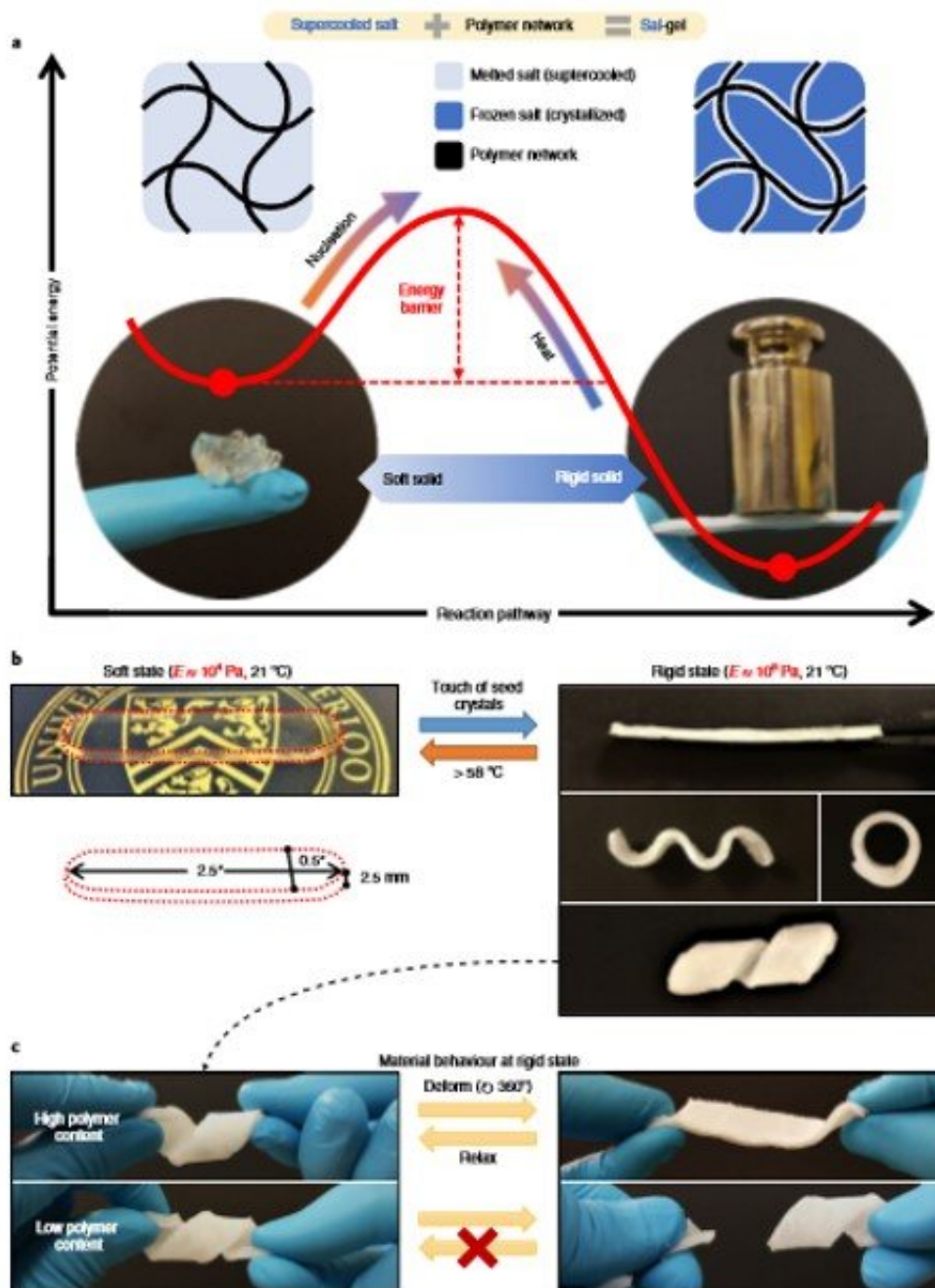


A hybrid material that switches reversibly between two stable solid states

August 7 2019, by Thamarasee Jeewandara



Material behaviors of sal-gel. (a) An illustrative plot of potential energy as a function of reaction pathway, characterized by an energy barrier between two stable solid states with distinct mechanical properties. The squares depict the conceptual molecular portraits of sal-gel, where the salt is melted in the soft state and frozen in the rigid state. The photographs illustrate the mechanical behavior of sal-gel, which is flexible enough to be folded onto itself in the soft state but stiff enough to hold a weight of 200 g in the rigid state. (b) On-demand shape-fixing of sal-gel (P10L10) by manipulating its shape in the soft state and then fixing the shape by touching the gel with salt seed crystals. The fixed shape can be reversed by heating the gel (>58 °C). (c) At high polymer content (P30L10), the material is elastic and flexible, deforming when twisted but returning to the original fixed shape when the force is released. At low polymer content (P10L10), the fixed shape is rigid and inflexible and breaks on twisting. Credit: Nature Materials, doi: 10.1038/s41563-019-0434-0

Solid matter typically contains a single, stable solid state for a specific set of conditions. Materials scientists envision that new materials with interchangeable solid states will be advantageous for diverse technical applications. In a new report now published on *Nature Materials*, Fut (Kuo) Yang and colleagues in the interdisciplinary departments of Chemical Engineering, Bioengineering and Biotechnology in Canada and China described the development of a two-in-one hybrid material.

They composed the material with a polymer impregnated with a supercooled [salt solution](#) known as "sal-gel." The material assumed two distinct but stable and reversible solid states under varying temperatures (-90 degrees C to 58 degrees C) and pressures. When the scientists stimulated nucleation, the material shifted from a clear, soft solid to a white hard state that was 10^4 times stiffer than the original (15 kPa vs. 385 MPa). They reversed the hard solid back to soft consistency via

transient heating to demonstrate reversibility of the transition. The study explored the concept of robust physical metastability of a liquid state and Yang et al. extended the work to sugar alcohols to form stimuli-responsive and non-evaporating "sug-gel." Such two-in-one hybrid materials will be useful in soft robotics and adhesive applications.

