[SQUEAKING]

[RUSTLING]

[CLICKING]

JUEJUN HU: OK, so in the last lecture, we talked about essentially the material that you use to make the breakable screens. [LAUGHS] So essentially, Gorilla glass, right? But there are also a lot of other competing glass materials from other companies essentially exhibiting similar properties. The whole idea is that you do this ion exchange to get a very large surface compressive stress, which helps you to essentially prevent the crack propagation. Now, I just want to start by mentioning that this ion exchange process does a couple of things.

OK, what I'm showing you here, this is the Weibull plot of essentially glasses with and without the ion exchange process. So if you look at Weibull plot, there are two things you can tell here. One is that the curve gets shifted towards the right side for the chemically strengthened glass, which indicates that you have now a higher strength. It can withstand essentially higher stress without fracturing. Makes sense, right?

Now the second thing is you notice the slope of the line. The slope of the line increases. If you remember, the slope essentially corresponds to the Weibull modulus. And the larger the modulus, the more consistent the glass material is. Essentially, it means that the glass material, they have a much narrower distribution of defects. So that's also what's shown here.

Essentially, with the ion exchange process, it essentially will give you a more reproducible or more consistent product finish compared to untreated. If it's just a regular soda lime glass, it's a much wider distribution of defects in terms of size and severity. So that's why people like to use these strengthened glasses, which is now a standard on most consumer electronic products. They are the cover glass materials.

Now, next thing I want to do, I want to actually draw a little comparison. Glasses do not come without competitors. For a long time, people have been talking about alternative carbon materials. And sapphire is the one that really stands out. In fact, if you go back about 10 years, there was a lot of discussions about Apple is going to switch to sapphire in the iPhone cover materials.

If you look back in like 2014, 2015-ish kind of time frame, Apple actually invested in a company, this one, GT ASF, GT Advanced Materials. The link is actually no longer working, but I decided to leave it there because the company has already been acquired. So Apple actually invested in that company several hundred of millions of dollars just to essentially crank up the manufacturing capability for sapphire screens.

It unfortunately did not really work out. If you look back the news, there was actually a lot of drama in that whole deal there. The company eventually filed for bankruptcy, but it doesn't mean that sapphire is going away. Apple still uses sapphire for some of their products, especially Apple Watch. So any of you have the Apple Watch? No? Just one, OK. I don't know which model you have.

AUDIENCE: It's old.

JUEJUN HU: OK. [LAUGHS] They have essentially two product lines. One is the lower-end model. They use aluminum casing. On that one, they still use the strengthened glass. They also have a higher-end model that uses either stainless steel or titanium. That one-- sapphire screen. I don't know which one you have, but you can try to scratch it. No. [LAUGHS] If you scratch it and it leaves a scratch, then it's glass. No, don't try it.

AUDIENCE: It's pretty scratched, so I'm going to say is not sapphire.

JUEJUN HU: It's probably glass, then. Don't try it. That's the best way to create surface defect that eventually lead to catastrophic failure.

AUDIENCE: It is rough. It might happen. [LAUGHS]

JUEJUN HU: Probably. Do your fractography. There you go. OK, so now what I want to do, I want to actually draw a little bit of a comparison between these two commonly used cover materials. And in the end, what I tried to show you here is that Apple actually made some rational choices.

There's a good reason why they use this specifically for Apple Watch in the higher-end models. So starting by looking at optical properties, refractive index, sapphire has a slightly higher refractive index. What does that mean? Refractive index actually impacts optical reflection. The higher refractive index, the more reflection you get.

So for glass, typical, normal, surface-normal refraction is about 4% based on the refractive index value. For sapphire, it's about 7.5%, 8%. So it's not a big difference. And you can potentially mitigate it with essentially anti-reflection coatings. But glass does have a slightly lower surface reflectance compared to sapphire.

Next part is density. So sapphire has higher density. Now for a cover material, you want it to have a smaller mass because everyone wants lighter consumer electronic devices. Again, it doesn't really make a big difference for small consumer electronic devices like Apple Watch. For larger devices like iPad, that weight actually adds up.

All right, next one, this is one of the most important metric here-- fracture toughness. So sapphire has a fracture toughness that's more than 2 times higher or 3 times higher compared to glass materials. And that's why if you actually read news report, some people were actually claiming sapphire is 3 times stronger compared to strengthened glass. We should give credit to authors of those articles because they actually did their homework. They actually looked up their fracture toughness, and that's where they draw their quantitative conclusion.

Now, however, what we have mentioned in the last lecture, if you recall, the glass, the fracture toughness was actually measured using ion-strengthened glass samples. It did not account for the fact that if you have compressive stress, it actually helps to prevent crack propagation. So the apparent fracture toughness or the apparent ability for glass to resist crack propagation is higher than what's actually specified by that number there. So the 3 times higher fracture toughness or 3 times stronger, that's not a totally fair comparison.

Now, in fact, we can compare this kind of availability of glass to resist fracture by looking at their strength here. So you can look at tensile strength. Unfortunately, I didn't find the number for strengthened glass. But flexural strength is what's more relevant. So flexural stress is basically the maximum surface stress the material can withstand before it breaks during bending.

So you can think of it as the ability of material to resist bending. Don't try it. You're not going to break it anyway. But if you compare them, sapphire and strengthened glass actually has quite comparable flexural strength. So in that regard, their performance is similar in this case, the ability to essentially withstand any kind of deformation.

Now, next one, the modulus, this is where you can make quite a bit of difference. Sapphire is a very stiff material. It has a Young's modulus that's 5 times higher compared to typical glasses. So what's the consequence? If you're trying to just look at the strength of essentially the screen, stand-alone screen, whether sapphire or glass, they are more or less similar because they have similar flexural strength.

However, when you put them in an electronic device, there are other materials that actually goes around the screen. So when you actually drop it-- I'm not going to try it-- if you actually drop it, then what actually deforms is not just your screen, but it's essentially the whole form. So now imagine if you have your screen as the most stiff component.

For example, if you have a sapphire, then when you actually drop it, most of the stress is going to be exerted on your screen because this is a stiff material, stiffest the material that has the least deformation. It will resist deformation most. And if you think about the Young's modulus of other materials like aluminum, aluminum has a Young's modulus of about 70 gigapascal.

