Multicomponent Blends based on Polyactic Acid, Polyhydroxybutyrate and thermoplastic Starch

Introduction
Currently, biodegradable polymers have raised great interest as the decreasing reserve of fossil raw materials and also common use of petrol-based polymer materials have great impact on the environment. Therefore, application of polymers, highly resistant to degradation, results in a large amount of municipal and industrial plastic waste which is then being stored for many years in nature or in landfills. Material recycling is only partial solution of full ecological application of polymers, including polymer waste elimination. Biodegradable polymers based on renewable raw materials seem to be the best solution of this serious ecological problem including polymer waste processing.1 Biodegradable materials have many special suitable properties for some application but processing properties, brittleness and sensitivity to water and air moisture limit their application on an industrial scale.2 Polyactic acid (PLA) is a biodegradable polyester with high strength and high modulus. The current method for PLA preparation is more ecological than the other processes with regards to the emissions of carbon dioxide, i.e. the synthesis of monomer (lactic acid) from glycerol using cascade bio- and chemocatalysis.3 In addition, if D,L-PLA is synthesized, amorphous product with improved toughness is obtained; but again, the elongation at break (ε) does not achieve values higher than tens of percents in this case. Also, the effect of physical ageing of PLA causes rapid decrease of PLA flexibility in a very short time period (several hours) after the melt processing of PLA regardless of the PLA synthesis method.4

Starch is usually used in biodegradable polymer blends to improve biodegradability as well as to reduce the price of the final material. On the other hand, it decreases the mechanical properties of the blends. To improve starch dispersion in polymer matrix and physical properties of the blend, thermoplastic starch (TPS) is applied. TPS is usually prepared by mixing of native starch with plasticizers in a twin-screw extruder at elevated temperatures. The mixture of glycerol and water is usually used as the plasticizer.5

Polyhydroxybutyrate (PHB) is a biodegradable thermoplastic polymer with a strong potential for industrial purposes due to its relatively high crystallinity (50–70 %), excellent gas barrier and physical properties similar to those of polypropylene, but its thermal stability during the melt processing is very low and similarly to PLA, high fragility of PHB limits its applications in thin wall products like packaging films. The processability and mechanical properties of PHB can be improved by its combination with other polymers in the polymer blends.

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Combination of PHA, especially PHB with TPS is rather problematic due to high sensitivity of PHB to degradation via the alcoholysis degradation mechanism in the presence of alcholic OH groups. Polyls which are usually used as starch plasticizers cause strong degradation of PHB. Janigova et al. found that degradation of PHB is strongly accelerated by presence of glycerol which is stronger prodegradant than water. Glycerol leads to much faster alcoholysis of ester bounds in the main chain of PHB than in case of hydrolysis by water. According to the work, also ethylene glycol is a stronger prodegradant than glycerol. Therefore, blending of TPS with the PHB containing polymeric matrix needs to find an effective modification which will be able to protect PHB polymer against alcoholysis degradation. According to patent application, the addition of anhydrides during the blend preparation leads to improved dispersion of TPS as well as to better mechanical properties.

In this work, blends based on PLA and PHB containing plasticized starch were prepared using a twin-screw extruder. The phthalic anhydride was used as protective modifier. The prepared pellets were used to prepare films using a single-screw extruder. The objective of the present work was to study the influence of concentration of the main components in the composition on mechanical properties of PLA/PHB blends containing plasticized starch. The method of the design of experiment was chosen in order to obtain a comprehensive description of the studied system.

### Experimental

#### Materials

<table>
<thead>
<tr>
<th>PLA (PLA 4042D; product of Nature Works, USA): m.p. = 150–162°C; M = 120000 g.mol⁻¹; MFI = 8 g per 10 min</th>
<th>Starch (Meritena 100; product of Amylum, Slovakia): M = 692 g.mol⁻¹; pH: 6.7; particle size: 5-20 µm; surface area: 1.79 m²/g. PHB (product of Biomer, Germany): M = 290000 g.mol⁻¹; Tₘ = 175°C; MFI = 15-30 g per 10 min</th>
</tr>
</thead>
</table>
had the width of 70 mm and the height of 0.55 mm. The polymer melt was extruded on the surface of a chill-roll chilled with water at 15°C.

### Mechanical properties measurement

Tensile strength at break (σb) and elongation at break (εb) were measured according to standard STN ISO 527 using a Zwick machine at the cross-head speed of 50 mm min⁻¹. Test specimens had shape of the strips, 15 mm wide and 100 mm long. Working distance at extensometer was 30 mm. Mechanical properties were measured 24 hours after the film preparation and also after one week, two weeks and one month of storage at 23°C and 50% of RH to determine the storage time influence.

