Optimizing Natural Rubber Blends for Examination Gloves: Vacuum Radiation for Mechanical Strength and Solvent Barrier

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Abstract

Natural rubber (NR) is emblematic of sustainability compared to synthetic rubber. However, the tradition of adding sulfur as a vulcanization ingredient results in the release of toxic substances and the potential for health issues. In this study, a feasible strategy was proposed to replace sulfur and discover a safe bulk modification process for NR films. The results have shown that the NR particle size was disintegrated to below 10 nm by gamma irradiation. High tension strength up to 24.45 MPa was observed in the vulcanized NR blend film, which could be elongated up to 800% strain after exposure to an optimum dose of 14 kGy. In comparison to commercial NR latex and nitrile gloves, the vulcanized NR/SIS films exhibited better chemical resistance ability against hexane, methanol, toluene, and acetone, as revealed by the permeation test. The appearance of amorphous regions and highly oriented NR crystallites was observed through transmission electron microscopy. Findings from this study propose the vacuum radiation strategy that can replace conventional vulcanization methods, resulting in NR films with high mechanical and barrier performance. Furthermore, the emission of toxic substances is reduced by this green process, making it practically useful for potential chemical-resistant examination glove applications.

Keywords: Natural rubber blend; Vulcanization; Radiation; Mechanical strength; Solvent barrier; Permeability

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1. Introduction

Natural rubber (NR) has been the subject of growing interest because of its relatively higher elasticity, greater sustainability and biodegradability compared to synthetic rubber. As NR latex examination glove market continues to rise, the making of glove exhibiting superior mechanical properties and excellent barrier properties are sought. According to the international standard, ASTM D3578-19, the produced gloves must meet the minimum requirement of tensile strength of 18 MPa, Young's modulus of less than 5 MPa, and elongation at break of 500%. [1] To this end, gloves with advanced mechanical properties have been produced via the sulfur vulcanization method and have been extensively studied. For instance, Roslim and coworkers reported sulfur loading of 1.50 phr increased the tensile modulus of NR. [2] Yamano et al. demonstrated the tensile strength of NR increased from 20 MPa to 30 MPa at vulcanization temperature of 130°C due to increased crystallinity of NR. [3] Previous study revealed that sulfur-cured thermoplastics vulcanizates had the highest tensile strength, elongation at break, storage modulus, and rubber elasticity due to the presence of sulfidic linkages.[4] Another study has revealed that sulfur-vulcanized NR composite with a 30wt% loading exhibited the lowest salt solution and water absorption, measuring less than 10%. [5] In a recent study, Supramaniam and coworkers fabricated an innovative self-healing glove using epoxidized natural rubber, demonstrating its chemical resistance comparable to that of nitrile and NR latex gloves.[6] Although the sulfur-vulcanized NR gloves have shown good mechanical performance, the addition of sulfur could increase NR degradation time in the natural environment and decrease microbial activity due to the formation of strong sulfide crosslinks in the rubber chains.[7] Additionally, the emission of gaseous sulfur compounds leads to increased carbon emissions into the environment and causes inflammation of the respiratory system, contributing to environmental and health problems.[8]

The alternative route to sulfur vulcanization by exposing NR to gamma irradiation was widely studied to modify the structure of NR by polymerization, grafting, and crosslinking processes.[9] Previous studies have highlighted the potential of low gamma irradiation dose as an energy-saving approach to enhance the mechanical properties of NR latex. For instance, a 6 kGy gamma irradiation dose has been demonstrated to enhance the tensile strength of NR latex films, achieving up to 27 MPa with a 94% crosslink density.[10] Additionally, a higher dose of 12 kGy resulted in an increased modulus for pure NR latex.[11] Aside from the irradiation dose, the presence of oxygen during irradiation also plays a crucial role in regulating the crosslinking rate. In the presence of oxygen, its combination with carbon radicals can form peroxide radicals, hence causing the oxidative degradation of NR.[12] This reduces the thermoxidative stability of the NR and hence, NR degrades more quickly. A previous study has reported that an oxygen environment decreases the creep elongation in an irradiated elastomer after 3 years of exposure to air compared to a non-oxidized sample under the same conditions.[13] Meanwhile, a sample packed in vacuum condition before irradiation showed low antioxidant activity.[14] A recent study revealed the pre-irradiation of NR latex films in air degraded the mechanical strength and elongation at break of NR samples due to the formation of carbonyl, aliphatic esters, ketones, and carboxylic acids.[15] Thus, if the sample condition during irradiation can be controlled, it could potentially prevent oxidative degradation and therefore, enhance the mechanical properties of the irradiated material.

This research aimed to alter blends of NR and poly(styrene-isoprene-styrene) (SIS) block copolymer using low-dose gamma irradiation to widen its functionality for chemical-resistant examination glove application. The SIS block polymers were chosen because SIS are attractive polymers that can self-assemble to form nanoscale morphologies such as gyroids, lamellae, or micelles [16] making it suitable for the development of lightweight gloves. This blend is produced via a solution blending method modified from our previous study, [17] which leads to an easier and energy-saving fabrication process compared to conventional melt mixing. Differing from previous reports, we effectively vulcanized NR/SIS films in vacuum condition as the green process by removing oxygen before irradiation to increase crosslinking probability and produce a rubber network mainly constructed by hydrogen bonding and C-C crosslink at room temperature. Establishing the potential of NR/SIS blend films as highly chemical-resistant examination gloves were emphasized.

2. Methods

2.1. Materials

Natural rubber (NR) latex with 62% dry rubber content was provided by the Raymintex Plant, Malaysian Nuclear Agency. The poly(styrene-isoprene-styrene) (SIS) triblock copolymer with multiarmed configuration and average degree of polymerization of 19,000 was acquired from Sigma Aldrich. The viscosity was 14.5 poise and the density was 0.92 g/mL. Toluene, hexanediol diacrylate, potassium laureate, calcium chloride 2-hydrate, and distilled water were purchased from R&M Chemicals. Commercial gloves made of disposable NR latex and synthetic nitrile butadiene rubber with a palm thickness of 0.48 mm were used for comparison in this study.

2.2. Fabrication of irradiated NR/SIS blend films

The NR/SIS blends were fabricated using the solution blending method. In brief, the NR latex (200 g) was first coagulated with calcium chloride (36 g), washed with distilled water, and dried in an oven (70°C) for 24 h to remove excess moisture. The dried NR with a total weight of 100 g was then cut, added in toluene (400 ml), and stirred for 30 minutes at 100°C. After NR was dissolved in toluene, the SIS, hexanediol diacrylate as sensitizer, potassium laureate as stabilizer, and distilled water were added in sequence in 30, 3.5, 0.06 and 3.5 parts per hundred rubbers (phr), respectively. The mixture was stirred continuously for three hours at 100°C and 300 rpm speed using a magnetic stirrer (Favorit). The NR/SIS blend solution was put on a clean glass plate and casted carefully using a film cast knife (BYK Gardner 2327) to form a NR/SIS film with an approximate dimension of 210 mm x 148.5 mm x 0.5 mm. The film was dried at room temperature for 24 h to remove solvents. After the drying process, the thickness of NR/SIS blend films was measured with a digital vernier caliper (Mitutoyo). The dried NR/SIS blend films of 0.48 mm in thickness comply with the specification of palm thickness for NR examination gloves according to an international standard of EN ISO 374-1:2016.[6] The films were then packed in a vacuum plastic bag and gases were sucked out using a single stage vacuum pump (Value, VE115N) with the pressure of 15×10^{-5} Pa (high vacuum) and time of 120 seconds. For ambient condition, the samples were packed in polyethylene bags. The blend films were then irradiated at 4, 8, 14, and 16 kGy irradiation doses using a cobalt-60 gamma cell (MDS Nordion, GC 220 E) at Universiti Kebangsaan Malaysia. The energy of Co^{60} is 4 MeV with a dose rate of 1.0 kGy/hour. The irradiation was performed in tightly closed reaction tubes at room temperature and under normal condition.

2.3. Materials characterizations

The average particle size was determined with a Zeta Sizer Nano ZS (Malvern Instrument) based on the dynamic light scattering theory. The angle of detection was varied from 30 to 140 in one step and size measurement ranged from 0.3 nm to 10 µm was used.

