

Comparison of Properties of Natural Rubber Compounds with Various Fillers

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One of the most important phenomena in rubber science is the reinforcement by rigid entities such as carbon black, clays, silicates and calcium carbonate. Thus, these fillers are added to rubber formulations to optimise properties that meet a given service application or a set of performance parameters.

In this study, it was observed that the degree of reinforcement by addition of fillers depended on the filler characteristics which in turn affected the strength of the rubber:filler interaction. The two main filler characteristics that affected reinforcement were the filler particle size and surface activity. The reinforcing effect of starch was considerably lower than that of carbon black due to its large particle size and its low dispersive component of surface energy.

Key words: reinforcement; rubber; strength; starch; calcium carbonate; silica clays; carbon black

In recent years, there has been a growing interest in renewable resources and recyclable new materials available at a competitive price. The potential benefits of using naturally occurring materials are many. The use of renewable, rather than petrochemical resources, will extend the non-renewable petrochemical supplies. It is also possible that less energy will be required to produce and process the biomaterials, so reducing carbon dioxide release by energy production and hence, reducing global warming. Biodegradability is an additional benefit of many renewable biological sources of polymers.

It is possible that the world's agriculture industry could produce sufficient material

that could be used as a renewable resource for polymer and filler feed stock. Agriculture offers a broad range of commodities, including trees, crops, farm and marine animals, that have many uses. Plant based materials have been used traditionally for food and feed and are increasingly being used in pharmaceuticals. The three major plant-based polymers are protein, oil and carbohydrates (starch and cellulose).

With the change in emphasis to more biodegradable packaging material and with the concern that the raw material for industrial polymers should be made from cheap renewable resources, starch has dominated commercial development in this area¹. Hence, it is possible

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that starch could be used as a renewable filler in rubber compounds.

Fillers which are commonly used in rubber compounding include carbon black and mineral types such as silica, calcium carbonate (whiting) and clay. Fillers are used as a reinforcement or a cheapening aid for rubber. Fillers can be divided into three categories, reinforcing, semi-reinforcing and non-reinforcing. There is no definite definition of a reinforcing filler, but it is a filler which generally increases stiffness and improves failure properties (tensile strength, tear resistance and abrasion resistance) of the final vulcanisate. The most commonly used reinforcing fillers are carbon black and silica.

Non-reinforcing fillers may be used to improve processing and to reduce compound cost. Examples of non-reinforcing fillers are clay, mica, talc and calcium carbonate. There are three characteristics, which determine the reinforcing capability of a filler, particle size, particle shape, and surface activity².

The specific activity of the filler is determined by the physical and chemical nature of the filler surface in relation to that of the elastomer. Non-polar fillers are best suited to non-polar elastomers; polar fillers work best in polar elastomers. Beyond this, general chemical compatibility is the potential for specific interaction between the elastomer and active sites on the filler surfaces.

An attempt to quantify the role of filler surface chemistry is to consider the so-called 'surface activity', which may be assumed to be assessed through the surface energy, γ_s , which consists of two components² i.e.:

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad \dots 1$$

where γ_s^d and γ_s^p are the so-called dispersive and polar (or specific) components, respectively.

Such properties can be measured by contact angle measurement and Inverse Gas Chromatography (IGC) in which the filler to be characterised is used as the stationary phase and the injected solute is the so-called probe².

In this study, the aim was to compare the performance of starch as a filler with other common fillers such as silica (VN2)[®], precipitated calcium carbonate and carbon black (N660), at the same volume loading.

Experimental and Sample Preparation

Natural Rubber (SMR L) and corn starch were supplied by the Malaysian Rubber Board (MRB) and National Starch and Chemical Company. The compound was based on a simple engine mount compound filled with 49 parts per hundred rubber (p.h.r.) carbon black. Compounds filled to the same volume loading with silica (54 p.h.r.) and calcium carbonate (73 p.h.r.) were also prepared for comparison purposes as shown in *Table 1*.

Mixing of the compounds was carried out in a Francis Shaw A KI Intermix while the viscosity and curing characteristics were assessed by Mooney Viscometer and Oscillating Disc Curemeter at 100°C and 150°C respectively. The compounds were cured with an electrically heated press to 90% cure at 150°C as obtained from the rheometer curemeter.

Measurement of Dynamic Properties

In this study the dynamic rheology, of the uncured compounds was analysed using a rubber processing analyser (RPA 2000) Mosanto, USA, with a strain sweep of 1 – 100% at 100°C and at a frequency of 1 Hz.

TABLE 1. FORMULATION OF STARCH, CARBON BLACK, SILICA AND CALCIUM CARBONATE FILLED NR COMPOUNDS.

Material (p.h.r.)	Unfilled NR	NR/Starch	NR/Carbon Black	NR/Silica	NR/CaCO ₃
Rubber (SMR L)	100	100	100	100	100
Zinc Oxide	5	5	5	5	5
Stearic Acid	2	2	2	2	2
Starch	—	36	—	—	—
*Carbon Black N660	—	—	49	—	—
**Silica VN2 [®]	—	—	—	54	—
***Precipitated CaCO ₃	—	—	—	—	73
Anti Ozone Wax	2	2	2	2	2
6 PPD	1.5	1.5	1.5	1.5	1.5
TMQ	1	1	1	1	1
TBBS	0.7	0.7	0.7	0.7	0.7
TMTD	0.5	0.5	0.5	0.5	0.5
Sulphur	1.7	1.7	1.7	1.7	1.7

* Carbon Black N660 (Sterling V N660 from Cabot Company)

