facts

Bio-based citrate plasticiser CITROFOL® BII in sealants and adhesives

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Abstract

Being "green" is no longer a tactic used to gain a competitive advantage, it is mainstream practice and the fundamental expectation of manufacturers and consumers. A growing number of companies, including retailers and also manufacturers, are using supplier scorecards to systematically measure the sustainability of their suppliers. It is based on the performance in areas such as water consumption, greenhouse gas emissions, waste generation and energy consumption[1]. In cooperation with the independent institute myclimate – The Climate Protection Partnership (Switzerland), Jungbunzlauer evaluated the data according to valid life cycle assessment standards. The results can be used in order to generate an Environmental Protection Declaration (EPD), which will disclose the potential impact on the environment[2].

The topics sustainability and renewable raw materials are getting more and more attention. Due to these reasons Jungbunzlauer conducted trials for citrate esters for the use in sealant and adhesive applications. The performance of Jungbunzlauer's citrate esters is an additional advantage, which fully complies with petrochemical-based premium product requirements. For decades now, the production of citrate esters and the frequent monitoring in terms of processing and quality management have given no cause for objections concerning quality and availability.

The objective of these investigations was to demonstrate that bio-based, non-phthalate citrate ester plasticiser CITROFOL® BII (tributyl O-acetylcitrate, ATBC) can be used in the following:

1. Water-based acrylic sealant
2. Polyurethane sealant
3. Vinyl acetate adhesive (food contact approved)

These are usually produced with petrochemical-based plasticisers like phthalates or benzoates. Samples were prepared and tested in order to determine their processing performance and the properties of the final sealant or adhesive, using CITROFOL® BII against diisononyl phthalate (DINP), dipropylene glycol dibenzoate (DPGDB) and dibutyl phthalate (DBP) as control standards.

All test results demonstrate an equal or even slightly better performance for the citrate ester compared with the standards in terms of rheology, curing behaviour, shore hardness, tensile strength and elongation, among others.

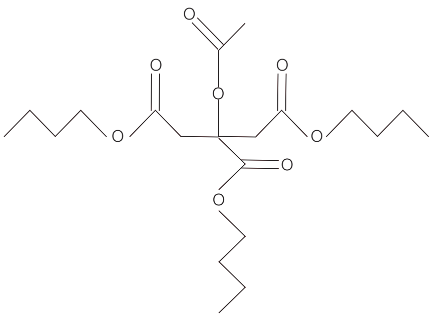
If an adhesive or sealant solution with a higher content of bio-based materials and a low carbon footprint without compromising on processing and key performance parameters is required, then citrate esters could represent a valuable alternative.

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, alkylsulphonic phenyl 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 their application performance. With the focus shifting onto bio-based plasticisers, the preferred choice nowadays are citrate esters, which have been known 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 hydroxyl group.



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

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, 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 wallpapering 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 and polyurethane sealants and a vinyl acetate adhesive.

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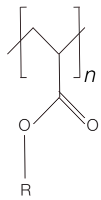
1. ACRYLIC SEALANT

Experimental phase

The basic plasticiser evaluation was conducted using DINP as a standard control versus CITROFOL® BII (tributyl O-acetylcitrate) in a water-based general purpose acrylic 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
562.0 g	filler



Both mixtures were blended under appropriate conditions using a laboratory dissolver to create a homogeneous, paste-like final product without any anomalies. Both paste-like 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 3 mm thick and cured at 23°C at 50% relative humidity – so-called standard conditions – before testing.

Results

Rheology/application

No abnormalities, such as heat effects or viscosity issues, emerged during the preparation of the sealant samples.

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 deviations, however the viscosity of CITROFOL® BII seems to be a little lower compared to DINP. Furthermore, film-formation time and joining time did not vary significantly. After the curing process, both DINP and CITROFOL® BII exhibited a similar shrinking behaviour, and in addition, no offensive odour could be detected from either paste formulation.

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 an early determination of tensile strength and elongation. However, a more meaningful result will be achieved after four weeks.

Testing of both products during the hardening and storage period revealed no discoloration of the samples. CITROFOL® BII does not contain any unsaturated or aromatic units, which often lead to discoloration, and is well-known for its good compatibility with and inertness to other formulation components.

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Table 1: Perfomance properties of DINP and CITROFOL® BII

Properties	DINP	CITROFOL® BII
Pasty state		
Odour	Odourless	Odourless
Viscosity (plate/plate)	3035 Pa·s	2379 Pa·s
Cured state		
Shore hardness A (after four days)	18	16
Adhesion properties on		
Concrete	Easily removable Leaves no residue	Easily removable Leaves no residue
Floor tile	Poorly removable	Poorly removable
Wood (spruce & beech)	Poorly removable	Poorly removable

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 were slightly in favour of CITROFOL® BII. Shore hardness was similar for both plasticisers.

Semi-quantitative adhesion testing to various substrates such as concrete, a floor tile and wood (spruce and beech) also showed a comparable performance for 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.