So that's comparable to glass but much lower than sapphire. So it means that essentially sapphire on the aluminum casing form is going to withstand a lot larger stress compared to glass. Now what about stainless steel? Stainless steel has a Young's modulus higher than 200 gigapascal. So the mismatch is a lot smaller.

So you see that actually makes sense that for stainless-steel-cased Apple Watch, people will actually use a sapphire screen because the modulus mismatch is a lot less compared to casing and the screen there. In fact, it's not just Apple. If you look at other premium electronic manufacturers like Samsung, they make similar choices. They have sapphire screens on their Galaxy Watch or whatever, the high-end models. So again, out of that reasoning, it makes sense that they use it for casing with high Young's modulus.

Now last one, this is where sapphire really shines-- hardness. Sapphire is one of the hardest materials, I think, basically, only second to diamond. And this, of course, shows up as a very high Vickers hardness. Harness essentially means that it's a lot more scratch resistant.

And surface scratches is usually the defect that eventually leads to breaking of your phone screen or your whatever, iPad screen. So the risk, if you put, for example, your phone in your wallet, in your pocket, along with other stiff materials like your keys, or I don't know where you put it in your pocket, but the risk of causing surface scratch is higher for glass compared to sapphire.

So despite the fact that people have made major strides over the past few years in terms of the strength of screens, my recommendation is still, try not to put it with something that's sharp and stiff. It may not break it immediately, but it may cause more surface cracks. And in those cracks eventually is where the defects will nucleate. And that's where the Griffith's crack comes along. You will get stress concentration and everything. So again, that's where sapphire really wins.

AUDIENCE: Is that why screen protectors are a thing?

JUEJUN HU: Yes.

AUDIENCE: Because it just prevents the scratches.

JUEJUN HU: Not really. The screen protectors essentially is like, they take the scratches on the screen protectors so the underlying glass doesn't get damaged. So yes, but the downside is that you reduce light transmission. That's the biggest thing, I think. So it's really up to you.

I don't use any screen protector because I feel like people essentially make so much effort trying to make it more scratch resistant and make it highly transparent. They put all kinds of coatings to increase light transmittance, and you just put a screen protector on top of that to negate all those efforts. So out of respect for the glass engineers, I decided not to put the screen protector.

AUDIENCE: Why do you want to match your casing and screen's Young's moduli?

JUEJUN HU: So basically, what happens when you actually drop it, the whole thing deforms. If everything deforms more or less with the same extent, then you have the same level of strain.

AUDIENCE: Oh, OK.

JUEJUN HU: But if one thing is particularly stiff, everything else is soft in the extreme case. Essentially, all the soft parts can easily deform, but then the stiff part actually withstand the much larger stress compared to anything else.

AUDIENCE: OK.

JUEJUN HU: So you actually don't want that. You want everything to deform more or less to the same extent. That's why ideally everything should have more or less the same mechanical stiffness.

AUDIENCE: Yeah, that makes sense. OK, cool.

JUEJUN HU: Yeah. So that's a good reason why people should use one material or the other. Make sense? Now, outside these apparent quantitative material properties, obviously, there's also a perception difference for these two materials. Sapphire, to the years of known material scientists, it's a precious gemstone. Now, to us it's basically nothing more than Al2O3.

I'm actually surprised people are not calling alumina, why they call it a sapphire screen. They should call it alumina screen. Anyway, so sapphire does give people a feeling. In fact, people call it a luxury cover material. Nobody calls glass a luxury cover material, even though they last for billions of years.

So anyway, that's also part of the reason they're used in the high-end models. Also, sapphire is indeed more expensive than glass. The cost of sapphire substrates or windows has gone down very significantly over the past couple of decades, not because of the display industry, in fact, because of the lighting industry, LEDs.

Blue LEDs, gallium nitride, is often grown on sapphire substrate. So because of the economy of scale coming from LED industry, that's why sapphire gets a lot cheaper over the past two decades. And that's what makes it viable to actually make it even out of screens. But still, anyway, it's still more expensive than glass. That's why it also makes sense Apple puts it only in essentially the high-end models.

OK, so that's the comparison here. But now what I also want to mention is that, again, people have been working on glasses for decades, these strengthened glasses. They've come up with new ways to further improve the glass properties beyond what I have listed in the previous table. So one example here, Corning has this line of products they call scratch-resistant glasses.

The first generation is what they label as SR+. The more recent one they have a DX+. Unfortunately, they did not give much information about what DX+ is. We know it's derived from SR+. So that's why I'm using SR+ still as an example, even though it's a somewhat outdated product.

So what they are showing here, essentially, this is a little demonstration experiment. If you use the regular Gorilla Glass, you start to scratch it, this is essentially the scratches that happens using different forces you apply on the glass screen. You see a very large scratch happening here. If you use either the Gorilla Glass SR+ or this one, ALCM. It stands for Alternative Luxury Cover Material, basically sapphire.

You see that you don't get any scratches on these two materials. And so they did not give much information about why this glass material is more scratch resistant compared to the untreated Gorilla Glass. But as an MIT engineer, we like to dig a little bit deeper, so I actually look at their product spec sheet. I found in one corner, they actually give this transmission spectrum here.

The main purpose they give that diagram is to show that the glass material actually has a high optical transmission compared to sapphire, basically because of that lower refractive index. But what I also noticed is that unlike untreated Gorilla Glass, which has a more or less flat spectrum, you see these fringes or fluctuations coming up on the transmission spectrum there. So my speculation is that this is not just one uniform glass material.

What happens is that there can be one layer or maybe multiple layers of some surface coating so that when the light comes through, it can get reflected either on the top surface or it can actually get reflected at the glass coating interface. Now, depending on the wavelength and thickness of the film, these two reflected light waves, they can interfere either constructively or destructively, which then lead to an intensity fluctuation as a function of wavelength.

So I actually wrote the Matlab code to try to fit this transmission spectrum. This is what I end up getting. So the vertical axis is essentially wavelength. So what this does, what you are seeing here, they correspond to the extremum positions and the transmission spectrum, the maximum/minimum.

