Jungbunzlauer

From nature to ingredients®

Thermoplastic processing of Polylactic Acid with CITROFOL®

Citrate esters as bio-based plasticisers

Biopolymers have a variety of possible applications due to their renewable characteristics and their potential biodegradability. Biopolymers are polymers that are either bio-based, biodegradable, or both. Unmodified biopolymers suffer from thermo-mechanical sensitivity during processing and often show poor physical and chemical resistance. Plasticisers can improve the handling and processing of biopolymers. Ideally, they are bio-based and biodegradable to tailor the properties of biopolymers into the desired range, like the CITROFOL® esters. Citrate esters are already applied in bio-based polymers with a positive impact on the processing and final product properties. Besides their compatibility with various polymers, their quick compostability without harm to air, soil or water is of benefit as well.

Polylactic Acid (PLA)

Polylactic acid (PLA) is one of the most promising biopolymers for the coming years (figure 1). PLA is biodegradable under (industrial) composting conditions, transparent, soluble in various solvents and allows for the ability to incorporate fibres. The physical and mechanical properties of PLA are comparable to polystyrene (PS) or polyethylene terephthalate (PET). Possible applications for PLA include use as packaging material or consumer goods.

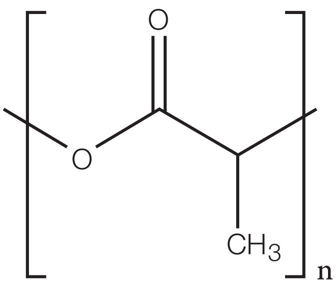

Figure 1: Chemical structure of PLA

Compounding and processing of plasticised PLA

To investigate the influence of plasticisers on PLA, two different PLA grades, Luminy® L105 and Luminy® L130, (obtained by Total Energies Corbion) were used. Both high-heat PLA types differ in their molecular weight and are especially suitable for injection moulding processes. As plasticisers CITROFOL® AI (triethyl citrate) and CITROFOL® BII (tributyl O-acetylcitrate) were used in the concentrations 10 and 15 wt.% and compared to the benchmark polyethylene glycol (PEG) 1000. PLA was dried before use to prevent polymer degradation during processing caused by residual moisture presence.

Based on a two-step manufacturing process, the plasticising effect of the citrate esters on PLA was investigated with regard to the processability and the end properties. In the first step, plasticised PLA granulate was produced via melt compounding. Therefore, PLA was melted in a co-rotating twin-screw extruder and the respective plasticiser was added using a liquid dosage unit. Afterwards, the plasticised granulate was melted again and injection-moulded to prepare the desired test specimens. Finally, the thermal, mechanical and rheological properties of the test specimens were analysed.

Benefits at a glance

Processing behaviour

The compounding of the two different PLA grades with all tested plasticisers in all concentrations was successful. Additionally, the CITROFOL® esters show significant benefits. As they are clear, practically colourless, oily liquids, no additional melting step is required, contrary to the benchmark PEG 1000 which is solid at room temperature. Figure 2 shows the measured motor load of the compounder during the processing of plasticised PLA. In general, the motor load of the extruder device could be significantly reduced with the addition of plasticisers, especially in the case of the citrate esters with a concentration of 15 wt.%. This may result in an easier processing as well as lower energy consumption, contributing to a more sustainable process.

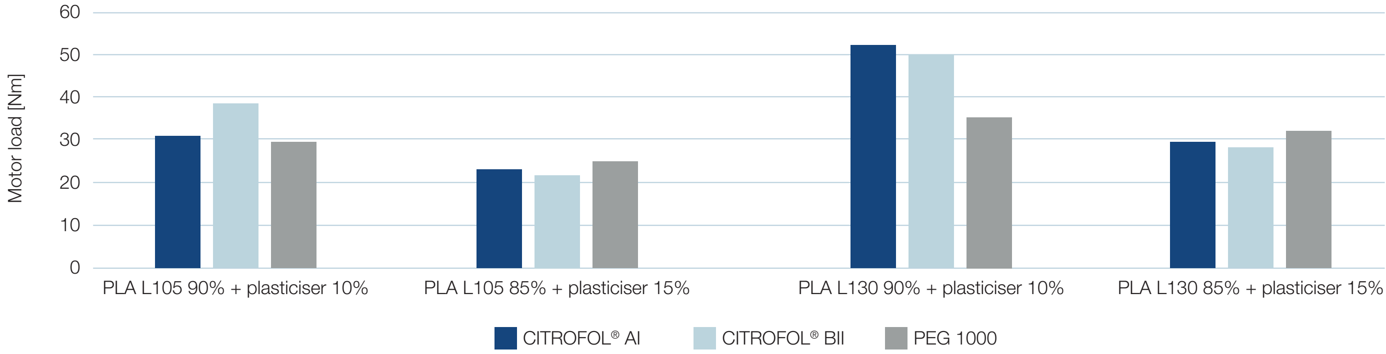

Figure 2: Motor load during processing for the plasticised PLA compounds

Mechanical properties

Mechanical properties like the elongation at break or the tensile strength are important characteristic values for polymers since they define their potential end application. With the addition of plasticisers, these values can be modified to create tailored polymers with desired characteristic profiles.

