Determination of radioactivities in gamma vulcanized natural rubber latex (GVNRL) for the assessment of radiological safety

D Toyen1,2 and K Saenboonruang1,3,*

1 Department of Applied Radiation and Isotopes, Faculty of Science, Kasetsart University, Bangkok, Thailand 10900
2 Scientific Equipment and Research Division, Kasetsart University Research and Development Institute (KURDI), Kasetsart University, Bangkok, Thailand 10900
3 Specialized center of Rubber and Polymer Materials for agriculture and industry (RPM), Faculty of Science, Kasetsart University, Bangkok, Thailand 10900

*Corresponding author: kiadtisak.s@ku.th, fscikssa@ku.ac.th

Abstract. Due to great potentials of utilizing products made from gamma vulcanized natural rubber latex (GVNRL) in applications that require less use or less release of hazardous chemicals during rubber vulcanization, the radiological health risks in rubber producers/users caused by radioactivities from natural radioisotopes containing in GVNRL must be thoroughly determined and evaluated. As a result, this work determined the activity concentrations of $^{226}\text{Ra}$, $^{232}\text{Th}$, and $^{40}\text{K}$ in GVNRL samples that were pre-vulcanized with 12-kGy and 24-kGy gamma irradiation using gamma spectroscopy. The results showed that the average radioactivity concentrations (± standard deviation) of $^{226}\text{Ra}$, $^{232}\text{Th}$, and $^{40}\text{K}$ in GVNRL samples were 30.8±1.5 (31.2±2.7) Bq kg$^{-1}$, 89.1±0.6 (89.7±0.4) Bq kg$^{-1}$, and 95.4±1.6 (93.2±2.2) Bq kg$^{-1}$, respectively. These results implied that GVNRL vulcanized with 12-kGy and 24-kGy gamma irradiation had statistically similar radioactivity concentrations and higher gamma doses did not result in increasing radioactivities. Furthermore, when compared these results with the values from non-vulcanized natural rubber latex (NRL), of which the activity concentrations of $^{226}\text{Ra}$, $^{232}\text{Th}$, and $^{40}\text{K}$ were 29.9±1.2 Bq kg$^{-1}$, 95.2±1.1 Bq kg$^{-1}$, and 96.2±1.0 Bq kg$^{-1}$, respectively, it could be concluded that the use of gamma irradiation for rubber vulcanization did not statistically increase or change activity concentrations of the mentioned radioisotopes, thus, it is radiologically safe for related personnel to work or use GVNRL products.

1. Introduction
Gamma vulcanized natural rubber latex (GVNRL) has gained much attention in recent years, mainly due to its preferable characteristics compared with typical sulfur-vulcanized or peroxide-vulcanized natural rubber latex, including being safer during production and use, less hazardous chemicals used and released, more environmental-friendly, and free from accelerator-induced allergies [1-3]. Examples of the uses of GVNRL include surgical latex gloves, stretchable food covers, and pharmaceutical packaging.

Despite being safer in terms of chemical-free products, issues related to the elevation of natural radionuclides such as $^{226}\text{Ra}$, $^{232}\text{Th}$, and $^{40}\text{K}$ in environment and consumer’s products, which also include...
non-vulcanized natural rubber latex and GVNRL, have become serious concerns for the health safety of human and living organisms. The elevation of these radionuclides in the present circumstances could be due to several factors such as the increase in use of fertilizer in agriculture, more residues left from mineral and coal mining, and possible byproducts from gamma irradiation [4-6]. Examples of reports, which showed the activity concentrations of these natural radionuclides in plants and consumer’s products include

- the average activity concentrations of $^{226}$Ra, and $^{40}$K in medicinal plants in Nigeria were $25.0 \pm 3.2$ Bq kg$^{-1}$ and $172 \pm 6$ Bq kg$^{-1}$, respectively, \cite{7} and
- the average activity concentrations of $^{226}$Ra, $^{232}$Th, and $^{40}$K in commercial infant formulas in Malaysia were $1.87\pm0.17$ Bq kg$^{-1}$, $0.89\pm0.13$ Bq kg$^{-1}$, and $213.00\pm2.09$ Bq kg$^{-1}$, respectively \cite{8}.

Although there already is widely available data on activity concentrations of several plants and products, the report on radioactivities in natural rubber latex (NRL) and GVNRL is still unavailable as no official reports have yet been released to the public, posing uncertainty in safety to workers and users who might have direct contact or use these GVNRL products in daily basis. As a result, this work aimed to determine and to compare the activity concentrations of $^{226}$Ra, $^{232}$Th, and $^{40}$K in both non-vulcanized NRL and GVNRL using gamma spectroscopy. The results obtained from the measurement would be thoroughly discussed and reported in this work.

