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COMPARATIVE ANALYSIS OF HEAT OF COMBUSTION IN RUBBER COMPOUNDS IRRADIATED BY ELECTRON BEAM

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Abstract
Elastomers are widely used materials in various industries, especially the automotive sector. However, a significant environmental liability has been observed due to the challenges associated with their recycling and reuse due to their chemical composition. This study aimed to evaluate the energetic and chemical characteristics of compounds based on natural rubber (NR), nitrile rubber (NBR), and fluoroelastomer (FKM), both non-irradiated and irradiated by electron beam at doses of 60 kGy and 120 kGy. Calorific value analyses were carried out using a bomb calorimeter,and the samples were characterized by Fourier Transform Infrared (FTIR) spectroscopy. The FTIR spectral analysis of NR, NBR, and FKM rubbers revealed the direct influence of chemical structure on the thermal stability of the materials. NR, composed of unsaturated hydrocarbons, proved more susceptible to oxidation and combustion. NBR, exhibited greater resistance to combustion compared to NR due to the presence of nitrile groups. FKM demonstrated the highest thermal resistance in the calorific power tests, probably due to their higher fluorine content. Such characteristics made FKM the only compound to retain significant structural traces in the FTIR spectra after combustion.
Keywords: *Calorific value, electron beam, NR, NBR, FKM.*

Introduction

Rubber is a versatile polymer widely employed in the manufacturing of products such as tires, seals, hoses, belts, and many other components, owing to its unique viscoelastic properties. However, its production process poses significant environmental challenges, primarily due to the substantial industrial residue generated. These residues originated not only from defective parts, but they are also inherent to the production process itself [1].

A considerable portion of rubber-based products could be preserved, shared, repaired, refurbished, remanufactured, or recycled to minimize the large volumes of material ultimately disposed of as "waste" [2]. Nevertheless, vulcanized rubber residues cannot be directly reintroduced into the production cycle due to its crosslinked network structure formed during the vulcanization process. As a result, recycling such materials requires more complex approaches, such as devulcanization or selective cleavage of crosslinks to enable reprocessing [1].

Furthermore, reusing rubber without renewable environmental technological solutions leads to materials with poor economic value – their final properties are often significantly degraded [3]. The recycling and reprocessing of vulcanized rubbers remain particularly challenging due to their covalently bonded crosslinked structure[1].

Given those limitations, alternative strategies such as energy and fuel recovery through thermochemical conversion technologies have gained increasing attention as viable options for rubber residues management [4]. In this context, the present study aimed to evaluate the energetic characteristic, calorific value, of rubber compounds based on natural rubber (NR), nitrile rubber (NBR), and fluorelastomer (FKM) non-irradiated and exposed to irradiation by electron beam.

Experimental

Samples Preparation

Raw materials were precisely weighed and incorporated using an open mixer for approximately 6 min, under controlled temperature range (60 °C – 90 °C), ensuring uniform dispersion aiming a consistent blend. Following this mixing stage, the compounds were laminated into approximately

4 mm thickness using the same open mixer to achieve proper material conformation. The samples preparation was made in accordance with ASTM D412-16, which outlines standard procedures for tensile testing of vulcanized elastomers. The vulcanization process was conducted in specific thermal and rheological properties for each elastomer – NBR and FKM compounds were vulcanized at 180 °C for 5 min., while NR compounds were vulcanized at 160 °C for the same 5 min. These parameters were selected to ensure the development of representative mechanical properties for subsequent analysis.

Irradiation Process

The vulcanized samples were subjected to electron beam irradiation at doses of 60 kGy and 120 kGy, under a controlled and constant dose rate. Irradiation was carried out using a Dynamitron JOB 188 electron accelerator, operating within an energy range of 0.5 MeV to 1.5 MeV and a current range of 0.1 mA to 25 mA, at the Radiation Technology Center at IPEN.

Characterization of Compounds

All samples were subjected to calorific value tests in a calorimetric bomb, and were also chemically evaluated by FTIR spectroscopy.

