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Effect of DEET on the Crystallinity of Bicomponent Poly(lactic acid) Monofilaments

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Abstract. Reduction of malaria will require outdoor protection against infective mosquito bites. This might he provided by wearable mosquito repelling textiles, e.g., anklets that protect the lower limb regions. Towards this goal, melt-biodegradable, DEET-containing bicomponent PLA monofilaments, with a sheath-core structure, were spun on a laboratory rig. It is expected that the sheath degree of crystallinity and crystalline morphology affect the release rate of the DEET. Consequently, the effect of DEET was investigated by means of DSC. It was found that DEET greatly increases the mobility of the PLA chains, resulting in a lowered Tg, a lowered cold crystallization temperature and an increased degree of crystallinity. Furthermore, the presence of DEET favored the formation of the α´-crystal structure.

INTRODUCTION

Current indoor vector control methods, recommended by the World Health Organization (WHO), include insecticide-treated nets (ITNs) and residual indoor spraying (IRS). Despite their success, there is a growing concern that the worldwide malaria incidence rate has remained constant for the past few years [1]. This residual malaria incidence will require effective outdoor protection. Wearable repellent textiles, covering the lower limb regions, might prevent infective mosquito bites outdoors [2-5]. Socks, knitted in part with mosquito repellent bicomponent fibers, demonstrated the potential for such effective outdoor protection. They retained repellence for more than six months even when washed repeatedly [3]. However, these fibers were spun from non-biodegradable polymers. Biodegradable alternatives are preferred in view of the worldwide concern about the impact of plastics on the environment.

In this study, bicomponent poly(lactide) (PLA) monofilaments containing the mosquito-repellent DEET were produced via melt spinning. The difference in solubility behavior between amorphous poly(D,L-lactide) (PDLLA) and semi-crystalline poly(L-lactide) (PLLA) was exploited to produce monofilaments with a sheath-core structure (PLLA-PDLLA) [6] as shown schematically in Fig. 1. It is expected that the degree of crystallinity and crystalline morphology will have a significant impact on the migration and release characteristics of DEET. However, the influence of DEET on the development of these attributes when melt-spinning bicomponent PLA filaments is unknown. Therefore, this aspect was investigated by means of differential scanning calorimetry (DSC).

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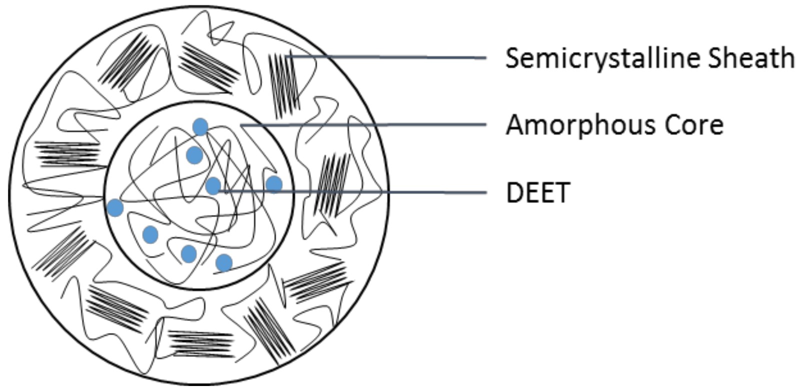

Figure 1. Schematic of the DEET-containing sheath-core structured filament.

EXPERIMENTAL

The monofilaments were spun using an in-house designed-and-built piston melt-spinning device at the Leibniz-Institute for Polymer Research in Dresden. Two commercially available PLA grades from NatureWorks were used. One was a semi-crystalline grade and the other one was an amorphous grade. In the case of the bicomponent filaments, the volumetric flow rates of the semi-crystalline sheath and the amorphous core were kept equal. A total mass flow rate of approximately 0.8 g min^{-1} was maintained in all experiments. The take-up speed for all reported experiments was 500 m·min^{-1}.

The preparation of the DEET-containing core material involved the dissolution of the DEET in the amorphous PDLA pellets at 130 °C in Petri dishes to produce material with 10 wt. % and 20 wt. % DEET content, This was based on knowledge of the PLA-DEET phase diagram evaluated in earlier work [6-8]. Complete dissolution was achieved within five minutes. After cooling, the resulting DEET-containing disc of approximately 3 mm was cut into pellets for use in the piston-melt-spinning device.

All DSC scans were performed on a model Q2000 from TA Instruments. The samples, weighing ca. 2-3 mg, were sealed in 50 µL aluminum pans and heated from -30 °C to 230 °C at a heating rate of 10 K min^{-1}.

