Analyze That episode transcript

Let’s talk about Polymers – Analytical techniques and processing for material understanding

This transcript has been lightly edited for clarity, readability, and length. The content reflects the original discussion and technical intent of the speakers.

Maximillian Ries: Welcome to Analyze That, the podcast where we don’t talk about materials, but we measure them and try to truly understand them.
Today it's all about polymers, probably the most versatile material on the planet. But before we dive in, let's quickly introduce ourselves and as usual, ladies first.

Alexandera Mueller-Ewers: Hi, I'm Alexandra Mueller-Ewers. I'm a business development manager for extrusion and rheology. I've been working now, quite for some time in rheology and it's a topic that never stops being interesting. There is a famous phrase “panta rhei”, everything flows and that pretty much describes rheology.

Maximilian Ries: My name is Maximillian Ries. I'm a business development manager for molecular spectroscopy. I studied physics in Berlin, and I did my PhD in optical spectroscopy. And what fascinates me most is how much molecular information you can extract just from light interacting with matter.

Together, we look at polymers from two different but highly complementary perspectives.

Alexandera Mueller-Ewers: And that's exactly what today's episode is about. We will discuss which characterization techniques really matter for polymers. In many cases, a single method is not enough. And we will explain how combining two different techniques can give you a deeper insight.

So, we will start with processing, especially lab-scale extrusion. Then we move into rheology. We will talk about the different techniques in spectroscopy. And Maximilian will give us more insights into microscopy. And at the end of this episode, we will turn into real-time process analytics.

Maximilian Ries: Polymers are complex materials. They are elastic, multiphase, they are full of additives and they are highly sensitive to processing conditions. If we look at the material in development, everything starts with the concept.

So, for today, as an example, let's take glass fibre-based polymers, which we all know are difficult to recycle. Probably most people have seen pictures of tractors burying wind turbine rotor blades, and we all agree that it would be desirable to replace those materials with recyclable fibres designed for recycling. And once we select material and define what we want to do, usually the development begins with the extruder.

Alexandera Mueller-Ewers: Yes, and that's a moment when an extruder can turn an idea into reality. On paper, the formulation or idea might look perfect, but it's then inside the extruder where we find out if it works. In the extruder, here we melt the polymer, we mix and add additives, we create blends, and most importantly, we define the thermal and mechanical history. And that history directly shapes the final performance.

Now, imagine you have just developed a brand-new material. Maybe it's expensive. Maybe you only have a few grams from synthesis. You wouldn't put it straight into a massive industrial extruder producing hundreds of pounds per hour. And that's why lab- scale extrusion is so powerful. It gives you the flexibility to test different process conditions.

For example, you can adjust the temperature step by step, modify screw elements or change shear conditions - and really understand how the material behaves. And you can do all of that with as little as 20g, for example, and run your material under real processing conditions for later scale-up. While you can start with a very small amount, a lab-scale extruder can also run at throughput of up to 50 kg per hour if needed.

Maximilian Ries: That's smart because your equipment grows with your application. And then depending on the task, you can also change the equipment. I know there are mixers and single screw systems, but I don't really understand which ones I use. Can you give me a little bit of explanation?

Alexandra Mueller-Ewers: That's a good question. And it really depends on what you want to achieve. So, in addition -as you just said- to the extruders, we have lab mixers and they can play an important role especially when the focus is on fusion or thermal behaviour, like in PVC applications for example.

However, if you are mainly shaping and transporting a relatively homogeneous polymer melt, a single-screw extruder is often sufficient. It's robust, it's cost efficient and widely used in production.
But if you are developing a new formulation, if you want to add fillers, fibres, additives, or if you're working with recycled materials, for example, then you typically need a twin-screw extruder. Twin-screw extruders give you a much better mixing; you have a better control over shear and a greater flexibility in configuration.

The intermeshing screws allow a very precise control over mixing for the residence time and energy input. This is important when you are working with sensitive additives, for example, or high filler loadings, or if you have material that degrade easily.

Maximilian Ries: So, if you take our example of a polymer composite based on recyclable fibers, we would use a twin-screw extruder because we want to explore our material, right? Now we optimized the formulation, we adjusted the processing parameters and proudly we produced our first strands or pellets.
The next step is to answer the key question: are the new properties of our material comparable or are they even superior to the previous formulations?

