Applicability of composite and nanocomposite materials to reusable liquid propellant tanks

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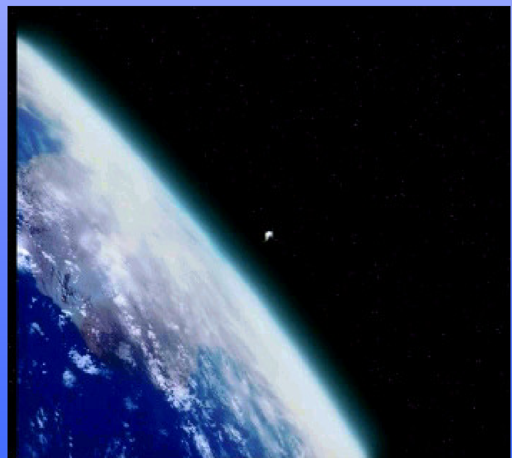


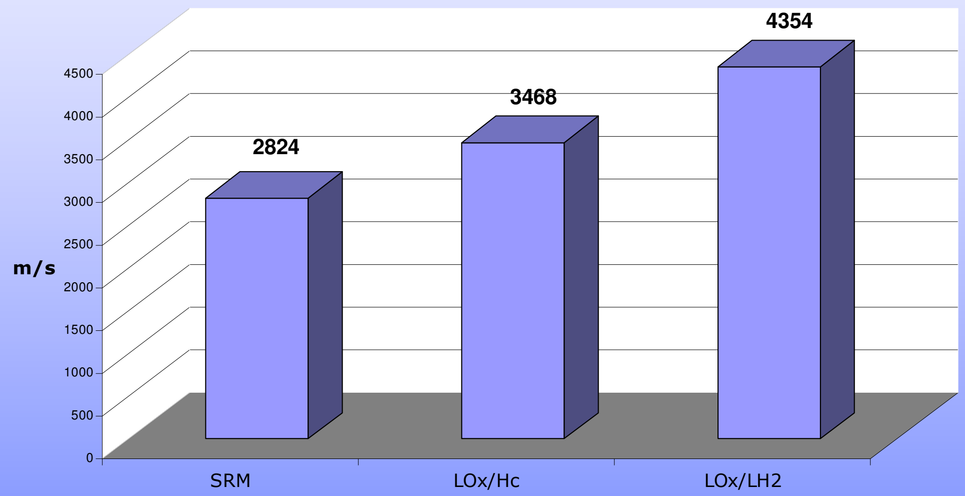
OUTLINE

- Frame and Introduction
- CIRA previous experience
- Status of the Project
- Future work

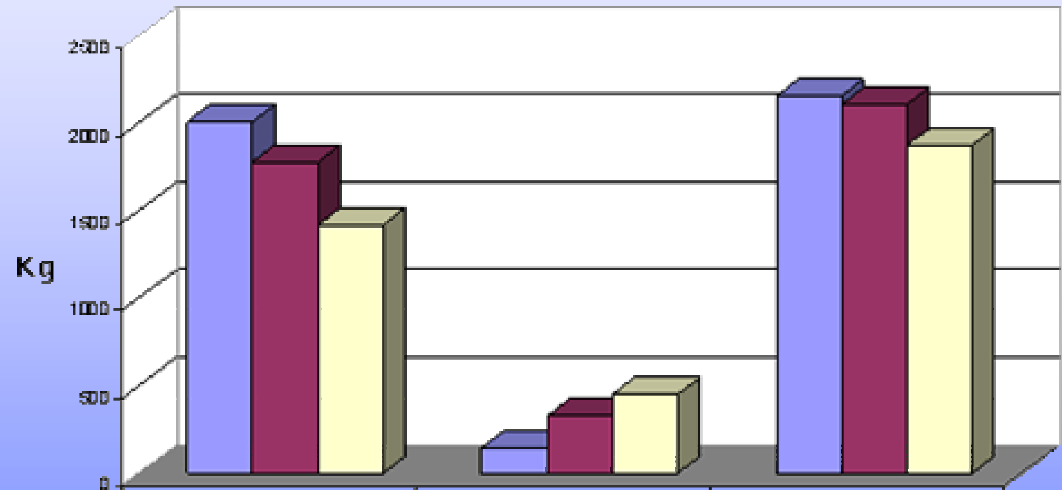
INTRODUCTION - FRAME

Liquid propulsion based on LH2/LOX or LHC/LOX is expected to be the standard for next generation of reusable launchers

Motor Vacuum ISP



Motors Propellant/DRY/Total masses



	1	2	3
SRM	2006.8	148.9	2155.7
LOx/Hc	1778	330	2108
LOx/LH2	1424	450	1874

Looking at mass distribution it is evident that a reduction in tank weight could be the key improvement to RLV cost reduction

INTRODUCTION - OBJECTIVE

Metallic cryotanks, based on Al-alloys, represent the mature technology for cryogenic propulsion.

