Universitatea Politehnica Timişoara
Faculty of Mechanical Engineering

CHARACTERIZATION OF SUSTAINABLE ELASTOMERIC MATERIALS USED FOR SEALING PERIPHERAL COMPONENTS IN PROTON EXCHANGE MEMBRANE FUEL CELL SYSTEMS

Summary of the PhD Thesis PhD Student:
Eng. Daniel FOLTUŢ

PhD Supervisor:
Prof. Dr. Ing. Dragoş Uţu
Prof. Dr. Ing. Viorel-Aurel Serban +

Contents

1 INTRODUCTION, BACKGROUND AND MOTIVATION

Chapter 1 presents the background and motivation of the chosen topic, emphasizing the role of PEMFC systems in electric mobility and the critical importance of sealing components.

The transition toward a low-carbon economy has become a defining global objective of the 21st century. With increasing concerns about climate change, fossil-fuel depletion, and energy security, attention has shifted toward technologies that enable efficient, clean, and renewable energy conversion and storage. Among these, hydrogen technologies—and particularly Proton Exchange Membrane Fuel Cells (PEMFCs)—have gained strategic significance due to their potential for decarbonizing transport, stationary power, and industrial processes.

Hydrogen offers the unique advantage of acting as both an energy carrier and a storage medium, complementing intermittent renewable energy sources such as wind and solar. When used in PEM fuel cells, hydrogen can be converted directly into electricity with only water and heat as by-products, making it one of the cleanest power-generation pathways currently available. Global investments in the energy transition reflect this technological momentum. The global energy system is facing pressing challenges from multiple directions: rising greenhouse-gas emissions, increasing demand for mobility, and the need for sustainable, secure energy supply. In response, investment into the energy transition has surged. According to the International Energy Agency (IEA), it is estimated that clean-energy investment in 2024 exceeded US $2 trillion, and that total energy investment (including fossil fuels) may surpass US $3 trillion in the same year [1–3].

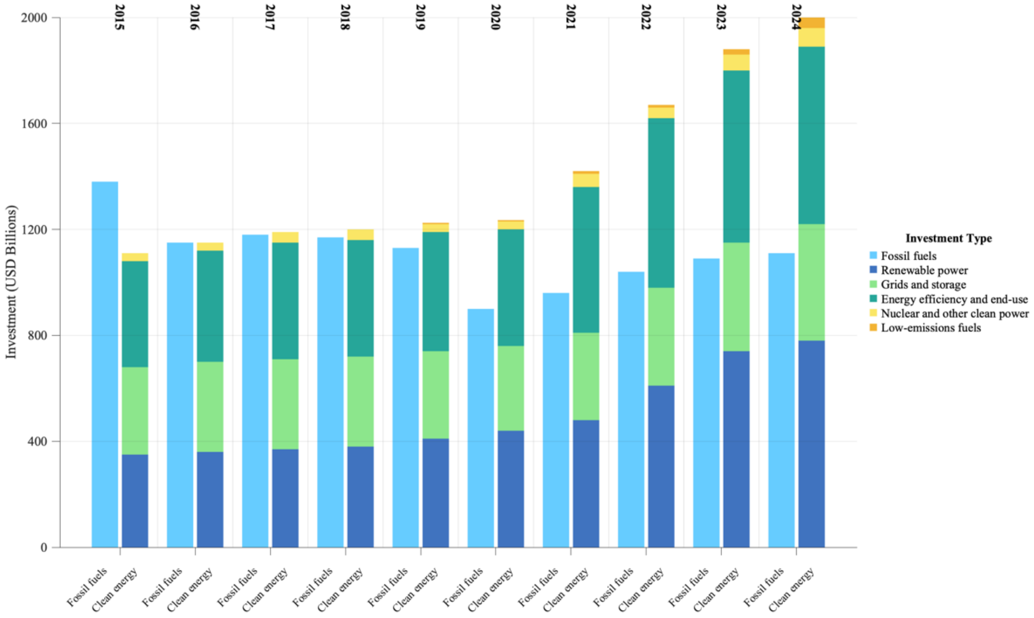

Figure 1.1. Comparison between fossil fuel and clean energy investments, 2015-2024

These figures indicate a major shift in capital flows toward renewables, electric mobility, energy storage and hydrogen-based technologies. Within this broader transformation, hydrogen and electrochemical energy systems play a pivotal role. The global demand for hydrogen surpassed 97 million tonnes in 2023 and is projected to approach 100 Mt in 2024, underscoring the scale of existing industrial hydrogen usage while signaling growth potential in low-emissions hydrogen production [4]. Meanwhile, the market for proton-exchange-membrane fuel cells (PEMFCs)—pivotal for hydrogen conversion in transport and stationary applications—was valued at US $4.3 billion in 2024 and is forecast to grow to approximately US $10.3 billion by 2034, representing a Compound Annual Growth Rate (CAGR) of approximately 9% [4,5].

Nevertheless, despite technological progress and stronger market signals, critical challenges remain for hydrogen and fuel-cell-based systems. Foremost among these are the high capital cost and complexity of stack manufacture and hydrogen infrastructure. The capital cost of Proton Exchange Membrane (PEM) electrolyzer stacks can be a significant portion (e.g., 46%) of the total electrolyzer cost.

Beyond cost, a critical and often under-recognized challenge is the **durability and reliability of peripheral components** (seals, gaskets, polymers). These components, while sometimes overlooked compared to core elements like catalysts and membranes, are essential for maintaining gas tightness, structural integrity, and system efficiency. They operate in harsh environments characterized by large temperature ranges, high humidity, chemical exposure (such as acidic or oxidative conditions), and mechanical stresses including vibrations, compression, and cyclic loading [6–8].

Material degradation and failure under harsh operating conditions—such as elevated temperature, high humidity, chemical exposure, and mechanical cycling—remain among the most critical challenges affecting the lifetime and economics of fuel-cell systems. Elastomeric sealing materials represent a relatively small subsystem, yet their performance has a disproportionately large influence on system reliability and maintenance cost. Even when the electrochemical components of a PEMFC achieve high efficiency, failure of seals or gaskets can cause gas leakage, cross-contamination, or electrical shorting, leading to rapid performance decay and safety risks. The environment in which these materials operate is extremely demanding, typically involving temperatures of 60–90°C, high humidity, acidic condensates, and repeated mechanical compression cycles, all of which accelerate both chemical and physical degradation [7–9].

In this context, **Proton Exchange Membrane Fuel Cell (PEMFC)** systems have emerged as a leading solution for electric mobility. PEMFCs convert hydrogen and oxygen electrochemically into electricity, producing only water vapor and heat as by-products. This direct conversion of chemical to electrical energy eliminates the combustion step, enabling higher efficiency and zero tailpipe emissions [10,11]. By 2024, the worldwide fleet of fuel-cell electric vehicles (FCEVs) exceeded 85,000 units, with major deployments in Japan, South Korea, the United States, and several EU member states.

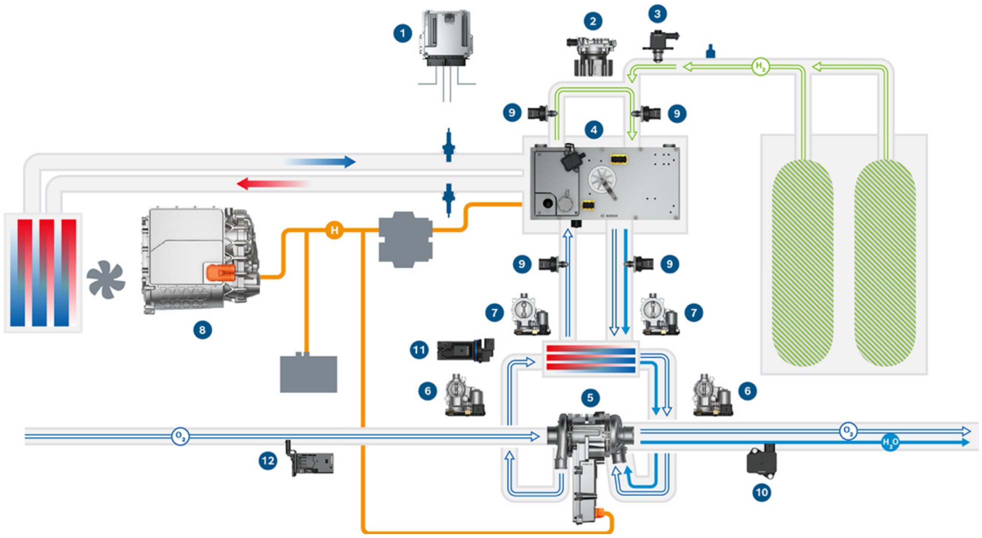

Figure 1.2. The PEMFC automotive system

A PEMFC powertrain integrates the fuel-cell stack, hydrogen tanks, DC/DC converter, traction inverter, electric motor, and auxiliary battery. The system relies heavily on the Balance-of-Plant (BoP) components, such as the electric air compressor, humidifier, stack-isolation and control valves, and thermal management systems. Specifically, the **cathodic air circuit** presents some of the most aggressive conditions for sealing materials due to the presence of compressed, hot, humid air that may contain acidic degradation products from the membrane.

Europe’s regulatory and industry frameworks project substantial expansion of hydrogen fuel cell vehicle deployment through 2035. The EU’s “Fit for 55” package establishes technology-neutral CO2 emission reduction targets. Industry projections anticipate that approximately 45,000 to 50,000 hydrogen-powered medium and heavy-duty trucks and buses will be deployed across the European Union by 2030, with the fleet expanding to approximately 850,000 units by 2035 [12–16].

