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Cross-Linked Hydrophobic Starch Granules in Blends with PLA

The majority of native starch is used in the food sector and in the paper industry. Only a small amount is used in polymer engineering. One reason for the reluctance of the plastics processing industry to use starch as a filling material in polymer blends is the unsatisfactory mechanical behavior of starch when combined with thermoplastics. Another reason is the hydrophilicity of starch. In order to make these materials capable of competing, an amelioration of the mechanical properties is compulsory. By means of modifying the native starch and optimizing the compounding process, it is possible to improve the performance of starch blends, and, thus, increase the number of application areas of these materials. For this reason, native starch was modified with a cross-linking agent using a laboratory mixer. Subsequently, the modified starch and poly(lactic acid) were compounded using a co-rotating twin screw extruder. Cross-linking of the native starch in the laboratory mixer resulted in an increase in the mechanical strength of the starch blends. In addition, the blends with cross-linked starch displayed lower moisture absorption levels than blends with native starch as a filling material.

1 Introduction

In the last 30 years, thermoplastic starch and native starch have been used for compounding starch blends (Bin-Dahman et al., 2015; Lai et al., 2006; Roy et al., 2011; Schwach and Avérous, 2004; Yu et al., 2006). In contrast to the processing of native starch as a filling material, thermoplastic starch is made during the compounding process by adding water and plasticizers to induce chemical destructuring in addition to thermomechanical destructuring (Avérous and Halley, 2009; Feldmann and Fuchs, 2015; Huneault and Li, 2012). However, the largest proportion of native starch is still used in the food sector and in the paper industry (Chen et al., 2010; Ellis et al., 1998). Only a small portion is used in polymer engineering for short-dated products, like “loose-fills”. Reasons for the reluctant utilization are the hydrophilic properties of starch as well as the insuf-

ficient mechanical properties of starch blends (Avérous and Halley, 2009; Fink et al., 2009; Mathew and Dufresne, 2002; Nabar et al., 2006; Zerroukhi et al., 2012).

Several methods exist for the improvement of the properties of native starch (Hu et al., 2016; Lawal et al., 2015; Sujka et al., 2015). Chemical Modification, ultrasonic and microwave treatment, ball milling, oxidation, enzymatic hydrolysis, annealing, and gamma irradiation are just some options for adapting the properties of starch to the requirements of its application areas (Radosta et al., 2016; Salimi et al., 2016; Shi et al., 2015; Sujka et al., 2015; Yang et al., 2015). Another option for utilizing native or thermoplastic starch is to blend it with hydrophobic plastics, like polyolefins, or with bioplastics, like poly(lactic acid) (PLA) (Beg et al., 2016; Lai et al., 2015; Mittal et al., 2015; Sangeetha et al., 2016). Starch blends with PLA contain hydrophilic starch and hydrolysis-sensitive PLA. There are several provisions that must be adhered to before and during the processing of these materials. For instance, pre-drying the starch prior to compounding it on a twin screw extruder is important to prevent possible hydrolysis of the PLA from being induced by the water contained in the moist starch (Liu et al., 2010; Wang et al., 2007; Yu et al., 2011). During the drying process, the selected temperature has a very great significance since the moisture content can be minimized only by sufficiently high temperatures and not by a prolonged drying time (Kovács and Tabi, 2011).

The mechanical properties of starch blends with PLA vary on a wide range depending on the starch/PLA type and content, the moisture content of the starch prior to compounding, the moisture content of the blend during examination, etc. (Huneault and Li, 2012; Sangeetha et al., 2016; Yu et al., 2006). Due to their partially insufficient mechanical properties and the moisture-sensitive behavior of starch blends with PLA, these materials face a low level of acceptance in the plastics processing industry for use in medium-term or even long-term products.

In order to expand the areas of application, several research projects focused on improving the properties of starch blends with PLA. Options for modifying the blends include using additives like maleic anhydride (Zhang and Sun, 2004) or poly(ethylene glycol) (Jacobsen and Fritz, 1996). In the past, another reagent for the modification of cross-linked native starch was epichlorohydrin (Kartha and Srivastava, 1985; Kuniak and Marchessault, 1972). Owing to its very high toxicity, cross-linking starch using epichlorohydrin is a matter of

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marginal interest today, even though the improvement of the mechanical properties was promising while using this reagent. Additional disadvantages of using epichlorohydrin during the modification of starch are the preliminary work needed and the duration of the cross-linking reaction.