Alexandra Mueller-Ewers: And then after the extrusion we start with the characterization. We usually prepare defined test samples. For example, using injection molding for small sample volumes. This allows us to produce consistent sample geometries with only a small amount of material. And with these samples we can perform mechanical or rheological tests in a consistent way.

Maximilian Ries: So, I totally understand what we're doing with the mechanical. But what exactly does the rheology characterize?

Alexandra Mueller-Ewers: So, rheology is the science of flow and deformation. In other words, everything flows. And in material processing, that's exactly what we deal with in every day in practice. It means understanding how a material behaves when it's processed, pumped, and stretched or shaped. But rheology goes far beyond simply measurement of the viscosity.

Depending on what we want to investigate with a rotational shear rheometer, we mainly use two different shear-based measurement modes.

First, we have the rotational test. Here we apply, for example, a shear rate and we measure the shear stress or the other way around depending on the application. And with these two values we can calculate the viscosity. So it allows us to determine the shear viscosity, and this tells us how easily the material flows.

In oscillation, that's the second possibility, we apply a small back and forth deformation to the material, and we measure its elastic and viscous response. This is a so-called storage modulus for the elastic response and the loss modulus for the viscous response.

So, this measurement allows us to distinguish between the elastic and the viscous contributions of the material. In other words, we can see how dominat the elastic part is and how strong the viscous part is. And that's when things become really interesting, when both contributions are present, then we are dealing with a so called visco-elastic material. And that's exactly what makes polymer so fascinating and sometimes also challenging to handle, because they don't behave purely like a liquid or a solid, but rather somewhere in between.

Maximilian Ries: Okay. So it totally makes sense that we have to understand the viscous and elastic behavior. Let's assume we are going into one extreme. What happens if my polymer is getting too elastic? If I have too much elasticity, can this cause problems in our process environment?

Alexandera Mueller-Ewers: Yes, absolutely. So in extrusion, if we have too much elasticity, this can lead to flow instabilities. For example, die swell, here the extrudated strands expands after leaving the die, or the extrudate can develop surface defects like sharkskin**.** So, when we understand the visco elastic behavior of our material, then we can adjust the material or the process and we can prevent these effects.

Maximilian Ries: And the melt flow index that I usually get as a parameter during processing, that alone is not enough to capture these effects?

Alexandera Mueller-Ewers: No, the melt flow index gives you just one number under one specific condition. It doesn't give you information about the viscoelasticity or how the material behaves under different deformation rates, for example. Rheology goes much further. It gives you insights into melting and crystallization. You can determine the glass transition T_g. You can follow curing reactions in real time or you can get even information about the molecular weight and its distribution.

Maximilian Ries: Yeah. And most probably as always, this is still not the whole story. Right now, we have talked about processing that is shear-dominated. However, there are other processing methods, such as film blowing, that involve different deformation modes.

Alexandera Mueller-Ewers: And this brings us to extensional rheology. In many industrial processes, you just mentioned one, for example, film blowing another one would be foam extrusion. The material isn't sheared, it's stretched. So under shear, polymers often become thinner. They flow more easily under extension.

However, many polymers behave very differently. They exhibit strain hardening. So in other words, that means the more you stretch them, the more they resist. And that resistance, often so called melt strength, determines whether a film remains stable or whether a foam holds or collapses. So while shear rheology tells us how a material flows, extensional rheology tells us how well it holds together, under stretching. And one of the reason why rheometers are so useful it’s the versatility: they can measure polymer films, polymer solids, or polymer solutions. In addition someone can also measure films or fibers in elongation - all on the same platform across a very wide temperature range.

Maximilian Ries: Can you also reveal what's happening inside the sample on a molecular level?

Alexandera Mueller-Ewers: No, this is what we can’t do. But we can combine rheology with spectroscopic methods, for example, with Raman or FTIR. That way, we don't just observe the change in mechanical properties, whether a material becomes stiffer or softer. We can, at the same time, track what's happening on the molecular level.