Importance of Elastomeric Gaskets in PEMFC Operation

Within a PEMFC stack, each membrane-electrode assembly (MEA) is surrounded by gaskets that ensure a gas-tight seal between bipolar plates and prevent mixing of hydrogen, oxygen, and coolant [17]. These gaskets play a decisive role in maintaining electrical insulation and the necessary compressive load on the stack. The operating environment inside a PEMFC is harsh: temperatures of 60–90°C, high relative humidity, and exposure to mildly acidic condensates formed by membrane degradation and catalyst reactions [18]. Under such conditions, elastomeric gaskets must retain their mechanical integrity, resist chemical attack, and minimize leakage to ensure long-term fuel-cell performance and safety.

In addition to the internal sealing elements, a complete PEMFC stack is integrated with several peripheral components that manage reactant distribution, humidification, heat exchange, and pressure control. One of the most critical of these subsystems is the **air-management assembly**, which regulates the flow and pressure of the oxidant stream through an air valve (or throttle valve). The sealing elements designed for this air valve must endure repeated dynamic compression, contact with humid and acidic air streams, and extended service times at moderate temperatures.

Need to Investigate Sustainable Sealing Materials

Ethylene-propylene-diene monomer (EPDM) rubber is the most widely adopted material for fuel-cell sealing applications due to its excellent thermal stability, elastic recovery, and resistance to ozone, oxidation, and polar media [19]. However, the demanding environment within a PEMFC can lead to oxidative chain scission, surface cracking, and leaching of ionic species from the polymer matrix. These degradation phenomena progressively weaken the mechanical integrity of gaskets and shorten stack service life [18,20].

In parallel, the environmental impact of conventional elastomer compounding, especially the use of virgin carbon black derived from fossil sources, has become an increasing concern. To mitigate this, "ECO" EPDM systems have been developed that incorporate **Circular Carbon Black (CCB)** or **Recycled Carbon Black (RCB)** recovered from end-of-life tires. Beyond EPDM, **Thermoplastic Vulcanizates (TPVs)** and **ECO-TPVs**—hybrid materials comprising dynamically cross-linked EPDM dispersed in a thermoplastic matrix—are emerging as promising alternatives due to their potential for recyclability and easier processing [21,22].

2 STATE-OF-THE-ART ANALYSIS

Chapter 2 deals with the state of the art in the field of PEMFC sealing, presenting theoretical aspects regarding operating environments, current elastomeric materials, degradation mechanisms, and sustainability considerations in rubber manufacturing. Moreover, an introduction to the tribological and chemical challenges of peripheral components is made.

The concept of converting chemical energy directly into electrical energy predates many other modern electrochemical systems, starting with Sir William Grove in 1839. However, significant advancements occurred in the mid-20th century with Francis Thomas Bacon's alkaline fuel cell and General Electric's development of the first PEMFC using sulfonated polystyrene membranes [23–25]. The 1990s saw a major revival driven by environmental concerns, leading to the development of chemically stable Nafion® membranes and the first commercial FCEV prototypes [26–28].

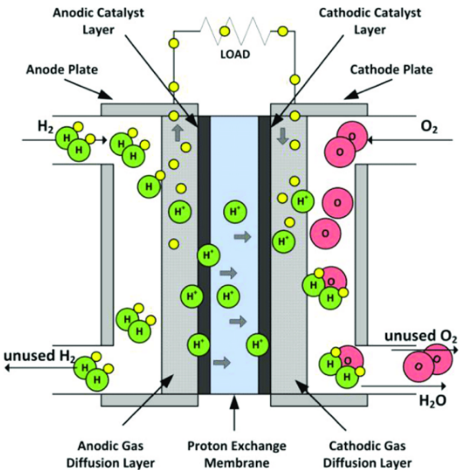

Figure 2.1. Schematic representation of a PEMFC

A PEMFC converts the chemical energy of hydrogen directly into electrical energy through electrochemical oxidation-reduction reactions. Its core unit, the membrane-electrode assembly (MEA), is the locus of these reactions.

The fundamental operation involves hydrogen oxidation at the and oxygen reduction at the cathode. The theoretical open-circuit voltage is 1.229 V, but practical cell voltages range between 0.6 and 0.8 V due to activation, ohmic, and mass-transport losses [29].

The internal operating environment of a PEMFC is defined by a combination of thermal, mechanical, and chemical stressors.

Temperature: Typically ranges between 60–90°C. The cathodic oxygen reduction reaction is strongly exothermic. In automotive systems, turbo-compressors can raise air inlet temperatures to over 100°C before thermal equilibrium [30].

Humidity: High relative humidity is essential for proton conductivity in PFSA membranes. Water transport occurs through electro-osmotic drag and back-diffusion, creating a wet environment. Dynamic load changes induce hydration cycling, subjecting seals to swelling and deswelling.

Pressure: Cathode pressures of 2–3 bar are used to enhance kinetics. Cyclic pressure variations impose repeated compressive deformation on gaskets and O-rings.

Chemical Environment: Intrinsically acidic and oxidative. PFSA membranes release sulfonic acid groups into condensed water, producing pH levels as low as 2–4. Additionally, the presence of hydrogen peroxide and hydroxyl radicals from incomplete oxygen reduction can cause severe chemical attack on elastomers [9].

Balance-of-Plant (BoP) and Peripheral Components

While the MEA defines electrochemical performance, the Balance-of-Plant (BoP) manages reactant supply, thermal regulation, and water distribution. BoP hardware may represent 40–60% of total system mass and cost [28,31].

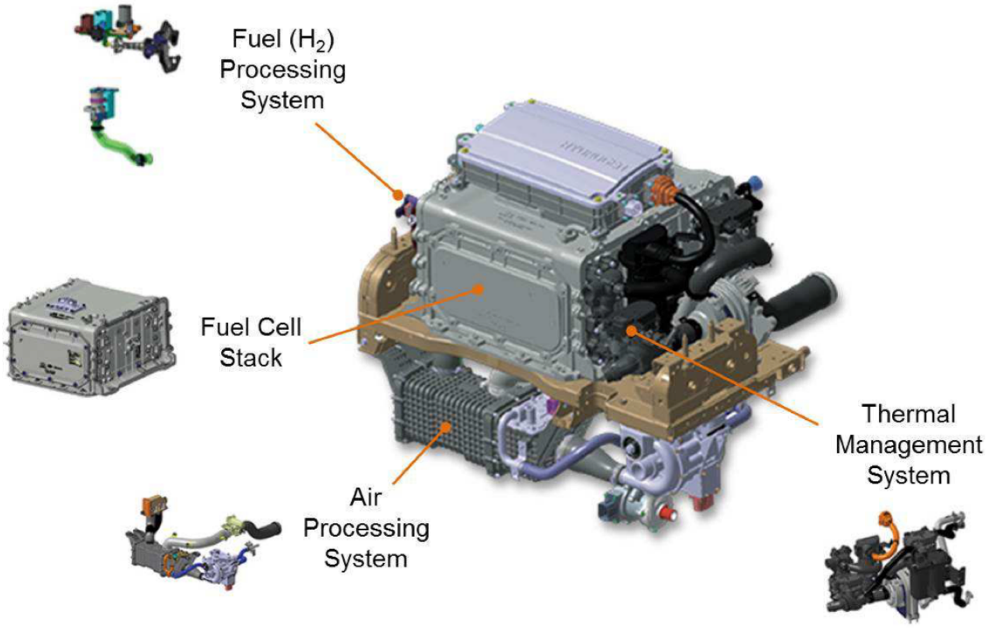

Figure 2.2. Typical PEMFC powertrain

Within the BoP, the **Air Flux Level Control Valve** is a critical component. It regulates the precise flow of compressed air to the cathode. This valve operates in a highly aggressive environment: temperatures from -40°C to 120°C, high oxygen concentration, near-saturated humidity, and exposure to acidic condensates. The elastomeric sealing elements inside this valve must maintain extremely low leakage rates while enduring millions of sliding and compressive cycles against polymeric housings (often PA66GF30) [32]. This is the main application of this thesis.

Figure 2.3. Air Valve for PEMFC systems

Sealing Concepts and Material Requirements

Seals are classified as static (between stationary components) or dynamic (accommodating relative motion). For a seal to remain leak-free, the contact stress must exceed the internal medium pressure. In PEMFCs, sealing failure modes include:

Stress Relaxation: Time-dependent decay of sealing force.
Compression Set: Irreversible deformation after load removal.
Chemical Degradation: Oxidative chain scission and crosslink modification.
Tribological Wear: Abrasion and surface fatigue in dynamic seals.

Elastomeric Materials for Air-Valve Sealing

Several elastomers are evaluated for PEMFC sealing:

EPDM (Ethylene Propylene Diene Monomer): Offers superior resistance to humidity, steam, acidic environments, and oxidation due to its saturated backbone. It is the dominant choice for static seals but can exhibit stress relaxation under cyclic loads.

TPV (Thermoplastic Vulcanizate): Composed of crosslinked EPDM dispersed in a polypropylene matrix. It offers improved tribological performance (lower friction) and processability but may have lower chemical resistance due to the polypropylene phase [33].

Silicone Rubbers (VMQ): possess flexibility and thermal stability but degrade quickly in acidic/humid environments above 100°C [34].

Fluoroelastomers (FKM): Excellent chemical resistance but poor low-temperature flexibility and dynamic compliance [35].

Comparatively, EPDM remains the most balanced material for cathodic-side sealing, provided wear and stress relaxation are managed. TPV is a strong candidate for dynamic applications where friction is a primary concern.

