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Research Article

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Study of Thermal Oxidative Ageing and Gamma Irradiation Effects on Styrene Butadiene Rubber/Boron Carbide Based Composites

Hafiz Muhibb ullah Zulkafal[1]*, Muhammad Asif[2], Tariq Yasin[2], Saima Kanwal[3], Muhammad Afzal Khan[1] and Khalid Iqbal[1]

[1]*Department of Physics, The Islamia University of Bahawalpur, Pakistan*
[2]*Department of Metallurgy and Material Engineering, Pakistan Instiute of Engineering and Applied Sciences, Pakistan*
[3]*Institute of Chemical Sciences, Bahauddin Zakariya University, Multan, Pakistan*

Abstract

Purpose: Nuclear radiations have broad applications in our daily life, while unwanted radiations are harmful for man as well as environment. The main objective of this study is to search better shielding material for transportation of radioactive substances, to form a light weight safety dress for workers and defence solutions.

Materials and methods: Composite of Styrene-Butadiene Rubber (SBR) containing 20 parts per hundred (phr) Boron Carbide (B_4C) was prepared using Two Roll Mill. Thermo-oxidative ageing was performed at Pakistan Institute of Engineering and Applied Sciences (PIEAS) using ageing oven in air at circulation speed of 15 rev/min. Thermal oxidative ageing of samples were carried out at 70°C for 12 days in ageing oven. Gamma ageing of samples were carried out by using Gamma irradiation facility at Pakistan Radiation Services (PARAS) Lahore. This was performed using ^{60}Co gamma irradiator in air at a dose rate of 1.02 kGy/h. The polymer composite are subjected to various doses of gamma radiation ranging from 100 to 400 kGy. Mechanical properties measurement were carried out for this composite are The tensile strength, elongation at break and young's modulus were measured using universal tensile testing machine. The solvents used in this study are: Acetone, chloroform, distilled water, kerosene oil, methanol, 12% NaOH, 10% H_2SO_4 and Xylene for Swelling measurements of composite at room temperature about 24 h to 48 h. Neutron attenuation properties of the composite were investigated using BF_3 detector in Pakistan Research Reactor-1 (PARR-1). Monte-Carlo simulation code (MCNP-5) and MCBEND was used to calculate the simulated results. Comparison of experimental and simulated result shows a good agreement with each other.

Results: Monte Carlo simulation results are matching to the experimental results and it is seen that addition of boron carbide increase the attenuation of thermal neutrons to about 167% than unloaded sample. Normally no swelling for water, 12% NaOH, 10% H_2SO_4 and Ethanol proves good for these environments. Mechanical characteristics are also favorable and show bearable behavior of the composite.

Conclusions: On the basis of experimentally observed behavior, characteristics and response to radiation, it can be concluded that styrene butadiene rubber/boron carbide based composites are the excellent materials for shielding radiations.

Keywords: SBR/B_4C composite; Radiation shielding; Thermo-oxidative aging; Gamma aging; Mechanical properties

Introduction

The nuclear materials have broad applications in our daily life. Nuclear radiations have beneficiary to medicine, industry, research and for many other purposes, while unwanted radiations are harmful for man as well as environments [1]. These unwanted radiations i.e., X-Rays, Gamma rays and neutrons emitted from nuclear materials causes ionization of the medium through a complicated mechanism and emits secondary charged particles [2]. The ionizing ability of these radiations focused the attention of many researchers in the field of nuclear energy to shield these radiations in order to keep the radiation workers and environments safe [3]. Already used materials for radiation shielding are normally lead, reinforced concrete, iron, graphite. But these materials posture problems of heaviness, space limitation, manufacturing and movement problems. Therefore the demand for reliable shielding material has been growing during the last decade [4]. Specifically, shielding materials for ionizing radiations such as high energy neutrons produced from nuclear reactors and related instruments/facilities, fusion reactors, cyclotrons, and space radiations have been explored [5]. Many studies have been carried out to understand and use of different materials for shielding radiation. These studies also define the physical and chemical properties of composite materials. Haghighat et al. explains effect of adding α-cellulose powder to styrene–butadiene rubber (SBR) compounds physical and chemical properties [6]. Reichmanis et al. examine different polymers and determine the specialty of polymers to show definite response on radiation exposure and chemical changes occurring in polymers [7]. Yasin et al. utilized styrene-butadiene rubber (SBR) mixed with waste tire rubber (WTR) and number of SBR/WTR blends was prepared by varying the ratios of WTR, cross linked by gamma rays and investigated the absorbed dose and physical properties [8]. Huang et al. investigated the boron carbide composite materials reinforced by carbon fiber and showed that carbon fiber reinforced composite materials had outstanding performance due to higher strength, lighter weight and better conductivity [9]. Abdel et al. experimented using different Composites of ethylene-propylene diene rubber and low density polyethylene with two different concentrations of boron carbide powder and investigated gamma and slow neutron

