

Properties and Weldability of Plasticized Polylactic Acid Films

Neda Stoehr,¹ Benjamin Baudrit,¹ Edmund Haberstroh,² Michael Nase,³
Peter Heidemeyer,¹ Martin Bastian¹

¹German Plastics Center, Research and Development, 97076 Wuerzburg, Germany

²RWTH-Aachen University, Faculty of Mechanical Engineering, 52072, Aachen, Germany

³University of Applied Science Hof, Faculty of Engineering, 95028 Hof, Germany

Correspondence to: N. Stoehr (E-mail: n.stoehr@skz.de)

ABSTRACT: The objectives of the presented work were to investigate films based on polylactic acid (PLA) and polyethylene glycol (PEG) in order to improve ductility and weldability of PLA films. The effect of plasticizer amount on the thermal, rheological, and mechanical properties of PLA plasticized films was investigated. The PEG content does affect the glass transition and the cold crystallization temperature of PLA in blends, while the melting temperature was not affected by the addition of PEG. The complex viscosity of the neat PLA granules and of plasticized films showed strong temperature and angular velocity dependence. The Young's modulus and tensile strength of plasticized films were improved with increasing plasticizer concentration, while the elongation at break stays rather constant. Plasticized PLA films were furthermore heat welded. These investigations showed that plasticized PLA films can be welded by heat welding. The obtained weld strength is strongly depending on the PEG amount as well as on selected welding parameters. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40394.

KEYWORDS:

Received 6 September 2013; accepted 5 January 2014

DOI: 10.1002/app.40394

INTRODUCTION

Polylactic acid (PLA) is a commercially available bio-based material that could become a material of choice, especially in packaging applications due to its good clarity, high strength, and moderate barrier properties.¹ Its low toxicity, along with its environmentally friendly characteristics, has made PLA an ideal material for food packaging and film wrap, as well as for other consumer products.^{2–5} PLA is characterized by excellent optical properties and high tensile strength but unfortunately, it is rigid and brittle at room temperature due to its glass transition temperature (T_g) close to 55°C.⁶ Another drawback is its inherent brittleness and poor toughness, which impede its wide application. Developing packaging materials requires high flexibility at room temperature and thus, there is no tolerance for the polymer film tearing or cracking when subjected to stress during package manufacturing or wider use.^{6–8} Therefore, the modification processes that toughen PLA have drawn great attention.^{9–11} Blending with flexible polymers is the method most extensively used to improve the mechanical properties of PLA. However, many of these blends are immiscible and have poor mechanical properties. Besides blending, plasticization is an economical and easy method of modifying PLA. To improve the ductility of PLA-based materials, numerous researches have been made to modify PLA properties via plasticization.⁸

A large number of substances have been investigated as the potential plasticizers for PLA: substances of relatively low molecular weight (bishydroxymethyl malonate (DBM), glucose monoesters and partial fatty acid esters, and citrates^{12,13}) as well as substances of relatively high molecular weight (polyethylene glycol (PEG),^{13–15} poly(propylene glycol) (PPG),¹⁶ atactic poly(3-hydroxybutyrate) (a-PHB),^{17,18} polyester diol (PED), poly(diethylene adipate) (PDEA),¹⁹ tributyl citrate-oligoester (TbC-oligoesters), diethyl bishydroxymethyl malonate.^{8,12}

Since the use of plasticizers with low molecular weight has been associated with their migration, plasticizers with rather high molecular weight and low mobility are more frequently used.

As already mentioned, PLA is often used in the packaging industry. In the packaging production, it is essential that the package can be tightly welded, and that the weld is sufficiently strong to withstand handling during distribution. Therefore, the weldability of PLA as well as of modified PLA materials is an important property with regard to packaging materials.¹²

By heat welding, two films are pressed together between heated platens to achieve fusion at the interface between the films. In order to get a sufficient amount of molten material, films must be exposed to elevated temperatures without undergoing

degradation, which may be particularly challenging in case of biomaterials.

Furthermore, the flow properties of the molten material have a large influence on the weld strength. These flow characteristics could be changed by use of different additives and plasticizers and hence act on weld quality.

The objective of this work was to test systematically changed recipes based on PLA and PEG (4,000 g/mol) as one of the plasticizers frequently used in film application²⁰ in order to improve the ductility as well as the weldability of PLA.

EXPERIMENTAL

Materials

PLA was provided by NatureWorks under the reference 4032D. The average molecular weight of 179,000 g/mol and the polydispersity index of 2.12 were determined by gel permeation chromatography in chloroform at 23°C. The plasticizer used was Polyethylene glycol (PEG) 4000 supplied by IMPAG Import GmbH. Irganox 1010 and Irgafos 168 were received from BASF and used as stabilizers.

Melt Blending

Prior to processing, neat PLA granules were dried in a dry-air drying oven at 80°C until the required residual moisture content (under 250 ppm) was achieved. Compounds containing 5.3, 7.9, and 10.6 phr plasticizer (PEG 4000) were prepared using a Leistritz corotating twin-screw extruder ($L/D = 45$; $D = 18$ mm). To maintain the stability of compounds, Irganox 1010 and Irgafos 168 were used (each 0.2 phr). PLA, stabilizers, and plasticizer were introduced into the extruder at the controlled rate using a loss-in-weight feeder. The temperature in the feeding zone was 45°C in order to prevent premature melting of the plasticizer and reached a maximum of 200°C. The melting temperature was also 200°C. A vacuum was pulled on the vent port of the extruder to remove residual moisture. The employed screw speed was 300 rpm. The molten polymer was formed into a strand by a single-filament die and the strand was then cooled in a water bath before granulation. A pelletizer was used to cut the extruded strands into small pellets. The compound granules were dried in a dry-air drying oven at 80°C until the required residual moisture content (under 250 ppm) was achieved. Compound granulates were then stored in sealed coated opaque plastic bags (to prevent moisture absorption) at ambient temperature.

Cast Film Extrusion

For the production of cast film a single-screw extruder from Dr. Collin with a diameter of 30 mm and an L/D ratio of 30 was used. Compound granulates were extruded with a screw speed of 60 rpm. The temperature in the feeding zone was 60°C, reached a maximum of 190°C, and the temperature of the water entering the chill roll was 40°C. By adjusting the speed on the rewind stand, it was possible to control the thickness of the polymer films. The thickness of the polymer films is set to be 50 μm .

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed using differential scanning calorimeter Netzsch 204 F1 Phoenix. The samples with a weight at about 11 mg were put into aluminum

pan and hermetically sealed. The scans were carried out under nitrogen atmosphere. The samples were preliminary heated from -70°C to 210°C to erase previous thermal history, then cooled to -70°C and finally heated to 210°C , at a cooling/heating rate of 10 K/min. Thermograms were recorded and glass transition temperatures, crystallization temperatures, and melting temperatures evaluated.

