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Even as temperatures rise, this hydrogel material keeps absorbing moisture

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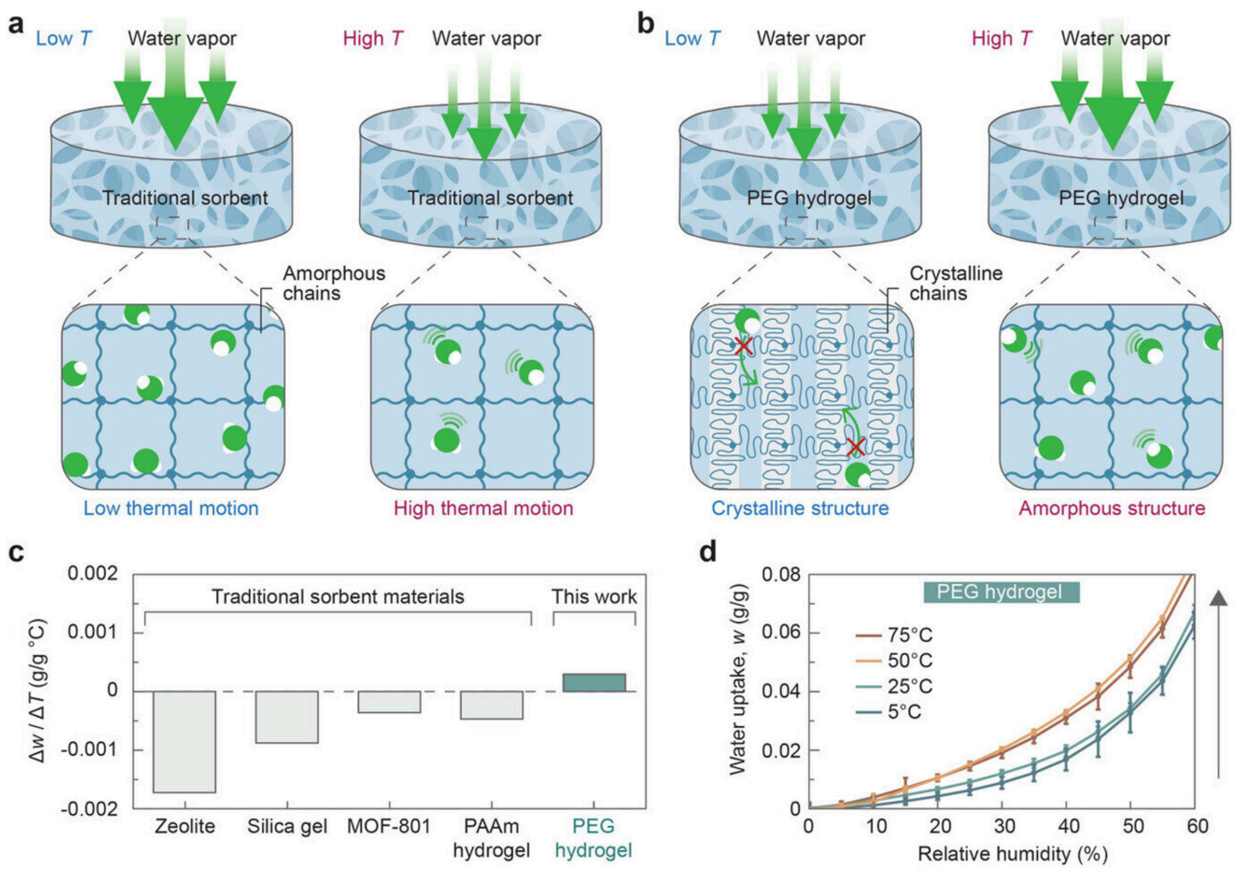

Dependence of water sorption on temperature. a) Schematic of traditional sorbents: sorption at a low temperature and desorption at a high temperature. b) Schematic of PEG hydrogels: desorption at a low temperature and sorption at a high temperature. The temperature-controlled phase transformation of nanocrystalline structures creates different interactions between the polymer and water molecules. When it is cooler than the melting point (T_m), the PEG chains are semicrystalline. When it is hotter than T_m, the PEG chains are amorphous. c)

Comparison of the temperature sensitivity of water sorption of four representative traditional sorbent materials[3, 6, 7, 9, 19] and the PEG hydrogel. The water uptake change (Δw) is obtained at ≈40% RH and the temperature change (ΔT) is ≈ 50 °C. d) Water vapor uptake isotherms of the PEG hydrogel in g g^{-1} (g of water per g of the dried PEG hydrogel, *w*) as a function of RH at temperatures of 5, 25, 50, and 75 °C. Arrow: temperature increases. Error bars: standard deviations of three independent measurements. Credit: *Advanced Materials* (2023). DOI: 10.1002/adma.202211763

The vast majority of absorbent materials will lose their ability to retain water as temperatures rise. This is why our skin starts to sweat and why plants dry out in the heat. Even materials that are designed to soak up moisture, such as the silica gel packs in consumer packaging, will lose their sponge-like properties as their environment heats up.