Using an MCR 300 rheometer (Anton Paar), blends' rheology was evaluated. A coneplate module with a 25 mm diameter and a 1° cone angle was employed. A Peltier Plate temperature controller (Model Viscotherm VT2) held the temperature measurement constant at 25.01°C. The tests for strain and frequency sweep were run.

An ISO 1817:2005 (E)-compliant swelling measurement was used to ascertain the gel content. This international standard describes methods of evaluating the resistance of vulcanized rubbers to the action of liquids by measurement of properties of the rubbers before and after immersion in test liquids. As soon as samples were weighed (W_1), they were submerged in 30 mL of toluene for 72 hours while being kept in the dark to reach equilibrium swelling. The samples were weighed (W_2) once more after swelling and then dried in the air for six days before being baked at 60°C. The dried sample's final weight, denoted as W_3, was used. The gel content was calculated using Equation (1):

$$\text{Gel content} = \frac{W_3}{W_1} \times 100 \qquad (1)$$

The crosslink density (υ) was calculated using Flory-Rehner relationship, according to Equation (2):

$$v = -\frac{In\,(1-V_R) + V_R + \mu V_R^2}{V_O\left(V_R^{\frac{1}{3}} - \frac{V_R}{2}\right)} \qquad (2)$$

where V_o is the molar volume of toluene (106.20 cm^3/mol), μ is the Flory−Huggins rubber-toluene interaction parameter (0.393), and V_R is the volume fraction of rubber in the solvent during equilibrium swelling according to Equation (3):

$$V_R = \frac{1}{1 + \left[\left(\frac{W_2 - W_3}{W_3} \times \rho_T/\rho_S\right)\right]} \qquad (3)$$

where W_2 is weight after solvent extraction, W_3 is weight after solvent evaporation, ρ_T is the sample density and ρ_S is the toluene density (0.865 g/cm^3).

According to ASTM D882 standard, the mechanical characteristics of blend films were measured using a universal testing machine (M350-10CT) (thickness less than 1 mm, width 40 mm, gauge length 50 mm). Using a pneumatic cutter, the NR/SIS films were formed into dumbells, which were then secured onto the tensile head with a 5 kN load cell. A tensile force was then applied to two grips that were 250 mm apart and the sample was positioned between them. The crosshead speed was set at 500 mm/min. Five specimens on average were used to record the mechanical characteristics data.

Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) were performed using a DTG-60H, simultaneous DSTG-TG apparatus (Shimadzu). The samples were weighed (6-10 mg) and placed in aluminium pan. The heating temperature was 30 to 600 °C at a heating rate of 10° C/min under inert N_2 flow (30 mL/min).

The ^{13}C-Magnetic Resonance (^{13}C-NMR) spectroscopy was measured with a Bruker 500 MHz NMR spectrometer (Billerica, USA) oscillated at 400.17 MHz. The spinning rate of 18±5 Hz with 1000 scans was set to acquire spectra. Samples were prepared in sample tube containing deteurated chloroform ($CDCl_3$) using a vortex mixer.

The transmission electron microscopy (TEM) analysis was performed using an FEI Talos L120C, fitted with a 120 kV emission gun. A 2 uL sample solution was dropped onto a carbon-coated copper grid without any staining reagent. The TEM grids were then dried overnight before imaging. The selected area electron diffraction (SAED) pattern was taken. The average diameter of the NR/SIS particles was measured using ImageJ software.

The X-ray diffraction (XRD) analysis was measured in a Bruker D8-Advance (Germany) using a monochromatic Cu Kα source ($\lambda = 0.1548$ nm) with an X-ray generator of 20 kV of voltage and 200 mA of current.

The functional groups of the blends was recorded using a Cary 630 Fourier Transform Infra-Red (FTIR) spectrometer (Agilent, USA) in transmission mode. Spectra were acquired in the region of 600-4000 cm^{-1} with a resolution of 4 cm^{-1}.

Using a field emission scanning electron microscope (FESEM) device (Zeiss, Supra 55VP) that ran at 24 kV of voltage and 10 A of current, the cross-section and surface morphologies of samples were examined. To avoid static charge, the samples were gold-sputtered at a 5 nm thickness.

A dead-end permeation setup was used to measure permeation at 27°C. Commercial gloves and casted NR/SIS films were cut into circles with a surface area of 0.0159 m^2 and placed on the Buchner funnel's porous plate. The samples were covered with two O-rings, and the vacuum system's pressure was set to 90 kPa with a total permeate volume of 30 mL. The film was removed after the permeation measurement and allowed to dry for 30 minutes before being stored. The permeability, P (L/hm^{2}bar) for various organic solvents through the samples was calculated using the following Equation (4):

$$P = \frac{w}{s \times t \times p} \qquad (4)$$

where w is total permeate volume (L), s is membrane area (m^2), t is filtration time (h) and p is pressure.

All quantum chemical calculations were carried out using Gaussian16 software. The ground state of NR and SIS structures were geometry optimized using density functional theory (DFT) with a hybrid B3LYP functional and 6-31 + G* basis set calculation. All the molecular structures were modelled using Gaussview version 5 software.

3. Results and Discussion

a) Strategy to control particle size and rheology properties of NR/SIS blends

The aim of our study was to form a NR/SIS rubber network by preparing the samples in vacuum condition and controlling the gamma irradiation dose parameter. The effects of particle size on rheology property of NR/SIS blends were investigated and shown in Figure 1. These properties are important to examine the flow behaviour of fabricated NR/SIS blend solutions for the glove manufacturing process. The unirradiated NR/SIS blend solution (control sample) had a binomial size distribution, with 40.71% of the particles having a size of between 4-6 nm and 59.10% having a diameter between 0.4 and 1 nm, as shown in Figure 1(a). This sample's particle size was higher than that of blends that had undergone irradiation. A high dose of 14 kGy radiation, meanwhile, caused the particle to fragment into smaller sizes, with the majority (54.03%) of the particles having a diameter of roughly 10 nm or less and the remaining 45.96% having a diameter of 0.68 to 64 nm. It was assumed that the change in blend particle size from micrometer to nanometer after 14 kGy was caused by the radiation energy being completely transferred to the exposed surface under vacuum conditions. Additionally, physical examination revealed that, as shown in the inset of Figure 1, all irradiated NR/SIS blend solutions were pale yellow and did not significantly differ from the color of unirradiated blend. This finding suggests that the samples did not degrade during the irradiation procedure because the vacuum environment prevented oxidation.

Figure 1(b) shows the viscosity of unirradiated and irradiated blends. In this case, the 14 kGy dose yielded the highest viscosity (220,910 mPa.s) in the NR/SIS blend compared to other doses (4, 8, 12 kGy) at the shear rate of 0.1/s, as depicted in the inset of Figure 1(b). When the particle size decreases, the degree of interaction between the particles increases, which results in a more viscous system.[18] Therefore, the highest viscosity of the 14 kGy-irradiated blend might be achieved by increased crosslinking structures between NR and SIS owing to smaller particle size brought by the irradiation. In another work, it was assumed the non-rubber components have promoted the formation of vulcanized intermediates.[19] Furthermore, the storage modulus, G’ was increased when strain increased (Figure 1(c)). The linear viscoelastic range of NR below 0.01% strain indicates that the NR/SIS chains were stable when a small deformation was applied. The critical G’ was the highest in the 14 kGy-irradiated blend (154,128 Pa) compared to the control sample (3.678 Pa). Similar results have also been obtained in previous studies.[20,21] Moreover, an increasing trend in G’ with increasing angular frequency was observed (Figure 1(d)), with the highest G’ (13,750 Pa) in 14 kGy-irradiated blend at 0.1 rads^{-1}. However, all blends became less viscous as the shear rate increased, implying a shear thinning behavior. This occurrence was ascribed to the destruction of the network, wherein the endpoints of chains weaken, and disengage from entanglements under conditions of high shear rates.

