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CITROFOL® – Citrate Esters as bio-based plasticisers for Polylactic Acid (PLA) applications

Background information

Recently, environmental concerns and increased consumer awareness with regard to sustainable products have fuelled the research as well as the development of renewable and biodegradable polymers. In particular, the replacement of ubiquitous fossil polymers with bio-based alternatives has become a focus of attention.[1]

Biopolymers are polymers that are either bio-based, biodegradable, or both. Due to their renewable character as well as their potential to biodegrade, they could prove useful in a variety of possible applications in the areas of packaging, consumer goods, agriculture, electronics, automotive coatings and adhesives.[2] The common market drivers for all these possible applications are plastic waste reduction, the development of sustainable carbon cycles, and the reduction of microplastics.[3]

Polylactic acid (PLA) and polyhydroxyalkanoates (PHA) are among the biopolymers most studied for their potential to replace fossil-based plastics.[4] Both are biodegradable, PHA in nature and PLA under industrial conditions. Furthermore, their physical properties, barrier properties and stretchability make them suitable for a broad range of applications. However, they suffer in their original state from thermo-mechanical sensitivity during processing and often show poor physical and chemical resistance. These limitations have until now hindered their widespread use, especially in the area of packaging applications.[5-7] Such shortfalls can be overcome by the use of suitable additives, such as plasticisers, that tailor the properties of biopolymers to the desired range.

Polylactic Acid (PLA)

PLA is an aliphatic polyester synthesised through the polymerisation of lactic acid (figure 1). Lactic acid serves as a monomer and is produced by bacterial fermentation of natural raw materials like sugar or starch.[8] In recent years, PLA has become one of the most commercially promising biopolymers as an alternative for petrochemical polymers because it exhibits good physical and mechanical properties that are comparable to commodity polymers – for example poly (ethylene terephthalate) (PET) and polystyrene (PS).[9-11] Furthermore, PLA is biodegradable under industrial composting conditions, has a very low toxicity profile, good barrier properties to aromas, and is highly transparent.[11,12] Moreover, PLA's thermal and rheological properties allow it to be processed using a wide range of industrial techniques, such as injection moulding, extrusion, thermoforming, fibre spinning and calendaring.[13,14] Nevertheless, PLA usage can be limited in its original state because of its brittleness, which poses severe limitations in terms of processability and end-use mechanical performances.

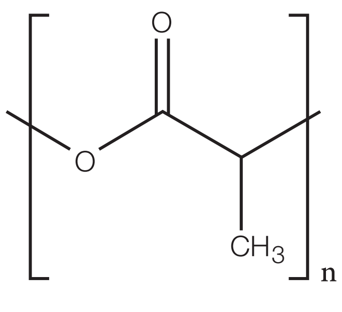

Figure 1: Molecular structure of PLA

To overcome these issues several strategies have been developed. In general, plasticisers are widely used as additives for polymeric materials as they enhance their flexibility, processability, and ductility.[15] The addition of plasticisers to fine-tune polymer properties is often preferred over other strategies like copolymerisation. Additivation is much more cost-effective and flexible than copolymerisation, which entails a new synthesis and scale-up for each desired change of the polymer properties. Different types of plasticisers such as poly (ethylene glycol) (PEG),[16-17] citrate esters,[18-22] oligomeric lactic acid[23] and triacetin[21, 23] have already been investigated for their ability to improve the flexibility of PLA.

Usability of plasticisers

However, it is important to choose the right plasticiser for a particular application. Firstly, good miscibility of the plasticiser and the polymer is essential to guarantee a homogeneous blend. Moreover, an efficient plasticiser should reduce the glass transition temperature (T_g) and melting point (T_m) of the plasticised material.[24, 25] This enables easier processing at lower processing temperatures and a broadening of the processing window for polymers with only a small gap between melting temperature and the start of thermal degradation. Additionally, especially in the case of biomedical applications, the plasticisers used should be non-toxic and should show minimum migration behaviour as the latter would cause the material to return to the brittleness of pure PLA.[26] A further advantage of plasticisers is that they can improve the compatibility between hydrophilic fillers, for instance reinforcing fibres, and the hydrophobic PLA matrix.

Ideally, citrate esters are intended for use in combination with biopolymers should be bio-based as well. The use of fossil plasticisers would dilute the overall bio-content of the final product and might limit its biodegradability. For this reason CITROFOL® citrate esters represent the perfect choice of plasticiser for biopolymers.

