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EFFECT OF GAMMA IRRADIATION ON CROSSLINK DENSITY AND CHEMICAL CHARACTERISTICS OF GADOLINIUM OXIDE-NATURAL RUBBER VULCANIZATE COMPOSITE

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ABSTRACT
EFFECT OF GAMMA IRRADIATION ON CROSSLINK DENSITY AND CHEMICAL CHARACTERISTICS OF GADOLINIUM OXIDE-NATURAL RUBBER VULCANIZATE COMPOSITE*.* Natural rubber is a polymer that has been widely used in various industrial applications because of its high flexibility. In this study, vulcanizates were developed from SiO_2-reinforced natural rubber with added Gd_2O_3. Vulcanizate composites containing 0, 5, and 10 phr of Gd_2O_3 were fabricated to evaluate the combined effect of inorganic fillers and gamma irradiation. All composites were irradiate with gamma rays at a dose of 100 kGy and were evaluated for their chemical characteristic, swelling behavior, and crosslink density. Fourier Transform Infrared (FTIR) analysis showed that gamma irradiation induces significant structural changes in the natural rubber vulcanizate. These changes were confirmed by the emergence of new absorption peaks assigned to O-H and C=C groups in the FTIR spectra. Swelling and crosslink density measurements showed that gamma irradiation increased the vulcanizate's crosslink density, indicating the formation of a stiffer polymer network. On average, the crosslink density increased by approximately 11%, accompanied by a 9.07% decrease in swelling. These finding highlight the synergistic role of SiO_2 and Gd_2O_3 under gamma irradiation in improving the integrity of natural rubber based composites.

Keywords: FTIR, gamma irradiation, Gd_2O_3, natural rubber, SiO_2.

INTRODUCTION

Natural rubber is a polymer that has been widely used in various industrial applications due to its high flexibility and abundant availability [1]. However, its poor resistance to heat, oxidation, and radiation necessitates modification through vulcanization [2] and reinforcement with inorganic fillers such as silica (SiO_2) and gadolinium oxide (Gd_2O_3). The addition of SiO_2 has been shown to improve the mechanical strength, dimensional stability, and thermal durability of rubber materials [3], [4], [5]. Meanwhile, Gd_2O_3 provides protection against neutron radiation due to its large neutron absorption cross section [6], [7].

The Gd_2O_3-filled natural rubber vulcanizate composite was developed for neutron shielding applications, particularly in Am-Be (Americium–Beryllium) source capsule containers. However, Am-Be sources also emit high-energy gamma rays [8], the protective material must exhibit strong resistance to both types of radiation. Previous studies have confirmed the excellent neutron attenuation of Gd_2O_3-filled natural rubber, with a thermal-neutron HVL of about 1.9 mm [6]. Since the neutron shielding performance is well established, this study focuses on the gamma radiation aspect. Unlike neutrons, gamma rays interact with polymers through photoelectric effect, compton scattering, and pair production [9].

Gamma radiation is known as an alternative method for modifying polymer structures to obtain materials with specifically tailored properties [10]. Several studies have reported that gamma radiation can enhance the physical properties of materials without the use of additional chemicals. Gamma radiation has a very high penetration ability, and it is well known that the interaction between gamma rays and polymers induces the formation of free radicals, which can subsequently lead to chain scission and crosslink formation [11], [12], [13]. The formation of crosslinks is one of the important parameters related to the mechanical properties of rubber.

Several studies have reported that ionizing radiation, such as γ-rays, promotes cross-linking between polymer chains, leading to improved thermal, chemical, and mechanical resistance [14]. Structural, thermal, and mechanical analyses of medical-grade polymers after gamma irradiation have shown that increased crosslink density reduces chain mobility and enhances dimensional stability [15]. In elastomer systems, ethylene- propylene-diene monomer (EPDM) and styrene-butadiene-styrene (SBS) blends irradiated at 100–150 kGy exhibited increased crosslinking in the EPDM phase, while the SBS phase showed resistance to further network formation, indicating that variations in crosslink density are strongly influenced by polymer chemistry and composition [16]. To evaluate the crosslinks formed as a result of gamma irradiation, the crosslink density was determined using the swelling method [17].

