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Review

Bridging Chemistry and Reliability: A Framework for Evaluating and Optimizing Polymers in Hydrogen Energy Systems

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Abstract

Hydrogen energy systems rely extensively on polymeric materials for storage, sealing, transport, and tribological applications; however, their long-term reliability is strongly influenced by hydrogen–polymer interactions. This review presents a comparative analysis of polymers with and without hydrogen bonding, focusing on how molecular architecture governs hydrogen compatibility, transport behavior, and degradation mechanisms under high-pressure environments. Hydrogen-bonded polymers, such as polyamides, polyurethanes (PU), and polyimides, exhibit high mechanical strength and thermal stability due to strong intermolecular interactions but are susceptible to hydrogen-assisted chemical degradation and embrittlement. In contrast, non-hydrogen-bonded polymers, including polyethylene, polypropylene (PP), polytetrafluoroethylene (PTFE), and Polyether ether ketone (PEEK), demonstrate excellent chemical inertness and low hydrogen reactivity, yet experience diffusion-driven damage such as blistering and fatigue softening. This study establishes a unified framework linking molecular structure, hydrogen transport, and failure mechanisms, revealing a fundamental trade-off between mechanical integrity and chemical stability. Advanced strategies, including polymer blending, nanofiller reinforcement, and multilayer composites, are proposed to optimize durability, permeability, and overall hydrogen compatibility.

Keywords: hydrogen exposure; polymer degradation; hydrogen bonding; hydrogen embrittlement; polymer permeability; tribological behavior; polyamide; PTFE; polymer nanocomposites; hydrogen storage; fuel cell infrastructure

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1. Introduction

Hydrogen has emerged as a cornerstone of the clean-energy transition due to its high gravimetric energy density (120 MJ kg^{-1}), zero carbon emissions, and versatility in storage and conversion technologies [1,2]. It is increasingly deployed in fuel-cell electric vehicles (FCEVs), compressed-gas storage systems, pipeline networks, and hydrogen refueling stations (HRSs) [3,4]. These applications, however, require materials that can maintain mechanical and chemical integrity under extreme service environments, often close to 70 MPa pressure and experiencing thousands of pressurizations–depressurization cycles [5–7]. The long-term durability of hydrogen systems is therefore dictated not only by metals but also by polymers, which are widely used as liners, seals, hoses, coatings, and membranes throughout the infrastructure [8–10].

Polymers are attractive in hydrogen applications because of their low density, design flexibility, processability, corrosion resistance, and electrical insulation. In Type IV composite pressure vessels, for example, polyamide-6 (PA6) and polyamide-11 (PA11) are frequently employed as liners owing to their moderate hydrogen permeability and good toughness [11]. High-density polyethylene (HDPE) and cross-linked polyethylene (PEX) are used for pipelines and valve components because of their ductility and resistance to chemical attacks. In addition, polytetrafluoroethylene (PTFE), polyether–ether–ketone (PEEK), and polyoxymethylene (POM) are utilized in valves, bearings, and tribological interfaces within compressors and delivery units, where their low friction coefficients ensure mechanical reliability under dynamic loading [12]. Despite these advantages, long-term hydrogen exposure can significantly alter polymer performance through permeation, swelling, blistering, micro-void formation, embrittlement, and tribochemical degradation, leading to leakage or catastrophic component failure [13,14]. The extent and mechanism of hydrogen-induced degradation are strongly governed by polymer molecular structure, particularly the presence or absence of hydrogen-bonding interactions between chains.

Hydrogen-bonded polymers such as polyamides, polyurethanes (PU), polyimides (PI), and polybenzimidazole (PBI), possess polar functional groups (–CONH–, –OH, –NH–) capable of forming strong intermolecular networks [15,16]. These interactions impart high stiffness, thermal stability, and low creep, desirable for liners and membranes [17–19]. However, the same polar sites also act as hydrogen-reactive centers, susceptible to hydrogen-assisted bond scission, oxidation, and plasticization, which can lead to local embrittlement and micro-cracking under pressure cycling [20–22].

Non-hydrogen-bonded polymers, including polyethylene (PE), polypropylene (PP), PTFE, PEEK, and POM, lack polar groups and are stabilized primarily by van der Waals or dipole–dipole forces [23,24]. Among them PTFE and PEEK exhibit excellent chemical inertness and low hydrogen solubility, making them suitable for gas transport and sealing [25,26]. Nevertheless, these materials may undergo diffusion-controlled blistering, surface pitting, and fatigue softening due to hydrogen ingress and rapid decompression [27,28].

Extensive testing efforts by DOE, PNNL, SNL, and ORNL have standardized evaluation protocols for polymer compatibility in hydrogen [9]. Tests typically involve exposure pressures of 17–103 MPa and temperatures from −40 °C to +85 °C, encompassing steady-state permeation, mechanical cycling, and in situ tribological assessment. These studies demonstrate that polymer degradation is not purely chemical but multiphysical driven by the interplay of hydrogen diffusion, thermal relaxation, mechanical stress, and surface friction. An in situ tribometry under 28 MPa H_2 revealed that PTFE and PEEK maintain stable friction coefficients, whereas PA6 and POM exhibit increased wear rates due to hydrogen-induced micro-cracking and reduced surface toughness [12]. Similarly, long-term aging tests on HDPE and PA11 pipelines confirmed that hydrogen exposure modifies crystallinity and elastic modulus, yet catastrophic degradation is minimal below 50 MPa [29].

Despite substantial progress, several critical knowledge gaps remain. The combined effects of pressure, temperature, humidity, and decompression rate are not yet fully captured by current test standards, resulting in inconsistent property data among laboratories. The tribochemical coupling of hydrogen diffusion with mechanical wear is poorly understood, particularly for dynamic sealing and compressor applications. Moreover, compositional variables such as additives, fillers, and polymer blending significantly influence hydrogen compatibility but remain under-explored. Addressing these challenges requires a holistic framework linking molecular interactions, environmental conditions, and multi-scale degradation mechanisms.

Therefore, this review aims to provide a comprehensive comparative assessment of polymeric materials under hydrogen exposure, emphasizing the influence of hydrogen

bonding on degradation behavior, performance, and quality. The review (i) categorizes polymers with and without hydrogen bonding; (ii) examines their mechanical, chemical, and tribological degradation mechanisms under hydrogen environments; (iii) analyzes operational conditions affecting hydrogen diffusion and damage; and (iv) evaluates material suitability and quality for use in hydrogen storage, distribution, and conversion systems. This systematic synthesis not only consolidates the fragmented understanding of hydrogen–polymer interactions but also offers design guidelines for next-generation hydrogen-resistant polymer systems that balance strength, impermeability, and long-term durability.

2. Polymers with and Without Hydrogen Bonds

Hydrogen plays several critical and diverse roles in relation to polymers, influencing their properties through noncovalent bonding, acting as a reactant or agent in polymerization and degradation [18,30]. On the other hand, polymers without hydrogen bonds often have simpler, non-polar structures, leading to properties like increased water repellency and chemical stability [31].

This Figure 1 presents the energetic scale of different bonding interactions in polymers, measured in kcal·mol^{-1}. It compares the strength of covalent bonds, hydrogen bonds, and van der Waals interactions. The placement of bonds along the scale illustrates how different interactions influence the structural integrity, thermal stability, and mechanical properties of polymers.

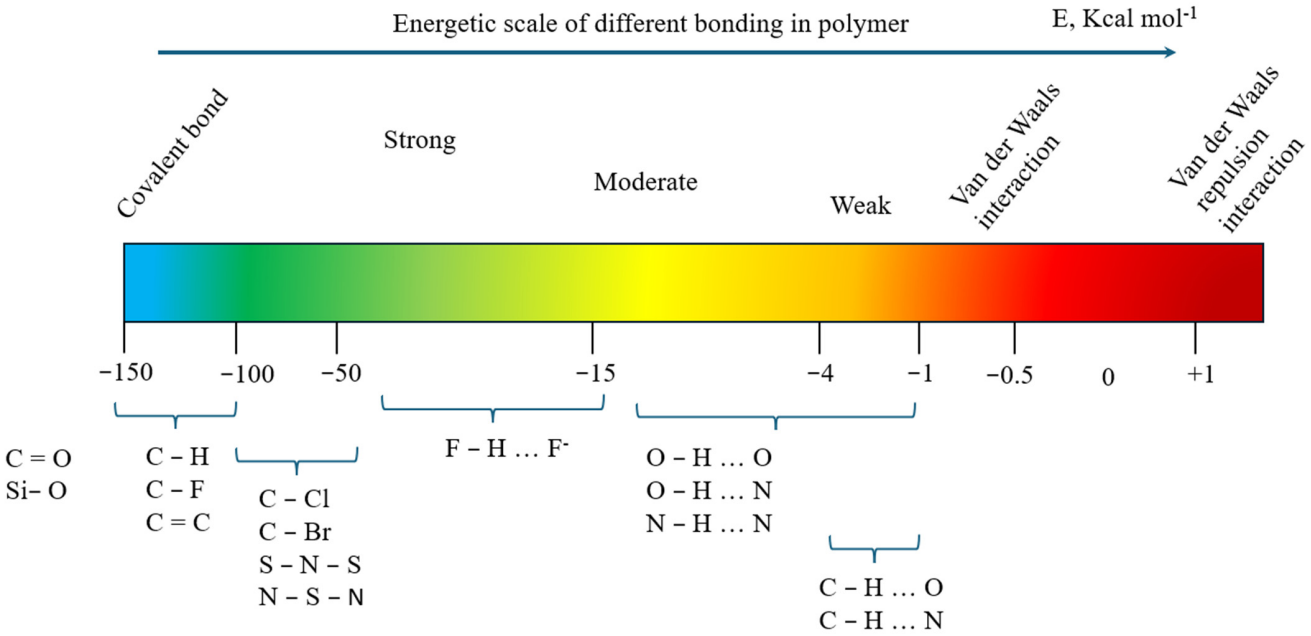


Figure 1. Energetic Scale of different bonding interactions in polymers, adapted from [32]. The color bar represents the relative bonding energy scale in polymers, where blue/green regions indicate stronger attractive interactions and yellow/red regions indicate progressively weaker or repulsive intermolecular interactions.

Figure 1 presents the energetic scale of bonding interactions in polymers, expressed in kcal·mol^{-1}, ranging from strong covalent bonds to weak van der Waals interactions. The horizontal axis illustrates a continuous decrease in bond strength from left to right, highlighting how different intermolecular and intramolecular forces govern polymer structure and properties. At the highest energy range (≈ -150 to -50 kcal·mol^{-1}), covalent bonds such as C–C, C–H, and Si–O dominate. These bonds form the polymer backbone and are responsible for the fundamental structural stability of all polymers. Moving toward lower energies, hydrogen bonds (≈ -4 to -15 kcal·mol^{-1}) appear in the intermediate region,

representing moderate-strength intermolecular interactions such as O–H···O, N–H···O, and N–H···N. Although weaker than covalent bonds, hydrogen bonds are significantly stronger than van der Waals forces and play a critical role in enhancing interchain cohesion, stiffness, and thermal stability. At the weakest end of the spectrum (≈ -0.5 to -4 kcal·mol^{-1}), van der Waals interactions dominate. These include dispersion forces and weak dipole interactions such as C–H···O and C–H···N. Polymers governed by these interactions exhibit lower intermolecular cohesion, leading to higher chain mobility, lower stiffness, and increased permeability. The energetic hierarchy shown in Figure 1 provides a clear basis for distinguishing between hydrogen-bonded and non-hydrogen-bonded polymers. Hydrogen-bonded polymers (e.g., polyamides, polyurethanes, and polyimides) contain polar functional groups that form moderate-strength intermolecular interactions, creating a physically cross-linked network that results in high mechanical strength, elevated glass transition temperature (T_g), and reduced chain mobility. However, these same polar sites can act as reactive centers under hydrogen exposure, increasing susceptibility to hydrogen-assisted degradation. In contrast, non-hydrogen-bonded polymers (e.g., polyethylene, polypropylene, PTFE, and PEEK) lack strong polar interactions and are governed primarily by van der Waals forces, leading to greater chain flexibility, lower stiffness, and enhanced gas diffusion pathways. Despite their lower mechanical cohesion, these polymers exhibit superior chemical inertness due to weak interaction with hydrogen. These fundamental distinctions form the basis for the comparative analysis of polymer properties presented in Section 2.