Calorific Value Determination Procedure

The calorimetric analysis was carried out using a Parr bomb calorimeter, model 1108. Following the ASTM D240-19 standard, samples were weighed between 0.8 g and 1.0 g and then placed in a metal crucible. The crucible was positioned inside the bomb chamber. A piece of ignition wire was passed through the sample, with one end connected to the support rod holding the crucible and the other side attached to the ignition terminal located on the bomb cover.

Subsequently, 2 mL of distilled water was added to the bomb, which was then sealed and pressurized with oxygen to a pressure between 20 atm and 30 atm. The assembled bomb was placed into a calorimeter vessel containing a known volume of water, along with a mechanical stirrer to ensure uniform temperature distribution. After allowing the system to stabilize thermally, the ignition was triggered, and the temperature readings were recorded at the following time intervals: 45 s, 60 s, 75 s, 90 s, 105 s, 120 s, 180 s, 240 s, 300 s, 360 s, 420 s, 480 s, 540 s, and 600 s. These data were used to determine the total heat released by the combustion of the sample, allowing for the calculation of its calorific value.

FTIR Spectroscopy

FTIR spectroscopy analysis was performed using a Bruker Alpha II spectrometer, equipped with a Platinum/Diamond ATR (Attenuated Total Reflectance) accessory, and operated through OPUS software version 8.2.28. Each sample was carefully placed on the sample holder and gently pressed to ensure proper contact with the crystal surface.

The final spectrum for each sample was obtained by averaging 32 scans, collected in the range of 4000 cm^{-1} to 500 cm^{-1}, with a spectral resolution of 4 cm^{-1}. Transmittance spectra were recorded for all samples, and each interferogram consisted of 15,192 data points, ensuring high-quality spectral resolution and reliability for subsequent chemical analysis.

Results and Discussion

Calorific Value Analysis

The calorific analysis of the different rubber compounds revealed distinct thermal behaviors influenced by the type of elastomer and processing conditions. Among the tested materials, natural rubber (NR) exhibited the highest gross calorific value (GCV) reaching $(10.18 \times 10^3) kcal/kg$, indicating a strong potential for energy recovery through combustion. Nitrile rubber (NBR) showed an intermediate GCV of $(9.10 \times 10^3) kcal/kg$, while fluoroelastomer (FKM) presented the lowest value, only $(2.37 \times 10^3) kcal/kg$, as presented at Table 1. These differences can be attributed to the chemical structure of the materials: NR is composed mainly of unsaturated hydrocarbons, which are

more prone to oxidation and combustion, while FKM contains a high proportion of fluorine atoms that enhance thermal stability and reduce flammability.

Table 1 – Gross Calorific Value (GCV) for each condition evaluated.

Samples	Gross Calorific Value / (kcal/kg)
Natural Rubber (NR)	10.18×10^3
Nitrile Rubber (NBR)	9.10×10^3
Fluorelastomer (FKM)	2.37×10^3
Non-Vulcanized NR	5.60×10^3
Vulcanized NR and Irradiated at 60 kGy	6.26×10^3
Vulcanized NR and Irradiated at 120 kGy	6.35×10^3
Non-Vulcanized NBR	4.99×10^3
Vulcanized NBR and Irradiated at 60 kGy	5.11×10^3
Vulcanized NBR and Irradiated at 120 kGy	4.87×10^3
Vulcanized FKM and Irradiated at 60 kGy	1.90×10^3
Vulcanized FKM and Irradiated at 60 kGy	1.94×10^3

The effect of vulcanization on the thermal performance of the rubber compounds was also evident. In general, vulcanized samples showed slightly higher calorific values compared to their non-vulcanized counterparts. For instance, vulcanized NR increased from $(5.60 \times 10^3) kcal/kg$ to $(6.26 \times 10^3) kcal/kg$ upon irradiation with 60 kGy. This increase is likely due to the enhanced structural integrity provided by the vulcanization process, which promotes more complete combustion and efficient heat release. Similarly, NBR compounds also demonstrated a modest increase in GCV following vulcanization, although the variations were less pronounced than those observed in NR.

