

Macroporous Polymeric Oxygen Scavenger Material

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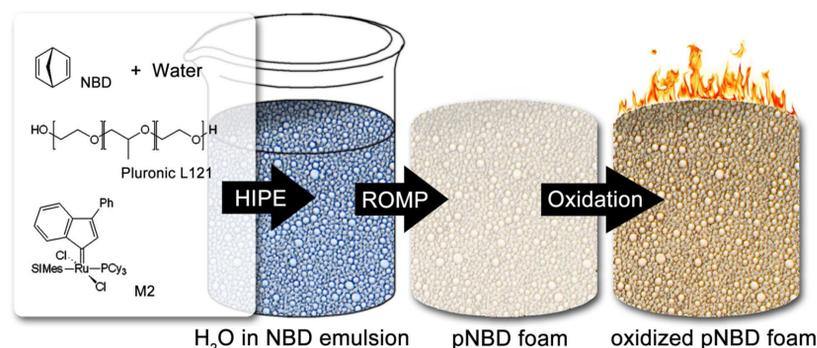
Introduction

Oxygen can have considerable detrimental effects on goods prone to oxidation, in particular food. Oxygen scavengers (sometimes referred to as oxygen absorbers) are therefore a mean to maintain food product quality. Reduced oxygen contents decrease the food metabolism, reduce oxidative rancidity, inhibits oxidation of labile vitamins and pigments, and, maybe most importantly, inhibits the growth of aerobic microorganisms. Most oxygen scavengers are based on iron powders containing catalysts, which react with some water from the surroundings to produce a reactive hydrated metallic reducing agent that scavenges oxygen and irreversibly converts it to a stable oxide. Such oxygen scavengers are capable of reducing oxygen levels to less than 0.01% (100 ppm_(v)) which is much lower than the typical 0.3–3.0% (3000 – 30000 ppm_(v)) residual oxygen levels achievable by modified atmosphere packaging (MAP). However, the oxygen scavenging capability is rapidly lost in case too much water is present. The iron powder is packed in a highly oxygen permeable sachet to separate it from the food, which constitutes another disadvantage of possible accidental ingestion of the contents by the consumer. This has considerably hampered their commercial success, particularly in North America and Europe. As an alternative, in particular for protecting liquids, various non-metallic reagents and organometallic compounds that have an affinity for oxygen have been incorporated into bottle closures, crown and caps or blended into polymer materials so that oxygen is scavenged from the bottle headspace and any ingressing oxygen is also scavenged. However, it should be noted that the speed and capacity of oxygen scavenging plastic films and laminated trays are considerably lower compared to iron based oxygen scavenger sachets or labels.¹

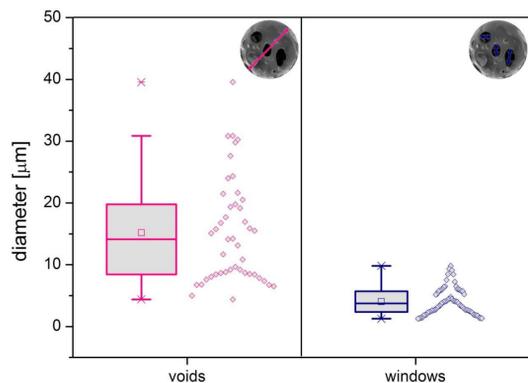
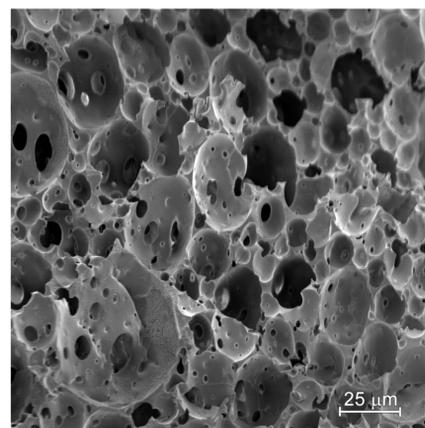
Herein, a hitherto unprecedented polymeric material for oxygen removal, namely a macroporous poly(norbornadiene) foam prepared by curing of a high internal phase emulsion of norbornadiene (NBD) in water via Ring-opening Metathesis polymerization (ROMP) is described.

Preparation

Foams of 80% nominal porosity were prepared by adding 7.5 g (81.4 mmol) of NBD and 0.525 g of the surfactant Pluronic L121 (7 wt% in respect to NBD) into a 250 mL three necked round bottom flask.² Subsequently, the mixture was stirred with a mechanical stirrer at 400 rpm while 30 mL distilled water were added dropwise. Afterwards, stirring was continued for 1 h. Then, 1.93 mg (0.002 mmol) of the initiator M2 dissolved in 200 µL toluene was added under severe agitation. The pinky viscous mixture was poured into molds and cured at 40 °C for 2h. The resulted white monoliths were put into acetone for 10 min and subsequently dried under vacuum at room temperature.