** Silica VN2[®] (Ultrasil VN2[®] from Degussa Corporation)

*** Precipitated Calcium Carbonate from Longcliff LTD

6 PPD - N-(1,3-Dimethylbutyl)-N-phenyl-*p*-phenylenediamine

TMQ - 2,2,4- Trimethyl- 1,2- dihydroquinoline polymerised

TBBS - N – tert –butyl-2 benzothiazolsulfenamide

TMTD - Tetramethylthiuram disulfide

Measurement of Physical Properties

The stress strain properties and tear strength of the compounds were measured by using a Hounsfield 500L testing machine with a cross – head speed of 500 mm/min in accordance to *BS 903:Part A2*, while the hardness of the compounds was measured by the Shore Type A Durometer according to *BS ISO 7619-1:2004*. Compression set was determined according to *ISO815:1991*. For the rebound resilience test, a Wallace Dunlop tripsometer was used to measure the rebound resilience according to *BS 903: Part A8*.

SEM Studies

Examination of the tensile fracture surface was carried out using a Leica Cambridge scanning electron microscope. The surfaces were examined after first sputtered coating with gold to avoid electrostatic charging and poor image resolution.

Measurement of Surface Energy

The surface energy of the natural rubber and starch was estimated by the measurement

of the contact angle formed at a three - phase interface with various liquids which gives the polar, γ_s^p and dispersive components, γ_s^d . The fluids used were triply distilled water and Diiodomethane (DIM). At least 10 drops were placed on each sample by using a computer controlled dispensing unit in a Contact Angle System. The software was also used to collect, store and process the contact angle data, θ_{water} and $\theta_{\text{diiodomethane}}$ to calculate the dispersive and polar components of the surface energy.

Measurement of Rubber Filler Interaction

The measurement of the surface activity and rubber filler interaction was determined by the bound rubber test. The solvent used for the bound rubber determination was toluene. For the determination, 0.23 g of uncured rubber compound was placed individually in 60 mL of the solvent in labelled bottles and allowed to swell until the equilibrium state was obtained. The solvent was removed after this period and the samples were then dried in a fume chamber for 9 h. The samples were further dried in an oven at 85°C for 24 h, and allowed to stand for an extra 24 h at 25°C before they were re-weighed.

The amount of bound rubber (in terms of % of initial rubber content of the compound) is given by :-

$$BDR (\%) = \frac{m_0 - (m_2 - m_3)}{m_0} \times 100$$

where;

m_0 = weight of rubber in sample

m_2 = weight of the unextracted sample

m_3 = weight of the dried and extracted sample

$m_0 = m_2 \times 100 / \text{cpd}$

cpd = sum of all ingredients in the formulation (in p.h.r.)

RESULTS AND DISCUSSION

Filler Characteristics

Table 2 shows the average particle sizes of the fillers used in this investigation. Due to the very small particle size, aggregation and agglomeration can be observed in carbon black, silica and calcium carbonate filler (Figure 1a, c and d). Starch has a relatively large particle size in comparison with the other fillers, as shown in Figure 1b. Hence, since a large particle size means a smaller surface area for interaction with the rubber, it is expected that the starch filled rubber will have relatively poor strength and stiffness.

Apart from the particle size, the particle shape and surface roughness can also affect rubber reinforcement. Starch particles being roughly spherical or polygonal, smooth surfaces and lack of porosity, so there is little or no trapped rubber present to increase the effective filler concentration (Figure 1b). Hence there is likely to be little increase in reinforcement due to geometric factors and filler size.

The contact angles of liquid on natural rubber are listed in Table 3. The values listed were the average of three contact angle measurements. The contact angles of the liquids on the material surface depend on the surface energy of the liquid in relation to that of the solid. In the case of natural rubber, a greater contact angle was obtained with water than with Diiodomethane (DIM). The greater contact angle obtained with water indicated greater cohesion between the molecules of the liquid than the molecular adhesion between liquid and solid. The strong hydrogen bonding in water was responsible for its high cohesion and only ionic and highly polar surfaces that offer equivalent or even stronger bonding interactions would be wetted very effectively by water.

TABLE 2. AVERAGE PARTICLE SIZE OF THE FILLERS USED IN THE EXPERIMENT

Filler	Average Primary Particle Size (nm)
Precipitated Calcium Carbonate	20 – 400 ³
Starch	15000 – 20000
Silica (VN2) [®]	20 – 25 ³
Carbon Black (N660)	61 – 100 ⁴

TABLE 3. THE CONTACT ANGLE MEASUREMENT AND SURFACE ENERGY OF NATURAL RUBBER AND STARCH

Sample	Θ (degree)				γ_s^p mN/m	γ_s^d mN/m	γ_s mN/m
	Diidomethane	Water	Formamide	Glycerol			
Natural rubber	71.10	89.50	–	–	4.24	22.27	26.51
Starch ⁵	35.00	25.00	31.00	10.00	38.50	25.20	59.70

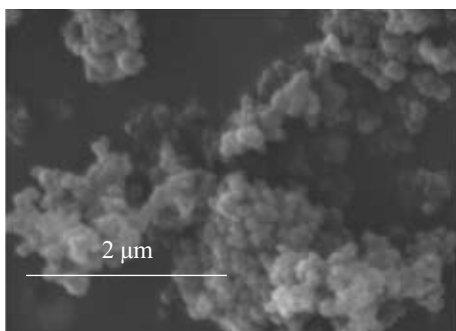


Figure 1a. SEM micrograph of Precipitated Calcium Carbonate.

