

## **CaCO<sub>3</sub> FROM SEASHELLS AS A REINFORCING FILLER FOR NATURAL RUBBER**

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### **ABSTRACT**

Bio-composites, due to their sustainably renewable nature, have attracted considerable attention due to their low cost and bio-degradability. CaCO<sub>3</sub> from seashells is a 'green' calcium carbonate that could enhance the mechanical and thermal properties of composites. The mixing of natural rubber (NR) with CaCO<sub>3</sub> using melt blending enhanced the hardness and tensile strength of the composites. The glass transition temperature did not have a significant effect on the composites, while the composites with filler of 355 μm in size showed the highest melting point in differential scanning calorimetry (DSC) analysis.

**Keywords:** Natural rubber; calcium carbonate; seashells; mechanical properties; thermal properties.

### **INTRODUCTION**

Natural rubber (NR) is an important elastomers and widely utilized in a variety of rubber products. NR is often reinforced by incorporating a filler to improve its mechanical properties, such as modulus, hardness and tensile strength [1]. Generally, the reinforcing phase, in the form of particles, fibers or flakes, is embedded within the rubbery matrix phase. The newly obtained material exhibits unique properties with the overall properties being better than the individual properties [2-4]. The efficiency of the reinforcing fillers depends on several factors, such as the shape of the filler, the surface area and the particle size. The most often used reinforcing fillers are carbon black and silica (SiO<sub>2</sub>) [5-7]. Renewable resources, such cornstarch, wood, and chitin, were previously the fillers of choice in polymers. The benefits of these fillers include their low cost, light weight and biodegradability [8-12]. Shells or exoskeletons from marine products, such as shrimp and cuttlebone, which are composed of different chemicals depending on their source, are used as fillers in NR. The exoskeletons of most crustaceans principally comprise calcium carbonate (CaCO<sub>3</sub>), being typically more than 80% CaCO<sub>3</sub> by weight [13]. Therefore, no complex extraction process is necessary to use the product. Sometimes, an extraction process is used to determine the chemicals or eliminate other contaminating substances as in the case of chitin/chitosan. The protein content and pigments can cause problems in further utilization, especially in pharmaceutical and biomedical applications [14]. For this reason it should be removed. Chitin or CaCO<sub>3</sub> is known as a biocompatible material because of its low antigenicity, low toxicity and biodegradability. Several studies have reported using chitin as a filler. CaCO<sub>3</sub> is used in rubber as a de-tackifying agent to improve the rheology and

processability, and impact strength, and also to reduce the cost of the formulation. It is also used as inert filler for tablets and dietary calcium supplement or antacid. An important use of CaCO<sub>3</sub> for environmental applications is to neutralize acidic conditions in water and to de-sulfurize flue gas and waste-water treatments [15]. This study aims to assess the possibility of using biodegradable CaCO<sub>3</sub> from product waste as a substitute for commercialized CaCO<sub>3</sub> to be the filler in NR by studying the mechanical and thermal properties. The mechanical studies focus on the tensile properties and hardness, while differential scanning calorimetry (DSC) analysis will study the  $T_g$  and  $T_m$  behavior of the composites.

## EXPERIMENTAL SET-UP

### Experimental Procedure

Standard Malaysia Rubber 10 (SMR-10) was used as the raw NR and supplied by Lee Rubber Sdn. Bhd., Kelantan. The NR was cut into small pieces with a weight of 100 phr for each sample using a cutter machine. The seashells were collected from Teluk Kalong Beach, Kemaman. Other chemicals were obtained commercially. The three major steps were preparation of the samples, mixing and characterization.

#### Preparation of Samples

In preparing the samples, the seashells were washed with distilled water several times to remove sand and dirt and were then dried in an oven overnight. Then, they were crushed into a powder and the powder foam was sieved using a 355  $\mu\text{m}$  size sieve. The effects of CaCO<sub>3</sub> loading between 10 phr to 60 in 100 phr of NR were studied using the tensile test to obtain the optimum percentage.

