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Formulation, preparation and mechanical characterization of Nitrile -Butadiene (NBR) rubber nanocomposites.

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Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

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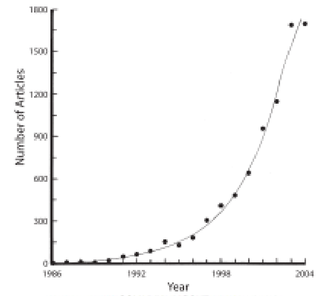
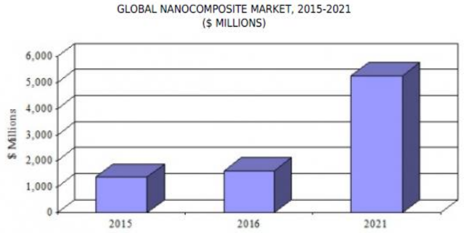
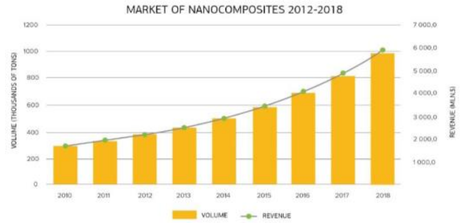
Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

1- Introduction: Nanocomposites, definition, market, materials and applications..

- **Nanocomposites are composites (Matrix+Reinforcement) in which at least one of the phases shows dimensions in the nanometre range (1 nm = 10^{-9} m).**
- **Nanocomposites are a sub- category of composite materials.**
- **the interest in nanocomposites started at around 1986 with the publication of 2 papers on the subject.**
- **In 2004, nanocomposites publications number reached some 1700 papers.**
- **Now, nanocomposites publications number exceeds some 15000 papers, together with some 5000 patents.**
- **Nanocomposites global market is expected to reach some $ 5.3 billion by 2021 (733.220 metric tons) from $ 1.6 billion in 2016 (308.322 metric tons) and $ 1.4 billion in 2015 (261.779 metric tons) .**
- **Composite materials: some $ 60 billion and 8 MT/Y.**







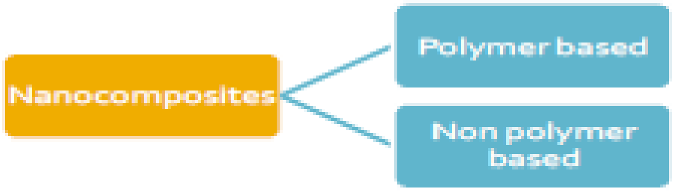
Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

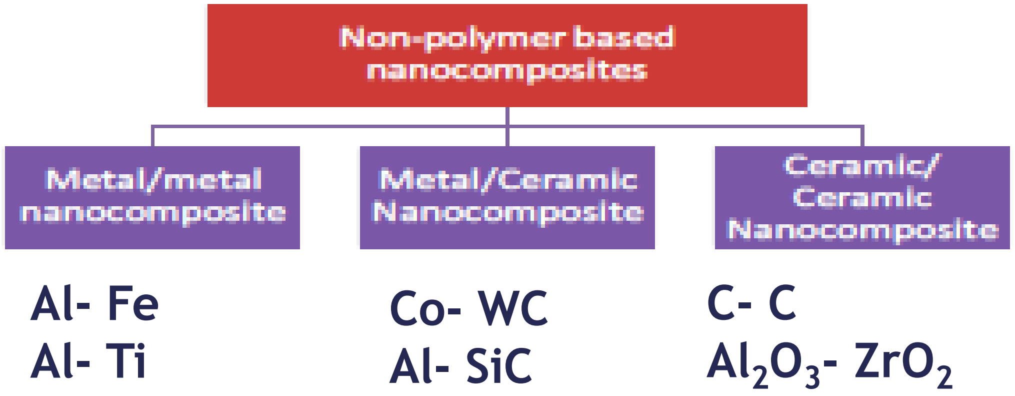
- 1- **Introduction: Nanocomposites, definition, market, materials and applications.**

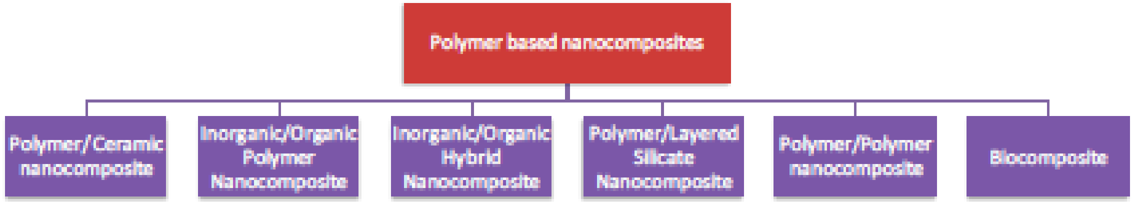
Classification of nanocomposites:

- **Polymer based nanocomposites,**
- **Non polymer based nanocomposites.**

The key constituent of nanocomposites is the nanofiller which distinguishes them from composite and generates their characteristic features.







Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

- 1- **Introduction: Nanocomposites, definition, market, materials and applications.**

Nanofiller constitent of nanocomposites covers:

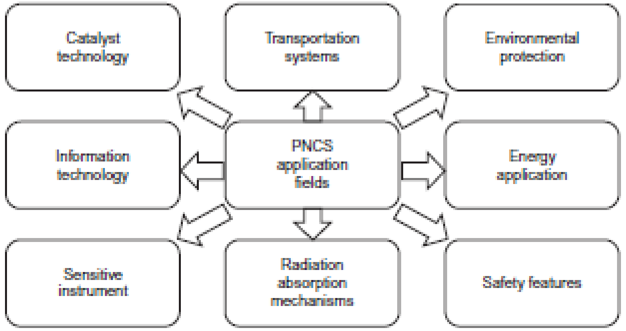
- - CB,
- - Silica,
- - Nanoclay,
- - CNTs,
- - Graphene, Graphene oxide,
- - Nano- oxides: TiO2, ZnO, Al2O3, …
- Biofillers:: Cellulose, wood, Coir, …

