Developing PFAS compliant Elastomeric Materials for Hydrogen Service: Addressing Diffusivity with 2D Nanomaterial Reinforcement

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1. Introduction

The global transition toward a low-carbon energy system has accelerated the search for scalable, clean energy carriers capable of supporting future industrial, transportation and power-generation demands. A recent publication by the World Economic forum on transforming energy demand reported that the net global energy demand is expected to increase by 8% - 33% by 2050, although this would not be met by even tripling the current renewable energy sources to meet adequate sustainable energy, it eventually mounts the pressure on global economies, mainly the OECD countries to work on energy efficiencies and push for greener technologies to honour the Paris agreement. Among the technologies emerging from this shift, hydrogen has gained significant prominence due to its high energy density, broad applicability across sectors, and its potential to substantially reduce greenhouse-gas emissions when produced from renewable or low-carbon pathways. As nations outline strategic roadmaps to decarbonise heavy industry, mobility and heating, hydrogen is increasingly positioned as a cornerstone of future energy infrastructure. This rapid momentum has stimulated parallel growth in the technologies required to produce, transport, store and utilise hydrogen safely and efficiently.

However, hydrogen's unique physical properties—including its low molecular weight, high diffusivity, and capacity to permeate and embrittle materials—pose stringent demands on the selection and design of engineering components. Elastomers are among the most critical materials in this context, serving as seals, gaskets, membranes and hoses throughout the hydrogen value chain. Their ability to maintain flexibility, integrity and low permeability under conditions of high pressure, rapid decompression and sub-zero temperatures are essential for preventing leakage and ensuring operational safety. Yet conventional rubber formulations often suffer from hydrogen-induced swelling, blistering and cracking, particularly under cyclic pressure exposures or in low-temperature service. As the hydrogen economy expands, the limitations of existing elastomers have become increasingly evident, revealing a need for materials engineered specifically for hydrogen environments. While qualification methods have historically been borrowed from the oil and gas sector—such as rapid gas decompression (RGD) testing—there remains no unified or application-specific standard for hydrogen-service elastomers. Moreover, the shift toward operating pressures up to 100 MPa and temperatures sub –50°C introduces challenges that conventional recipes and filler systems are not designed to withstand. This has created a significant materials-development gap at a time when industries urgently require reliable sealing solutions to support the deployment of hydrogen technologies.

This paper examines the formulation, performance requirements and material-selection strategies necessary for developing elastomeric compounds tailored for low-temperature hydrogen service. Through an understanding of hydrogen–rubber interactions, permeation and decompression mechanisms, compounding principles and test methodologies, this work aims to support the creation of safer, more durable materials for next-generation hydrogen systems. As the sector moves toward wider industrialisation, advances in elastomer technology will be essential to enabling robust hydrogen infrastructure and unlocking the full potential of a clean-energy hydrogen economy.

2. Understanding the Challenges

Hydrogen being one of the smallest molecules pose a high level of permeation and swelling within any materials, particularly elastomers. While this presents a significant challenge by increasing the risks of swelling and diffusion, it can also offer advantages in high-pressure and rapid decompression environments.

Figure 1: Samples with Fractures caused due to Rapid Gas Decompressions (RGD)

In certain cases, elastomers exposed to hydrogen may avoid the fracture patterns typically observed with larger gas molecules such as CO_2 or CH_4, which are commonly evaluated in Oil & Gas qualification testing. Another key challenge relates to the extreme service temperatures associated with hydrogen applications. Current industry demand increasingly requires reliable performance at temperatures as low as –50 °C and below. Although cryogenic conditions (< –120 °C) fall well outside the operational limits of elastomeric materials, and therefore outside the scope of this study, they underscore the severity of the environments being considered.

Additional challenges include the emerging regulatory landscape—particularly proposed PFAS restrictions, which may limit the use of fluor polymers such as FKM. High-pressure hydrogen systems also necessitate robust resistance to Rapid Gas Decompression (RGD). Furthermore, a lack of service-validated test methodologies tailored specifically to hydrogen environments continues to complicate material selection and qualification.

3. Experimental Approach

To develop new materials capable of meeting low-temperature hydrogen service requirements and to address the challenges from a materials-performance perspective, we first benchmarked our current commercial elastomer grades, which are already deployed globally in demanding RGD applications. Building on this baseline, several next-generation formulations were produced, including new FKM compounds manufactured using non-fluoro surfactant technology, FKM materials incorporating graphene dispersions, and Clwyd-IP EPDM formulations designed for enhanced extreme low-temperature capability. The specific material iterations assessed in this study are listed in Table 1. A target hardness of 90 IRHD was selected for all compounds to enable consistent comparison.