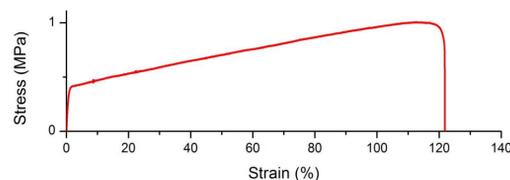


Characterization of the foams



Box-whisker/bee swarm plot of void and window size distribution (median: horizontal line in the box; quartiles: upper and lower limit of the box, the boxes represent a restricted area where half of the overall values are included; average: □; whiskers: 1.5-IQR. Bee swarm plot showing a one-dimension dispersion of densely packed and non-overlapping data points)

Scanning electron micrograph of the pNBD-foam, median (average) void diameter: 14.2 (15.2) µm, median (average) window diameter: 3.75 (4.14) µm; values retrieved from the plot on the right.



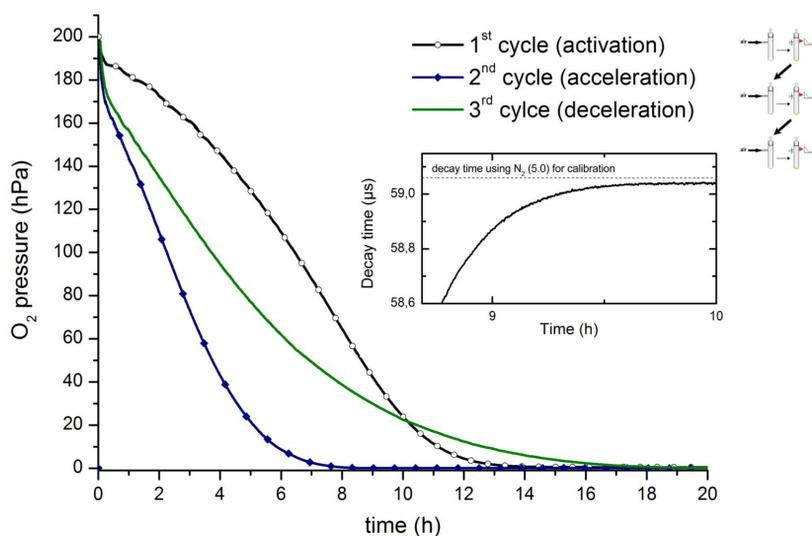
mechanical properties

Young's modulus	68 ± 9 MPa
ultimate tensile strength	1.07 ± 0.03 MPa
max strain	105 ± 11 %
0.2 % offset yield point (MPa)	0.45 ± 0.08
elongation @ yield point (%)	0.45 ± 0.10
modulus of toughness (MJ/m ³)	0.86 ± 0.08

Mechanical properties were assessed by stress strain testing at room temperature at a rate of 5 mm/min. HIPE was casted into Teflon molds (shouldered tensile test specimens, of 5 mm width at breaking point, thickness of 3 mm, 43 mm gage length, 62 mm distance between shoulders and 100 mm overall length).



Photograph of cylindrical specimens after self-inclination at room temperature during drying under ambient conditions.



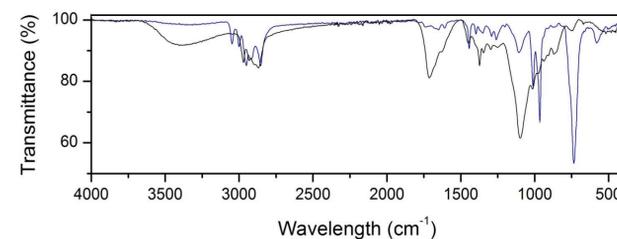
Monitoring of the oxygen partial pressure over time the pNBD-foam (626 mg) was placed in an air-filled tightly closed reaction vessel (volume 270 mL) with two optical sensor spots mounted (a sensor spot with a dynamic range from 1000 hPa to 1 hPa (PyroScience) and a trace sensor spot (homemade³) with a dynamic range from 50 hPa to 0.003 hPa). The lifetime of the optical sensor material was read out throughout the vessel's wall using the optical oxygen meters FireStingO2. After the 1st cycle the vessel was evacuated and refilled with air and the 2nd cycle was recorded this procedure was repeated to obtain the 3rd cycle.

Inset: life time measurement from the trace sensor spot revealed final oxygen levels of at least 0.0003 vol%, i.e. 3 ppm (0.003 hPa is the LOD of the oxygen trace sensor).



Oxygen scavenging

Weight balance	
volume of O ₂ provided	160 mL
mass pNBD foam provided	0.6258 g
mass pNBD foam obtained	0.8115 g
weight increase	23 wt%
mass O ₂ incorporated	0.1857 g
O ₂ incorporation per repeating unit	1.2
final O ₂ content	less than 3 ppm _(v)



IR spectra of unoxidized (blue) and oxidized (black) pNBD-foams.

Conclusion

Emulsion templated norbornadiene was cured via ROMP yielding macroporous poly(norbornadiene) foams of 80% porosity exhibiting appealing stiffness combined with considerable ductility. The foams are readily oxidized in the presence of oxygen and can therefore be used to scavenge oxygen. The presented material is, to the best of our knowledge, the first example of a purely organic oxygen scavenger material which distinctly surpasses the performance of typically applied state-of-the art oxygen scavengers by providing an approx. 2 orders of magnitude lower final oxygen level in about the same time. The disclosed measurement setup might also serve for a fast evaluation of oxidation inhibitor additives for plastic goods.

References

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