# The Effect of Egg Shell Powder on Rheological Properties for (NR50/NBR50/ESP) and (NR50/NBR50/ESP/CB-20pphr) Composites

Mohammed Jomaa Mohseen  $^{1*}$ , and Sameer Hassan Hadi Al-Nesrawy  $^2$ 

<sup>1</sup>Department of Physics, College of Education for pure science, University of Babylon, Babylon, Iraq. <u>mohammed.mohseen.pure416@student.uobabylon.edu.iq</u>

<sup>2</sup>Department of Physics, College of Education for pure science, University of Babylon, Babylon, Iraq.

Pure.samir.hassan@uobabylon.edu.iq

 $\textbf{*Corresponding author email:} \ \underline{Pure.samir.hassan@uobabylon.edu.iq}$ 

تأثير مسحوق قشر البيض على الخواص الريولوجية لمتراكبات (NR50/NBR50/ESP) و (NR50/NBR50/ESP/CB-20pphr)

Accepted: 14 / 8/2023 Published: 31/12 /2023

#### **ABSTRACT**

#### Background:

This study used eggshell powder(ESP) as reinforcement filler in (NR/NBR) blend to investigate the effect of this filler material on rheological properties.

## Materials and Methods:

MSR 20 NR (50 pphr) was utilized, and (50 pphr) of NBR (1052, with 33 percent acrylonitrile contents) as a basic, carbon black N375(CB-20 pphr) was used. Eggshell powder (ESP) is a (97%) calcium carbonate (CaCO3) powder, two groups of samples were prepared with (0, 10, 30, and 50 phr) loading ratios of ESP and (CB-20 phr).

#### **Results:**

The results revealed that all properties decreased with increasing ESP and CB loading ratios except cure rate index(CR) properties increased with increasing loading ratios.

#### Conclusion:

From the results obtained Eggshell powder (ESP) was utilized in composites as biofillers. The eggshell powder (ESP) and CB-20 pphr used as reinforcement in the group (A) and (B) composites have been studied for their mechanical and rheological properties. As the loading ratios for (ESP) and (CB-20pphr) increased, the rheological parameters such as the smallest torque (ML), the ideal the Additionally assessed the maximum torque (MH),optimum cure time (Tc90), and scorch time (Ts2) all dropped, but the cure rate index (CR), which was rising.

## **Keywords:**

Composite, Eggshell powder, Calcium carbonate, Rheological properties, Carbon black.



# 1. INTRODUCTION

NBR is commonly used in numerous industries because of its simplicity of production and resilience to chemicals and oils. But neat NBR only exhibits weak tensile properties, and is grease resistant. Over the past few years, a significant amount of research has been done to develop new polymeric materials with improved specific properties for particular purposes. The easiest method for combining the best qualities of many existing polymers—that is, mixing polymers—receives a lot of attention. Despite reports of an increase in miscible mixes [1].

Composites often consist of two (or more) separate components that, when combined, create a new substance that differs greatly from its component elements in every way. This combination has the advantage of integrating the filler's high stiffness and strength into the composite [2].

Due to advances in science and technology over the past (20) years, more synthetic polymers have been manufactured globally. A very wide range of polymer composite materials are used for structural applications in the aerospace, building, and automotive industries because of their strength, high specific stiffness, and lightweight nature [3].

Today, composite materials are widely used in almost every sector of the military, automotive, construction, and packaging industries. Low density, high specific strength and stiffness, strong corrosion resistance, and enhanced fatigue properties are the main benefits of composite materials. They have successfully replaced numerous traditional metals because of these qualities. Polymer composites have been created for decades by reinforcing polymers with a variety of micronscale particles [4].

Rubber reinforcement with stiff materials such as carbon black, clays, silicates, and calcium carbonate is one of the most significant phenomena in material science. These reinforcement agents or fillers are included in rubber compositions to enhance their attributes so that they meet a particular application for a service or a set of performance criteria. Even though the primary objective was to lower the cost of molding chemicals, the amount of selective active fillers and how they affect the physical qualities of rubber are now given priority [5].