Sustainability in Synthetic Rubbers

The transition to sustainable energy systems demands eco-friendly materials. Conventional EPDM relies on petrochemical feedstocks. Sustainability pathways include:

Sustainable Feedstocks: Bio-based monomers (terpenes, vegetable oils) or CO2-based rubbers [124, 127].

Sustainable Fillers: Replacing virgin Carbon Black (CB) with Recycled Carbon Black (rCB) from end-of-life tires or Circular Carbon Black (CCB) produced from tire pyrolysis oil. rCB offers a low carbon footprint but often suffers from high ash content and surface heterogeneity, which can compromise mechanical reinforcement [36,37]. CCB acts as a "drop-in" solution with properties closer to virgin black.

Research Gaps Identified

Recent literature has expanded the understanding of elastomer degradation in fuel cells. Studies have shown that acidic condensates initiate chain scission in EPDM [38,39].

However, significant **gaps** remain:

Lack of Integrated Studies: Most studies isolate degradation modes (chemical OR mechanical). Few assess the synergistic effects of acidic, thermal, and tribological stress.

Leaching Characterization: There is insufficient data on the specific molecular identification of organic leachates from sustainable elastomers that could poison catalysts.

Tribology against Composites: Limited research exists on the wear of elastomers against glass-fiber reinforced plastics (PA66GF30), the standard material for BoP housings.

Sustainable Variants: The performance of EPDM reinforced with circular vs. recycled carbon black under PEMFC-specific acidic conditions is largely uncharacterized.

Addressing these gaps is the primary focus of the experimental program detailed in the subsequent sections of this thesis.

---

3 SCOPE AND OBJECTIVES OF THE THESIS

Chapter 3 outlines the scope and specific objectives of the doctoral research.

For the development and comprehensive characterization of sustainable elastomeric sealing materials intended for Proton Exchange Membrane Fuel Cell (PEMFC) applications, the experimental program was structured to systematically evaluate material behavior under simulated service conditions. This chapter details the materials selection, accelerated aging protocols, analytical techniques, and testing methodologies employed to fulfill the scope of the doctoral research.

3.1 Scope and Specific Objectives

The primary scope of this work was to investigate the behavior of sustainable elastomeric materials, with a focus on Ethylene Propylene Diene Monomer (EPDM) and Thermoplastic Vulcanizates (TPV), under the specific conditions required for sealing peripheral components of PEMFC systems. A central aspect of the research was to assess the viability of utilizing circular and recycled carbon black as reinforcing fillers without compromising the critical performance metrics of the seals.

To achieve this, the following specific objectives were pursued:

Comparative analysis of elastomeric sealing materials: A critical evaluation of current commercial solutions versus sustainable alternatives.

Characterization of mechanical behavior under aging: Evaluation of changes in tensile strength, elongation, hardness, and compression set induced by thermal and acidic aging protocols.

Evaluation of tribological performance: Assessment of the coefficient of friction and wear rates of EPDM and TPV against glass-fiber reinforced polyamide (PA66GF30) to simulate dynamic valve sealing.

Assessment of chemical stability and leaching potential: Investigation of organic and ionic leaching from ECO-EPDM elastomers using HPLC and conductivity measurements to estimate membrane contamination risks.

Correlation of results: Integration of mechanical, tribological, and chemical data to identify the most robust sustainable material formulation.

4 METHODOLOGY OVERVIEW

Chapter 4 describes the methodology and equipment used to achieve the experimental study. This chapter offers an outline concerning the applied investigation methods and presents different experimental techniques, such as accelerated aging protocols, chemical analysis (HPLC, HWET), and tribological testing, which can provide important information on the quality and performance of sustainable sealing materials.

The experimental methodology was designed to replicate the aggressive environment of the PEMFC cathodic air loop. This involved a multi-stage process:

Material Selection & Preparation: Sourcing and preparation of standard and sustainable elastomer samples.

Accelerated Aging: Exposure of samples to thermal stress and acidic immersion for extended durations.

Physicochemical Characterization: Tracking of mass/volume changes, hardness evolution, and leaching behavior.

Mechanical & Tribological Testing: destructive and non-destructive testing to quantify performance degradation.

Microstructural Analysis: Advanced microscopy to visualize degradation mechanisms.

Each phase was carefully planned in chronological order. Material preparation and conditioning preceded aging protocols. After aging, specimens underwent mechanical testing, swelling and leaching evaluation, wear testing, microstructural analysis, and thermal analysis. The design ensures reproducibility: detailed descriptions of materials, preparation, testing conditions, measurement procedures, and data analysis are provided to allow replication by other researchers.

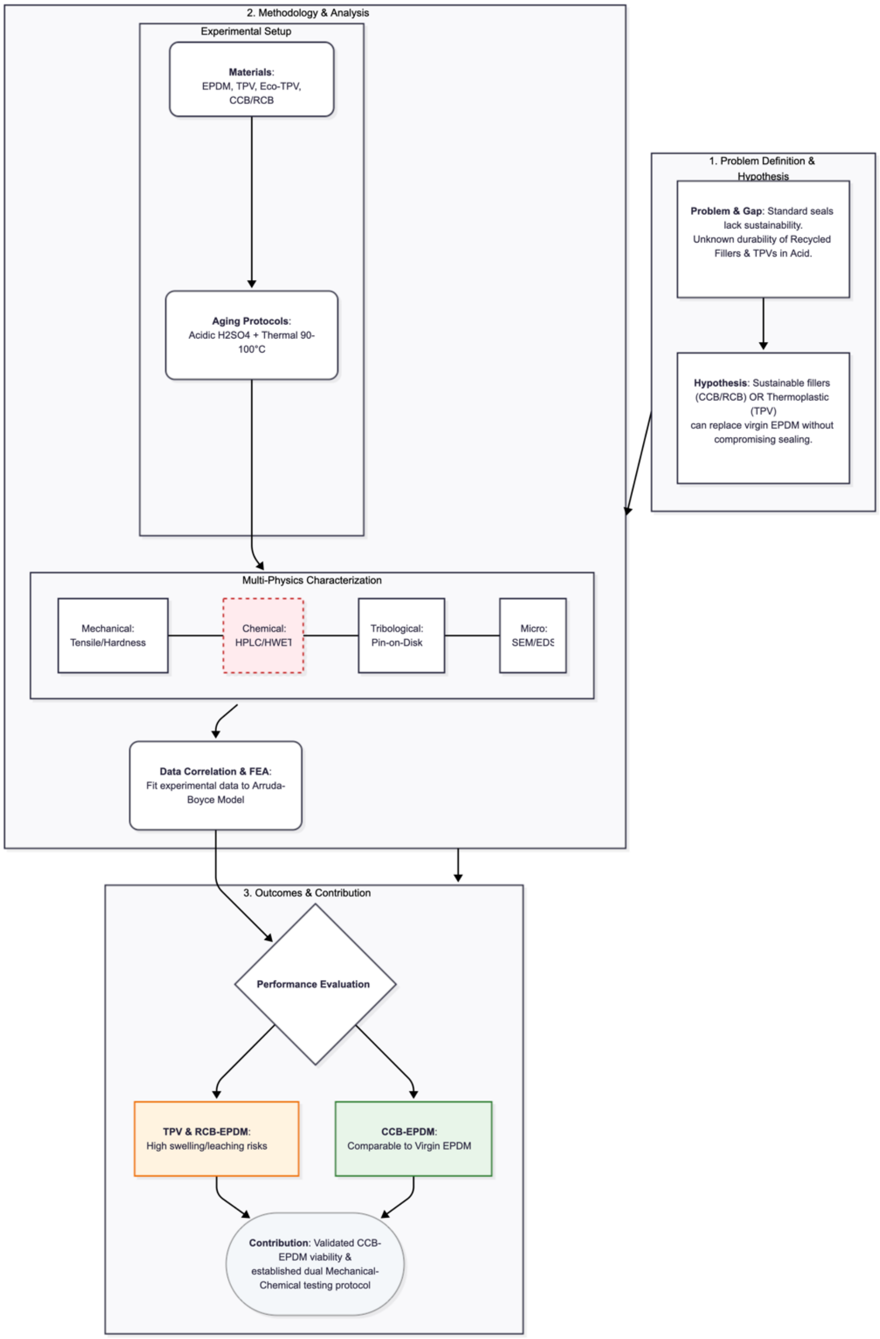

Figure 4.1. Experimental Methodology

4.1 Materials

The study investigated three distinct categories of elastomeric materials, selected based on their relevance to automotive sealing and potential for sustainability.

4.1.1. Thermoplastic Styrenic Elastomer (TPS)

Initial thermal aging studies were conducted on a Thermoplastic Styrenic Elastomer (TPS) grade provided by Kraiburg. Dumbbell-shaped specimens were prepared according to ISO 37 Type 2 standards. This material served as a baseline for understanding the thermal degradation mechanisms of thermoplastic elastomers.

4.1.2. EPDM-H, TPV, and Eco TPV

The core investigation focused on three commercially relevant sealing materials:

EPDM-H: A standard peroxide-cured Ethylene Propylene Diene Monomer rubber, characterized by a saturated backbone providing high resistance to heat, ozone, and oxidation.

TPV (Thermoplastic Vulcanizate): A material consisting of a crosslinked EPDM phase finely dispersed within a thermoplastic polypropylene (PP) matrix, offering processability advantages.

Eco TPV: A sustainable variant containing at least 15% post-consumer recycled content, designed to lower the carbon footprint while targeting comparable mechanical performance.

4.1.3. Low-Friction (LF) Variants

For the tribological study involving dynamic sealing contacts (e.g., air control valves), specialized low-friction formulations were used:

LF EPDM: Density 1.06 g/cm^3, Hardness 62 Shore A.

LF TPV: Density 0.96 g/cm^3, Hardness 80-87 Shore A.