Fibers	Role	Density (g/cm^3)	Diameter (nm)	Tensile Modulus (Ga)	Tensile strength (Gpa)	Tensile strain (%)	Price/kg
Carbon fillers							
Carbon black [8,9]	Mechanical, electrical	0.12–0.65	10–400	—	0.010–0.030	—	4
Carbon fibers [1]	Mechanical	1.6–2.2	>10^3	600	4	5	20
Carbon nanotubes [1]	Mechanical	0.8–2.0	1–20	1500	63	—	>3000
Graphene [1]	Mechanical, electrical, thermal	2.2	—	1000	—	—	>2000
Inorganic fillers							
Aluminum oxide [10]	Thermal	3.95–4.1	50	375	2.6	—	2
Calcium carbonate [11]	Flame	2.71–2.85	400–3000	69.9	—	—	2
Halloysite [1]	Mechanical	2.6	10–70	600	—	—	1
Kaolin [12]	Mechanical	2.6	—	170	—	—	1
Nanoclay [13]	Mechanical, thermal	2–3	—	Up to 300	—	—	60
POSS [14]	Mechanical, thermal	—	1.5	—	—	—	700
Silica [15]	Thermal	2.2–2.65	30–100	90	1.6	—	100
Talc [16]	Thermal	2.5–2.8	>10^3	57.31	—	—	0.8
Titanium oxide [17]	Thermal, permittivity	3.78–4.23	30–40	41.77	53.11	—	4000
Zinc oxide [18]	Mechanical, thermal, electrical	5.61	100	250	—	—	2000
Biofillers							
Cellulose [19,20]	Mechanical	1.5	>10^3	150	0.5	20	100
Coir [21]	Mechanical	1.2	>10^3	6	0.18	30	100
Husk [22]	Mechanical	1.8–2.1	>10^3	22	—	—	0.1
Wood [23]	Mechanical	0.3–1.3	500–2000	13	0.24	—	1

- The development of effective nanocomposites is directly linked to the availability and the properties of these nanoreinforcements, which should be able to be dispersed in a polymeric matrix at a nanoscale level.
- Many nanofillers are currently available, between those, in terms of high performances; Graphene, Graphene oxide, carbon nanotubes are (CNT) the most promising, while CB, silica and layered silicate (MMT) are the most common and established.

Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

- **1- Introduction: Nanocomposites, definition, market, materials and applications.**
- **Nanocomposites applications are numerous in various fields like packaging, automotive industry, energy, building and dentistry.**
- **Nanocomposites applications rely mainly on some of their features:**
- **- Their intrinsic mechanical properties (transportation, automotive),**
- **- Their intrinsic reduced permeability against gases (packaging),**
- **- Their functionalities.**



	Nylon 6	Cloisite® Nanocomposite (5%)
Tensile Strength (MPa)	82	101
Tensile Modulus (MPa)	2756	4657
Flexural Modulus (MPa)	2431	3780
HDT, °C	57	96

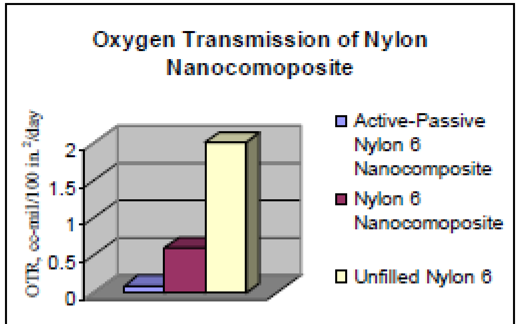


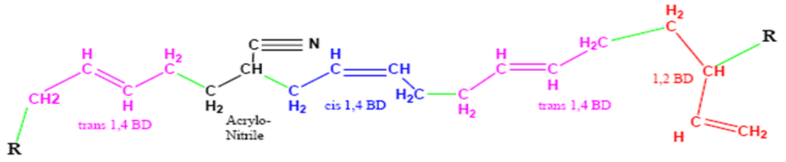
Figure 2 (Source: Plastics Technology, 2001)

Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

2- NBR rubber nanocomposite/ composite: Materials and methods.

NBR is a copolymer elastomer with good chemical and Thermal resistance.

- NBR Krynac 3370F rubber- LANXESS,
- CB N330- Richon,
- Silica aerosil 200- Degussa,
- Vulcanic tuff- Syria,



Krynac 3370F rubber

Analytical balance

Aerosil 200

Grinding machine

Sieving set

Vulcanic tuff

Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

3- NBR rubber nanocomposite/ composite formulation.

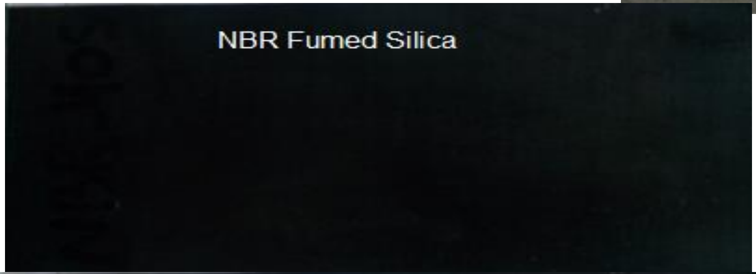
Constituents	Content (phr)
NBR Krynac 3370F	100
Carbon Black N330 (group 1)	0,10,20,30,40,50,75,100
Fumed Silica (group 2)	0,10,20,30,40,75
Volcanic tuff (group 3)	0,10,30, 50,75
ZnO	3
Stearic acid	2
DOP	10
IPPD	1
DPG	1
S(98%)	2.5

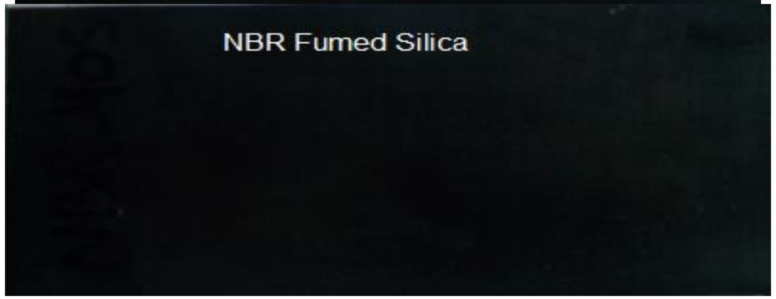
Phr: Parts per hundred rubber by weight;
DPG: Diphenyl guanidin
IPPD: N-isopropyl- N'-phenyl-p phenyleneDiamne

Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

4- NBR rubber nanocomposite/ composite mixing ,vulcanization and forming .