Lightweight composite materials can potentially assure significant mass and cost reduction: they took advantage of an high specific strength and the possibility to be employed in automated manufacturing processes (i.e. Filament winding) far less expensive than conventional techniques used with metal alloys.

CIRA promoted "Cryo" project in the frame of USV PROGRAM

The project has the final objective of designing, manufacturing and testing of a scaled demonstrator composite tank for LOX aimed at:

- Weight reduction (Composite Structure)
- Manufacturing cost reduction (Filament Winding)

Technology Needs

- To contain, without leakage, cryogenic propellants for times required by launch mission.
  Very low temperature (90 K) and high cyclic thermal loads (ΔT_{max}= 300 K)

- To sustain a suitable number of flight/abort cycles.
  Reusability RLV requirement and Air-frame integration

- Carrying capacity of structural loads as well as internal pressure, axial and lateral inertia loads, which the launcher is subject to during the acceleration phase

- Suitable permeability in order to border the liquid leakage rates within the limit set for the specific safety requirements

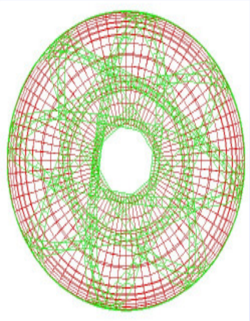
- Feasibility property in relation to the fabrication limits imposed by the technological processes employed in modern manufacturing industries.

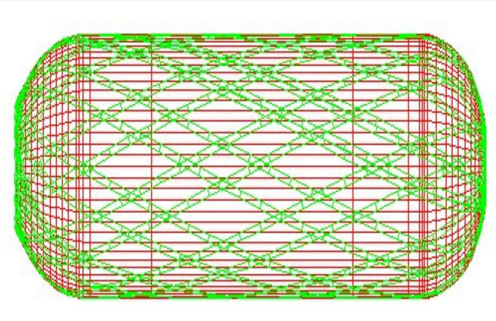
INTRODUCTION - OBJECTIVE

TANK REQUIREMENTS

DIMENSIONS

Cylindrical Height	8000 mm
Cylindrical Internal Diameter	5400 mm
Thickness (reference value)	3.5 mm





TANK DESIGN HYPOTHESIS

1 - Linerless tank

All loads, chemical resistance and barrier performances are demanded to CFRP.

2 - "Linered" tank

Load resistance is demanded to CFRP. Chemical resistance and barrier performances are demanded to the internal liner.

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CIRA-NASDA PREVIOUS EXPERIENCE

• **Materials selected by NASDA**

•CFRP BESFIGHT IM600/Q133

•Plaster mandrel

•**Design**

•Design optimisation

•Cure cycle optimisation

Tank design

An aided design of the tank was realized using a filament winding simulation code (ARIANNA).

CIRA-NASDA PREVIOUS EXPERIENCE

Ground testing
Reusability
critical areas

Permeability

Temperature behaviour

Micro cracking

Voids at leakage points

During the test campaign some leakage points were detected :

- Pre-preg ageing
- Not well adjacency among fibres.

<u>Process quality control and understanding of basic phenomena!!</u>

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  - Applicability of nanocomposite materials as internal liner.
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Material pre-screening

CFRP materials →

EPOXY	CYANATE-ESTER
Bryte EX 1522 Thiokol UF 3339-100	Bryte EX 1515

➢ The laboratory scale tests are carried out with the double aim to provide a database, as complete as possible, in order to support the FE design phase of the tank, and to identify the influences that typical CFRP parameters, such as Tg, kinetic cure, CTE, mechanical properties, density cracks etc. have on the cryogenic behaviour of the material as well as on its barrier performances.

