

Thermotropic polyesters and polylactide

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Summary

Fiber-reinforced composites, characteristically having high specific stiffness and strength, are interesting as a more sustainable solution (compared to for example metals) in various applications. However, upon end-of-life, recycling of fiber-reinforced composites is challenging. For example, thermomechanical recycling of glass fiber-reinforced composites results in deterioration of the mechanical performance, as breaking of the glass fibers during the process decreases the aspect ratio of the fibers. Moreover, processes required for the recovery of the reinforcing phase are energy intensive and the matrix phase is often lost. Thermoplastic LCP reinforced composites, on the other hand, are melt processable and, in theory, provide an opportunity for recycling without loss of mechanical performance. Mechanical performance of the thermoplastic composites is found to be strongly dependent on the morphology that is formed due to flow fields during melt processing. However, variations in the melt viscosity of the different components at a specific shear rate impose a challenge in the reproducibility of the morphology (and the mechanical performance) on recycling. In the past, liquid crystalline polymers (LCPs) have been used to produce reinforced thermoplastic composites, as LCPs are more easily oriented upon flow than regular polymers. However, reproducibility of the LCP based composites properties upon recycling and reprocessing has not yet been assessed.

In this thesis, the potential of LCP reinforced thermoplastic composites is explored with the aim to identify important parameters for the production of reprocessable thermoplastic composites. For the study thermoplastic composite consisting of thermotropic polyesters and polylactide (PLA) is investigated. The study focusses on improving our understanding of 1) the formation and relaxation of interchain orientation of LCPs under deformation, 2) the formation of the morphology during melt processing, and 3) the role of the thermal- and viscoelastic behavior of the blends components in these processes. This knowledge is highly relevant when developing suitable LCP – PLA systems for the production of recyclable LCP reinforced thermoplastic composites.

The processes governing the molecular alignment and relaxation of an aromatic-aliphatic thermotropic polyester under shear flow has been followed using a combination of *in situ* polarized microscopy and *in situ* Wide-angle X-ray Diffraction (Chapter 2). The domain texture of the LCP initially stretches upon startup of the shear flow with a simultaneous increase in interchain orientation. Subsequently the polydomain texture breaks up at higher degrees of deformation, while the degree of interchain orientation remains constant. Though the polydomain texture of LCPs is

influenced by the applied shear rate, the final degree of interchain orientation is independent of the shear rate. During relaxation, the stretched domains of the LCP first contract and subsequently coalesce. The relaxation of the LCP orientation does not start instantaneously and only decreases upon coalescence of the LCP domains. The relaxation of orientation is faster when a finer texture is formed (i.e. when higher shear rates are applied), and this interdependence will have significant implications for the processing of LCPs and LCP-polymer composites.

The morphological development of two different LCPs in a PLA matrix in different processing steps is characterized in detail, and is interpreted within a theoretical framework based on the capillary number (α) and the viscosity ratio (λ) (Chapter 3). The use of LCPs with a lower viscosity and concomitantly a lower λ results a finer dispersion, but also results in accelerated relaxation of the LCP domains within the matrix. Crystallization of the LCP, resulting in a sudden increase in λ that prevents droplet deformation, negatively affects the reinforcement in an injection molding process. LCPs that are amorphous in nature typically do not show sudden increase in λ . Therefore, compared to semi-crystalline LCPs, amorphous LCPs are likely to be more suitable as the dispersed phase in an injection molding process. Extensional flow, such as experienced in melt spinning, is found to be highly efficient in the formation of LCP fibrils, regardless of the viscosity ratio between the LCP and polymer matrix (PLA). In shear flow, on the other hand, deformation of droplets is only possible for viscosity ratios below 3.8.