Figure 1: Mechanical properties of DINP and CITROFOL® BII

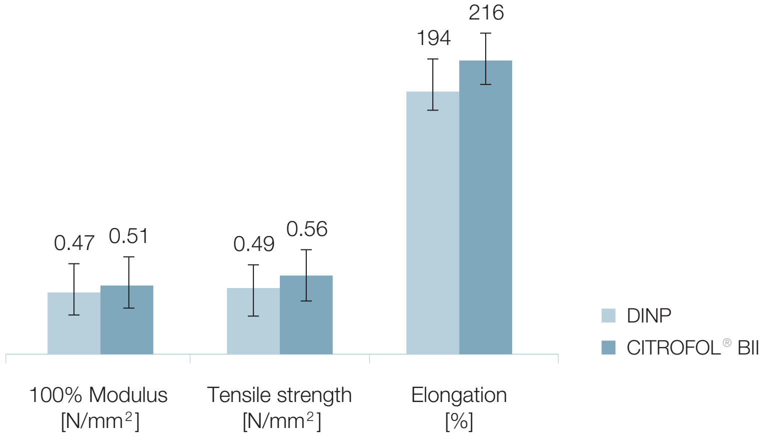

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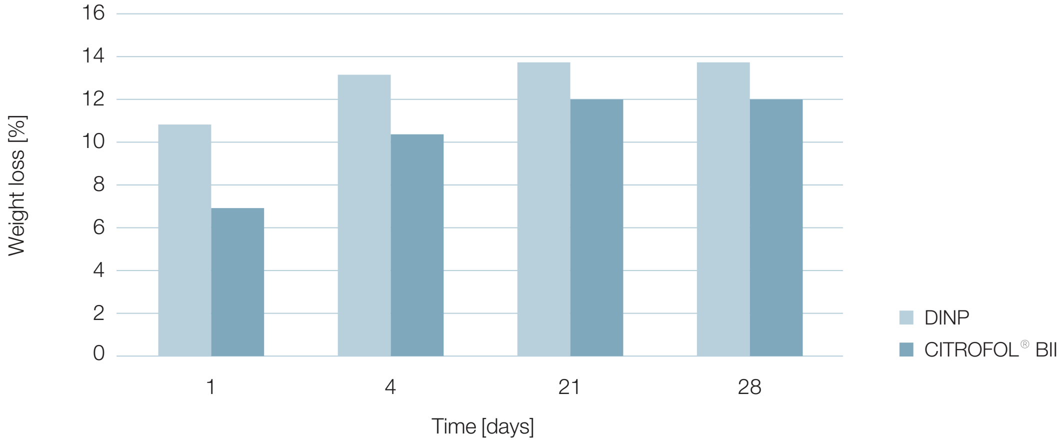
Figure 2: Weight loss during setting time

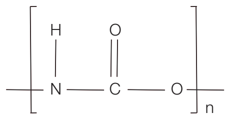


2. POLYURETHANE SEALANT

Experimental phase

The plasticisers were tested against a standard polyurethane prepolymer, produced from methylene diphenyl diisocyanate and a trifunctional polypropylene ether glycol, with a 2.65 % content of free isocyanate groups in the following formulation:

30 g	polyurethane prepolymer (% NCO = 2.65)
20 g	plasticiser
49 g	filler
1 g	desiccant



The polyurethane sealant mixtures and test samples were prepared in a similar way to the acrylics under point 1.1. Only the test programme differs slightly.

Results

The sample preparation with DINP and CITROFOL® BII showed equal performance for both substances, which was also the case for the curing process (seven days at 23°C and 50% relative humidity) and mechanical test results. Testing results for both plasticiser series showed a tensile strength of around 1.6 N/mm² and maximal elongations of approximately 460%.

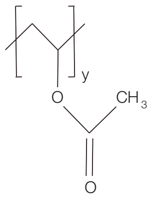
A further storage period of an additional 28 days under standard conditions did not cause any significant changes in the mechanical properties. The CITROFOL® BII series appeared to tend towards a higher tensile strength of approximately 2.1 N/mm².

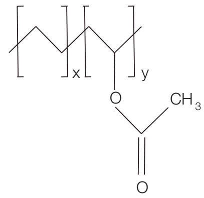
If the samples are stored for an additional 28 days after the usual curing time at an elevated temperature of 70°C, reduced elongation to 400% and a tensile strength of around 2.0 N/mm² will be observed.

3. VINYL ACETATE AND ETHYLENE VINYL ACETATE ADHESIVES

Experimental phase

CITROFOL® BII has been tested both in water-based homopolymer vinyl acetate (VAC) and as well in a copolymer ethylene vinyl acetate (EVA) formulation with the petrochemical plasticisers dibutyl phthalate (DBP) and dipropylene glycol dibenzoate (DPGDB). The VAC and EVA emulsion systems used, each with 40% water and 60% polymer content, were blended with the plasticiser in a ratio of 90:10.





