facts

Sealant with bio-based citrates

Jungbunzlauer

From nature to ingredients®

Abstract

The objective of these investigations was to demonstrate how a bio-based, non-phthalate citrate ester plasticiser can be used in a water-based acrylic sealant, which is usually produced with petrochemical-based plasticisers like phthalates. As with the preparation of the sealant samples, all testing was carried out regarding its processing performance and the determination of the final sealant properties using CITROFOL® BII (tributyl O-acetylcitrate also acetyl tributylcitrate or ATBC) and Di-isononylphthalate (DINP) as control standard.

All test results exhibit an equal or even slightly better performance for the citrate ester than for the standard DINP in terms of rheology, curing behaviour, tensile strength and elongation, for example.

If a sealant solution is required with a higher content of bio-based materials and a low carbon footprint without compromising on processing and key performance parameters, then citrate esters could represent a preferable alternative.

Jungbunzlauer
From nature to ingredients®

Introduction

Plasticisers are an important product group for the processing and final properties of polar polymers. They serve to reduce glass transition temperatures and contribute to flexibility and elasticity.

The most widely produced plasticisers are phthalates, with a market share far above 80% worldwide. Besides phthalates, other chemicals such as trimellitates, benzoates, adipates, alkyl sulfonic acid phenol esters and phosphates comprise the fossil fuel based plasticiser market. The usage and acceptability of bio-based products in technical application is growing, not least due to environmental trends and continuous adaptations in order to improve consumer protection, but also due to the creditability of the application performance. With the focus shifting to bio-based alternatives for plasticisers, the preferred choice nowadays for a material are citrate esters, which have been known about for many decades, and are available in commercially large-scale quantities at reasonable and competitive prices.

Jungbunzlauer is the largest global producer of citric acid and citrate esters, which are well-known under the brand CITROFOL®. Citric acid is produced via fermentation of sugar or starchy materials, and consists of three carboxyl groups and one hydroxyl group. Firstly, alcohol (e.g. n-butanol) is used for the esterification of the carboxyl groups, and in a possible second step acetic anhydride can be used for the acetylation of the hydroxy group.

Citrate esters are biodegradable with an excellent toxicological and eco-toxicological profile, versatile and highly compatible with numerous polymers and other plasticisers. They are particularly characterised by highly efficient solvation, and the low-migration and non-VOC options allow them to be used according to technical requirements.

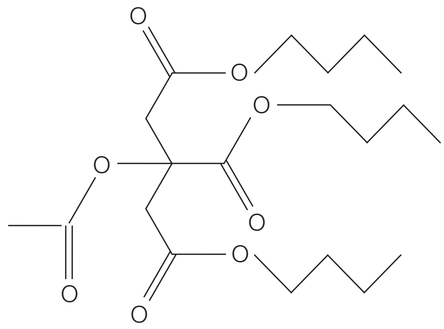
As a result of their high safety profile, CITROFOL® esters are being used more and more in technical applications where phthalate plasticisers were traditionally used. Competition from ever more advanced alternatives to common plasticisers has resulted in ever more diverse applications.

Citrate esters are used as primary plasticisers particularly for the processing of flexible polyvinylchloride (PVC) for sensitive applications such as medical devices, food packaging and toys. Besides technical PVC applications such as wallpaper and flooring, citrate esters are also used in polymeric systems based on acrylics, polyurethane, polyvinyl acetate, cellulose acetate, nitro cellulose, polylactic acid and polyhydroxy alkanoates, to mention but a few. The following investigations will give an overview of their usage in acrylic sealants.

Experimental phase

The basic plasticiser evaluation was conducted using DINP as a standard control versus CITROFOL® BII (tributyl O-acetylcitrate) in an acrylic-based formulation also containing an emulsifier, a dispersing agent, a pigment and a filler, described in the following:

317.0 g	acrylic polymer
97.5 g	plasticiser
3.0 g	emulsifier
6.0 g	dispersing agent
14.5 g	pigment
562.0g	filler



CITROFOL® BII
(IUPAC name: tributyl 2 acetyloxypropane-1,2,3-tricarboxylate)

Both mixtures were blended under appropriate conditions using a laboratory dissolver to create a homogeneous, pasty final product without any anomalies. Both pasty materials were transferred into cartridges typically used for the application of sealants.

