

Design Aspects of a Failure Resistant 70 MPa Type IV Composite Overwrapped Pressure Vessels for Hydrogen Storage

A Thesis Submitted

in Partial Fulfilment of the Requirements

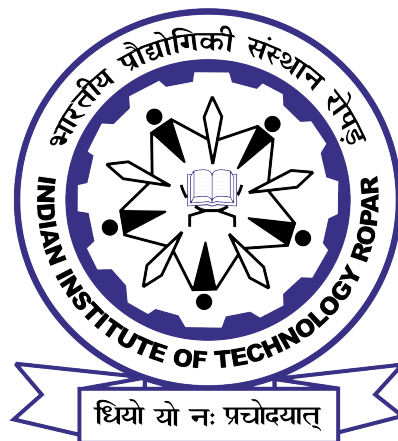
for the Degree of

DOCTOR OF PHILOSOPHY

by

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(2017MEZ0017)



DEPARTMENT OF MECHANICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY ROPAR

October, 2024

Mukesh Kumar

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*This thesis is dedicated to my teachers and parents
(For their endless love, support, and encouragement)*

Declaration of Originality

I hereby declare that the work being presented in the thesis entitled **Design Aspects of a Failure Resistant 70 MPa Type IV Composite Overwrapped Pressure Vessels for Hydrogen Storage** has been solely authored by me. It presents the result of my independent investigation and research conducted during the period from January 2018 to June 2024 under the supervision of Dr. Dhiraj K. Mahajan, Associate Professor, Department of Mechanical Engineering. To the best of my knowledge, it is an original work, both in terms of research content and narrative, and has not been submitted or accepted elsewhere, in part or in full, for the award of any degree, diploma, fellowship, associateship, or similar title of any university or institution. Further, due credit has been attributed to the relevant state-of-the-art, collaborations with appropriate citations and acknowledgments, in line with established ethical norms and practices. I also declare that any idea, data, fact, or source stated in my thesis has not been fabricated, falsified, or misrepresented. All the principles of academic honesty and integrity have been followed. I fully understand that if the thesis is found to be unoriginal, fabricated, or plagiarized, the Institute reserves the right to withdraw the thesis from its archive and revoke the associated Degree conferred. Additionally, the Institute also reserves the right to appraise all concerned sections of society of the matter for their information and necessary action. If accepted, I hereby consent for my thesis to be available online in the Institute's Open Access repository, on an inter-library loan, and the title & abstract to be made available to outside organizations.



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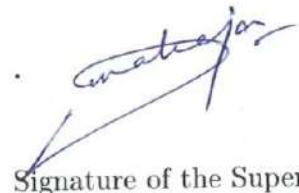
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Thank you
Mukesh Kumar

Certificate

This is to certify that the thesis titled **Design Aspects of a Failure Resistant 70 MPa Type IV Composite Overwrapped Pressure Vessels for Hydrogen Storage**, submitted by **Mukesh Kumar (2017MEZ0017)** for the award of the degree of **Doctor of Philosophy** at Indian Institute of Technology Ropar, is a record of bonafide research work carried out under my guidance and supervision. To the best of my knowledge and belief, the work presented in this thesis is original and has not been submitted, either in part or full, for the award of any other degree, diploma, fellowship, associateship, or similar title at any other university or institution.

In my opinion, the thesis has reached the standard fulfilling the requirements of the regulations relating to the Degree.



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Lay Summary

Hydrogen has emerged as a zero-emission solution for light to heavy-duty transport as well as various stationary applications. Type IV composite overwrapped pressure vessels (COPVs) are standardized to store gaseous hydrogen (H_2) at a nominal working pressure (p_{nwp}) of up to 70 MPa or more so as to achieve a competitive driving range for commercially available hydrogen fuel cell electric vehicles (HFCEVs) and hydrogen internal combustion engine vehicles (HICEVs). As per various national and international standards, Type IV COPVs are tested up to the burst pressure (p_b) which is around 2.25 times of p_{nwp} to provide a sufficient factor of safety for regular operations at p_{nwp} .

Although Type IV COPV for H_2 storage has been standardized and commercialized, there are several challenges associated with it such as high cost, limited temperature range of usage, safety, etc. which are linked to the materials, design, and manufacturing processes used to fabricate these COPVs. Therefore, a good understanding of the role of materials used for their manufacturing, design along with the manufacturing defects on their failure behavior under critical operational conditions of high-pressure H_2 is absolutely necessary. Materials used for manufacturing Type IV COPV include hydrogen embrittlement resistant metals used for the manufacturing boss (required for holding the gas filling valve), a suitable grade of polymer used for manufacturing liner to control the H_2 permeation, and carbon fiber-reinforced plastic (CFRP) that has a suitable matrix material along with the suitable grade of fibers as reinforcement to provide the required strength for holding high-pressure H_2 . Design aspects of COPVs include length to diameter ratio, shape of dome section and coupling of metallic boss with polymeric liner. Manufacturing defects on the other hand, can include defects in the polymeric liner, gaps at the interface of various components of COPV, sharp thickness variation in CFRP winding, etc. These defects are known to cause several kinds of failures in Type IV COPVs that include buckling of the liner, reduced p_b , leakage of gas, as well as an overall reduction in the operational life.

This thesis aims to address the critical challenges of developing a failure resistant Type IV COPV with p_{nwp} of 70 MPa focusing on materials, design aspects, and manufacturing defects. A computational framework is developed that considers manufacturing defects, and design variation and correctly accounts for H_2 permeation in the liner material to significantly improve our understanding of complex phenomena happening in Type IV COPVs during operational life. At first, a small Type IV COPV with an internal water volume of 18 liter is designed progressively using netting analysis, classical laminate theory, and finite element analysis, to elucidate the role of design parameters and defects responsible for its failure at the p_b . Next, a novel hydrogen transport model has been developed to investigate the transport behavior of hydrogen in polymer liner material to predict the optimal thickness of the liner required to control the H_2 permeation. Lastly, the role of defects in polymer liner and at the liner-composite interface has been analyzed

under the filling-defilling cycles of Type IV COPVs.

Abstract

Hydrogen has emerged as a zero-emission solution for light to heavy-duty transport as well as various stationary applications. Type IV composite overwrapped pressure vessels (COPVs) are standardized to store gaseous hydrogen (H_2) at a nominal working pressure (p_{nwp}) of up to 70 MPa or more so as to achieve a competitive driving range for commercially available hydrogen fuel cell electric vehicles (HFCEVs) and hydrogen internal combustion engine vehicles (HICEVs). As per various national and international standards, Type IV COPVs are tested up to the burst pressure (p_b) which is around 2.25 times of p_{nwp} to provide a sufficient factor of safety for regular operations at p_{nwp} .

Although Type IV COPV for H_2 storage has been standardized and commercialized, there are several challenges associated with it such as high cost, limited temperature range of usage, safety, etc. which are linked to the materials, design, and manufacturing processes used to fabricate these COPVs. Therefore, a good understanding of the role of materials used for their manufacturing, design along with the manufacturing defects on their failure behavior under critical operational conditions of high-pressure H_2 is absolutely necessary. Materials used for manufacturing Type IV COPV include hydrogen embrittlement resistant metals used for the manufacturing boss (required for holding the gas valve), a suitable grade of polymer used for manufacturing liner to control the H_2 permeation, and carbon fiber-reinforced plastic (CFRP) that has a suitable matrix material along with the suitable grade of fibers as reinforcement to provide the required strength for holding high-pressure H_2 . Design aspects of COPVs include length to diameter ratio, shape of dome section and coupling of metallic boss with polymeric liner. Manufacturing defects on the other hand, can include defects in the polymeric liner, gaps at the interface of various components of COPV, sharp thickness variation in CFRP winding, etc. These defects are known to cause several kinds of failures in Type IV COPVs that include buckling of the liner, reduced p_b , leakage of gas, as well as an overall reduction in the operational life.

To gain a competitive edge on Type IV COPVs, simulation-assisted manufacturing technologies must be developed to reduce test requirements, boost production rates, and reduce rejections or failures under service conditions. To improve such understanding, in this thesis, at first a small Type IV COPV with an internal water volume of 18 liter is designed progressively using netting analysis, classical laminate theory, and finite element analysis, to elucidate the role of various design parameters and defects responsible for its failure at the p_b . The failure behavior of Type IV COPV is found to be highly sensitive to the placement of the CFRP lay-up, the outer shape of the metallic boss that interacted with the CFRP winding while the junction points of the liner, boss, and CFRP winding are shown to be the hot spots for failure. Lastly, failure prevention strategies at these hot spots are discussed in terms of the CFRP failure criteria.

Next, a novel modeling framework is developed and implemented using UMATHT (user-defined material with heat transfer) subroutines in the commercial FE solver Abaqus. UMATHT is used to solve the H_2 permeation equation, following the analogy between heat transfer and the diffusion equation. The variation in hydrogen transport properties in liner material based on the morphological properties of polymer with applied pressure has been implemented in the model to investigate the H_2 permeation mechanism. The developed modeling framework is first calibrated w.r.t experimental data available in the literature, and thereafter, the model with calibrated constants is extended to simulate the optimal thickness of liner material for a 70 MPa p_{nwp} Type IV COPV.

Lastly, to explore the mechanism of H_2 permeation and failure based on pre-existing micro-defects in the polymeric liner material, two defect cases are considered for analyzing the role of defects in polymer liner and at liner-composite interface under filling-defilling cycles of Type IV COPVs. A quarter model of the cross-section of cylindrical part of the Type IV COPV with both the defects incorporated is subjected to an operational filling and defilling cycle typically associated with Type IV COPV. A multi-variable H_2 permeation analysis is conducted using the extended governing equations of Fick's law for hyper-elastic polymeric liner material and defilling-induced blistering model. Filling is carried out up to 70 MPa in 5 minutes, and maintained for several hours, then fast defilling is carried up to a minimum pressure up to 2 MPa as followed in realistic situations. Simulation results provide an understanding of H_2 pressure build-up inside defects during the filling and defilling cycle clearly highlighting the effect of location of micro-defects on damage initiation under operational conditions of Type IV COPVs.

List of Publications

Journal Publications

- **Mukesh Kumar**, and Dhiraj K. Mahajan, Role of Design and Manufacturing Defects on Failure Behavior of Type IV COPV for H₂ Storage (To be Submitted)
- **Mukesh Kumar**, and Dhiraj K. Mahajan, Modeling of H₂ Permeation in Liner Materials of Type IV Composite Overwrapped Pressure Vessel (To be Submitted)
- **Mukesh Kumar**, and Dhiraj K. Mahajan, Role of Micro-Defects on Blistering Behavior of 70 MPa Type IV Composite Overwrapped Pressure Vessels due to H₂ Permeation (To be Submitted)

Patent

- Dhiraj K. Mahajan, Srikant Shekhar Padhee, Ravi Mohan Prasad and **Mukesh Kumar**, A Leak Proof Liner-Boss Assembly for Type IV Hydrogen Storage Tank, Patent Grant No. 478710, Application No. IN202011022281, Date of Grant: 07/12/2023, Country of filing: India.

International and National Conferences

- **Mukesh Kumar**, Dhiraj K. Mahajan, Role of Polymeric Liner Defect on Failure Behavior of Type IV Composite Overwrapped Pressure Vessels. ASATM-2023, 11th to 13th January 2023, NTU Singapore
- **Mukesh Kumar**, Dhiraj K. Mahajan, Modeling of Hydrogen Permeation in Liner Materials of Type IV Composite Overwrapped Pressure Vessels, National Conference on Energy Materials and Devices, 16th to 18th December 2022, Department of Physics, IIT Jodhpur, Rajasthan, India
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Workshop

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- Automation of Finite Element Analysis from 23rd to 27th August 2019, Centre for Continuing Education, IIT Madras, India

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Nomenclature & Abbreviations

β	Pressure coefficient
ϵ_o	Mid-plane strain vector
Δt	Time increment
η	Concentration coefficient
γ	Chain immobilization factor accounting for the amorphous part
μ	Chemical potential of hydrogen in the polymer
μ^0	Reference chemical potential
ϕ	Crystallinity of semicrystalline polymer
ϕ_f	Crystallinity of semicrystalline polymer after pressurization
ϕ_i	Crystallinity of semicrystalline polymer before pressurization
ρ_a	Amorphous phase density of polymeric material
ρ_c	Crystalline phase density of polymeric material
ρ_s	Semicrystalline density of polymeric material
σ_{90}	Stress in the hoop layer
σ_α	Stress in the helical layer
σ_{p_b}	Stress at p_b
σ_p	Stress at p_{nwp}
τ_a	Characteristic parameter accounted for the enhancement of diffusion path in polymeric material
J	Hydrogen flux
ζ	Coefficient of concentration expansion
A	Laminate extensional stiffness
A_f	Cross-sectional area of tow
B	Laminate coupling stiffness
C	Hydrogen concentration

C_i	Hydrogen concentration on inside boundary of the sample
$C_O - C_t$	Concentration difference
C_t	Hydrogen concentration at time, t
C_O	Initial hydrogen concentration in material
C_o	Hydrogen concentration on the outside boundary of sample
D	Laminate bending stiffness
d	Filament diameter
D_o	Overall diffusion coefficient for hydrogen in polymer
D_{sc}	Diffusion coefficient for hydrogen in semicrystalline polymer
dp	Depressurization rate
$F.I$	Tsai Wu failure index
FV_f	Free volume available in the polymer after pressurization
FV_i	Free volume available in the polymer before pressurization
k	Curvature vector
L	Total length of the cylinder
M	Resultant couple moment
N	Order of polynomial of the Ogden model
n	Filament per tow
N_s	Number of spool
n_t	Total number of layers
N_X	Resultant force component in hoop direction
N_Y	Resultant force component in axial direction
n_{he}	Number of helical layers
n_{ho}	Number of hoop layers
p_b	Burst pressure
p_{nwp}	Nominal working pressure
R	Universal gas constant

r	Radial distance along the diameter which varies in the dome
R_b	Radius of the boss
R_c	Outer radius of the polymeric liner over which the filament is wound
r_{iv}	Internal radius of boss that interacts with the valve
SR	Stress ratio
T	Absolute temperature
t_c	Total thickness of composite in cylindrical part
t_f	Thickness of single tow fibers
$t_h(r)$	Helical layer thickness buildup in the dome
t_{90}	Total hoop layer thickness
t_α	Total helical layer thickness
V_f	Fiber volume fraction
V_H	Partial molar volume of hydrogen in polymer
W_f	Bandwidth of single tow
1-D	One dimensional
12000	12K
2-D	Two dimensional
3-D	Three dimensional
CF	Carbon fiber
CFRP	Carbon fiber reinforced plastic
CLT	Classical laminate theory
COPV	Composite overwrapped pressure vessel
EPDM	Ethylene propylene diene monomer
FE	Finite element
FEM	Finite element method
FW	Filament winding
GC	Gas chromatography

H ₂	Gaseous hydrogen
HDPE	High-density polyethylene
HE	Hydrogen embrittlement
HPHP	High-pressure hydrogen permeation
hr	Hour
HTM	Hydrogen transport model
L	Liters
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
NA	Netting analysis
NTP	Normal temperature and pressure
PA6	Polyamide 6
PE	Polyethylene
PET	Polyethylene terephthalate
PU	Polyurethane
RVE	Representative volume element
s	Second (sec)
TGA	Thermal desorption analysis
UD	Unidirectional
UMATHT	User defined material for heat transfer
WA	Winding angle

Chapter 1

Introduction

1.1 Introduction

The world is facing the greatest challenge of climate change due to the excessive use of fossil fuels (coal, oil, and natural gas). This has led to increased usage of renewable energy sources to meet the energy requirement. However, the irregular, seasonal variation of most known renewable sources (including solar, wind, geothermal, hydro, tidal, and biomass) leads to an imbalance between energy supply and demand. Green H_2 as a clean energy source overcomes both the shortcomings of conventional and renewable energy sources. It has thus been identified as the most important energy vector. It also has the highest specific energy (nearly 142 MJ/kg, almost 3 times more than gasoline). It generates water as a by-product, making it one of the most environment-friendly fuels, with the potential to fulfill all types of energy requirements for global needs [3, 4].

Green H_2 can be produced using any renewable energy source; however, its efficient utilization is significantly challenged due to issues associated with its value chain (such as cost of production, storage, transmission, utilization, and safety). One of the challenges for bulk H_2 production is storage and transportation for its effective utilization. Due to its low volumetric energy density, the volume required for storage at normal temperature and pressure (NTP) (20°C , 0.10 MPa) is quite large e.g., approximately 11,000 liters (L) water volume is required to store 1 kg of H_2 at NTP with a density of 0.09 kg/m^3 [5]. For mobile applications, a typical hydrogen fuel cell electric vehicle (HFCEV) e.g. a sedan gives a mileage of 100 kms per kg of H_2 [6]. Thus storage of H_2 is required at very high pressures to be utilized for mobile applications such as as a fuel in hydrogen internal combustion engine vehicles (HICEV) or as an energy medium in the case of HFCEV. As an example, H_2 stored at 70 MPa requires 24 L of water volume to store 1 kg of H_2 at 20°C with a density of 42 Kg/m^3 [7].

Based on the components of the gaseous H_2 storage pressure vessels (PVs), they are classified into four categories, i.e., Type I, Type II, Type III, and Type IV PVs, as illustrated in the schematic shown in Fig. 1.1. In Type I to Type III PVs (as shown in Fig. 1.1(a), 1.1(b), 1.1(c)), H_2 remains in physical contact with the metallic material that can cause hydrogen embrittlement (HE) at high pressure, thus limiting their storage capacity [8, 9]. Residual moisture in stored H_2 is prone to corrosion and HE, leading to the reduction in the strength and fracture toughness of metallic materials, which may lead

to catastrophic failure of Type I, Type II, and Type III PVs. In addition, a higher density of metals causes more weight, making them unsuitable for vehicular applications [10, 11]. Type II and Type III PVs have a carbon fiber reinforced plastic (CFRP) wrapped over the metallic liner to increase the pressure rating H_2 storage compared to Type I PV.

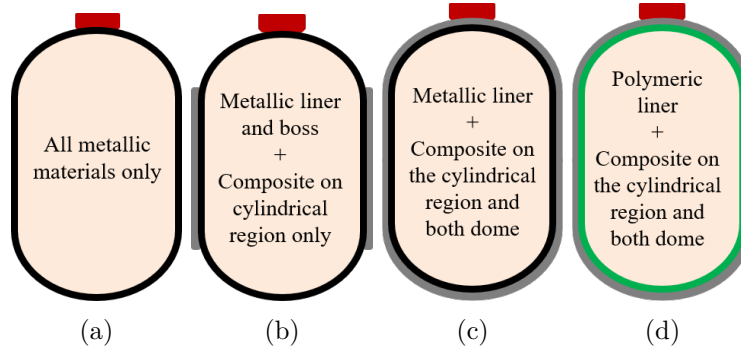


Figure 1.1: Schematic of types of PVs for hydrogen storage with integrated parts and corresponding materials. The metallic boss, metallic liner, composite, and polymeric liner are shown in red, black, gray, and green colors, respectively.

The most promising candidate for high-capacity gaseous H_2 storage is the Type IV composite overwrapped pressure vessel (COPV) as shown in Fig. 1.1(d) [5]. In Type IV COPVs, the polymeric liner material provides the H_2 permeation barrier, while high strength fibers (e.g. carbon fiber) based reinforced plastic composite winding envelops the liner-boss assembly to provide the required strength to hold highly pressurized H_2 . These COPVs are standardized and utilized efficiently nowadays for various mobile applications (e.g., cars, buses, trains, drones) as onboard H_2 storage. Type IV COPVs offer several advantages compared to their counterparts, such as high gravimetric energy density, lightweight, improved cycle life, corrosion resistance, etc. However, there are also several challenges associated with it such as high cost, limited temperature range of usage, safety, etc. which are linked to the materials, design, and manufacturing processes used to fabricate these COPVs. These issues need to be solved to further improve their performance with regards to the storage capacity, safety, and applications by reducing the unit cost.

Due to the proprietary nature of work done by several companies who have commercialized Type IV COPVs, most of the parameters associated with the materials, design, and manufacturing processes such as H_2 permeability rate of polymeric liner material, boss-liner interface design, and composite wrapping orientations are little known or not available in the open literature. However, several experimental and simulation studies related to academic research are reported in the open literature related to the design and testing of Type IV COPVs based on their capacity, operating parameters, and selection of materials. For the design calculations, the netting analysis (NA) and classical laminate theory (CLT) are used for finding the overall thickness and stresses in the composite wrapping for given operating conditions, respectively [12, 13]. CFRP with unidirectional (UD) fibers has unique strength properties that meet the requirement

of high p_{nwp} of these COPVs. To validate the p_{nwp} of COPVs, they are tested using a hydraulic medium in a controlled environment up to the burst pressure (p_b), defined as the maximum pressure required for initiating a failure in PVs. For enhanced safety, p_b is set at $2.25 \times p_{nwp}$ or more as per various national and international standards (ISO 19881) for COPVs.

Finite element (FE) simulations are commonly used to optimize COPVs design that involves optimizing the boss design, winding sequence, liner-boss interface design as well as the failure behavior using selective failure criterion at the p_b [14, 15]. An improper boss design and liner-boss interface cause leakage and failure of the costly Type IV COPVs. For storing 5.6 kg of usable H_2 at 70 MPa, the cost comparison of baseline components of Type IV COPVs, which includes carbon fiber, resin matrix, selling, general and administrative (SG&A), scrap, manufacturing, boss, and liner (without boss) is shown in Fig. 1.2. As shown, 76% of the total cost of Type IV COPV is contributed by carbon fiber used as reinforcement of plastic matrix in CFRP based overwrapping.

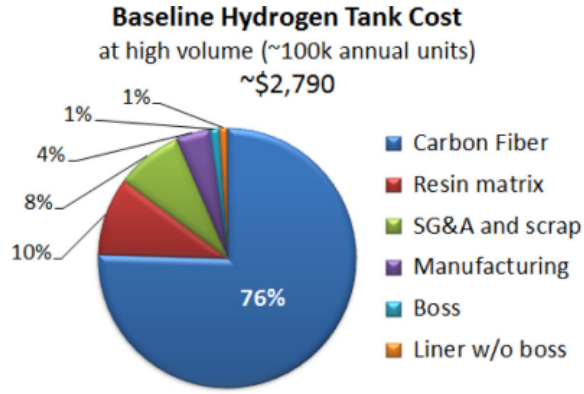


Figure 1.2: An illustration of a typical Type IV hydrogen COPV with a wall showing the polymer liner core wrapped with fiber-reinforced composite [1].

The polymeric liner of Type IV COPV protects the metallic boss and the composite material from direct physical contact with H_2 to avoid HE and leakage. However, due to the small size of H_2 molecule, it can permeate through most materials, including polymeric liners. Several studies have focused on the H_2 permeability in polymers under low-pressure conditions, and little is discussed in the open literature about the behavior of these materials under high-pressure H_2 . It is reported that the H_2 permeation properties of semi-crystalline polymer material (permeability, diffusivity, and solubility) are functions of the operating pressure of H_2 gas [16, 17, 18]. Excessive H_2 permeation in polymeric liners can cause various kinds of failures in Type IV COPV, such as liner buckling, blistering at the interface of composite winding and liner, and cavitation in the liner (as shown in Fig. 1.3 [19]) that are generally promoted by various manufacturing defects observed in the liner, such as the inclusion of air, foreign particles, and others [20, 21, 22]. This results in liner collapse and failure of Type IV COPVs during the operational cycles (filling-defilling) [2].

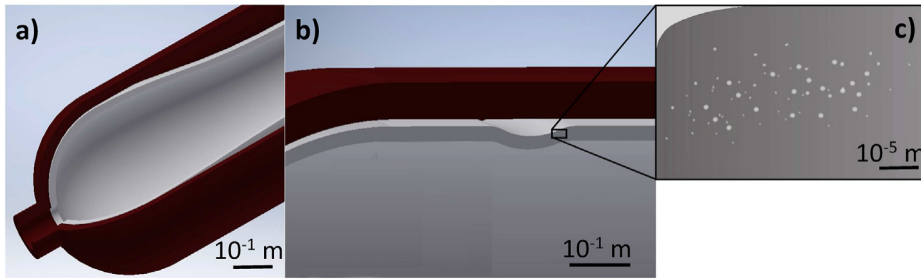


Figure 1.3: Schematic of Type IV COPV under (a) buckling, (b) blistering, (c) cavitation (scale mark is approximate) [2].

The failure of this costly H_2 storage system causes a huge economic loss along with increasing the risk of causing catastrophic failure. These factors make Type IV COPV an active area of research to further improve their performance w.r.t storage capacity, cost reduction, safety, and applications while taking practical issues like manufacturing defects into consideration.

1.2 Background and Motivation

Development of Type IV COPVs involves multiple materials, components, and manufacturing processes as mentioned above. Since the beginning of the PhD, author was involved in development of a Type IV COPV with p_{nwp} of 70 MPa as part of a sponsored project¹ where the role of author was to design and fabricate the components of COPV such as bosses, design of Filament Winding (FW) on a prefabricated liner-boss assembly along with providing support in the fabrication and testing of the designed COPV. A brief description of the design, manufacturing and testing process adopted for a custom-made Type IV COPV is mentioned below:

1.2.1 Experimental work on design, fabrication, and testing of Type IV COPV

An 18 L internal water volume capacity Type IV COPV with p_{nwp} of 70 MPa is chosen for design, fabrication, and testing work. Considering the non-availability of in-house manufacturing facilities like rotomolding and FW machinery, a pre-fabricated roto-molded polymer liner made of HDPE material (as per the design offered) was procured from an international vendor (Crompton Mouldings, U.K). A custom-designed metallic boss was then fabricated at IIT Ropar. A schematic of metallic boss and polymeric liner is shown in Fig. 1.4 (a detailed description is shown in Fig. 3.5). Metallic bosses were pasted over liner using structural adhesive (3M DP460) after treatment of the contact surface on boss to generate roughness using emery paper. The procured polymer liner and fabricated liner-boss assembly are shown in the Fig. 1.5.

¹Project No. 5815; Title: Design, development, and demonstration of Indigenous hydrogen storage and fuel cell system for mobile and stationary applications of 5 kW capacity

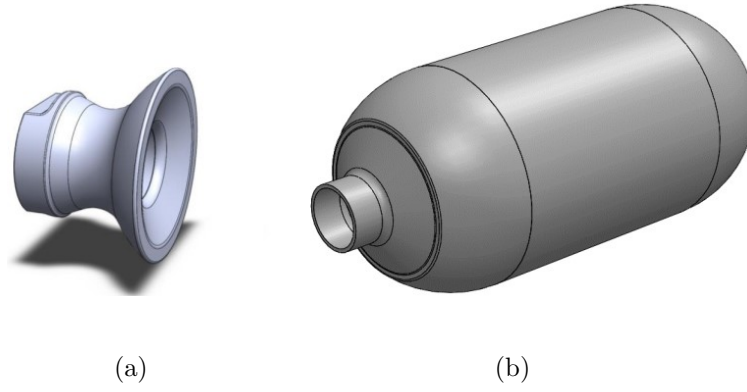


Figure 1.4: A schematic of (a) metallic boss, and (b) polymeric liner.



Figure 1.5: (a) Polymer liner procured from Crompton Mouldings, U.K., and (b) liner-boss assembly fabricated at IIT Ropar.

On the liner-boss assembly, wet FW was performed at CNC Technics Pvt. Ltd, Hyderabad, India as per the optimized winding sequence provided to CNC Technics by the author. Optimization of winding sequence was obtained through finite element analysis (FEA) performed using WCM plugin in ABAQUS simulation software. The liner-boss

assembly undergoing FW process at CNC Technics is shown in Fig. 1.6.



Figure 1.6: Winding of CFRP on the liner-boss assembly during FW process.

Following steps were followed during the FW process at CNC Technics:

1. Fiber Type: The carbon fibers T700S-12K-50C from Toray were considered for FW. The bobbins of carbon fiber were placed on the creel system.
2. Resin Preparation: A 2:1 blend of epoxy (LY556) and hardener (XY54) was utilized as the resin (matrix) material for fiber impregnation towards wet winding.
3. Mandrel Mounting: The liner-boss assembly was mounted on the 4-axis FW machine, supported by the chucks. It ensured that the liner-boss assembly was securely held during the winding process, allowing for precise control during the fiber placement.
4. Band Width: A single spool of fiber was used for winding with a bandwidth of 2 mm at the pay-out eye mounted on the carriage that moves along the axis of the rotating mandrel.
5. Winding: Fibers were wound on the mandrel surface (according to the optimized winding pattern obtained from FEA), completing the manufacturing of Type IV COPV.

After the completion of composite wrapping, the Type IV COPV was subjected to curing in an oven for 1 hour at 100 °C as shown in Fig. 1.7. The fabricated Type IV COPV was tested for identifying the burst pressure while hydraulically pressurizing up to 157.5 MPa at GEM Pressure Systems Pvt Ltd., Hyderabad, India. The site of p_b test and remote monitoring arrangement during testing is shown in Fig. 1.8. During the test, a leakage of water was observed from the dome region at the pressure values of 10 MPa only confirming the leakage of water from open end boss-liner interface. Due to financial constraints, only

one Type IV COPV was developed and tested. However, the observed failure of tested COPV provided several insights into the role of boss design, manufacturing, winding defects, and interfaces in Type IV COPV. This failure actually formed the basis for setting the objectives and scope of this thesis work as mentioned in following sections.



Figure 1.7: Curing of fabricated composite cylinder after wrapping to cure the epoxy resin.

1.3 Objectives and Scope

This thesis aims to address the critical challenges in design and development of a Type IV COPV with p_{nwp} of 70 MPa, focusing on possible defects in such vessels that may lead to early failure. As explained in the introduction and shown in the background work, several parameters are crucial for the development of failure resistant Type IV COPVs. Besides mechanical failure at burst pressure, polymeric liner material failure due to H_2 permeation has been reported during their operational cycles. The improper selection of material, liner thickness, and defects during manufacturing can lead to costly failure of these storage systems. A computational framework that considers manufacturing defects and correctly accounts for H_2 permeation in the liner material can significantly improve our understanding of complex phenomena happening in Type IV COPVs during their operational life. Thus, based on computational studies, this work aims at improving the cycle life, cost, and safety aspects of Type IV COPVs by developing a modeling framework that accounts for the manufacturing defects and H_2 permeation in liner material to simulate the failure behavior of Type IV COPVs.