I extracted it from that plot. And essentially, I just did the fitting. So if everything falls on one line, it says that this is indeed caused by reflectance. I basically fitted to this very simple model there. OK, so while we still don't know exactly why you have this scratch-resistant property, we can at least conclude, based on my fitting, that there's actually a surface coating layer, which is about 2.3 microns in thickness and has a refraction index 0.03 higher or lower compared to a substrate glass.

So it's plausible that this coating is also a coating with a higher hardness, so they prevent essentially any scratches on the glass surface. Again, this is speculation, but it makes sense because that's the only difference I see between this glass material and the untreated Gorilla.

Now let's take a look at another trick. This one I think is much more ingenious. This actually does engineer the glass intrinsic properties to get the damage resistance. So this is another line of products. They call it native glass materials with native damage resistance, NDR. So at the bottom, again I'm showing you what happens here. If you just scratch on glass material without this capability, you get large scratches. With this capability, the scratch is more confined.

Microscopically, if you look at what happens, this is a cross section of the scratch. On other materials without this capability, you see lots of microcracks forming. And that happens because when you actually try to scratch it, you apply this essentially compressive stress. Then, stress accumulation exceeds the strength of the material at the surface, which eventually leads to a formation of microcracks.

On the other hand, if it is glass with NDR, you see this region here, this part, this is the region with a lot of plastic deformation. Essentially, the cracks is inhibited because the plastic formation helps to absorb a lot of the deformation. So this is a glass that can induce a considerable amount of plastic deformation, essentially, in the form of densification.

So how does it work? So the trick goes back to when we talk about borosilicate glasses. So when we talk about borosilicate glasses, we mentioned that boron has this boron anomaly. It can essentially switch between two kinds of microstructure moieties. It can either be forming essentially a B3.

I show them in there. You can actually have a non-bridging oxygen. Or it can induce this B3 to B4 conversion. You form a fourfold coordinate boron atom which give rise to a more tightly connected network, which gives you essentially a higher density, among other properties, like lower thermal expansion coefficients. So the trick they play is that they essentially add boron into the glass network.

And they engineer chemistry so that when you actually apply stress, the stress actually induces a transformation from B3 to B4. In the process, the density of glass increases because of increased network connectivity. And this is the plastic deformation. It's a permanent plastic deformation.

So it's a stress-induced chemical transformation which also brings in a densification. So that's why this material can now actually absorb a lot more deformation while inhibiting the formation of cracks, which I think is a pretty smart trick. They actually use the structural transformation to help prevent the crack formation. Any questions about that before I move on?

OK. So now, besides being scratch resistant or damage resistant, I want to mention that the other advances that people were able to accomplish is to make bendable phone screens. So this is actually from a news release by Samsung. I think this is about 2020 or something. They essentially unveil what they claim is the first foldable phone with a glass screen, the Z Flip.

In the news release, you can see that you can essentially fold the phone in half. They claim that they were able to bend the laws of physics to get glasses to be bendable. Is that really the case? Well, we can take a look. First, actually, I'm going to show you a little YouTube video. The key trick that you can actually get these glasses to be really flexible and foldable is to make them extremely thin. This one has no sound.

[VIDEO PLAYBACK]

Internet connection is not very good. Oops. So this company specializes in laser processing of these ultra-thin glasses. So you can see that they can actually use the surface patterns to help relieve the stress. They have actually some data to show that. You can see the stress distribution with the surface patterning helping to release the stress at the edges. But they were able to bend it to a very small bending radius. And it's completely flexible.

[END PLAYBACK]

So what's the physics here? Are we actually breaking any physical laws? If you think about if you bend a sheet of glass, that's mechanics 101. What happens? On the top surface, you have essentially tensile strain. At the bottom surface, you get compressive strain. If the glass is uniform, then right in the middle, you have what's called a neutral plane or neutral axis, where the stress essentially goes to 0.

So if a glass were to break, this top surface where you have tensile stress is usually where any kind of defect is going to initiate. So the strain level on the top surface, the strain, epsilon, on the top surface, this is actually given by-- basically, if we label the glass thickness, this is, let's say, d; the radius of the bending here, let's label it as r-- then, the strain on the top surface will just be given by epsilon equals to 1/2 thickness normalized by the bending radius.

That's just a very simple equation for mechanics that gives you what's the strain on the top surface. So now let's plug in some numbers and see what the strain is. And from there, we can calculate the stress. So for these ultra-thin glasses, their thickness is of the order of 25 to 30 microns. Let's just take, let's say, 30 microns. So 30 microns is 0.03 millimeters.

In terms of bending radius, we see that they can be bent to a very tight bending radius, down to about 1 millimeter. So let's just take a rounded number. This is 2 times 1 millimeter gives you 2 millimeters. So it's pretty straightforward to calculate that the strain now on the surface is 1.5%.

Now what about the stress? So we need to know the Young's modulus if we want to infer what the stress is. So come back here. The Young's modulus for glass, 60 to 75 gigapascals. Let's just say 60 gigapascals. Then the stress is going to be E times epsilon. So what does that correspond to? So it will be 60 times 1.5. So it becomes a 0.9 gigapascals, or 900 megapascals.

So if you have a glass sheet that has not been chemically strengthened, this would be the level of tensile stress the glass will see. However, you notice that this glass material, once they are properly strengthened, they can have a compressive stress of the order of 900 megapascals or above. So it means even under these pretty extreme bending conditions, the surface is still almost in a tensile stress-free state or even still in a compressive stress state.

Because of the native compressive stress, you have to add it on top of this stress here. So if you're under neutral condition or under compressive stress condition, obviously you're not going to get a lot of crack propagation. So that's why we see that there's really no breaking of physical laws.

The whole idea is that as long as you make the glass material thin enough and also apply large enough surface compressive stress through chemical strengthening, you will be able to prevent any crack initiation, even under these predicted bending conditions. So the whole idea is to get a very thin piece of glass that has a thickness that's 30 microns, about 1/3 of a sheet of paper. So it's really very, very thin.