Rheological Characterization

Rheological measurements were carried out on Haake Mars from ThermoFischer Scientific. These measurements were run with 20 mm parallel plate geometry and a gap of 1.0 mm. The complex viscosity was monitored over angular velocity. In order to keep the response in the viscoelastic linear domain, the applied deformation was kept at around 0.01. Samples were dried prior to testing in order to remove the moisture.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) of the plasticized PLA films was performed using a Mettler Toledo DMA/SDTA861e. The samples dimensions of $19.5 \times 4.0 \times 0.05$ mm³ were mounted in the tensile mode. Measurements were performed at frequency of 1 Hz and the temperature program was run from -10°C to 120°C , at a heating rate of 2 K/min. The amplitude was 5 μm and the autostrain was set to 120%. The viscoelastic properties such as the storage modulus (E') and mechanical loss factor ($\tan \delta$) were recorded as a function of temperature.

Heat Welding (Sealing) (HS)

All joints were prepared using a HSG/ETK laboratory heat sealer from Brügger. The heat platens used were flat and 2.0 mm in width. The weldability of the material as a function of welding process variables like die temperature, die pressure, and dwell time were investigated. The ranges of die temperature, die pressure, and dwell time were 85–130°C, 1.0–3.5 MPa, and 0.05–0.9 s, respectively. All joints were made by welding a film to an identical film between two platens set to the same temperature. After welding, the joints were cooled to room temperature at ambient conditions.

Tensile Testing

The tensile test is the commonly used test for determining mechanical properties of materials. Properties that are directly calculated via a tensile test are, among others, Young's modulus, tensile strength, and elongation at break. Strength is defined as a stress, which is measured as force per unit area, but can be reported just as a force or as a force per unit width. In this study strength will be reported as a force per unit width.

Tensile testing of the plasticized PLA films as well as of the welded samples was conducted on a tensile tester from Zwick Roell at 23°C and 50% relative humidity. The shape of the samples was rectangular, with a width of 15 mm. The gauge length was 50 mm and the crosshead speed was 100 mm/min. For the determination of the Young's modulus of the plasticized PLA films, a testing velocity of 1 mm/min between 0.05% and 0.25% elongation was used. The tensile tests were measured in accordance with ISO 527 for the films and DIN EN ISO 55529 for the welded samples. Values for Young's modulus, tensile strength, elongation at break, and weld strength were evaluated from the scans. Reported values are the average of five or more measurements.

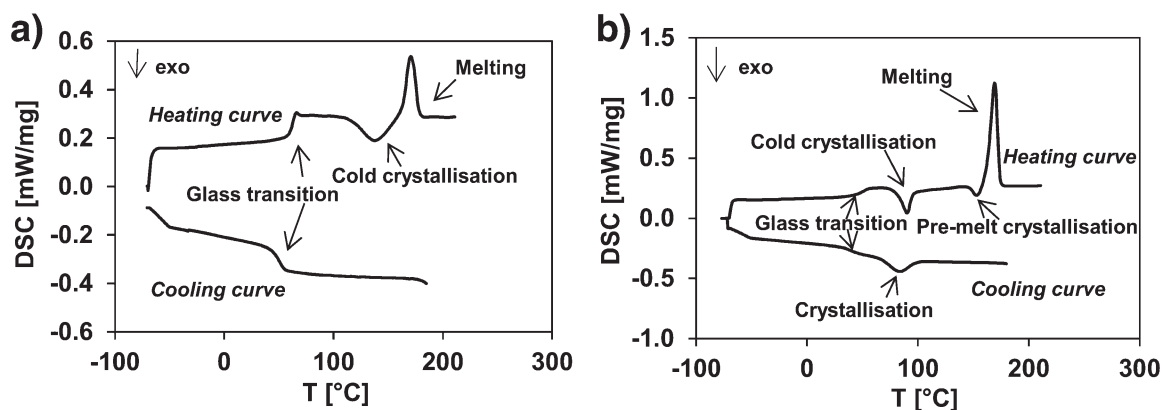


Figure 1. DSC thermograms for (a) neat PLA granules and (b) PLA film plasticized with 5.3 phr PEG during cooling and second heating.

Scanning Electron Microscopy

Fracture surfaces of the plasticized PLA films were examined by scanning electron microscopy (SEM) using a Zeiss Supra 40VP scanning electron microscope at an operating voltage of 15 kV. The fractured surface of the film was prepared by tensile test. Each surface was coated with a thin layer of gold, and was then observed with SEM. The composition was checked by energy-dispersive X-ray spectroscopy (EDX) using an X-ray microanalysis unit.

RESULTS AND INITIAL DISCUSSION

Differential Scanning Calorimetry

The thermal properties of neat PLA granules and plasticized PLA films were studied by differential scanning calorimetry. Corresponding differential scanning calorimetry (DSC) thermograms are shown in Figure 1. The DSC thermograms for all plasticized PLA films were found to look very similar. Thus only DSC thermogram of PLA film plasticized with 5.3 phr PEG is shown as an example.

The thermogram of neat PLA granules as well as of plasticized PLA film display a shift in the signal baseline related to the glass transition, an exothermic peak of cold crystallization and an endothermic melting peak. An additional exothermic peak of premelt crystallization was detected only by plasticized PLA films.

The neat PLA (granules) is characterized by a glass transition temperature (T_g) at around 63°C. The obtained result is in line

with previously published result.²¹ As expected increasing the amount of PEG leads to decrease of T_g (see Figure 2). In addition, thermograms of plasticized PLA films display only one glass transition temperature. This implies the full compatibility of the polymer and the plasticizer as reported by Hassouna et al. and Pillin et al.^{8,22}

According to Figure 1(a) exhibit neat PLA (granules) an exothermic broad peak of cold crystallization (T_{cc}) at around 137°C. The T_{cc} at 120°C was reported by Kulinski et al.²³ In this study, already processed and not neat PLA was investigated. Furthermore, it was observed that for all of the plasticized films there was a depression of the cold crystallization temperature [see Figure 1(b)], which is dependent of the plasticizer content (Figure 3).

Furthermore it was found that the PEG content does not affect the melting temperature (T_m) of PLA in blends.

As already mentioned, an exothermic peak of pre-melt crystallization at around 152°C was detected only by plasticized PLA films. The premelt crystallization temperature seems to be independent of the plasticizer content.

The neat PLA (granules) exhibits no crystallization peak upon cooling, while by the plasticized PLA films crystallization peak upon cooling appears at around 89°C. This indicates that PEG acts as a nucleating agent for PLA crystallization.