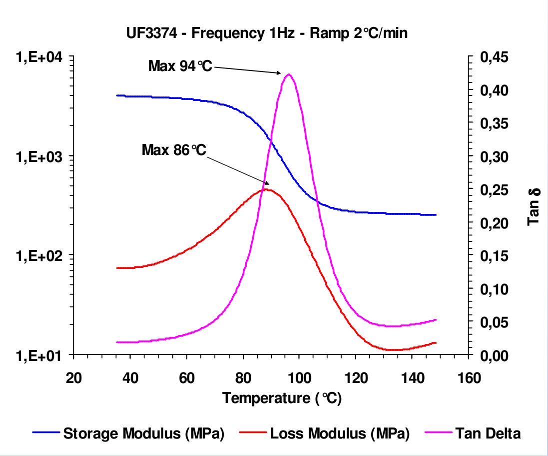
The laboratory testing involves:

- ***thermal analysis,***
- ***optical and electron microscopy,***
- ***mechanical testing,***
- ***barrier property characterisation.***

Results of the CFRP Characterisation

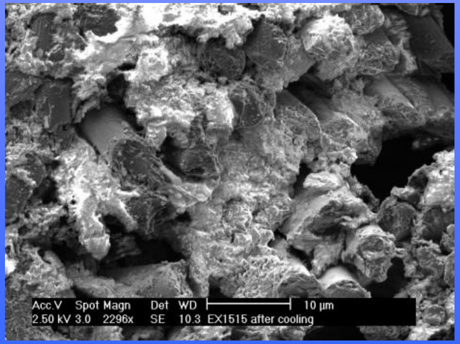
➢Characterization laboratory-scale: Thermal analysis

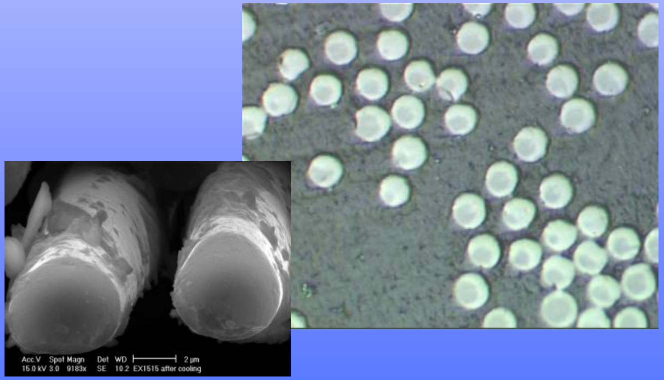
This work has addressed the issue of understanding the processing limit of B-staged tow prepreg candidate for cryogenic application and defining their optimal cure cycles.



➢Characterization laboratory-scale: non destructive analysis

NDE, optical and electron analysis have been performed in order to optimize the process manufacturing and to evaluate cracks and defects in the sample specimens prior and after cryogenic exposure.





Cooling effects: local fiber/matrix debonding

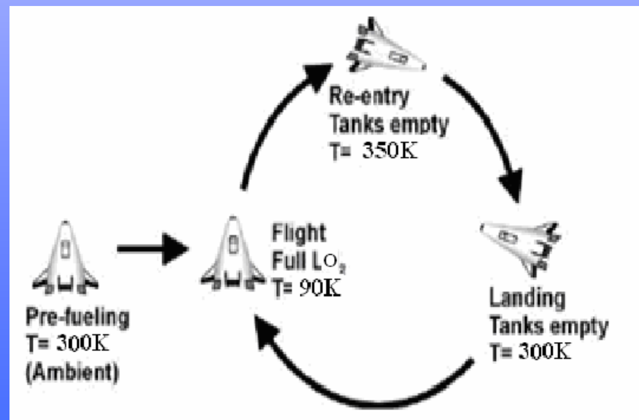
Results of the CFRP Characterisation

Mechanical tests

Test matrix

E_1	LONGITUDINAL YOUNG'S MODULUS
σ_1^R	LONGITUDINAL TENSILE AND COMPRESSION STRENGTH
E_2	TRANSVERSE YOUNG'S MODULUS
σ_2^R	TRANSVERSE TENSILE AND COMPRESSION STRENGTH
σ^a	APPARENT TENSILE STRENGTH
G_{12}	IN-PLANE SHEAR MODULUS
τ_{12}	IN-PLANE SHEAR STRENGTH

- PRISTINE
- CONDITIONING A
  6-hours immersion in liquid nitrogen
- CONDITIONING B (10 times)
  Quenching from 300K to 77K by immersion in liquid nitrogen for 6 hours
  Heating up to 300K
  Heating up to 350K in 10 minutes
  Cooling back to 300K

