

Variation Effect of Carbon-Silica Dual Phase Fillers on the Rheological and Mechanical Properties of Natural Rubber Matrix Composites

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Abstract: The effect of variation of Carbon-Silica Dual Phase Fillers (CSDPF) on the mechanical properties of natural rubber compounding was investigated. The natural rubber for the compounding process was sourced locally. Five different batches were prepared by varying the amount of carbon black and silica fillers present in them. These samples were subjected to different rheological and mechanical tests from where the samples with optimum rheological and mechanical properties were determined. It was found out that sample with higher proportion of carbon black followed by sample with equal amount of the carbon black and silica has the best rheological and mechanical properties. These observations were due to higher polymer-filler interactions and lower filler-filler interactions taking place in the compounds.

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1. Introduction

The pressure to meet the ever-more stringent requirement for increase in wear resistance, reduction in rolling resistance and improvement in wet skid resistance for tyres in general have been transferred to the filler supplies. These requirements can only be met by new fillers that can impact high tensile strength at high temperature and improved resilience of natural rubber compounds. It has been established that the wear resistance of filled rubber compounds is essentially determined by the filler characteristics, especially surface activity and morphology. High surface area carbon black with large interfacial area between fillers and the polymer generally shows high interaction with the hydrocarbon polymer used in tyres (Wang, et al,1991). It is also recognized that highly structured product generally gives a higher polymer- filler interaction when it is incorporated into the polymer (Wolff, et al ,1993).

There are increasing reports in the literature that significant improvements of multiple structural functions can be achieved with new hybrid multiscale composites which incorporate nanoscale reinforcements as well as conventional micron scale fibre or particle reinforcements. For example, while fibre-dominated properties (i.e., longitudinal tensile strength and elastic modulus) of conventional unidirectional polymer composites with micron size fibre reinforcements are excellent, the corresponding matrix-dominated transverse tensile strength and

longitudinal compressive strength properties are often poor. However, these traditionally poor properties can be significantly improved by (a) replacing the neat resin polymer matrix with a nanocomposite matrix, and/or by (b) growing nanoreinforcements like carbon nanotubes on the surface of the fibers (Vlasveld et al, 2005; Zhao et al, 2005; Uddin and Sun, 2008; Uddin and Sun, 2010; Liu et al, 2008).

Carbon black poses high surface area with concurrence of high surface activity, results in improved wear resistance in the practical loading range. This can be observed from the abrasion resistance of filled natural rubber compounds. Tyre rolling resistance has become a major concern during the last decade as for environmental issues and energy savings. For conventional carbon blacks there is generally a trade-off between wear resistance and rolling resistance. Carbon black impacts high abrasion resistance to the compound but such compound has low rolling resistance (Meng, et al, 2000)

Although, it has been reported that the application of silica in tyre compounds has not been successful due to its incompatibility with natural rubber but in the last few years, silica has been used with styrene butadiene rubber (SBR) in passenger tread compounds to improve rolling resistance and wet interaction. This source is attributed to its surface modification with coupling agents. Compared to carbon black, with similar surface area and structure, silica fillers show a very low polymer-filler interaction

and a strong tendency to agglomerate, forming a developed filler network in the compounds. This results in poor compound process ability, poor mechanical properties such as low tensile strength and abrasion resistance, and unacceptable dynamic properties (Wang, et al, 1999). However, surface modification with coupling agents such as bi-functional saline, bis- (3-triethoxysilypropyl)-tetrasulfane (TESPT) lowers the filler-filler interaction by covering the polar surface with organo-grafts, and enhances the polymer-filler through creation of chemical linkages between the filler surface and polymer chains (Wolff, et al, 1993).

The optimum fillers for natural rubber tread compounds are the combination of fillers that possess high polymer-filler and low filler-filler interactions. The former ensures higher abrasion resistance while the latter ensures low hysteresis, hence lower rolling resistance. In this regard, the carbon-silica dual phase fillers (CSDPF) provide the best balance of properties for natural rubber-based tyres applications⁸. These fillers, instead of containing typical 90-99% elemental carbon as in traditional carbon black with oxygen and hydrogen as minor constituents, there is silica phase finely distributed in the carbon phase.

The choice of proper curing system materials to accommodate the time required for mixing, forming, moulding and processing of the selected materials to form the product and at the same time minimized the time necessary to cure the material to obtain the optimal physical properties is the work of the compounder (Alkadasi et al, 2004).

This work was carried out to study the effect of the variation of carbon-silica proportions during natural rubber compounding. This was done with the aim of obtaining high polymer-filler and low filler-filler interactions in the hydrocarbon elastomers, compared to the conventional fillers used in tread compound and, hence enhancement of the rheological and mechanical properties of the final product.