2.1. Polymers with and Without Hydrogen Bonding

As illustrated in Figure 1, hydrogen bonding occupies an intermediate energy range between strong covalent bonds and weak van der Waals interactions, making it a key factor governing intermolecular cohesion and polymer performance [18]. Polymers containing hydrogen-bonding functional groups (e.g., –CONH–, –OH, –NH–) form interchain networks through directional interactions, whereas non-hydrogen-bonded polymers rely primarily on van der Waals and dipole–dipole forces [23,33–36]. This fundamental difference leads to distinct structure–property relationships, particularly relevant for hydrogen environments. Table 1 provides a unified comparison of representative polymers, highlighting how intermolecular interactions influence their thermal and mechanical properties.

Table 1. Comparison of common polymers with hydrogen-bonding capability, their functional groups, and key material properties such as glass-transition temperature, tensile strength, and thermal/chemical characteristics [21,37–68].

Polymer/H-Bonding Type	Functional Groups	Hydrogen Bond Type	Typical T_g (°C)	Tensile Strength (MPa)	Key Properties
Nylon-6/Nylon-6,6 (Polyamide)/HB	–CONH–	Intermolecular H-bonds between amide groups	47–75	75–90	High strength, high crystallinity, good abrasion resistance, moisture sensitive
Polyurethane (PU) /HB	–NH–COO–	Intra- & intermolecular	−50 to 50	30–60	Elastic, hydrogen bonding enhances hardness and T_g
Poly(vinyl alcohol) (PVA)/HB	–OH	Extensive intermolecular	85–90	30–70	Water soluble, good film forming, high T_g
Poly(acrylic acid) (PAA)/HB	–COOH	Strong intermolecular	100–106	~45	Highly hydrophilic, forms H-bonded networks
Polyamide-imide (PAI)/HB	–CONH–, –CO–, –NH–	Strong intermolecular	340–441	160–200	Excellent thermal stability and strength
Poly(ethylene oxide) (PEO)/HB	–O– (ether)	Weak intermolecular (via oxygen)	−60	1–20	Flexible, weak hydrogen bonding with water
Poly(vinyl pyrrolidone) (PVP)/HB	–C=O (lactam)	H-bond acceptor	176	2–3	Highly polar, good adhesion, hygroscopic
Kevlar (Aramid)/HB	–CONH– (aromatic amide)	Strong directional H-bonding	>300	3000	Exceptional strength, high modulus, thermal stability

Table 1. *Cont.*

Polymer/H-Bonding Type	Functional Groups	Hydrogen Bond Type	Typical T_g (°C)	Tensile Strength (MPa)	Key Properties
Polyethylene (PE)/NHB	–CH_2–CH_2–	van der Waals	−125	10–30	Flexible, non-polar, high ductility
Polypropylene (PP)/NHB	–CH(CH_3)–CH_2–	van der Waals	−10	30–40	Semi-crystalline, low density, good chemical resistance
Polystyrene (PS)/NE	–CH_2–CH(Ph)–	π–π stacking, dipole	95–105	35–55	Rigid, transparent, brittle
Poly(methyl methacrylate) (PMMA)/NHB	–$COOCH_3$	Dipole–dipole	105	50–80	Transparent, hard, poor impact resistance
Poly(tetrafluoroethylene) (PTFE)/NHB	–CF_2–CF_2–	van der Waals	~120	20–35	Chemically inert, low friction
Polycarbonate (PC)/NHB	–O–C(=O)–O– (no H donors)	Dipole–dipole	145–150	60–70	Tough, transparent, impact resistant
Poly(ethylene terephthalate) (PET)/NHB	–CO–O– (ester)	Dipole–dipole	70–80	55–75	Strong, semi-crystalline, moisture resistant
Polyvinyl chloride (PVC)/NHB	–CH_2–CHCl–	Dipole–dipole (C–Cl)	80	45–60	Rigid, flame retardant, chemical resistant
Polytetrafluoroethylene (PTFE)/NHB	–CF_2–CF_2–	van der Waals (very weak)	−110 °C to 130 °C	20–35	Chemically inert, extremely low friction, excellent hydrogen resistance
Polyether ether ketone (PEEK)/NHB	–O–Ph–O–Ph–CO–Ph–	Dipole–dipole + aromatic interactions	~143	90–100	High strength, high thermal stability, good chemical resistance

HB = Hydrogen bonded, NHB = Non-hydrogen bonded.

The comparison in Table 1 reveals a clear structure–property trade-off governed by intermolecular interactions.

2.1.1. Mechanical and Thermal Behavior

Hydrogen-bonded polymers generally exhibit higher tensile strength and thermal stability due to strong intermolecular cohesion. For example, Kevlar demonstrates tensile strength on the order of ~3000 MPa, significantly exceeding that of non-hydrogen-bonded polymers such as polyethylene (~10–30 MPa). Similarly, hydrogen-bonded systems tend to exhibit higher glass transition temperatures due to restricted chain mobility. In contrast, non-hydrogen-bonded polymers rely on weaker van der Waals interactions, resulting in lower stiffness but greater flexibility. Their lower intermolecular cohesion allows easier chain movement, which is beneficial for ductility but limits mechanical strength.

2.1.2. Chain Mobility and Transport Behavior

The absence of hydrogen bonding in non-polar polymers leads to higher segmental mobility and increased free volume, facilitating gas diffusion. This makes materials such as polyethylene and PTFE more susceptible to hydrogen permeation and diffusion-driven damage. Conversely, hydrogen-bonded polymers exhibit reduced chain mobility, which limits diffusion pathways and lowers permeability. However, this advantage is offset by the presence of polar functional groups that can interact with hydrogen and environmental species.

2.1.3. Chemical Stability and Hydrogen Interaction

A key distinction lies in chemical reactivity. Hydrogen-bonded polymers contain polar groups that can act as interaction sites for hydrogen and reactive species, making them more vulnerable to hydrogen-assisted degradation mechanisms such as bond scission and oxidation. Non-hydrogen-bonded polymers, by contrast, are generally chemically inert, particularly fluoropolymers such as PTFE, where strong C–F bonds resist hydrogen interaction. As a result, these materials exhibit superior resistance to chemical degradation but remain susceptible to physical damage mechanisms such as blistering and microvoid formation.

2.2. Quality Assessment of Polymers with and Without Hydrogen-Bonded Polymers in Hydrogen Environments

When exposed to H_2 environment, Hydrogen-bonded polymers show excellent mechanical strength and high thermal stability, but only moderate chemical stability because hydrogen can disrupt their polar bonds and accelerate oxidation. In contrast, non-hydrogen-bonded polymers offer excellent chemical stability and strong resistance to hydrogen and radicals, although their mechanical performance is generally moderate due to lower stiffness. Their thermal stability varies widely, depending on crystallinity and backbone structure. Overall, hydrogen-bonded polymers excel structurally but are chemically vulnerable, while non-bonded polymers are chemically inert but mechanically less robust. Table 2. compares the overall material quality of polymers with and without hydrogen bonding when used in hydrogen environments.

Table 2. Quality assessment comparison of polymers with and without hydrogen-bonded polymers in hydrogen environments.

	with Hydrogen Bond		Without Hydrogen Bond	
Quality Aspect	**Performance**	**Assessment**	**Performance**	**Assessment**
Mechanical strength	Excellent	High tensile and fatigue resistance	Moderate	Ductile but lower modulus
Chemical stability	Moderate	Sensitive to hydrogen-induced oxidation and H-bond disruption	Excellent	Inert to H_2 and radicals
Thermal stability	High	Stable up to 200 °C (aromatic polyamides, imides)	Moderate	Melting range 120–200 °C
Gas permeability	Low	Suitable for liners and barriers	Very low	Excellent hydrogen barrier (PTFE, PEEK)
Long-term durability	Moderate	Degrades with moisture and hydrogen cycling	High	Stable under pressure cycling

3. Application of Polymers with and Without Hydrogen Bonds in H_2 Systems

Polymers play critical roles in modern hydrogen technologies, including storage, distribution, sealing, membranes, and fuel-cell components as shown in Figure 2 [69,70]. Their application strongly depends on molecular structure particularly the presence or absence of hydrogen bonding, which dictates permeability, mechanical strength, chemical stability, and resistance to hydrogen-induced degradation [71–73].

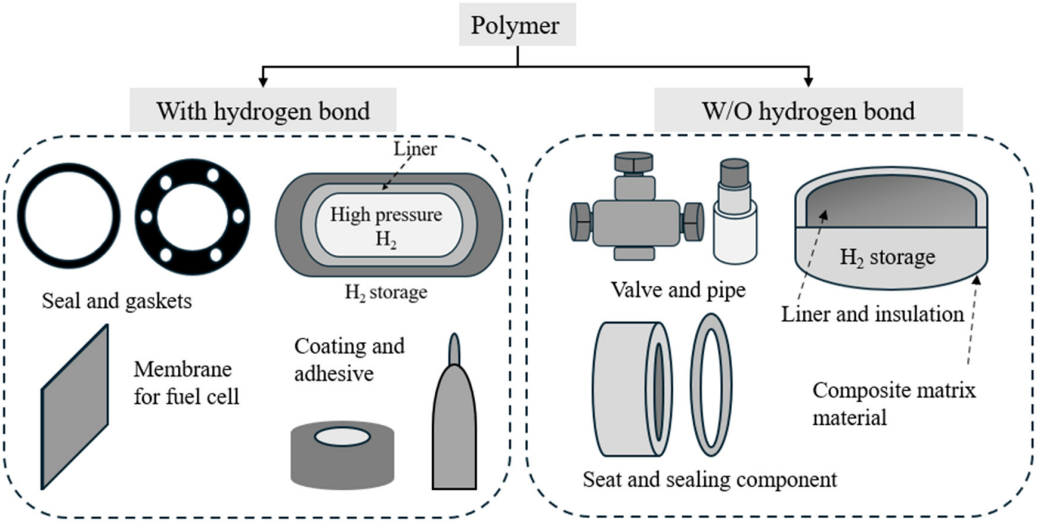


Figure 2. Classification of polymers with and without hydrogen bonding, used in various hydrogen system components.

3.1. Polymers with Hydrogen Bonding

These bonds confer high mechanical strength, dimensional stability, and thermal resistance, making such polymers excellent candidates where structural integrity and barrier control are required under hydrogen pressure. Table 3 shows the Applications of hydrogen-bonded polymers in hydrogen systems, emphasizing their functional roles, benefits, and constraints in high-pressure and fuel-cell environments.

Table 3. Applications of hydrogen-bonded polymers in hydrogen systems, highlighting functional roles, advantages, and limitations.

Application Area	Polymer System	Functional Role	Advantages	Limitations	Ref.
Hydrogen Storage Liners	Polyamide-6, Polyamide-11	Inner liner materials for composite high-pressure tanks (Type IV)	Low hydrogen permeability; high mechanical strength	Moisture sensitivity; potential hydrogen-induced embrittlement	[11,74]
Seals and Gaskets	Polyurethane (PU), Polyamide-imide	Flexible sealing under cyclic pressure conditions	Good elasticity; chemical resistance; fatigue resistance	Hydrogen-bond network disruption leads to aging and degradation	[75,76]
Membranes (Fuel Cells/Electrolysis)	PVA, Polybenzimidazole (PBI), Nafion-based blends	Proton exchange membranes or gas separation barriers	High proton conductivity; good dimensional stability	Hydration-induced swelling; chemical degradation over time	[77–79]
Coatings and Adhesives	Polyimides, Polyurethane (PU)	Protective coatings for hydrogen-exposed metal components	High adhesion; excellent thermal and chemical stability	High cost; moisture-sensitive curing; long-term durability concerns	[80,81]

3.2. Polymers Without Hydrogen Bonding

Their inertness and low hydrogen reactivity make them favorable for hydrogen containment and transport, where chemical compatibility and low gas permeability are required rather than strong cohesive bonding. Application of these polymers are shown in Table 4.

Table 4. Applications of non-hydrogen-bonded polymers in hydrogen systems, highlighting functional roles, advantages, and limitations.