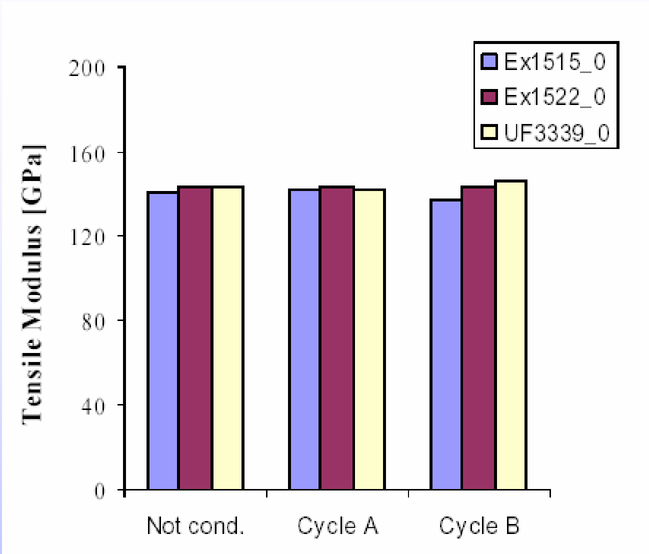


Results of the CFRP Characterisation

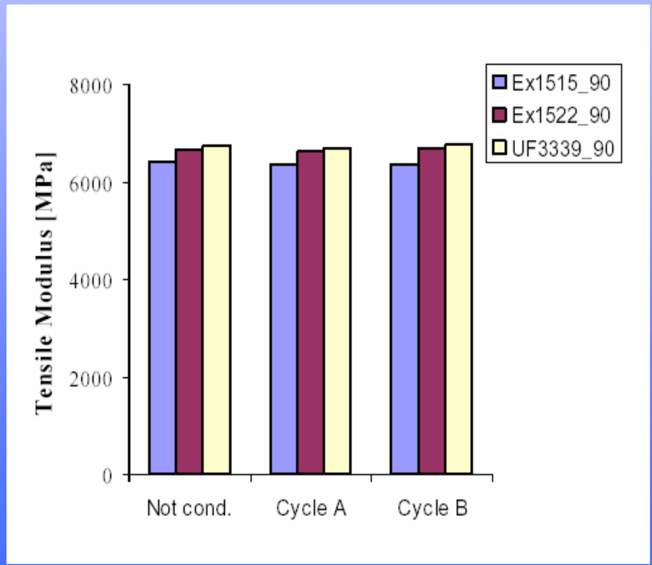
- As thermal cycling is introduced to the laminate, one would expect for the value of Young's modulus to decrease if cracks were forming, since the bounds holding the material together are breaking apart effectively making it less stiff.

- After reviewing all of the data, the conclusion was that the selected advanced materials, does not exhibit any crack growth after 10 cycles of the launcher flight.

- Mechanical tests on the selected CFRP materials will be performed at 90K using a cryogenic mechanical testing machine (Colonnetti CNR Turin).



Longitudinal tensile tests



Transversal tensile tests

Mass transport behaviour characterisation

- The mass transport behaviour represents the main concern when thinking of polymer composites as materials for tank building. A barrier performance even a bit less than optimal could actually lead to a dramatic failure of the tank.

- Moreover, the polymeric matrix is characterised by a non-zero permeability to low molecular weight gases, which has to be measured and be kept under allowable values.

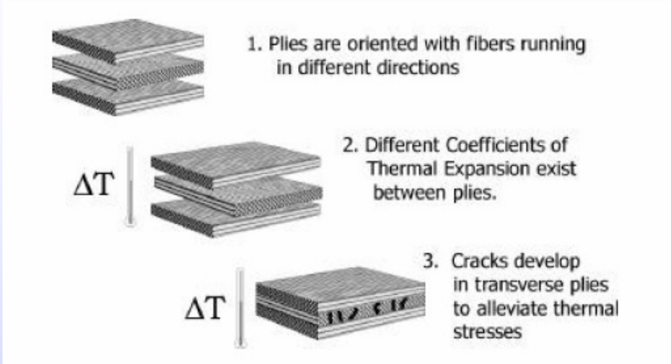
- The barrier performance can be estimated at different levels ranging from the macroscopic behaviour to the intrinsic material-related phenomena (multi-scale approach):