The current industry standard industrial rubber for enhancing strength and toughness, abrasion resistance, and durability is composed of carbon black and silica. Researchers are looking at new varieties of organic fillers as a replacement for the petroleum hydrocarbon product carbon black notwithstanding its benefits because of environmental concerns [6].

Recent environmental and economic considerations have given the use of waste materials in polymeric products significant significance. To create new useful composite materials, some of these wastes have been included in the polymer matrix, for example, Bagasse, rice husk ash, fly ash, tire rubber waste, and paper sludge are examples of waste materials are all examples of trash. Eco composites are mostly made from non-toxic, biodegradable natural resources [7].

It has been determined that food wastes are the cause of several health and environmental issues. According to the United Nations' Food and Agriculture Organization (FAO). The majority of food waste includes some kind of valuable mineral. Finding a different way to extract valuable minerals from these food wastes is, therefore, necessary to avoid the high disposal costs and environmental issues. Eggshells are one of the numerous food wastes that include several bioactive chemicals with high economic potential. Approximately (94–96%) of an eggshell is estimated to be CaCO<sub>3</sub>, which is a key ingredient in many manufacturing sectors [8].

For Pure and Applied Sciences (JUBPAS)

Because of its chemical makeup and accessibility, ES has the potential to be used in large quantities as a filler in composite applications that are low-cost, lightweight, and load-bearing. To enhance the mechanical and physical characteristics of styrene-butadiene rubber, polyester resin, and polypropylene eggshell powder (ESP) have been utilized as a filler in recent research [9].

This research work used eggshell powder(ESP) as reinforcement filler in (NR/NBR) blend to investigate the effect of this filler material on rheological properties.

# 2. Materials and Methods

#### 2.1. Materials

MSR 20 NR (50 pphr) was utilized, and it was provided by Perlis, Malaysia. (50 pphr) of NBR (1052), with a (33) percent acrylonitrile content, was obtained from Nantex Industry Co., Ltd. in China. Iran's Doudah contributed the carbon black N375. It is evaluated in line combined with [ASTM D136 and D135] standards for DBP and iodine absorption, respectively. N375 (CB-20 pphr) was used. Durham, UK provided the stearic acid (99.4%) and zinc oxide (97%) for the product. Flexsys, a Belgian company, provided 98 percent of 6PPD N-(1, 3-dimethyl butyl)-N-phenylenediamine for this study. oxydiethylenebenzothiazole (MBS). ITT, India provided the most (98.2%) of the 2-sulfonamide. oil processing. Sodium was imported from Al- Meshrak, CO-Iraq.

Eggshell powder (ESP) is a (97%) calcium carbonate (CaCO<sub>3</sub>) powder that was developed in the Alkhora Company's facility in Baghdad. It has great mechanical qualities, is lightweight, and is simple to produce.

## 2.2. Preparation method

Acrylonitrile Butadiene Rubber (NBR) (50 pphr) and vulcanization ingredients, such as sulfur, zinc oxide, citric acid as an activator, 6PPD as an antioxidant, MBS as an accelerator, and oil droplets as plasticizers, were utilized in this design as the basic material fabric; the batch is then supported with the aid of eggshell powder (ESP) at specific loading ratios to attain (NR50/NBR50/ESP).

To prepare the composite, it was added to the fundamental materials with one-of-a-kind loading ratios (0, 10, 30, and 50 pphr) to gain (NR50/NBR50/ESP) within the It was produced to acquire (NR50/NBR50/ESP/CB-20 pphr) inside the institution (B) utilizing identical loads ratio of ESP with carbon black (CB-20 pphr) in another pattern as group (A). Tables (1) and (2) include a summary of it.