In this study, the surface of native potato starch granules was modified with the mildly toxic cross-linking agent glycidyl ether and a suitable catalyst. After cross-linking the starch using a laboratory mixer, the modified starch and poly(lactic acid) were compounded using a co-rotating twin screw extruder. Subsequently, the starch-filled PLA blends were processed into samples in an injection molding machine. The influence of the cross-linking process on the impact strength, tensile properties and moisture absorption was investigated. The aim of the analyses was to enhance the compatibility between starch and PLA to improve the mechanical properties and to reduce the moisture absorption, and, in turn, to expand the areas of application of starch blends with PLA.

2 Materials and Methods

2.1 Materials

PLA (Ingeo Biopolymer 3052D, CAS 9051-89-2) was obtained from NatureWorks LLC, Minnetonka, USA, and was used as the plastic matrix for the starch blends. Predominantly corn starch was used as raw material for the synthesis of PLA. The PLA has had a D-Lactide content of 4.3%, a MFI of 56.5 g/10 min (5 kg/200 °C) and a molecular weight of 1,39E+05 g/mol. Native potato starch (Superior, CAS 9005-25-8) was obtained from Emsland-Stärke GmbH, Emlichheim, Germany, and was used as the filling material. The composition of the starch was 0,34% ash, 0,078% phosphorus, 0,08% protein and 22% amylose. The glycidyl ether 1.4-bis [(2.3-epoxypropoxy)methyl]cyclohexane (Polypox R 11, CAS 14228-73-0) from the Dow Chemical Company, Midland, USA, was used as cross-linking agent. Imidazole (Glyoxalin, 1,3-Diaza-2,4-cyclopentadien, CAS 288-32-4) from Carl Roth GmbH + Co. KG, Karlsruhe, Germany, was used as catalyzer in the laboratory mixer during the cross-linking process.

2.2 Starch Preparation

The native potato starch was pre-dried in a convection oven (Heraeus Function Line) at 105 °C for at least 24 h until a

moisture content below 1 wt% was achieved prior to beginning the cross-linking process in the laboratory mixer (model FML 10, Zeppelin Systems, Kassel, Germany). The moisture content was measured using a moisture measuring device (model MA 100, Sartorius, Goettingen, Germany).

2.3 Modification in the Laboratory Mixer

A laboratory mixer was loaded with the pre-dried starch. The starch was heated to defined temperatures (140 °C, 160 °C, 180 °C, 200 °C, 220 °C) by means of friction (3 600 min⁻¹). After reaching the particular temperatures, the mixer was paused and a mixture of cross-linking agent and catalyzer was added using a syringe. A total of 1 wt% of cross-linking agent was used in the mixer in relation to the starch amount. The amount of catalyzer was 4 wt% relating to the amount of cross-linking agent. After adding the components, the laboratory mixer was started again (1 800 min⁻¹) for 5 min. Afterward, the modified starch was extracted and stored in hermetically sealed bags in order to once again be stored in an airtight container to prevent moisture absorption prior to the compounding process.

2.4 Compounding

The blends were compounded with a ZSE 18 HPe (Leistritz, Nuremberg, Germany) co-rotating twin screw extruder that had a screw diameter of 18 mm and a processing length of 40D. Prior to compounding, the PLA was dried (60 °C) using an air dryer system (model TR-Dry-Jet Easy 15, Toro Systems, Igensdorf, Germany) until a moisture content of 0.1 wt% remained. The starch (50 wt%) and the PLA (50 wt%) were fed into the barrel of the extruder using a gravimetric dosing system. The rotation speed of the screws of the extruder equaled 200 min⁻¹. The polymer strand was cooled down on a discharge conveyor and was granulated using a strand granulator (model SGS 25-E, Scheer, Korntal-Muenchingen, Germany). In addition to the blends with modified starch (MST), a blend with native starch (ST) was compounded for reference purposes (Table 1). A screw configuration that included kneading and mixing elements was used (Fig. 1). The adjusted temperatures for the compounding process ranged from 170 to 200 °C (Fig. 1). The average melt temperature, which was measured with a sensory element in the extrusion die (200 °C), was 204 °C. The throughput was 2.5 kg/h on average. The moisture