The preparation of the test samples for mechanical testing (tensile strength, 100% modulus, elongation at break) was done according to standard procedures. The sealant mixture was applied onto a plate, squeegeed to a film 3mm thick and cured at 23°C at 50% relative humidity before testing.

Jungbunzlauer
From nature to ingredients®

Results

Rheology/Application
During the preparation of the sealant samples no conclusive findings emerged, such as heat effects or viscosity issues. Both formulations can be manually pressed out of the used sealant cartridges in a similar way and the rheology measurements (oscillating plate/plate methodology) showed no noteworthy deviations, viscosity with CITROFOL® BII seems to be a little lower. Furthermore, film-formation time and joining time do not vary significantly. After the curing process both exhibited a similar shrinking behaviour, and in addition, no offensive odour could be detected from either the DINP or the CITROFOL® BII paste.

The solidification process is dependent on the rate of water evaporation, and after four days the inherent cohesion of the acrylic particles was already sufficient to allow for the determination of tensile strength and elongation. However, a more meaningful result will be achieved after four weeks.

During the hardening and storage period, no discoloration of the samples was observed during the testing of either DINP or CITROFOL® BII. CITROFOL® BII does not contain any unsaturated or aromatic units, which often lead to discoloration, and is well known for its good compatibility with other formulation components without any reaction.

Properties	DINP	CITROFOL® BII
Pasty state		
Odour	odourless	odourless
Viscosity (plate/plate)	3035 Pa*s	2379 Pa*s
Cured state		
Shore hardness A (after 4 days)	18	16
Adhesion properties on		
Concrete	easy removable without residue	easy removable without residue
Floor tile	poorly removable	poorly removable
Wood (spruce & beech)	poorly removable	poorly removable

Jungbunzlauer
From nature to ingredients®

Performance properties

Mechanical properties/Adhesion to specific surfaces

The results after a curing time of 28 days in terms of maximum tensile strength, 100% modulus and elongation at break are slightly, but not significantly, in favour of CITROFOL® BII. Shore hardness is similar for both plasticisers.

Semi-quantitative testing of adhesion to various substrates such as concrete, a floor tile and wood (spruce and beech) also showed a comparable performance from DINP- and ATBC-based sealant formulations. While the adhesion to concrete was poor for both systems, adhesion to the floor tile and wooden surface was much better. This was already noted during removal of the cured sealant layers from the latter two surfaces, as a greater amount of force was required to remove both sealant systems and a greater amount of sealant residue remained on the surfaces.