Table 1. presented the loading ratio of the components of group (A) composites

No.	Materials	A1	A2	A3	A4
1	NR	50	50	50	50
2	NBR	50	50	50	50
3	Zinc Oxide	4	4	4	4
4	Stearic acid	1	1	1	1
5	MBS	1	1	1	1
6	6PPD	0.5	0.5	0.5	0.5
7	Carbon black	0	0	0	0
8	Process oil	3	3	3	3
9	ESP	0	10	30	50
10	Sulfur	1.5	1.5	1.5	1.5

Table 2. presented the loading ratio of the group (B) composites' constituents

No.	Materials	B1	B2	В3	B4
1	NR	50	50	50	50
2	NBR	50	50	50	50
3	Zinc Oxide	4	4	4	4
4	Stearic acid	1	1	1	1
5	MBS	1	1	1	1
6	6PPD	0.5	0.5	0.5	0,5
7	Carbon black	20	20	20	20
8	Process oil	3	3	3	3
9	ESP	0	10	30	50
10	Sulfur	1.5	1.5	1.5	1.5

## 2.3. Rubber batch preparation

The eggshell wastes amassed domestically were washed very well many times with water, dried in the sun for several days, and then divided into tiny pieces. The eggshell and its membranes were separated from the trash eggshell bits using mechanical stirring. The eggshell fragments were dried for an hour at (100°C) in a furnace after the membranes were removed. The dried eggshell fragments were then ground into powder in a very centrifugal mill. The eggshell powder became positioned in a field furnace for (2 hours) at four hundred°C. heat treatment changed into executed on the ESP to enhance the homes of the eggshell powder. Fig.(1,a,b) display the eggshell powder (ESP) earlier than and after heat treatment, respectively.





Figure(1): Photographs of egg shells powdr heat treatment at 400 °C: a)before treatment and b)after treatment

The composites have been created with the aid of combining the substances in a applying them to the (Comerio Ercole Busto Avsizo, Italy) rubber batch laboratory (2-Rolls). The diameter is one hundred fifty mm in line with the roll, and the period is three hundred mm. Well, mixing turned into done in line with [ASTM D15], the temperature turned into regulated at (50-5) °C, and for all types of batches, the materials collection to the architecture and the time needed for each material had been documented.

## 3. Results and Discussion

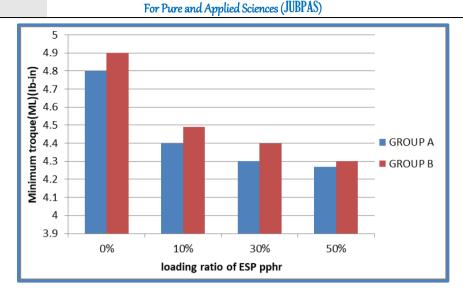
Rheology provides information about minimum and maximum torque, scorching time, curing time as well as curing rate, and maximum torque(MH) is related to the stiffness, crosslinking density, and viscosity of the compound under testing. Minimum torque(ML) indicates the processability of the material; the higher it is the lower the material's processability. Scorch time(Ts2) and cure time(Tc90) measure the time taken to begin and end vulcanization, respectively and cure rate time(CR) determines how long vulcanization takes. The following equation presents a simple approach to describing the cure rate index [10].

$$CR = 100/(Tc90-Ts2)$$
 .....(1)

#### 3.1. Rheological properties

## 1. Minimum Torque(ML)

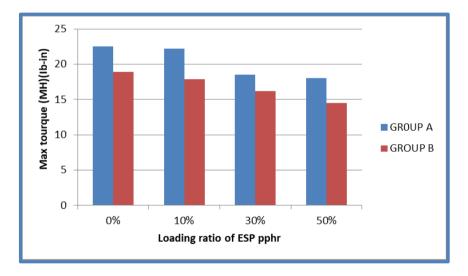
In accordance with [ASTM D-2705], oscillating disc rheometer measurements of all rheological characteristics were made at (160°C), (10 bar) of pressure, and (12 min). Fig.(2) illustrates the fluctuation of the loading ratios (ESP) and (CB-20pphr), where (ML) is the measured minimum torque. Torque and viscosity are reduced as a result of the correlations between the rubber chain's cross-linking density and the loading ratio of (ESP) and (CB), which speeds up the vulcanization process. (ML) decreases as the (ESP) and (CB) loading ratio rises. As a result, the rate of vulcanization rose quickly in these samples as the (ESP) loading ratios continued to rise; This conduct is in line with what the researcher has discovered [11].