Forming mold



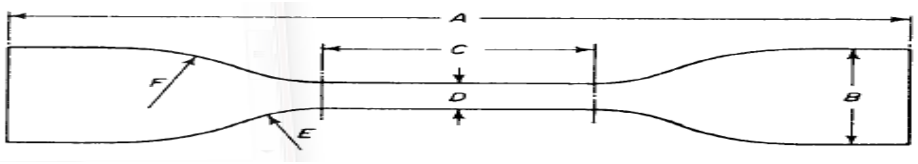


NBR rubber sheets: 15x9.5x0.25 cm^3

Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

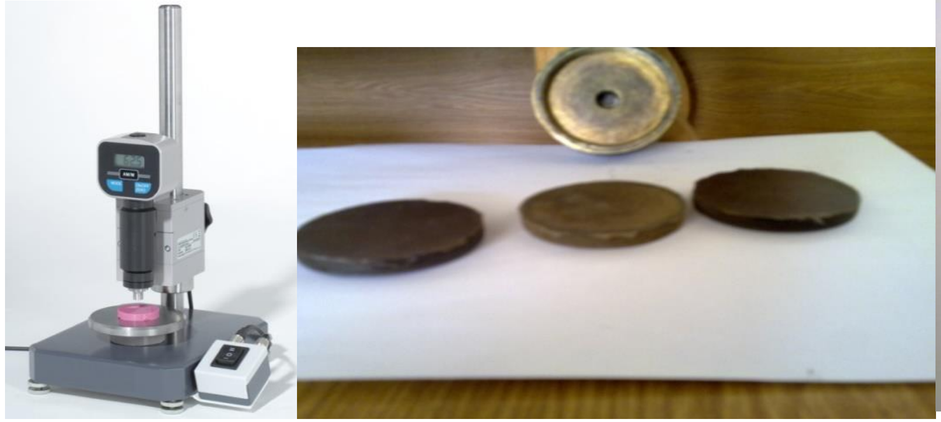
5- NBR rubber nanocomposite/ composite physical and mechanical characterization.

- Specific gravity,
- Tensile test ASTM D412,
- Hardness Shore A DIN 53505.



Tensile sample

Dimensions (mm)	
Sample length A	75
Endings width B	12.5 ±1
Length of the effective portion C	25 ±1
width of the effective portion D	4±0.1
The outer radius E	8 ±0.5
The inner radius F	12.5 ±1
thickness	2.5 ± 0.1

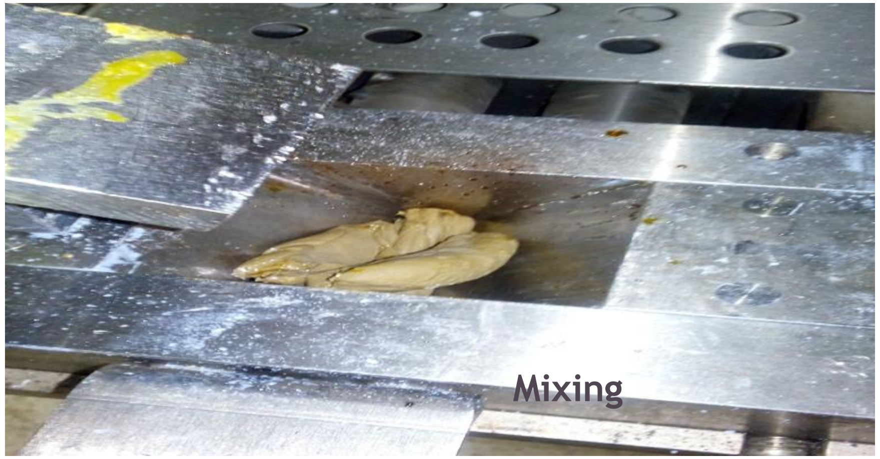


Hardness tester and samples

Mechanical testing machine

Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

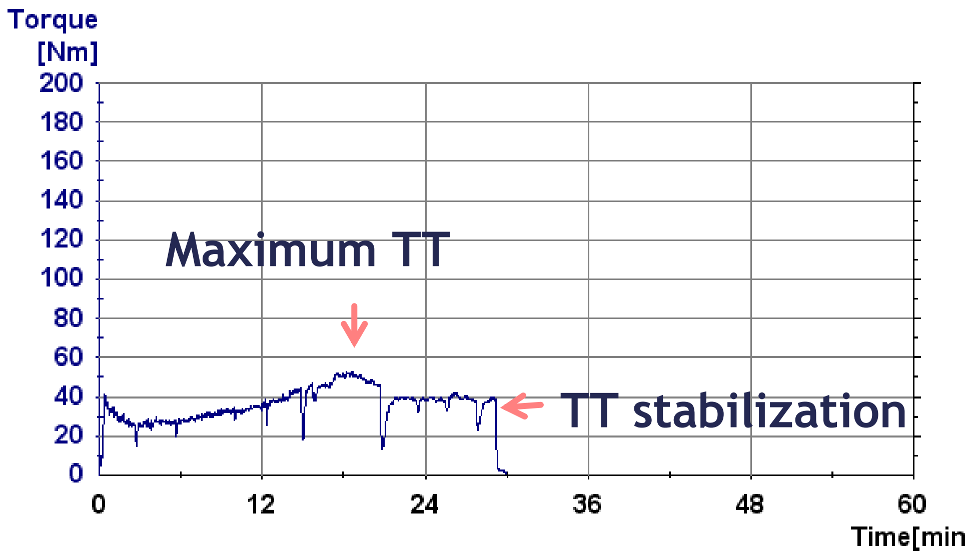
5- NBR rubber nanocomposite/ composite physical and mechanical characterization: Methods.