### Results and discussion

To protect PHB against to alcoholysis degradation, it is necessary to add an effective modifier to the blend. Based on results in work8, the phthalic anhydride was used in all prepared blends. Effect of main components concentration on the blend properties was studied using methodology of design of experiment (DoE) while the 3-factor 5-level DoE was used for experimental area description. The regression equations obtained from DoE evaluation were used for optimisation procedure. The following weight ratios were chosen as factors of experiment:

\[
\begin{align*}
x_1 &= \text{PHB} \\
x_2 &= \text{PLA} \\
x_3 &= \text{Starch} \\
x_4 &= \text{ATBC}
\end{align*}
\]

where PHB is the weight of polyhydroxybutyrate, PLA is the weight of polylactic acid, starch is the weight of corn starch without any additives, ATBC is the weight of acetyltributylcitrate.

The condition of Doe listed in table 1 were calculated according to desired concentration ranges of the blend components:

- PLA from 40 to 60 wt%
- PHB from 5 to 20 wt%
- Starch from 10 to 30 wt%

For each blend glycerol (plasticizer for starch) and phthalic anhydride (modifier) were used in constant relative amount as follow:

- weight ratio Glycerol/Starch was kept 40/60
- weight ratio PHAN/(Starch+Glycerol) was kept 1/100

Composition of all blends prepared in DoE is listed in the table 2.

All blends and films with composition according to table 2 were prepared. Mechanical properties are listed in table 3 and 4.

The results were further processed by analysis of variance (ANOVA) and by regression analysis. The following regression-
on model was applied for the used type of DoE.

\[ Y = b_0 + \sum_{i=1}^{4} b_i x_i + \sum_{j=1}^{4} b_{ij} x_j + \sum_{i=1}^{4} b_{ii} x_i^2 \]

where \( b_0, b_i, b_{ij}, \) and \( b_{ii} \) are regression coefficients, \( k \) is the number of factors (in our case \( k = 3 \)).

Standard tables of ANOVA were calculated for all measured parameters. Table 5 shows ANOVA table for tensile strength at break for films measured 24 hours after film preparation where:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( \varepsilon_{b1} ) (1d)</th>
<th>( \varepsilon_{b2} ) (1w)</th>
<th>( \varepsilon_{b3} ) (2w)</th>
<th>( \varepsilon_{b4} ) (1m)</th>
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</table>

Fig. 1: Dependence of \( \sigma_b \) on starch and PHB content in PLA/TPS/PHB blends, measured one day after film extrusion (concentration of ATBC: 15%, \( x_3 = -1,682 \)).

Fig. 2: Dependence of \( \sigma_b \) on starch and PHB content in PLA/TPS/PHB blends, measured one day after film extrusion (concentration of ATBC: 23%, \( x_3 = 0 \)).

Fig. 3: Dependence of \( \varepsilon_b \) on starch and PHB content in PLA/TPS/PHB blends, measured one day after film extrusion (concentration of ATBC: 30%, \( x_3 = 1,682 \)).

Fig. 4: Dependence of \( \varepsilon_b \) on ATBC content (factor \( x_3 \)) and PHB content (factor \( x_1 \)) in PLA/TPS/PHB blends, measured one day after film extrusion.
s1 - the variability of the linear part of the equation
s2 - the variability of the non-linear part of the equation
SR – a residual variability
SE – an experimental variability
SLF – variability correspond to the lack of fit
sb0, sbi, sb iiasbij - standard deviations of regression coefficients
bc0, bci, bciia bcij - critical values of regression coefficients (significance level 0.05)
Fcrit – critical values of F criteria (significance level 0.05)
s – the sum of squares
f – the number of degrees of freedom
s^2 – the variance

The same analysis was done for all measured properties. Results of regression analysis for all evaluated properties are shown in the tables 6 and 7. The coefficients typed in bold (tab. 6 and 7) are statistically significant at a significance level of 0.05%.

Dependencies of tensile properties of PLA/PHB/TPS flat films measured 24 hours after the preparation are shown in Figs. 1-4 in form of 3D diagrams. The tensile strength at break (σb) was influenced by all three factors without mutual interactions. The tensile strength was increased and passed the maximum depending on the starch content of the blend. Tensile strength at break was simultaneously decreased by increasing concentration of both PHB and ATBC (Fig. 1-3). All coordinates are in the coded values.

Based on the obtained results, we can see that it is possible to achieve tensile strength at break at the level of 18 MPa by a suitable combination of the composition of the mixture. The elongation at break depends only on the PLA/PHB ratio (factor x1) and on the concentration of the plasticizer in the blend (factor x3). The increasing PHB concentration caused decreasing elongation at break. The concentration of ATBC affects this property only in relation to the PHB concentration (only interaction x1/x3 is significant). By increasing the concentration of PHB in the PLA/TPS blend, it appears that the plasticizer is reallocated between these two polymers, which must necessarily affect the properties of the mixed material where the two polymers form the matrix. The change in starch concentration in the blend does not have a statistically significant effect on PLA/PHB/TPS foil flexibility. Based on this investigation it can be assumed that TPS is sufficiently deformable in the domain during the tensile test and TPS domains do not act as significant stress concen-
The total flexibility of the material is given only by the flexibility of the polymer PLA/PHB matrix.

