechanical properties by mixed filler depends not only on the filler types, but also appears to depend upon the filler content. It is interesting to note that at 60 °C (working temperature) the loss tangent or loss energy (tan δ), which is directly proportional to the heat build up and rolling resistance, decreased with increasing the loading of gypsum and precipitated silica in compound no.10 (Mix 10) and no.12 (Mix 12), respectively (Maingam, B.,

1994 and Bice. J-A. E., 1997). The results suggest that water existing as dihydrated form in the molecular structure ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) of gypsum or physisorp in silica can contribute to decrease heat build up in rubber compound. This brings the clue why silica filled-NR compounds exhibit the reduction in rolling resistance. In other words, heat build up is tempered by water adsorped in silica. The hydarted form of water in gypsum ensures the exist of water and thus more effective to reduce heat build up. In turn, water, especially in physisorp form, may be the cause of lowering modulus and hardness since it can soften the filler.