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A Compressive Review on Swelling Parameters and Physical Properties of Natural Rubber Nano composites

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Abstract

The research covered most of the recent scientific research related to strengthening the natural rubber and improving its physical properties. The swelling properties played a substantial role in decreasing the efficiency of the elastomer compounds as a result of immersing or contacting these compounds with organic solvents. Using nanoparticles for inorganic fillings is essential with a view to expanding the industrial applications of natural rubber Nano-composites. The research covered the latest methods that researchers have used to reduce rubber swelling to the lowest levels. The paper discussed the relationship between swelling properties and mechanical, electrical, curing, and morphology properties. The research also discussed the relationship between swelling properties and the concentration of the filter used to harden the rubber matrix, the swelling capacity, and the type of Nano-composite. All results, which discussed by previous studies showed that improving the thermal, electrical and mechanical properties of the Nano-composites of natural rubber leads to a reduction in the swelling problems of the natural rubber compound, and that selecting or modifying the properties of the filler material gives encouraging and strong results towards reducing the rates of swelling.

Key Words: Natural Rubber; Nano-composites; Swelling Parameters; Mechanical Properties;Thermal Properties

1. Introduction

Polymers are characterized by flexible and unique properties compared to the properties of other engineering materials, in order to enhance these properties and enable polymers, especially elastomers, to expand their properties in the rubber industry; their properties are enhanced by inserting organic or organic nanoparticles into the polymeric matrix [1-7]. But this phenomenon based on many factors as structure, formation, reinforcing particle size, filler - elastomer interaction, Filler dispersion, etc.[8-12] . In general, Nano-composites are characterized by the presence of at least one dimension of dispersal particles in the range of Nano-materials [13-15]. On the other hand, polymer compounds have received wide attention in terms of scientific research because these materials allows to design high- execution materials based on their enhanced properties, compared to the raw material due to good particle dispersion and surface chemistry properties, which leads to high interference between the filler particles and chains of polymer [16-21]. The economic importance of natural rubber (NR) is widespread and is used in many industrial applications, whether alone or mixed with other materials. Among the most important of these applications is its use in the manufacture of tires and adhesives as a result of its having a high molecular weight with of cis-1,4-polyisoprene units which It is considered essential in its structural construction [22, 23] . Jeffrey, et al studied adding grapheme oxide platelets to the natural rubber matrix for preparing the Nano composites by latex co-coagulation according to consolidate the vulcanizing factor (in one of two processes: solution pretreatment or two-cylinder milling). The treatment results showed a good composite morphology and dispersal of the graphene oxide platelets in the natural elastomers matrix [14]. Bokobza worked on a reviewing study for improvement of the electrical, mechanical, and thermal conductivity of natural rubbers by silicate

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layers, that the process of strengthening rubber with fillers. In addition of, improves the performance of vulcanized rubber, reduces swelling, and limits the movement of polymer matrix chains due to their more available, high surface area to volume ratio, low cost, and the potential of complete separation (exfoliation) of silicate layers [25]. Bokobza, studied the addendum multi-walled carbon nanotubes (MWNTs) to natural rubber to progress the electrical and tensile specifications of the rubber compounds. The author noted that the electrical percolation threshold is reached at less than 1 phr of multi-wall carbon nanotube, which led to enchantment the aspect ratio, tensile stress and reduced the elongation at break compared to rubber without additives [26, 27]. In addition, reinforcement of natural rubber with cellulose Nano crystals (CNCs), especially when strengthening isolated natural rubber CNCs), is preferential acid-hydrolysis, the results led to a high aspect ratio CNC was removed from soy hulls, high tensile execution nano-composites were gained, precipitation of CNC plays an important job in the tensile specifications of the rubber compounds [28,29]. Used the bagasse whiskers with natural rubber for absorption moisture from the soil, the increase in moisture absorption continues by rubber thin-film until five percentage of whiskers loading while decreased at a higher capacity, the participation of cellulose whiskers raises the average of degeneration of rubber in soil [30] . Rajasekar, et al used Nano clay to harden natural rubber and improve its properties. The well dealing of nanoparticles in the rubber compounds is a noteworthy factor that leads to a remarkable amelioration in the characterizations of the rubber. Furthermore, a kind of compatibility can be used between natural rubber and epoxy resin (ENR) that can be safely used to exfoliate the Nano-layer .The morphological study demonstrated that intercalation of Nano plasma into the ENR and increased incorporation of modified Nano clay composite into the nitrile rubber matrix leads to exfoliation of the Nano layer [31] . Xiaodong et al prepared Nano composites from natural rubber and carbon black, which are both electrically conductive and hierarchical in 3D by integrating cellulose Nano composites through latex synthesis technology. These compounds have a very low filtering threshold for electrical conductivity, high fluid sensing capacity, fast response, and high reproducibility, so they are of great importance in the application of sensors, simple and low-cost, and performance can be improved using natural cellulose resources [32].

