This highlight refers to the PhD by Ivanna Lins Colijn (2023, cum laude)

Multiscale investigation and characterization of nano-particle reinforced bioplastics: Toward a circular economy

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Background

The discovery of plastics has revolutionized the world we live in due to their astonishing properties including mouldability, durability, price, and strength in combination with light weight. However, our consumption pattern in combination with the (often) non-biodegradable/compostable nature of plastics is no longer compatible. A circular bio-economy offers an escape from our current reality where fossil fuels have adverse effects on the environment, and plastic pollution negatively impacts life on the planet. There is a clear demand for plastics as well as a desire to reduce the impact on the planet. We therefore need to ask ourselves what these novel materials should look like and what their role is within a circular economy.

At present, much can be gained by recycling, reusing, or reducing traditional fossil-based plastics. In a polluted world where fossil sources are scarce and oil prices are heavily fluctuating, it is advisable to focus on biobased materials for the long(er) term. Bio-based (biodegradable/compostable) plastics are particularly relevant because of their lower footprint compared to their fossil-based counterparts. Today, the use of bioplastics is still a niche, mainly because their functionality does not compare favourably to their intended use.

The addition of nanoparticles to biobased polymers led to nanocomposites with enhanced mechanical, thermal, and barrier properties, and has the potential to make the use of bioplastics mainstream (Yanat & Schroën, 2021, 2023).

Method

Within the thesis, we investigated and characterized the multiscale physical and chemical properties of nanoparticle reinforced plastics through multidisciplinary research that is divided into three parts:

- Part I: Model systems
- Part II: Biobased systems
- Part III: Plastic products and society

Improved material properties are observed when nanoparticles are homogeneously dispersed in the polymer matrix. In practice however, nanoparticles tend to aggregate. The first part of this thesis is dedicated to model systems to investigate the effect of various design parameters on nanoparticle dispersion, and how the resultant nanocomposite structure affects material properties. In the second part of the thesis, we focussed on the development of fully biobased and compostable nanocomposites consisting of PLA and chitin nanocrystals. The last part of this thesis was dedicated to plastic materials in society (Colijn, 2023).

Results

In practice, nanocomposite design often relies on trial-and-error approaches, despite the various theoretical frameworks available. We reviewed these frameworks and summarized experimental techniques to measure fundamental properties. Nanoparticle dispersion is predominantly affected by thermodynamic factors; for optimal nanoparticle dispersion, the nanoparticle – polymer interaction forces need to be higher than the interaction forces between the nanoparticles themselves. This clearly illustrates we should look beyond the famous 'like-dissolves-like theory'. Kinetic effects – such as shear forces – can bring nanoparticles to a new 'equilibrium', but these effects are of lesser importance in nanocomposite design (Colijn et al., 2023; Colijn & Schroën, 2021).

Molecular dynamics simulations highlight that nanoparticle – polymer interactions affect nanoparticle dispersion, which is key to the creation of enhanced materials properties. Favourable interactions increased the polymer density at the nanoparticle interface, thus resulting in an increased interphasial layer thickness; this leads to the formation of nanoparticle bridges and increased glass transition temperature, correlating to more stable materials (Colijn, 2023).

We showed that interphasial relaxation times were 10^2 – 10^3 times longer in nanocomposites than in neat polylactic acid (PLA). As such, nanoparticles essentially play the role of long-lived physical crosslinks. Nanoparticle dispersion highly affected nano- and bulk scale dynamics inside polymers (Colijn et al., 2024). The nano- and bulk scale dynamics were practically independent of the enthalpic component. We hypothesized that individual interphasial regions can affect each other, an effect that is enhanced by improved dispersion and higher nanoparticle loading. That leads to thought-provoking indications that dispersion is more important than nanoparticle – polymer interactions, whereas the latter is generally considered most important (Colijn et al., 2024).

In practise, nanoparticle aggregates can potentially be broken up during industrial processes. Ultrasound can easily deliver the critical energy input needed to break up chitin nanocrystal aggregates, whereas the energy input generated during polymer extrusion is expected to be too low (Colijn et al., 2021). Thus, other methods than those classically applied in industry should be considered to achieve chitin nanocrystal dispersion. Modifying chitin nanocrystals with fatty acids differing in carbon chain length was used to achieve this; particles modified with the longest fatty acid showed highest hydrophobicity, and dispersibility (Colijn et al., 2022a).

Generally, particle addition to the base polylactic acid polymer resulted in brown colour formation, which was reduced when the particles were modified (Colijn et al., 2023). This was likely the result of better dispersibility of modified chitin nanocrystals, and reduced reactivity. Overall, the addition of chitin nanocrystals improved barrier properties and provided high UV protection without this being at the expense of mechanical strength (Colijn, 2023).

