[SQUEAKING]

[RUSTLING]

[CLICKING]

JUEJUN HU:

So let's continue our discussion on glass strengthening. So in the last lecture, we highlighted there are three different techniques, or three different groups of techniques, for strengthening glass materials. You can either engineer the chemistry to enhance the intrinsic material parameter K1c. Or you can try to essentially decrease or eliminate the defects, surface cracks. And the third one is that also, even if there are surface defects, if you apply surface compressive stress, you can prevent the opening of cracks, and therefore essentially apparently make the glass material more strong.

So let me elaborate a little bit and talk about all the different techniques. Let's start from the first one. How do you actually engineer the intrinsic glass chemistry to boost its K1c?

So in the previous lecture, we have already given you an analytical expression of what K1c looks like. So effectively, K1c is a material constant. And it depends on two parameters in a brittle material, which is gamma the surface energy, and E is the elastic modulus.

Now, gamma is directly dictated by the bond energy, because when you are trying to form new surfaces, you are essentially spending energy to break chemical bonds. And the excess energy you accumulate is basically because of the chemical bonds. They are now essentially dangling on the surface. The electrons are no longer paired with one another to lower the overall energy.

So the basic material theory says that gamma is directly proportional to the chemical bond energy. So therefore, in order to increase K1c, an immediate way is to basically increase the chemical bond energy. You have stronger chemical bonds, you tend to increase gamma.

It turns out stronger chemical bonds also tend to increase elastic modulus as well, which is understandable. But the correlation is actually a lot weaker because elastic modulus has to do with specific shape of essentially the interaction potential between the different atoms. But in general, rule of thumb, if you want to have material that's actually mechanically stronger, can resist crack propagation, you want something with strong chemical bonds, which also makes a lot of intuitive sense.

Now, even for the same chemical bonds, I also want to mention that the network topology also play a role in dictating the mechanical properties of glass materials. So this is most clearly seen by this plot here, where we are essentially looking at the variation of the elastic modulus as a function of arsenic percentage in arsenic selenium [INAUDIBLE] [? glass. ?] So there are three curves here.

E is a Young's modulus. K is essentially the volumetric modulus. G is the shear modulus. So it's quite remarkable that if you look at all three curves, they all peak where arsenic corresponds to 40% So this is actually the As2Se3 composition.

Now, if you recall, this also corresponds to where you have a mean coordination number of 2.4, the magic number. This is actually quite a common phenomenon if you look at some other groups of glass materials. What I'm showing you here, if you focus on these black dots here, these are actually the binary germanium selenide glasses.

And it's plotted in these two plots here. This one is basically the toughness measured by indentation method-- I talked about it in the last lecture as a function of the mean coordination number. On this one on the right side, this is basically brittleness, similarly inferred from limitation measurements as a function of mean coordination [? number. ?]

What we are seeing here is that a critically connected glass network also corresponds to the point where you have the maximum toughness and the lowest brittleness. The two are correlated together. It's less brittle.

You can actually accommodate more plastic deformation. You absorb more energy. Therefore, it becomes tougher. So the takeaway message is that the network topology also plays a significant role in dictating the intrinsic glass mechanical properties there as well.

All right, so that's about the glass chemistry. Now we'll spend a bit more time discussing about how to introduce a compressive stress on glass surfaces to prevent crack propagation. And there are, in general, three different ways that people do it. You have thermal toughening, chemical toughening or ion exchange, as well as so-called intrinsic toughening. OK, so let me go through them one by one.

So thermal toughening is probably the easier. It's basically how you actually create any kind of tempered glasses. You have a glass pane. You heat it up to a high temperature above the glass transition temperature. So then you quickly cool it down.

And because of the difference in terms of cooling rate from the outside and the interior, you eventually build up a gradient of stress inside the material here. The surface will be compressive stress. The interior will be tensile stress

The typical stress profile will be what I'm illustrating here. As I'll show you in the next few slides, the stress profile, theoretically, it will follow like a parabolic shape So because of the parabolic shape, you can actually easily calculate the surface layer that's under compressive strain will be about 20% of the overall thickness of the glass pane. So on each side, you have basically 20% of region that's under compressive strength. And inside, there's about 60% of the thickness that's under tensile strength.

One basic rule coming from mechanics saying that because of equilibrium, the requirement for doing equilibrium, if you look at a thin pane of glass that's uniform in composition, the area under the curve must be the same for compressive and tensile stress. So effectively, we're saying that these two triangular regions here, the area should add up to the same area as the area under this curve here in the middle. That's just because of simple mechanical equilibrium requirements.

Now, what that also means is that, because there's a very significant thickness of the material under large compressive strain on the surface, 20%. The magnitude of the tensile strain inside the glass is also very significant, just to counterbalance the surface compressive strain. So this is actually one of the main problems with thermally tempered glasses Because glass materials, if you have any kind of intrinsic defects under compressive strain, great, it's not going to open.

Under tensile strain, however, any kind of defects can easily propagate because it's getting opened. The crack tip is getting opened by this intrinsic tensile strain. So the tensile strain region essentially becomes Achilles heel for thermally tempered glasses

You already see the example when you're looking at the Prince Rupert's drop. In Prince Rupert's drop the tail essentially allows you to access the tensile strain region inside. So if you accidentally break the tail, it quickly propagates and the whole thing breaks apart.

So as we'll see later, a thermally tempered glass has the issue of spontaneous breakage, even though the probability is low. But they do sometimes spontaneously break basically because of defects in the tensile strength region. So because of that, you obviously don't want a cell phone to explode suddenly in your pocket.

So that's why people come up with an alternative technique for applications like smartphone screens. The technique they use is called ion exchange or chemical toughening. And in this case, what you do is immerse your glass material into essentially a molten salt bath. If it's a glass containing sodium, you can put it in, for example, a potassium salt bath.

And then the potassium ion diffuses in the glass. Sodium ion also diffuses. So eventually, potassium is going to occupy the original site occupied by the sodium ions. And potassium is bigger. So then that can essentially create this compressive strain on the surface. Simple.

Now, what I want to highlight here is this strain profile-- stress profile. You have very high compressive stress on the surface. But the thickness of this layer, this is called K steps, the surface layer where you have compressive stress. K step typically is pretty small for chemically toughened glass. It's of the order of a few tens of microns.