Previous study have also reported that gamma radiation can induce changes in the chemical structure of the rubber matrix. These chemical changes can be analyzed using Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectrum is essential for identifying specific functional groups in polymers and detecting the formation of new bonds after gamma irradiation [18]. Thus, this study specifically aims to evaluate how gamma irradiation influences the crosslinking behavior and chemical structure of Gd_2O_3-SiO_2-natural rubber vulcanizates.

METHODOLOGY

Vulcanizate composite fabrication

All materials were weighed and mixed using a *two-roll mill* (Berstorff, Germany) at a temperature of 70±5 °C. The masticating process SIR 100 parts per hundred rubber (phr) was carried out for 1-3 minutes. Subsequently, the other ingredients were added step by step to the rubber sample and mixed using the same procedure. The order of ingredient addition was as follows: (1) ZnO 5 phr and stearic acid 2 phr; (2) silica powder 70 phr and minarex oil 8 phr; (3) antilux 3.5 phr, PEG 5 phr, TMQ 2 phr, TiO_2 10 phr and Gd_2O_3; (5) MBTS 1.35 phr; and (6) sulfur 3.2 phr and SI-69 5 phr. After mixing, the resulting rubber composite sheet was removed, covered with plastic sheet, and left for one day at room temperature. The sample was then vulcanized using *a* hot press vulcanizing machine (Kobe Machinery, Japan) at 150 °C and a pressure of 100 kg/cm^2 to produce a rubber vulcanizate. The vulcanizates were prepared both without Gd_2O_3 (0 phr) and with Gd_2O_3 added at concentrations of 5 phr and 10 phr.

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR analysis was performed on thin rubber layers in the wavenumber range of 4000–600 cm^{-1} with a resolution of 4 cm^{-1} using a Bruker Tensor 27 FTIR Spectrometer (Germany).

Swelling and crosslink density

Crosslink density was influenced by the physical properties of the rubber and was calculated based on the equilibrium swelling of the rubber sample. In this study, samples measuring 30 mm x 5 mm x 2 mm were cut and weighed before being immersed in toluene for 72 hours at room temperature. After immersion, the samples were removed from the toluene, wiped, and left to reach equilibrium weight, and then weighed. The swelling ratio was determined in Equation (1). Each test was performed in triplicate to ensure the accuracy and reproducibility of the results.

$$\zeta\ \% = \frac{m_2 - m_1}{m_1} \times 100 \quad (1)$$

The Flory Rehner equilibrium swelling equation showed the quantitative relationship between the swelling measurements and the crosslink density. The equation used to calculate the crosslink density was expressed in Equation (2).

$$\nu_e = \frac{\ln(1-V_r) + V_r + \chi {V_r}^2}{V_S(\sqrt[3]{V_r} - 0.5V_r)} \quad (2)$$

In this equation, V_r was the volume fraction of the swollen rubber, V_S was the molar volume of toluene (106.3 ml/mol), χ was the Flory/Huggins interaction parameter between toluene and natural rubber (0.393). The rubber volume fraction (V_r) was calculated using Equation (3).

$$V_r = \frac{(m_1/\rho_1)}{(m_1/\rho_1) + (m_2/\rho_2)} \quad (3)$$

The weight of swollen rubber, m_2, was then measured, followed by the measurement of the dry rubber weight, m_1, where ρ_1 was the density of the dry polymer sample and ρ_2 was the density of the solvent.

Gamma Irradiation

Gamma irradiation of the samples was carried out using a Cobalt-60 gamma chamber, installed at the National Research and Innovation Agency of Indonesia (BRIN). The Gd_2O_3–SiO_2 natural rubber vulcanizate composites were irradiated in air at room temperature. The irradiation was performed at a total dose of 100 kGy with a gamma radiation rate of 2.1 kGy/h.

RESULT AND DISCUSSION

FTIR analysis

Filler–rubber bonding generally increases the effective crosslink density, a change that is often reflected in FTIR spectra. Figure 1 shows the typical absorption bands observed in natural rubber-based vulcanizate. Strong bands between 3000–2800 cm^{-1} correspond to C–H stretching vibrations, while the peak at 1470–1410 cm^{-1} is characteristic of the $–CH_2$ group [11]. The band at 1020–1080 cm^{-1} arises from C–O stretching vibrations, and the region around 720–570 cm^{-1} indicates a C–S vibrations [2]. Figure 2 also shows the appearance of an O-H absorption band in the range of 3500-3000 cm^{-1} and a C=C absorption peak at 1635 cm^{-1} after gamma irradiation. Quantitative analysis indicated that the intensity of the C=C peak at 1635 cm^{-1} increased by approximately 55.46%. The growth of –OH and C=C peaks in Figure 2 after irradiation are consistent with a scenario in which gamma-induced radicals react within a constrained matrix to produce oxidized groups (–OH) and additional crosslinks.