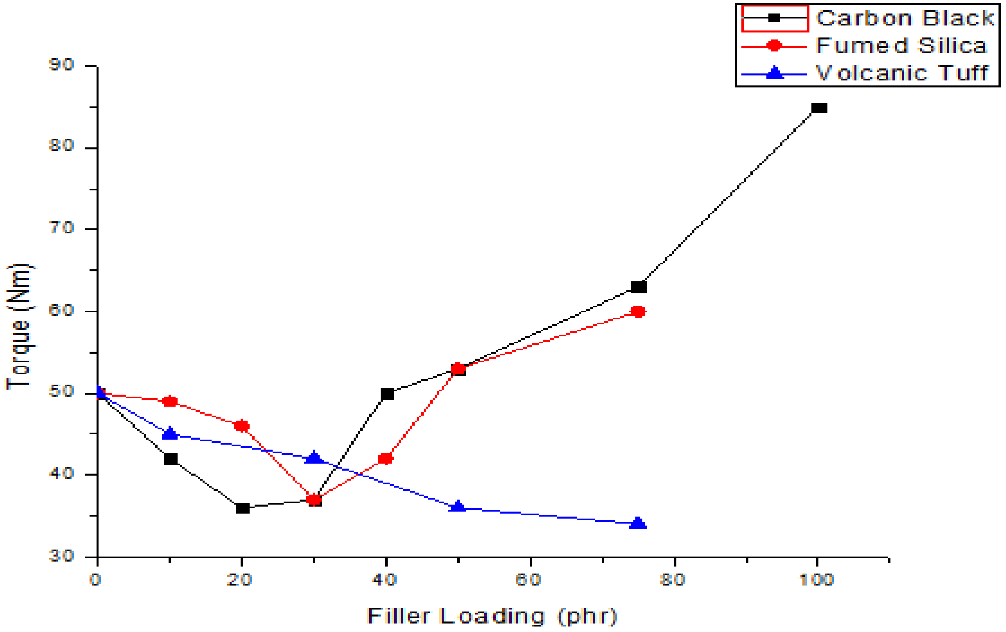
Hardness tester

Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

6- Un-vulcanized NBR rubber nanocomposite/ composite characterization: Torsion torque .



Torsion torque (TT) curve of 10 phr silica during mixing: maximum value of 50 Nm after 18 minutes



Effect of filler type and content on maximum torsion torque value during mixing

Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

7- Vulcanized NBR rubber nanocomposite/ composite physical and mechanical properties characterization.

Sample	Specific weight (g/cm^3) experimental	Specific weight (g/cm^3) theoretical	Tensile Strength (MPa)	Strain (%)	Young modulus @ (100%) (MPa)	Young modulus @ (300%)(MPa)	Toughness (J)	Hardness (A)Shore
NBR0	1.07	1.07	2.25(0.71)	182 (67)	1.36(0.17)	0	0.50(0.31)	53
NBR10C	1.11	1.11	4.83(0.45)	366 (25)	1.42(0.07)	1.25(0.07)	1.82(0.25)	55
NBR20C	1.14	1.15	7.03(2.48)	412(153)	1.74(0.20)	1.63(0.14)	3.08(2.19)	61
NBR30C	1.14	1.19	12.58(3.15)	452(122)	2.96(0.67)	2.77(0.45)	6.31(3.50)	65
NBR40C	1.19	1.22	19.21(2.99)	479 (70)	3.81(0.63)	3.86(0.41)	10.06(2.85)	67
NBR50C	1.21	1.24	20.48(3.45)	484(148)	3.58(1.02)	4.09(0.85)	9.94(4.05)	75
NBR75C	1.30	1.31	18.02(5.77)	274 (68)	6.79(1.51)	6.42(3.58)	6.69(3.05)	85
NBR100C	1.37	1.36	14.08(1.46)	109 (14)	13.37 (6)	0	2.51(0.63)	86
NBR10S	1.11	1.12	5.02(0.63)	434 (55)	1.45(0.09)	1.16(0.10)	2.43(0.55)	57
NBR20S	1.15	1.17	8.12(1.84)	490 (85)	2.04(0.17)	1.68(0.11)	4.60(1.66)	63
NBR30S	1.19	1.21	18.05(1.53)	797 (59)	2.23(0.10)	1.90(0.17)	13.89(1.74)	67
NBR40S	1.21	1.25	22.12(4.31)	817(182)	2.28(0.52)	2.26(0.45)	18.76(6.42)	73
NBR50S	1.27	1.29	25.40(2.66)	(85) 755	3.57(1.29)	3.18(0.70)	19.88(3.08)	87
NBR75S	1.35	1.37	24.98(4.70)	478 (60)	6.07(0.41)	5.31 (0.65)	16.31(4.82)	87
NBR10VT	1.25	-	3.62(0.77)	263 (53)	1.85(0.36)	0	1.09(0.31)	53
NBR30VT	1.15	-	3.28 (0.46)	257 (35)	1.69(0.23)	0	0.97(0.20)	58
NBR50VT	1.25		3.49 (0.25)	339 (63)	1.51(0.16)	1.05 (0.48)	1.34(0.31)	64

Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

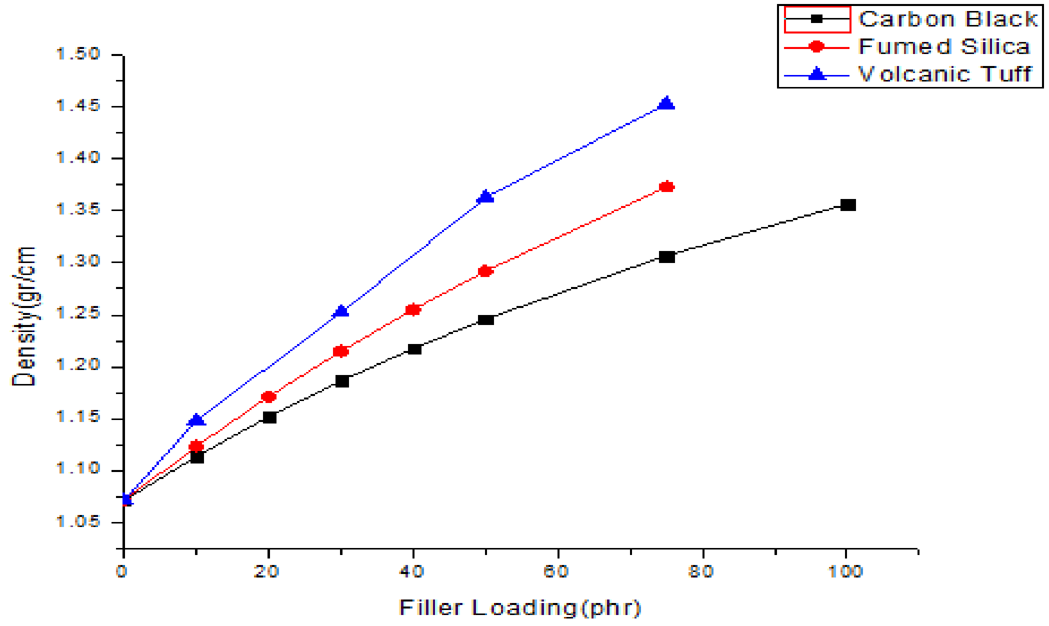
7- Vulcanized NBR rubber nanocomposite/ composite physical and mechanical properties characterization: Specific gravity.