Table 1:

Clwyd RGD Grade Materials	Next Generation materials
FFKM	FKM
FKM (Copolymer)	NFS FKM + Graphene
FKM LT	EPDM
AFLAS	EPDM + Graphene
EPDM	LT EPDM + Graphene
NBR	HNBR + Graphene
HNBR	FFKM LT + Graphene

Each material underwent a comprehensive characterisation programme, including tensile and tear testing (tensile strength, 100% modulus, elongation at break, and tear resistance), compression set

and heat-ageing evaluations under conditions tailored to the polymer type, and determination of glass transition temperature via Differential Scanning Calorimetry (DSC). Additional low-temperature performance analysis was performed using the Gehman torsional method, reporting the temperature corresponding to a torsional stiffness of 70 MPa. Hydrogen permeation was measured in accordance with ISO 15105-1 after steady-state conditions were established. Finally, rheological behaviour relevant to processing and mould-flow characteristics was assessed using a Rubber Process Analyser (RPA) via a frequency sweep at 100 °C and 2.8% strain.

4. Results & Analysis

4.1 *Clwyd's benchmark materials*

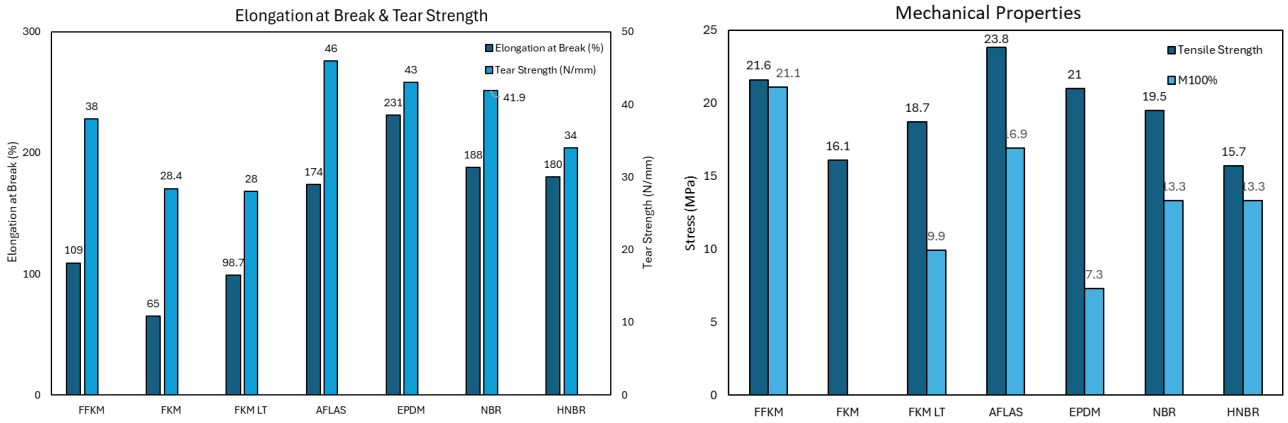

Figure 2: Tensile properties and Tear Strength of the Benchmarking RGD Clwyd Materials