Now, one thing I do want to mention, though, about this particular phone here, Z Flip, if you look at the way the process is demonstrated here, the screen is actually not one single-layer material. They actually put two layers there, essentially a glass that they also put on top a polymer layer as a protective coating to prevent surface damage.

Downside is, polymer, of course, is soft. It's not scratch resistant, even compared to glass. And that's why the phone actually gets quite a bit of criticism because of the poor ability to withstand the surface scratches. But that's the trade off there.

So now, let's move beyond cover materials and let's look at, these are glass materials with extremely high K steps. You may recall that K steps is basically the diffusion distance of the ions during the ion exchange process. So these are glass materials with very high fracture resistance compared to typical materials because of large K steps and extremely high level of surface stress.

So these are the materials that are used for some high-end applications, for architectural applications, for example. They are also the materials people use on essentially military vehicles as the window materials. They can actually be bulletproof because of very, very high level of surface stress. So let's take a look at the chemistry here and see how they were able to achieve these extremely high K steps.

Look at the K steps here. These are typically hundreds of microns K steps. And in the extreme case, you can even get 1-millimeter-thick K steps. So to get to this high K steps, these are all aluminum silicate glasses. As we mentioned, you have alumina there because you want to essentially boost the glass transition temperature so you don't get glass relaxation even if you do a high temperature treatment. You can use high temperature to expedite the ionic diffusion process.

So that's why you see that pretty consistently, they all contain alumina. Also, the other thing is that you notice that they always contain a couple of percent or few percent of magnesium oxide or calcium oxide. This is what we mentioned in last lecture. Empirically, people have found out that adding this rare-earth oxide helps the diffusion of alkaline ions.

And then in terms of the ion exchange process, you also notice that they use a mixed ion bath for these ones with very high K steps. This is also something we mentioned in last lecture. If you do a mixed ion bath, this will actually also help to increase the diffusion of the ions into the surface. Now, despite all this treatment, this process still takes a very long time just because of the kinetics of diffusion process.

So look at the time it takes to process the glass materials. They range from one day to the case of half a month for the ion strengthening process. They just allow ion to essentially penetrate through this large surface thickness. So that's an extreme example where you can actually get to this very high strength glass materials.

Now these are actually some quantitative data just to show you that in this first plot here, this is just to illustrate that this kind of mixed ion bath actually helps with promoting the diffusion kinetics. So you see these dots here. You can see from the horizontal axis here, this is basically the depth below surface where the ion has diffused into.

You can clearly see that if you mix into a mixed ion bath with sodium or potassium, you get more penetration into the glass material compared to the ones using only one kind of ionic species. Weibull plot again. So on the Weibull plot, we also see that we can get much higher strength. These are the points that actually correspond to strengthened glass materials.

These are the ones that are actually not strengthened. With mixed ion bath, these are the ones with the highest strength, the green dots. These are actually with the mixed ion bath. So they're high strength. At the same time, you also see the same thing, improved Weibull modulus, indicating that the material after ion exchange becomes more consistent, in terms of quality.

All right, so these are for essentially flat-panel glasses, how you use chemical strengthening to increase its ability to resist fracturing. The other case where ion or chemical strengthening or ion exchange is widely used is for glass containers, especially vials used for pharmaceutical applications. This is one case where you cannot do conventional thermal tempering.

Because of the geometry, inherent strange geometry and non-uniform thickness of a vial, if you do thermal tempering, it's going to lead to a very non-uniform cooling profile, therefore leading to non-uniform thermal stress. So that's why people basically use a chemical toughening to strengthen these vials for pharmaceutical applications.

So what I'm quoting here, this is actually an article that's from 2020, essentially at the peak of COVID, where people are actually racing to develop vaccines against COVID. One of the issues they faced there is not just to scale up the manufacturing of the vaccine itself, but also the container that actually contain those vaccines. And this is not a small problem because you need billions of glass containers so that they were able to ship this COVID virus products to around the world.

The requirement is also pretty stringent here. For this vials used to contain vaccines, they need to withstand a very wide temperature range. You may recall that a lot of the vaccines, they had to be stored at cryogenic temperatures. For example, Pfizer's vaccine, they have to store at negative 70 degrees Celsius. They also need to withstand high temperatures because these containers need to be sterilized. And they usually sterilized at high temperature, 200, 300 degrees Celsius.

So unlike everyday-use glass material, which usually sees a much narrower temperature window, all the pharmaceutical vials, they have to be specified to operate from negative 100 degrees Celsius to positive 400 degrees Celsius, which is a very wide temperature range compared to other kind of glass products.

They also operate in a potentially chemically corrosive environment. They have been in contact with aqueous solution for a long period of time. So you don't want any kind of components from the glass to actually leach into the solution. They also have to have a very high resistance to surface damage, essentially resistant to wear and tear.

And most of their requirements actually come from the manufacturing side. You can imagine that if you have a very delicate glass product, then you have to be very, very careful in handling them during manufacturing and during packaging. So that actually lowers the throughput. So to use high throughput process, they also require the glass with very high surface strength.

So that's why-- this is one example-- for example, Corning actually developed this special line of glass they call Valor Glass. It has several important features that make it suited for this particular kind of pharmaceutical applications here. The first one is that it's boron-free.

Now we have mentioned about boron, essentially like Pyrex glass. Pyrex glass is used in a lot of these applications when you're dealing with chemicals because of essentially you have this tightly connected network. It has good thermal shock resistance. It's also more chemically resistant. However, when it comes to pharmaceutical vials, people don't like to use boron because it can cause a problem of so-called delamination.

So why do you get delamination? First thing, it has to do with the manufacturing process of these vials. So if you have a regular glass bottle, the way you make it is by blow molding. You blow compressed air through the parison and it conforms to the shape to get the bottle. Blow molding is not used for this pharmaceutical vials for a few reasons.

First thing, blow molding, borosilicate glass typically has a much higher glass transition temperature, so it means the processing temperature is a lot higher. So it makes it a more challenging process. Second is that blow molding typically causes very large plastic deformation or very large deformation, viscous deformation, during the process.