| Notation | Starch content | PLA content | Max. temperature in mixer |
|---------------------|------------------------|-------------|---------------------------|
| 50ST/50PLA | 50 wt% native starch | 50 wt% PLA | – |
| 50MST(140 °C)/50PLA | 50 wt% modified starch | 50 wt% PLA | 140 °C |
| 50MST(160 °C)/50PLA | 50 wt% modified starch | 50 wt% PLA | 160 °C |
| 50MST(180 °C)/50PLA | 50 wt% modified starch | 50 wt% PLA | 180 °C |
| 50MST(200 °C)/50PLA | 50 wt% modified starch | 50 wt% PLA | 200 °C |
| 50MST(220 °C)/50PLA | 50 wt% modified starch | 50 wt% PLA | 220 °C |

Table 1. Compounded starch blends

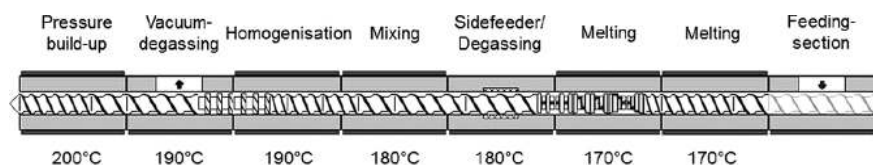


Fig. 1. Screw configuration and temperatures

contents of the starch blends after compounding were below 0.1 wt%.

2.5 Injection Molding

To prevent moisture from influencing the results, the starch blends were dried in an air dryer system (60 °C) for 24 h as a precaution prior to injection molding. Subsequently, test specimens were assembled according to DIN EN ISO 527-1A for the mechanical and analytical investigations using an injection molding machine (Allrounder 270 S, Arburg, Loßburg, Germany) with a screw diameter of 25 mm and a clamping force of 350 kN. A hot runner needle valve nozzle was used to prevent the sprue from tearing in the runner. The cycle time was approximately 50 s, including a cooling time of 25 s. In addition to the starch blends, specimens made of pure PLA were assembled for reference purposes. The process temperatures are shown in Table 2. After assembly, the specimens were stored in an airtight container to prevent possible moisture absorption.

2.6 Characterization

The starch blends were investigated while in a dry state and at room temperature.

2.6.1 Thermogravimetric Analysis of Starch

The thermal stability of the native starch when exposed to different temperatures (140 °C, 160 °C, 180 °C, 200 °C, 220 °C) was investigated using a TGA-Module Q 500 (TA Instruments, New Castle, USA) to evaluate the maximum temperatures for the cross-linking process in a synthetic air atmosphere. Prior to beginning the testing cycle, the native starch samples were heated to 100 °C at a heating rate of 10 K/min to pre-dry them. This temperature was sustained for 90 min, as was a constant weight. Then, the starches were heated further at a heating rate of 8.5 K/min until their specific temperatures were reached (140 °C, 160 °C, 180 °C, 200 °C, 220 °C) in order to evaluate the degradation of the materials. A heating rate of 8.5 K/min

was used because it corresponds well to the heating rate the materials are exposed to during the modification process in the laboratory mixer.

2.6.2 Differential Scanning Calorimetry of the Crosslinking Reaction

Differential scanning calorimetric (DSC) investigations were carried out using a DSC 1 (Mettler Toledo, Columbus, USA) at heating rates of 4.5, 6.0, 7.5, 9.0 K/min in a temperature range of 140 to 220 °C in a nitrogen atmosphere. Mixtures of cross-linking agent and catalyzer (mixture ratio analogous to ratio described in 2.3) were investigated to obtain evidence of the temperature and time required for the cross-linking reaction to run its course, and to evaluate the reaction kinetics. Model-free kinetics has been used to transfer the results of the regular DSC measurements into a diagram showing the conversion of the reaction between cross-linking agent and catalyzer. Model-free kinetics is a suitable tool to describe chemical reactions (Vyazovkin, 2006).

2.6.3 Scanning Electron Microscopy

The blend morphology was investigated using a scanning electron microscope (SEM) MV2300 (CamScan Electron Optics, Beaverton, USA). Fractured (freeze-fractured surface) samples were sputter coated with gold prior to the examination. Images with a magnification of 250 were taken to evaluate the distribution of the starch and the bonding between the starch and the PLA matrix.