So what that means is, if you think about it from the same perspective of essentially mechanical equilibrium, Again, the area under either tensile or compressive strain has to be equal. But because the surface compressive layer is so thin, the magnitude of tensile strain in the interior of the glass pane is much smaller. So because of that, you pretty much eliminate any risks of spontaneous breakage because of the large tensile strain in the glass material. So that's why your cell phone is not going to explode suddenly in your pocket.

All right, now last one-- intrinsic toughening, this usually applies to essentially selective modification of the chemical property on the surface of glass. This can be done by crystallization. And as I mentioned in the last class, glass ceramics is one way to actually strengthen glass materials.

In fact, if you look at some of the high-end smartphone products, Apple has, what's called Ceramic Shield-- I don't know if you heard that brand name. In some of their more recent generation of phones, it has Ceramic Shield. It's basically a glass.

The screen is made of pure glass. It's glass ceramics. Samsung is following suit. I think Corning has a new product called gorilla Armor, which is basically also glass ceramics. So you can essentially create a gradient in terms of chemical properties.

You can, by essentially diffusion, create a chemical gradient, and use that to actually help to create a compressive stress on the surface. So we're mostly focusing on the first two categories because they are the most commonly used examples in strengthening glass materials. So I'll start from the first one.

So thermal tempering is probably the most widely used for everyday products like architectural glasses or everyday home appliances. And the reason is that it's quite simple to make compared to chemical tempering. It's actually much lower costs.

So the way it works, let's start by looking at this plot here. This is basically what I'm plotting here, two things-- temperature profile and the stress profile inside a flat pane of glass. You first start by heating up to somewhere around 600, 650 degrees Celsius for soda-lime glass.

Now, for soda-lime glass, let me remind you that it's Tg. It's about 510 degrees Celsius. So what is Tg? If you recall, it is also called the straining point.

It means that if you heat up the glass material above the Tg, any internal stress is going to relax. Below Tg, the stress will take too long to relax. So you can actually build up internal stress.

So therefore, if you heat it up above Tg, you have a uniform temperature initially. And then the stress should also be 0 because all the stress gets relaxed. Then you start to cool down.

Now, when you start to cool down, you build up the temperature gradient like what I'm showing here. Initially, the temperature is still high. So there should still be no stress at all.

Now, the profile of this temperature here, we argue that this should be an ideal case scenario where the glass is uniform. And this probably doesn't depend on temperature. This curve should have exactly a parabolic shape.

You can prove it mathematically. But in fact, it's quite easy to explain, just intuitively here, why this is a parabolic shape. If you think about a pane of glass, and this is the temperature curve, by symmetry, you can think of the heat coming from this side, this half of the glass. They should escape from this surface. So if you look at one point here, let's say [? A, ?] then across this surface, the heat released will be proportional to essentially the slope of the temperature curve here, just by Fourier's law.

Now, the amount of heat released comes from the thickness of the glass pane. So you can expect that the amount of heat that you need to release across a particular surface inside the glass pane here should be proportional to the thickness of the shaded area. The larger the shaded area, the more heat you have to escape just because you have more material if you have uniform cooling there.

So what that means is that the heat dissipation rate, or the slope of this curve, should be proportional to the thickness of this shaded area. That's exactly the curve of a parabola. The slope of parabola scales linearly with the horizontal coordinate. Does that make sense? So that's why we argue that this must be a parabolic shape, [INAUDIBLE] the ideal scenario.

So now in this case, as I said, at high temperature, essentially the temperature is non-uniform, but stress is zero. You start to cool down. If things happen in more or less an ideal manner, then this temperature profile is going to stay constant. It's going to decrease uniformly across the entire glass pane.

Now, if you decrease-increase across the glass pane uniformly, it means that the entire piece of glass is contracting in a uniform manner, as long as the temperature profile stays the same shape. You just drop down. So in this case, there's still no stress.

You only start to build up stress when the surface gets close to room temperature. When the surface gets to room temperature, it will not cool down anymore. So contraction will stop, but the inside is still at high temperature because of the parabolic shape. So the inside will continue to cool down and it will continue to contract.

So in this process, this is when you actually build up this stress gradient. The surface becomes compressed. The inside has tensile stress.

So the key takeaway message here is that when you're doing the thermal tempering process, you do not build up the stress under high temperature. You actually build up stress when the material is cooled down close to room temperature. So only when you start to have essentially the surface start to reach room temperature, that's when you actually build up the stress there.

All right, so this plot, essentially, I give you the equation. I already tell you that the temperature profile should have a parabolic shape. So as a result, if the thermal expansion is uniform again, then the stress profile should also follow the same parabolic shape.

So then, from the argument of mechanical equilibrium, the area under the tensile and compressive stress curve should be equal. You can then determine where this kind of zero stress plane should be. And that's where we come up with the conclusion that about 20% of the glass thickness on the surface is under compressive strain.

All right, so now, here's a few important conclusions we can draw from this very simple equation here. The first thing is that assuming, again, we have this ideal parabolic stress distribution curve, what you will see is that the surface stress, they should scale quadratically with the thickness of the glass. So in this case, sigma, this is basically the surface stress. X is essentially the horizontal coordinate which corresponds to thickness of the glass. So the thicker the glass, the larger the stress gradient you can actually build up. And hence, the higher the surface compressive stress

So this can be demonstrated by what I'm showing on the right-hand side plot here. For the right-hand side plot, what I'm showing here is essentially a surface stress measured on essentially soda-lime glass panes. That's cooled down just simply using an air quench.

So it's pretty straightforward. You just get a glass pane, put it there. Just through convective cooling, it cools down from the furnace. So each of these curves correspond to a different glass thickness, ranging from about 2 millimeters all the way to about more than 1 inch in thickness.

Now, you do see that the stress increases as you go to thicker and thicker glass panes. However, if you compare, for example, this top one, this one is more than 10 times thicker than the bottom curve here. So if it follows this quadratic relation, the surface stress should be 100 times higher than the thinner glass pane, which obviously is not the case. So that means that our ideal theory, this kind of parabolic stress distribution, it has not taken into account some practical considerations there.

It turns out what happens there is actually because of viscoelastic relaxation because we know glass, around the glass transition regime, is actually viscoelastic material. And what viscoelastic material does is that it can relax. So even if you start to build up this kind of stress and strain gradient, because of relaxation phenomena, essentially the strain or the stress you build up would gradually decay over time.

So that's why when you actually get to the final steady state, the steady state stress you will measure is much less compared to what you would calculate just based on the simple theory there. So that's why if you only use a simple convective cooling, that's actually a limit on how much stress you can actually build up. This can be seen from this plot here where you increase the glass thickness. You get diminishing returns in terms of building up the surface stress.

