# Biobased flexibilisers for PLA

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While biobased additives have been used in conventional polymers since the start of their industrial production [1], for natural-based polymers the use of biobased additives is an ideal and sustainable choice. The most well-known 100 % biobased and biodegradable polymer is polylactic acid (PLA) which has found its way into numerous applications including building and construction materials, food and beverage packaging, and electronics and appliances to name but a few.

A characteristic challenge of PLA that has limited its broader application is brittleness [2]. Several strategies have been proposed to overcome this issue such as blending PLA with other polymers. However, this requires the use of compatibilisers and the resulting blend might not be 100 % biobased or it may no longer be biodegradable [2, 3]. This article outlines recent application tests to determine the effects on PLA utilising 100 % biobased flexibilisers.

## Application test design

The authors' target was to reduce the brittleness of PLA by utilising additives meeting the following requirements.

- The additive is biodegradable.
- The additive is 100 % biobased.
- The authors have anticipated the additive to be considered a valuable additive solution only if these positive features of both biodegradability and biobased origin of PLA are fully preserved.
- The additive's polarity is well-adjusted to the polarity of the polymer substrate in order to ensure optimum compatibility.
- The additive is composed of polymeric molecules according to the REACH definition. The polymeric nature of the additive molecule, once compounded into the polymer substrate, reduces the tendency of the additive to migrate from the polymer substrate bulk to its surface. This reduces undesired phenomena such as leaching, extraction of the additive, and resulting consequences such as loss of effect and stickiness of the plastics surface.

The results of this development project are 100 % biobased flexibilisers MC 2178 and MC 2192. These products are liquid polyester molecules fully composed of biobased monomers. They differ in the average molecular weight and therefore, in their viscosity. MC 2178 has a viscosity of approx. 700 mPas, MC 2192 has a viscosity of approx. 5,000 mPas, both measured at 20°C according to DIN 53019 (Brookfield method).

The following additives were tested as reference materials in addition to MC 2178 and MC 2192:

- Glycerine
- Triacetin (Glycerine triacetate)
- ESBO (Epoxidised soybean oil), typically used as secondary plasticiser in PVC
- ATBC (Acetyl tributyl citrate)
- PBAT, biodegradable polymer often used in blends with PLA

Triacetin and ATBC were tested despite the fact that these additives are hardly available as 100 % biobased. Acetic acid and butanol used for synthesis typically have a petrochemical feedstock. The same applies to the building blocks adipic and terephthalic acids of PBAT which is the only solid polymer among the tested products. This leads to the following biobased carbon contents, calculated with the molecular formula except PBAT:

100 % for glycerine, ESBO, MC 2178 and MC 2192

33 % for triacetin, with only glycerine but not acetic acid to be biobased

30 % for ATBC, with only citric acid but neither acetic acid nor butanol to be biobased

< 50 % for PBAT [4]

## Potential additives were tested in the following manner:

1) PLA pellets, injection moulding grade, MFR 22 g/10 min at 210°C and 2.16 kg, were dried according to the supplier's recommendation. 10 % of additive was dosed via a liquid feeding system and compounded into the PLA in an extrusion process. The maximum temperature during compounding was 200°C.

2) Injection moulding of sheets 100 x 100 x 3 mm at 190–195°C. Shore D hardness was tested shortly afterwards.

3) Tension rods were punched from the injection moulded sheets. Prior to punching, the sheets were tempered to 50°C.

4) Tension rods were stored at 20°C and 50 % RH for several days before mechanical data were tested according to ISO 527 (tension rod type 5A). Young's modulus, maximum tensile strength ,and elongation at maximum tensile strength were determined.

| | Shore D hardness |
|---|---|
| Virgin PLA (no flexibiliser) | 84.7 |
| + 10 % Glycerine | 81.5 |
| + 10 % Triacetin | 83.8 |
| + 10 % ESBO | 79.3 |
| + 10 % ATBC | 83.7 |
| + 10 % PBAT | 79.9 |
| + 10 % MC 2178 | 84.4 |
| + 10 % MC 2192 | 84.7 |