***Corresponding author:** Hafiz Muhibb ullah Zulkafal, Department of Physics, The Islamia University of Bahawalpur, Pakistan, Tel: +923024388245; E-mail: muhibbiub@yahoo.com

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radiation shielding properties with temperature variations and explains dependence of electrical and thermal properties for these composite materials [10]. Kipcak et al. explain the behavior of boron carbide and compared boron carbide prepared using different techniques and investigated the shielding behavior of boron carbide [11]. Gwailey et al. explains maximum degree of swelling (*Q*), penetration rate (*P*) and the average diffusion coefficient (*D*av) for composites of natural rubber and boron carbide with different concentrations [12] Many reports, journals and monographs have been studied on radiation shielding some organizational reports are mainly used for the basis of this study are, The Radiation Shielding Information Center (RSIC) at Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA. National Council on Radiation Protection and Measurements (NCRP) Beheads, Maryland, USA. Radiation protection and shielding Division of the American Nuclear Society (ANS), La Grange park Illinois, USA. OECD Nuclear Energy Data Bank, Gif-Sur-Yvette, France and the European shielding information services, Ispra, Italy. All these organizations have published data using different materials for shielding of ionizing radiations.

Hence a trial was made to prepare a composite material of SBR/B_4C containing 20 phr of B_4C. This composite to be tested for thermal neutrons as shielding material and show excellent attenuation properties against thermal neutrons due to high absorption cross-section of boron (^{10}B thermal neutron cross section=3837 barn) [10].

Despite the use of these composite materials for radiation shielding applications, their long term properties are affected by Heat, Solvents, Acids, Neutron and Gamma environments and more importantly combination of all these which will degrade the material structure and cause fracture in the material [13]. The heat and radiation can affect the physical properties of the composite material, therefore the study of thermal oxidative aging and Gamma aging on physical properties of composite material is necessary [14].

In present work, the neutron shielding properties of SBR/B_4C composite have been tested by using thermal neutron radiation technique at Pakistan Atomic Research Reactor-1 (PARR-1). PARR-1 is a research reactor operating at power of 10 MW and core flux is 1×10^{14} n/cm^2/sec. A monochromatic energetic beam of neutrons with thermal core flux of 1×10^5 n/cm^2.sec is bombarded on various thicknesses of the material and the transmitted beam of neutrons was collected by BF_3 detector. The simulated results were made by MCNP-5 and MCBEND. The simulated and experimental results are also compared in this work. The mechanical properties, swelling index in different solvents and the effects of Gamma ageing and thermal oxidative ageing on physical properties of the composite material were also studied.

Materials and Methods

Styrene butadiene (SBR-1502) with 23% styrene contents were supplied by Kumho Petrochemical Co., Ltd, Korea was used as matrix. B_4C was supplied by sigma Aldrich and used as neutron shielding material. Sulphur was used as cross-linking agent. The recipe of this study also contained other accelerator's, additives i.e., Zno, Stearic acid, 6-PPD. Zno and stearic acid act as activator and accelerator and their concentration used were 5 phr and 1 phr. 6-PPD were act as anti-oxidant and amount used were 1 phr. Solvents and other chemicals used were of commercial grade.

Sample preparation

First mastication of SBR was done on two roll rubber mixing mill at 25°C for 15 minutes. Then Zno, stearic acid, paraffin oil, MBT, MBTS, 6-PPD and boron carbide were mixed except sulphur. Sulphur was mixed at the end before making sheets on hot press. The total duration of mixing was 30 minutes. The compound was pressed to 2 mm thick sheet using hot press at 150°C and 15 MPa pressure for 20 minutes.