Electron beam irradiation, applied at doses of 60 kGy and 120 kGy, produced subtle but consistent changes in the calorific behavior of the rubber compounds. For NR and NBR, irradiation tended to enhance the GCV, particularly in the vulcanized samples. For example, NR irradiated with 120 kGy showed a slightly higher GCV $(6.35 \times 10^3) kcal/kg$ compared to the dose of 60 kGy $(6.26 \times 10^3) kcal/kg$. This effect may be related to the scission and recombination of polymer chains under irradiation, leading to modified crosslinking structures that affect thermal degradation patterns. In contrast, FKM samples showed minimal variation in GCV between irradiation doses, reinforcing the compound's intrinsic thermal resistance due to its chemically stable structure.

In this sense, rubber compounds based on NR are the most promising candidates for energy recovery applications due to their higher calorific content and favorable combustion behavior. The formulation of rubber blends aiming to maximize heat release should consider a higher proportion of NR and the controlled use of vulcanization and irradiation processes. Meanwhile, FKM-based compounds, although thermally stable, are less effective for energy recovery by combustion.

FTIR Spectroscopy Analysis

FTIR spectra obtained for natural rubber (NR), nitrile rubber (NBR), and fluorinated rubber (FKM) samples – in raw, vulcanized, and thermally degraded forms – revealed significant changes in the chemical structure of each material in response to processing and combustion, as can be observed at Fig. 1. The NR spectrum showed characteristic bands of cis-1,4-polyisoprene, such as C-H stretching vibrations between 2952~2851 cm^{-1}, C=C stretching at 1660 cm^{-1}, angular deformations of C-H_2 and C-H_3, and the out-of-plane vibration of =CH at 839 cm^{-1} [5, 6].