Application Area	Polymer System	Functional Role	Advantages	Limitations	Ref.
High-Pressure Hydrogen Pipes and Valves	High-density polyethylene (HDPE), polypropylene (PP), polycarbonate (PC)	Hydrogen transport and distribution lines	Chemical inertness; flexibility; low cost	Hydrogen diffusion and permeability increase with temperature	[10,82,83]
Sealing Components and Valve Seats	Polytetrafluoroethylene (PTFE), polyether ether ketone (PEEK)	Low-friction seals and valve seats	Excellent chemical resistance; low wear; low friction	Creep under high pressure; low elasticity	[27,84]
Liner or Insulation Layers	Polyethylene terephthalate (PET)	Structural barrier layers or outer jackets	Good dimensional stability; transparency; moderate strength	Higher permeability compared to polyamides or polyethylene	[85]
Composite Matrix Materials	Epoxy resins or fluoropolymer blends	Matrix materials for carbon-fiber hydrogen storage vessels	Strong adhesion to fibers; enhanced gas barrier properties	Brittle behavior under impact; limited toughness	[86]

4. Degradation of Polymers in Hydrogen Environments

Hydrogen exposure affects polymers through a variety of physical and chemical mechanisms, depending on the molecular structure, crystallinity, crosslinking, and environ-

mental conditions [72,87,88]. A generalized schematic illustrating the hydrogen-induced degradation mechanisms in hydrogen-bonded and non-hydrogen-bonded polymers is presented in Figure 3.

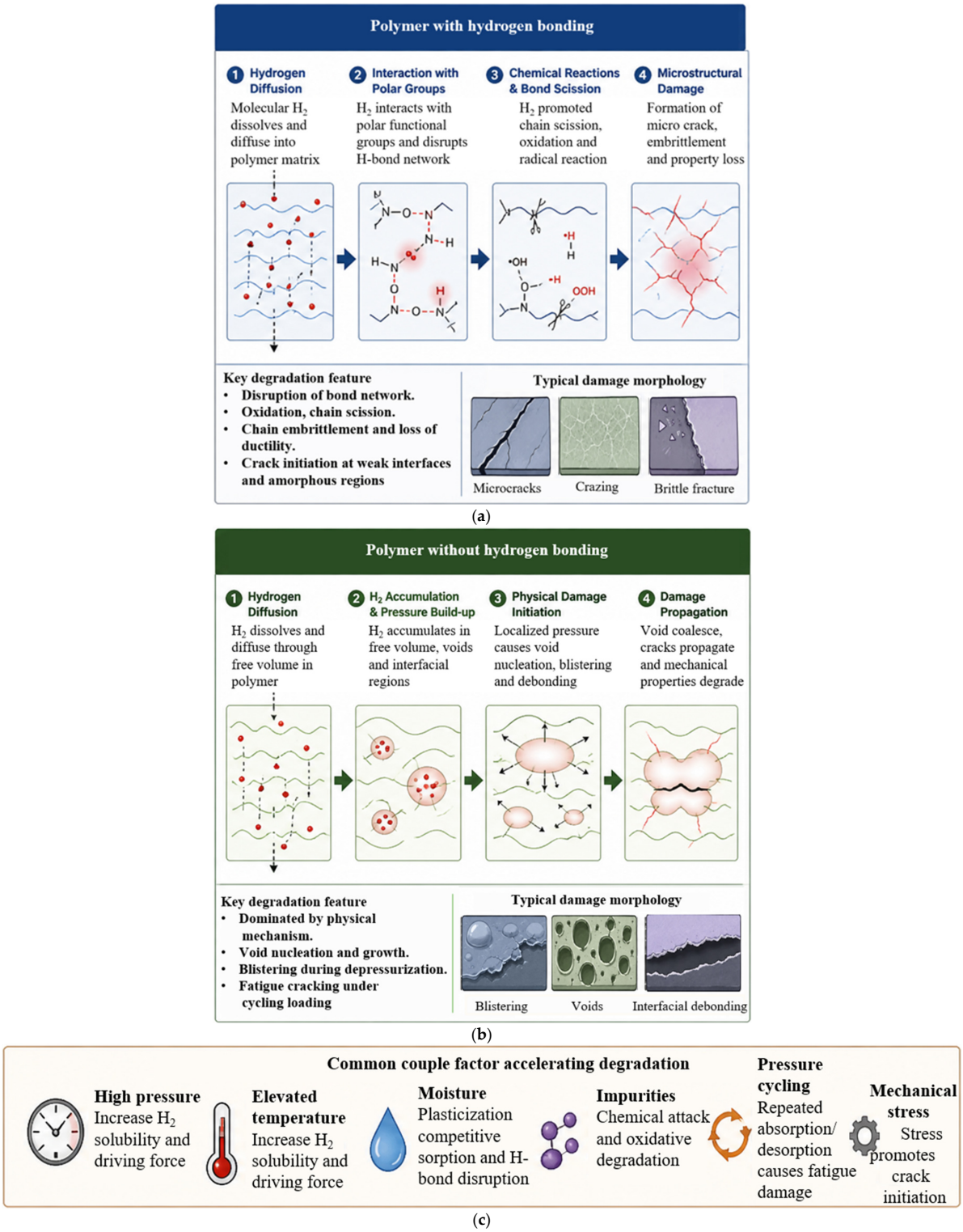


Figure 3. Generalized hydrogen-induced degradation pathways in polymers, comparing (**a**) hydrogen-bonded polymers, (**b**) non-hydrogen-bonded polymers, and (**c**) common factors influencing fast degradation. The red dots represent hydrogen (H_2) molecules, the red dashed arrows indicate hydrogen diffusion pathways through the polymer matrix, the blue and green lines denote polar and nonpolar polymer chains, respectively, while the shaded circles and red zigzag symbols indicate void/cavity formation and crack initiation sites.

The degradation pathways illustrated in Figure 3 provide a mechanistic basis for understanding how hydrogen–polymer interactions evolve from molecular-scale processes to macroscopic material failure. As shown, hydrogen diffusion, interaction with polymer structure, and subsequent microstructural damage collectively govern the degradation behavior of polymers in hydrogen environments. These processes do not occur independently but manifest as three strongly coupled degradation modes: mechanical, chemical, and tribological degradation. The relative contribution of each mode depends on polymer molecular architecture, particularly the presence or absence of hydrogen bonding, as well as environmental conditions such as pressure, temperature, and cycling history.

Accordingly, the following sections analyze these degradation modes in a systematic manner, beginning with mechanical degradation, followed by chemical and tribological effects.

4.1. Mechanical Degradation

4.1.1. Mechanical Degradation of Hydrogen-Bonded Polymers

Hydrogen-bonded polymers exhibit high initial strength and modulus because of their cohesive intermolecular networks (–NH···O=C or –OH···O–). However, when exposed to hydrogen environments, these bonds are disrupted by diffusing hydrogen molecules and radicals, leading to [87,89] hydrogen-assisted embrittlement due to the weakening of amide or urethane linkages. Microcrack initiation and reduced elongation at break caused by localized stress around hydrogen-rich regions. Swelling and softening from hydrogen diffusion coupled with moisture, weakening interchain bonding and decreasing crystallinity. Ultimately, the hydrogen-bond network degradation leads to reduced tensile and fatigue strength. Polyamide 6 and 6,6 show ~20–40% loss in tensile strength after prolonged hydrogen exposure [11,21].

4.1.2. Mechanical Degradation of Non-Hydrogen-Bonded Polymers

These polymers depend mainly on van der Waals interactions for cohesion, which makes them less chemically reactive but mechanically vulnerable to hydrogen diffusion and pressure cycling [8,23,90]. Blistering and microvoids form due to differential hydrogen solubility in amorphous vs. crystalline regions. Fatigue softening and crack propagation occur under cyclic decompression conditions. Despite lower chemical sensitivity, mechanical integrity deteriorates due to physical stress accumulation. PE and PP maintain most of their chemical integrity but show increased brittleness under high-pressure hydrogen cycling [13,91].

4.2. Chemical Degradation

4.2.1. Chemical Degradation of Hydrogen-Bonded Polymers

Hydrogen can directly interact with polar functional groups, accelerating:

- Chain scission and oxidation at amide, urethane, or hydroxyl sites.
- Hydrogenolysis reactions, particularly in presence of catalytic metals, causing reduction of carbonyls and loss of backbone integrity.
- Loss of hydrogen-bond network stability, promoting irreversible molecular rearrangement.

Such chemical degradation results in a decline in molecular weight, reduced T_g, and loss of dimensional stability. Examples: Polyurethane and PVA exhibit discoloration and chemical softening after long-term exposure in hydrogen-rich or humid hydrogen atmospheres [91].

4.2.2. Chemical Degradation of Non-Hydrogen-Bonded Polymers

Chemically inert polymers such as PTFE, PE, and PP show minimal reactivity to molecular hydrogen. However, under plasma or high-temperature hydrogen environments, atomic hydrogen can cause surface etching and carbon–hydrogen bond scission. Radical-assisted oxidation may occur when hydrogen exposure is combined with oxygen contamination, slightly degrading surface chemistry. Overall, chemical degradation is minor compared to mechanical fatigue. Examples: PTFE and HDPE exhibit minimal chemical alteration even after extended exposure to 70–100 MPa hydrogen [13].

4.3. Tribological Degradation

4.3.1. Tribological Degradation of Hydrogen-Bonded Polymers

Tribological degradation arises due to hydrogen-induced changes in viscoelasticity and surface energy. Increased surface wear results from reduced toughness and cohesive strength after H-bond disruption. Hydrogen-induced microcracking at sliding interfaces accelerates delamination wear.

Reduced lubricity occurs when absorbed hydrogen alters interfacial adhesion, especially in polyurethanes and polyamides used as seals or coatings. Such effects lead to higher friction coefficients and wear rates under dry or boundary lubrication conditions. Nylon and polyurethane seals display 30–50% higher wear rate after hydrogen cycling [21].

4.3.2. Tribological Degradation of Non-Hydrogen-Bonded Polymers

Tribological degradation in non-polar polymers mainly results from surface morphology changes rather than chemical effects. Hydrogen diffusion and desorption can cause blistering and pitting on the surface, increasing roughness. Reduced wear resistance arises due to microcrack coalescence in semi-crystalline regions.

However, low-friction polymers such as PTFE retain their lubricity because hydrogen does not significantly alter the C–F surface bonds. Examples: PTFE and UHMWPE remain stable tribologically, making them preferred candidates for hydrogen valve seats and bearings [11,92]. Table 5 provides a comparative summary of hydrogen-induced degradation mechanisms in polymers with and without hydrogen bonding.

Table 5. Summary of hydrogen bonding effects on the chemical, mechanical, and tribological properties of polymers.

Property Domain	with Hydrogen Bonding	Without Hydrogen Bonding	Key References
Mechanical	Hydrogen-assisted embrittlement, chain scission, reduced ductility	Diffusion-induced microcracks, fatigue softening	[11,21,74]
Chemical	Bond cleavage at polar sites, oxidation, hydrogenolysis	Minimal chemical change; possible surface etching	[13,93]
Tribological	Increased wear due to microcracks and adhesion loss	Surface pitting, roughness increase, minor friction change	[21,94,95]

Hydrogen-bonded polymers offer high strength and temperature resistance but are chemically vulnerable because hydrogen disrupts polar linkages. Non-hydrogen-bonded polymers, though chemically inert, are mechanically limited by gas diffusion and pressure-induced cracking. Therefore, hybrid or composite materials—such as fluoropolymer-reinforced amides or nanofiller-modified PUs—represent promising directions for developing durable hydrogen-compatible materials for seals, liners, and fuel-cell components.

5. Conditions of Hydrogen Exposure

Polymeric materials used in hydrogen systems are continuously subjected to a complex combination of thermodynamic, mechanical, and chemical stresses. The behavior of a polymer under hydrogen depends strongly on exposure conditions, namely pressure, temperature, time (or number of cycles), decompression rate, and environmental coupling (e.g., humidity or gas composition). These parameters govern hydrogen solubility, diffusivity, and the resulting microstructural damage such as swelling, blistering, or chain scission. A comprehensive understanding of these conditions is thus essential for establishing performance standards and predictive lifetime models for polymeric components.