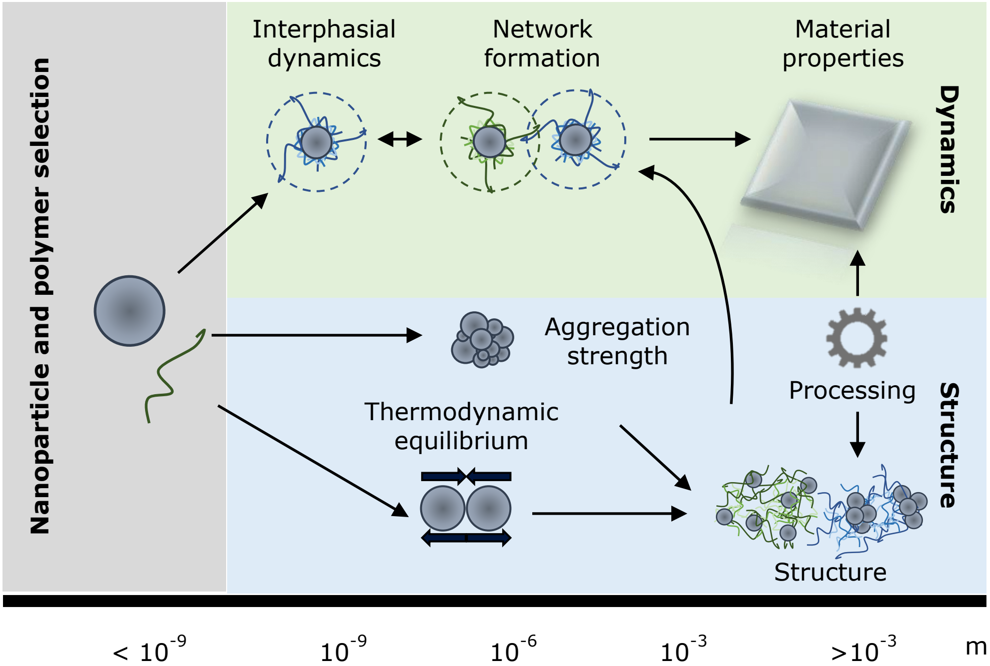

Figure 1: Overview of the various scales and driving forces affecting the formation of nano-composite plastic materials (Colijn, 2023).

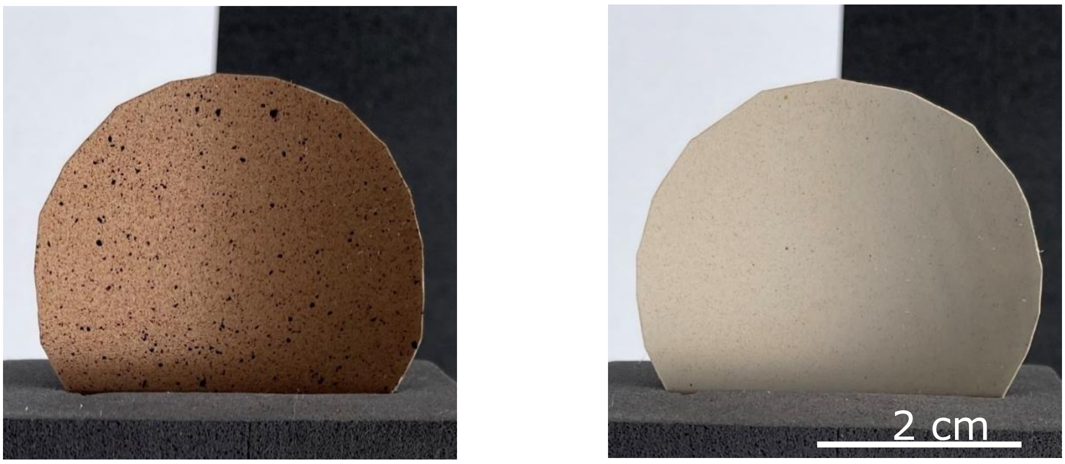

Figure 2: (a) Large chitin nanocrystal aggregates visible at 5 wt.%; (b) fatty acid surface modification (C18:0) improves dispersibility and film transparency (Colijn et al., 2023).

Plastics play an important role in the transition from a linear economy toward a circular one, but ideas about this role differ among actors. We studied these ideas as a form of futurity framing of traditional media and international academic papers. The futurity frame of a linear economy focussed on today's issues with plastics such as their non-biodegradability. Within the vision of a transition toward a circular economy, actors focus on the processes and steps required for change including consumer behaviour, social structures, and waste management systems. In both visions, actors envision plastics as part of our future circular economy. Academic papers focus mainly on alternatives forms of plastics, whereas newspapers mainly report on closing the loop for traditional forms of plastic. We observe a missed opportunity to combine both visions to develop alternative biobased and biodegradable forms of plastics that can be recycled. The further development of this future vision of recyclable bioplastics and biodegradable plastics by industry, academics, governments, and NGOs, including citizens, may contribute to a more fully circular biobased plastic economy (Colijn et al., 2022b).

Outlook

Fundamental insights can be used to rationally design nanocomposite materials. On the smallest scale enthalpic and entropic factors are important for interphasial and overall nanocomposite architecture, and collectively affect material dynamics; it seems important to maximize the polymer density near the nanoparticle surface to reduce interphasial dynamics.

In order to get improved materials, interphasial properties need to be translated to the bulk, and we illustrate that the overall nanocomposite dispersion state plays a crucial role in this. In well-dispersed systems interphasial layers interact with each other, potentially via overlapping interphasial zones, polymer bridges, or communicate via entanglements (if applicable). Eventually, a pseudo-percolation network is formed which reduces the dynamics of most of the material. From this, we concluded that nanoparticle dispersion is the key factor for nanocomposite design, and various thermodynamic and kinetic routes are available to facilitate that. This leads to altered mechanical, barrier, and thermal properties. Additionally, nanoparticles can give optical, antioxidant, and/or antimicrobial features if the nanoparticle possess such functionality.

Before novel materials - such as bio nanocomposites - can successfully be introduced into society, other factors should be investigated as well including scalability, accessibility, end-of-life possibilities, sustainability, toxicology, and consumer acceptance and handling. We conclude that the rational design of nanocomposites needs to be approached in a truly multifaceted way that combines various fields of science to be successful.

Acknowledgement

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