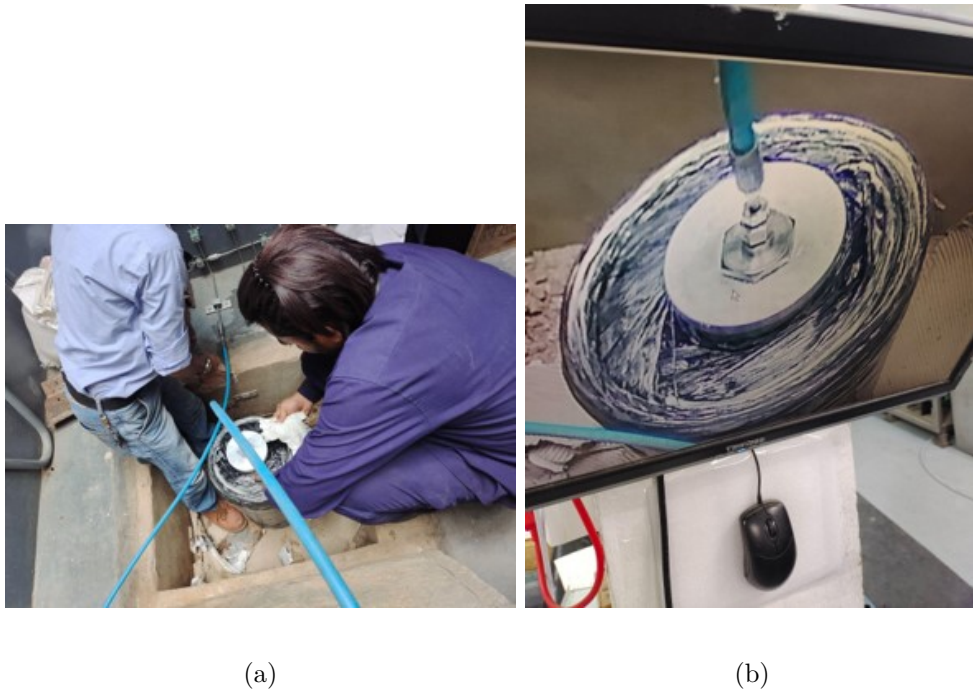


Figure 1.8: (a) Picture of site preparation for burst test and (b) remote monitoring of cylinder during burst test.

The defined objectives of this thesis work are summarized as follows:

1. Development of a computational framework that accounts for manufacturing defects to investigate the mechanical failure at p_b .
2. Development of a novel material modeling framework of H_2 permeation through the liner material that accounts for polymer morphology, density, and thickness to achieve the desired permeation limit in Type IV COPVs.
3. To analyze the role of H_2 permeation on manufacturing defect-based failure in liner and liner-composite interface under filling-defilling cycles of Type IV COPVs.

1.4 Outline of the thesis

The research objectives of the present work are structured and elaborated in five chapters, as outlined below:

In **Chapter 1**, a general introduction, background, objectives and scope, and layout of the thesis is provided. The challenges associated with the onboard gaseous H_2 storage are explained along with the motivation for this thesis.

In **Chapter 2**, the design and material aspects related to the failure of Type IV COPVs for high-pressure applications are summarized. The chapter also describes failures associated with H_2 permeation phenomena and pre-existing defects relevant to Type IV COPVs during operation.

Chapter 3 focuses on Objective 1, where a computational investigations were performed

to simulate possible scenarios of manufacturing defects in Type IV COPV and their effect on the failure behavior at p_b .

Chapter 4 focuses on the development of the H_2 permeation model in a commercial FE software, ABAQUS. The modeling framework considers the gradients of concentration and pressure-driven mass diffusion at a constant temperature. Variations in the diffusion coefficient are implemented in the model based on operational parameters and the structural properties of the liner material. The modeling framework incorporates H_2 permeability reduction in liner material with increasing H_2 pressure.

Chapter 5 extends objective 2 towards safety concerns involving Type IV COPV that are crucial due to the occurrence of decompression damage, influenced by the H_2 transport properties in liner material and H_2 gas operating parameters. The influence of pre-existing micro-defects present inside the polymeric liner and at the interface of polymer-composite on H_2 permeation through the wall of Type IV COPV is investigated for a given H_2 filling and defilling cycle using FE simulation. This comparative study provided a valuable understanding of the role of defect size and location to avoid catastrophic failures during the operational cycle of Type IV COPVs for onboard H_2 storage applications.

Chapter 6 Summarizes the findings in this thesis and discusses the future scope of the work.

Chapter 2

Literature Review on Failure Study of High Pressure Type IV COPVs

2.1 Introduction

High pressure Type IV COPVs, primarily used for storing and transporting gases such as H_2 and hydrogen-blended compressed natural gas (HCNG) in various applications, face several technical challenges. The studies, along with recent work on the design, manufacturing defects, and H_2 permeation-based failure analysis of Type IV COPVs, are summarized in the following sections.

2.2 Design and Failure Study of Type IV COPVs

Type IV COPVs use a polymeric liner and boss assembly, over which composite layers are wrapped by filament winding (FW). The inner carbon fiber (CF) layer, which is thicker, provides the strength needed to resist the stored H_2 gas pressure of Type IV COPVs, while the thinner outer glass fiber (GF) layer protects it from damage caused by drops or impacts [23, 24, 25]. The blow-moulded polymeric liners (BMPLs), glued to the metallic boss, caused failure during cyclic pressure tests. The failure occurred due to a crack oriented perpendicular to the liner's parison pinch-off seam in the hemispherical dome region. This crack originated from the parting line of the mold and was further exacerbated by a gap in the glued region [26].

Recently, the topology optimization of boss has been reported to ensure safety and sealing behavior [27]. The boss design and the liner interface have been analyzed to enhance the performance with the connection of CFRP [28]. The heat-treated aluminium alloys (e.g., Al6061-T6, Al6082-T6, 7075-T6) are anodized via methods like sulphuric acid anodizing or plasma electrolytic oxidation to form oxide layers, which electrically isolate the two electrically conductive materials having dissimilar electrochemical potential [29, 30]. This barrier disrupts the electrochemical pathway or contact between the aluminium alloy (anode) and CFRP (cathode), preventing contact-based galvanic corrosion (GC) in the presence of electrolytes like water present in atmospheric air [31]. Without such protection, aluminium undergoes oxidation, forming porous aluminium hydroxide and leading to gradual mass loss and interface failure [32, 33]. During H_2 cycling tests of Type IV COPVs, grounding the metallic end boss (which supports the filling/defueling valve)

can mitigate triboelectric charging that originates from frictional interactions between high-velocity H_2 and the polymer liner, generating significant surface potentials. The resultant electrostatic discharge (ESD) poses an ignition risk due to H_2 's wide flammability range (4–75% volume in air) [34]. Grounding the end boss provides a conductive pathway to neutralize accumulated charges, prevent sparking, reduce ESD-induced damage, and minimize risks of fatigue cracking and deterioration, as recommended by ISO 19881 and the safety of H_2 storage technologies [35]. The study has reported on torque enhancement of liner-boss with CFRP coupling, considering SUS31603 and AA6061-T6 as boss materials. S31603 boss material has been recommended for better performance in fatigue loading [36].

Among CF, GF, and kevlar fiber (KF) reinforced plastic composite materials, it has been predicted using FEA that KFRP has been evaluated for critical buckling load for larger applications [37]. The weight reduction and performance enhancement were achieved using larger sizes of CF among T700S, T800S, and T1100G with an increase of V_f by 60%. Furthermore, the stress concentration at the dome-cylindrical interface was reduced to an p_{nwp} of 70 MPa, with a p_b value of 157.5 MPa. The measured critical stresses were 2574 MPa, 3126 MPa and 3391 MPa, which are safer compared to the tensile strength of 2860 MPa, 3290 MPa, and 3460 MPa, respectively [38]. Advanced fiber placement (AFP) reinforces high-stress zones (e.g., dome-cylinder interfaces) in high-pressure Type IV COPVs, enhancing structural integrity while minimising CF usage. Towpreg/prepreg winding—using epoxy-impregnated fibers enables rapid, low-void fabrication, outperforming wet winding in cycle times and consistency. T700, M40, IM7, T800, and T800S CFs achieve tensile strengths up to 4950 MPa and moduli of 275 GPa (IM7), balancing stiffness and elongation (1.4–2.0%) [39]. AFP excels in precision thermoset layups, while towpreg's cost-performance efficiency makes it ideal for H_2 storage COPVs and aerospace structures. This improvement is attributed to these materials' higher tensile strength, modulus, and lower yield strain [40].

Composite failure is categorized based on the various mechanisms like delamination, matrix and fiber cracking [41], etc. In Table 2.1, the experimental (Exp.), analytical, and FEA studies are summarized based on the design and failure criteria of Type IV COPV. Non-destructive testing (NDT) employs independent failure criteria associated with various failure modes, including Tsai-Wu, Tsai-Hill, Azzi-Tsai, Hoffman, and Chamis [42]. The Puck failure criterion analyzes inter-fiber failures by categorizing matrix cracking into stress-dependent modes and distinguishes them from fiber failures [43, 44]. While enabling precise failure prediction, its implementation in FEA requires complex user-defined subroutines, extensive material testing for parameter calibration, and struggles with modeling progressive damage degradation [45, 46, 47].

Table 2.1: Various design parameters and failure criterion used for Type IV COPVs.

Test parameters	Material & component	Design & analysis parameters	Method and software
p_{nwp} 70 MPa	Nylon 6, CFRP	WA, thickness, Max. principal, and Eq. stress	ANSYS [48]
p_{nwp} 70 MPa	CFRP	CLT thick wall model, Stress component	ABAQUS, Analytical [49]
p_b 8.0 MPa	Nylon, ABS, GFRP, AL	Load cycle, deformation	Exp. [50]
p_b 47 MPa	HDPE, GFRP, Boss	Tsai-Wu, Tsai-Hill, Max. stress, stacking sequence	ABAQUS WoundSim & Exp. [51]
p_b 60.5 MPa	HDPE, CFRP	Stress, stacking sequence	ABAQUS WCM & Exp. [52]
p_b 158 MPa, 2.25	HDPE, CFRP, Boss	Stress along fiber direction, doilies layer	ABAQUS [53]
p_{nwp} 52 MPa, 2.25	PA6, CFRP, Boss	Max. principal stress, predefined crack effect	ABAQUS WCM2017 & Exp. [54]
p_{nwp} 20.7 MPa, 2.0	HDPE blend, CFRP, AA	Tsai-Wu, von Mises stress	Abaqus6.8, WCM [55]
p_{nwp} 166.95 MPa, 2.25	PA6, 316L, CFRP	Progressive failure, strain criteria	Exp., ANSYS [56]
p_{nwp} 70 MPa	HDPE, CFRP, Boss	Failure strain	Abaqus WCM[57]
p_b 166.11 MPa	PA6, CFRP, AA Boss	Cylinder-dome interface failure	Exp., Analytical [58]
p_{nwp} 70 MPa	PE, CFRP, Boss	Dome thickness prediction, Tsai-Wu failure	FEM [59]
p_b 113.4 MPa	HDPE, CFRP	Transverse shear stress, interface failure	Abaqus, Analytical [60]
p_b 185 MPa	PA6, CFRP, Boss	Tsai-Wu failure criteria	Abaqus, WCM [46]
p_{nwp} 70 MPa, 2.25	HDPE, CFRP	Tsai-Wu failure criteria	Analytical, ANSYS14.0 [61]
p_b 166.19 MPa	PA6, AA, CFRP	Displacement 6 mm without damage	ABAQUS2017 [62]
Thermo-mech. load, p_{nwp} 70 MPa	PU, CFRP, 316L	Temperature affects p_b	Abaqus, WCM [41]
p_{nwp} 70 MPa	HDPE, CFRP,	Equivalent stress	MATLAB, Abaqus [63]
p_b 40 MPa	HDPE, CFRP	Tsai-Hill, von Mises stress	MATLAB [64]
p_b 26.76 MPa	HDPE, CFRP	Max. stress, Max. strain	Abaqus, WCM, Exp.[65]
p_{nwp} 20 MPa	Graphite/epoxy	Hoop, axial, von Mises stress, Tsai-Hill	ANSYS [66]

Tsai-Wu criterion is widely acknowledged for its precision in predicting failure pressure in composite materials. Although this criterion is inherently conservative, it plays a crucial role in ensuring safety throughout the design process [67]. The stress and Tsai-Hill failure indices were analyzed for a symmetrical cross-ply graphite/epoxy composite cylinder, focusing only on the first two layers. The Tsai-Hill failure index values for the second layer are 2.07 when the ends of the domes are fixed and 1.84 when they are free as a boundary condition [66]. A 2-D axisymmetric model with a total composite thickness of 32.54 has been analyzed for p_b of 117 MPa [54]. The 1/36 part of Type IV COPV without boss has been analyzed using FEA and burst at 60.5 MPa near the head, and the error is 9.6% with the Exp. test [52]. A blend of 95 wt.% LLDPE and 5 wt.% HDPE material rotomolded liner with a prototype of 1 litre and actual liner of internal water capacity 22 litres has been tested for p_b . The theoretical and Exp. thickness of the polymeric liner is estimated to be in the range of 15–16 mm and to withstand a maximum pressure of 2.0–2.2 MPa. CFRP wrapped over the liner and tested using FEA for 20.7 MPa with a safety factor of 2.0, and it has been reported that the Tsai-Wu failure index value was critical for the second layer [55]. Utilizing ANSYS composite pre/post (ACP), the prepreg winding configuration (angle, orientation, arrangement, and number of layers) has been analyzed for stress analysis. The ultimate strength of the composite is 1979 MPa, corresponding to applied p_{nwp} 70 MPa; for hoop layers, the maximum principal stress generated is 1874.2 MPa, which results in p_b 73.91 MPa. The low helical angle provides a durable result compared to other helical angles. The boss geometry is missing through the analysis [48]. The closed-form analytical model was used to analyze the cylindrical part of Type IV COPV. The symmetric and asymmetric models were analysed and validated using the FEA tool [49]. A Type IV COPV with 3-D printed polyamide and acrylonitrile butadiene styrene (ABS) liner with GFRP wrapped and tested for 8.0 MPa [50]. A rotomolded polymeric liner with end bosses was wrapped with GFRP and tested for 47 MPa for various stacking sequences utilizing WoundSim ABAQUS [51]. The CFRP with 2.0 mm thickness of LLDPE, LLDPE/HDPE, and HDPE liner material has sustained the pressure of 20, 30, and 40 MPa for the yield stress of 10, 15, and 25 MPa, respectively [64].

Research and development efforts for Type IV COPVs continue to address diverse application requirements – such as H₂ storage, aerospace, and automotive – across varying geometric configurations (water capacity, diameter, and length). Each configuration demands unique design and manufacturing parameters, even for dimensional adjustments (e.g., length or diameter) at a fixed water capacity, necessitating validation of process parameters and design integrity. Modifications to fiber specifications (e.g., CF, KF, or GF), fiber precursors, fiber manufacturers, structural materials, or cylinder designs require full type approval testing. While minor variations may qualify for reduced testing as per ISO 11119-3. To minimize reliance on physical trials, simulation-driven optimization-such as FEA for stress distribution and progressive damage modeling, is critical for achieving scalable, high-performance Type IV COPV development.

2.3 Hydrogen Permeation-Induced Failure Study of Type IV COPVs

H₂ permeation through the polymeric liner material is a critical challenge of high-pressure Type IV COPVs. High-pressure high-permeation (HPHP), thermal decomposition analysis (TDA), and FE-based methods are most common in analysing the H₂ permeation behavior through the polymeric liners. BMPLs with a length of 720 mm, a diameter of 365 mm, and a uniform thickness of 3.5 mm were analyzed for H₂ permeation using RC's BlowView software. The analysis found a pressure-independent permeation rate of 17.2 Nml/hr/l (normalized liters of H₂ per hour per litre of tank volume), while the pressure-dependent analysis showed a maximum reduction to 3.5 Nml/hr/l [68]. These values should be compared to the regulated maximum allowable limit at 20 °C, which is 8.0 Nml/hr/l [69]. According to ISO 11119-3, the allowable H₂ permeation rate for Type IV COPVs with polymeric liners is ≤ 2 ml/hr per liter of water capacity, which is notably higher than the ≤ 0.25 ml/hr/l limit specified for air, nitrogen, or CNG. The permeation through the semicrystalline polymers is a complex phenomenon due to its little-known behavior under high-pressure conditions. The diffusion occurs exclusively in the amorphous regions of the polymer, with crystalline regions acting as effective barriers; thus, highly crystalline HDPE liners are more effective at reducing H₂ permeation. However, while increased crystallinity decreases H₂ permeation, it can also negatively impact the liner's mechanical properties, such as elongation [70].

Nylon exhibits good mechanical properties and H₂ barrier performance, but absorbs water due to the carbonyl oxygen in its amide groups. Moisture absorption is typically measured to qualify liner materials selection according to ISO 62 [71]. The absorbed moisture acts as a plasticizer, causing the plastic to swell and resulting in decreased strength and stiffness [72]. As more water accumulates, the free volume within the polymer matrix increases, and the intermolecular bonds are weakened, which reduces the H₂ barrier properties and causes dimensional changes [73, 74]. To address this, surface modification techniques such as direct fluorination have been applied to polymer materials. These methods have been shown to significantly reduce water uptake, thereby improving the long-term performance of Type IV COPV liners [75, 76, 77]. At low temperatures (−40 °C and 0 °C), brittle fracture occurs in both neat PA6 and PA6/organo-modified montmorillonite nanocomposite liner materials [78].

Explosive decompression failure (XDF) is a common failure mechanism in liner materials during cyclic pressure testing under conditions ranging from 2 MPa to $1.25 \times p_{nwp}$ [79]. The pressure relief time critically influences the H₂ permeability and structural integrity of PA6 and PA11 liners in Type IV COPVs. At 6-second decompression, H₂ permeability decreased due to microstructural damage (tiny holes in PA6 and clustered holes in PA11), while 60-second and 3600-second cycles caused $< 2\%$ permeability change but introduced

cracks. Tensile strength remained stable, but nominal strain surged by 100% (PA6) and 53% (PA11) under rapid decompression, indicating strain-rate sensitivity. Optimal pressure relief times (60–3600 s) balance permeability control and structural stability, which are crucial for designing durable H₂ storage systems [80]. In recent years, extensive Exp. and numerical studies have investigated H₂ permeation through polymeric liners and polymer blends, highlighting its critical role in the failure mechanisms of Type IV COPVs under cyclic decompression loading. The literature on H₂ permeation and its contribution to liner and Type IV COPV material failures, such as delamination of liner-composite, blister formation, XDF and cavity formation, is summarised in Table 2.2.

In summary, ongoing research is addressing critical challenges in the design, manufacturing and permeation-based failure study of Type IV COPVs for high-pressure H₂ storage through numerical modeling, and design optimization.

Table 2.2: Hydrogen permeation-induced failure study of Type IV COPVs material.

Liner	Operating parameters	Test, Failure parameters	Method, Software
HDPE	70 MPa, 27°C, 55°C, 72 hrs.	Collapse, buckling,	Exp. and FE [81]
PE grades	90 MPa, 30°C, 24 hrs	Liner-Composite Interface Permeation wrt pressure and crystallinity	HHP and TDA [18]
HDPE, PA	87.5 MPa, 25°C, 13 hrs	Depressurization-induced blistering	COMSOL [20]
HDPE, PET, PA6	86 MPa, -30 to 85°C, 16.38 hrs	Permeability vs pressure for various Young's modulus	Exp. HPT [82]
EPDM	27 MPa, 25°C, 13 hrs	XDF with volume fraction of cavity	FE Abaqus [83]
HDPE, PA, EPDM	87.5-0.1 MPa, 50-25°C, 13 hrs	XDF cause cavitation, depressurization	Numerical [21]
HDPE Elastomer	0.71 MPa, 25°C, 5.83 hrs 9 MPa, 25°C, 13 minutes	Permeation and Fracture Decompressed at different rates, pressure	COMSOL, Exp. [84] Exp. [85]
HDPE, LDPE	10.3 MPa, 25°C, 1 seconds	Permeability and diffusivity wrt pressure	Numerical [86]
HDPE	100 MPa, -40 to 85°C, 7 days	Permeability and strength wrt pressure	Exp. [87]
HDPE	90 MPa, 30°C, 24 hrs	HTM properties	Exp. [88]
EPDM	10 MPa, 30°C, 24 hrs	Failure in polymer	Exp. [89]
CFRP	196 MPa, 23°C	Permeability, damage, orientation	Exp. [90]
EPDM	5.75 MPa, 25°C, 13.9 hrs	Concentration	Exp. [91]
PE100, PA11	2-0.5 MPa, 20-50°, 450 days	Permeability vs time, temperature	Exp. [92]
HDPE	2 MPa, 20-50°C, 4 hrs	Permeability, diffusivity formulation	Exp. [93]
PA6, PA12	35 MPa, 65°C, 7 days	CTE difference, delamination	Abaqus [2]
BMPL HDPE	70 MPa, 20°C, 48 hrs	Effect of pressure on permeability	NRC's BlowView [68]
PA6, PA11	70-1 MPa, 15°C, 7 days	Effect on decompression on permeability & strength	Exp. [80]

Chapter 3

Role of Manufacturing Defects on Failure Behavior of 70 MPa Type IV COPV for H₂ Storage

3.1 Introduction

To achieve sustainability with respect to world's energy requirement in future, it is important to develop storage systems for H₂ that can store H₂ without any loss. This is particularly difficult due to the small size of H₂ gas molecules, that can lead to easy diffusion or leakage of H₂ in any gaseous storage system. In addition, gaseous H₂ need to be stored at high pressure to provide sufficient quantity of H₂ required for meeting the operational requirements. Such high pressure storage of H₂, can lead to the premature failure of a pressure vessels (PVs) made completely of metals, called Type I PVs, due to hydrogen embrittlement phenomenon [94, 95, 96, 97, 98]. Looking at such limitations, several new technologies are being explored for large-scale H₂ storage. These include Type II PVs that has a metallic vessel wrapped with fiber reinforced plastic (FRP) based composite over cylindrical part, Type III composite overwrapped PVs (COPVs) that has metallic liner (vessel) wrapped with FRP composite over both dome and cylindrical part, Type IV COPVs that has plastic liner wrapped with FRP composite over both dome and cylindrical part, cryo, cryo-compressed and materials-based storage, among other alternatives [99, 100].

Among various options available, Type IV COPV is one of the prime option available for H₂ storage so as to provide a competitive driving range for fuel cell electric vehicles (FCEVs). A major design requirement for Type IV COPVs is the necessary demonstration of a burst pressure, p_b , that is more than 2.0 times their nominal working pressure, p_{nwp} , as per the international standards for refillable composite gas cylinders [101]. One of the main advantages of these COPVs is that they allow FCEVs to be quickly refueled while providing driving range comparable to IC engine based vehicles [102]. However, they are costlier due to the high usage of carbon fiber (CF) material, which contributes to 70% of their cost. Additionally, because of its plastic liner, it has low toughness, low damage tolerance, and is vulnerable to impact loads. The p_b test is one of the top-rated tests other than free-fall drop impact, bullet penetration, extreme temperature pressure cycling, bonfire test, etc. to qualify the Type IV COPV as per international standards.

Unlike metallic PVs (Type I, II, III), Type IV COPVs exhibit significant performance variations with slight changes in geometry, material composition, and design parameters. Several experiment and simulation based studies are available in the literature that discuss the design process and assess the performance of mechanical behavior of complex multi-material structures of Type IV COPVs [65, 103, 53, 56, 104, 105, 106]. Many of these studies focus on the design of individual parts such as polymer liner [55], dome shape [107, 59, 60], CF stacking sequence [47, 108], etc. for their performance evaluation. The manufacturing methods used for polymeric liner development affects the performance of Type IV COPVs. Typically, highly efficient high-pressure Type IV COPV is produced using filament winding (FW), and it can be very difficult to maintain accuracy due to several manufacturing design variables, including volume fraction (V_f), winding angle (WA), stacking sequence, bandwidth [109], cut-uncut helical layers [110], ply-drop location [47], and the requirement of an ideal relationship between FW tension [111] and winding time. The fiber bandwidth (BW) is related to the number of tangent points, which directly affects the cylinder-dome interface and fiber placement near the polar boss region. It is known that a decrease in BW increases the layer thickness of the dome region [112]. An increase in the number of tangent points reduces fiber overlap and enables smooth thickness distribution along the circumferential direction [113]. The V_f , WA, and strength properties are random parameters directly related to the manufacturing uncertainties of composite layup [114]. The conventional netting analysis (NA) for the design and manufacturing of the dome-cylinder interface shows a jump due to a sharp geometry change. This causes the failure at the dome-cylinder interface due to secondary stresses and differences in stiffness [60, 115, 116]. These COPVs are designed based on safe and unsafe burst modes. In the case of safe burst mode, the failure occurs along the axis of the center of the cylindrical part in the circumferential direction, resulting in the boss going inward of Type IV COPV [15]. In case of unsafe mode, failure occurs in the dome region, which could lead to the ejection of the boss due to the liner-boss junction and dome-cylinder interface failure [56, 106, 15, 117, 118]. The dome-cylinder interface failure is found to be due to thickness transition which can be prevented by the use of doily layers (strips of CF as shown in black color in Fig. 3.1) placed to ensure the safety of COPVs [53, 119, 120, 121, 122, 123]. A few failure behaviors of Type IV COPVs are also studied concerning various factors that control their burst strength [56, 124], and failures such as liner collapse during decompression [2].

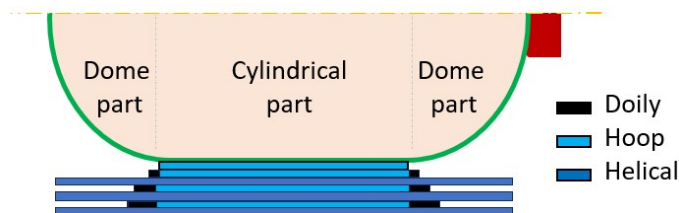


Figure 3.1: A schematic of doily layer inserted with hoop and helical layers on liner-boss assembly.

In finite element analysis (FEA), a half or full axisymmetric model was generally considered for the symmetric polymeric mandrel, and a symmetric load case was considered [46, 125, 126]. The failure criterion was employed to ensure the strength of a safe COPV design, although the majority of the literature only took the stress, strain, and deformation-based criterion into account for its design and analysis. The static burst pressure and thermo-mechanical loading were considered and analyzed by ABAQUS tools and experimentally tested. In the analysis, a gap was reported at the polymeric liner-boss junction and the boss-composite interface, but we didn't consider as a serious issue and part of the research [15, 46, 63, 127, 128].

The air gap was detected by reverberation NDT at the aluminium-polymer liner interface. Interfacial strength is reported in very few works of literature for metallic liner-composite interactions [129] and thermoplastic PA6 liner and composite material [46, 130]. Manufacturing defects arise in a composite layup during the FW process on the liner-boss assembly due to the shape or improper design of the liner-boss assembly. It could be caused by the filament slipping while being wound, the hoop winding being placed incorrectly at the end of the cylindrical section, the air gap between the liner-boss connection, and other factors [47]. The uniformity and defect detection on the LDPE and HDPE polymer liner samples were detected by ultrasonic NDT, which contains an artificial defect [131]. Application of putty, a patch, filler, or sleeve material is used to repair a damaged area of gas pipelines for metal or polymer pipelines and also for COPVs [132, 133].

Despite such vast studies available in the literature, the role of design and manufacturing defects on failure behavior of Type IV COPVs is not clearly understood. To ensure safety and further improvement in the upper pressure limits of H₂ storage, it is important to understand the role of design parameters and manufacturing defects on their failure behavior at p_b . In this paper, few critical design and manufacturing defects such as shape of composite winding, metallic boss and possible gap at the liner-metallic boss-composite winding interface are considered in an 18 litre Type IV COPV to analyse their individual role in failure. Such defects are found to be hot spots for failure of Type IV COPVs which is characterized in terms of Tsai-Wu failure criterion for composite winding. These findings are then corroborated with the experimental failure observed in a similar Type IV COPV to provide guidelines for developing a failure resistant Type IV COPV.

This chapter is organized as shown in Fig. 3.2 and follows: after providing a brief introduction to the topic and relevance of this work, the following section provides the analytical relationships related to NA, CLT, and failure criteria that form the basis of designing the proposed Type IV COPVs. The list of material properties, dimensions of various parts, and FE modelling details are then provided in the next section. The results section provides the distribution of equivalent von Mises stress and Tsai-Wu failure

index ($F.I$) based investigations in the composite winding, followed by discussion and conclusions.

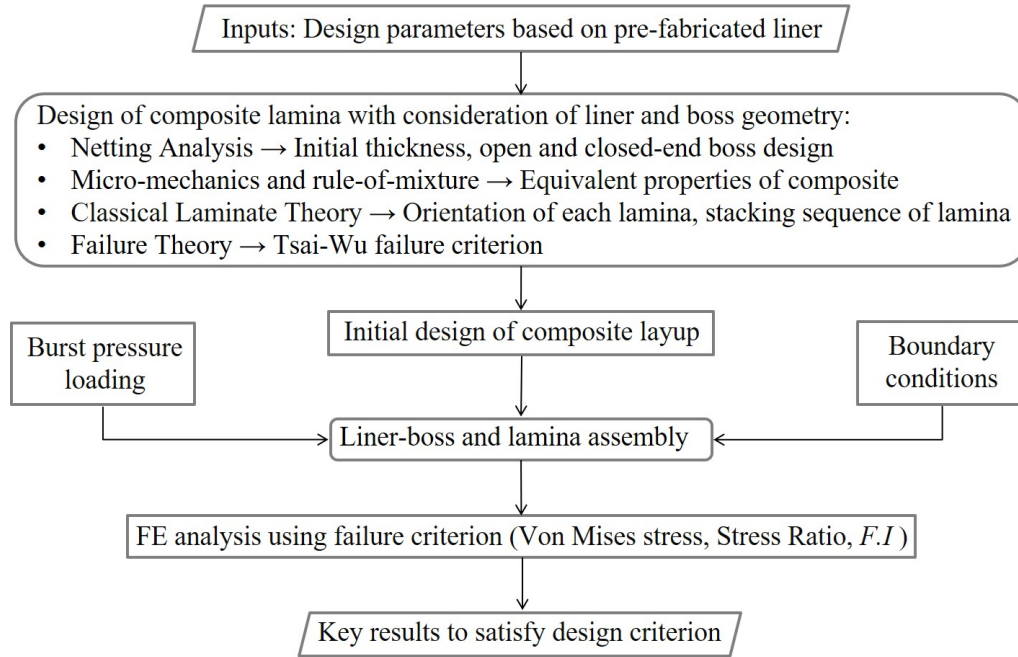


Figure 3.2: A schematic flow diagram for design and analysis of Type IV COPV.