5.1. Pressure Effects

Hydrogen is stored and distributed under pressures typically ranging from 35 to 70 MPa in commercial systems and up to 100 MPa in test facilities [14,96,97]. Increasing pressure elevates the hydrogen chemical potential, enhancing gas dissolution within the polymer matrix according to Sieverts' law:

$$C_{H_2} = k_s \sqrt{P_{H_2}} \quad (1)$$

where C_{H_2} is the equilibrium hydrogen concentration, k_s is Sieverts' constant, and P_{H_2} is the applied hydrogen pressure. At high pressures, the free volume within the polymer chains decreases due to hydrostatic compression, which may initially reduce diffusivity (D) but increases stored hydrogen content. During decompression, the sudden expansion of dissolved gas can nucleate internal cavities, producing micro-voids and blisters, a failure mode observed in polyamide liners of Type-IV tanks and HDPE pipelines after cyclic exposure between 35 and 70 MPa [14,96,97].

5.2. Temperature Effects

Temperature strongly influences both diffusivity (D) and permeability (P) of hydrogen through an Arrhenius relationship [71]:

$$D = D_0 exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

$$P = S \times D \quad (3)$$

where E_a is the activation energy for diffusion, R the gas constant, and S the solubility coefficient. Typical E_a values for polymers lie between 15 and 45 kJ mol^{-1}, depending on molecular structure and crystallinity. Elevated temperature increases chain mobility, enhancing diffusion and swelling but may also accelerate oxidation and chain scission in hydrogen-bonded polymers (e.g., polyamides, polyurethanes) where polar groups promote radical formation. For example, permeability of PA6 rises by nearly an order of magnitude between 25 °C and 80 °C, whereas non-polar PTFE exhibits only marginal change due to its low cohesive energy and stable C–F bonds [11,98].

5.3. Exposure Time and Pressure Cycling

The duration of hydrogen exposure and the number of pressure cycles significantly affect material response. Under steady-state conditions, diffusion tends to reach equilibrium; however, repeated loading–unloading induces cyclic expansion and contraction of the polymer network, leading to fatigue softening and gradual loss of stiffness. Long-term tests on HDPE and PA11 pipes exposed to 40–50 MPa hydrogen for up to 13 months showed moderate decreases in elastic modulus (≈10–15%) and crystallinity without catastrophic cracking [14]. Conversely, rapid pressurization–depressurization can produce cavitation

and delamination, particularly in amorphous or hydrogen-bond-rich materials where molecular relaxation is slower. These effects are magnified in cryogenic or sub-ambient environments (−40 °C), where hydrogen solubility increases while polymer ductility decreases [13].

5.4. Decompression and Rapid Venting

Upon rapid pressure release, supersaturated hydrogen within the polymer matrix desorbs violently, generating gas-phase nucleation and interfacial debonding. This decompression damage manifests as surface blistering, whitening, or micro-cracks, commonly observed in polyamide liners after fast refueling simulations and in HDPE seals after 10,000 pressure cycles [14,99]. The severity of damage depends on the decompression rate (dP/dt)—typically >10 MPa s^{-1} in rapid venting—where mechanical stresses exceed yield strength before gas diffusion can equilibrate. Composite liners are particularly susceptible at polymer–fiber interfaces, where mismatched elastic moduli promote debonding and blister coalescence.

5.5. Environmental Coupling and Mixed-Gas Effects

In practical hydrogen systems, polymers are rarely exposed to pure hydrogen; instead, they operate under coupled chemo–thermo–mechanical environments involving high-pressure hydrogen, temperature fluctuations, moisture, and trace impurities [72,100]. These combined effects significantly alter hydrogen transport, degradation pathways, and long-term reliability, often in ways that cannot be predicted from single-variable testing alone.

5.5.1. Competitive Sorption and Moisture Effects

In hydrogen-bonded polymers such as polyamides, polyurethanes, and polyimides, water molecules strongly compete with hydrogen for polar sorption sites (e.g., –CONH–, –OH groups) [101,102]. Due to their higher polarity, water molecules preferentially occupy these sites, leading to:

- Plasticization of the polymer matrix, increasing chain mobility and reducing glass transition temperature.
- Disruption of intermolecular hydrogen-bond networks, weakening mechanical integrity.
- Enhanced diffusion pathways, indirectly increasing hydrogen permeability under humid conditions.

While hydrogen itself has relatively low solubility in polar polymers, the presence of moisture amplifies degradation by coupling swelling, softening, and chemical instability, ultimately accelerating fatigue and embrittlement during pressure cycling [103].

5.5.2. Mixed-Gas and Impurity Effects

Hydrogen infrastructure often contains trace gases such as methane (CH_4), oxygen (O_2), hydrogen sulfide (H_2S), and ammonia (NH_3), each of which interacts differently with polymer systems [104]:

- Hydrogen–methane mixtures: Methane reduces polymer swelling due to its larger molecular size, but hydrogen dominates diffusion, leading to complex dual-gas transport behavior.
- Oxygen contamination: Promotes oxidative degradation, particularly in hydrogen-bonded polymers, accelerating chain scission at polar functional groups.
- Hydrogen sulfide (H_2S): Can induce chemical attack and localized degradation, especially in elastomers and polar polymers.
- Ammonia (NH_3): Strong polarity enhances interaction with hydrogen-bonded networks, further destabilizing intermolecular bonding.

These interactions demonstrate that degradation in hydrogen environments is not purely pressure-driven but governed by synergistic chemical interactions and competitive adsorption phenomena.

5.6. Thermodynamic and Chain Dynamic Effects on Hydrogen–Polymer Interactions

The behavior of polymers under hydrogen exposure is not governed solely by external conditions such as pressure and temperature, but also by intrinsic thermodynamic driving forces and chain dynamics, which together dictate hydrogen sorption, transport, and the resulting degradation mechanisms.

5.6.1. Thermodynamic Driving Forces for Hydrogen Sorption and Transport

Hydrogen uptake in polymers is controlled by the chemical potential gradient between the external gas phase and the polymer matrix. At equilibrium, hydrogen concentration follows Sieverts' law (Equation (1)). However, transport is more fundamentally governed by the gradient in chemical potential (μ), such that hydrogen flux can be expressed as [105]:

$$J = -cB(c)\frac{d\mu(c)}{dx} \quad (4)$$

where $B(c)$ denotes the concentration-dependent mobility of hydrogen. The variables J, B, and μ are expressed as functions of the quantities indicated in parentheses. This formulation highlights that hydrogen diffusion depends not only on concentration gradients but also on polymer–gas interactions and local free energy landscapes.

In hydrogen-bonded polymers, polar functional groups introduce enthalpic interactions, increasing hydrogen affinity but also promoting localized trapping and chemical reactivity. In contrast, non-hydrogen-bonded polymers exhibit weak interactions with hydrogen, and transport is dominated by entropy-driven diffusion through free volume. This distinction explains why hydrogen-bonded systems show moderate solubility but lower diffusivity, whereas non-polar systems exhibit low solubility but relatively higher diffusivity. The overall permeability (P) remains governed by Equation (3) [71,106].

The balance between these parameters is strongly influenced by molecular structure, crystallinity, and environmental conditions.

5.6.2. Free Volume and Thermodynamic Stability

The fractional free volume of polymers plays a central thermodynamic role in hydrogen transport. Regions with higher free volume provide energetically favorable sites for hydrogen accommodation, reducing the local chemical potential and facilitating diffusion. Semi-crystalline polymers exhibit heterogeneous thermodynamic environments, where [107,108]:

- Amorphous regions dominate hydrogen sorption and diffusion.
- Crystalline regions act as barriers due to dense molecular packing.

This leads to anisotropic transport behavior and explains why polymers such as HDPE and PA systems show pressure- and temperature-dependent permeability trends. Increasing temperature enhances chain mobility and entropy, thereby increasing diffusivity, while simultaneously reducing gas solubility in some systems. The competition between these effects governs the observed permeability behavior under realistic conditions.

5.6.3. Chain Dynamics and Segmental Mobility

Chain dynamics influence hydrogen transport through segmental mobility and relaxation behavior. Hydrogen-bonded polymers exhibit restricted chain mobility due to strong intermolecular interactions, resulting in high glass transition temperature (T_g), reduced

segmental motion and lower hydrogen diffusivity. However, under hydrogen exposure, particularly in the presence of elevated temperature or moisture, these intermolecular bonds may be disrupted, leading to localized plasticization, increased chain mobility, and subsequent mechanical degradation [109].

In contrast, non-hydrogen-bonded polymers possess greater intrinsic flexibility, characterized by lower T_g, higher segmental mobility and increased diffusion rates. While this facilitates hydrogen transport, it also promotes diffusion-driven damage mechanisms, including swelling, microvoid formation, and fatigue softening during cyclic pressurization [110].

5.6.4. Coupled Diffusion–Relaxation Behavior

The interaction between hydrogen diffusion and polymer relaxation introduces time-dependent, coupled behavior that is critical under service conditions. When hydrogen diffusion occurs faster than polymer relaxation, internal stresses accumulate, leading to micro void nucleation, blistering during decompression and crack initiation at weak interfaces. Conversely, when relaxation processes occur on comparable or faster timescales, the polymer can partially accommodate hydrogen-induced stresses, reducing damage severity. These effects are particularly pronounced under rapid decompression and cyclic loading, where mismatches between diffusion kinetics and mechanical response drive failure mechanisms observed in liners, seals, and pipelines [111,112].

5.6.5. Implications for Hydrogen Exposure Conditions

The thermodynamic and chain dynamic behavior of polymers provides a unifying framework linking the environmental factors discussed in Sections 5.1–5.5. Specifically:

- Pressure controls chemical potential and hydrogen uptake.
- Temperature governs both thermodynamic equilibrium and chain mobility.
- Time and cycling determine the extent of diffusion–relaxation coupling.
- Environmental coupling (humidity, impurities) modifies both thermodynamic interactions and dynamic response.

As a result, hydrogen compatibility must be understood as a multi-parameter, multi-physics problem, where thermodynamics and chain dynamics jointly dictate long-term performance. This perspective reinforces the need for integrated testing and modeling approaches that capture not only hydrogen transport but also the evolving mechanical and physicochemical state of the polymer under realistic operating conditions.

6. State of the Art in Hydrogen–Polymer Interaction Studies

Recent investigations have focused on the mechanical degradation, gas permeation, and tribological behavior of common polymers such as HDPE, UHMWPE, PEEK, PTFE, PA6, EPDM, and NBR under high-pressure hydrogen conditions (up to 90 MPa). Two prominent mechanisms affect polymer performance. The first is permeation and diffusion. Studies have demonstrated that hydrogen permeability and diffusion coefficients in polymers deteriorate with increasing pressure due to hydrostatic compression reducing the free volume available for gas transport [84,85]. The second mechanism is related to mechanical and tribological degradation. In situ tribometry and tensile testing revealed increased wear and friction in hydrogen-exposed EPDM, PTFE, and PEEK materials, primarily due to embrittlement, blistering, and surface interactions with counterface metals [86,87]. Advanced measurement methods, such as high-pressure hydrogen permeation testers and in situ tribometers, have enabled accurate characterization of polymers in practical FCEV and HRS environments.

6.1. Common Test Methods for Hydrogen Exposure in Polymers

To evaluate the impact of hydrogen on polymeric materials, several experimental methods have been developed and standardized. These include the following.

Hydrogen Permeation Testing: High-pressure permeation test systems are used to determine permeability, diffusivity, and solubility. ISO 15105 and ASTM D1434 [113] are commonly used standards. Tests can be performed under steady-state or transient conditions. Specialized autoclaves are used to simulate hydrogen storage pressures (35–90 MPa) [96].

In Situ Tensile Testing: Custom-built high-pressure chambers allow real-time mechanical testing under hydrogen atmosphere. Tensile stress–strain behavior is measured to assess embrittlement, yield strength loss, and fracture characteristics [114]. High-Pressure Tribometry: In situ tribometers evaluate the wear and friction performance of polymers in hydrogen environments. Parameters such as wear rate, coefficient of friction, and transfer film formation are monitored under varying loads and pressures [115].

Hydrogen Cycling and Fatigue Testing: Long-term exposure and cyclic pressurization tests assess mechanical fatigue, crack growth, and healing potential. These tests mimic operational conditions in hydrogen refueling stations or on-board storage [116].