Maximilian Ries: That's super exciting. And before we go there, let me briefly clarify for our audience what molecular spectroscopy does.
Spectroscopy essentially measures the interaction of light and matter. Depending on the frequency of the light, different atomic or molecular excitations are probed. If you take ultraviolet or visible light, you have an interaction with the electronic transitions that largely determine material’s color. And this is the main reason why UV-Vis systems are widely used to control the optical properties of materials and monitor material degradation, for example through aging.

If you use infrared light, on the other hand, that would interact with vibrational states of molecules and provide a unique fingerprint for each material, depending on the atoms involved, the type of the bond, and also the surroundings of the bond. The technique is called Infrared Spectroscopy or Fourier Transform Infrared Spectroscopy (FTIR), and together with Raman spectroscopy, they are the number one techniques that are used for polymer identification.

Alexandera Mueller-Ewers: Okay, now I have to ask, could you explain what is the difference between FTIR and Raman?

Maximilian Ries: Sure, how much time do I have? If you take a high level view, then infrared spectroscopy measures the direct absorption of infrared light, and it requires a change in the dipole moment of the molecular bond.
On the other hand, Raman spectroscopy analyzes the inelastically scattered light from the laser interacting with a molecule. Here the key requirement is a change in the polarizeability during the vibration of the bond. So it implies that in both techniques, in principle, you measure the same bonds, but through a different mechanism.
I brought an example of a spectrum measured with FTIR and Raman spectroscopy. And as you can see, both techniques can be used to identify that the material really is PET. However, you will also notice that some bonds, such as the carbonyl group, are very pronounced in FTIR, but weaker in Raman since these bonds have a lower polarizability.

On the other hand, you have a polymer backbone which consists mainly of carbon-carbon bonds, and since these bonds are between identical atoms, they have no permanent dipole moment. They show a weaker infrared intensity, but they can produce very strong Raman signals simply because of the significant polarizeability changes. So since these techniques look at chemical bonds, so they must be used for, for monitoring reactions or structural changes. Right.

Alexandera Mueller-Ewers: So they must be used for monitoring reactions or structural changes. Right?

Maximilian Ries: Yes and this is what leads us to hyphenated techniques. I would say it is a passion of both of us. Because with hyphenated techniques, we don't just see the mechanical changes, but we can also observe at the same time what is happening on the molecular level. So let's imagine we are heating a polymer and you observe a drop in viscosity with rheology. Well, you see the drop. But then, if you simultaneously measure with Raman or FTIR, we can correlate the mechanical changes directly with their molecular origin.

Alexandera Mueller-Ewers: Yeah, and I think a great example is a curing reaction. With rheology, we can clearly see the transition from a liquid to a solid, the material stiffens and network forms. Spectroscopy shows what's happening on the molecular level, for example, the decrease in reactive groups as crosslinking progresses. Suddenly, we are not just measuring the stiffness, we are watching the formation of the network in real time. So, where do you see the biggest advantage of combining rheology with Raman or FTIR?

Maximilian Ries: So let's take your curing example. And with the FTIR technique, we can see whether the network formation is mainly driven by a decrease in the monomer concentration or by intramolecular reactions, which usually become more dominant in the later stages of curing. And this insight then allows us to optimize the curing process, for example, by simply deciding whether to increase the monomer concentration, or later on adjust the temperature to enhance the molecular mobility.

When it comes to structural ordering, like crystallization, for example, then Raman spectroscopy allows us to track molecular ordering directly. For instance, through specific bands that indicate crystalline domains. Realogically, we notice a strong increase in the storage modulus as the sample transitions from a melt to a solvent. Now, when we combine both techniques, we can correlate this rise in the storage modulus with the development of molecular order and for some systems, that combination then reveals intermediate structural stages, for example, from an amorphous to a crystalline state, or from one polymorph to another which a single technique would miss.

Alexandera Mueller-Ewers: So, in other words, Raman reveals molecular ordering. But what if we really want to quantify crystallinity?

Maximilian Ries: Then we would use X-ray diffraction. Raman spectra do not provide us with a direct measurement of a lattice constant, because lattice parameters are on the same length scales as X-ray wavelengths, and it is the diffraction patterns that allow us to determine lattice spacing and quantify crystallinity using X-ray diffraction.

As you know, the manufacturing conditions directly influence the crystallinity of materials and the crystallinity of a material strongly affects the mechanical and thermal and barrier properties of the product. And therefore, XRD helps us to link the processing parameters directly to the final material performance.