The counter-body selected for these tests was **Polyamide 66** reinforced with 30% glass fibers (PA66GF30), machined into 6 mm diameter balls, replicating the mating surface found in automotive housings.

4.1.4. Sustainable ECO EPDM (CCB and RCB)

To specifically address the impact of filler sustainability, two custom ECO EPDM compounds were manufactured by Arlanxeo. Both used the same base polymer and peroxide crosslinking system but differed in their reinforcing filler:

CCB EPDM: Reinforced with **Circular Carbon Black**, obtained via advanced pyrolysis of end-of-life tires (ELT). This filler is characterized by controlled particle morphology and high purity.

RCB EPDM: Reinforced with **Recycled Carbon Black**, recovered through conventional pyrolysis routes. This filler typically exhibits a broader particle size distribution and higher ash content.

Table 2.1. Initial properties of ECO EPDM compounds

Property	**CCB EPDM**	**RCB EPDM**
Tensile Strength (MPa)	15	12
Elongation at Break (%)	271	262
Hardness (Shore A)	77	75
Microhardness (IRHD)	47	45

4.2 Accelerated Aging Protocols

To simulate the service life of PEMFC peripheral components, accelerated aging protocols were implemented.

4.2.1. Thermal Aging

Thermal aging was performed to isolate the effects of temperature from chemical attack. TPS samples were aged according to ISO 188 for 168 hours at 100°C. For the EPDM, TPV, and ECO EPDM series, a more rigorous protocol was applied: samples were exposed to dry heat in a convection oven at 90°C for 1000 hours. This temperature was selected to represent the upper limit of the cathodic air stream exiting the compressor.

2.4.2. Chemical Aging (Acidic Immersion)

To reproduce the corrosive environment created by membrane degradation products and acidic condensates, samples were fully immersed in aqueous sulfuric acid (H_2SO_4) solutions. Three concentrations were chosen to span the range of potential operating conditions:

0.001 M H_2SO_4: Simulating mild condensate, pH value aprox 2.24.

0.1 M H_2SO_4: Representing moderate acidity, pH value aprox 0.84.

1 M H_2SO_4: Simulating severe local acidity or water accumulation, pH value aprox 0.10.

All chemical aging tests were conducted at a constant temperature of **90°C for a duration of 1000 hours**.

4.3 Chemical Analysis and Leaching Characterization

Assessing the release of contaminants is critical for preventing catalyst poisoning. The following techniques were employed:

4.3.1. Mass and Volume Change (Swelling)

Swelling behavior was quantified by measuring the mass and volume of specimens before and after a 1000-hour immersion. For EPDM, TPV, and Eco TPV, measurements were performed both in air and in water using the Archimedes principle (with a sinker for buoyant samples). The percentage volume change (ΔV_{100}) was calculated to determine the extent of fluid uptake and network relaxation.

4.3.2. pH Tracking

The pH of the aging solutions was measured before and after immersion using a Mettler Toledo FiveEasy pH meter. Changes in pH were used to indicate either the leaching of alkaline species (fillers, additives) or the absorption of acid by the polymer matrix.

4.3.3. Hot Water Extraction Test (HWET)

To evaluate ionic leaching under neutral conditions, a Hot Water Extraction Test was performed. Specimens were immersed in deionized water (initial conductivity below 1.0 μS/cm) at 80 °C for 168 hours. The electrical conductivity of the water was monitored at regular intervals (0, 24, …, 168 hours) using a portable conductivity tester. A threshold of 5 μS/cm was established as the maximum acceptable limit for compatibility with PEMFC cooling circuits.

4.3.4. High-Performance Liquid Chromatography (HPLC)

Organic leachates released from the ECO EPDM materials were analyzed using an Agilent 1260 Infinity II HPLC system equipped with a UV–Vis diode-array detector (DAD). A reversed-phase C18 column (Teknokroma) was used. Leachate solutions from acid immersion tests were filtered (0.45 μm) and diluted with acetonitrile. UV absorbance was monitored at wavelengths including 230 nm to detect aromatic and unsaturated organic compounds. This qualitative and semi-quantitative analysis allowed for fingerprinting of organic contaminants released by recycled fillers.

4.4 Mechanical Testing

Mechanical properties were evaluated to assess structural integrity retention after aging.

4.4.1. Tensile Testing

Tensile tests were conducted using an Instron universal testing machine equipped with a video extensometer for precise strain measurement. Specimens were dumbbell-shaped (ISO 37 Type 2). Tests were carried out at a crosshead speed of 500 mm/min under standard laboratory atmosphere (23 °C, 50% RH). Measured parameters included tensile strength (MPa), elongation at break (%), and modulus at 100% elongation (M100). For the EPDM-T material used in stiffness and FEA calibration studies, additional tests were performed at temperatures of −40 °C, 23 °C, 80 °C, and 125 °C to assess temperature-dependent stiffness.

4.4.2. Compression Set

Compression set, a critical parameter for sealing longevity, was measured according to ISO 815-1A. Type B specimens (6.3 mm thickness, 13 mm diameter) were compressed by 25% and maintained at 125 °C for 72 hours. The permanent deformation after recovery was calculated, providing a direct measure of the material's loss of elasticity.

4.4.3. Hardness Testing

Changes in surface hardness were evaluated using two methods: Shore A hardness (ISO 48-4) and microhardness (IRHD) according to ISO 48-2, to detect near-surface degradation gradients.

4.4.4. Dynamic Mechanical Analysis (DMA)

Viscoelastic properties (storage modulus E′, loss modulus E″, and tan δ) were determined using a single-cantilever configuration. A temperature sweep from 20 °C to 160 °C was performed at a heating rate of 5 K/min and a frequency of 1 Hz.

4.4.5. Tribological Testing

To simulate the dynamic friction occurring in air control valves, tribological tests were performed using a DUCOM TR-20 Micro Pin-on-Disk tribometer under a ball-on-disk configuration. The counterbody was a 6 mm diameter ball made of PA66GF30 (polyamide 66 with 30% glass fiber). Tests were conducted under dry sliding conditions at three normal loads: 1 N, 3 N, and 6 N; and at three rotational speeds: 92, 183, and 286 RPM (corresponding to linear sliding speeds of approximately 0.05, 0.10, and 0.15 m/s). The duration of each test was 30 minutes. During the tests, the coefficient of friction (CoF) evolution over time was recorded. After the sliding tests, mass loss was measured and specific wear rates were calculated.

4.5 Microscopy and Surface Analysis

Microstructural changes induced by sliding and aging were investigated using scanning electron microscopy (SEM). For the TPS materials, a FEI INSPECT S microscope was used; for EPDM, TPV, and related elastomers, a Thermo Fisher Axia ChemiSEM was employed. Prior to imaging, samples were sputter-coated with gold to prevent charging. SEM imaging was performed at various magnifications (from 500× up to 5000×) to observe surface cracking, filler exposure, and changes in roughness. In addition, SEM was coupled with energy-dispersive X-ray spectroscopy (EDS) to map elemental composition (C, O, S, Si, Zn) on the surfaces of aged samples, providing insight into oxidation, filler migration, or acid uptake.

4.6 Thermal Analysis (TGA / DSC)

Thermogravimetric analysis (TGA) was performed using a STA 449 F1 instrument to evaluate thermal stability and to determine decomposition temperatures under nitrogen atmosphere. The tested temperature range was from 30 °C up to 900 °C. Differential scanning calorimetry (DSC) was conducted on a TA Instruments Discovery DSC 25P. Thermal scans ran from −60 °C to 200 °C, allowing determination of glass transition temperatures (Tg), melting points, and any changes in crystallinity or crosslinking induced by aging.

This comprehensive experimental framework provided both quantitative and qualitative data to assess wear, surface degradation, chemical changes, and thermal properties, thereby supporting the evaluation of sustainable elastomer feasibility for fuel-cell sealing and related applications.

5 RESULTS AND DISCUSSIONS

Chapter 5 presents the experimental program concerning the mechanical, chemical, and tribological behavior of the materials, the results obtained during this study (including the specific effects of circular versus recycled carbon black), and highlights the most important aspects.

The experimental program yielded a comprehensive dataset detailing the mechanical, chemical, and tribological response of sustainable elastomeric sealing materials under simulated PEMFC operating conditions. This chapter presents the key findings, focusing on the comparative performance of EPDM, TPV, and Eco-friendly variants, with particular emphasis on the impact of circular versus recycled carbon black fillers.

5.1 Thermoplastic Styrenic Elastomer (TPS): Thermal Aging Behavior

Initial investigations on TPS provided a baseline understanding of how thermoplastic elastomers degrade under thermal stress, a critical factor for components near heat sources in the engine bay.

Tensile Response:

Tensile testing performed at varying strain rates (5, 50, and 500 mm/min) revealed a consistent pattern of thermo-oxidative stiffening. As illustrated in Figure 3.1, thermal aging at 100 °C for 168 hours induced a significant increase in the stress required to deform the material, indicating a reduction in chain mobility and an effective increase in network crosslink density.