[Stiffness changing materials](#) offer a solution to engineer paradoxical shape adaptability and load-bearing capabilities that are important for a variety of technical areas including [soft robotics](#), [adhesion/adhesives](#) and [aeronautics](#). Sustaining the mechanical response of such [smart materials](#) is, however, limited by the requirement for an external stimulus. A solution to create two-in-one solids is to explore the mechanical or structural metastability of such materials. This is observed with [origami- or kirigami-inspired](#) metamaterials that can transform their stiffness via changes in topological states.

To obtain dual stable states, the underlying mechanism must form an energy barrier between the two, where each state rested at an energetic minimum. For instance, liquid crystallization can meet this requirement where the liquid initially required formation of a sufficiently large cluster of crystalline atoms or molecules. The free energy gain of transforming the crystalline phase must then overcome the free energy cost of creating an interface between the [liquid and the crystal](#). Scientists could overcome the [energy barrier](#) between the interfaces by inducing self-assembly via [secondary nucleation](#) (formation of new crystals from existing crystals) for liquid-to-crystalline transformations and with heat for crystalline-to-liquid transformation. The process is comparatively more difficult for phase transformations with pure solids whose crystalline and non-crystalline phases are both solids.

Soft-to-Hard Transitional Contact

Demonstrating the joining of sal-gel
in the soft state to a golf ball and the
subsequent lifting of the gel in the
soft or rigid state

Soft-to-hard transition on contact of sal-gel. Credit: Nature Materials, doi: 10.1038/s41563-019-0434-0

As an example material, [sodium acetate trihydrate](#) is a phase-changing material (PCM) commonly known as "hot ice," as it releases heat during freezing with well-known capacity to supercool. Although the solid has a melting point of 58 degrees C, it can remain stable as a supercooled liquid at room temperature for years, with application in [seasonal energy storage](#). Yang et al. provided the solid sodium acetate trihydrate an additional solid form by using a compatible polymer network to produce a printable and light-weight [hybrid material](#) known as sal-gel. The material could interchangeably switch its effective stiffness without external stimulation, allowing the scientists to fully leverage the phase transition and metastability of the salt.