2. Reviewing the Important Swelling Parameters

The swelling properties limit the physical properties of rubber compounds after their immersion in organic solvents. Therefore, it is very important to determine the efficiency of these compounds for resistance to decomposition or dissolving in organic solvents. In this work, the samples were weighed accurately before immersion (initial mass) and after their immersion in a specified amount of toluene for 24 hours (swelling mass). The samples are placed in a drying oven at a temperature of 60 ° C for 24 hours as a period times then , the mass of solvent that was absorbed by the rubber compound after the end of the immersion period (de- swollen mass) was determined by weighing the dried samples, then determining the swelling properties according to the following steps:

a) Determination of the swelling ratio (SI) of rubber after immersion in the solvent by the following relation [33]:

$$S1 = (W1 - W2)/(W\ 2)\ \ 100\% \qquad (1)$$

Where SI is the swelling index in [%]; W1 and W2 are the swollen and initial mass in (g).

b) Determination of the mole percentage uptake of the solvent Qt can be defined with the following relation [33-35]:

$$Qt = (W2 - W2) / (W1- Wm)\ 100\% \qquad (2)$$

Where Qt is the mole uptake in [%]; Wm is the solvent molar mass of toluene in (g/mole).

c) Determination of the solubility fraction SF [%] can be defined with the following relation [33, 36]:

$$Sf = (W2- W3) / W2 \quad 100\% \qquad (3)$$

Where: SF is the solubility fraction [%]; W2 and W3 are the initial and de-swollen mass in (g).

d) Measurement of the volume fraction of rubber can be defined with the following relation [33, 35, 37]:

$$Vr = 1/((1+Pp/Sp)(W2/W1 -1)) \qquad (4)$$

Where:

Vr is the volumetric fraction of the rubber compound sample after swelling [-]; SP and PP represent the density of the solvent and the polymer samples in (g/cm3).

e) Determination of cross-link density per unit volume (mole/cm3) can be defined with the following relation [35,37]:

$$V=-(\ln (1-Vr) +Vr+XVr \hat{}2)/(V0 (Vr\hat{}(1/3) -2 (V r) /f)) \qquad (5)$$

Where V represent the crosslink density per unit volume (mole/cm3).

VO represent the molar volume of solvent (for toluene is VO = 106.9 cm3/ mole).

f represent the functional crosslinks, f = 4, Suppose information of a tetra-function crosslink.

χ represent the Flory-Huggins rubber–solvent interaction parameter (0.37 for a sulfur cross-linked SBR- toluene pair) [37].

3. Relationships between the Swelling Parameters and Physical Properties of NR Nano composites.

3.1 Effect of Swelling Media on NR Nano Composites Properties.

LeCorre et al. studied the effect of chemical solvents such as toluene, which is a suitable material for natural rubber and water that cannot dissolve natural rubber, on the swelling behavior of these compounds depending on the mass of the absorbed solvent as a function of time. This mass is recorded as a time function of the square root according to the following: [38].

3.1.1 Toluene

LeCorre et al. studied the influence of solvents such as toluene and water on the physical specifications of NR after filling by starch Nano-crystals. The authors used many Nano-composites during the experiment. Some of the Nano-composites behaved well, but some compounds had poor behavior towards chemical solvents because they were not reinforced by nanoparticles such as (NR100) or weak (like NR95) while there are compounds in which the absorption of solvents decreased significantly from P21-NR95 to M70-NR70 (see results at Table 1) [38]. Figure 1 shows the relationships between the uptake(mol %) at many periods of time (hours) of immersion the samples insolvent for (a) toluene, (b) water, and the relationships between the uptake(mol %) at many root square of half-time t-1/2 (s-1/2) for (c), and (d). In this Figure, two regions can be set: the first zoom of the rapid imbibition kinetics of t <10 hr., and the second, the plateau-like plateau of the second zoom when equilibrium is reached after 10 hours. The uptake % of the unfilled material reached the highest ratio at NR-100, while M27- NR70 achieved the lowest ratio. This is evidence of the role of toluene in dissolving rubber compounds such as natural rubber. The same swelling behavior occurs when the relationship between uptake% and the square root of the half-time t-1/2 (s-1 /2) [38]. Xiaodong et al. prepared a three-dimensional hierarchical conductive structure from the natural rubber/carbon black Nano composites for the application of liquids and tension sensing as shown in Figure 2. The models of the Nano composites were submerged in the toluene solvent at different periods; the researchers noted that the density of luminance reduced with the time passed after 12 minutes of immersion, which indicates a decrease in conductivity with an increase in the rate of swelling of the samples. After that, the authors removed the samples from the immersion solution and wiped the residual solvent on the samples using tissues. It was observed that the light intensity improved with the passage of the drying time as the samples shrink. Figure 3 illustrates the response against time and the logarithmic resistance in time t / initial resistance (Rt / R0) against time during the immersion and drying process of the reinforced natural rubber by black Nano carbon and cellulose (CB @ CNs / NR). The authors note a large change in the resistance of Nano composites and a decrease in the performance of the conduction networks during immersion due to the effect of swelling, and that the fluid sensing process can be controlled by increasing the CB @ CNs loading ratios, thus obtaining a faster response to the sensing of the stimuli [32] .

3.1.2 Water

All compounds of NR are described by their absorption of water during the immersion period and the rate of absorption increases if the rubber matrix is not filled (NR100). According to Figure 1b, the absorption kinetics in the first stage is up to 5 hours and in the second stage after this period, the ability of the natural rubber to absorb water is medium. Moreover, Table 1 represents the results of absorption and diffusion of the solvent in the rubber compounds. There was no wide difference between the absorption of the SNC / NR95 Nano composites and the NR Nano composites adsorption. [38].