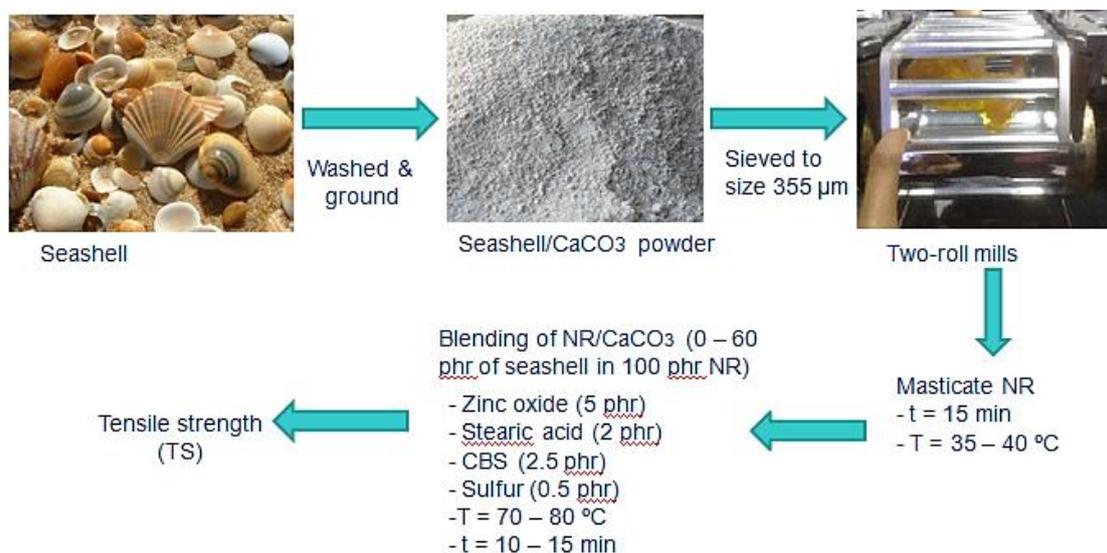


Figure 1. Initial study to find the optimum percentage of CaCO<sub>3</sub> in the NR blend.

After obtaining the optimum amount of CaCO<sub>3</sub> (40 phr CaCO<sub>3</sub>), the research was furthered to form NR/40 phr CaCO<sub>3</sub> composites with different grain sizes of the CaCO<sub>3</sub>: 112  $\mu\text{m}$ , 355  $\mu\text{m}$ , 800  $\mu\text{m}$  and 1000  $\mu\text{m}$  with optimum NR loading measured in the initial process.

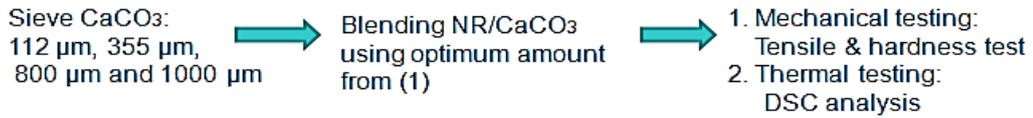


Figure 2. Flow chart shows preparation of NR / 40 phr CaCO<sub>3</sub> blends with different grain sizes of the filler.

The samples were compounded via melt blending using a two-roll mill at 35–40 °C with four chemicals of fixed amounts added continuously during mixing to assist in acceleration and crosslinking. Initially, the NR was masticated in the mill for 15 min. Thereafter, the rubber was blended with zinc oxide (5 phr), stearic acid (2 phr), cyclohexylbenzothiazole-sulfenamide (CBS) (2.5 phr), CaCO<sub>3</sub> and sulfur (0.5 phr). The mixture was plasticized for 10–15 min and thin-passed several times at 70–80 °C. Last, the obtained samples were hot-pressed using a 1-mm thick mold to form sheet samples.

#### Characterization Process

All prepared samples were tested using Shore durometer hardness testing, in accordance with ASTM D2240 [16], as the measure of a resilient material’s resistance to indentation. Each sample was tested three times to achieve measurement accuracy. During the hardness testing, the sample was put on a flat surface. The Shore durometer hardness tester was pressed onto the sample. After 15 seconds, the reading was shown by the durometer. Tensile testing measures the force required to break a plastic sample and the extent to which the sample stretches or elongates to that breaking point. The samples were cut into dumbbell shapes by using the ASTM D412 standard cutter [17]. The tensile test was undertaken using an Instron Universal Testing Machine.



Figure 3. Instron Universal Testing Machine for tensile testing and the dumbbell shaped samples.

Thermal analysis was undertaken using DSC employing a Mettler Toledo to determine the temperature of a sample to glass transition ( $T_g$ ) and the melting point ( $T_m$ ). During DSC characterization, the weighed sample was put into an aluminum pan. The pan was clamped using the clamp pan in the DSC equipment and the experiment was run at temperatures of -80 °C to 500 °C at a heating rate of 10 °C /min.

$$\text{Tensile strength (MPa)} = \frac{\text{Pulling force (N)}}{\text{Sample width (mm)} \times \text{Sample thickness (mm)}} \quad (1)$$

$$\text{Tensile modulus (MPa)} = \frac{\text{Stress (Pa)}}{\text{Strain difference}} \quad (2)$$

$$\text{Sample heat flow (q)} = \frac{\text{Temperature difference between samples}}{\text{Resistance of the thermoelectric disk}} \quad (3)$$

