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Research Article

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Application of Acrylonitrile Butadiene Rubber for Management of Industrial Waste Silica

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Abstract

Some glass factories have drilled and milled silica mixed with water, their treatment depends on precipitation, filtration etc. New concept for recycling of waste have paid attention to taking samples from different steps of traditional treatment, water evaporation of samples have been carried out. Investigation of attained powdered using EDX showed that, about 95.87% of sample was silica while particle size analyzer proved that it was not exceeding 73 micrometer. Silica powder mixed with Acrylonitrile Butadiene Rubber using miller and moreover thermal compression were performed to achieve maximum compatibility and constant thickness of the composite. Electron beam irradiation of the samples with different doses 25 and 100 KGy were carried out. Mechanical investigation using stress strain technique, showing that pure silica composite was more than waste silica composite of step one by small value. Thermal characterization was studied using thermal gravimetric analysis proved that improvement of the silica waste / NBR composite than that of pure composite and also for electrical properties of the composite which have the same behavior. These results confirmed application of waste silica instead of pure one with NBR composites and management of environmentally problem such as water polluted with waste silica.

Keywords: Composite; Silica waste; Recycling; Irradiation; Thermal behavior

Introduction

Polymer materials have served mankind for decades. They are used in a wide range of industrial applications including packaging, transportation, construction, pharmacy and the food industry world wide. Elastomers are probably the most versatile and useful groups of polymers ever known to man. These materials are used to manufacture articles such as tires, isolation bearings, roofing sheets, seals, electrical cables and hovercraft skirts. Raw elastomers, e.g. natural rubber (NR), have poor properties and must be reinforced. Reinforcement gives improvement in properties such as tear strength, abrasion resistance, stiffness and hardness [1]. This is brought about by the inclusion of solid particles for example carbon black. Fillers and curing agents to a large extent control the technical properties of rubber compounds [2-8]. Particularly, as a chemical-free biomacromolecule, natural rubber latex (NRL) has been used in manufacturing medical products such as medical gloves, condoms, blood transfusion tubing, catheters, injector closures and safety bags due to its excellent elasticity, flexibility, antivirus permeation, good formability and biodegradability [9-11]. More recently, with the worldwide spread of the epidemic diseases such as Acquired Immure Deficiency Syndrome (AIDS), hepatitis B, Severe Acute Respiratory Syndrome (SARS) and avian influenza A (H5N1), it becomes increasingly important and urgent to develop high performance NRL protective products. Low tensile strength and poor tear resistance are the other major drawbacks encountered in NRL products, especially for medical gloves and condoms. Attempts have been made to use carbon black [12], ultra-fine calcium carbonate [13], modified montmorillonite [14], silica [15] and starch [1] to reinforce dry NR or NRL. However, these traditional reinforcement materials are not so effective for NRL. Therefore, it is essential to exploit new ways to enhance the ageing resistance and mechanical properties for NRL products. Further, such reinforcements are related to the secondary structure of filler particles (agglomerate) [16-18] and the rubber/filler interactions [19-21]. Silica is also known as an effective filler of rubber reinforcement. Since silica does not have any radical and lone electrons, it does not show any ESR signals. Thus silica filled rubber systems are suitable for the investigation of chain scission of rubber molecules during the deformation. For silica filled rubber systems, the rubber/filler interactions can be controlled by the introduction of coupling agent [22-24].

Tribological studies on SiO_2 / acrylate nanocomposites show that friction leads to the gradual loss of SiO_2 nanoparticles [25]. In the case that SiO_2 nanoparticles are applied in tires, one may expect them to be released by wear. It has been shown that many of the particles released by the interaction between tires and road pavement are <100 nm [26,27]. Furthermore, nanoparticles may be released when nanocomposites are subjected to wear, such as sanding in the case of coatings and abrasive use in the case of dental fillings [28-30]. Thus, it would seem proper to consider the impact of nanoparticlate TiO_2 and amorphous silica after release. There is evidence that amorphous SiO_2 nanoparticles may be hazardous to humans [31–33] and may exhibit ecotoxicity [34]. A main molecular mechanism of cytotoxicity in case of both amorphous SiO_2 and TiO_2 nanoparticles in the absence of light appears to be oxidative damage linked to reactive oxygen species, whereas TiO_2 particles exposed to light and/or UV radiation may also damage cells due to photo catalytically enhanced oxidation [35-44]. Changes of the nanoparticulate surface, which may be introduced to achieve a better performance of nanocomposites e.g. [45-48], may in turn affect hazard. All in all, amorphous SiO_2 and TiO_2 nanoparticles can be hazardous, with actual hazard to a considerable extent dependent on surface characteristics and in case of TiO_2 also on crystal structure. Claims that nanocomposites are 'environmentally safe'