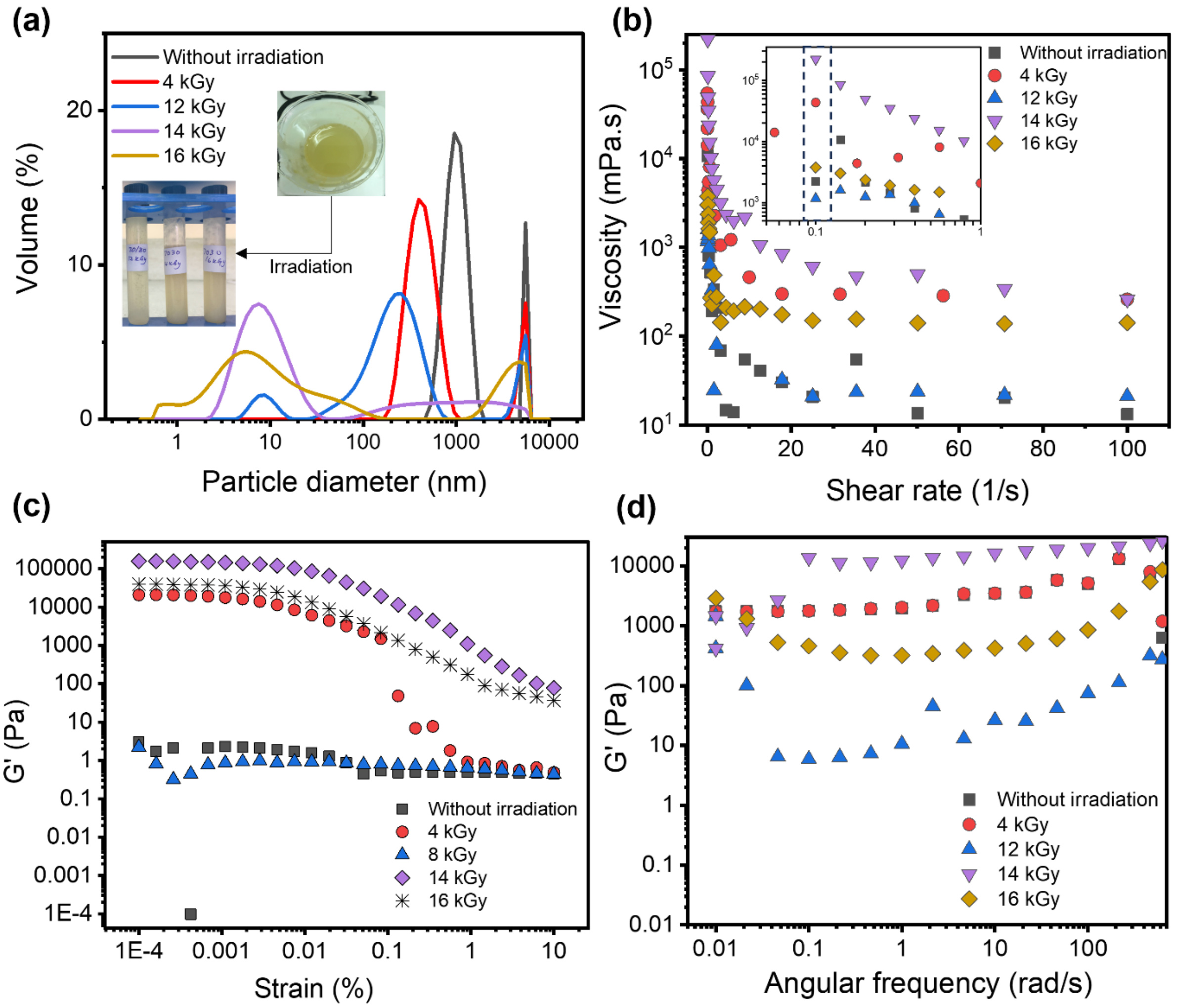

Figure 1 (a) Particle size, (b) viscosity, (c) G’ curves vs strain and (d) G’ curves vs angular frequency for control and vulcanized NR/SIS blends

b) Gel content, crosslink density, thermal and mechanical properties analyses

The swelling test was used to determine the amount of undissolved rubber in a solution and estimate the crosslinking density within the blend system. From Figure 2, the gel content of the irradiated NR/SIS films increased, indicating that they could maintain their shape in toluene without deterioration for three days. The optimum 14 kGy dose produced the maximum gel content, 45.38%, and crosslinking density, 34.9×10^{-5} mol/cm^3, compared to the control film. The resistance to toluene might be due to the increase in crosslinking density and reduced mobility of polymer chains due to the crosslinking.[22]

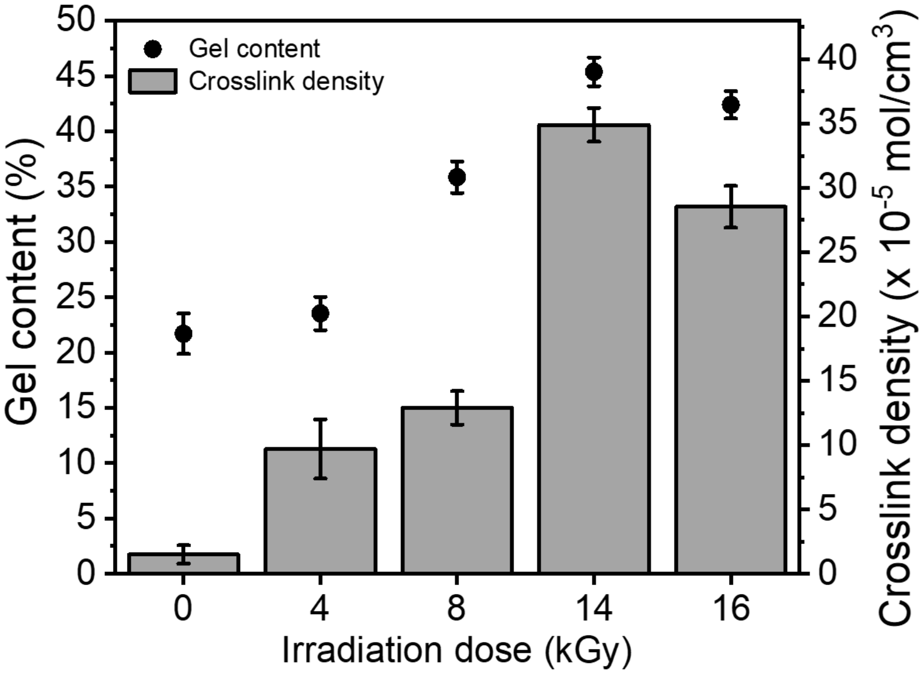

Figure 2 Increasing gel content and crosslink density of vulcanized NR/SIS blend films

In Figure S1, the TGA curves below 300°C exhibit two minor degradation steps attributed to the degradation of the HDAA (100–140°C) and potassium laureate (150–180°C) stabilizers. A significant degradation step occurs at around 300–400°C, with a small shoulder observed at approximately 420°C, associated with isoprene and PS degradation, respectively. For all samples of the blends, the TGA curves indicate that the onset temperature, T_{onset}, of the third degradation peak ranges from 300–350°C. The maximum degradation temperature, T_{max}, in the DTG curve of the 14 kGy-irradiated blend increased slightly from 6°C to 363.24°C and 369.27°C, and about 51.83% of the isoprene units were degraded. The higher T_{max} implies that the 14 kGy dose induced higher thermal stability in the blend due to radiation-induced crosslinking. Similar increases in T_{max} have been found in previous studies.[22,23]

The stress-strain behavior reflects the mechanical performance of NR/SIS blend films. Representative stress-strain curves for the control and irradiated blend films are plotted in Figure 3. The neat NR film had a less steep stress-strain curve indicating its soft feature. A noteworthy scenario was that the optimum dose of 14 kGy under vacuum condition led to a steeper curve with longer strain (Figure 3(a)), with a tensile strength (σ_s) is increased by about 157.91%, 24.45 MPa after irradiated up to 14 kGy as compared to control film, 9.48 MPa, as given in Table 1. In fact, the 14 kGy-vulcanized NR/SIS film in vacuum had a σ_s at least two times higher, 24.45 MPa compared to the 14 kGy-vulcanized film in ambient condition, 8.85 MPa (Figure 3(b)). Furthermore, the Young's modulus (E) of this vulcanized film due to radiation increased from 0.65 MPa to 4.55 MPa. This finding agrees with previous works.[24,25] This observation was augmented with the maximum gel content, 45.38%, and crosslinking density, 34.9×10^{-5} mol/cm^3, in the 14 kGy-vulcanized film. The enhanced ability of the vulcanized films to withstand high tension force proves that the vacuum condition during the irradiation process generates crosslinking.

