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Development Of MOF/Polymer Adsorbent Membranes For Industrial Drying Processes

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Introduction

Metal Organic Frameworks (MOFs): hybrid materials consisting of **metal clusters connected by organic linkers** to form 3D structures.
Properties:

- High specific surface area
- High porosity
- Low density
- High volatility

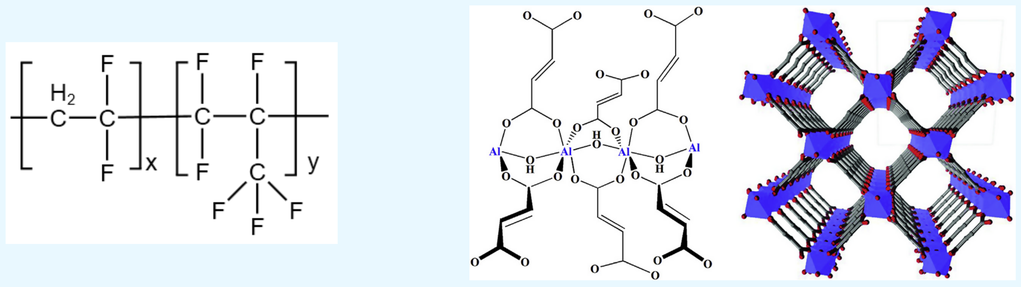
In **technological applications** the use of MOF in form of very fine powder is limited in due to the difficulties in the handling and confinement of the powder.
Thus it is **crucial to:**

- **Stabilize the MOF** (keeping its properties of interest intact)
- Do it in a supported form that is physically and chemically stable

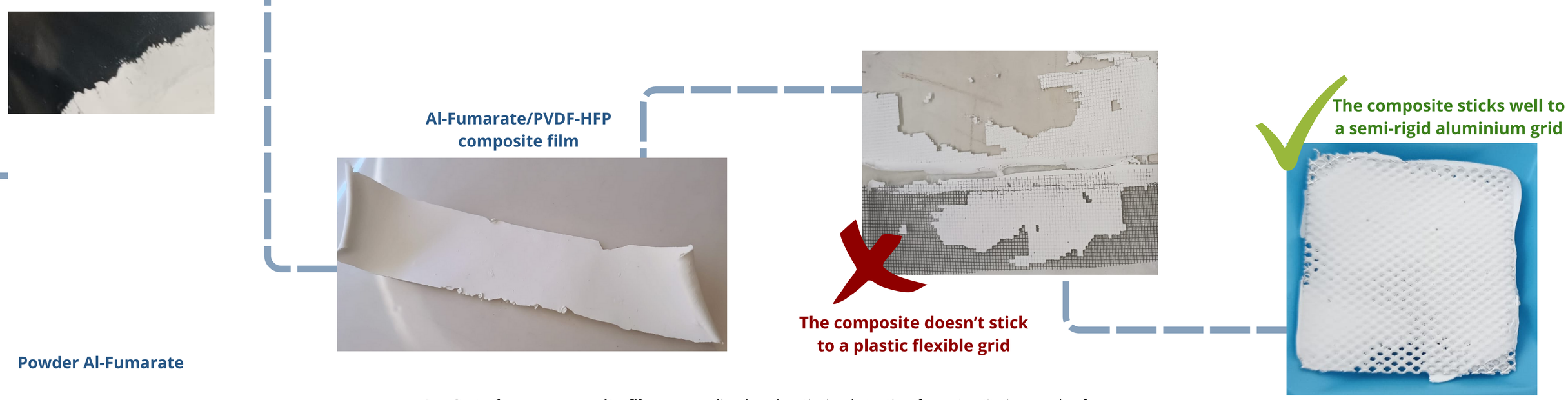
The purpose of this work **is to design and develop an innovative MOF/polymer composite** to be used in the realization of an **innovative desiccant module.**

Materials and Methods

Aluminium fumarate and **PVDF-HFP** were used to prepare MOF/polymer adsorbent membranes. Different samples in form of a **film** were obtained by casting the composite mixtures at various MOF load. The N2 adsorption/desorption analyses allowed to select the **maximum MOF loading** corresponding to the **minimal detriment of specific surface properties**.
Despite its brittleness to shear, the composite films resulted a quite versatile form for adding semi-rigid support to the material. Multiple types of supports were tested, differing in material and stiffness.



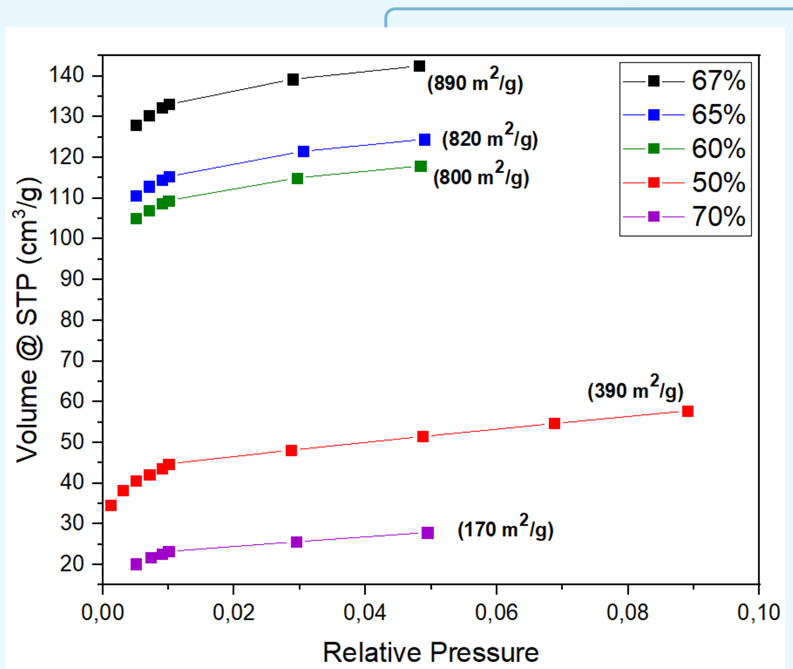
Chemical structures of PVDF-HFP (on the left) and Aluminium Furmarate (on the right)



