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Elasto-Plast

TPE boosts toughness of PLA tapes

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PLA (polylactic acid) is produced from biomass and has special piezoelectric properties, i.e. it can convert mechanical strain into electrical charges. At present, these properties are hardly exploited. The **BIOHARV**-project[1] optimises the formulation and production processes of PLA-based mono-oriented films, tapes and fibres to enable the use of these materials in new micro-energy recovery applications for the power supply of smart and communicating sensors.

PLA has many advantages, in addition to its renewability, it has high mechanical strength and is relatively easy to process. However, its inherent brittleness is an important drawback that significantly limits a wide application of the material. This brittleness also proved problematic in the production and processing of PLA tapes for energy recovery prototypes. The tapes were very difficult to handle due to splitting along the machine (i.e. longitudinal) direction. A common strategy to improve the properties of (bio-based) plastics is to mix them with plasticisers or more flexible polymers. This is also an efficient, cost-effective way to increase the toughness of PLA. The use of flexible polymers is particularly interesting because of the limited loss in tensile strength and modulus of elasticity compared to the application of plasticisers, provided that a fine morphology and suitable compatibility of mixtures can be obtained.[2]

An interesting type of materials in this context are thermoplastic elastomers (TPE), a collective term for plastics that are elastic at room temperature and become plastic and can be reshaped when heated. These plastics combine the properties of classic elastomers (flexibility, elasticity) with the processability of thermoplastics. Most conventional thermoplastics exhibit rather low wear resistance and flexibility. TPE can be used as an alternative to meet these desired requirements. In addition, the impact strength of conventional thermoplastics can be improved by adding a TPE. The **ELASTOPLAST**-project[3] aims at gathering knowledge about the relationship between morphology, process conditions and product properties of TPE as well as the new developments in of the field of this unique technology. The main goal of the project is to familiarise companies with the rich possibilities that TPE offer to increase product properties or improve the processability of classical polymers.

[1] www.gotos3.eu/bioharv
[2] Ming Wang, Ying Wu, Yi-Dong Li & Jian-Bing Zeng (2017): Progress in Toughening Poly(Lactic Acid) with Renewable Polymers, Polymer Reviews, DOI: 10.1080/15583724.2017.1287726
[3] https://interreg-elastoplast.eu/

The acquired knowledge from both above mentioned projects was used to develop PLA tapes with improved mechanical properties. For this purpose, a SEBS-based TPE (Thermolast®K TF7ADN from the Kraiburg company) was selected, as it previously gave good results in PLA injection moulding applications. This TPE was compounded with PLA (Luminy® L130 from the Total Corbion company) in different proportions (from 1 to 10%) and then processed via tape extrusion. The effect of the TPE became apparent at macroscopic level starting from a concentration of 5%. The tapes (thickness 40-70 µm, width 11-14 mm) evolved from transparent, slightly undulated tapes that split very easily along the machine direction to matte-white, smoother tapes that no longer show any cracks, even at higher draw ratio (DR), as shown in Figure 1.

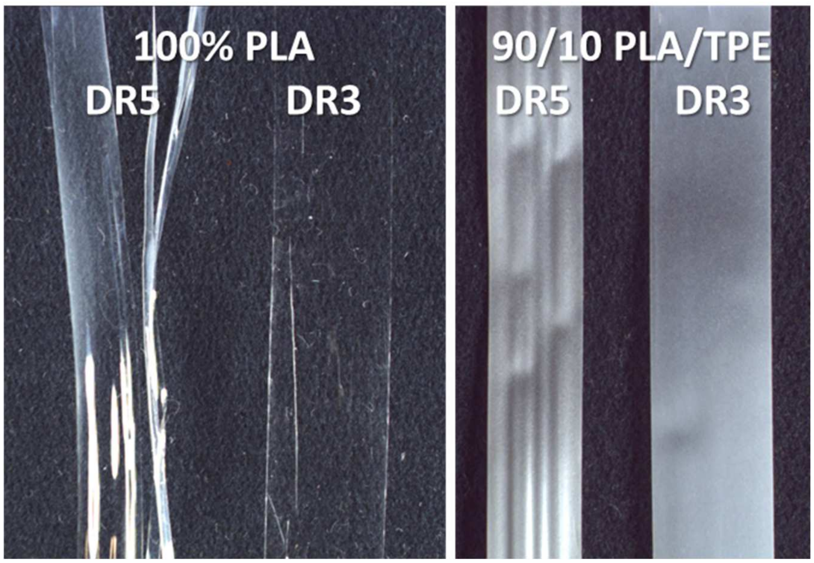

Figure 1 Pure PLA tapes (left) versus 90/10 PLA/TPE-blend tapes (right) with draw ratio (DR) 3 and 5.

The mechanical properties of the materials were determined by means of tensile tests in the machine direction of the tapes. The resulting tensile strength (tenacity) and modulus of elasticity (E-mod) of PLA tapes with TPE content ranging from 0 to 10% are shown in Figure 2. The tensile strength appears to show a slight upward trend with increasing TPE content, although the differences are very small, while the modulus of elasticity appears to be unaffected. The TPE therefore has little or no effect on the mechanical properties in the machine direction of the tape.