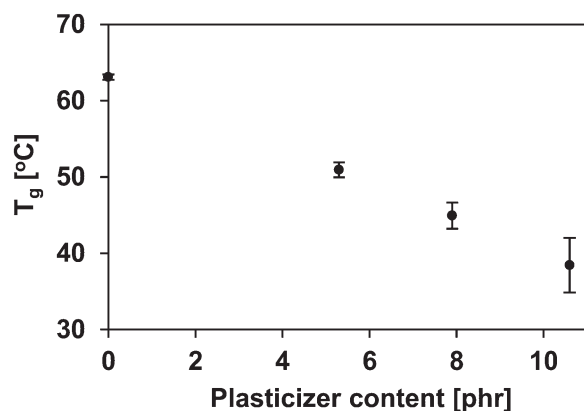


Figure 2. Effect of plasticizer content on the glass transition temperature.

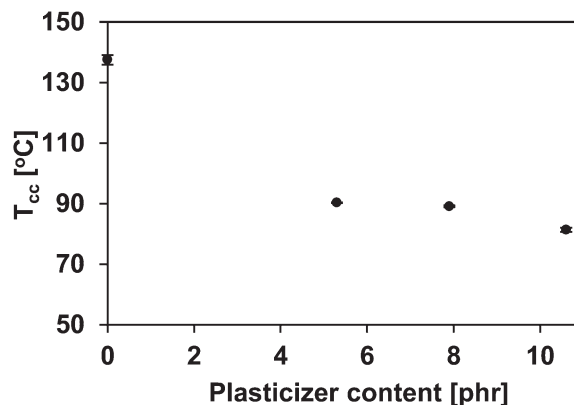


Figure 3. Effect of plasticizer content on the cold crystallization temperature.

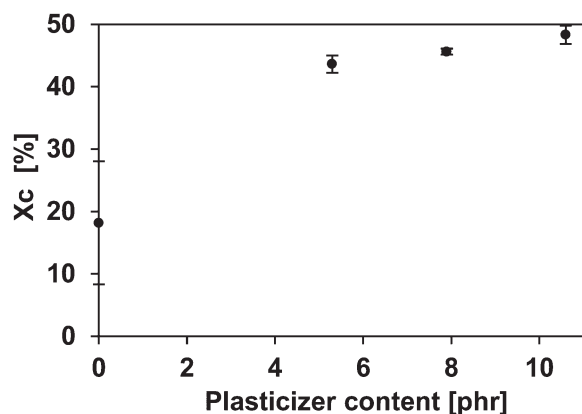


Figure 4. Effect of plasticizer content on the crystallinity.

The increase of PLA chain motion due to the increased amount of PEG (lower T_g) allows an easier rearrangement of PLA chains to crystallize.⁸ In addition it was found that the crystallinity (X_c) of PLA increased with the presence of PEG (see Figure 4). Moreover, the neat PLA showed crystallinity of about 18%. This result is in compliance with PLA crystallinity of about 14% reported by Xiao et al.²⁴ Degree of crystallinity was calculated based on the enthalpy of fusion of 100% crystalline PLA being equal to 93 J/g.²⁵ As the previous thermal history of a polymer affects the measured degree of crystallinity, data obtained from second heat has to be used in order to compare materials directly to each other. Thus, the enthalpies of fusion obtained during second heating were used in order to calculate crystallinity.

Rheological Characterization

The dynamic oscillatory shear measurements were performed on the neat PLA granules and plasticized films to investigate their response to the dynamic shearing.

The complex viscosities, $|\eta^*|$, of the neat PLA granules as a function of angular velocity, ω , at various temperatures are shown in Figure 5. The $|\eta^*|$ of the neat PLA (granules) shows strong temperature as well as angular velocity dependence, revealing a Newtonian plateau at low angular velocity. The neat PLA exhibits a zero-shear viscosity around 6 kPa s measured at 180°C. This result is in line with previously published results.¹

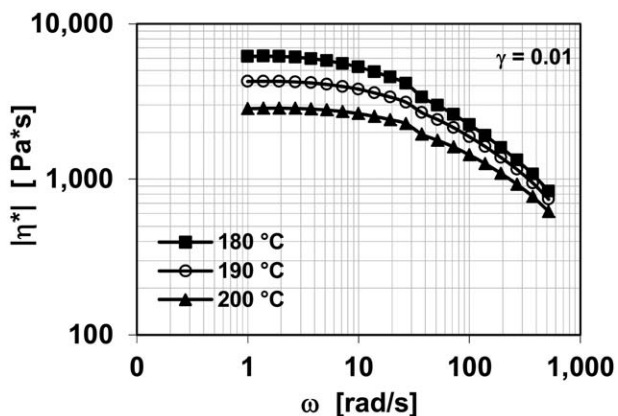


Figure 5. Complex viscosity for neat PLA granules at different temperatures.

As shown in Figure 6 the $|\eta^*|$ of the plasticized PLA films at 190°C is overall lower than that of the neat PLA granules within the angular velocity range studied and $|\eta^*|$ decreases with the plasticizer content, showing that the effect of the PEG on the complex viscosity is very pronounced. As expected the presence of plasticizer decreased the viscosity of PLA (Figure 6). The plasticized PLA films viscosity curves have a Newtonian plateau at low angular velocity.

As already mentioned in order to produce plasticized PLA films compound granulates were fabricated using a corotating twin-screw extruder. After that, the extruded compound granules were dried in a dry-air drying oven at 80°C until the required residual moisture content (under 250 ppm) was achieved. Compound granulates were then stored in sealed coated plastic bags (to prevent moisture absorption) at ambient temperature. Accordingly, after a few weeks a single-screw extruder was used concerning production of cast film without prior drying.

The complex viscosities, $|\eta^*|$, of the Compound (granules) and plasticized PLA film containing 10.6 phr PEG as a function of angular velocity at 190°C are shown in Figure 7. As could be seen from Figure 7 second processing method (film extrusion) had a strong influence on viscosity. Since the films were produced without prior drying of compound granules, it could be expected that they absorbed some moisture. The additional complication during processing is the potential for molecular weight decrease due to shearing and the hydrolytic sensitivity of the polymer bonds. The presence of moisture during processing can reduce the molecular weight and thus the viscosity is also reduced. The presence of moisture during processing leads to the loss in viscosity to a great extent when processing is done without prior drying.

The effect of the plasticizer content on zero viscosity, $|\eta_0^*|$, is shown in Figure 8. It could be seen that the zero viscosity slightly decrease with increasing plasticizer content.