CITROFOL® – benefits of a bio-based plasticiser

CITROFOL® citrate esters are bio-based, safe and environmentally friendly. They are listed in international chemical inventories such as REACH. Citrate esters are produced by acidic esterification of citric acid and either ethanol or n-butanol. All raw material can be obtained from renewable resources. A further acetylation step can lead to more esters. CITROFOL® types are clear transparent, odourless and colourless liquids as well as non-VOCs (volatile organic compounds) with excellent storage stability. Therefore they are the preferred choice for sensitive products like toys, medical devices or food packaging and also for pharmaceutical applications and personal care. Moreover, all CITROFOL® esters are non-GMO, vegan, kosher and halal. With regard to their application as plasticisers, they are versatile in use and characterised by their positive toxicological and eco-toxicological profile. Hence they offer a good alternative to petrochemical-based plasticisers like phthalates, benzoates or adipates. CITROFOL® esters are already applied in bio-based polymers like cellulose acetates and nitrocellulose, where they have a positive impact on the processing and final product properties. Besides their broad compatibility with various polymers, their rapid compostability without harm to air, soil or water is unique and perfectly aligned to the increasing end-of-life requirements for many products manufactured with biopolymers.

Table 1: Properties of citrate esters

Chemical name	**CITROFOL® AI** Triethyl citrate	**CITROFOL® AII** Triethyl O-acetylcitrate	**CITROFOL® BI** Tributyl citrate	**CITROFOL® BII** Tributyl O-acetylcitrate
Synonym	TEC	ATEC	TBC	ATBC
CAS No.	77-93-0	77-89-4	77-94-1	77-90-7
Molecular formula	$C_{12}H_{20}O_7$	$C_{14}H_{22}O_8$	$C_{18}H_{32}O_7$	$C_{20}H_{34}O_8$
Molecular weight [g/mol]	276.3	318.3	360.4	402.5
Flash point [°C]	150	188	206	218
Boiling Point [°C]	287	326	309	331
Pour point	-40	-43	-63	-57
Colour	Colourless	Colourless	Colourless	Colourless
Appearance	Clear, viscous liquid	Clear, oily liquid	Clear, oily liquid	Clear, oily liquid

In principle, all CITROFOL® citrate esters are suitable for the plastification of PLA. Their characteristic properties can be found in table 1. Citrate plasticisers are readily soluble in PLA is due to the polar interactions between the ester groups of PLA and the plasticiser.[27]

1 Basic data for the thermoplastic processing of PLA

1.1. Goal of study

The aim of the study is to generate a basic data set on the processing of PLA plasticised with citrate esters and compare this to a commonly used benchmark.

1.2. Materials, compounding and methods

1.2.1. Materials

In order to investigate the influence of plasticisers on PLA, two different PLA grades, Luminy® L105 (MFI (210°C, 2.16 kg) = 70 g/10 min) and Luminy® L130 (MFI (210°C, 2.16 kg) = 23 g/10 min), were purchased from TotalEnergies Corbion. The two high-heat PLA types differ in their molecular weight but are both especially suitable for injection moulding processes. CITROFOL® AI (triethyl citrate) and CITROFOL® BII (tributyl O-acetylcitrate) were used as plasticisers in the concentrations 10 and 15 wt.% and compared to the benchmark polyethylene glycol (PEG) 1000. PEG 1000 was obtained from Carl Roth. PLA was dried before use to prevent any polymer degradation during processing caused by residual moisture presence.

1.2.2. Compounding and processing of plasticised PLA

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. For this, PLA was melted in a co-rotating twin-screw extruder and the respective plasticiser was added using a liquid dosing unit. The plasticised granulate was then melted again and injection-moulded to prepare the desired test specimens. Finally, the thermal, mechanical and rheological properties of the test specimens were analysed.

1.2.3. Test methods for the characterisation of the compounds and test specimens

Mechanical properties

Important for the evaluation of polymers are their mechanical properties, e.g. the tensile strength, the elongation at break and the Young's modulus. The measurements of the mechanical properties were carried out using a mechanical testing machine (Zwick Z2.5 tensile tester) using a cross-head speed of 10 mm/min. All tests were conducted according to DIN EN ISO 527-2, with five test specimens per sample. The test specimens had an overall length of 6 cm and a width of 1 cm (figure 2).

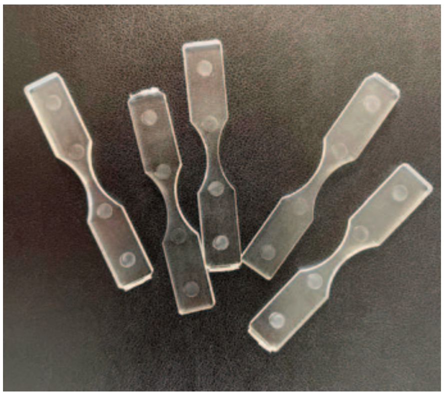

Figure 2: Test specimen for mechanical testing

Thermal properties

All thermal properties (glass transition temperature (T_g) and melting temperature (T_m)) were investigated via differential scanning calorimetry (DSC) following DIN ISO 11357. For these tests, a DSC Polyma 214 (NETZSCH Co., Germany) with a heating range of -40°C to 220°C and a heating rate of 10 K/min was used. The 2nd heating curve was always used for analysis of the thermal properties.