2.6.4 Moisture Absorption

To investigate the moisture absorption, five specimens of each starch blend and the pure PLA were stored in a conditioning cabinet SC 340 MHG (Weiss, Reiskirchen, Germany) for fifteen days (27 °C, 65 % RH) according to DIN EN ISO 291. Prior to testing and after every five days during the testing period, the samples were weighed using a laboratory scale (Sartorius).

| Zone 1 °C | Zone 2 °C | Zone 3 °C | Zone 4 °C | Hot runner °C | Mold °C | Melt °C |
|--------------|--------------|--------------|--------------|------------------|------------|------------|
| 200 | 200 | 210 | 210 | 220 | 20 | 225–230 |

Table 2. Process temperatures used in the injection molding process

2.6.5 Tensile Tests

Tensile tests were carried out using a testing machine (model UPM 1446, Zwick Roell, Ulm, Germany) at a speed of 5 mm/min according to DIN EN ISO 527. Five samples of each starch blend and the pure PLA were tested. The tensile strength, Young's modulus, and the elongation-at-break were determined.

2.6.6 Impact Tests

The Charpy impact strength of the materials was measured using an instrumented impact test pendulum (Zwick Roell). According to DIN EN ISO 179-2, ten specimens of each blend were investigated.

3 Results and Discussion

3.1 Thermogravimetric Analysis of Starch

The TGA thermogram of native starch when exposed to different temperatures is shown in Fig. 2. The starch samples heated to 200 °C and 220 °C displayed degradation during the testing cycle. Also, a discoloration of both samples was observable.

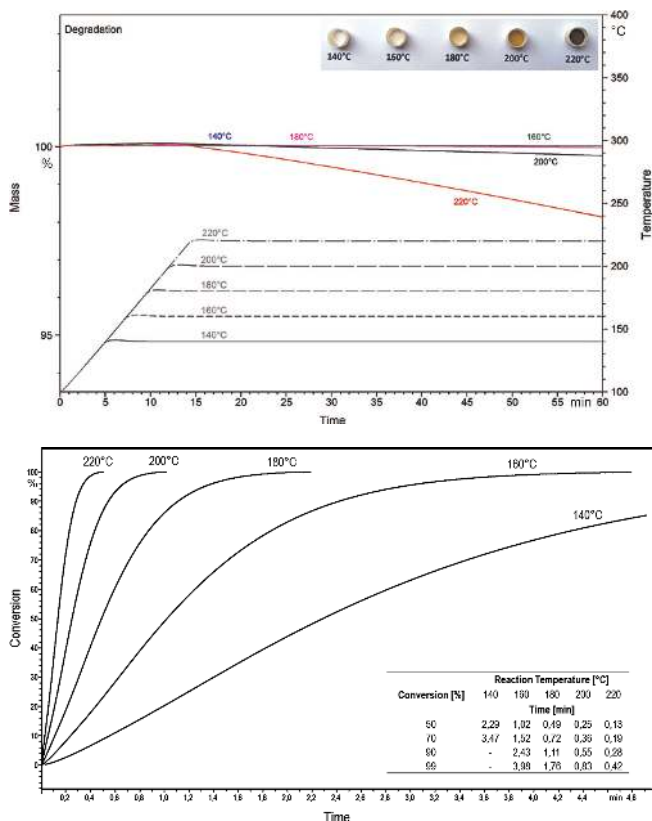


Fig. 2. TGA thermogram of the thermal stability of native starch at different temperatures (top) and DSC thermogram of the cross-linking reaction between the cross-linking agent and catalyzer (bottom)

Based on the duration of the starch modification process in the laboratory mixer, only starch that was heated to 220 °C should display degradation during the modification process. The conducted investigations showed that native starch can be processed using a wide range of temperatures and limited period of time.