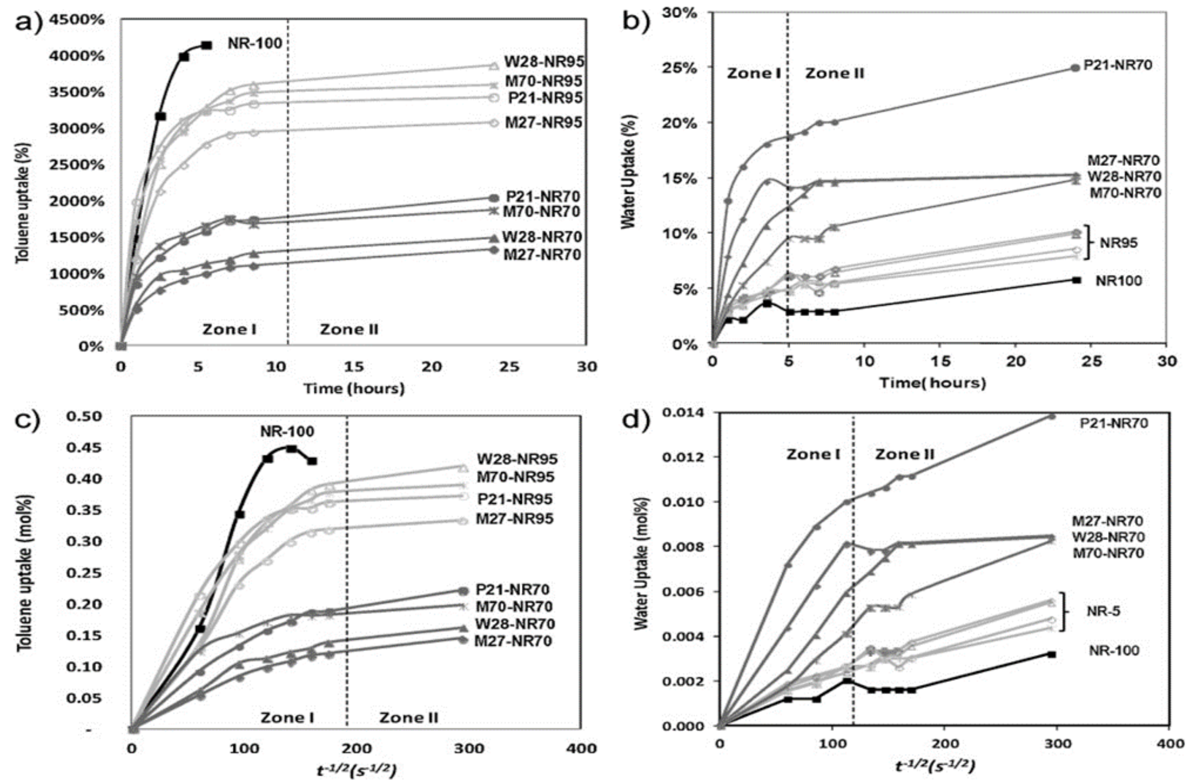

Fig. 1 shows the relationships between the uptake(mol %) at many periods time (hours) of immersion the samples in solvent for (a) toluene , (b) water , and the relationships between the uptake(mol %) at many half time t-1/2 (s-1/2) for (c) , and (d) [38] .

Table 1. Toluene and water adsorption characteristics of starch Nano-crystals / natural rubber Nano- composites [38].

Samples	Toluene				Water			
	TU [mol%]	***D*** toluene [10^{-8} $cm^2.s^{-2}$]	***S*** [%]	***P*** toluene [10^{-8} $cm^2.s^{-2}$]	TU [mol%]	***D*** water [10^{-8} $cm^2.s^{-2}$]	***S*** [%]	***P*** water [10^{-8} $cm^2.s^{-2}$]
NR100	∞	4.2	∞	∞	0.32	0.04	6	0.24
NR-100*	∞	40	∞	∞	-	0.04	7	0.28
M1-NR95*	-	12.8	3290	42.112	-	0.29	8	2.32
P21-NR95	37	1.64	3428	5621.92	0.48	0.14	9	1.26
M27-NR95	33	2.73	3071	8383.83	0.56	0.16	10	1.6
W28-NR95	42	1.35	3866	5219.1	0.55	0.14	10	1.4
M70-NR95	39	1.72	3592	6178.24	0.44	0.14	8	1.12
M1-NR70*	-	3.4	1320	4488	-	5.61	22	123.42
P21-NR70	22	1.29	2043	2635.47	1.39	3.33	25	83.25
M27-NR70	14	4.61	1.332	6140.52	0.85	1.22	15	18.25
W28-NR70	16	3.17	1.488	4716.96	0.84	1.15	15	17.25
M70-NR70	20	0.84	1.865	1566.6	0.82	0.65	15	9.75

WU= molar water uptake, TU= molar toluene uptake, D= diffusion coefficient of a solvent molecule through a polymer membrane, P = permeability coefficient of the solvent in the NR, S= sorption coefficient