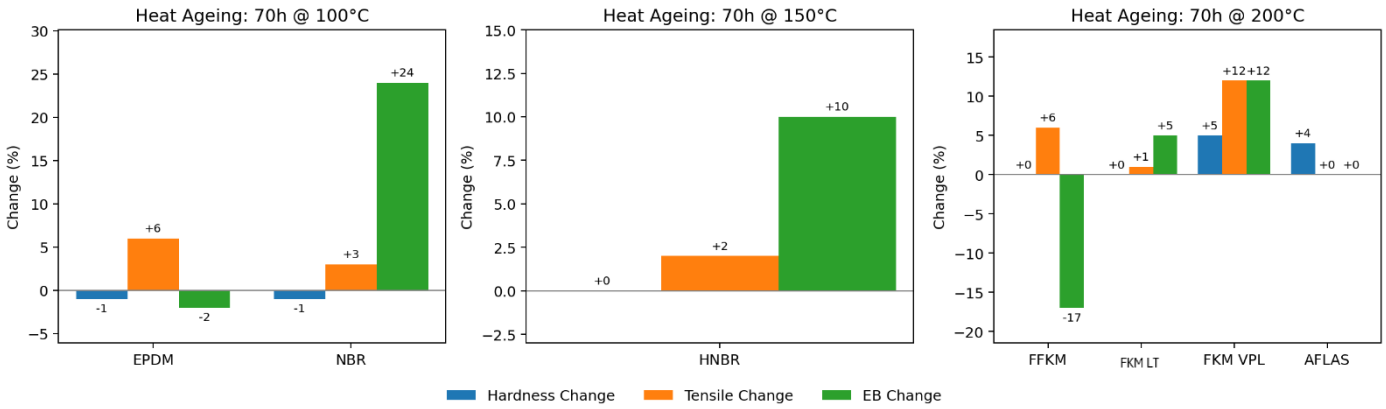

Figure 3: Heat Ageing properties of Benchmarking materials

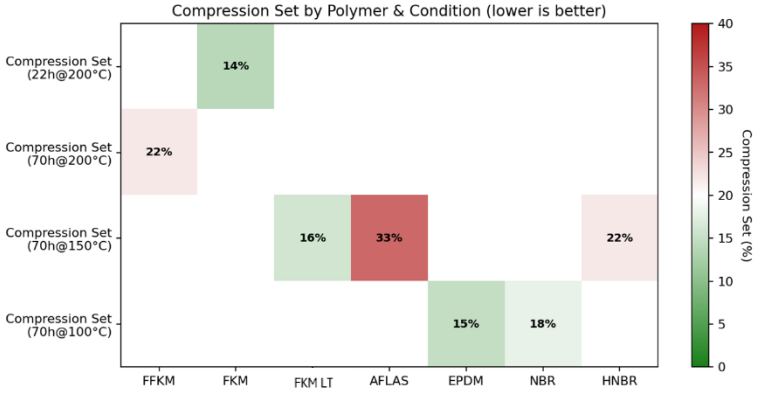

Figure 4: Compression set properties of Benchmarking materials

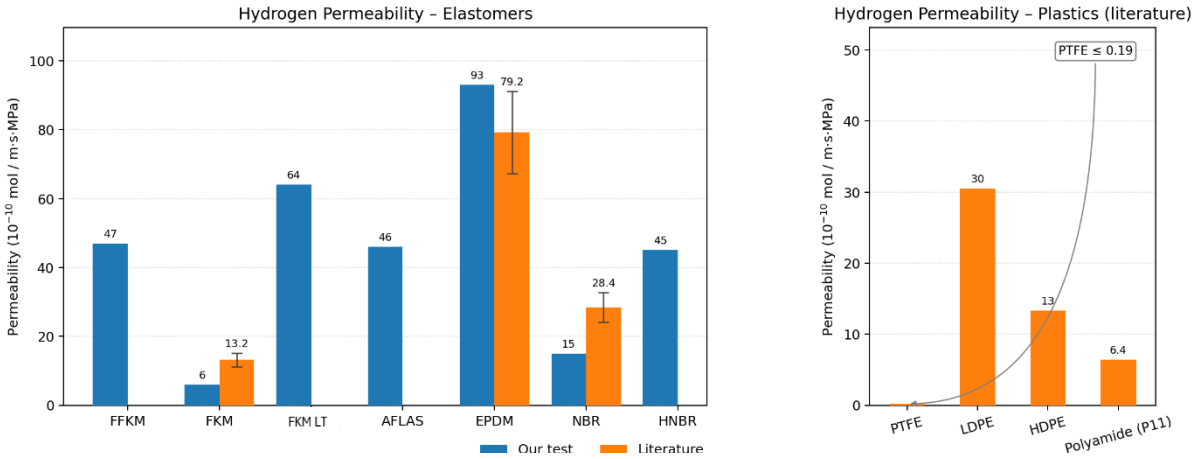

Figure 5: H_2 Permeation tested on materials

The materials, being relatively high-hardness elastomers with carefully tailored filler loadings, polymer architectures, and crosslink densities, exhibit the expected high modulus and strong heat-ageing resistance characteristic of RGD-qualified compounds. Selection of a suitable formulation ultimately depends on the specific service environment, including operating temperature range, the fluids in contact, and processing requirements. Compression-set behaviour likewise varies with polymer type and formulation, reflecting the differing thermal stability and chemical resistance inherent to each base polymer. Across the tested materials, FKM demonstrates the lowest hydrogen permeation rate, outperforming NBR and the other elastomers evaluated. These material iterations were chosen to align with current industrial offerings for high-pressure hydrogen systems, where high-temperature capability and chemical compatibility are also critical performance drivers. When benchmarked against previously reported literature values [1–3], the Clwyd materials show superior hydrogen-barrier performance, influenced strongly by polymer family, filler loading, and crosslink density; notably, FKM ranks only behind PTFE, widely regarded as one of the best-performing materials for hydrogen service.

