Hydrothermal Aging of SAPO-34/Nexar Composites in Thermal Energy Storage Systems

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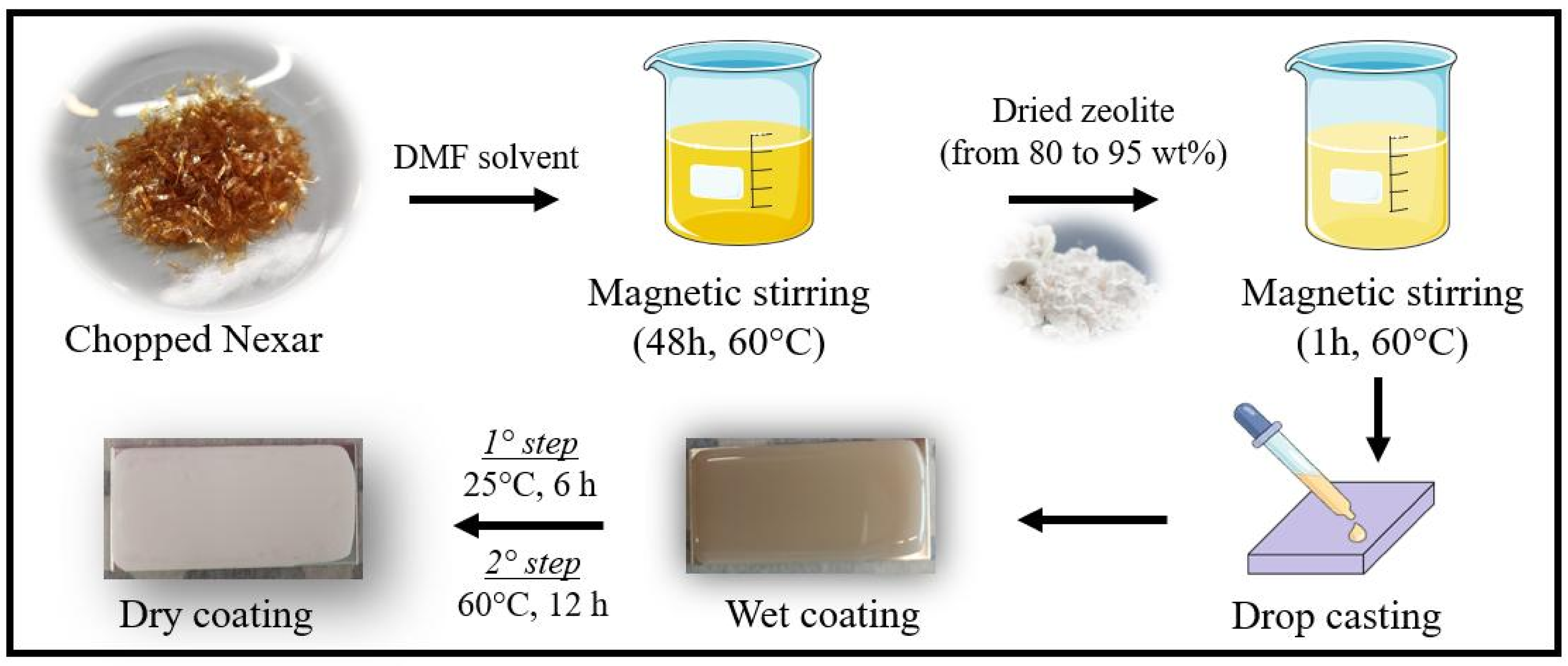
INTRODUCTION