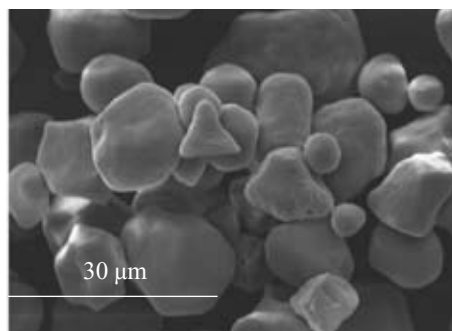


Figure 1b. SEM micrograph of Starch.

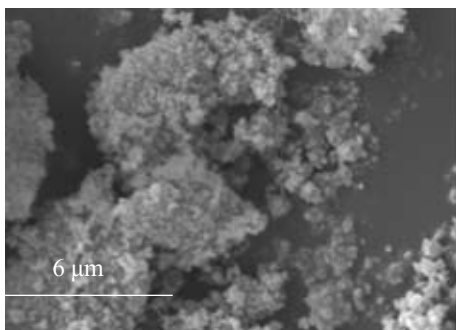
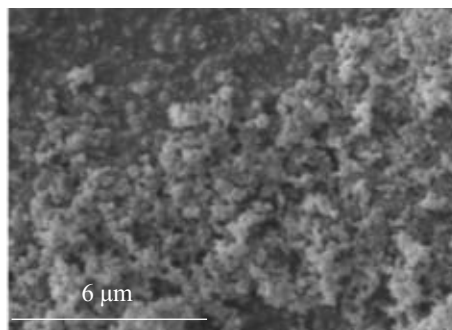

Figure 1c. SEM micrograph of Silica VN2[®].


Figure 1d. SEM micrograph of Carbon Black N660.

Since NR is non-polar, it cannot interact in this way with water, hence the high contact angle. The relatively low contact angle observed for the DIM on NR indicates that there is greater molecular adhesion between non polar rubber and non polar DIM liquid than the cohesion between the molecules of the DIM. The stronger adhesion between the liquid and solid will tend to minimize the contact angle and wet the solid sample. Generally, the high dispersive component (γ_s^d) of the surface energy of natural rubber indicates that a relatively large interaction can be obtained with non polar materials or substances.

Attempts were made to measure the surface energy of starch by using the contact angle method on a pellet of compacted starch. It was observed, however, that a rapid absorption of the water inside the compact occurred immediately after the deposition of the water drop. *Figure 2a* shows the phenomenon of capillary action in a porous starch pellet prepared for the measurement. Initially, water was absorbed quickly into the porosity (*Figure 2b*). Then swelling occurred, resulting in a mushroom-like structure appearing on the top of the starch surface (*Figure 2c*). Thus the contact angle measurement is dominated by capillary absorption, rather than being a measure of surface energy. The absorption behaviour is likely to be related to the intergranular porosity, holes and cracks in the compacted material, as observed by Roman *et al.*⁶ in his compaction study in pentosan and wheat flour. For this reason, the correct surface energy could not be determined for any of the powders such as carbon black, silica and calcium carbonate by contact angle measurement. However, Carvalho *et al.*⁵ managed to measure the surface energy of starch by preparing a non-porous sample of starch. The starch was initially processed at 150 – 160°C in a Haake Rheomix 600 batch mixer equipped with roller rotors operating at 50 r.p.m. for 6 min and pressed at 160°C.

The mixing, plasticising and pressing at a high temperature reduces the porosity. In his experiment, Carvalho *et al.*⁵ found that the surface energy of starch was 59.70 mN/m with the dispersive component 25.20 mN/m and 38.20 mN/m for the polar component. It is clear that the starch is much more polar than natural rubber, and would be expected to have higher adhesion to a polar rubber with a higher specific component in its surface energy, such as epoxidised natural rubber or nitrile rubber.

Given the problems of measuring contact angles for powders, a more reliable surface energy can be obtained from the Inverse Gas Chromatography technique which is widely used nowadays⁷. In this technique, the material to be examined is placed in a chromatographic column and studied using test solutes. The test solutes are injected into the flow of carrier gas and transported over the surface of the material. The retention time, which is influenced by interactions between the solute and stationary phase, is then used to determine the surface energy⁷. Literature values for the surface energy and the dispersive and polar components for the starch, carbon black, calcium carbonate and silica are presented in *Table 4*.

To date, there is no complete compilation of polar and dispersive components for the individual fillers. The data in *Table 4* shows some of the surface characteristics of the fillers measured by the Inverse Gas Chromatography technique^{8–12}. For carbon black, the dispersive component of surface energy is higher than other fillers, due to the fact that there are relatively few polar groups on the surface. It was estimated that for a typical furnace black, 95% of the surface is available for Van der Waals interactions, while not more than 5% of the surface corresponds to polar sites¹³. The relative size of the components of surface energy in *Table 4*, suggests that the physical interaction between carbon black and non-

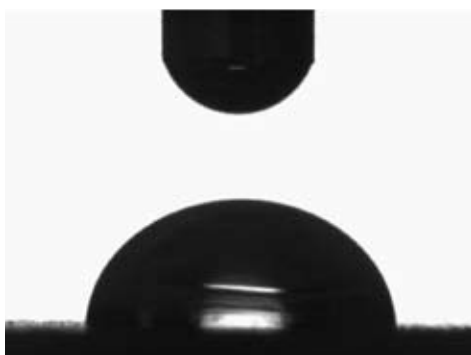


Figure 2a. $t = 0$ second.



Figure 2b. $t = 1.5$ seconds.



Figure 2c. $t = 2.5$ seconds.

Figure 2. Contact angle measurement of water on a compacted starch pellet.

