EFFECT OF EGG SHELLS POWDER ON SOME MECHANICAL AND PHYSICAL PROPERTIES OF NATURAL RUBBER (NR)

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ABSTRACT

In this research, the effect of egg shells powder on some mechanical and physical properties of natural rubber, that comprised each of tensile strength, modulus of elasticity, elongation, hardness, resilience and specific gravity, were studied. The egg shells were collected and dried by exposed to sun for (3) days and they were milled by electrical mill, the set of sieves were employed to get on egg shell powder by the suitable size. The egg shell powder was added to NR from 5 wt % to 25 wt % and then tensile, hardness, resilience and specific weight tests were carried out for prepared specimens. The results showed that the hardness and modulus of elasticity, specific weight increased with increasing of the powder. The hardness was (35 IRHD) for pure rubber, while was (49.3 IRHD) at percent of powder (25 wt %) . It was observed that the tensile strength, elongation and resilience decreased with increasing of powder. The tensile strength was (21.96 MPa) for pure rubber, while was (9.21 MPa) at percent of powder 25 wt %. This work exists with a good replacement for synthetics fillers avoiding their toxicity and their highly cost and reducing of the environmental pollution.

Keywords: Natural Rubber (NR); Egg Shells Powder (ESP); Mechanical; Physical Properties.

الخلاصة

تم في هذا البحث دراسة تأثير إضافة مسحوق قشور البيض على بعض الخواص الميكانيكية والفيزيائية للمطاط الطبيعي والتي شملت كل من مقاومة الشد، معامل المرونة، الاستطالة، الصلابة، الارتدادية والوزن النوعي. تم تجميع القشور وتجفيفها عن طريق وضعها معرضة لأشعة الشمس لمدة (3) أيام ثم تم طحنها بطاحونة كهربائية وتم الحصول على مسحوق بالحجم الحبيبي المناسب عن طريق منظومة مناخ كهربائية.
1. INTRODUCTION:

Raw dry rubber is seldom, if ever used in its original state for any engineering application. Rubber manufacture involves the addition to rubber many ancillary materials called additives. This is to allow the rubber compounds to be satisfactorily processed and when vulcanized improve the application properties of the rubber articles. Additives in rubber include; vulcanizing agents, accelerators, activators/retarders, antidegradents, fillers, plasticizers and other ancillary ingredients. One of the most important additives and second largest following the base polymer in rubber compounding is the filler. Fillers improve processability, physical mechanical properties such as tensile properties, hardness, flex fatigue, tear and abrasion resistances, and may cheapen the final product. They achieve performance enhancement by forming strong chemical bonds with the rubber, that is, strong filler elastomer interactions. The fillers used in rubber compounding can be classified into reinforcing and non-reinforcing types. A) reinforcing filler is one which increases the tensile strength, hardness and abrasion resistance of the rubber article. The finer the particle size the more reinforcing a filler is. Examples of reinforcing filler include; carbon black and silica. B) Non-reinforcing fillers cause reduction in strength properties but may increase hardness and modulus of the rubber product. They are usually applied as diluents or extenders to generally reduce cost, examples include the whitings (CaCO₃) and china clay [Blow et al, 1982, Bello, 2001, Whela et al,1979].

The eggshell contributes 11% of the total weight of egg. The major constituent present in the shell is CaCO₃, which accounts around 91% of the total weight. India, currently ranks fourth in world in egg production with an annual production of 17,32,500 tons of egg. By taking 11% of the weight, nearly it comes around 1,90,000...
tons of eggshell waste is created. This material goes as a waste and leads to pollution since it favours microbial action [S.Sasikumar].

**Table 1:** Chemical Analysis for Egg Shell Powder [Jayasankar, 2010].

<table>
<thead>
<tr>
<th>Element</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>50.7</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.09</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.02</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.19</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.24</td>
</tr>
<tr>
<td>SrO</td>
<td>0.13</td>
</tr>
<tr>
<td>NiO</td>
<td>0.001</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.57</td>
</tr>
<tr>
<td>Cl</td>
<td>0.219</td>
</tr>
</tbody>
</table>

Many investigators have studied effect of additives on mechanical properties of polymer and the new usage of egg shell powder in the engineering application.

