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Polymers and composites for hydrogen economy: a perspective

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Abstract
This paper provides authors' perspective on the current advances and challenges in utilising polymers and composites in hydrogen economy. It has originated from '*Polymers and Composites for Hydrogen Economy*' symposium organised in March 2025 at the University of Warwick. This paper presents views from the event and thus provides a perspective from academia and industry on the ongoing advances and challenges for those materials in hydrogen applications.

Keywords Polymers, Composites, Hydrogen economy, Hydrogen transport, Hydrogen storage

Introduction

Search for alternative and sustainable energy resources to satisfy increasing world energy demands and address global climate changes, drives the transition to infrastructure for renewable and alternative fuel energy sources. Hydrogen has been considered as an important energy carrier that can contribute to alternative energy sources [1]. While political and socio-economical challenges will play a key role in future exploitation of hydrogen in the energy sector, the specific role and contribution of hydrogen will also rely upon the infrastructure used for production, transport, storage and propulsion with hydrogen. The properties of engineering materials used to manufacture future hydrogen infrastructure will be one of key enablers of hydrogen economy.

Metallic materials have probably been the most studied for hydrogen transport (pipelines) and storage (tanks) applications, but can suffer from several issues when interacting with hydrogen such as hydrogen embrittlement [2]. Polymer-based materials and their composites have attracted significant attention because of their good chemical resistance, lightweightness, and flexibility in manufacturing various designs and geometries. In the following, we will provide our perspective on recent advances with those materials in hydrogen transport and storage, and remaining challenges that need to be addressed including *hydrogen emission regulations*, *structural integrity*, *sealing challenges*, *experimental testing challenges*, and *predictive modelling*.

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Polymers and composites for hydrogen transport via pipeline networks

The primary role of the so called transportation pipeline is a cost-effective (i.e. cost per mile) transport method [3] to deliver high volumes to the end user (industry, heating, power, transportation) especially when significant transportation distances are considered. Those large pressure and large diameter pipelines differ from so called distribution pipelines (small pressure and small diameter) that serve small end-user customers. In 2024, around 5,000 km of onshore hydrogen pipelines have been in operation, mainly in Europe and the US, with further plans to reach, for example 31,000 km of pan-European hydrogen pipelines by 2030 (see the *European Hydrogen Backbone* initiative [4]), 700 km pipeline in China, 5600 km in West Africa, or 2,000 km in Oman [3].

Furthermore, since various factors (for example, the transition to net zero emissions) drive lower consumption of natural gas (NG), there are plans to repurpose part of the existing extensive NG pipeline infrastructure for hydrogen service [5] to reduce investment costs, shorten lead times and reduce environmental impact (instead of installing new pipes) - for example, 60% of the total German hydrogen pipeline network covering 7600 km (by 2032) will result from repurposing of NG pipelines. Det Norske Veritas' (DNV) Hydrogen Forecast expects that by 2050 more than 50% of pipelines globally will be repurposed from existing NG pipeline networks.

Polymers (mostly HDPE) have been traditionally used in low pressure pipes in utility systems such as NG distribution. More recently, they have also been considered as liners and coatings for hydrogen repurposed steel pipelines systems and non-metallic pipeline networks to protect pipeline infrastructure from corrosion and mechanical damage (e.g. caused by friction, or erosion), and also improve flow efficiency. Pipe-in-pipe (PIP) and inner coating of steel pipelines approaches are two of major options that can involve polymers to ensure safe operation of repurposed metallic pipelines. Both approaches aim to form a physical barrier between the steel and transported gas – in the PIP approach, a protective thermoplastic polymer material (e.g. HDPE or polyamide (PA)) is fitted as a tubular element into a tubular section of the pipeline, either during pipe manufacturing or rehabilitation; on the other hand, in the coating solution approach a barrier material is applied onto the surface of the inner pipeline wall, e.g. via a fusion bonded epoxy coating – however, that approach has been traditionally used during the production process of the pipes, and its feasibility for existing pipelines is uncertain. Besides liners and coatings, compatibility of elastomeric seals in pipeline repurposing may become another challenge. Those materials are typically considered when different components are joined together, and the largest units affected by this include compressor stations and valves – the latter (and associated sealing materials) may require the most significant changes during repurposing process.

