



## Evaluation of Styrene/Butyl-Acrylate as Modifier Additive in (NBR) Compounds Vulcanizates



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**S**TYRENE/BUTYL acrylate (SBt) was prepared using *in-situ* seed emulsion polymerization and precipitated in an excess of methanol. The prepared (SBt) was utilized as modifier additive for acrylonitrile–butadiene rubber (NBR) in different dosage i.e. 5 phr, 10 phr, 15 phr and 20 phr. The rheometric and the physicomechanical characteristics of the vulcanizates include tensile strength, elongation at break, and swelling in toluene and motor oil were studied at room temperature before and after aging at 90 °C for up to 7 days. Moreover, morphology and dielectric properties of the modified (NBR) vulcanizates were investigated as well. It was discovered that 20 phr of the Styrene/butyl acrylate (SBt) that incorporated with (NBR) has the highest physicomechanical characteristics as well as dielectric parameters.

**Keywords:** (NBR), (SBt), Dielectric properties, Physicomechanical properties, Morphology.

### Introduction

Elastomers are polymers with an elastic property, compared with other materials; they have an obvious low Young's modulus and high yield strain (1). This term is often used interchangeably with the term rubber. They are amorphous and expected to be very permeable polymers, there is a considerable segmental bouncing because they are existing above their glass transition temperature. At ambient temperatures, they are soft and deformable. There are mostly applicable for seals, adhesives, and molded flexible parts. Moreover, the thermosets step required vulcanization that is a form of crosslinking or thermoplastic and so-called thermoplastic elastomer (TPE). Firstly, the important advantages of TPEs over the conventional thermoset (vulcanized) elastomers, firstly that they can ease and speed the processing. Secondly, there are recyclable, has lower energy costs for processing, and has available standard uniform grades, that is not generally available in the conventional thermosets.

Eventually, in order to improve the properties of elastomers, some materials are incorporated such as stearic acid, zinc oxide, processes aid, Sulfur, carbon black (HAF), antioxidant (PBN), high-quality accelerator, such as n-cyclohexyl-2- benzothiazole sulfonamide (CBS), and tetramethylthiuram disulfide (TMTD).

Besides the previously mentioned elastomers, there is another kind of rubber called nitrile rubber (NBR) or also known as Buna-N, Perbunan, nitrile rubber. NBR products are typically the beaver of automotive industries (2). By selecting NBR with the appropriate acrylonitrile content, NBR can be utilized by rubber compounder in a wide variety of application requiring lubricants, fuel, and chemical resistance, especially for automotive manufacturing. Within a temperature range of –40°C to +125°C, NBR articles can afford the stark automotive applications. Industrially, NBR has been utilized in different applications such as roll-up covers, hydraulic pipes, conveyor

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belts, graphic arts, hydraulic packer, O-rings and seals for all kinds of plumbing and appliance applications (2).

Nowadays, the applications of NBR increases annually. Likewise, unsaturated thermoset elastomers, NBR are requested to be formulated with various ingredients and further processes in order to fabricate functional articles. Extra components classically contain reinforcement fillers, plasticizers, stabilizers, and curing frameworks. Moreover, in order to produce the final rubber products, processing includes mixing, extrusion, the formation of the needed shapes, and finally. The mixing and the processing steps are usually performed on open roll-mills or internal Brabender. The final products that behold in the market include seals, grommets, pipes or tubing and calendered sheet goods or various sponge articles (3). Different NBR producers can be produced only by varying its polymerization temperatures to make "hot" and "cold" polymers. In NBR, mostly the acrylonitrile (ACN) and butadiene (BD) proportions varied according to the specific oil, fuel resistance, and low-temperature necessities (4). Furthermore, NBR polymers that carry a third monomer, e.g. divinylbenzene, methacrylic acid, are also displayed. Each modification contributes uniquely different properties, for example, some NBR elastomers are hydrogenated to decrease the chemical reaction of the polymer vertebrae and an essential improvement to their heat resistance will be performed.

The ACN content is a primary standard that appoint the grade of NBR. The ACN level allocates various basic properties, including lubricates, solvent impedance, low-temperature, flexibility-glass transition temperature, and abrasion impedance (5-6). The higher the provide ACN content, the higher the improved properties such as the resistance of solvent, along with higher glass transition temperature. The aim of this research is to investigate the impact of styrene-butyl acrylate before and after aging also study the morphology of the modified NBR, on the characteristics of NBR vulcanizates with freaked reference include the mechanical, rheological and electrical characteristics.

## **Material and Experimental Techniques**

### *Materials*

Acrylonitrile-Butadiene Rubber (NBR)

Perbunan N3310 with acrylonitrile content  $\approx$  34%, was obtained from Bayer AG (Germany). ZnO, Stearic acid, elemental sulfur (S), and phenyl-  $\beta$ -naphthyl amine (PBN), N-cyclohexyl-2-benzothiazole sulphenamide (CBS), carbon black (HAF), were of technical grade were obtained from local rubber company.

Styrene (St), butyl acrylate ((Bt)), acrylic acid (AA), cetyl alcohol, dioctyl phthalate (DOP), DawFax, Sodium bicarbonate, Potassium persulfate were used as fine chemicals imported from Sigma Aldrich. The used monomers were distilled to remove the inhibitor

### *Experimental techniques:*

#### *Preparation of the styrene butyl acrylate copolymer*

The copolymer latexes based on styrene (St), butyl acrylate (Bt), acrylic acid (AA), were prepared by *insitu* seed emulsion polymerization technique with solid content of 50%. Typically, the copolymer synthesis has been carried in two steps; pre-emulsion step and *insitu* seeded emulsion polymerization step. In the pre-emulsion step, 30% of distilled water, Daw fax emulsifier, and the monomers (St and Bt) were added into glass beaker and mixed for 30 min using high speed homogenizer. (7)

The acyclic acid monomer (AA) was added during continuous homogenization. In the *insitu* seeded emulsion polymerization step, distilled water, cetyl alcohol emulsifier,  $\text{NaHCO}_3$ , 50% of the initiator, and 10% of the pre-emulsion were added into four necked flask equipped with continuous stirring under reflux. (8)