As illustrated in Figure 5, polymer selection has a significant impact on diffusion behaviour: despite all being fluoro-polymers, FKM copolymer demonstrate better performance than FFKM, low-temperature-grade FKMs, or AFLAS (FEPM). While the favourable diffusion performance of fluoro-elastomers supports their continued use, the emerging PFAS regulatory landscape highlights the need to further accelerate the development of alternative materials for future hydrogen applications.

4.2 *Next generation Materials*

PFAS (per- and polyfluoroalkyl substances) are broadly defined as materials containing at least one fully fluorinated methyl (–CF_3) or methylene (–CF_2–) carbon atom. Although often described as “forever chemicals,” their exceptional chemical resistance and inert behaviour have historically made them highly valuable in sealing applications, particularly in environments involving corrosive or otherwise aggressive media. However, low molecular-weight PFAS species can persist in the environment, leading to bioaccumulation and associated risks to living organisms, including humans. While high-molecular-weight fluoro-polymers themselves are not considered bioaccumulative, their conventional manufacture relied on low molecular-weight fluorinated surfactants, which have raised environmental and regulatory concerns. In response, modern fluoro-polymers are now produced using non-fluorinated surfactant technologies, making them strong candidates for compliance with the ongoing PFAS restriction proposals under consideration by ECHA.

Clwyd has evaluated a new generation of non-fluoro-surfactant FKMs, further enhanced through the incorporation of two-dimensional nanomaterial dispersions within the elastomer matrix. Graphene, when effectively dispersed, is known to create a tortuous diffusion pathway, thereby reducing permeation of gases and fluids through the material. In this study, graphene was introduced at a 5 wt% loading into our existing high-performance RGD-qualified grades to assess whether diffusion behaviour could be further improved, with performance compared directly against the original compounds. The full set of material iterations is presented in Table 1. Additional formulations include Clwyd's previously developed low-temperature EPDM grades, engineered for exceptional flexibility at very low temperatures, which were also modified with graphene to enhance hydrogen-barrier performance. These EPDM-based materials are intended as potential alternatives to VMQ for applications requiring reliable sealing below –60 °C.

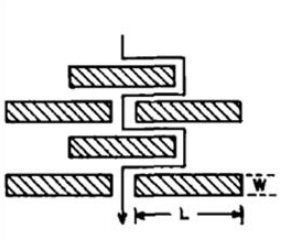

Figure 6: Schematic of Graphene creating Tortuous pathway

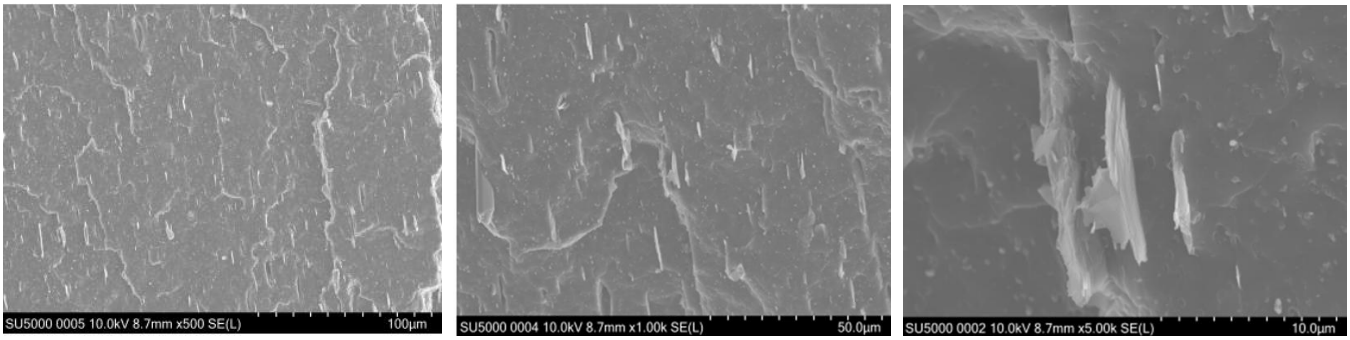

Figure 7: SEM images of Graphene dispersion in Clwyd rubber matrix.