Pipeline networks made of polymer composites can further provide reduced hydrogen permeation (compared to unreinforced polymers), enhanced mechanical strength, improved flow efficiency, and corrosion resistance. However, their performance in hydrogen-transporting pipelines will depend on several design variables such as constituent material properties, lay-up or manufacturing methods used. With a roll out of an extensive hydrogen transport pipeline network, all those design variables will have impact on health, safety and environment (HSE) criteria of the future hydrogen transport infrastructure.

Hydrogen emission

There is an increasing amount of evidence that hydrogen emission to atmosphere can have an indirect warming effect on the climate [6] with recent chemistry models aiming to predict increase in atmospheric hydrogen [7]. That increase in hydrogen can come from fugitive emissions that include both unintended emissions (e.g. from pipelines and storage tanks), and through deliberate purging or venting [8]. An assessment of emission rates for different elements in hydrogen economy chain (e.g. production, transport and storage, etc.) were summarised in [8]. Controlling hydrogen emission in non-metallic pipeline networks and storage systems over time requires criteria for allowable emission - while there exists an international standard [9] limit (6 cm^3 (STP) $h^{-1}L^{-1}$) on emission rates for compressed hydrogen fuel containers in land vehicles, a corresponding one for non-metallic pipeline systems or storage tanks for aerospace are not yet available to our best knowledge. This is related to gas barrier characteristics of polymers and their composites as discussed below.

Gas barrier resistance of polymers

While a significant amount of understanding of gas permeation characteristics of polymers has been gained since [10] to correlate structure-transport property characteristics, much less progress has been done for hydrogen. However, the knowledge gained can be expected to be applicable to hydrogen permeation in polymers, with the main polymer characteristics affecting the transport process as summarised below.

Generally, gas barrier resistance is suggested to increase with the level of **crystallinity**, which acts as an impermeable gas-blocking structure that increases the path length of gas penetrants (i.e. tortuosity) - which is also strongly affected by the size and distribution of the crystalline phase rather by the crystallinity itself [11].

While **molecular weight** is believed to have little effect on permeability, it is indirectly related to both **density** [12] and **molecular branching** - the chain architecture (branching *versus* linear) plays a critical in determining how molecular weight affects density. Generally, higher density reduces gas permeability and increases with both crystalline degree and density of the amorphous phase - the latter quantity dictates how much free volume between polymer molecules is available for gas permeation. Then, bulky side-chain molecules can hinder chain dynamics and thus decrease permeation of gases, compared to linear chains. Furthermore, permeability is also reduced with increased **crosslinking degree** [13] that affects chain mobility, and depends on the gas molecule size. **Molecular orientation** [14–16] can significantly affect permeability, especially when crystallites are present. Also **polar groups** can reduce permeability where polarity results in dense packing and reduced rates of groups motions [17] - notably polyamides such as PA6 and PA11 have higher hydrogen barrier performance than HDPE despite their lower crystallinity, due to their higher amorphous density and polarity [18]. Finally, incorporation of **fillers** and **plasticizers** can significantly affect permeation rates – 2D nanofiller such as nano-clay or graphene can significantly reduce permeation rates in polymers by creating more tortuous diffusion paths [19, 20], with the effect depending on the type, shape, and loading of the filler and its interaction with the polymer. Plasticizers typically increase permeation by reducing polymer density and lowering the *glass transition temperature* (GTT) - permeation rates increase with temperature because of increasing chain mobility and free volume, especially above GTT.

Permeation through composites

Continuous fibre-reinforced polymer composite materials can be utilised in manufacturing of offshore pipes for transport of green hydrogen harnessed through electrolysis powered from renewable resources. A comprehensive permeation assessment was conducted by Strohm for their thermoplastic composite pipes (TCP) made of high-density polyethylene (HDPE) reinforced with E-glass fibres [+/-53°] over a range of pressures and temperatures using full-scale TCP specimens. Their studies have revealed an approximately ten-fold reduction in hydrogen permeation when compared to traditional unreinforced pipes. With enhanced gas barrier characteristics combined with corrosion resistance and superior fatigue life those composite pipes are considered as robust and reliable solution for the offshore hydrogen infrastructure. Further work is needed to understand better the parameters controlling permeation across the scales, including the effects of fibre volume fraction, fibre sizing, composite lay-up, as shown in Fig. 1 - optimising those parameters through relevant manufacturing approaches can result in further enhancements of gas barrier characteristics.