3.2 Mathematical Formulation Used for Design of Type IV COPVs

In this section, the analytical relations used for the design of Type IV COPV based on NA and CLT are discussed first. Based on these relationships, the design parameters of COPV are selected for FE modeling.

3.2.1 Prediction of composite thickness based on netting analysis

FW is a widely used technique for manufacturing axisymmetric composite PVs using continuous unidirectional (UD) fibers. The inner liner geometry acts as the base geometry and serves as a mandrel for the FW process. The NA is a preliminary sizing step to estimate the thickness of the helical and hoop layers for a given p_b and ultimate fiber strength. A few assumptions are adopted when performing NA, as mentioned below [107, 13]:

1. There are negligible or low shear stresses at the interface between matrix and fiber, and the matrix does not contribute to carrying any part of the load in tension.
2. The fiber and the matrix have equal strain during tensile and compressive loading.
3. Load sharing contribution from the polymeric liner is considered to be non-existent.

4. COPV is designed for p_b using the ultimate strength of the fiber.
5. All the materials used in the structure obey Hooke's law.
6. The fibers are straight and continuous.

The schematic of a COPV section with inner radius R_c subjected to internal pressure p and helical layers wound at an angle α is shown in Fig. 3.3(a). The stresses in the hoop and helical layers are σ_{90} , and σ_α respectively. The dome part is only wound by helical layers as shown in the schematic Fig. 3.3(b), where R_b is the outer boss radius, F_a is the axial force that varies with radial distance r of the dome region from the axis of rotation along y-direction and F_c is the circumferential force in the cylindrical part. Due to only helical winding, the fiber strength in the dome part is unable to achieve a level similar to that in the cylindrical part. This is compensated by an increase in the thickness of the helical layer with a decreasing radius in the dome part.

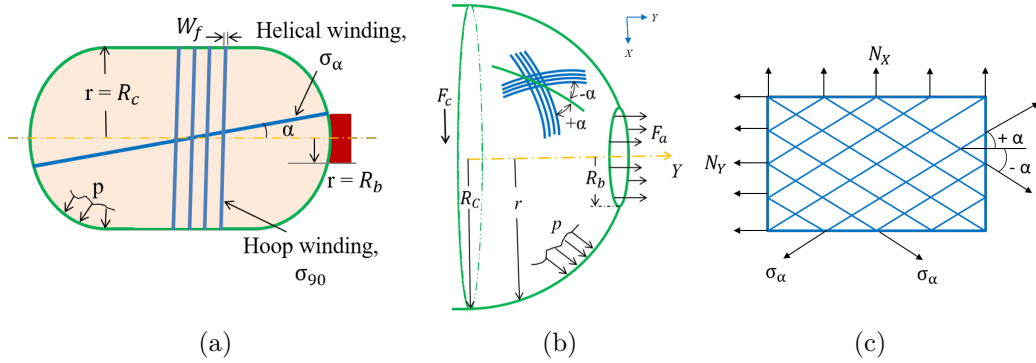


Figure 3.3: Schematic of COPV with winding over (a) the polymeric liner part, (b) only the dome part along with associated geometrical parameters, and (c) free body diagram of a netting-based element.

For the cylindrical part of COPV, a free body diagram of a unit length is shown in Fig. 3.3(c). The total helical (t_α) and hoop (t_{90}) layer thickness in cylindrical part is given as [13], where $F_a = pR_c/2$ and $F_c = pR_c$ are the axial and circumferential forces, respectively:

$$t_\alpha = \frac{pR_c}{2\sigma_\alpha \cos^2 \alpha} \quad (3.1)$$

$$t_{90} = \frac{pR_c(2 - \tan^2 \alpha)}{2\sigma_{90}}, \quad (3.2)$$

Based on this, the total thickness (t_c) of the composite in the cylindrical part is given as:

$$t_c = t_\alpha + t_{90} = \frac{pR_c}{2\sigma_\alpha} \left[\frac{1}{\cos^2 \alpha} + (2 - \tan^2 \alpha) \right] = \frac{3pR_c}{2\sigma_\alpha} \quad (3.3)$$

where it is assumed that $\sigma_\alpha = \sigma_{90}$ are the same as per NA. The thickness of the tow fibers (t_f) impregnated with resin with volume fraction (V_f), cross-sectional area (A_f), number of spools (N_s) is given as:

$$t_f = \frac{N_s A_f}{W_f V_f} \quad (3.4)$$

where W_f is bandwidth, as shown in Fig. 3.3(a). With the decrease in radius from the cylindrical part to the boss end there is variation in WA. This results in an increase in the thickness and decrease in BW of the composite in the polar region of the dome region which changes the dome geometry [134, 112]. Helical layer thickness buildup $t_h(r)$ as a function of radius r in the dome section is given as:

$$t_h(r) = \frac{t_{90} \cos \alpha(R_b)}{\cos \alpha(r)} \frac{R_c}{r + 2W_f \left(\frac{R_c - r}{R_c - R_b}\right)^4} \quad (3.5)$$

where $\alpha(r)$ and $\alpha(R_b)$ are WA at a varying radius r in the dome part and at the end of the dome part respectively. Using Clairault's method, the variations of WA with radius r in the dome section are given as [135]:

$$\alpha(r) = \sin^{-1}\left(\frac{R_b}{r}\right) + \delta \left(\frac{r - R_b}{R_c - R_b}\right)^n \quad (3.6)$$

where friction effect is included by an exponential factor n for wet winding and its value is zero for frictionless winding for dry winding based on prepregs [136, 137]. δ is the WA deviation from frictional to frictionless helical winding [138]. The variation of WA over the dome part to ensure the no fiber slippage $\alpha(r)$ is given as [139]:

$$\alpha(r) = \sin^{-1}\left(\frac{R_b}{r}\right) \quad (3.7)$$

The linear density (TEX) is 800 g/km for Toray 700S 12,000 (12K) CF. The amount of resin and fiber required depends on the CFRP properties and the path of the filament wound. Based on these relationships, the parameter values obtained for winding of Type IV COPV by considering a T700S-12K filaments per tows with a single spool ($N_s = 1$) of UD CF at p_b are given in Table 3.1. Using Eq. 3.4 the bandwidth of a single tow is 2.01 mm. Maximum load is carried by UD fibers in the fiber's direction. Matrix materials are isotropic, transferring loads equally in all directions. In contrast, composite materials (fiber/epoxy), are highly orthotropic, with properties that vary depending on the direction of the load. Therefore, the design of these composites using FW plays a significant role in affecting the load-bearing characteristics of the overall system. NA provides the first approximation of design parameters of the Type IV COPV without considering the stiffness discontinuities between the hoop and helical layups, dome-cylinder transition, and non-pressure loads such as bending or axial compression [13, 140].

3.2.2 Classical laminate theory based stress analysis

CLT-based FE modeling of composite winding removes such limitations of NA. The organized stack and structured arrangement of the UD composite layer is named lamina, where the stack is defined by the orientation of each layer's fibers. A schematic of layerwise

Table 3.1: Composite layup design description from netting analysis for a given load, material, and geometrical parameters.

Parameters	Units	Values
Filament diameter, d	μm	7
Filament per tow, n_f	(-)	12K
Cross section area for 12K filament, A_{12K}	mm^2	0.46
Volume fraction of carbon fiber V_f	(-)	0.66
Cross section area for single tow, A_f	mm^2	0.69
Individual layer thickness, t_f	mm	0.34
Burst pressure, p_b	MPa	157.5
Total hoop layer thickness, t_{90}	mm	12.24
Total helical layer thickness, t_α	mm	25.16
Total thickness in cylindrical part, t_c	mm	37.4
Total number of hoop layers, n_{ho}	(-)	36
Total number of helical layers, n_{he}	(-)	76
Total number of layers, n_t	(-)	112

composite winding is shown in Fig. 3.4(a) along with a single layer that has the WA, α in Fig. 3.4(b). For stress analysis, the local stiffness matrices for all layers in the local (1, 2) coordinate system are set up in global (X, Y) coordinate systems.

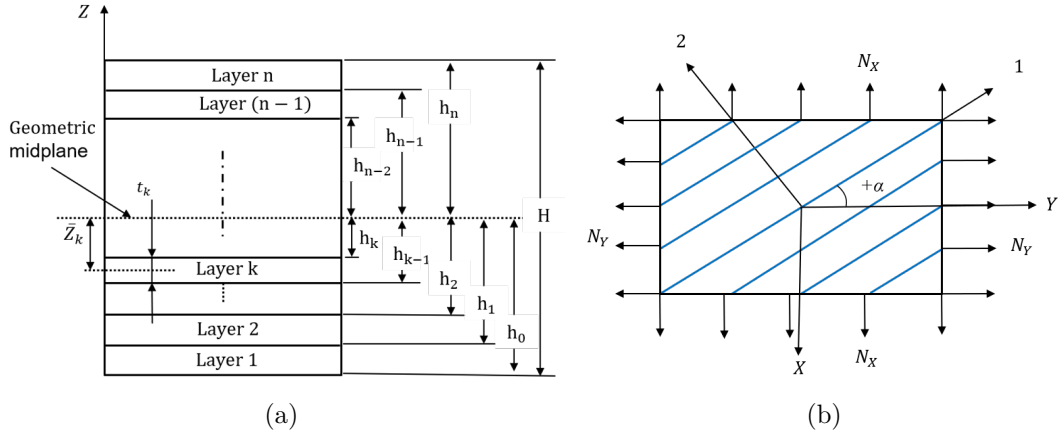


Figure 3.4: Schematic of CLT for (a) multi-layer lamina, (b) a schematic diagram with local (1,2) and global (X, Y) coordinate system.

The CLT is based on the following assumptions:

1. Normal lines to the midplane (see, 3.4(a)) before and after deformation remain straight and normal to the plane of deformation.
2. Each layer is perfectly bonded.
3. The thickness of the layer is constant throughout the laminate.
4. Each layer obeys Hooke's law.

In CLT, the resultant normal force components (see Fig.3.4(b)) take the geometry and loading effect in cylindrical or dome geometry to estimate the stress-strain behavior. CLT

enables the calculation of stresses and strains within layers of composite winding of the Type IV COPVs subjected to varying pressures of the gas. Further, the global stiffness matrix of the layer is set using the force and moment equilibrium over the layer as per Eq. 3.8. The relation of loads, **ABD** matrix, and strain component is written in matrix form as [141]:

$$\begin{bmatrix} N \\ M \end{bmatrix} = \begin{bmatrix} A & B \\ B & D \end{bmatrix} \begin{bmatrix} \epsilon^o \\ k \end{bmatrix} \quad (3.8)$$

where ϵ^o is the mid-plane strain vector, k is the curvatures vector, A is the laminate extensional stiffness, B is the coupling stiffness, D is the bending stiffness, and M is the resultant couple moment. The applied normal resultant loads (N_X and N_Y) for the cylindrical and hemispherical dome parts are shown in Eq. 3.9 and Eq. 3.10 respectively [12].

$$N_X = pR_c; N_Y = pR_c/2 \quad (3.9)$$

$$N_X = N_Y = pR_c/2 \quad (3.10)$$

The resultant stress components are evaluated by the **ABD** matrix. The composite design using CLT in Abaqus and governing equations of composite layup are included in FEA using the UVARM subroutine (required to specify user-defined output variables at all material calculation points of elements). The CF composite layups with proper sequencing of laminate, and orientation play an important role in understanding the critical stress responsible for the strength of Type IV COPV.

3.2.3 Tsai-Wu failure index

In the present study, the Tsai-Wu failure index ($F.I$) is used to estimate the failure of Type IV COPV at different H₂ gas pressures. $F.I$ determines the integrity of composite orthotropic lamina. It accounts for strength tensors and can distinguish between tensile and compressive strengths. The general form of quadratic $F.I$ criteria is expressed as [14]:

$$F.I = F_{11}\sigma_{11}^2 + F_{22}(\sigma_{22}^2 + \sigma_{33}^2) + 2F_{22}\sigma_{22}\sigma_{33} + 2F_{12}\sigma_{11}(\sigma_{22} + \sigma_{33}) + F_1(\sigma_{11} + \sigma_{22}) + F_2\sigma_{33} + F_{66}\sigma_{12}^2 < 1 \quad (3.11)$$

where σ_{ij} denotes the stress components and the coefficients are calculated using the following relationship:

$$F_1 = \frac{1}{\sigma_{1t}^*} - \frac{1}{\sigma_{1c}^*}, F_2 = \frac{1}{\sigma_{2t}^*} - \frac{1}{\sigma_{2c}^*}, F_{11} = \frac{1}{\sigma_{1t}^*\sigma_{1c}^*}, F_{22} = \frac{1}{\sigma_{2t}^*\sigma_{2c}^*}, F_{66} = \frac{1}{\tau_{12}^{*2}}, \quad (3.12)$$

$$F_{12} = -\frac{0.5}{\sqrt{\sigma_{1t}^*\sigma_{1c}^*\sigma_{2t}^*\sigma_{2c}^*}}$$

Here, the allowable tensile and compressive strengths in two material directions are

denoted by σ_{1t}^* , σ_{2t}^* and σ_{1c}^* , σ_{2c}^* , while τ_{12}^* is the allowable shear strength.

3.2.4 Stress ratio

Stress ratio (SR) is defined as the ratio of stress in fiber at specified minimum burst pressure (σ_{pb}) to stress in fiber at p_{nwp} (σ_p) and its value is 2.25 for CF material of 70 MPa Type IV COPVs as per ISO 19881 standards [101, 1].

$$SR = \frac{\sigma_{pb}}{\sigma_p} \quad (3.13)$$

3.3 Design Aspects and Finite Element Method used for the Analysis of Type IV COPV

The design of COPV using the FE method consists of the following steps: CAD model development, material assignment to all parts, meshing, specifying boundary conditions, and interactions between parts. The estimation of failure is obtained based on the set failure criteria with increased pressure of H₂ gas to the p_b . Each of these steps used for the analysis of COPV is detailed in the following part of this section.

3.3.1 CAD model and material properties

CAD modeling of Type IV COPV consists of the development of the geometric model of HDPE liner, and the open-end, and closed-end metallic bosses, as shown in Fig. 3.5. The shape of the liner and bosses selected for the design of the COPV is motivated by the ongoing experimental research work on the manufacturing and failure behavior of Type IV COPV in our research group, along with the work available in the literature [142, 143]. The open-end boss hosts the gas filling valve with radius r_{iv} as marked in the zoomed view of the open-end dome section. The COPV considered in this work has an 18 L water volume capacity. The thickness of the HDPE liner is considered to be 5 mm, which is sufficient to act as a H₂ permeation barrier [1].

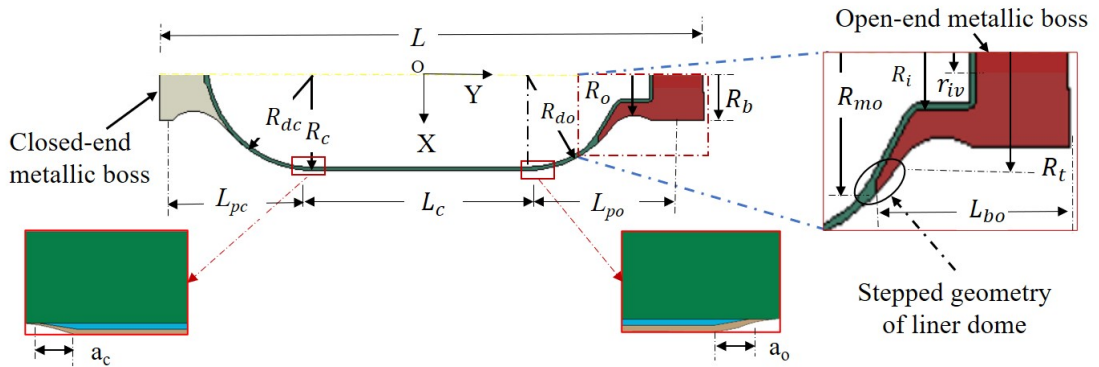


Figure 3.5: A 2-D CAD model of the liner-boss assembly of Type IV COPV used in this study.

The maximum radial and axial dimensions of the boss are named R_{mo} and L_{bo} respectively. The turnaround radius of helical layers wrapping direction is considered to be the outer surface of the open and closed-end bosses, also termed as polar boss region. Dimensions R_c , R_b , R_o , R_{do} and R_{dc} mark the radius of the cylindrical part of the liner, radius of the polar boss end region, boss minimum outer radius, open-end metallic boss dome radius, and closed-end metallic boss dome radius, respectively. The transition radius, R_t marked in the zoomed view of the open-end dome section is considered for bosses from the beginning of the fillet. The open-end boss has a geometry such that it is placed over the stepped dome of the liner. The stepped geometry of the liner dome leads to an increased wall thickness in the vicinity of the step and also provides better gripping of the boss, which will be discussed later. The considered geometry of the boss on the closed end of the COPV maintains the symmetry of the composite winding on both domes of the liner. While the total length of COPV is marked as L , the cylindrical section of COPV has length L_c , and the open-end and closed-end boss sections have lengths L_{po} and L_{pc} , respectively. The initial parameters considered for the CAD modeling of COPV are mentioned in Table 3.2. The lengths a_o and a_c marked at both ends of the cylindrical section in the insets of Fig. 3.5 describe the tapered end of the hoop layer plies. This end type of hoop layer is used for designing the composite winding of COPV with the ply drop location at the end of the cylindrical section.

Table 3.2: Design parameters of liner-boss assembly with composite specifications used for Type IV COPV design (all dimensions are in mm).

L	L_c	L_{po}	L_{pc}	L_{bo}	R_c	R_b	R_o	R_{mo}	R_t	R_i	r_{iv}	a_c	a_o	t_c
672	274	177	179	132	121	60	53.46	87.71	75	34	12	2.0	2.0	38.08

It is to be noted that the cylindrical section of COPV hosts both hoop and helical layers of composite, while the dome section hosts only the helical layers. This leads to a difference in the thickness of winding in cylindrical (t_c) and dome sections (t_h), as highlighted in the 3-D model of COPV in Fig. 3.6. In the FE analysis result section, it will be discussed about the removal of the sharp transition in composite winding thickness at the interface of cylindrical and dome sections [47].

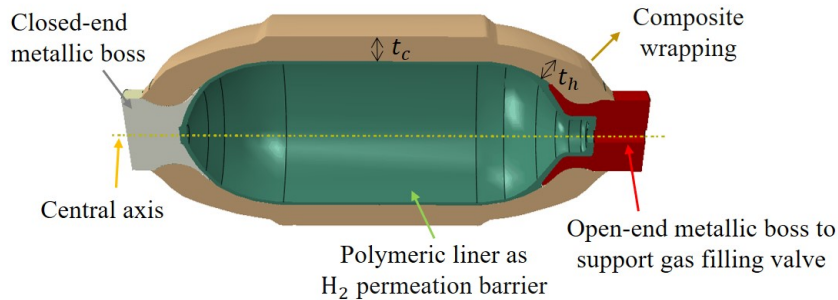


Figure 3.6: A 3-D Type IV COPV model with integrated parts.

The selected HDPE material for the polymeric liner can achieve the US, DOE targets of permeation limit (0.05 (g/hr)/Kg of H₂) at p_{nup} as per ISO 11119-3 [82]. It is a better choice over PA6 and PA12 in terms of low-to-high temperature performance requirement of -40°C to 85°C, making it a better choice for H₂ storage in Type IV COPVs [144, 145, 146]. Aluminum alloy grade Al6061-T6, which is heat-treated, is considered the boss material. It has a lower density and higher thermal conductivity than stainless steel, resulting in higher thermal diffusivity, which allows it to release the maximum temperature (limited to 85°C) reached inside the 70 MPa Type IV COPVs during fast filling. It is best suited due to its good strength, and toughness under a high-pressure H₂ environment, showing good resistance to HE as per GB/T 35544 safety standards [88]. Toray T700S CFs with 12K tows (T700S-12K-50C) are considered as reinforcement material. In contrast, compatible epoxy LY556 and XY54 hardener combined are considered as a matrix material in the ratio 2:1 for composite wrapping with V_f of 66% [147, 148]. Matrix helps in transferring the load from one reinforcement to another. The CF and matrix should have high interfacial bonding for reliable usage. Material properties assigned for the aluminum metallic boss [149, 150], matrix [148], polymeric liner [88], CF [147], and subsequently the composite lamina are mentioned in Table 3.3 and 3.4 respectively. The failure behavior of composite wrapping is governed by its strength properties as mentioned in Table 3.5 that are used for calculating the $F.I.$

Table 3.3: Mechanical properties of the metallic boss (Al6061-T6), matrix (LY556-XY54) and polymeric liner (HDPE) material used for Type IV COPV.

Property (Units)	Al6061-T6 [149]	LY556-XY54 [148]	HDPE [88]
Elastic modulus (GPa)	74.12	3.5	0.65
Poisson's ratio (-)	0.28	0.34	0.41
Tensile strength (MPa)	281	72.2	24.1
Density (kg.m ⁻³)	2700	1200	942

Table 3.4: Mechanical properties of T700S-12K-50C carbon fiber reinforcement and composite lamina.

Properties (Units)	Carbon fiber [147]	Composite lamina
Elastic modulus in fiber direction, E_{11} (GPa)	235	156.3
Elastic modulus in transverse direction, E_{22} (GPa)	28	11.2
Elastic modulus in transverse direction, E_{33} (GPa)	28	11.2
Shear modulus, $G_{12} = G_{13}$ (GPa)	50	4.02
Shear modulus, G_{23} (GPa)	10	3.91
Poisson's ratio, $\nu_{12}=\nu_{13}$ (-)	0.23	0.27
Poisson's ratio, ν_{23} (-)	0.3	0.43
Density, ρ (kg.m ⁻³)	1800	1596

For the creation of a composite layout, a node-set was created on the outer surface of the liner-boss assembly (see Fig. 3.5), over which the composite layers interact. Based

Table 3.5: Strength properties of the composite lamina.

Strength properties of composite lamina (Units)	Value [151]
Longitudinal tensile strength, σ_{1t}^* (MPa)	3234
Longitudinal compressive strength, σ_{1c}^* (MPa)	2400
Transverse tensile strength, σ_{2t}^* (MPa)	111
Transverse compressive strength, σ_{2c}^* (MPa)	290
Shear strength, τ_{12}^* (MPa)	50

on the design data from the NA as given in Table 3.1, the inputs are provided for all the composite layers in the WCM plugin. As an input for the composite layers, a minimum helical WA was determined using ratio R_b/R_c as per Clariuts principle and evaluated WA is 25° , considered as reference angle [13]. The hoop layers are placed at a uniform WA of 90° with constant thickness in the cylindrical part. The hoop layers cover the cylindrical part, while helical layers cover both the cylindrical as well as the hemispherical dome parts [152]. Helical layers WA along the cylindrical part remain the same, while across the dome part, it starts to decrease progressively from the cylindrical tangent line to the top end of the boss as per Eq. 3.7. The thickness of each layup is 0.34 mm. The composite layups are sequenced to achieve the same overall thickness in the cylindrical part as per NA. The N_s for the 1-41 layer and the 42-112 layer are 1 and 2, respectively. The number of layers (n), layer type (hoop/helical), composite material, WA, BW, and N_s are summarized in Appendix-I.

3.3.2 Boundary condition and meshing

To simulate the static burst test, an axisymmetric Type IV COPV model is considered for simulations. The boundary conditions applied are shown in Fig. 3.7. As shown, pressure is applied on the inner periphery of the polymeric liner. If the COPV was not structurally damaged at the minimum p_b , then the internal pressure was increased until the burst to obtain the maximum burst pressure ($p_{ult.}$). Both hoop-helical winding and the liner-boss assembly are meshed using four-noded axisymmetric reduced integration elements, CAX4R. Convergence studies were performed to select the mesh size for the simulation model.

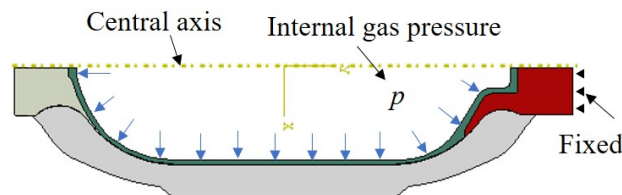


Figure 3.7: Load and boundary condition used to simulate p_b test of Type IV COPV.

3.3.3 Manufacturing defects found and need to analyze using FEA

To understand the role of manufacturing defects, several possible defects are considered in the design of the Type IV COPV. These defects include the sharp transition in the composite winding at the transition zone of the cylindrical and dome part (D1), possible gaps at the multi-material junction of the plastic liner-metallic boss-composite winding on the open-end dome (D2) and closed-end dome (D3) side, the shape of the metallic boss in contact with the composite winding at the open-end (D4) and closed-end (D5) dome sides, as shown in Fig. 3.8.

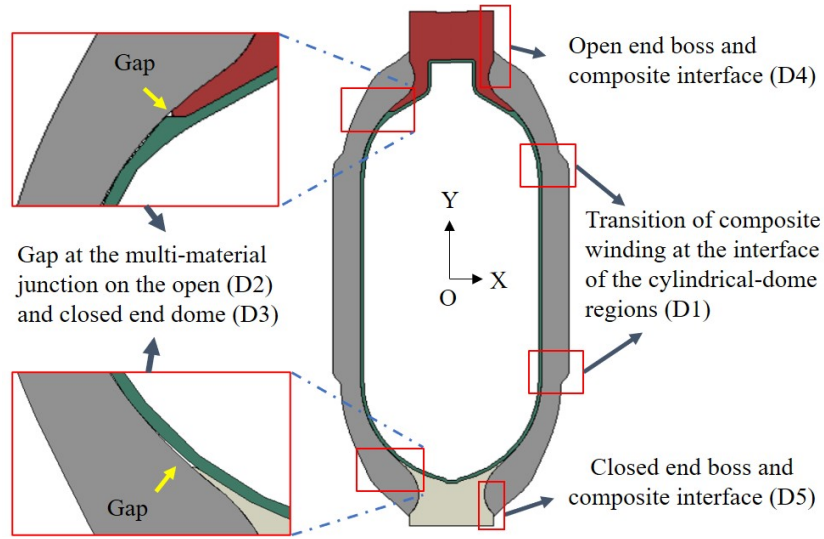


Figure 3.8: Manufacturing defects considered in the liner-boss-composite model.

For studying the role of defects D1, D2, D3, D4, and D5; all interfaces between two different materials of the Type IV COPV are considered to be permanently bonded. The effect of individual defects on failure behavior is studied through five different simulation cases. For case I: the defects D1, D2, and D3 are considered in the model. For case II: only D2 and D3 defects are considered, while the transition in the composite winding at the transition zone of the cylindrical and dome part of COPV is made smooth. For case III, defects D2 and D3 are further removed by filling the gaps with different sleeve materials to analyze the failure behavior of composite layers. In case IV, the design variation of the open (D4) and closed-end (D5) metallic bosses are studied to understand the failure at the boss-composite coupling region. The following assumptions are considered in modelling and FEA:

1. Boss on the closed end of the COPV maintains the symmetry of the composite winding on both domes of the liner.
2. 2-D axisymmetric Type IV COPV modelled due to symmetry and to reduce computational time.

3. Boundary conditions are applied on one open end of the boss to implement the realistic conditions.
4. All the interfaces (liner-boss, boss-composite, and liner-composite) are rigidly bonded thoroughly.

3.4 Results

To understand failure in Type IV COPV, the $F.I$ of the composite winding is tracked till the p_b . For case I, Fig. 3.9(a) shows the contour plot in the composite winding, and Fig. 3.9(b) shows the variation of $F.I$ in the first hoop (Layer Number 1: Hoop) and the first helical layer (Layer Number 5: Helical) in the composite winding.

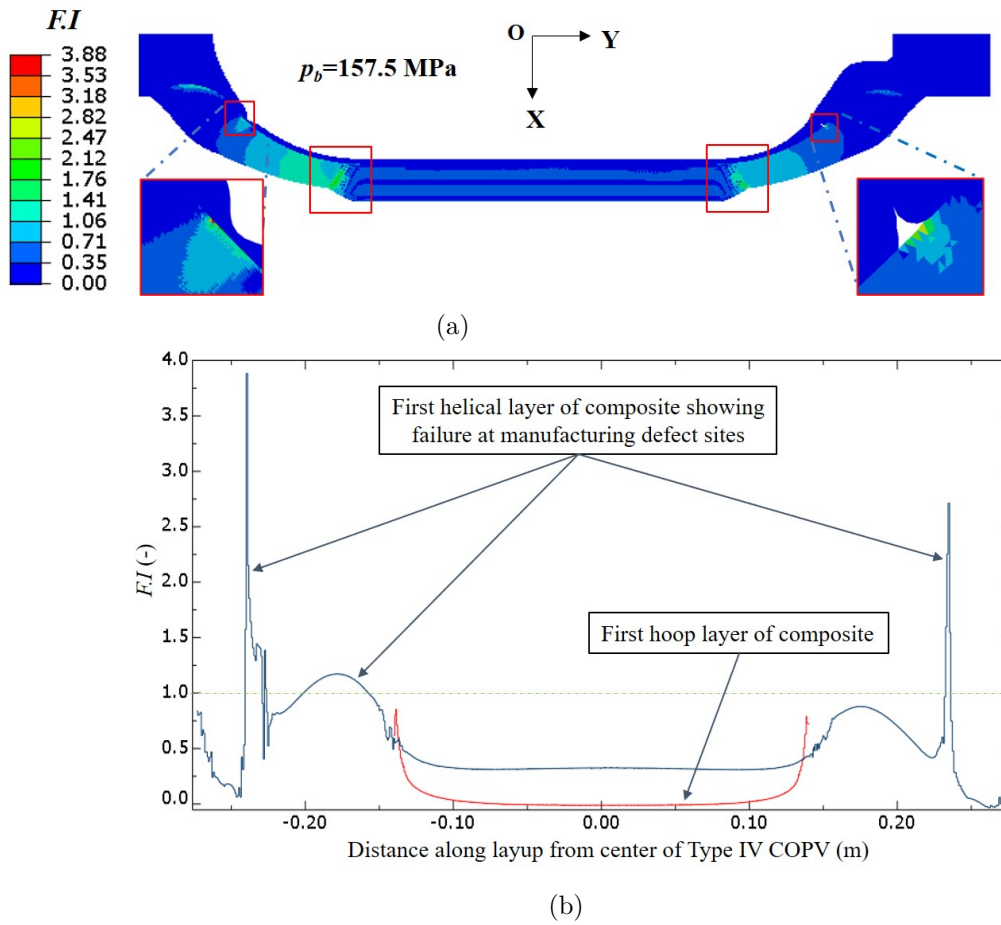


Figure 3.9: (a) Contour plots of $F.I$ in composite layers, and (b) variation in the $F.I$ along the first helical and first hoop layer of Type IV COPV with manufacturing defects considered as per case I.