## RESULTS AND DISCUSSION

### Mechanical Properties of Samples

All samples were successfully prepared using a two-roll mill. In the initial stage, the NR/CaCO<sub>3</sub> composites were prepared with different filler loadings using the 355 μm filler size. This step was undertaken to find the optimum amount of CaCO<sub>3</sub> to give the highest tensile strength. Figure 4 shows the tensile strength of the samples. Using 100% NR, the tensile strength was 20 MPa but with increasing filler loading, a uniform increase was seen, due to reinforcement effect of CaCO<sub>3</sub> filler to NR, until 40 phr CaCO<sub>3</sub> was loaded [18]. It can be seen that the CaCO<sub>3</sub> particles could be fully wetted by the NR matrix, especially at low loading. The rubber chain could penetrate into the pores of the CaCO<sub>3</sub> and become a part of the filler (bound rubber). The presence of an organic component, such as chitin, is speculated to give a good reinforcement effect to the seashell particles during mixing with NR [19]. The further addition of CaCO<sub>3</sub> filler decreased the tensile strength due to agglomeration in the filler particles, thereafter being less wetted and less penetrated by natural rubber chains, which had a detrimental effect on the tensile strength [19]. According to these results, further studies should be undertaken using a 40 phr load of CaCO<sub>3</sub> in NR composites to study the effect of different sizes of filler on the mechanical and thermal properties.

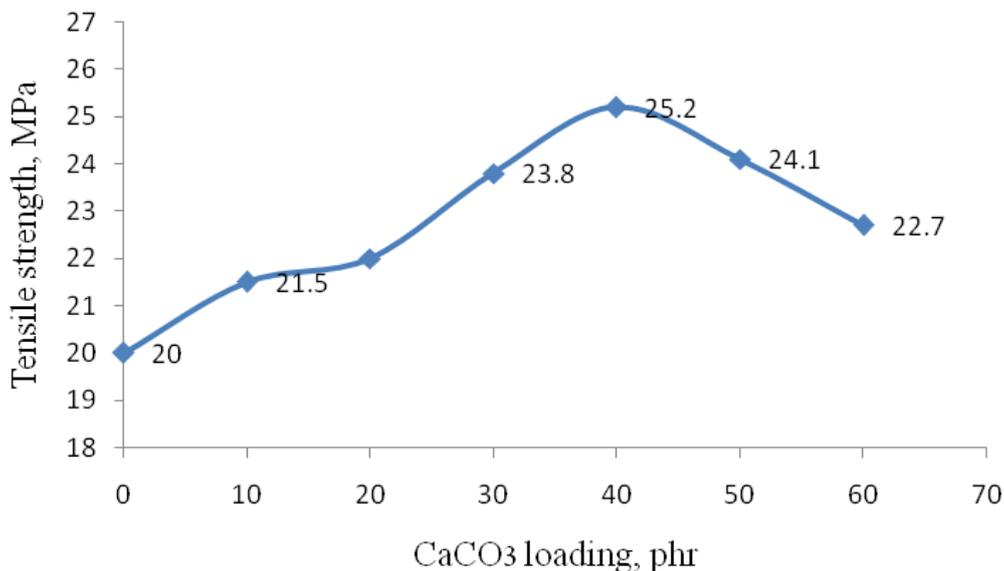


Figure 4. Effect of CaCO<sub>3</sub> loading on tensile strength of NR/CaCO<sub>3</sub> composites.

Table 1 shows the results from the hardness and tensile tests of 100% NR and NR/40 phr CaCO<sub>3</sub> with different sizes of filler: 112 μm, 355 μm, 800 μm and 1000 μm. It is clearly seen that the increase in size of the filler enhanced the hardness and tensile modulus properties of the composites due to the decrease in elasticity of the NR. From

the hardness test, the composites are seen to be able to resist deformation during indentation. The increment in modulus is due to the degree of crosslinking and the more homogenous CaCO<sub>3</sub> filler distribution in the NR [20]. Increases in modulus often bring about decreases in elongation in filled-rubber materials [15]. This was proved by the results of elongation at break in Table 1. Only the addition of the 112 μm filler showed a significant effect on elongation, but for the next replenishment, a declining trend was shown. This is because the small sized filler would not cause disruption to the entangled polymer chains sliding freely when subjected to extension. The enhancement to the tensile strength was seen with the increasing filler size up to 355 μm and decreased for further loading with composites containing 800 μm and 1000 μm sizes of CaCO<sub>3</sub>. This can be explained in that the smaller size of filler has a higher surface area which interacts well with the polymer matrix. The presence of the higher size filler highly affects the dispersed phase which finally affects the mechanical properties. In fact, as widely reported, filler aggregations, acting as local defects and reducing the interfacial area, could adversely affect the functional properties of final composites, hence, their reduction in the obtained analysis [21].

Table 1. Mechanical properties of NR/40 phr CaCO<sub>3</sub> with different CaCO<sub>3</sub> filler sizes.

