Chemistry: Challenges and Solutions
Unit 13: Modern Materials and the Solid State
Crystals, Polymers, and Alloys
Hosted by Ainissa Ramirez

We often think of chemistry as dissolving, precipitating, evaporating, or condensing. In fact, many chemical or physical reactions involve fluids – liquids and gases.

But look around. Most of the matter we use in daily life – our food, our clothes, the ground we walk on, is solid.

Chemists are engineering new solid materials every day. Whether crystals, polymers, or advanced metal alloys, these materials help us to explore the universe, and make advances in healthcare.

TREVOR CASTOR: With drugs being encapsulated in polymers, taking insulin will be like eating food.

These new materials are all are governed by the chemistry of the solid state.

[Title: Unit 13 – Modern Materials and the Solid State]
[SEGMENT 1]

AINISSA RAMIREZ: Solids offer so many possibilities because in a solid the individual atoms, molecules, or ions are organized in definite arrangements. And there's so many kinds of atoms to choose from. And so many possible arrangements.

I'm Ainissa Ramirez, a materials scientist. And here we are, where the rubber meets the road – in a machine shop. My work is based on the chemistry of solids. Solid-state chemistry offers many, many ways to create or modify the properties of solid materials. Let me show you an example.

Here I have a piece of metal wire. There's nothing special about it. I can twist it, I can bend it and it keeps its shape. In fact, that's one of the characteristics of a solid. Solids keep their shape, while liquids and gases take the shape of their containers. But let's see what happens when we raise its temperature. It returned to its original shape. Let's see that again. When I apply heat to it, it returns to its original configuration. That's why we call it a "shape memory alloy." It's an alloy, or mixture of two or more different metals, that remembers its shape.

In this material, the atoms can take different arrangements, depending on the temperature. We call these phase changes. That's something you're already familiar with, like when ice melts into water.

At cool temperatures, the atoms of the shape memory alloy go into one phase, which looks like this. But when the metal is heated, the atoms go into a different phase, which looks like this. Why does the phase change? Remember that atoms in a solid, even though they are held in a definite arrangement, are always jiggling in place. If you increase the temperature, they jiggle more. Then they need a little more room. In a shape memory alloy, they spontaneously rearrange themselves into a more open configuration. What do we see at a macroscopic level? The material stiffens and “remembers” its original shape.

To get a better handle on the way solids work; let’s start with what holds them together – their bonds. And what better place to do that than in a mineral collection?

[SEGMENT 2: Atomic Arrangements]

RAQUEL ALONSO-PEREZ: The public is always very excited by the different shapes and colors of the minerals. But from a geochemist’s point of view, these shapes and colors are the results of the highly ordered atomic arrangement and chemical composition of these natural solid substances, which are usually formed by inorganic processes, by nature.

Here we have one example, halite, which is common salt, the one we all use for cooking in our kitchen.

Notice how the shape of the crystal, or what we call the external symmetry, is in the form of a cube. So if we look at the atomic level, what we see is the cubic arrangement of sodium, chloride, sodium, chloride. By the repetition of that unit cell, we will get the final shape of the crystal.

Salt is one of many minerals held together by ionic bonding, a type of solid where positive and negative ions are held together by mutual Coulombic attraction in a regular pattern.

RAQUEL ALONSO-PEREZ: In my research, I’m looking at garnets, this is another type of mineral with an ionic bonding and cubic symmetry but they usually form the dodecahedron, or twelve-sided, habit.

The huge variety of shapes that the crystals of minerals adopt is simply the expression of one unit cell over and over. Ionic compounds are held together by ionic bonds, but that is only one kind of bond that holds solids together. A different type of bonding holds metals together: metallic bonding.

RAQUEL ALONSO-PEREZ: Gold has a different type of bonding, which is called metallic bonding, and which is responsible for these unique properties of metals such as malleability and high electroconductivity.