Thermo-oxidative ageing was performed at Pakistan Institute of Engineering and Applied Sciences (PIEAS) using ageing oven in air at circulation speed of 15 rev/min. Thermo-oxidative ageing was performed for 2-12 days. Gamma Irradiation was performed at Pakistan Radiation Services using ^{60}Co gamma irradiator (Model JS-7900, IR-148, and ATCOP), in air at a dose rate of 1.02 kGy/h. The polymer composite are subjected to various doses of gamma radiation ranging from 100 to 400 kGy.

Swelling measurement

Tiny pieces of sample of approximately uniform size and weight were accurately weighed (W_1) by using an electric balance of least count 10^{-4} g and immersed in 50 ml of respective solvent at room temperature for 24 h to 48 h. After that the sample was taken out and placed between two pieces of filter paper. Then the sample was placed in weighing bottle and reweighed (W_2), the degree of swelling (SI%) was calculated by using the defined equation [14]:

$$\text{Swelling Index (SI \%)}=(W_2\text{-}W_1/W_1) \times 100 \quad (1)$$

The solvents used in this study are: Acetone, chloroform, distilled water, kerosene oil, methanol, 12% NaOH, 10% H_2SO_4 and Xylene.

Mechanical properties

Mechanical properties measurement were carried out by cutting five dumbbell shaped specimens of 2.5 μm thick with the help of steel die of standard width 6.3 mm. The tensile strength, elongation at break, tears strength and young's modulus were measured using universal tensile testing machine, Model AURA10, maximum load 10 KN were performed according to ASTM method D-412 for tensile and D-624 for tear strength [15]. The cross head speed was 300 mm/min at room temperature (25°C). Thermal oxidative ageing of samples were carried out at 70°C for 12 days in ageing oven. Gamma ageing of samples were carried out by using Gamma irradiation facility at Pakistan Radiation Services (PARAS), Lahore.

Neutron attenuation properties

Neutron attenuation experiment was performed at PARR-1. PARR-I utilized thermal neutron irradiation technique by using diffractometer arrangement to study the neutron shielding properties of SBR/B_4C composites. The thermal neutrons were obtained with 10 MW from core flux of 1×10^{14} n/cm^2/sec and were converted to mono-energetic (thermal range) neutron beam through a mono-chromator (Cu^{220} crystal) [16]. Neutron beam of wavelength 1.2 A_0 was bombarded on various thicknesses of the samples for equal interval of time. The transmitted beam was collected with a BF_3 detector (Reuter Stokes, USA) with Ortec timer counting system. At full power, neutron flux of 1×10^5 n/cm^2/sec was obtained, and made incident on our mono-chromator crystal. It specifically diffracts neutron of thermal energy range at wavelength of 1.270 A.

Results and Discussion

Attenuation measurement

The attenuation of neutrons in SBR/B_4C composite material is calculated. The linear attenuation coefficient was calculated from the slope of graph plotted between Ln (I/I_0) and X in centimeters as shown in Figures 1 and 2. Absorption coefficient is calculated for the sample of composite formed experimentally and also using Monte-Carlo simulation code (MCNP-5) and MCBEND. All these results are listed in the Table 1 also contains the values of relaxation length which is calculated by using the formula.

$$\lambda=1/\Sigma \quad (2)$$

The half value thickness is mentioned in the Table 1 was calculated by the relation:

$$X^{1/2}=0.693/\Sigma \quad (3)$$

It can be seen from the Table 1 that the value of Σ_a for samples without B_4C is 2.49 cm^{-1}, whereas for loaded sample of 20% B_4C is 6.15 cm^{-1} which shows the increase in absorption of thermal neutron in the shielding material consequently addition of B_4C increase the attenuation coefficient of neutron. The relaxation length (1/Σ) decreased from 0.40 cm (for SBR_0) to 0.16 cm (for SBR_{20}). Similarly half value thickness ($X^{1/2}$) decreased from 0.27 cm (for SBR_0) to 0.11 cm (for SBR_{20}). This is very low and the lowest value of half value thickness is desirable for material used in shielding radioactive source [17]. Also comparison of results is made with simulated results as shown in Table 1 and can be seen that there is no large difference present between these values.

