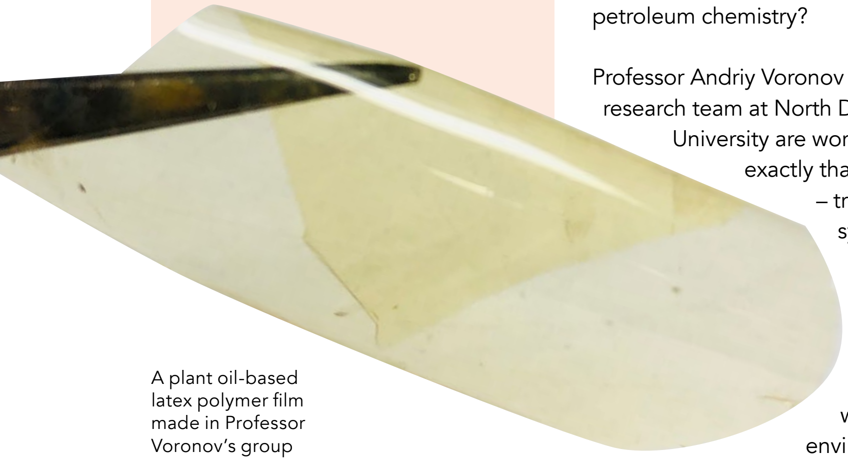
High performing monomers and polymers from plant oils

We often think of fossils fuels as a source of energy, but one of the key uses of fossil fuels is as a starting point for the synthesis of new chemical compounds. These range from plastics to pharmaceutical products. In recent years, there has been a push to move to more sustainable chemical feedstocks. Professor Andriy Voronov at North Dakota State University is one of the researchers leading the way to find strategies to make high performance chemicals from renewable feedstock with lower environmental impact.



A plant oil-based latex polymer film made in Professor Voronov's group

Many materials, such as plastics, start their lives as part of the sludgy black mixture that is crude oil. Crude oil is a very rich source of hydrocarbon compounds, chemicals that contain the elements carbon and hydrogen. From this soup, thousands of different chemical compounds can be created, ranging from high-value pharmaceuticals to the building blocks of plastics like polyethylene and nylon.

While crude oil and other hydrocarbon fuels like natural gas are a rich chemical feedstock, these are all finite resources and often very energy-intensive to process into useful compounds; they also accumulate waste due to their non-biodegradable nature. Great progress has been made in finding renewable alternatives for energy generation, but can the same thing be done for petroleum chemistry?

Professor Andriy Voronov and his research team at North Dakota State University are working on exactly that problem – trying to synthesise materials from renewables with lower embroiled energy, and with a lower environmental impact. In his research, he has developed a new strategy for making vinyl monomers in a single step reaction by converting plant oils into monomers. Then, the monomers are used in a polymerisation step to produce acrylic polymers.

POLYMER PRODUCTION

The plastics that we know are examples of polymers – materials made from a pattern of repeating subunits known as monomers. The commonly used plastic polyethylene that is very often employed to produce drinking bottles and plastic bags gets its name from its monomer subunit ethylene. In the polymer, hundreds or thousands of monomer units are joined together to form long chains. Depending on the density and length of these chains, the final plastic can have different properties. For example, a high density of chains makes polyethylene very lightweight and strong, suitable for bottles, but a low density of chains can make something as flexible as a carrier bag.

Professor Andriy Voronov has found a method to make acrylic monomers from plant oils using just a one step synthetic process. Plant oils are an excellent starting material as many of them are inherently abundant, often inexpensive, and non-toxic. They also have the intrinsic but important property of being biodegradable. The challenge of using them to make high performance polymers – where consistency of properties such as the chain length is key – is how to deal with the more complex and inconsistent starting materials. Chemically, oils are composed of triglycerides (esters of fatty acids and glycerol).

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Plant oils are extracted from seeds, like rape seed oil (pictured). The oils are used as raw materials for the synthesis of monomers.

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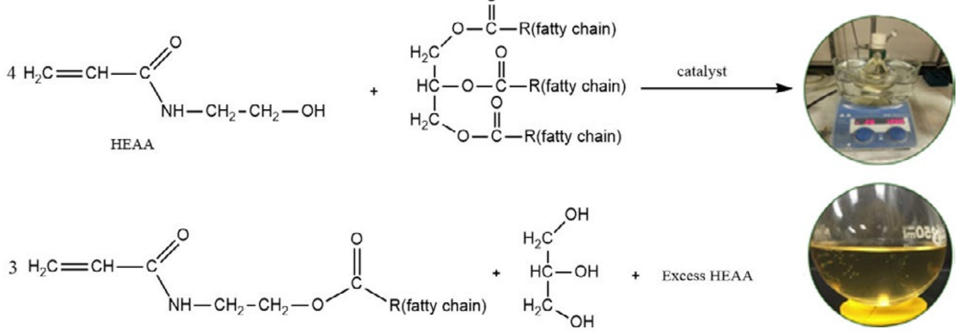
Once oils are turned into monomers, the monomers are then used to create polymers and polymeric materials, which have many different and important applications.



Oils are composed of triglycerides, esters of fatty acids and glycerol.

Successful polymer synthesis is all about control and industrial production plants invest significantly in technologies to allow precise control over each step of the reaction. As the monomers react together to start building the chain, there is always a risk of unwanted side reactions. Some of these might make other unwanted chemical species, but others may lead to termination of the chain growth process. While this is desirable once the chain has reached the intended length, if it happens too early the reaction mixture could deteriorate.