3.2 Differential Scanning Calorimetry of the Crosslinking Reaction

The DSC thermogram of the cross-linking agent and the catalyzer is shown in Fig. 2. The reaction proceeds considerably faster as the temperature increases. The five minute holding time in the laboratory mixer is insufficient for an entire conversion of the cross-linking agent to take place at 140 °C. At 200 °C and higher, an entire conversion of the cross-linking agent occurs within one minute. In order to achieve a faster conversion of 100 % of the material, either the temperature or the hold-up time can be increased. In regards to the thermal stability, see 3.1/ Fig. 2, a maximum temperature of 200 °C should be used for the modification process in correlation with the process parameters (heating rate, hold-up time etc.).

3.3 Scanning Electron Microscopy

The recorded micrographs are shown in Fig. 3. The blend with native starch (Fig. 3A) displays poor adhesion between the starch granules and the PLA matrix. Gaps between the blend partners are clearly visible. In contrast, the blends with modified starch (Fig. 3B to F) exhibit much better adhesion between the starch granules and the PLA matrix. The distinguishable holes in the material (Fig. 3 B to F) are caused by an excavation of the starch granules during fracturing. This phenomenon was already described by Kovács and Tabi (2011), Wu (2011) and Yu et al. (2011). Regarding the distribution of the starch granules in the PLA matrix, no significant differences between the blends are visible regarding the used process parameters. The distribution of the starch granules in the PLA matrix is homogeneous in all blends. Intact and deformed starch granules are visible in the micrographs of all blends. The carried out investigations represent proof that using the described methods and process parameters does not lead to considerable destructuring of the starch granules.

3.4 Moisture Absorption

The results of the moisture absorption investigation shown in Fig. 4 verify the expected lower moisture absorption level of pure PLA compared to the starch blends. All materials reached their highest level of moisture absorption within the first five days of the testing cycle. The blends with modified starch, except for 50MST(140 °C)/50PLA (possibly uncompleted reaction, see 3.2/ Fig. 2), displayed lower moisture absorption levels than the blend that contained native starch (50ST/50PLA). However, the moisture absorption level dropped as the process temperature increased during the modification process in the laboratory mixer. This behavior indicates the occurrence of