Large deformation means that there's also a much higher residual stress, as you can see from the bottle. I showed you the plastic bottle. It has lots of residual stress in blow-molded bottle there. And those residual stress can eventually lead to cracking and damage of the material. So for pharmaceutical industry where they absolutely want everything to be perfect, you cannot do that.

So for these kind of vials, the process to make it is so-called converting. Converting essentially means that you have a long glass tube. They start out by cutting it into sections. They then sealed one end and then shape it into the vial shape. So that process gives you less deformation and less residual stress compared to a blow-molding process.

However, the conversion process involves high temperature treatment. You need to have high temperature to actually induce viscous deformation and seal it at one end. So during high-temperature treatment, boron can preferentially leach out from the glass and it actually vaporizes in the form of borosilicate.

So this vaporized boron, some of it can get redeposited in parts of the glass container which has a lower temperature during the process. So this redeposited boron is then going to attach to the surface of container forming these islands or patches with chemical inhomogeneity. Then, the remaining glass will become boron-depleted. So boron-depleted portion becomes more susceptible to chemical attack.

Remember, when glass comes into contact with aqueous solution, any kind of alkaline atom can leach reach out into the solution there, and it eventually increases the pH value, which accelerates a chemical attack. So then essentially these weaker part of the glasses, they will then delaminate from the glass container surface and essentially form small tiny little flakes that goes into the solution.

So delamination turns out to be one of the biggest problems that compromised the yield of this kind of vaccine product. So that's why Corning want to go with this kind of boron-free formulation, which helps you to essentially minimize this kind of a boron volatilization issue and reduce this kind of delamination impact. So that's one thing.

Second thing is that they also develop a proprietary surface coating, which helps you to prevent any kind of wear and tear. As I said, this is important for increasing the manufacturing throughput. And they also do ion exchange to enhance the mechanical strength. If you look at the ion exchange process they use, this is actually a picture taken from their factories where they're actually manufacturing these glass vials.

You see these huge cassettes where they essentially put down these vials, essentially layer by layer, and then they put all of them into a huge molten salt chemical bath here. So this is a very highly parallel process, completely automated, that gives you extremely high throughput. So you can actually manufacture billions of these bottles during a short period of time.

All right, so far we've been talking about different kinds of strengthening processes by inducing compressive stress. I want to mention that to get the optimal performance of glass materials, you can also try to combine it with other materials to create a composite that helps you to further boost their properties, reduce damage. The most simple form of this kind of composite materials is lamination.

So in laminated glass, basically you have alternating layers between glass and polymers. You have a glass, put a polymer sheet, sandwich it between another layer of glass. You can repeat the process to get multilayer laminates. Now the advantage, there are twofold advantage here. One is that these soft polymers essentially helps you absorb the deformation and helps you spread it over the larger glass sheet.

Also, even if you fracture one pane of glass, the polymer tends to hold the broken pieces together so that you don't have large shards falling down, which may potentially injure people. So that's why this kind of laminated glass, this is a standard glass material people use in architectural applications. So I'm actually giving you one example here.

This is the Skywalk at Grand Canyon. Any of you have been there? It doesn't matter. Most of the building classes, they are actually laminated glass. But in the Skywalk, they have basically a glass bridge with glass bottom. You can actually walk on top of Grand Canyon and you can look down, take pictures, post them on Instagram or whatever. That's what it's for. So, not going to go there?

AUDIENCE: No.

[LAUGHTER]

JUEJUN HU: Not going to pay to go there, right?

AUDIENCE: No.

JUEJUN HU: OK. So that's one example. Now, you can also make this laminated glass actually bulletproof. I will show you a little video here.

[VIDEO PLAYBACK]

- What you might not know is performance flattening.

- It's not very targeted.

- Meet Trent Kimball from San Antonio, Texas. He's the head of a firm that makes armored cars.

- We'll take a common, everyday vehicle, take out the entire interior and put in our armored materials in the doors, the windows, the roof, the floor, the fuel tanks, and basically make it a cocoon of armor for the occupants inside the vehicle. These vehicles are going to politicians, businessmen, celebrities, and we've even offered them for the Pope.

- One day, Trent got so tired of people asking him if the glass in his vehicles could really stop a bullet, he decided to prove it.

- My name is Lawrence Caso. This is my AK-47. And today I'm gonna shoot my boss. Don't try this at home.

[GUNSHOTS]

- The only time I've had a little bit of fear enter my body was actually looking at the shooter, and the shooter's eyes got really big. So that's the only time I actually felt a little bit nervous.

- Shooting at my boss is actually pretty interesting. I bet there's a lot of people who would like to do it, but I like my boss. He's pretty cool, so I'm glad he's OK.

- Yes, Trent lived and uploaded this astonishing clip to the internet, where it has almost 6 million hits. But exactly how did that windshield save his skin?

- The way you make glass absorb the energy from something like an AK-47 is that you have to make laminated glass. So you'll have a layer of glass, and then you'll have a layer of a material called polycarbonate, and then you'll have another layer of glass, and another layer of polycarbonate, and then so on and so on and so on to make a thick window.

- This is a composite. And composites are used when you want the properties of two different materials, you want to put them together for different purposes.

[GUNSHOT]

If you were to just to have a thin piece of plastic, a bullet would easily penetrate that. If you just have a piece of glass, the bullet would cause it to completely shatter. You put those together and the glass disperses that force of that bullet over a larger area, and then the plastic can absorb that force.

- Aside from the AK-47 the M16 and other military-type weapons, we can also stop the hand grenades and also right up to the 50-caliber round.

- So thanks to the laminated glass, Trent dodged not one, but three bullets from a lethal semi-automatic rifle. The really scary part was still to come.

- I did not tell my wife. She wasn't going to know until after.

[GUNSHOT]

Now she says we can't do it again.

[END PLAYBACK]

JUEJUN HU: OK, so now this is actually some scientific literature to prove that indeed, laminated glass actually helps increase the strength of glass products. So you can see from here, if you have a monolithic piece of glass versus glass with laminates and different thickness of the polymer layers, you can see an apparent increase of the fracture strength. So this is scientifically validated. You can actually help improve the strength.

Now I just want to mention that you can actually take this design to another level. In addition to increasing the strength of glass materials, you can also use it to actually create highly flexible and bendable glass devices by using essentially this kind of a laminated or multi-layer design.