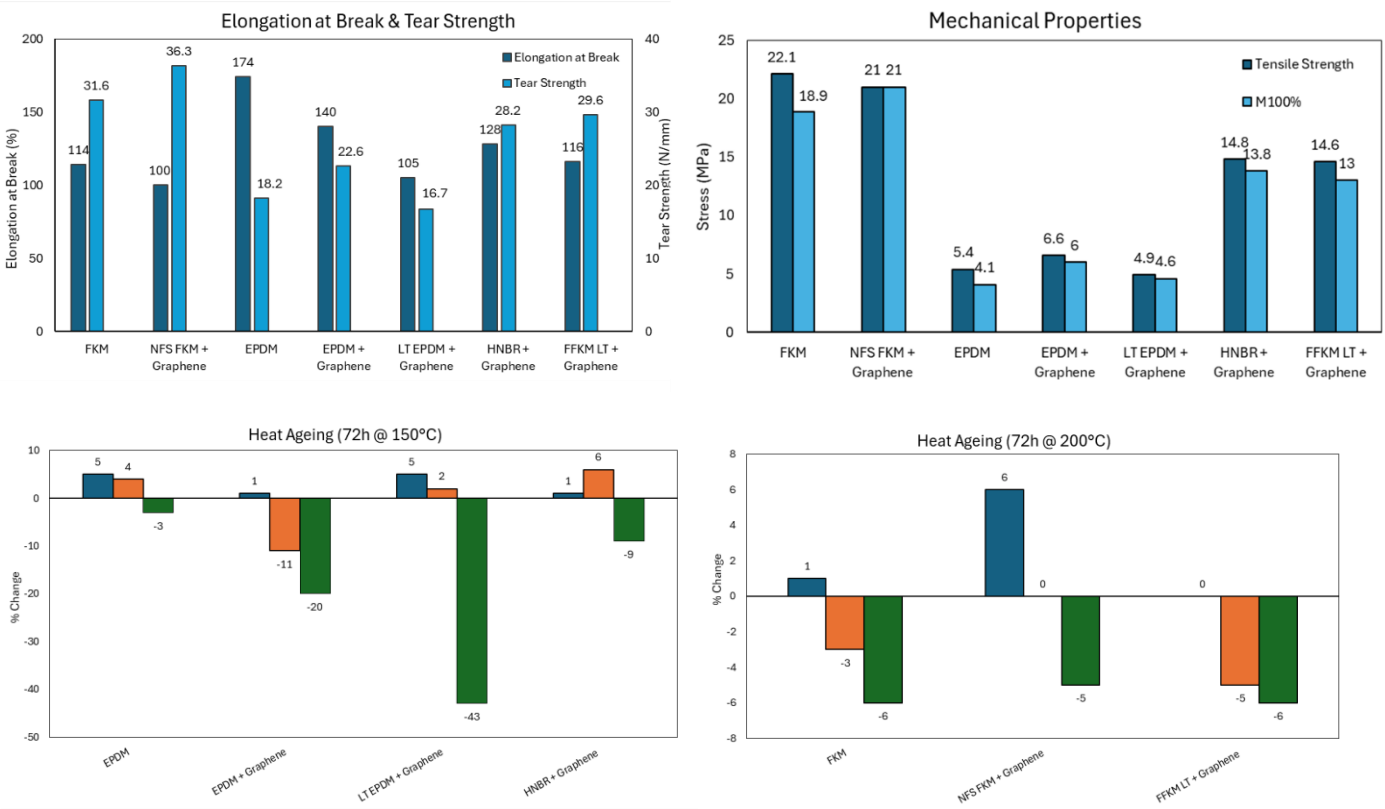

Figure 8& 9: Tensile and Heat Ageing properties

SEM imaging confirms that the graphene is uniformly and effectively dispersed within the elastomer matrix. Achieving good dispersion is essential, as it enables the formation of a tortuous diffusion pathway that enhances the material's barrier properties. Both the grade of graphene selected and the mixing protocol employed play a critical role in obtaining this level of dispersion. As shown in Figure 8, the graphene-modified materials exhibit notable improvements in tensile strength and tear resistance, particularly within the FKM and EPDM formulations. This enhancement is likely due to the localized graphene domains restricting crack propagation through the matrix. A slight reduction in elongation at break is observed across all graphene-containing compounds compared with their respective controls, which correlates with the corresponding increase in 100% modulus associated with graphene reinforcement.