The maximum stress you can build up is of the order of about 30 megapascals, which is still quite remarkable because the atmospheric pressure is what? It's like 0.1 megapascal. So this is, like, 300 times atmospheric pressure in terms of compressive stress on the glass surface if it's a thick [INAUDIBLE]. So it is a lot. But people want to do better.

Oh, by the way, before I go to the next point, I also want to mention one quick thing. Also, our simplified theory also ignores one important consideration here about fictive temperature. So I have mentioned about the assumption of this kind of parabolic stress buildup. The glass should be uniform. The inside and outside should have the same properties throughout the cooling process.

It is not because the surface actually cools down faster effectively. Inside cools down slower. So that means that the structure of the glass is also different. The surface should have a fictive temperature that's actually higher compared to the inside.

You can think about it. Yeah, OK. You should know it by this point. You can draw your cooling plot, and then figure it out.

So now if you have a fictive temperature gradient, what does that translate to? Actually, different fictive temperature means different structure. The larger the fictive temperature, the larger the volume.

So that's also going to change because of volume difference. That's also going to contribute to essentially an actual accumulation of the stress there. So that's actually additional contribution that we have not taken into account due to this essentially cooling rate gradient in our simplified theory of a parabolic stress distribution.

Anyway, so coming back to my point here, if you just do a simple convective cooling, the glass you get, this is called a thermally tempered glass. And you can only build up a maximum stress. Actually, as I said, it's about 30 megapascals, give or take. So this kind of heat-strengthened glass has a limited surface stress up to between 24 to 52 megapascals. So this is actually regulated, by the way.

So ASTM actually has a standard that specifically defines two classes of thermally tempered classes. One is called heat-strengthened glass. The other is called tempered glass.

For heat-strengthened glass, this is done usually just using simple convective cooling. The surface stress is relatively low. I mean, it's still very high pressure there, very high compressive stress, but it's smaller compared to tempered glass. So it gives you a strength that's about twice stronger compared to annealed glass.

Annealed glass essentially means that there's no internal stress. It's just a soda-lime glass without any specific treatment. So it's not strengthened.

Now, you can also go to a tempered glass. A tempered glass, by this regulation, it should have a surface stress greater than 69 megapascals. And it gives you about four to five times stronger compared to annealed glass.

Now, to get to the tempered glass, you cannot just do a simple convective cooling. You have to use essentially some way to actually accelerate the cooling process to build up even more stress. The typical way of doing it, you can either use compressed air. You can use essentially forced cooling, and blow compressed air to expedite the cooling.

You can also do a liquid quenching. In that case, you either use a mineral oil or you actually use some salt solutions like potassium nitrite or sodium nitrite. Those are typical compositions that you would use to quench these glasses.

There's more recent techniques people are also using. People also using things like fork cooling. So fork cooling, they essentially spray very tiny little droplets of liquid onto a surface of glass to actually help with cooling down.

That's a more recent technique. People are also using actually solids as a cooling media. So in that case, they actually put in a fluidized bed. In the fluidized bed, you have these tiny little beads, usually made of alumina. They have a small diameter of a few hundred microns.

Under appropriate conditions, the collection of particles behaves like liquid. And then you can essentially put it in there. And then these particles are going to roll across the glass surface and induce cooling there. So those are the more recent techniques compared to the liquid or forced air, compressed air cooling OK. Yes.

AUDIENCE: What are the, I guess, constraints on mineral oil or salt solution [INAUDIBLE]? Is it just water is too good in [INAUDIBLE] glass [INAUDIBLE].

JUEJUN HU: Good question. I actually don't know exactly why they use that specific chemical formula for cooling there. I have to look it up. That's a good question.

I know that that's what they use, the chemical formula. I don't know exactly why they actually use it. So let me look it up. I can't answer your question right now.

AUDIENCE: And for the salt solutions, if you're quenching from a high enough temperature, is there any chemical strengthening that happens at the same time?

JUEJUN HU: I would say no, or [? at least ?] quite minimally. In fact, what happens is that we will see, for chemical strengthening, it requires probably more extreme conditions. And also, it requires much longer duration.

You can also use-- in fact, we are going to show you one example where people use supercritical fluid to do strengthening [INAUDIBLE] chemical strengthening. And in that case, people usually use [? hours ?] for diffusion to take place. During the quenching process, maybe like surface monolayer, but that's really negligible. Yeah.

OK, so bottom line, tempered glass is stronger. It has more stress. And you can actually see that from actually the breaking behavior of thermally strengthened glass and tempered glass.

For thermally strengthened glass, when it breaks, it's behaving in a way very similar to just an untreated glass. You end up with big shards with sharp edges and corners, which can be dangerous to users, of course. For thermally tempered glass, when they break, they tend to break into small pieces, tiny little pieces, in lots of cases, also with rounded corners. So it's actually safer to use this.

There are downsides, though. For thermally tempered glass, they have the risk of spontaneous breaking. That happened to me actually. Like, the microwave oven glass door in my home? One day, we wake up and it's completely shattered for no reason.

Well, there's actually a reason. We won't talk about it. But apparently, nobody tried to touch it or whatever.

It just broke. OK, so it does happen. Any tempered glass products, it could break spontaneously.

The reason for that is because of-- well, we're going to talk about it in a second. But before that, I want to mention that that's actually because of the very high tensile stress inside the material. If you have large compressive stress on the surface, obviously, you have high tensile stress.

The tensile stress region is the Achilles heel for this kind of thermally tempered glass. And because of defects that we're going to talk about in a couple of slides, that's what's causing this kind of spontaneous breakage in the tempered glass. For heat-strengthened glass, because of the stress is very low, you don't have that risk.

Now I'm actually going to show you-- I already showed the YouTube video there. The reason I want to show this YouTube video is because Prince Rupert's drop, which you see in the Glass Lab demo, represents the ultimate or extreme example of thermal tempering of glasses. So because of this extremely fast cooling rate, you're actually starting not from 600 C.

You're starting from molten glass which is even higher temperature. So you quickly cool down through a liquid. This gives rise to extremely high compressive stress build-up in the Prince Rupert's drop. And it's so strong that it can actually withstand bullets. So I'm going to show you this video here.

[VIDEO PLAYBACK]

- All right, Keith. This is Prince Rupert's drop.

JUEJUN HU: This is the real one.

