

Learn About ...

Superabsorbent Polymers

Absorbers and super absorbers

If you spill a drink, your first impulse is probably to grab one or more paper napkins or paper towels to soak up, or absorb, the liquid. If the spill is large, several paper towels will be needed. Even a “quicker-picker-upper” can absorb only a small amount of liquid, before it is saturated (has absorbed all it can). What makes materials more or less absorbent in the first place? The answer is in their chemistry. We can harness the chemistry of polymers to build a better absorber: a super absorber.

The word “polymer” means “many parts” (from the Greek: poly = many, meros = parts). A chemical polymer is a molecule made of many repeating units, monomers (mono = one, meros = parts), linked together through chemical bonds. It is useful to think of polymers as chains – a good analogy is a chain of paperclips (the monomers), Figure 1. Polymers are very versatile. They can form materials that are rigid like plastic water bottles or materials that are flexible, like plastic grocery bags. Note that polymeric materials are often called “plastics”.

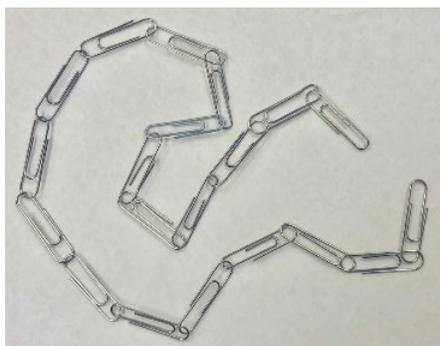


Figure 1. A chain of paperclips linked end-to-end like the individual molecules (monomers) that are chemically bonded to form a chemical polymer chain.

Some polymers occur naturally. The most common polymer on Earth, cellulose, is a polymer of glucose molecules and is made (as a result of photosynthesis) by essentially every green plant. Cellulose forms part of a plant’s rigid structures, the wood in a tree trunk, for example. Other familiar materials composed of cellulose include cotton, linen, rayon, and paper. You’ll note that these materials can absorb water, but if a soaked cotton or paper towel is gently squeezed, most of the absorbed water gets squeezed out. These materials absorb only a relatively small amount of water and lose it easily.

Unlike cellulosic materials, superabsorbent materials can hold hundreds of times their own weight in liquid and lock it in so that it doesn't escape when the material is squeezed, Figure 2. These materials are composed of man-made polymers that are specially designed (see next section) to give the materials their superabsorbent properties. A common example of a superabsorbent polymer is sodium polyacrylate (available in several materials under such trade names as WATER LOCK). Some of these polymeric materials can absorb 800 times their own weight in distilled water.

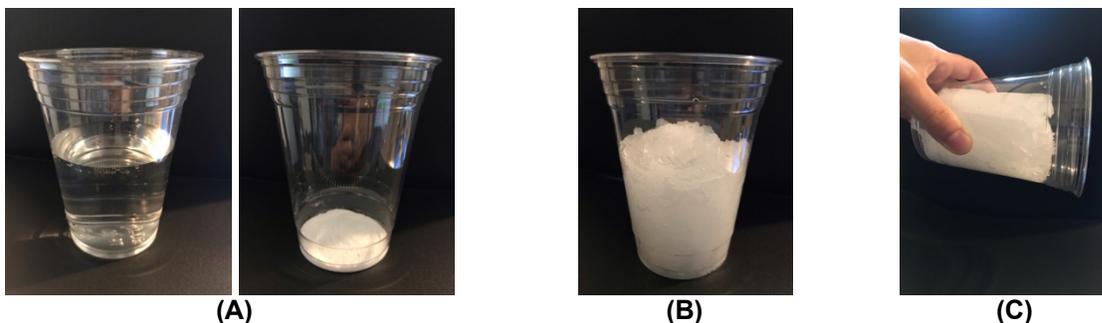


Figure 2. (A) 250 mL of distilled water and 3.5 g of sodium polyacrylate polymer (white solid) are (B) mixed and stirred to mix well. (C) Cup with water and polymer mixture is tilted to show that the gel does not flow.