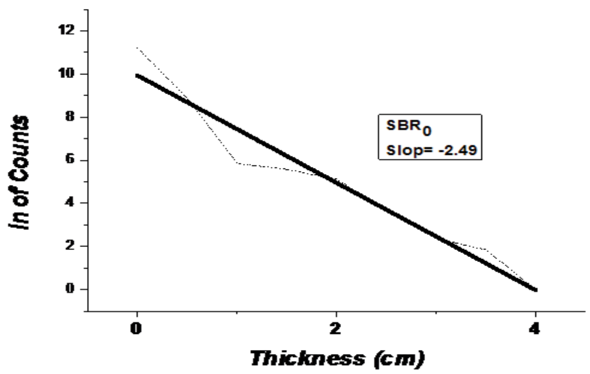

Figure 1: Variation of count rate with thickness of the material.

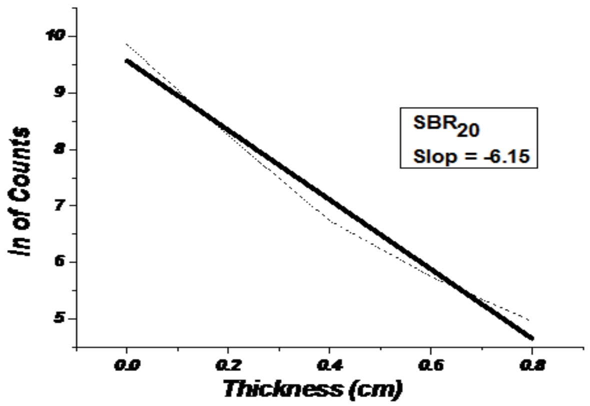

Figure 2: Variation of count rate VS thickness of the material.

The above Figures 1 and 2 shows count rate for SBR_0 and SBR_{20} with the increasing thickness in centimeters. On the basis of these graphs attenuation measurements are taken for SBR_0 and SBR_{20}. It can be seen that addition of boron carbide increase the attenuation of thermal neutrons to about 167% than unloaded sample.

Swelling, measurements

The study of polymers against solvents is very important for their practical use. A cross-linked polymer absorb certain amount of liquid when it is in contact with polymer matrix depending upon molecular weight of liquid and cross-linking density of polymer. Liquid will penetrate into the structure of the polymer matrix depending upon the cohesive energy density of the liquid. Due to the penetration of liquid into the polymer matrix the mass and dimension of the matrix will changed which lead to the destruction and deformation of the sample microstructure. As a result of interaction of polymer matrix with liquid, liquid will absorb into the polymer matrix and remove soluble constituents. The degree of swelling of SBR_0 and SBR_{20} against various solvents at different time says 24 hr and 48 hr is shown in Figures 3 and 4. It can be seen from both the Figures that almost no swelling was seen in the following solvents: water, 12% NaOH, 10% H_2SO_4 and Ethanol. Whereas, it absorb Kerosene, chloroform, xylene and acetone at different absorb rate depending their cohesive energy density. High degree of swelling was observed in chloroform and xylene. High degree of swelling means composite absorb large amount of that material so matrix is not suitable for use in that environment.

Thermo-oxidative aging

Effect on tensile properties: High temperature ageing have considerable affect on physical properties of the composite material, such as reduction in molecular mobility, increase in creep rate and tendency for brittle failure increases. It also affects the resistivity of the polymer containing metallic fillers. The effect of high temperature aging on tensile strength of the composite can be seen in Figure 5.

In this graph decrease in tensile strength is observed as a function of aging time. A sharp decrease in the value of tensile strength has been observed due to exposure of heat. This might be because of the removal of paraffin oil or other ingredients from the polymer matrix. As the paraffin oil remove from the polymer matrix and comes on the surface. It increases the adhesion on the surface which reduces the elasticity of the polymer composite as shown in Figure 6. It has reduced the %elongation at break and increased the Young's modulus and hardness as shown in Figures 7 and 8. It has also been observed that variation in the values of %elongation at break and micro hardness is seen for first four days and then no considerable change is observed. Also, decrease in tensile strength may be due to the degradation of the polymer structure due to breakage of C-S bond due to high temperature or may be due to the decrease in orientation process of the polymer

Sample Type	Density (g/cm^3)	Mass Absorption coefficient (cm^2/g)	Relaxation length (cm)	Half Value thickness (cm)	Absorption coefficient (Σ_a) (cm^{-1})		
					Experimental	MCNP-5	MCBEND
SBR_0	1.04	2.39	0.40	0.27	2.49	2.79 ± 0.03	2.82 ± 0.004
SBR_{20}	1.31	4.69	0.16	0.11	6.15	6.75 ± 0.01	6.77 ± 0.007

Table 1: Attenuation characteristics of B_4C loaded SBR composites.