TABLE 4. DISPERSIVE COMPONENT AND SPECIFIC INTERACTION OF THE SURFACE ENERGY OF FILLERS BY IGC TECHNIQUE

Sample	γ_s^d at (mJ/m ²) Dispersive Component	I^{sp*} MeCN at 150°C (mJ/m ²) Specific Component
Starch ⁹	32.5 (35°C)	—
Carbon ¹ Black N660 ^{10,11}	124.7 (20°C)	158.0
Ultrasil VN2® (Silica) ^{11,12}	22.9 (20°C)	252.0
Precipitated Calcium Carbonate ⁸	84.2 (20°C)	—

I^{sp*} - Specific components of surface energy with polar probe acetonitrile (MeCN)

polar or low polarity rubbers will be much stronger than for the other fillers. The next highest dispersive component is observed for the calcium carbonate, suggesting that a greater interaction could be obtained with calcium carbonate in NR than with silica or starch.

On the other hand, silica has a much greater specific component of surface energy, due to the hydrogen bond interaction between the –CN group of the polar probe and silanol groups¹¹. By contrast, the interaction of polar rubbers with silica is likely to be stronger than with carbon black, although the overall interaction would be dependent on the balance of both specific and dispersive components.

Bound Rubber Content

The amount of bound rubber for a given elastomer depends on a number of factors such as surface area, structure and surface energy of the filler and the dispersion state. *Figure 3* shows that the highest bound rubber content is for carbon black. This might be expected since carbon black has the highest dispersive component of surface energy of all the fillers and so would be expected to interact most strongly with the non-polar NR (*Table 3*). However, it is surprising that the next highest bound rubber content is for silica, which has the lowest dispersive component of surface energy (*Table 4*). The reason for the higher than expected bound rubber content is likely to be poor dispersion of the silica and the presence of agglomerates that physically “trap” rubber (*Figure 6*). Poor dispersion is confirmed by the SEM micrograph in *Figure 4*, which shows the presence of agglomerates and non uniform silica dispersion in the NR compound. Agglomeration of the silica is likely because of its very small particle size and very high specific component of surface energy, which results in strong inter-particulate interaction.

Wolff¹⁰ also found a lower bound rubber content for silica filled than carbon black filled natural rubber compounds. He attributed the lower bound rubber content of the silica filled compounds to strong filler:filler interaction and relatively weak filler rubber interactions in comparison to the black filled compounds. Calcium carbonate has a lower bound rubber content than the silica, which may be due to less agglomeration caused by a larger average particle size and possibly lower specific surface energy (this value not known). Starch has the lowest bound rubber content due to both its low dispersive component of surface energy and large particle size, which would expose a lower surface area for interaction with the rubber and minimise agglomeration.

Viscoelastic Properties of the Uncured Compound

Many properties of uncured, filled compounds can provide useful information about the rubber:filler interaction, without the complication of chemical crosslinking that is introduced during curing.

The influence of fillers on the dynamic modulus of the uncured compound can be seen in *Figure 5*. It is observed that storage modulus increases with addition of silica, carbon black, calcium carbonate and starch. While the storage modulus of the unfilled compound is insignificantly changed upon increasing strain amplitude, it decreases for the filled rubber, showing typical non-linear behaviour. The decrease in modulus with increase in strain was attributed by Payne¹⁴ to the structure of fillers and may be visualised as filler – filler linkage of physical nature which are broken down by straining. The structure was further clarified by Medalia¹⁵ that interaggregation association by physical forces and not the structure or aggregate bulkiness as generally termed in the rubber industry. It is understandable that the

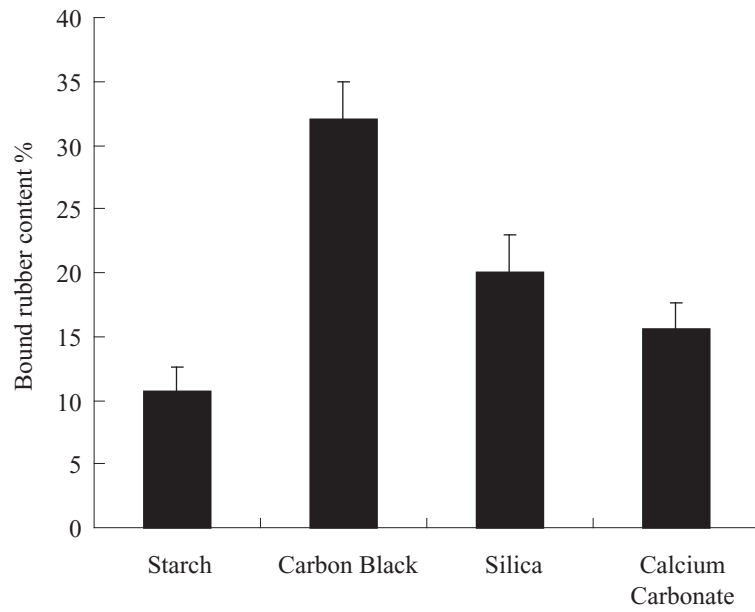


Figure 3. Effect of fillers on bound rubber content of NR.