When evaluating the heat-ageing performance of the graphene-modified materials relative to their control compounds, a slight increase in the change in elongation at break is observed—consistent with the behaviour previously noted for these formulations. Overall, however, the mechanical properties after ageing remain broadly comparable between the graphene-filled and control materials and can be further optimised through formulation adjustments. Among the polymers tested, FKM shows the least sensitivity to graphene incorporation under heat-ageing conditions. Compression-set results (Figure 10) indicate a modest increase in compression set for the graphene-containing compounds compared with their respective controls, suggesting that while graphene enhances strength-related properties, it may slightly stiffen the network under compressive strain.

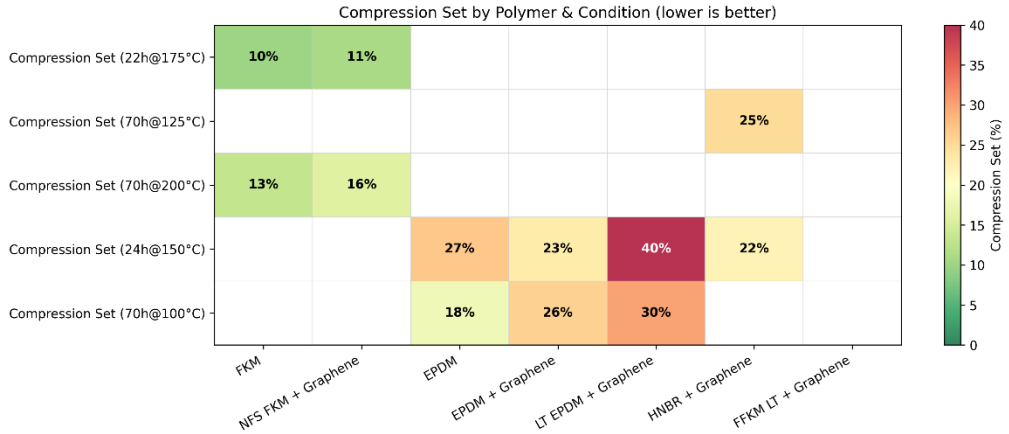

Figure 10: Compression set properties

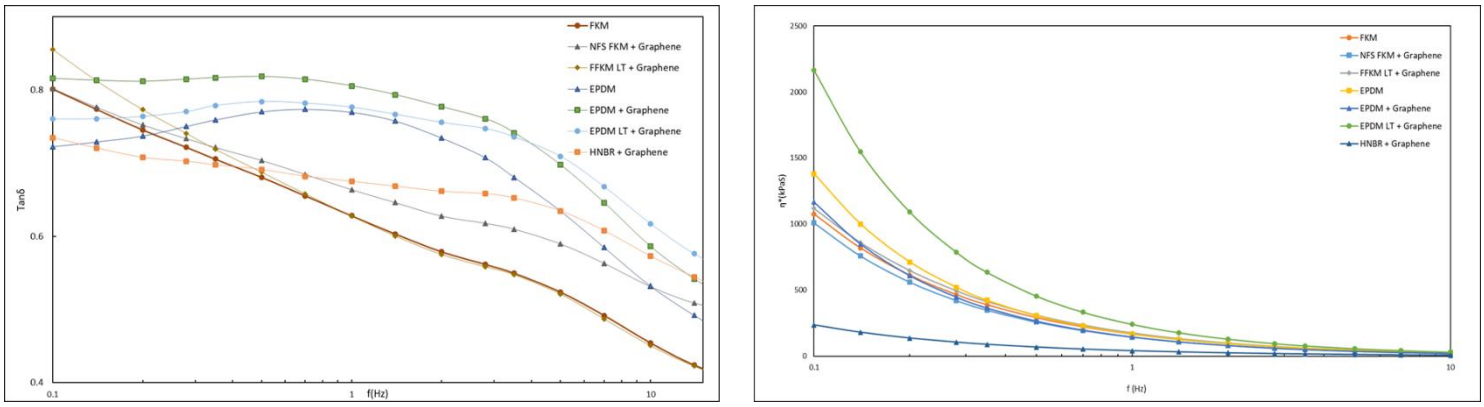

Figure 11: Frequency sweep vs Tan δ and Complex viscosity (η). From RPA at 100°C, 2.8%*

Ensuring good processability is essential when developing new elastomer formulations, particularly with respect to extrusion behaviour and mould flow, so that the materials remain industrially viable. To evaluate these characteristics, the compounds were analysed using a Rubber Process Analyser (RPA) through a strain-sweep test, assessing changes in tan δ and complex viscosity (η*). A higher tan δ at lower frequencies is generally indicative of improved processability, while a lower complex viscosity in the same frequency range reflects enhanced flowability within a mould.