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[49-50], 'environment(ally)-friendly' or 'eco-friendly' and that TiO_2 nanoparticles are 'non-toxic' do not seem to have a firm foundation in empirical data. Moreover, traditional methods of particulate control such as wastewater treatment plants and filters are often not well suited to efficiently catching TiO_2 and SiO_2 nanoparticles. There is only very limited research into the performance of recycled nanocomposites which contain organic polymers. One study has considered recycling of layered silicate-thermoplastic olefin elastomeric nanocomposites, focusing on mechanical performance [51]. In this study it was found that though degradation of the nanocomposite during recycling occurred, mechanical properties remained significantly better than those of the neat polymer. More in general one might expect that the oxidative properties of titania and silica nanoparticles are conducive to polymer degradation and will increase thermal degradation over the level occurring in neat polymer when recycling involves heating [45,52,53].

Our results aims to manage the silica waste resulting from manufacturing of glass crystals. The silica waste has different particles size which used as filler with synthetic rubber to improve their mechanical characteristics. Irradiation with electron beam has applied to achieve compatibility and finally cross-linking. Thermal behavior of waste silica / NBR composites have been studied and compared with that of pure silica to show its availability to replace with them.

Experimental Approach

Materials and methods

Materials: A commercial grade acrylonitrile-butadiene rubber (Europrene N3345) with 34 % acrylonitrite content was used as the matrix polymer it was purchased from Enichem Company INC., Italy. The recipe of this study contained also other additives, namely: ZnO, stearic acid (from El-nasr Phosphate Company (Egypt). Pentaerthenol triacrylate (PETriA) from Aldrish (Germany) used as sensitizer. The first two additives act as accelerators as well as activators and their content was 5 phr and 1 phr, respectively.

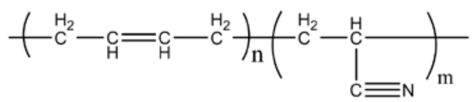

Diagram showing the formula of NBR

Sample Preparation: NBR, ZnO, stearic acid and silica followed by sensitizer were mixed on a rubber mill (300 x 470 mm). The blends composite sheets were then compression molded into sheets of 4 mm thickness at 160°C under a pressure of for 10 min. Irradiation by Electron beam accelerator was carried out for achieve optimum com.

Powdered characterization

EDX Measurements: Oxford-tests attached to Scan Electron Microscope (SEM), Joel- 5400, Japan.

Calibration data:- Gain factor: 49.996, Live time: 80 Seconds.

Sample data:- Total spectrum count: 875722, Live time: 70 Seconds, System resolution: 173 eV, Accelerating voltage: 20.00 KV.

Particle size analyzers: The particle size analysis for different types of silica was carried out by using Quantachrome porosimeter (Pore Master 60) from Florida, (USA) depending on automatic mercury intrusion under high pressure 60, 000 psia.

Mechanical properties measurements

Hardness measurements: Samples of at least 1 mm in thickness with flat surface were cut for hardness test. The measurement was carried out according to (ASTM D2240, 2000) used to examine by analogue manual instrument of hardness tester with thin pin it is termed Baxio USA. The unit of hardness is expressed in (Shore A).

Tensile measurements: Five individual dumbbell-shaped specimens were cut out from the sheets using a steel die of standard width (4 mm). The minimum thickness of the test specimens was determined by gauge graduated to one hundredth of the mm. A bench mark of 1.5 cm was made on working part of each test specimen. The ultimate tensile strength and elongation at break point were determined at crosshead speed 500 mm / min on a rubber tensile testing machine Instron Machine model 1195, (England). The measurement was carried out according to (ASTM D-412-66T), in which the standard deviation was ±5%.

Electrical properties

AC impedance spectroscopy measurements over a frequency of 10^6 Hz using a system 3532 Hioiki bridge LCR hi tester. Each composite sample was cut into sections 2.5 cm × 2.0 cm prior to being mounted in the cell.