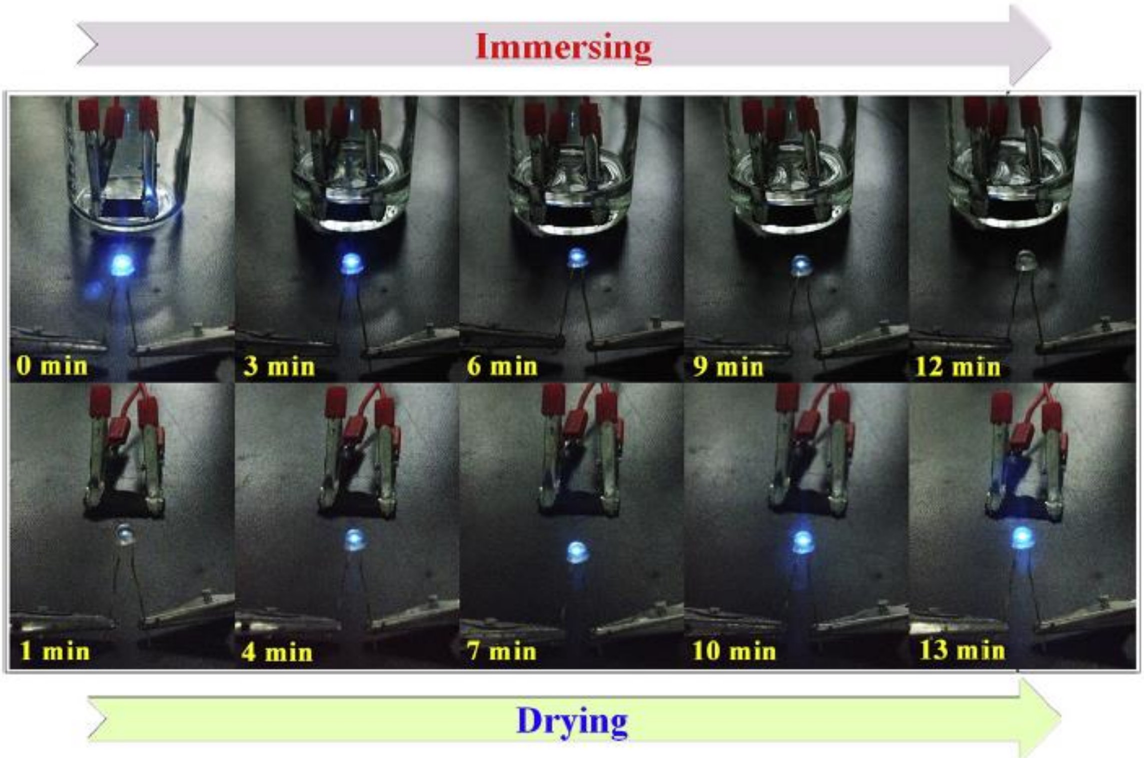

Fig. 2 shows the Photographs of Carbon black and cellulose / Natural rubber during the immersing the samples in toluene and drying in the hot-air at many time periods [32] .

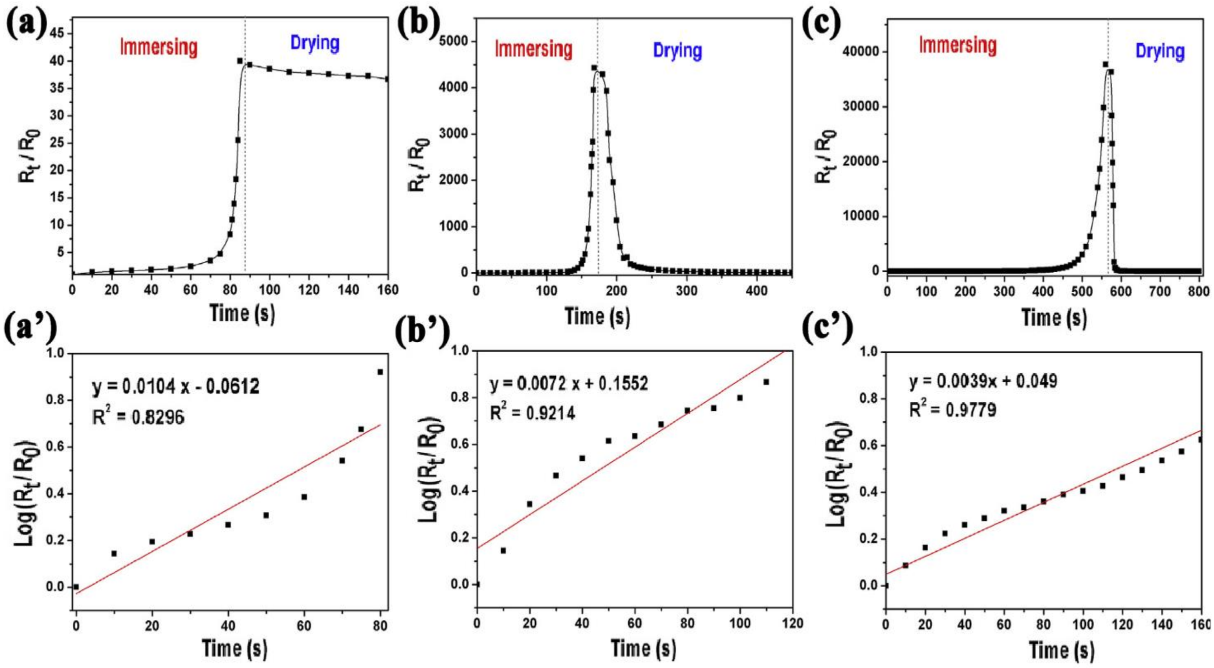

Fig.3 Responsively against immersion periods and drawing of log (Rt/R0) for many Nano composites [32].