Structural integrity of hydrogen transport infrastructure

Under certain conditions of temperature, pressure and gas/liquid type (e.g. dense and supercritical CO_2 phase), thermoplastic polymer pipelines can experience Rapid Crack Propagation (RCP) [21]. The RCP has been regarded as the most catastrophic type of failure of a pipeline - fracture can initiate from micro-defects and potentially run along the pipeline for several hundred meters. The phenomenon is understood as a competition between the velocities of decompression wave and crack tip - i.e. when the crack tip velocity (function of material toughness) is higher than the decompression wave velocity, the fracture front maintains its pressure/stress and continues to propagate - the propagation either stops naturally when the crack tip velocity eventually drops below the decompression wave velocity, or through some crack arrestors - composite overwraps are used as such arrestors on steel pipes to stop RCP. There is significant experience with RCP while transporting methane in low pressure NG distribution networks, but only limited testing has been completed to determine the

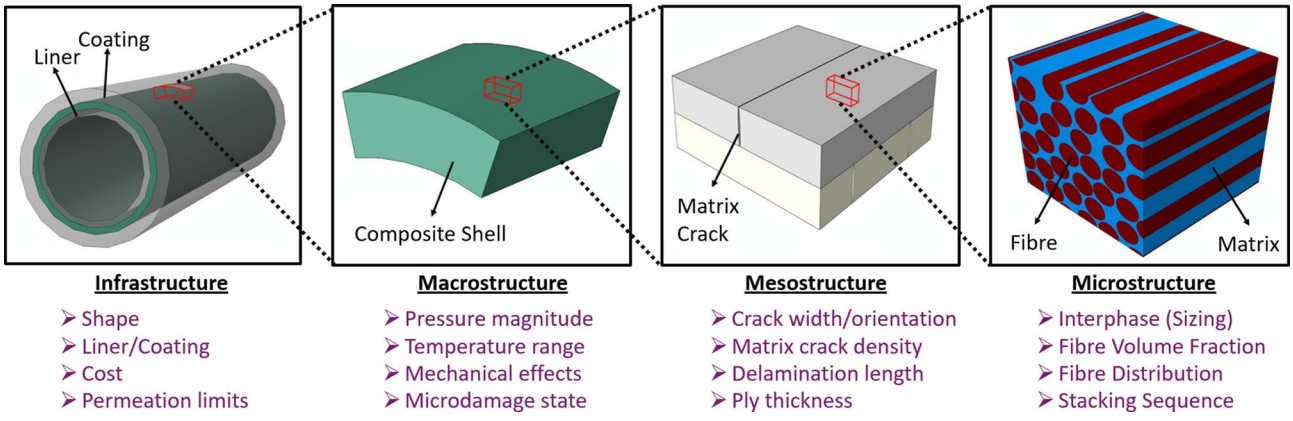

Fig. 1 Design parameters affecting composite permeability across the scales

decompression wave behaviour in hydrogen. Composite pipes have shown to have resistance to RCP when tested with CO_2, which has decompression behaviour that exaggerates the probability of RCP.

Pressurisation/depressurisation cycles can also lead to Rapid Gas Decompression (RGD) damage that can affect structural integrity of hydrogen pipelines. A major implication of RGD damage in high-pressure composite pipelines systems can be blistering and buckling of thermoplastic polymer liners. This temperature- and depressurisation rate-dependent phenomenon is introduced through the sorption and diffusion of gas by the liner, and its accumulation in the pre-existing interfacial defects (e.g. microvoids/microcavities), or constrained swelling. Initially it results in a pressure that is equivalent to the bore pressure - at decompression rates much larger than the diffusion rate in the liner, the pressure difference at the (pipe/liner) interface is introduced - if the difference reaches some critical value it can then lead to the formation of cavities, pores and bubbles resulting in the decohesion of the liner from the composite shell. RGD damage has been extensively explored for elastomeric materials (since [22]), and also to some extent for thermoplastic pressure barriers for unbonded flexible pipes. The microvoiding is frequently observed as material whitening [23] with a typical void size between 0.30 and 0.75 μm, and it is believed to initiate because of triaxial stress. As the cavity size can adversely affect polymer properties (e.g. tensile strength), it may be suggested that future work should focus on setting acceptance criteria for maximum void size and maximum void content in thermoplastic polymer systems subject to RGD. One fresh avenue to explore the problem may be by exploiting research related to microcellular foaming on amorphous thermoplastics [24].