But one material appears to uniquely resist heat's drying effects. MIT engineers have now found that polyethylene glycol (PEG)—a hydrogel commonly used in cosmetic creams, industrial coatings, and pharmaceutical capsules—can absorb moisture from the atmosphere even as temperatures climb.

The material doubles its water absorption as temperatures climb from 25 to 50 degrees Celsius (77 to 122 degrees Fahrenheit), the team reports.

PEG's resilience stems from a heat-triggering transformation. As its surroundings heat up, the hydrogel's microstructure morphs from a crystal to a less organized "amorphous" phase, which enhances the material's ability to capture water.

Based on PEG's unique properties, the team developed a model that can be used to engineer other heat-resistant, water-absorbing materials. The group envisions such materials could one day be made into devices that harvest moisture from the air for drinking water, particularly in arid desert regions. The materials could also be incorporated into heat pumps and air conditioners to more efficiently regulate temperature and humidity.

"A huge amount of energy consumption in buildings is used for thermal regulation," says Lenan Zhang, a research scientist in MIT's Department of Mechanical Engineering. "This material could be a key component of passive climate-control systems."

Zhang and his colleagues detail their work in a study appearing today in *Advanced Materials*. MIT co-authors include Xinyue Liu, Bachir El Fil, Carlos Diaz-Marin, Yang Zhong, Xiangyu Li, and Evelyn Wang, along with Shaoting Lin of Michigan State University.

Against intuition

Evelyn Wang's group in MIT's Device Research Lab aims to address energy and water challenges through the design of new materials and devices that sustainably manage water and heat. The team discovered PEG's unusual properties as they were assessing a slew of similar hydrogels for their water-harvesting abilities.

"We were looking for a high-performance material that could capture water for different applications," Zhang says. "Hydrogels are a perfect candidate, because they are mostly made of water and a polymer network. They can simultaneously expand as they absorb water, making them ideal for regulating humidity and water vapor."

The team analyzed a variety of hydrogels, including PEG, by placing each material on a scale that was set within a climate-controlled chamber. A material became heavier as it absorbed more moisture. By recording a material's changing weight, the researchers could track its ability to absorb moisture as they tuned the chamber's temperature and humidity.

What they observed was typical of most materials: as the temperature increased, the hyrogels' ability to capture moisture from the air decreased. The reason for this temperature-dependence is well-understood: With heat comes motion, and at higher temperatures, water molecules move faster and are therefore more difficult to contain in most materials.

"Our intuition tells us that at higher temperatures, materials tend to lose their ability to capture water," says co-author Xinyue Liu. "So, we were very surprised by PEG because it has this inverse relationship."

In fact, they found that PEG grew heavier and continued to absorb water as the researchers raised the chamber's temperature from 25 to 50 degrees Celsius.

"At first, we thought we had measured some errors, and thought this could not be possible," Liu says. "After we double-checked everything was correct in the experiment, we realized this was really happening, and this is the only known material that shows increasing water absorbing ability with higher temperature."

A lucky catch

The group zeroed in on PEG to try and identify the reason for its unusual, heat-resilient performance. They found that the material has a natural melting point at around 50 degrees Celsius, meaning that the hydrogel's normally crystal-like microstructure completely breaks down and transforms into an amorphous phase. Zhang says that this melted, amorphous phase provides more opportunity for polymers in the material to grab hold of any fast-moving water molecules.

"In the crystal phase, there might be only a few sites on a polymer available to attract water and bind," Zhang says. "But in the amorphous phase, you might have many more sites available. So, the overall performance can increase with increased temperature."

The team then developed a theory to predict how hydrogels absorb water, and showed that the theory could also explain PEG's unusual behavior if the researchers added a "missing term" to the theory. That missing term was the effect of phase transformation. They found that when they included this effect, the theory could predict PEG's behavior, along with that of other temperature-limiting hydrogels.

The discovery of PEG's unique properties was in large part by chance. The material's melting temperature just happens to be within the range where water is a liquid, enabling them to catch PEG's phase transformation and its resulting super-soaking behavior. The other hydrogels happen to have melting temperatures that fall outside this range. But the researchers suspect that these materials are also capable of similar phase transformations once they hit their melting temperatures.

"Other polymers could in theory exhibit this same behavior, if we can engineer their melting points within a selected temperature range," says team member Shaoting Lin.

Now that the group has worked out a theory, they plan to use it as a blueprint to design materials specifically for capturing water at higher temperatures.

"We want to customize our design to make sure a material can absorb a relatively high amount of water, at low humidity and high temperatures," Liu says. "Then it could be used for atmospheric water harvesting, to bring people potable water in hot, arid environments."

More information: Xinyue Liu et al, Unusual Temperature Dependence of Water Sorption in Semicrystalline Hydrogels, *Advanced Materials* (2023). DOI: 10.1002/adma.202211763

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