So what I'm showing you here on the left-hand side, this is how you would actually make a foldable glass device, as I mentioned. I showed you on the board. Basically, you bend it. At the top, you have a tensile strength, bottom, the compressive strength, in the middle, you have a neutral plane or neutral axis where stress essentially vanishes.

Now, this design is actually useful because people use it to create all type of flexible electronic or flexible photonic device designs. What they will do is they can put their device, which is very sensitive strength, you don't want to damage it. They will try to locate it right in the middle here at the neutral plane where the stress vanishes.

So then regardless of how you actually bend your structure, your critical device is not going to get damaged because the actual stress on that is actually 0. Now, one downside about this design here is that your devices must be embedded in your substrate. This could be an issue, for example, if you have devices that actually dissipate lots of heat. Usually the flexible material around it is some kind of polymer, which is pretty terrible thermal conductor.

And putting something that generates heat embedded in a poor thermal conductor is never a good idea. You also have some applications where you actually want your device to interact with surrounding environments. For example, for sensing applications like for biomedical applications, you want to have the device actually exposed on the surface or near the surface rather than embedded very deep in the substrate.

So that's why an alternative design that was proposed here is to essentially create this kind of laminate structure. You have two stiff layers on top and bottom. In between, you put a very low Young's modulus material, sort of like rubber. Now when you bend it, what this new theory tells you is that instead of having just one single neutral axis, you actually have multiple planes of this kind of neutral axis here where the stress actually goes to 0.

What's also more important is that by tuning the thickness and moduli of the different layers, you can tune the position of these neutral planes, essentially versatilely across the entire stack. So this allows you to put devices that's actually much closer to the surface compared to the classical neutral-plane design I'm showing on the left-hand side.

So in this slide, I'm going to show you one demo. In this case, this is actually from my group. We were able to actually bend these flexible devices made out of glass materials. We can bend it down to an extremely small bending radius of 0.3 millimeters, and we can also essentially bend them for hundreds and thousands of cycles without seeing any damage, essentially leveraging this kind of a multi-neutral axis design.

So this is for essentially to bend the glass. For some other applications, you not only want your material to be bendable, you also want it to be stretchable. So for example, for a lot of biomedical applications, people are trying to do epidermal integration, essentially putting the device directly on top of human skin. Human skin is actually a material that can easily withstand a large plastic deformation.

So to match that, it means that your device should now be able to bend. It should be able to stretch and compress. So how do you create a stretchable device out of a stiff material? What you would do is now instead of doing multilayer lamination, you now change the in-plane configuration of the device. And the inspiration comes from the fact that, for example, if you think about a helix springs.

Stainless steel is pretty stiff material in a bulk form, but if you shape it into this helical shape, you can actually stretch it and compress it with a very large strain. So what we did is you can now essentially create basically this kind of in-plane photonic springs. You essentially generate this kind of meandering shape of glass materials here. And when you actually stretch it, what we have shown is that it will deform essentially both in-plane and out of plane. And in doing so, the level of actual stress exerted on the glass material can be very, very small.

On top of that, what we also do is that for some devices, you may have some critical devices where you absolutely don't want any kind of mechanical deformation. So what we can do is we can actually embed these critical devices that you don't want to deform in a stiff material. So eventually the configuration will be like you have these kind of stiff islands locally. They are interconnected together by these kind of meandering structures.

So when you actually stretch it, essentially the meandering structure absorbs all the deformation while keeping the stiff islands completely intact, free of stress. So that's the strategy we have demonstrated. You can actually essentially create the structures out of essentially brittle glass material, but you can essentially create very long, large elongation, and you can also stretch them for thousands of cycles without seeing any kind of damage.

So we've talked about two different kinds of strategies of how to change the configuration of glass materials to accommodate normal mechanical attributes. You can either do a outer plane structural engineering by lamination. You can also change the in-plane structure, like in the case of stretchable devices. You can combine the two.

You can combine both lamination and also in-plane structuring. So this is shown in this example here. So in this paper, the authors essentially develop a toughened glass material inspired by this natural material nacre. So nacre is the material that is found inside the inner layer of the shells, seashells. It's essentially the lustrous material that people also call it the mother of pearl.

So nacre, actually the main ingredient is calcium carbonate, limestone. But nacre, it turns out it's actually quite flexible and it's also very tough. So how do you make limestone essentially flexible and tough? So the trick here, if you look at the microstructure of nacre, it consists of multiple layers. And then within each layer, it's also not a monolithic piece. You have these kind of little platelets, essentially little plates.

In between, you infiltrated with essentially a polymer material. So when you actually try to bend it or try to deform it, these platelets can essentially shift with respect to each other to absorb this kind of deformation there. So that's actually one of the configurational designs that the authors explored. So what they did is they started out essentially from just a typical flat sheet glass. They use laser writing to engrave these changes in these glass materials here without completely etching all the way through.

So they are still connected as one piece. They then go through the typical lamination process to form a multilayer structure. And in the end, when you actually start to bend it, because the glass pieces, they are only connected together through this the deep trenches, so when you actually bend it, they essentially break and separate into individual pieces. So that's how they create this kind of nacre-like microstructures.

They choose this kind of a glass material and the polymer material to have a very similar refractive index. So when the light goes through it, it barely sees this kind of microstructure there with minimal amount of scattering because of index matching. So that's why, if you look at the optical transmission diagram here, this kind of laminated material, 3D material, they still have optical transmittance that's fairly close or reasonably close compared to untreated glass.

But they do exhibit much enhanced properties when it comes to resisting damage during mechanical deformation. So at the bottom here, you see that on top row, this is when you try to apply stress on one point on different kind of materials. You have a plain laminated glass, borosilicate and PMMA. At the bottom, you have this one. This is actually an nacre-like material.

You clearly see that all the other cases, you generate lots of defects and cracks. In this case, the material remains intact. In terms of the mechanism, this can actually help absorb this kind of deformation here. I have this little video. And also I show the simulation result on the left-hand side. The bottom line is what I said. When you actually try to bend it, the platelets inside each laminate layers, they can essentially shift their position with respect to each other.