Specific weight of NBR rubber nanocomposites/ composites increases generally with filler content (carbon black, fumed silica and volcanic tuff).

The specific weight values of the NBR rubber composites with volcanic tuff are higher than those with carbon black and fumed silica.

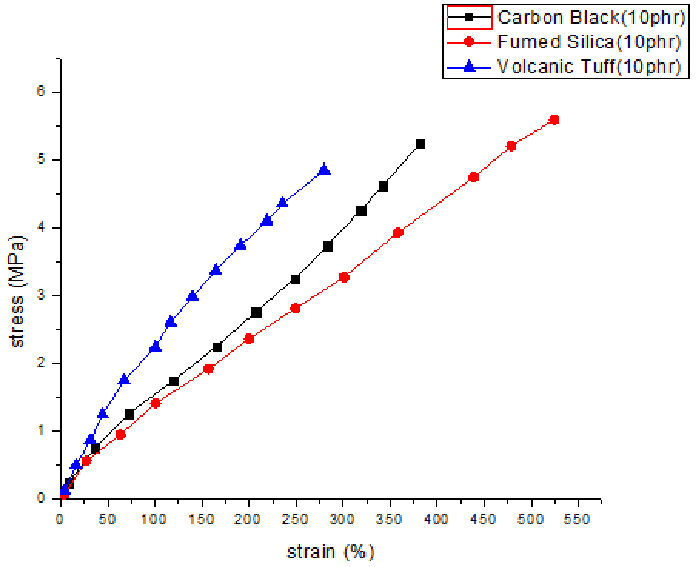
The increase in specific weight results from the fact that the densities of carbon black and fumed silica and volcanic tuff are higher than that of NBR Krynac 3370F rubber and that the order of specific weight of these powders (assuming non porous volcanic tuff grains after grinding) is:

volcanic tuff ≥ fumed silica > carbon black.

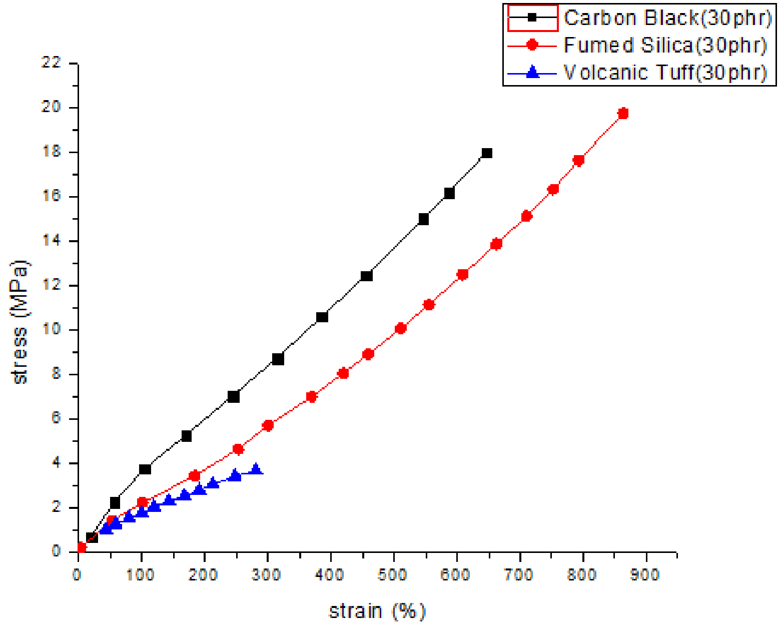


Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

7- Vulcanized NBR rubber nanocomposite/ composite physical and mechanical properties characterization: Tensile strength.



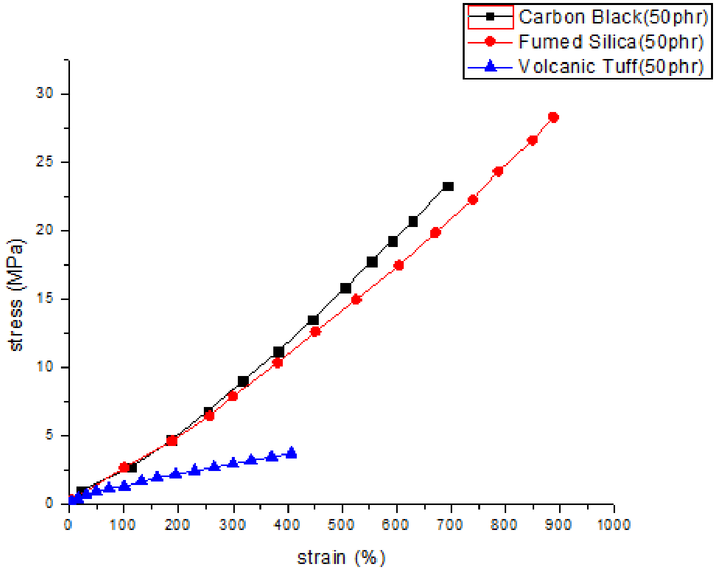
Stress-strain curves of NBR- 10 phr fillers