The hybrid material transformed to a rubber-like form on melting for on-demand shape-fixing with a change in stiffness greater than 10^4 times. The feature is highly desirable for "two-in-one" solids compared to previously developed [stiffness-changing materials](#). The new material is relevant for the ever-growing performance to miniaturize and increase performance density of multifunctional materials.

Material Behavior at Rigid State

Demonstrating the difference between samples with low and high polymer content in their rigid states

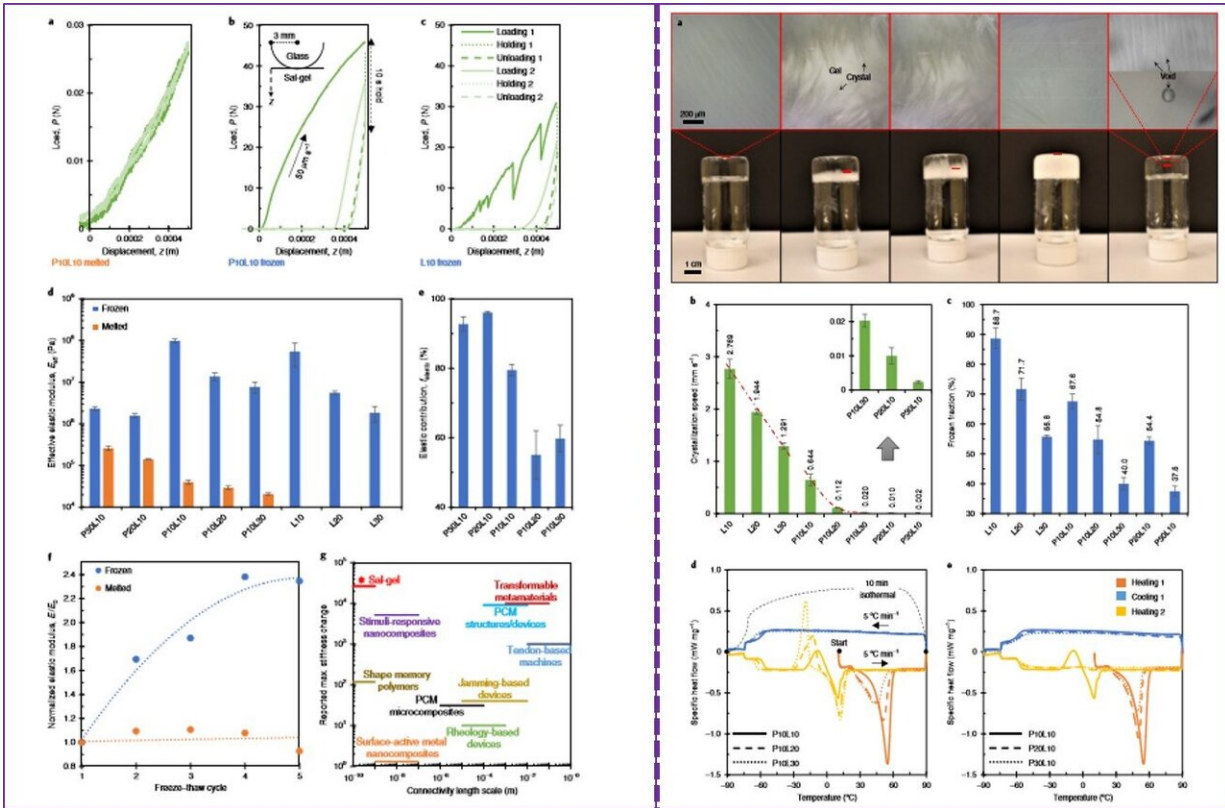
Sal-gel properties at the rigid state. Behavior at low polymer content vs. high polymer content. Credit: Nature Materials, doi: 10.1038/s41563-019-0434-0

The scientists prepared sal-gel by mixing melted sodium acetate trihydrate with polymer pre-cursors of [poly\(acrylic acid\)](#) and a liquid mixture of acetic acid with water. The resulting gel mixture remained transparent, suggesting the constituents to be miscible with each other. The resulting gel had two solid states; a transparent soft state and an opaque rigid state that resisted deformation. The scientists transformed the sal-gel from its soft state to the rigid state via secondary nucleation through the touch of sodium acetate trihydrate seed crystals. Upon contact with a seed crystal, nucleation occurred immediately for crystallization to proceed from the point-of-contact across the entire material.