- Prince Rupert's drop, the [INAUDIBLE]. Papers submitted from 1660 to the Royal Society. So this is the very early stuff.

- Hey, it's me, Destin. Welcome back to *SmarterEveryDay.* I am in the basement of the Royal Society in London, England. And this is Keith, the head librarian. And he has a special paper written by who?

- Sir Robert Moray.

- And it's about the Prince Rupert's drop.

- That's right.

- Can you show it to me?

- Yep, so here we have an account of the glass drops by Sir Robert Moray.

- Will you show me the drawing? The famous drawing?

- So just turn over the pages. "So is a kingdom one and strong, but when the top is broken shivers into men."

- So the strength of the Prince Rupert was recognized way back in the day, [? even in ?] the beginning of the Royal Society. [INAUDIBLE]

- It is.

JUEJUN HU: Don't tell me that.

[LAUGHTER]

- I was fascinated by them.

- They were fascinated back then. I'm still fascinated now. But today, we're going to use some of the best technology that we have available. We're going to use a high-speed camera and record a bullet striking the bulb over Prince Rupert's drop at several hundred thousand frames per second. Let's go get smarter every day.

All right, goggle up. Science is about to happen. The first video I made about the Prince Rupert's drop here at Lookout Mountain [INAUDIBLE] was about why the Prince Rupert's drop was so strong. Today, we're going to test the limits. If you haven't seen that video, you really need to watch it because you have to understand what we're dealing with before this video will make any sense.

This is the setup. I've got a .22 rifle aimed at a Prince Rupert's drop. I've got a high-speed camera right here. This is a v2511 We're going to run it over 100,000 frames per second.

So I've got the rifle aligned so that we should hit the Prince Rupert's drop. The resolution is going to be a little bit lower, because that's what you have to do in order to get so much speed. But it should be awesome.

Here we go. Get your goggles on. Let's do it. My Prince Rupert's drop is wobbling, so I have to time the bullet.

[MUSIC PLAYING]

[GUNFIRE]

All right. [INAUDIBLE] look at that.

JUEJUN HU: [INAUDIBLE] slow motion. Look at the bullet [INAUDIBLE]. And this is what happened? The bullet shatters.

AUDIENCE: And then [? there's ?] [INAUDIBLE].

[MUSIC PLAYING]

JUEJUN HU: So the Prince Rupert's drop is intact by creating this elastic [INAUDIBLE] probably to tail.

[LAUGHS]

- The bullet did not break the Prince Rupert's drop. It looks like it creates a shockwave that runs down the tail. And then the tail shakes, breaks, and then breaks it back the other way. I'm going to do this several more times because that is beautiful. That gun is pointed in the general direction of the high-speed camera. So I'm a little nervous about that point.

JUEJUN HU: Don't try that at home.

[GUNFIRE]

- Just make sure [INAUDIBLE] [? Everything ?] looks good. Look at the high-speed now. God! It's awesome!

[LAUGHS]

Dang! That is beautiful. It's beautiful and it's material science. And if those jokers back in the 1600s had this kind of technology, they would have written way more interesting letters to each other. Not that they didn't do a good job because they're awesome.

JUEJUN HU: OK, we can skip the video. He's just going to try to shoot it multiple times. I think we can move over here. There's somewhere [? where it is ?] more clear.

OK, let me try to show you something, a slightly different video here. So the same guy obviously gets fascinated with this kind of experiment. He then somehow got an AK-47 and then tries to shoot Prince Rupert's drop.

- Welcome back to *SmarterEveryDay.* I've been waiting on a sunny day to do this. If you remember the last video, I fired a .38 special versus a Prince Rupert's drop and the Prince Rupert's drop won. Well, we're going to fix that today. We've got the high-speed camera back out.

[END PLAYBACK]

JUEJUN HU: Let me call that fractal luminescence. It has nothing to do with amorphous structure. It has to do with polar chemical bonds. So if I have [? a ?] polar chemical bond, it means that I have charge transfer between the atoms.

So we actually break it quickly. Turns out some of the charges actually remain on the two paths. And those charges have to relax somewhere.

So eventually, they relax essentially by going across the bandgap. And that goes into the form of photons. So that's basically what happens there. OK, so bottom line, what you have seen here-- Prince Rupert's drop is extremely strong. It actually shatters the bullet.

So about nine years ago, a group from Purdue University figured that maybe they should try to quantify how much stress is actually on the surface of Prince Rupert's drop. And what's the amount of force it can withstand before it actually really breaks? So they actually published a paper. And this one actually got a lot of public attention. They were able to actually directly measure the stress level on Prince Rupert's drop and use that to actually compute the maximum amount of compressive load they actually withstand before it actually breaks.

I'm a bit more worried about how they actually measured the compressive stress. The way they measured compressive stress is using a technique of photoelasticity. This is a very, very common way of measuring stress and strain in transparent materials like glass or plastics.

The way it works is that you have of polarized light source. So when a polarized light source [INAUDIBLE] on the material, in this case, if it's no stress, then the light will just go through. It comes out as transparent. Nothing really happens.

However, if you apply stress, you're essentially changing the density of electron clouds. If you're changing the density of electron clouds, you're going to change the polarizability when they respond to oscillating electromagnetic waves. So essentially, it means that the refractive index is changing when you actually apply this kind of stress [INAUDIBLE]. Makes sense?

You essentially compress the electron. You think of a compressed electron. If you compress electron, the reason you have refractive index is because the electrons are responding to oscillating electromagnetic field due to the light. So if that behavior changes, you change the refractive index.

Now, the key thing to take away is that this kind of change happens not in an isotropic manner. It happens anisotropically. Because you apply compressive stress, you can imagine that you're squeezing material in this direction. But the material expands in the other directions.

So now you expect the material actually becomes anisotropic, even though it started out isotropically. It becomes a uniaxial material that goes along the direction of the other stress. It has a principal axis aligned with that direction.

So what photoelasticity is looking at is essentially birefringent materials or birefringence in materials. Birefringence just means that the material has anisotropic refractive index distribution. So if a polarized light [INAUDIBLE] on a birefringent material, it's going to split into two radiations or two light beams.

One is called ordinary light beam, the other called extraordinary light beam. They will then propagate along slightly different directions. So then when they come off the material, if you put another polarizer at the end, the two beams are going to recombine at the polarizer and they will interfere. So now it depends on how much birefringence you have, which alters the path lengths of the two different light beams.

