Sustainably dyed and functionalized biobased poly (lactic acid) fibers for textile applications

Summary

Innovative textile products and fabrication techniques are the need of the hour to make the textile field more sustainable. Although biobased polymers such as PLA is being investigated for various textile applications, the processes used currently in textile productions are not always sustainable. Conventional exhaust dyeing of PLA can lead to hydrolytic degradation and obtaining satisfactory color performance is therefore challenging. Furthermore, the effluents from the process are toxic and leads to water pollution.

Colorants are multifunctional meaning they can impart other functionalities like electrical conductivity, and anti-microbial properties, when the right ones are used. With the outburst of Covid-19 virus, the need for masks with very low fiber diameter and antibacterial functionality skyrocketed. Electrospinning is an upcoming way for producing such materials but solution electrospinning is commonly used now and this is not environmentally friendly because of the use of solvents. Melt electrospinning has shown potential but the low electrical conductivity and high viscosity of polymer melt makes it challenging.

To overcome both these challenges, in this thesis, a novel approach to use multifunctional colorants for manufacture of potentially sustainable PLA textiles was investigated and the following objectives were accomplished:

- Evaluation of dope dyeing process as a sustainable alternative to conventional exhaust dyeing of PLA
    - A dope dyed knitted fabric was successfully developed
        - It was observed that dope dyeing did not lead to loss in performance and no degradation happened, unlike exhaust dyeing, where degradation was observed
        - The properties of the filaments and knitted fabrics were influenced by process parameters more than the colorants used
    - The performance of the selected biobased and potential biobased colorants were comparable to fossil-based colorants
- Investigation of the effect of multifunctional colorants on rheological, and electrical properties of PLA and the diameter of the fibers fabricated in melt electrospinning
    - Addition of colorants led to reduction of fiber diameter

    - A prototype of melt electrospun PLA fiber web with antibacterial properties was produced using the 600 nozzle pilot-scale melt electrospinning device
- A comparison of melt spinning and melt electrospinning process was performed and the key similarities and differences between the processes were identified

The colorant used and its weight percentages influenced the diameter of the fiber obtained from the melt electrospinning process, whereas the colorant used did not influence the properties of the melt spun yarn. Overall, the potential of colorants to perform as multifunctional additives that impart color, antibacterial properties and work as a nucleating agent in PLA was demonstrated and a short overview is given in the following summary.

The various textile production techniques used to produce fibers with different diameters was presented in **Chapter 1,** the current state of the art on important processes (melt spinning and electrospinning) involved in production of fibers for conventional textile applications and submicron, and nanofibers for filtration application were discussed.

In **Chapter 2**, the dope dyeing of PLA was focused on. The low thermal stability of PLA and its hydrolytic degradability posed challenges for its conventional exhaust dyeing. Therefore, dope dyeing was proposed as a more sustainable and suitable alternative. The impact of colorants on thermal, rheological, and mechanical properties of PLA multifilaments and fabrics were investigated. A mix of fossil-based, potential biobased, and a biobased colorants (a total of 5 colorants) were used to perform dope dyeing. It was observed that three of the colorants used worked as a nucleating agent to promote crystallization in PLA at lower cooling rates. However, they did not affect the mechanical properties and crystallinity of the melt spun yarn and the draw ratio used played a more dominant role in determining these. It was demonstrated that unlike exhaust dyeing, dope dyeing using the selected colorants did not lead to hydrolytic degradation of PLA. Color stability tests (BWS, UV-stability) tests performed on the dyed yarn and the fabric revealed that the potential biobased and actual biobased colorants performed as good as the fossil-based colorants. The results obtained in the study show the potential of dope dyeing as a sustainable dyeing technique for dyeing PLA to produce conventional textiles.

Chapter 3 was a proof-of-concept study designed to investigate the effect of colorants on electrical conductivity of PLA. Lab-scale melt electrospinning of PLA was performed using potential biobased dyes at different concentrations. The electrical conductivity of PLA increased upon addition of colorants. Addition of quercetin, and alizarin did not lead to any degradation of PLA. However, addition of hematoxylin led to degradation but the finest fibers (16.04 μm in diameter) were produced by adding 2% (w/w) hematoxylin, reducing the average fiber diameter by 77% compared to pure PLA. The crystallinity of the lab-scale melt electrospun fiber was measured to be very low (8.87%), meaning the orientation was low in the fiber. Although the crystallinity was low, the study revealed the potential of biobased dyes as additives to increase the electrical conductivity of PLA.

In **Chapter 4,** the effect of dyes and pigments on the melt electrospinning performance of PLA was investigated. Pigments such as copper pthalocyanine are expected to have higher electrical conductivity than the dyes but are harder to disperse in the polymer and dyes are easier to disperse. Since when conductive additives are added, the electrical conductivity of the polymer compound depends on the additive and the degree of dispersion, the potential of dyes and pigments were compared here. It was observed that the addition of pigments led to higher electrical conductivity compared to the selected dyes. However, the diameter was lower with fibers containing dyes. This was attributed to the aggregate formation, which was observed through SEM images in case of pigments. The diameter of the pure PLA fibers was > 100 μm, and the best result was achieved with composite A1, which formed fibers 52.5 μm in diameter. Based on the results, it was determined that, among the colorants tested, dyes performed better and a scale-up was therefore performed with dyes.

Chapter 5 focused on scaling up the melt electrospinning of PLA with colorants to the 600-nozzle pilot scale device. Curcumin, alizarin, and quercetin were the dyes used since dyes were observed to perform good in lab scale and they offered an additional antibacterial functionality. Spinning trials showed that the addition of dyes produced narrower fibers in the resulting fiber web, with a minimum diameter of ~9 μm for the fiber containing 3% (w/w) of curcumin. Furthermore, it was also observed that the PLA fiber web containing 5% (w/w) curcumin was antibacterial against *S. Aureus*. Our work provides insight into the scaling up of the melt electrospinning process from the laboratory to pilot scale, and shows the potential of multifunctional colorants to develop environmentally friendly microfiber webs with antibacterial properties for filtration and biomedical applications.