**(Sarkawi and Yusof Aziz, 2003)** studied utilizing ground rice husk, without burning it as filler in rubber compounding by evaluating the rheological behaviour and physical properties of rice husk powder (RHP)-filled rubber vulcanisates. For comparison purposes, commercial silica was used at 40 and 50 pphr whilst carbon black was used at 50 pphr. The results showed that the physical properties of RHP-filled vulcanisate are still inferior to carbon black-filled vulcanisate but some of the properties are comparable to silica-filled vulcanisate. The RHP also offers processing advantages over silica.

**(Ahmed, 2004)**, made an investigation into the properties for unsaturated polyester resin reinforced with rice husk. Results showed that composite materials of rice husk gain better mechanical properties compared with composite prepared from unsaturated polyester resin without filler.
(Suzuki, 2005), studied the effect of rubber/filler interactions on the stress-strain behavior for silica filled styrene-butadiene rubber (SBR) vulcanized in relation to the chain scissions of rubber molecules during deformation. The tensile stress increases with increasing the interfacial interactions between rubber's molecules and silica surface, and simultaneously the chain scission becomes remarkable.

(AL-Maamory, 2006) studied effect of reinforcement of novolac, silica, carbon and nylon fiber on some mechanical properties of NBR. He was obtained that the increasing percent of silica increases physical and mechanical properties. The rebound resilience was increased with increasing of novolac and silica percent and it was decreased with increasing carbon black percent.

(Osabohien et al, 2007) investigated the cure characteristics and the physico-mechanical properties of natural rubber, standard Nigerian rubber, SNR10 filled with cherry seed shell (CSS) and standard carbon black CB (N330). The tensile strength of both CSS and CB-filled vulcanizates increased to a maximum at 40 phr filler content before declining. The moduli (M100 and M300), specific gravity (S.G), hardness and abrasion resistance increased while the elongation at break and Dunlop resilience decreased with increasing filler content for both vulcanizates.

(Hanim, et al., 2008) prepared of polypropylene/calcium carbonate (PP/NPCC) nanocomposites using a co-rotating twin screw extruder at filler loadings of 5, 10 and 15 weight %. The impact strength and modulus of PP showed some improvement with the incorporation of the nanofiller while the tensile strength deteriorated.

(Jayasankar et al, 2010) studied the possibility of using Egg Shell Powder, Rice Husk Ash and Fly Ash as partial replacement in the conventional Concrete. They were concluded that RHA, Fly ash and ESP mixed cubes has equal strength with that of conventional concrete cubes in certain categories. The main objectives of this work are to investigate:

- Practicability of utility from waste materials (egg shells), that they consider pollutes of the environment, in the engineering applications.
- Use of a new fillers (egg shells powder) for improvement the mechanical and physical properties of polymer instead of traditional material, with a consequent reduction in cost.
2. EXPERIMENTAL PART

2.1: Preparation of the master batch

The master batch was comprised of natural rubber and some additives that were used according to international standard. Table (2) shows typical formulation of the natural rubber compound ingredient [Babbit, 1987].

Table (2): Typical formulation of the natural rubber compound ingredient.

<table>
<thead>
<tr>
<th>Compounding ingredients</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Natural Rubber</td>
<td>100</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>2</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>5</td>
</tr>
<tr>
<td>MBTS</td>
<td>1</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.75</td>
</tr>
</tbody>
</table>

The stearic acid and zinc oxide were used as activating material, MBTS (2,2-Dibenzothiazyl disulphide) was as accelerating material, while the sulphur was used as vulcanizing material.