Remarkably, the σ_s obtained in this work is significantly higher than previous works that produced the σ_s of 12 kGy-irradiated neat NR latex (12.9 MPa),[24] and rubber blend filled with dicumyl peroxide accelerator (1.3 MPa).[26] Moreover, the 14 kGy-vulcanized NR/SIS film passed the mechanical properties required by international standard of ASTM D3725 for examination gloves, as the σ_s of this blend (24.45 MPa) exceeded the minimum σ_s and E requirement of 18 MPa and less than 5 MPa, respectively. As previously found, the nanosized particles (below 10 nm) in this vulcanized NR/SIS blend film might accelerate chemical interaction between gamma ray and nanoparticles. A previous research found that a nano-NR composite have higher flexural modulus compared to a micro-composite because nanosized particles have better ability to shield gamma ray than microsized particles.[27]

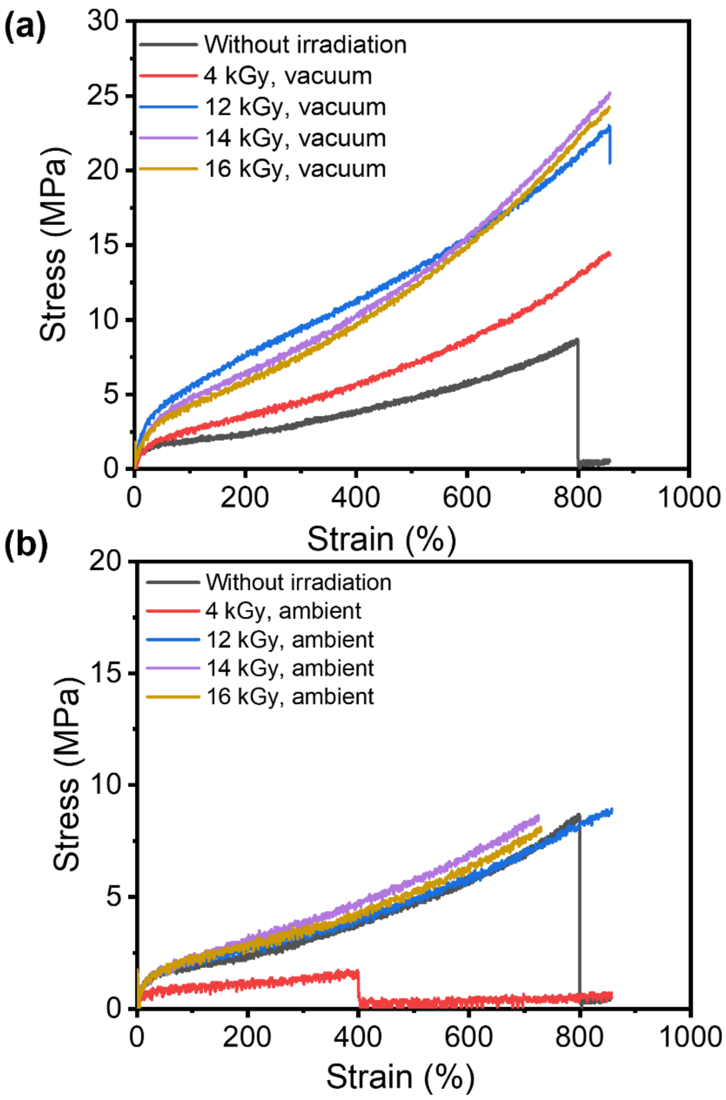

Figure 3 Enhanced mechanical properties of vulcanized NR/SIS films after irradiated at (a) vacuum and (b) ambient conditions

Furthermore, the strain of vulcanized NR/SIS blend films in vacuum condition increased after irradiation with values around 850% irrespective of increasing the dose than control blend film, 800%. This is similar to the work of Rahman and coworkers who suggested an increase in elongation at break of NR latex gloves was due to the higher crosslink density that led to higher strain concentration and more force needed to pull the sample.[28] However, the insignificant change in strain values after the irradiation might likely be due to the presence of proteins in NR, which limit the compactness of the rubber network.[29] Based on these results, the crosslinking process under vacuum could be enhanced by preserving the irradiated blend and preventing oxidative degradation in vulcanized NR/SIS blend films. Ambient oxygen primarily participates in the radical termination process,[30] while oxygen facilitates oxidative degradation through a peroxide radical mechanism.[12,31] Therefore, an oxygen-free environment (vacuum medium) could prevent oxidative degradation and promote crosslinking. This hypothesis is further supported by the disappearance of the -OH peak at 3200–3400 cm^{-1}, as discussed in the FTIR analysis (Figure 5).

Table 1 Mechanical properties of the control and vulcanized NR/SIS blend films

Condition	**Irradiation dose (kGy)**	**Tensile strength (MPa)**	**Young modulus (MPa)**	**Elongation at break (%)**
Control	0	9.47 ±0.25	0.65± 0.06	857.09± 20.33
Vacuum	4	14.4± 0.1	2.31± 0.17	733.01± 10.21
	12	22.25± 0.58	4.55 ±0.15	708.83± 12.33
	14	24.4±5 0.10	4.87± 0.14	671.94± 20.10
	16	23.47± 1.80	4.65± 0.27	642.86± 47.12
Ambient	4	1.65± 0.17	1.15± 0.14	400.01± 0.24
	12	8.56± 0.14	1.71± 0.05	857.16± 0.31
	14	8.85± 0.34	1.93± 0.10	757.10± 0.10
	16	7.96± 0.23	1.97± 0.12	856.56± 19.63

c) Monitoring chemical structure and crystallinity of vulcanized NR/SIS film

The crystallinity investigation of the blends was investigated using TEM and XRD analyses. The TEM was used to see the formation of NR crystals and self-assembly of SIS block copolymer in NR phase. As seen in Figure 4(a), through the solution blending method, the SIS was self-assembled into spherical micelles of various diameters ranging approximately 4.76 – 5.93 nm. Francis and co-workers have reported a similar finding, the PS-*b*-PI$_3$ copolymer presented as nanostructures in epoxy matrix in the 200–500 nm diameter range.[32] Another research study also showcased the creation of nanostructures when surfactants were incorporated.[33] Consequently, employing a liquid medium, such as toluene, in the polymer blend preparation process holds promise for nanostructure formation. Additionally, TEM analysis confirmed the presence of NR crystalline structures in the blend that had been vulcanized at 14 kGy, as illustrated in Figure 4(b). At high magnification (inset of Figure 4(b)), the NR crystal planes showed majority of the *d*-spacing value of 0.23 nm from the (040) plane with several orientations. A previous study also found the (040) plane of NR had a similar d-spacing of 0.23 nm.[34] The formation of NR crystalline planes could be due to the promising generation of crosslinking where the formation process is controlled by the irradiation dose and vacuum condition. More importantly, the vacuum condition helps the crosslinking process by the method of radical preservation. The crystalline nature of NR and SIS block copolymer was investigated by selected area electron diffraction (SAED) as shown in Figure 4(c) which identified the orthorhombic structure of NR from the (040) plane. Furthermore, the presence of the halo pattern might be associated with amorphous SIS nano micelles. This observation indicates that the vacuum condition and 14 kGy irradiation dose have formed a new polycrystalline material. Therefore, it maximized the σ_s and E of vulcanized NR/SIS films with values of 24.45 MPa and 4.55 MPa, respectively.

To validate the crystalline nature of NR in a bulk quantity of the blend films, X-ray diffraction (XRD) was used. As given in Figure 4(d), the XRD spectrum of control blend film showed an amorphous peak with a broad feature at $2\theta = 18.28°$, corresponding to NR peak and similar to the neat NR spectrum from our previous study.[22] The 14 kGy-vulcanized film at ambient condition also featured similar amorphous NR peak. Furthermore, it is noteworthy the vacuum condition induces crystallinity in the 14 kGy-vulcanized blend with the presence of NR sharp peak at a similar $2\theta = 18.28°$. Upon analysis, the sharp NR peak at $2\theta = 18.28°$ in this blend film matched the NR crystal with a d-spacing of 0.23 nm corresponding to the (040) NR plane of an orthorhombic lattice from TEM analysis, as discussed previously (Figure 4(b)). It is also interesting to mention that a high intensity wide-angle X-ray diffraction peak at 18.28° corresponding to aged NR was reported by Musto and coworkers.[35] Meanwhile, the formation of another sharp NR peak at $2\theta = 31.2°$ in the 14 kGy-vulcanized blend at vacuum condition was also found by previous study.[36] Previous study shows the propagating radicals exhibit sufficient reactivity to interact with double bonds during irradiation.[37] Therefore, it is presumed during the exposure of 14 kGy of radiation dose, the vacuum can preserve the irradiated NR/SIS blend films by allowing propagating radicals to sustain longer in vacuum condition, and then increasing free radical activities, especially crosslinking. Therefore, these results from TEM and XRD successfully prove that the vacuum condition during irradiation could improve the crystallinity of NR blend films.