Finally, it is noteworthy to mention that both RCP and RGD damage are influenced by material properties, especially their toughness and fracture resistance – thus, the prevention of RCP and RGD damage can be achieved by tuning those properties alongside component geometry. Also, while normally some interconnected mechanisms are considered when designing for the two phenomena (e.g. allowable initial defect arising from RGD that is acceptable for certification against RCP), more holistic material design strategies may be needed to address simultaneously both RCP and RGD damage.

Cryogenic hydrogen storage with composite tanks

Since the first hydrogen liquefaction by James Dewar in 1898, at least 26 Nobel prize awards were related to cryogenic science and technology with many directly connected to liquid hydrogen [25]. This has provided impetus for the development of techniques to store liquid gases and applications of liquid hydrogen e.g. for propulsion in the aerospace sector. The Aerospace Technology Institute's (ATI) FlyZero project backed by the UK government concluded that green liquid hydrogen is the most viable zero-carbon emission fuel with the potential to scale to larger aircraft utilising fuel cell, gas turbine and hybrid systems [26]. Composite materials offer promising means to reduce weight of liquid hydrogen (LH2) tanks (compared to metallic ones) but their resistance to permeation and microcracking remain the main challenges. Particularly, composite layers in the tank are susceptible to various forms of microdamage (e.g. transverse matrix microcracks [27–29] resulting from the differences in thermal expansion coefficients and decreased mobility and ductility of the polymeric matrix [30]). The microdamage can lead to the change in vacuum-based insulation characteristics by increasing conduction and convection, and thus lead to hydrogen boiling and runaway from the tank.

NCC (National Composites Centre) have highlighted several future research challenges/directions in relation to the cryogenic tank development - from the flight-worthy perspective those can be divided into four groups (as summarised in Fig. 2: (1) material degradation from thermal cycling that can lead to the microdamage network

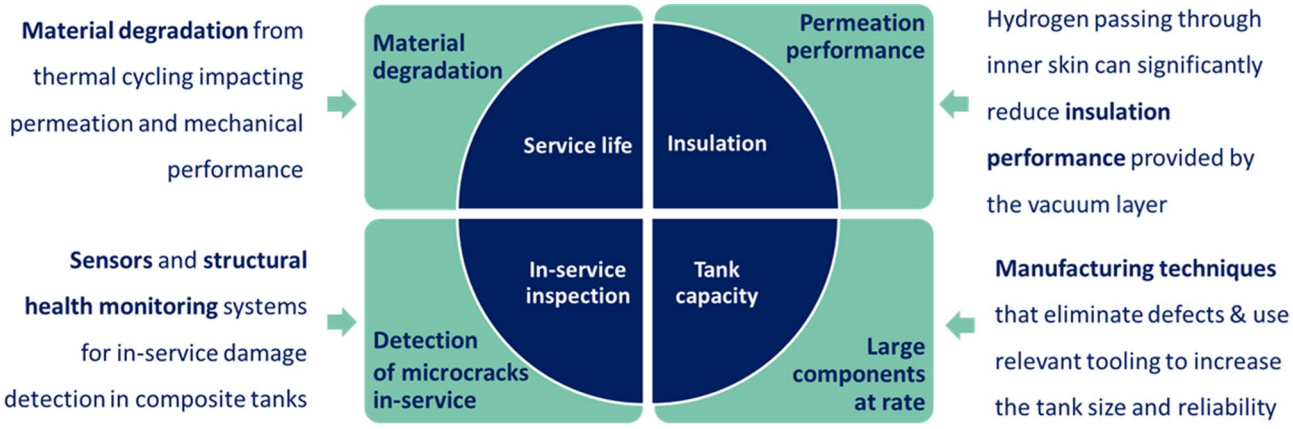

Fig. 2 Some challenges for the flight-worthy development of composite-based cryogenic tanks

causing increases in hydrogen permeability and affect structural integrity of the tank (e.g. reduction in stiffness and strength) - one of the solutions may be new resin technologies to produce matrix materials with enhanced mechanical properties (e.g. strength, durability) [31, 32], reduced toxicity and hydrogen repellence of molecular hydrogen through increased resin polarity; (2) interaction between hydrogen permeability and thermal insulation performance - i.e. increasing permeability can lead to temperature changes in the tank by affecting thermal conduction and convection governed by the vacuum insulation; (3) improved manufacturing techniques for composites to eliminate voids and microcracking with the possibility of using thin-ply laminates [33, 34]; and (4) methods development for in-service detection of microdamage states in composite tanks utilising advances in structural health monitoring approaches [35], combined with artificial intelligence [36].