The determination of the mechanical properties was conducted according to DIN EN ISO 527-2. For the unplasticised PLA as well as for the specimens with 10 wt.% plasticiser very low values for the elongation at break (1.9 to 2.2%) were obtained. Figure 3 demonstrates the significant increase of these values with a plasticiser usage concentration of 15 wt.% for all tested plasticisers. CITROFOL® BII shows the highest improvement for the elongation at break for PLA L105 whereas for PLA L130 CITROFOL® AI yielded the highest effect. In general, the citrate esters show a superior behaviour compared to PEG 1000.

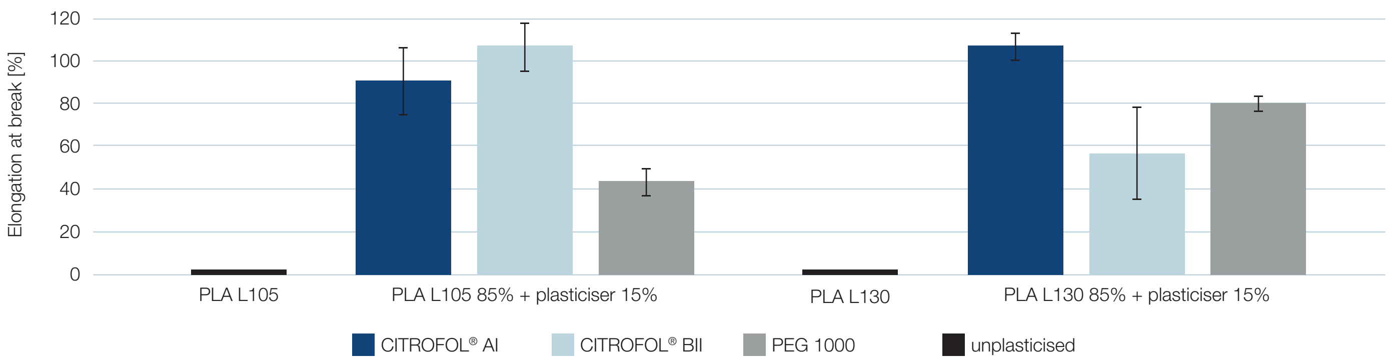

Figure 3: Elongation at break of plasticised PLA compounds

Figure 4 shows the results for the tensile strength. The tensile strength of PLA decreases with the addition of plasticiser. Similar to the elongation at break, 15 wt.% plasticiser have significant impact, whereas 10 wt.% only show a small reduction in the values, compared to the unplasticised PLA. For PLA L105 the reduction of the tensile strength with CITROFOL® AI is comparable to those containing PEG 1000 (with 10 and 15 wt.%). CITROFOL® BII exhibits the lowest reduction in tensile strength for PLA L130.