You may get constructive interference. You may get destructive interference. So you will essentially come up with essentially a bright, dark pattern if you use essentially monochromatic laser light to illuminate material. So for that, you can infer how much stress you have. Or if you illuminate it using essentially a white light source, you come up with color patterns, color fringes like what I'm showing here, because different [? colors ?] essentially interfere differently.

So I can actually show you how that works. I brought along with me-- I'm going to show you. I have of polarized light source. Any of you want to guess what's the polarized light source?

My screen. Most of your laptop screens are polarized. You can come around here and take a look. We can probably take a video after later. Oh I know.

So this is basically just white, nothing. This is a polarizer. OK, this is [INAUDIBLE] the polarization direction line, turn around, stuck. OK, so now we'll do it in a cross polarized orientation.

We'll put it like this. You put the component that actually has intrinsic stress or strain in there. And then you will see color fringes immediately.

It's very strange very, very-- strange. Now the reason this is a very heavily strained. Remember how these are made? It's the same way as blow molding. That's a technical term. You have a [INAUDIBLE], and then you blow it.

So there's very large plastic deformation takes place when making this kind of containers. So that's why there's lots of residual stress. And that's why you see a very strong photoelasticity there.

This is for amorphous polymer. I also bring along with me another piece I got from Amazon. This is actually a glass [? butcher ?] ball made of a thermally tempered glass.

I mean, it's a lot more uniform, so you don't see a lot of stress accumulation. However, I probably need someone to help me hold in this orientation here. Orthogonal direction.

So in most regions, you don't see any stress there. I mean, a little bit. You see a little bit of color change right at the corner. Now you can rotate it by 90 degrees, you actually see a different pattern there, slightly different color. Rotate it.

So this is where you actually get more stress accumulation, obviously, because of geometry, because the cooling is not very uniform at corners. So that's why you accumulate more stress there. So you can use this way actually to analyze any [? residual ?] stress, any transparent component by just buying that.

That's like half a dollar polarizing film. And with a laptop, you do that. You can get polarized light, actually.

AUDIENCE: [INAUDIBLE].

JUEJUN HU: You can get natural polarized light. Just look at reflected light on water surfaces and that kind of stuff. The reflected light in lots of cases is polarized. I won't go into why. If you're interested in learning, why, go to my 346 class.

[CHUCKLES]

OK, so that's basically how they actually quantify the strain level in Prince Rupert's drop. I will directly jump to the conclusion. This is a surface stress they measure. They measure surface stress up to 700 megapascals, which is 7,000 times atmospheric pressure-- enormous.

And that's why-- now if you look at the [? converse ?] tool, how much compressive load this Prince Rupert's drop can withstand? A tiny little bit. It can withstand the compressed load exceeding 10,000 newtons. That's more than a ton.

So in order to break that Prince Rupert's drop from the front side, you need to put a load of more than a ton to break it. That's why next time, if you see on YouTube, people will try to, they try to put all kinds of things. They try to smash it, they do whatever, it doesn't break.

That's far from breaking. You need a ton of mass to actually really break it. So don't be too surprised if you see that kind of video. OK, so bottom line-- this is essentially compressive strength at its finest. You can really get to extremely, extremely strong glasses by just doing this kind of treatment.

All right, now [? it comes ?] back, I have mentioned that there's a Achilles heel for Prince Rupert's drop because they break spontaneously. Here comes the problem. So if you have any defects inside the material, if you have any cracks in the tensile strain region, then those cracks can very easily propagate, and then lead to eventually catastrophic failure.

Now unfortunately, there's one kind of defect that's almost universally present in all glasses. It's very difficult to eliminate. It's a nickel sulfide. Now, nickel sulfide, where it comes from, people are not totally clear.

People sometimes add a little bit of sulfur in the glass batch. Sulfur is called the fining agent. It helps to reduce viscosity of glass melt, so it makes it a bit easier to process. So sometimes people intentionally add a little bit of sulfur there.

But nickel is an impurity. Where does it come from? People don't really know. It may be coming from a raw ingredient.

It may be coming from the stainless steel handling instruments, some powders getting there or whatever. But there's trace amounts of nickel anyway. So in the end, it forms this nickel sulfide in the form of inclusion.

The reason nickel sulfide is so problematic is because when you look at this phase diagram here, it has two phases. It has a phase-- this is the high-temperature phase. This is the low-temperature phase.

So when you are processing a glass, when you're doing a thermal tempering process, the temperature, if you recall, we heat up to about 600 C. And then start to cool down right. 600 C nickel sulfide is in a high temperature phase.

Now, when you start to cool down, it now has a tendency to convert to the low-temperature phase. It's a slow process because it's usually kinetically inhibited. But once it converts into the low temperature phase, the volume increases. The two phases have a significant volume difference.

Now, with increased volume, it's going to essentially create microcracks by squeezing on the glass matrix around it. These microcracks is where the problem happens. They can essentially nucleate much larger cracks, eventually leading to catastrophic failure, because they're located in the inside of the glass where nothing prevents it from opening.

Now, you can try to reduce the incidence of this kind of breakage by having high purity glass ingredients and all that stuff. It's quite difficult. It's quite expensive as well.

The more common way people are trying to eliminate this kind of failure is using a process called heat soaking. Heat soaking is quite simple. Essentially, you preheat all the thermally tempered glass pieces, try to accelerate the phase transition of a nickel sulfide to convert into low-temperature phase.

So if there are any pieces that has this kind of inclusion there, they may break during the thermal heat soaking process. And therefore, you can only pick up the good ones. Unfortunately, that process does not eliminate all the faulty parts.

So that's why all the thermally tempered glass products, whether it's the door on the microwave oven or door in your shower room or whatever, architectural glasses all have the risk of spontaneously breaking. Even though the probability is very, very low, it does happen. OK, so don't be too surprised if you see some glass pieces suddenly break into small pieces.

What do you do? Remember what I said in the last class. Do your fractography. So this is an example of a nickel sulfide inclusion Well, in fact, you can actually really do it for photography.

So what you would do? Typically, if you have some glass broken due to this kind of nickel sulfide intrusion, the breaking pattern has this kind of butterfly geometry. It looks like a butterfly in the center here.

The reason it looks like a butterfly is because-- we can zoom in a little bit. This is actually what happens. Right at this point, right here, the intersection of several of the radial cracks, this is where the defect initiates. If you look carefully, most likely you see a nickel sulfide defect right there

Now, the reason you have this butterfly pattern is because when the crack forms, initially, it propagates radially outwards from the point of defects. And then because you have a lot of compressive strain in a thermally tempered glass, this compressed strain means that there's lots of elastic energy. This elastic energy has to be released during fracture.