The polymerization reaction was carried out at 80°C using thermo stated water bath for 30 min under a blanket of Nitrogen atmosphere. The remaining pre-emulsion and initiator were step wise added into the reactor within 3h. The recipe used for preparation of the co-polymer latexes was deionized water 50.4, (St) 26.5, ((Bt)) 19, (AA) 1.8, Daw Fax emulsifier 2.2, cetyl alcohol 0.4, Sodium bicarbonate 0.1, Potassium persulfate 0.2. (9)

The prepared co-polymer was precipitated using excess of methanol and dried in well ventilated oven at 90°C till constant weight. (10)

### *Mixing and Vulcanization*

Laboratory two-roll mill (470 mm diameter and 300 mm working distance) was used for rubber mixing. The speed of the slow roller is 24 rev./min with a gear ratio of the tow roll 1:1.4. Care was taken to ensure complete mixing of rubber ingredients on the mill. The vulcanization was carried out in a heated platen press under a pressure of about 4 MPa and temperature 162 °C.

### *Rheometric characteristics:*

Monsanto Oscillating Disc Rheometer model-100 was used to determine Rheometric characteristics: Maximum torque ( $M_h$ ), minimum torque ( $M_l$ ), scorch time  $t_{s2}$ , optimum cure time ( $t_{c90}$ ) and the cure rate index (CRI) were determined according to ASTM method D 2084-10.

### *Physico-mechanical properties*

a-The mechanical properties (tensile and elongation) were determined using Zwick tensile testing machine (model-1425), according to ASTM D 412-10.

b- Swelling of the rubber vulcanizates in toluene was determined according to ASTM D 471-12a.

The samples were immersed in both toluenes at room temperature for 24 hours or in motor oil at 100°C for seven days.

The swelling value (S.V.) was calculated as follows:

$$S.V. = [(W_i - W_o)/W_o] \times 100$$

Where:

$W_o$  = weight before swelling

$W_i$  = weight after swelling

C-Thermal oxidative aging was carried out according to ASTM D 573-10 at 90°C for different time periods up to 7 days in electric oven with good air circulation.

### *Scanning Electron Microscopy (SEM)*

The electron microscope model JXA 840A JEOL electron probe micro analyzer, Japan, was used to inspect the prepared vulcanizates. The fracture surfaces were gold coated to avoid

electrostatic changing during examination. The samples were mounted on a standard specimen stub, coated with a very thin layer of gold.

### *Dielectric measurements*

Dielectric parameters  $\epsilon'$  and  $\epsilon''$  were performed from 100Hz up to 3.8MHz using a Hioki (Ueda, Nagano, Japan) model 3532 High Tester LCR.

## **Results and Discussion**

### *Rheometric characteristics*

The styrene-butyl acrylate copolymer was added to the unvulcanized NBR at different doses (5 phr, 10 phr, 15 phr and 20 phr). The mixing process was achieved in a laboratory roll-mill according to the usual protocol. The rheological characteristics of the mixed NBR products are demonstrated in **Table 1**. The data in **Table 1** shows that the rheometric characteristics greatly depend on the concentration of styrene-butyl acrylate copolymer. It can be seen that the styrene-butyl acrylate copolymer accelerates the vulcanization process as the values of  $t_{c90}$  are decreased with the incorporation of SBt. This is confirmed by the increase of cure rate index values. This can be explained on the basis of the SBt act as an activator of the curing system used. On the other hand, the minimum torque was slightly decreased, while the maximum torque slightly increased as the dose of styrene-butyl acrylate copolymer was increased.

**Table 2** shows both the tensile strength and elongation at break for the prepared samples. It is clearly seen that the incorporation of styrene-butyl acrylate copolymer in NBR compounds has improved the physicomechanical characteristics of the resulted vulcanizates, the values of the tensile strength of the vulcanizates were slightly increased as the dose of styrene-butyl acrylate copolymer were increasing. This can be ascribed to the increase in the stiffness of the NBR vulcanizates. On the other hand, the values of elongation at break were slightly decreased with the increase of the concentration of SBt. This confirms the increase of the stiffness of the NBR vulcanizates. The swelling behavior of NBR vulcanizates versus the concentration of (SBt) in toluene in one hand and in motor oil, on the other hand, is given in **Table 2**. It is clearly seen that the swelling values are slightly increased. This may be due to the chemical nature of (SBt). On the other

hand, the soluble fraction in toluene is clearly decreased. This may be due to the interaction of SBt with the rubber and its ingredients.

#### *Scanning electron microscopy (SEM)*

The morphology of the NBR either unmodified or modified with styrene-butyl acrylate copolymer was studied using (SEM) technique. **Figure 1** shows the SEM images of unloaded NBR with styrene-butyl acrylate copolymer. **Figure (2-3)** demonstrate that the modified NBR with styrene-butyl acrylate copolymer. This scans showed that (SBt) was well dispersed in NBR matrix.

#### *Aging of rubber vulcanizates:*

The effect of styrene-butyl acrylate copolymer and the aging characteristics of NBR vulcanizates were investigated. The NBR vulcanizates were exposed to high thermal aging in an oven with valid air circulation at the temperature 90 °C for 7 days. On the physicomechanical characteristics of the aged samples were allocated and represented. The measured values of tensile strength and elongation at break for all aging periods were illustrated in Figure (7-8) after represented.

The results illustrate that the tensile strength increased from 71% for NBR without modification till 107% of the NBR loaded with 20 phr of styrene-butyl acrylate copolymer, while elongation at break gradually decreases with aging time in the whole aging period. It is worthy to notice that, the NBR vulcanizates modified with styrene-butyl acrylate copolymer have a great efficiency to protect the rubber vulcanizates against thermal aging. It is clearly seen as the chain of (SBt) increases the stiffness of NBR vulcanizates increases, but the elongation gradually decreased with aging time.