Sealing hydrogen in transport and storage applications

To satisfy high-pressure requirements in hydrogen transport and storage applications, technological advances in polymeric materials for hydrogen sealing are required. Elastomeric materials have found use in several pressure retaining applications where sealing of gases remains the biggest engineering challenge because of their extremely low viscosity ([37]). An example are elastomeric O-rings with high endurance and integrity for use in high-pressure hydrogen seals. The main material challenges for elastomers in high-pressure hydrogen transport and storage applications are related to the resistance to: (1) gas leakage and (2) rapid gas decompression (RGD) damage.

Gas emission in sealings can generally be connected with gas permeation in the bulk and interfacial gas emission around the seals (especially at low temperatures due to their shrinkage). The formulation of a given elastomer compound can have a significant effect on the permeation - thus, it cannot be assumed that all elastomers in a family will behave in the same way [38, 39]. RGD damage in elastomers can lead to localised damage (e.g. microcavities) that can grow into cracks and result in ultimate failure of the seal [40] - the process is influenced by the temperature (loss of strength), pressure (above 50 bar), and decompression rate (as soon as larger than the diffusion rate). Historically, RGD damage testing focussed on methane/carbon dioxide mixtures rather than hydrogen. Recent work by James Walker & Co. [38, 39] has demonstrated that there is good correlation between resistance to RGD damage under hydrogen and methane/carbon dioxide mixture when assessed using the ISO23936–2 [41] test protocol.

While sealing in non-sub-zero conditions allows exploiting excellent elastomeric properties such as flexibility, resilience and elastic recovery, that is not the case in sub-zero hydrogen sealing applications. Whilst the materials are generally capable of surviving low temperatures without damage, they cannot effectively react to pressure changes at temperatures much below their GTT - therefore, special care must be taken when designing sealing systems for such operating conditions [37, 42, 43].

Two key issues needs addressing (1) increase in material brittleness and loss of mechanical integrity starting from temperatures below -150°C; and (2) material differential contraction when cooled leading to gaps that can pave the way for hydrogen emission - the latter can be tackled through careful optimisation of thermal expansion coefficient and seal design to minimise potential emission paths.

Chemically, hydrogen has no effect on most elastomers [44] - however the *American Petroleum Institute* (API) has recently published the 25th edition of API 6D that specifically includes an annex (M) (*Specification for Valves*) describing a formal qualification protocol for the use of non-metallic seals used in hydrogen service valves - it is anticipated it will be adopted for elastomers for hydrogen sealing.

Experimental challenges

The ability to perform accurate, reliable, and repeatable measurements is critical for the industry to evaluate and certify polymeric and composite materials for use with hydrogen [45]. However, the lack of experimental harmonization, extreme thermal and chemical environments present unique experimental and material-specific challenges. Challenges related to experimental protocols for measuring permeation and mechanical characteristics for those materials are summarised below.

Measuring hydrogen permeability under cryogenic conditions

While hydrogen permeation through polymer systems have been meaningfully recorded at ambient temperatures and elevated pressures (e.g. [46, 47]), significantly less is known about their behavior under cryogenic conditions [48].

To accurately assess intrinsic material permeability at cryogenic temperatures, advanced experimental techniques are essential. This necessity arises from the challenge of distinguishing true steady-state permeation from transient transport mechanisms driven by microcracking and thermal contraction. Standard extrapolations based on Arrhenius-type behaviour often fail to capture these second-order effects, especially in anisotropic composite systems. Therefore, empirical testing protocols must be refined to isolate intrinsic transport properties, enabling reliable material certification for hydrogen applications.

This includes developing representative sample geometries and sealing methods that mitigate defect-driven leakage pathways.

Currently, there is a severe lack of infrastructure capable of performing such tests as only around eight specialist labs worldwide have the required capability. Furthermore, the absence of an international testing standard for hydrogen permeability at cryogenic temperatures, hinders comparative assessment. Below are just some of the key experimental challenges to be addressed.

