

Thermotropic polyesters and polylactide

Citation for published version (APA):

de Kort, G. W. (2021). *Thermotropic polyesters and polylactide: a route to sustainable and reprocessable reinforced composites*. [Doctoral Thesis, Maastricht University]. Maastricht University. <https://doi.org/10.26481/dis.20210125gk>

Document status and date:

Published: 01/01/2021

DOI:

[10.26481/dis.20210125gk](https://doi.org/10.26481/dis.20210125gk)

Document Version:

Publisher's PDF, also known as Version of record

Please check the document version of this publication:

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Chapter 7 – Valorization addendum

The previous chapters of this thesis describe my findings over the past four years regarding the development of reprocessable reinforced thermoplastic composites based on liquid crystalline polymers and poly(lactide) with the underlying goal to boost the development and implementation of sustainable plastic materials. Chapters 2 through 4 investigate the orientation and relaxation of LCPs, identify feasible processing routes and crucial LCP properties for the production of reinforced thermoplastic composites, demonstrate the reprocessability of LCP-PLA composites and identify the boundary conditions for their reprocessability. The viscosity of the two thermoplastic polymers, as well as their ratio and their respective temperature dependence are identified as the key parameters that determine the morphology and performance of the composite, given that the processing conditions are kept the same. These parameters need to remain constant over the course of multiple processing cycles to maintain the performance of the composites upon reprocessing. As the processing temperatures of typical LCPs are high and PLA is susceptible to thermal degradation, this can pose a challenge.

To address this issue a versatile method to produce LCPs with a low processing temperature has been developed, which is described in Chapter 5 and these LCPs are used to produce reinforced composites with PLA in Chapter 6. This method is based on the chain extension of a liquid crystalline prepolymer with carboxylic end-groups with bis(2-oxazoline)s, which allows control over the molecular weight and chain architecture of the final LCP. The backbone of the prepolymer consists of several different aromatic monomers, including bent and substituted monomers, some of which were biobased, that are incorporated randomly into the chains. This results in nematic glasses with excellent mechanical performance and processing temperatures below 190 °C, which corresponds to the minimum processing temperature of semi-crystalline PLLA. The thermal degradation of the PLLA upon reprocessing is therefore minimized. The composites based on PLLA and the chain extended LCPs possess good mechanical properties, comparable those of short glass fiber-reinforced thermoplastic polymers and proved to be reprocessable. This similarity provides a clear range of applications where these composites can potentially be used. As we consider these materials a viable and more sustainable alternative to other reinforced composites, a patent application has been filed on chain extended thermotropic LCPs with a low processing temperature and their in use thermoplastic composites.

7.1 Potential and challenges regarding industrial implementation of LCP reinforced thermoplastic composites

From a material science point of view, chain extended LCPs are highly suitable to produce reprocessable reinforced composites with PLA or other thermoplastic materials. However, that alone is not sufficient to make the transition from a scientific study to actual market implementation. In order to achieve that the material needs to fit an unmet need, open a new market, have superior properties, or achieve the same at a lower cost. Several factors that favor the implementation of reprocessable LCP reinforced thermoplastic composites include:

1. The materials meet a societal need for materials that combine sustainability and performance.
2. There is a clear market for these composites based on their mechanical performance.
3. The composites can be processed via commonly used techniques.
4. The properties of the materials can be tuned towards a specific application.

Depending on the product and processing route, however, changes in product design and mold design might be required to obtain products with the desired properties, as the LCP morphology is determined by the flow fields the molten blend experiences during processing. Overall, the industrial production and actual application of PLA-LCP composites seems feasible and these composites can be implemented easily to replace existing materials. However, additional factors, such as the economic viability of these composites and the technical feasibility of the recycling process, need to be addressed.

Typically, thermotropic mainchain polyesters are relatively expensive. As a result, these materials are used when outstanding thermal properties or mechanical performance is required, but this has limited the implementation of these materials in other applications. The high cost of these polymers is in part related to the monomers used (eg. 6-hydroxy-2-naphthoic acid, or 4,4'-dihydroxy biphenyl) and in part to the stringent synthesis conditions that are required. The liquid crystalline prepolymers that have been developed have the potential to overcome this challenge. The concept is based on the use of several different monomers to create a random backbone and suppress the processing temperature. Therefore, a wider range of monomers can be incorporated, circumventing the need for the use of certain expensive, aforementioned fossil-based monomers that are commonly used in commercial LCPs. The low

processing temperature and molecular weight of the prepolymers limits the melt viscosity during the synthesis and allows for lower synthesis temperatures: the conditions required to produce the polymers are less stringent. These two factors make the liquid crystalline prepolymers relatively cheap to produce, at the very least in comparison to typical commercial LCPs.