Rheological measurements

For the measurement of the viscosity, a parallel-plate rotational rheometer (Discovery HR20 by TA Instruments) with a 25 mm parallel plate was used. All measurements were conducted according to DIN ISO 51810. The frequency sweep was measured over a range of 0.1 to 100 Hz at a temperature of 190°C.

1.3. Results

Processing behaviour with respective advantages

While the compounding of the two different PLA grades with all tested plasticisers in all concentrations was successful, the CITROFOL® esters exhibited significant additional benefits. As they are clear, practically colourless, oily liquids, no additional melting step is required, in contrast to the benchmark PEG 1000 which is solid at room temperature. Figure 3 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 by the addition of plasticisers, especially in the case of the citrate esters at a concentration of 15 wt.%. This may result in easier processing as well as lower energy consumption, contributing to a more sustainable process.

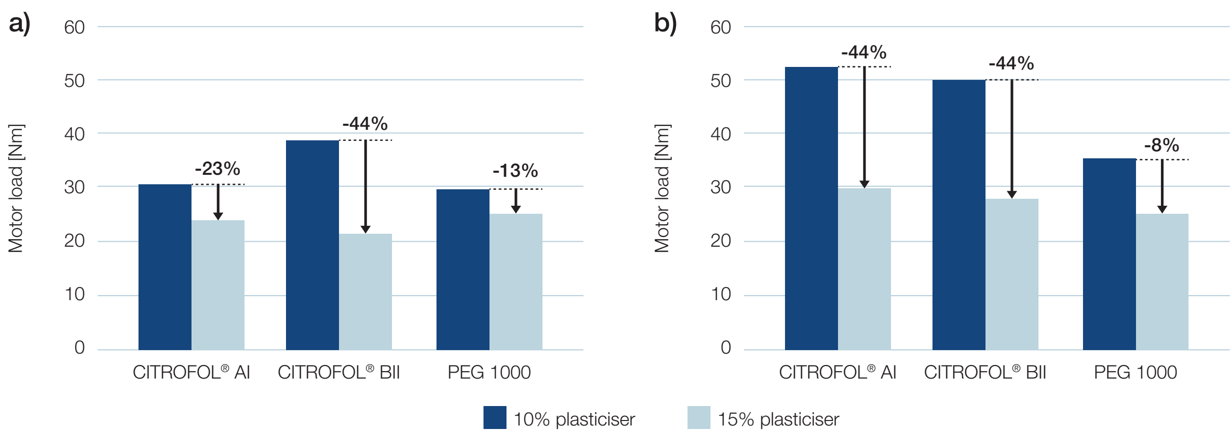

Figure 3: Torque during processing of original PLA L105 (left, a)) and PLA L130 (right, b)) both unplasticised and plasticised with different plasticisers in various concentrations

Rheological properties

The complex viscosity of the plasticised granulates was determined as it is also a critical factor for evaluating the processing of a polymer. The results for PLA L105 and PLA L130 are depicted in figure 4. It is clear that the addition of the plasticisers resulted in a reduction in the viscosity of both PLA types. The values obtained for PLA L130 are higher as the molecular weight of PLA L130 is higher, too. Compared to PEG 1000, the two CITROFOL® grades offer acceptable alternatives. Low viscosities may enable easier processing and also improved incorporation of higher amounts of fillers that are essential for the production of tailor-made polymer compounds. In addition, low viscosities are especially advantageous for the production of thin-walled parts.