A familiar use of sodium polyacrylate is as the main component in the core of most disposable baby diapers, adult incontinence briefs, and some feminine hygiene products. (The patent for this application was filed jointly by Carlyle Harmon of Johnson & Johnson and Billy Gene Harper of Dow Chemical in 1966.) The outside of such diapers (see the figure) is usually composed of a few different polymers, such as polypropylene and polyethylene, that enclose the superabsorbent core, usually sodium polyacrylate or a combination of polymers including sodium polyacrylate, that gives these products their amazing absorbing power.

Try the [Superabsorbent Diapers Home Experiment](#) to investigate this absorbency. Or, as a quick, simple experiment, try placing a disposable diaper in a basin of water or under a running faucet for about 1 minute.

What does the center core feel like?

How has the weight of the diaper changed?

What other observations can you make?

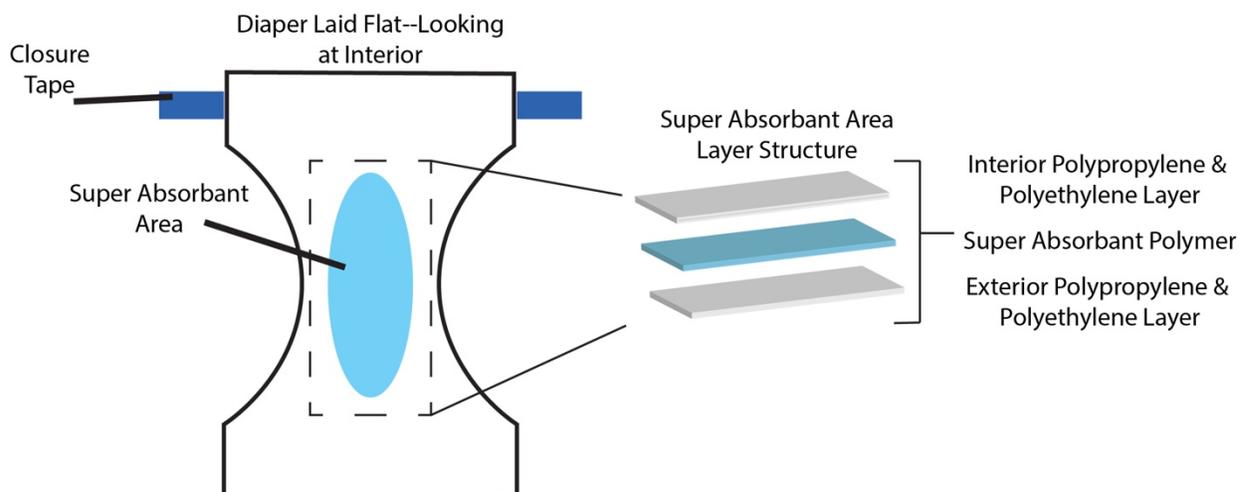


Figure 3. The construction of a superabsorbent, leakproof diaper holds the superabsorbent polymer between fabric layers in a core “pocket”.

How absorbers and super absorbers work

In a cellulose polymer chain, Figure 4(B), each glucose monomer has three alcohol (-OH) groups. These make the chain polar and readily able to make hydrogen bonds to adjacent chains to form multi-chain fibers. Although each hydrogen bond is weak, there are so many of them that the chains are held together. The fibers are what make it possible, for example, to spin cotton thread that can be woven into a cotton cloth.