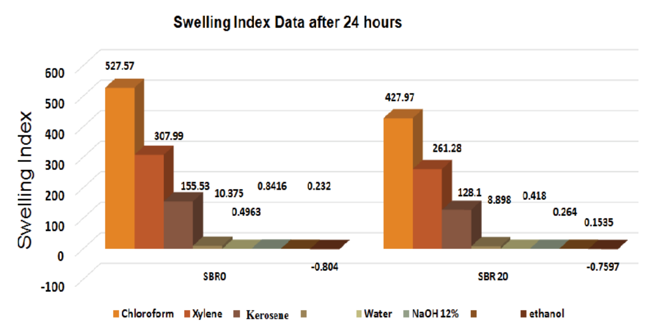

Figure 3: Swelling index data after 24 hours.

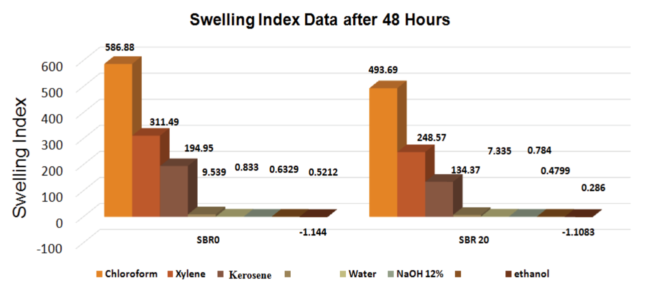

Figure 4: Swelling index data after 48 hours.

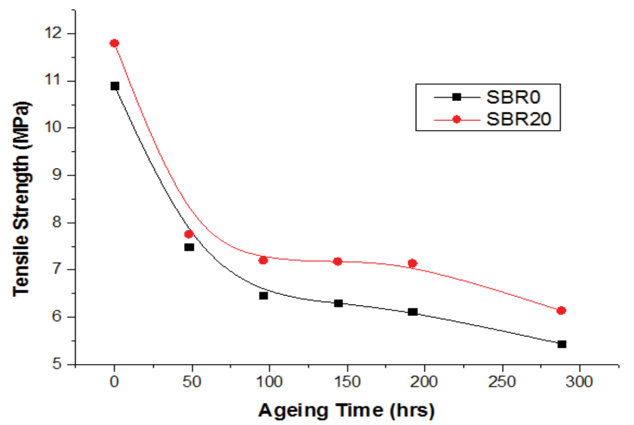

Figure 5: Variation in tensile strength as function of aging time.

matrix which may occur at high level of cross-linking. After specific ageing time the trend of properties remains constant because of the establishment of equilibrium.

Gamma aging

Tensile properties: Gamma irradiation of polymer composites may have considerable effects on tensile properties of polymer composites such as degradation of the polymer matrix through chain scission or increase in the tensile properties through cross-linking. The data obtained for variation of tensile strength at various doses and can be seen that tensile strength of the control sample decrease with irradiation of dose upto 100 kGy. As the dose increases from 100 kGy to 400 kGy it can be seen that no appreciable change has been observed but the value is still decreasing for polymer composites. At high dose these chemicals may come out of the composite and results in decrease in the elasticity of the composite and decrease in tensile strength. The data obtained for variation of tensile strength at various doses is shown in Figure 9. The effect of gamma dose on %elongation at break is shown in Figure 10 which shows that gamma irradiation on SBR/B_4C sample