To conduct the initiation experimentally, Yang et al. used a wooden stick

with a small amount of fine crystal dust at the tip. Since the phenomenon originated from the sample surface, they assumed a two-fold cause; where at first, the free energy cost for nucleation greatly lowered at the gel's surface due to reduced surface area. Thereafter, on contact, the surface experienced an enormous [amount of kinetic energy](#). As long as the gel remained lubricated, the scientists could prevent unwanted crystallization. Yang et al. reversed the sal-gel to its soft state by heating it above the melting point and used these properties to fix the shape of the gel on-demand. They tuned the physical properties of the frozen state by manipulating the polymer content of the gel to withstand deformation and return to its fixed shape upon stress release.

The research team tested the [mechanical behavior](#) of the two states of the sal-gel system under similar environments using [indentation](#). They compared the melted and frozen sal-gel, where a visible plastic deformation formed on the frozen state, which disappeared after melting. Using measurements Yang et al. showed a significant change in stiffness between the two states. Although the frozen sal-gel was stiff, it was less brittle for indentation without cracking compared to a polymer-free frozen salt control.



LEFT: Mechanical behaviors of sal-gel. (a–c), Typical load–displacement curves for melted (a) and frozen (b) P10L10, and frozen L10 (c) samples in indentation tests. (d,e), Mechanical characterization of sal-gel of different compositions with effective elastic moduli extracted from the initial loading curves (d) and elastic contributions of material response in the frozen state (e). (f), A plot of relative change in elastic modulus for a P10L10 sample over five freeze–thaw cycles. (g), The change in stiffness of sal-gel compared with other stiffness-changing materials/devices with respect to the length scale of connectivity. These (with their respective key references) include shape-memory polymers, stimuli-responsive nanocomposites, surface-active metal nanocomposites, PCM microcomposites, transformable metamaterials, rheology-based devices, jamming-based devices, PCM structures/ devices and tendon-based machines^{28,29}. The error bars represent one standard deviation ($n \geq 3$) RIGHT: Crystallization behavior of sal-gel. (a), Microscopic and macroscopic images of the growth of salt crystals in sal-gel from a single nucleation point over time. The images on the far right are from the same sample with fully re-melted crystals. Each microscopic image corresponds to the locations marked in red in the