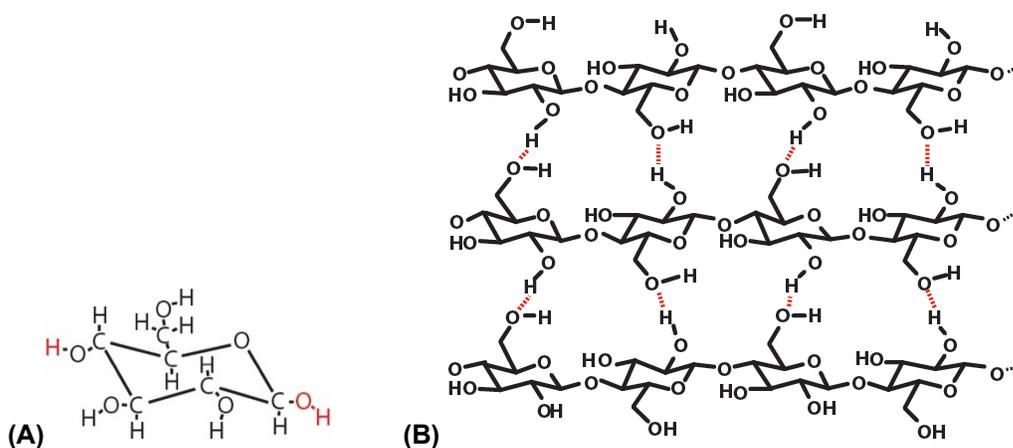


Figure 4. (A) A glucose molecule with the atomic symbols for all atoms shown. (B) Hydrogen bonds (shown dotted) between three cellulose polymer chains form a microfibrillar structure. The glucose monomer structures are shown in an abbreviated skeletal form that omits carbon atom labels and all hydrogen atom labels except those bonded to hetero (non-carbon) atoms. Forming the bond between two glucose monomers requires the loss of a water molecule, H-OH, with the -OH coming from one glucose and the -H from its partner. This is shown in color in (A).

When a cotton cloth is immersed in water, water molecules can enter the tiny spaces between the woven threads. The entry of water is aided by capillary action in these tight spaces and by the polarity of the surrounding threads that can hydrogen-bond to the water. (Materials that interact to attract water molecules are called “hydrophilic”, water-loving, from the Greek hydros = water, philia = love.) When the soaking wet cloth is removed from the water, these weak interactions continue to hold much of the water. But the water is readily lost when the cloth is squeezed and the spaces holding the water are compressed and expel the water. Other cellulosic materials absorb and easily lose water in similar ways.

In contrast to hydrogen-bonded fibrous cellulosic materials, superabsorbent sodium polyacrylate polymer is composed of a three-dimensional mesh-like network of many polymer chains linked through chemical bonds. Each polymer chain, Figure 5(B), is composed of acrylic acid and sodium acrylate monomers, Figure 5(A). One way to produce these chains is to start by polymerizing (making polymer from) acrylic acid monomer. Then these polyacrylic acid chains are mixed with enough sodium hydroxide solution to react with some (but not all) the carboxylic acid groups to give ionic sodium acrylate groups. Note that these polymer chains have a “backbone” of carbon atoms singly-bonded to one another with either a carboxylic acid or carboxylate ion group bonded to every other carbon. The backbone of singly-bonded carbons is flexible and allows the chain to bend and fold, as shown in the structural representations, Figures 5(B) and 6.

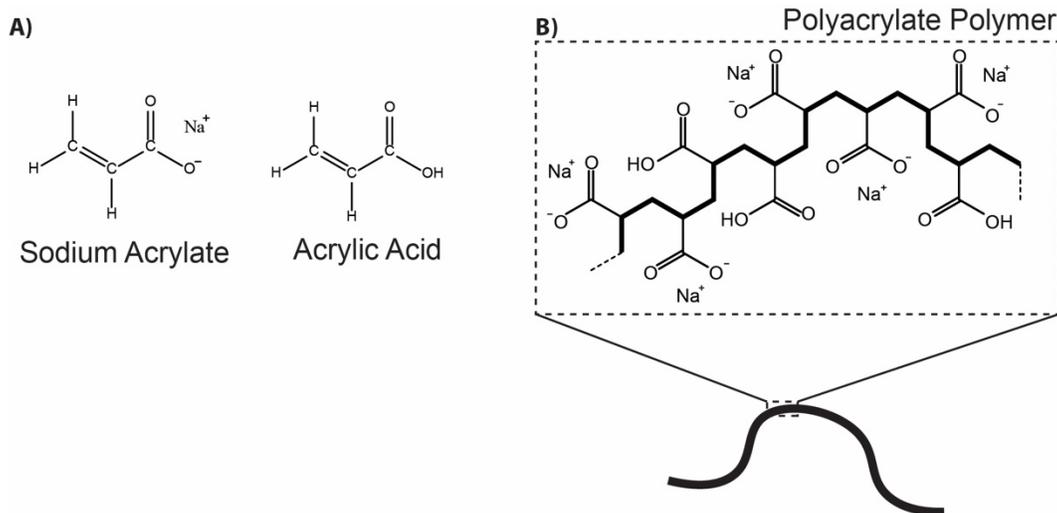


Figure 5. (A) Acrylic acid and sodium acrylate monomer. (B) Abbreviated skeletal molecular structure of a short length of a polyacrylate polymer chain with the carbon-carbon singly-bonded backbone bonds shown in heavier type. The wormlike sketch is a schematic representation of an entire polymer chain.