Dynamic Mechanical Analysis (DMA)

Figures 9 and 10 show the experimental dynamic mechanical values of the storage modulus (E') and the loss factor ($\tan \delta$) at 1 Hz for the plasticized PLA films.

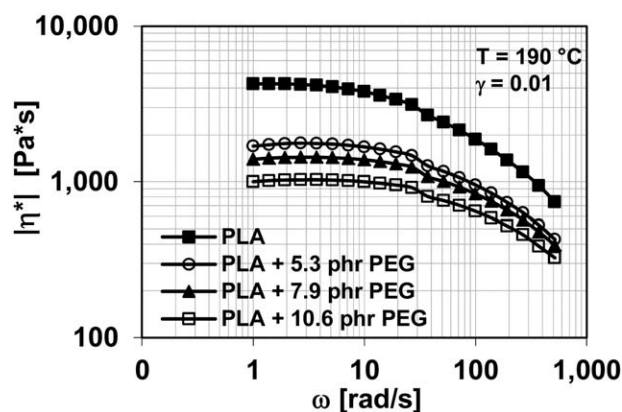


Figure 6. Complex viscosity for neat PLA granules and plasticized films modified with 5.3, 7.9, and 10.6 phr PEG.

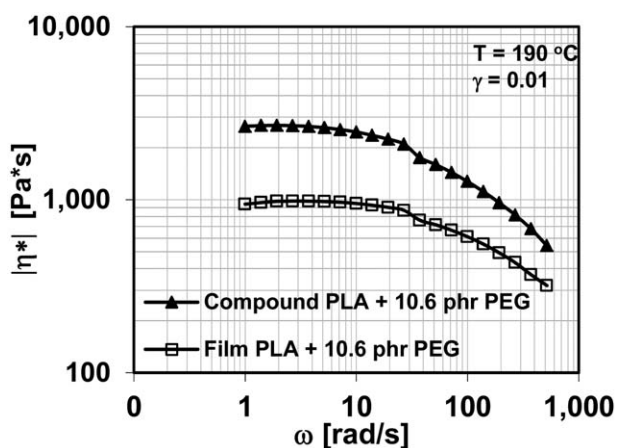


Figure 7. Complex viscosity for Compound (granulates) and film modified with 10.6 phr PEG.

The α -relaxation (maximum of $\tan \delta$ values at 1 Hz)—associated with the glass transition—can be observed at 58.9, 55.1, and 52.0°C for the films plasticized with 5.3, 7.9, 10.6 phr PEG, respectively. As expected, increasing the amount of the plasticizer resulted in the reduction of glass transition temperature. Figure 11 displayed that increasing plasticizer content decreased the T_g linearly.

Most polymers usually display, after T_g a second plateau region in the E' curve. The extension of this plateau will depend on the crystallinity and molecular weight of the polymer until the respectively limiting processes of melting or degradation takes place.²⁶ The increase in chain mobility of the plasticized films above T_g favors the activation of the cold crystallization process, which proceeds as temperature increases. After T_g the storage modulus of the plasticized films increases due to the increase in crystallinity (see Figure 9).

Mechanical Properties and Scanning Electron Microscopy

Exemplary force-elongation dependencies for the plasticized PLA films are plotted in Figure 12. The film plasticized with 5.3 phr PEG showed tensile strength at 40 N/15 mm and elongation at break at 2.4%, indicating thus a limited viscoelastic region. The increase of plasticizer content changed the tensile behavior. As expected, exhibit films plasticized with 7.9 and 10.6 phr PEG higher elongations at break and thus a longer

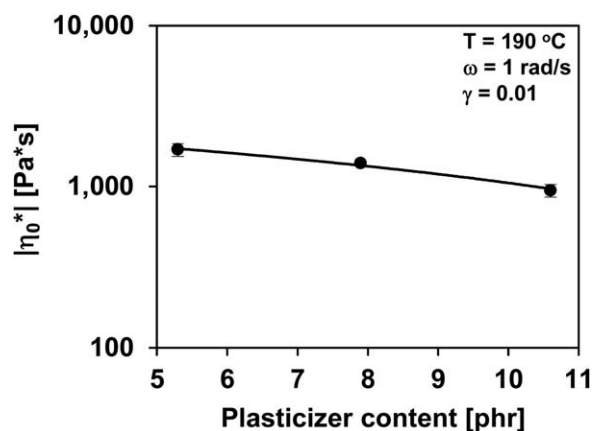


Figure 8. Effect of plasticizer content for films on the zero-shear viscosity at 190°C.

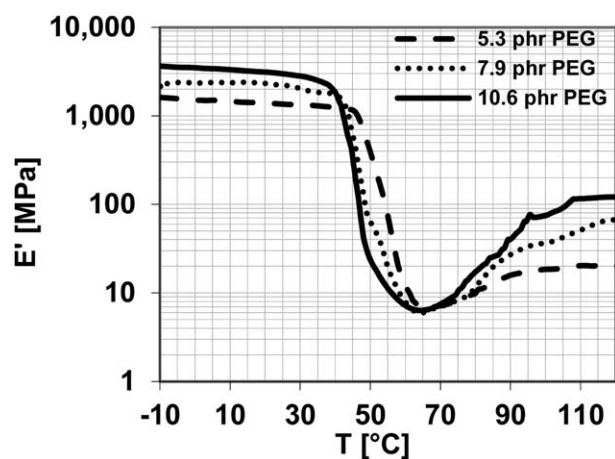


Figure 9. Temperature dependence of storage modulus for plasticized PLA films measured at 1 Hz.

viscoelastic region compared to film plasticized with 5.3 phr PEG.

The Young's modulus and tensile strength of the plasticized PLA films increase with increasing plasticizer concentration, while considering the standard deviation the elongation at break stays rather constant (see Figure 13).

The mechanical properties were in close agreement to Li et al.¹ Tensile modulus at 3.7 GPa, tensile strength at 70 MPa and elongation at break around 5 % of injection-molded PLA were reported by Li et al.¹ In addition they blended PLA with PEG (3,350 g/mol) in presence of talcum and investigated the effects of PEG concentration on mechanical properties. Tensile modulus, tensile strength, and elongation at break as a function of formulation and molding temperature were in the range between 2.39 and 4.23 GPa for the tensile modulus 37.3 and 60.5 GPa for the tensile strength and 6.2 and 40.4% for the elongation at break.