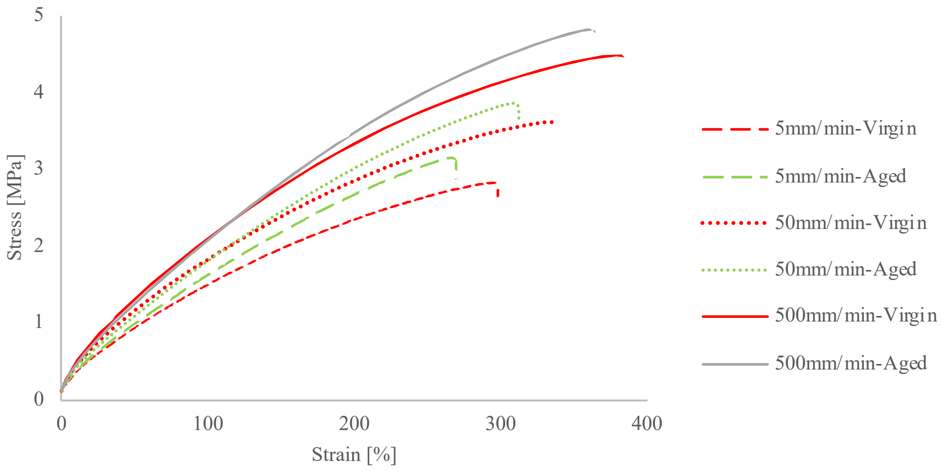

Figure 5.1. TPS tensile response dependence on load speed and sample state

Specifically, the ultimate tensile strength (UTS) increased by approximately 9-14% depending on the strain rate, while elongation at break decreased. For example, at a test speed of 5 mm/min, the UTS rose from 2.78 MPa (virgin) to 3.17 MPa (aged). This behavior suggests a dominant crosslinking mechanism or physical aging process in the styrenic hard domains, which restricts chain mobility and increases rigidity at the expense of ductility.

Microstructural Degradation:

Scanning Electron Microscopy (SEM) confirmed surface-level degradation. Aged samples exhibited increased surface roughness and the formation of micro-cracks and voids, which act as stress concentrators and precursors to macroscopic failure.

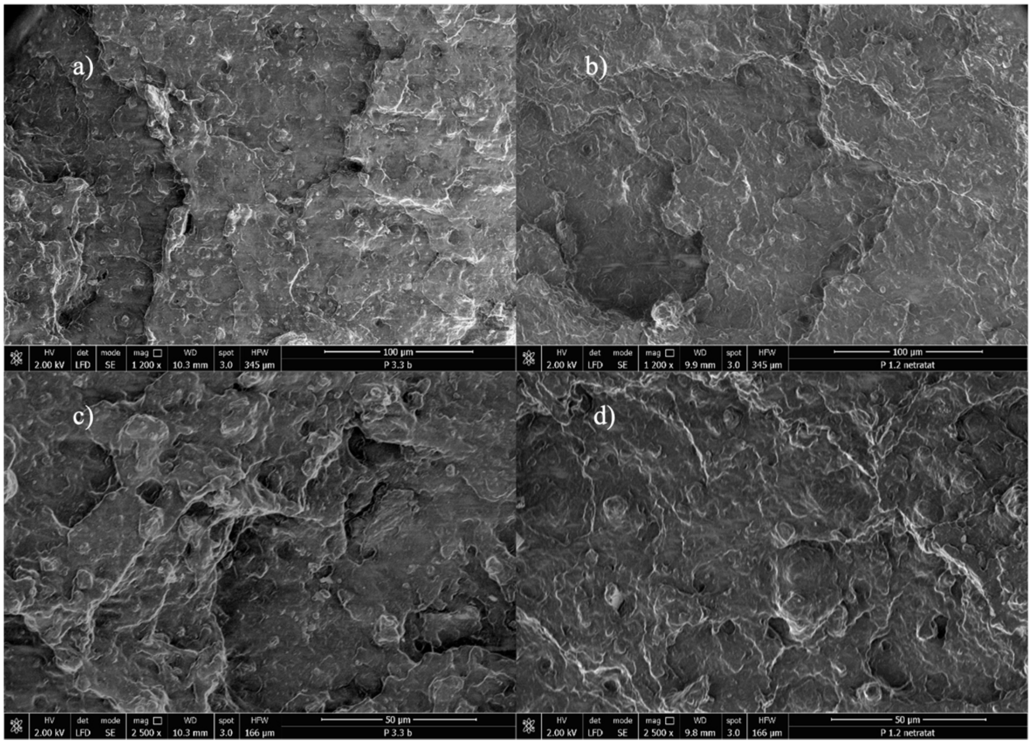

Figure 5.2. SE micrograph of TPS/SEBS a) aged, magnitude 1200x; b) unaged, magnitude 1200x; c) aged, magnitude 2500x; d) unaged, magnitude 2500x

Thermal analysis (TGA) identified the onset of matrix decomposition at approximately 470 °C, confirming that the material's thermal stability limits are well above typical PEMFC operating temperatures, although long-term oxidative aging remains a concern for mechanical compliance.

5.2 Chemical and Thermal Stability of EPDM-H, TPV, and Eco TPV

The core comparison between thermoset rubbers (EPDM-H) and thermoplastic vulcanizates (TPV, Eco TPV) highlighted significant differences in chemical resilience under acidic conditions.

5.2.1. Swelling Behavior

Immersion in sulfuric acid solutions at 90 °C for 1000 hours produced varied swelling responses, directly correlating with the material's polarity and filler–matrix interaction.

EPDM-H: Demonstrated superior chemical inertness. Even in the most aggressive 1 M H_2SO_4 solution, weight change (WEC) was limited to 1.88% and volume change (VC) to 1.64%. In mild acid (0.001 M), slight negative volume changes (approximately −1%) were observed, potentially due to the extraction of low-molecular-weight species or post-curing network densification.

TPV: Showed moderate swelling, reaching approximately 5.2% WEC in 1 M acid.

Eco TPV: Exhibited the highest susceptibility to acid ingress, with weight increases exceeding 6% and volume expansion of 6.5% in 1 M H_2SO_4.

These results confirm that while the crosslinked EPDM phase in TPVs provides some resistance, the continuous polypropylene matrix and the presence of recycled content in Eco TPV create pathways for acid penetration and degradation.

5.2.2. Mechanical Property Retention

Tensile testing after aging reinforced the swelling data. EPDM-H maintained its structural integrity best, with tensile strength remaining above 17.8 MPa (from an initial 18.8 MPa) after 1000 hours in 1 M acid.

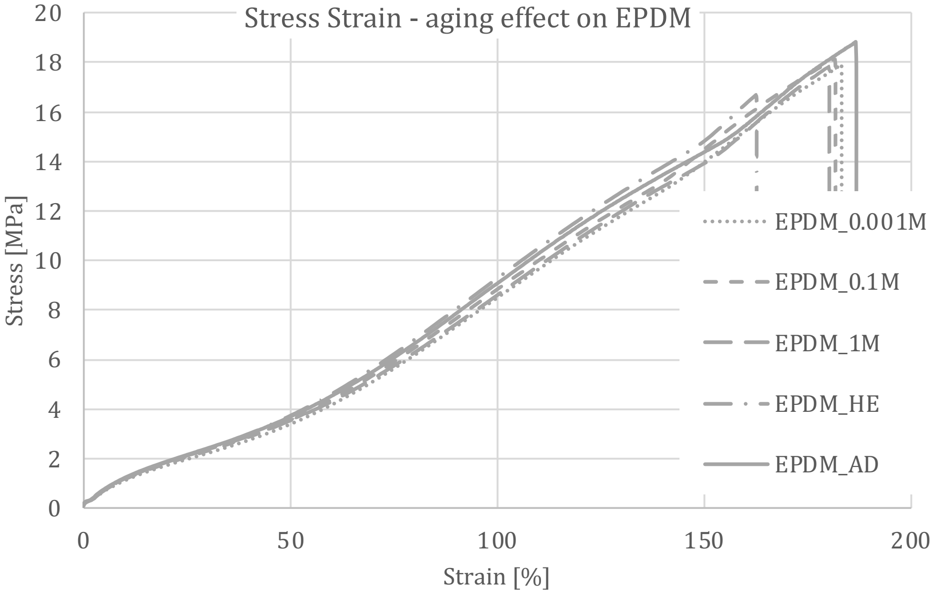

Figure 5.3. Stress–strain curves for EPDM-H under different aging conditions

In contrast, TPV and Eco TPV showed gradual strength loss. Eco TPV’s tensile strength dropped from 7.85 MPa to 7.15 MPa under mild acid exposure, reflecting degradation of the thermoplastic phase. However, elongation at break remained relatively stable for all materials, suggesting that the degradation mechanism primarily affects the load-bearing matrix rather than the extensibility of the elastomeric network.

5.2.3. Hardness and Compression Set

Hardness measurements revealed distinct aging trajectories.

TPV: Retained its hardness most effectively (less than 5% change), likely due to the high crystallinity of the PP phase, which resists softening.

Eco TPV: Suffered significant softening (15–20% decrease in Shore A), consistent with plasticization caused by absorbed acid.

EPDM-H: Showed moderate softening but excellent elastic recovery.

Compression-set tests (ISO 815-1A) highlighted EPDM-H’s superiority for static sealing. EPDM-H exhibited the lowest permanent deformation, whereas Eco TPV showed the highest compression set, indicating poor recovery after load removal — a critical flaw for long-term sealing reliability.

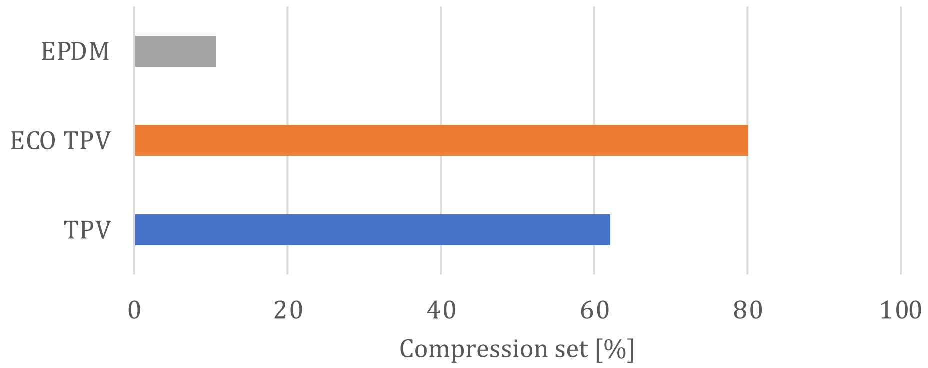

Figure 5.4. Compression-set values for EPDM-H, TPV, and Eco TPV

5.3 Sustainable ECO EPDM: The Impact of Circular vs. Recycled Filler

A pivotal finding of this thesis is the divergent performance of EPDM compounds reinforced with Circular Carbon Black (CCB) versus Recycled Carbon Black (RCB). Despite sharing the same base polymer, the filler origin dictated the material's chemical stability.