Achieving and maintaining **hermetic sealing** under cryogenic hydrogen conditions is a major challenge affecting test precision across test houses [49]. Polymeric and composite samples are particularly prone to sealing issues due to surface roughness and uneven thermal contraction during cooling, leading to microleaks and raising data uncertainty.

Cryogenic temperatures lead to extremely low diffusion rates, significantly increasing **experimental timescales** and reducing throughput - halving sample thickness reduces thermal time-lag by a factor of four (quadratic dependence). However, in fibre-reinforced composites, reducing plies below a critical threshold alters their behaviour [33, 50] making samples unrepresentative of full-scale laminates. Thus, unlike metals, composites may require a minimum representative thickness to yield reliable permeability measurements. Non-linear regressional fits may need to be developed to reduce experimental time.

Characterisation of mechanical properties under cryogenic conditions

Mechanical properties of composite materials change drastically at cryogenic temperatures due to reduced molecular mobility, altered failure mechanisms, and embrittlement effects. Initial results from uniaxial tensile tests on polymer composites show that at 77 K the failure strain decreases three-fold, while the Young modulus increases three-fold compared to room temperature; at 20 K the failure strain reduces eight-fold and modulus increases four-fold, indicating increased brittleness and stiffness. These results are consistent with molecular-scale phenomena such as decreased chain mobility. For testing at cryogenic temperatures typically a cryostat attached to a mechanical testing frame would need to be employed. The use of liquid nitrogen allows for testing at 77 K while the use of liquid helium enables the temperature of 4 K to be achieved by full immersion of the composite specimens. For tests at 20 K, special temperature control systems need to be employed, like that developed by Materials Reliability Inc. and National Physical Laboratory. Another approach for cooling materials to liquid hydrogen temperature is by cryo-cooler-based systems in dry-cryostats. Moreover, there is need to utilise in-situ gripping systems with minimal thermal gradients, enabling accurate strain localization. The development of advanced strain imaging at cryogenic temperatures is needed to enhance non-contact strain field mapping during testing. Furthermore, fatigue and impact resistance at cryogenic temperatures remain critical for better understanding of microdamage processes but remain as under-explored areas.

Modelling hydrogen permeation across the scales

Robust predictive multiscale modelling capability for hydrogen permeation in polymers and composites can (1) reduce time-consuming experimental testing, and (2) allow less conservative design and reduce material usage.

Various theoretical concepts and models have been devised to capture gas-solid interaction in amorphous polymers (either in a glassy or rubbery state) - that includes free-volume models, sorption models (e.g. dual mode) with varying degree of complexity (e.g. to include effects of gas mixtures) in combination with Sanchez-Lacombe (SL) (rubbery state) and non-equilibrium lattice fluid model (NELF) (glassy state), as summarised in [51]. While some of these models have been extended to semi-crystalline polymers they are yet to capture the full picture of gas transport in those systems.

Molecular dynamics (MD) simulation tools have been utilised to obtain more insight into sorption, solubility, diffusivity and permeation in semi-crystalline polymers. In contrast to macroscopic approaches such as equations of state for sorption and free volume models for diffusion that are computationally cheap but require extensive input information, molecular models, on the other hand, are fully predictive but have a high CPU load. For a more detailed analysis of the different tools available in the prediction of gas sorption, diffusion and permeation in polymers we refer to a recent review [52]. Most molecular methods simulate separately the solubility and diffusivity in a nanometer-sized polymer box and evaluate the permeability as the product between the two. More recent molecular methods estimate the permeability directly by calculating the flux of gas molecules across the polymer slab kept at a gas constant concentration difference [53]. In modelling semi-crystalline polymers, one has to consider that the crystal phase has negligible solubility, diffusivity and permeability compared to the amorphous phase. Furthermore, the connection to the crystal phase constrains the amorphous phase affecting its density and permeability [54, 55].