The changes in the swelling data and swelling in oil obtained during the aging period are given in Figure (9-11). From these data, it can be clearly seen that the swelling values decrease with increasing the (SBt) content this indicates further cross-linking during the thermal aging time in the whole aging period. On the other hand, the higher value of soluble fractions can be attributed to the solubility of the (SBt) in the organic solvent. Also shown that from the obtained data the swelling in the motor oil reduces with the increment of the (SBt) content this attributed to the further cross-linking of NBR vulcanizates.

#### *Dielectric measurements*

The dielectric constant ( $\epsilon'$ ) was measured as a function of frequency ( $f$ ) at room temperature, and it was observed that the value of  $\epsilon'$  is opposite to the common rule wherein  $\epsilon'$  decreases with increasing frequency. Here, we observed that the value of the dielectric constant ( $\epsilon'$ ) increases with the increasing frequency, as shown in Figure (4). This may be ascribed to either the increase of the number of dipoles that contributed to the polymerization or to the increase the ability of the dipoles structure to respond to the applied electric field. Moreover, it is clear that ( $\epsilon'$ ) increases with the increment of (NBR) content in the blend. The step up in  $\epsilon'$  with the incorporation of rubber is due to the increase in C = N dipoles, which results in an increment in the orientation polarization and the existence of interfacial polarization. (11)

From **Figure 5**, it is obvious that the curves relating ( $\epsilon'$ ) and  $\log(f)$  are broader than Debye curves (12), referring that more than one relaxation process is present. These processes could be ascribed to the mechanisms related to the main chain and its related motions (13-15).

One of the available mechanisms is related to the Maxwell-Wagner impact that often persists in low-frequency region for heterogeneous systems. The alternating current is the origin of this process where it is the reason of phase formation with an applied potential due to the variation in the permittivity and sensitivities of the blends.

This circumstance has also been noticed for both discrete polymer and NBR as a result of the existence of peroxide in NBR that is frequently added-up for the rubber curing and in addition to other impurities such as catalysts and antioxidants that are also offered during the polymerization and oxidation processes (16-17).

We found that the dielectric loss ( $\epsilon''$ ) increases with frequency from 100Hz till showing a peak at ~1KHz for all samples. Likewise, the movable electronic transport such as an electronic bouncing gets to be less that has the ability to follow the relevant electric field reversal, (electron faster than the field), that is common properties of all dielectrics oblivious to the relaxation mechanism. The peak frequency of the relaxation was shifted to a lower value with the increase of additives. This suggests that the additives slowed the segmental mobility of polymer chains in the samples i.e.

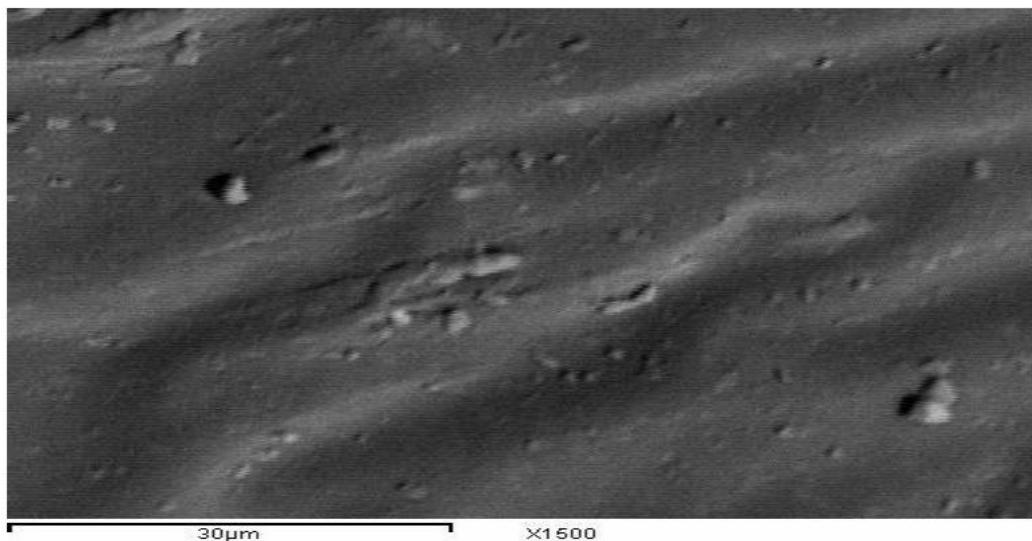
**TABLE (1): The Rheometric characteristics of the rubber mix of (NBR) vulcanizates with styrene butyl acrylate co-polymer.**

Ingredient	Formulation	N1	N2	N3	N4	N5
(NBR)		100	100	100	100	100
styrene butyl acrylate co-polymer	----	5	10	15	20	
Minimum torque ( $M_L$ ), dNm	6	5.5	5.5	5	4.5	
Maximum torque ( $M_H$ ), dNm	50	53	53	53	51	
Optimum cure time ( $T_{C90}$ ), min	25	20.5	20	20	19	
Scorch time ( $t_{S2}$ ), min	2.25	2.75	2.75	3.5	3.5	
Cure rate index (CRI), min <sup>-1</sup>	4.94	5.63	5.8	6.06	6.45	

Stearic acid 4, Zinc oxide 5, processes aid 3, Sulfur 2, HAF 40, PBN 1, CBS 1, TMTD 0.8

**TABLE (2): The Physico- mechanical properties of the rubber mix of (NBR) vulcanizates with styrene butyl acrylate co-polymer.**

Properties	Formulation	N1	N2	N3	N4	N5
Tensile strength, (MPa)		12.68	12.93	13.95	14.68	14.3
Elongation at break, %		463	500	500	456	431
Equilibrium swelling in toluene, %		118	130	123	123	129
Soluble fraction in toluene, %		3.93	3.77	2.81	1.86	1.75
Swelling in motor oil, %		1.91	2.24	2.5	2.6	2.29