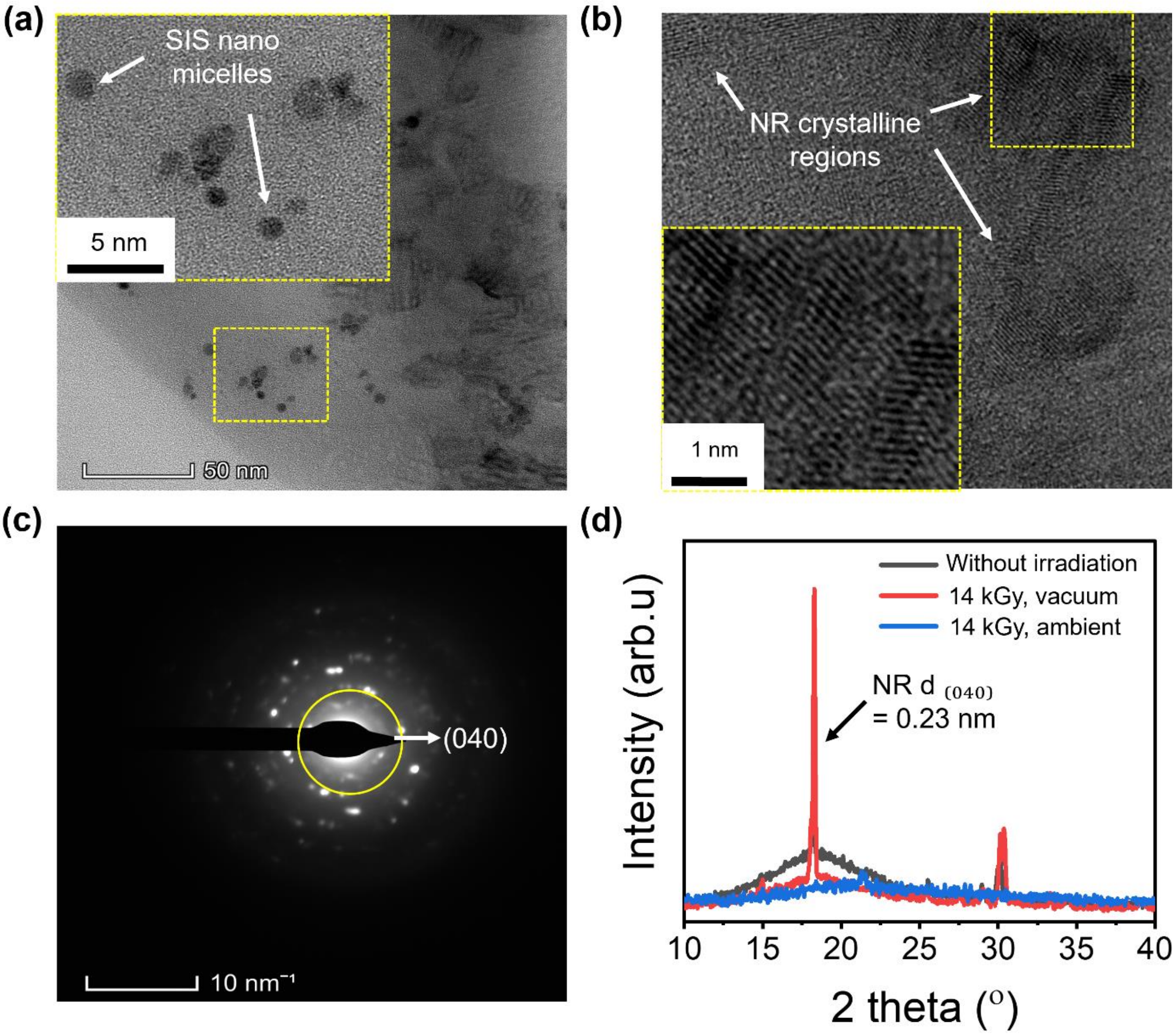

Figure 4 Crystallinity investigation by TEM and XRD. (a) TEM image showing SIS micelles, (b) TEM image showing crystalline regions and the (040) NR crystal plane with the lattice distance 0.23 nm, (c) selected area electron diffraction pattern, and (d) XRD pattern of control and 14 kGy-vulcanized blends at vacuum and ambient conditions

To determine the specific interaction between the rubber components and SIS block components after irradiation, FTIR and ^{13}C-NMR analyses were carried out. The FTIR spectra of the 14 kGy-vulcanized film under vacuum condition (Figure 5) confirmed the presence of C-C crosslinking, indicated by a C-C stretching peak of the isoprene unit at 930 cm^{-1} (marked with a red circle). This peak was not present in the control film. Furthermore, the hydroxyl (-OH) and lipid (vR1(C=O) OR_2) groups, observed at 3200–3400 cm^{-1} and 1722 cm^{-1}, respectively, disappeared in the 14 kGy-vulcanized blend film under vacuum condition. It is confirmed that the removal of oxygen and lipid components during irradiation under vacuum condition has prevented oxidative degradation in the NR/SIS films. Previous study revealed lipid components can cause oxidation and deteriorates the NR.[38] Moreover, the increased peak intensities of the Amide II protein (β N-H+ ν C-N) and C=C-H stretching peaks from NR at 1588 and 836 cm^{-1}, respectively, in the 14 kGy-vulcanized film at vacuum condition implied that more H-bonds from non-rubber components has formed in the sample. Therefore, a synergistic effect of H-bond interactions and crosslinking in NR chains might form a polymer network and improve the rheology, mechanical, and thermal properties of the 14 kGy-vulcanized blend film. A similar synergistic effect between non-rubber and rubber components has been found previously. [29]

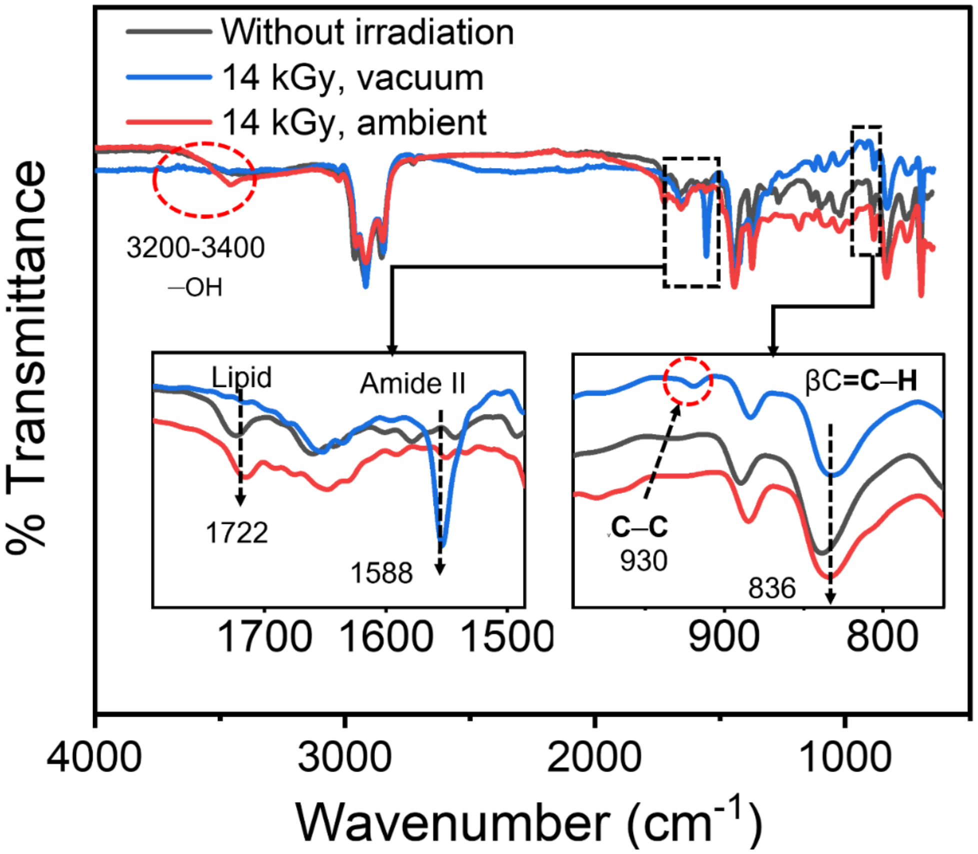

Figure 5 FTIR spectra showing increased hydrogen bond interactions from amide II proteins at 1588 cm^{-1} and new C-C stretching peak at 930 cm^{-1} in 14 kGy-vulcanized film