✓ **leakage phenomena**

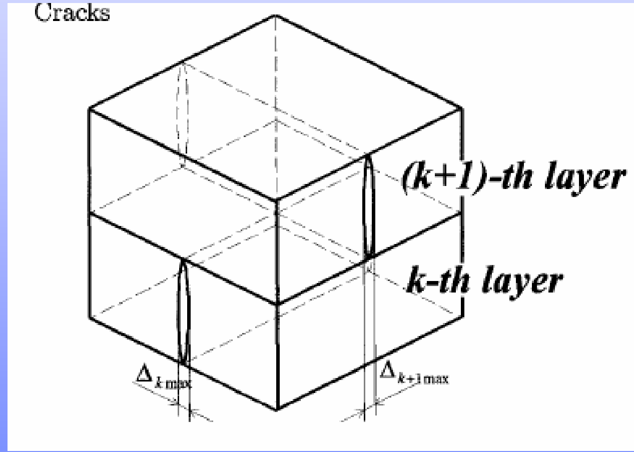
✓ **permeability behaviour**

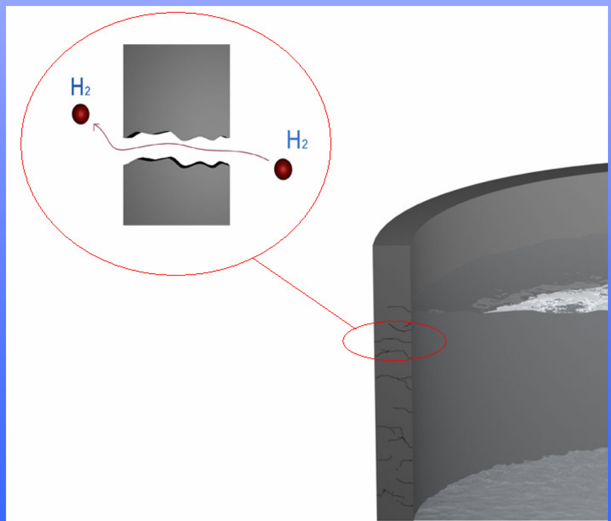
Mass transport behaviour characterisation

- The extension of composite materials to cryogenic tank building is not an ordinary issue. Composite materials particularly suffer from severe thermal stresses, which may cause matrix micro-cracking.



- In the case of leakage, gas or liquid flows through the leak path consists of continuously connected matrix cracks in each layer, which results in a sequence of connecting passages between both sides of the laminate.



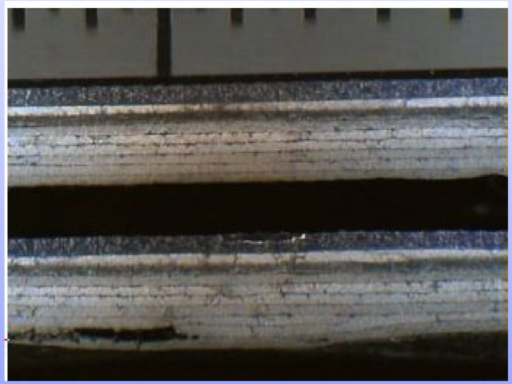


- Increase of the propellant leakage can be cause by the enlargement of crack-opening displacements caused by mechanical and thermal loads, increase of crack density and decrease of temperature.

Mass transport behaviour characterisation

Leakage phenomenon

➢ The leakage test is necessary as it recreates the operative conditions of the actual tank, and serve as an evaluation tool for the effectiveness of both material and process parameters.



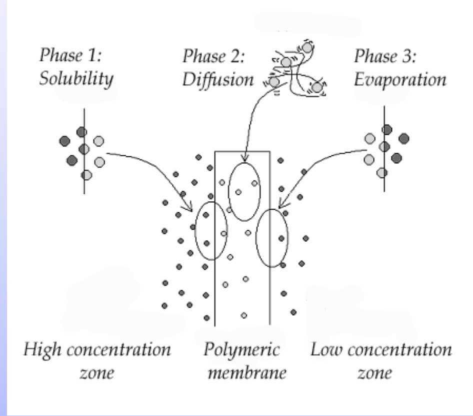
➢ In the leakage phenomenon the effects of intrinsic permeability, defects formed during the manufacturing process and microcracking arising from thermal cycling load are merged.

Water proof test up to 6 bar on a UF3339/IM7 tank-like specimen with ± 50 lamination sequence, previously conditioned.
No cracks or leakage areas were observed.

Mass transport behaviour characterisation

Diffusion/permeability

➢ If there are layers without cracks in the laminate, leakage does not take place, and diffusion alone can be present.