2. Experimental

2.1. Materials and chemicals
High-ammonia (HA) NRL supplied by the Rubber Authority of Thailand (RAOT) was used as the main matrix. Other chemicals that were also used in this work were 99.9% n-butyl acrylate (n-BA) supplied by BASK (Thailand) and 10% potassium hydroxide (KOH) supplied by Gammaco (Thailand) Co., Ltd.

2.2. Preparation of GVNRL mixtures
NRL was continuously stirred using a top stirrer with a rotating speed of 300 rpm for 60 minutes. 0.25 phr of KOH was added to the NRL and stirred for another 10 minutes. Then, 5 phr of n-BA, which acted as a gamma vulcanization accelerator was added to the mixture and the stirring was continued for 40 minutes. The NRL mixture was later transferred to 5-L plastic containers and irradiated with gamma rays using a $^{60}$Co source at the accumulated doses of 12 and 24 kGy, respectively. It should be noted that the gamma irradiation was carried out at the Thailand Institute of Nuclear Technology (Nakhon Nayok, Thailand) and the dose rate of $^{60}$Co source used in this work was 2.1 kGy hour$^{-1}$. After the gamma irradiation finished, the GVNRNL mixtures as well as the non-vulcanized NRL were kept in separate 500-mL Marinelli-type beakers and stored in a freezer at the temperature of $-4^\circ$C for at least 30 days to let $^{226}$Ra, $^{232}$Th, and their progenies reach secular equilibriums prior to gamma spectroscopy.

2.3. Determination of activity concentrations
The activity concentrations of natural radionuclides of interest were determined using a reverse electrode, closed-end, coaxial HPGe gamma spectrometer (Canberra; Model GR2519; Serial number 12946022; 51.7 mm crystal diameter; 58.5 mm length), which have a relative efficiency of 20% and an energy resolution of 1.9 keV (FWHM) at the 1.33 MeV peak of $^{60}$Co. The measurement was carried out inside a 12-cm thick cylindrical lead shield with a movable cover to reduce external and background radiation. The detector was connected to a 16k channel integrated multichannel analyzer (Canberra; Model DSA1000). Spectra of gamma rays emitted from the samples were analyzed using the Genie 2000 (3.2) software, in which the calibration of the energy and efficiency was performed using a mixed gamma standard-type EG-ML developed by Eckert & Ziegler (California, USA). All measurements were performed with a 60,000 s counting time period.

The activity concentrations of $^{226}$Ra, $^{232}$Th, $^{40}$K, and $^{137}$Cs in the samples were calculated using Eq.1 [4]:

\[ \text{Activity Concentration} = \frac{C}{t} \]

where $C$ is the count rate and $t$ is the total counting time.
\[ A = \frac{N_{net}}{m \times t \times P_{\gamma} \times \varepsilon_{\gamma}} \]  

(1)

where \( A \), \( N_{net} \), \( m \), \( t \), \( P_{\gamma} \), and \( \varepsilon_{\gamma} \) are the activity concentration (Bq kg\(^{-1}\)), the net count of gamma rays at the respective energy per second (cps), the mass of the sample (kg), the collection time (s), the probability of the transition of the interested radionuclide at the respective gamma energy, and the efficiency of the gamma spectrometer at the respective gamma energy, respectively. The values of \( \varepsilon_{\gamma} \) for a respective gamma energy are shown in Figure 1.

3. Results and discussion

The activity concentrations of \(^{226}\text{Ra}, ^{232}\text{Th}, \) and \(^{40}\text{K}\) in both non-vulcanized NRL and GVNRL are shown in Table 1 and the contributions of each radionuclide to the total activity concentration are shown in Figure 2.

| Sample (gamma vulcanizing dose) | Activity concentration (Bq kg\(^{-1}\)) | Total activity concentration (Bq kg\(^{-1}\)) |
|---------------------------------|--------------------------------------|-----------------------------------------------|
|                                 | \(^{226}\text{Ra}\) | \(^{232}\text{Th}\) | \(^{40}\text{K}\) |                                  |
| NRL (0 kGy)                    | 29.9±1.1       | 95.2±1.2       | 96.2±1.0       | 221.3±3.3                   |
| GVNRL (12 kGy)                 | 30.8±1.5       | 89.1±0.6       | 95.4±1.6       | 215.3±3.7                   |
| GVNRL (24 kGy)                 | 31.2±2.7       | 89.7±0.4       | 93.2±0.4       | 214.1±3.5                   |
| Average                        | 30.6±1.8       | 91.3±0.7       | 94.9±1.0       | 216.9±3.5                   |

Figure 1. Efficiencies of the gamma spectrometer at respective gamma energies

Figure 2. Contributions of \(^{226}\text{Ra}, ^{232}\text{Th}, \) and \(^{40}\text{K}\) in non-vulcanized NRL and GVNRL to the average total activity concentration.