In general, the recycling of plastic products faces one challenge: the material needs to be collected and separated effectively, with the additional difficulty that most products are not designed with recycling in mind. One of the main reasons for the inferior properties of thermomechanically-recycled plastics, in addition to the effects of degradation, is the contamination of the materials, either via the inclusion of different polymers or via the introduction of incompatible additives. Although the LCP-PLA composites are reprocessable, their properties are prone to change upon the introduction of contaminants. In order to tackle this challenge, not only for the materials studied in this thesis but for the recycling of plastics in general, a joined effort is required: polymer producers, product designers, plastic processors, recycling companies and regulatory bodies need to work together to develop products and materials that are both separable and recyclable in an efficient manner. To this day, the lack of such a joined effort prevents the efficient recycling of plastics without deterioration of material properties and the implementation of recycled plastic materials into high quality products remains limited.

7.2 Room for improvement: backbone composition and prepolymer molar mass

In this thesis, it has been demonstrated that chain extension of liquid crystalline prepolymers can be used to produce versatile LCPs with good mechanical performance. In turn, these LCPs can be used to produce reprocessable reinforced thermoplastic composites. However, in the main text of the thesis only a single prepolymer is discussed, whereas different combinations of chain architecture, chain composition and prepolymer molar mass are easily produced. To demonstrate the versatility of this method and to give an indication of the effect of the prepolymer molar mass on the final properties a set of prepolymers was synthesized (Figure 7.1). The chemical composition of the backbone differs from the prepolymer described in Chapter 5, the main differences being that no aromatic-aliphatic monomer is incorporated, and the amount of 4-hydroxy benzoic acid is higher. This composition was chosen to improve the mechanical performance of the LCPs, while maintaining the ability to be processed at low temperatures. Liquid crystalline prepolymers with molecular weights of

1 kg mol⁻¹, 5 kg mol⁻¹ and 10 kg mol⁻¹ were synthesized via the incorporation of decreasing amounts of isophthalic acid into the polymer backbone. Via a similar procedure as described in Chapter 5, the chain extension reaction with a stoichiometric amount of **IaOx** was carried out via reactive extrusion and the obtained LCPs were injection molded into dogbones.

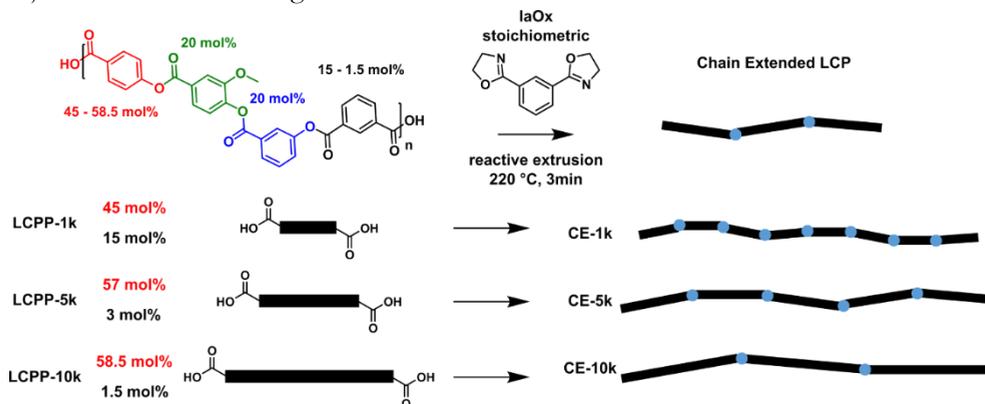


Figure 7.1 Chemical composition of the produced liquid crystalline prepolymers and schematic representation of their chains.

Increasing the molecular weight of the prepolymer has a positive effect on the tensile modulus of the chain extended LCP (Figure 7.2a). The chain extended LCPs that were obtained using a prepolymer with a molar mass of 10 kg mol⁻¹ can reach a tensile modulus of 18.8 GPa. This value exceeds the stiffness obtained for any of the other LCPs described in this thesis, including commercially available thermotropic polyesters. The change in stiffness is not exclusively caused by the effect of prepolymer molecular weight, as there is a difference in the microstructure of the different LCPs (Figure 7.2b). Although both LCPs have an orientation along the injection direction, the sample based on the 1.0 kg mol⁻¹ prepolymer is less oriented. Additionally, the increased amount of 4-hydroxy benzoic acid resulted in the formation of a small fraction of crystalline material. Despite the introduction of crystallites, these materials remain processable at low temperatures (200 – 220 °C). These findings clearly demonstrate that further research into this type of LCP can provide versatile materials with even better mechanical properties.