2. Materials and Method

2.1. Materials

Materials employed in this research work include: Natural rubber, Peptone 66, Zinc Oxide, Stearic acid, Carbon black (N326), Silica (Si69), 2,2,4-Tri Methyl Dihydroquinoline (TMQ), Polyvinyl inhibitor (PVI) and Sulphur (insoluble sulphur).

2.2. Equipment

The equipments used are: Monsanto Rheometer, Monsanto Instron Machine, Two Roll Mill, Compression Moulding Machine, Tripsometer, Duraton, Mercer Gauge, Weighing Balance, Knife and Duraton 2000I Tensometer.

2.3. Method

The total mass of the compound prepared per batch was 600Kg. Five different batches were produced by varying the mass of the filler in the compound as shown in Table 1 below.

2.3.1. Mixing and Compounding

The mixing and compounding of the raw materials was carried out on a two rolling mill. After weighing, the natural rubber was charged into the mill for several minutes to reduced mastication and particle size of the rubber as well as increase cross linking density so that it will allow high polymer-filler dispersion. Peptone66, zinc oxide and stearic acid (activator) were added to the rubber compound after 20 minutes of mixing. After proper blending, the filler (either carbon black or silica or both depending on the batch to be produce) was introduced into the mill followed by the addition of TMQ, the accelerator (insoluble sulphur) and the polyvinyl inhibitor to complete the compounding process.

2.3.2. Material Testing

After compounding, samples were cut from each batch of the composites produced and various rheological property tests were carried out on the samples at the different stages of the production process. Mechanical tests were also carried out on the cured samples.

3. Result Analysis

3.1. Rheological properties

Rheological tests are carried out on uncured compounds to know whether the compound mix was carried out correctly and to also provide some information concerning the vulcanized product that will be produced after curing. Rheological properties are the properties that have to do with the flow of materials in their liquid states. These properties have a lot of influence on the properties that will ensue after the materials have been cured.

Cure is often called vulcanization or cross-linking. It is an intermolecular reaction caused by the introduction of chemicals (usually sulphur and zinc oxide or morfax) which link or tie independent chain molecules together causing the polymer to form molecular networks. The critical parameters relating to the curing process are; the time elapsed before the curing process starts, the rate at which the process occurs and the extent to which the cross linking occurs. There must be sufficient time before the process begins to allow the mixing of all the ingredients of the rubber compound, the forming of the ultimate product and moulding before curing takes

place. The process should be rapid but well controlled. Curing is a process in which polymer molecules are cross-linked by the addition of sulphur or other equivalent curative agents. This makes the bulk materials harder, durable and more resistance to chemical attack. From Table 1 and Figure 1, it was observed that sample A with carbon black of 180.82 Kg of the total weight of the composite has the least curing time of 0.9 minute and hence, the best curing time. This early curing time was due to high polymer-filler interaction that exists between the natural rubber and the carbon black. This was followed by sample C with equal mass of carbon black and silica (90.41 Kg each) which cured at 1.35 minutes. Sample B with 180.82 Kg silica takes the longest time to cure and does not cure as at 1.6 minutes but burnt to form ashes due to the lower polymer-filler interaction which makes it difficult for silica to disperse effectively into the matrix of the polymer.

3.1.1. Curing Time

Figure 3 show the minimum and maximum torque of the natural rubber compounds containing different filler contents. Minimum torque is a measure of the reinforcing efficiency of the vulcanizates and the number of sulphur cross link that will be form in the compound. It is the lowest points on the graph that also measure the viscosity of the uncured compounds. Viscosity is the resistance of a fluid to flow under stress. It is a temperature dependant property. Materials are less viscous at high temperature. From the Figure, it was observed that sample C with equal mass carbon black and silica and sample D with 108.49 Kg of carbon black and 72.33 Kg of silica has the highest minimum torque of 2.58 lb while sample B has the least value of 1.05 lb.

The maximum torque measures the stiffness of the cured compound and the number of sulphur cross link that are formed in the compound. A compound with higher stiffness will have good rolling resistance properties which are indicated by higher maximum torque. From Figure 3, it was observed that sample D followed by sample A has the best maximum torque of 12.04 lb and 10.79 lb respectively.

3.1.2. Scorch Time

Scorch time is the parameter that is used to monitor premature cross linking between the filler and polymer when sulphur and accelerator have not been added (Alkadasi et al, 2004). It is the time required at a specific temperature or heat history for a rubber to form incipient cross linking. It was observed that sample E with 108.49 Kg silica and 72.33 Kg of carbon black have the best scorch time of 0.87 minute

followed by sample C with equal amount of both carbon black and silica (90.41 Kg) having a scorch time of 0.71 minute while sample B with 180.82 Kg silica has the least scorch time of 0.18 minute. The scorch time indicate some interference effect to the cross linking formation caused by the presence of the silica in sample B as shown in the Figure 2. Monsanto Rheometer was used to determine the scorch time and from the results, it was observed that all the sulphur cured formulations adopted have sufficient time to permit mixing, forming and flowing of the compound into the mould before curing except for sample B.

