Study of rubber/calcium carbonate composites

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Abstract. Fillers have been widely used in the rubber industry for many applications such as tile floor, vehicle tire, etc. Calcium carbonate (CaCO₃) is one of the important inorganic powders and it is widely used as filler in order to reduce the cost in rubber industry. The objective of this study is to investigate physical and mechanical properties of the rubber composites with CaCO₃ powder. We studied the CaCO₃ additive in natural rubber (NR) with 25, 50, 75 and 100 parts per hundred rubber (phr). The effect of CaCO₃ on the properties of rubber composite, such as Mooney viscosity, bound rubber, Mullins effect and Payne effect, was investigated. The result of Mullins effect of rubber composite filled with CaCO₃ is in good agreement with the result of bound rubber: higher bound rubber leads to higher stress to pull the rubber composites. The Payne effect shows that the value of different storage moduli (ΔG’) of rubber compound filled with 25 phr CaCO₃ is the lowest due to weaker filler network. While, the NR supplemented with 100 phr CaCO₃ represents more significant ΔG’ with the strain increasing. This type of material could be applied for tailoring the properties of rubber products.

1. Introduction
Natural rubber (NR) is a major agricultural product, which is widely used in industry, for example, tile floor, tire, glove, pillow and mattress, medical products, etc. NR obtained from Hevea brasiliensis consists of cis-1,4-polyisoprene and nonrubber components (proteins, phospholipids, sugar, salt, etc.). Until now, there are no synthetic materials that can replace natural rubber obtained from plants [1]. NR is often reinforced by incorporation of filler to improve its mechanical properties: modulus, hardness, tensile strength, abrasion resistance and tear resistance [2].

Recently, fillers have been widely used in the rubber industry for many purposes such as improvement of mechanical properties, efficient production and reducing cost of rubber products. Generally, there are three main groups of filler, including reinforcing fillers, semi-reinforcing fillers, and non-reinforcing fillers. Efficiency of the reinforcing filler depends on several factors such as particle size, surface area and shape of filler [3]. Among commercial fillers, carbon black and silica (SiO₂) are the most important reinforcing fillers. They are added to improve the mechanical properties of rubber compounds. However, there are some fillers that can be used as none or semi-reinforcing fillers (such as clay, talc, and calcium carbonate, etc.) for either reducing cost or improving mechanical properties [4]. Calcium carbonate (CaCO₃) is one of the important inorganic powders and widely used as filler in paints, plastics, and rubber industry in order to reduce the material cost [5]. The main aim of this work
is to study the effect of CaCO$_3$ in rubber composites on the properties, in particular physical and mechanical properties.

2. Experimental
For the sample preparation, the natural rubber (NR) grade STR 5L was first masticated with a two-roll mill at 70°C for 5 minutes. Composite samples were prepared by mixing NR with CaCO$_3$ at 25, 50, 75 and 100 phr for 10-15 minutes (totally four samples). All samples were then cut into form of testing sheets. For scanning electron microscopy analysis (SEM: FEI, Quanta 450 FEI), rubber samples were cut into small pieces, and coated with gold for the morphology analysis. Mooney viscosity was determined by using Mooney viscometer of the rubber compounds. Bound rubber was considered a quantitative measure of the filler surface activity and the rubber-filler interaction. Bound rubber was determined by immersing 1 gram of rubber composite in 100 ml of toluene solvent at room temperature for 7 days. After dissolution, a piece of rubber that is insoluble in toluene was filtered and weighed [6]. Mullins effect of the rubber composite was measured using Universal Testing Machine with strain range: 1–100% in cycle mode. Payne effects of CaCO$_3$ supplemented rubber composite was analyzed using rubber process analyzer under temperature 60 °C, frequency 1 Hz, strain range: 1–100%. The value of different storage moduli ($\Delta G'$) means $G'_\text{max} - G'_\text{min}$.

3. Results and discussion
Before using as rubber filler, the CaCO$_3$ material was analyzed by scanning electron microscopy (SEM). This proves the narrow size distribution around 1 micron of particles (data not shown). Analysing the Mooney viscosity of NR with CaCO$_3$ additives the results show steady increase of viscosity of the rubber composites between 58-62 a.u. for the composition of 25-100 phr of filler (Figure 1). The CaCO$_3$ are solid particle fillers, as expected, when mixed with NR, the product has increased viscosity. This relates to the hydrodynamic effect [7], which causes the increase in the rubber viscosity when supplemented with none-reactive solid additive. This also suggests good blending of used compounds.

![Figure 1. Linear increase of the Mooney viscosity and bound rubber content with increased amount of the CaCO$_3$ (25-100 phr) in NR.](image-url)

The bound rubber refers to the fraction of polymer which cannot be extracted with a good solvent from a rubber-filler mix. To evaluate the interaction between filler particles and NR, the bound rubber
of uncrosslinked composites was measured by extraction with toluene at room temperature. The percentages of bound rubber in all samples (25-100 phr of CaCO₃) are also summarized in Figure 1. The highest bound rubber is for natural rubber samples with 100 phr CaCO₃ added. These results are in good agreement with the Mooney viscosity analysis.

The Mullins effect is a phenomenon observed in rubber material where the stress-strain equilibrium changes with the softening. This is regarded as a strain-induced softening character and is observed in elastomeric polymers when forces are repeatedly applied to a material which leads to weaken of rubber material. The Mullins effect was analyzed by stress strain curve (3 loops of go-return curves) for natural rubber with addition of CaCO₃ at 25, 50, 75 and 100 phr respectively (data not shown). When increasing CaCO₃ in NR, the stress of NR composites tends to be increased, especially at high loading of CaCO₃ (75 and 100 phr).

The Payne effect is a feature of the stress-strain behavior, which is related to the shape change by causing strain in the rubber with fillers. This phenomenon is regarded to the storage modulus (G') and loss modulus (G'') in shear deformation conditions. The reason for this phenomenon is the formation of a network formed by filler-filler interaction in the composites at low strain. In real life, this means the energy loss (Tan delta) and the efforts are to maximize this effect in filled rubber [8]. For instance, the result of shear modulus of the NR composites corresponding to the amount of CaCO₃ filler shows differences. This phenomenon is caused by the filler–filler networks and adsorption–desorption of polymeric chains at the filler interface of the rubber composites. Looking at the Payne effect results (Figure 2), the value of different storage moduli (ΔG') of rubber compound filled with 25 phr CaCO₃ is the lowest due to weaker filler network. While, the NR supplemented with 100 phr CaCO₃ represents more significant ΔG' with the increasing of strain. The value of damping factor (Tan delta) corresponds to energy loss showed that CaCO₃ particle at 100 phr has more pronounced values. Energy loss from the straining also produced heat caused increasing of temperature, higher ΔG' higher Tan delta.

![Figure 2. Payne effect as a function of strain for NR with CaCO₃ particles at 25-100 phr.](image)

**4. Conclusions**

In this research, we found that the Mullins effect of rubber composite filled CaCO₃ is in good agreement with the result of bound rubber, higher bound rubber of rubber composite higher stress to pull the rubber composites. From the Payne effect point of view, the value of different storage moduli (ΔG') of rubber compound filled with 25 phr CaCO₃ is the lowest due to weaker filler network, while the NR supplemented with 100 phr CaCO₃ represents more significant ΔG', higher ΔG' higher Tan delta.
5. References

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