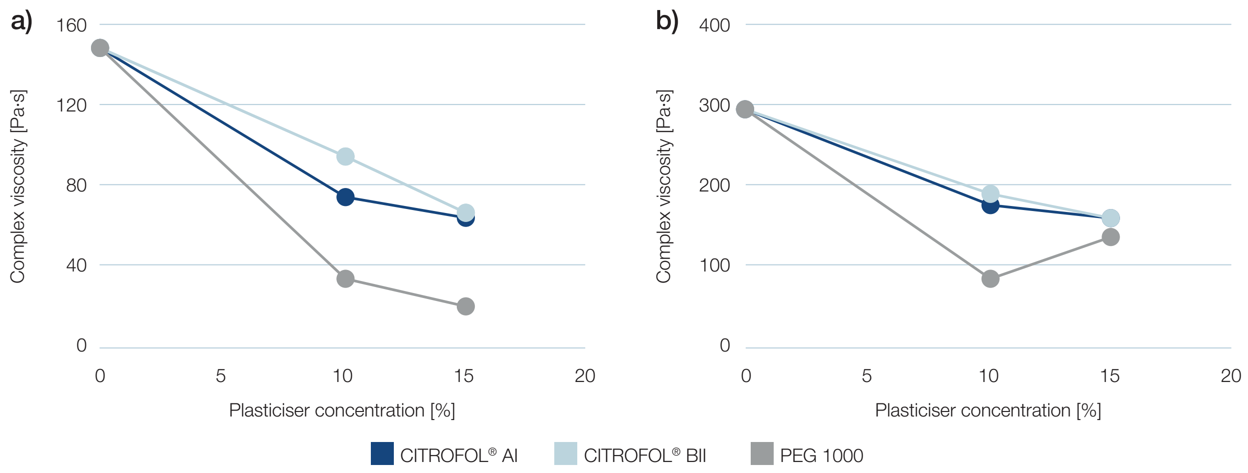

Figure 4: Complex viscosities of original PLA L105 (left, a)) and PLA L130 (right, b)) both unplasticised and plasticised with different plasticisers in various concentrations

Mechanical properties

Mechanical properties like elongation at break and 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.

Very low values for elongation at break (1.9 to 2.2%) were obtained with both unplasticised PLA and the specimens with 10 wt.% plasticiser. Figure 5 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 greatest effect. In general, the citrate esters show superior behaviour compared to PEG 1000.

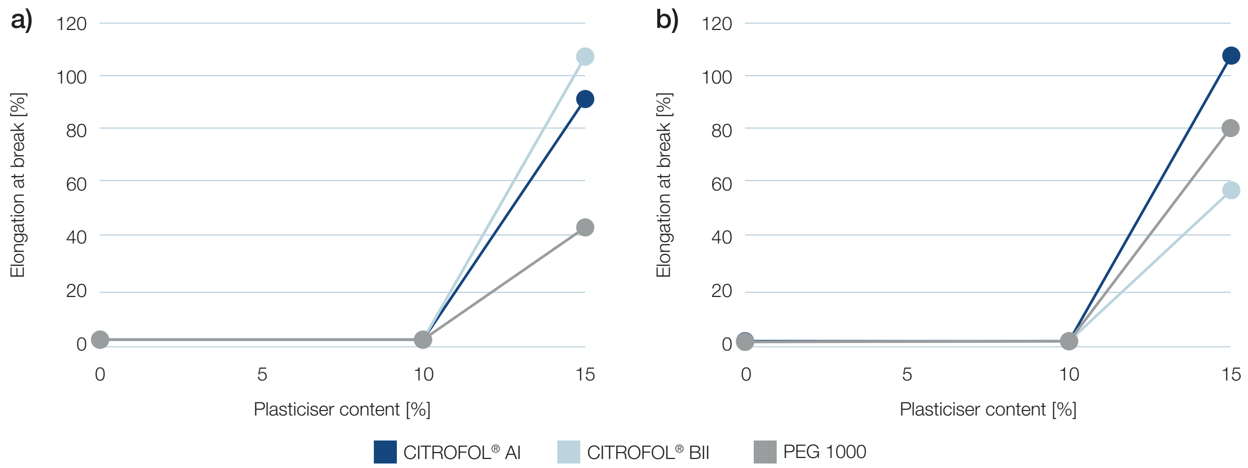

Figure 5: Elongation at break of original PLA L105 (left, a)) and PLA L130 (right, b)) both unplasticised and plasticised with different plasticisers in various concentrations

Figure 6 shows the results for tensile strength. The tensile strength of PLA decreases with the addition of plasticiser. Similar to the elongation at break, 15 wt.% plasticiser has a significant impact, whereas 10 wt.% only shows 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 specimens containing PEG 1000 (at 10 and 15 wt.%). CITROFOL® BII exhibits the lowest reduction in tensile strength for PLA L130.