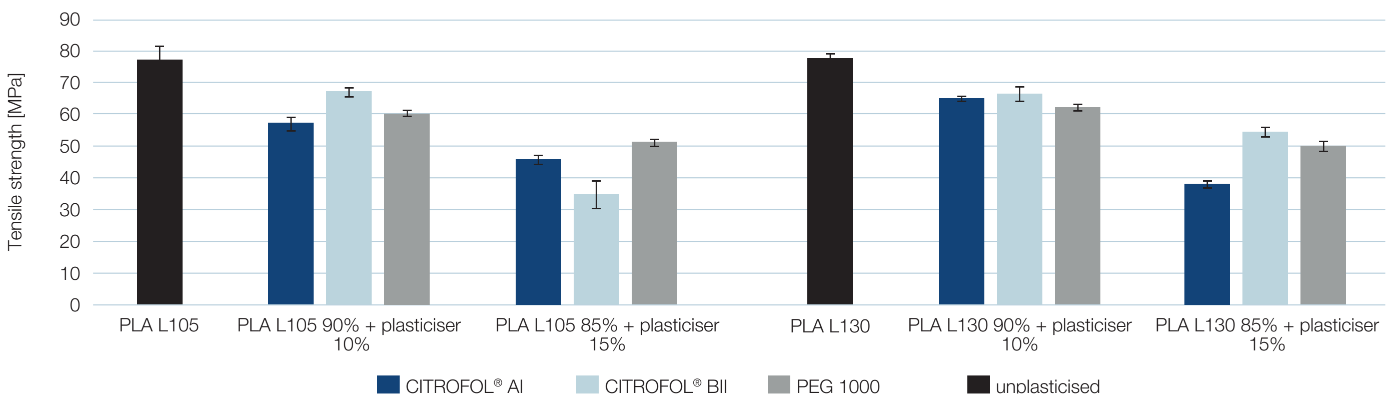

Figure 4: Tensile strength of plasticised PLA compounds

Thermal properties

Thermal properties like glass transition temperature and melting temperature are also critical parameters as they give an indication if the processing window can be broadened with the addition of plasticisers. This allows for an enhanced processing of the polymer material. With increasing plasticiser concentration, the melting temperature is reduced (figure 5). The level of reduction depends hereby on the type of plasticiser. Citrate esters demonstrate a higher efficiency, i.e. stronger reduction, which leads to a larger gap between degradation temperature and melting temperature. This results in a broader processing window and hence in an easier processing of the polymer melt.

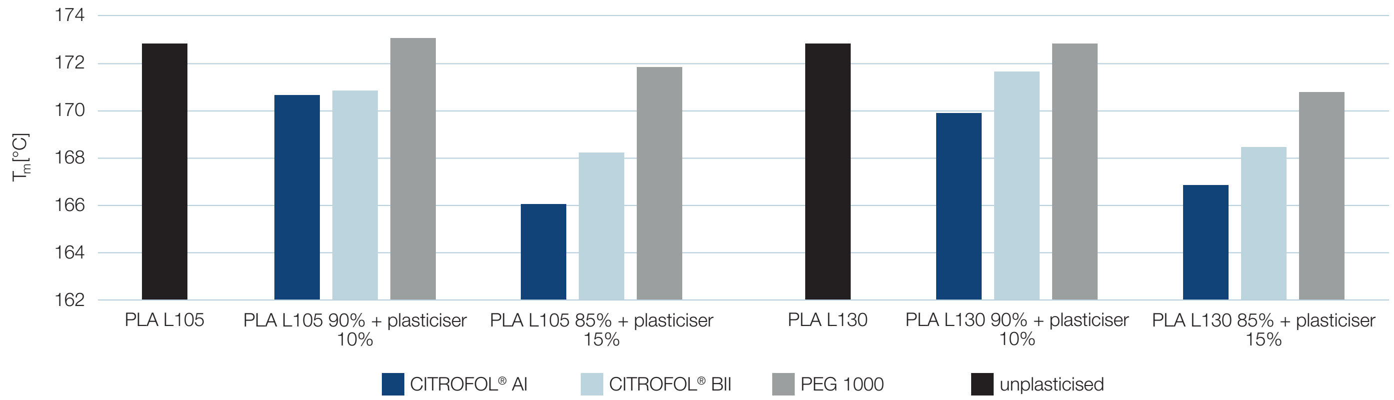

Figure 5: Melting temperatures of plasticised PLA compounds

However, a reduction of the melting temperature usually comes with a reduction of the glass transition temperature. This can be unfavourable, in particular for end applications where such temperatures can be reached, e.g. warm food packaging. Our study demonstrated that in most cases the CITROFOL® esters showed a less pronounced impact on the glass transition temperature compared to PEG 1000 (up to 10°C), although having a higher efficiency in the reduction of the melting temperature.

This study showed that the used citrate esters are compatible in combination with different types of PLA. A significant improvement in the mechanical properties was achieved with the addition of 15 wt.% citrate esters. In addition, an improved processing and reduced melting temperatures were observed.

About Jungbunzlauer

Jungbunzlauer is one of the world's leading producers of biodegradable ingredients of natural origin, which enable its customers to manufacture healthier, safer and more sustainable products. Jungbunzlauer belongs to the largest global producers of citric acid and citrate esters, which are well-known under the brand CITROFOL®. Product innovation and continuous process improvements in our state-of-the-art plants result in unique high quality products. Citrate esters have an excellent toxicological and eco-toxicological profile, but also provide good versatility and compatibility with numerous polymers. They are particularly characterised by highly efficient solvation, low migration and non-VOC attributes. CITROFOL® grades offer a sustainable alternative to petrochemical- based plasticisers. Therefore, they are the preferred choice for sensitive products like toys, medical devices, food packaging, pharmaceutical applications and personal care. Moreover, all CITROFOL® esters are non-GMO, vegan, kosher and halal.

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