**Figure (1): SEM of unloaded (NBR) with styrene butyl acrylate co-polymer**

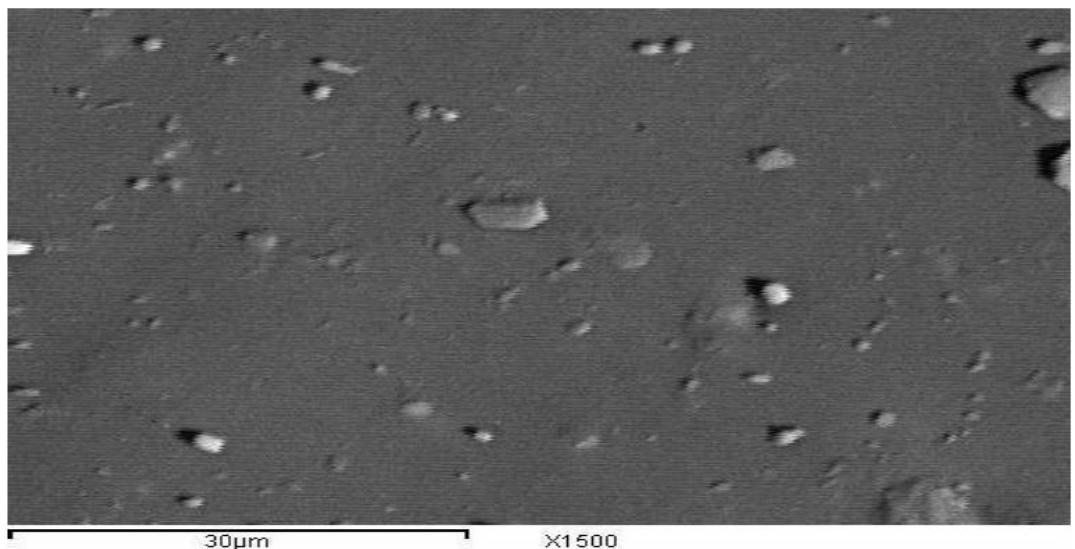


Figure (2): SEM of (NBR) modified with 15 phr styrene butyl acrylate co-polymer

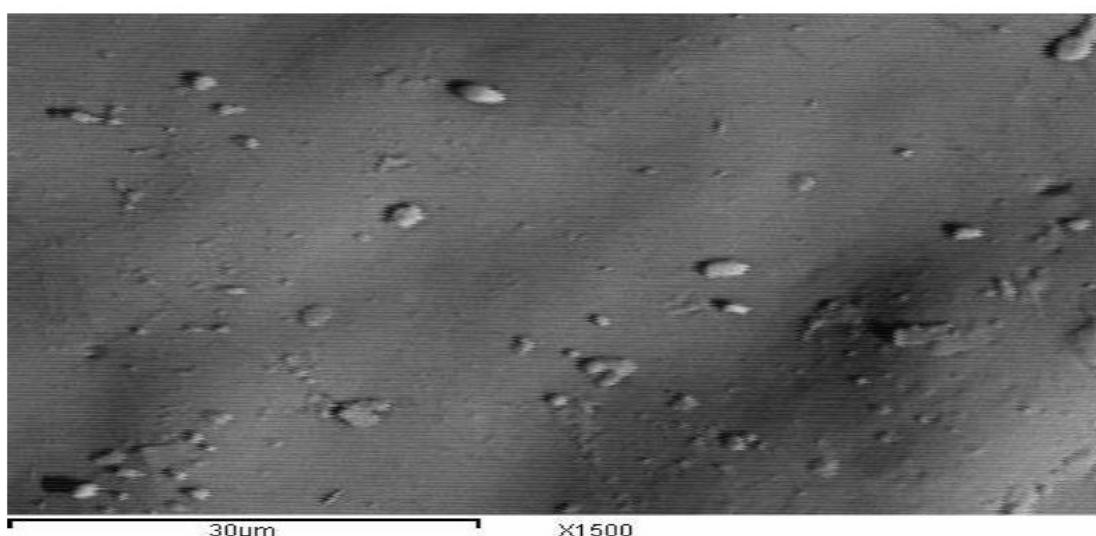
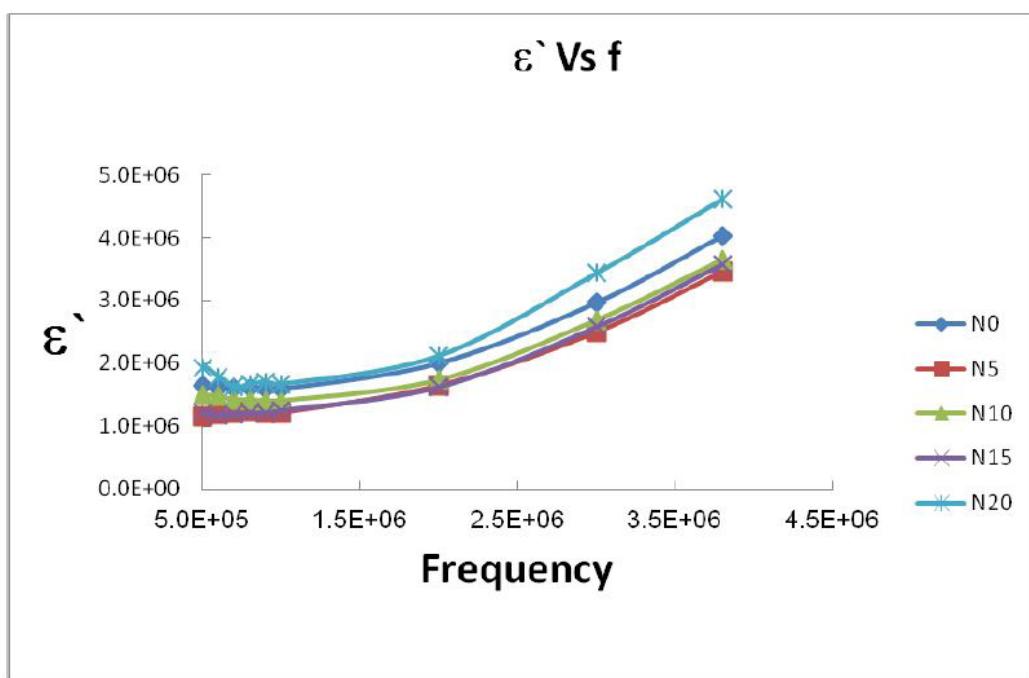
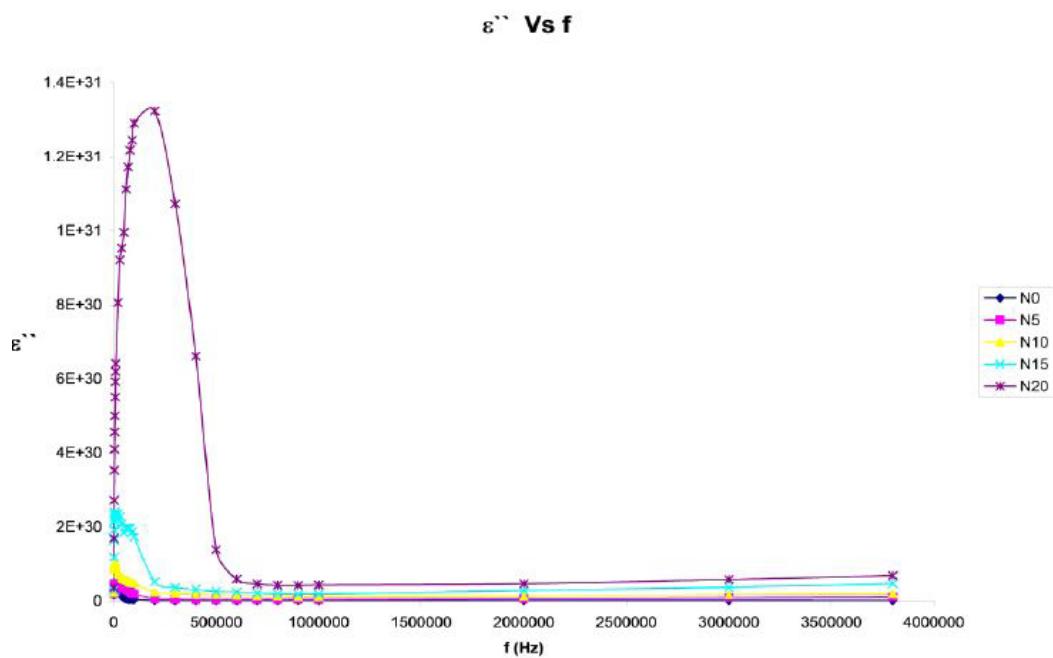