Thermal Properties measurements

Thermal Gravimetric Analysis: Shimadzu TGA -50, Japan, was used to characterize the thermal stability of the different composites. Thermal analysis was carried out using a thermal gravimetric analysis (TGA) apparatus, samples of 0.98 - 1.5 mg were encapsulated in aluminum pans and heated from 50 up to 500°C at heating rate 10°C /min.

Results and Discussion

Silica powdered characterization

Chemical characterization of waste silica and pure by EDX (Table 1): It is apparent that waste silica of step one contain 95.87 % silica which is less than pure silica by 2.19 %. it has traces of aluminum, sulfur, titanium, copper, zinc and tin while the latter 4 elements have disappeared completely in pure silica. Silica of step two differ from that of step one by raising of aluminum concentration to about 16% which is due to adding of alum to clarify the silica- water suspension as this drilled silica is desired to get ride off. Metal traces of step two silica such as titanium has about double value of step one while copper and zinc are triple time of step one. Tin have disappeared completely in silica of step two while sulfur has the same value in step one and step two. Silica of step two has 79.09 % value of its weight so it decreased by 18.97 % from the pure silica.

Particle size analyses of the silica (waste and pure one) (Table 2): As it seen from table 2 waste silica of waste silica of step one and two is larger than pure silica while silica of step two (73 µm) is larger than that of step one (66 µm). It may due to adding alum have important role for precipitation of more silica particles have larger and smaller particle size. Particle size of step two has larger particle size which may due to different traces of metals by higher ratio than that of step one waste silica. The included trace metals included higher atomic radius than pure silica besides their ability to form a complexes such as aluminum. Aluminum has a capability to react with acids and alkali which raise their probability to form higher particle sized compounds. Surface area of waste silica particles are varied with a large range compared to pure silica.

No.	Element	Element % of Pure silica	Element % of waste silica step 1	Element % of waste silica step 2	Atomic % Pure silica	Atomic % waste silica step 1	Atomic % waste silica step 2
1-	O	15.43	8.79	11.26	37.15	27.05	26.09
2-	Al	0.8	0.96	11.63	1.34	1.75	15.98
3-	Si	44.4	39.26	40.16	60.89	68.82	53.00
4-	S	0.51	0.16	0.17	0.62	0.24	0.2
5-	Ti	-------	0.68	2.36	--------	0.7	1.83
6-	Cu	--------	0.69	2.73	--------	0.54	1.6
7-	Zn	-------	0.74	2.83	--------	0.56	1.35
8-	Sn	--------	0.85	0.0	--------	0.35	0.0

Table 1: Constituents of pure silica and waste silica taken from 2 steps of waste treatment.

No.	Pure silica	waste silica step 1	waste silica step 2
Particle size	52 µm	66 µm	73 µm

Table 2: Particle size of pure and waste silica.

Rubber composite characterization

Nitrile butadiene rubber (NBR) is a family of unsaturated copolymers of 2 propenenitrile and various butadiene monomers (1,2-butadiene and 1,3 butadiene). Although its physical and chemical properties vary depending on the polymer's composition of nitrile (the more nitrile within the polymer, the higher the resistance to oils but the lower the flexibility of the material), this form of synthetic rubber is generally resistant to oil, fuel, and other chemicals. Its resilience makes NBR a useful material for disposable lab, cleaning, and examination gloves. It is used in the automotive industry to make fuel and oil handling hoses, seals, and grommets. NBR's ability to withstand a range of temperatures from −40°C to +108°C makes it an ideal material for extreme automotive applications. Nitrile butadiene is also used to create moulded goods, footwear, adhesives, sealants, sponge, expanded foams, and floor mats. Nitrile rubber is more resistant than natural rubber to oils and acids, but has inferior strength and flexibility. Nitrile gloves are nonetheless three times more puncture-resistant than rubber gloves [54]. Nitrile rubber is generally resistant to aliphatic hydrocarbons. Nitrile, like natural rubber, can be attacked by ozone, aromatic hydrocarbons, ketones, esters and aldehydes.