*Table 1: Shore D hardness of injection moulded PLA sheets*

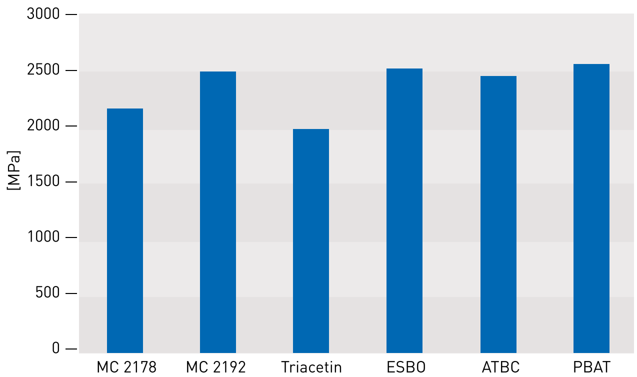


*Figure 1: Young's modulus of PLA tension rods containing flexibilisers*

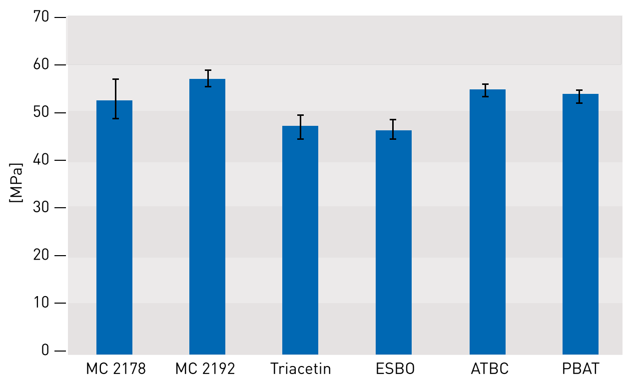


*Figure 2: Peak tensile strength of PLA tension rods containing flexibilisers*

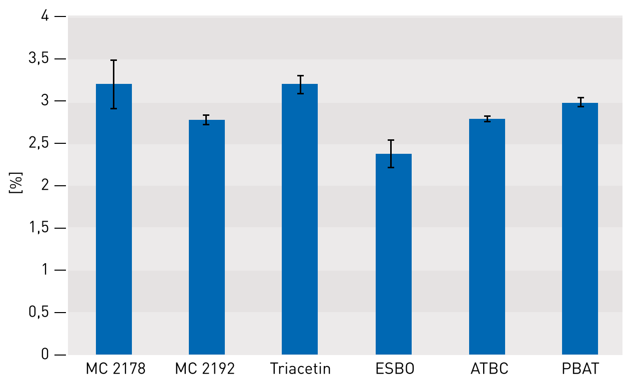


*Figure 3: Elongation at peak tensile strength of PLA tension rods containing flexibilisers*

Steps 1) and 2) were conducted at the Emery Oleochemicals' application lab located in Loxstedt, Germany while steps 3) and 4) were done at an external lab.

## Improved mechanical properties with biobased flexibilisers

Shore D hardness was determined for all samples. From the results shown in Table 1, it can be concluded that the additives, though working as plasticisers in other polymers, decrease the hardness of PLA only to a very minor extent.

Regarding the mechanical values, no tension rods could be punched from the injection moulded sheets made from virgin PLA without the addition of flexibiliser. Despite heating the sheets to 50°C to increase flexibility, these samples cracked. The samples made from PLA with glycerine as flexibiliser showed serious exudation. As glycerine was apparently not compatible with PLA, those tension rods were not tested further. All other flexibilisers were compatible with PLA at room temperature for prolonged storage.

## Mechanical properties

The tension rods were used to evaluate tensile strength and elongation. In this study, Young's modulus, peak tensile strength, and the corresponding elongation measured at this peak tensile strength were examined. Both tensile strength at break and elongation at break showed high standard deviations in their respective single values and therefore, cannot be considered.

Comparing MC 2178 and MC 2192 in Figures 1-3, MC 2178 provides a lower Young's modulus and a higher elongation, while MC 2192 provides a higher peak tensile strength. The reason for this difference in performance is the molecular weight of the two flexibilisers. Triacetin is quite comparable to MC 2178 but with a slightly lower peak tensile strength. ESBO provides both low peak tensile strength and elongation. ATBC and PBAT offer a similar performance to MC 2178 and MC 2192.

This study provides a good initial overview of the different flexibilisers' capabilities but should not replace lab and production trials at bioplastics compounders and converters.

## Summary

The features of all flexibilisers tested with 10 % dosage in PLA are summarised in Table 2.

MC 2178 and MC 2192 prove to be beneficial flexibilisers for PLA with the additional favourable characteristic of being 100 % biobased.

## Conclusion: Benefits of 100 % biobased flexibilisers MC 2178 and MC 2192

This study has proven that the use of 100 % biobased and biodegradable flexibilisers MC 2178 and MC 2192 in PLA provide comparable or superior mechanical properties compared with PLA containing conventional flexibilisers. Food contact compliance is currently being prepared. It is notable that all polymeric building blocks of MC 2178 and MC 2192 already comply with food contact regulations according to FDA CFR 21 and EU 10/2011.

### References


[1] https://greenpolymeradditives.emeryoleo.com/about-us/

[2] Effect of Different Compatibilizers on the Properties of Poly (Lactic Acid)/Poly (Butylene Adipate-Co-Terephthalate) Blends Prepared under Intense Shear Flow Field, Hezhi He et al., Materials 2020, 13, 2094 https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&ved=2ahUKEwiN9tHxq_buAhXOwAIHHdH5DbsQFjABegQIBRAD&url=https%3A%2F%2Fwww.mdpi.com%2F1996-1944%2F13%2F9%2F2094%2Fpdf&usg=AOvVaw1alhS5kXm3yZiRWc90aYzx

[3] IMPROVEMENT OF MECHANICAL PROPERTIES OF POLY(LACTIC ACID) BY ELASTOMER, Penwarat Sennan et al., The Malaysian Journal of Analytical Sciences, Vol 18 No 3 (2014): 669 – 675 http://www.ukm.my/mjas/v18_n3/Penwarat_18_3_21.pdf

[4] https://www.bio-based.eu/market_study/media/files/15-05-13_Bio-based_Polymers_and_Building_Blocks_in_the_World-nova_Booklet.pdf


i https://greenpolymeradditives.emeryoleo.com/additives/

*Table 2: Mechanical data of PLA tension rods with different flexibilisers*

| | Biobased Carbon Content [%] | Compatibility with PLA | Mechanical Properties |
|---|---|---|---|
| MC 2178 | 100 | + | Higher elongation than MC 2192 |
| MC 2192 | 100 | + | Higher peak tensile strength than MC 2178 |
| Glycerine | 100 | - | not determined due to exudation |
| Triacetin | < 50 | + | Similar to MC 2178, but lower peak tensile strength |
| ESBO | 100 | + | Lowest peak tensile strength and elongation |
| ATBC | < 50 | + | In general similar to MC 2178 and MC 2192 |
| PBAT | < 50 | + | In general similar to MC 2178 and MC 2192 |