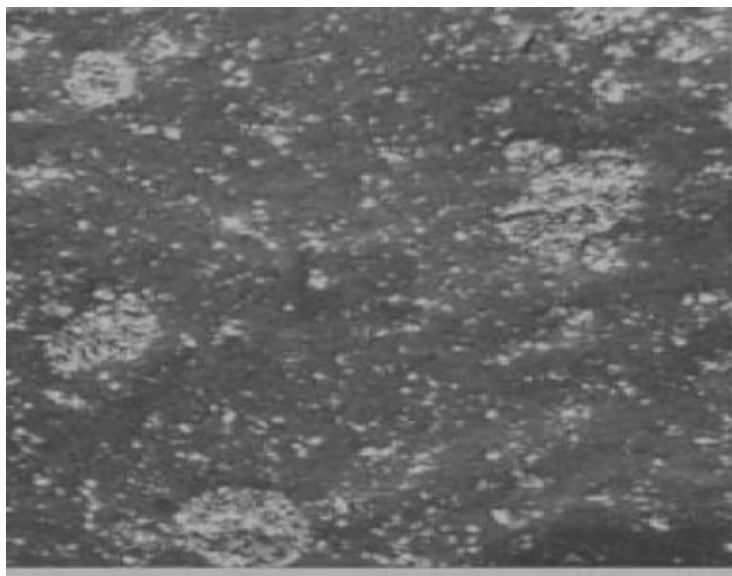


Figure 4. SEM image of Cut Surface of NR/Silica Compound.

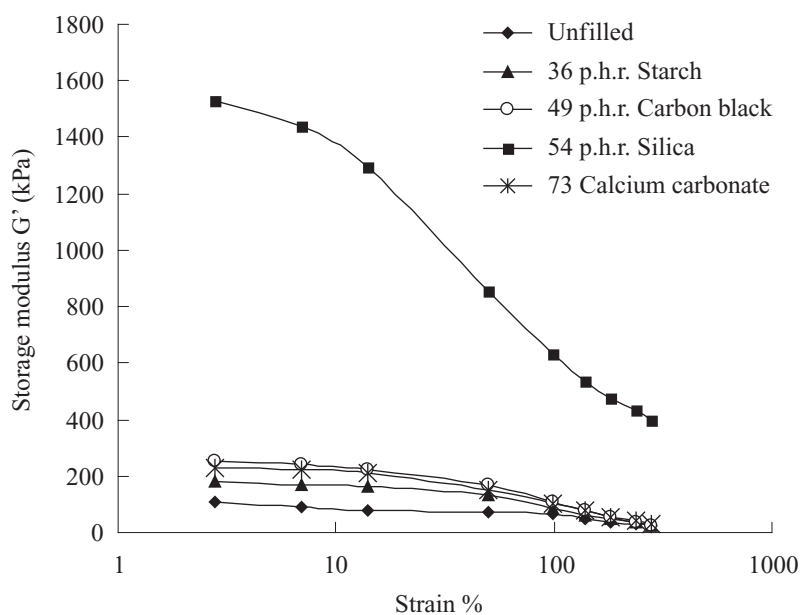


Figure 5. Strain dependence of G' of different fillers with similar volume loading.

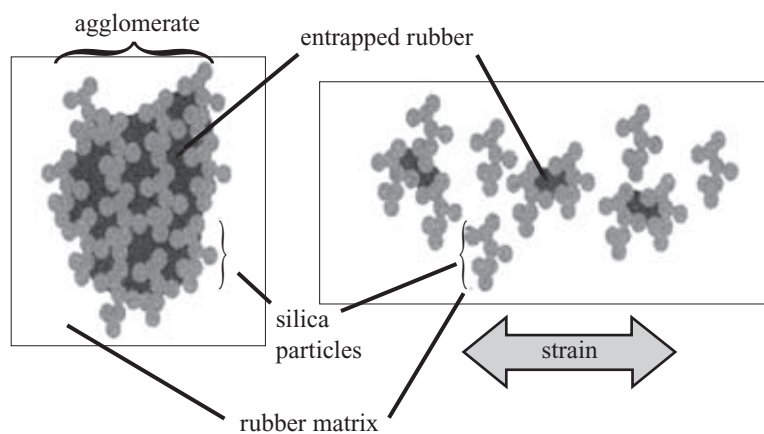


Figure 6. Immobilisation of rubber matrix due to agglomeration².

rubber trapped or caged in the filler network or agglomerates would be at least partially “dead”, losing its identity as an elastomer and behaving as a filler in terms of stress-strain properties.

Therefore, the effective volume of the polymer bearing the stresses imposed upon the sample is reduced by filler networking, resulting in increased modulus which is governed primarily by the filler concentration. The breakdown of the filler network by increasing strain amplitude would release the trapped rubber so that the effective filler volume fraction and hence the modulus would decrease. This mechanism suggests that the Payne effect can serve as a measure of filler networking which originates from filler-filler interaction as well as polymer-filler interaction. This observation can be verified by the changes in effective volume of filler upon filler loading and their strain dependence.

Figure 5 shows that the highest modulus and greatest Payne effect are obtained with silica (VN2)[®]. The results discussed in the previous two sections would suggest that the high dynamic stiffness is due to strong filler: filler interactions leading to agglomeration and increase in modulus by immobilising rubber between particles thus increasing the effective volume fraction of the filler (*Figure 6*). However, as the strain increases, some of the silica agglomerates are broken down and the trapped rubber is released. Hence, a lower modulus is obtained at higher strain as shown in *Figure 5*.

The compound containing carbon black (N660) has the greatest stiffness of the remaining compounds. This is attributed to relatively strong interactions between the rubber and the carbon black, as seen in the results of the bound rubber test and deduced from the dispersive component of surface energy.

The lowest modulus is for the starch filled compound and this could be due to both weak rubber:filler and weak filler:filler interactions, which attributed to its surface characteristics. Neither agglomerations nor the high dispersive component of the surface energy could contribute to high modulus and strong rubber filler interaction. Although starch might be expected to exhibit a high filler:filler interaction *via* hydrogen bonding, the large particle size minimises the effect.

