Effect of urea-based activators on reinforcing activity of silica in natural rubber-based compounds

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ABSTRACT

Silica-filled rubber compounds has a high demand for making white and colored rubber products. Silica-filler has high reinforcing ability compared to other white-fillers. Traditionally, polyethylene glycol (PEG) is used to block the acidic silanol groups covering the surface of silica to prevent agglomeration of filler. The present research made an attempt to replace PEG with commercially available urea-based activator Rhenofit-1987. Similar to PEG the Rhenofit-1987 structure includes hydroxyl groups. Additionally, it has amine groups which accelerate vulcanization by building additional links with rubber. To check the reinforcing activity of Rhenofit-1987, the series of Natural rubber-based silica-filled compounds were prepared by partially and fully replacing PEG with Rhenofit-1987. Obtained test results showed improved tensile and tear strength of compounds consisting of Rhenofit-1987 which confirm that Rhenofit-1987 has better reinforcing activity of silica than PEG.

KEY WORDS: PEG; NR; Silanization; Reinforcement

INTRODUCTION

Elastomers refer to the group of polymers that exhibit rubbery or elastic behavior, including natural rubber and synthetic rubbers. Formulation continues to expand the field of each kind of new or conventional rubber. Formulation areas have constantly focused on improving rubber physical properties and performance. (Bawadukji NA, Jabra R., 2017)

Sri Lanka is one of the nine major producers of Natural Rubber (NR) in the world with a current global market share of around 0.7%. *(Plantationindustries.gov.lk. 2017).* Numbers of products are made out of white and colored rubber compounds such as tubs, sheets, gloves, solid tires for vehicles, for operations in food, pharmaceutical and other related production or service areas.

To achieve desirable processing characteristics and adequate properties, large quantities of fillers are compounded with rubber. The mostly used fillers for white and coloured rubber compounds are mineral fillers like silica, precipitated calcium carbonate (CaCO3) and china clay, kaolin.

Fillers can have chemically or adsorptive bound functional groups on their surface. The carbon black surface consists of phenolic, hydroxyl, quinone, carboxyl, lactone groups and reactive hydrogen bonds which can react with rubber molecules chemically resulting a high level of physical interaction. Silica consists of silanol and siloxane groups on its surface. As silica is polar in nature, its interaction towards non-polar rubber is very less. The reason for this is absence of strong interaction between organic NR and

inorganic filler. Advantage of silica when compared to other white fillers refers to its ability to reinforce rubber up to certain extent due to complex silanization process taking place between inorganic silica and organic rubber

in the presence of bonding promoters and activating agents. Compounding the silica with NR involves silanization reaction that combines several reactions such as silica-silane reaction, silane-rubber coupling and cross linking between polymers.

In the presented research, the attention was brought to optimization of silanization reaction through application of urea-based activator. Due to the presence of strong polar groups in this activator, it is supposed to block the acidic silanol groups covering the surface of the silica and prevent agglomeration of filler. Additionally, to that, urea compounds accelerate rubber curing and increase density of crosslinks due to having an amine group in its structure. Because of aforementioned reasons, the interaction of silica with rubber will be increased leading to compounds with suitable level of strength, abrasion, tear

resistance and other properties *(Rowland, Faiman, and Jablonowski 1994: Kaewsakul, Sahakaro, Dierkes, and Noordermeer, 2013).*

METHODOLOGY

Batch 1 – 100% PEG as the activator

Batch 2 – 50% PEG replaced by Rhenofit-1987

Batch 3 – 100% Rhenofit-1987 as the activator

Three batches were prepared according to the formula in

Table 1- Rubber compounding formula

Compound	Amount (g)
Reed smoked sheet rubber	450
Stearic acid	9
Silica	225
Silane coupling agent	22.5

Petroleum resin (C-9)	4.5
Antioxidant (SP oil)	9
Activator (Rhenofit-1987: PEG)	22.5
Master 1	**742.5**
Master 1	675
Zinc oxide	22.5
Master 2	**697.5**
Master 2	697.5
TBBS	9
Sulphur	13.5
Final mix	**841.5**

	Hardness (Shore A)	Rebound Resilience (Rebound height, mm)	Tensile strength (MPa)	Tear strength (N/mm)	Abrasion (weight difference, g)
Batch 1	81.83	21.33	7.4631	26.70	0.489
Batch 2	83.00	21.00	7.4659	29.52	0.621
Batch 3	78.17	15.67	8.7721	39.00	0.537

Before adding activator, raw materials were mixed for 20 minutes maintaining the temperature between 150^0C to 160^0C in internal mixture. Then after cooling down, activator was mixed using two roll mills. Finally, with 675g of Master 1, Master 2 and Final mix were prepared using two roll mills.

Rheological properties of the prepared batches were obtained using moving die rheometer, t_{90} at 160^0C. Then batch 1 and 2 were cured for 8.52 minutes and batch 3 was cured for 8.68 minutes at 160^0C in compression molding machine while obtaining sheet and die samples. Hardness (Durometer), Rebound resilience (Vertical Rebound Tester), Tensile Test (Universal tensile testing machine), Tear strength (Universal testing machine) and Abrasion (DIN abrasion tester) tests were conducted for the cured samples of the prepared three white rubber batches.

RESULTS AND DISCUSSION

Experimental results are shown in *Table 2*. By analyzing the results following observations were obtained.

- Hardness had been increased from Batch 1 to Batch 2 and had decreased in Batch 3.
- Rebound resilience was almost same in Batch 1 and Batch 2 and it had drastically decreased in Batch 3.
- Tensile strength had been slightly increased in Batch 2 but it had drastically increased in Batch 3.
- Tear strength had increased with the use of Rhenofit 1987 from Batch 1 to Batch 3.
- Abrasion resistance had increased in Batch 2 and then decreased in Batch 3.

Batch 1 was made using PEG as the activator, while other two samples were made replacing PEG partially and fully with the urea-based activator Rhenofit 1987. Through the observation of results, it could be seen that the hardness, tensile strength, tear resistance and abrasion was increased when PEG is replaced 50% by the urea-based activator. The reason for the increased properties would be due to the urea-based compound achieving the expected results by reducing the filler-filler interaction as well as increasing the crosslinking and vulcanization properties of NR.

When only Rhenofit was used as the activator, there is a visible reduction in hardness, rebound resilience and abrasion and properties of the compound was shifted from elastomeric properties to plastic properties. Rhenofit 1987 consists short chains than PEG. Results shows that it exceeds the activity of PEG. It could be concluded that when the amount of Rhenofit 1987 used, is as same as the amount of PEG, an excess amount of Rhenofit can remain in the compound and could result in increase of softening of the rubber which ultimately leads to increased plastic properties.

CONCLUSION

By looking at the results it can be concluded that the reinforcing activity of silica-based NR was increased by using the urea-based activator.

Results indicated that the optimum amount of Rhenofit 1987 which should be used in compounding the silica rubber is not similar to the amount of the traditional activator (PEG). Series of tests should be conducted to find the optimum amount of urea-based compound to be used to increase the properties of the rubber compound. Quality of the end product could also be enhanced by using a blend of PEG and Rhenofit 1987. But the optimum ratio of the two activators should be experimentally determined.

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