The highly ionic and polar polyacrylate polymer chains are fairly soluble in water. To prepare the insoluble superabsorbent polymer material the chains are cross-linked (connected to one another) at a few places. Figure 6 illustrates one possible way to create these cross-links with the connector molecule, $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$. The linker is bonded to the

polymer chains by ester bonds between the alcohol groups on the linker and a carboxylic acid group on the chains. Like the polymer chains, the linkers are flexible strings of singly-bonded atoms. The cross-linked, bulky, high molecular mass material is insoluble in water. When dry, the resulting three-dimensional mesh-like structure collapses on itself as a powdery solid material.

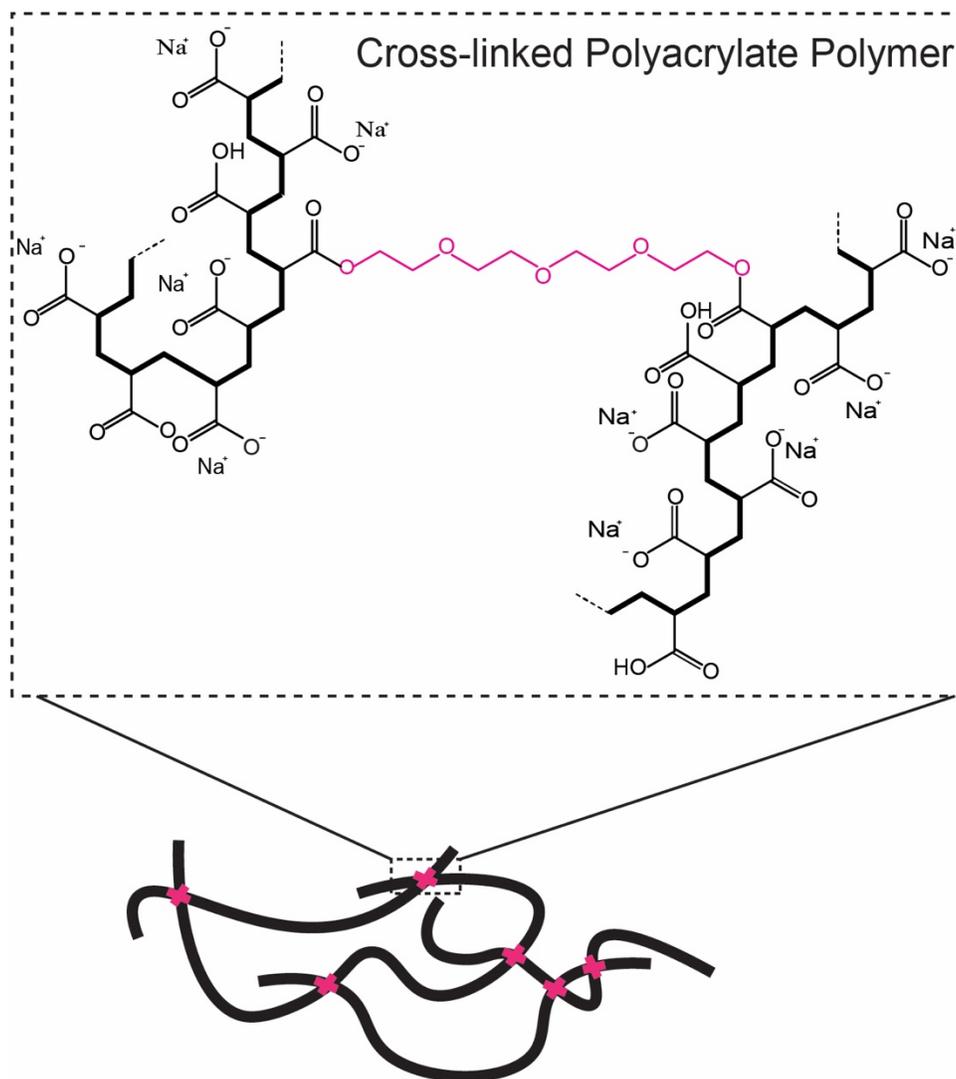


Figure 6. The cross-linking molecular structure between two polymer chains is shown in color. The pink "X"s in the schematic sketch represent the sites of cross-links creating the mesh work of many interconnected polymer chains in superabsorbent polyacrylate polymer material.