3.1.3 Oil and Solvents

Rajasekar et al. Dissolved natural rubber epoxide (ENR) in some chemical solvents such as toluene using the continuous mixing technique of the solutions and strengthened it with the Nano clay after having good dispersion of the filler in the polymer matrix and this Nano composite was named (ENR-

Nano-clay composites (EC)). A new compound was combined with an NBR matrix with the presence of a curing agent such as sulfur. This work gave encouraging results towards reducing swelling rates, especially in oil and chemical solvents at test temperatures 25 and 100 degrees Celsius, as shown in Figure 4. Their high resistance to oils characterizes Nano composites such as NBR / 10EC and other chemical solvents at all absorption temperatures compared to NBR compounds without fillers [31]. On the other hand, Stephen et al studied combining natural rubber with XSBR or mixing it in certain proportions such as 70/30 NR / XSBR by adding silicate nanoparticles and determining the resistance of these compounds to chemical solvents such as benzene, toluene, and xylene.

The authors noted that the Qt (%) of the rubber compounds decreases with increasing the molecular weight of unfilled and Nano composites, these results indicated more dissipation of nanostructured silicates in the polymer matrix. In addition of, high interaction of a polymer chain with the layers of silicates, therefore limiting of the solvent Qt (%) of polymer, according to the above results the order of solvent benzene > toluene > p-xylene shows these results in Figure 5 [35].

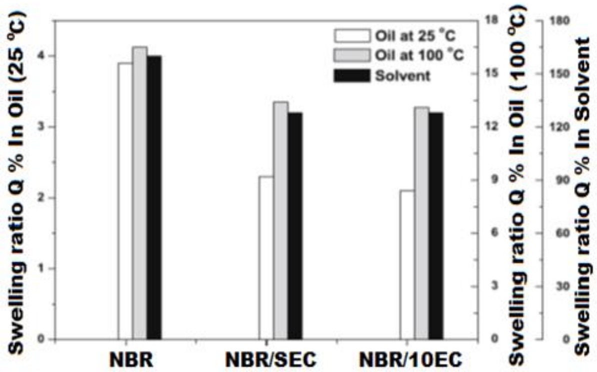

Fig.4. The swelling percentage of the polymer compounds and chemical solvents [31]

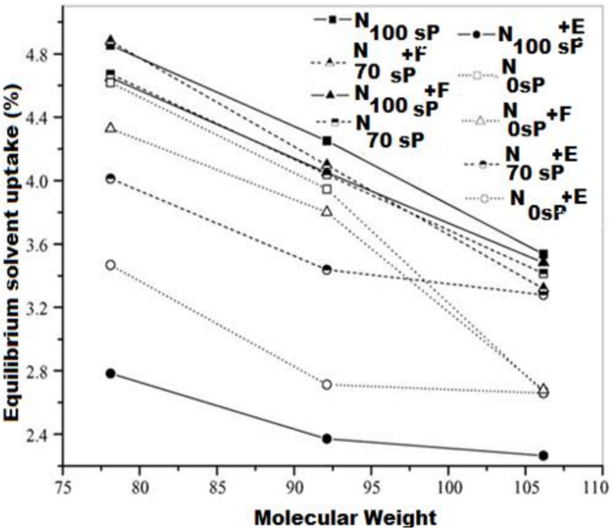

Fig. 5. The relationships between the solvent uptake and solvents molecular weight for many polymers Nano composites [35].

3.2. Relationships between the Swelling Capacity and NR Nano-composites

Bernal-Ortega, et al. Studied the relationship between the structure of natural rubber compounds and the specifications of styrene-butadiene rubbers reinforced with MWCN particles. The authors noted that the crosslink intensity of the Nano composites improves dramatically with the increase of the ratio of the MWCN, according to the NMR (nuclear magnetic resonance) to determine the density of the crosslinks of the Nano composites, these testing results lead to a reduction of the swelling effect and an increase in electrical conductivity. The NMR examination, which determines the density of crosslinks, is a great indicator for determining the swelling ratio of the elastomeric compounds by determining the relationship between the amount of swelling in the filled samples and the unfilled samples according to swelling experimentally, the swelling behavior for reinforced compounds through the Equation 6:

$$\frac{1}{MC}{}^{SW}{}'filled \qquad (6)$$

Also, the swelling behavior of unreinforced compounds through the Equation 7:

$$\frac{1}{MC}{}^{SW}{}'unfilled \qquad (7)$$

By analyzing the above relationships, we believe that the non-reinforced nanoparticles have a similar degree of swelling restriction for each sample, therefore the swelling ratio depends on the reinforcing nanoparticles of the rubber compound, which in turn increases the density of crosslinks:

Swelling Restriction Ratio=

$$\frac{\frac{1}{Mc}{}^{SW}{}'filled - \frac{1}{Mc}{}^{SW}{}'unfilled}{\frac{1}{Mc}{}^{SW}{}'unfilled} \qquad (8)$$

Where the molecular weight of network chain between cross-links (Mc) . Through Figure 6, which shows the swelling ratio calculated according to equation 8, the inflation resistance rates of NR compounds are high, and this result is due to the role of CNT in restricting swelling, also the resistance ratio of NR compounds with CNT is five times that of its resistance in the presence of carbon black (CB). Based on the foregoing, the result of the swelling ratio is related to the density of crosslinking on the surface of the reinforcing material and the rubber fraction interfering with the surface of these particles. Therefore, a comparison can be made between the different filling systems (CNT, CB, and Silica). [1].