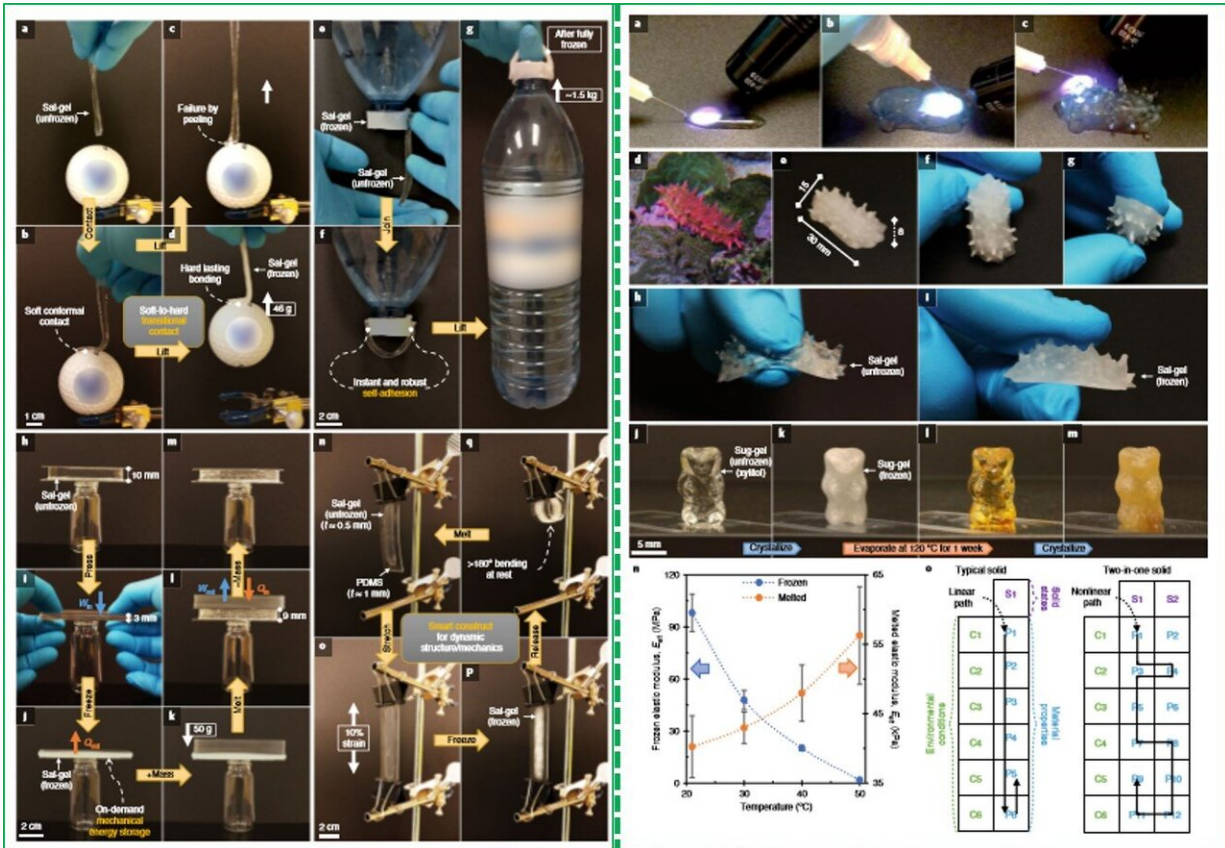
macroscopic photographs. (b), Crystallization speed for different samples. The dash-dotted red line highlights the trends from L10 to L30 and from P10L10 to P10L30. (c), Fraction of frozen salt for different samples. (d,e), Specific heat flow obtained from differential scanning calorimetry for different samples with distinct liquid (acetic acid) (d) and polymer content (e). The error bars in (b) and (c) represent one standard deviation ($n \geq 3$). Credit: Nature Materials, doi: 10.1038/s41563-019-0434-0

After further characterization of the hybrid material, the scientists showed that when more acetic acid liquid was present in the mixture, the sal-gel became softer and less elastic. When they repeatedly froze and thawed the gel, they did not observe lasting damage in the polymer network, although the material became stiffer with repeated [freeze-thaw cycles](#).

The scientists then investigated the crystallization behavior of the sal-gel and observed the growing crystals to push aside the polymer network without rupturing or damaging the network. The salt hydrate demonstrated thermal behaviors similar to [water freezing in hydrogels](#), where the addition of more polymer and diluent led to less crystallization. The thermal behaviors indicated a strong stability of sal-gel with supercooling greater than 150 degrees C.

The sal-gel demonstrated soft-to-hard transitional contact, instant and robust self-adhesion, mechanical energy storage alongside the capacity to form smart constructs. A major advantage of the hybrid material was its self-contained nature, which easily allowed additive manufacture. As a proof-of-principle, Yang et al. fabricated a synthetic sea cucumber using three-dimensional doodling by delivering un-crosslinked sal-gel solution using a syringe to crosslink the solution in the lab using an ultraviolet light source thereafter. The resulting print closely resembled a living sea cucumber in appearance and mechanics, where the dermis switched

between a transparent soft and opaque rigid state.