The flexible mesh is, however, capable of expanding to give a larger three-dimensional structure containing a lot of empty spaces. This property and the polar and highly ionic character of the polymer account for its superabsorbency. When the dry, superabsorbent polyacrylate polymer material interacts with water, polar water molecules are attracted to the polar polymer. Water can enter folds and gaps in the structure and form hydrogen bonds with carboxylic acid and carboxylate anion groups. This is much like the interactions of water with the cellulosic materials

discussed above, with two major exceptions: the flexible, mesh-like polymer structure can expand to accommodate more water and the water inside the mesh is a fairly concentrated “salt” solution of mobile sodium cations and fixed carboxylate anions, Figure 7.

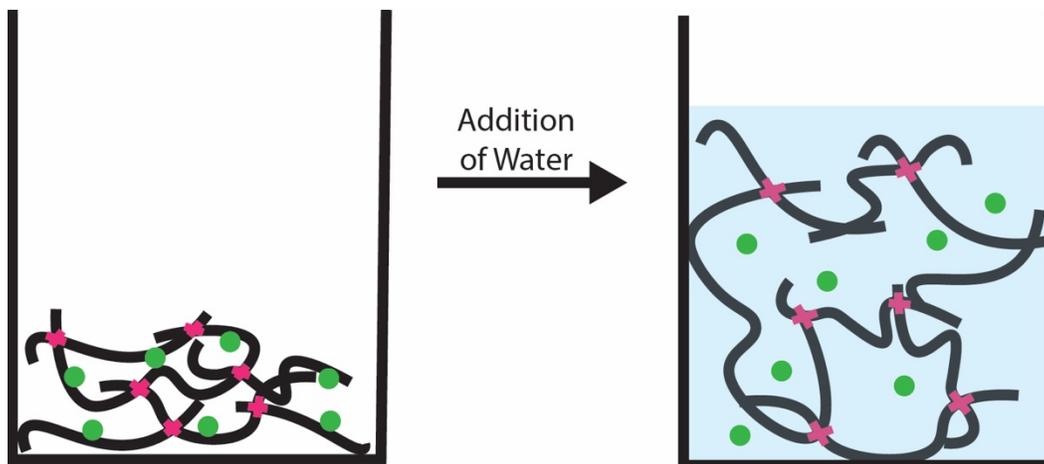


Figure 7. Schematic molecular level representation of water absorption by the polyacrylate polymer shown in Figure 2. The dry sodium polyacrylate cross-linked polymer on the left is a compact solid. Its sodium cations (green dots) are associated with the carboxylate anions on the chains and are not free to move about. On the right, distilled water has been added, water has entered the polymer mesh, and the polymer has expanded a great deal as water fills the spaces within the mesh to produce a gel. The sodium cations have dissolved into the water to form a fairly concentrated solution. Since the sodium cations are attracted by the carboxylate anions, very few of them leave the gel.

Movement of large amounts of pure water into the sodium polyacrylate polymer mesh is a result of the ion imbalance between the high concentration salt solution inside the polymer mesh compared to the water outside the polymer. The entry of water into the mesh network occurs by a process very like **osmosis**, the diffusion of water across a semi-permeable membrane. The net movement of water in osmosis is from the side of the membrane with the lower salt concentration to the side with the higher salt concentration—from the outside to the inside of the sodium polyacrylate polymer mesh. This is because the attractions between polar water molecules and ions restrict the freedom of movement of the water molecules compared to the motion they would have in pure water (or a lower salt concentration). Restricted motion is unfavorable, so net diffusion occurs in the direction to dilute the high salt solution and provide more freedom to the water molecules. (In thermodynamic terms, the entropy of the concentrated solution is increased by dilution and natural processes occur in a direction to increase entropy.)

The transformation of the polymer from a fine powder to a gelatinous mass is visually striking, especially as the gel swells to many times its original size.