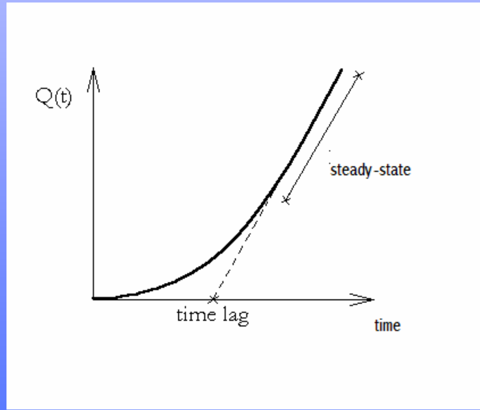


➢ The permeation through a polymer is a thermodynamic process. It involves:

- the solubility
- the diffusion
- the dissolution

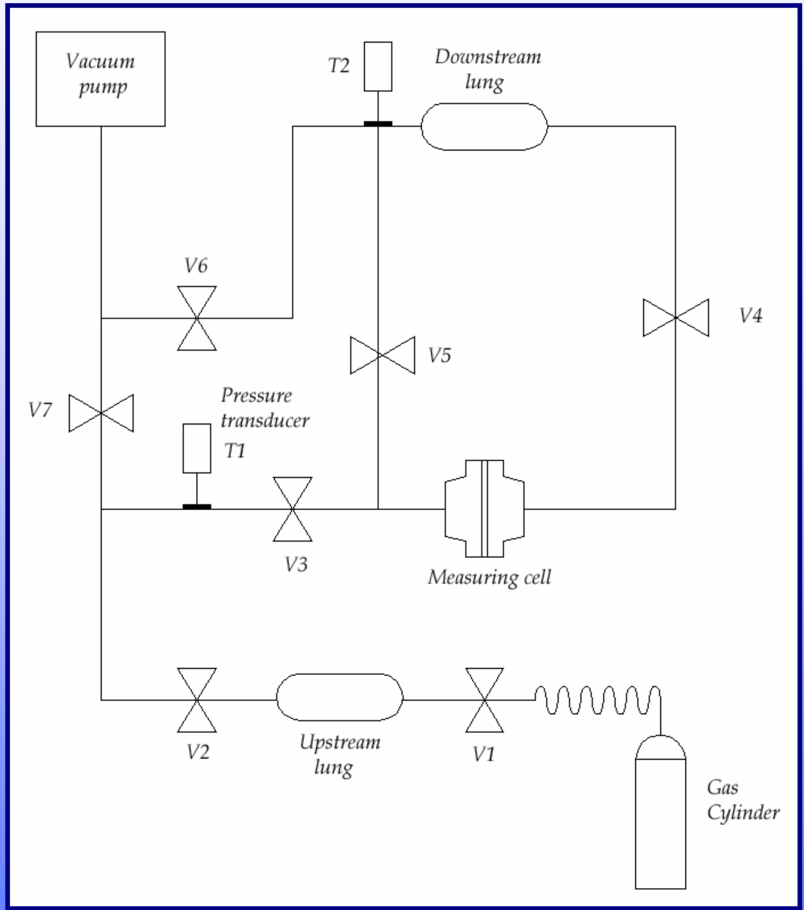
➢The Time Lag Method allows one to determine the permeability (*P*), solubility (*S*), and diffusivity (*D*) coefficients. The time lag is simply the amount of time required for a gas to permeate through a membrane.

➢ The integral technique measures the accumulation of the permeate gas (pressure) as a function of time.



➢ The data is separated into two sections, the first region representing transient diffusion and the second steady-state diffusion.

Mass transport behaviour characterisation



➢ Preliminary permeability experiments have been performed: solubility, diffusion and permeability in the membranes have been evaluated in the 30°-80°C temperature range. The data at cryogenic temperature can be estimate by the Arrhenius-type relation.

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  - ➢ Applicability of nanocomposite materials as internal liner.
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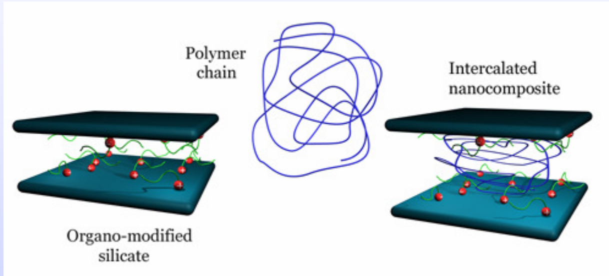
Nanocomposite, in cryogenic propellant storage, could provide:

- increased stability by preventing chemical degradation in aggressive liquid fuel environments
- increased gas barrier properties, originated by an increase in the diffusive path that a penetrant molecule must travel in the presence of filler and a decrease in mobility of macromolecules driven by interaction between nanoparticles and polymeric chain.
- better mechanical properties

Applicability of nanocomposite materials for the liner solution

Type of nanocomposites considered in this work

Polymer-layered nanocomposites are produced promoting the intercalation of the polymer chain, or of a subsequently polymerized precursor, within the galleries of layered host crystals, organo-modified in order to enhance their affinity with the polymer.