And this helps to prevent the formation of cracks. You can clearly see from here this laminate has to move with respect to each other. This one is just a plain laminated sheet without this in-plane structuring. So this is one example to show you that by combining this actually out-of-plane and in-plane structuring, you can get to glass components that offer unique mechanical attributes.

All right. I'm going to wrap up here for this section here on glass strengthening. The key takeaway message here is that we spend lots of time essentially talking about these different kind of strengthening techniques. So you want to be able to understand the differences between these strengthening methods. You have essentially a thermal tempering.

For thermal tempering, there are two subcategories there. You can have heat-strengthened glass versus tempered glass. They really differ only by the amount of surface stress you accumulate. But for tempered glass, large surface stress also means that there's very large tensile stress region inside the glass material, which may cause spontaneous breaking, while the risk of spontaneous breaking is actually nonexistent for the case of heat-strengthened glass.

For chemically strengthened glass material, they don't break spontaneously because of the smaller surface thickness of the chemical stress there. And one important difference I also want to highlight here is the temperature for the heat treatment. All of them involve treating the glass material at high temperature. But for heat strengthening, you need to heat it up to above the glass transition temperature. So a high temperature is actually stress free.

You only accumulate this stress when you actually cool down such as the surface starts to approach the room temperature. That's when the temperature gradient is converted into the thermal stress. Versus chemical strengthening-- the process has to take place below the glass transition temperature, because you don't want any of the stress coming from the ion exchange process to get relaxed in this process. So that's a key difference here. The heat treatment temperature is different from these different processes.

Any more questions about strengthening? OK. So we still have a bit of time. I think I actually have some time to quickly go over the P-set. OK, so first question is really straightforward. You all get it right one way or the other. I just want to mention that you can actually be a bit more quantitative. So co-working is not a way to actually make amorphous material pieces because of the strain softening.

You can either do casting or you can do essentially a thermoplastic forming. So for casting, you can actually try to calculate what is the critical thickness you can cast without inducing crystallization. This data, this is what I found from online. You can also find the kinetics of crystallization by looking at the TT diagram for vitreloy. It turns out vitreloy is one of probably most widely used metallic glass compositions, so its data is pretty much everywhere.

In fact, in my class when I show this TT diagram, the example I use is vitreloy. So you can actually get the critical cooling curve, critical cooling rate from this plot here. Plug it back. What you find out is that you can cast a vitreloy medallion up to 2.2 centimeters thickness without inducing crystallization. That's why it's called bulk metallic glasses. They really have quite good ability to resist crystallization. So you can treat them using conventional process.

Now another route, you can do thermoplastic forming, for example, compressive molding. Compression molding should work pretty well because medallion is a pretty open structure. You can have two pieces, just press it and then it will mold. Again, you can do some quantitative calculation here. To predict the compressive molding process compatibility, you need to know how long the glass can stay at a state without crystallization during the process, at the right viscosity value.

So you start out by essentially looking at the viscosity value for compression molding from the slides. Then you go to the Angel plot, which I also have in the slides. This one is vitreloy, so basically this slide here. So from that, you can then read out for this particular viscosity value what's the corresponding temperature. Then with that temperature, you then go back to TT diagram. You can then read out what's the time it takes for it to crystallize.

Then that gives you the time window you can actually perform your compressed modeling without a risk of crystallization. So that's the calculation I did. We figured that we can actually get to a process window about more than three minutes, which should be more than enough for simple compressed molding process. So that's why we conclude this compressed molding process is compatible with structuring with vitreloy.

You can also do injection molding. Injection molding requires lower viscosity, which then means that you have to go to higher temperature. In fact, as a result, you have a narrow time window. In this particular case, this is probably also not quite preferred because the processing temperature is actually above the nose temperature, which means that when you are trying to cool it down, you have to go through this nose temperature, which potentially has a much higher risk of crystallization. So it's not quite preferred but potentially also viable.

So that's the first one. Second one, basically we write our code. One thing I noticed is that for some of you, your answer shows a little bump in the cooling curve. That should not happen because when the glass relaxes, it should always relax towards the quotation mark, "equilibrium state," which is a supercooled liquid state.

For this particular example here, the supercooled liquid state has a volume smaller than the glassy state, so the volume should always decrease when it relaxes. So it should not go back up. Volume always goes down. So double check your code. Maybe probably it's just a sign error or something. I want to spend a little bit of time talking about this guy here, about the heat released in the heat treatment process.

So heat released, this is directly related to enthalpy change. This is the amount of heat that's actually released. So this can be written as, the heat released, it should be this one. The heat flux, I should say, it should be the enthalpy change over time. So then this can be written, you can write it in this form here. Convert it into two derivatives here.

The first one, dH/dT, this is actually quite straightforward. This basically is the slope of the enthalpy temperature curve. The second one is just your heating rate. It's a bit easier to try to plot the heat flux as a function of time, rather than as a function of temperature. It gets pretty confusing as a function of temperature because we are heating, cooling, and reheating. So the curve becomes a bit messy.

I should be a bit more clear, I apologize. We should try to plot it as a function of time, rather than as a function of temperature. So I should have made it a bit less confusing. But anyway, if you try to plot it as a function of time, you need to look at the sign of these two factors here. So for this one, first term, we have mentioned that the shape of the curve for enthalpy is quite similar to that of volume.

So we can basically go back to this plot here that shows how the volume changes as a function of temperature and essentially plot it, in this case, also for enthalpy. The caveat is that when I'm plotting this plot here, you notice that this last line is completely flat. Now, it's not supposed to be completely flat. The reason it's flat is because we neglect any kind of thermal expansion of the glassy state.

Now, same thing for enthalpy. The slope of the line corresponds to the heat capacity of the glassy state, which is not zero. So we should essentially artificially add that slope back. So what we have will be something like this. You have this curve here. It goes back to the glass line. And then when you heat it back up, it will retrace this line here, goes back down, come here, and goes back, like that. This is what it should be looking like.

So now we can divide it into a few different regimes and try to plot this diagram separately. So first regime is when we are cooling down. This is our regime 1. Second is when you start to reheat it up. Now during reheating process, you notice that there's actually a maximum point. So around this maximum point, the sign of the slope of the curve actually changes sign.