Gamma irradiation induces free radicals in the polymer chains via bond scission. In the first step, high-energy photons break covalent bonds (C–C, C–H) along the polyisoprene backbone, producing chain radicals (R•). Two radicals on different chains can recombine to form a new covalent link (R–R), effectively creating an intermolecular crosslink [19]. Alternatively, a polymer radical may abstract hydrogen from another chain (propagating a radical) or react with oxygen to form peroxide/alkoxyl radicals, eventually yielding –OH groups. This is why we observe new –OH absorbance (3500–3000 cm^{-1}) and a C=C band at 1635 cm^{-1} after irradiation: they signal that radicals have partly oxidized and partly reformed double bonds. In sum, the schematic sequence is Figure 3.

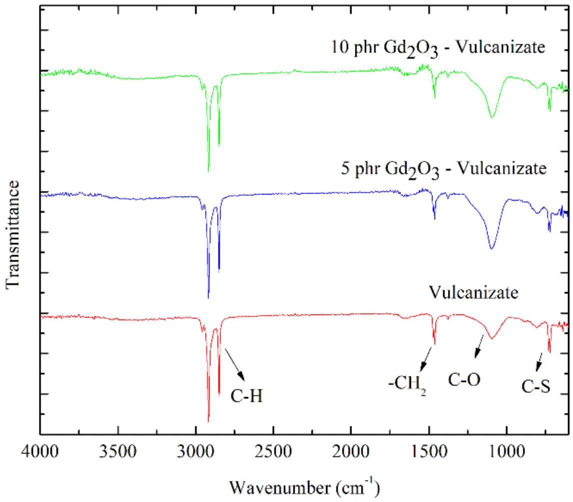

Figure 1. FTIR spectra of Gd_2O_3-SiO_2-natural rubber vulcanizate composites before gamma irradiation.

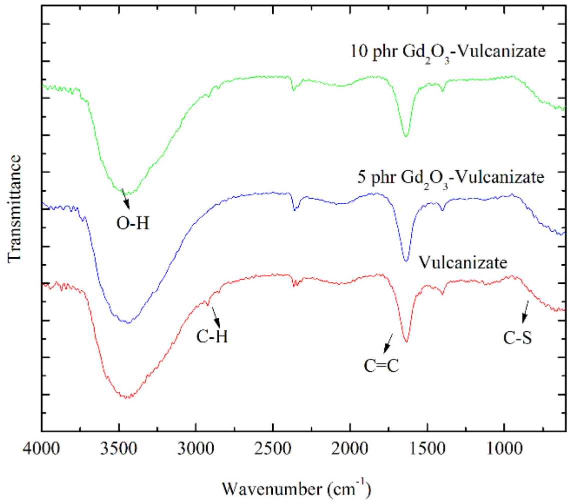

Figure 2. FTIR spectra of Gd_2O_3-SiO_2-natural rubber vulcanizate composites after gamma irradiation 100 kGy.

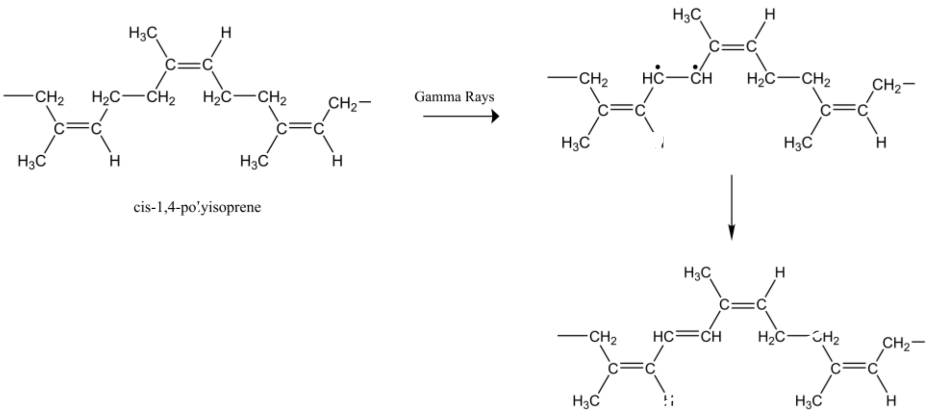

Figure 3. Schematic Representation of the Free Radical Reaction Mechanism.