RESINS

- EC97 produced by Camattini, Italy, (polyurethane epoxy-terminated resin having a reduced gas permeability)
- DER 331 produced by DOW, that is an epoxy resin

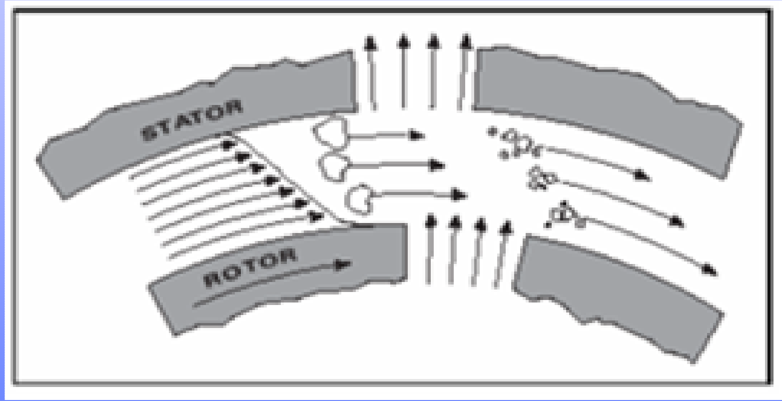
NANOFILLER

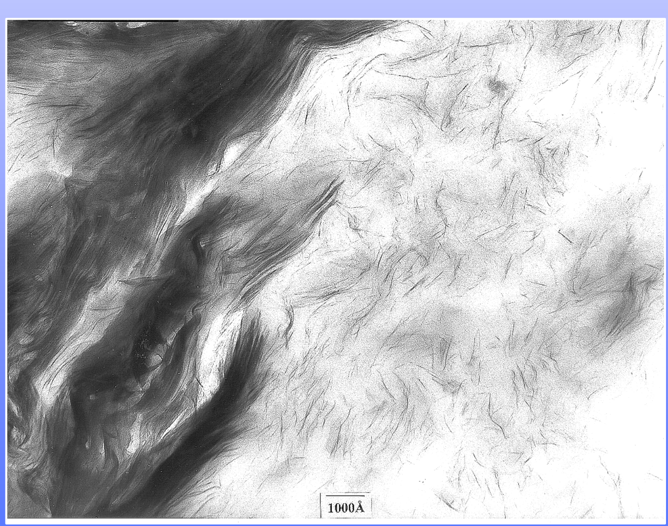
- Hydrotalcite PURAL MG61HT from SASOL (moral ratio Mg/Al = 2/1) modified in house with ABS.
- Dellite AP (commercial organo-modified montmorillonite produced by Laviosa Chimica, modified with a primary ammonium salt)

Nanocomposite Sample Preparation

The polymer-clay mixtures were dispersed with a high performance dispersion device (Ultra turrax D25 basic, IKA WERKE) with a S25N-18G dispersion tool for 5 to 10 minutes at a variable speed ranging from 13500 to 24000 rpm.

Mechanical blends at 3 and 6wt% of each nanofiller were prepared for each of the two matrices selected





Platelets Peel Apart

Nanocomposite Sample Characterization Permeability

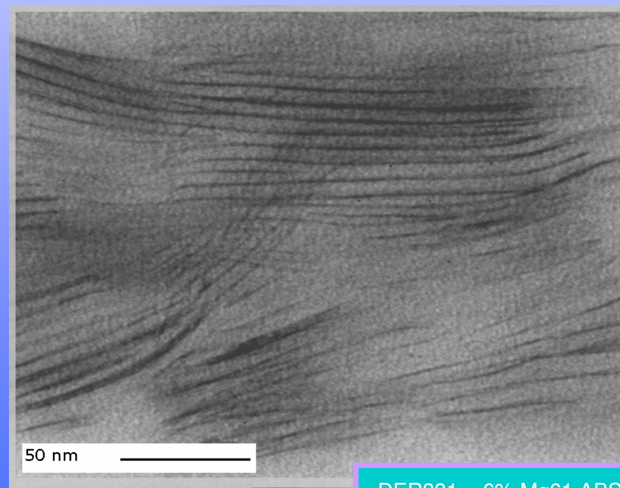
System	Average Permeability ($cm^3 x cm/cm^2 x sec x Pa$)
DER 331	2,72E-15
DER 331+ 3% Mg61ABS	2,61E-15
DER 331 + 6% Mg61ABS	2,22E-15
DER 331+ 3% Del AP	2,58E-15
DER 331 + 6% Del AP	2,50E-15