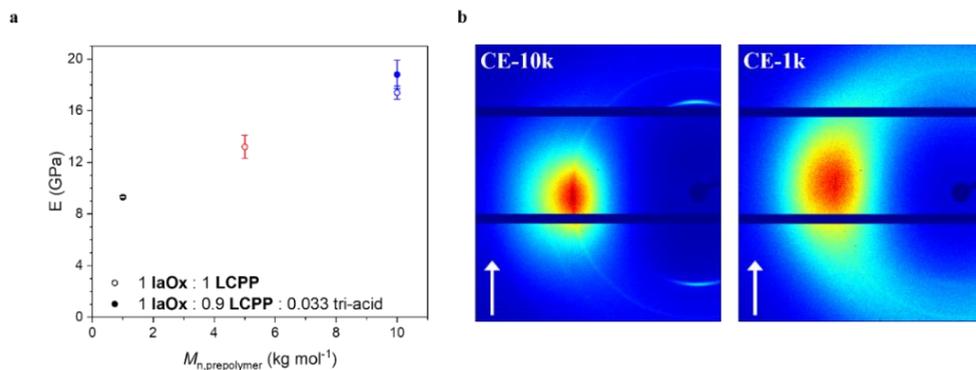


Figure 7.2 (a) Stiffness (E) as a function of prepolymer molecular weight. (b) 2D-WAXD patterns of injection molded samples consisting of chain extended LCPs with different prepolymer molecular weights.

7.3 Towards different applications: cholesteric prepolymers

When chain extending liquid crystalline prepolymers in the presence of tri- or multi-functional reagents it is possible to produce strong liquid crystalline networks. Such networks have interesting properties for film and coating applications: they are strong and are likely to possess good chemical and thermal resistance. The introduction of a chiral mesogenic monomer in the polymer backbone can induce the cholesteric phase, which can be used to produce brightly colored films without the use of pigments. As the color of the material depends on the microstructure of the material, these materials are potentially useful as sensors.

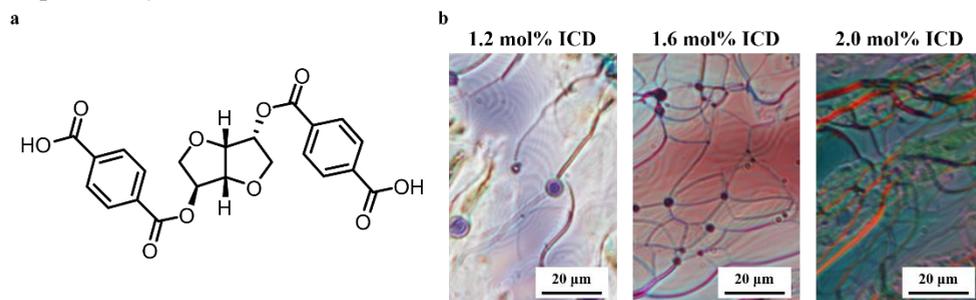


Figure 7.3 (a) Structure of the isosorbide-based chiral dopant (ICD). (b) Cholesteric textures of liquid crystalline prepolymers containing different amounts of ICD, viewed under crossed polarizers at 250 °C.

To explore this possibility an isosorbide-based chiral dopant (ICD, Figure 7.3a) was synthesized and subsequently incorporated in different liquid crystalline prepolymers. The synthesis procedure and monomers used closely resemble those of the other prepolymers described in this thesis. The introduction of the chiral monomer resulted in a distinct change of the observed texture in polarized optical microscopy. In the absence of ICD, nematic Schlieren textures were observed. However, when ICD was

built into the polymer backbone, cholesteric fingerprint or oily streak textures are observed (Figure 7.3b).