When nano or micro particles are dispersed with polymers, a core shell structure tends to be formed in which nanoparticles covered with polymeric chains under certain conditions such as those used for self-assembly. By employing this approach, Caruso et al. [55] developed core-shell materials with given size, topology, and composition. Han and Armes [56] and Rotstein and Tannenbaum [57] studied polypyrrole, polystyrene and silica nanocomposites, respectively, and also confirmed the formation of this core-shell structure. In the present study, SiO_2 nanoparticles act as cores or templates to adsorb NBR particles to develop a bulk NBR/SiO_2 microcomposite. There is electrostatic adsorption stage in this process figure 1 [58]. Electron beam irradiation play very important role in cross linking of NBR and silica; irradiate the composite make a homolitic and heterolytic fission upon NBR rubber which firstly surrounded the silica mechanically and thermally. Positive charged arising by irradiation on NBR adsorbed on negatively charged silica powdered. Positively charged trace metals which have investigated by EDX may play an important role for tightly compatiblization to NBR especially waste silica taken from step two (Figure 1).

Mechanical properties of rubber composites

Hardness properties: Hardness and 300% modulus of all vulcanizates are illustrated in table 3. As expected, the gum gives the lowest hardness and modulus while hardness and modulus increase noticeably when pure silica is added to the NBR. At 40 % amounts of filler, step one vulcanizate exhibits nearly equal stiffness with waste silica step two silica-filled composite. In addition, the results showed that small difference of hardness between step one waste silica composites when it compared with composite of pure one. Hardness of composite increased upon 100 KGy irradiation using Electron beam irradiation as it seen in table 3. This is thought to be due to the decrease in crosslink density when high silica loading is used at 25 KGy. In a previous study, crosslink density of NR vulcanizates gradually decreases when silica loading is more than 20 phr [59]. The explanation is given as the adsorption of zinc complex on the silica surface, thus lowering the sulfur vulcanization efficiency. (Table 3)

Stress strain of rubber composite (Figure 2) (Table 4): It is well known that the stress–strain curves for silica filled rubber systems are affected by the crosslink density of rubber matrix [60,61], the size of agglomerates formed by the silica [62,63] and rubber / silica interactions [64,60]. These effects can be controlled by the contents of curing agents, the number of silanol groups on silica particles and the introduction of coupling agent. Irradiation by electron beam have advantageous role for cross linking and so on composite stress strain. Waste silica composites have improved mechanical character than that of pure one which represented by two samples first of which (sample 1) irradiated by 25 KGy. While second one which irradiated by 100 KGy was termed sample 4. The irradiated samples with 100 KGy dose have higher stress value while that irradiated with 25 KGy have higher strain value it may due to incomplete cross linking between inorganic particles and the rubber understudy. These results may be explained by higher cross-linking have attained by higher irradiation dose in the range of 100 KGy.

Electrical behaviors of rubber composite: The dielectric behavior of composite materials can be also changed depending on the particle size of the added particles. Some degree of dielectric enhancement

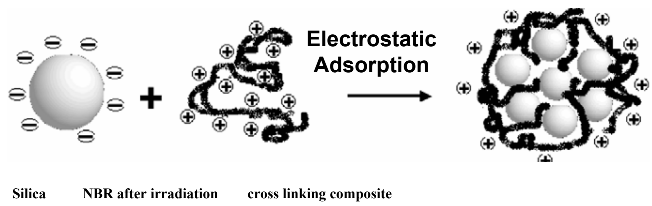

Figure 1:

No.	Sample	Hardness (Shore-A)
1-	NBR with no additive and irradiation at 25KGy (Blank)	38
2-	NBR with no additive and irradiation at 100KGy (Blank)	41
3-	NBR with pure silica additive and irradiation at 25 KGy	54
4-	NBR with waste silica step 1 additive and irradiation at 25 KGy	51
5-	NBR with waste silica step 2 additive and irradiation at 25 KGy	54
6-	NBR with pure silica additive and irradiation at 100 KGy	62
7-	NBR with waste silica step 1 additive and irradiation at 100 KGy	59
8-	NBR with waste silica step 2 additive and irradiation at 100 KGy	64

Table 3: Study of hardness of pure and waste silica /NBR composite.