The first helical layer is in direct contact with the junction of the plastic liner and the metallic boss where due to defects D2 and D3, a sharp jump in $F.I$ (> 1) is observed, thus confirming the site of failure. The site of defect D1 also shows a high value of $F.I$ (> 1), which confirms another site of failure in Type IV COPV for case I. The unsymmetrical variation of $F.I$ in the composite layup is due to a slight variation in the shape of the open

and closed-end domes of the plastic liner. For case I, the von Mises stress contour in the composite winding is shown in Fig. 3.10(a) while the variation of von Mises stress in the first hoop and first helical layer is shown in Fig. 3.10(b). It is shown that while the hoop layers carry the maximum load in the composite winding, it is the helical layers that lead to the failure.

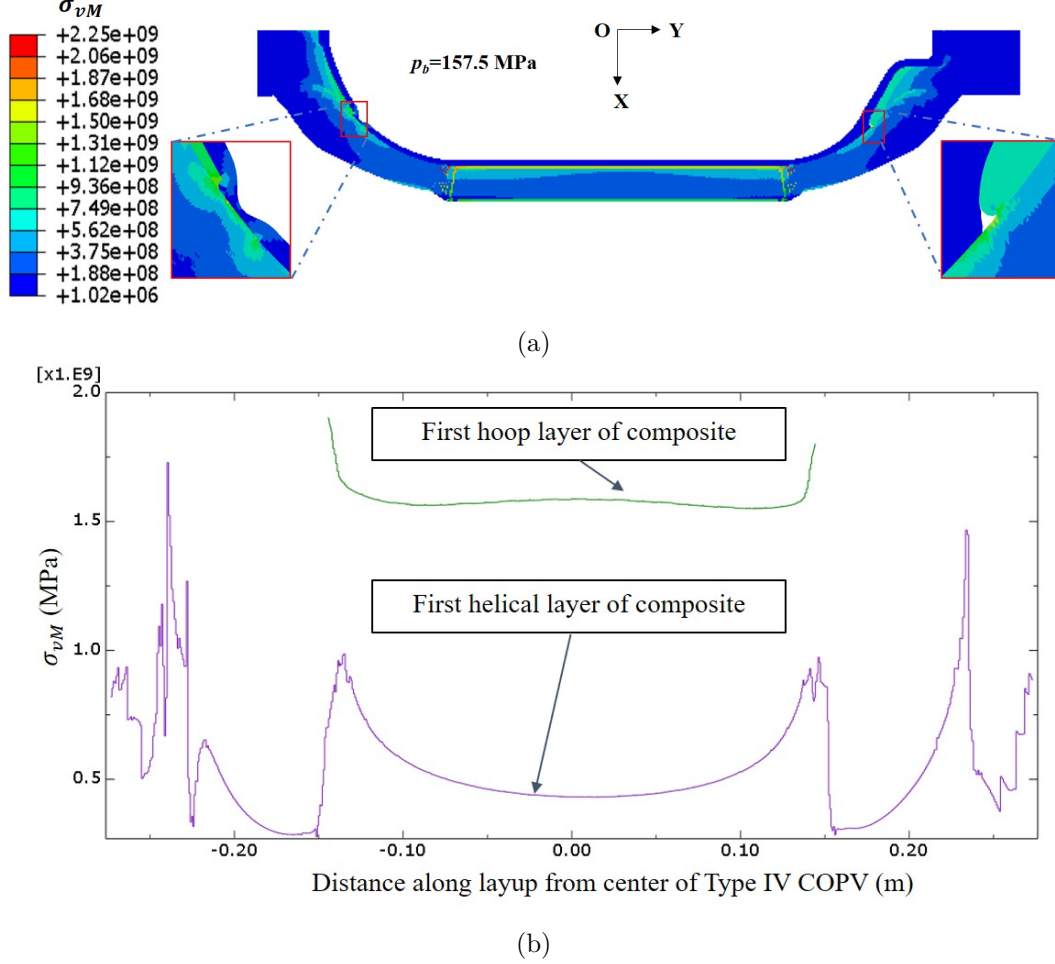


Figure 3.10: (a) Contour plots of von Mises stress in composite layers, and (b) variation in the von Mises stress along the first helical and first hoop layer of Type IV COPV with manufacturing defects considered as per case I.

In case II, our objective is to highlight the role of sharp transition (D1) of the composite winding in the transition zone of the cylindrical and dome part of COPV on failure. To achieve this, defect D1 is removed from the designed COPV while maintaining the other two defects, D2 and D3, as in case I (see Fig. 3.11). To remove the sharp transition, the hoop ply drop locations on both open- and closed-end domes are modified by the nominal retraction length. The length of nominal retraction for the L_{pc} region and L_{po} region is denoted by a_c and a_o , respectively, [47].

The composite layer thickness build-up at different locations in the open and closed dome part of case II is shown in Fig. 3.11, respectively. The thickness of the composite in the cylindrical part is 38.08 mm. The ply-drop in the dome region after the dome-cylindrical

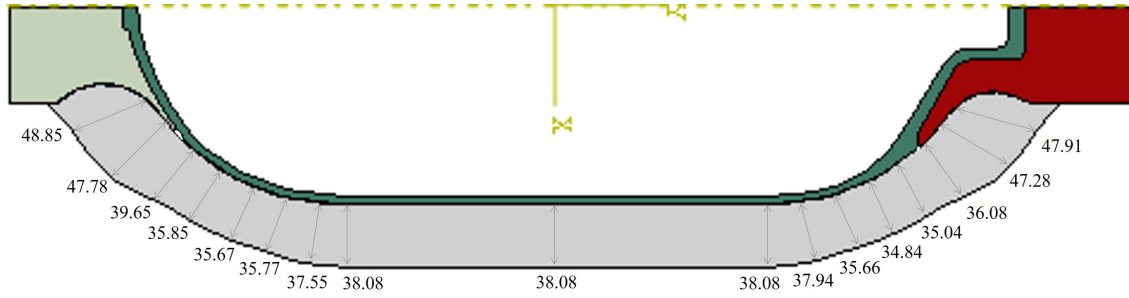


Figure 3.11: Design of Type IV COPV with the removal of manufacturing defect D1 from the cylindrical-dome part transition, with thickness buildup at different locations for safer design for open dome part and closed dome part.

interface region acts as a doily. The variation in the ply drop location of each hoop layer accounts for the smooth transition of composite layers. In addition, the maximum thickness build-up on the polar end bosses ensures that there will be no ejection of bosses from the dome ends at p_b . For case II, while the failure is prevented at the D1 defect site, the $F.I$ of helical fiber at the liner-metallic boss junction shows a sharp rise due to the localization of stresses at the D3 defect site, as shown in Figs. 3.12 and 3.13. The D3 defect site leads to maximum damage as a sharp jump, as shown in the contour plot in $F.I$. (> 1) and the high $F.I$. in Figs. 3.12(a) and 3.12(b), respectively.

The contour and line plots for the first hoop and helical layer and von Mises stress are shown in Fig. 3.13(a) and 3.13(b), respectively. These figures also showed the role of defective geometry at the liner-metallic boss junction on the propensity of failure. While the gap at the D2 defect site is much smaller and shielded by the thickest part of the liner, the gap at the D3 defect site is much larger and flatter, with a thin layer of the liner covering it. During pressurization, the plastic liner at the D3 defect site filled the gap while sharply increasing the stress level at the edge of the D3 defect site.

To prevent the failure of Type IV COPV from these gaps as defect sites, it is proposed to fill these gaps with suitable sleeve material as in case III with defects D2 and D3 removed. An axisymmetric model of Type IV COPV, with the gaps at the liner-metallic boss junction filled by a sleeve material, is shown in Fig. 3.14. The following materials are considered sleeve material: Al6061-T6 (same as boss material), resin (Epoxy LY556 and XY54 hardener mixture, same as used for CFRP matrix material), HDPE (same as plastic liner material), and Teflon, the properties of which are mentioned in Table 3.8) [153]. The selection of the sleeve material is performed based on the reduction of $F.I$ to be within the safe limit ($F.I < 1$) as shown in Fig. 3.15. The resin and Teflon as sleeve material show the lowest $F.I$ values (within the safe limit) throughout the first helical layer of composite, with Teflon showing a slightly lower value on the open dome region compared to resin material. Based on these results, Teflon material was used to fill the gap for further analysis of the role of other defects in COPV.

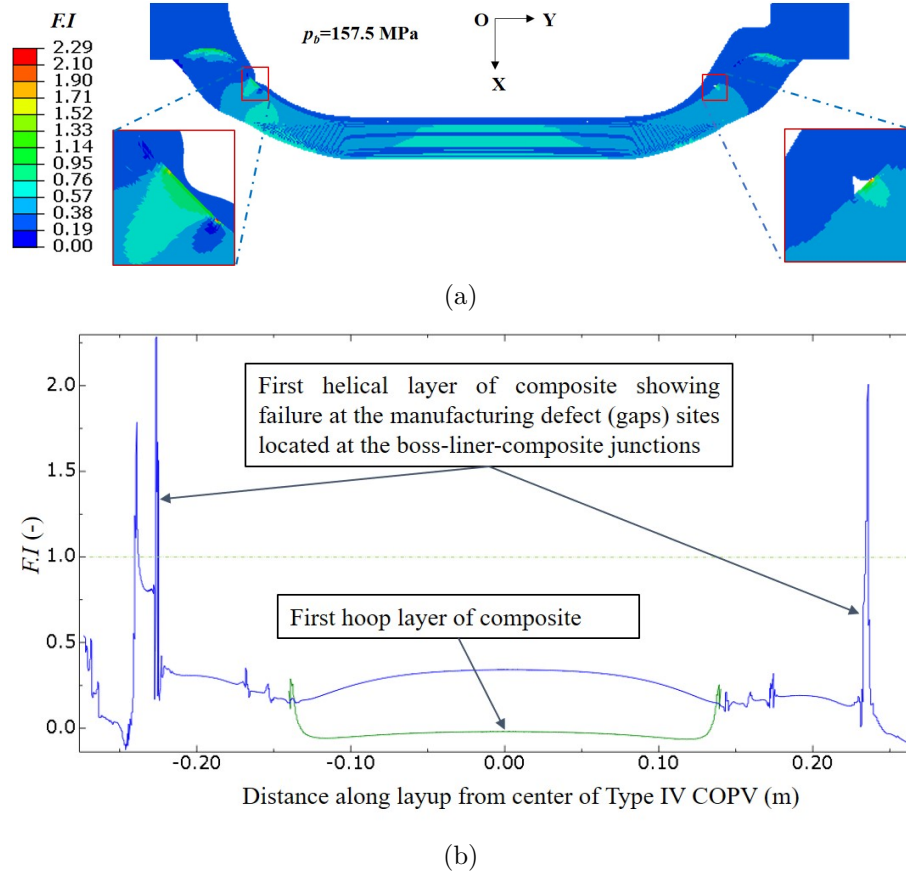


Figure 3.12: Variation of $F.I$ of Type IV COPV with the removal of sharp transition at dome-cylinder interface manufacturing defect (a) the contour plot variation, and (b) the line plot for the first helical and hoop layer.

Table 3.6: Mechanical properties of the sleeve material.

Material grade	Elastic modulus (GPa)	Poisson's ratio (-)	Tensile strength (MPa)	Density (kg.m^{-3})
Teflon [153]	3.65	0.25	2.4	760

Due to the lack of a specific standard and the absence of sufficient relevant literature for the design and manufacturing of metallic bosses, it is crucial to understand the role of the boss profile in the failure of Type IV COPV. In case IV, the role of open and closed boss geometric profile (that interacts with the composite) on the failure behavior of COPV is studied at the minimum required $p_b = 157.75$ MPa. With the removal of manufacturing defects associated with the composite winding and liner-boss junction, it is crucial to understand the role of the shape of metallic bosses in the failure of COPV. In case IV, the role of open-end and closed-end boss profiles (that interact with the composite winding) on the failure behavior of COPV is studied at the p_b . Three different profiles of open-end and closed-end bosses are studied as shown in Fig. 3.16. These include a straight profile of bosses where they connect with the composite winding along with a sharp transition into the flange region (referred to as A1A2 profile of bosses in Fig. 3.16(a)), straight profile of bosses where they connect with the composite winding along with a fillet based transition

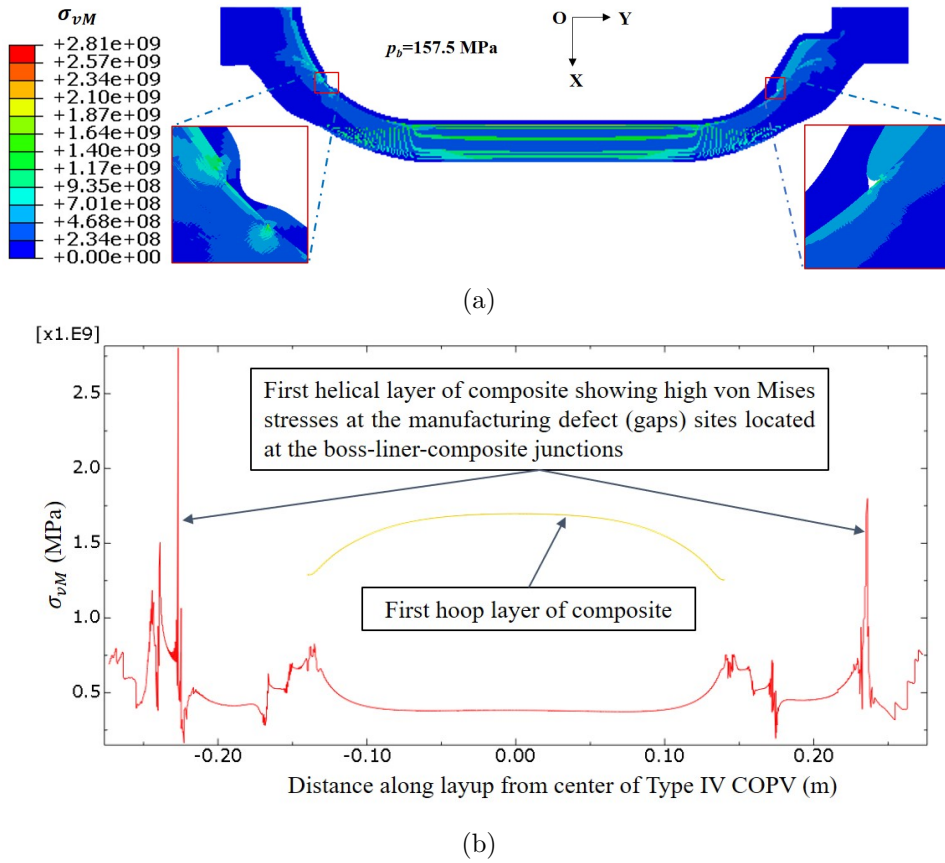


Figure 3.13: von Mises stress distribution in composite layers and plastic liner after removal of sharp transition at dome-cylinder interface manufacturing defect (a) contour plot variation and (b) line plot for the first helical and hoop layer.

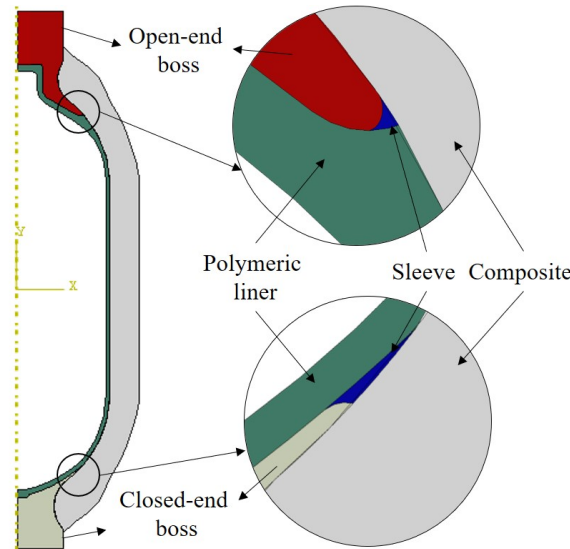


Figure 3.14: Type IV COPV axisymmetric model with sleeve material used to fill the liner-boss-composite materials gap.

into the flange region (referred as B1B2 geometry of bosses in Fig. 3.16(b)) and concave profile of bosses where they connect with the composite winding along with a fillet based transition into the flange region (referred as C1C2 geometry of bosses in Fig. 3.16(c)),

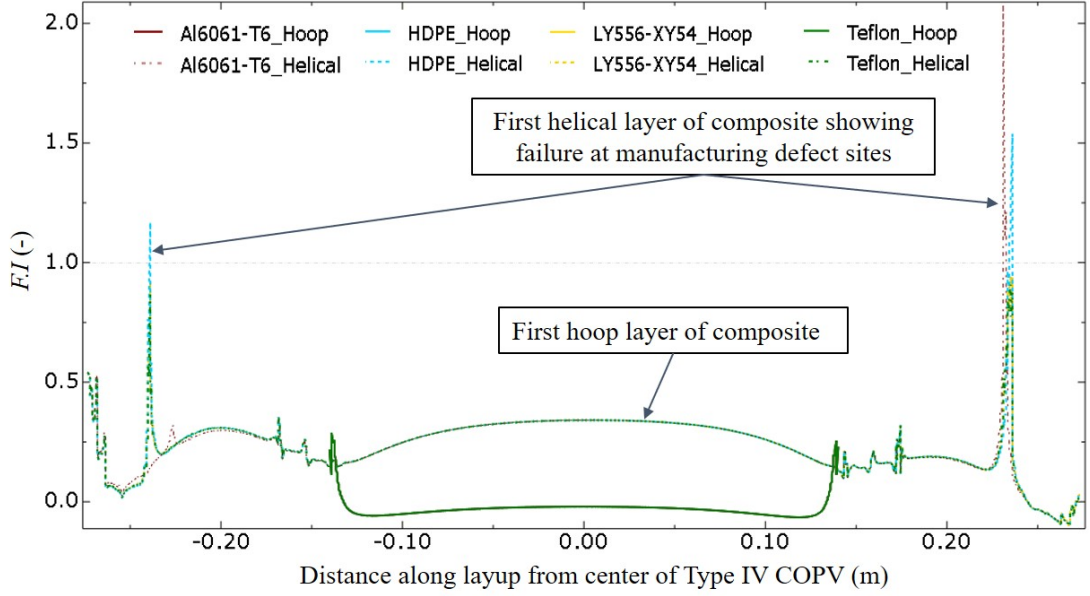


Figure 3.15: $F.I$ at multi-material interface of both end domes.

which is also used in case I, II and III. The design parameters of three profiles of open-end and closed-end bosses studied in case IV are given in Table 3.7. Fillet radius R_f , with the corresponding coordinates of the center point (x_f, y_f) , arc angle θ_f , boss inner radius R_i are shown in Table 3.7 along with the dimensions of R_o , R_{do} and R_{dc} , as defined in sub section 2.3.1 .

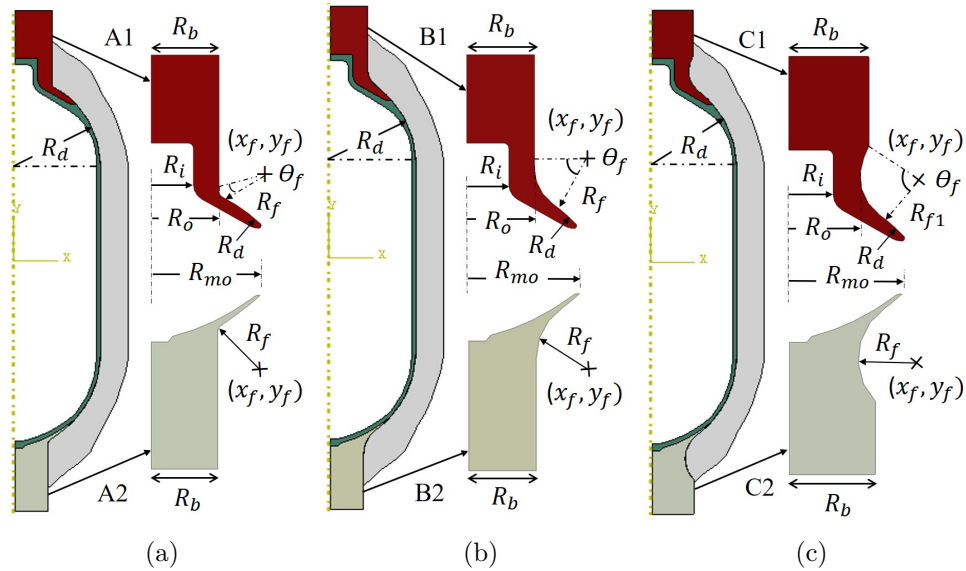


Figure 3.16: Various composite-boss interface designs for the open dome end and closed dome end, (a) pure cylindrical type, (b) cylindrical with curvature in starting of the composite, (c) curvature provided with cylindrical profile with more thickness.

The $F.I$ contour plots for A1A2, B1B2, and C1C2 boss shapes are shown in Fig. 3.17. A rise in $F.I$ to unsafe values for the A1A2 profile indicates that the sharp corner in the

Table 3.7: Design parameters of three profiles of open-end and closed-end bosses studied in case IV.

	A1A2		B1B2		C1C2	
Features	A1	A2	B1	B2	C1	C2
R_f (mm)	5	5	33.74	41.21	33.74	41.21
x_f, y_f (mm)	(60, 200)	(50, -300)	(90, 220)	(90, -320)	(90, 200)	(90, -310)
R_b (mm)	53.46	53.46	53.46	53.46	60	60
θ_f ($^\circ$)	63.04	55.94	54.09	56.63	93.08	105.85
R_i (mm)	34	34	34	34	34	34
R_o (mm)	53.46	53.46	53.46	53.46	53.46	53.46
R_b (mm)	53.46	53.46	53.46	53.46	60	60
R_{mo} (mm)	87.71	87.71	87.71	87.71	87.71	87.71
R_d (mm)	124	125.5	124	125.5	124	125.5

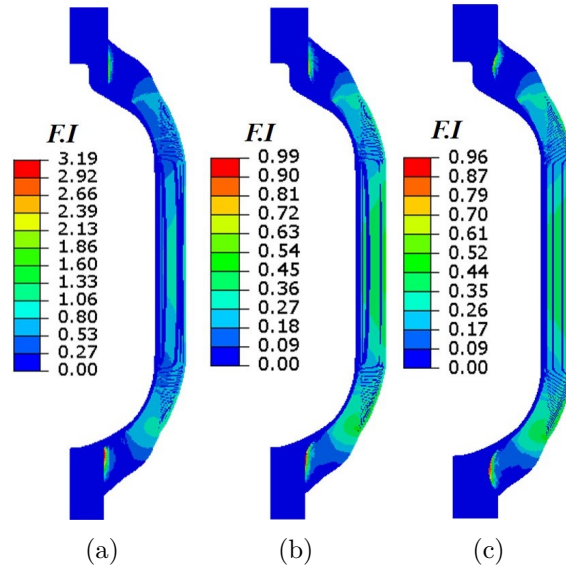


Figure 3.17: $F.I$ variation for composite-boss interface designs for the open dome end and closed dome end, (a) pure cylindrical type, (b) cylindrical with curvature in starting of composite, (c) curvature provided with cylindrical profile with more thickness.

boss profile to connect the straight section with the flange section is not desirable. The rounded corner in the boss profile B1B2 prevents such a sharp rise in the $F.I$ value and is further reduced by using a C-type curved profile C1C2 of the boss to satisfy the safe limits at the minimum required p_b . $F.I$ plot along the first helical and hoop layers of composite that interacted with different boss profiles are shown in Fig. 3.18.

The manufacturing defects in the Type IV COPV in the transition zone of composite winding (D1), the gaps in the liner-boss-composite winding junction (D2 and D3), and at the boss-composite winding interface (D4 and D5) are fixed. The von Mises stress distribution in composite after removal of all defects is shown in Fig. 3.19 (a) and (b). The stresses are reduced for the first hoop and helical layer, and the maximum equivalent stress is generated in the cylindrical section only. This shows the result of a safe design per the COPV design rule. This also validates the safety criteria of the Type IV COPV design.

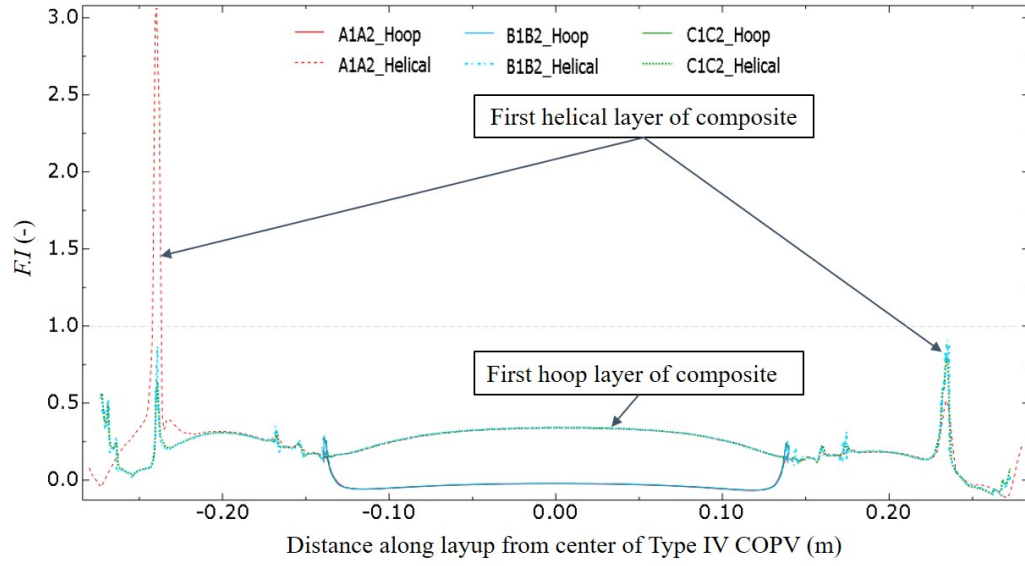
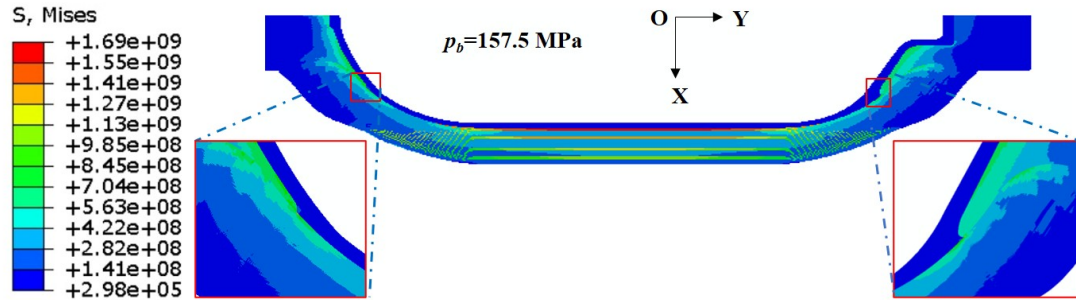
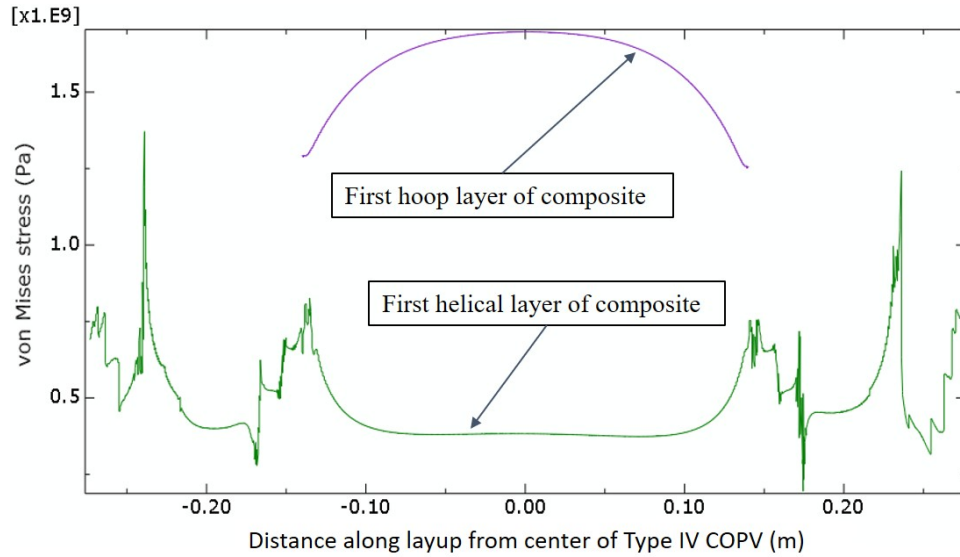


Figure 3.18: $F.I.$ for various profiles of boss shape.



(a)



(b)

Figure 3.19: von Mises stress distribution in composite layers after removal of all manufacturing defects (a) contour plot variation and (b) line plot for the first helical and hoop layer.

After fixing all defects, Type-IV COPV was tested above the minimum required p_b to evaluate the maximum burst performance of the proposed design [15]. The $F.I$ value and contour for the composite assembly at a design p_b load of 157.5 MPa, 159.25 MPa, 161 MPa, and 162.75 MPa are shown in Fig. 3.20 (a), 3.20 (b), 3.20 (c) and 3.20 (d), respectively. The Type IV COPV model demonstrated safe performance under pressure, sustaining a p_b of 157.5 MPa with a SR of more than the minimum required of 2.25.

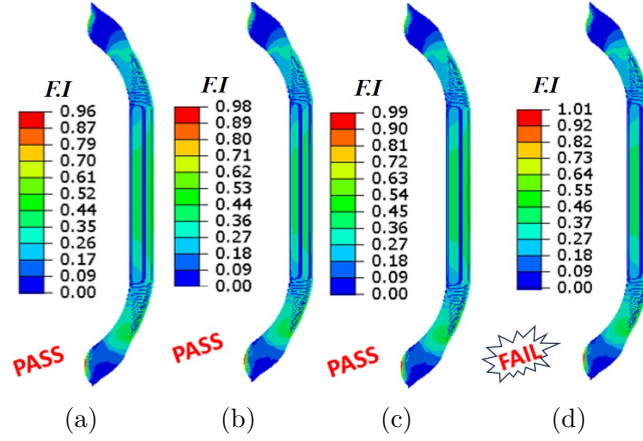


Figure 3.20: $F.I$ at various design pressures (minimum p_b to ultimate $p_{ult.}$ value).