RESULTS AND DISCUSSION

DSC scans of the bicomponent (semicrystalline sheath and amorphous core) PLA monofilaments, with different DEET contents in the core, are shown in Fig. 2(a). Figure 2(b) shows corresponding DSC scans for the monocomponent (amorphous core only) monofilaments. As can be observed from Figs. 2(a) and (b), the presence of DEET had a significant effect on the glass transition temperature (Tg) measured for the filaments. For PLA-only filaments, the Tg was about 56 °C which is in good agreement with literature values [9]. However, the Tg shifted to significantly lower temperatures when DEET was present in the fiber cores. Average Tg-values of 33 °C and 22 °C were recorded for DEET present at 10 wt. % and 20 wt. %, respectively. As expected, only a single lower Tg-value was observed for the monocomponent core-only filaments (see Fig. 2(b)). Noteworthy is the fact that this was also the case for the bicomponent filaments in Fig. 2(a). This suggests that DEET was present at comparable levels in both the amorphous core polymer and the semicrystalline sheath portion, resulting in similar Tg-values. The lowered Tg-values indicates that the DEET notably increased the mobility of the PLA chains.

Perusal of the cold-crystallization exotherm, observed between 60 and 90 °C in Fig. 2(a), reveals a shift to a lower temperature together with a decrease in the magnitude of the event. The exotherm in this region is attributed to the formation of α´-crystals [9, 10]. The lowered crystallization temperature further supports the notion that the presence of DEET increased the chain mobility. The decrease in the magnitude of this event, should be viewed in conjunction with the smaller exothermic event located at 156 °C (observed for the DEET-free filaments) and the melting peak following it at a slightly higher temperature. The smaller exothermic event is associated with the transition of the disordered α´-phase to the α-crystals [10, 11]. This phenomenon disappears with increasing DEET content. The melting peak at 168 °C in the DEET-free filaments represents the melting of α-crystals. The lower temperature shoulder, observed for the sample with a DEET content of 10 wt. %, is attributed to the melting of α´-crystals [9-11].

This shoulder dominates in the sample containing 20 wt. % DEET. The reduction in the cold-crystallization event of α´-crystals during the DSC heating scan, the disappearance of the transition exothermic event and the increased α´-melting peak suggests that the formation of α´-crystals is favored in the presence of DEET.

As can be seen from Fig. 2(a), the presence of DEET increased the degree of crystallinity of the spun fibers. This was deduced from the decrease in the area difference between the endothermic and exothermic events with increasing DEET content. This is also evident from Fig. 2(b) where crystallization is even induced in the supposedly amorphous core-only fibers containing 20 wt. % DEET. It serves as further proof that the DEET greatly increases the mobility of the PLA chains, enhancing crystallization, as quantified in an independent PLLA-DEET crystallization study [12]. These observations are of major importance since a higher degree of crystallinity implies a lower rate of migration and therefore also lower rate of release of the DEET from the bicomponent fibers.

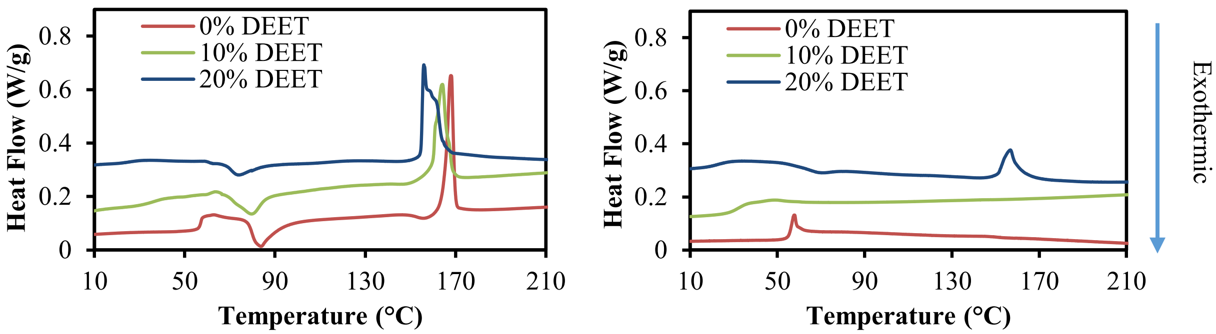

Figure 2. DSC heating scan of (a) bicomponent sheath-core and (b) monocomponent core-only PLA filaments with varying DEET content in the amorphous core.

CONCLUSIONS

The presence of DEET significantly increased the chain mobility of PLA chains, not only in the amorphous core material, but also in the semi-crystalline structure constituting the sheath. This was indicated by fact that only a single Tg value was observed at significantly lower temperatures for both bicomponent filaments and amorphous, core-only monocomponent filaments. Correspondingly, the presence of DEET also caused a decrease in the cold-crystallization temperature of α´-crystals in the sheath and an overall increase in sheath crystallinity. Moreover, crystallization was even induced in the amorphous core when the DEET content was 20 wt. %. Additionally, the α´-crystal structure appears to be favored in the presence of DEET. The present work about melt-spun bicomponent DEET-containing PLA fibers provides valuable knowledge for further reduction of outdoors-occurring malaria infections, being an alternative, e.g., for application of electrospun fibers [13], or extruded strands.

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