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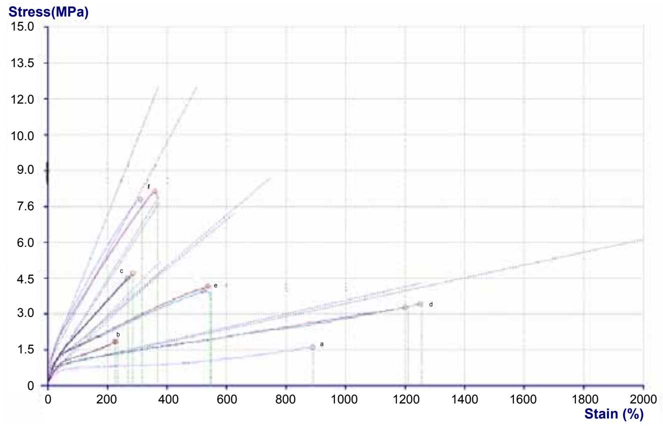

a) Pure silica at 25 KGy irradiation
b) Waste silica discharged from step one at 25 KGy irradiation
c) Waste silica discharged from step two at 25 KGy irradiation
d) Pure silica at 100 KGy irradiation
e) Waste silica discharged from step one at 100 KGy irradiation
f) Waste silica discharged from step two at 100 KGy irradiation

Figure 2: Stress strain curve NBR/ silica composites.

was reported for composite materials with dispersed Al_2O_3, SiO_2, TiO_2 particles as the particle size decreases from a typical bulk value to a nanometer scale [65,66]. The dielectric differences between nanometer-sized and bulk-sized particles can be seen in the Cole-Cole plot. The dielectric enhancement is attributed to the dipoles associated with the interfaces of the nanometer-sized particles, which are created because of the presence of dangling bonds, twisted bonds or bonds with adsorbed foreign molecules. In the case of heterogeneous systems, where materials of different electrical properties contact each other, the charges at the interfaces can additionally build-up [67]. For the investigated systems such dipoles can result from the rubber-filler ionic interactions when silica was used. Therefore we assume that the concentration of dipoles present in the system varies with the amount of added silica, that is reflected by the relaxation strength, $\Delta\varepsilon = \varepsilon 0 - \varepsilon\infty$ calculated from Cole-Cole plots for α- relaxation. The highest value of the relaxation strength was obtained for the vulcanizates filled with silica synthesized from 40% of silica, as one would expect as shown in table 4. Therefore, this behavior could result from the highest amount of silica, charges on its surface and its interactions with rubber chains. The Cole-Cole plot for the investigated systems demonstrates a major deviation from semicircle, especially at low frequencies, which indicates not only a large distribution of relaxation times, but can be also due to the presence of nanometer size particles. The differences in the positions of Cole-Cole for the investigated systems could be the result of the volume fraction of particles as well as the distribution of the particles morphology, shape or structural interactions. Irradiation dose has an important role for composite compatiblization 100 KGy is advantageous dose over 25 KGy and so electrical conductivity is less in larger dose. Pure silica/NBR composite is less in EC comparing to that of waste silica composite. Waste silica of step two is higher in EC than waste silica step one composite which may due to more concentration of trace metals in this composite as it seen in table 4. (Table 5).

Thermal behaviors

Thermal gravimetric analysis (Figure 3): The thermal and thermo oxidative ageing resistance of NBR / SiO_2 composite can be assessed, respectively, from the investigation of thermal and thermo oxidative decomposition. There is only one obvious thermal decomposition step of NBR molecular chains, primarily initiated by thermal scissions of C–C chain bonds accompanying a transfer of hydrogen at the site of scission.

40% pure silica – Nitrile butadiene rubber composite have differentiated into 5 divisions as seen in figure 3. Each division could be expressed on loss of some fragments of the composite (as CO, CO_2, CH_4, H_2O…etc). First division showed loss of 1.85% of the original weight by raising the temperature to 269°C expressed on working temperature which may be explained by loss of water content included through the composite. Second division illustrated gradual low decrease of weight which was 3.5% from the original value due to heating into 382°C. The third division described convex curve, loss of weight through which was 17% by increasing the temperature to 438°C. 48% weight loss was observed via the fourth divisions which have occurred by raising the temperature into 477°C which may due to loss of the majority of the organic fragments. The fifth division illustrated the tail of the thermo gram which ended at 484°C and the weight loss reached to 65% of the original weight.