The ^{13}C-NMR spectra were recorded to analyze the chemical structure based on carbon groups of the neat NR and NR/SIS blends. As shown in Figure 6, the carbon signals detected at δ = 32.23, 135.16, 125.03, 26.38, and 23.4 ppm corresponded to C1, C2, C3, C4 and C5 of *cis*-1,4-PI. All signals were similar as reported in the previous study.[7] The appearance of major peaks at δ = 135 and 129 ppm belonging C2 and C3 of benzene rings from PS confirmed that the SIS was successfully grafted onto NR chain. Furthermore, in the expanded spectra range from 30-41 ppm, both control and 14 kGy-vulcanized blend films showed new carbon peaks at δ = 40.26 and 32.53 ppm associated with secondary carbon (C2) of isoprene units and methylene (C8) of the benzene ring.[39] It was noticed that the C2 and C8 peaks were slightly shifted at higher location from 32.16 to 32.52 ppm and from 40.26 to 40.65 ppm, respectively, after the blend was exposed to a 14 kGy irradiation dose. From a mechanistic point of view, here, the gamma-ray penetrated the carbon nuclei and reduced their electron densities. The de-shielding phenomenon has also been found in another study.[9] However, the mechanism of the de-shielding phenomenon requires further investigation.

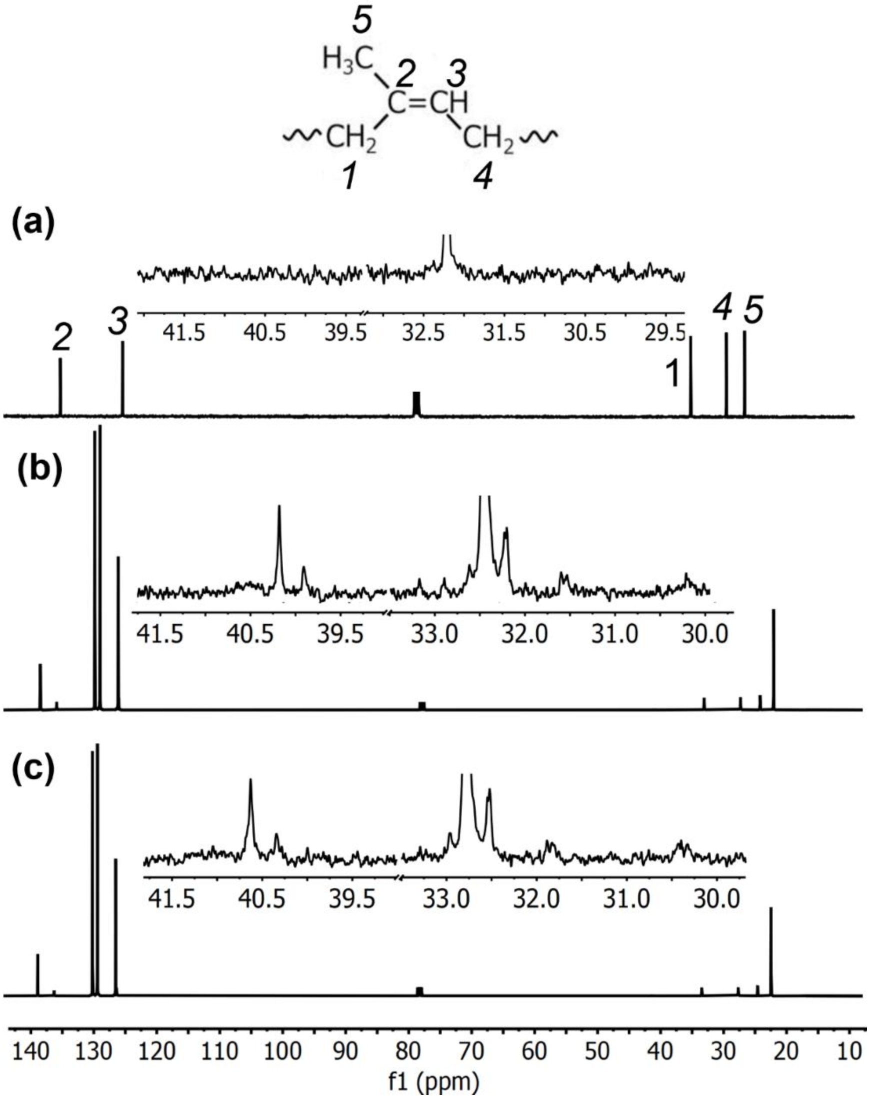

Figure 6 ^{13}C-NMR (a) neat NR (b) control NR/SIS and (c) 14 kGy-vulcanized NR/SIS films

Figure 7 depicts the sequence of events leading to the desired vulcanized rubber network of the blend film. During the preliminary experiment, we found that the direct incorporation of SIS in a toluene solution with NR latex is difficult because of instant coagulation. Therefore, NR latex must be coagulated first to convert into solid NR and the neutralization process of rubber particles with calcium chloride ions must be allowed to rupture its membrane. The toluene may assist the self-assembly of SIS nano micelles onto NR latex chains and forms a homogenous NR/SIS blend solution. Finally, the plausible mechanism of the vulcanization process could therefore be a synergistic effect of H-bond interactions and C-C crosslinking in NR chains that was confirmed by FTIR and C-NMR analyses, enabling the formation of a rubber network within a vulcanized NR/SIS structure.

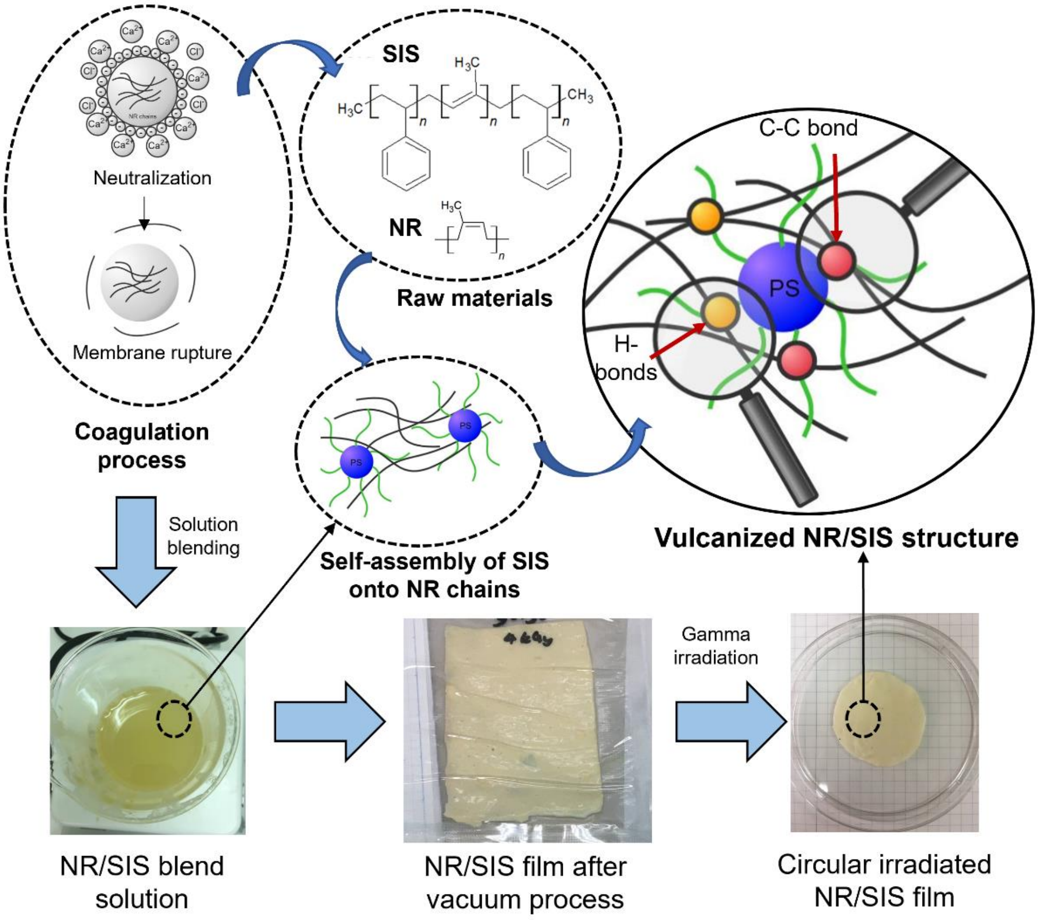

Figure 7 Schematic illustration of process for vulcanization process between SIS nano micelles and NR latex chains for producing high mechanical strength of NR/SIS blend film