Morphology of tensile fracture surfaces were studied by scanning electron microscopy (SEM) (see Figure 14). Figure 14(a) showed, as typical brittle fracture, the relatively smooth fracture surface of film plasticized with 5.3 phr PEG, indicating that little plastic deformation

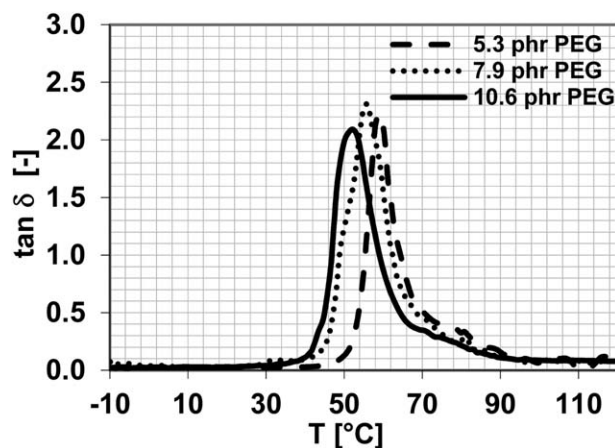


Figure 10. Temperature dependence of loss factor $\tan \delta$ for plasticized PLA films measured at 1 Hz.

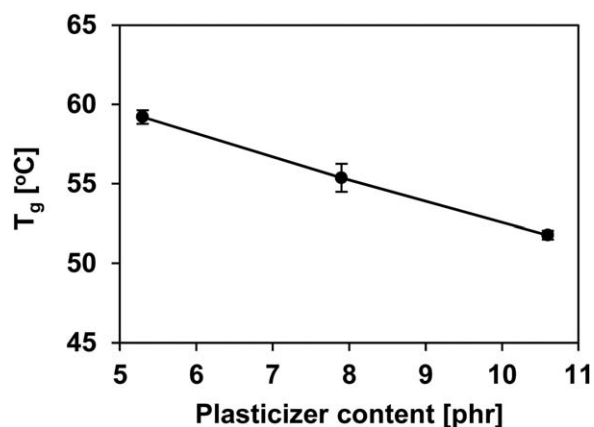


Figure 11. Glass transition temperature obtained by DMA measurements as a function of the plasticizer content.

had taken place during the tensile test. A few fibrils can be seen which were formed during crazing. Also some fibrils could be observed for the plasticized PLA film containing 7.9 phr PEG [see Figure 14(b)]. Such fibril-like structures have been reported in other modified PLA blends.^{27–29} Compared with film with 5.3 phr PEG, the fracture surfaces of film with 7.9 phr PEG was slightly rougher showed more structure because of larger plastic deformation caused by more crazes. This was in good agreement with their slightly higher elongation at break, compared with film with 5.3 phr PEG. Fracture surface morphology of film with 10.6 phr PEG [see Figure 14(c)] showed no

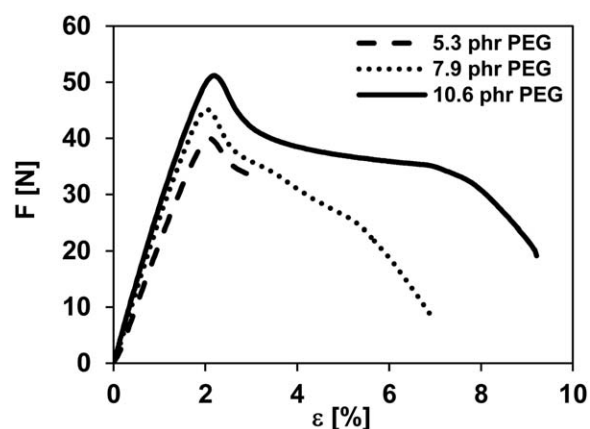


Figure 12. Force–elongation plot for plasticized films.

fibrils. Instead many cracks perpendicular to tensile direction can be observed, which is the result of the propagation of massive microcracks. In order to identify these massive microcracks the length of the scale in the Figure 14(c) was changed to 10 μm. Forming of massive microcracks or microvoids can absorb much energy. Therefore it behaved as brittle fracture with slightly high elongation at break. The obtained results are in line with previously published results.^{27–29}

Heat Welding (Sealing)

A range of the welding parameters (die temperature, die pressure, and dwell time) for each PLA plasticized film have been

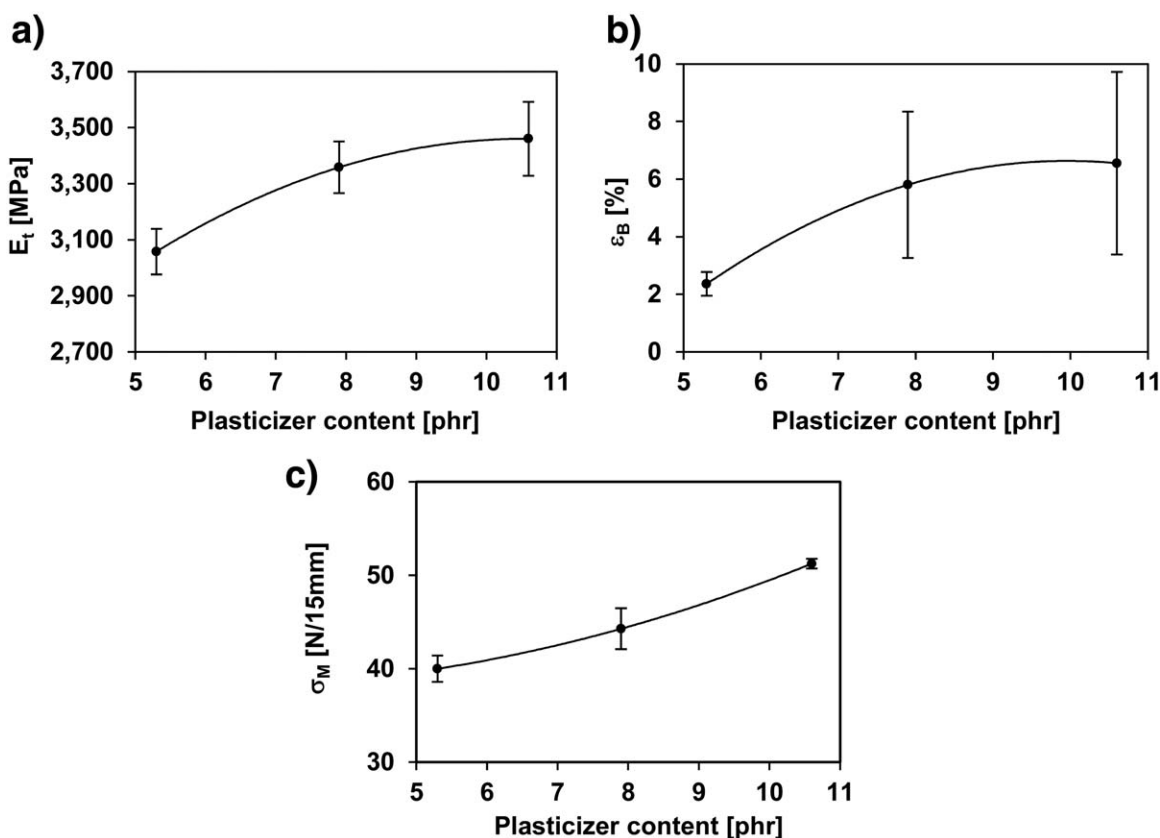


Figure 13. (a) Young's modulus as a function of the plasticizer content. (b) Elongation at break as a function of the plasticizer content. (c) Tensile strength as a function of the plasticizer content.