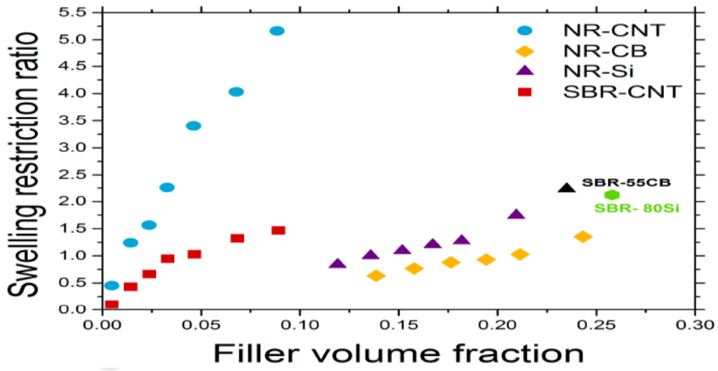

Fig. 6. Shows the relationship between swelling limitation and filler volume fraction for many Nano composites [1].

3.3 Relationships between the Crosslink density and swelling ratio.

Kang et al. Creation of new Nano composites with high kinetic properties during mechanical mixing. Graphene (GE) nanoparticles were used in the mixing process with natural rubber. The role of graphene particles was important for accelerating crosslink reactions and forming a bonding network in Nano composites. This method led to transfers the loading from the rubber matrix to the reinforced material, and increasing of the torque (ML), maximum torque (MH) as well as increasing the difference between the torque and the maximum torque (M) [36]. On the other hand, increasing of the density of the crosslinks is related to the dispersion of additive graphene nanoparticles and exfoliation in the rubber matrix, which is indicated by the measurements of the swelling equilibrium, curing rate, and the torque difference (M). In addition to the good interference between the graphene nanoparticles and NR matrix. Figure 7 shows a crosslinks density are measured using the Flory - Rehner equation (Equation 5) which increased with graphene loading and swelling ratios which decreasing with graphene loading. For the purpose of comparison, the authors explained that the increase in the density of crosslinks amounted to 69.8% at 5 phr of graphene compared to the percentage of these crosslinks in pure natural rubber, while the rate of swelling decreased by 35.8% [36]. That is means the fixing of rubber chains and preventing their movement gives graphene sheets a winding path and reducing swelling rates [39-41].

Jinrong et al studied the effect of adding graphene (GE) on the kinetics of chemical reactions that occur during vulcanization of natural rubber (NR) using sulfur as a curing agent. Through this process, the equilibrium swelling of rubber immersed in toluene was reducing [42]. The natural rubber latex / Nano clay was re-vulcanized and using a freeze-drying technique by Pojanavaraphan and Magaraphan, the authors found that the increase in hardness was significant compared to the hardness of pure NR. The results indicate the high hardness of the Nano composites as a result of the excellent interaction between the polymer and the surface of the filler material, which leads to strengthening the rubber matrix, increasing the maximum torque and increasing the crosslinking, this process was done by heat treatment and by microwave. Table 2 shows the swelling rates results, which calculated according to equation 2, the swelling ratios gradually decrease with the increase in the content of the nanoparticles due to the diffusion and good dispersion of the nanoparticles in the rubber matrix and the growth of crosslinking. During the treatment process, the rate of swelling decreases with the highest crosslinking density and reaches its peak at NR / 3 MMT [43], these results support the hypothesis that increased crosslinking strengthens the rubber matrix [43-46].

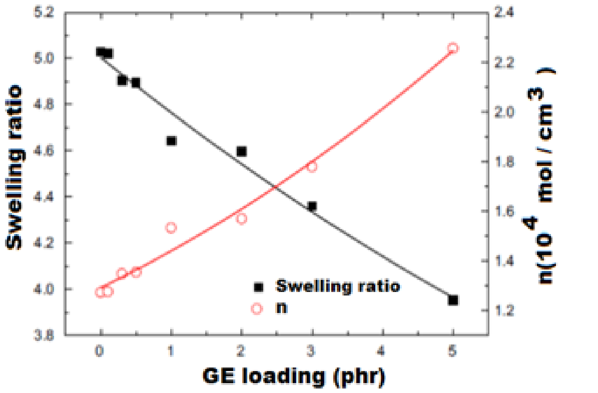

Fig. 7 Shows relationship between density crosslinks and equilibrium swelling ratio for many Nano composites as function of graphene loading [42]

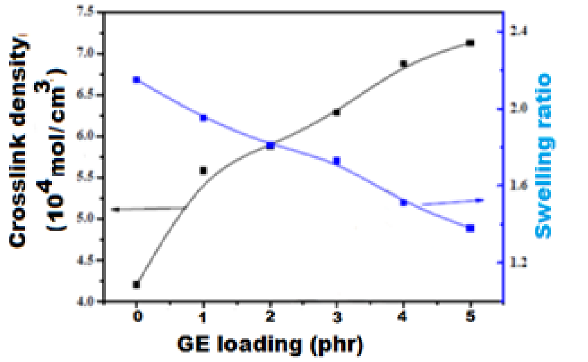

Fig. 8 Shows relationship between numbers of crosslinks and swelling ratio for many Nano composites as function of graphene loadings [36].