The outermost electrons in a metal atom can move freely between nearby positive metal atom nuclei, as if they are a sea of negative charge; these electrons are attracted to all the positively charged nuclei, not just one. The collective attraction between the sea of electrons and the lattice of nuclei holds the metals together.

RAQUEL ALONSO-PEREZ: Other types of metals, such as silver and copper, have the same type of properties. The third known type of bonding is the covalent bonding, which results from the shared electrons between atoms. This type of bonding is responsible for the great stability, insolubility, and high melting point of diamonds.

A covalent network solid is made of many atoms held together in large, regular lattices by covalent bonds.

RAQUEL ALONSO-PEREZ: The covalent bonding is the strongest bonding that we know and that's why diamonds are the hardest mineral known on Earth.

A fourth type of solid, molecular solids, are held together by intermolecular forces, also called Van der Waals forces. These solids, unlike diamonds, are soft, low-density, and usually have low melting points.

RAQUEL ALONSO-PEREZ: Graphite has a structure which consists of parallel layers of strongly bonded carbon atoms that are separated from each other by a large distance. That large distance is the result of a weak Van der Waals bonding. Because of this weakness, and these parallel layers in between, graphite can be used for many applications, especially for writing, in our pencils.

[SEGMENT 3: Carbon Nanotube Sensors]

AINISSA RAMIREZ: We've seen how pure carbon can come in different forms, or allotropes. One form, diamond, is hard and clear. One form, graphite, is soft and gray. And one form, carbon nanotubes, is created in the laboratory to have very particular, and useful, properties.

Carbon nanotubes can help solve an age-old problem, a problem found here at Carver Hill Orchards and at many other places where fruit is harvested, processed, or sold.

Currently, it's estimated that 30% to 50% of the Earth's fresh produce never makes it to the table. Often, fruits and vegetables get thrown away because they've gone bad. But a key to solving this problem centers on a plant hormone, ethylene, a gas emitted by ripening fruit.

JOSEPH AZZARELLI: Ethylene even in very small quantities can trigger the process for ripening, and ultimately death, of the fruit that we all consume on a daily basis.

Researchers at the Swager Lab, at MIT, are working to develop a sensor chip to detect ethylene.

JOSEPH AZZARELLI: The reason that we're interesting in detecting ethylene is that, if we can start to understand how a fruit is responding to its environment, then we can start to think about: what's the expiration date of that fruit? When do we harvest it? When do we ship it? How do we package it? All of these decisions can lead to greater efficiency in the food supply chain and ultimately could reduce food waste around the world.

Key to the team's ethylene sensor are carbon nanotubes, tiny cylinders of linked carbon atoms.

JOSEPH AZZARELLI: Our research uses single wall carbon nanotubes as materials in the sensors that we fabricate. I have here a molecular model of a single walled carbon nanotube. This model is about a meter long, so it's about a billion times the size of a real single walled carbon nanotube. The single-walled carbon nanotube is made up of carbon atoms And the way that this molecular model is represented is one of these little black spheres here is a single carbon atom, and this is the bond to another single carbon atom.

The single walled carbon nanotubes are very sensitive to having their electronic structure perturbed or disrupted by another molecule. So for instance, if I have a receptor molecule on or near the surface of the single-walled carbon nanotube, and I have ethylene, come by and attach to that receptor molecule, I'll disrupt the electronic structure of the nanotube, and I'm going to make it harder for electrons to move from point A to point B on this essentially nanowire that I'm holding here. That's useful because then we can measure that response with simple electronics.

In order to see how ethylene disrupts the conductivity of the carbon nanotubes, researchers first combine the carbon nanotubes with an ethylene-selective material to make a pellet. Then they use this pellet to draw the sensing material directly on to the chip.

JOSEPH AZZARELLI: So this right here is a sensor chip. That is basically just a piece of copy paper that has had gold electrodes deposited on it. That's where we put our sensing material, that's been specifically designed to interact with ethylene and only ethylene.