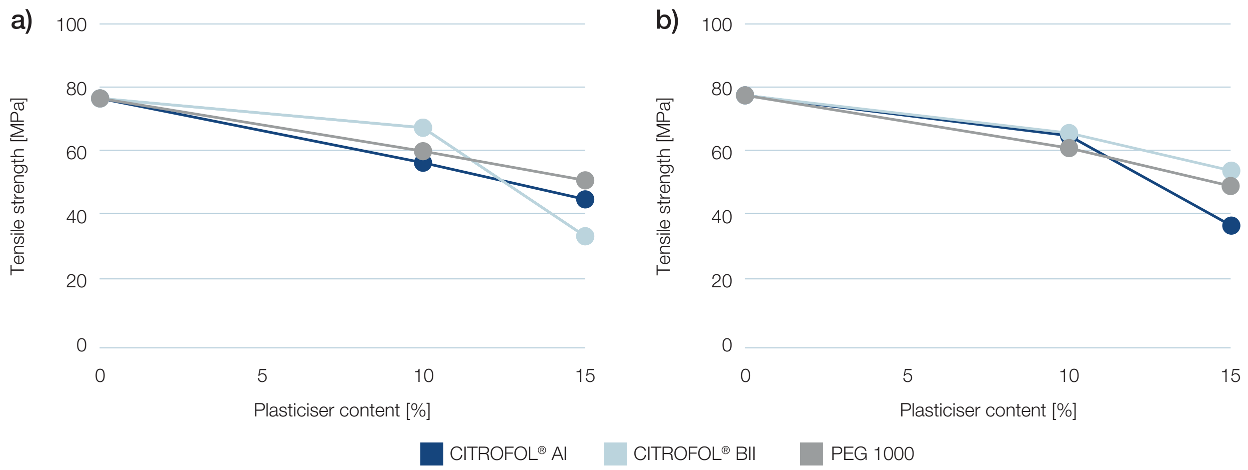

Figure 6: Tensile strength of original PLA L105 (left, a)) and PLA L130 (right, b)) both unplasticised and plasticised with different plasticisers in various concentrations

Thermal properties

Thermal properties like glass transition temperature and melting temperature are also critical parameters as they give an indication as to whether the processing of the polymer material can be improved by the addition of plasticisers. With increasing plasticiser concentration, the melting temperature is reduced (figure 7). The level of reduction depends on the type of plasticiser. Citrate esters demonstrate a higher efficiency, i.e. greater reduction, which leads to a larger gap between degradation temperature and melting temperature. This results in a broader processing window and hence in easier processing of the polymer melt.

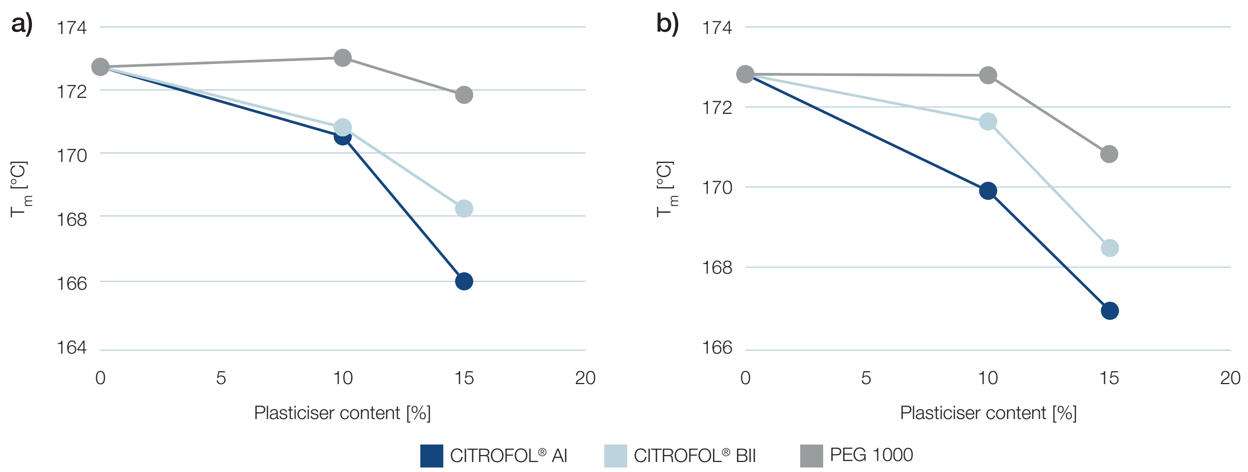

Figure 7: Melting temperatures of original PLA L105 (left, a)) and PLA L130 (right, b)) both unplasticised and plasticised with different plasticisers in various concentrations

However, a reduction in the melting temperature is usually accompanied by a reduction in the glass transition temperature. This can be unfavourable, in particular for end applications where such temperatures can be reached during product use, 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), while having a higher efficiency in the reduction of the melting temperature (figure 8).