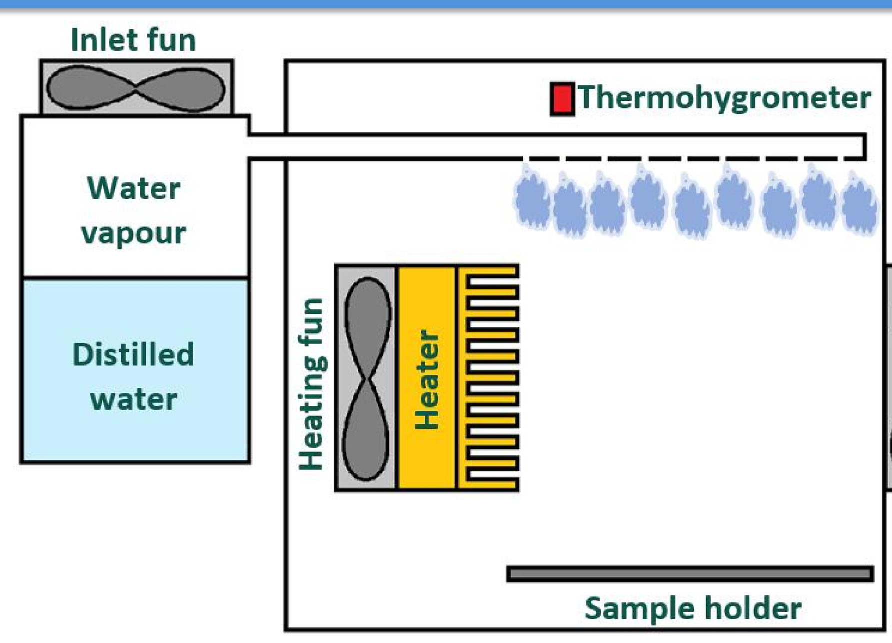
Efficient Thermal Energy Storage (TES) systems are vital for advancing energy efficiency and integrating renewable sources. Within this context, innovative composite coatings offer a promising avenue to enhance TES system effectiveness and longevity. Tris study focuses on developing and characterizing novel composite coatings, specifically tailored for TES applications, consisting of a sulfonated pentablock terpolymer (Nexar) matrix, known for its excellent water vapor permeability, filled with SAPO-34 zeolite filler, a microporous substance with high heat exchange capabilities at lower temperatures. A significant challenge for adsorbent coatings and composite materials lies in their susceptibility to aging, particularly when the polymeric matrix is crucial for maintaining structural and functional integrity. Prolonged exposure to adsorbates like water vapor can severely degrade the coating's performance. Therefore, rigorously assessing the composite's aging response is indispensable for confirming its practical viability.

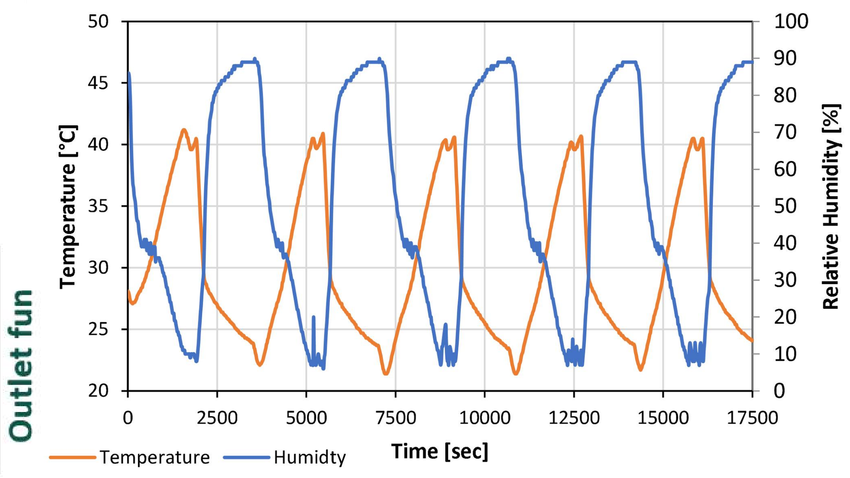
EXPERIMENTAL PART

For coatings preparation (300 - 500 µm thick), Nexar polymer was dissolved in N,N-Dimethylformamide (DMF) at 60°C for 48 hours. Dehydrated SAPO-34 zeolite powder (5 - 10 µm) was incorporated into this solution (80 - 95 wt%) and stirred for an hour at 60°C. The composite suspension was drop-casted onto aluminum plates and dried in two stages, first at ambient temperature for 3 hours and then overnight at 60°C.
The coatings underwent testing, before and after aging, to assess their:

- Mechanical performances (scratch and pull-off test)
- Thermal stability (thermogravimetric analysis - TGA)
- Adsorption properties (dynamic vapor sorption - DVS)





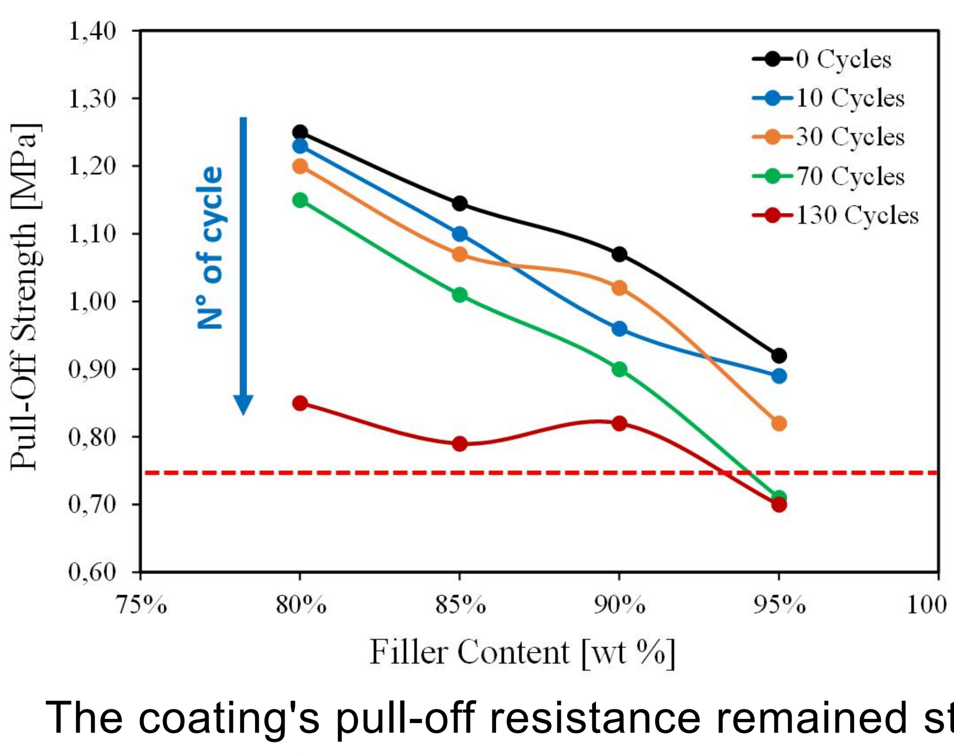


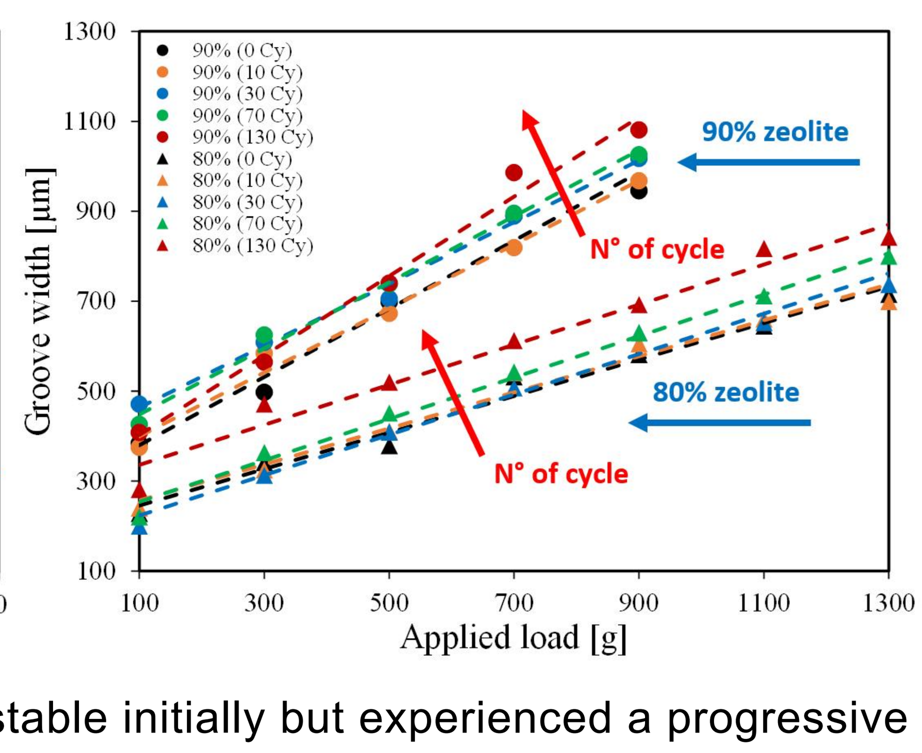
"Dry" conditions 40 °C e 20% RH
"Wet" conditions 30 °C e 90% RH

A prototype climatic chamber was developed to simulate wet/dry cycles. This chamber is thermally insulated and connected to a steam generator. Inside, a heating element coupled with a fan maintains the set temperature, while a second fan exhausts internal humidity to the outside.

- **Phase "To Dry":** The steam generator is switched off. The outlet fun and the heating element are active. Once Dry conditions are reached, the next phase begins.
- **Phase "Dry":** Dry conditions are maintained.
- **Phase "To Wet":** The heating element is switched off and the steam generator is switched on. Once Wet conditions are reached, the next phase begins.
- **Phase "Wet":** Wet conditions are maintained.