Table 1. Composition of the samples.

Samples	Natural Rubber(Kg)	Carbon Black(Kg)	Silica(Kg)
A	384.71	180.82	34.47
B	384.71	-	180.82
C	384.71	90.41	90.41
D	384.71	108.49	72.33
E	384.71	72.33	108.49

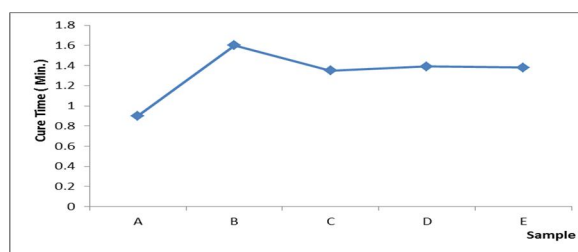


Figure 1. Curing Time for the Different Batches of the Samples Produced.

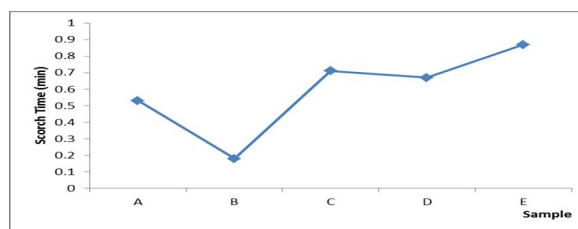


Figure 2. Scorch Time for the Different Batches of the Samples Produced.

3.1.3. Torque at a given Time

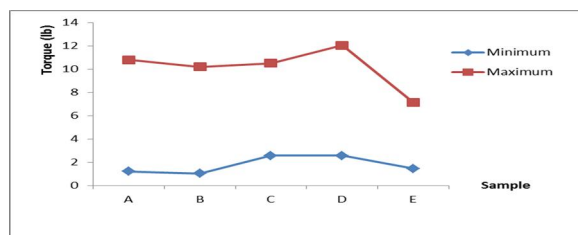


Figure 3. Torque Properties of the Different Batches of the Samples Produced.

3.1.4. Specific Gravity

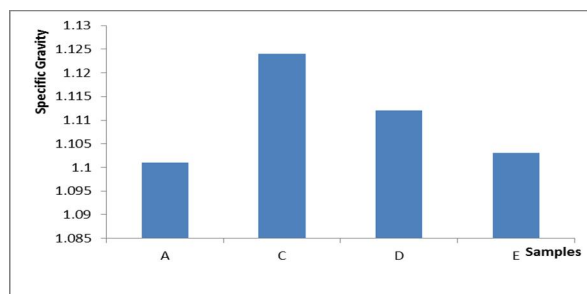


Figure 4. Variation of Specific Gravity with Samples

Figure 4 revealed the variation of specific gravity with the samples. Specific gravity is the ratio of the weight of a compound to the weight of an equal volume of water at a standard condition. It is a measure of thorough mixing and incorporation of compounds. From the Figure, sample C followed by sample D have the best specific gravity values of 1.124 and 1.112 respectively. These samples have the best mixing and incorporation.

3.1.5. Ultimate Tensile Strength

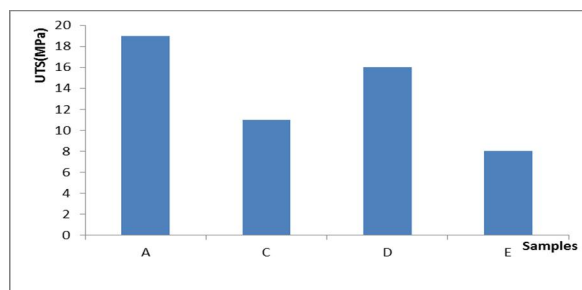


Figure 5. Variation of Ultimate Tensile Strength with the Samples

The ultimate tensile strength of the samples was shown in Figure 5. Tensile stress is the force per unit cross sectional area of the tensile test specimen. It is a measure of the stress required to fracture or break the material. Ultimate tensile strength is the maximum stress the material can withstand before fracture or failure occurs. Monsanto Instron Machine was used for the determination of the tensile properties. It was observed from the test that sample A followed by sample D have the best ultimate tensile strength values of 19 MPa and 16 MPa respectively. As shown in Figure 5, the high tensile strength observed in the two samples (A and D) is due to the high carbon black content. Generally carbon black possesses high abrasion resistance which is impacted into the composite.

3.1.6. Young's Modulus of Elasticity

Modulus of elasticity measures the load require to stretch the polymeric substance to a set extension per cross sectional area. It expresses the resistance to stiffness of the composites. The results of the test as shown in Figure 6 revealed that sample D has the best Young's modulus of elasticity of 14 MPa followed by sample A with a value of 12 MPa. The high modulus of elasticity of the two samples was due to the high polymer-filler interaction and low filler-filler interaction that exist in the compounds while sample E shows the least modulus of elasticity because of poor polymer-filler interaction and high filler-filler interaction.