d) Solvent permeation and FESEM analyses

Taking advantage of high mechanical performance, the NR/SIS films passed the international standard of ASTM D3725 for examination gloves. The permeation behavior of NR/SIS films was tested to assess the ability of glove material chemical resistance when in contact with solvents. It was found that permeability values and irradiation doses varied considerably, even the average film thickness was similar (0.48 mm). From Figure 8 (a), the control film has the highest permeability values of all solvents ranged from 4500-2500 L/m^2 h^1 bar^1. Meanwhile, all solvent permeability of the vulcanized NR/SIS films decreased after exposure under 4-14 kGy irradiation dose. Within the overall trend, the 14 kGy-vulcanized film demonstrated the lowest permeability to methanol (2000 L m^{-2} h^{-1} bar^{-1}), acetone (2300 L m^{-2} h^{-1} bar^{-1}), hexane (2700 L m^{-2} h^{-1} bar^{-1}), and toluene (3000 L m^{-2} h^{-1} bar^{-1}) compared to other doses of vulcanized films. A comparison of the results obtained from this study with previous works using NR/nitrile rubber membrane, [38] and NR/low density polyethylene membrane, [40] showed that NR/SIS films performed resonably well against most permeants. Furthermore, as shown in Figure 7(b), for methanol, the 14 kGy-vulcanized film exhibited better chemical resistance compared to commercial nitrile (3300 L m^{-2} h^{-1} bar^{-1}) and NR latex powder free gloves (3700 L m^{-2} h^{-1} bar^{-1}). A similar result has been obtained in another recent study that the NR latex gloves with thickness of 0.44 -0.46 mm had higher permeability compared to nitrile gloves. [6] Therefore, the improved solvent permeability of vulcanized films than commercial gloves implied the crosslinking via gamma irradiation has increased the chemical resistance performance of NR/SIS films. This could be explained by the fact that crosslinking reduces the mobility of rubber chains and limits the available free space. Hence, solvents take time to permeate through the films.

Moreover, the difference in solvent permeabilities through 14 kGy-vulcanized films could be explained by considering their polarity as the polarity of solvents also important. The 14 kGy-vulcanized film exhibited higher chemical protection against polar solvents (methanol and acetone) compared to nonpolar (hexane) and aromatic (toluene). The highest penetration of toluene molecules in all vulcanized films is expected since its solubility parameter (8.9 cal cm^{-3})$^{1/2}$ close to natural rubber (8.9 cal cm^{-3})$^{1/2}$. Hexane solvent also have higher permeability through this film compared to methanol. Similar result was also obtained by NR/nitrile rubber membrane produced by Maria and coworkers.[38] As the 14 kGy-vulcanized film had no -OH functional group, as revealed by FTIR analysis (Figure 5), its weaker polarity made hexane permeate this film faster than the higher polarity of methanol with a -OH functional group. Another study also found that nonpolar malathion in pesticides permeates nonpolar NR latex glove more quickly and lower the breakthrough times than polar nitrile glove. [6]

The permeability behavior of fabricated vulcanized NR/SIS films could be correlated to their morphologies. Based on the cross-sectional FESEM image in Figure 8(c), the presence of pores approximately 100 µm in the control film might be the reason for the faster penetration of solvents compared to vulcanized films. Meanwhile, the 14 kGy-vulcanized film exhibited dense and nonporous structure (Figure 8(c)), which limited the free space for the permeation process and therefore, this film showed better chemical resistance compared to other tested films. FESEM image of the surface of 14 kGy-vulcanized film revealed that PS appeared as flakes were randomly dispersed and adhered tightly to NR matrix (Figure 8(d)). The improved adhesion between PS and NR in the 14 kGy-vulcanized film could be a result of increased crosslinking degree and crystallinity based on swelling and TEM analyses.

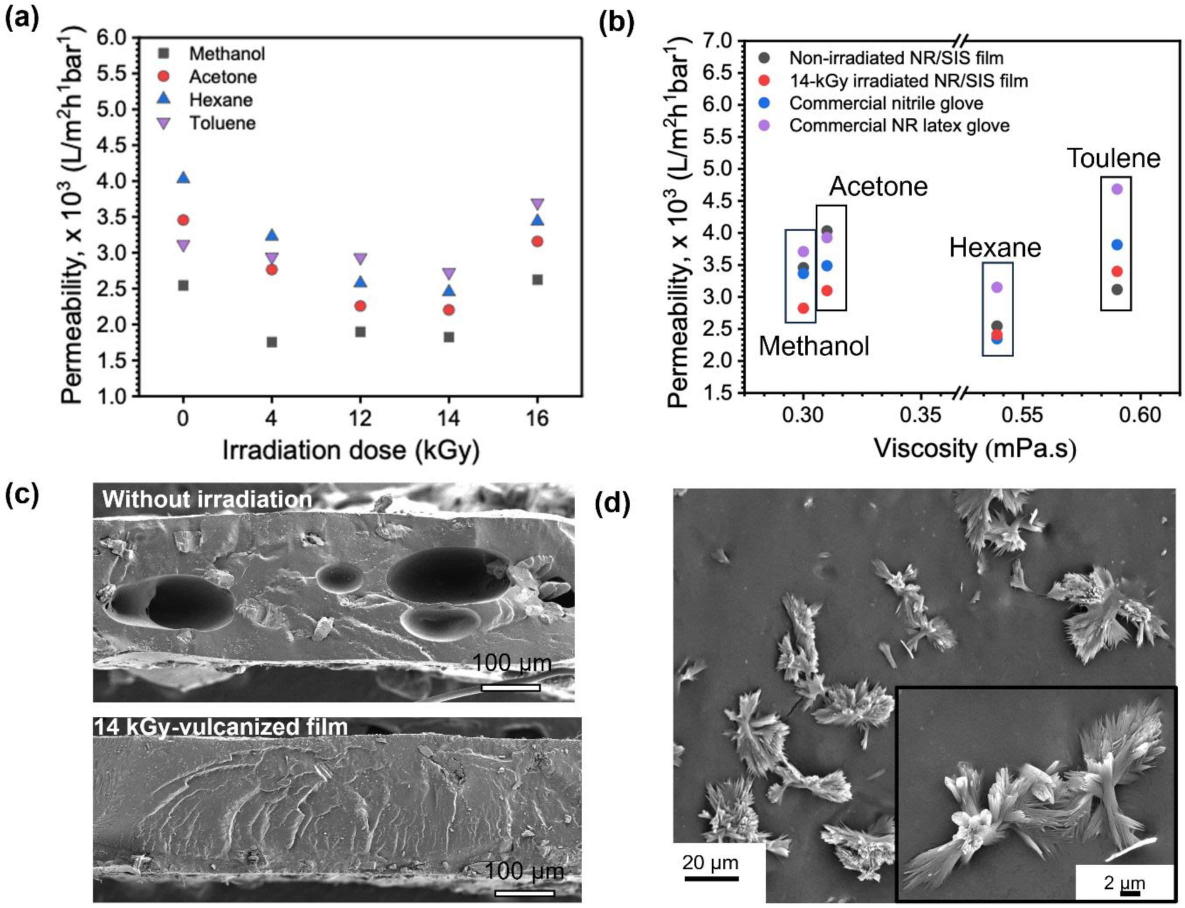

Figure 8 Solvent permeation and FESEM analyses. (a) the 14 kGy-vulcanized film demonstrated the lowest permeability values, (b) a comparison between

vulcanized films with commercial NR latex and nitrile gloves, (c) the cross-sectional FESEM image showing the presence of pores in the control sample and dense structure in the 14 kGy-vulcanized film, and (d) The tight adherence of PS flakes to the NR matrix