In **Chapter 6,** an insight into similarities and differences between melt spinning and melt electrospinning was pondered. It was observed from DSC studies, that although the pigments acted as nucleating agents at a cooling rate of 10 °C/min, the nucleation efficiency started to decrease once the cooling rate was increased to 30 °C/min and it was even lower at a cooling rate of 60 °C/min. The cooling rates in melt spinning exceed 200 °C/min and it was observed that the nucleating agent did not have sufficient time to promote crystallization. Drawing applied during the process led to stress induced crystallization and proved more effective. In case of melt electrospinning, it was observed that having nucleating agent could be detrimental to the process. When the polymer crystallizes, its viscosity increases multiple-fold and the electrical conductivity decreases. Both have negative influence on melt electrospinning process and since nucleating agent speeds up the crystallization process, it could reduce the time the polymer jet has for whipping during processing. Therefore, performing the process without nucleating additives could be more beneficial. Based on calculation of the processing parameters, it was observed that the melt drawing ratio was higher in melt electrospinning but the drawing rate was higher in melt spinning than melt electrospinning. Furthermore, the results showed that the crystallinity of yarn obtained from melt spinning was higher leading to the hypothesis that in order to obtain melt electrospun fibers with good mechanical properties, both high melt draw ratio and drawing rates are necessary. Integration of a climate chamber could be the next step in achieving this.

Outlook

Dope dyeing is generally expected to be more sustainable than exhaust dyeing since lesser amount of water and chemicals are used for processing. However, high temperatures are needed to perform the mixing process and large amounts of materials are required to clean the extruder, when the color needs to be changed. Taking this into account, dope dyeing would be suitable for producing yarns in larger quantities and exhaust dyeing would be suitable to produce dyed yarns at lower quantities. Although, no toxic chemicals are used in dope dyeing, cleaning the extruders to change the color of the yarn is challenging and a lot of polymer and cleaning materials are required for this. In order to get a clear idea on how sustainable this can be, a life cycle assessment (LCA) study would be necessary. Since the colorants are extracted from different resources, and have different toxicity levels, it would be necessary to perform LCA for each individual scenario to identify the hotspots. In the current research work, potential biobased colorants were used. Together with colleagues, we also performed a LCA study on extraction and dyeing with a biobased colorant. A madder root extract was prepared and we performed dyeing with this extract. It was observed during this study that the extraction of the colorant was a major hotspot that needed to be optimized to make the biobased colorants more sustainable. Furthermore, when the sugars presented in the extract are not fully removed, exhaust dyeing still worked but dope dyeing did not work. It led to burnt brown color. Therefore, more research to improve the yield of biobased colorants during extraction is necessary to bring them to the market. Nucleating agents, based on colorants, have been shown to influence the crystallinity in PP even when melt spinning at higher speeds. Even though the colorants used in this thesis proved to be nucleating at lower cooling speeds, it was not the case during melt spinning. In this thesis, we used colorants that melt during melt spinning of the polymer and colorants (with higher melting point) that do not melt during melt spinning. When using colorants that melt during processing, we observed that there was plasticizer effect on the polymer melt. However, for the colorant to act as a nucleating agent, they need to crystallize very fast under melt spinning conditions and then nucleate the crystallization of PLA. This can be quite challenging. Therefore, using colorants that do not melt during melt spinning could have more potential to work as nucleating agents at these higher cooling speeds. Further investigation is necessary into the crystallization and crystal structure of colorants to determine what characteristics of a colorant are necessary for them to function as nucleating agents and improve the mechanical properties of melt spun PLA filaments. Apart from process optimization, next steps could be investigating the performance of PLA based textiles. Tailoring the crystallization of PLA and heat setting can help influence the biodegradation of PLA. This can lead to very interesting textile products, where the age of the product could potentially be tailored.

Melt electrospinning is still under developmental stage. Our research showed that the use of colorants had a positive influence on the diameter of the fiber web. In future attempts, a combination of more than one colorant can be used to investigate a potential synergetic effect. One more alternative could be use of an antibacterial colorant and a nanoadditive such as graphene to improve the electrical conductivity even further. Colorants such as curcumin, and alizarin are also pH sensitive. Their color changes based on the pH they are used in. Since wounds have different pH during the healing process, melt electrospun anti-bacterial wound dressing made with these colorants could serve as smart wound dressing materials. A second optimization step can come from the machine modification. For ex., an integration of a climate chamber to control the temperature below the spinneret could promote production of thinner fibers through melt electrospinning. Optimizing the design of the current spinning nozzle to reduce the dwell time of the polymer inside can reduce thermal degradation and make the process more versatile for other polymers. A two-side approach to modify the material and the machine simultaneously can help make more innovative sustainable melt electrospun textile materials. Although, melt electrospinning shows a lot of promise for producing fibers suitable for filtration application, to the best of our knowledge, no such filter exists in the market currently. Investigating the performance of melt electrospun nonwovens as filters can be a good follow-up to the current results of the thesis. Using colorants as multifunctional additives to make anti-bacterial filters has great potential in the field of air filtration for hospitals and also medical masks. During Covid pandemic, disposal of filters was a big challenge and using biopolymers such as PLA to produce one material filters can be a positive step towards solving this issue. Overall, this thesis showed the potential of using colorants to make PLA based textiles. Further investigation in this field could lead to new interesting textile products based on PLA.