And they get released in the form of surface energy. That's why thermally tempered glass breaks in such a different way compared to conventionally annealed glasses. It doesn't break in large shards. So as the crack propagates, the excess elastic energy is released in the form of essentially this kind of secondary cracks that go in this direction, in the orthogonal direction.

So because of the interaction of these two sets of cracks, that's why you tend to form this kind of butterfly-like pattern there. But this is where the defect originates. All right, makes sense? OK, I forgot to do my fractography analysis when I saw my microwave door open. I really should have done that.

[CHUCKLES]

Anyway, so it's exactly because of this issue here of spontaneous breakage when they come up with some applications, like consumer electronics, cover glasses for your phones. People want to come up with a different way to do strengthening. That's where ion exchange or chemical strengthening come in. So I've already basically mentioned about this simple process here.

The most common way of doing it is you immerse your glass products in a molten salt bath. So if the glass contains sodium, you put it in a potassium salt bath. Also, if you cannot contain lithium, you can put it in a sodium salt bath.

People also use mixed salt baths. Lithium glass can be simultaneously [? ion ?] exchanged in a mixed salt baths of sodium and potassium, for example. So then through interdiffusion process, you build up the surface compressive strain in the region where you have [INAUDIBLE] diffusion of the ions.

The kinetics is described basically by interdiffusion. So what I'm listing here is the interdiffusion coefficient. Now, for those of you who have taken 3.033, kinetics, or 3.030. What's the name of the equation for interdiffusion coefficient? Pop quiz.

AUDIENCE: [INAUDIBLE] [? Einstein. ?] No. [INAUDIBLE]

JUEJUN HU: [INAUDIBLE] equation. OK, this is not [INAUDIBLE] equation.

[CHUCKLES] It doesn't matter. This is called the--

AUDIENCE: [INAUDIBLE] Einstein.

JUEJUN HU: Nernst-Planck. Close. It's about the same time. They all lived [? within the ?] same time. But we don't credit everything to Einstein, OK?

[CHUCKLES]

AUDIENCE: [INAUDIBLE]

JUEJUN HU: So now the reason the coefficient is a little bit different from [INAUDIBLE] equation is because [INAUDIBLE] equation describes essentially charged neutral particles, like atoms when they interdiffuse. That's what you use. For ions, because they actually carry charge, what that means is [INAUDIBLE] ions move, the charge distribution also modifies.

And when you change charge distribution, you change internal electric fields. And the electric field is going to modify again the motion of the ions. So they are inter-linked together.

So that's why for any interdiffusion process in a charged species, you should not use [INAUDIBLE] equation. But rather, you should use the Nernst-Planck equation. That's what I'm [INAUDIBLE] there.

Now, what I want to mention is that if you look at the Nernst-Planck equation, let's see what actually happens. So suppose you look at the glass surface where you have about the N is essentially the amount. N is the molar fraction of the ions. D is the diffusion coefficient of each of the ions.

So if you have about the same amount of sodium and potassium ions, then if you look at the denominator here, we know that D, the diffusion coefficient of sodium, should be larger than the diffusion coefficient of potassium. Because they're smaller, it's a lot easier to squeeze around. So that's why you expect D sodium to be larger.

So therefore, the denominator, this term should be dominant. So if this term is dominant, you can cancel out this DNa, the diffusion coefficient of sodium in both numerator and denominator. What is left behind basically becomes the diffusion coefficient of potassium.

This also makes sense. What is this? In the interdiffusion process, the overall kinetics is basically dictated by the slower diffusion species, which is the bigger ion. Interdiffusion process, the diffusion coefficient more or less equals to a [? decay, ?] the diffusion coefficient of potassium or the heavy ion species.

All right, so now if you notice a diffusion coefficient, what you can also do again goes back to your kinetics class. You can use it to now estimate what is the diffusion length. Diffusion length is given basically a square root of diffusion coefficient and tau. Tau is basically your time of the diffusion process. So the longer you diffuse, the longer you go through the process, the thicker the surface compressive layer gets.

And that diffusion length has a name. It's called K steps in the context of a chemically strengthened glass. So K steps is basically the thickness of the surface compressive layer.

For soda-lime glass, it's typically, as I said, about 30 microns-ish. People try to modify it by changing glass chemistry, which I'll talk about in the next slide. You can increase the K steps to close to maybe, like, 100 microns in a lot of consumer electronic products. In extreme cases, they can even reach something like about a millimeter for things like glass windows used in military vehicles. They need extremely high compressive stress.

Now, there's one thing I also want to mention about this process here, which is different from thermal tempering process. Remember for thermal tempering process, you heat it up to above the glass transition point because you want all the stress to relax at high temperatures. And you cool down to build up the stress gradient.

In the chemical toughening process, you never, never exceed Tg. Why? Above Tg stress, you're going to get relaxed. So if you do your ion diffusion above Tg, then while you're actually diffusing, the stress is also actively getting relaxed. You get nothing.

So that's the main difference there. Chemical strengthening has to be performed below Tg. So you retain the stress throughout the process. Thermal tempering has to go above Tg.

Now, we know that diffusion is a thermally activated process. So higher the temperature, the faster it diffuses. The faster it diffuses, the larger the K steps, the stronger the glass product gets. So that's actually motivation for people to raise the temperature during the ion exchange process just to expedite diffusion.

Now, Tg sets a limit. You cannot really go above Tg. So if you want to get the more efficient chemical strengthening process for ion exchange, you need to find glass materials with higher Tg, which means that you can afford doing ion exchange at relatively high temperatures to expedite the kinetics. So we're going to talk in the next slide about some of the strategies, how to essentially boost the ion diffusion kinetics. But before that, I just want to mention a couple of quick things.

One is that in this kind of simple model, we assume the diffusion coefficient is the constant. In fact, it's not. It also depends on compressive strength. It's quite intuitive. If you have compressive strain, you actually impede diffusion. You can squeeze on ions, slow down the diffusion kinetics, which makes sense.

The other thing I also want to mention here is about the advantages of this process, why people want to use chemical strengthening versus thermal tempering. The first one, obviously, is that they don't break. They don't explode spontaneously, number one, because of the much lower level of tensile strength inside the glass material-- first thing.