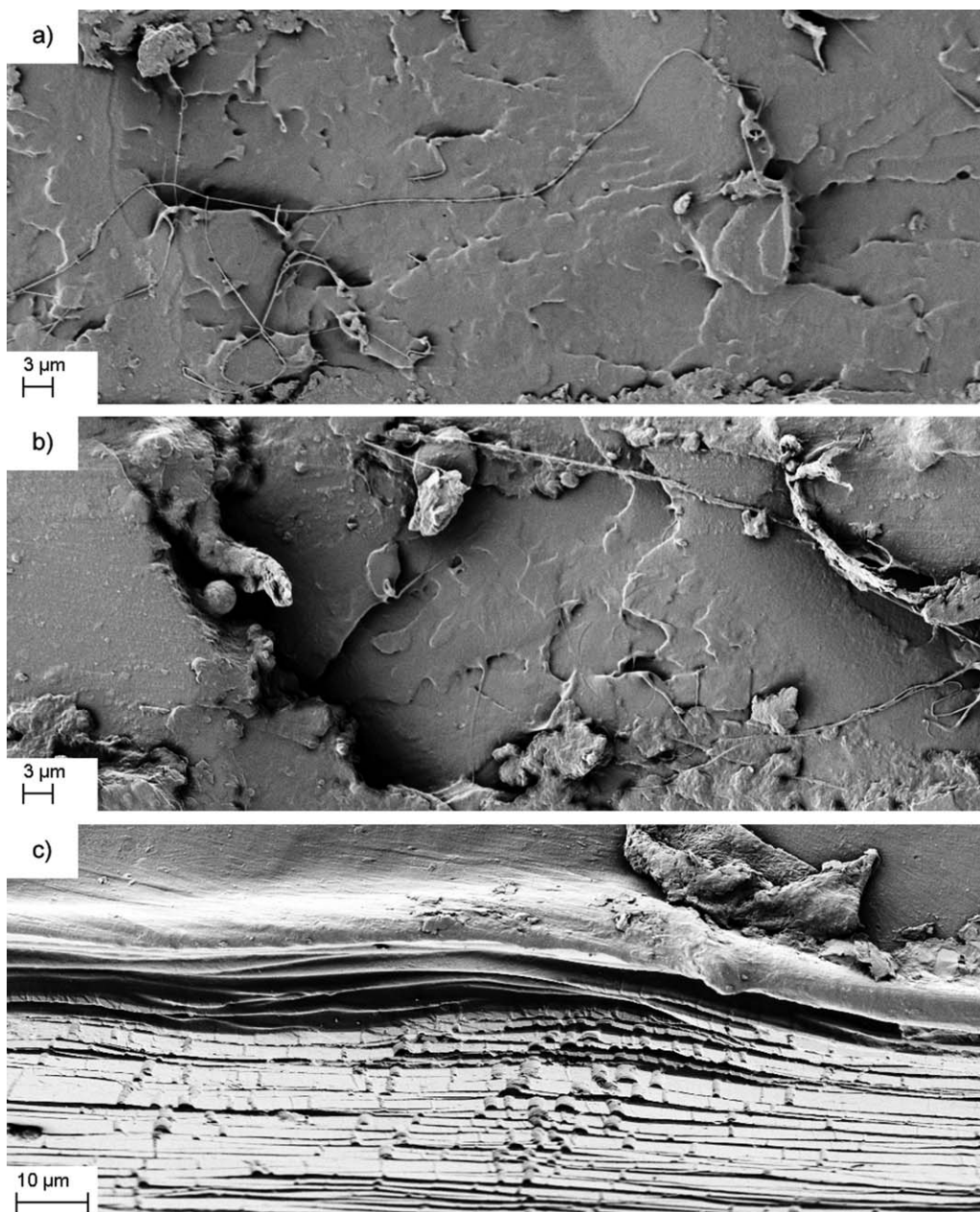


Figure 14. SEM micrographs for films modified with (a) 5.3 phr PEG, (b) 7.9 phr PEG, and (c) 10.6 phr PEG.

analyzed, in order to determine if there are any differences in the weldability of films with increasing plasticizer concentration.

It was possible to weld all tested films in a die pressure range from 1.0 to 3.5 MPa and dwell time range from 0.05 to 0.9 s. The only difference was observed in minimal and maximal die temperature. Furthermore, these investigations showed that a higher amount of PEG leads to a decrease in the minimum and maximum applied die temperature (see Figure 15).

The weld strength as a function of the die temperature at various dwell times and at constant die pressure (1.0 MPa) for the plasticized PLA film with 10.6 phr PEG is shown in Figure 16.

The first appearance of measurable weld strength was observed at 1.0 MPa, 85°C, and 0.05 s. Increasing the dwell time from 0.05 to 0.5 s at 85°C die temperature leads to a notable improvement of the weld strength. The weld strength remains rather constant, while increasing the dwell time from 0.5 to 0.9 s at 85°C. At 100°C die temperature the weld strength remains nearly unchanged, while dwell time increased. Increasing the dwell time from 0.05 to 0.5 s at 110°C die temperature weld strength dropped.

The weld strength as a function of the die temperature at various dwell times and at constant die pressure (1.5 MPa) for the plasticized PLA film with 10.6 phr PEG is shown in Figure 17.