As shown in Table 1, the activity concentrations of \(^{40}\text{K}\) were higher than the values of \(^{226}\text{Ra}\) and \(^{232}\text{Th}\), ranging from 93.2±0.4 Bq kg\(^{-1}\) to 96.2±1.0 Bq kg\(^{-1}\) with the average value of 94.9±1.0 Bq kg\(^{-1}\). Interestingly, the activity concentrations of \(^{232}\text{Th}\) was only slightly less than the values of \(^{40}\text{K}\), with the average activity concentrations of 91.3±0.7 Bq kg\(^{-1}\), while \(^{226}\text{Ra}\) had the least activity concentrations, with the average value of 30.6±1.8 Bq kg\(^{-1}\). The total activity concentrations contributed from natural radionuclides of interest ranged from 214.1±3.5 Bq kg\(^{-1}\) to 221.3±3.3 Bq kg\(^{-1}\), with the average total...
activity concentration of 216.9±3.5 Bq kg⁻¹, in which ⁴⁰K contributed the highest percentage of activity concentrations to the total value (44%). The contributions from each radionuclide to the total activity concentration are shown in Figure 2.

The higher values of ⁴⁰K were expected as K is an essential element and the most abundant inorganic mineral nutrient in plant cells due to its functions as a stabilizer in metabolism and an osmoticum contributing to cellular hydrostatic pressure, growth, and environmental changes, leading to high accumulation of K in all parts of the plants, which could be transferred and accumulated in NRL [9]. On the other hand, for ²²⁶Ra and ²³²Th, the results showed that they also significantly accumulated in both non-vulcanized NRL and GVNRL, as seen by their contributions of 14% and 42% to the average total activity concentrations, respectively. Their accumulations could be explained by the fact that although ²²⁶Ra and ²³²Th are not essential elements for plants, they are chemically similar to some essential elements such as calcium, resulting in possible transportation of these radionuclides along with other elements. Another interesting result shown in Table 1 was that when the activity concentrations of each radionuclide in non-vulcanized NRL and GVNRL (both 12-kGy and 24-kGy gamma doses) were compared, the values were not statistically different. This behaviour was observed because both 12-kGy and 24-kGy gamma irradiation used during the vulcanization could not activate or produce radioactive isotopes inside the NRL, resulting in relatively unchanged total activity concentrations in all samples. As a result, it could be concluded from the overall results that, in terms of radiological safety, GVNRL was safe for production and usage as they had similar total activity concentrations as the non-vulcanized NRL.

4. Conclusions
In this work, the activity concentrations of ²²⁶Ra, ²³²Th, and ⁴⁰K in non-vulcanized NRL and GVNRL that were gamma irradiated with the accumulated doses of 12 kGy and 24 kGy, respectively, were determined using a gamma spectroscopy. The results showed that ⁴⁰K had the highest activity concentration and contributed the most percentage to the total values. The results also indicated that using gamma irradiation for rubber vulcanization did not statistically changed both individual and total activity concentrations from the natural radionuclides of interest. Hence, based on the overall results, it could be concluded that GVNRL was safe for both production and usage.

5. References
[1] Intharapat P, Kongnoo A and Kateungngan K 2013 J. Polym. Environ. 21 245-58.
[2] Ibrahim S, Badri K, Ratnam C T and Ali N H M 2018 Radiat. Eff. Defects Solids. 173 427-34.
[3] Moonlek B and Saenboonruang K 2019 Radiat. Eff. Defects Solids. 174 452-66.
[4] Saenboonruang K, Phonchanthuek E and Prasandee K 2018 J. Environ. Radioact. 184-185 1-5.
[5] Saenboonruang K, Phonchanthuek E and Prasandee K 2018 Chiang Mai J. Sci. 45 821-31.
[6] Poltabtim W and Saenboonruang K 2019 Chiang Mai J. Sci. 46 778-86.
[7] Njinga R L, Jonah S A and Gomina M 2015 J. Radiat. Res. Appl. Sci. 8 208-15.
[8] Priharti W, Samat S B, Yasir M S and Garba N N 2016 J. Radioanal. Nucl. Chem. 307 297-303.
[9] Dreyer I and Uozumi N 2011 FEBUS. J. 278 4293-303.

Acknowledgements
Authors would like to acknowledge financial supports from the Faculty of Science, Kasetsart University under the Undergraduate Research Matching Fund (URMF). Authors also would like to thank the Thailand Institute of Nuclear Technology (TINT) for the technical support and the Specialized Center of Rubber and Polymer Materials for Agriculture and Industry (RPM), Faculty of Science, Kasetsart University, for publication support.