From Figure 11, it can be observed that the graphene-modified materials exhibit tan δ values comparable to those of the control compounds, indicating similar viscoelastic behaviour under processing-relevant conditions. A comparable trend is also seen in the complex viscosity data. Notably, the graphene-containing formulations show slightly lower complex viscosities, which can be

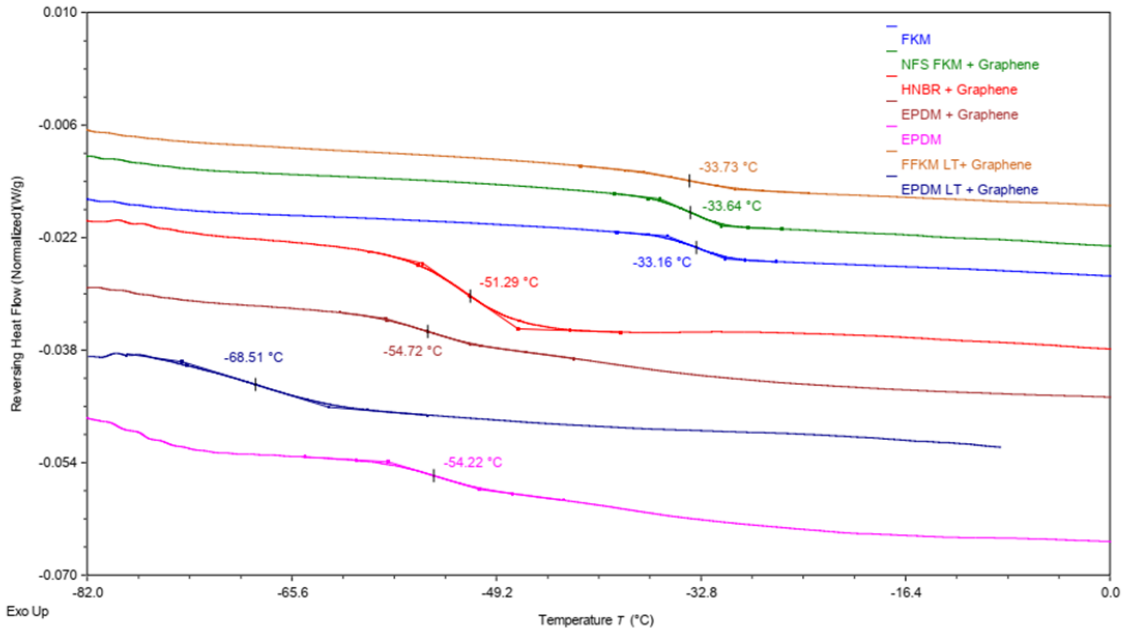

Figure 12: DSC sweep and Glass transition temperatures (Tg) of materials.

attributed to the effective dispersion of graphene within the elastomer matrix. This reduction in η* supports improved flow characteristics, confirming that these materials remain industrially processable while still delivering the enhanced performance benefits associated with graphene incorporation.

Table 2

Materials	°C at 70 MPa Torsional Mod
FKM	-33.16
NFS FKM + Graphene	-33.64
EPDM	-40.7
EPDM + Graphene	-38.6
LT EPDM + Graphene	-54.8
HNBR + Graphene	-35.5
FFKM LT + Graphene	-26.3

Analysis of the glass transition temperatures shows that Clwyd's low-temperature EPDM exhibits a Tg of –68.5 °C, significantly lower than that of standard EPDM grades, which typically demonstrate a Tg around –55 °C. These specialised formulations were selected to optimise low-temperature performance across the elastomer portfolio, a trend that can also be observed for FKM, FFKM and HNBR materials included in this study. Importantly, the incorporation of graphene does not appear to influence the Tg of any of the compounds, indicating that the nanomaterial reinforcement affects mechanical and barrier properties without altering the fundamental thermal transition behaviour of the polymers.

