Jungbunzlauer

From nature to ingredients®

Thermoplastic processing of Cellulose Acetate 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.

Cellulose Acetate

Cellulose Acetate (CA) is an acetate ester of cellulose, obtained by acetylation of the cellulose hydroxyl groups with acetic anhydride in acetic acid and in the presence of a strong acid catalyst. Cellulose diacetate (CDA) corresponding to an average of two acetate esters per cellulose monomer unit is the grade with the highest commercial relevence and is therefore commonly referred to as cellulose acetate (figure 1). CA is a biopolymer primarily derived from wood pulp and is widely used in consumer goods, including plastic films, textiles and cigarette filters, frames for glasses and the food packaging segment.

Neat cellulose acetate exhibits good mechanical properties, e.g. a high Young's modulus and a high tensile strength; however, the material has a narrow temperature window between its glass transition temperature that is important for processing and its degradation temperature. Its inherent stiffness and brittleness demands the addition of plasticisers to ensure a good processing and optimised resilience in the end application.

Citrate esters exhibit a powerful potential as plasticisers. They are toxicologically harmless and bio-based. Therefore, they are ideal candidates for the thermoplastic processing of Cellulose Actetate. In this study, the influence of different citrate esters on the plasticisation of CA with respect to relevant end properties was investigated.

Compounding and processing of plasticised CA

In this study, CA powder (CA-398-30) from Eastman Chemical Company (Kingsport, Tennessee) was used. Different concentrations (15, 20, 25, 30 wt.%) of CITROFOL® AI (CF AI; triethyl citrate) and CITROFOL® AII (CF AII; triethyl O-acetylcitrate) were used as plasticisers and compared to the reference Triacetin (TA; gylceryl triacetate). The production of plasticised CA consisted of two steps. In a first step, a dry blend was prepared via mixing CA with the respective plasticiser in a mixer for 3 min. In the second step, the dry blends were melt extruded using a single screw extruder and then granulated. Afterwards, the desired test specimens were prepared by melting and injection moulding of the granulate. Finally, the thermal, mechanical and rheological properties of the test specimens as well as their migration potential were analysed.