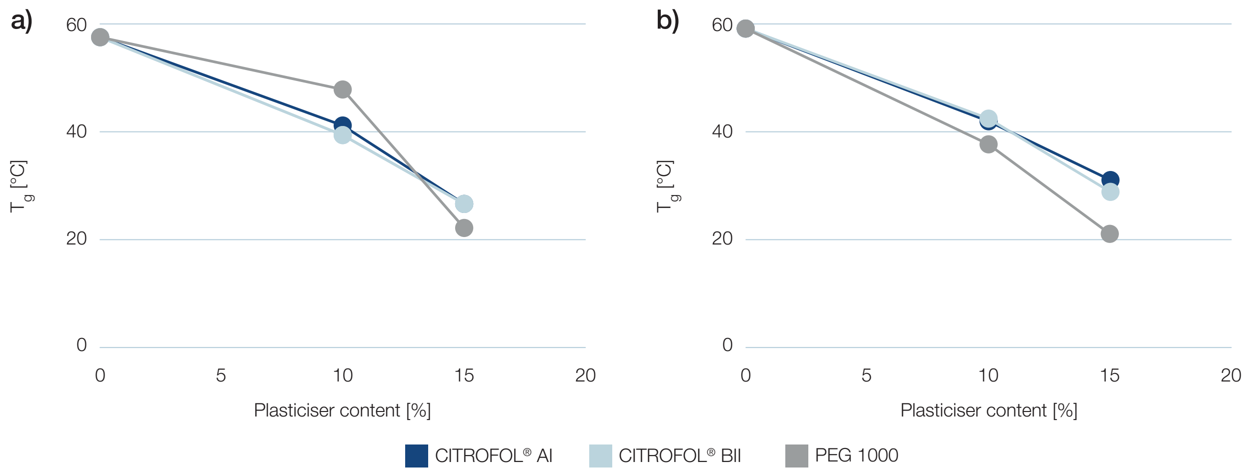

Figure 8: Glass transition temperatures of original PLA L105 (left, a)) and PLA L130 (right, b)) both unplasticised and plasticised with different plasticisers in various concentrations

This study revealed that the citrate esters used show good compatibility with different PLA types and therefore represent powerful alternatives to state-of-the-art plasticisers. While their compatibility is comparable to that of PEG 1000, CITROFOL® AI and CITROFOL® BII outclass PEG 1000 in all other tested properties (figure 9). A significant improvement in mechanical properties was achieved by the addition of 15 wt.% citrate esters to PLA, which exhibited a higher elongation than PLA plasticised with PEG 1000. Furthermore, improved processing and reduced melting temperatures were observed with CITROFOL® AI and CITROFOL® BII resulting in a broader processing window. An additional advantage of citrate esters is that no extra heating step for dosage is needed as the products are liquid in their delivery form. Finally, the citrate esters exhibit a significant sustainability advantage due to their high bio-based content.

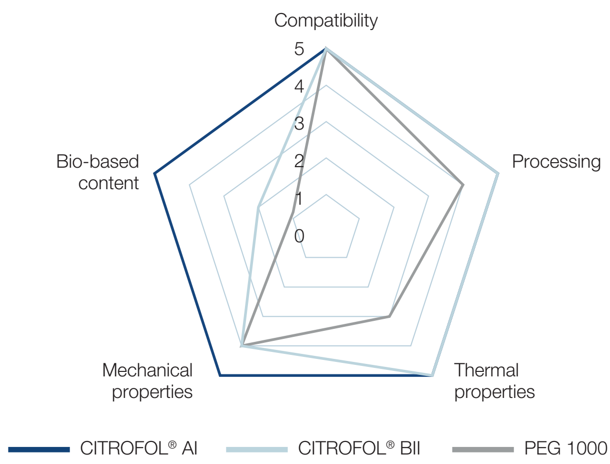

Figure 9: Overview of properties improved in PLA plasticised with CITROFOL® AI and CITROFOL® BII versus PEG 1000 (score 1–5, 1 = poor, 5 = excellent)

2 Foaming of plasticised PLA

In the second part of the study, the performance of CITROFOL® citrate esters in the foaming process of PLA was investigated. The main application field of PLA is packaging. Foamed packaging is a particularly important segment as the boxes obtained demonstrate good mechanical protection of the contents and at the same time weigh less and cost less because less plastic is needed. In the food packaging market, foamed boxes offer high thermal insulation and are particularly good at keeping hot food hot.

Until now the foamed packaging market has been dominated by expanded polystyrene (EPS) and expanded polypropylene (EPP) – a dominance mainly driven by their inherent properties and the low material costs. However, this type of packaging waste has a considerable adverse impact on the environment, as most of the EPS and EPP foams are utilised for single-use packaging applications e.g. in the food, personal care, agriculture, and fishing equipment segment. This waste accumulates over time. It takes EPS, for example, over 100 years to degrade. Furthermore, upon disintegration, hazardous chemicals may be released into the environment, adversely affecting human and animal health.

Overall, stronger regulations, in particular for single-use plastics, have led to a steadily increasing importance of sustainable and ideally biodegradable alternatives to EPS and EPP – like plasticised PLA – that help to reduce plastic waste while maintaining the desired functionality of the packaging during use.

2.1. Goal of study

In this study, the effect of CITROFOL® AI on the process of foaming PLA was investigated. For this purpose, PLA plasticised with CITROFOL® AI in combination with a blowing agent was processed via foam extrusion. The samples were characterised and the results were compared to those obtained with unplasticised foamed polystyrene (PS). One main goal was to show that foaming is possible with plasticised PLA and that mechanical properties like elongation at break can be improved.