Additional low-temperature performance was assessed using the Gehman torsional test, which measures the change in a material's torsional stiffness as temperature decreases. The temperature at which the torsional modulus reaches 70 MPa is commonly used as a practical indicator of low-temperature elasticity. As shown in Table 2, Clwyd's low-temperature EPDM achieves a torsional modulus temperature of –54.8 °C, significantly outperforming standard EPDM grades, which typically fall within the –38 °C to –35 °C range. These results further demonstrate the potential of these optimised EPDM materials to serve as viable alternatives to VMQ in certain hydrogen applications requiring reliable performance at sub-zero temperatures.

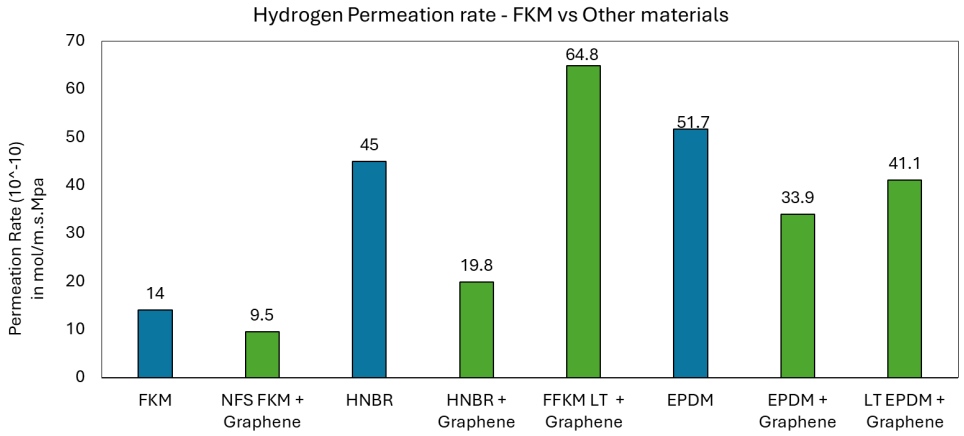

Figure 13: H_2 Permeation rates from ISO 15105-1 test.

Figure 13 presents the hydrogen permeation rates for the next-generation material grades, clearly showing that the incorporation of graphene enhances barrier performance across all polymer systems evaluated. This improvement is consistent with the expected mechanism, whereby well-dispersed graphene creates a tortuous diffusion pathway that restricts gas transport through the elastomer matrix. Quantitatively, the addition of graphene reduces permeation by approximately 31% in FKM, 34% in EPDM, and 56% in HNBR compared with their respective control formulations. Although the Clwyd IP low-temperature EPDM employs an alternative base formulation, it still demonstrates a meaningful improvement in permeation performance, with a 20% reduction relative to its control material.

5. Conclusions

From the results analysed across the next-generation material formulations, it is evident that elastomers originally tailored for high-pressure Rapid Gas Decompression (RGD) service—and validated under such conditions—also demonstrate strong potential for hydrogen applications. Their suitability, however, remains highly dependent on the specific demands of the end-use environment, including service temperature, media compatibility, and chemical exposure. The newly developed non-fluoro-surfactant FKM grades show performance comparable to current commercial FKMs, consistent with findings from earlier studies, and the incorporation of graphene further enhances their hydrogen permeation resistance.

The improved barrier performance observed in the graphene-containing compounds aligns with SEM evidence confirming effective dispersion of graphene within the matrix, enabling the formation of a tortuous diffusion pathway. Beyond permeation, graphene reinforcement also contributes to increased tear strength, modulus, and tensile properties, likely due to its ability to inhibit local crack initiation and propagation. Importantly, these enhancements are achieved without compromising

processability, as demonstrated by RPA measurements, exhibit improved mould-flow characteristics.

Clwyd's low-temperature EPDM innovation shows a Tg of –68 °C, positioning it as a strong candidate to replace VMQ in hydrogen sealing applications, particularly where both low-temperature elasticity and superior chemical resistance are required. Collectively, these results highlight the potential of advanced elastomer formulations—especially graphene-modified and non-fluoro-surfactant fluoro-elastomers—to meet the evolving demands of hydrogen systems, from extreme temperatures to stringent permeation requirements.

6. Future studies

Continuing this evaluation, we are advancing the work through a collaborative Innovate UK–funded project with the University of Manchester and the Henry Royce Institute. This effort involves assessing the permeation performance of the developed materials using a bespoke test system capable of operating from –30 °C to +200 °C and at pressures up to 200 bar. This setup enables systematic investigation of the effects of temperature, pressure, and decompression rate on material behaviour, allowing us to evaluate performance under conditions that more closely replicate real-world field applications.

7. References

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