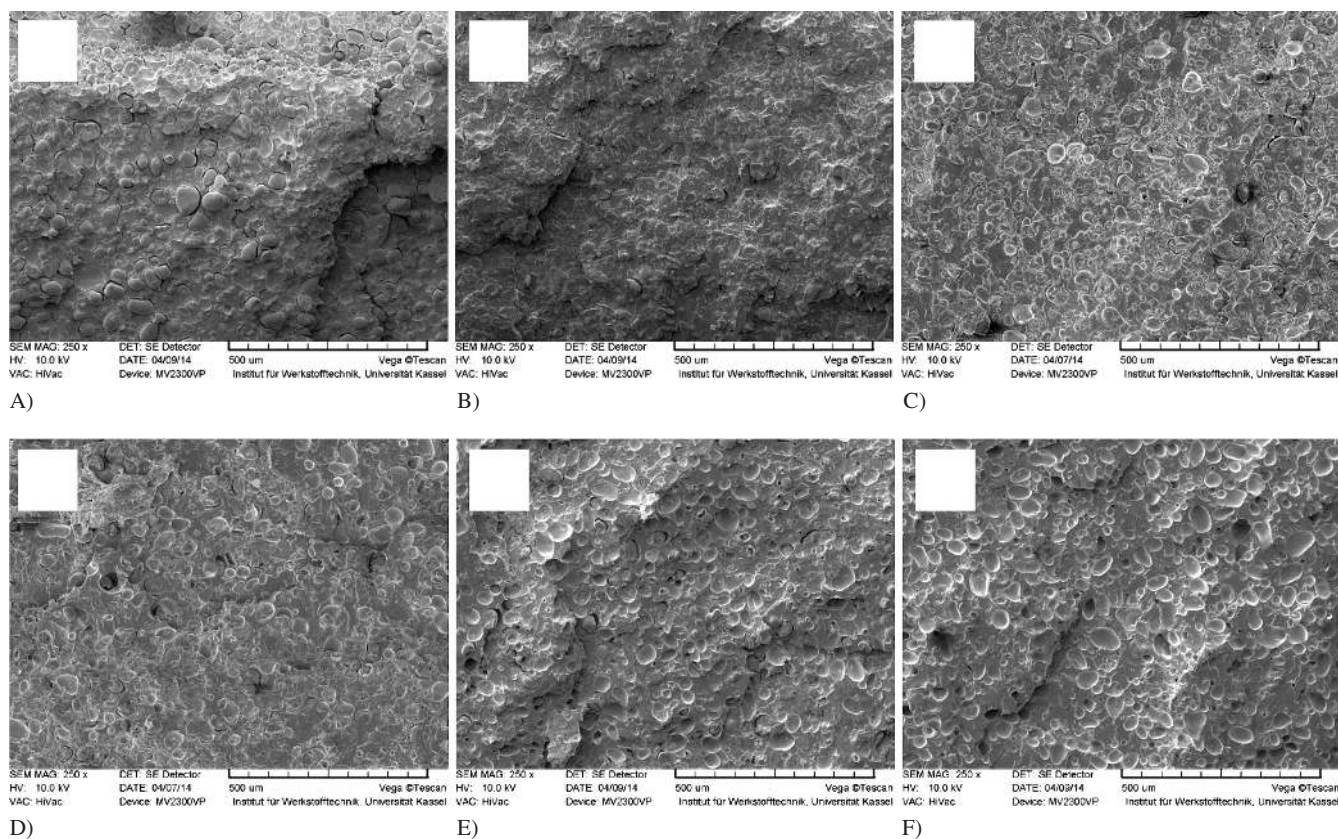


Fig. 3. Distribution of the starch and the embedding between the starch and the PLA matrix: 50ST/50PLA (A), 50MST(140°C)/50PLA (B), 50MST(160°C)/50PLA (C), 50MST(180°C)/50PLA (D), 50MST(200°C)/50PLA (E), 50MST(220°C)/50PLA (F)

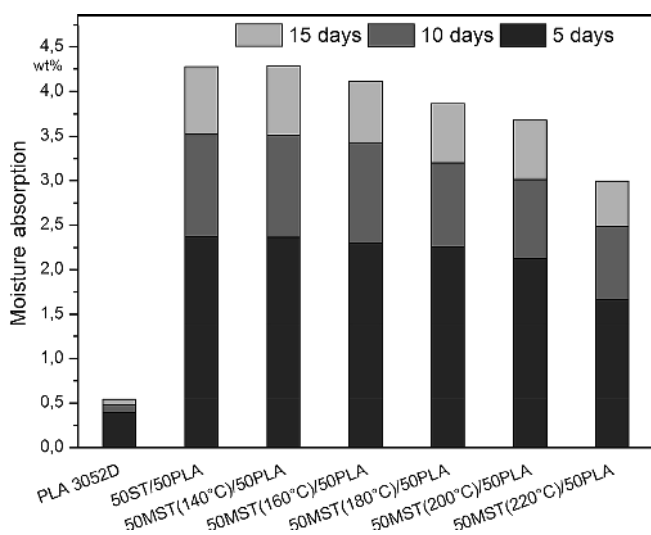


Fig. 4. Moisture absorption levels of the starch blends and the pure PLA during the fifteen-day testing cycle

a successful cross-linking reaction starting at 160 °C and continuing thereafter. One of the reasons 50ST/50PLA achieved the highest moisture absorption level in comparison to the remaining blends is the poor binding of the starch granules to the PLA matrix (see Fig. 3). Obviously, the gaps between the blend

partners offer the moisture extensive space for permeation. This behavior was also observed by Ke and Sun (2001).

3.5 Mechanical Properties of Starch/PLA Blends

The tensile strength and elongation-at-break results measured during tensile tests are displayed in Fig. 5. 50ST/50PLA (42 MPa) shows a significantly lower tensile strength (~22%) than pure PLA (54 MPa), whereas the blends with modified starch exhibit equal or even superior tensile strengths compared to pure PLA, which is a surprising result considering that the starch portion in the blend amounted to 50 wt%. The elongation-at-break of pure PLA was the highest value of all investigated materials. All blends with modified starch, including 50MST(140 °C)/50PLA, display higher levels of elongation-at-break (~25%) compared to the blend containing native starch (50ST/50PLA). Yet, the blends with modified starch show clearly more brittle behavior than pure PLA. The results obtained for the tensile strength and elongation-at-break indicate a successful cross-linking process for the modified starches. However, this behavior did not occur for all blends with modified starch during the moisture absorption investigation.