The second thing is that because of the surface compressed layer of [INAUDIBLE] thing, any kind of photoelastic changes or birefringence effect is a lot weaker because it's such a thin layer. So in some kinds of high [? energy ?] applications, these actually lead to less distortion of the images or less essentially better optical quality. So that's one consideration there.

The last thing I also want to mention is that for glass pieces that have strange geometries, not like a flat plane-- you may have glass containers, for example, if you want to strengthen those kinds of irregular shaped glass products, people usually don't use thermal tempering because this irregular geometry means that cooling is not uniform. You're going to build up lots of internal stress, like what I've shown there. The corner is actually where the stress [? gets ?] built up. So if you an irregular shape, you can imagine, there is a lot of residual stress, which is harmful for the glass.

So for strengthening of, for example, bio bottles that people use in the pharmaceutical industry, chemical strengthening is what they do. They immerse the whole thing into the chemical salt bath. The surface is going to get uniformly diffused with the ionic species. So that's why, for these reasons, people use chemical strengthening. Yes.

AUDIENCE: Are there-- is thickness of the glass a constraint on thermal tempering as well?

JUEJUN HU: Of course. Yeah, I mean, the case that--

AUDIENCE: If it's too thin like for your phone or something?

JUEJUN HU: Yeah, then you also build up a lot of tensile stress. Yeah, and it's quite apparent that the case depth has to be considerably smaller than half of the glass [INAUDIBLE] thickness if you want to eliminate the risk of loss of tensile strength, so same idea. Yeah

And by the way, the other reason people don't use chemical strengthening also, it's a more expensive process. [INAUDIBLE] temperature is really simple [INAUDIBLE]. That's why. So in architectures-- for example, in my microwave oven, that's why they use thermal tempering, not chemical tempering.

Now, one last thing I also want to mention here is-- you see this bullet point. It says that only applies to alkaline earth glasses, which makes sense. For alkaline, that's what people use most commonly across the industry. For example, with sodium, you use potassium ion exchange. That's the most common one. Lithium, you can use sodium or you can use potassium.

Alkaline earth is really actually a new process. It only was developed less than a decade ago. And the motivation behind it is that actually, for some high-end applications-- especially in electronics, people want glass formulations that's free of alkaline ions.

The reason people don't like alkaline ions is that they are actually very mobile. They tend to diffuse very, very fast. And if you have glass containing sodium, the sodium can easily diffuse, for example, into amorphous silicon, which is what you use to make transistors, and eventually, essentially harm the electronic properties of semiconductor materials.

So for those applications, people want alkaline-free glass. But they still want to chemically toughen it to get better mechanical properties. So that's why this is where the alkaline earth based ion exchange process comes into play.

Now, the process was only developed less than 10 years ago, basically, because the alkaline earth sources tend to have high melting points. They tend to decompose. They also can be highly corrosive, whatever.

But the problem is this high melting point. Their melting point is higher than the Tg of most glasses. So now you see what the problem is.

If you try to do a molten salt bath, the strain will be relaxed all the time. You just cannot accumulate stress. So that's why people tend to aqueous solutions of alkaline earth ions.

But for aqueous solution, normally, you cannot get to the temperatures needed to expedite the diffusion process. So what they will do is put it in basically a pressure cooker. By applying a large pressure, 45 megapascals, you can essentially raise the boiling point of the liquid.

In fact, when they do it, they do it in a supercritical fluid. So essentially, that's a state where you cannot tell the difference. There's no clear difference between gas phase and liquid phase. There's one simple fluid phase. So at that high temperature, still, it takes like hours in the aqueous salt bath to get the diffusion [? there. ?]

So that's why. That answers your question. If you just do it in the thermal tempering process, there's very little salt diffusion because there's simply not enough time.

Now, the other interesting finding also, if you look at this particular one, they are using barium ions to replace calcium ions in the glass to build the compressive stress. When the barium ion diffuses, it not only replaces the calcium ion, it also displaces some of the boron ions, which is normally not what you would expect. But this is a borosilicate glass, by the way. So anyway, there's some interesting materials studies if you want to see more details. This is actually the seminal paper that actually describes this process developed for alkaline earth ion exchange.

OK, so now, next slide, I'm trying to summarize how we actually increase the K steps. Increasing K steps is actually important because increased K steps essentially means that you have a thicker surface layer that's under compressive strain right. This usually also gives rise to higher surface compressive strain, and therefore stronger glass products after the process.

So increasing the K steps is really a kinetic problem. You're trying to expedite the diffusion kinetics. So some common ways-- you can essentially apply additional external stimuli.

You can use electric fields. You can use ultrasonication. You can use microwaves. They can also expedite diffusion processes. That's one way people are doing it.

Now, the second one, for a lot of these consumer electronic products, people typically use aluminum silicate glasses. Now, the reason they use aluminum, you may recall that in the early lectures when we talked about aluminum silicate glasses, aluminum is somewhat similar to boron. It can exist in two different kinds of states.

It can either form non-bridging oxygen acting as a network modifier. Or it can get converted into these four-fold coordinated states, and it increases the connectivity of the network. So it is exactly the latter property that was actually used in this case here.

So for this application, they typically use an alkali-alumina ratio of about 1. If you go back to the lecture, this ratio corresponds to where you have the maximum amount of four-fold coordinated alumina. So having more four-fold coordinated alumina means that you have better network connectivity.

And therefore, you increase the Tg of the glass. By increasing the Tg of the glass, you can now do your ion exchange process at high temperatures without worrying about stress relaxation. And that's how you can expedite the kinetics, by just essentially leveraging the Arrhenius law.

Now, the next one, you can use ion pairs with less size disparity, which also makes sense. If you have the two ions [? and ?] the exchange process has a huge size difference, it becomes very difficult for one ion, the bigger one, to actually squeeze through the pocket left behind by the smaller one. So if you do a lithium-sodium pair, this is kinetically faster compared to a sodium-potassium pair. Next bullet point-- yes?

AUDIENCE: If you use a smaller replacement ion, [INAUDIBLE] trade-off of, it's less effective

JUEJUN HU: [INAUDIBLE] less effective in that regard.

AUDIENCE: But it's much easier.

JUEJUN HU: But you get much larger K steps, less amount of a compressive strength in general. So that's the trade-off there. Or in fact, what people will do-- let me get to the last point. People actually do mixed salt baths

So for example, in a glass containing lithium, you put it in salt baths containing both sodium and potassium. So the sodium will go in deeper. It'll give you a large K steps.