The effect of a strong filler:filler interaction in the silica filled compound can also be observed in the high viscous modulus or loss modulus (G'') and viscosity values in *Figure 7* and *8*. Payne¹⁶ believed that the energy loss during dynamic strain is substantially controlled by the breakdown and reformation of the aggregate contacts. In fact, Kraus derived an equation for viscous modulus based on the breakage rate of interaggregate contacts and the rate of reagglomeration which is related to the strain as mentioned in Men Jiao Wang report¹⁷. He also claimed that once the strain is high enough, the filler:filler network is destroyed to such an extent that cannot be reconstructed in the dynamic strain cycle. Such breakdown of the filler network is responsible for the decrease in viscous modulus observed in *Figure 7* for all the filled compounds, except the silica filled one.

The viscosity values of the compounds shown in *Figure 8* follow the same pattern as the dynamic viscous modulus. In the case of the viscosity measurement, the continuous deformation will result in filler – filler network breakdown, but any strong filler:filler interactions are likely to result in agglomerates that will increase viscosity by immobilising the rubber.

Figure 9 gives the $\tan \delta$ for the same compounds. This figure shows that the breakdown of the inter-aggregate bonding

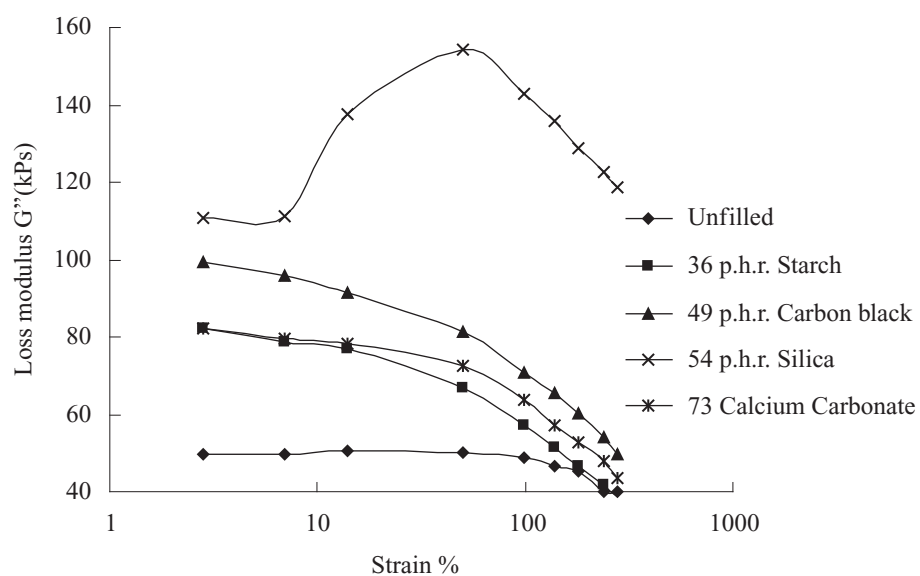


Figure 7. Strain dependence of G'' of different fillers with similar volume loading.

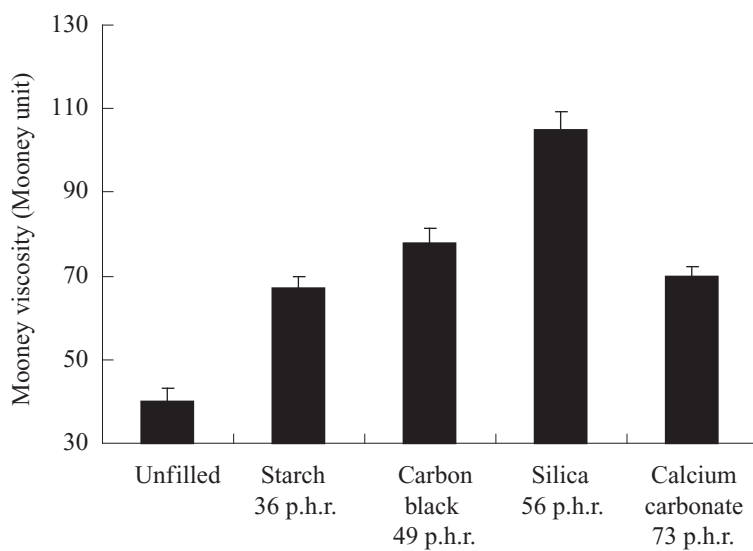


Figure 8. Effect of fillers on the compound viscosity.

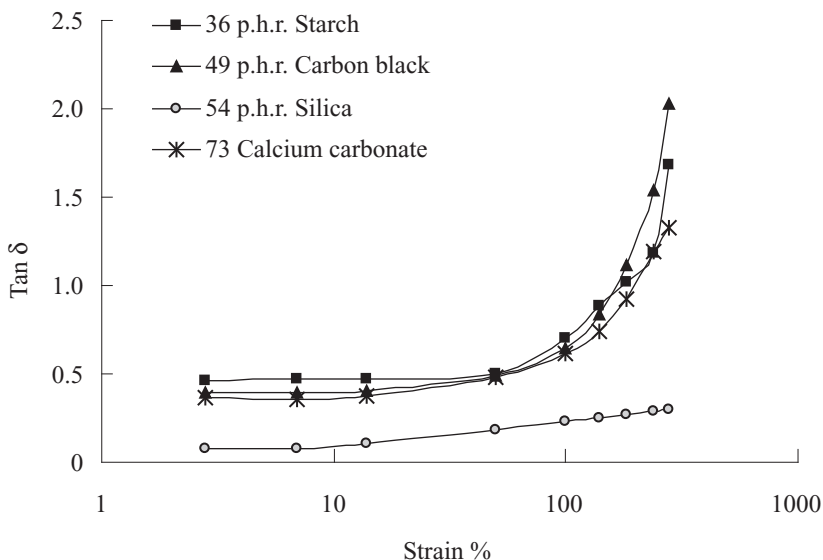


Figure 9 Strain dependence of $\tan \delta$ of different fillers with similar volume loading.

of the silica over a broad range of strain amplitudes indicates that the silica:silica interaction differs strongly from the Van der Waals bonding of carbon black aggregates.