Young’s modulus and the impact strength of the starch blends and the pure PLA are displayed in Fig. 6. Based on the elongation-at-break, pure PLA shows the highest impact strength (15 kJ/m²) of all of the investigated materials. In con-

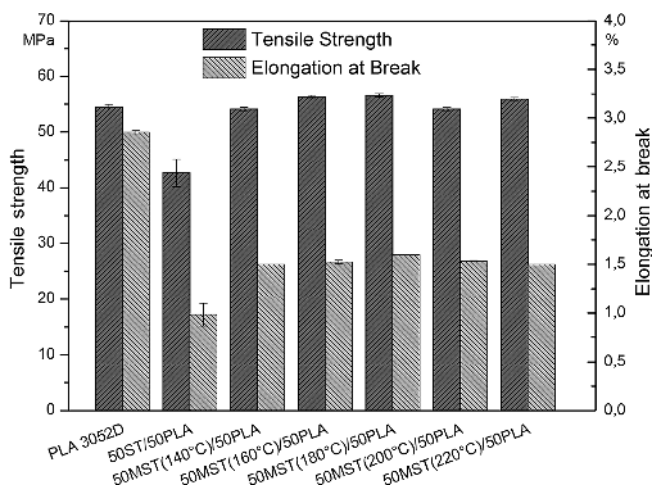


Fig. 5. Tensile strength and elongation-at-break values of the starch blends and pure PLA

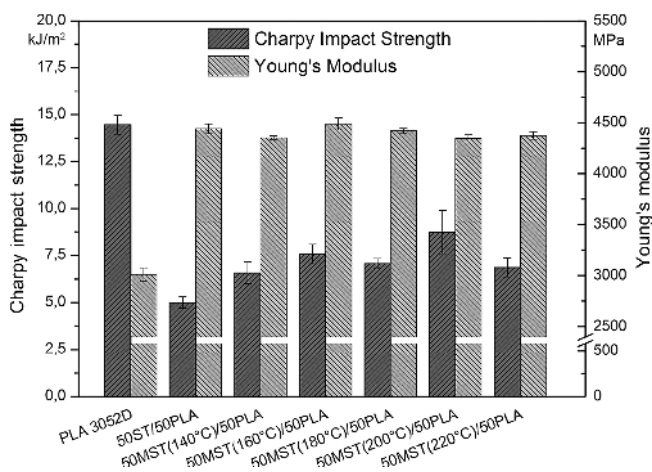


Fig. 6. Charpy impact strength and Young's modulus of the starch blends and pure PLA

trast, the blend with native starch 50ST/50PLA (5 kJ/m²) displays the lowest impact strength. All blends with modified starch show impact strengths that are 21 to 44 % higher than that of the blend with native starch. The blend 50MST (200 °C)/50PLA (8.7 kJ/m²) displays the highest measured impact strength of the blends with modified starch. As was expected, the starch blends (approx. 4400 MPa) have significantly higher Young's moduli (~30 %) compared to pure PLA (3000 MPa) (Thakore et al., 1999). There were no significant differences between the blends with modified starch and the blend with native starch in regards to Young's modulus.

4 Summary and Conclusions

The investigations were performed to evaluate the influence of the hydrophobic cross-linked potato starch in the compounding process with PLA in a co-rotating twin screw extruder. The compatibility between the starch and the PLA was significantly improved.

- The basic principle of hydrophobic crosslinking hydrophilic polymer blend components before compounding could be proven in the development of bioplastics.
- Pure PLA, a starch blend with native starch (50 wt%), and blends with modified starch (50 wt%), which were cross-linked while exposed to different temperatures, were studied.
- The thermogravimetric analysis showed the thermal stability of native potato starch at different temperatures.
- The results from differential scanning calorimetry illustrated the correlation between the time and temperature required for the cross-linking reaction of the native starch.
- It was shown that the blends with modified starch, which were cross-linked at 160 °C and higher, have lower moisture absorption levels compared to the blend with native starch.
- The blends with modified starch displayed equal or even higher tensile strengths than pure PLA, whereas the blend with native starch showed significantly lower properties.
- The elongation-at-break and impact strength of blends with modified starch were enhanced in comparison to the blend with native starch.
- As expected, the Young's modulus of all starch blends were higher than that of pure PLA.

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