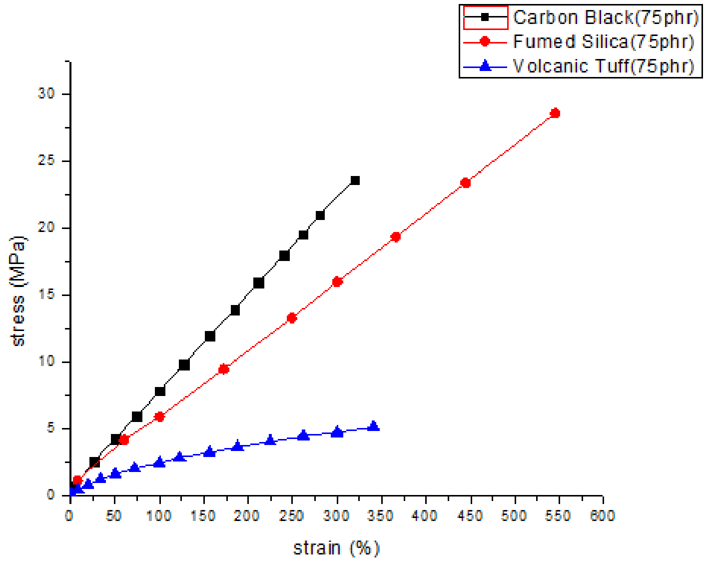
Stress-strain curves of NBR- 30 phr fillers

Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

7- Vulcanized NBR rubber nanocomposite/ composite physical and mechanical properties characterization: Tensile strength.



Stress-strain curves of NBR- 50 phr fillers

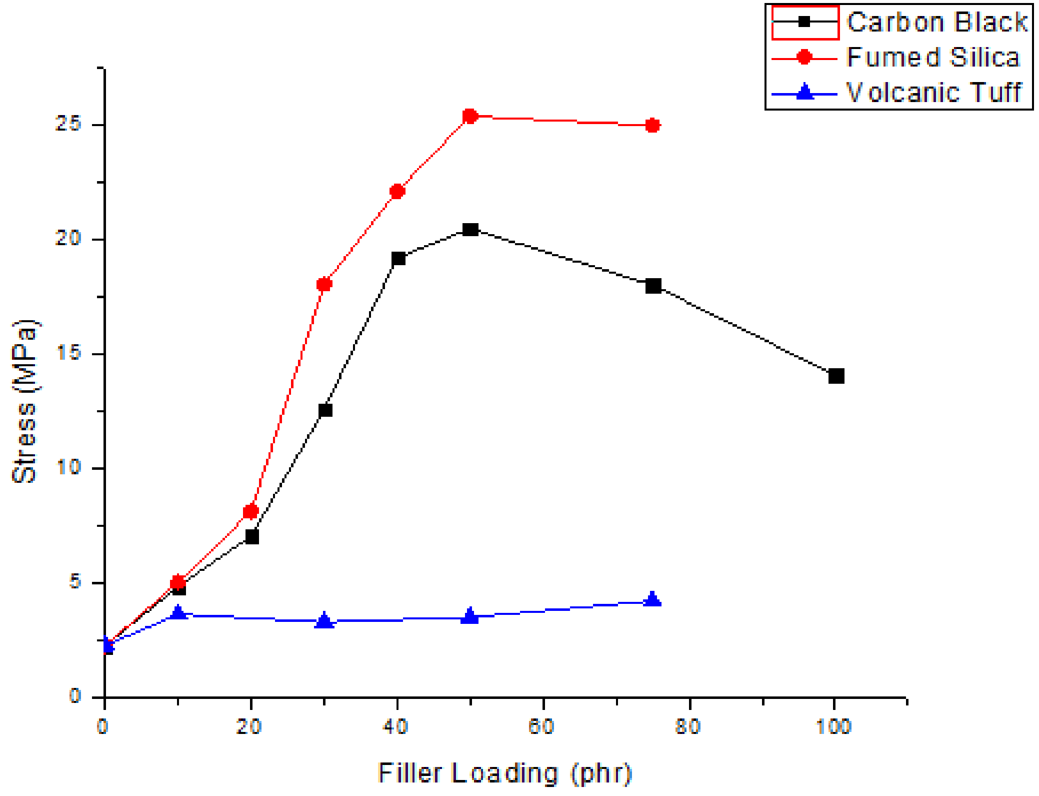


Stress-strain curves of NBR- 75 phr fillers

Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

7- Vulcanized NBR rubber nanocomposite/ composite physical and mechanical properties characterization: Tensile strength.

- ✓ NBR rubber nanocomposite tensile strength increases clearly with CB content up to 20.48 MPa at 50 phr CB ratio.
- ✓ nano silica improves significantly the tensile strength of NBR rubber nanocomposite up to 25.34 MPa at 50 phr ratio..
- ✓ NBR rubber nanocomposite strengthening with fumed silica is more effective than that with CB.
- ✓ This can be attributed to the polarity of NBR rubber that enhances mutual interactions between rubber and polar groups on silica particles. On the other hand, the higher specific surface of silica particles contributes to that.
- ✓ volcanic tuff effect on NBR rubber composite tensile strength is very weak.
- ✓ CNT- NBR nanocomposite: 8.09 MPa at 5 phr.
- ✓ Treated nanoclay- NBR nanocomposite: 9- 15 MPa at 18 phr.



Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

7- Vulcanized NBR rubber nanocomposite/ composite physical and mechanical properties characterization: Strain at break.