5.3.1. Swelling and Acid Resistance

RCB EPDM consistently swelled more than CCB EPDM. In 0.1 M H_2SO_4, RCB EPDM showed a weight increase of 6.30% compared to just 3.61% for CCB EPDM. This behavior is attributed to the higher heterogeneity, ash content, and surface polarity of the recycled filler, which facilitate water and acid uptake.

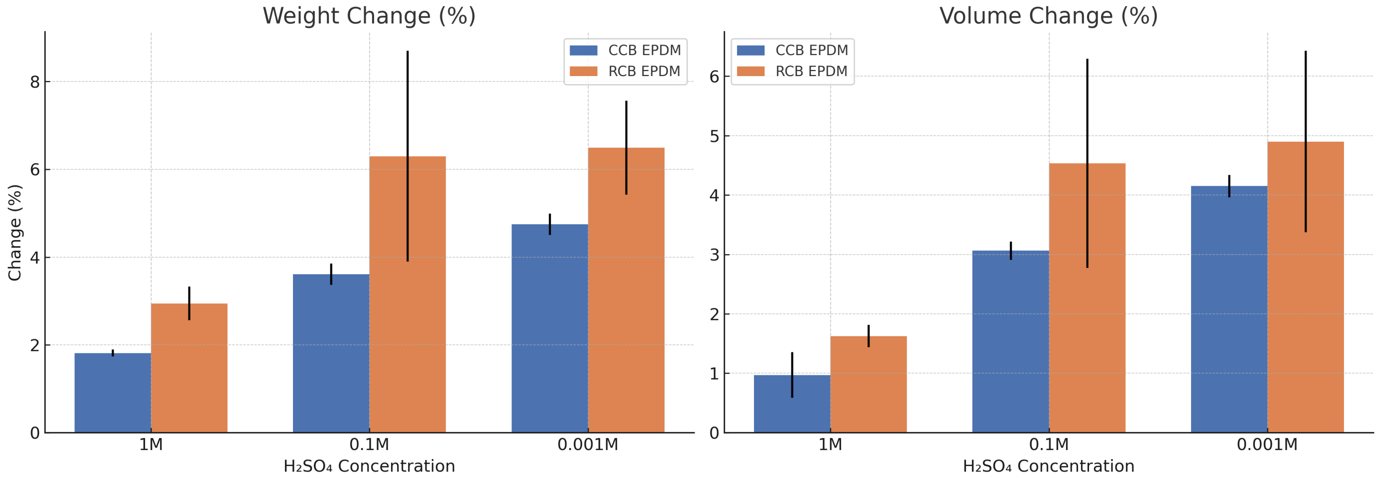

Figure 5.5. Weight and volume change of CCB EPDM and RCB EPDM

5.3.2. Leaching Behavior: Ionic and Organic Release

The potential for catalyst poisoning was assessed through leaching studies.

Ionic Leaching (HWET): RCB EPDM released ionic species much faster than CCB EPDM. The electrical conductivity of the extraction water for RCB EPDM exceeded the critical 5 µS/cm threshold within 48 hours, whereas CCB EPDM remained below this limit for nearly 100 hours.

pH Evolution: Immersion of RCB EPDM caused an alkaline drift (pH increase) in the acid solutions, suggesting the leaching of basic impurities such as metal oxides or ash from the recycled filler. Conversely, CCB EPDM induced a slight pH decrease or stability.

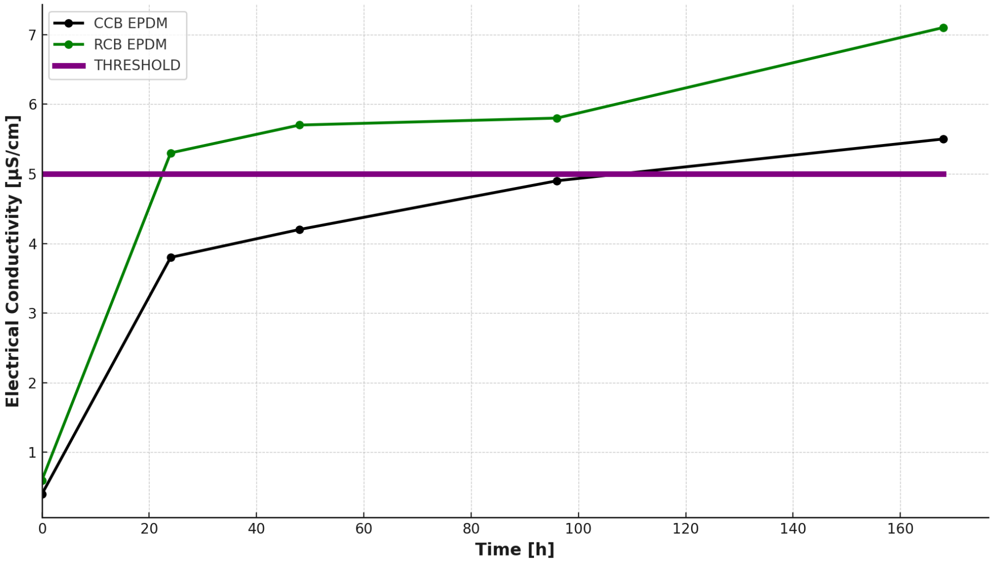

Figure 5.6. HWET result for CCB EPDM and RCB EPDM

Organic Leaching (HPLC): Chromatographic analysis (HPLC-DAD) detected significantly higher levels of organic leachates from RCB EPDM in mild to moderate acid concentrations. This confirms that the recycled filler introduces not only ionic impurities but also extractable organic compounds, such as residual oils and PAHs, that pose a contamination risk to the fuel cell membrane.

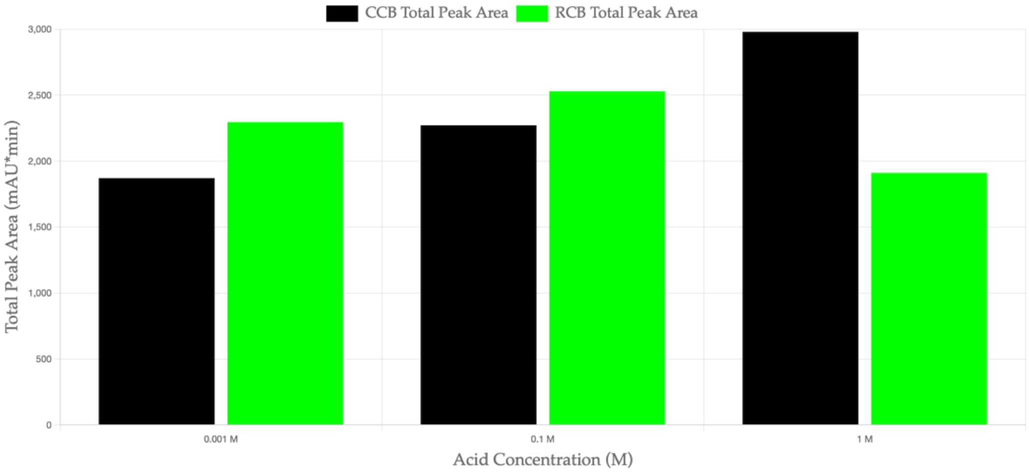

Figure 5.7. Total peak area of organic leachates from CCB and RCB EPDM

5.3.3. Mechanical Degradation of Sustainable Variants

While fresh RCB EPDM exhibited slightly higher initial stiffness, it suffered greater property loss upon aging. After 1000 hours in 1 M acid, RCB EPDM lost approximately 32% of its tensile strength and became noticeably brittle. CCB EPDM retained approximately 83% of its strength and maintained a smooth stress–strain response, demonstrating that circular carbon black can offer durability comparable to virgin fillers.

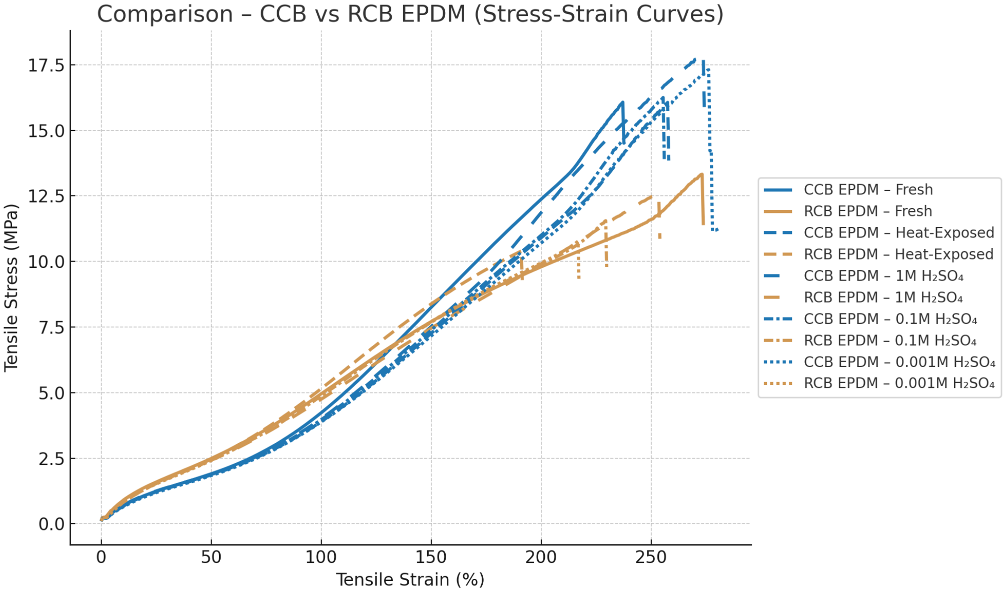

Figure 5.8. Comparative stress–strain behavior of CCB EPDM and RCB EPDM in aged states

5.4 Tribological Performance

For dynamic applications like the air control valve, friction and wear are defining performance metrics. The ball-on-disk tests against PA66GF30 revealed a clear trade-off.