e) Molecular modelling of vulcanized NR/SIS molecule

The simulation of crosslinking mechanism between NR and SIS using DFT theory was illustrated in Figure 9. The proposed optimized model for NR/SIS molecule as shown in Figure 9(a) exhibited a total energy of -2534217.068 kcal/mol. After forming the NR/SIS molecule, the bond dissociation energy (BDE) of C-C and C-H groups at different locations was calculated. It was observed that the C-H bond (location 6) of NR/SIS molecule had the lowest BDE value of 90.160 kcalmol^{-1}, as shown in Table 2. This indicates that the endothermic reaction takes place when the electrons and other ions are absorbed during the gamma irradiation. Meanwhile, the BDEs of C-C bonds at locations 1, 3, and 7 were negative values, making their dissociations highly unfavorable as energies were released (exothermic reaction). During the irradiation, the C-H bond was dissociated and NR/SIS macroradical was generated, as shown in Figure 9(b). The macroradical became the potential crosslinking point, allowing the recombination process and a potential new C-C bond was introduced. Therefore, an optimized vulcanized NR/SIS molecule with a new C-C crosslink junction that exhibited the minimum energy of -1281744.784 kcalmol^{-1} was formed, as illustrated in Figure 9(c). The potential energy graph in Figure 9(d) showed the energy transition from reactant (NR/SIS molecule) to transition state (NR/SIS macroradical) and finally formed product (vulcanized NR/SIS molecule). The potential energy difference between the reactant and product was found of 676,062.43 kcalmol^{-1}.

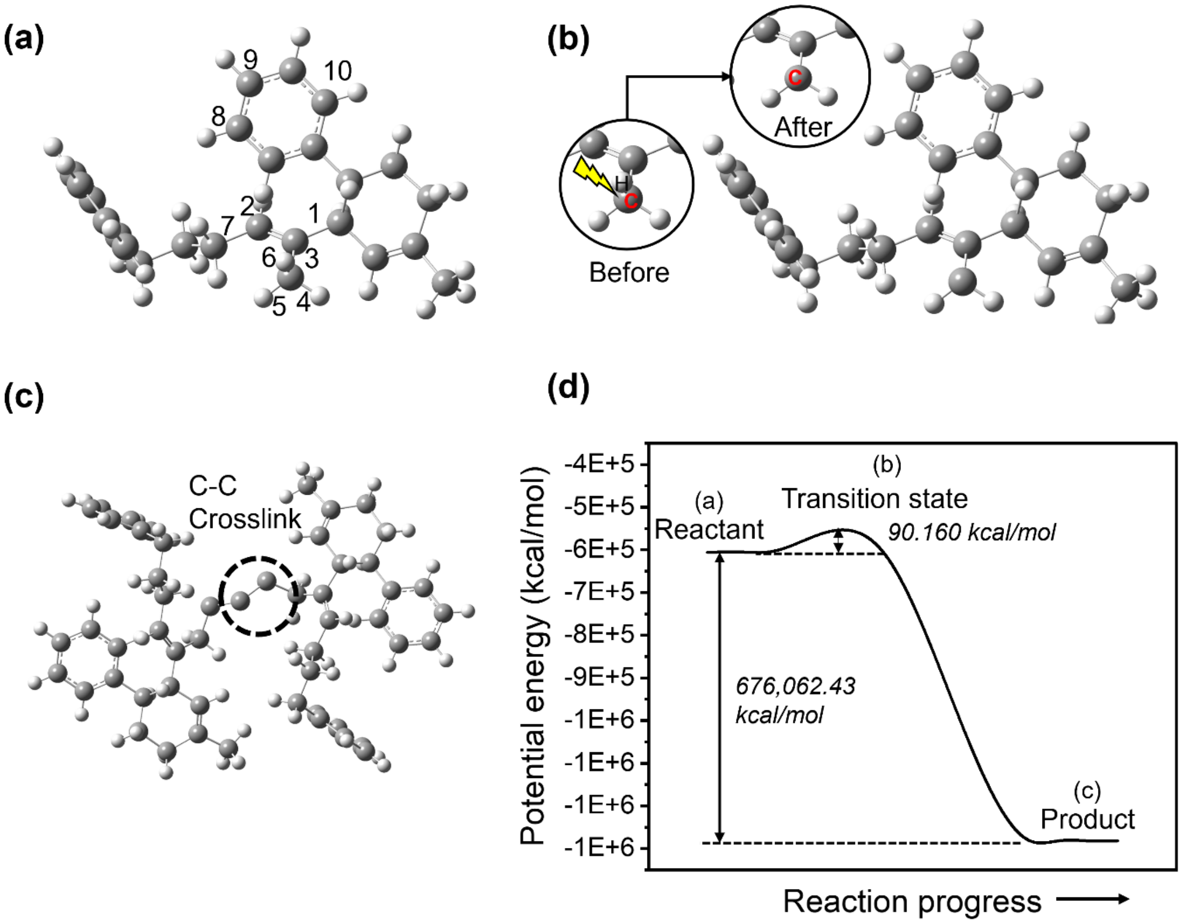

Figure 9 (a) Optimized model for NR/SIS molecule, (b) Possible dissociation location for NR/SIS molecule during irradiation forming macro-NR/SIS radical, (c) Optimized structure of vulcanized NR/SIS molecule with C-C crosslink and (d) Potential energy graph of reactant, transition state and product during vulcanization process

Table 2 The calculated bond dissociation free energies of NR/SIS molecules at different C-H and C-C locations

	Bond location	E (Hartree)	G_{total}^{298K} (Hartree)	G_{corr}^{298K} (Hartree)	BDE, ΔG^{298K} (kcalmol^{-1})
	H radical	-0.49	-0.49	0	-
	CH_3 radical	-39.97	-39.92	0.05	-
	NR radical	-195.47	-195.36	0.10	-
NR/SIS	1 C-C	-734.92	-734.57	0.35	-433.87
	2 C-H	-964.54	-964.11	0.42	106.59
	3 C-C	-925.44	-925.04	0.40	-115.6
	4 C-H	-964.55	-964.12	0.43	103.09
	5 C-H	-964.55	-964.13	0.42	99.73

6 C-H	-964.57	-964.14	0.4	90.16
7 C-C	-617.46	-617.20	0.26	-513.80
8 C-H	-964.54	-964.11	0.43	107.77
9 C-H	-964.54	-964.11	0.43	110.22
10 C-H	-964.54	-964.11	0.43	108.25

4. Conclusions

In conclusion, the NR/SIS blend films successfully underwent modification utilizing the gamma irradiation method. The vulcanized films underwent a thorough evaluation of their performances in terms of crystallinity, chemical structure, physical, mechanical, thermal, and chemical resistance. The findings showed that, in comparison to commercial gloves, the NR/SIS film vulcanized with the ideal dose (14 kGy) exhibited improved chemical resistance against hexane, methanol, and acetone. Additionally, this film outperformed the ASTM D3270 minimum standards for commercial examination gloves in terms of tensile strength (24.5 MPa), Young's modulus (4.45 MPa), and elongation at break (800%). Additionally, the ideal dose caused blend particles to fragment into smaller sizes, smaller than 10 nm, and increasing viscosity (220,910 mPa.s). As shown by the presence of highly orientated NR crystallites with d-spacing of 0.23 nm, TEM examination of the sample revealed considerable changes in crystallinity brought about by gamma irradiation. By eliminating hydroxyl and lipid groups, the vacuum condition successfully shielded the vulcanized NR/SIS films against oxidation, as shown by FTIR measurements. This ground-breaking chemical-resistant polymer is an excellent example of the possibilities of the vulcanization process modification using improvised gamma irradiation. The method makes producing gloves safer because it does not involve dangerous sulfur or accelerators.

Acknowledgements

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Table of Contents

This manuscript introduces the ability of the vacuum radiation strategy as a green process that can replace conventional chemical vulcanization methods, resulting in natural rubber (NR)/poly(isoprene-*b*-styrene-*b*-isoprene) (SIS) films with high mechanical and barrier performance. The proposed method is an interesting, fast reaction time and energy-saving method because the samples packed in vacuum condition before the irradiation have produced vulcanized NR/SIS blend films. Moreover, this approach is greener than the conventional sulfur vulcanization method because it does not contain vulcanization agents.