EC97	8.19E-15
EC97 + 3% Mg61ABS	7,51E-15
EC97 + 6% Mg61ABS	5,47E-15

Measure performed with a MOCOM OX-TRAN 2/60
(carrier flux: 10cc/min; sample surface area: 10 cm2; T=23°C)

$$\frac{P_n}{P_p} = \frac{1-\phi_s}{1+\frac{2L}{6W}\phi_s\left(S+\frac{1}{2}\right)}$$

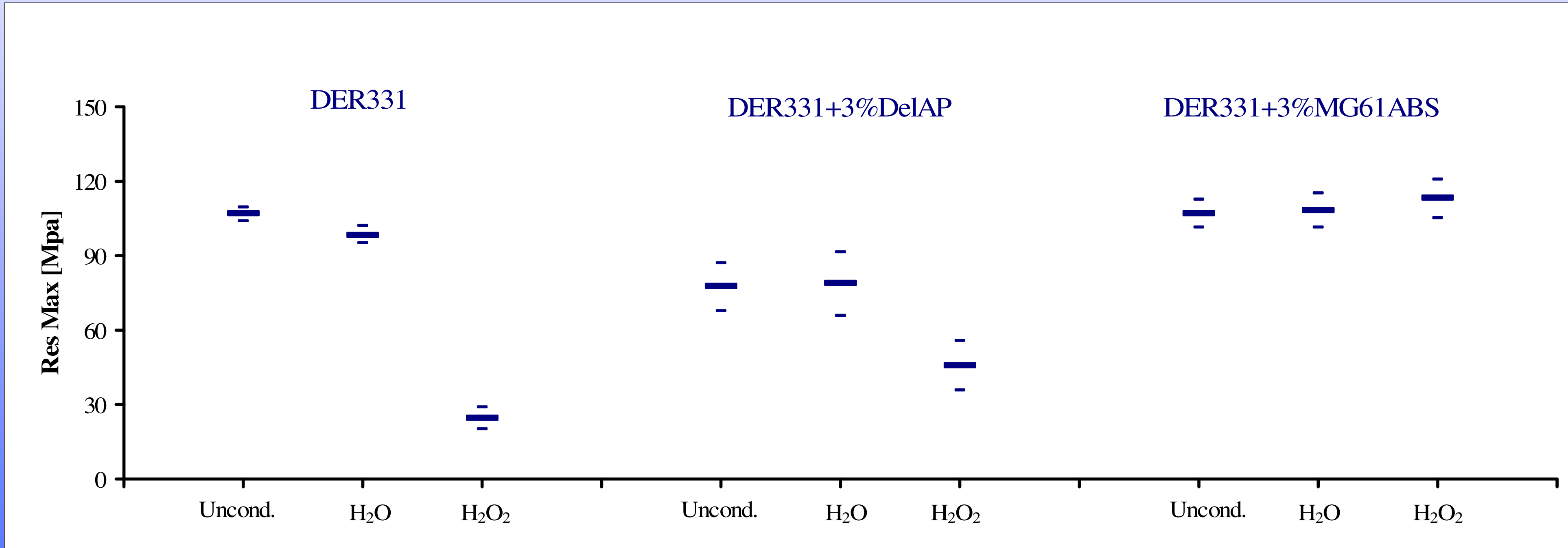
Bharadwaj model (2001): *Pn/Pp* is the relative permeability, *L* and *W* are the mean diameter and the thickness of the platelets, ϕ_s is the volumetric fraction of platelets, *S* is an order parameter



DER331 + 6% Mg61 ABS
110000 x

Nanocomposite Sample Characterization
Chemical resistance

➢ Preliminary tests at ambient temperature were performed by evaluating nanocomposites mechanical properties (flexural) prior and after exposure to hydrogen peroxyde.



The addition of 3wt% of nanoclay prevent from matrix degradation

Conclusions and future work

- The selected composite materials does not show matrix microcrack, delamination or increase of the porosity size caused by the thermal cycles at cryogenic temperatures. This aspect is very important to prevent leakage phenomena in the tank wall and to satisfy the reusable requirements.

- The preliminary results obtained on nanocomposite materials show significant improvements in:

  - ✓ the barrier properties
  - ✓ the chemical resistance to oxygen

- An on-ground qualification campaign will be performed with liquid oxygen on the final scaled prototypes with the aim to verify the compliance of the project product with the fixed requirements.

Thank you for your attention!