Figure 3b and illustrated thermo gram of waste silica of 40% ratio with NBR forming a composite. The thermo gram attained could be characterized into 4 divisions. First division showed 1.85% loss of weight by raising the temperature into 357°C and 373°C for the first and second steps of silica/ treatment respectively. This loss of weight described working temperature of the composite that proved their availability with wider range of temperature than pure silica-NBR

Specimen No.	Specimen Description	E-Mod MPa	Yield MPa	Yield %	Break MPa	Break %
1	Pure silica at 25 KGy	1.145	1.847	228.8	1.847	234.4
1		1.28	1.847	225	1.847	226.1
2	Step one silica at 25 KGy	-------	0.1912	-------	1.618	890
3	Step two silica at 25 KGy	0.2845	3.289	1200	3.289	1210
3		0.2694	3.421	1250	3.421	1256
4	Pure silica at 100 KGy	1.917	4.705	286.1	4.705	286.1
4		1.990	4.487	267	4.487	269.6
5	Step one silica at 100 KGy	1.033	3.977	523	3.784	546
5		1.062	4.170	537	4.125	548
6	Step two silica at 100 KGy	3.137	7.79	310.5	7.59	315
6		2.628	8.12	359.0	7.84	368

Table 4: Study of tensile of pure and waste silica /NBR composite.

No.	Sample	Electrical conductivity µ Simon / Cm
1-	NBR with no additive and irradiation at 25KGy	$4x10^{-12}$
2-	NBR with no additive and irradiation at 100KGy	$6x10^{-12}$
3-	NBR with pure silica additive and irradiation at 25KGy	$8x10^{-11}$
4-	NBR with pure silica additive and irradiation at 100 KGy	$5x10^{-11}$
5-	NBR with waste silica step 1 additive and irradiation at 25 KGy	$3x10^{-9}$
6-	NBR with waste silica step 1 additive and irradiation at 100 KGy	$9x10^{-10}$
7-	NBR with waste silica step 2 additive and irradiation at 25 KGy	$6x10^{-9}$
8-	NBR with waste silica step 2 additive and irradiation at 100 KGy	$2x10^{-9}$

Table 5: Study of Electrical conductivity of pure and waste silica /NBR composite.

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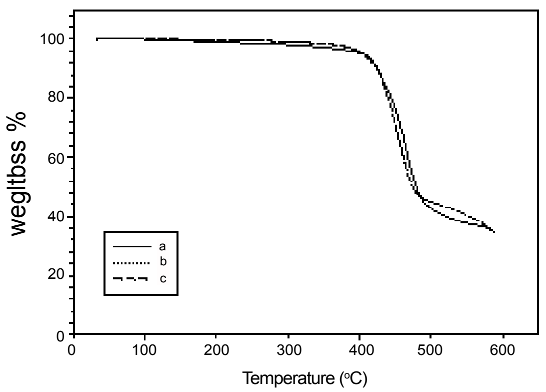

a) Pure silica
b) Waste silica discharged from step one
c) Waste silica discharged from step two

Figure 3: Thermo-gravimetric analysis of NBR/ silica composites.

composite. While second step waste silica-NBR composite has more thermal stability than step one waste silica-NBR composite. The second division showed 16.5 and 16% loss of weight by heating the composite to 433°C and 435°C for step one silica silica composite and second one in regular manner. There were dramatic weight decrease ended at 47.5% for the first step waste silica-NBR composite and 52% weight decreased was attained by the second step waste silica-rubber composite. This division (Third division) attempt more thermal stability of the first step waste silica / NBR composite than that of step one's silica composite. The fourth division described weight loss which ended at 65% weight loss from the original value for the two thermograms by heating the temperature into 586°C. The two thermograms attempt more compatibility of waste silica than pure one through the composite with NBR.

Conclusion

This work aims to examine the availability to replace pure silica used for NBR reinforcement by waste silica discharged from glass and crystal factories. This study managed two problems, first of which to overcome a serious environmentally one. The second problems depend on cost benefit point of view, through which it could be using no cost waste silica instead of somewhat expensive pure one. This study included evaporation silica suspension to attain silica powdered which have particle size in the range of 50 to 75 micrometer. Mixing the attained silica powdered from two points of waste silica discharges with nitrile butadiene rubber in the ratio of 40 %. Electron beam irradiation with different doses (25 and 100 KGy) was exposed on the composites for achieve optimum compatibility and finally cross-linking. 100 KGy irradiation dose have better results than 25 KGy. Mechanical properties showed more or less change of tensile strength and hardness by comparing pure silica composites by waste silica one. Thermal and electrical characterizations of the waste silica composite were improved. The attained results confirmed using the waste silica instead of pure one for reinforces NBR to carry out composites having different applications.

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