Blistering/Cavitation Evaluation: Post-decompression inspection using SEM or micro-CT scans identifies internal voids, cracks, or blisters formed due to rapid pressure drops [117]. Thermal and Spectroscopic Analysis: Techniques like DSC, FTIR, and XRD are used to identify chemical and morphological changes pre- and post-exposure, such as crystallinity shifts or oxidation [21].

6.2. Limitations and Challenges

Despite progress, several limitations hinder widespread implementation:

- Measurement Constraints: Non-steady-state methods like TDA fail for highly fractured specimens post decompression, making steady-state high-pressure permeation tests more reliable but complex and cost-intensive [85].
- Material Diversity: Studies often focus on a narrow range of commercial polymers, limiting the generalizability of findings across different formulations and manufacturing methods.
- Surface and Interface Effects: Limited understanding exists regarding the role of fillers, additives, and counter face materials on tribological behavior in hydrogen environments.
- Long-Term Durability: Most studies are short-term and lack real-world cycling or environmental exposure data, particularly involving temperature-pressure-humidity fluctuations.

6.3. Future Research Direction

From the reviewed literature, several study gaps emerge. Firstly, there is a lack of standardized protocols for testing polymer performance under dynamic hydrogen pressure cycling. Secondly, insufficient multi-physics models coupling diffusion, mechanical degradation, and tribological wear mean applications for polymers handling hydrogen are not optimal. Furthermore, there is limited exploration of the nanocomposite or hybrid polymer systems with enhanced hydrogen resistance. Transportation, use, and storage of hydrogen under high pressure states in polymers remain underdeveloped. Finally, there is the absence of comprehensive failure maps correlating polymer chemistry, morphology, and service conditions.

6.4. Room for Improvement and Future Research

To improve the performance and reliability of polymer components in hydrogen systems. Material innovation is important. The development and testing of high-performance thermoplastics, vitrimers, and polymer nanocomposites specifically engineered for hydrogen barrier and mechanical resilience is paramount.

Testing enhancements are imperative. It is important to design integrated high-pressure test rigs capable of simultaneously evaluating permeation, wear, and mechanical behavior.

Modeling and simulation advancements are key. We need to advance the predictive modeling tools that account for coupled physical-chemical-mechanical effects in hydrogen environments.

Standardization and benchmarking are needed for uniform understanding and compatibility of solutions. The establishment of international test standards for polymers under hydrogen exposure are needed. Such standards should be analogous to ISO19880-5 and GTR 13 for component-level requirements.

7. Polymer Quality for Hydrogen Environments

The overall quality and suitability of polymers for hydrogen applications depend on their ability to maintain mechanical integrity, chemical stability, and low hydrogen permeability during long-term service. Comparative evaluation of polymers with and without hydrogen bonding reveals distinct strengths and limitations that govern their performance in storage, transport, and conversion systems.

7.1. Hydrogen-Bonded Polymers: Strength Versus Reactivity

Polymers containing strong intermolecular hydrogen bonds such as polyamides (PA6, PA11, PA66), polyurethanes (PU), polyimides (PI), and polybenzimidazole (PBI) exhibit superior mechanical strength, high glass-transition temperatures, and dimensional stability.

These features make them desirable for liners, membranes, and sealing components in pressurized or electrochemical hydrogen systems. However, their polar functional groups (–CONH–, –OH, –NH–) also make them chemically active under hydrogen exposure. Hydrogen diffusion and reactive radicals can disrupt the hydrogen-bond network, leading to partial loss of crystallinity, micro-cracking, and embrittlement. Consequently, their "quality index" in hydrogen environments is rated as high for short-term mechanical performance but moderate for long-term chemical stability. Table 6 provides a consolidated quality assessment of hydrogen-bonded polymers, emphasizing their superior mechanical strength and low gas permeability, while also identifying chemical stability as a limiting factor under prolonged hydrogen exposure.

Table 6. Quality assessment of hydrogen-bonded polymers in hydrogen environments.

Quality Aspect	Performance	Assessment
Mechanical strength	Excellent	High tensile and fatigue resistance
Chemical stability	Moderate	Sensitive to hydrogen-induced oxidation and H-bond disruption
Thermal stability	High	Stable up to 200 °C (aromatic polyamides, imides)
Gas permeability	Low	Suitable for liners and barriers
Long-term durability	Moderate	Degrades with moisture and hydrogen cycling

7.2. Non-Hydrogen-Bonded Polymers: Stability Versus Strength

Non-hydrogen-bonding polymers lack polar functional groups and therefore interact weakly with hydrogen molecules. Their chemical inertness, low hydrogen reactivity, and minimal radical susceptibility translate into excellent stability and low permeability, making them ideal for piping, liners, and valves in hydrogen infrastructure.

On the other hand, absence of cohesive H-bonds limits their mechanical modulus and temperature tolerance. Under cyclic high-pressure conditions, these materials may exhibit diffusion-driven microvoids or surface blistering, but without significant chemical decomposition.

Their quality rating is therefore excellent for chemical and tribological performance, yet moderate for structural applications requiring stiffness or high-temperature endurance. Table 7 summarizes the quality assessment of non-hydrogen-bonded polymers in hydrogen environments.

Table 7. Quality assessment of non- hydrogen-bonded polymers in hydrogen environments.

Quality Aspect	Performance	Assessment
Mechanical strength	Moderate	Ductile but lower modulus
Chemical stability	Excellent	Inert to H_2 and radicals
Thermal stability	Moderate	Melting range 120–200 °C
Gas permeability	Very low	Excellent hydrogen barrier (PTFE, PEEK)
Long-term durability	High	Stable under pressure cycling

7.3. Comparative Quality Evaluation

To provide a unified perspective on polymer performance in hydrogen environments, a comparative evaluation of hydrogen-bonded and non-hydrogen-bonded systems is presented in Table 8. This comparison highlights the fundamental structure–property trade-offs governing hydrogen compatibility, particularly the balance between mechanical robustness, chemical stability, and transport behavior.

Table 8. Comparative performance of hydrogen- and non-hydrogen-bonded polymers under hydrogen exposure conditions.

Criterion	Hydrogen-Bonded Polymers	Non-Hydrogen-Bonded Polymers
Structural integrity	High (reinforced by H-bond network)	Moderate (dependent on crystallinity)
Hydrogen compatibility	Moderate (reactive polar sites)	Excellent (chemically inert)
Permeability	Low–moderate	Very low
Degradation tendency	Chemical (chain scission, oxidation)	Physical (blistering, diffusion cracks)
Service temperature range	Wide (−50 °C to 200 °C)	Narrower (−80 °C to 120 °C)
Overall hydrogen environment quality rating	High mechanical, moderate chemical	High chemical, moderate mechanical

7.4. Quality Optimization Strategies

Enhancing polymer performance in hydrogen environments requires advanced material design strategies that address the coupled challenges of hydrogen permeability, mechanical integrity, and long-term durability. These strategies operate across multiple length scales, from molecular-level interactions to macroscopic structural design. While

significant improvements have been reported, each approach presents inherent trade-offs that must be carefully managed for practical applications.

7.4.1. Polymer Blending

Polymer blending provides a versatile approach to combine the complementary properties of hydrogen-bonded and non-hydrogen-bonded systems. Blends such as polyamide (PA)/polytetrafluoroethylene (PTFE) and polyurethane (PU)/polyether ether ketone (PEEK) leverage the high mechanical strength of hydrogen-bonded polymers and the chemical inertness of non-polar polymers. These systems have demonstrated approximately 20–40% reductions in hydrogen permeability, while maintaining moderate tensile strength and flexibility [26,118].

The improvement arises from phase-level synergy, where the dispersed non-polar phase disrupts continuous diffusion pathways, while the hydrogen-bonded phase maintains structural integrity. However, achieving optimal performance requires precise control of phase morphology and interfacial adhesion. Poor compatibility between phases can lead to phase separation, weak interfaces, and mechanical degradation, particularly under cyclic pressure and thermal loading. Long-term stability is further challenged by differential swelling and thermal expansion between phases.

7.4.2. Nanofiller Reinforcement

Nanofiller incorporation is among the most effective strategies for enhancing both barrier and mechanical properties. The addition of nanomaterials such as graphene, carbon nanotubes (CNTs), silica (SiO_2), and layered silicates introduces tortuous diffusion pathways, significantly increasing the effective path length for hydrogen transport.

Graphene/polyamide nanocomposites, for example, have shown 30–60% reductions in hydrogen permeability, along with 10–50% increases in modulus and tensile strength, depending on filler content and dispersion quality. Similar improvements have been reported for clay-filled and silica-reinforced systems. These enhancements are primarily attributed to the high aspect ratio of nanofillers and strong interfacial interactions, which restrict polymer chain mobility and reduce free volume [119,120].

Despite these benefits, the effectiveness of nanofillers is highly dependent on uniform dispersion and strong interfacial bonding. Agglomeration of nanoparticles can create defect regions and stress concentration sites, which may counteract barrier improvements and initiate mechanical failure. Additionally, high filler loadings can increase viscosity during processing, complicating manufacturability and scalability.

7.4.3. Cross-Linking Engineering

Cross-linking introduces a network structure that restricts polymer chain mobility and reduces free volume, thereby improving resistance to hydrogen diffusion and swelling. Chemically cross-linked systems such as cross-linked polyethylene (PEX) and epoxy networks typically exhibit 10–30% reductions in permeability, along with improved thermal stability and creep resistance.

The primary mechanism involves the formation of a three-dimensional network that limits segmental motion and suppresses diffusion pathways. This also enhances dimensional stability under high-pressure hydrogen exposure. However, excessive cross-linking can lead to increased brittleness, reduced fracture toughness, and limited recyclability, which may be detrimental in applications involving cyclic loading or impact stresses.

7.4.4. Surface Modification

Surface modification techniques, including plasma treatment, chemical grafting, and fluorination, provide a targeted approach to enhance hydrogen resistance without alter-

ing bulk properties. These methods can reduce hydrogen permeation at the surface by approximately 10–30%, primarily by forming low-energy or chemically inert surface layers.

For example, plasma fluorination introduces a fluorinated surface that reduces hydrogen solubility and improves chemical resistance. However, these modifications are inherently surface-limited, and their effectiveness may degrade over time due to abrasion, environmental exposure, or pressure cycling. As a result, surface treatments are often used in combination with bulk modification strategies.

7.4.5. Multilayer Structures and Coatings

Multilayer composite systems represent one of the most effective strategies for achieving high-performance hydrogen barriers. These systems combine a low-permeability inner layer (e.g., PTFE, EVOH) with a mechanically robust outer layer (e.g., polyamide, polyurethane), enabling simultaneous optimization of barrier and structural properties.

Such architectures can achieve up to an order-of-magnitude ($\approx 10\times$) reduction in hydrogen permeability compared to single-layer systems. The improvement arises from serial resistance to diffusion, where each layer contributes to the overall barrier performance.

However, multilayer systems are particularly susceptible to interfacial degradation mechanisms, including delamination, interfacial peeling, and crack propagation along layer boundaries. These issues are exacerbated by mismatches in thermal expansion coefficients and mechanical properties, especially under cyclic pressure and temperature conditions.

7.4.6. Crystallinity and Morphological Control

Increasing the degree of crystallinity is an effective way to reduce hydrogen permeability by limiting diffusion through densely packed crystalline regions. Semi-crystalline polymers such as HDPE and polyamides can achieve 20–50% reductions in permeability through controlled crystallization.

The mechanism involves the creation of impermeable crystalline domains, forcing hydrogen to diffuse through the amorphous phase. However, increasing crystallinity often leads to reduced toughness and increased brittleness, which may compromise mechanical performance under dynamic loading conditions.

7.4.7. Fiber-Reinforced and Hybrid Composites

Fiber-reinforced polymer composites, such as carbon fiber-reinforced polymers (CFRP), are widely used in hydrogen storage applications (e.g., Type IV tanks). These systems provide multi-fold increases in mechanical strength (typically >2–5$\times$) while maintaining relatively low weight.

Hybrid systems combining polymer matrices with solid lubricants or barrier fillers can also provide multifunctional performance, including improved wear resistance and reduced hydrogen permeability. However, these systems require careful optimization of fiber–matrix and filler–matrix interfaces to avoid debonding and performance degradation.

7.4.8. Emerging Self-Healing and Vitrimer Systems

Emerging materials such as self-healing polymers and vitrimer networks offer new opportunities for improving long-term durability. These systems utilize dynamic covalent bonds that enable stress relaxation and damage repair, achieving ~80–100% recovery of mechanical integrity after microcrack formation [121].