The cholesteric prepolymers had a pearlescent appearance and reflected a range of wavelengths of light dependent on the ICD concentration, resulting in brightly colored films and pieces of material (Figure 7.4a). Conform theory an increased amount of ICD in the polymer resulted in a decrease in the pitch length and correspondingly a decrease in the wavelength of light that was reflected (Figure 7.4b). Interestingly, upon solvent casting the films were initially colorless. Upon heating the chains were able to rearrange within one minute, yielding brightly colored cholesteric films. Deformation of the molten films resulted in the disappearance of the color, due to the disruption of the helical structure. The helical structure quickly reforms while in rest, restoring the films color. In essence, this very simple observation describes a basic mechanical sensing device, displaying the potential of these materials. The different cholesteric prepolymers are miscible, because of the similarity of the chain compositions. This allows mixing of different polymers to tune the pitch and reflected wavelength of the material, which provides a simple route to obtain a broader range of colored films, as shown in Figure 7.4c.

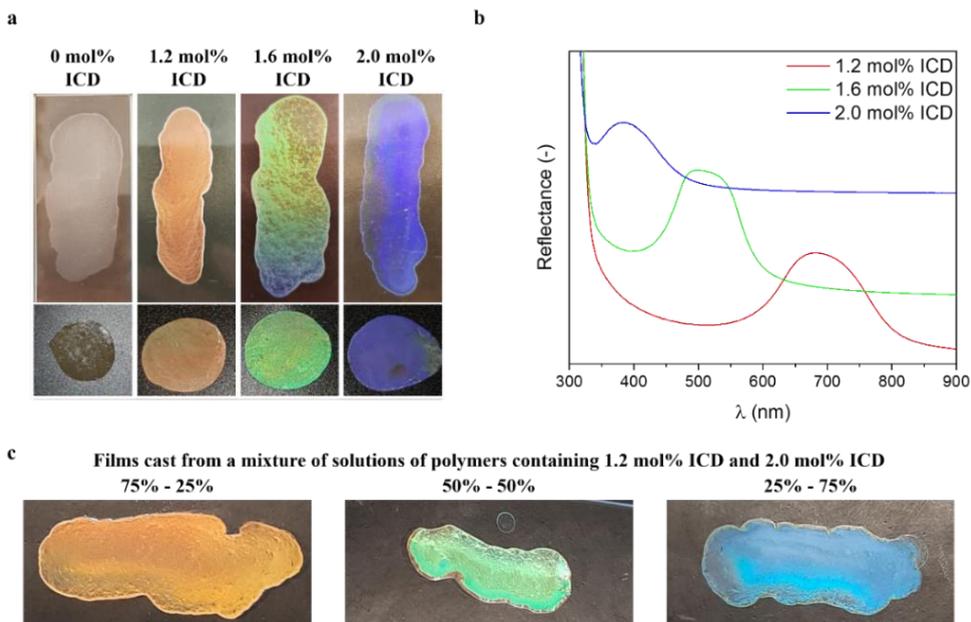


Figure 7.4 (a) Photographs of solvent cast films (top) and melt-pressed pieces (bottom) of cholesteric liquid crystalline prepolymers containing different amounts of ICD. **(b)** Reflectance as a function of wavelength of solvent cast films of cholesteric liquid crystalline prepolymers. **(c)** Photographs of solvent cast films. The color was varied by mixing different amount of solutions containing the 1.2 mol% ICD prepolymer and the 2.0 mol% ICD prepolymer.

7.4 Closing remarks

I sincerely hope that I have been able to show to you, reader of this thesis, that the knowledge gained and the materials developed have the potential to contribute to the more sustainable use of plastic materials in the future and that these materials provide an interesting starting point for further study on account of their versatility and properties. However, regardless of how interesting they are or how excellent their performance, these are not going to solve the problem that we, as humanity, face regarding the sustainable use of plastic materials and other resources. As a concluding statement, I wish to convey to you, dearest reader, the following message: If we truly wish to create a sustainable future, a bright future for the coming generations, we have to face the possibility that we need to change our ways in a drastic manner. Although much remains to be gained by the work of scientists, their efforts need to be supported by both industry and society to have the required impact. It is unfair to rely exclusively on the work of scientists and the development of new technologies to solve our problems regarding sustainability. It is unfair, as all of us have helped create these problems and contributed to them. We must start considering the possibility that we need to change the way we utilize our resources, the way we approach materials and energy, the way we consume, and maybe most importantly the way we desire growth. For generations we have sought prosperity through growth, but growth can never be limitless in a system that knows boundaries. As the growth of a fish is limited by the size of the bowl in which it swims, so humanity's growth is limited by the boundaries of our planet. Let us strive to respect those boundaries until we are ready to overcome them. Thank you.