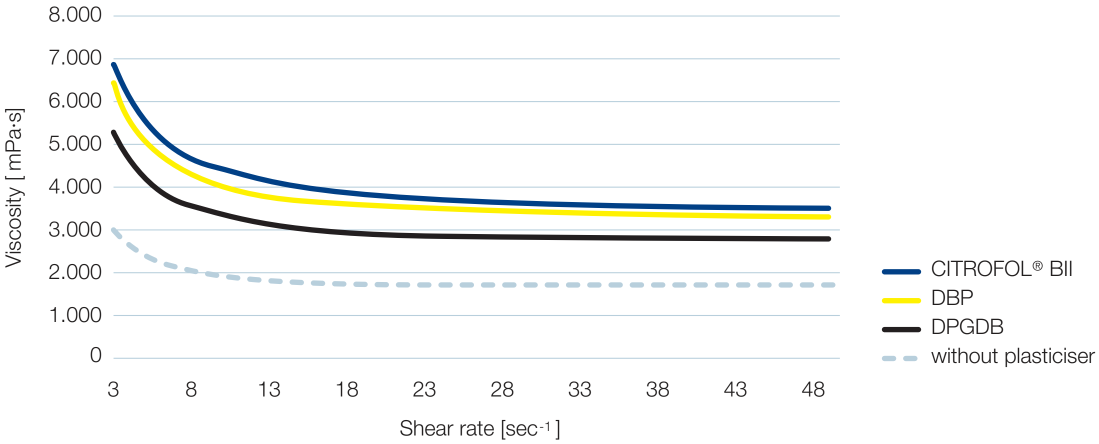
Results

All plasticisers tested showed excellent compatibility with one another in the VAC and EVA emulsion. The observed set and open times revealed no differences in the performance of CITROFOL® BII compared to DPGDB and DBP, and this was also the case for the semi-qualitative adhesion test of gluing two cardboard sheets together and pulling them apart manually after a certain while.

Whereas the viscosity behaviour of the plasticisers were equal for the VAC emulsion, the testing with the EVA emulsion revealed significant differences as demonstrated in the graph below.

All plasticisers caused a viscosity increase for the EVA system, but the largest effect can be observed for CITROFOL® BII. In comparison to DPGDB in particular, the viscosity increase with CITROFOL BII was considerably higher, which could provide benefits in terms of formulation changes and related cost improvements.

Figure 3: Viscosity of an EVA emulsion with 10% plasticiser content



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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 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, tributyl O-acetylcitrate – CITROFOL® BII – was among the first plasticisers 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 polyhydroxyalkanoates (PHA), open up new opportunities for the use of citrate esters, especially if bio-based components and/or biodegradability are required.

In addition, CITROFOL® BII is REACh registered, and is listed worldwide in multiple regulatories (food contact approved). As a non-VOC, it is particularly suited for interior applications when low or no emission is required.

Conclusion

The primary plasticiser CITROFOL® BII has great potential to perform well in water-based acrylic and vinyl acetate emulsions as well as in polyurethane, used for the manufacturing of sealants and adhesives. The evaluation of the most interesting processing requirements and end-product properties demonstrated the same or even better results compared with the standard plasticisers DINP, DBP and DPGDB.

Renewable raw material solutions have paved the way for niche applications and conquer more and more technical areas, including sealants and adhesives, where petrochemical-based plasticisers formerly dominated.

References

[1] Challener, C; "Get to grips with the green imperative"; ICIS Chemical Business 18–24 April 2016; ASC Supplement 11–12

[2] Gibson, J; "Sealant lead in PCR development"; ICIS Chemical Business 18–24 April 2016; ASC Supplement 16–17.

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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.

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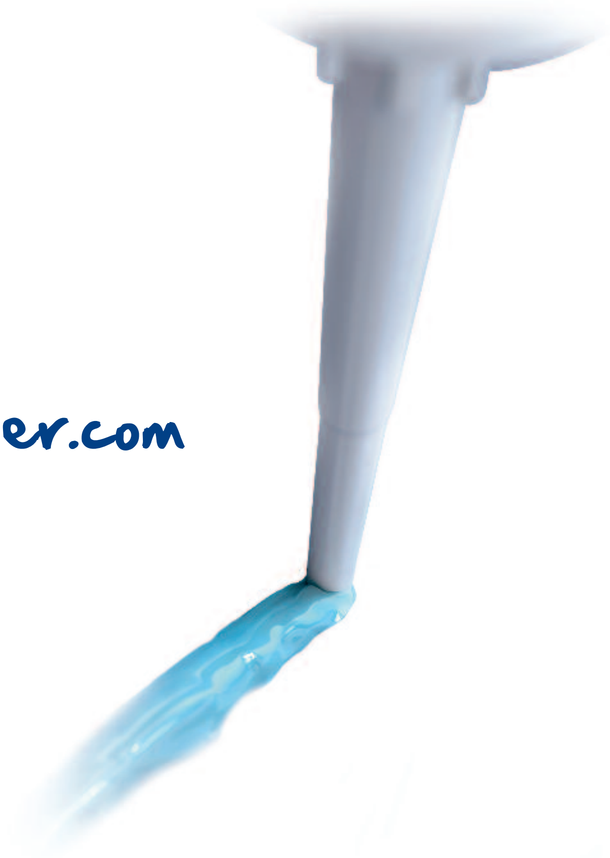

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