Fig. 1: Tensile strength – 100% Modulus – Elongation at break

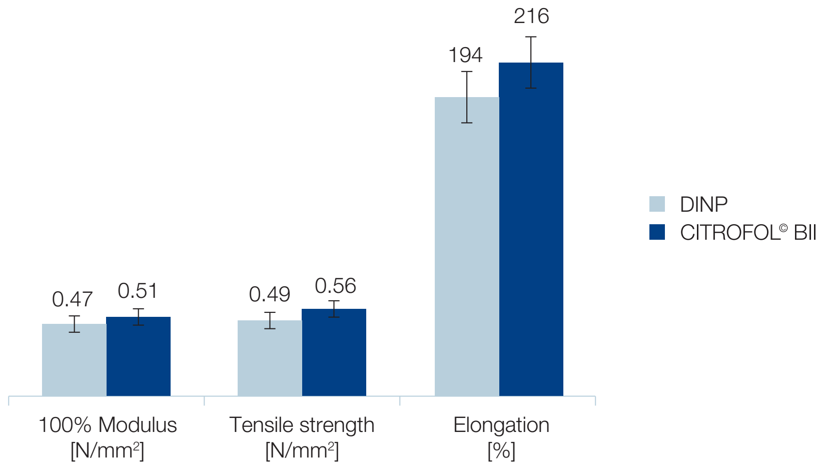
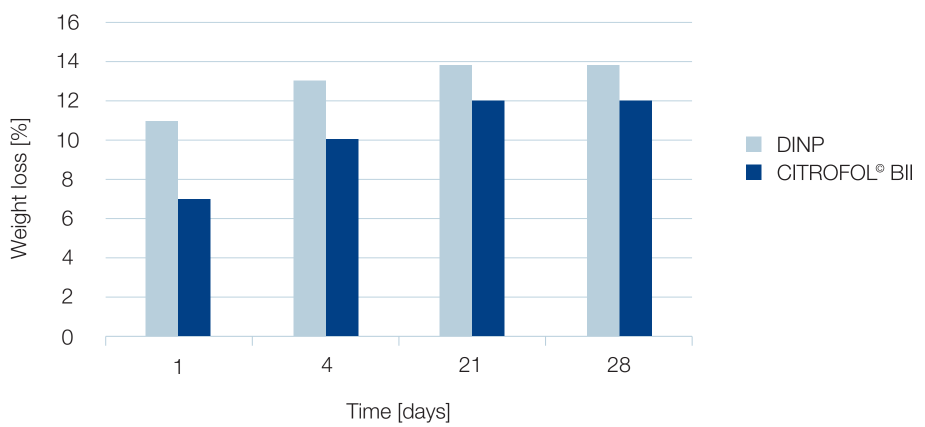


Fig. 2: Weight loss during setting time



Jungbunzlauer

From nature to ingredients®

Health, safety and the environment

Known for their safe ecological profile and lack of adverse effects on health during their handling and use, citrate plasticisers are registered in major national chemical inventories and as well as in certain application-specific registries. Citrate esters are readily metabolised within the human body into non-toxic constituents.

Based on a risk assessment, ATBC was the first plasticiser to receive approval from the Scientific Committee as an alternative to phthalates for toys in Europe. CITROFOL® BII is also certified in accordance with DIN EN 13432 (related to ASTM D6400) and can be used as a plasticiser for manufacturing compostable materials that do not produce adverse effects on water or soil. Biopolymers, for instance polyhydroxy alkanoates (PHA), open up new opportunities for the use of citrate esters, especially if bio-based components and/or biodegradability are required.

Conclusion

The primary plasticiser CITROFOL® BII has great potential to perform well in water-based acrylic sealants. The evaluation of the most interesting processing requirements and end product properties demonstrated at least the same or even better results compared with the standard phthalate DINP.

What is more, CITROFOL® BII is REACH registered, as well as having received worldwide listing in multiple regulatory bodies (food contact approved). As a non-VOC, it is particularly suited for interior applications, when low or no emission is required.

Finally, competition from ever more advanced alternatives to common plasticisers has resulted in ever more diverse technical applications, including sealants and adhesives, where petrochemical or phthalate based plasticisers were traditionally used.

About Jungbunzlauer

Jungbunzlauer is one of the world's leading producers of biodegradable ingredients of natural origin. We enable our customers to manufacture healthier, safer, tastier and more sustainable products. Due to continuous investments, state-of-the-art manufacturing processes and comprehensive quality management, we are able to assure outstanding product quality. Our mission "From nature to ingredients®" commits us to the protection of people and their environment.

The Author

Dr. Klaus Klingberg – Product Manager Specialties, Jungbunzlauer Ladenburg GmbH
klaus.klingberg@jungbunzlauer.com

Discover more on
www.jungbunzlauer.com

The information contained herein has been compiled carefully to the best of our knowledge. We do not accept any responsibility or liability for the information given in respect to the described product. Our product has to be applied under full own responsibility of the user, especially in respect to any patent rights of others and any law or government regulation.

Headquarters **Jungbunzlauer Suisse AG** · CH-4002 Basel · Switzerland · Phone +41-61-2955 100 · headquarters@jungbunzlauer.com

www.jungbunzlauer.com

Jungbunzlauer
From nature to ingredients®