The effect of the molecular weight of the PLA matrix on the morphology and the performance of the composites is studied using a commercially available LCP and several different PLA matrices (Chapter 4). Two distinct regimes, dependent on the LCP/PLA viscosity ratio are identified: In the first regime ($\lambda < 1$), a higher matrix viscosity results in a slightly coarser morphology. However, the overall mechanical performance is not influenced as the LCP retains a fibrillar morphology, and the degree of molecular orientation of the LCP remains high. In the second regime ($\lambda > 1$), a lower matrix viscosity results in a less effective deformation of the LCP droplets during processing. When the viscosity ratio exceeds a value of 3.8 the LCP droplets can no longer be deformed by the matrix: the application of shear flow results in a nodular LCP morphology. In the second regime, the mechanical performance of the thermoplastic composite decreases with decreasing molecular weight of the matrix. These two regimes are retained upon repeated processing (thermomechanical recycling) of the composite materials. However, changes in morphology and performance are observed because of the decrease in the PLA viscosity due to the decreasing molecular weight of the PLA with the number of reprocessing cycles. Reprocessing of LCP reinforced thermoplastic

composites, without any loss of mechanical performance could be achieved under the condition that the viscosity of the PLA matrix remains sufficiently high to satisfy the condition of $\lambda < 1$.

In Chapter 4 of this thesis, the viscosity ratio of the blend is identified as a key parameter for recyclability, whereas Chapter 3 shows that an amorphous LCP is to be preferred over a semi-crystalline LCP. This suggests that improvements in the reprocessability of composites can be made by selecting LCPs with a low processing temperature and a tunable viscosity. Such LCPs are presented in this thesis (Chapter 5): control over the LCP viscosity is achieved via a chain extension reaction of an amorphous liquid crystalline prepolymer using bis(2-oxazoline)s as coupling agents. The chain extension can be easily carried out via reactive extrusion, and molecular weight can be controlled via the molar ratio of liquid crystalline prepolymer to bis(2-oxazoline). The resulting LCPs are found to have excellent mechanical properties. With the increase in the molecular weight of the LCP, a transition in the viscoelastic behavior from an unentangled nematic melt to a constrained melt is observed. Interestingly, in the constrained melt, a minimal loss in the orientation parameter is observed even upon heating the chain-extended LCPs to temperatures well above their glass transition temperature.

To assess the effect of the LCP viscosity on the morphology in more detail, composites of the new LCPs (as reported in Chapter 5) with PLA have been produced, and the reprocessability of the LCP-PLLA composites is demonstrated (Chapter 6). In accordance with their viscosity ratios, a suitable fibrillar morphology is obtained via injection molding for all composites, even forming fibrils with sub-micron diameters in the case of the LCPs with lower molar mass. Effective reinforcement is achieved and the stiffness and strength of the thermoplastic composites increased when using LCPs with a higher viscosity. Interestingly, the expected decrease in strain at break that typically accompanies polymer matrix reinforcement is not observed when using LCPs with higher molar masses ($M_w > 40 \text{ kg mol}^{-1}$ according to GPC analysis). The relaxation of the interchain orientation of the LCP in a PLA matrix is evaluated in detail via *in situ* Wide-angle X-ray Diffraction. The viscosity of the matrix phase is found to be the dominant parameter. In blends, the mechanism by which the interchain orientation of the LCP decreases differs from that of LCPs without matrix. It is related to the relaxation of the fibrillar LCP morphology within the PLA melt and is affected by the stereoregularity and crystallinity of the matrix. The presence of the LCP is found to affect the cold crystallization of the PLLA matrix. Although no increase in nucleation or crystallization rate is observed, the orientation and growth of the PLLA crystallites is affected.

In this thesis, the potential of LCP reinforced thermoplastic composites is explored with the aim to identify important parameters for the production of reprocessable thermoplastic composites. The thesis conclusively demonstrates that for the combination of a thermotropic polyester and PLA, it is feasible to use amorphous LCPs with a low processing temperature. The use of a suitable LCP (viscosity slightly lower than the molten matrix, amorphous) allows the formation of the required fibrillar morphology under different processing conditions, and simultaneously limits the thermal degradation of the PLA matrix phase. Recycling of LCP-PLA composites without loss of mechanical performance is demonstrated, under the condition that the viscosity ratio remains below one. Based on these findings, a system is developed to produce amorphous LCPs with a tunable viscosity. The effectiveness of the LCPs in composites with PLA is demonstrated. These findings, investigated in a specific system, are of a generic nature and can therefore be translated to other polymer-polymer system.