Figure(2): The **ESP** A-(NR50/NBR50/ESP) Bcorrelation between the groups (NR50/NBR50/ESP/CB-20 pphr), respectively, and the minimum torque (ML) and loading ratio.

## 2. Maximum Torque(MH)

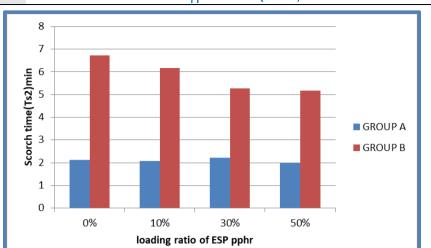
The maximum torque (MH) decreased when the ratios of (ESP) and (CB-20pphr) loading rose, as shown in Fig.(3). The rubber substance started to volcanize and become an elastic solid as the torque increased, which is what led to this behavior. The findings suggest that there might be a molecular chain separation. This behavior supports the study's conclusions [12].



Figure(3) shows the variance in maximum torque (MH) for ESP groups A-(NR50/NBR50/ESP) and B-(NR50/NBR50/ESP/CB-20 pphr) with respect to the loading ratio.

#### 3. Scorch Time(Ts2)

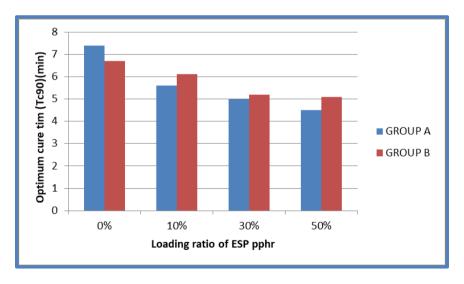
Fig.(4) shows the relationship between the loading ratio of (ESP) and (CB-20pphr) and the optimal scorch time (Ts2) indicates that treatment should begin in opposition gradually As can be observed, this increases the loading ratio of (ESP). As a result, both values for treatment duration and the ideal scorch time (Ts2) increased, as did the vulcanization rate slowed down. This behavior is compatible with the researcher's theory [13].



Figure(4) shows how the loading ratio of the ESP groups A-(NR50/NBR50/ESP) and B-(NR50/NBR50/ESP/CB-20 pphr) affects the change of scorch time (Ts2).

#### 4. Optimum cure time(Tc90)

Fig.(5) shows revealed the ideal cure time (Tc90) reduced when ratios of (ESP) and (CB-20pphr) loading rose. This occurred because the values of the optimum cure time (Tc90) fell as the vulcanization rate accelerated. This action is consistent with the study's conclusions [14].



Figure(5) shows how the loading ratio of the ESP groups A-(NR50/NBR50/ESP) and B-(NR50/NBR50/ESP/CB-20 pphr) affects the optimum cure time (Tc90).

#### 5. Cure rate index(CR)

It is visible that the CR (cure rate time) increased as the (ESP) loading ratios increased, and this behavior was accounted for by a rise in the rate of vulcanization. Fig.(6) displays the link between the CB-20 pphr, ESP loading ratios, and cure rate time (CR). This backs up the study's conclusions **[15]**.

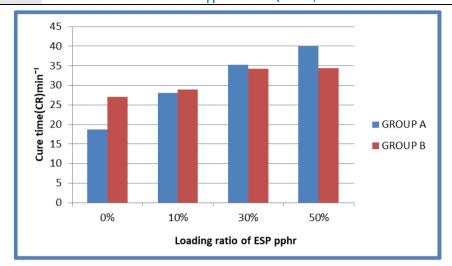
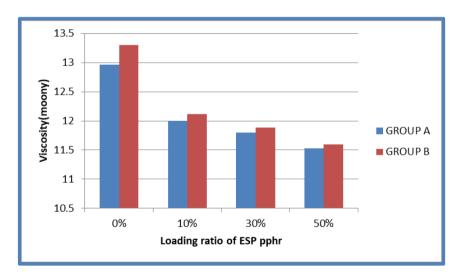


Figure (6) shows how the loading ratio of the ESP groups A-(NR50/NBR50/ESP) and B-(NR50/NBR50/ESP/CB-20 pphr) affects the cure time (CR).