So what we're going to do now is we are going to inject the gas on to the sensor chip. And we'll see the response on the computer. When we have current on the y-axis, and we expose the sensor to the gas, we actually are restricting the flow of electrons through that sensor. And therefore the current, that is the number of electrons that are flowing through it at any given point in time, is decreasing.

So we see this nice drop in the curve, representing the presence of the gas, and therefore the reduced current of the sensor.

Carbon nanotubes that detect ethylene may someday spawn new efficiencies in harvesting and marketing fresh produce.

JOSEPH AZZARELLI: Given the number of resources that go into growing food, the number of resources that go into shipping food, and the number of resources that go into simply displaying it for purchase, we feel that any even incremental improvement that you can make, in reducing food waste is a worthwhile pursuit.

[SEGMENT 4: Early Plastics]

AINISSA RAMIREZ: Here we are at the Historical Society in Leominster, Massachusetts, called the "Comb City," and for good reason. In the late 1800s, there were many companies here that made combs and other personal accessories.

PAUL J. BENOIT: This is how the first combs were made. Cattle horn, nothing unusual about it.

AINISSA RAMIREZ: As the worldwide demand outstripped the supply of bone, horn, and other natural raw materials, a man-made material called celluloid was a workable substitute. It is a polymer, a material composed of long chains of smaller molecules which, when heated, becomes soft and pliable, a plastic.

In 1901, the Viscoloid Company opened here, to manufacture celluloid combs and other products. It soon grew to be one of the largest plastics complexes in the world.

PAUL J. BENOIT: And just went gung ho on making all the previous items that were made out of horn or metal or whatever out of celluloid and went on the market. And celluloid was very popular.

AINISSA RAMIREZ: Today, plastics are a multi-billion dollar industry. The exact geometry of polymer chains gives each plastic its desired properties. We can see this joining, or polymerization reaction, happening in front of our eyes.

[SEGMENT 5: Making Nylon]

DANIEL ROSENBERG: Today we’re going to make a polymer. A polymer! A polymer!

A polymer is a long chain molecule made up of monomers.

A monomer is a small molecule that's reactive. And it can react with other monomers in order to make a chain of molecules that gets longer and longer and longer and eventually winds up being an enormously long chain which we call a polymer.

The polymer we're going to make today is nylon. Nylon was one of the first synthetic fibers made, and it revolutionized fashion and it changed the world. So we're going to make it out of two solutions and a beaker. Now I could pour these two solutions together and it would form a blob. But we're going to take advantage of the fact that this monomer solution - hexamethylenediamine – is in water, and the other monomer solution, diacid chloride, is in hexane. Hexane floats on water. And so if I pour the water first, and then slowly pour in the hexane, we'll get two layers of solution. And where the two layers meet, the monomers react to form a polymer.

Hexamethylenediamine is a six-carbon chain, with an amine group on either end. And those amine groups are reactive, but not towards each other. And you can think of them as little hooks. And the diacid chloride is a six-carbon chain with an acid chloride on either end. And those acid chlorides are reactive but not with each other. They're like little loops ready to react. When I mix these two solutions, the hooks of the amines, and the loops of the acid chlorides link up and become a single molecule.

So if I reach in and I grab the interface, it's like a thin sheet of nylon. And as I pull it up it frees up the two liquid surfaces, So that more monomers can react… and more monomers can react. And I just keep pulling the polymers out as a thread. And as I keep pulling with my handy dandy spool, I can just keep moving the polymer, allowing the monomers to react. And I get a nylon thread.

So, when we reach the end of one or the other of the solutions, the reaction is over.

[SEGMENT 6: Pharmaceutical Polymer Research]

Polymers are often used in manufacturing highly durable, long-lasting materials. But some polymers are intentionally made to break down at a controlled rate, under specific conditions. Advances in polymer science are opening the way for new drug delivery systems.

Trevor Castor at Aphios Corporation has developed an innovative way to encapsulate insulin in polymer nanoparticles.