Molecular methods alone cannot account for the overall tortuosity due to length and time restrictions they can represent. Tortuosity can thus be estimated using one of the various analytical models available for semi-crystalline or filled polymers (e.g. Nielsen) [56], or by employing direct continuum-based (e.g. finite element/volume)

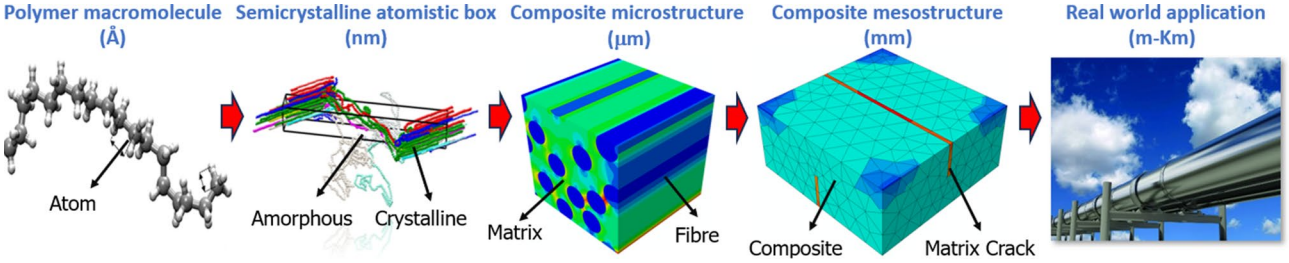

Fig. 3 Predictive modelling framework across the scales to capture chemical and physical nature of polymers (e.g semi-crystalline, free volume) and couple it with the continuum representation of polymer composites for real-world hydrogen applications

simulation utilising the representative volume element (RVE) concept, both for semi-crystalline polymers [57] and composites [58], also with uncertainty quantification [59]. Those methods can account for tortousity as a function of the crystalline degree, shape, orientation for semi-crystalline polymers, and volume fraction, shape, orientation or distribution of the reinforcement for composites. Coupling them with diffusion coefficients obtained from molecular simulations, can help to add the chemical detail and additional physical mechanisms, including connectivity between crystal and amorphous phase [60], to provide a more complete picture and prediction of transport properties in real-world applications, as shown in Fig. 3.

Concluding remarks

This paper has attempted to provide a perspective from academia and industry on the advances and remaining challenges in the field of polymers and composite materials for hydrogen transport and storage. The primary unresolved practical challenges and fundamental issues have been identified and can be summarised as follows:

- Hydrogen emission to atmosphere can have an indirect warming effect on the climate with increases in anthropogenic hydrogen stemming from unintended emissions such as from pipelines and storage tanks. This requires development of further regulatory thresholds for allowable emission criteria, as well as further research into improving hydrogen gas barrier resistance of polymeric materials across a wide range of pressures and temperatures.
- Technological advances in polymeric materials for hydrogen sealing are required in hydrogen transport and storage applications, including enhancements in mechanical integrity at temperatures below −150° C, and/or optimised differential contraction when cooled to eliminate gaps that can pave the way for hydrogen emission
- Whereas resistance to permeation has been found (by the authors) to be the most sensitive metric and design driver for flight-worthy composite hydrogen tanks, future research efforts should be directed to investigate it further, and if needed develop material and design solutions for the tanks that concurrently optimise for hydrogen barrier performance, structural integrity, and thermal insulation accounting for the multi-faceted impact of microcracking
- Establishing post-manufacture methods quantifying the quality of manufactured parts for cryogenic storage tanks, to assess if existing manufacturing-induced defects are allowable for their in-service performance (mechanical, transport), will be key towards certification of flight-worthy tanks
- Current resins are not capable to meet either the permeation or mechanical degradation requirements when cycled to liquid hydrogen temperatures. Matrix material capable of achieving the required permeation rates, whilst being able to withstand thermal cycling without sustaining a significant loss of mechanical or gas barrier properties are required. The two routes being explored are formulations of new systems specifically geared to these applications, or modifications of existing systems to achieve the required properties
- While preventing from rapid crack propagation (RCP) and rapid gas decompression (RGD) damage can be achieved by tuning both material properties and geometry in reinforced thermoplastic pipes (RTPs) for hydrogen transportation, more holistic material design methodologies that consider interconnected mechanisms and are material agnostic, may need to be explored
- Further research is needed to develop physically-sound multiscale approaches that seamlessly combine molecular and continuum approaches by exploring recent advances in artificial intelligence/machine learning, to form an experimentally-validated predictive modelling platform to accelerate design of future hydrogen infrastructure, and reduce experimental burden.

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Author contributions
Authors 2-8 contributed equally to this work by providing relevant sections and reviewing the manuscript, as originally written by the first/corresponding author 1.

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Data availability
No datasets were generated or analysed during the current study.

Declarations

Competing interests
The authors declare no competing interests.

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