Figure (3): SEM of (NBR) modified with 20 phr styrene butyl acrylate co-polymer



**Figure 4:** The variation of the real part of the dielectric constant  $\epsilon'$  as a function of frequency for pure NBR and NBR-SBT samples with different concentrations.



**Figure 5:** The variation of the imaginary part of the dielectric constant  $\epsilon''$  as a function of frequency for pure NBR and NBR-SBT samples with different concentrations.

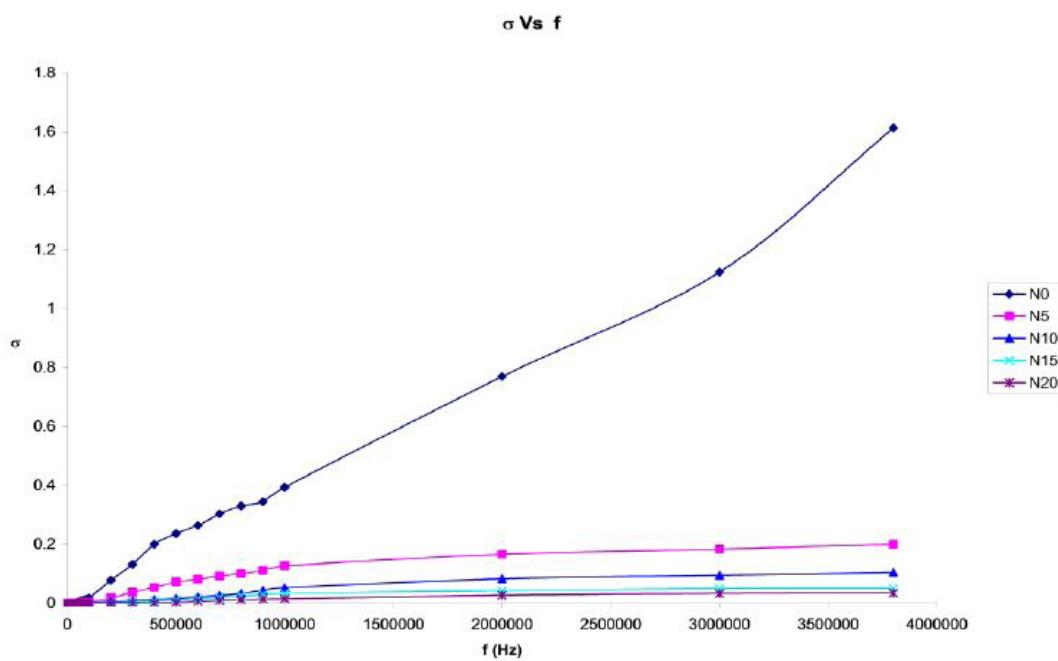


Figure 6: The variation of ac conductivity as a function of frequency for pure NBR and NBR-SBT samples with different concentrations.