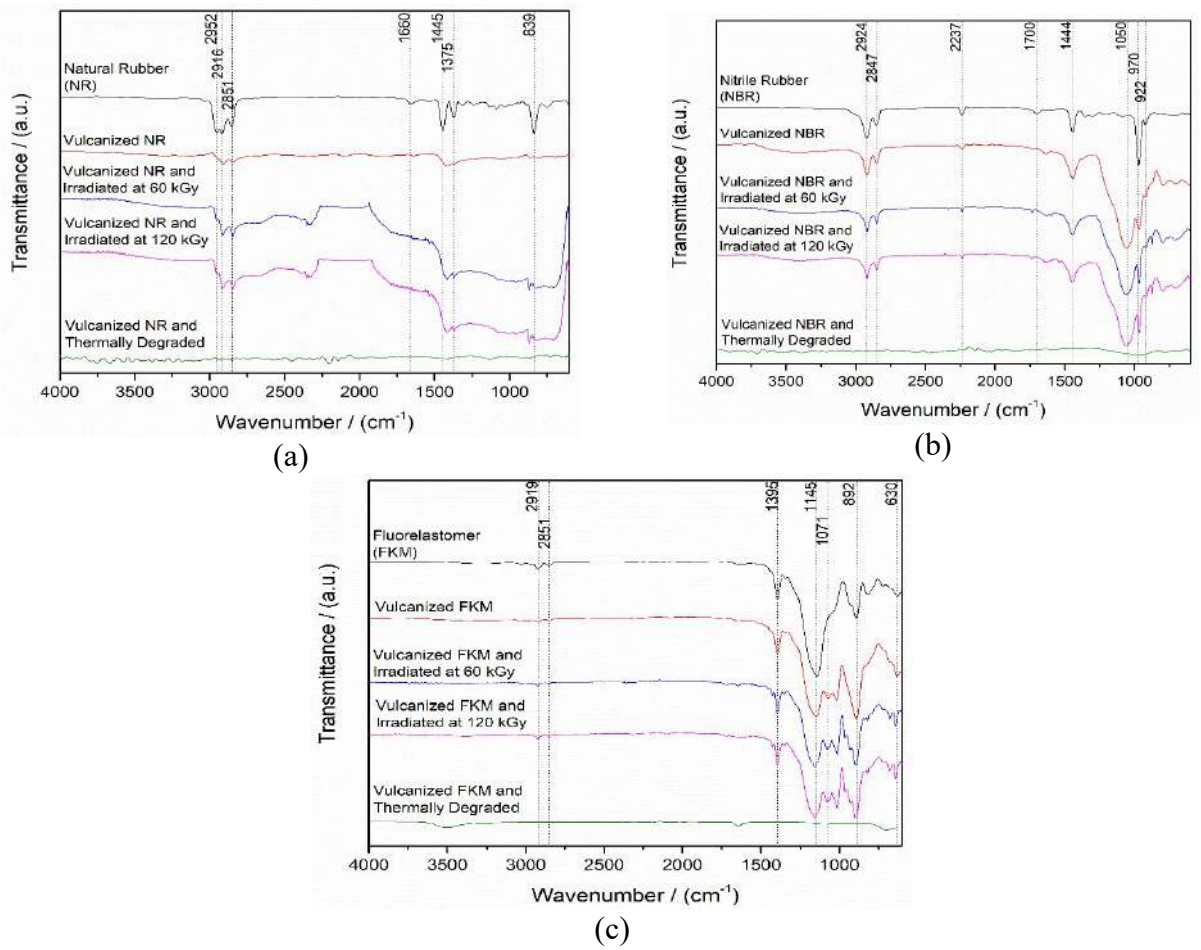

Figure 1 – Transmittance spectra obtained by FTIR spectroscopy analysis for; (a) NR samples; (b) NBR samples; and (c) FKM samples.

After vulcanization, NR displayed a reduction in the intensity of these bands, indicating partial consumption of double bonds due to crosslinking with S atoms. Bands expected for C-S and S-S bonds (661~600 cm^{-1}) confirmed the formation of crosslinks [7]. New absorptions in the region of 3500~3000 cm^{-1} suggested the formation of hydroxyl groups (O-H), indicating the onset of oxidation for thermally degraded samples. Post-combustion spectra showed near-total elimination of organic bands, consistent with complete degradation of the polymer matrix and the presence of inorganic residues [8]. For NBR, the spectra exhibited typical unsaturated chain features, and a nitrile (C≡N) stretch at 2231 cm^{-1}, along with bands attributed to butadiene and residual monomers. Vulcanization led to slight spectral changes, preserving the nitrile band, but reducing the intensity of others, indicating interactions with S atoms [9]. The increased intensity at 1050 cm^{-1} reflected greater C-C bond presence. Compared to NR, NBR's structure showed greater resistance to vulcanization, aligning with its known higher chemical stability and confirmed by previews gross calorimetric value discussed before. Following thermal degradation, the spectrum of vulcanized NBR closely resembled that of NR – an almost complete disappearance of well-defined bands, replaced by spectral noise, confirming extensive carbonization and irreversible breakdown of polymer chains. This indicates that despite its greater chemical resistance, NBR is still thermally degradable under extreme conditions. Fluorelastomers (FKM) exhibited distinct spectral features, as observed at Figure 1c, especially below 1500 cm^{-1}. Strong bands such as the -CF_2 stretch (1395 cm^{-1}) and C-F vibrations (1145 cm^{-1}, 1071 cm^{-1}, 1017 cm^{-1}, and 630 cm^{-1}) reflected its highly fluorinated and stable structure. The absence of unsaturation bands highlighted its saturated and chemically resistant nature. After vulcanization, FKM maintained nearly all structural bands, with enhanced clarity, confirming its robust chemical structure [5, 9]. Post-combustion spectra of FKM still exhibited residual features, particularly in the C-F vibration region, demonstrating its superior thermal stability compared to NR and NBR. These results support the use of FKM in harsh environments, such as in the automotive and aerospace

industries, due to its exceptional thermal and chemical resistance. No significant variations were observed in the FTIR spectra between the irradiated and non-irradiated samples for both FKM and NBR. However, the irradiation process led to notable modifications in the spectrum of vulcanized NR.

Conclusions

Rubber compounds based on natural rubber (NR) exhibit the highest potential for energy recovery due to their superior gross calorimetric value and combustion efficiency, especially when formulations maximize NR content and optimize vulcanization and irradiation conditions. FTIR analysis highlights the key role of chemical structure in thermal behavior: NR's unsaturated hydrocarbons favor combustion, but reduce thermal stability, while nitrile rubber (NBR) offers moderate resistance through its nitrile groups. Fluoroelastomer (FKM), although chemically and thermally robust due to its fluorinated structure, has low gross calorimetric value and limited energy recovery potential. These insights support the development of more effective and sustainable strategies for managing rubber residues through thermo-energetic valorization.

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