The baseline safety margin and the progressive load analysis for the failure threshold of the estimated p_b corresponding to p_{nwp} are as follows:

- Baseline safety margin: At p_b of 157.5 MPa, the maximum $F.I$ reached 0.96, which is below the critical threshold ($F.I < 1$).
- Failure threshold for progressive applied load: Structural failure ($F.I > 1$) occurs at a p_b of 162.75 MPa, establishing this as the critical burst pressure limit, where the $F.I$ reaches 1.01 and the corresponding SR is 2.32 (> 2.25).

The $F.I$ for all the cases that are considered for the manufacturing defects are summarized in Table 3.8. In Table $F.I$ are mentioned as 3.88, 2.29, 2.19, 1.54, 0.98, 0.96, 3.19, 0.99, and 0.96 for case I, II, III(AA), III(HDPE), III(Resin), III(Teflon), IV(A1A2), IV(B1B2), and IV(C1C2) respectively. In brackets of case III and case IV represent the different sleeve materials and the various shape of boss shapes that interacted with the composite material, respectively.

Table 3.8: $F.I$ for different cases considered for manufacturing defect.

Case	I	II	III	III	III	III	IV	IV	IV
			(AA)	(HDPE)	(Resin)	(Teflon)	(A1A2)	(B1B2)	(C1C2)
<i>F.I</i>	3.88	2.29	2.19	1.54	0.98	0.96	3.19	0.99	0.96

3.5 Discussion

The work is motivated by the ongoing experimental work on the development of Type IV COPVs with $p_{nwp}=70$ MPa using a pre-fabricated liner. The pre-fabricated liner considered in the experimental work has a neck (see, Fig. 3.6) with an opening for gas input on one of the dome while the other dome is closed. The metallic boss with a threaded opening for the valve is then bonded over the liner neck using a suitable adhesive on the open-end dome side. A metallic boss having a similar geometric profile but without an opening is also attached on the other side of liner to maintain symmetry during FW. FW of liner-boss assembly is then performed using the filament winding sequence. The Type IV COPV thus obtained is then subjected to burst test as per ISO 19881 standard [101] with increasing hydraulic media (water) pressure till $2.25 \times p_{nwp}$. During burst test, it was observed that the fabricated COPV failed much earlier than the expected failure pressure. The failure in the form of leakage of hydraulic media from the open-end boss region was observed during experiment. Based on these experimental observations, the simulation framework presented in this paper is designed to elucidate the role of manufacturing and design defects on the failure behavior of a Type IV COPV at p_b using FE analysis. The analysis presented can be used as guidelines on how failure can be prevented in expensive Type IV COPV by doing suitable design modifications.

To analyze the failure of Type IV COPV during burst test, interactive failure theory was used to predict failure sites as Tsai-Wu failure index $F.I$ (see, Eq. 3.11). By critically investigating the failure observed during testing, it was found that the site of the hydraulic media release from the COPV is the open-end metallic boss and FW coupling (D4 defect site) which is caused by the release of hydraulic media from the valve mounting zone of the liner at first and then from the adhesive joint between the liner and the open-end metallic boss (which seems to have failed during pressurization of COPV due to expansion of the COPV) followed by the final release from the open-end metallic boss and FW coupling site. Though the coupling of liner-metallic bosses was considered to be permanent in FEA, the shape of the boss considered in experiments leads to highest stresses levels at the D4 and D5 sites on the dome part of metallic boss. Due to this, during experiment, once the adhesive bond between liner and metallic boss is opened during pressurization, the media finds the way to easily escape the COPV from the coupling of open-end metallic boss and FW.

While the experimentally observed failure can be partially explained based on FEA analysis of a defect free COPV (with D1, D2, and D3 defects removed), the following findings are also relevant for developing a failure resistant COPV:

1. The hoop layers only cover the cylindrical part and helical layers cover cylindrical as well as hemispherical dome parts. This results in more thickness in the cylindrical part and less thickness in the dome part [154]. Due to this, at the interface of cylindrical and dome parts, a stress concentration region is created leading to high

F.I observed at these defect sites. Such a defect can be removed by shifting the drop location of hoop plies from the end of the cylindrical part to the dome part just after the dome-cylindrical transition region or by using dollies at the dome-cylindrical transition region, as shown in Fig. 3.1.

2. The gap at the multi-material interfaces of Type IV COPV can act as a failure site. The hoop layers in the cylindrical zone appear to be undamaged due to this gap, in contrast to the helical layers in the dome region. Such a gap can be filled with matrix material of FW or a similar material (Teflon) to prevent the failure.
3. The role of the boss shape and its interaction with the composite analyzed in case IV and with boss shape design A1A2 were found to be unsafe. The design was found to be safe for B1B2 and C1C2 boss shapes. It was observed that the boss design parameters are an important parameter for safety and considers the number of parameters in designing (shown in Table 3.7).
4. After a safer design, maximum p_b capability was examined, and it was observed that the design could withstand a maximum p_b of 161 MPa and was safe for p_b of 157.5 MPa. It is observed that the design failed at p_b of 162.75 MPa. The p_b can be improved with consideration of various design modifications and manufacturing defect minimization.

3.6 Conclusion

This work proposes a design solution for Type IV COPV for H₂ storage with p_b of more than 150 MPa. The precisely calculated theoretical design parameters based FE modelling considers the possible manufacturing defects to perform failure analysis. It was found that equivalent von Mises stress and *F.I* shows large variation along the composite winding due to shape of liner and boss, composite geometry, and their interfaces. The findings from this work are summarized as follows:

1. The sharp transition at the cylinder-dome interface model exhibits the worst load-bearing capability. The ply drop location when shifted from the end of the cylindrical part to the dome part near the dome-cylindrical part transition region can help to prevent the failure at the dome-cylindrical interface region.
2. Even a small gap at the multi-material interfaces of Type IV COPV can act as failure site, as shown in the case III of this work. This calls for a high precision winding systems required for filament winding of Type IV COPVs to prevent any such defects during the winding process and by having such a contact between liner-metallic boss-FW such that no gaps are possible.
3. While the simulations are performed using non-geodesic dome as per the design of liner used in experiments, the geodesic dome is essential for transitioning the failure

from dome region (as high F.I value is observed in dome region of a defect free COPV) to cylindrical part of Type IV COPV to make it a safe design.

Chapter 4

Modeling of H_2 Permeation through the Liner Materials of 70 MPa Type IV COPV

4.1 Introduction

The polymeric liner in Type IV COPV, serves as a structural element during the FW process. It functions as a non-load bearing member with major role to provide a strong permeation barrier for high-pressure gaseous hydrogen (H_2). It is in direct physical contact with the H_2 and has the remarkable ability to prevent leaks [155]. Besides acting as a permeation barrier, it also protects CFRP layers and metallic bosses from direct contact with H_2 . The gradual loss of H_2 from Type IV COPV can decrease safety and reliability, since, it is flammable in air and explosive at NTP in the concentration range of 4-75% and 15-59%, respectively [100].

The manufactured and finished Type IV COPV (as per ISO 11119-3) are filled with H_2 up to p_{nwp} and kept in a sealed chamber (a schematic shown in Fig. 4.1) for 500 hours at NTP/vacuum and monitored for H_2 permeation/leak. It could be measured using (a) gas chromatography (GC) based on the volumetric method, (b) weight loss or pressure sensor (manometric method), (c) thermal desorption analysis (TDA), and (d) high-pressure H_2 permeation (HPHP) setup.

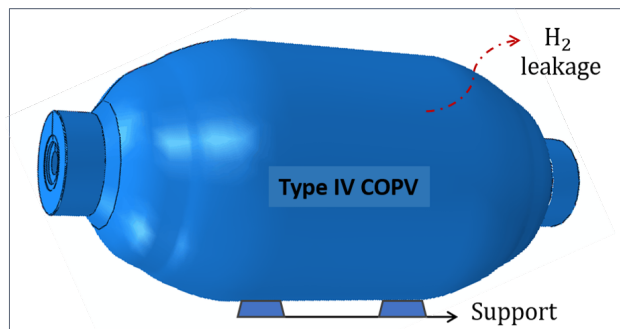


Figure 4.1: An illustration of a typical Type IV H_2 COPV kept in a sealed chamber for permeation testing.

The polymeric liner is made up of elastomers, thermoplastics, and thermosetting polymers, which can store and transport H_2 in the acceptable temperature ranges of -40°C to 85°C and pressure up to 90 MPa for several cycles in Type IV COPVs [19, 87]. These polymeric liner materials are used in various applications such as food packaging, pipes, drug delivery, beverage [125, 156], and industries exposed to chemical and cryogenic temperatures that cause failure due to leaks at critical operating conditions [157]. Polymeric liner materials such as PA6 [47, 125, 62, 158], PE [59], LLDPE [55], LDPE [55, 64], HDPE [65, 55, 60, 64, 63, 61, 57, 65, 159, 160], polyurethane (PU) [41], PET [161] etc., are combined with Type IV COPVs and performed various mechanical tests. Very few reports are available on analyzing the safety and structural integrity of polymeric liners separately [146]. Various research articles show the study of permeation on polymers such as PA6 [146, 162], PET [156, 163, 164, 165], LDPE [166, 86], HDPE [86] materials, etc., according to various low-pressure applications [167].

Most of the earlier literature worked on the non-dependence of diffusivity and solubility on the H_2 concentration in the polymer matrix. It was reported that the solubility is independent of the H_2 pressure lower than 10 MPa [168]. H_2 exposure up to 90 MPa, influences the mechanical as well as transport properties due to compression, which causes severe failures in HDPE materials [87, 169, 88]. The exposure time, depressurization rate for H_2 (10–90 MPa) affect the permeation properties of LDPE, LLDPE, MDPE, HDPE, UHMWPE (PE100 grade), and EPDM [18, 88, 83]. HDPE is a widely used common liner material for storing H_2 at pressures up to 90 MPa because of its excellent toughness, low permeability, and ease of manufacture. Thermal and mechanical cyclic loading is responsible for H_2 permeation through CFRP and polymer [170]. The effect of concentration (C), pressure (p), and temperature (T) content on sorption, diffusion, permeation, and conductivity was analyzed during the fast filling of COPV [20, 2, 81], for that aging has been studied under a H_2 environment for PA11 and PE100 [171]. The physical and mechanical properties of the polymers change at high-pressure H_2 , i.e., plasticization. The pressure of gas in polymers also affects the glass transition temperature T_g of the polymer during the temperature-dependent test [87]. Operational variables (C , and p), material characteristics (crystallinity, orientation, crosslinking), thickness [168], blending variables (organic or inorganic filler, complex side chain addition) [154], transport variables (permeability coefficient: P_e , diffusion coefficient: D_{eq} , and solubility coefficient: S), manufacturing methods (roto molding, blow molding, or injection/extrusion molding [172], 3-D printing [173], ultrasonic fusion bonding), and handling and packaging procedures also influence barrier performance. Any material and design changes in these COPVs, H_2 interaction, and compatibility must be taken into account for polymer liners and CFRP wrapping, as well as changes in the static, cyclic, and fatigue strength of the material due to the presence of high-pressure H_2 [174].

Due to the small molecular size of H_2 , it gets dissolved, and its penetration is unique to the polymeric liners. H_2 penetration rates and its saturation in the liner material are

encouraged by prolonged storage and require higher barrier coefficients. A semicrystalline polymer sample has a higher diffusion of H_2 governed by the diffusion model and the sorption mode during cyclic loading [82, 84]. Henry's law dissolving in an equilibrium zone and Langmuir-type sorption in a non-equilibrium region make up the dual-mode sorption model (reflected due to excess free volume), which strongly depends on pressure [17, 175]. Gas diffusion through polymeric liner material involves complex nonlinear diffusion consisting of the governing equations such as Henry's law, Fick's 2nd law, a yield criterion, and non-linear transient diffusion based on Langmuir sorption [176]. High pressure results in an increase in H_2 concentration and a decrease in free volume (FV). It also affects the transport properties (P_e , D_{eq} , and S) of polymeric material. For high-pressure H_2 permeation testing, it takes a costly, complex assembly of the setup, significant time, prototype sample preparation, and other safety concerns [177]. However, because of the proprietary nature of the research carried out by commercial organizations, the characteristics of H_2 permeation and their behavior at high pressure are still not available in the literature. Therefore, it is important to analyze and understand the role of polymer microstructure in the H_2 multi-operational parameter-driven permeation model. To determine whether the liner specimen can maintain its H_2 barrier qualities and permeability over the COPV lifetime, H_2 permeation measurements must be taken at predetermined intervals.

In this work, the process of H_2 permeation and the barrier mechanism of polymeric liner material is analyzed by considering factors such as C , p , crystallinity, morphology, etc. that affect the transport properties of the Type IV COPV wall material. A coupled framework of H_2 transport model (HTM) has been developed for FEA using the user material's thermal (UMATHT) subroutine. A procedure for H_2 transport modeling framework is shown in Fig. 4.2.

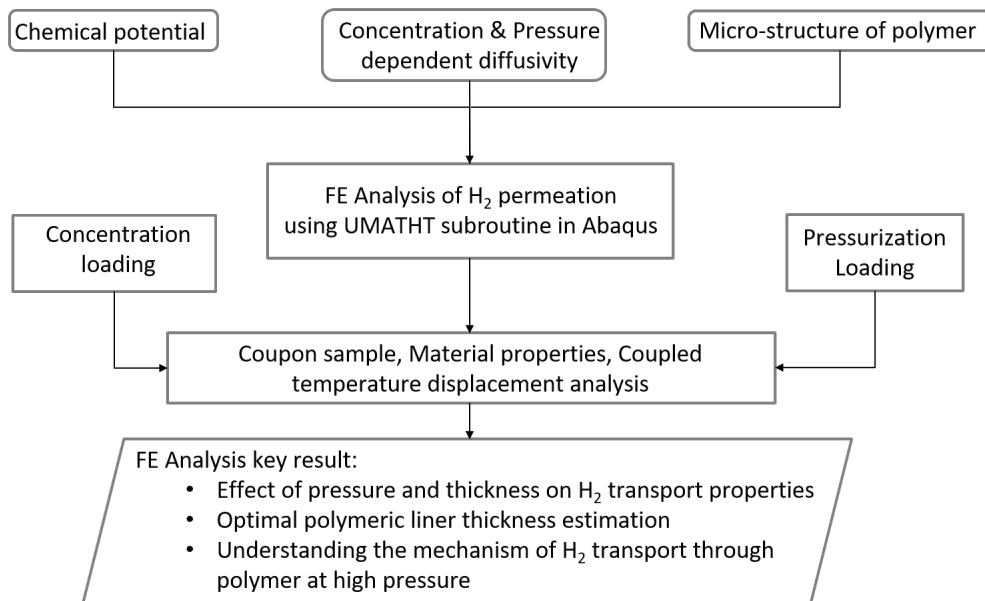


Figure 4.2: A schematic of hydrogen transport modeling framework.

The mathematical framework developed has been validated by experimental results of transport properties reported in the literature, and permeation tests are performed by pressurizing one side of the coupon with H_2 from 10 MPa to 90 MPa. The simulation framework attempts to conclude the effective H_2 transport properties through the wall of a polymeric liner to improve the structural integrity and permeation limit of 70 MPa Type IV COPVs to achieve the DoE, USA targets for the light-duty FCVs [82]. The loss can be recovered or minimized by proper maintenance of permeability and understanding the proper mechanics of permeation to achieve desired gravimetric and volumetric targets.

4.2 Mathematical Modelling to Implement in FE Analysis

To simulate the complex H_2 diffusion through a polymer at critical pressure and C , there is a need for a simplified and well-defined mathematical model to implement in commercial software like Abaqus. The UMATHT subroutine can correlate our mathematical modeling with the variables of H_2 diffusion through Abaqus. The limitations of the earlier approach ignore the effect of pressure gradient, variation in diffusivity, and crystallinity of the polymeric liner material on the permeation measurement [84].

4.2.1 Methods of permeability prediction and process of H_2 diffusion through polymeric liner material

The permeability test was performed on the disc-shaped polymeric liner coupon sample utilizing the permeation test bench (as per ISO 15105) in which the sample is placed inside the permeation cell. This high-pressure gas permeation (HPGP) cell consists of two chambers, in which H_2 is at p_{nwp} in one chamber directly exposed with the polymeric sample and the other chamber is at NTP, as shown in Fig. 4.3. The H_2 diffusing through the polymer sample was then collected in the chamber at NTP and the p or flux (J) vs time plot was used to calculate the H_2 transport properties of the polymeric liner material [178]. The TDA method is a simple non-steady state permeability measurement technique in which the H_2 permeates out from all directions after being taken out of the pressure chamber, and it is a less accurate type [18, 22]. The following processes are involved in the diffusion of H_2 through a dense polymer, according to permeation measurements that revealed a permeation coefficient:

1. At high penetrated C and p , the H_2 adsorbs into the polymer surface;
2. Penetrate molecule gets diffused through the polymer via C and p gradients;
3. Desorption of the penetrated molecule takes place in the atmosphere at NTP from the polymer surface.

The schematic of polymeric material, state of gaseous (H_2) (p , C), and steps involved in the diffusion through the polymer are shown in Fig. 4.3(a) and (b). In Fig. 4.3(a), the polymer material (shown in green) has thickness L , and the left side of it, named the

feed side, contains H_2 at a p , and C and right sides of polymeric material are named as permeate side exposed to atmospheric NTP. In Fig. 4.3(b) of step I, the adsorption takes place on the left side of the polymeric material (feed side: at $X=0$), in step II, the diffusion takes place; and in step III, that is the right side of the polymeric material (permeate side: at $X=L$), the desorption takes place to the permeate side.

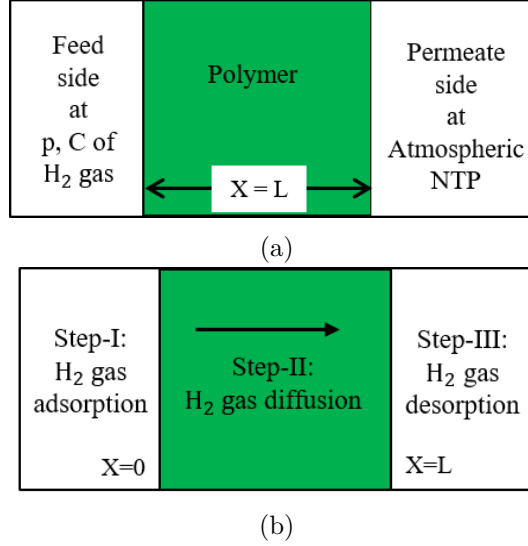


Figure 4.3: (a) H_2 interaction with the polymeric sample at a given state, (b) steps involved in the diffusion process.

4.2.2 Governing equation for H_2 diffusion in terms of chemical potential

To consider the effect of the C and p -driven diffusion model, the equivalent term used in mathematical modeling is termed “chemical potential”, and it is defined as the movement of molecules from a surface area with a higher potential to a surface area with a lower potential; this process is known as diffusion. At constant temperature, the chemical potential μ (Eqn.(4.1)) and gradient of chemical potential $\nabla\mu$ (Eqn.(4.2)) are written as [179]:

$$\mu = \mu^0 + RT \ln C - V_H \sigma_H \quad (4.1)$$

$$\nabla\mu = \nabla(RT \ln C) - \nabla(V_H \sigma_H) \quad (4.2)$$

where μ_0 is the standard chemical potential. Fick’s first and second laws explain this diffusion process for a steady and transient state. The H_2 flux (J) vector is proportional to the rate at which the gradient of chemical potential changes, $\nabla\mu$ and the expression is written as Eqn.(4.3) [180]:

$$J = -\frac{D_{eq}C}{RT} \nabla\mu = -\frac{D_{eq}C}{RT} \left(\frac{\nabla C}{C} RT - V_H \nabla\sigma_H \right) \quad (4.3)$$

where D_{eq} is the diffusion coefficient for H_2 , R is the universal gas constant, J defines the number of H_2 molecules passing through a unit area per unit of time, C is the number of

moles of H₂ per unit volume, and V_H is the partial molar volume of H₂ in the polymer at room temperature T for a system for compression of the polymer by the pressure of the penetrant [161]. The extended form of Fick's second law, unsteady state, non-linear, second-order partial differential equation specifies a non-zero value for the hydrostatic stress/pressure gradient and C -induced diffusion as written in Eqn. (4.4):

$$J = -\frac{D_{eq}}{RT}(RT\nabla C - CV_H\nabla\sigma_H) = -D_{eq}\nabla C + \frac{D_{eq}CV_H}{RT}\nabla\sigma_H \quad (4.4)$$

The hydrostatic stress is the average of all three normal stress components, and it causes a compression effect on the polymer. It is written as:

$$\sigma_H = \frac{1}{3} \sum_i^3 \sigma_{ii} = \frac{\sigma_{11} + \sigma_{22} + \sigma_{33}}{3} \quad (4.5)$$

The value of i ranges from 1 to 3 and corresponds to all three normal stress components. The analysis considered a plane stress condition $\sigma_{33} = 0$ i.e., the stress generated is unaffected by out-of-plane normal and shear components. The polymer chains are compressed for the applied hydrostatic pressure, restricting their mobility. As a result, the diffusion of H₂ molecules through the polymer becomes slower. Diffusion depends on various factors, including the specific polymer, its molecular structure, crystallinity, and the nature of the gas. The unique characteristics of the polymer, such as its structure, crystallinity, and interactions with H₂, might influence the complex relationship between V_H and compressibility. The simplified expression for V_H is written as Eqn. (4.6) [181]:

$$V_H = \left(\frac{\partial V}{\partial n}\right)_{T,p} = V_s \frac{\partial}{\partial C} \left(\frac{\Delta V}{V_0} + \beta_{T,p}\right) \quad (4.6)$$

where V is the volume of a polymer-gas system containing “ n ” moles of H₂, V_0 is the volume of penetrant free polymer at $p = 0$ and $C = 0$, V_s is the volume of an ideal gas at NTP, $\Delta V = V - V_0$ is the volume of penetrant inside the polymer, $\beta_{T,p} = -\frac{\partial}{\partial p}(\ln(V))_{T,n}$; compressibility of the H₂ containing polymer. Fick's second law is obtained from Fick's first law of diffusion. The mass conservation equation is written as:

$$\frac{\partial}{\partial t} \int_V (C) dV + \int_S J \cdot n dS = 0 \quad (4.7)$$

Applying the divergence theorem, the final implementation of the H₂ transport model results:

$$\frac{\partial C}{\partial t} - \nabla \cdot (D_{eq} \nabla C) - \nabla \cdot \left(\frac{D_{eq} C V_H}{RT} \nabla \sigma_H \right) = 0 \quad (4.8)$$

The H₂ transport governing equation model is abbreviated as Eqn. (4.8). The FE formulation for this HTM is given in Appendix I, A.1. Abaqus FE software uses mass diffusion to solve equations but doesn't currently support diffusion-stress-based coupled analysis for polymeric materials. The software explores diffusion-stress analysis based on an analogy between heat transfer and diffusion equations. For the specific form of coupled

governing equation for the H_2 in polymer, user-defined material, and variables have to be implemented using UMATHT subroutines to define coupled field variables. These field variables are calculated by the URDFIL and UVARM subroutines and shared with the UMATHT using common blocks. The auxiliary UEXTERNALDB subroutine allows for reading external files and initializing some variables used during the calculations. The internal H_2 pressure is applied to the internal polymeric surface of the COPV model.

4.2.3 Henry's law for polymer- H_2 interaction and time-lag method for transport properties estimation

There is no dissociation of H_2 molecules on the surface of the polymer during the polymer- H_2 interaction and the molecular interaction takes place at a given p , and C , as shown in Fig. 4.4.

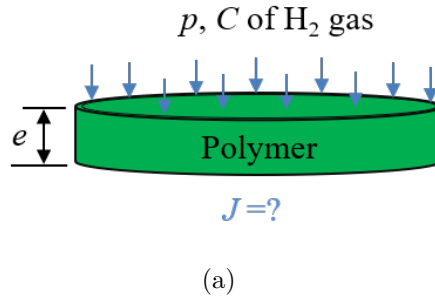


Figure 4.4: H_2 interaction with polymeric coupon sample.

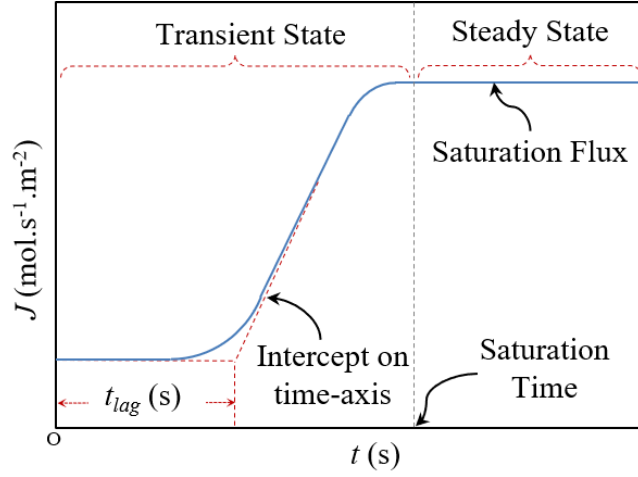
The molecular interaction model takes care of the H_2 intake in the liner material using Henry's law for polymer-gas interaction, given as (Eqn. (4.9)):

$$C = S.p \quad (4.9)$$

where solubility S is the capacity of the liner material to accept solute H_2 molecules per unit volume per unit pressure. The schematic plot of J across the polymer sample with respect to time is shown in Fig. 4.5. The initial curve represents the unsaturated/transient state of the H_2 molecule inside the polymer and after the material becomes fully saturated with H_2 , it shows a steady state represented by a horizontal flat curve. The e (m) is the thickness of the sample, and t (s) is the time. The permeability P_e ($\text{mol.m.Pa}^{-1}.\text{m}^{-2}.\text{s}^{-1}$) is the rate at which gas molecules permeate through the polymer material per unit pressure per unit area for a given thickness. It is estimated using the saturation J value multiplied by sample thickness wrt pressure, as written in Eqn. (4.10):

$$P_e = \frac{J.e}{p} \quad (4.10)$$

The time lag method was used to estimate the transport properties corresponding to the saturation J reached at saturation time, t_{sat} [182]. It is the time at which the gas molecule starts reaching out of the polymer sample to permeate sideways from the feed side. It



(a)

Figure 4.5: H_2 flux vs. time plot for permeation testing by the time-lag method.

includes adsorption, diffusion, and the path followed by H_2 molecules to reach out of the polymer sample or on the permeate side surface of the sample. At saturation state (t_{sat} , J), the J value will be maximum and the change in J value is negligible (the maximum J variation is less than 1%). Most commonly, the diffusivity values are estimated using the time-lag method, corresponding to the J vs. time plot. The value of the intercept on the time axis is called time lag, t_{lag} , and estimated using Eqn. (4.11) [183]:

$$t_{lag} = \frac{e^2}{6D_{eq}} \quad (4.11)$$

The accuracy of this method has been described by analytical and FE Abaqus-based software results for J vs time [184, 185, 186]. The time lag is the characteristic time that depends on D_{eq} , e , and the inflection point [182]. There are various time lag models available for permeation analysis, as described by the Taylor series, the singular point method, the tangent method extrapolated on the time axis, and the precise equation described by the sigmoidal plot. The singular points are considered at the 0.63 times saturation J value [187]. The solubility change for H_2 molecules inside the polymer was evaluated using the relation between the P_e , D_{eq} , and S as expressed in (4.12) [177]:

$$Pe = D_{eq} \cdot S \quad (4.12)$$

4.2.4 Effect of concentration and pressure on diffusivity

The diffusivity is the capacity of the material to let gas flow through it. It is almost constant at NTP. But for the transition and peak loading, the diffusivity properties change from material to material [188]. The diffusivity of the H_2 gas-polymer system depends on H_2 concentration inside the material as well as p and it is expressed as Eqn. (4.13) [16, 17]:

$$D_{eq}(C, p) = D_{sc} \exp(\beta_h p + \eta C) \quad (4.13)$$

where D_{sc} is the diffusion coefficient for semi-crystalline polymeric material at atmospheric pressure and with no invasive gas content, β_h is the pressure coefficient, and η is the concentration coefficient. If these two modes are independent of one another, the constant β can be written as $\beta = \beta_h + \eta.C$. This relation follows the straight line and “ β ” is evaluated from the slope. The term “ η ” and, correspondingly, “ $\exp(\eta C)$ ” denote an increase in the number of molecules dissolved in the polymer that results in the rise of plasticization [16, 17]. The term “ $\exp(\beta_h p)$ ” considers the contribution of the hydrostatic pressure only on diffusion. As per the kinetic theory of penetrating gases in the solid polymer in terms of the pressure coefficient is estimated by [189] $\beta_h = \frac{V^*}{RT}$, where V^* is the activation volume, R is the universal gas constant, and T is the room temperature or the temperature of the surroundings [178, 190]. The V^* parameter related to pressure coefficient affects yield and strain rate dependency of polymeric behavior in compression [191]. As a result, we can calculate β from the extrapolated value of slope $\frac{\ln(P_e)}{p}$, as shown in Fig. 4.6. The logarithmic permeability ($\ln(P_e)$) is calculated from the permeability coefficients at 10 to 90 MPa, taken from the paper by Fujiwara et al. [18].

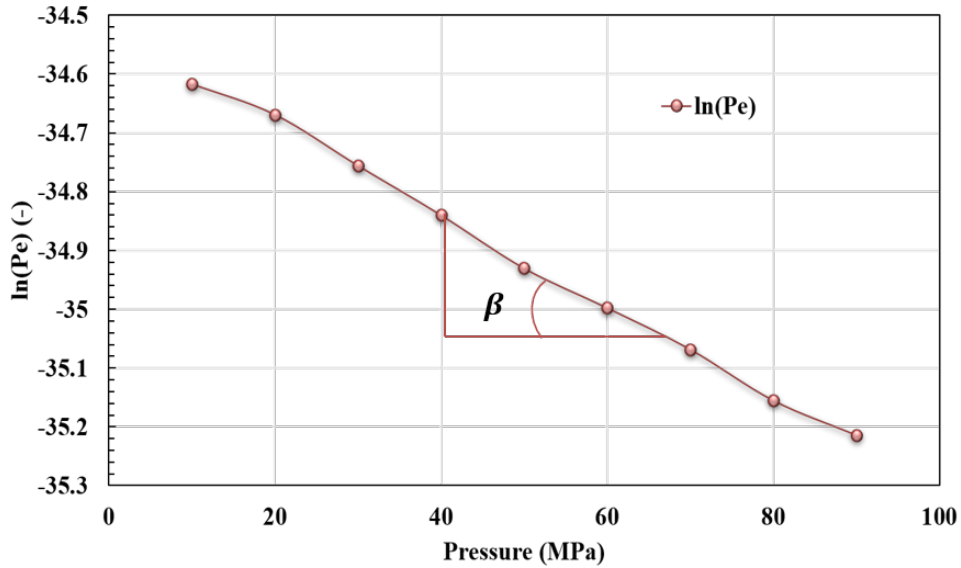


Figure 4.6: Diffusivity dependent on C and p w.r.t to its coefficient of semicrystalline polymer.