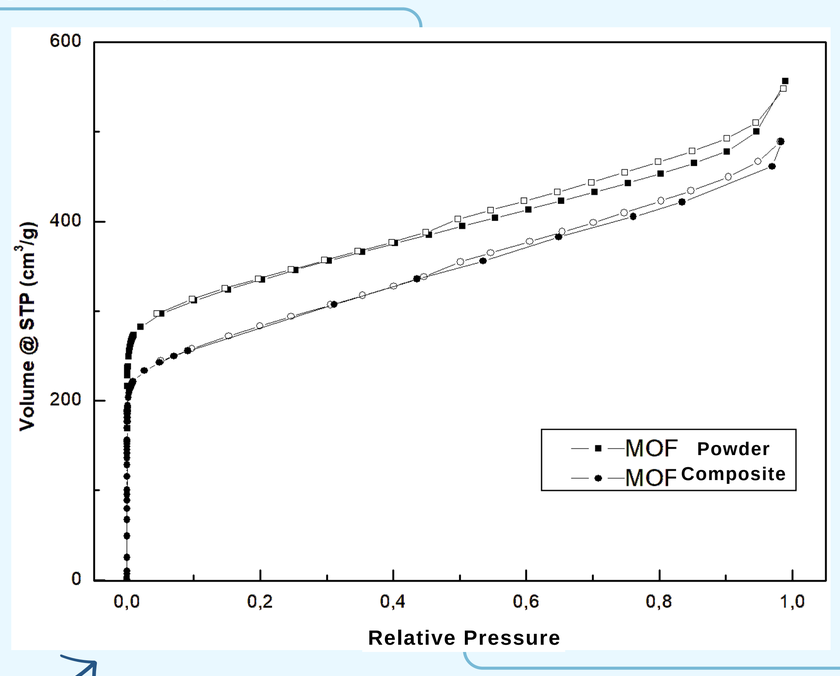
A MOF/polymer composite film was realized and optimized starting from A MOF in powder form.
Different types of grids were tested as able to support the composite film and strengthen it in a dimensionally stable form.

Characterization

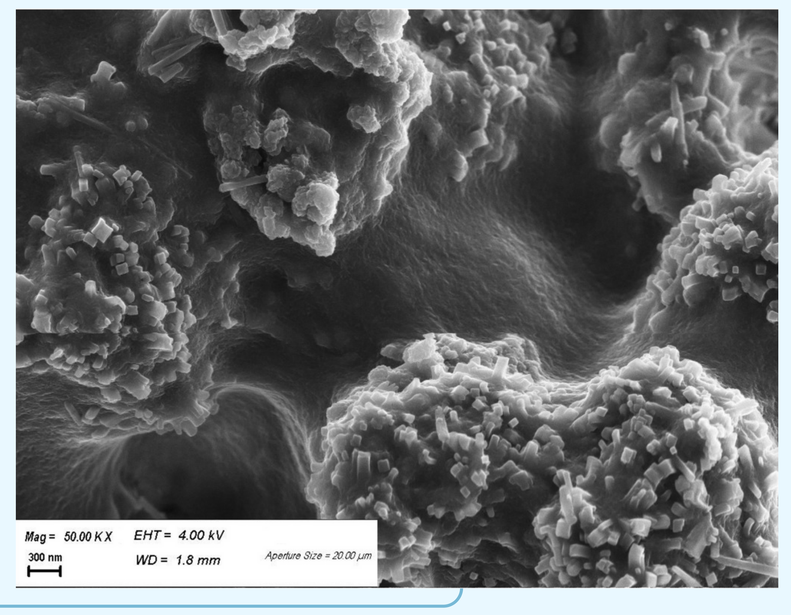
N_2 adsorption/desorption analyses at 77 K



Comparison of BET surface areas for composite samples at different MOF load



SEM analysis of the composite film



The composite at 67% w/w load results the best sample in terms of surface area. Its complete isotherm is compared to the free MOF one (on the left). SEM image (on the right) show Al-fumarate particles only partially embedded in the polymeric matrix, as desired to mantain the MOf adsorption properties

Results and Discussion

The samples were characterized by nitrogen adsorption measurements at 77 K and by SEM. The BET surface area **increases with the amount of MOF load up to 67% w/w** and dramatically decreases at 70% w/w. This reveals the existance of a **threshold effect** in maintaining the adsorptive properties for the Al fumarate when embedded in the polymer matrix.
By comparing the best sample at 67% MOF load with the MOF in form of free powder, it can be seen that the **adsorptive properties are minimally reduced**, resulting the composite suitable for adsorption applications.
In agreement with these results, SEM images show that **MOF particles are partially anchored to the polymer matrix** and are otherwise exposed to the outside with the major part of their external surface available for adsorption.

Conclusions

To address the technological issues connected with the use of the Al-fumarate as adsorbent material in drying prototypal devices, a challenging approach for supporting the MOF on a stable support was developed. The realization of a composite material at **high MOF loading with minimal decrease of surface properties was achieved**. Work is in progress for the characterization of the mechanical properties of the film as fixed on semi-rigid grids. In addition, preliminary results (not reported), show **appreciable features in terms of water vapour adsorbtion isotherms**. Much efforts are currently devoted to the realization and testing of an innovative desiccant module based on the supported MOF/polymer composite.

References

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