The mixing was carried out on laboratory mill (Comerio Ercole Busto Asvio, Italian's made), the roll dimensions were: outside (150mm), working distance (300mm), speed of the slow roll (24 rpm) and gear ratio (1.4). The roll mill had the facility of controlling the gap distance between the rolls and the rolls temperatures. The program of mixing and homogenizing were carried out according to the following steps:

1) The rubber was passed between two rolls many times with decreasing a mill roll opening to 0.2 cm, at 70°C.
2) The stearic Acid was added to rubber between rolls with the continuous mixing.
3) Zinc oxide was added and the mixing was carried out continuously.
4) MBTS and sulfur were added respectively.
5) After the master batch was completed, the egg shells powder was added to rubber according to sample with the continuous mixing.
6) The composite material was rolled continuously with decreasing a mill roll opening for final homogenized.
7) The composite material was cooled at room temperature.
2-2. preparation of the egg shells powder

The egg shells powder was obtained from the egg shells that they were collected and dried by exposed to sun for (3) days, and they were milled by electrical mill, the set of sieves were employed to get on egg shells powder by the suitable size. The grain size in the research was (75 µm), that it was resulted from sieve had mesh (200). The egg shells powder were used (5, 10, 15, 20 and 25) wt %.

2-3. Samples preparation of the tensile test:

The tensile samples were prepared by using laboratory mill. Take the materials from the mill as a sheet. To homogenize the sheet thickness and to complete the vulcanization, it was used hydraulic press. The sample was pressed under pressure was equaled (200 psi) at (145 °C) for (45 min). The sheet pressed with mould consists of two parts each of them in the dimensions of test sample, the part dimensions of (200×200×5) mm .

Two test samples were cut from the sheet. The cutting was made by using hand press type Wallace Test Equipment.

Tensile properties were determined according to ASTM-D412 by using the Monsanto Tensometer T10. Dumbbell-shaped specimens were conditioned at room temperature. A cross head speed of 50 mm min⁻¹ was used. The average of three samples was used during the test.

This testing equipment was controlled by a microprocessor together with a plotter and pneumatic sample holder. It is designed for testing tensile strength, modulus and elongation percentage at break, this microprocessor together with a plotter and pneumatic sample holder assists in obtaining a written record of each test more independent of the operator, who supplies dimensional and identification information and fits the test piece in the testing equipment before starting the test. This gives improved consistency compared with manual methods of measuring extension and mechanical methods of measuring loads.

2-4. Samples preparation of the hardness, resilience and specific gravity

The samples were prepared as following steps:
1. Preheating for molds at 150°C, the mold had dimensions (length, width, thickness) were (200,180,6.5) mm respectively, the mould had nine circler disk equality in volume, the disk diameter was (45 mm), and it's thickness was (3 mm).

2. The composite material was putted in mold that putted under hydraulic press, it was used pressure equal (200 psi) and temperature (150°C) for (30 min) to complete the vulcanization.

3. The samples were existed from the mold and it was remained for 24 hours for cooling before the test operation.

The International Hardness test is used in measurement of the penetration of rigid ball into the rubber specimen under specified conditions. The measured penetration is converted to the International Rubber Hardness Degrees (IRHD). The scale of degrees is so chosen that zero represents a material having elastic modulus equal to zero and 100 represents a material of infinite elastic modulus. Thus the scale covers all the normal range of hardness.

Wallace Dead Load Hardness Testers was used to test of hardness samples according to ASTM D-1415.

Determination of specific gravity yields for Archimedes base which states that the apparent loss in weight of a body immersed in a liquid equal to the weight of the liquid displaced [Craig, 1963]. When the weight of the body and the weight of equal volume of water is known, therefore the specific gravity can be determined which is, by the definition, the ratio of:

Weight of a given vol. of body/Weight of equal vol. of water

Thus, S.G = [Wt. of body in air/(Wt. in air–Wt. in water)] * S.G of liquid

Monsanto-Densitorn was used to test of specific gravity samples.