Vitrimers, in particular, combine the structural stability of thermosets with the reprocessability of thermoplastics, making them promising candidates for hydrogen-resistant materials. However, their performance is often temperature-dependent, and challenges related to processing, long-term stability, and industrial scalability remain.

7.4.9. Overall Assessment and Design Trade-Offs

While these optimization strategies demonstrate significant improvements in hydrogen barrier performance and mechanical durability, their practical implementation requires balancing permeability reduction, mechanical integrity, processability, and long-term reliability. Key challenges include:

- Nanofiller dispersion and agglomeration.
- Interfacial adhesion in blends and multilayer systems.
- Durability under cyclic pressure and thermal loading.
- Scalability and manufacturing complexity.

These considerations highlight the need for integrated material design approaches and multi-field-testing methodologies, ensuring that optimized materials can perform reliably under realistic hydrogen service conditions.

8. Conclusions

Hydrogen–polymer interactions are fundamentally governed by molecular architecture, particularly the presence or absence of hydrogen bonding, which dictates the balance between mechanical strength, chemical stability, and hydrogen transport behavior. Hydrogen-bonded polymers provide high structural integrity, thermal resistance, and barrier performance due to strong intermolecular cohesion; however, their polar functional groups render them vulnerable to hydrogen-assisted chemical degradation, including bond scission, oxidation, and embrittlement under prolonged exposure. Conversely, non-hydrogen-bonded polymers exhibit excellent chemical inertness and stable tribological performance, with minimal reactivity toward hydrogen, but are limited by diffusion-induced physical damage such as blistering, microvoid formation, and fatigue softening under cyclic pressure conditions.

The comparative analysis demonstrates that no single polymer class satisfies all performance requirements for hydrogen environments. Instead, hydrogen compatibility emerges as a multi-dimensional property governed by the interplay of diffusion, mechanical stress, thermal effects, and interfacial behavior. This inherent trade-off underscores the necessity of hybrid material design strategies. Approaches such as polymer blending (e.g., hydrogen-bonded/non-bonded systems), nanofiller incorporation (graphene, SiO_2), and multilayer composite architectures (e.g., fluoropolymer barrier layers combined with structural polymers) offer promising pathways to simultaneously enhance barrier performance, mechanical durability, and chemical resistance.

Future research should focus on developing multi-functional polymer systems through controlled molecular design, establishing standardized testing protocols under realistic hydrogen cycling conditions, and advancing multi-physics modeling frameworks that couple diffusion, chemical degradation, and tribological wear. Additionally, the integration of self-healing polymers, vitrimer networks, and smart sensing materials represents an emerging frontier for improving long-term reliability. These advances are essential for enabling safe, durable, and high-performance polymer components in next-generation hydrogen storage, transport, and energy conversion systems.

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References

1. Sun, H.; Wang, Z.; Meng, Q.; White, S. Advancements in hydrogen storage technologies: Enhancing efficiency, safety, and economic viability for sustainable energy transition. *Int. J. Hydrogen Energy* **2025**, *105*, 10–22. [CrossRef]
2. Angelico, R.; Giametta, F.; Bianchi, B.; Catalano, P. Green hydrogen for energy transition: A critical perspective. *Energies* **2025**, *18*, 404. [CrossRef]
3. Wang, Y.; Yuan, H.; Martinez, A.; Hong, P.; Xu, H.; Bockmiller, F.R. Polymer electrolyte membrane fuel cell and hydrogen station networks for automobiles: Status, technology, and perspectives. *Adv. Appl. Energy* **2021**, *2*, 100011. [CrossRef]
4. Pang, Y.; Martinez, A.; Wang, Y. Hydrogen refueling stations/infrastructure. In *Fuel Cells for Transportation*; Elsevier: Amsterdam, The Netherlands, 2023; pp. 575–597.
5. Sun, B.; Zhao, H.; Dong, X.; Teng, C.; Zhang, A.; Kong, S.; Zhou, J.; Zhang, X.-C.; Tu, S.-T. Current challenges in the utilization of hydrogen energy-a focused review on the issue of hydrogen-induced damage and embrittlement. *Adv. Appl. Energy* **2024**, *14*, 100168. [CrossRef]
6. Ahad, M.T.; Bhuiyan, M.M.H.; Sakib, A.N.; Becerril Corral, A.; Siddique, Z. An overview of challenges for the future of hydrogen. *Materials* **2023**, *16*, 6680. [CrossRef]
7. Bridgeland, R.; Chapman, A.; McLellan, B.; Sofronis, P.; Fujii, Y. Challenges toward achieving a successful hydrogen economy in the US: Potential end-use and infrastructure analysis to the year 2100. *Clean. Prod. Lett.* **2022**, *3*, 100012. [CrossRef]
8. Kulkarni, S.S.; Choi, K.S.; Kuang, W.; Menon, N.; Mills, B.; Soulami, A.; Simmons, K. Damage evolution in polymer due to exposure to high-pressure hydrogen gas. *Int. J. Hydrogen Energy* **2021**, *46*, 19001–19022. [CrossRef]
9. Simmons, K.L.; Kuang, W.; Burton, S.D.; Arey, B.W.; Shin, Y.; Menon, N.C.; Smith, D. H-Mat hydrogen compatibility of polymers and elastomers. *Int. J. Hydrogen Energy* **2021**, *46*, 12300–12310. [CrossRef]
10. Dagdag, O.; Kim, H. Recent Advances in the Hydrogen Gas Barrier Performance of Polymer Liners and Composites for Type IV Hydrogen Storage Tanks: Fabrication, Properties, and Molecular Modeling. *Polymers* **2025**, *17*, 1231. [CrossRef] [PubMed]
11. Dong, C.; Liu, Y.; Li, J.; Bin, G.; Zhou, C.; Han, W.; Li, X. Hydrogen permeability of polyamide 6 used as liner material for type IV on-board hydrogen storage cylinders. *Polymers* **2023**, *15*, 3715. [CrossRef]
12. Duranty, E.R.; Roosendaal, T.J.; Pitman, S.G.; Tucker, J.C.; Owsley, S.L., Jr.; Suter, J.D.; Alvine, K.J. In situ high pressure hydrogen tribological testing of common polymer materials used in the hydrogen delivery infrastructure. *J. Vis. Exp. JoVE* **2018**, *133*, 56884.
13. Menon, N.C.; Nissen, A.; McArthur, K.; Mills, B.; Ryan, F.; Simmons, K. Evaluation of Common Thermoplastic Polymers in High-Pressure Cycling Hydrogen Under Ambient and Cold Environments as Applicable to the Hydrogen Infrastructure. In *Proceedings of the ASME 2024 Pressure Vessels & Piping Conference, Bellevue, WA, USA, 28 July–2 August 2024*; American Society of Mechanical Engineers: New York, NY, USA, 2024.
14. Castagnet, S.; Grandidier, J.-C.; Comyn, M.; Benoît, G. Effect of long-term hydrogen exposure on the mechanical properties of polymers used for pipes and tested in pressurized hydrogen. *Int. J. Press. Vessel. Pip.* **2012**, *89*, 203–209. [CrossRef]
15. Coleman, M.M.; Painter, P.C. Hydrogen bonded polymer blends. *Prog. Polym. Sci.* **1995**, *20*, 1021–1051. [CrossRef]
16. Painter, P.C.; Park, Y.; Coleman, M.M. Hydrogen bonding in polymer blends. 2. Theory. *Macromolecules* **1988**, *21*, 66–72. [CrossRef]
17. Tajima, R.; Nakagawa, S.; Yoshie, N. Multiple hydrogen bonds as tools to enhance the mechanical and mechanoresponsive properties of polymers. *Polym. J.* **2025**, *58*, 1–13. [CrossRef]
18. Wan, Q.; Thompson, B.C. Control of properties through hydrogen bonding interactions in conjugated polymers. *Adv. Sci.* **2024**, *11*, 2305356. [CrossRef]
19. Sandoz-Rosado, E.; Beaudet, T.D.; Andzelm, J.W.; Wetzel, E.D. High strength films from oriented, hydrogen-bonded "graphamid" 2D polymer molecular ensembles. *Sci. Rep.* **2018**, *8*, 3708. [CrossRef] [PubMed]
20. Zheng, J.; Png, Z.M.; Oh, X.Y.; Zuo, H.; Li, Z. Recycling homocarbon backbone polymers toward a circular materials economy. *Chem* **2025**, *11*, 102406. [CrossRef]
21. Dawicka, N.; Kurc, B.; Gross, X.; Tomasz, J.; Siwińska-Ciesielczyk, K.; Kołodziejczak-Radzimska, A. Analysis of the Strength of Polyamide Used for High Pressure Transmission of Hydrogen on the Example of Reinforced Plastic Hoses. *Materials* **2025**, *18*, 1402. [CrossRef]
22. Byrne, N.; Ghanei, S.; Espinosa, S.M.; Neave, M. Influence of hydrogen on vintage polyethylene pipes: Slow crack growth performance and material properties. *Int. J. Energy Res.* **2023**, *2023*, 6056999. [CrossRef]
23. Tsioptsias, C. Thermochemical transition in non-hydrogen-bonded polymers and theory of latent decomposition. *Polymers* **2022**, *14*, 5054. [CrossRef]
24. Patil, S.; Gainaru, C.; Böhmer, R.; Cheng, S. Evidence for supramolecular dynamics of non-hydrogen bonding polar van der Waals liquids. *J. Chem. Phys.* **2025**, *163*, 134501. [CrossRef]
25. Primc, G. Strategies for improved wettability of polyetheretherketone (PEEK) polymers by non-equilibrium plasma treatment. *Polymers* **2022**, *14*, 5319. [CrossRef] [PubMed]