TREVOR CASTOR: Traditionally insulin is introduced in the body as an injection. You have to find a secure place to do an injection, making sure that your insulin product is refrigerated; you have to worry about the potential of creating an infection. And if you have to inject that every day it becomes difficult to maintain that type of adherence.

What our hopes and ambitions is really to improve the quality of life of diabetics. So that taking insulin will be like eating food, basically. This is part of the holy grail of biotechnology

Normally insulin, if swallowed, would be quickly broken down in the digestive system, and never reach the bloodstream. Aphios researchers are enveloping insulin in a polymer that resists the digestive acids and enzymes long enough to make it into the bloodstream.

TREVOR CASTOR: So what we have done here at Aphios is to encapsulate insulin in biodegradable polymer nanoparticles. We take a polymer and we mix it with a solution of insulin, and the insulin is encapsulated in the polymer.

One of these biodegradable polymers I speak of is polylactic acid. And it's a long-chain polymer. So it's a repeating unit of lactic acid. And it can break down. It's biodegradable.

It is a considerable challenge to find a polymer that is resistant to digestion, can attach itself to insulin, and eventually degrades to release the insulin, all while being harmless to people.

TREVOR CASTOR: We've done experiments to show that these nanoparticles do survive in the stomach, because the biopolymer is resistant to the pH of the stomach. And from there, because they are small, they will be transported into the bloodstream. In the bloodstream the particles will degrade with time, and the polymer will be released, and insulin will be released from the polymer.

The solution of insulin-polymer nanoparticles is freeze-dried to form a powder, from which a time-release insulin pill will be made.

TREVOR CASTOR: It's almost like an onion. Where you have layers of polymer covering the insulin. And as the biodegradable polymer degrades, it releases layers, and insulin is released as a result.

Biodegradable polymers could be the key to making ingestible pills that would improve the lives of people with diabetes and other life-long conditions.

TREVOR CASTOR: I would like to see drugs being encapsulated in polymers, to control blood pressure, to control cancer, to control a number of diseases.

Where we can take them on a daily basis very much like I now take aspirin.

[SEGMENT 7: High Temperature Alloys]

AINISSA RAMIREZ: Materials scientists are constantly striving to create new, and more useful, solids. One promising area is the creation of alloys - mixtures of two or more metals. The exact mix can be fine tuned to give the desired properties. We're at the Smithsonian Astrophysical Observatory Central Engineering Facility, where alloys are used in building spacecraft and advanced telescopes.

The engineering team is looking for materials that can survive the mission of the Solar Probe Plus spacecraft. The Probe is planned to go nearer to the Sun's surface than any other spacecraft has ever gone.

ANTHONY W. CASE: The Solar Probe Plus spacecraft is going to go within nine and a half solar radii of the surface of the sun, which is well within the orbit of Mercury. At that location it's going to have more than 500 times the brightness of the sun than we see here on Earth and so the entire front of the spacecraft that's seeing the sun is going to get extremely hot.

Temperatures this close to the Sun could be as high as 1,700 degrees Celsius, or 3,092 degrees Fahrenheit. On board, the spacecraft will be sophisticated research instruments, including ones known as SWEAP.

ANTHONY W. CASE: The SWEAP Suite, or the Solar Wind Electrons, Alphas and Protons investigation, is a suite of four instruments that are on the Solar Probe Plus spacecraft, designed to measure the solar wind plasma that's flowing outward from the Sun. So the Solar Probe Cup, or SPC, is one of those instruments. And it's designed to hang out from behind the heat shield and look directly at the Sun.

The problem is that not only do we you see what you're trying to measure in terms of science; you also see the very hot surface of the Sun, that's illuminating you at all times. So at the very front of the instrument we've got a heat shield made of niobium looking directly at the Sun, which gets up to temperatures of greater than 1700 degrees Celsius. If you go to the back of the cup – which is only about a few inches behind that heat shield – we're down to about 700 degrees Celsius.