Wallace R2-Dunlop Tripsometer takes the form of an out of balance metal disc revolving on virtually frictionless bearing and which acts as a slow moving pendulum. The test piece is placed against a rigid support so that it receives a blow at its centre. A circular scale is provided for measuring the angle of displacement. The measured quantity is the angle to which the disk rebounds after the hammer strikes the specimen. Tests are carried out according to ASTM D1054.
3. RESULT AND DISCUSSION:

3.1 Tensile Strength:

Figure (1) shows decreasing in the tensile strength as ESP % increases. According to [Liang, 2002], the strength of particulate-filled polymer composites depends, to a great extent, on the interfacial adhesion between the matrix and the filler which will facilitate the transfer of a small section of stress to the filler particle during deformation. In this study, no coupling agent has been added into the NR/ESP and in the absence of any coupling agent, the interfacial adhesion between the NR matrix and the ESP have obviously not been improved. That is agreement with [Hanim, 2008]. Without the chemical modification, there is simply adhesion of the polymer to the filler through weak bonding, i.e., Van der Waals or induction interactions [Barone, 2005].

![Tensile Strength Graph](image)

Fig.(1): Effect of ESP on the tensile strength of NR

3.2 Elongation:

From Fig. (2), it can be seen that the elongation at the break decreased with increasing filler loading. Increased filler loading in the (NR) matrix resulted in the stiffening and hardening of the composite and the recipe take away form ductile.
Fig.(2): Effect of ESP on elongation of NR.

3.3 Modulus of Elasticity:

From Fig. (3), it can be seen that the Young’s modulus increased with the increasing (ESP) loading. The increased modulus corresponds to more filler where its intrinsic properties as a request agent exhibit high stiffness (modulus) compare to polymeric material. This is because at a high filler loading, the composite will be able to withstand greater loads and the recipe tends to brittle as ESP% increases. This behaviour is similar to a result reported by [Liang, 2002] and [Hanim, 2008].

Fig.(3): Effect of ESP on modulus of elasticity of NR

3.4 Shore Hardness:

Figure (4) shows increasing of hardness as ESP% increases. This is due to increasing the surface area of ESP in contact with rubber. The explanation of such
behavior agrees with the results of modulus of elasticity because hardness gives indication to modulus of elasticity for rubber under simple strain condition.

![Graph showing the effect of ESP on hardness of NR.](image1)

**Fig.(4): Effect of ESP on hardness of NR.**

### 3.5 Resilience:

From Fig. (5), the resilience decreased with increasing filler (ESP), this is also expected as mentioned earlier. The deterioration in resilience is most probably related to the presence of agglomerates at higher filler concentration. As expected, addition of the ESP increased the stiffness of the NR gradually with increasing filler content.

![Graph showing the effect of ESP on rebound resilience of NR.](image2)

**Fig.(5): Effect of ESP on rebound resilience of NR.**
3.6 Specific Gravity:

Fig.(6) shows increasing of specific gravity with increasing ESP%. This can be explained as follows the particle interfere between rubber chains and make it denser per unit volume.

![Graph showing specific gravity vs ESP%](image)

**Fig.(6): Effect of ESP on specific gravity of NR.**

4. CONCLUSIONS:

In this paper, effect of egg shells powder on some mechanical and physical properties of natural rubber was investigated. Based on the analysis in the present experimental work, the following conclusions can be deduced:

1. The egg shells as a useful material instead of a waste material (harm to the environment) that they were hurled in many hundred tons annually had been used in an engineering applications.
2. The tensile strength, elongation and resilience were decreased with increasing egg shells powder percent. The tensile strength decreased from (22.4 MPa) to (9.7 MPa) with increasing ESP from (5 wt %) to (25 wt%).
3. The modulus of elasticity, hardness and specific gravity were increased with increasing ESP. The hardness was increased from (36.9 IRHD) to (58.3 IRHD) with increasing ESP from (5 wt%) to (25 wt%).
REFERENCES:
Suzaki, N-, J. polymer, 46, 193,(2005).