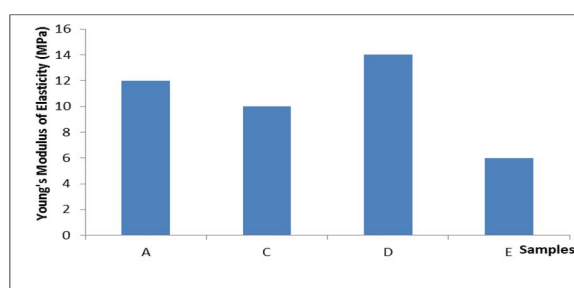


Figure 6. Variation of Young's Modulus of Elasticity with the Samples

3.1.7. Elongation at Break

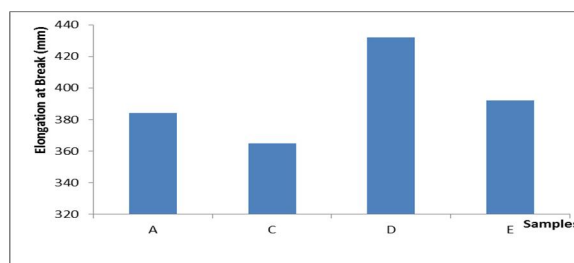


Figure 7. Variation of Elongation at Break with the Samples

This is the maximum stretch a material can attain before fracture. The result of the test in Figure 7 shows that sample D with a value of 432 mm has the best elongation at the break followed by sample E with a value of 392 mm. These samples possess the best capability to stretch to the maximum length before breaking.

3.1.8. Resilience

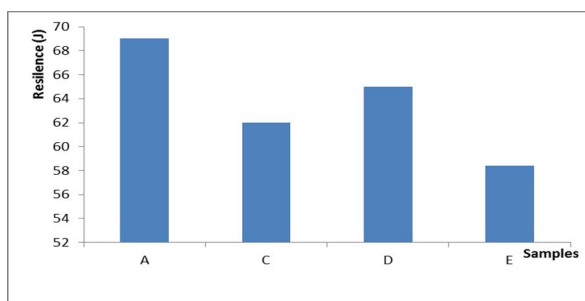


Figure 8. Variation of Resilience with the Samples

Resilience is the ability of a material to return to its normal energy level when the applied stress that causes its deformation is removed. From Figure 8, it was observed that sample A and sample D with values of 69 J and 65 J respectively have the best resilience properties.

3.1.9. Hardness

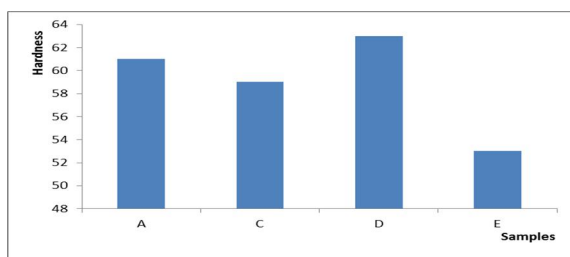


Figure 9. Variation of Hardness with the Samples

The hardness of a material is a measure of the resistance of the material to indentation. Duration 2000I was used for the determination of the hardness values. It was observed from Figure 9 that, sample D and sample A with values 63 HDN and 61 HDN respectively gave the best hardness value.

4. Conclusion

This research work was carried out to study the reinforcement efficiency of carbon-silica dual phase filler for the improvement of the mechanical properties of natural rubber compounding for the production of automobile tyres.

From the results of the various rheological tests carried out, it was observed that sample C which is the mixture of equal amount of carbon and silica has the best rheological properties followed by sample D that contains 108.49 Kg of carbon black and 72.33 Kg of silica. These show that the mixture of these two fillers enhanced the rheological properties of the blends.

The results of the mechanical tests show that sample D that contains 108.49 Kg of carbon black and

72.33 Kg of silica has the best mechanical properties followed by sample C that contains equal amount of carbon black and silica and, sample A that contains only carbon black of 180.82 Kg.

The results show that the mixture of carbon and silica to form dual phase compounds in the production of carbon-silica dual phase filler reinforced natural rubber composites enhanced the rheological and the mechanical properties of the composites more than the individual fillers. Carbon black was observed to be more effective in the reinforcement of the natural rubber than silica.

Thus, for a filled compound, carbon-silica dual phase fillers gave the best performance and improvements in production of tread compounds than the conventional fillers (carbon or silica) due to the high polymer-filler interaction and lower filler-filler interaction that exist in the formulation. The mixture of carbon black with silica brings about improvement in the bonding strength between the matrix and the filler and, hence, the ensuing properties.

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