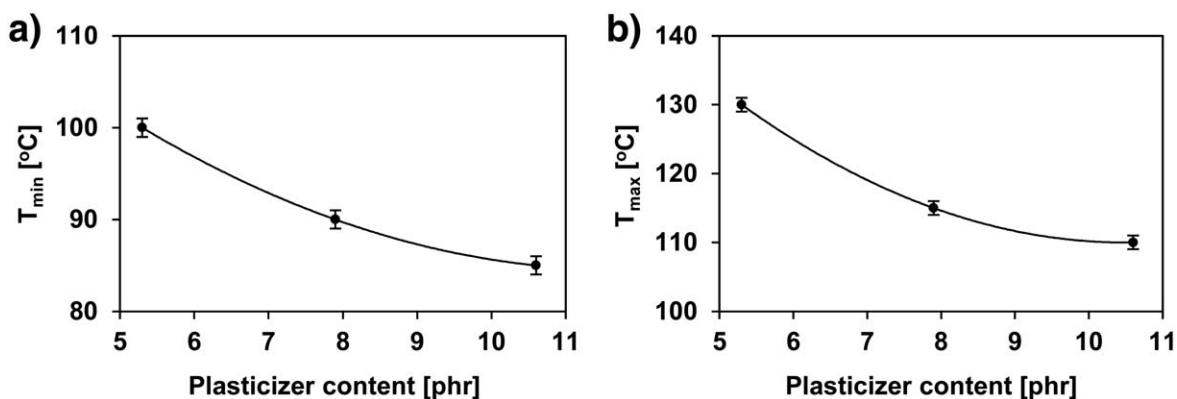


Figure 15. (a) Minimum and (b) maximum applied die temperature during welding as a function of the plasticizer content.

At medium (1.5 MPa) die pressure, dwell time and die temperature have stronger influence on the strength in comparison with low (1.0 MPa) die pressure. As seen in Figure 17 increasing the dwell time from 0.05 to 0.5 s at 85°C die temperature weld strength remains constant. Further dwell time increase from 0.5 to 0.9 s at 85°C leads to weld strength increase. At 100°C die temperature increasing the dwell time leads to lower weld strength. Elevating the dwell time from 0.05 to 0.5 s at 110°C die temperature resulted in a weld strength decrease.

According to Figure 18 dwell time and die temperature have influences on the weld strength at high (3.5 MPa) die pressure too.

These results suggest that the obtained weld strength strongly depends on welding parameters. During heat welding dwell time, die temperature and die pressure are of high importance. The similar tendency was found for the PLA films plasticized with 5.3 and 7.9 phr PEG. Thus these results will not be discussed in detail.

As already mentioned different die temperatures were used in order to weld films with different plasticizer amount. Mutual die temperature for all films investigated was 100°C. In order to determine the influence of a PEG concentration of the weldability of the films the weld strengths obtained at 100°C die temperature, 1.5 MPa die pressure and 0.05, 0.5, or 0.9 s dwell time were compared (see Figure 19).

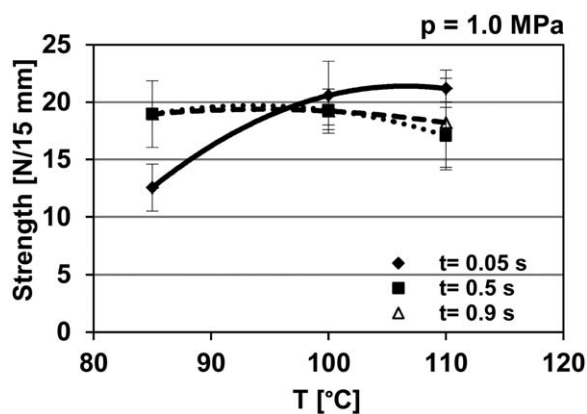


Figure 16. Weld strength at 1.0 MPa die pressure, different die temperatures, and dwell times from welded film modified with 10.6 phr PEG.

As shown in Figure 19 the weld strength appears to be dependent on plasticizer amount (for each observed dwell time). Increasing plasticizer content leads to an increase in weld strength.

Furthermore, in order to determine the influence of increasing plasticizer concentration of the weldability of films, all weld parameters were taken into account and the best weld strength in dependency of material was chosen as representative result. The weld parameters used in order to achieve these best weld strengths are listed in Table I.

According to Figure 20, it was found that a higher amount of PEG leads to an increase in the strength of the welded samples as well as the nonwelded films.

These weld strength values were compared to the base material strength. Hence, it could be determined, if increasing PEG content only leads to an improvement in mechanical properties of the films or in weldability as well.

Comparing best weld strength with the strength of nonwelded film (quasi welding factor) it was found that higher amount of PEG leads slightly to improvement of weldability. Because of the large standard deviation it could also be concluded that the weldability stays rather unchanged (see Figure 21).

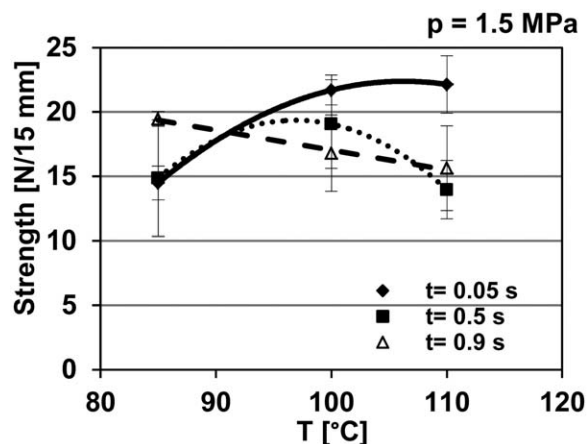


Figure 17. Weld strength at 1.5 MPa die pressure, different die temperatures, and dwell times from welded film modified with 10.6 phr PEG.

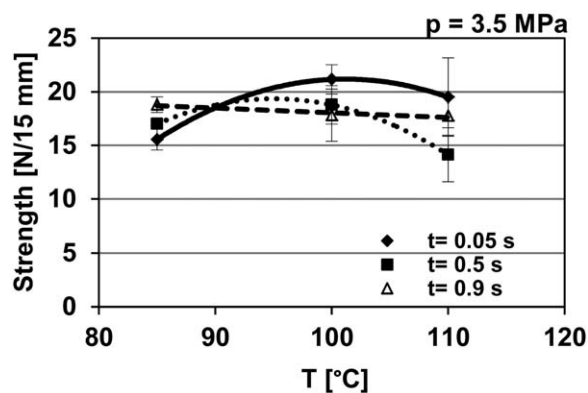


Figure 18. Weld strength at 3.5 MPa die pressure, different die temperatures, and dwell times from welded film modified with 10.6 phr PEG.

FINAL DISCUSSION AND CONCLUSION

The PEG content does affect the glass transition temperature (T_g) and the cold crystallization temperature (T_{cc}) of PLA in blends, while the melting temperature (T_m) was not affected by the addition of PEG. The addition of PEG as a plasticizer resulted in decrease in T_g , due to improved chain mobility. Moreover, it was found that T_{cc} decrease with increasing plasticizer content, which is consistent with the fact that PLA crystallizes more easily at lower temperatures due to enhanced chain mobility as the plasticizer level increases.

However, the addition of PEG caused the crystallization upon cooling. This indicates that PEG acts as a nucleating agent for PLA crystallization.