26. Moskvitin, L.V.; Koshkina, O.G.A.; Slesarenko, S.V.E.; Arsentyev, M.A.; Trakhtenberg, L.I.; Ryndya, S.M.; Magomedbekov, E.P.; Smolyanskii, A.S. Thermoradiationally Modified Polytetrafluoroethylene as a Basis for Membrane Fabrication: Resistance to Hydrogen Penetration, the Effect of Ion Treatment on the Chemical Structure and Surface Morphology, Evaluation of the Track Radius. *Membranes* **2023**, *13*, 101. [CrossRef] [PubMed]
27. Tang, H.; Wang, M.; Li, Y.; Wang, Y. A Study on the Effect and Suppression of Hydrogen Permeation Behavior on the Friction Characteristics of PEEK/PTFE Composites via Molecular Dynamics Simulation. *Polymers* **2024**, *16*, 1000. [CrossRef]
28. Wilson, M.A.; Frischknecht, A.L. High-pressure hydrogen decompression in sulfur crosslinked elastomers. *Int. J. Hydrogen Energy* **2022**, *47*, 15094–15106. [CrossRef]
29. Klopffer, M.-H.; Berne, P.; Castagnet, S.; Weber, M.; Hochstetter, G.; Espuche, E. Polymer pipes for distributing mixtures of hydrogen and natural gas. Evolution of their transport and mechanical properties after an ageing under an hydrogen environment. In *Proceedings of the WHEC 2010: 18. World Hydrogen Energy Conference: Building Bridges to the Hydrogen Energy Economy, Essen, Germany, 16–21 May 2010*; U.S. Department of Energy Office of Scientific and Technical Information: Oak Ridge, TN, USA, 2010.
30. Mabesoone, M.F.; Palmans, A.R.; Meijer, E. Solute–solvent interactions in modern physical organic chemistry: Supramolecular polymers as a muse. *J. Am. Chem. Soc.* **2020**, *142*, 19781–19798. [CrossRef]
31. Speight, J.G. *Handbook of Industrial Hydrocarbon Processes*; Gulf Professional Publishing: New York, NY, USA, 2019.
32. Afonin, A.V.; Vashchenko, A.V.; Sigalov, M.V. Estimating the energy of intramolecular hydrogen bonds from 1 H NMR and QTAIM calculations. *Org. Biomol. Chem.* **2016**, *14*, 11199–11211. [CrossRef]
33. Moldoveanu, S.; David, V. Solvents, buffers, and additives used in the mobile phase. In *Selection of the HPLC Method in Chemical Analysis*; Moldoveanu, S.C., Ed.; Elsevier: Amsterdam, The Netherlands, 2017; pp. 393–450.
34. Galante, M.; Tkatchenko, A. Anisotropic van der Waals dispersion forces in polymers: Structural symmetry breaking leads to enhanced conformational search. *Phys. Rev. Res.* **2023**, *5*, L012028. [CrossRef]
35. Liu, C.-S.; Pilania, G.; Wang, C.; Ramprasad, R. How critical are the van der Waals interactions in polymer crystals? *J. Phys. Chem. A* **2012**, *116*, 9347–9352. [CrossRef] [PubMed]
36. Li, Q.; Tan, S.; Gong, H.; Lu, J.; Zhang, W.; Zhang, X.; Zhang, Z. Influence of dipole and intermolecular interaction on the tuning dielectric and energy storage properties of polystyrene-based polymers. *Phys. Chem. Chem. Phys.* **2021**, *23*, 3856–3865. [CrossRef]
37. Kuo, S.-W. Hydrogen-bonding in polymer blends. *J. Polym. Res.* **2008**, *15*, 459–486. [CrossRef]
38. Wang, S.; Tang, S.; He, C.; Wang, Q. Cyclic deformation and fatigue failure mechanisms of thermoplastic polyurethane in high cycle fatigue. *Polymers* **2023**, *15*, 899. [CrossRef]
39. Tsioptsias, C.; Fardis, D.; Ntampou, X.; Tsivintzelis, I.; Panayiotou, C. Thermal behavior of poly (vinyl alcohol) in the form of physically crosslinked film. *Polymers* **2023**, *15*, 1843. [CrossRef]
40. Phattarateera, S.; Xin, L.; Amphong, C.; Limsamran, V.; Threepopnatkul, P. Comparative studies of starch blends on the properties of PVA films. *Carbohydr. Polym. Technol. Appl.* **2023**, *6*, 100340. [CrossRef]
41. Iritani, K.; Nakanishi, A.; Ota, A.; Yamashita, T. Fabrication of Novel Functional Cell-Plastic Using Polyvinyl Alcohol: Effects of Cross-Linking Structure and Mixing Ratio of Components on the Mechanical and Thermal Properties. *Glob. Chall.* **2021**, *5*, 2100026. [CrossRef]
42. Chan, C.K.; Chu, I.M. Effect of hydrogen bonding on the glass transition behavior of poly (acrylic acid)/silica hybrid materials prepared by sol–gel process. *Polymer* **2001**, *42*, 6089–6093. [CrossRef]
43. Huang, Q.; Wan, C.; Loveridge, M.; Bhagat, R. Partially neutralized polyacrylic acid/poly (vinyl alcohol) blends as effective binders for high-performance silicon anodes in lithium-ion batteries. *ACS Appl. Energy Mater.* **2018**, *1*, 6890–6898. [CrossRef]
44. Bai, L.; Zhai, L.; He, M.H.; Wang, C.O.; Mo, S.; Fan, L. Thermal expansion behavior of poly (amide-imide) films with ultrahigh tensile strength and ultralow CTE. *Chin. J. Polym. Sci.* **2020**, *38*, 748–758. [CrossRef]
45. Vrandečić, N.S.; Erceg, M.; Jakić, M.; Klarić, I. Kinetic analysis of thermal degradation of poly (ethylene glycol) and poly (ethylene oxide) s of different molecular weight. *Thermochim. Acta* **2010**, *498*, 71–80. [CrossRef]
46. Gucci, F.; Grasso, M.; Russo, S.; Leighton, G.J.; Shaw, C.; Brighton, J. Electrical and mechanical characterisation of poly (ethylene) oxide-polysulfone blend for composite structural lithium batteries. *Polymers* **2023**, *15*, 2581. [CrossRef] [PubMed]
47. Huang, S.; Zhou, L.; Li, M.C.; Wu, Q.; Kojima, Y.; Zhou, D. Preparation and properties of electrospun poly (vinyl pyrrolidone)/cellulose nanocrystal/silver nanoparticle composite fibers. *Materials* **2016**, *9*, 523. [CrossRef]
48. Jayalath, I.N.; Vaidyanathan, R.; Blum, F.D. Thermal Behavior of Polyvinylpyrrolidone on Reduced Graphene Oxide. *J. Polym. Sci.* **2025**, *63*, 1898–1907. [CrossRef]
49. Zhang, C.; Jiang, Y.X.; Sun, J.P.; Xiao, H.; Shi, M.W.; Long, J.J. Investigation of the influence of supercritical carbon dioxide treatment on meta-aramid fiber: Thermal decomposition behavior and kinetics. *J. CO2 Util.* **2020**, *37*, 85–96. [CrossRef]
50. Chadwick, S.S. Ullmann's encyclopedia of industrial chemistry. *Ref. Serv. Rev.* **1988**, *16*, 31–34. [CrossRef]
51. Liu, P.; Lu, R.; Huang, T.; Cong, P.; Jiang, S.; Li, T. Tensile and tribological properties of polytetrafluroethylene homocomposites. *Wear* **2012**, *289*, 65–72. [CrossRef]

52. Calleja, G.; Jourdan, A.; Ameduri, B.; Habas, J.P. Where is the glass transition temperature of poly (tetrafluoroethylene)? A new approach by dynamic rheometry and mechanical tests. *Eur. Polym. J.* **2013**, *49*, 2214–2222. [CrossRef]
53. Yuan, M.; Galloway, J.A.; Hoffman, R.J.; Bhatt, S. Influence of molecular weight on rheological, thermal, and mechanical properties of PEEK. *Polym. Eng. Sci.* **2011**, *51*, 94–102. [CrossRef]
54. Yu, Y.H.; Liu, S.J. Polyetheretherketone for orthopedic applications: A review. *Curr. Opin. Chem. Eng.* **2021**, *32*, 100687. [CrossRef]
55. Kuo, S.W.; Xu, H.; Huang, C.F.; Chang, F.C. Significant glass-transition-temperature increase through hydrogen-bonded copolymers. *J. Polym. Sci. Part B Polym. Phys.* **2002**, *40*, 2313–2323. [CrossRef]
56. Saha, J.K.; Rahman, M.M.; Haq, M.B.; Al Shehri, D.A.; Jang, J. Theoretical and experimental studies of hydrogen bonded dihydroxybenzene isomers polyurethane adhesive material. *Polymers* **2022**, *14*, 1701. [CrossRef]
57. Chen, L.; Lin, Z. Polyethylene: Properties, production and applications. In *Proceedings of the 2021 3rd International Academic Exchange Conference on Science and Technology Innovation (IAECST), Guangzhou, China, 10–12 December 2021*; IEEE: Piscataway, NJ, USA, 2021.
58. Ashby, M.F. *Materials and Sustainable Development*; Butterworth-Heinemann: Oxford, UK, 2022.
59. Perozziello, G.; Kruhne, U.; Luciani, P. *Microfluidics for Cellular Applications*; Elsevier: Amsterdam, The Netherlands, 2023.
60. Hosseinzadeh, H.; Salehi, A.M.; Mehraein, M.; Asadollahfardi, G. The effects of steel, polypropylene, and high-performance macro polypropylene fibers on mechanical properties and durability of high-strength concrete. *Constr. Build. Mater.* **2023**, *386*, 131589. [CrossRef]
61. Singh, A.; Chauhan, A.; Gaur, R. A comprehensive review on the synthesis, properties, environmental impacts, and chemiluminescence applications of polystyrene (PS). *Discov. Chem.* **2025**, *2*, 47. [CrossRef]
62. Yang, Y.; Liu, Z.; Hao, Y. *Flame Retardant Selection for Thermoplastics, in Flame Retardant Selection for Polymers*; Elsevier: Amsterdam, The Netherlands, 2025; pp. 27–61.
63. Edo, G.I.; Yousif, E.; Al-Mashhadani, M.H. Polymethyl Methacrylate (PMMA): An Overview of Its Biological Activities, Properties, Polymerization, Modifications, and Dental and Industrial Applications. *Regen. Eng. Transl. Med.* **2025**, 1–27. [CrossRef]
64. Li, W.; Li, J.; Xing, H.; Wang, K.; Zhang, Y.; Liu, J. Simultaneously enhancing fire retardancy, acid and alkali resistance of polypropylene/aluminum trihydrate composite by microencapsulated red phosphorus. *J. Vinyl Addit. Technol.* **2025**, *31*, 199–210. [CrossRef]
65. Feng, Z.; Cai, W.; Gao, J.; Jiang, G.; Qi, L.; Li, J.; Hu, Y.; Chu, F.; Xing, W. Achieving scratch resistance and flame retardancy in transparent polycarbonate through P/N/Si synergistic coating. *Prog. Org. Coat.* **2025**, *204*, 109247. [CrossRef]
66. Mohajan, H.K. Polyethylene Terephthalate (PET): An Overview on Production, Consumption, and Recycling. *Art Soc.* **2025**, *4*, 33–35.
67. Chen, M.; Jabeen, F.; Rasulev, B.; Ossowski, M.; Boudjouk, P. A computational structure–property relationship study of glass transition temperatures for a diverse set of polymers. *J. Polym. Sci. Part B Polym. Phys.* **2018**, *56*, 877–885. [CrossRef]
68. Wang, W.; Zhao, G.; Ma, X.; Ren, D.; Nie, M.; Han, R. Polyamide 6 as a liner material for type IV hydrogen storage cylinders: Performance challenges and modification strategies. *Polymers* **2025**, *17*, 1848. [CrossRef]
69. Habib, A.A.; Sakib, A.N.; Mona, Z.T.; Bhuiyan, M.M.H.; Kazempoor, P.; Siddique, Z. Hydrogen-Assisted aging applied to storage and sealing materials: A comprehensive review. *Materials* **2023**, *16*, 6689. [CrossRef]
70. Jana, S.; Parthiban, A.; Rusli, W. Polymer material innovations for a green hydrogen economy. *Chem. Commun.* **2025**, *61*, 3233–3249. [CrossRef]
71. Sgambitterra, E.; Pagnotta, L. Permeability: The driving force that influences the mechanical behavior of polymers used for hydrogen storage and delivery. *Energies* **2024**, *17*, 2216. [CrossRef]
72. Balasooriya, W.; Clute, C.; Schrittesser, B.; Pinter, G. A review on applicability, limitations, and improvements of polymeric materials in high-pressure hydrogen gas atmospheres. *Polym. Rev.* **2022**, *62*, 175–209. [CrossRef]
73. Dutton, R. Materials degradation problems in hydrogen energy systems. *Int. J. Hydrogen Energy* **1984**, *9*, 147–155. [CrossRef]
74. Li, J.; Lv, R.; Gu, C.; Liu, Y.; Li, J.; Li, X. An Ageing Test Standards Analysis on Thermoplastic Liners of Type IV Composite Hydrogen Storage Tanks. *Energies* **2023**, *16*, 2818. [CrossRef]
75. Gauthier, M.M. (Ed.) Advanced Thermoplastics. In *Engineered Materials Handbook Desk Edition*; ASM International: Almere, The Netherlands, 1995.
76. Board, N. *Polymers and Plastics Technology Handbook*; Asia Pacific Business Press Inc.: Delhi, India, 2004.
77. Kaiser, R.; Ahn, C.-Y.; Kim, Y.-H.; Park, J.-C. Towards Reliable Prediction of Performance for Polymer Electrolyte Membrane Fuel Cells via Machine Learning-Integrated Hybrid Numerical Simulations. *Processes* **2024**, *12*, 1140. [CrossRef]
78. Tellez-Cruz, M.M.; Escorihuela, J.; Solorza-Feria, O.; Compañ, V. Proton exchange membrane fuel cells (PEMFCs): Advances and challenges. *Polymers* **2021**, *13*, 3064. [CrossRef]
79. Sajid, A.; Pervaiz, E.; Ali, H.; Noor, T.; Baig, M.M. A perspective on development of fuel cell materials: Electrodes and electrolyte. *Int. J. Energy Res.* **2022**, *46*, 6953–6988. [CrossRef]
80. Sezer Hicyilmaz, A.; Celik Bedeloglu, A. Applications of polyimide coatings: A review. *SN Appl. Sci.* **2021**, *3*, 363. [CrossRef]