2.2. Materials, compounding and methods

2.2.1. Materials

For these tests, a high-heat PLA type (Luminy® L175 obtained from TotalEnergies Corbion) was tested. The PLA granulate was dried before use (80°C, 4-5 h) to prevent polymer degradation during processing caused by residual moisture presence. CITROFOL® AI was used in the concentrations 10 wt.% and 15 wt.%.

2.2.2. Compounding and processing of foamed PLA with plasticisers

The processing consisted of several steps. In the first step, plasticised PLA granulate was produced via melt compounding. Here, PLA was melted in a twin-screw extruder and the plasticiser was added using a liquid dosing unit. Thermal analysis with DSC measurements was performed for characterisation of the prepared compounds. This was followed by the foam extrusion process. The plasticised granulate was melted again and mixed with the blowing agent sodium hydrogencarbonate ($NaHCO_3$) in different concentrations (1–2 wt.%) and 1 wt.% calcium carbonate ($CaCO_3$) as nucleation agent. The foamed strands were characterised in respect of their thermal properties via DSC. Furthermore, their density was measured and microscope images were taken to obtain information on pore sizes and distributions. In the next step, the cast foil extrusion process was conducted to prepare foamed foils. Finally, the mechanical properties and density of the foils were analysed, and microscope images were taken. The composition of the different samples is illustrated in table 2.

Table 2: Composition of prepared samples

Trial	Compound	Compound [wt.%]	Blowing agent [wt.%]	Nucleation agent ($CaCO_3$) [wt.%]
CF AI-10-2-1	PLA with 10 wt.% CITROFOL® AI	97	2	1
CF AI-15-1-1	PLA with 15 wt.% CITROFOL® AI	98	1	1
PS-1	Polystyrene	99	1	-
PS-2	Polystyrene	98	2	-

2.2.3. Methods

Microscopy
Microscopy was performed using a Keyence VHX-950-F microscope with a magnification factor of 20 or 50.

Density
The density of the samples was determined using a Mettler Toledo XSR 225 analytical scale via the Archimedean density principle.

Mechanical properties
For the PLA basic data set, the measurements of the mechanical properties were carried out with a mechanical testing machine (Zwick Z2.5 tensile tester) using a cross-head speed of 10 mm/min. All tests were conducted according to DIN EN ISO 527-3, with five test specimens per sample.

2.3. Results for cast foils

The preparation of a cast foil made from PLA could be successfully demonstrated. The best results were obtained with a combination of PLA with 10 wt.% CITROFOL® AI, 2 wt.% $NaHCO_3$ and 1 wt.% $CaCO_3$ (figure 10) and with 15 wt.% CITROFOL® AI, 1 wt.% $NaHCO_3$ and 1 wt.% $CaCO_3$ (figure 11). The foils show a homogenous closed surface and the foam cells are clearly visible in the profile. The maximum expansion of the foils is limited by the tool gap. With higher plasticiser concentrations the foils become softer, leading to undesirable holes in the foil surface.

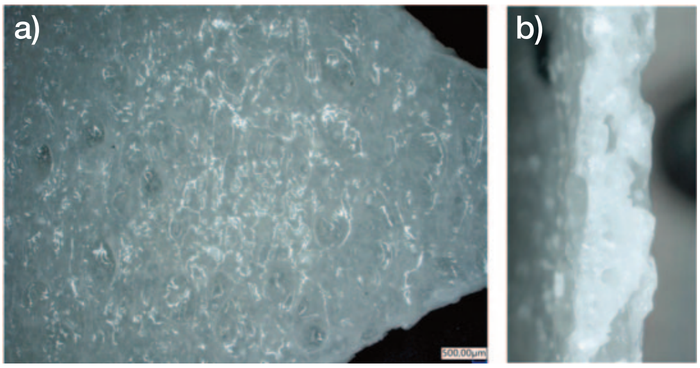

Figure 10: PLA cast foil with 10 wt.% CITROFOL® AI, 2 wt.% $NaHCO_3$ and 1 wt.% $CaCO_3$, a) top view, b) cross-section

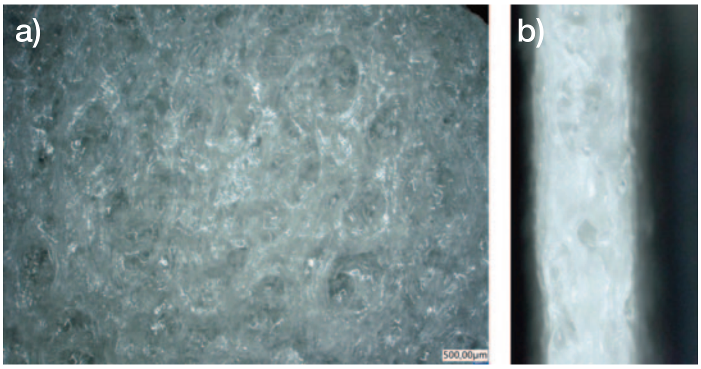

Figure 11: PLA cast foil with 15 wt.% CITROFOL® AI, 1 wt.% $NaHCO_3$ and 1 wt.% $CaCO_3$, a) top view, b) cross-section