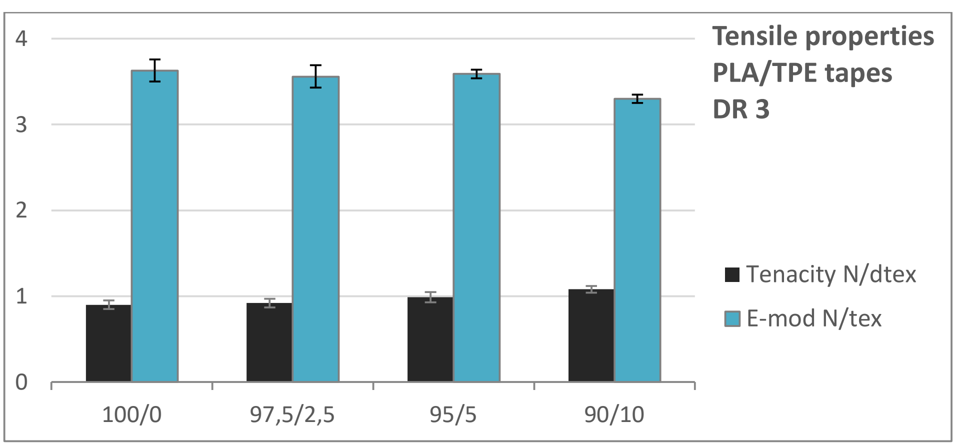

Figure 2 Tensile strength (Tenacity, N/dtex) and modulus of elasticity (E-mod, N/tex) of different PLA/TPE-blend tapes (DR 3).

Due to the limited width of the tapes, it is impossible to determine the strength in the cross (i.e. transverse) direction using the universal testing machines applied for standard tensile tests on yarns (EN ISO 2062) or plastics (ISO 527). It was therefore decided to perform tensile tests in the cross direction of the tapes using DMA ("dynamic mechanical analysis"), a technique that enables the characterisation of smaller samples. The results are presented in Figure 3. The stress-strain plot of 100% PLA clearly shows the course of a brittle fracture, while the 90/10 PLA/TPE tape shows a tough fracture with plastic deformation. The maximum force the materials can undergo is similar, but the maximum elongation of the 90/10 PLA/TPE tape is ten times higher than the elongation of the pure PLA tape. It can therefore be concluded that the TPE has a positive effect on the mechanical properties in the cross direction of the tape.

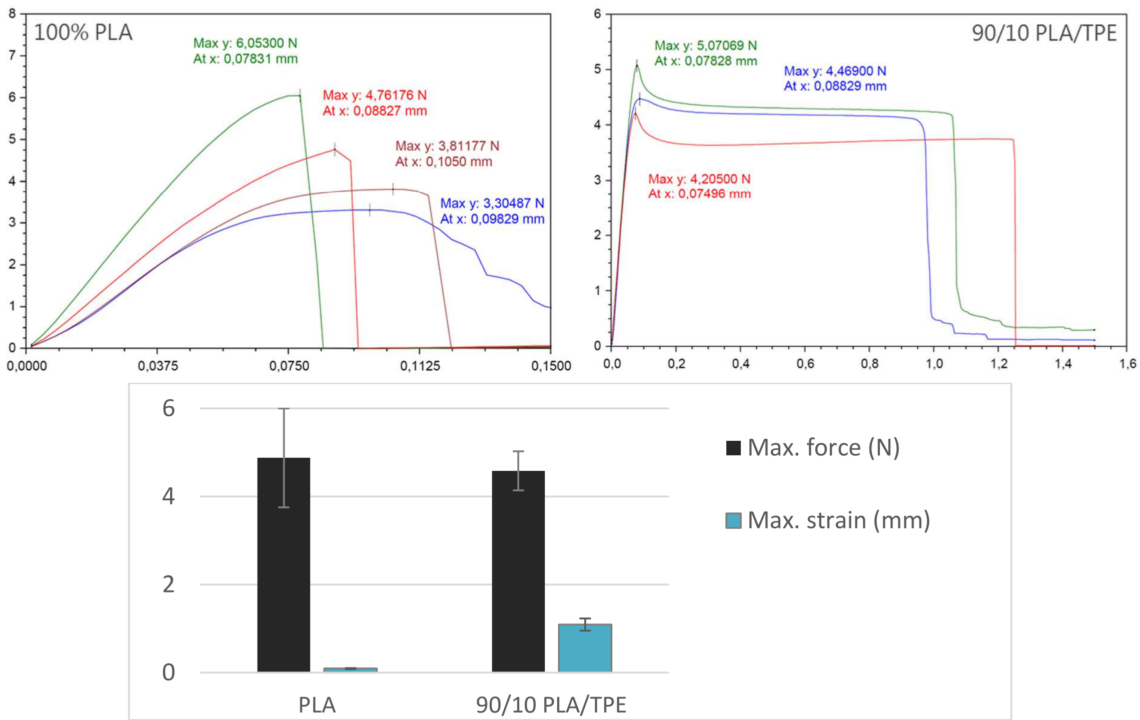

Figure 3 Results of DMA measurements: stress-strain plots (top) and maximum force and deformation (bottom) for 100% PLA and 90/10 PLA/TPE tapes (DR 3).