LEFT: Applications of sal-gel. (a–d), Demonstration of the soft-to-hard transitional contact of sal-gel. A thin strip of unfrozen sal-gel (a, P10L10) is lowered into contact with a golf ball (b) and is then lifted off while the gel is unfrozen (c) or frozen (d). (e–g), Demonstration of the instant and robust self-adhesion of sal-gel. A strip of unfrozen sal-gel (P10L10) is pressed against a frozen sal-gel (P10L10) that has been wrapped around a bottle cap (e); the unfrozen gel adheres on contact by freezing (f) and is able to lift up a bottle of water weighing around 1.5 kg after it is fully frozen (g). (h–m), Demonstration of sal-gel for mechanical energy storage. A very thick strip of unfrozen sal-gel (h, P10L10) is first compressed (i) and then frozen (j) to store mechanical energy. A weight is then added on top of the frozen gel (k). On heating, the gel lifts the weight (l), producing work. On removing the weight, the gel returns to its uncompressed original thickness (m). (n–q), Demonstration of sal-gel for

forming smart constructs. A very thin strip of unfrozen sal-gel (P10L10) is chemically bonded to a flat piece of silicone rubber (n). After stretching the rubber (o) and freezing the gel in situ (p), the flat piece of rubber curves onto itself on the release of external forces (q). RIGHT: Practical implications of sal-gel. a–c, Demonstration of the processability of sal-gel for additive manufacturing by fabricating a synthetic sea cucumber via three-dimensional doodling. d–g, Qualitative comparison of a living spiny sea cucumber (*Pentacta anceps*) (d) with the sal-gel sea cucumber at different viewing angles (e–g). h,i, Photographs of the fabricated sea cucumber at the two different solid states: a transparent and easily depressed soft state (h) and an opaque and firm rigid state (i). j–m, A sug-gel gummy bear incorporating more than 90 wt% of sugar alcohol liquid content displays the same dual mechanical behaviour as the sal-gel (j,k); this system is practically non-evaporative (l) and can still crystallize after prolonged overheating (m). n, Elastic modulus of frozen (blue) and melted (orange) sal-gel as a function of temperature. (o), Illustration of the material properties (P1–P12) of a typical material with a single solid state (S1) and two-in-one solid materials with two solid states (S1 and S2) with environmental conditions (C1–C6). Note the nonlinear response path of material properties allowed in two-in-one materials with respect to the linear response path of typical solids. The error bars in n represent one standard deviation ($n \geq 3$). Credit: Nature Materials, doi: 10.1038/s41563-019-0434-0

They extended the concept of sal-gel to other materials using the sugar alcohol [xylitol](#) as the PCM (phase-changing material). Using the sugar alcohol, they prepared a sugar-gel (sug-gel) gummy bear with two-solid state behaviors. When the scientists overheated the construct to 120 degrees C to accelerate evaporation for a week, the gummy bear's volume did not visibly change and still remained capable of dual-state behavior.

To translate sal-gel into practical applications, Yang et al. should resolve two technical issues relative to evaporation and sensitivity, which affected the implementation of the material. The issues were partially

addressed by coating the sal-gel with lubricant to optimize and increase its stability, they aim to further engineer the material in the future and fully resolve the limitation. The research team also increased the flexibility in design and functionality in the two-in-one solid, compared to normal solids with a single solid state.

In this way, Fut (Kuo) Yang and co-workers strategically constructed a solid framework inside a functional liquid—supercooled melted salt (sodium acetate trihydrate) by forming a compatible polymer network of poly(acrylic acid) to create the hybrid material sal-gel. Synergistic interactions of the materials at the molecular level allowed Yang et al. to leverage the liquid properties and explore its phase transition and metastability.

The hybrid construct showed unusual material behavior to switch between two stable solid states with varying mechanical properties that could co-exist under similar environmental conditions. The stiffness states did not require continuous stimulation, allowing new capabilities for advanced applications. While the present work focused on the transformation of supercooled liquid, Yang et al. expect to extend the approach to other liquids with different functionalities to diversify the range of mechanically switchable materials.

More information: Fut Yang et al. A hybrid material that reversibly switches between two stable solid states, *Nature Materials* (2019). [DOI: 10.1038/s41563-019-0434-0](https://doi.org/10.1038/s41563-019-0434-0)

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