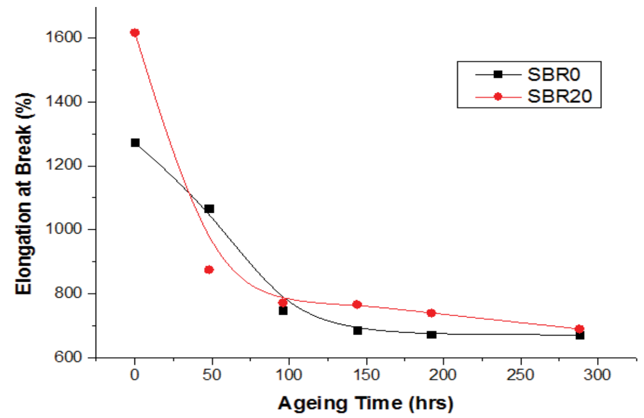

Figure 6: Variation in %elongation at break with aging time.

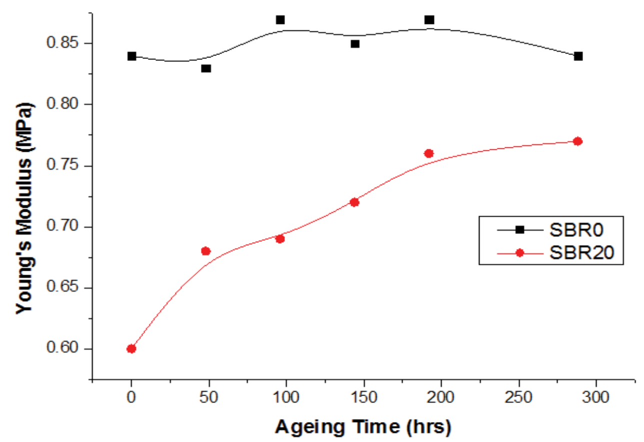

Figure 7: Variation in Young's modulus with aging time.

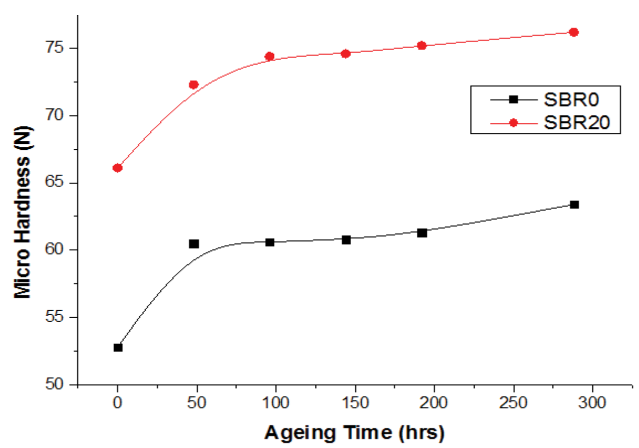

Figure 8: Variation in micro hardness with aging time.

lead to reduce %elongation at break (Eb) at start for the value of 200 kGy and then almost constant trend is seen. The trend for irradiation of gamma on styrene butadiene rubber with loaded and unloaded boron carbide is shown in Figure 10.

The effect of gamma dose on Young's modulus for SBR/B_4C sample shows that as the dose increases from 0 to 100 kGy the response is linear and then increasing concave shape graph can be seen for 100-400 kGy values, hardness increases sharply at start for 200 kGy and then almost constant trend is seen as shown in Figures 11 and 12.

This behavior revealed that contribution of induced cross-linking due to irradiation is less in comparison with chain scission. Also, it may be due to removal of paraffin oil and other ingredients from the composite matrix due to deposition of energy and adhesion on the surface of the polymer matrix increases which will increase the hardness and reduce the tensile strength and %elongation at break.

Conclusion

The mentioned and briefly explained results enabled us to conclude that SBR/B_4C composites show considerable up-gradation in properties in comparison with un-loaded rubber. The desirable characteristics like increased attenuation of thermal neutron, excellent retardation against high gamma doses, with standing ability in different environments even in high temperatures with no noticeable changes occurring in physical and chemical properties and interaction with different materials proves better ability for shielding. So it can be concluded that styrene butadiene rubber /boron carbide based composites are the excellent materials for shielding radiations.