[View a close-up video of the diaper polymer gelation and swelling in water.](#)

What limits the amount of water that can be absorbed (and, hence, the size of the gel)?

If distilled water is being absorbed, the solution inside the polymer mesh is always saltier than the water outside. Thus, movement of water into the mesh to further dilute the ion concentration continues to be favorable. However, there is a limit to how much the flexible polymer chains and cross-links can be extended, so there is a physical limitation to the maximum amount of space available for water within the mesh. Once the space is filled, the movement of water in and out of the gel stops. The water inside is “locked” in the mesh by all the ionic and polar attractions and no more can enter, because there is no room. “Locking” water almost irreversibly into a semi-solid gel in the core of disposable diapers is essential for keeping moisture away from the baby’s skin.

Effect of salt on absorbency

Remember that net movement of water into the superabsorbent polymer mesh depends on the ionic imbalance between the solutions inside and outside the mesh. As you can imagine, ions in the water being absorbed compromise the performance of super absorbers. A sodium polyacrylate super absorber can absorb up to 800 times its own weight in *distilled* water, but much less, if the water contains ions—only 300 times its weight in unfiltered tap water, and the polyacrylate mixture in diapers typically absorbs only about 30 times its weight in urine. Figure 7 illustrates the absorbency differences among various solutions. Tap water contains trace amounts of various dissolved ions (the maximum amount of total dissolved solids in drinking water recommended by the EPA is 0.05%). Urine has an average salt concentration of approximately 0.9% and is represented in Figure 8 by a 0.9% salt solution.

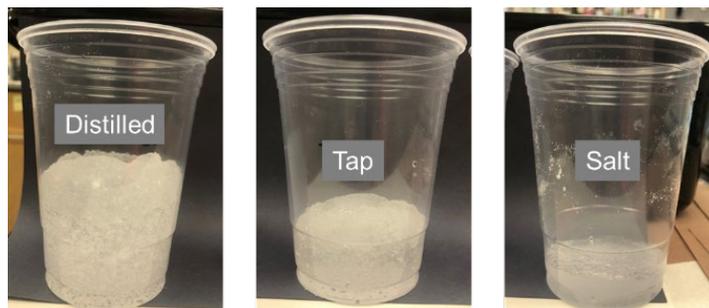


Figure 8. These results illustrate the difference in water absorbed by the same amount of cross-linked polyacrylate polymer mixed with distilled water, tap water, and a 0.9% solution of salt (sodium chloride).

Sprinkling a bit of table salt (sodium chloride) on a gelled sodium polyacrylate superabsorbent polymer that is swollen with absorbed water has a dramatic effect—the gel quickly transforms to a loose mush. Adding sodium chloride directly to the outside of the hydrated polymer produces a much higher ion concentration on the outside surface of the polymer than on the inside. As a result, water molecules quickly diffuse out of the polymer matrix, causing it to collapse. Acidic compounds, such as vinegar, have an even more potent effect as they both reduce the osmotic effect and react with the polymer carboxylate groups to lower the ionic character of the polymer.

pH changes during superabsorbent polymer transitions

An acid-base buffer solution contains comparable concentrations of a weak acid and its conjugate base (that is, the negative ion formed by loss of the acidic H^+ from the acid). The sodium polyacrylate polymer structure shown in Figure 5 has exactly this characteristic. The chains have both carboxylic acid, $-COOH$, and carboxylate anion, $-COO^-$, side groups. The polymer differs from a traditional buffer solution only because the conjugate acid and base are not floating freely in solution, but have to remain attached to the polymer chain as they interact with surrounding water.

In experiments where superabsorbent polymer powder is added to distilled water in small increments, the pH of the mixture (measured with pH meter or indicators) is initially about 8.6 and drops steadily as more polymer is added. When the gel has formed, the pH is near 7.0 and remains constant as more polymer is added with no discernible change in the viscosity of the gel. Addition of a small amount of salt, NaCl, causes the gel to break up rapidly to form a watery mush with a pH of about 6.0.