## 6. Viscosity

According to relationship, Viscosity = ML x 2.7 . Fig. (7), shows the viscosity dropped as the loading ratios for Both (ESP) and (CB-20pphr) grew. relationships between the cross-linking density and the (ESP) and the rubber chain were used to explain this behavior, which in turn increased torque and viscosity and accelerated the vulcanization process, this is agreement with the researcher [16].



Figure(7) shows how the viscosity of the ESP groups A-(NR50/NBR50/ESP) and B-(NR50/NBR50/ESP/CB-20 pphr) varies with loading ratio.



# **Acknowledgments:**

Acknowledgment and appreciation to University of Babylon.

# **Ethics**

The Research is not involving the studies on human or their data and all authors commented on previous versions of the manuscript and All authors read and approved the final manuscript.

# 4. Conclusion

Eggshell powder (ESP) was utilized in composites as biofillers. The eggshell powder (ESP) and CB-20 pphr used as reinforcement in the group (A) and (B) composites have been studied for their mechanical and rheological properties. As the loading ratios for (ESP) and (CB-20pphr) increased, the rheological parameters such as the smallest torque (ML), the ideal the Additionally assessed the maximum torque (MH), optimum cure time (Tc90), and scorch time (Ts2) all dropped, but the cure rate index (CR), which was rising.

# Conflict of interests.

There are non-conflicts of interest.

# Reference

- S. P. Thomas, S. Thomas, C. V Marykutty, and E. J. Mathew, "Evaluation of effect of various [1] nanofillers on technological properties of NBR/NR blend vulcanized using BIAT-CBS system," J. Polym., vol. 2013, 2013.
- P. A. Fowler, J. M. Hughes, and R. M. Elias, "Biocomposites: technology, environmental [2] credentials and market forces," J. Sci. Food Agric., vol. 86, no. 12, pp. 1781–1789, 2006.
- [3] M. Y. Amir Hashim and M. D. Morris, "NR latex vulcanisation-prevulcanisation and postvulcanisation of dipped NR latex films.," 1999.
- H. P. S. A. Khalil, P. Firoozian, I. O. Bakare, H. M. Akil, and A. M. Noor, "Exploring biomass [4] based carbon black as filler in epoxy composites: Flexural and thermal properties," Mater. Des., vol. 31, no. 7, pp. 3419–3425, 2010.
- [5] M. S. Sobhy, D. E. El-Nashar, and N. A. Maziad, "Cure characteristics and physicomechanical properties of calcium carbonate reinforcement rubber composites," Egypt. J. Sol, vol. 26, no. 2, pp. 241–257, 2003.
- [6] S. Kamaruddin, M. H. Zakaria, A. B. Chai, and J. H. Ho, "Comparative study of engineering properties using natural rubber (NR) and specialty rubber reinforced biocomposite material," AIP Conf. Proc., vol. 2284, no. October, 2020, doi: 10.1063/5.0027892.
- P. Intharapat, A. Kongnoo, and K. Kateungngan, "The potential of chicken eggshell waste as a [7] bio-filler filled epoxidized natural rubber (ENR) composite and its properties," J. Polym. Environ., vol. 21, pp. 245–258, 2013.
- [8] T. Zaman, M. Mostari, M. A. Al Mahmood, and M. S. Rahman, "Evolution and characterization of eggshell as a potential candidate of raw material," Cerâmica, vol. 64, pp.



236-241, 2018.