Dependence of elongation at break (εb) of PLA/PHB/TPS flat films measured 24 hours after the preparation is shown in Fig. 4.

Different situation was observed in mechanical properties measured one week after film preparation. The properties of the films depended significantly only on the concentration of ATBC (factor x3) one week after film extrusion. Tensile strength at break was linearly decreased with increasing content of plasticizer and elongation at break was passed over the maximum. The simple dependencies of the two monitored parameters on the ratio x3 in the coded coordinates are shown in the figures 5 and 6.

The tensile strength was slightly decreased with the storage time and the elongation at break reached the maximum in the area around the coded level x3 = -1 which corresponds to the real concentration of ATBC in polymer matrix PLA/PHB of 18.5%.

After two weeks of storage time tensile strength at break (Fig. 7) depends only on concentration of plasticizer but elongation at break (Fig.8) depends on factor x2 and x3 (starch and ATBC content).

It was shown, that the mechanical properties depend not only on the composition of the blend but also on the storage time. Changes occur mainly in extremely low or extremely high concentration ranges of these components. This is particularly evident from Fig. 4, 6 and 8, where the elongation at break was decreased after one or two weeks of storage at the edges of the experimental space and remains at approximately 200% in the centre of the experimental space. It can be assumed, that these effects can be connected to liquid additives (ATBC, glycerol) re-distribution between polymers (PLA, PHB and starch) during the storage time. The physical ageing can also take a role in mechanical properties changes.

Regression equations calculated based on experimental data evaluation (DoE) were used to determine an optimal blend composition. Based on the DoE, information about the effect of observed factors on the mechanical properties and their changes during short-term storage was obtained. In addition, a system of equations was obtained which describes the dependence of the properties on the composition of the blend. Using the algorithm of Solver routine from Microsoft Excel, two optimized blends were simulated and calculated as follows:

OPTσ – optimization criterion - the maximum tensile strength at break without any limits

OPTε – optimization criterion - the maximum value of the elongation at break at tensile strength at break after two weeks of storage of at least 14 MPa.

Based on required limits given above, the coded levels of each factor were calculated (tab. 8) using Solver from MS Excel. The calculated composition of the blends in the coded coordinates of the factors was recalculated to weight composition (tab. 9). The blends were then prepared under the same conditions as the blends for the DoE and mechanical properties were measured. Comparison of measured and calculated values of tensile properties is shown on Fig. 9-12.

Based on the obtained results it can be concluded, that the mathematical models adequately describe the experimentally obtained values of mechanical properties, which is demonstrated by close values of the measured mechanical properties with the values calculated with respect to the experimental variability (Figs. 9, 10). Tensile strength at break (blend OPTσ) measured one month after extrusion is almost the same as the value measured one day after preparing of film and achieves 15 MPa (Fig. 9). In case of the blend OPTε the measured value of elongation at break is even slightly higher than the calculated value one month after film storage (Fig. 10).

The measured tensile strength values (blend OPTσ) are very close to the calculated and even one month after the extrusion on the strength is 15 MPa (Fig. 11). This corresponds to the minimum tensile strength at break criterion given in the optimisation procedure (14 MPa). The Fig. 12 shows the measured and calculated values of elongation at break. The value (εb) was slightly decreased due to the storage time. The elongation at break va-

![Fig. 9: Measured and calculated values of tensile strength at break for the optimized blend OPTσ, from one day to one month after extrusion.](image)

![Fig. 10: Measured and calculated values of elongation at break for the optimized blend OPTε, from one day to one month after extrusion.](image)
lue did not fall below the calculated value, not even one month after the film preparation. Vice versa, the measured value is even slightly higher and reaches 170%.

**Conclusion**

Based on the obtained results, it can be concluded that an addition of PHB influences the properties of biodegradable PLA/TPS polymer blends. Results of DoE show that there is an optimal composition within which maximal elongation at break can be reached. The blends exhibited sufficient tensile strength and elongation at break also at higher starch content. Values of elongation at break remain at approximately 200% in the centre of the applied experimental space. Therefore, the materials can be considered suitable for packaging applications in terms of their flexibility. With the addition of PHB, acceptable value of tensile strength can be achieved, also in case of higher starch content. The effective modification using phthalic anhydride is able to protect PHB polymer against alcoholysis degradation due to the action of glycerol. The DoE regression equations were used for optimization of blend composition with respect to the required mechanical properties. The mathematical models describing the real dependencies of mechanical properties on blend composition are sufficiently accurate. Therefore, it will be possible to calculate the composition of the mixtures with respect to the required properties for individual application with sufficient precision. The presented combination of polymers represents a biodegradable material based fully on renewable polymeric raw materials providing suitable mechanical properties including flexibility of the thin wall products. Blending of PHB with PLA in combination with plasticized starch increases the application potential of renewable biodegradable thermoplastics on an industrial scale.

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**References**