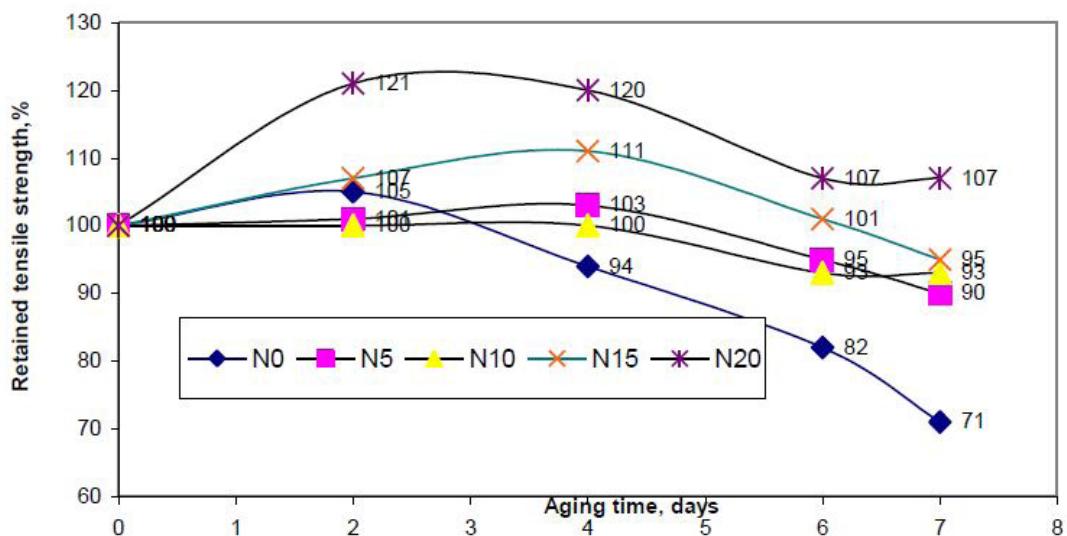
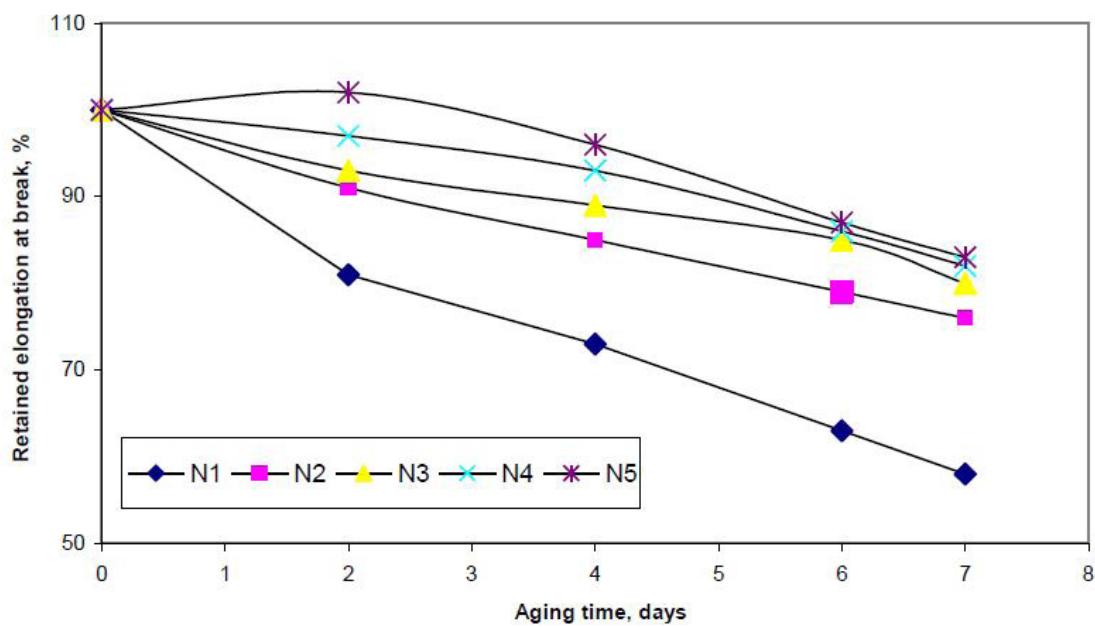
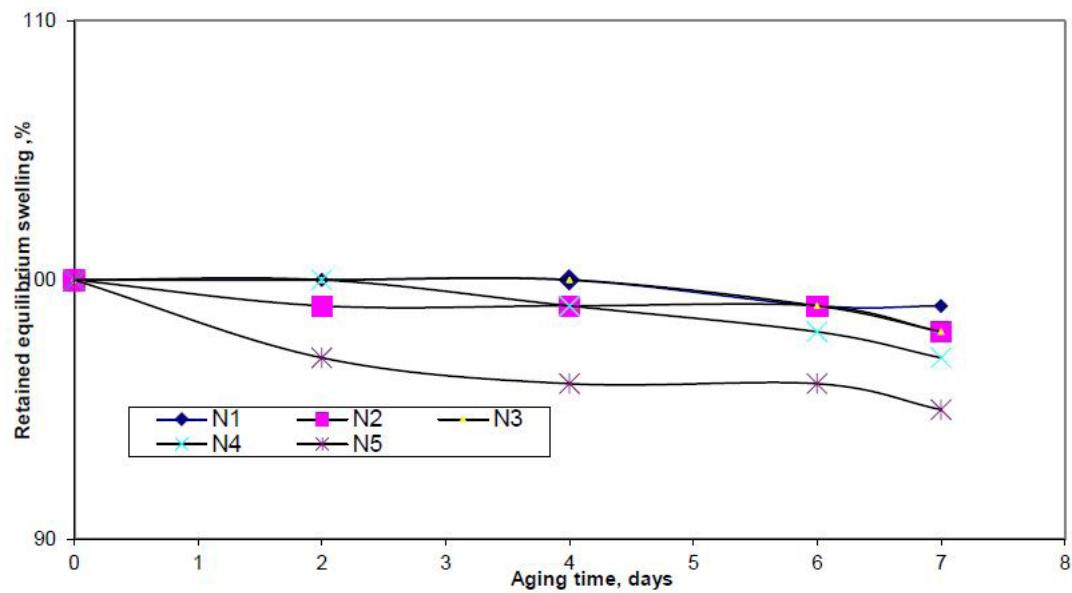


Figure (7): Retained tensile strength of NBR vulcanizates containing styrene butyl acrylate copolymer vs. time after aging, (days)



**Figure (8):** Retained elongation at break of NBR vulcanizates containing styrene butyl acrylate co-polymer vs. time after aging, (days)



**Figure (9):** Retained equilibrium swelling in toluene of NBR vulcanizates containing styrene butyl acrylate co-polymer v.s. aging time, (days)