So that's why we should have two regimes here. The first one is when you actually more or less retrace this curve. And then the third regime is when you see significant structural relaxation during the last transitional regime. And then the fourth regime, of course, is when you actually are cooling it back down.

So now let's take a look at the sign of each of the terms during these four processes here. So first process, cooling, the slope of the curve is positive. This is regime 1. So the slope of a curve is positive. dT/dt, this is a cooling process, so temperature decreases with time, so this should be negative.

So overall, the dH/dt for the heat flux, this should be a negative. Now it should be negative because during cooling the material obviously releases heat to the environment. So negative sign essentially just means that the material is releasing heat.

Second regime, so for the second regime here, dH/dt is still positive. But dT/dt, this is the reheating process, so it becomes positive. So then what we have, this is a positive 0. It means that the material is now absorbing heat because you're reheating it up.

OK, regime 3, for regime 3 what's different here is that this curve, dH/dt, now has a negative slope. This is the reheating process. So while the temperature is increasing, you're actually releasing heat because you essentially the glass material is relaxing.

It's relaxing to this more stable supercooled liquid state. In the process, it's releasing excess enthalpy to the environment. That's why it becomes negative. Finally, the last process here, process number 4, again, you have a positive slope for dH/dT. dT/dt, this is cooling, so it should be negative. So it should also be negative.

Now let's try to stitch things together and try to plot this diagram here. So this will be our dH/dt. This will be our heat flux basically as a function of time. So let's see what happens. So first part, this is going to be a negative, but initially, you get a larger slope.

So for constant cooling rate, initially you get a larger negative heat flux. And then you should smoothly reduce to a lower level because now you are essentially converting from supercooled liquid to glass. And glass has a smaller heat capacity.

Now, go to regime 2. I should probably make it a bit narrower. I don't have that much space on board. So this is regime 1, regime 1. Now regime 2, in regime 2, we have a positive. Initially, regime 2, the curve actually more or less retraces the curve in regime 1.

So it means that the heat flux essentially just flips signs, but the magnitude is the same. And then eventually, because the dH/dt starts to decrease and eventually flips sign, it means that the heat flux should also decrease and eventually flips signs. So this would be regime 2.

So that means regime 3, regime 3 and 2, they should be continuous. It's basically one same process. So the curve should also be continuous. It should continue to extend. And eventually it should reach some kind of maximum slope here. And then the slope would then decrease again. So it means that it should reach a maximum and then goes back. So this will be regime 3.

Finally, for regime 4, regime 4, this would also be a negative, started out negative. And then the slope increases and then decreases again. Oh, sorry. I should make it a bit more dramatic. In the end, the slope is the same as the regime 2 and regime 1.

So it should come back to the same level. So it should go larger and then eventually comes back to the same level. It should come back to the same level as the final plateau of regime 1. So that's what the curve is going to look like. This is the more complex problem in the whole P-set here.

AUDIENCE: I was only a little bit wrong.

JUEJUN HU: I think you more or less get it right. You get the idea. Part of your confusion, I should really say that you should plot it as a function of time, not as a function of temperature. If you plot it as function of temperature, it gets really confusing which way it's going and all that stuff.

All right. Last question here, this one is straightforward. Basically, you just want to prevent the formation of ice crystals by amortizing it. The interesting part is that I was actually reading about this technology called cryonics. Maybe you all heard of it. It's also called, I think, cryogenic sleep or cryogenic hibernation, which appears in lots of science fiction.

Basically, it's saying if you want to go into a hibernation state, if you can quickly freeze it, then you can wake back up after a few decades, as long as you heat up. Now, the biggest barrier why that doesn't work is because of crystallization. So when you actually try to freeze body fluids, essentially it forms ice crystals. And these tiny little sharp ice crystals, they can pierce through the cell membrane and then eventually leading to it becoming nonfunctional.

So the whole idea for people working in that field is to create some material, some liquid, that can go into a glassy state as you go to cryogenic temperature. So when you go back up, you prevent any kind of formation of crystals. So amorphization, amorphous material is quite important there, if you want to realize essentially eternal life through cryonics. So that's why amorphous material is important. It's eternal. We have seen that.

We still have five minutes. I think I can actually do the demo. Now, this lecture is about glass strengthening. Next lecture is actually about amorphous, about metallic glasses. I'm not going to go into details there because we don't have enough time, but I can show you a little demo. So metallic glasses has a lot of unique mechanical attributes. That's why I have a chapter dedicated to metallic glasses.

So what I have here, on top this is a sheet of metallic glass, vitreloy. It's sitting on an aluminum truck. I have with me a little bowl made of stainless steel. What I will do, I will let it bounce back, initially starting on, let it bounce back on the aluminum. OK, I'll do it again, pretty boring. OK, now I turn to the face where I have metallic glass. I'll do exactly the same thing.

I'll try again. You can do aluminum again. I don't know if it was properly filmed. Why do you see the difference?

AUDIENCE: Because the glasses have really high modulus, elastic modulus.

JUEJUN HU: What limits the height of the ball bouncing back?

AUDIENCE: Plastic deformation.

JUEJUN HU: OK. What does plastic deformation do?

AUDIENCE: It absorbs energy.

JUEJUN HU: Exactly. If it absorbs energy, then it doesn't bounce back nearly as high. The basic physics behind it, it's because aluminum, when actually the ball impinge on the surface, it causes lots of plastic deformation. That's why it causes dents. It absorbs energy. But for metallic glass, it doesn't have a proper mechanism to induce large plastic deformation.

We mentioned about this because it doesn't have any kind of dislocations. So you don't have the typical dislocation motion mechanism to actually cause plastic deformation. And that's why metallic glasses tend to have much higher elastic limit and higher yield strength. So this experiment actually shows what happens when you actually have a material that doesn't deform plastically.

Essentially, all the energy gets stored in the form of elastic energy, so it will bounce back with minimal amount of internal damping. I'm going to stop here. And in the next lecture, we are going through more details about the actual structural model of amorphous metal and its mechanical attributes. All right, thank you.