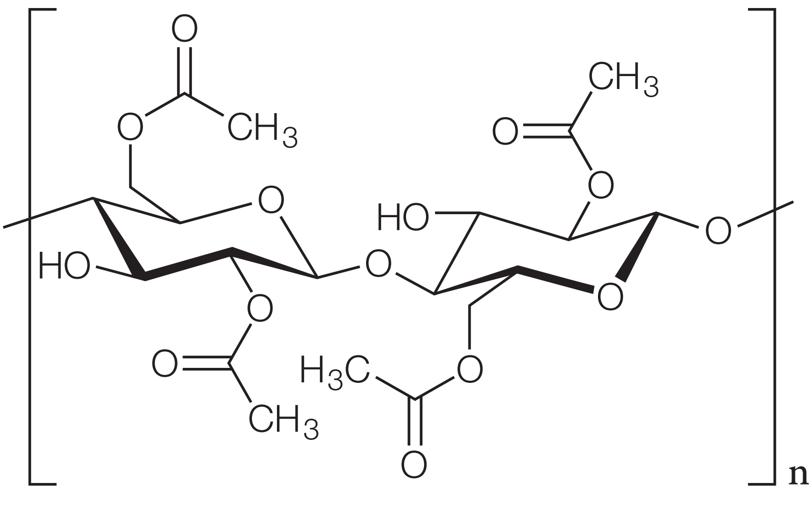

Figure 1: Chemical structure of Cellulose Diaceate

Benefits at a glance

Processing behaviour

In figure 2a, the melting temperatures during the processing and the qualitative assessment of the processing behaviour is illustrated. CITROFOL® AI and Triacetin showed a very stable processing with no material inhomogeneity at a concentration of 20 wt.% and higher. In the case of CITROFOL® AII, a minimum concentration of 25 wt.% was necessary to ensure a stable process. For all three tested plasticisers, a concentration of 15 wt.% was not efficient enough as process instabilities and material inhomogeneties were observed. To overcome these issues, the processing temperature was increased. This, however, resulted in a stronger yellowing of the processed material. On the other hand, with increasing plasticiser concentration the melting temperature decreased. This demonstrates that the processing temperature window of CA improves with the addition of plasticisers as the gap between the melting temperature and the degradation temperature increased, resulting in less yellowing of the processed material. These findings were reproduced with dynamic mechanical analysis (DMA) measurements, where a decrease of the glass transition temperature with increasing plasticiser concentration could be seen. Figure 2b shows the torque (determined in a pre-test with a Micro Compounder) as a function of the plasticiser content. All tested plasticisers showed the same trend. The torque of the device was significantly reduced with the addition of plasticisers. This may result in an easier processing as well as lower energy consumption, contributing to a more sustainable process.

a)

wt.%	TA	CF AI	CF AII
15	205	205	215
20	200	200	210
25	190	190	195
30	190	190	190

not possible

with issues

without issues

b)

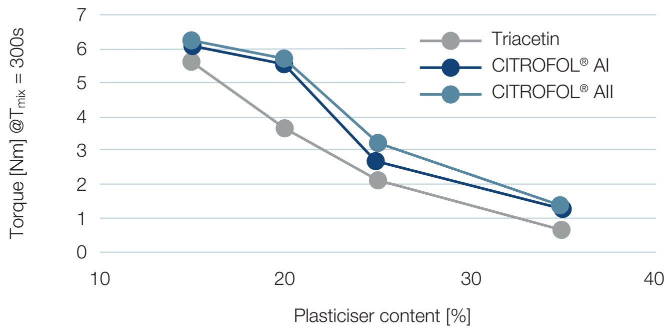

Figure 2: a) Melting temperatures in °C during processing and qualitative assessment of the processing behaviour
b) Torque determined after a processing time of 300s dependent on the plasticiser content

Migration

For the migration tests, round test specimens (diameter = 25 mm, height = 1 mm) were stored at 80°C for 21 days in a convection oven. After given timeframes, the sample surface was cleaned removing any substances that potentially migrated to the surface and the weight difference of the sample was determined. The results are depicted in figure 3.

The larger the molecular weight of the plasticiser, the lower is the migration behaviour and hence the weight loss. According to this experiment, CITROFOL® AII exhibits the lowest mass change over the storage period, whereas the benchmark TA showed the highest mass loss, which is consistent with the molecular weight of the tested compounds.

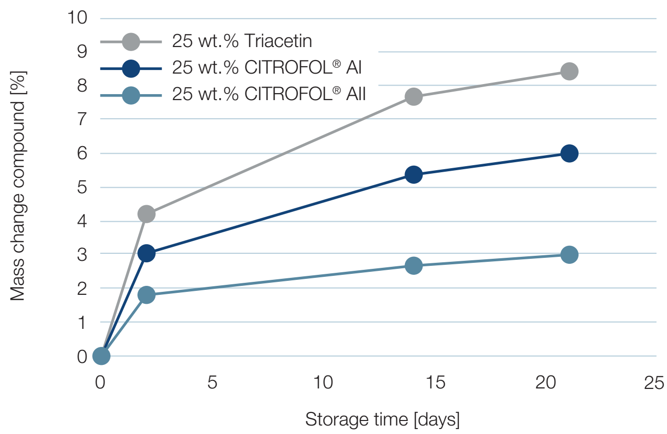

Figure 3: Mass change of different compounds over a storage period of 21 days at 80°C

Charpy impact strength

The Charpy impact strength was performed according to DIN EN ISO 179. The tests for the unnotched samples were carried out with a 4J hammer, whereas for the notched samples a 1J hammer was used. In figure 4, the results of the Charpy impact strength are illustrated. In general, the impact strength increases with increasing plasticiser concentration. A brittle-to-tough transition occurs between 20 and 30 wt.% plasticiser content. Interestingly, the samples with CITROFOL® AI showed an unexpectedly high level of impact strength in comparison to TA, even for low plasticiser concentrations.