Density measurements

Another important property of cast foils is their density. The results for the PLA cast foils are shown in figure 12. As expected, the density of all prepared cast foils is lower than that of pure PLA granulate. The density of the PLA cast foils is relatively high compared to that of foils made from unplasticised polystyrene. But the density of the two PLA foils is comparable at about 1.0 g/cm^3. Another interesting point is that the density of the polystyrene cast foil increases massively (from 0.44 g/cm^3 to 0.71 g/cm^3) when the blowing agent concentration is increased (from 1.0 wt.% to 2.0 wt.%). One explanation for this would be that the concentration of the blowing agent is too high, which results in increased coalescence, leading to fewer foam cells inside the cast foils and hence ultimately to increased density.

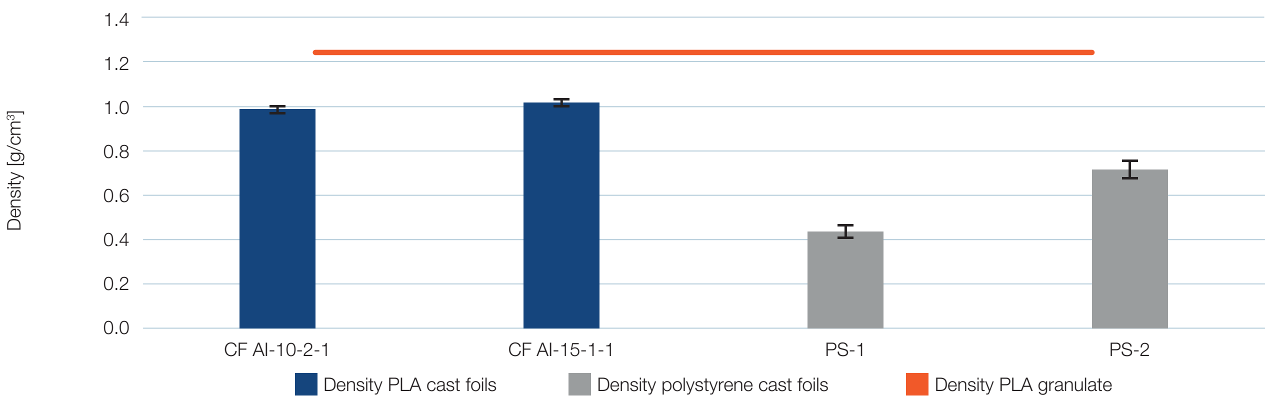

Figure 12: Density of plasticised PLA and polystyrene cast foils

Mechanical properties

The preparation of defined test specimens is necessary for the investigation of mechanical properties. It was not possible to create such specimens from the polystyrene cast foils because the foils were too brittle, so that when punching out the specimen the foils/specimen just broke. For this reason, the mechanical properties were investigated only for the PLA cast foils. The results are shown in table 3.

As expected, the elongation at break increased with a higher plasticiser concentration (from 13 to 28%). Also the tensile strength was lower for the PLA cast foil plasticised with 15 wt.% CITROFOL® AI (8.8 MPa) compared to the one plasticised with 10 wt.% CITROFOL® AI (12.6 MPa). The same was true for the Young's modulus. Higher values were measured for the cast foil with the lower CITROFOL® concentration.

Table 3: Mechanical properties of PLA cast foils

Compound	Young's modulus [MPa]	Tensile strength [MPa]	Elongation at break [%]
PLA with 10 wt.% CITROFOL® AI, 2 wt.% $NaHCO_3$, 1 wt.% $CaCO_3$	413 ± 30	12.6 ± 1.9	13 ± 4
PLA with 15 wt.% CITROFOL® AI, 1 wt.% $NaHCO_3$, 1 wt.% $CaCO_3$	234 ± 21	8.8 ± 0.5	28 ± 8

This study revealed that the foaming of plasticised PLA is in principle possible, despite the low melt strength of the polymer melt, which is especially critical for foaming. It was successfully shown that homogenous cast foils can be prepared from PLA plasticised with CITROFOL® AI. Plasticiser concentrations between 10 and 15 wt.% seem to be optimal, as these have a positive impact on the processability and final properties of this application. For commercial applications it is crucial to further decrease the densities of the foamed materials. Physical foaming instead of chemical foaming should be taken into consideration. It would also be beneficial to find an optimal temperature programme for the compounding steps in order to improve the stability of the overall process and of the very promising final products.

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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 is among the largest global producers of citric acid and citrate esters. Its products 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. They are therefore 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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