Swelling and crosslink density

Table 1 shows the swelling values and crosslinking density of Gd_2O_3-SiO_2-natural rubber vulcanizate composites at variation 0, 5, 10 phr Gd_2O_3. In general, after the addition of Gd_2O_3, the swelling value decreases while the crosslink density increases. This shows the influence of Gd_2O_3 on the structure of the vulcanizate composite which becomes stiffer. In addition, Table 1 also shows a decrease in swelling values from the range of 89-97% to 84%, and an increase in crosslink density from the range of 690-800 mol/m^3 to 800-900 mol/m^3 after the gamma irradiation process. The increase in crosslink density indicates that gamma irradiation leads to more effective crosslink formation in the rubber matrix by generating free radicals, which subsequently recombine to form a denser polymer structure. This observation is consistent with previous studies, which have reported that gamma irradiation significantly increases the crosslink density in natural rubber/styrene-butadiene rubber blends [20]. Similarly, in a study on 50/50 natural rubber/styrene-butadiene rubber, gamma irradiation enhanced the crosslink density, resulting in improved mechanical strength and thermal stability of the vulcanizates [21].

In addition, the presence of SiO_2 plays an important role. SiO_2 fillers are known to interact with rubber both physically and chemically. Well-dispersed silica increases the number of effective crosslinking sites and the composite modulus. Previous study have reported that silane treatment combined with urea on silica markedly enhanced crosslink density and mechanical strength in polyisoprene, as confirmed by FTIR and cure analysis [22]. Another study showed that combining silica with graphene oxide substantially increased the cure rate and NR crosslink density via improved filler–rubber interactions [23]. By contrast, Gd_2O_3, as a heavy metal oxide, has few surface chemical groups available to bond chemically with rubber, so its influence is principally physical.Thus, although Gd_2O_3 does not directly form chemical crosslinks, it can indirectly affect crosslink formation by constraining the polymer chains and increasing the bound-rubber fraction.

Tabel 1. Result of swelling and crosslink density test Gd_2O_3-SiO_2-natural rubber vulcanizate composites before and after gamma irradiation.

Gd_2O_3 Content (phr)	*Swelling* (%)		Density (g/cm^3)		Crosslink density (mol/m^3)	
	Before	After	Before	After	Before	After
0	97.00±4.76	84.33±3.73	1.37±0.02	1.59±0.06	816.02±66.12	829.71±92.20
5	91.64±5.09	84.05±4.84	1.41±0.06	1.51±0.08	848.01±19.63	889.06±163.43
10	89.26±7.23	84.02±6.32	1.65±0.06	1.51±0.18	691.51±136.19	884.10±79.05

CONCLUSION

Natural rubber vulcanizate composites reinforced with SiO_2 and incorporated with Gd_2O_3 at concentrations 0, 5, and 10 phr were successfully fabricated. Based on the FTIR analysis, the appearance of O-H and C=C absorption bands indicated changes in the chemical structure caused by gamma irradiation. The results of the swelling and crosslink density tests showed an increase in crosslink density and a decrease in swelling values. These finding demonstrate that gamma irradiation plays an important role in strengthening the rubber vulcanizate structure through the formation of stable free radicals. However, this study was limited to FTIR, swelling, and crosslink density analyses, which provided only preliminary insights into the material's chemical and physical changes. Further research involving mechanical, thermal, and morphological characterizations is required to gain a more comprehensive understanding of the effects of gamma irradiation on the overall performance of the vulcanizate composites.

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AUTHOR CONTRIBUTION

Dira Amanda: Investigation, Formal analysis, Visualization, Writing – original draft; Tetty Kemala: Conceptualization, Formal analysis, Validation, Supervision, Writing – review & editing; Jaka Rachmadetin: Formal analysis, Supervision, Writing – original draft, Writing – review & editing, Funding acquisition; Sulistioso Giat Sukaryo: Resources, Conceptualization; Adi Cifriadi: Resources, Methodology; Mohammad Khotib: Supervision, Supervision Writing – review & editing; Kuat Heriyanto: Project administration, Visualization; Achmad Ramadhani: Investigation, Methodology

DECLARATION

Conflict of Interest: The authors have no competing interests to declare.

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