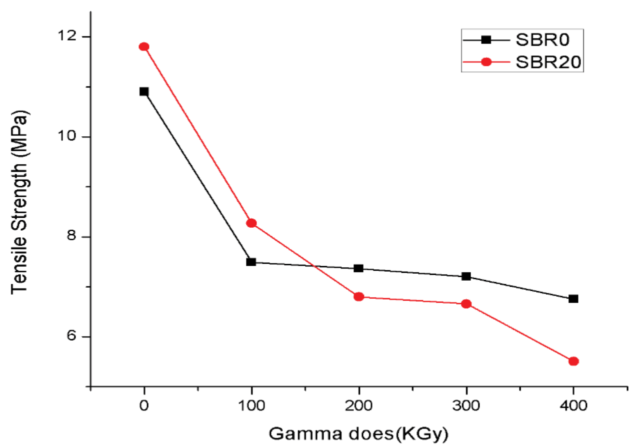

Figure 9: Variation in tensile strength with gamma dose.

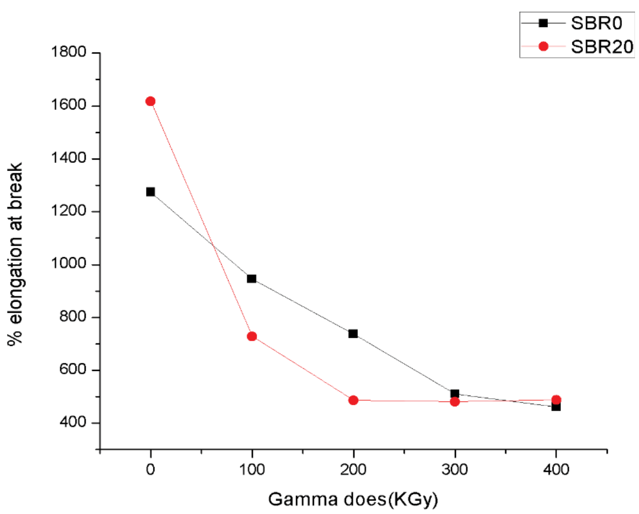

Figure 10: Variation in % elongation at break with gamma dose.

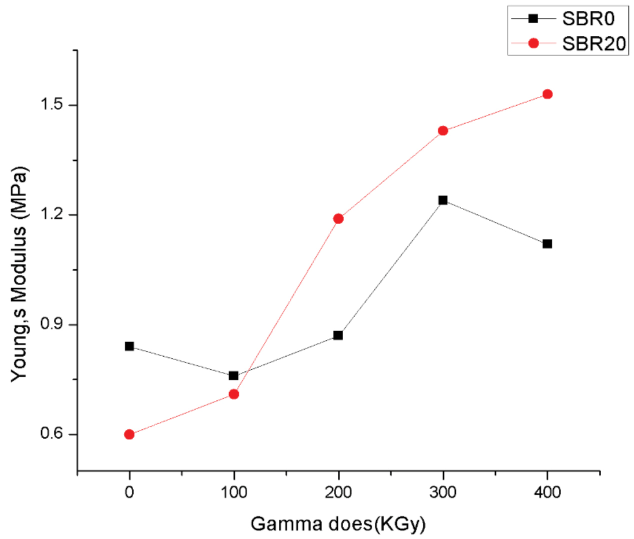

Figure 11: Variation in % young's modulus with gamma dose.

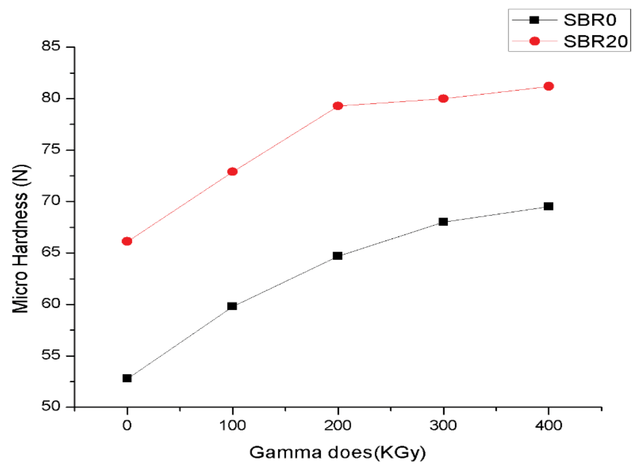

Figure 12: Variation in micro hardness with gamma dose.

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