So, it's being heated from the front, and it's being very rapidly cooled from the back. Not only do we have to withstand very high temperatures at the front of the cup, we have to withstand very large gradients in temperature throughout the cup.

To find materials able to survive the Sun's heat, and return useful data requires testing materials in a vacuum chamber at temperatures up to the full range they will experience during the mission.

ANTHONY W. CASE: Inside this tent is what we call the Solar Environment Simulator, or SES. This is a vacuum chamber. So we can set our instruments in there and we can pump out all of the air. So we get down to less than a billionth of the amount of air we have in the room here. There's a big window on the front of the SES, which allows us to shine in four modified IMAX film projectors, so we can produce solar illumination onto the instrument. IMAX film projectors are meant to take light and display it on a screen that's really large. But we've modified that by using lenses to focus the light down into a small area.

RADIO: All right, lamp two is on; lamp three is on; lamp four is on…

RICHARD GATES: This is the first time we've set up the four projectors all at once.

Right now we're probably within 90% of what the probe's going to see. We'll probably run six projectors in order to get the maximum amount of light that the probe will see in flight as it gets the closest to the Sun.

The scientists use the simulator to test different materials.

ANTHONY W. CASE: Typically when we build space flight environments we use aluminum. I have an example of aluminum back here and this is a piece of aluminum that we've used in the Solar Environment Simulator before. Unfortunately this particular piece got a little hot during one of the tests. And you can see along the edge here that it got melty, it cracked. And this is not a material that we could use in an instrument like the SPC that's going to fly that close to the Sun.

For the instruments to survive the mission, the team must rely on a specialized branch of material science, high temperature alloys.

One alloy that these scientists work with is called TZM. This stands for titanium, zirconium, molybdenum. TZM is 99% molybdenum. By itself, molybdenum can withstand very high temperatures. But it is also very brittle, so it is difficult to work with. Adding a small amount of titanium and zirconium, just 1% of TZM, makes the material much stronger while still being able to withstand high heat.

Plansee U.S.A. supplies TZM for the SWEAP project.

STEPHEN C. MCCROSSAN: TZM has extremely high strength at high temperatures. Owing to the addition of the alloyed ingredients, titanium and zirconium. If you were to expose a piece of steel or copper to the kind of temperatures that the SWEAP instrument is exposed to, those materials would droop or maybe even be melted at the temperature where the TZM materials are still holding on to their strength and able to function in the intended application.

A crystal is an ordered arrangement of atoms or molecules. A solid like pure Molybdenum consists of many adjacent crystals called grains. The places where the grains meet are called grain boundaries.

If the grains or their boundaries slip, the material as a whole can deform, or experience “creep.” The risk of creep increases at high temperatures. Material scientists know that mixing very small amounts of Titanium and Zirconium with Molybdenum decreases creep.

ANTHONY W. CASE: So the Solar Probe cup is made of a simple cylinder of Molybdenum TZM. And then fine mesh grids that are on the inside of the cup made of tungsten.

One of the considerations when we choose materials to make a cup out of is that chemically we don’t want to pick materials that are very active or interesting materials, we want them to be as inert as possible. So we want to choose things like molly TZM, sapphire, tungsten, these sorts of materials that don’t interact when we place them together in a very hot thermal environment and in the vacuum of space.

The team will continue to test the strength of materials for SWEAP to make sure they can survive the mission, while it travels closer to the sun than ever before.

ANTHONY W. CASE: The Solar Probe Plus mission is scheduled to launch in 2018. The mission is about seven years long. And will reach its first close approach to the sun within about three months after launch.

[WRAP-UP]

AINISSA RAMIREZ: As we have seen, materials science takes advantage of many branches of chemistry - polymer science, metallurgy, crystallography, and many others - to continue the human quest that we began in our first unit.

The possibilities are endless. Whether combining different polymers into composite materials, creating new alloys, or building finely tuned nanostructures, there's an infinite variety of new applications waiting to be discovered, as chemistry continues to find new solutions to society's challenges.

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