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Process influences on the structure, piezoelectric and gas-barrier properties of P(VDF-TrFE) (81-19) copolymer

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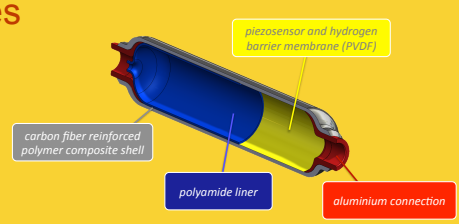
Objective and Challenges

Development of a novel gas-barrier membrane based on a piezoelectric polymer, to be used as a self-sensing liner for a high pressure hydrogen storage vessel.

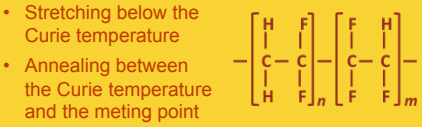
Challenges were to find a material and a processing method to reduce the gas permeability of the polymer without loosing its piezoelectric performance.



Material and Process

Copolymer of poly(vinylidene fluoride) and trifluoroethylene (PVDF-TrFE) (81-19 mol%) with crystalline polymorphisms including α and polar all-trans β piezoelectric phases.

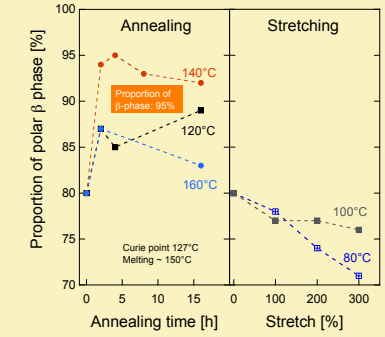
- Stretching below the Curie temperature
- Annealing between the Curie temperature and the meting point

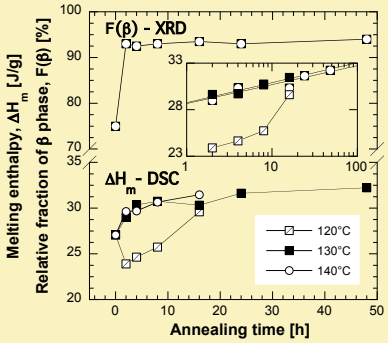


Structure

Calorimetry and XRD analyses show that annealing between the Curie temperature and the melting point enabled to increase the proportion of the piezoelectric crystalline β phase up to 95%.

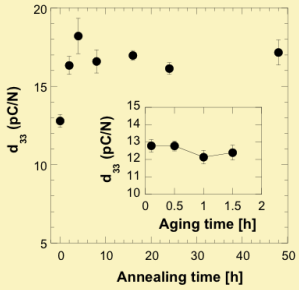
In contrast, complex stretching treatments led to a decrease of the amount of β phase.





Piezoelectricity

The piezoelectric coefficient d_{33} of the polymer increased by more than 30% after annealing for 4 h at 140°C, and it was stable upon aging.



Conclusions

An optimal annealing process was elaborated to increase the proportion of the piezoelectric crystalline β phase in a PVDF-TrFE (81-19) copolymer, based on fundamental calorimetry and *in-situ* XRD analyses.

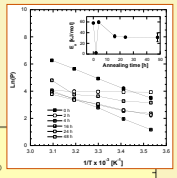
A combined improvement of the piezoelectric performance (+30%) and of the gas-barrier properties (x 10) was obtained after annealing the PVDF-TrFE copolymer for 4 h at 140°C.

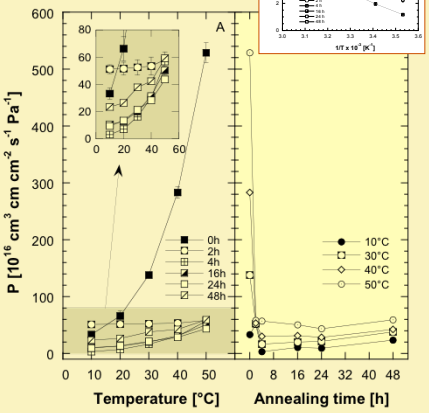
The gas-barrier performance of the annealed copolymer is outstanding. A PVDF-based piezoliner was produced and integrated in a working demonstrator of a self-sensing carbon fiber reinforced composite pressure vessel.

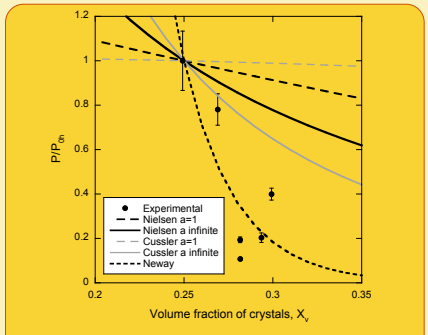
Gas-barrier Properties

The oxygen permeability of the polymer was reduced 10 fold after annealing for 4 h at 140°C, which is remarkable.

The activation energy for oxygen transport was also reduced twofold after annealing.







The oxygen permeability of PVDF-TrFE (normalized with respect to the permeability of the solvent cast polymer) decreases faster with increasing volume fraction of crystals than classic Nielsen and Cussler model predictions (a is the aspect ratio of the crystals; 'Neway' is an empirical exponential model).

Acknowledgements & References

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