Alexandera Mueller-Ewers: So, X-rays don't just tell us about structure, they can also show the composition.

Maximilian Ries: Yes, absolutely right. Besides X-ray diffraction, we can also use X-ray fluorescence, which adds elemental insights. So as x-rays have much higher energies than ultraviolet or visible light, they can ionize inner-shell electrons, which are deeper, if you want to say, than the electrons that produce the color. And when the vacancies of these electrons, they are filled by electrons from higher energy levels, characteristic X-rays are emitted with energies that are specific to each element.

And as you can easily understand, this is particularly useful if you want to do elemental fingerprinting or if you want to quantify additives such as flame retardants, fillers, pigments, or even detecting heavy metals and contaminations throughout production.

Alexandera Mueller-Ewers: So far, everything we have discussed gives us bulk information. But polymers are rarley homogeneous. We have multilayer films, composites and defects, and they all require spatial resolution.

Maximilian Ries: Yeah. And that's exactly where microscopy techniques really change perspective. So, if we start with Raman and FTIR microscopy, they provide us with the chemical imaging at the micrometer scale. They are particularly powerful in identifying layers, blends, crystalline domains, and also in failure analysis and unknown inclusions in the sample.

Alexandera Mueller-Ewers: So, that tells us a lot about the chemistry of the material. But what if we want to understand the elemental composition, especially at the surface?

Maximilian Ries: Yeah, that's a good question. Again, we can use X-ray techniques for surface and elemental composition, surface chemistry and elemental composition. We would go and use XPS, which is X-ray photoelectron spectroscopy. And we can analyze the top few nanometers only and reveal chemical states at the surface. So that's very crucial if you want to think about adhesion or additive migration and coating performance**.**

And if you are aiming more for morphology, then you would use scanning electron microscopy(SEM). This provides ultra high-resolution imaging down to a nanometer level. And it can also be equipped with elemental mapping, which is ideal for studying filler dispersion or contaminations.

But now let’s zoom out a little bit again and have a look at our materials outside the analytical lab and really look at them under manufacturing conditions.

Alexandera Mueller-Ewers: Yes. Once the process is running at scale, we want analytical insight in real-time. So, to maintain consistent quality the process itself must become analytically transparent.

Maximilian Ries: For example, residual monomers or reaction gases, they can be tracked with online gas analysis using process mass spectrometer.

And with Raman and near-infrared analyzers, you can perform molecular analysis directly in the production process. And that would mean continuous monitoring during reactive extrusion, looking at additive concentrations that are changing, compositional changes without interrupting the process.

Alexandera Mueller-Ewers: From a rheological perspective, this is just as important. Under manufacturing conditions, flow behavior is a key quality indicator. With an online process rheometer, we can track the viscosity and the melt flow index directly in the melt stream under real production conditions. And this enables faster adjustments- we have fewer out of spec batches and a more stable process overall.

So aside from inline intelligence, we also need dimensional and structure control. Gauging systems allow continuous monitoring of thickness and basis weight in film or sheet production.

Maximilian Ries: So in other words, analytics is no longer something that validates production afterwards. It becomes part of the control strategy itself. We know that processing defines structure and structure defines properties and chemistry defines everything that's underneath. So, there is no single technique that can capture this level of complexity.

If we go back to rheology, we use it to explain the flow instability. If we go and take spectroscopy methods, we can reveal the molecular structure and with X-rays we can quantify crystallinity and composition. And if we really want to look into details, we take microscopy and we resolve spatial heterogeneity.

Alexandera Mueller-Ewers: So, and with inline systems, we can close the loop. When we bring these perspectives together, measurements turn into real material understanding. And that integrated approach - from R&D to production - is exactly what enables smarter development, faster troubleshooting and more stable manufacturing.

Maximilian Ries: Thank you very much for listening to Analyze That. We hope this episode gave you a clear understanding of polymer characterization from early-stage development, where we have very small sample amounts all the way to full-scale production.

If you're interested and want to learn more about polymer analysis and characterization techniques, please visit our website and it leaves us with the last words.

Alexandera Mueller-Ewers: See you next time

Maximilian Ries: and stay curious!