Table 2 Results of the thermal and microwave curing for natural rubber and it is Nano composites, which represented by swelling ratios and crosslink densities [43].

Materials	Thermal curing		Microwave curing	
	Swelling ratio	Ve (mol /cm^3)	Swelling ratio	Ve (mol /cm^3)
NR	23.98	3.51*10^{-6}	28.69	2.43*10^{-5}
NR/1MMT	22.60	3.57*10^{-6}	27.76	3.14*10^{-5}
NR/1MMT	21.02	3.65*10^{-6}	17.60	4.56*10^{-5}
NR/1MMT	17.32	5.08*10^{-6}	15.48	5.66*10^{-5}

.

3.4 Relationships between the Mechanical Properties, Concentration Gradients, and swelling ratio

Natural rubber was mixed with purified attapulgite (PAT) in a double-cylinder plastic mixer at 450 ° C, which named (PAT-450) and also at 850 ° C, which named (PAT-850) by Wang and Chen. The authors concluded that PAT particles have a significant impact on the mechanical specifications of NR Nano composites, as it improves the curing conditions of NR, increases the impedance to chemical solvents, and improves the tensile strength compared to the specifications of purely natural rubber. The authors discussed the results of the effect of adding PAT to the natural rubber and verifying the swelling rates. Figure 9 shows the relationship of the swelling ratios to the periods of immersion of the samples in the toluene solvent. The rates of swelling in the second section of the figure above due to the decrease in the concentration gradient and then reaching a state of equilibrium for the swelling rates with the increase of the periods of immersion. These results give an impression of the relationship between the tensile properties of Nano composites and their comparison with natural rubber compounds. The PAT particles act as a barrier to prevent the toluene from penetrating the Nano composite and increase the swelling rates as the residence time of PAT-450 and PAT-850 Nano composites in the solvent up reaching the equilibrium state is much less than the natural rubber residence time in the solvent to reach to the equilibrium state. [47].

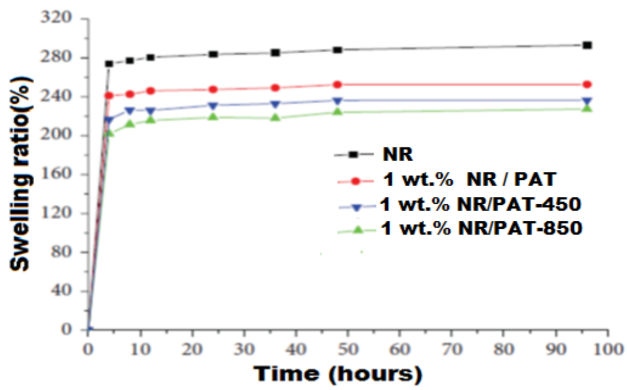

Fig. 9 Shows the swelling ratio of different Nano composites as a function of period's immersion times [47] .

Fibers are one of the important filler materials for natural rubber to improve its physical properties, including increasing its resistance to swelling, and in order to achieve the best performance of the fiber as a reinforcing material, the fibers must be guided and aligned at a certain guiding angle in order to obtain the highest adhesion strength between the fibers and the rubber, reduce swelling ratios and obtain high mechanical properties Jacob and his colleagues developed an empirical equation for the purpose of measuring swelling rates depending on the fiber guide angle (θ) when using short fibers in natural rubber reinforcement.

$$a^2 = (a_T^2 - a_L^2)\sin 2_\vartheta + a_L^2 \qquad (9)$$

Where aL and aT are the longitudinal and transverse dimensional swelling ratios. Figure 10 swelling variation as a function of θ, the results were calculated by using (equation 9). For all Nano composites prepared the swelling ratio increased with increasing the orientation (θ), the range of short fibers orientation from 0° to 90°. According to the gum compound, which did not contain fibers, was placed above the lines corresponding to the other mixes. The results showed that short fibers were more restricted in their ability to transport solvent into the composite than long fibers. [48].

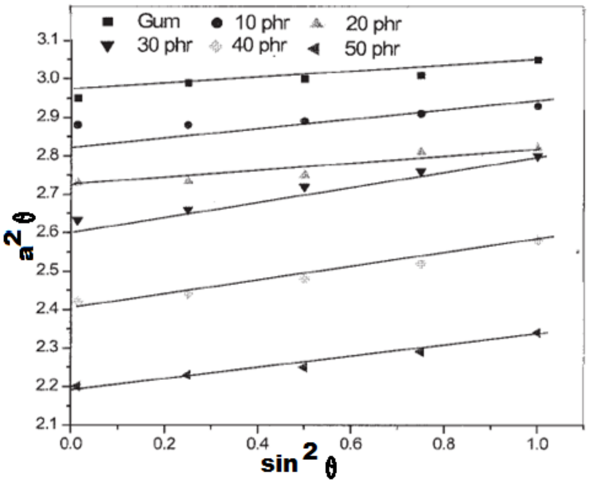

Fig. 10 Swelling variation as a function of θ [48] .