The slope of $\ln(P_e)$ and hydrostatic applied pressure is almost linear from 10 to 90 MPa. This represents the behavior of the given gases for the given polymer following Henry’s law. So, the variation of the slope is constant and nearly the same, with a value of $-8.0 \times 10^{-9} \text{ Pa}^{-1}$ for a given penetrating molecule in a given polymer material [17]. It was observed that an increase in applied pressure on the polymer resulted in a decrease in the permeability coefficient. Its increased compactness at high pressure results in a decrease in the FV and an increase in density [146]. The compression of the polymer

slows down the segmental motion, which in turn reduces the diffusion of H_2 through the polymer material. The morphology of semi-crystalline polymers is as shown in Fig. 4.7.

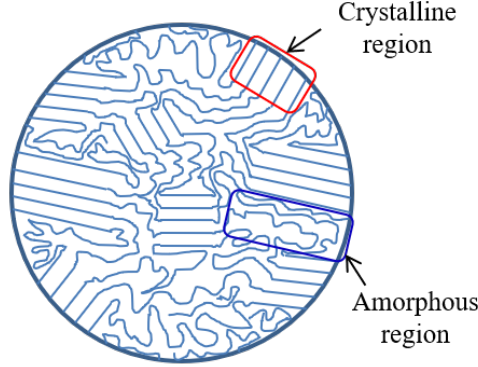


Figure 4.7: Morphology of semicrystalline polymer, consists of crystalline and amorphous region.

The p effect reverses the C effect. Segmental motion speeds up the mobility of H_2 entrance inside the polymer. Therefore, it is reasonable to assume that the molecular size of the penetrant will influence η and β_h . The few constants are estimated from the literature study of experiments (Exp.), but the literature is available for certain pressures only. The fitting of these parameters has been performed to evaluate the Exp. value due to very few published literature data available and few reports for the detailed study of high-pressure H_2 behavior inside the polymeric liner materials. Atmospheric temperature (T in K), partial molar volume (V_H in $\text{m}^3.\text{mol}^{-1}$), hydrostatic stress coefficient (β_h in Pa^{-1}), activation volume (V^* in m^3), universal gas constant (R in $\text{N.m.mol}^{-1}.\text{K}^{-1}$), diffusivity coefficient (D_{eq} in $\text{m}^2.\text{s}^{-1}$), and solubility (S in $\text{mol.m}^{-3}.\text{Pa}^{-1}$) parameters for the H_2 -polymer interaction material model at the minimum reference pressure of 10 MPa is provided in Table 5.4 [16, 17, 191].

Table 4.1: H_2 transport material properties of the polymeric liner material.

Para.	T	V_H	β_h	V^*	R	D_{eq}	S
Value	300	2.78×10^{-6}	4×10^{-8}	1.38×10^{-9}	8.314	1.35×10^{-10}	6.87×10^{-6}

4.2.5 Effect of crystallinity on diffusivity

In a polymer membrane, the Pe , D_{eq} , and S of gases often decrease with increasing crystallinity because they cannot diffuse and dissolve in the crystalline domain. As the degree of crystallinity increases, the permeability decreases [87, 161]. Due to a reduction in the volume percentage of the amorphous region, the polymer becomes more crystalline when compressed at high pressure, and it reverts to its initial condition when decompressed to low pressure [154]. Due to the shrinkage of the FV at high pressure, permeability

reduces with a drop in diffusivity [87]. The crystallinity ϕ_i of a semicrystalline polymer structure, as shown in Fig. 4.7, consists of amorphous and crystalline regions and is written as Eqn. (4.14) [177]:

$$\phi_i = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \quad (4.14)$$

where, ρ_c is crystalline phase density, ρ_a is amorphous phase density, ρ_s is semi-crystalline density. The crystallinity parameters are shown in Table 4.2 for HDPE polymer material [16, 165, 17]. Michaels and Bixler proposed a relationship between the overall diffusivity D_{eq} and the diffusivity function of operating parameters at NTP is D_o as shown in Eqn. (4.13) and (4.15) [192].

Table 4.2: HDPE crystallinity parameters require density, crystalline, and amorphous region.

Parameters	ρ_s	ρ_a	ρ_c	ϕ_i
Units	kg/m ³	kg/m ³	kg/m ³	%
Values	942	850	1000	52.62

The semi-crystalline diffusivity in terms of chain immobilization factor and tortuosity factor is expressed as (4.15) [193]:

$$D_{sc} = \frac{D_o}{\gamma\tau} = \frac{D_o}{2(1 + \tau_a\phi_i)} = \frac{D_o}{2(1 + 7.75\phi_i)} \quad (4.15)$$

where τ_a is a characteristic parameter and considered for the enhancement of diffusion path due to crystallinity, which is equal to 7.75, and δ is chain immobilization factor accounting for the amorphous part with $\gamma, \tau > 1$ [193, 194]. A tortuosity factor τ expresses how the penetrant molecules go around crystallites by using the amorphous component [195]. It is the measure of the maximum distance that a diffusing molecule must travel, and it is a function of the crystallinity ϕ_i [193]. For 1-D diffusion analysis, a 2-D rectangular model has been considered, in which the permeation has been allowed through the thickness direction. The crystallinity is the function of density and the density is related to volume. The volume consists of area multiplied by thickness, and the area remains the same in the analysis. Therefore, the final crystallinity of the semicrystalline polymer under high pressure directly affected by sample thickness can be expressed as Eqn. (4.16):

$$\phi_f = 100 - \left(\frac{FV_f}{FV_i} \phi_i \right) \quad (4.16)$$

where FV_i and FV_f are free volumes available in the polymer before and after pressurization, respectively.

4.3 FE Modelling Framework to Validate the Experimental Results

In this thesis work, FE simulation framework aims to study the H_2 permeation behavior of the polymeric liner material. The HDPE material was subjected to pure H_2 at a wide range of pressure and the other side was exposed to NTP, for a long duration to get saturated inside the polymer. After gas begins to diffuse from one end (feed side) to the other side (permeate side) through the sample thickness e , the rate of gas penetration reaches equilibrium, known as transmission rate or gas permeation rate. The polymer liners behavior under high pressure of H_2 inside Type IV COPVs for permeation has been analyzed. For this, HDPE material is a better choice among various liner materials studied (HDPE, LDPE, MDPE, LLDPE) in the literature [18], for the permeation behavior. The behavior of different polymer samples by Fujiwara et al. (2020) and (2021) [18, 88], under H_2 pressure up to 90 MPa with constant temperature conditions has been investigated. To validate the experimental results of available literature [18, 88], the present study aims to model the FEA framework and model validation. A transient coupled temperature displacement model is used for the analysis in Abaqus software. At first, H_2 permeation behavior through the HDPE polymer material was studied up to 90 MPa with the considerations of material properties (S , D_{eq} , ρ , ϕ) at given operational parameters (H_2 pressure and C) [82]. Secondly, a safer value within the permeation limit for optimal thickness was evaluated for the HDPE liner of Type IV COPV for p_{nwp} 70 MPa.

A 2-D rectangular cross-section is adopted as a representative volume element (RVE) of the polymeric liner material in a Type IV COPV to streamline the FE model. This approach focuses on capturing essential through-thickness diffusion and stress behavior while avoiding curvature-related geometric complexities. The following points justify the plane strain condition for this geometry:

1. Physical representation of a long cylinder wall:

This condition matches the physical scenario of a long cylindrical vessel wall or a coupon cut from its midsection, where the middle region does not deform longitudinally but only in-plane (radial and circumferential directions). The RVE represents a small segment of the liner wall or a coupon extracted from a cylindrical vessel's midsection. In such cases, hydrostatic compression generates dominant in-plane stresses, while axial deformation remains negligible key feature replicated by the plane strain model.

2. Constrained deformation along length:

The ends in the length (z) direction are assumed to be constrained, resulting in negligible out-of-plane strain ($\epsilon_{zz} = 0$, $\epsilon_{xz} = 0$, $\epsilon_{yz} = 0$). Aligning with the plane strain assumption. This restriction mirrors the behavior of a long cylindrical vessel, where midsection deformation occurs only in-plane, causing strains (radial ϵ_{yy} and

circumferential ϵ_{xx}).

3. Focus on in-plane stress and diffusion coupling:

By eliminating out-of-plane strain effects, the model captures the dominant in-plane stresses (radial σ_{yy} and circumferential σ_{xx}) and their effect on diffusion. This is particularly important for studying hydrostatic compression and the resulting through-thickness stress gradient in the liner material.

4. Simplified geometry with high aspect ratio:

The cross-section length ($d = 16$ mm) significantly exceeds the thickness ($e = 1.5$ mm), yielding an aspect ratio $d/e > 10$. This minimizes edge effects and prioritizes analysis of radial (through-thickness) diffusion and stress gradients [196].

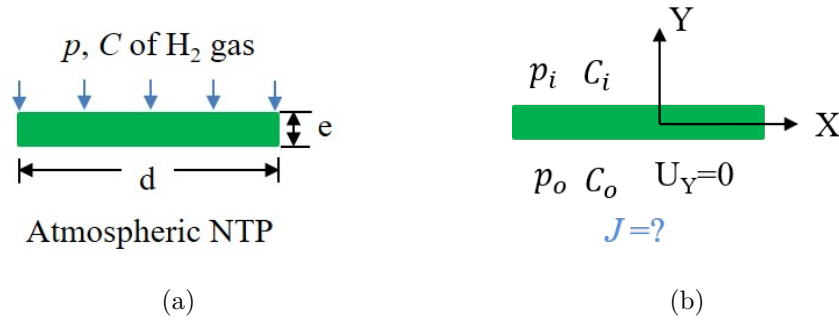


Figure 4.8: Schematic representation of rectangular coupon sample (a) geometric parameters and physical loading condition, and (b) cartesian coordinate system with boundary condition.

Load and boundary conditions applied for H_2 permeation simulations through polymeric liner samples are shown in Fig. 4.8(a) and Fig. 4.8(b). It was assumed that the diffusion through the 2-D RVE model is only in the radial direction, i.e., across the wall thickness. The diffusion through polymer is considered 1-D, i.e., unaffected by length of the sample. The applied C and p as loaded on the feed side remain constant. The assumptions considered in the FE model development are summarized:

1. A 3-D geometry is considered as a 2-D RVE model for 1-D diffusion;
2. A simple sorption model (Henry's law) is considered for H_2 interaction with polymer;
3. The diffusion across the edges of a 2-D sample is very low or negligible;
4. CFRP restricts the displacement across the radial/thickness direction;
5. Applied concentration on feed side remains constant.

The thickness is negligibly small compared to the length of the sample; therefore, the J at the side edges of the polymer sample is considered to be negligible. The zero displacement boundary condition (across the radial/thickness direction, i.e. $U_Y=0$) is provided on the polymer sample of the permeate side. The J variation with time to H_2 saturation is

evaluated using an extended diffusion model on the test coupon sample. The initial C inside the test sample material is zero. In the present FE analysis, H₂ captures boundary nodes at the surface of the test sample. The difference in C of H₂, i.e., $C_O - C_t$, is caused by diffusion from one node to the next. The time increment directly affects the accuracy of results; the time starts from 0 sec to a time of 3 weeks (near 500 hours) and is chosen at a time-step Δt of 60 sec.

The selection of non-metallic polymeric liner materials is standardized by ISO 11114-5 based on H₂ compatibility. The Ogden material model is selected for the hyperelastic polymeric liner. Generalized, Ogden's strain density energy function is written as [22]:

$$W(\lambda_1, \lambda_2, \lambda_3) = \sum_{p=1}^N (\mu_p / \omega_p) (\lambda_1^{\omega_p} + \lambda_2^{\omega_p} + \lambda_3^{\omega_p} - 3) \quad (4.17)$$

where μ_p is the constant shear moduli, ω_p is the dimensionless constant, λ_i is the principal stretches, and N is the number of terms. Material parameters $\mu_1 = 51.125$ MPa, $\omega_1 = 3.55$. The HDPE exhibits linear elastic behavior up to the yield point, and its yield strength is 24.1 MPa [88]. It shows a similar yield strength in tension and compression within the elastic range due to its thermoplastic nature.

A 4-node plane strain thermally coupled quadrilateral, temperature-displacement element CPE4T type, was chosen for the mesh for a 2-D cross-section liner material in the FE model. A linear element type was selected to minimize the computational time. In the mesh-independent study, the output does not change significantly for the 0.1 mm element size. FEA was done with the following mesh and element specifications, as shown in Table 4.3.

Table 4.3: FE mesh and element type specifications.

FE mesh model	Element type	Number of element	Number of node
2-D rectangular	CPE4T	280035	278005

4.4 Result and Discussion

The HDPE sample has been tested at various pressures for a set amount of time to reach saturation state, and the amount of H₂ that permeates through the material is then measured by saturated J . Finally, the model is used to determine whether the liner's steady-state leakage rate may reach the permeation limit by estimating the thickness. After modeling and simulating this, the H₂ transport properties are evaluated using the time-lag method.

The contour plot for H₂ concentration variation along the thickness of the test coupon sample driven by C and p at the inner surface (feed side) due to polymer-gas interaction

after a long time is shown in Fig. 4.9(a). The H_2 concentration (Conc) are 140, 284, 403, 519, 660, 787, 867, 999, and 1110 mol.m^{-3} corresponding to applied gaseous pressures of 10, 20, 30, 40, 50, 60, 70, 80, and 90 MPa as shown in Fig. 4.9 (b), (c), (d), (e), (f), (g), (h), (i) and (j) respectively. At the initial time stage, the H_2 diffusion is very slow, and after some hours H_2 starts diffusing through the barrier and goes into a saturation state. The contour for J inside the polymer is shown in Fig. 4.10. The C of H_2 corresponds to times of 6.63, 8.13, 10, 11.66, 13.03, 13.46, 14.31, 14.85, 15.5, 15.91, 16.66, 17.63, 18.26, 19.01, 20.3 minutes (min) and more than a week, as shown in Fig. 4.10 (i), (ii), (iii), (iv), (v), (vi), (vii), (viii), (ix), (x), (xi), (xii), (xiii), (xiv), (xv), and (xvi) respectively. The arrow ($\rightarrow$) represents the direction of movement of H_2 . The contour will look similar for all p , and the corresponding C values will differ.

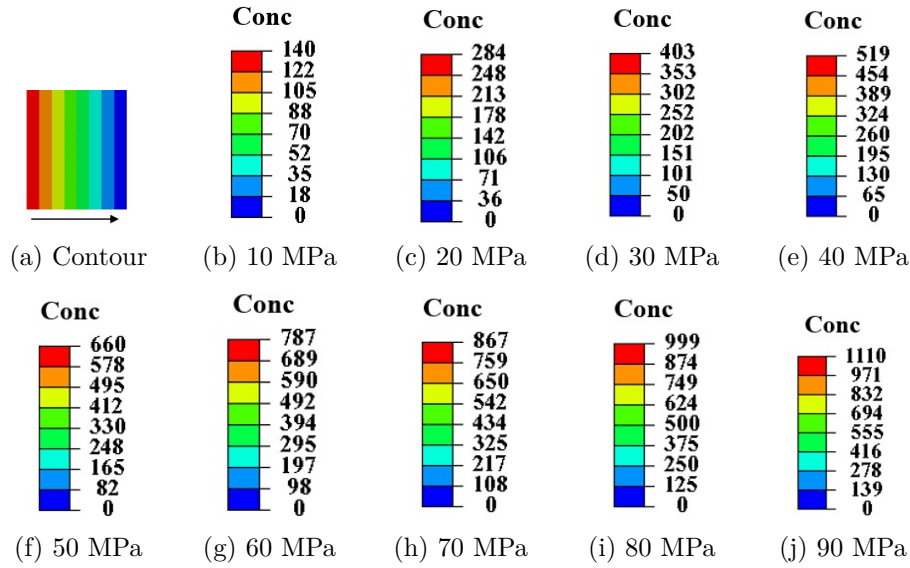


Figure 4.9: Contour for C of H_2 across the thickness of the sample, corresponding to an increase in pressure 10, 20, 30, 40, 50, 60, 70, 80, and 90 MPa.

The C of H_2 inside the polymer increases with time, and after several hours it reaches a saturation state, which means the J becomes constant with time, which is visible in Fig. 4.11 (a). This steady state J , after several hours, remains constant and is known as saturation J inside the sample. The zoomed view of an unsaturated region is shown in Fig. 4.11 (b), and the J rate increases with an increase in p and corresponding C value in the unsaturated region. An unsaturated state is also known as a transient state, in which the J changes with time. The zoomed region shows the unsaturated J , and after the 2.5×10^5 sec, the horizontal line signifies the constant J , showing the saturation of J inside the polymeric liner material. With the increase in applied pressure from 10, 20, 30, 40, 50, 60, 70, 80, and 90 MPa, the corresponding J values are 6.16×10^{-6} , 1.16×10^{-5} , 1.61×10^{-5} , 1.98×10^{-5} , 2.25×10^{-5} , 2.52×10^{-5} , 2.74×10^{-5} , 2.87×10^{-5} , and 2.96×10^{-5} $\text{mol.m}^{-2}.\text{s}^{-1}$, respectively. Using the saturation J value corresponding to the pressure applied and the thickness of the sample, the H_2 permeability was evaluated using Eqn. (4.10).

The pressure is increased from 10 MPa to 30 MPa, and the J profile and saturation time

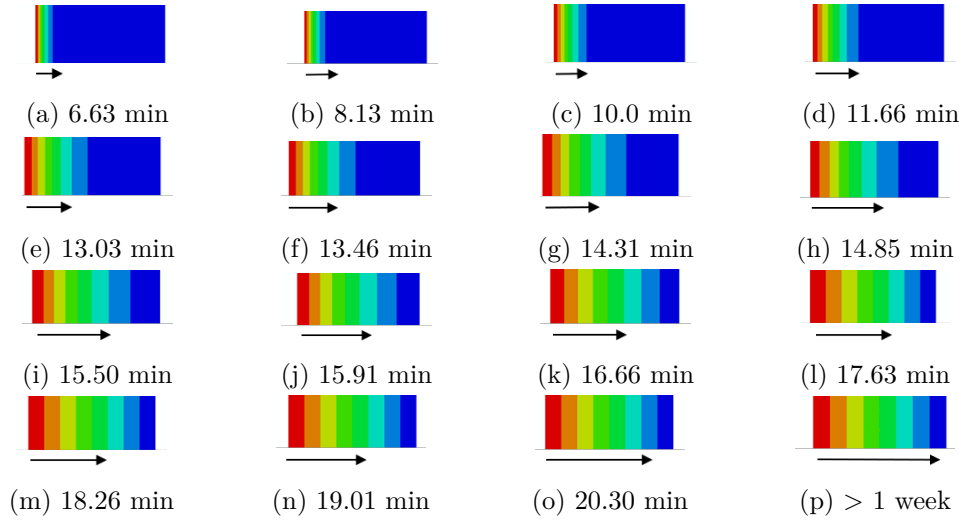


Figure 4.10: H_2 flux contour across the thickness of the sample with increases in pressure with time at 10 MPa.

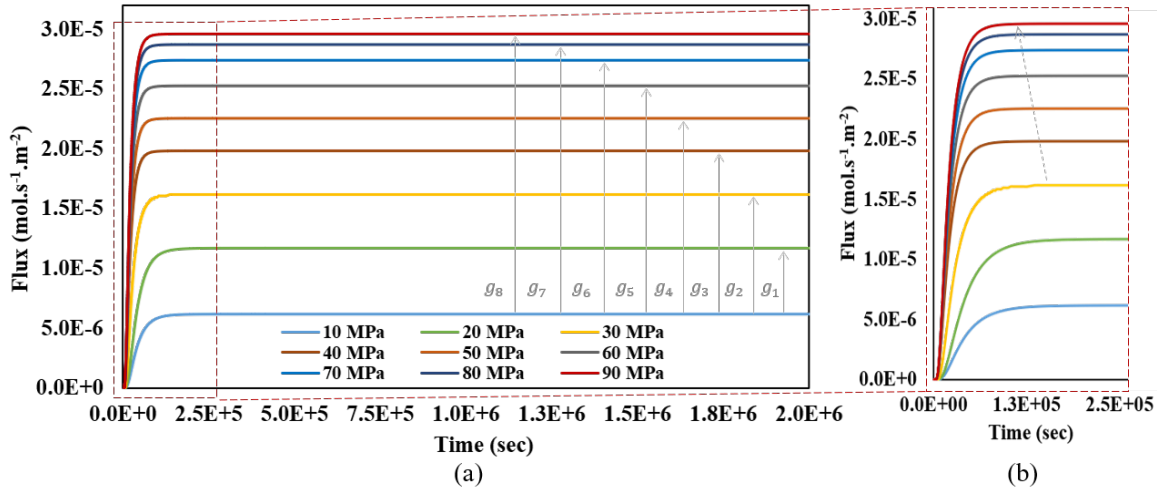


Figure 4.11: Contour for H_2 flux for various pressures (a) till saturation reached and (b) the unsteady state in zoomed view.

also increase. At 30 MPa, there is non-uniformity (shown in Fig. 4.11(b)) due to exceeding the HDPE yield strength of 24.1 MPa. It is observed that it affects the distribution of H_2 in the polymer but does not affect the saturation J value. The H_2 that occupies the amorphous region now starts to feel more compression due to an increase in applied p . This causes the fast flow of H_2 and the rate of J to increase with pressure, corresponding to the increase in pressure at and above 30 MPa. More H_2 on the feed of the polymer causes a higher rate of polymer-gas interaction, and diffusion will be faster. This shows the reduction in saturation time with an increase in J value (as shown in Fig. 4.11(b) by the left inclined arrow). The difference in saturation J value corresponding to the next-to-previous applied pressure is decreasing. The saturation J increased, corresponding to an increase in pressure (shown by an upward arrow “ $\uparrow$ ” in Fig. 4.11 (a)) as compared to an initial applied pressure of 10 MPa. The difference in the saturation J value is

0.55×10^{-5} , 1.0×10^{-5} , 1.36×10^{-5} , 1.63×10^{-5} , 1.91×10^{-5} , 2.12×10^{-5} , 2.25×10^{-5} , and 2.34×10^{-5} $\text{mol.m}^{-2}.\text{s}^{-1}$ (for the gap $g_7 > g_6 > g_5 > g_4 > g_3 > g_2 > g_1$) corresponding to an increase in applied pressure of 20, 30, 40, 50, 60, 70, 80 and 90 MPa, respectively, to the reference J value of 6.16×10^{-5} $\text{mol.m}^{-2}.\text{s}^{-1}$ for 10 MPa. The relative changes are 0.89, 1.62, 2.47, 2.65, 3.46, 3.84, 4.08, and 4.24, corresponding to the applied pressure 20, 30, 40, 50, 60, 70, 80, and 90 MPa, respectively, to the reference pressure of 10 MPa. Fig. 4.12 shows the variation of permeability of HDPE material with the applied pressure at a constant temperature. The model was able to fit the points of the FEA and the Exp. values that are reproduced from the Fujiwara et al. 2020, and 2021 papers. The dependence of permeability with applied pressure can be easily understood using the expressions shown in Eqn. (4.10).

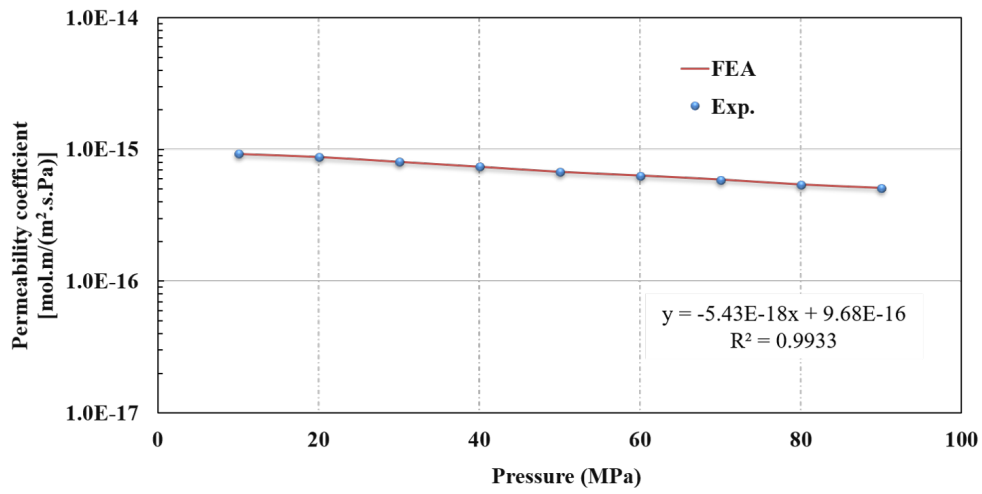


Figure 4.12: Permeability variation with an increase in H_2 pressure for HDPE.

It was observed that the permeability decreased with an increase in pressure due to an increase in the crystallinity of HDPE. The polymer chains get compact due to the increase in density due to decrease in thickness, which means there is a reduction in the FV , increasing crystallinity. The diffusivity value was evaluated using Eqn. (4.11) for a given sample thickness and time-lag value utilizing the J plot as shown in Fig. 4.11 (corresponding to an intercept on the time-axis as shown in Fig. 4.5(b)). The diffusivity variation with the applied pressure is shown in the Fig. 4.13. The solubility was evaluated using the relation between P_e , and S using the Eqn. (4.12). The variation of the solubility coefficient with an increase in pressure for HDPE is shown in Fig. 4.14.

The permeability coefficient was observed to be an important parameter for H_2 permeation study through the polymer. Since it is directly related to saturated J value, the J value can capture the C , p , e , and ϕ (Eqn. (4.10), (4.2), and (4.13)). The diffusivity coefficient is evaluated using the unsaturated J plot and time-lag method (as shown in Eqn. (4.11)), which is an approximate type of analysis and therefore the diffusivity coefficient is less important as compared to the permeability coefficient. The solubility is independent

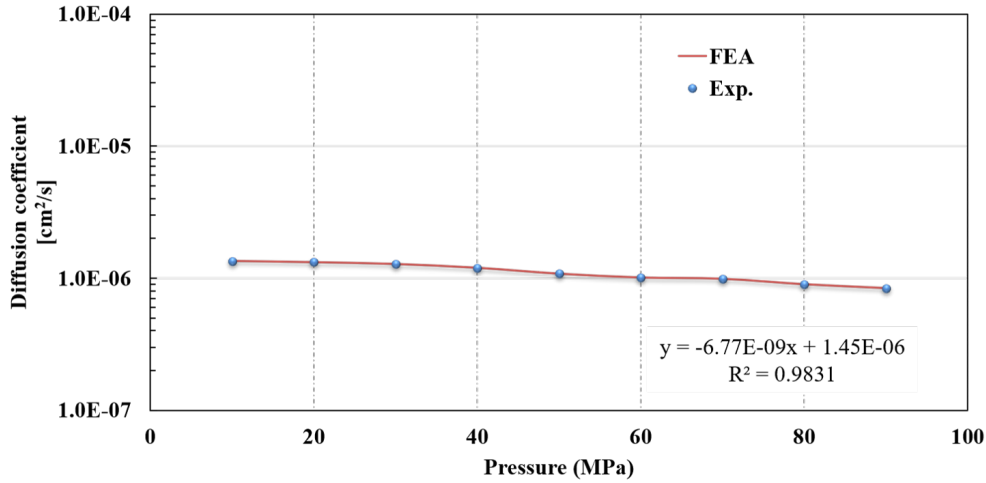


Figure 4.13: Diffusivity variation with pressure for HDPE polymer sample.

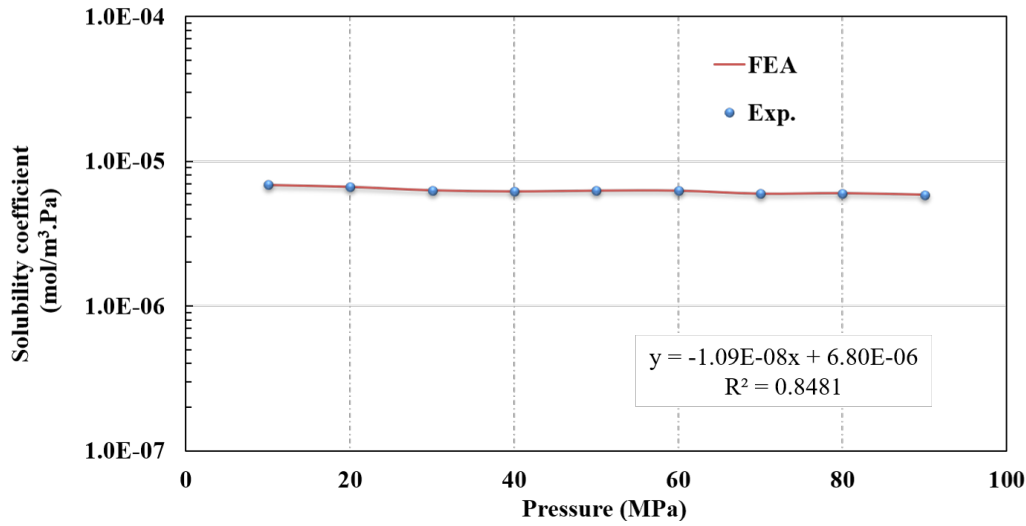


Figure 4.14: Solubility coefficient variation with pressure for HDPE polymer sample.

of J (either saturated or unsaturated), C , p , and ϕ parameters, and it is a function of permeability and diffusivity coefficients only. In general, solubility is the material property and it is nearly constant. In this case, the solubility variation is very low and almost constant, but the solubility decreases with an increase in pressure. This signifies that at extremely high pressure, a minimal alteration in the properties of HDPE material will impede the solubility of H_2 . So, solubility is the least essential parameter to consider for the H_2 permeation analysis through the polymer material (and can be easily understood by Eqn. (4.12)) and it was observed that it gives less accuracy.

Fig. 4.15 shows the variation of crystallinity with pressure. The hyperelastic nature of HDPE thermoplastic polymer shows a non-linear type of reduction of thickness with an increase in applied pressure. The reduction in free volume after pressurization, and the increase in crystallinity have been observed. This corresponding increase in pressure on the sample results in a decrease in sample thickness and an increase in crystallinity (evaluated using Eqn. (4.16)) from the initial crystallinity value of 52.62%.