But potassium will go more in the surface region. But that gives you a very high surface compressive stress. So that also helps.

Now, the last bullet point I want to mention here is to add some minor quantity of magnesium oxide or calcium oxide, about 2% usually, give or take. That's what people do. Why? There have been lots of studies about why that actually helps increase the diffusion kinetics.

I'm not going to go through details. I don't think it's fully settled yet. But in practice, that's what people do. Empirically, that's what they found.

So if you're happy with that, now let's actually look at one real-life example of a [? chemically ?] toughened glass. So the example I've given here is Gorilla Glass from Corning. Gorilla Glass was the one that was actually developed when Steve Jobs tried to approach Corning.

Essentially, when he was trying to make the first iPhone, and he was complaining about plastics being terrible, it creates all the scratches, he wants glass. So that's why he called Corning. And Corning made it for them.

And if you also remember, when we talk about the manufacturing of glass process, we talk about this fusion process-- [INAUDIBLE] fusion. Fusion process was really developed by Corning decades ago. It was shelved. Nobody found any use for that. Now, when they come to make Gorilla Glasses that's what they thought of when they reinvigorated or revived their process specifically for making high-quality cover glasses.

Over the years, Gorilla Glasses have developed many, many generations. They are all slightly different. They A little bit better one generation than the other.

I picked this one, Gorilla Glass 6. This is actually not the latest generation. The latest ones are the-- I think they have Gorilla 7i.

They also have Gorilla Armor 2. They have Gorilla Invictus 2. Their 3 is the latest ones. I'm not going to go through the differences there.

But the reason I picked Gorilla Glass 6 is because this is the one they have the most complete data online. The latest generations, they hide some of the data. So that's why I decided to pick this one here. But again, they are more or less the same if you look at the data that was published. So now let's go through them.

So first one-- viscosity. Essentially, they are looking at different reference points. These are the temperature reference points we talked about before-- softening point, annealing point, straining point. The key point I want to mention here is this guy, essentially annealing point.

Sorry, I should mention that this is basically the glass transition temperature. So for glass transition temperature, this is annealing point. It's not straining point.

I made a mistake the previous lecture. It should be annealing point. Straining point is beyond which you don't have any-- you don't have any further strain relaxation.

Annealing point is when you have an expedited relaxation of a strain. But bottom line, this is close to the [? essential ?] glass transition temperature. So for aluminum silicate glasses, the annealing point in this case is about 620 degrees Celsius, which is much higher compared to soda-lime glass, which is about 510 degrees Celsius. So that's why they can afford using high temperatures in the ion exchange process to get the large K steps.

In terms of the mechanical properties, you can look at density, Young's modulus, Poisson ratio, shear modulus. One little practice we can also do is in the previous lecture, I mentioned about this criteria of the ratio between the bulk modulus and shear modulus. The ratio turns out to be greater than 0.42, the critical number. So it should be brittle, which makes sense. The glass is [INAUDIBLE] brittle, although you also have a little bit of intrinsic ductility coming from the volume change during compressive stress, which we're going to cover.

Now, if you look at the hardness, hardness is basically the ability of the material to resist deformation. So you see that after the ion exchange process, the hardness actually increases, because when you're actually measuring hardness in this case, they are using viscous indentation method. Essentially, it's the pyramidal shape of the stylus to compress on the surface.

So you have a compressive stress on the surface. This compressive stress is going to resist deformation due to the stylus. And therefore, apparently, it will show up with a higher hardness. Makes sense?

OK, now next one, this is the more tricky one-- fracture toughness. The fracture toughness of all the Gorilla Glasses, [INAUDIBLE] you find, it's all around like 0.7 megapascal square root meter. It's basically the same as untreated soda-lime glass. Why?

The simple argument is that the fracture toughness is an intrinsic material parameter. So it should not depend on how you actually process it. In fact, I specifically asked my colleagues at Corning how they actually measure this fracture toughness number. It was done using a chevron-notch test, which is one of ASTM's standards. And it was done on a unstrengthened Gorilla Glass sample.

So when you look at this number, it really only measures the intrinsic glass material property. It hasn't taken into account the compressive stress yet. Realistically, if you look at the material under actual use conditions, you have lots of compressive stress essentially forcing on the tip of the crack. So if you apply your external load, which is our sigma infinity, in order to induce opening of the crack, your sigma infinity has to overcome the compressive stress. And then on top of that, the remaining amount has to exceed essentially the fracture stress of the glass.

So the compressive stress would actually increase the apparent ability for the material to resist breaking. But it does not get reflected in this measure number of fracture toughness. In fact, there are some people who are arguing, saying that you should not use unstrengthened glass to measure fracture toughness.

You should essentially do some calculations to look at correct geometry, account for compressive stress, and use that modified fracture stress to actually calculate the fracture toughness. Most people don't accept that. That's why. They still do the untoughened glass.

Now this is something to keep in mind. Because if you look at some news reports, they will just be citing this number as figure of merit to gauge a glass material's ability to resist fracturing or resist damage. This is not quite accurate because this is measured on the unstrengthened sample.

All right, so now about chemical strengthening, finally here, you can see it has a compressive stress on the surface of maximally exceeding 900 megapascals. This is even higher than what you can get using in the Prince Rupert's drop. So you can really get to a very, very high compressive stress with chemical toughening process.

The K steps, it's also larger compared to soda-lime glass. We mentioned soda-lime glass, the K steps is around 30 microns. You can actually get close to 100 microns with this kind of a modified formula there. Yes.

AUDIENCE: Can you [INAUDIBLE] do [INAUDIBLE] in [? after you ?] do it. [INAUDIBLE]

JUEJUN HU: To do what?

AUDIENCE: [INAUDIBLE]

JUEJUN HU: Yes, nobody really does that. That's the point about why would you actually want to do that?

[CHUCKLES]

Because if you do a thermal tempering, and then you do a chemical toughening, you combine the worst aspects of both. You get a large tensile stress region inside, which may be prone to damage. And then the amount of stress you accumulate on the surface, this is pretty much kept. That's very high stress. You get lots of relaxation already at that high stress level.

So by combining both, I don't think you can get too much additional out of it. So that's why. And also, it's just simply, more expensive. Why not just do a simple chemical toughening? So that's why people usually do one but not the other

We actually [? ran on ?] time. Any more questions? OK, I will stop here. In the next lecture, we are going to talk a little bit about the comparison of the sum of the different carbon materials beyond glasses.