The results indicate that, the surface activity and particle size are the predominant factors affecting the strength of the filler:filler and filler:rubber interactions.

Cure Properties

The cure properties of the filled compound are presented in Table 5. Table 5 shows that the highest minimum torque is observed for the silica filled compound, which correlates with the highest viscosity as shown in Figure 8. Sombatsompop *et al.*¹⁸ discovered that a higher minimum torque was obtained for a silica filled NR compound than for one filled

with fly ash. As with the loss modulus and viscosity results, the high value was attributed to a silica filler network or silica aggregates formed as a result of interparticulate hydrogen bonding. The relatively low torque ($M_H - M_L$) observed with starch and calcium carbonate is due to the relatively weak filler:filler and filler:rubber interactions as discussed in the previous section.

Table 5 shows that the silica filled compound exhibits the longest optimum cure and scorch times, which may be due to the adsorption of accelerator on the silica surface¹⁹⁻²¹. Since the silica surface is acidic, due to its silanol groups, it forms strong hydrogen bonds with the amide groups on basic accelerators such as CBS and TBBS. A second more important reason is that sulphur cure is an alkaline process, which is retarded and ultimately totally blocked by the acidity of the silanol groups. Due to the

TABLE 5. CURE PROPERTIES OF FILLED NR COMPOUNDS

	Unfilled	Starch	Carbon Black	Silica	Calcium Carbonate
Cure time, t_{90} (min)	8.17	6.05	6.31	21.15	5.46
Scorch time, t_{s2} (min)	4.56	4.09	4.11	8.01	4.23
Max. torque, M_H (dNm)	58.24	65.51	85.4	87.33	73.43
Min. torque, M_L (dNm)	13.7	15.54	22.7	28.69	21.59
$M_H - M_L$ (dNm)	44.5	49.9	62.7	58.64	51.84

adsorption, the availability of the accelerator for vulcanisation will be decreased.

Choi *et al.*²² speculated that the situation becomes worse when the absorption of the CBS on the silica tends to accelerate the dissociation of the N-S bond of CBS and causes a lesser amount of CBS to be available for any crosslinking reaction to take place, as shown in *Figure 10*. In another study, he also discovered that for a silica filled compound without coupling agent, reversion increases with TBBS accelerator content²³.

The difference between the maximum torque and minimum torque in the rheograph is known as delta torque (Δ Torque) and is generally related to the crosslink density. Despite the aggregation of silica, which resulted in a high minimum torque, the delta torque value for the silica filled compound is lesser than that of the carbon black filled blend. It is likely that the absorption of curing agent on silica is responsible for the lower crosslink density.

Stress-Strain Properties of the Cured Compound

Hardness can be used as a measure of small strain stiffness. *Table 6* shows that the hardness is greatest for the silica filled compound and as

with the properties of the uncured compound discussed previously, this is attributed to its strong filler network and agglomeration of the silica. The starch filled compound has the lowest hardness due to the weak interaction with the rubber and large particle size, as discussed earlier.

Figure 11 shows the tensile stress-strain properties of the compounds with different fillers. The stress of the carbon black and silica filled compounds are similar at elongations up to 100%. This is contrary to the hardness and dynamic modulus results, which indicate the silica compound is much stiffer than the others. The relatively lower stiffness of the silica filled compound observed in the tensile test may be due to a combination of poor dispersion and weak interaction between the silica and the rubber, which results in de-bonding. De-bonding would not be expected to occur at the low strains of the hardness test and is also less likely to occur under the shear deformation of the dynamic test.

Above 100% elongation, the tensile stress of the carbon black filled compound steadily increases with strain, due to the strong rubber: filler interaction and good dispersion. However, the silica filled compound breaks at very low elongations because of the poor dispersion of the silica and weak silica:rubber interaction. The agglomerates cause high stresses to

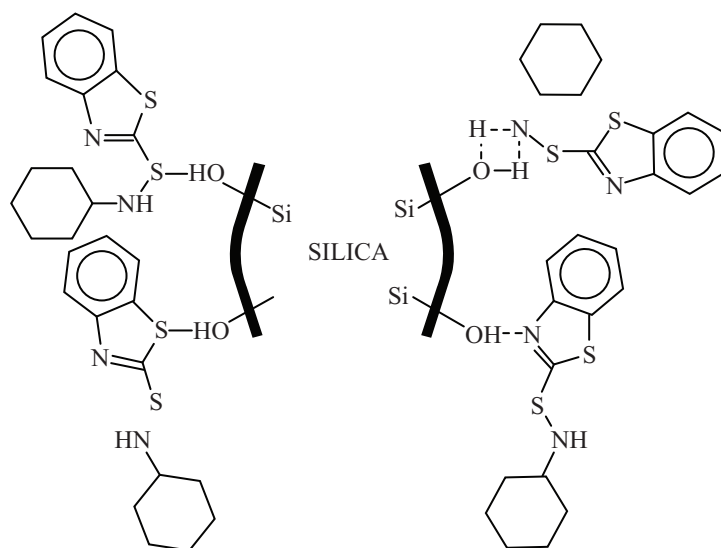


Figure 10. Dissociation of the N-S bond of CBS by hydrogen bonding with silica²².