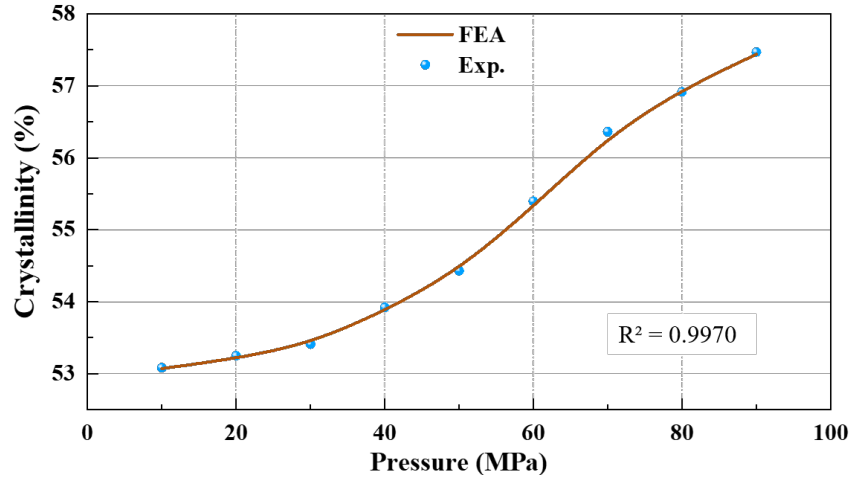


Figure 4.15: Variation of pressure affecting the crystallinity of polymer sample..

The actual thickness of the sample at atmospheric pressure is 1.5 mm, and it decreases to 1.34, 1.33, 1.32, 1.31, 1.29, 1.27, 1.24, 1.22, and 1.21 mm corresponding to an increase in pressure 10, 20, 30, 40, 50, 60, 70, 80, and 90 MPa respectively. This is due to the semi-crystalline nature and free volume available inside the polymer sample. The decrease in thickness of polymeric liner material is allowable due to H_2 gas pressure, as per ISO 11114-5. The Exp. output (P_e , D , and S) values are available for all the pressures, but crystallinity values are available with an interval of 20 MPa. Therefore, crystallinity values at the other pressure are taken by averaging the previous to the next value and only two decimal places are considered.

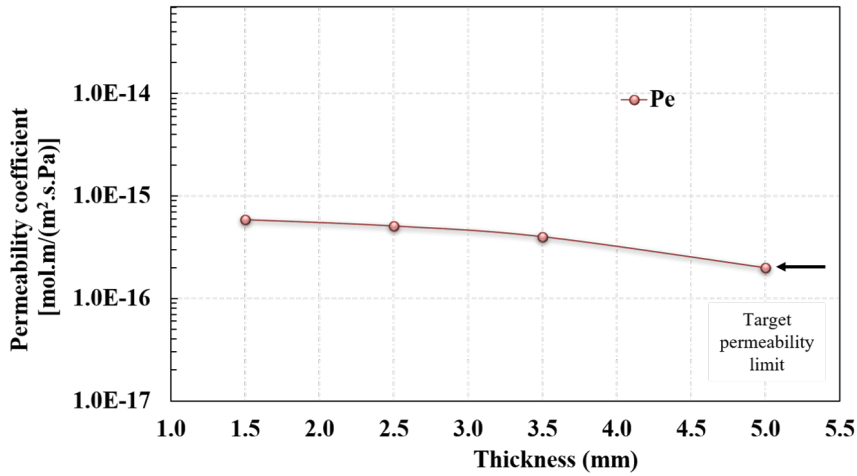
The FEA values are considered for two decimal places for most of the parameters that are not directly or significantly affected. The FEA analysis was performed, and the results were compared with the Exp. data reported in the published paper of Fujiwara et al. 2020, 2021. The H_2 transport parameters (Para.) at the various applied pressures for HDPE material for Exp. and FE simulation specifications are shown in Table 4.4. The unit used for pressure (p) is MPa, permeability (P_e) is $\text{mol.m.Pa}^{-1}.\text{m}^{-2}.\text{s}^{-1}$, diffusivity (D) is $\text{cm}^2.\text{s}^{-1}$, solubility (S) is $\text{mol.Pa}^{-1}.\text{m}^{-3}$ and crystallinity (ϕ) is %. The difference between the Exp. and FEA for permeability, diffusivity, solubility, and degree of crystallinity is nearly 0.01 for each pressure and the error is less than 1 %. In the r-square (r^2) regression fit value lies between 0 and 1 [186]. Using the linear fit, the r^2 values for permeability, diffusivity, and solubility, are 0.9933, 0.9831, and 0.8481 respectively. For the crystallinity variation, the r^2 value is 0.9970 using the nonlinear regression fit with a logistic function. This shows that the regression value is closer to 1, which shows linear variation. The developed permeation FEA model matches the results of Exp. with accuracy.

The current thickness of the HDPE sample is 1.5 mm and has been analyzed for H_2 transport behavior up to 90 MPa, but this thickness is not sufficient to satisfy the criteria of a permeation barrier for 70 MPa p_{nwp} Type IV COPVs. So, to satisfy the safety criteria

Table 4.4: Experimental data and FEA simulation study parameters for the various pressures.

Para.	$P_e (\times 10^{-16})$		$D (\times 10^{-6})$		$S (\times 10^{-6})$		$\phi (\%)$	
p	Exp.	FEA	Exp.	FEA	Exp.	FEA	Exp.	FEA
10	9.25	9.24	1.35	1.34	6.87	6.89	53.08	53.07
20	8.78	8.76	1.31	1.33	6.65	6.58	53.24	53.21
30	8.05	8.08	1.28	1.27	6.28	6.36	53.41	53.42
40	7.40	7.43	1.20	1.19	6.17	6.24	53.92	53.87
50	6.76	6.76	1.08	1.09	6.25	6.20	54.43	54.44
60	6.32	6.31	1.01	1.02	6.25	6.18	55.39	55.32
70	5.88	5.87	0.99	0.95	5.96	6.17	56.36	56.30
80	5.40	5.38	0.90	0.91	6.0	5.91	56.91	56.95
90	5.08	4.98	0.84	0.83	5.57	5.53	57.47	57.44

of H₂ permeation barrier limit as per DoE USA targets, there is a need for more thickness of the sample. Therefore, by keeping all parameters, thickness of the polymeric liner material is increased. The increase in thickness variation as 1.5 mm, 3 mm, and 5 mm results in a reduction of permeability values as 5.87×10^{-16} , 4.60×10^{-16} , and 1.97×10^{-16} mol.m.Pa⁻¹.m⁻².s⁻¹ respectively as shown in Fig. 4.16.

Figure 4.16: Permeability coefficient variation with thickness at p_{nwp} of 70 MPa.

The permeability values decreased with the increase in thickness due to more time taken by the H₂ molecule to reach to permeate side of the polymer sample. The compression effect at 70 MPa of applied pressure, the density increases due to the compactness of the polymer. The effective diffusivity coefficient with a variation of sample thickness is shown in Fig. 4.17. It is observed that the increase in the thickness of the polymer sample resulted in a sufficient, significant reduction in permeability and diffusion coefficient. The 5 mm thickness of HDPE finds a suitable material for the liner to build a 70 MPa Type IV COPV material. The maximum value of thickness is recommended up to 6 mm and the permeation test coupon sample should be of the same thickness of liner as per ISO 11114-5 to resist the H₂ permeation through the polymeric liner material.

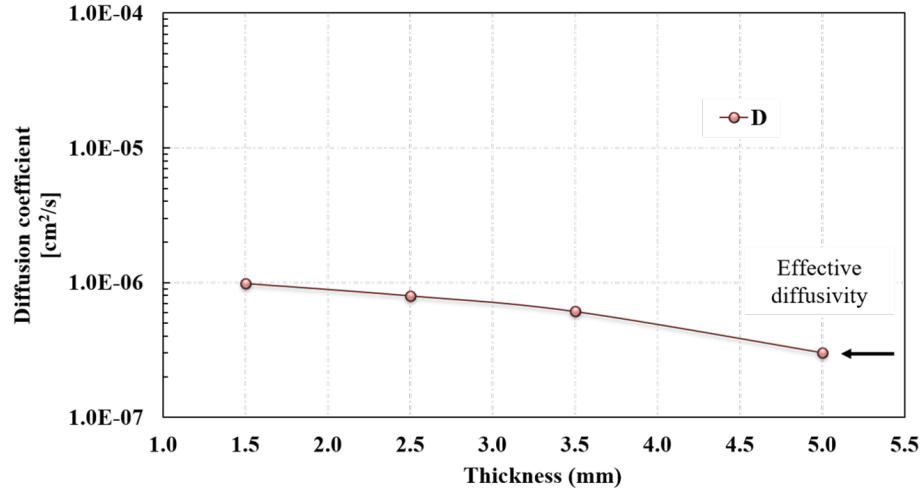


Figure 4.17: Diffusivity coefficient variation with thickness of the sample, at p_{nwp} of 70 MPa.

4.5 Conclusion

The developed HTM is utilized in the FE simulation framework with the consideration of gradient of C and p -driven H_2 diffusion at a constant temperature. The variation in diffusion coefficient was implemented in the model based on the operating conditions and the morphology of the polymer material for H_2 storage at 70 MPa p_{nwp} in Type IV COPV. The material properties and structural characteristics were implemented from the experimental data of Fujiwara et al. 2020, 2021, which showed a good H_2 permeation barrier performance for HDPE. It was observed that permeability decreases with an increase in pressure from 10 to 90 MPa for a given thickness of 1.5 mm for the polymeric liner material. The permeability shows a linear variation for an increase in pressure, with an accuracy of 99.33% for linear fitting. The model also captured the variation of crystallinity with an increase in pressure due to the reduction in the free volume present in the HDPE material due to compression at high pressure. The results of Exp. data validated by the developed FE analysis model and the percentage error was less than 1%. The permeability for 1.5 mm thickness is $5.87 \times 10^{-16} \text{ mol.m.Pa}^{-1}.\text{m}^{-2}.\text{s}^{-1}$ at 70 MPa of applied pressure and the required permeability value as per the DoE target for the 70 p_{nwp} for Type IV COPV material is $3.32 \times 10^{-16} \text{ mol.m.Pa}^{-1}.\text{m}^{-2}.\text{s}^{-1}$ (0.05 (g/hr)/kg). Therefore, the thickness variation was performed for 70 MPa p_{nwp} by keeping all the parameters that show the permeability limit within a safer limit, which is $1.97 \times 10^{-16} \text{ mol.m.Pa}^{-1}.\text{m}^{-2}.\text{s}^{-1}$ for the optimal thickness of 5 mm for polymeric liner material. The H_2 takes a longer time to diffuse and to cross the higher thickness, which achieves the desired limit. So, the developed model gives a FE framework to simulate H_2 transport behavior to understand the H_2 -polymer interaction mechanism for the selection of suitable liner material from the commercially available or newly developed material grade for Type IV COPV storage material.

Chapter 5

Role of Micro-Defects on Blistering Behavior in 70 MPa Type IV COPV due to H₂ Permeation

5.1 Introduction

H₂ storage poses a challenge due to its very small molecular size, allowing it to permeate through most materials easily and degrade their properties at critical operations [2, 92, 197]. Polymeric liner material provides exceptional H₂ leak prevention potential for 70 MPa Type IV COPVs [155]. During the manufacturing of polymeric liners using rotational molding, approximately 40% of the processing time is dedicated to removing macro- and micro-defects (air bubbles, voids, cavity, pore, and inclusions). There are air particles trapped in the melted polymer when the powdered polymer melts. To eliminate such defects, the mold is rotated biaxially, densification is performed, and curing is achieved by maintaining the mold at an elevated temperature [118, 198]. Large defects require more time to remove, limiting the range of plastic materials used in rotational molding [199, 200]. Still, the micro-defects remain in the polymeric liner material. The other manufacturing processes (blow molding, extrusion, injection) also consist of micro-defects that influence barrier performance and concern for safety at high pressure in Type IV COPVs [201]. In addition, studies have demonstrated that H₂ diffusion primarily occurs within the *FV* by hopping mechanism [202], which can be likened to the small holes between the polymer molecular chains [203, 177]. Due to manufacturing defects and a high cyclic loading rate, the polymeric liners experience stress, which may cumulatively reduce their durability and increase their susceptibility to micro-cracking.

Therefore, after p_b qualification and ensuring that the H₂ permeability is within the limit at p_{nwp} for the optimal thickness of liner material, the defilling test needs to be performed to check the effect of decompression to ensure the safety of Type IV COPV. High-pressure H₂ molecules can accumulate through the diffusion process, generating internal stresses in polymer liners and causing microscopic cavitation and macroscopic buckling. Pre-existing cavities contribute to liner-composite interface failures, such as debonding. Parametric analysis was performed for depressurization-induced blistering for liner materials (HDPE and PA) having thicknesses of 1, 2, 3, and 4 mm for the defilling rates of 1, 3, 5, and 13 hrs. 1 mm thickness showed an optimum value for all defilling rates to avoid blistering, but the

liner thickness requirement is more [20, 81]. The depressurization was performed at 0.004 to 5 MPa/min after 1 week saturation period from a pressure of 35 MPa to 17.5 MPa to analyze the blister formation at the liner-composite interface [2]. Depressurization rates ranging from 0.007 MPa/min to 0.7 MPa/min were investigated for a Type IV COPV with a polymeric liner thickness-to-external diameter ratio of 0.019 [2]. The volumetric capacity could be increased by reducing the empty p from 2 MPa to 0.3 MPa [169]. Depressurizing from p_{max} to ambient p_{min} can cause failures, which can result in crack initiation, growth, component failure, and full breakage. Controlling transport properties is crucial for preventing blister fractures and other types of H₂-induced damage, such as aging due to swelling, liner collapse, and more (as shown in Fig. 1.3) [19, 87]. Polymeric liners can be post-processed directly or indirectly to enhance their H₂ leak prevention capabilities, like fluorination (by surface mechanism) due to non-polar behavior of H₂ relative to HDPE material and others [204]. However, no specific standard is currently available for defect detection present inside the liner material and its role during H₂ permeation [155]. Therefore, it is essential to investigate the effect of H₂ permeation on the micro-defects, inclusion size, and location for the dynamic loading.

The regulations and codes that are currently in place for the design and testing of Type IV COPVs for H₂ storage do not specifically address the impact of micro-defects on H₂ permeation following polymeric lining manufacturing (ISO 11119-3). In the reported research work, the limitations of the earlier approach ignored the effect of the C and p gradient simultaneously that influence the H₂ transport properties during operations [84]. Therefore, in this thesis work, the improvement in liner technology utilized a developed HTM material model to investigate H₂ accumulation and the stress generated inside the defect. Utilizing the FE Abaqus tool, H₂ diffusion through Type IV COPV's RVE has been examined in this regard, taking into account complex nonlinear diffusion made up of the governing equations of Henry's law, Fick's second law, transient diffusion, and a hyperelastic behavior of liner material [176, 205].

5.2 Mathematical Model Used for the Analysis

Given the importance of polymeric liners towards the operational requirements of Type IV COPV, the role of pre-existing micro-defects present inside the polymeric liner and at the interface of polymer-composite on the failure behavior of Type IV COPV for a given H₂ filling cycle is simulated using FE simulation in this part of the thesis.

To simulate H₂ diffusion through a polymer at critical C and p , a well-defined mathematical model was developed in Chapter 4 and utilized in Chapter 5. The subroutine UMATHT can correlate our mathematical modeling with the variables of H₂ diffusion through the Abaqus interface.

5.2.1 Effect of hydrogen concentration on pressure buildup inside the defect

The H₂ accumulated inside the defect increases the p , generating stress. The stress (σ_c) and strain (ϵ_c) as a function of C of H₂ are expressed as [83]:

$$\sigma_c = E\epsilon_c \quad (5.1)$$

$$\epsilon_c = \zeta\Delta C \quad (5.2)$$

where ζ is the coefficient of C expansion and ΔC is the change in C inside the material.

5.2.2 Effect of pore pressure inside the defect

The safety and reliability of Type IV COPVs are crucial due to the occurrence of decompression damage and are influenced by the operating parameters. The p of H₂ in pre-existing defects may lead to the initiation and propagation of cracks. The effect of the decompression rate on preexisting defects that cause the development of p inside the defect is expressed as [20]:

$$p_{d,D} = \frac{C_i}{S} - p_i \quad (5.3)$$

where $p_{d,D}$ is p inside the defect, S is solubility of the liner material, and C_i is applied concentration. When the $p_{d,Y}$ exceeds $\frac{2}{3}\sigma_y$, blistering happens, and the relation is expressed as [85]:

$$p_{d,Y} = \frac{2}{3}\sigma_y \quad (5.4)$$

where σ_y is the yield strength of the polymeric liner material.

5.3 FE Modeling Framework

The presence of defects in polymeric liner material and liner-composite interface causes early failures due to the phenomenon of pressurization-depressurization. In this thesis work, a FE simulation framework aims to study the role of defects in the failure behavior of 70 MPa Type IV COPVs. A computational model for H₂ transport in COPV materials is implemented in Abaqus using UMATHT to model their failure behavior. The polymeric liner was subjected to direct contact with H₂ and the other side of RVE of Type IV COPV has been exposed to NTP, for a long duration to get H₂ saturation inside the polymer. After H₂ begins to diffuse through the sample from one end to the other, its penetration rate reaches equilibrium, known as the transmission rate or permeation rate, which is measured over the saturation time. The appropriate material properties, loads, and boundary conditions are defined to analyze the coupled transient temperature displacement analysis. The effect of material specifics at given operational parameters (C and p of H₂) on permeation behavior is studied up to 70 MPa [82]. The subsurface defect

lies inside and the near-surface defect lies on the surface of the liner material, respectively, as per ISO 11114-5:2022. Here, the sub-surface defect inside the polymeric liner material and a defect at the interface of liner-composite material are considered as case I, and case II, respectively. A damage-predictive model has been considered to estimate the blistering. This can reduce the number of physical tests and minimize the cost and time for Type IV design and testing. The assumptions considered in the model development are described:

1. A 3-D geometry is considered as 2-D RVE model for diffusion across the thickness;
2. A fixed type interaction between liner and CFRP considered;
3. The diffusion across the edges of 2-D model are very less or negligible;
4. The individual layer orientation effect is neglected.

5.3.1 Pressurization-depressurization cycle of hydrogen for Type IV COPVs

Filling is carried out up to maximum pressure (p_{max}) of 70 MPa in 5 minutes and maintained for several hours, then fast defilling is carried out to a p_{min} of 2 MPa at a constant temperature of 23 °C in Type IV COPVs [206]. To test the permeation rate of Type IV COPVs for more than 1 week, it remains at the same p_{nwp} to get H_2 saturation inside the wall [2, 81]. The linear depressurization rate is followed and evaluated from p_{max} , p_{min} , and the time of desorption (t_{deso}) [207]. The sample could be depressurized after saturation or a steady state is reached, as per ISO 1114-2:2022. Then defilling was performed at a maximum rate of 0.7 MPa/min from p_{nwp} to p_{min} within 1.63 hr [20, 2]. The p_{min} inside the Type IV COPVs remains at 2 MPa to avoid failure at the liner-composite interface [2]. In this thesis work, our purpose is to estimate the H_2 accumulation behavior inside the defect for the first cycle. The time instance of analysis is shown (in Fig. 5.1) by star mark “*” for the start of filling as A, just before reaching 70 MPa as B, start-between-end of saturation as C, D, E, F respectively, just during the start of depressurization as G, and at the end of depressurization-dwelling as H.

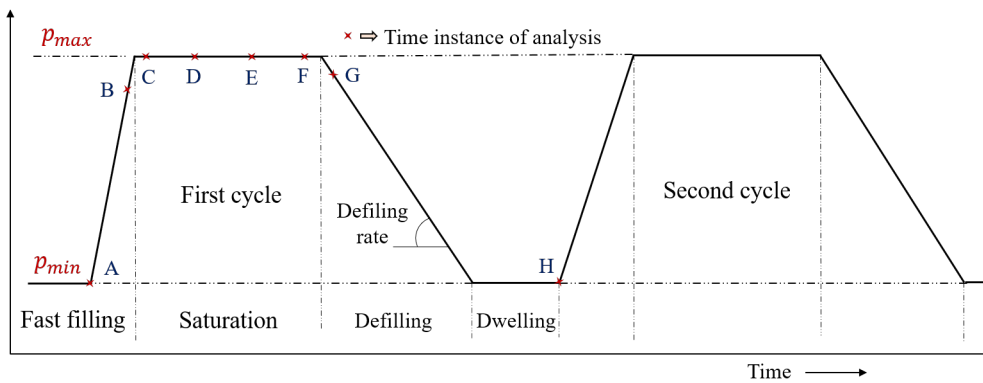


Figure 5.1: Typical pressurization-depressurization cycle of H_2 for Type IV COPVs.

The time instants are 1 s, 2.80 minutes, 9.16 minutes, 1.85 hr, 36 hr, 144 hr, 145 hr, 145 hr, and 217 hr respectively, corresponding to the filling-defiling process marked as A, B, C, D, E, F, G, and H respectively.

5.3.2 Geometrical coupon sample with loading and boundary conditions

To explore the mechanism of H_2 permeation, two micro-defects in the polymeric liner material are considered. Case I considers a circular defect at the middle of the polymeric liner, as shown in Fig. 5.2, and case II considers a semicircular defect at the liner-composite interface, as shown in Fig. 5.3. A quarter model of the cross-section of the cylindrical part of the Type IV COPV with both the defects incorporated is then subjected to an operational filling and defilling cycle.

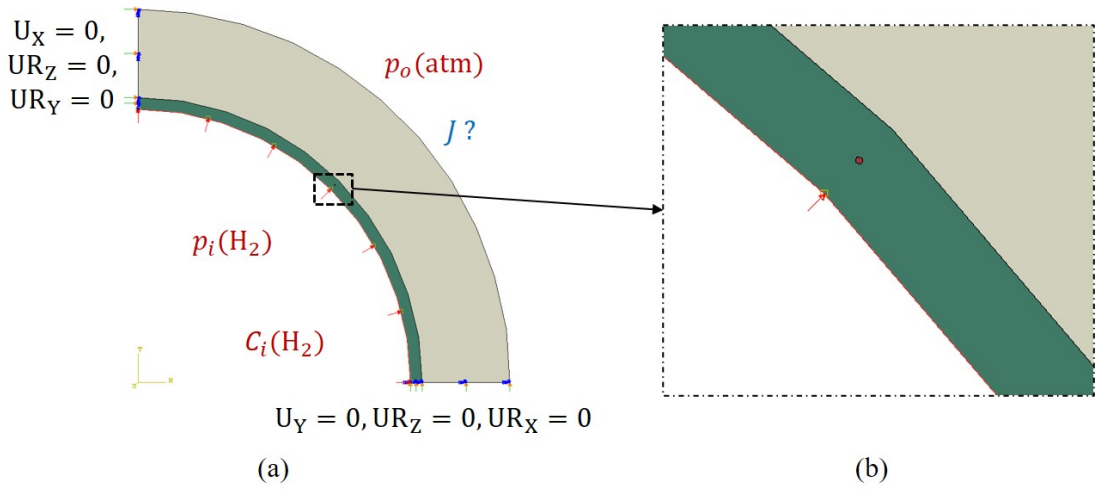


Figure 5.2: Schematic representation of (a) geometry, loading and boundary conditions, and (b) location of defect in polymeric liner material.

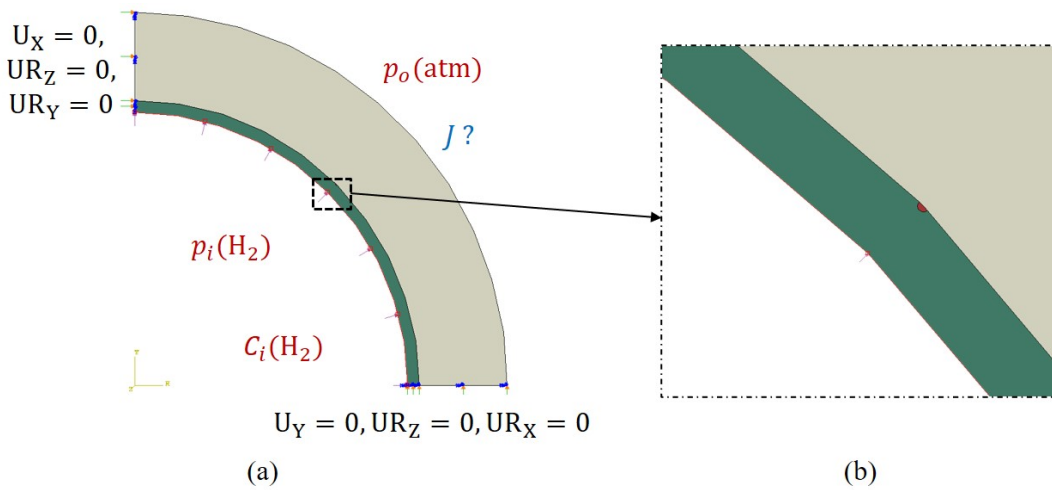


Figure 5.3: Schematic representation of (a) geometry, loading and boundary conditions, and (b) location of defect at liner-composite interface.

This model assumes that diffusion occurs in the radial direction across the wall thickness according to the loading and boundary conditions applied to the 2-D RVE model. On the innermost surface of the polymeric liner material, the loading conditions C_i and p_i were applied. The bottom and top surfaces are fixed in Y-direction ($U_Y = 0$, $U_{R_Z} = 0$, $U_{R_X} = 0$) and X-direction ($U_X = 0$, $U_{R_Z} = 0$, $U_{R_Y} = 0$), respectively. The initial concentration (C_O) within the RVE sample material is zero. In FE analysis, H₂ captures boundary nodes at the surface of the RVE sample. The difference in C of H₂ is $C_O - C_t$, caused by diffusion from one node to the next.

The circular defect size is 0.2 mm in diameter for case I and 0.1 mm for case II (less than 1 mm to be considered a micro defect) [208]. The other geometric parameters used in the FE model, are shown in Table 5.1

Parameters	Symbol	Liner	Defect	Composite	Units
Thickness	e	5	0.2 (diameter)	38.08	mm
Inner and outer radius	R_i, R_o	116, 121	-	121, 159	mm

Table 5.1: Geometrical parameters used in the FE model.

5.3.3 Mesh and element type used for modeling COPV material and defect

For H₂ diffusion, a 4-node plane strain thermally coupled quadrilateral, bilinear temperature-displacement element type, CPE4T, has been chosen for the meshing of CFRP material. A linear element type was chosen to minimize the computational time. A 4-node and 8-node plane strain thermally coupled quadrilateral, bilinear displacement, and temperature, hybrid, constant pressure element types CPE4HT and CPEH8T have been chosen for the meshing of liner material with defect at the center and defect at the liner-composite interface, respectively. This element type is useful for simulating phenomena like C -driven expansion or contraction of fluids in porous media, which can affect pore p . The type of element, number of elements, and number of nodes used for the polymeric liner, CFRP, and defect material are shown in Table 5.2.

Parameters	Liner (case I)	Liner (case II)	CFRP (case I)	CFRP (case II)
Element type	CPE4HT	CPEH8T	CPE4T	CPE4T
Number of element	5292	2000	100	216
Number of node	5521	2331	130	259

Table 5.2: FE model parameters used in mesh model.

The mesh-independent study plays a vital role in estimating the closer value in FE analysis. Here, we conducted the test for various mesh sizes in the range of 0.5-0.1 mm with an interval of 0.1 mm for the FE model. The model showed the mesh insensitiveness for the mesh size of 0.1 mm.

5.3.4 Material model used for polymeric liner, composite material, and defect

The polymeric liner material and the defect material are modeled as hyperelastic material, and the properties are shown in Table 5.3 [16, 17, 191]. The third-order Ogden model incorporates multiple strain energy terms to capture extreme deformations (expansion-contraction) and compressibility of pores or defects (behaves like soft materials). It enables better fitting of the nonlinear stress-strain behavior and softening/stiffening effects in hyperelastic materials [209], [210].

Ogden model	Symbol	Liner	Defect	Units
Order	N	1	3	-
Material constant	μ_i	51.125	-0.165, 0.289, 0.346	MPa
Material constant	ω_i	3.25	6.135, 20.13, 5.27	-

Table 5.3: Material model parameters used for polymeric liner, and defect.

The mechanical properties of the composite material are taken from Table 3.4. All composite layups are considered to have a single orientation, and the orientation effect on H_2 permeation is not incorporated. The H_2 transport properties of HDPE polymer are taken from the experimental study performed by Fujiwara et al. (2020) and (2021) [18] and [88] under p up to 70 MPa with constant temperature conditions. The atmospheric temperature (T) is 300 K, initial concentration (C_O) is zero, and universal gas constant (R) is $8.134 \text{ J.mol}^{-1}.\text{K}^{-1}$ for all materials. The initial diffusivity (D_o), solubility (S), and partial molar volume (V_H) specifications used for polymeric liner, defect, and composite material used in FE modeling are shown in Table 5.4 [16, 17, 191].

Parameters	Liner	Defect	Composite	Units
D_o	9.9×10^{-11}	9.9×10^{-9}	9.9×10^{-9}	$\text{m}^2.\text{s}^{-1}$
S	5.96×10^{-6}	5.96×10^{-4}	-	$\text{mol.m}^{-3}.\text{Pa}^{-1}$
V_H	2.78×10^{-5}	2.78×10^{-4}	2.78×10^{-7}	$\text{m}^3.\text{mol}^{-1}$

Table 5.4: Modeling parameters used for polymeric liner, defect, and composite material.

5.4 Results and Discussion

After modeling and simulating the H_2 permeation through the RVE sample of 70 MPa Type IV COPV with pre-existing defects, H_2 flux (J) is investigated with time. The contour of J variation is driven by C and p , and the H_2 -polymer interaction at the inner surface follows Henry's law. The contour for J across the thickness of the sample for a defect inside the polymer (case I), and for the defect at the interface of liner-composite (case II) are as shown in Fig. 5.4 and 5.5, respectively.

At the initial stage, J is very slow, and after some hours, H_2 starts diffusing in polymer and goes into a saturation state by maintaining a constant internal p of 70 MPa after filling.