3.4.1. Coefficient of Friction (CoF)

EPDM: Exhibited unstable friction behavior. The CoF increased with both load and sliding speed, rising from approximately 0.54 to over 0.83 at high speeds (0.15 m/s). This indicates a transition from adhesive friction to a deformation-dominated regime with significant thermal softening and stick-slip phenomena.

TPV: Demonstrated superior frictional stability. Its CoF remained lower (0.36–0.50) and less sensitive to velocity changes, particularly under higher loads (6 N). The thermoplastic matrix reduces adhesion and provides a lower-friction interface.

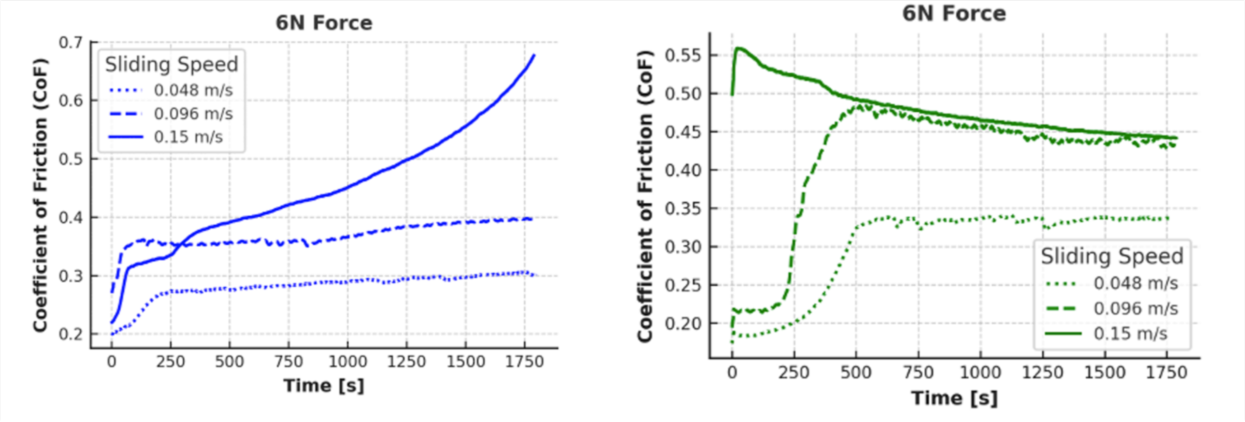

Figure 5.9. CoF vs. time for LF EPDM (blue) and LF TPV (green) at 6 N load

5.4.1. Wear Resistance

Wear volume calculations and mass loss measurements confirmed TPV's advantage in dynamic contacts.

- EPDM showed high specific wear rates, with broad wear tracks characterized by tearing, debris accumulation, and abrasive damage from the glass fibers in the counter-body.
- TPV exhibited significantly lower wear volumes and smoother, polished wear tracks.

The data suggests that TPV is the preferred candidate for dynamic seals where leak-tightness must be maintained during movement, while EPDM requires surface modification or lubrication to match this performance.

5.5 Finite Element Analysis (FEA) Calibration

To bridge the gap between material coupons and component design, experimental data was used to calibrate hyperelastic material models.

Model Selection:
The Arruda–Boyce model was identified as the most accurate constitutive law for capturing the nonlinear stress–strain behavior of the EPDM compounds. It provided a superior fit for both the initial stiffness and the large-strain hardening region compared to Mooney–Rivlin or Yeoh models.

Simulation of Seal Performance:
Using the calibrated Arruda–Boyce parameters, FEA simulations of a seal "push-in" assembly were performed. The simulations accurately predicted the insertion forces and contact pressure distribution, validating the experimental characterization. Specifically, the simulation highlighted the higher insertion resistance of TPV due to its higher stiffness, which correlates with the tribological findings.

5.6 Summary of Findings

The results collectively paint a detailed picture of material suitability for PEMFC applications:

- Static sealing: EPDM-H is the benchmark, offering unmatched chemical resistance and elastic recovery.
- Dynamic sealing: TPV excels in low-friction, low-wear applications but is vulnerable to acid attack.
- Sustainability: CCB EPDM (circular filler) is a viable, high-performance sustainable alternative. RCB EPDM (recycled filler) poses significant leaching and durability risks and requires higher purity standards before adoption in fuel cell stacks.

6 CONCLUSIONS

Chapter 6 points out the conclusions of this study and the personal contributions accomplished through this work.

The theoretical and experimental study realized in the context of this thesis addresses current tendencies in the development and manufacturing of sustainable sealing components for hydrogen mobility. The research focused on characterizing sustainable elastomeric materials, optimizing material selection for peripheral components in Proton Exchange Membrane Fuel Cell (PEMFC) systems, and evaluating their durability under simulated operating conditions.

In the current state of the art, sealing in PEMFC systems involves the use of specialized gaskets and O-rings made from synthetic rubbers, primarily EPDM, designed to withstand acidic environments, humid air, and temperature fluctuations. However, standard materials often rely on fossil-based feedstocks and virgin carbon black, contributing to a significant carbon footprint. Furthermore, the specific degradation behavior of thermoplastic vulcanizates (TPVs) and sustainable elastomers containing recycled fillers under the combined chemical, thermal, and tribological stresses of the cathodic air loop remained insufficiently characterized.

The present work dealt with the comprehensive characterization of functional elastomeric materials based on EPDM, TPV, and Eco-friendly variants (utilizing circular and recycled carbon black) using standardized aging and tribological testing methods. The study demonstrated that EPDM and its sustainable counterparts provide the necessary elasticity and chemical inertness for static sealing, while TPV variants offer distinct tribological advantages for dynamic applications. Moreover, the integrated testing approach provided a holistic view of material degradation, linking microstructural changes to macroscopic performance loss.

Personal Contributions

The original contributions of this study refer to:

Utilizing accelerated aging protocols (acidic immersion and thermal exposure) to evaluate the chemical stability of EPDM, TPV, and Eco-TPV functional materials under conditions relevant to the cathodic side of PEMFCs.

Validation of Circular Carbon Black (CCB) as a superior sustainable filler compared to Recycled Carbon Black (RCB). Experimental data proved that CCB-filled EPDM offers chemical and mechanical stability comparable to virgin materials, whereas RCB variants show higher swelling and leaching risks.

Advanced chemical characterization using High-Performance Liquid Chromatography (HPLC) and Hot Water Extraction Tests (HWET) to quantify organic and ionic leachates. This provided critical data on the risk of catalyst poisoning, often missing in standard material datasheets.

Comparative analysis of tribological behavior of low-friction EPDM and TPV against glass-fiber reinforced polyamide (PA66GF30), identifying TPV as a superior candidate for dynamic applications due to lower friction and wear.

Calibration of hyperelastic material models (Arruda-Boyce) based on experimental data to allow for accurate Finite Element Analysis (FEA) of sealing force retention and contact mechanics.

Correlation of mechanical, tribological, and chemical results to establish a rigorous selection methodology for functional sealing materials, ensuring a better understanding of component lifespan in the cathodic air circuit.

Specific Conclusions

Based on the experimental results, the following specific conclusions were drawn:

Material Stability: A careful selection of base polymers and filler systems was performed. EPDM-H was found to be the most chemically stable material, exhibiting the lowest volume change and mass uptake even after 1000 hours of immersion in 1 M sulfuric acid.

Thermoplastic Vulnerability: Eco TPV demonstrated the highest susceptibility to acid-induced swelling (over 6% mass increase), indicating the vulnerability of the thermoplastic phase to hydrolysis and oxidation. While TPVs offer processing advantages, their chemical resistance in acidic condensates is inferior to thermoset EPDM.

Impact of Filler Origin: Circular Carbon Black (CCB)–filled EPDM demonstrated superior stability compared to Recycled Carbon Black (RCB)–filled EPDM. RCB variants showed significantly higher swelling and microstructural degradation, attributed to the higher heterogeneity and impurity content of the recycled filler.

Leaching Risks: Leaching analysis via HPLC and conductivity measurements revealed that RCB EPDM releases significantly more ionic and organic species, particularly in the early stages of exposure. This indicates a higher risk for catalyst poisoning and membrane contamination compared to the cleaner CCB formulation.

Mechanical Retention: Mechanical testing confirmed that EPDM-H retains the highest tensile strength and elongation at break after aging. In contrast, TPV and Eco TPV experienced gradual strength loss due to the degradation of the polypropylene matrix.

Sealing Force: Compression-set results highlighted that EPDM-H offers the best elastic recovery, essential for static sealing. Eco TPV exhibited the highest permanent deformation, raising concerns about long-term sealing-force retention.