In mixtures with more water than the polymer can absorb, the polymer acts as a base and extracts a proton from water to form modestly basic solutions that become less basic as more polymer is added. When enough polymer is added and the gel forms, the mixture comes to equilibrium with no further change in pH. It seems counterintuitive that addition of more of a base (the polymer) makes the mixture less basic (lowers the pH). A possible explanation could be that the observed chemistry is between water outside each polymer mesh and only the carboxylate groups on the surface of the mesh. As more polymer is added, the individual polymer meshes begin to aggregate (as they must to finally form the gel) and the aggregates expose less surface to the surrounding water. Thus, the effective base concentration decreases and the pH goes down. When salt breaks up the gel, exchange of solution between the inside and outside of the polymer mesh is enhanced and the pH might be representative of the acid-to-base ratio of the polymer carboxyl groups and their acid equilibrium constant. This is food for thought and, perhaps, more investigation.

Beyond diapers: superabsorbent polymer applications

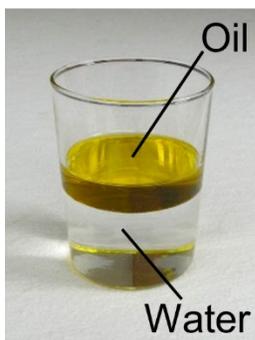
In the health fields, doctors and scientists are interested in using superabsorbent polymers to increase the absorbency of wound dressings. Superabsorbent polymers are also added to soil in drought-prone areas and to potting soil, as a way to “store” water. The soil can absorb water when it gets soaked and release water when it becomes dry. Super absorbers can be used in filtration units that remove moisture from automobile and airplane fuels.

As you can see, there are many important ways to use superabsorbent polymers to actively collect and remove water. Conversely the saturated gel itself has useful applications, holding a lot of water available in one place to put out a fire, for instance. Barricade Fire Blocking Gel is just one example of a handful of commercial products that use superabsorbent polymers to protect properties from wildfires. In 2018, there were 58,083 wildfires in the United States, which burned 8,767,492 acres. This includes the devastating Carr fire in northern California that ravaged 229,651 acres and destroyed over 1,000 homes. While it's true that over 80% of U.S. wildfires are caused by humans—arson, accidental sparks, improperly extinguished camp fires, cigarettes, etc.—changes in moisture and precipitation levels are also making dry areas drier,

helping fires spread and making them harder to put out. Therefore, fire protection will become increasingly important as a climate change adaptation strategy.

When Fire Blocking Gel superabsorbent granules mix with water, they form a wet gel that can be used to coat a variety of surfaces. Since water is locked in a semi-solid gel, it can be immobilized onto a variety of surfaces and remain stationary without damaging the structures. The gels are typically 95-99% water. When they come into contact with fire, they act as a physical barrier to save the structure.

To see a super absorber in action, try our [Superabsorbent Diapers Home Experiment](#). You can even check how well a polymer gel blocks heat yourself with the gel material you create in this experiment. Simply put some of the gel in a small Ziploc bag and place your hand at least 5 inches away from a hot surface both with and without the bag between you and the hot surface. Is there a difference in how much heat your hand feels? The Florida firefighter who invented Fire Blocking Gel was inspired by a dirty diaper that did not burn when the contents of the trashcan it was in caught fire.



A polymer chain mesh of water-loving (**hydrophilic**) molecules can absorb water on a super absorber scale. A similar approach can create super absorbers for liquids other than water. Scientists at Pennsylvania State University have been exploring a material called i-Petrogel that can be used to mop up and repurpose oil from huge oil spills in the oceans. They created a superabsorbent polymer made entirely from water-repellent (**hydrophobic**) molecules, which bind to oil, but repel water. The figure at the left shows the hydrophobic effect of cooking oil, which does not mix with water, but floats on the surface. i-Petrogel can absorb over 40 times its weight in crude oil and effectively stops the oil from spreading after a spill. Similar to the gelation and swelling of polyacrylate in water, i-Petrogel gels as it absorbs oil and then floats on the surface of the water. It can be recovered and sent to an oil refinery where the entire mass, including the petrogel, can be refined. Current methods of oil spill cleanup, including underwater dispersants and microorganisms, are not nearly as effective and economical as the potential of i-Petrogel. Just \$16 worth of i-Petrogel would recover ~\$85 worth of crude oil from otherwise wasted and toxic spills.

So, that was a lot to absorb! What other uses can you imagine for superabsorbent materials?

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