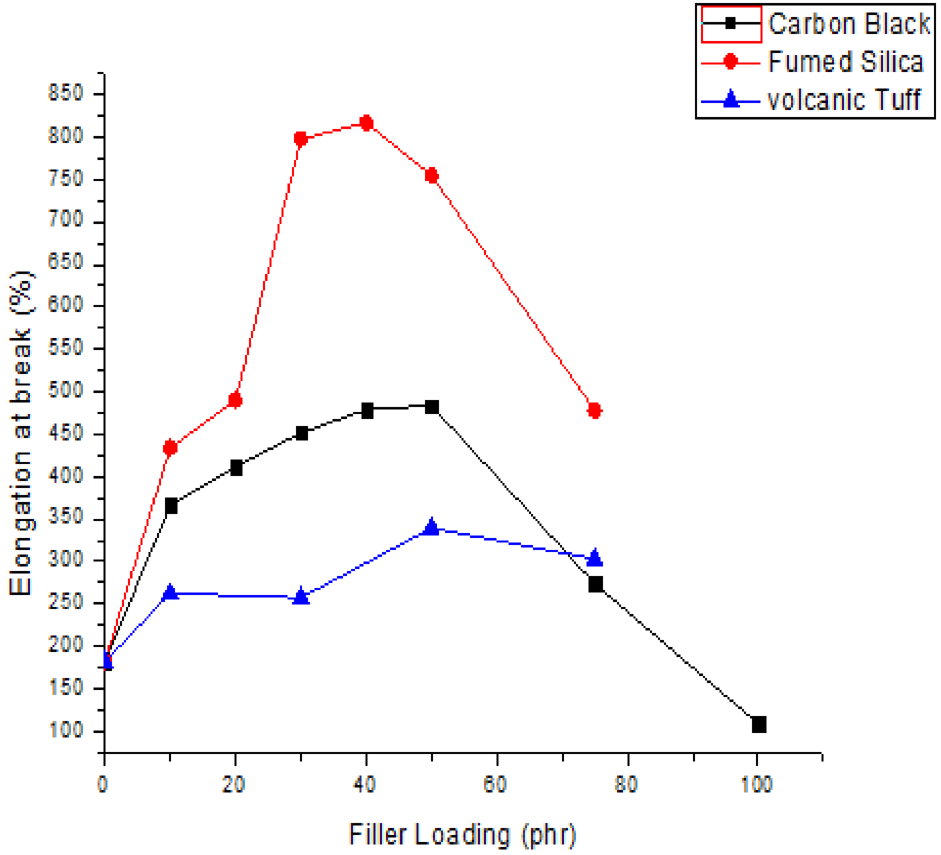
Up to 50 phr, increasing each filler content leads to a substantial increase of the elongation at break of NBR rubber nanocomposite/ composite

After that, the decrease of the strain is attributed to an increase in volume fraction of fillers particles and the inadequate rubber fraction to bind them effectively.

Fumed silica effect overcomes that of CB in the rubber nanocomposite elongation at break which is higher than 800% with fumed silica and 500% with the CB.

This behavior can be related to the difference in specific surface and active groups kind and quantity on CB and fumed silica and the potential impact of silica on reducing crosslinking density.

With volcanic tuff, the elongation at break remains within 200-300%. This could be related to its large micro particles dimensions and limited surface activity compared with both CB and silica particles.



Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

7- Vulcanized NBR rubber nanocomposite/ composite physical and mechanical properties characterization: Young modulus @ 100% strain and @ 300% strain.

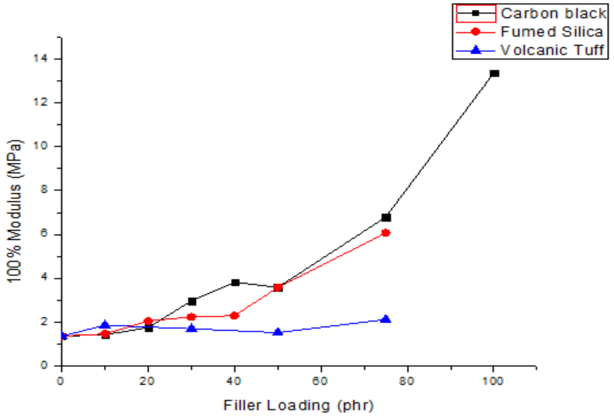
Young modulus at 100% strain increases similarly with both CB and fumed silica.

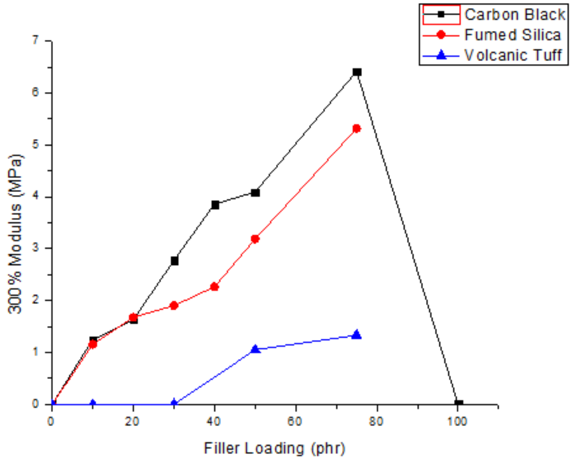
For Young modulus at 300% strain, CB effect overcomes that of fumed silica between 20 and 80 phr filler content.

Regarding volcanic tuff, its impact on NBR rubber composite Young modulus is very weak at 100% strain and at 300% strain, NBR rubber did not attained 300% strain level up to 30 phr volcanic tuff, where a limited increase in Young modulus is observed between 30-80 phr volcanic tuff.

Based on the above, the filler effect seems to be related to several factors:

- **filler ratio in rubber mixture,**
- **the mutual interactions between filler particles and rubber chains,**
- **filler potential impact on crosslinking density of the rubber.**





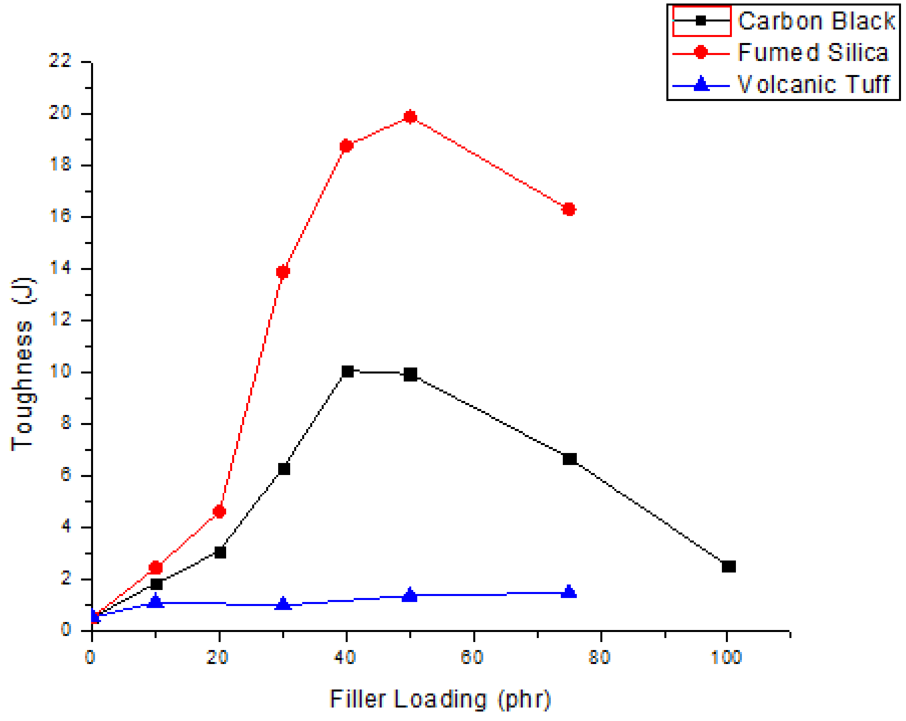
Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