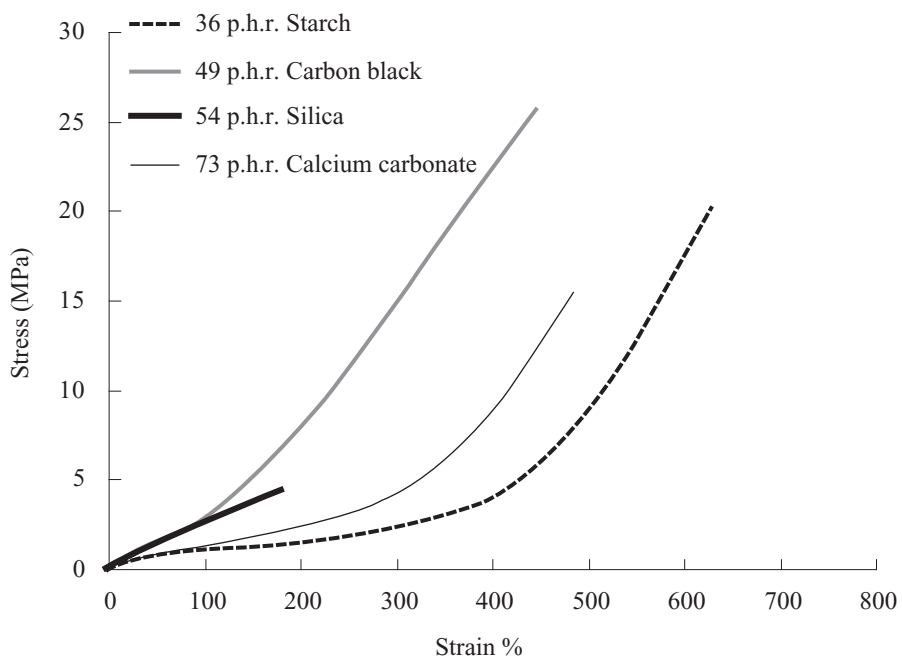


Figure 11. Effect of fillers on the tensile stress strain properties of the NR compound.

develop close to their surfaces and the weak interaction is likely to result in de-bonding and hence fracture initiation. As with the properties discussed in the previous sections, the calcium carbonate filled compound has generally low stiffness due to having a larger particle size than carbon black and silica as well as relatively weak interaction with the rubber. The starch filled compound has the lowest stiffness due to a weak interaction with the rubber and a particle size much larger than all the other fillers.

Despite the large difference in stiffness, the tensile strength is greater compared to the silica and calcium carbonate compound. Lower tensile strength is observed for the calcium carbonate and silica filled compounds, which may be due to the poor dispersion. *Figure 4* shows that in the case of the NR sample containing silica, the filler distribution is not uniform. Several agglomerates can be seen in this picture which could be sites of stress concentration, crack initiation and hence, result in low tensile strength.

In contrast to the tensile strength results, *Table 7* shows that the silica filled compound has the greatest tear strength. Yan *et al.*²⁴ also discovered that a silica filled NR compound had a higher tear strength and lower tensile strength than the one filled with carbon black. It is thought therefore, that dispersion is not the main factor that affects the tear strength. Perhaps the surface area and hysteresis are the most important factors in controlling the tear strength. In the case of crack propagation, the crack growth might be deviated due to strong filler:filler interaction or agglomeration.

Rebound Resilience

Table 7 shows that carbon black and silica filled compounds have a lower value of rebound resilience than the other compounds. According to Jacques²⁵ the incorporation of most particulate fillers into rubber leads to a reduction in resilience, particularly with the reinforcing fillers. The introduction of reinforcing filler reduces resilience or increases

TABLE 6. HARDNESS OF FILLED NR COMPOUNDS

Fillers	Hardness (Shore A)
Starch	50
Carbon Black	60
Silica	68
Calcium Carbonate	52

TABLE 7. PHYSICAL PROPERTIES OF THE CURED NR/FILLED COMPOUND

Fillers	Tear Strength (N/mm)	Resilience (%)
Starch	15.2 (± 3.2)	86.5 (± 0.8)
Carbon Black	30.8 (± 1.8)	60.1 (± 1.2)
Silica	60.5 (± 2.5)	69.3 (± 1.5)
Calcium Carbonate	22.8 (± 2.4)	87.2 (± 1.8)

hysteresis because of the energy consumed in polymer:filler friction and in dislodging polymer segments from the surface of an active filler. The greater rebound resilience of the compounds containing calcium carbonate and starch is due to the weaker rubber-filler interaction which means that less energy is dissipated by friction of the rubber on the filler surface.

CONCLUSIONS

- The reinforcing effect of starch is considerably lower than that of carbon black due to the large particle size of starch and its low dispersive component of surface energy. It is necessary to chemically or physically modify the surface of starch particles in order to increase the dispersability and activity of starch in the rubber compound.
- A consideration of surface energies suggests that starch will interact more strongly with elastomers containing polar groups.
- The agglomeration of silica in NR is caused by greater filler:filler interaction than rubber:filler interaction. The agglomeration leads to high stiffness and low tensile strength.
- Greater rubber:filler interaction in the carbon black filled NR contributes to good dispersion and a higher tensile strength than the silica filled NR.

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