3.5 Relationships between the swelling Behavior and Types of Filler Reinforcing.

Some modern methods such as situ polymerization or solution and melt intercalation that strengthen natural rubber use distinct types of fillers, such as layered silicate because the polymer chains are spread between the silica layers and give great cohesion strength to the Nano composite . Increase its mechanical properties, as well as significantly reduce the rates of swelling because the exfoliated layers Silica reaches 1 nm. Therefore, natural and synthetic silicates were used at 10 wt. % to strengthen natural rubber by Varghese and Kacsisrger-Ko. The authors found that the efficiency of silica layers in enhancing the properties of natural rubber exceeds that of the particles of commercial clays. Figure 11 shows the swelling behavior of natural rubber compounds reinforced with types of fillers such as clays and silica layers added to unfilled natural rubber (Gum) at 25 ° C. The authors discovered that the highest percentage of toluene absorption was for non-filled rubbers, this is normal behavior, and that the lowest toluene absorption is found in rubber compounds filled with silica layers (fluorhectorate). The reason, according to his achievement of results in the high toluene absorption rate in the gum, followed by lower rates in the rubber filled with commercial clay, is that there are no restrictions or hindrance to the toluene from penetration into the rubber compound and a change in the sample dimensions. On the contrary at the Nano composites reinforced with silica layers, the adoption of toluene facing the more resistance or penetration is limited. Figure 12 shows the change in the dimensions of the rubber compound samples after the toluene penetrated them, as the percentage of thicknesses and diameters of the samples increased after being immersed with the toluene at a temperature of 25 ° C. On the contrary [49], the increase in the diameter of the samples after immersion, as this variation occurs in the properties of compounds with a good orientation such as Fluorohectorite. [49, 50] .

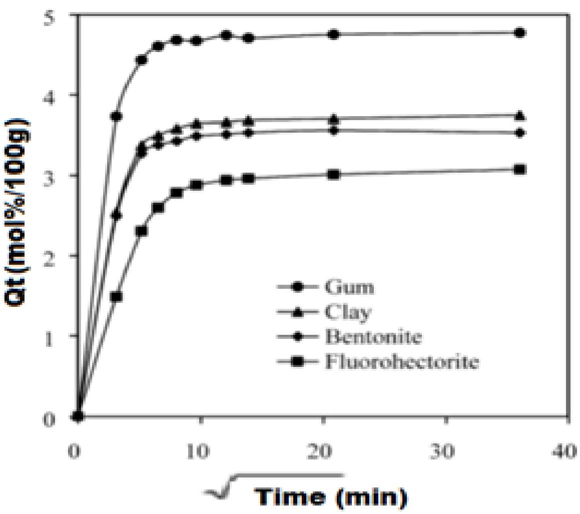

Fig. 11 Shows the changing the uptake (Qt) as a function square root of time immersion of different Nano composites [49] .

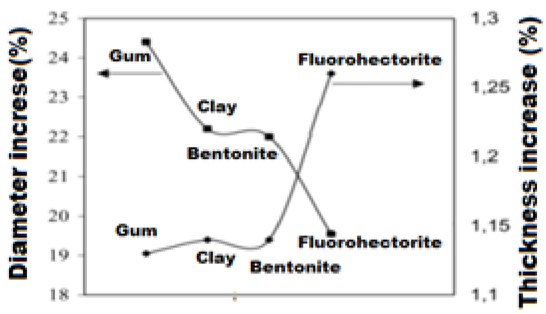

Fig.12. Shows the changing in the sample dimensions after immersion in toluene for different Nano composites [49].

4. Conclusion

In this paper, all the research related to the development of rubber technology was reviewed, including natural rubber because of its great importance in industrial applications. The following are the most important findings of researchers, which lead to reducing the problems caused by rubber swelling as a result of direct contact or immersion in organic solvents:

• Used the natural rubber (NR) as a Nano composite more important for economic purposes , because it is widespread and is used in many industrial applications, whether alone or mixed with other materials, and among the most important of these applications is its use in the manufacture of tires and adhesives as a result of its having a high molecular weight

• Improving the mechanical, electrical, and thermal conductivity of natural rubbers by silicate layers, that the process of strengthening rubber with fillers improves the performance of vulcanized rubber, reduces swelling.

• Used the bagasse whiskers with natural rubber for absorption moisture from the soil, the participation of cellulose whiskers increased the rate of degradation of rubber in soil.

• The reinforcement of the natural rubber by black Nano carbon and cellulose (CB @ CNs / NR) led to limited the swelling ratio.

• Reinforcement of the natural rubber NR; 'carboxylated styrene butadiene rubber XSBR' and their '70/30 NR/XSBR' by added the Nano-structured layered silicates led to more resistance against the chemical solvents.

• The regular dispersion of PAT particles in the polymer matrix, which contributes to improved rubber- filler interface and reducing the swelling ratio.

5. Conflicts of interest

There are no financial interests among the authors or any financial disputes regarding the research.

6. Formatting of funding sources

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7. References

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