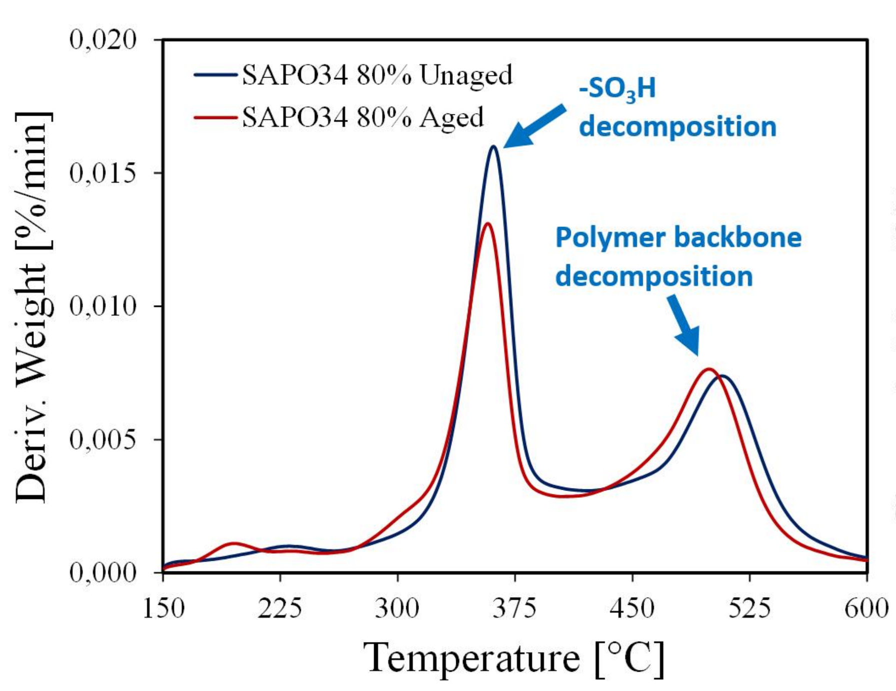
RESULTS & DISCUSSION

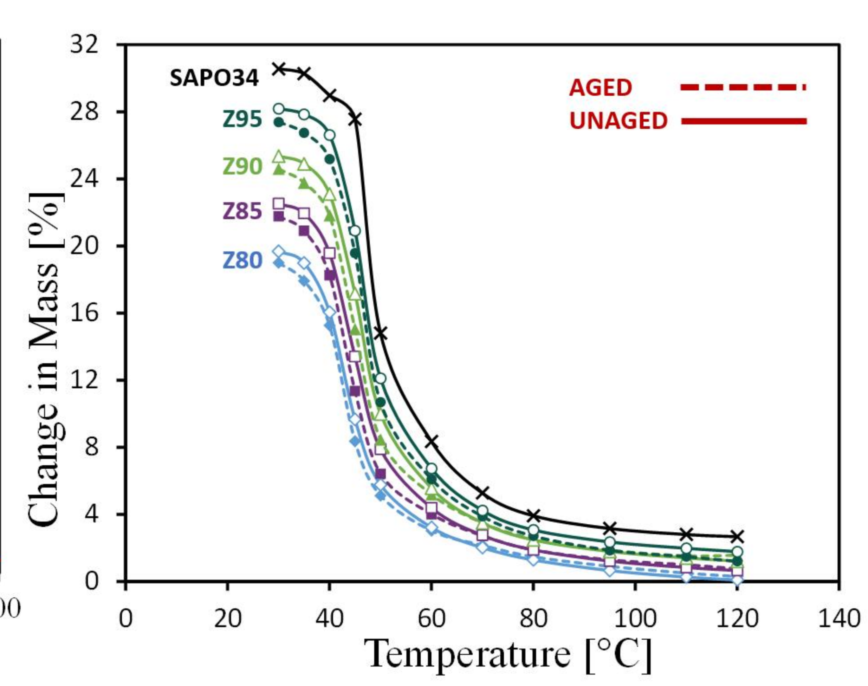




The coating's pull-off resistance remained stable initially but experienced a progressive decrease after 70 aging cycles, eventually stabilizing at 0.8 MPa. This reduction in adhesion is caused by vapor penetration at the interface. The 90% zeolite formulation proved to be the most mechanically stable, effectively balancing polymer permeability and matrix instability.
Concurrently, scratch test results indicated that deterioration is more pronounced in low-zeolite content coatings (a 25% groove increase) compared to high-zeolite content coatings (an average increase of 10%).

The thermal stability analyzed via TGA indicates that the curves for aged and unaged samples are essentially superimposable; however, limited deterioration of the polymer is evidenced by a slight shift (an advance of 3.6 °C and 8.0 °C in the decomposition peaks of the sulfonic groups and the polymer backbone, respectively).
The influence of aging on adsorption capacity was found to be slight, with the coatings showing a maximum reduction of only 2.9% - 3.5% after 130 cycles. This performance loss, potentially due to polymer degradation, is not sufficient to compromise its functionality.





CONCLUSION

- The coatings examined show a degradation of mechanical properties with an increasing number of aging cycles. However, the extent of this degradation depends on the zeolite content, as the coatings with the highest and lowest zeolite contents show a greater reduction in properties, though not enough to compromise their functionality.
- The adsorption isobars show a negligible reduction in maximum capacity, suggesting a possible polymer degradation. This is confirmed by thermogravimetric analysis (TGA), which highlighted a shift to lower temperatures in the degradation peaks, indicating a limited reduction in thermal stability.
- These more contained reductions in mechanical properties observed in the coatings with 90% by weight of zeolite, the composition chosen to balance mechanical integrity with water vapor adsorption capacity, are potentially compatible with thermochemical energy storage applications.

ACKNOWLEDGEMENT

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