81. Gomez-Lopez, A.; Panchireddy, S.; Grignard, B.; Calvo, I.; Jerome, C.; Detrembleur, C.; Sardon, H. Poly (hydroxyurethane) adhesives and coatings: State-of-the-art and future directions. *ACS Sustain. Chem. Eng.* **2021**, *9*, 9541–9562. [CrossRef]
82. Barth, R.R.; Simmons, K.L.; San Marchi, C.W. *Polymers for Hydrogen Infrastructure and Vehicle Fuel Systems*; Sandia National Lab. (SNL-CA): Livermore, CA, USA; Pacific Northwest National Laboratory: Livermore, CA, USA, 2013.
83. Patel, A.; Acharya, N. Metal coated and nanofiller doped polycarbonate membrane for hydrogen transport. *Int. J. Hydrogen Energy* **2018**, *43*, 21675–21682. [CrossRef]
84. Menon, N.C.; Hecht, E. *Dispenser Reliability: Materials R&D. A Hydrogen Fueling Infrastructure Research and Station Technology (H2FIRST) Report*; Sandia National Lab. (SNL-CA): Livermore, CA, USA; National Renewable Energy Laboratory (NREL): Golden, CO, USA, 2020.
85. Chapelle, D.; Feng, L.P.; Nardin, P.; Rauch, J.Y. Assessment of the gas permeation through thin coated polymeric membranes; Improvement of the gas barrier ability for hydrogen storage. In *Defect and Diffusion Forum*; Trans Tech Publications: Baech, Switzerland, 2012.
86. Dagdag, O.; Kim, H. Cryogenic Impact on Carbon Fiber-Reinforced Epoxy Composites for Hydrogen Storage Vessels. *J. Compos. Sci.* **2024**, *8*, 459. [CrossRef]
87. Hecht, E.S. *Review on the Effects of Hydrogen at Extreme Pressures and Temperatures on the Mechanical Behavior of Polymers*; Sandia National Lab. (SNL-CA): Livermore, CA, USA, 2013.
88. Abdullayev, E.; Fladung, T.; Noeske, P.-L.M.; Mayer, B. Investigation of Hydrogen Transport Behavior in Polyethylene Terephthalate Membrane by Prolonged Hydrogen Exposure Treatments. *Energies* **2024**, *17*, 6478. [CrossRef]
89. Xie, F.; Zhang, T.; Bryant, P.; Kurusingal, V.; Colwell, J.M.; Laycock, B. Degradation and stabilization of polyurethane elastomers. *Prog. Polym. Sci.* **2019**, *90*, 211–268. [CrossRef]
90. Zhang, X.; Zhai, L.; Li, H.; Qi, G.; Gao, X.; Yang, W. Molecular simulation study on the hydrogen permeation behavior and mechanism of common polymers. *Polymers* **2024**, *16*, 953. [CrossRef]
91. Figiel, Ł.; De Angelis, M.G.; Janssen, F.; Vehlow, D.; Giannis, S.; Skytree, L.; Walls-Bruck, M.; Douglas, A. Polymers and composites for hydrogen economy: A perspective. *J. Mater. Sci. Compos.* **2025**, *6*, 11. [CrossRef]
92. Yin, S.; Taylor, A.; Wong, J.S. Tribology of PTFE in Hydrogen Atmosphere. *Tribol. Int.* **2025**, *204*, 110481. [CrossRef]
93. Morsbach, S.; Giersch, D.; Zhang, K.A.; Schüßling, A.; Weberskirch, D.; Börger, A. Hydrogen compatibility of polymers for fuel cell vehicles. *Energy Technol.* **2022**, *10*, 2200018. [CrossRef]
94. Sawae, Y.; Morita, T.; Takeda, K.; Onitsuka, S.; Kaneuti, J.; Yamaguchi, T.; Sugimura, J. Friction and wear of PTFE composites with different filler in high purity hydrogen gas. *Tribol. Int.* **2021**, *157*, 106884. [CrossRef]
95. Wang, S. Blending Hydrogen in Urban Gas Pipeline System: Investigation of the Hydrogen Compatibility of PE Pipeline Material. *J. Pipeline Sci. Eng.* **2025**, *6*, 100297. [CrossRef]
96. Fujiwara, H.; Ono, H.; Onoue, K.; Nishimura, S. High-pressure gaseous hydrogen permeation test method-property of polymeric materials for high-pressure hydrogen devices (1). *Int. J. Hydrogen Energy* **2020**, *45*, 29082–29094. [CrossRef]
97. Fujiwara, H.; Ono, H.; Ohyama, K.; Kasai, M.; Kaneko, F.; Nishimura, S. Hydrogen permeation under high pressure conditions and the destruction of exposed polyethylene-property of polymeric materials for high-pressure hydrogen devices (2). *Int. J. Hydrogen Energy* **2021**, *46*, 11832–11848. [CrossRef]
98. Yuan, S.; Zhang, S.; Wei, J.; Gao, Y.; Zhu, Y.; Wang, H. Materials selection, design, and regulation of polymer-based hydrogen barrier composite coatings, membranes and films for effective hydrogen storage and transportation: A comprehensive review. *Int. J. Hydrogen Energy* **2024**, *91*, 555–573. [CrossRef]
99. Menon, N.C.; Kruizenga, A.M.; San Marchi, C.W.; Campbell, J.; Nissen, A.; Mills, B.E. *Polymer Behaviour in High Pressure Hydrogen Helium and Argon Environments as Applicable to the Hydrogen Infrastructure*; Sandia National Lab. (SNL-NM): Albuquerque, NM, USA, 2017.
100. Hmaimid, Z.; Varghese, R.T.; Finger, D.C.; Guðlaugsson, B.; Costa, D.A.; Ahmed, T.; Narayanan, J.A. A comprehensive review on the compatibility of polymeric materials for hydrogen transportation and storage. *Int. J. Hydrogen Energy* **2025**, *192*, 152366. [CrossRef]
101. Gilormini, P.; Verdu, J. On the role of hydrogen bonding on water absorption in polymers. *Polymer* **2018**, *142*, 164–169. [CrossRef]
102. Gardeniers, M.; Leone, N.; Kneepkens, R.; van Diepen, A.; Droste, J.; Hansen, M.R.; Rastogi, S.; Harings, J.A. Breaking the hydrogen bond barrier reversibly: Toward ultradrawable polyamides. *ACS Appl. Polym. Mater.* **2025**, *7*, 6825–6836. [CrossRef]
103. Zhang, X.; Yin, Z.; Xiang, S.; Yan, H.; Tian, H. Degradation of polymer materials in the environment and its impact on the health of experimental animals: A review. *Polymers* **2024**, *16*, 2807. [CrossRef]
104. Kass, M.D.; Keiser, J.R.; Liu, Y.; Moore, A.; Polsky, Y. Assessing compatibility of natural gas pipeline materials with hydrogen, CO_2, and ammonia. *J. Pipeline Syst. Eng. Pract.* **2023**, *14*, 04023007. [CrossRef]
105. Suzuki, A.; Yukawa, H.; Nambu, T.; Matsumoto, Y.; Murata, Y. Consistent description of hydrogen permeability through metal membrane based on hydrogen chemical potential. *Int. J. Hydrogen Energy* **2014**, *39*, 7919–7924. [CrossRef]

106. Zhang, H.; Geise, G.M. Modeling the water permeability and water/salt selectivity tradeoff in polymer membranes. *J. Membr. Sci.* **2016**, *520*, 790–800. [CrossRef]
107. Divine-Ayela, C.; Perez, F.; Striolo, A. Hop, skip, and jump: Hydrogen molecular transport through amorphous polyethylene matrices studied via molecular dynamics simulations. *Ind. Eng. Chem. Res.* **2023**, *62*, 19893–19906. [CrossRef]
108. Atiq, O.; Ricci, E.; Baschetti, M.G.; De Angelis, M.G. Molecular simulations of hydrogen sorption in semicrystalline high-density polyethylene: The impact of the surface fraction of tie-chains. *J. Phys. Chem. B* **2024**, *128*, 2799–2810. [CrossRef]
109. Otmi, M.A.; Willmore, F.; Sampath, J. Structure, dynamics, and hydrogen transport in amorphous polymers: An analysis of the interplay between free volume element distribution and local segmental dynamics from molecular dynamics simulations. *Macromolecules* **2023**, *56*, 9042–9053. [CrossRef]
110. Xu, H.; Yang, T.; Lei, Y.; Fu, X.; Liu, Z.; Li, S.; Jiang, L.; Lei, J. Mechanically-robust and humidity-tunable self-destructive polymers enabled by hydrogen-bond nanoconfinement. *Nat. Commun.* **2025**, *16*, 11135. [CrossRef]
111. Kulkarni, S.S.; Choi, K.S.; Simmons, K. Coupled diffusion-deformation-damage model for polymers used in hydrogen infrastructure. In *Proceedings of the ASME 2022 17th International Manufacturing Science and Engineering Conference, West Lafayette, IN, USA, 27 June–1 July 2022*; American Society of Mechanical Engineers: New York, NY, USA, 2022; Volume 85819, p. V002T05A003.
112. Kulkarni, S.S.; Choi, K.S.; Menon, N.; Simmons, K. A diffusion–deformation model with damage for polymer undergoing rapid decompression failure. *J. Mech. Phys. Solids* **2023**, *178*, 105348. [CrossRef]
113. Maes, C.; te Molder, M.; Luyten, W.; Herremans, G.; Winckelmans, N.; Peeters, R.; Carleer, R.; Buntinx, M. Determination of the nitrogen gas transmission rate (N2GTR) of ethylene vinyl alcohol copolymer, using a newly developed permeation measurement system. *Polym. Test.* **2021**, *93*, 106979. [CrossRef]
114. Kuang, W.; Nickerson, E.K.; Shin, Y.; Taufique, M.F.N.; Clelland, D.T.; Seffens, R.J.; Simmons, K.L. In situ investigation of high-pressure hydrogen-induced swelling in elastomers and its correlation with material properties. *Int. J. Hydrogen Energy* **2025**, *179*, 151315. [CrossRef]
115. Duranty, E.R.; Roosendaal, T.J.; Pitman, S.G.; Tucker, J.C.; Owsley, S.L.; Suter, J.D.; Alvine, K.J. An in situ tribometer for measuring friction and wear of polymers in a high pressure hydrogen environment. *Rev. Sci. Instrum.* **2017**, *88*, 095114. [CrossRef]
116. Guo, J.; Xing, L.; Hua, Z.; Gu, C.; Zheng, J. Optimization of compressed hydrogen gas cycling test system based on multi-stage storage and self-pressurized method. *Int. J. Hydrogen Energy* **2016**, *41*, 16306–16315. [CrossRef]
117. Castagnet, S.; Mellier, D.; Nait-Ali, A.; Benoit, G. In-situ X-ray computed tomography of decompression failure in a rubber exposed to high-pressure gas. *Polym. Test.* **2018**, *70*, 255–262. [CrossRef]
118. Zhang, H.L.; Hu, W.T.; Xiao, J.; Li, T.L.; Lin, Y.H. Revealing the hydrogen permeation mechanism in polyetheretherketone and polytetrafluoroethylene: From experimental validation to molecular-level interpretation. *Chin. J. Polym. Sci.* **2026**, *44*, 278–298. [CrossRef]
119. Yuan, S.; Sun, Y.; Cong, C.; Liu, Y.; Lin, D.; Pei, L.; Zhu, Y.; Wang, H. A bi-layer orientated and functionalized graphene-based composite coating with unique hydrogen gas barrier and long-term anti-corrosion performance. *Carbon* **2023**, *205*, 54–68. [CrossRef]
120. Alkrunz, M.; Sandaruwan, C.; Shajahan, S.; Al Tawil, B.; Khan, M.; Nulakani, N.V.R.; Anjum, D.; Schiffer, A.; Zweiri, Y.; Samad, Y.A. Additively Manufactured Graphene Enhanced Nylon with Inhibited Coiling, Entropically Favorable Linear Conformations for Hydrogen Barrier Applications. *Adv. Ind. Eng. Polym. Res.* **2025**, *8*, 573–587. [CrossRef]
121. Sharma, H.; Patel, R.; Rana, S. Epoxy Vitrimers: Effect of Thermal Cycling on Stress Relaxation and Self-Healing Properties. *ChemistrySelect* **2025**, *10*, e01491. [CrossRef]

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