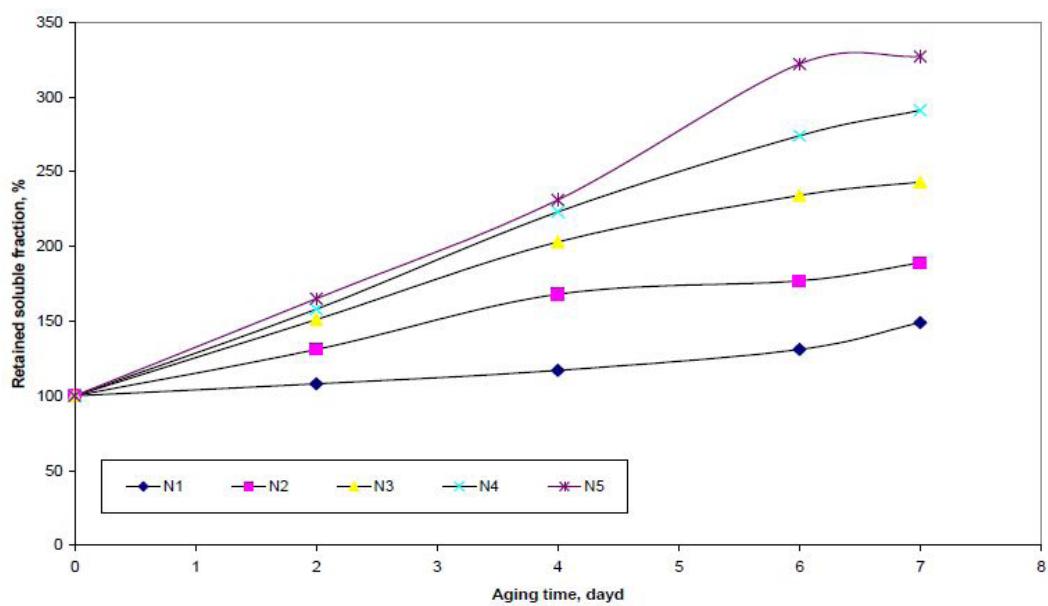


Figure (10): Retained soluble fraction in toluene of NBR vulcanizates containing styrene butyl acrylate co-polymer v.s. aging time, (days)

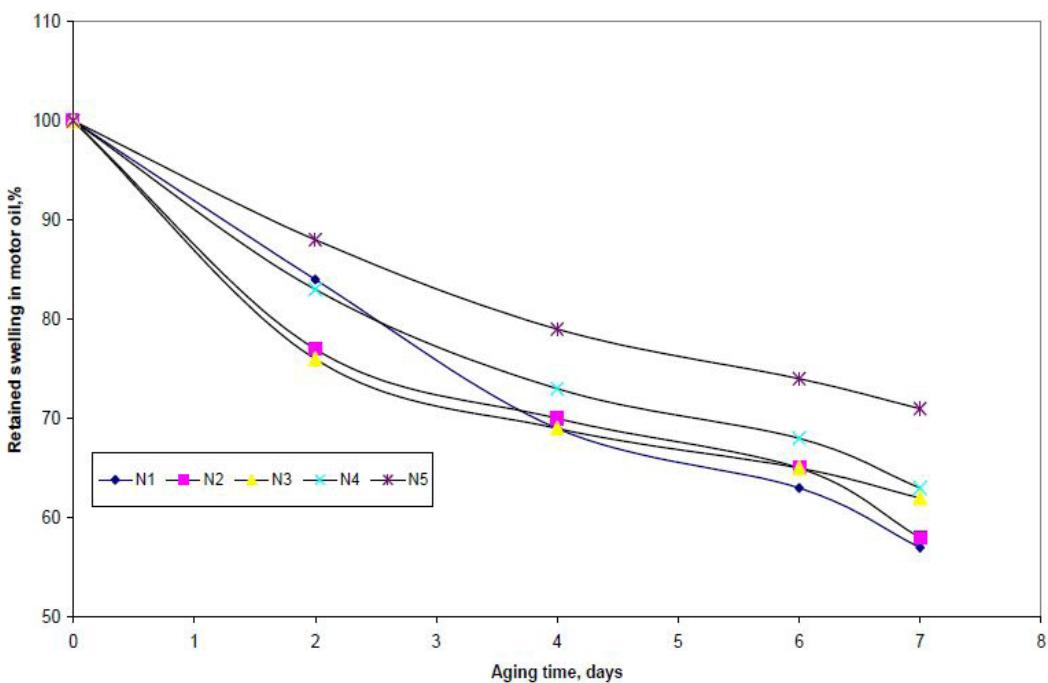


Figure (11): Retained swelling in motor oil of NBR vulcanizates containing styrene butyl acrylate co-polymer v.s. aging time, (days)

segmental relaxation is faster in the samples with lower additives.

This behavior has also been observed in many polymer-ceramic composites (18-19). It can be explained that the more additives, the more interfacial area is created and the polymer chains are detached into tiny portions that raise the conductive web work. Therefore, more dipoles can rotate, bouncing can be more hyper, and the dissipation of more energy can be realized. In fact, the dielectric loss is the measurement of energy dissipation for the bouncing or rotation of the molecules in the electric field. Furthermore, interface area and tiny or less dense domains of polymer chain could be noticed. Consequently, the improved bouncing of polymer molecules may cause the dielectric loss (20). Moreover, at higher frequencies, the ion vibration may have a high and even only impact on the dielectric loss. Thus, ( $\epsilon'$ ) has an inverse proportion to the value of frequency as it diminished, the values of frequency are the highest (21).

**Figure (6)** illustrates the variation of electrical conductivity  $\sigma$  with frequency for NBR with different additives. It has been observed that for NBR, electrical conductivity varies linearly with a frequency which indicates the high insulating nature of the material. With respect to other samples, the figure shows that the conductivity from 100 Hz up to 1MHz still varies linearly with a frequency indicating the insulating nature of the samples. Going up with frequency, from 1 MHz up to 3.8 MHz, the conductivity starts to be frequency independent, indicating the transition from an insulator to a semiconductor which could be attributed to the formation of conducting web work.