Different polymers have very different structural properties. If the mobility of a polymer chain is limited, the polymeric materials are brittle and rigid. If the mobility is higher, the resultant polymer is flexible. For more flexible polymers, one of the most popular applications is for coatings for a wide variety of materials. This means the polymer needs to be very resistant to protect the object underneath but must also have good adhesion to stick to the surface without flaking or chipping over time. The acrylic polymers derived from plant oils that are designed in Prof Voronov's lab have long aliphatic (hydrocarbon) chains with different amounts of double bonds (depending on the oil source) that provides the material flexibility. The hydrophobicity property is inherently based on the nature of the renewable resource used for the synthesis. These excellent properties can be used for waterproofing, improving flexibility, and adhesion and have many valuable applications.

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A FLEXIBLE BACKBONE

While Professor Voronov's plant oil-based acrylic monomers can be used directly for making already existing materials that are based on acrylic monomers, they

Setup for small pilot synthesis of plant oil-based monomer (10 litres).

Prof Voronov's development of a new synthetic approach opens the possibility of creating bio-based polymers, in a relatively straightforward way.

are also an excellent building block for making biobased polymeric structures. The designed plant oil-monomers have dual functionality – a vinyl bond that makes the polymer chains growing in free radical polymerisation, and double bonds in fatty acid chains that are preserved during polymerisation and can be used for post-polymerisation crosslinking reactions.

The acrylic monomers can also be mixed with both important petroleum intermediates or biobased vinyl compounds to make mixed polymer species (copolymers). Such copolymers allow the combination of the excellent water resistance of the plant oil-based acrylic polymers and their plasticity with desirable properties from the other polymer species. This means that the biodegradability and elasticity of the final copolymer produced can be tailored exactly for the specific application to make a sustainable polymeric material.

Another important feature of plant oil-based acrylic monomers is that they can undergo a reaction in an emulsion process to form emulsion polymers, otherwise known as latexes. An emulsion is formed when a compound does not dissolve in a solvent, it remains as dispersed droplets. One of the most well-known examples of an emulsion is milk, which is a dispersion of oil droplets in water. Emulsion polymerisation is a very useful process as it yields a ready-to-use final latex polymer and this type of polymerisation occurs readily in water. This means the emulsion polymers can be formed, applied to a surface, and a final polymer film or coating is left after drying. The plant oil-derived emulsion polymers have the benefit of being able to form films, which is highly desirable in applications, such as paints and coatings. For specific applications like paints for example, the hydrophobicity is required that makes plant oil-based monomers ideal candidates for material synthesis.

A GREENER FUTURE

Moving towards a circular industry, where chemical waste products also become chemical feedstocks, is a huge undertaking for chemical processing. Professor Voronov's development of a new synthetic approach is important not just because it opens the possibility of creating bio-based polymers, but because it does so in a relatively straightforward way.

One of the big challenges in sustainable chemical synthesis is finding reactions that are not just suitable for the benchtop, where a single scientist can make perhaps a few grams of product, but finding reactions that can be scaled up and automated to produce many kilograms of product every day. Having a single step synthesis makes this a much more realistic possibility as fewer steps mean better product yields and more efficient processes, as well as a greater degree of simplicity in the reaction automation. Since the reaction proceeds at mild conditions it does not require high energy consumption.

Professor Voronov has now patented the synthetic process. The performance of the plant-oil based monomers and polymers opens a wide range of opportunities for adhesives and coatings and even personal care products due to their inherent non-toxicity. This is an exciting period for the development of new synthesis tools and routes that make use of renewable, green feedstocks.

Behind the Research

Prof Andriy Voronov

E: andriy.voronov@ndsu.edu **T:** +1 701 231 9563 **W:** https://www.ndsu.edu/cpm/faculty/voronov/ **W:** https://cpmvoronov.wordpress.com/ **W:** https://lpnu.ua/en/icct

Research Objectives

Professor Andriy Voronov's research centres on sustainable polymeric materials for coatings, adhesives, bioplastics, and personal care products.

Detail

Address

Department of Coatings and Polymeric Materials,
North Dakota State University, NDSU Dep.2760
P.O. Box 6050, Fargo,
North Dakota 58108 USA

Bio

Professor Andriy Voronov works in Coatings and Polymeric Materials Department at North Dakota State University, Fargo, North Dakota, USA. He completed his degrees in Ukraine, and his PhD in Polymer Chemistry from Lviv Polytechnic National University.

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Collaborators

- Zoriana Demchuk, Ihor Tarnavchyk, Kyle Kingsley – Coatings and Polymeric Materials, NDSU
- Oleg Shevchuk, Vasylyna Kirianchuk, Ananiy Kohut, Stanislav Voronov – Department of Organic Chemistry, Lviv Polytechnic National University, Ukraine

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Personal Response

Are you looking to develop other types of monomers from plants?

" Synthesis of emulsion polymers from plant oil-based monomers provides an opportunity to replace petroleum-derived constituents in latex synthesis to make the resulting product more environmentally-friendly. However, due to the highly hydrophobic nature of plant oil-based monomers, synthesis of highly biobased latexes remains challenging. Recently, we reported on emulsion polymers with plant oil-based content of up to 60 % wt. While incorporation of plant oil-based fragments into the latex copolymers improves mechanical properties of the product, an excessive softening of polymeric materials can be experienced when incorporated plant oil-based fragments exceed level of 60 wt %. To this end, to further increase the biobased content in latexes without deteriorating the material's properties and performance, other biobased counterparts can be considered for copolymerisation with plant oil-based monomers. We are looking forward to further research and progress in this direction. "

NDSU NORTH DAKOTA STATE UNIVERSITY