Tribological Performance: Investigations revealed a distinct trade-off. TPV maintained a more stable and lower coefficient of friction under high load and speed conditions, making it suitable for dynamic valve seals. EPDM exhibited friction escalation due to thermal softening and adhesive wear, resulting in higher material loss at high PV factors.

Simulation: The Arruda–Boyce hyperelastic model was identified as the most accurate constitutive model for simulating the mechanical response of these elastomers in finite-element analysis, providing a reliable tool for predictive seal design.

Outlook

The theoretical and experimental study highlights current tendencies in the development of sustainable sealing components for hydrogen mobility. While EPDM remains the gold standard for chemical resistance, sustainable alternatives using circular fillers show great promise.

Future research directions include:

- Further optimization of Eco-EPDM formulations by investigating different loadings of circular carbon black to maximize mechanical performance.
- Experimental testing of these materials in an active fuel-cell stack to validate the leaching impact on actual electrochemical performance (OCV decay, voltage loss).
- Characterization of the long-term fatigue behavior of these elastomers under combined mechanical cycling and chemical exposure.
- Assessment of the influence of hydrogen gas permeation at high pressures (700 bar) on the structural integrity of sustainable EPDM variants.

7 SELECTIVE BIBLIOGRAPHY

1. International Energy Agency World Energy Investment 2024 2024.
2. BloombergNEF Energy Transition Investment Trends 2024 2025.
3. Chart: Global Investment in the Energy Transition… | Canary Media Available online: https://www.canarymedia.com/articles/clean-energy/chart-global-investment-in-the-energy-transition-surpasses-2t?utm_source=chatgpt.com (accessed on 30 October 2025).
4. Proton Exchange Membrane Fuel Cell Market Size, Trends, Share, Demand 2034 Available online: https://www.zionmarketresearch.com/report/proton-exchange-membrane-fuel-cell-market?utm_source=chatgpt.com (accessed on 30 October 2025).
5. PEM Fuel Cell Market Share, 2034 Statistics Report Available online: https://www.gminsights.com/industry-analysis/pem-fuel-cell-market?utm_source=chatgpt.com (accessed on 30 October 2025).
6. Energy; Directory, S. Fuel Cell Degradation Mechanisms 2024.
7. Hinds, G. Performance and Durability of PEM Fuel Cells: A Review; Teddington, Middlesex, United Kingdom, 2004;
8. Luo, C.; Choo, H.L.; Ahmad, H.; Sivasankaran, P.N. Towards Enhanced Durability: A Review of Fuel Cell Electric Vehicle Development. Next Energy 2025, 9, 100399, doi:10.1016/j.nxener.2025.100399.
9. Rangel, C.M.; Silva, R.A.; Travassos, M.A.; Paiva, T.I.; Fernandes, V.R. Fuel Starvation: Irreversible Degradation Mechanisms in PEM Fuel Cells. In Proceedings of the Proceedings of the 18th World Hydrogen Energy Conference (WHEC 2010); Essen, Germany, May 2010.
10. Global Investment in the Energy Transition Exceeded $2 Trillion for the First Time in 2024, According to BloombergNEF Report | BloombergNEF Available online: https://about.bnef.com/insights/finance/global-investment-in-the-energy-transition-exceeded-2-trillion-for-the-first-time-in-2024-according-to-bloombergnef-report/?utm_source=chatgpt.com (accessed on 30 October 2025).
11. International Energy Agency Global Hydrogen Review 2024 2024.
12. Council, H. Hydrogen: Scaling Up — A Sustainable Pathway for the Global Energy Transition; 2017;
13. Europe, H. CO_2 Emission Standards for Heavy-Duty Vehicles — Position Paper; 2023;
14. Analysis, I. In 2030, over 45 000 Heavy Trucks Will Run on Hydrogen in Europe 2023.
15. MobilityPortal.eu EU CO_2 Reduction Targets for Trucks and Buses 2024.
16. Commission, E. Heavy-Duty Vehicles – Transport Decarbonisation 2025.
17. Mechanical Durability of PEM Fuel Cells | Encyclopedia MDPI Available online: https://encyclopedia.pub/entry/25697 (accessed on 3 September 2025).
18. Foltuț, D.; Șerban, V.A. Mechanical Performance Degradation of ECO EPDM Elastomers in Acidic Fuel Cell Environments. Materials 2025, 18, doi:10.3390/ma18092071.
19. Pehlivan-Davis, S. POLYMER ELECTROLYTE MEMBRANE (PEM) FUEL CELL SEALS DURABILITY, Lounghborough University, 2016.
20. Foltuț, D.; Șerban, V.-A. Current Advancements in the Behavior Analysis of EPDM Elastomers in Peripheral Applications of the Cathodic Side of PEMFC Systems. Recent Prog Mater 2024, 06, 1–27, doi:10.21926/rpm.2404026.
21. Foltuț, D.; Șoșoi, G.-I.; Vălean, E.; Pospisil, J.; Pascal, D.-T.; Șerban, V.-A. Impact of Aging on Tensile Properties of EPDM, TPV, and Eco-TPV: A Comparative Study Across Diverse Environments. IOP Conf Ser Mater Sci Eng 2024, 1319, 012022, doi:10.1088/1757-899X/1319/1/012022.
22. Foltuț, D.; Uțu, I.-D.; Șerban, V.-A. Tribological Performance of EPDM and TPV Elastomers Against Glass Fiber-Reinforced Polyamide 66 Composites. Materials 2025, Vol. 18, Page 2515 2025, 18, 2515, doi:10.3390/MA18112515.
23. M.A., W.R.G.Esq. XXIV. On Voltaic Series and the Combination of Gases by Platinum. The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science 1839, 14, 127–130, doi:10.1080/14786443908649684.
24. Barak, M. Fuel Cells—Present Position and Outstanding Problems. Advanced Energy Conversion 1966, 6, 29–55, doi:10.1016/0365-1789(66)90011-7.
25. Niedrach, L.W.; Grubb, W.T. Ion Exchange Membrane Fuel Cells. Fuel cells. Academic, New York 1963, 253–298.

26. Peron, J.; Mani, A.; Zhao, X.; Edwards, D.; Adachi, M.; Soboleva, T.; Shi, Z.; Xie, Z.; Navessin, T.; Holdcroft, S. Properties of Nafion® NR-211 Membranes for PEMFCs. J Memb Sci 2010, 356, 44–51, doi:10.1016/j.memsci.2010.03.025.
27. Zhao, J.; Tu, Z.; Chan, S.H. Carbon Corrosion Mechanism and Mitigation Strategies in a Proton Exchange Membrane Fuel Cell (PEMFC): A Review. J Power Sources 2021, 488, 229434, doi:10.1016/J.JPOWSOUR.2020.229434.
28. Hong, B.K.; Kim, S.H. Recent Advances in Fuel Cell Electric Vehicle Technologies of Hyundai. ECS Trans 2018, 86, 3–11, doi:10.1149/08613.0003ecst.
29. Ramani, V.; Kunz, H.R.; Fenton, J.M. The Chalkboard: The Polymer Electrolyte Fuel Cell. Electrochem Soc Interface 2004, 13, 17.
30. Larminie, J.; Dicks, A.; McDonald, M.S. Fuel Cell Systems Explained; J. Wiley Chichester, UK, 2003; Vol. 2;.
31. Sery, J.; Leduc, P. Fuel Cell Behavior and Energy Balance on Board a Hyundai Nexo. International Journal of Engine Research 2022, 23, 709–720, doi:10.1177/14680874211059046.
32. Technologies, V. Stack Control Valve (SCV) – One-Pager 1.4 (ENG); 2025;
33. Qiu, D.; Liang, P.; Peng, L.; Yi, P.; Lai, X.; Ni, J. Material Behavior of Rubber Sealing for Proton Exchange Membrane Fuel Cells. Int J Hydrogen Energy 2020, 45, 5465–5473, doi:10.1016/J.IJHYDENE.2019.07.232.
34. Schulze, M.; Knöri, T.; Gülzow, E. Interaction of Sealing Materials with the Proton Exchange Membrane Fuel Cell Environment. J Power Sources 2004, 127, 213–221, doi:10.1016/j.jpowsour.2003.09.016.
35. Xu, Q.; Zhao, J.; Chen, Y.; Liu, S.; Wang, Z. Effects of Gas Permeation on the Sealing Performance of PEMFC Stacks. Int J Hydrogen Energy 2021, 46, 36424–36435, doi:10.1016/J.IJHYDENE.2021.08.137.
36. Costa, S.M.R.; Fowler, D.; Carreira, G.A.; Portugal, I.; Silva, C.M. Production and Upgrading of Recovered Carbon Black from the Pyrolysis of End-of-Life Tires. Materials 2022, 15.
37. bin Samsuri, A. Evaluation of Recycled Carbon Black (r-CB) Based on Styrene Butadiene Rubber, Natural Rubber and Nitrile Rubber Compounds. In Application and Characterization of Rubber Materials; IntechOpen, 2023.
38. Surehali, S.; Singh, A.; Biligiri, K.P. A State-of-the-Art Review on Recycling Rubber in Concrete: Sustainability Aspects, Specialty Mixtures, and Treatment Methods. Developments in the Built Environment 2023, 14, doi:10.1016/j.dibe.2023.100171.
39. Tan, J.; Chao, Y.J.; Van Zee, J.W.; Li, X.; Wang, X.; Yang, M. Assessment of Mechanical Properties of Fluoroelastomer and EPDM in a Simulated PEM Fuel Cell Environment by Microindentation Test. Materials Science and Engineering: A 2008, 496, 464–470, doi:10.1016/J.MSEA.2008.05.052.