- [9] A. S. M. Bashir, Y. Manusamy, T. L. Chew, H. Ismail, and S. Ramasamy, "Mechanical, thermal, and morphological properties of (eggshell powder)-filled natural rubber latex foam," *J. Vinyl Addit. Technol.*, vol. 23, no. 1, pp. 3–12, 2017, doi: 10.1002/vnl.21458.
- [10] S. H. Al-Nesrawy, M. Al-Maamori, and H. R. Jappor, "Effect of temperature on rheological properties of sbr compounds reinforced by some industrial scraps as a filler," *Int. J. Chem. Sci.*, vol. 14, no. 3, pp. 1285–1295, 2016.
- [11] M. H. Naeem and S. H. H. Al-Nesrawy, "Preparation of (Rubber Blend/Oyster Shell Powder) Composites and Study Rheological Properties," 2019.
- [12] E. F. Al-Nesrawy and S. H. H. Al-Nesrawy, "Rheological Properties Of (NR/SBR/CMC/CB) Nanocomposites," in *Journal of Physics: Conference Series*, 2021, vol. 1973, no. 1, p. 12161.
- [13] E. S. Bhagavatheswaran *et al.*, "The taste of waste: the edge of eggshell over calcium carbonate in acrylonitrile butadiene rubber," *J. Polym. Environ.*, vol. 27, pp. 2478–2489, 2019.
- [14] M. Balachandran and S. S. Bhagawan, "Mechanical, thermal, and transport properties of nitrile rubber–nanocalcium carbonate composites," *J. Appl. Polym. Sci.*, vol. 126, no. 6, pp. 1983–1992, 2012.
- [15] A. A. Abdelsalam, S. Araby, S. H. El-Sabbagh, A. Abdelmoneim, and M. A. Hassan, "Effect of carbon black loading on mechanical and rheological properties of natural rubber/styrene-butadiene rubber/nitrile butadiene rubber blends," *J. Thermoplast. Compos. Mater.*, vol. 34, no. 4, pp. 490–507, 2021, doi: 10.1177/0892705719844556.
- [16] E. F. Al-Nesrawy and S. H. Hadi Al-Nesrawy, "Rheological Properties of (NR/SBR/CMC/C.B) Nanocomposites," *J. Phys. Conf. Ser.*, vol. 1973, no. 1, 2021, doi: 10.1088/1742-6596/1973/1/012161.

ــوم الصـــر فــة والنط بيقيــة مــجلــة جــــامعة بــــابــل للعلــوم الصـــر فــة والنط بيقيــة مـجلــة جـــامعة بـــابــل للعلــوم الصــر فــة والنطـــــبيقيــة



# الخلاصة

## الخلفية:

استخدم هذا البحث مسحوق قشر البيض (ESP) كحشو تقوية في مزيج (NR / NBR) للتحقق من تأثير مادة الحشو هذه على الخصائص الربولوجية.

## طرق العمل:

تم استخدام ( MSR 20 NR 50 pphr ) من 1052 NBR ( مع (33) بالمائة من محتويات أكريلونيتريل ) كأساس ، أسود الكربون CB-20 pphr). مسحوق قشر البيض (ESP) عبارة عن مسحوق كربونات الكالسيوم 97٪ (CaCO3) ، تم تحضير مجموعتين من العينات بنسب تحميل (Phr 50 ، 30 ، 10 ، 00) من ESP و (CB-20 phr).

# <u>النتائج:</u>

أوضحت النتائج أن جميع الخواص انخفضت مع زبادة نسب تحميل ESP و CB فيما عدا زبادة خصائص مؤشر معدل الشفاء (CR) مع زيادة نسب التحميل.

# الإستنتاجات:

من النتائج التي تم الحصول عليها تم استخدام مسحوق قشر البيض (ESP) في المركبات كمواد بيولوجية. تمت دراسة مسحوق قشر البيض (ESP) و CB−20 pphr المستخدمان كتعزيز في مركبات المجموعة (أ) و (ب) لخصائصهما الميكانيكية والريولوجية. مع زبادة نسب التحميل لـ (ESP) و (CB-20pphr) ، فإن المعلمات الربولوجية مثل أصغر عزم دوران (ML) ، والمثالية التي تم تقييمها بالإضافة إلى أقصى عزم دوران (MH) ، ووقت المعالجة الأمثل (Tc90) ، ووقت الاحتراق (Ts2) انخفض جميعها ، لكن مؤشر معدل الشفاء (CR) ، الذي كان يرتفع.

## الكلمات المفتاحية:

مركب ، مسحوق قشر البيض ، كربونات الكالسيوم ، الخصائص الربولوجية ، أسود الكربون.