Size of CaCO <sub>3</sub> in NR/CaCO <sub>3</sub> composite (μm)	Hardness (Shore A)	Elongation at break (mm)	Tensile strength (MPa)	Tensile modulus (MPa)
0	10.8	349	20	1.9
112	10.83	380	24	2.0
355	11.37	375	25.2	2.2
800	13.57	358	21	2.6
1000	15.67	342	18.9	2.9

### Thermal Analysis of Samples

Figure 5 shows  $T_g$  and  $T_m$  from the DSC analysis. With regard to the  $T_g$ , the addition of CaCO<sub>3</sub> seashells as the filler produced no significant variation in  $T_g$  in the NR/40 phr CaCO<sub>3</sub> composites. The NR amorphous region was not influenced by the filler loading as has been seen in other articles [22] regardless of the nature of the polymeric matrix [23]. The melting point increased due to the higher size of the CaCO<sub>3</sub>. The maximum  $T_m$ , 401.120 °C, was reached for the 355 μm size filler. For the fourth and fifth samples, with the 800 μm and 1000 μm filler sizes, a slight decrease in  $T_m$  was shown. This can be explained by the aggregation in the blending decreasing the compatibility of the mixture. The viscosity of the blends increased because of the poor flowability of neat NR; hence, the diffusion rate of the CaCO<sub>3</sub> filler chains was reduced. The rigidity of the composites was enhanced with the increments in the filler size; hence, the increased melting point.

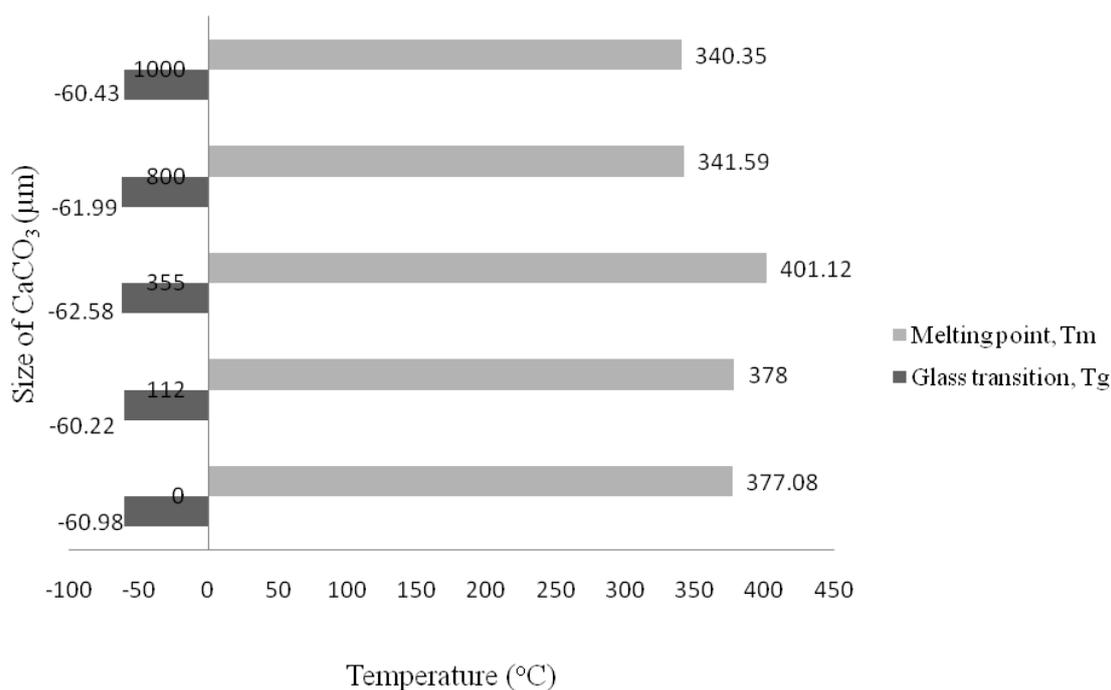


Figure 5. DSC analysis results for NR/40 phr CaCO<sub>3</sub> composites with different CaCO<sub>3</sub> sizes.

## CONCLUSIONS

NR-biocomposites were produced by blending NR with filler obtained from nature. In the resulting composites, initial studies showed the highest tensile strength in the 40 phr loading of CaCO<sub>3</sub> in NR. From the tensile strength and melting point analysis using different filler sizes, the optimum properties were given by the 355 µm NR/40 phr CaCO<sub>3</sub> sample and the melting point at 401.12 °C. The hardness reading increased with the increasing filler size to a maximum 15.67 Shore A shown by filler size 1000 µm. The tensile modulus showed the same trend. There was no significant difference in the glass transition for all composites. The author suggests that further studies should be undertaken using different nanometer sizes of filler that it is believed can enhance the properties of the composites.

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