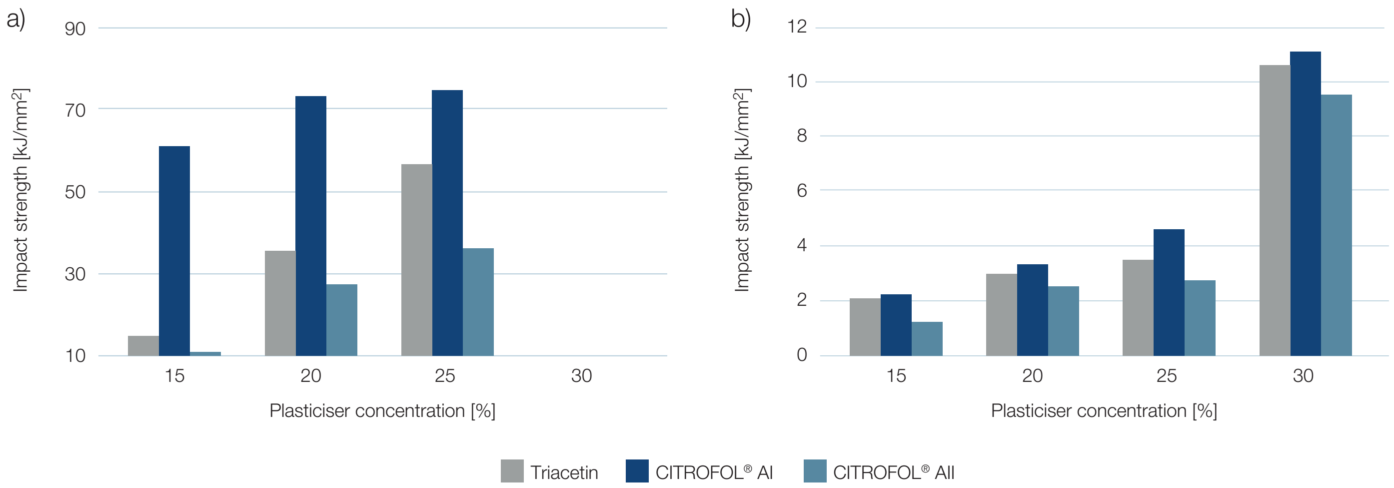

Figure 4: Charpy impact strength a) unnotched samples, b) notched samples

The study demonstrated that CITROFOL® AI is an excellent alternative to the benchmark Triacetin for the processing of Cellulose Acetate. All plasticised samples showed excellent optical properties with a high transparency. While parameters like processing, plastification and mechanical properties are also comparable to Triacetin, both CITROFOL® grades show a significantly improved migration inhibition. This feature helps to prevent brittleness and may increase the lifetime of a product. Moreover, combined with the low toxicological profile, it qualifies the CITROFOL® esters for the usage as plasticisers in sensitive applications.

Also in terms of sustainability, the CITROFOL® grades show unique advantage due to a significantly higher bio-based content. CITROFOL® AII contains 87% and CITROFOL® AI even 100% renewable carbon whereas Triacetin only contains up to 40% renewable carbon.

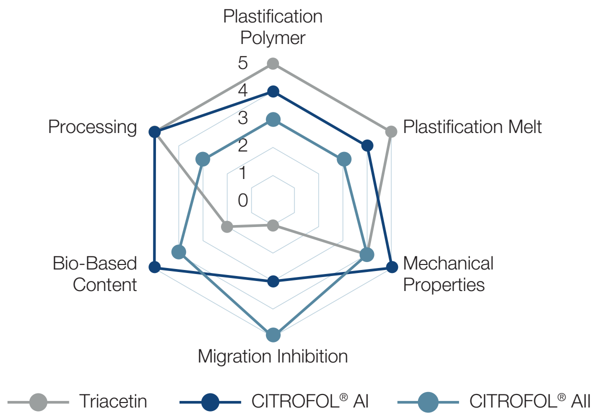

Figure 5: Spider diagram of all tested properties (ranking: 0=bad, 5=excellent)

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 producer 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 or food packaging, pharmaceutical applications and personal care. Moreover, all CITROFOL® esters are non-GMO, vegan, kosher and halal.

Headquarters **Jungbunzlauer Suisse AG** · CH-4002 Basel · Switzerland · Phone +41 61 295 51 00
For further information please contact: headquarters@jungbunzlauer.com · www.jungbunzlauer.com