In order to study the mixing of the TPE and PLA phases, SEM ("scanning electron microscopy") images were taken of the fracture surface of injection moulded test samples. On the electron microscopy images (see Figure 4), two phases can clearly be distinguished: (i) TPE particles dispersed in the (ii) PLA matrix. These rubbery particles can absorb and dissipate part of the distortion energy by means of plastic deformation. The final effect on material strength depends on particle size and dispersion as well as compatibility with the plastic matrix.[2]

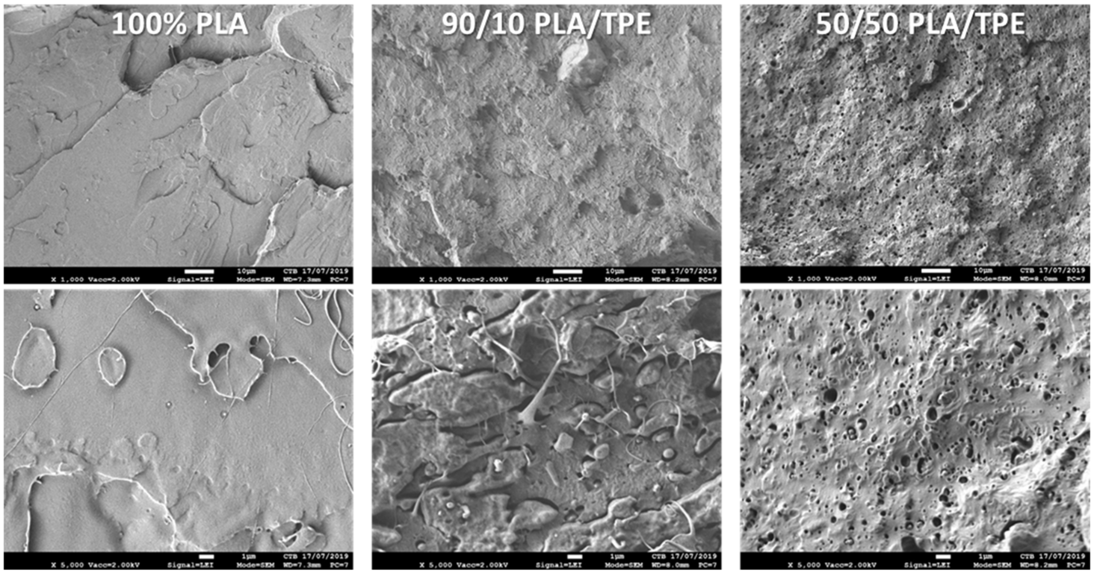

Figure 4 Scanning electron microscopy images of the fracture surface of 100% PLA, 90/10 PLA/TPE and 50/50 PLA/TPE injection moulded test samples.

Finally, piezoelectric energy recovery was evaluated by means of bending tests. Previous experiments with PLA films have already shown that both the crystallinity and orientation of PLA are important factors for higher energy recovery. A higher DR generally leads to a higher polymer chain orientation and crystallinity.[4]

The latter was also observed for both pure PLA and PLA/TPE blend tapes, where an increase in DR from 3 to 5 resulted in a twofold increase in crystallinity (from ±20% to ±40%). As the energy recovery measurements had not yet been completed at the time of publication, the data will be published in a follow-up article. However, the first results do not indicate a negative effect of the TPE on the energy recovery capacity of the tapes; on the contrary, the capacity generated by blend tapes generally appears to be higher than for pure PLA. Nevertheless, the effect of the TPE on energy recovery as well as the reproducibility of energy measurements needs to be further investigated before unambiguous conclusions can be drawn.

In general it can be concluded that the addition of 5 to 10% of the SEBS-based TPE TF7ADN leads to an improvement of the mechanical properties of PLA tapes, mainly in the cross direction. The blend tapes also don't show cracking at higher DR and are easier to handle for the production of energy recovery prototypes. Evaluation of the energy recovery is still ongoing, but the first results indicate a positive influence of the TPE on the generated power. Nevertheless, the effect of the TPE on energy recuperation as well as the reproducibility of energy measurements should be further investigated. In addition, different possibilities for further optimization of the crystallinity and the energy recovery capacity will be studied by means of extrusion trials on **Centexbel's monofilament extrusion line[5].**

The extrusion line has four sets of rolls and three ovens (two hot air- and one steam oven) which allows a 3-stage drawing process (instead of a 1-stage drawing). Moreover, the line offers the choice

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[4] Stubbe, B. et al, *Biobased piëzo-elektrsiche PLA-films voor opkomende IoT-toepassingen*, Unitex nr. 1/2019, p.13-16, 1/03/2019

[5] https://www.centexbel.be/en/pilot-platforms/extrusion-platform

between different cooling methods (water bath, chill roll or air cooling). Finally, it is also the intention to investigate alternative, bio-based TPE as well as the combination with MA-g-SEBS, which could possibly bring about a further improvement in mechanical properties through a better interaction between the two phases.

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