### Conclusions

On the basis of the investigated data, one can conclude the following:

- 1- Styrene butyl-acrylonitrile copolymers act as a significant modifier to NBR compounds.
- 2- The optimum dosage of styrene butyl-acrylonitrile in the NBR is 15 phr of styrene butyl-acrylonitrile to achieve overall reasonable characteristics.
- 3- Swelling in oil and toluene was slightly increased as the amount of styrene-butyl acrylate copolymer was increased.

- 4- The  $\epsilon'$  increases with the increase of (SBt) content. The increment in  $\epsilon'$  incorporated to the rubber is due to the increase in carbon – Nitrogen (C = N) dipoles that order for the increment in the orientation polarization and the existence of the interfacial polarization.

### References

1. Laurence McKeen; The Effect of Sterilization Methods on Plastics and Elastomers (Fourth Edition), Pages 305-351; (2018).
2. Mohammed H. Al- Maamori, Ali Abdul-Amir Al-Zubaidi, Ahmed Abdulameer Subeh; Effect of Novolac on Mechanical and Physical Properties of Nitrile Rubber (NBR)”; International Journal of Materials Science and Applications; 4(2-1) 43-47, (2015).
3. Brendan Rodgers, Walter Waddell; The Science of Rubber Compounding; The Science and Technology of Rubber (Fourth Edition), Pages 417-471; (2013).
4. “Ming Yu Huang; Fluorinated elastomeric blowout preventer packers and method”; US 8091855 B1, Jan, 10, (2012).
5. A. I. Hussain, A. H. Abdel-Kader and A.A. Ibrahim; “Effect of Modified Linen Fiber Waste on Physico-Mechanical Properties of Polar and non-Polar Rubber”; Natural and Science; 8; (8) 82-93 (2010).
6. Felipe N. Linhares, Cléverson F. S. Gabriel, Ana Maria F. de Sousa, Regina Célia Reis Nunes; Mechanical and rheological properties of nitrile rubber/ fluoromica composites; Applied Clay Science, 162, Pages 165-174; 15 September (2018).
7. Abd El-Shafey I. Ahmed, Ahmed I. Hussain, Ahmed M. El-Masry, and Ahmed Saleh; “Effect of changing mass ratio of styrene/butyl acrylate on the behavior of nano organo-silica in poly (styrene co-butyl acrylate) emulsion core-shell”; ARPN Journal of Engineering and Applied Sciences, Vol. 10, No. 14, (2015).

8. Abd El-Shafey I. Ahmed, Ahmed. I. Hussain, Ahmed M. El-Masry1 and Ahmed Saleh; “Thermomechanical properties of styrene-butyl acrylate/organo-silica nanocomposite films prepared by seed emulsion polymerization”; *Polymer Composite*; 2 May (2015), DOI:10.1002/pc.23560.
9. F.A El-Moeen, A.I. Hussain, EL Nashy, HA El-Wahhab, AERM Naser; “Nano-Emulsion Based on Acrylic Acid Ester Co-Polymer Derivatives As An Efficient Pre-Tanning Agent For Buffalo Hide”; *Arabian Journal of Chemistry*; 9 July 2014, DOI:10.1016/j.arabjc. 2014.05.024.
10. Mohamed Gmoaa Hussain, Ahmed I. Hussain, Said Teleb; “Preparation and Characterization of Some nano-emulsion Oracticles from Acrylate Ester as a Binder for Over Print Varnish Water Base” 5th International Conference on Advances in Chemistry and Applied Chemistry; October 21-23 (2014).
11. “A. A. Mansour, S. EL. Sabagh and A. A. Yehia; Dielectric Investigation of SBR-(NBR) and CR-(NBR) Blends”; *J. Elastomers and Plastics*.26, 367, (1994).
12. “Smyth, C. P.; Dielectric Behavior and Structure”; McGraw-Hill: New York, (1955).
13. “Younan, A. F.; Abd-El-Messieh, S. L.; Gasser, A. A., Electrical and mechanical properties of ethylene propylene diene monomer–chloroprene rubber blend loaded with white and black fillers”; *J Appl. Polym. Sic.*, 70, 2061, (1998).
14. “Mohamed, M. G.; Abd-El-Messieh, S. L.; El-Sabbagh, S.; Younan, A. F.; Electrical and mechanical properties of polyethylene-rubber Blends”; *J Apple Polym Sci*, 69, 775, (1998).
15. “El-Sabbagh, S.; Moktar, S. M.; Abd-El-Messieh, S. L.; Electrical and mechanical properties of grafted and ungrafted polyacrylamide-rubber blends”; *J Appl. Polym Sci*, 70, 2059, (1998).
16. “Abd-El-Messieh, S. L.; Younan, A. F., Dielectric relaxation and mechanical properties of natural and chloroprene rubber with some nitroaniline additives”; *J Apple. Polym. Sci*, 62,805, (1996).
17. “Abd-El-Aal, M. M.; Mokhtar, S. M.; Osman, B. S.; Dielectric relaxation of poly (tetrafluoroethylene–perfluorovinyl ether) films”; *Polym. Int.* , 39, 339, (1996).
18. “Boger A, Bisig A, Bohner M, Heini P, Schneider E, Variation of the mechanical properties of PMMA to suit osteoporotic cancellous bone”; *J. of biomater. Sci- Polym.* 19:9, 1125-42, (2008).
19. “Jancar J, Hynstova K, Pavelka V, Toughening of denture base resin with short deformable fibers”; *Compos Sci Technol*; 69:457-62, (2009).
20. “Chih-Wen Tang, Bin Li, Lili Sun, Brooks Lively, Wei-Hong Zhong; The effects of nanofillers, stretching and recrystallization on microstructure, phase transformation and dielectric properties in PVDF nanocomposites”; *Eur. Polym. J*.48, 1062-1072, (2012).
21. “S. C. Agarwal, S. Guha, K. L. Narasimhan; A.C conductivity in amorphous germanium”; *J. Non-Cryst. Solids* 18,429, (1975).