7- Vulcanized NBR rubber nanocomposite/ composite physical and mechanical properties characterization: Toughness.

Toughness of the NBR Krynac3370F rubber nanocomposite reinforced by fumed silica is clearly superior to that with CB.

It is, therefore, clear that increasing silica content leads to higher NBR rubber nanocomposite strain at break and higher toughness.

For volcanic tuff, its impact on NBR rubber composite toughness was very weak compared with CB and silica. This behavior is due to the low deformation at break of NBR rubber composite with volcanic tuff exhibiting large particle size of low specific surface.

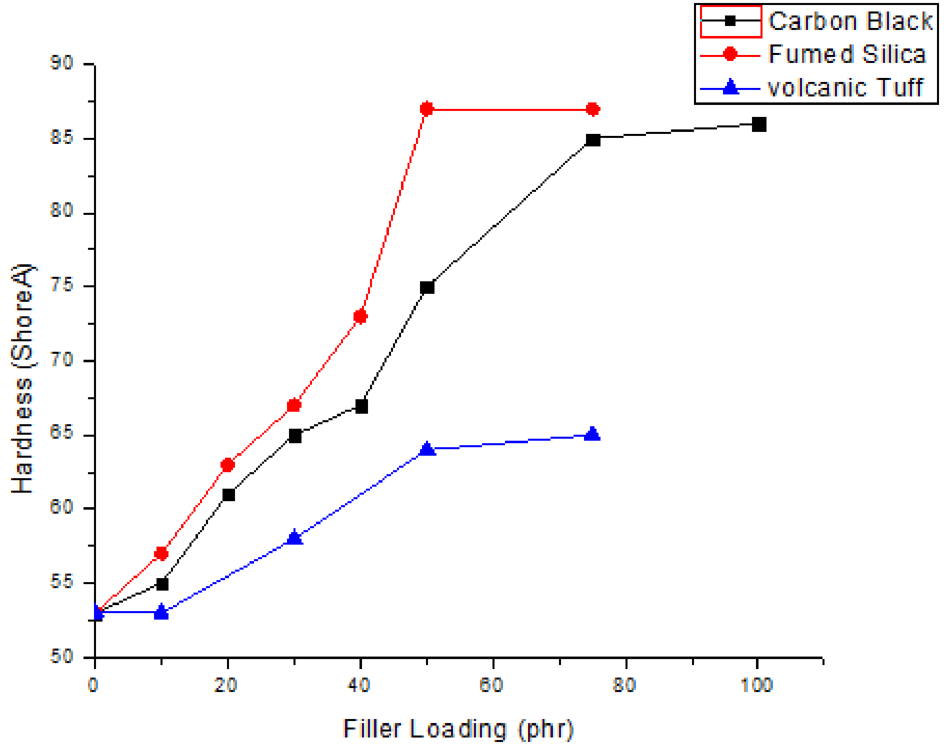


Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

7- Vulcanized NBR rubber nanocomposite/ composite physical and mechanical properties characterization: Hardness.

Increasing filler content in the three groups (carbon black, fumed silica and volcanic tuff), leads to a significant increase of NBR rubber nanocomposite/ composite hardness which reaches the value of 86 Shore A in the first group at 100 phr ratio, the value of 87 Shore A at 75 phr ratio in the second group and the value of 65 Shore A at 75 phr ratio in the third group.

The hardness increase is due to a good distribution of filler particles within the rubber structure as filler content is growing and to the multiple interactions between fillers surface functional groups and rubber chains. As the hardness of fumed silica particles is higher than that of carbon black, fumed silica effect on NBR rubber nanocomposite hardness overcomes that of carbon black.



Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

8- Conclusions.

- The experimental results confirm the possibility of changing the proportions of carbon black, fumed silica and volcanic tuff fillers in NBR Krynac 3370F rubber nanocomposite/ composite within a wide range of 0-100 phr allowing to change and improve NBR mechanical properties according to the requirements of different applications.
- The experimental results allowed the determination of the appropriate process conditions for the preparation of NBR rubber nanocomposites/ composites sheets and mechanical tests samples with carbon black, fumed silica and volcanic tuff.
- Experimental results showed the improvement of the mechanical properties and hardness of NBR rubber nanocomposites/ composites, particularly with carbon black and fumed silica.
- Volcanic tuff did not really increased mechanical properties, but preserved them up to 75 phr which reduce significantly NBR rubber composite cost.

Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

8- Conclusions.

- **The improvement in mechanical properties and hardness of NBR rubber nanocomposites/ composites has been realized without the use of silane coupling agent or compatibility agent between NBR rubber and reinforcing fillers.**
- **Experimental results in this study have shown the clear superiority of fumed silica in improving the mechanical properties of NBR Krynac 3370F rubber nanocomposites in comparison with carbon black.**
- **Nanocomposites, polymer based and non polymer based are now considered, both scientifically and industrially, as confirmed and promizing research and development axis.**
- **The growth of nanocomposites depend on the increase of nanofillers production capacity of and the decrease of their prices.**

Acknowledgement.

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Formulation, preparation and mechanical characterization of Nitrile – Butadiene (NBR) rubber nanocomposites.

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Thanking you for your attention