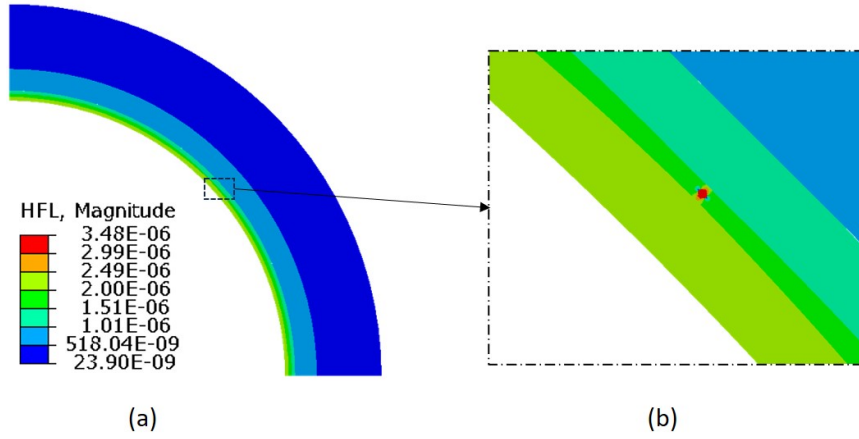


Figure 5.4: Contour for J (a) across the thickness of the sample, and (b) with defect at the center of polymeric liner material.

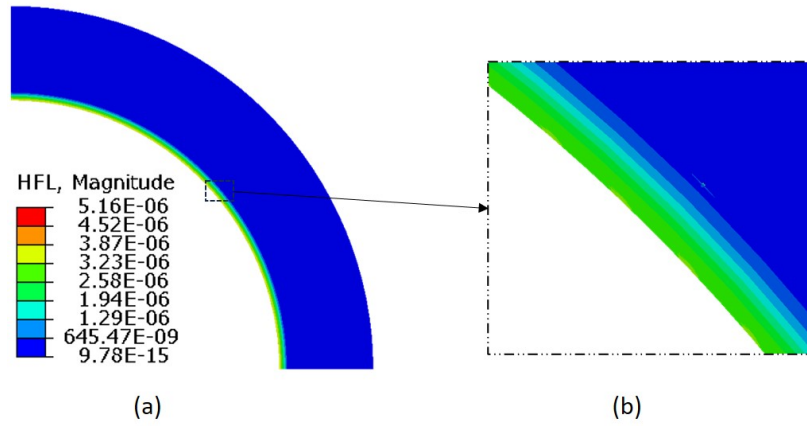


Figure 5.5: Contour for J (b) across the thickness of the sample, and (b) with defect at the interface of liner-composite material.

The J rate increases with time and after several hours, it reaches a saturation state inside the defect, which means the J is constant with time throughout the thickness of the RVE sample (as per Fig. 5.1). The J due to defect inside polymeric liner material and for the defect at the interface of polymeric liner-composite are 3.48×10^{-6} and 5.16×10^{-6} $\text{mol.s}^{-1}.\text{m}^{-2}$. The J of case II defect is higher since after the accumulation of H_2 , the p generated at the interface allows the passage of H_2 through the composite due to higher diffusivity. In case of a defect inside the polymer, the polymeric liner material does not allow H_2 to pass easily, and J is lower as compared to a semicircular defect at the liner-composite interface. This means J is not uniform due to defects present in the RVE. Also, the CFRP properties are assumed values that are not available in the literature for Type IV COPVs due to their porous behavior. So, the permeability prediction is not effective in these cases. Therefore, it is important to check the p generated by these defects and their effect on the yield behavior of the material to estimate the chance of blister formation due to pre-existing manufacturing defects.

The p variation in both defects is monitored during the operational cycle, as shown in Fig. 5.6. The p_{max} generated inside the defect for case I is 126 MPa, and for case II is 113 MPa. The p variation for case I starts from a 65 MPa value due to fast filling or sudden pressurization up to 70 MPa, and it increases during the saturation period at a faster rate due to the accumulation of H_2 inside the pre-existing circular defect of the polymeric liner material. Due to sudden decompression, a decrease in p value was found during the defilling period. The p_{min} of 20 MPa was applied on the boundary during dwelling period. Due to the accumulation of H_2 within the defect, the pressure value decreases linearly.

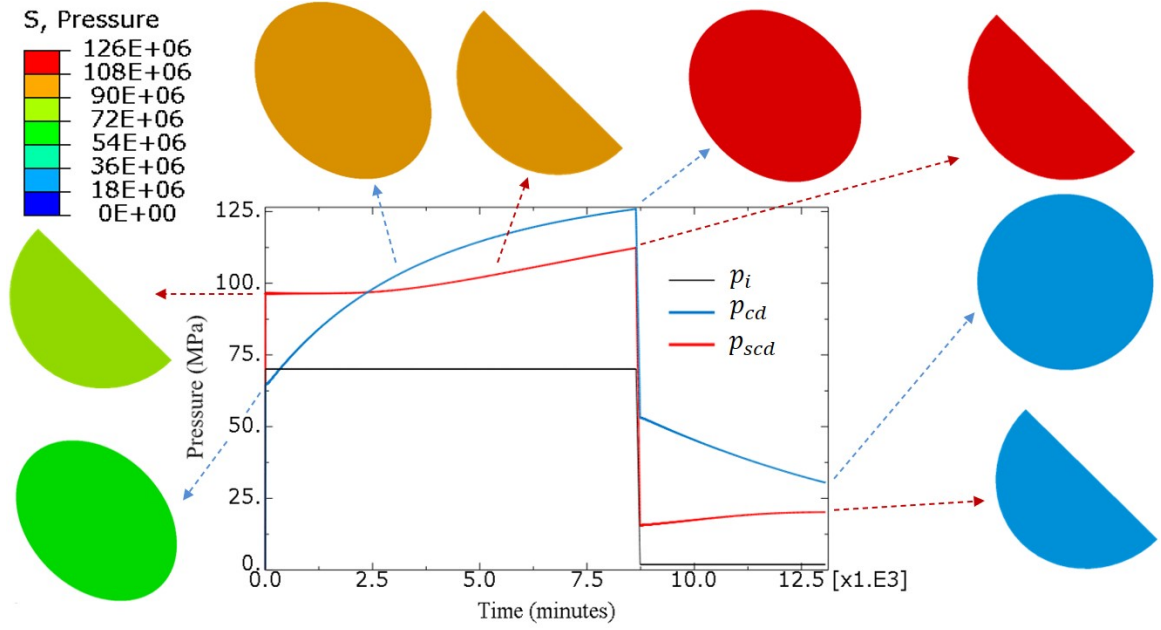


Figure 5.6: Pressure variation with time for the defect inside the polymer (p_{cd}) and defect at the liner-composite interface (p_{psd}) concerning the similar applied p_i for first cycle.

For a similar loading condition, the p variation with time for case II is shown in Fig. 5.6. The p value starts from 90 MPa due to sudden pressurization, and its value is much higher than that in case I. Because the defect position in case II is at the interface of the liner-composite and there is an increase in resistance, the stress value is exceeded. During the saturation period, the rate of increase of stress is low because the composite has a higher diffusivity, due to which H_2 accumulation is much lower at the interface. During decompression, the sudden drop in p value increased slightly in a linear fashion during the dwelling period because of the accumulation of H_2 in the interfacial semicircular defect.

The p generated is compared with the material yield limit, the theoretical decompression damage limit, and the permeation damage limit to identify the failure conditions [211, 205, 18]. The diffusive properties are based on theoretically calculated $p_{d,D}$ using Eqn. (5.3) for p_i 70 MPa, C_i 867 mol.m⁻³, S 1.8 × 10⁻⁶ mol.m⁻³.Pa⁻¹ obtained as 411.6 MPa. Material yield-based $p_{d,Y}$ using Eqn. (5.4) for the yield value of 24.1 MPa is 16.1 MPa. If p developed inside the defect exceeds $p_{d,Y}$ the yielding will begin. The p inside the

defect arises due to the diffusive properties of the polymeric liner material for H₂ gas. So, the failure is shown only if $p_{d,D}$ is greater than the theoretically calculated value of 411.6 MPa. The p_{max} generated inside the defect for cases I and II are 126 MPa and 113 MPa respectively.

The p generated at the defect site inside the liner material, at the end of the first cycle is nearly 126 MPa. In the next cycle, the pressure inside the defect has increased to 131 MPa as shown in Fig. 5.7. So, we can say that the pressure inside the defect increased by 416 MPa in 58th cycle, which is exceeding the $p_{d,D}$ of 411.6 MPa. This could be responsible for blister formation.

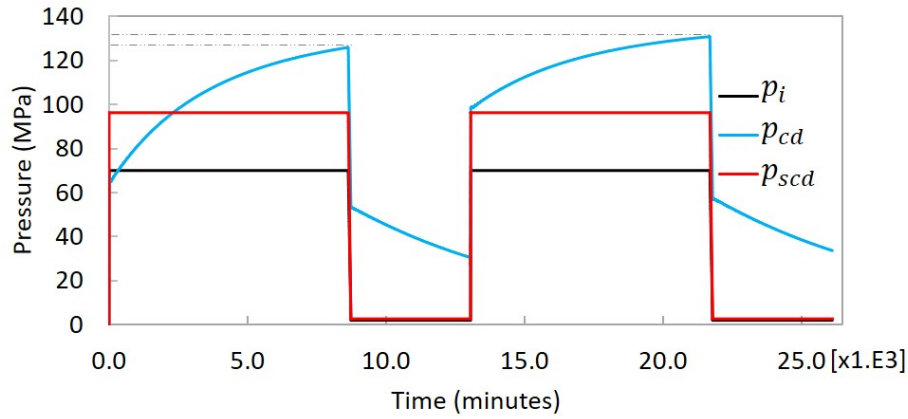


Figure 5.7: Pressure variation with time for the defect inside the polymer (p_{cd}) and defect at the liner-composite interface (p_{psd}) concerning the similar applied p_i for two cycle.

The applied H₂ concentration C_i , concentration due to defect inside polymer C_{cd} and concentration due to defect at the liner-composite C_{scd} are shown in Fig. 5.8. The H₂ concentration for fast depressurization rate (dp_1) of 0.7 MPa/min and slow depressurization rate (dp_2) of 0.07 MPa/min has not shown a significant change. For slower dp_2 the time taken is longer as compared to faster dp_1 , which results in slower drop of H₂ concentration with time. The defect present inside the polymeric liner material showed accumulation of more H₂ concentration, which results in pressure buildup inside the defect as per Henry's law.

Therefore, simulation results provide an understanding of p build-up inside defects during the filling and defilling cycle. These results provided insight into the effect of the location of micro-defects on predicting the chance of blister formation (and damage initiation) under the operational conditions of Type IV COPVs. The discussion of this chapter is as follows:

1. After p_b qualification and ensuring that the H₂ permeability is within the limit at p_{nwp} for the optimal thickness of liner material, the defilling test needs to be performed to check the effect of decompression and ensure the safety of Type IV COPV. Since defects are introduced during the manufacturing and processing of

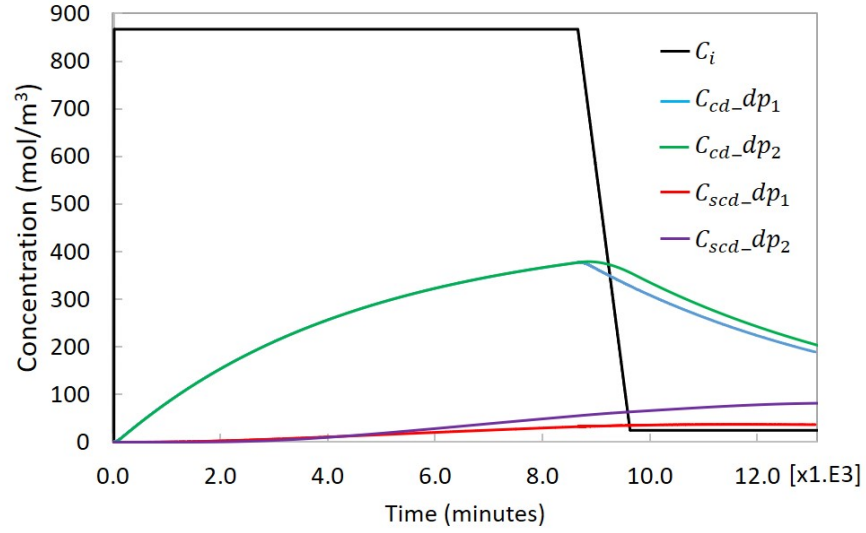


Figure 5.8: Concentration variation with time for the defect inside the polymer (C_{cd}) and defect at the liner-composite interface (C_{scd}) for single cycle.

the polymeric liner, this can cause 70 MPa Type IV COPVs to fail due to sudden decompression.

2. The H_2 permeation mechanism within a FE framework presents an HTM material model for polymers that can capture pressure and concentration-driven permeation.
3. The aspects of pre-existing micro-defects found in the liner material and at the liner-composite interface for a representative volume element (RVE) of a 70 MPa Type IV COPV have been investigated. The liner thickness is 5 mm, and the H_2 transport properties are based on the chapter 4 work.
4. The effects of pressurization and depressurization on H_2 permeation within these micro-defects lead to molecular H_2 saturation inside the material, and H_2 accumulation within the defects has been analyzed.
5. The role of the micro-defects location for a given H_2 filling cycle and the observation that H_2 saturation and accumulation result in pressure buildup within the defects have been examined. The defect at the interface shows very little accumulation of H_2 due to the porous nature of the composite. The composite has a higher diffusivity as compared to the polymeric liner material.
6. The results obtained from our study provide valuable insights into understanding the location of micro-defects, which can help to determine their potential to cause failure or remain acceptable during the operational cycle of Type IV COPVs in on-board applications.
7. In addition, the number of cycles estimated could cause blister formation for a given defect size, location, material properties, liner thickness, and loading conditions. For an increase in the number of cycles, the defect inside the polymeric liner material is

critical due to an increase in pressure buildup during each cycle, and for the defect at the liner-composite interface, the pressure decreased with an increase in the loading cycle.

8. Also, the effect of minimum and maximum decompression rates provided valuable insight into the defects present inside the liner and at the liner-composite interface. The defect present inside the liner material does not show a significant effect due to the rate of decompression. However, the interface shows a significant reduction in concentration variation within the defect present at the liner-composite interface. The slower rate of decompression shows a higher concentration value due to the increased saturation time inside the material.

5.5 Conclusion

The present chapter explores the simulation-assisted framework to understand the mechanism of H₂ transport through pre-existing micro defects in polymeric liner material and liner-composite interface, considering operational cycle requirements and safety concerns related to p_{nwp} of 70 MPa Type IV COPV. A multi-variable H₂ transport permeation analysis has been conducted using the extended governing equations of Fick's law for RVE of Type IV COPV material and the defilling-induced blistering model.

The analysis estimated the H₂ saturation inside the material and its accumulation within the defects. Such H₂ saturation and accumulation result in p build-up due to increased C within the defects. Although there is a minimal accumulation of H₂ in both cases, as it is released by the composite, it contributes to increased p and generates maximum stress within the defect. By analyzing this data, p_{max} is predicted that may develop within a defect. Even though the chosen defect size is small, it can initiate and contribute to failure. This information is valuable in understanding the location of micro defects that may lead to failure or be acceptable during the operational cycle for 70 MPa Type IV COPVs in onboard applications to avoid failure due to H₂ permeation.

Chapter 6

Conclusion and Future Scope

6.1 Conclusion

This thesis addresses critical challenges in the design and development of a Type IV COPV with p_{nup} of 70 MPa, focusing on manufacturing defects. It is shown that design parameters are crucial for defect-free manufacturing of Type IV COPVs and can significantly impact their performance. Besides mechanical failure at burst pressure, polymeric liner material failure due to H₂ permeation during operational cycles is modeled using a novel hydrogen transport material model (HTM) developed in this work. The elimination of manufacturing defects has been found to improve the high-pressure H₂ storage Type IV COPV performance and safety.

The first objective (Chapter 3) of this thesis work has proposed a design solution for prototype development of Type IV COPV having 18 L capacity to store 0.75 kg of H₂. The design and manufacturing aspects responsible for the failure at burst pressure of more than 150 MPa have been investigated through the utilization of numerical modeling. The NA was utilized to estimate the initial thickness required to sustain the burst pressure load in the circumferential and axial directions. The CLT has been utilized inside the Abaqus software to simulate the composite material with Tsai-Wu failure criteria. Upon analyzing the mechanism of failure, several design and manufacturing flaws associated with the Type IV COPV have been eliminated. Furthermore, the maximum possible burst pressure has been investigated after making the safer 70 MPa Type IV COPV.

In the second objective (Chapter 4) of this thesis work, a HTM modeling framework has been developed by implementing concentration as well as pressure-driven diffusion at a constant temperature. The developed modeling framework is implemented using UMATHT subroutines in the commercial FE solver Abaqus. This study uses the chemical potential method to simulate the effects of both concentration and pressure on the H₂ transport properties. The experimental work of Fujiwara et al. 2020, 2021 (Exp.) has been validated to verify the HTM for H₂ transport properties evaluated for the applied pressure of 90 MPa. This simulation results demonstrated the model's accuracy with the comparison with Exp. data. In addition, the role of the H₂ transport mechanism through the polymer is highlighted in this chapter. The simulation results revealed the effect of compression due to H₂ pressure on polymer transport properties. Further, using this HTM method, the minimum thickness required for the Type IV COPV polymeric liner material

to restrict the H_2 permeation limit at 70 MPa of p_{nwp} was determined.

The third objective (Chapter 5) has used HTM to examine the effects of pressurization and depressurization of H_2 on pre-existing micro-defects inside Type IV COPV. In this study, a representative sample of the cylindrical section of Type IV COPV has been subjected to cyclic loading (pressure and concentration) of H_2 and analyzed using the FE modeling framework. Such H_2 saturation and accumulation resulted in p build-up within the defect site. In contrast, the central defect of the polymeric liner material is more likely to accumulate H_2 . More specifically, due to the higher diffusivity of the CFRP material, defects at the liner-composite interface result in less H_2 accumulation and consequently less pressure buildup. Therefore, the defect location within the polymeric liner material is responsible for the chance of blister formation. Moreover, the results highlighted that the dynamic H_2 redistribution (driven by pressure and concentration) caused the pressure buildup inside the material due to the presence of pre-existing micro-defects, which could be responsible for the blistering and the failure of the 70 MPa Type IV COPVs.

6.2 Scope for future studies

The possible immediate extensions of the current work for the future include the following:

- The liner-boss and liner-CFRP interfaces will be examined to identify the root causes of interfacial failure. Interfacial strength will be enhanced by analyzing the mechanical effects of polymeric liner surface treatments under cyclic loading conditions. Additionally, the role of galvanic corrosion at the aluminium alloy-CFRP interface and its implications for structural integrity will be evaluated. Design refinements will focus on optimizing manufacturing quality to ensure the Type IV COPVs withstand the minimum required p_b with an optimum strength-to-weight ratio.
- The filament winding manufacturing parameters (e.g., tension, winding angle, cure cycle) associated with towpreg winding methods will be optimized to minimize defects (e.g., fiber misalignment, resin-rich zones) in CFRP composites. A systematic analysis of defect propagation mechanisms (e.g., void formation, interlaminar delamination) will be conducted to mitigate design- and manufacturing-related failures, ensuring structural integrity under critical operational loads.
- The generalized chemical potential method utilized in this thesis for the developed HTM will be extended to blended polymeric liner materials by incorporating specific theories and relations, such as the Nielsen model, to better understand the mechanism of H_2 permeation and enhance gas barrier performance for real-world industrial applications. To capture the local and nonlinear behavior of different blended polymers interacting with high-pressure gaseous H_2 , with glassy and rubbery phase behavior will be integrated using the dual-mode sorption model. In future

research, we plan to expand our analysis to include a larger dataset encompassing various industrial-grade polymers (such as PA6, EVOH, and PET) and their blends.

- The novel HTM model presented in this thesis will be extended into a coupled temperature-stress-diffusion model. The dynamics of the filling-defueling cycle and the associated failure scenarios of high-pressure Type IV COPVs, resulting from manufacturing defects within the polymer and at the polymer-composite interface, will be examined. This analysis will take into account the realistic bonding phenomena between the polymeric liner and the composite material.

These extensions aim to enhance performance parameters, reduce manufacturing and operational uncertainties for Type IV COPVs with p_{nwp} of 70 MPa for efficient H₂ storage solutions.

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Chapter A

Appendix

A.1 CFRP Winding Sequence Used for FW on Liner-boss Assembly of Type IV COPV

Sr.	n	Layer Type	Material	WA (°)	BW (mm)	N_s (-)
1	1-4	Hoop	CFRP	89.85	2.01	1
2	5, 6	Helical	CFRP	25.00	2.01	1
3	7-10	Hoop	CFRP	89.85	2.01	1
4	11, 12	Helical	CFRP	25.00	2.01	1
5	13	Hoop	CFRP	89.85	2.01	1
6	14, 15	Helical	CFRP	25.00	2.01	1
7	16, 17	Hoop	CFRP	89.85	2.01	1
8	18-20	Helical	CFRP	25.00	2.01	1
9	21	Hoop	CFRP	89.85	2.01	1
10	22-24	Helical	CFRP	25.00	2.01	1
11	25	Hoop	CFRP	89.85	2.01	1
12	26-28	Helical	CFRP	25.00	2.01	1
13	29	Hoop	CFRP	89.85	2.01	1
14	30-32	Helical	CFRP	25.00	2.01	1
15	33	Hoop	CFRP	89.85	2.01	1
16	34-36	Helical	CFRP	25.00	2.01	1
17	37	Hoop	CFRP	89.85	2.01	1
18	38-40	Helical	CFRP	25.00	2.01	1
19	41	Hoop	CFRP	89.85	2.01	1
20	42-44	Helical	CFRP	25.00	2.01	1
21	45	Hoop	CFRP	89.85	2.01	1
22	46-48	Helical	CFRP	25.00	2.01	1
23	49	Hoop	CFRP	89.85	2.01	1
24	50-52	Helical	CFRP	25.00	2.01	1
25	53	Hoop	CFRP	89.85	2.01	1
26	54-56	Helical	CFRP	25.00	2.01	1
27	57	Hoop	CFRP	89.85	2.01	1
28	58-60	Helical	CFRP	25.00	2.01	1
29	61	Hoop	CFRP	89.85	2.01	1
30	62-64	Helical	CFRP	25.00	2.01	1
31	65	Hoop	CFRP	89.85	2.01	1
32	66-68	Helical	CFRP	25.00	2.01	1
33	69	Hoop	CFRP	89.85	2.01	1
34	70-72	Helical	CFRP	25.00	2.01	1
35	73	Hoop	CFRP	89.85	2.01	1

Sr.	n	Layer Type	Material	WA (°)	BW (mm)	N_s (mm)
36	74-76	Helical	CFRP	25.00	2.01	1
37	77	Hoop	CFRP	89.85	2.01	1
38	78-80	Helical	CFRP	25.00	2.01	1
39	81	Hoop	CFRP	89.85	2.01	1
40	82-84	Helical	CFRP	25.00	2.01	1
41	85	Hoop	CFRP	89.85	2.01	1
42	86, 87	Helical	CFRP	25.00	4.00	2
43	88	Hoop	CFRP	89.85	4.00	2
44	89	Helical	CFRP	25.00	4.00	2
45	90	Hoop	CFRP	89.85	4.00	2
46	91	Helical	CFRP	25.00	4.00	2
47	92	Hoop	CFRP	89.85	4.00	2
48	93	Helical	CFRP	25.00	4.00	2
49	94	Hoop	CFRP	89.85	4.00	2
50	95	Helical	CFRP	25.00	4.00	2
51	96	Hoop	CFRP	89.85	4.00	2
52	97	Helical	CFRP	25.00	4.00	2
53	98	Hoop	CFRP	89.85	4.00	2
54	99	Helical	CFRP	25.00	4.00	2
55	100	Hoop	CFRP	89.85	4.00	2
56	101, 102	Helical	CFRP	25.00	4.00	2
57	103	Hoop	CFRP	89.85	4.00	2
58	104-112	Helical	CFRP	25.00	4.00	2

A.2 Finite Element Formulation of Hydrogen Transport Model for Polymeric Liners in Type IV COPVs

The FE equation for H_2 permeation is derived according to the standard FE formulation using Galerkin method. Let's consider a body with volume V bounded by surface S which consists of a part S_c where the hydrogen concentration is prescribed and a part S_j where the flux through the surface is prescribed by value 'j' such that

$$\mathbf{J} \cdot \mathbf{n} = j$$

Parts of the surface are such that $S = S_c \cup S_j$.

Weak Form

The weak form of the governing differential equation is derived by multiplying the equation by a test function δC and integrating over the volume V . This results in the following equation:

$$\int_V \delta C \left\{ \frac{\partial C}{\partial t} - \nabla \cdot (D \nabla C) + \nabla \cdot \left(\frac{DCV_H}{RT} \nabla \sigma_h \right) \right\} dV = 0 \quad (A.1)$$

We know that,

$$\nabla \cdot (\delta C D \nabla C) = \nabla \delta C D \nabla C + \delta C \nabla \cdot (D \nabla C) \quad (A.2)$$

and

$$\delta C \nabla \cdot \left(\frac{DCV_H}{RT} \nabla \sigma_H \right) = \nabla \cdot \left(\delta C \frac{DCV_H}{RT} \nabla \sigma_H \right) - \nabla \delta C \cdot \frac{DCV_H}{RT} \nabla \sigma_H \quad (\text{A.3})$$

$$\begin{aligned} \int_V \left\{ \delta C \frac{\partial C}{\partial t} - \nabla \cdot (\delta C D \nabla C) + \nabla \delta C \cdot (D \nabla C) + \nabla \cdot \left(\frac{\delta C DCV_H}{RT} \nabla \sigma_h \right) \right. \\ \left. - \nabla \delta C \cdot \left(\frac{DCV_H}{RT} \nabla \sigma_h \right) \right\} dV = 0 \end{aligned} \quad (\text{A.4})$$

Applying Gauss Divergence Theorem

$$\int_V \left\{ \delta C \frac{\partial C}{\partial t} + \nabla \delta C \cdot (D \nabla C) - \nabla \delta C \cdot \left(\frac{DCV_H}{RT} \nabla \sigma_h \right) \right\} dV + \int_S \delta C j dS = 0 \quad (\text{A.5})$$

From weak form derived earlier can be rewritten as

$$\int_V \delta C f dV - \int_V \nabla \delta C \cdot J dV + \int_S \delta C j dS = 0 \quad (\text{A.6})$$

Here, f is the function of C and $\dot{C}$.

Incremental form

The incremental form of the equation is derived by expanding the equation in terms of the incremental changes in concentration ΔC and its rate of change $\Delta \dot{C}$. The incremental form of $E=0$ in C and $\dot{C}$ is and j is known boundary condition. This results in the following equation:

$$E + \frac{\partial E}{\partial C} \Delta C + \frac{\partial E}{\partial \dot{C}} \Delta \dot{C} = 0 \quad (\text{A.7})$$

$$\begin{aligned} \int_V \delta C f dV - \int_V \nabla \delta C \cdot J dV + \int_A \delta C j dS + \int_V \delta C \frac{\partial f}{\partial C} \Delta C dV - \\ \int_V \nabla \delta C \frac{\partial J}{\partial C} \Delta C dV + \int_V \delta C \frac{\partial f}{\partial \dot{C}} \Delta \dot{C} dV = 0 \end{aligned} \quad (\text{A.8})$$

$$\begin{aligned} \int_V \delta C [\dot{C}] dV + \int_S \delta C j dS - \int_V \nabla \delta C \cdot \left[-D \nabla C + \frac{DCV_H}{RT} \nabla \sigma_h \right] dV \\ - \int_V \nabla \delta C \cdot \left[-D \nabla + \frac{DV_H}{RT} \nabla \sigma_h \right] \Delta C dV + \int_V \delta C \Delta \dot{C} dV = 0 \end{aligned} \quad (\text{A.9})$$

Discrete form

The discrete form of the equation is obtained by discretizing the weak form using the FE method. The interpolation function N_c is used to approximate the concentration C , and the gradient of the interpolation function B_c is used to approximate the gradient of C . The discrete form of the equation is given by:

$$\Delta C = N_c \{ \Delta C \}$$

$$\Delta \dot{C} = N_c \{ \Delta \dot{C} \}$$

$$\delta C = N_c \{ \delta C \}$$

and the gradient of shape function is

$$B_c = \nabla N_c \quad (\text{A.10})$$

$$\nabla \sigma_H = [B_c] \{ \sigma_H \} \quad (\text{A.11})$$

Rate of change of nodal mass concentration

$$\frac{\partial \{C\}}{\partial t} = \{ \dot{C} \} \quad (\text{A.12})$$

Since, previous equation holds for any δC , it must also hold for any δC . So,

$$\begin{aligned} & \int_V N_c \dot{C} dV \\ & + \int_S N_c j dS \\ & - \int_V B_c^T \cdot \left[-D_{eq} \nabla C + \frac{D_{eq} C V_H}{RT} \nabla \sigma_h \right] dV \\ & - \int_V B_c^T \cdot \left[-D_{eq} \nabla + \frac{D_{eq} V_H}{RT} \nabla \sigma_h \right] N_c \Delta C dV \\ & + \int_V N_c \Delta \dot{C} N_c dV = 0 \end{aligned} \quad (\text{A.13})$$

Matrix Form

The discrete form is then converted into a matrix form using the FE method. The matrix form is given by:

$$[M_c] \cdot \Delta \dot{C} + [K_1 + K_2] \cdot \Delta C = F \quad (\text{A.14})$$

Where $[M_c]$, $[K_i]$ and $[F]$ denote the concentration capacity matrix, mass diffusivity matrix, and H_2 flux matrix given by Eqn.

$$[M_c] = \int_V [N_c]^T [N_c] dV \quad (\text{A.15})$$

$$K_1 = \int_V B_c^T D_{eq} N_c dV \quad (\text{A.16})$$

$$K_2 = \int_V B_c^T \left[\frac{D_{eq} V_H}{RT} \nabla \sigma_h \right] N_c dV \quad (\text{A.17})$$

$$F = - \int_V B_c^T \cdot \left[-D_{eq} \nabla C + \frac{D_{eq} C V_H}{RT} \nabla \sigma_h \right] dV + \int_V N_c \dot{C} dV + \int_A N_c j dS \quad (\text{A.18})$$

Time integration

The matrix form is then integrated in time using the finite difference method. The resulting equation is given by:

$$([M_c] + \Delta t[K])\{C\}^{t+\Delta t} = [M_c]\{C\}^t + \Delta t\{F\} \quad (\text{A.19})$$

The time-varying hydrogen concentration is given by:

$$\{\dot{C}\} = \Delta t(\{C\}_{t+\Delta t} - \{C\}_t) \quad (\text{A.20})$$

Final equation

The final equation that ensures the symmetry of the left part is given by:

$$(\Delta t[M] + [K_1])\{C\}_{t+\Delta t} = (\Delta t[M] - [K_2])\{C\}_t + [F] \quad (\text{A.21})$$

This equation is used to solve the FE equation for H₂ permeation using the Abaqus FE software.