Furthermore, it was found that the increase of PLA chain mobility due to the greater amount of PEG allows an easier rearrangement of polymer chains to crystallize. Therefore, the crystallinity of PLA was found to be slightly increased if PEG content is elevated. These results are in line with the results obtained by mechanical tests. Due to increased crystallinity, the Young's modulus and the tensile strength of the plasticized films increase.

In order to weld films efficiently, film surfaces have to be brought into contact above their glass transition temperature. Therefore it could be expected that the materials with lower T_g could effec-

Table I. Weld Parameters

Plasticizer content (phr)	Die temperature (T) (°C)	Dwell time (t) (s)	Die pressure (p) (MPa)
5.3	130	0.9	1.5
7.9	100	0.5	3.5
10.6	110	0.05	1.5

tively be welded at lower die temperature. Since the T_g of investigated films decrease with increasing plasticizer content it was found that the minimum and maximum applied die temperature by welding decrease with increasing plasticizer content.

In addition, increasing plasticizer content leads to the increase in the weld strength for the films welded under the same conditions (100°C, 1.5 MPa, 0.05; 0.5 or 0.9 s). Theoretically, when the film surfaces are brought into contact above their glass transition temperature, the polymer chains diffuse across the contact area until the interface is indistinguishable from the bulk material and the polymer–polymer interface disappears, while the weld strength increases until it reaches the bulk material strength. The increased mobility of the polymer chains caused by increased PEG concentration (viscosity decrease with increasing plasticizer content) contributes the more effective diffusion of polymer chains during welding and thus results in increase of the weld strength.

By melt blending PLA with PEG 4000, it was possible to produce a polymer material which could be used for the production of the cast films.

As observed from differential scanning calorimetry, the PEG content does affect the glass transition temperature (T_g) and the cold crystallization temperature (T_{cc}) of PLA in blends, while the melting temperature (T_m) was not affected by the addition of PEG.

The addition of PEG as a plasticizer resulted in decrease in T_g . The thermograms of plasticized PLA films showed only one glass transition temperature, which indicated the full compatibility of the polymer and the plasticizer. Furthermore it was found that T_{cc} slightly decrease with increasing plasticizer content. The premelt crystallization process was detected only by plasticized PLA films. The premelt crystallization temperature

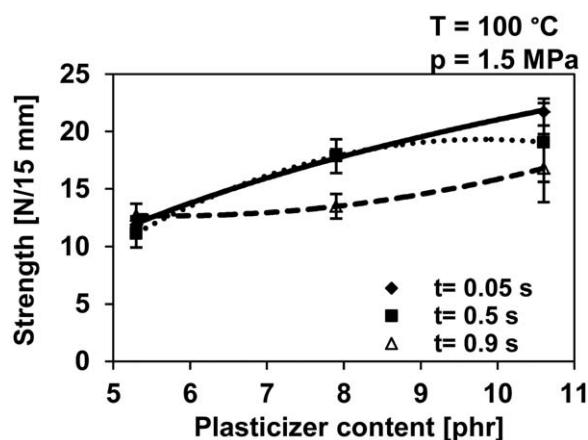


Figure 19. Weld strength at 1.5 MPa die pressure, 100°C die temperature and different dwell times as a function of the plasticizer content.

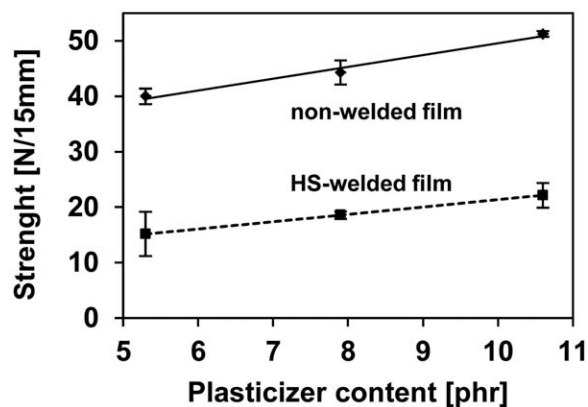


Figure 20. Best weld strength of welded films and tensile strength of base material as a function of the plasticizer content.

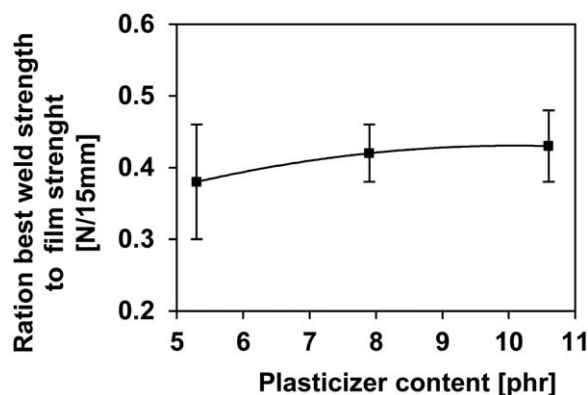


Figure 21. Ratio best weld strength to film strength as a function of the plasticizer content.

seemed to be independent of the plasticizer content. However the addition of PEG caused the crystallization upon cooling. This indicates that PEG acts as a nucleating agent for PLA crystallization. In addition, it was found that the crystallinity of PLA increased with the presence of PEG.

According to the rheological measurements the complex viscosity of the neat PLA granules as well as of plasticized PLA films shows strong temperature as well as angular velocity dependence. The complex viscosity of the plasticized PLA films at 190°C is overall lower than that of the neat PLA granules within the angular velocity range studied and the complex viscosity decreases with the plasticizer content, showing that the effect of the PEG on the complex viscosity is very pronounced. The presence of plasticizer decreased the viscosity of PLA.

DMA results confirmed that the increasing plasticizer content results in a reduction of glass transition temperature. Increase in the storage modulus of the plasticized films after T_g , indicates that the cold crystallization process took place.

The mechanical properties of plasticized PLA films could be improved with increasing plasticizer content. The Young's modulus and tensile strength of the plasticized PLA films increase with increasing plasticizer concentration, while the elongation at break stays rather constant.

The plasticized PLA films could effectively be welded by heat welding. The obtained weld strength is strongly depending on the PEG amount and the welding parameters. These researches show that higher amount of PEG in plasticized films leads to a decrease in the minimum and maximum applied die temperature during welding.

At 100°C die temperature, 1.5 MPa die pressure and 0.05, 0.5, or 0.9 s dwell time the weld strength appears to be dependent on plasticizer amount. Elevating plasticizer content leads to an increase in weld strength.

The best weld strength values (obtained from this research) were compared to the base material strength. Comparing these weld strength with the strength of nonwelded film (quasi welding factor) it was found that the higher amount of PEG leads slightly to improvement of weldability.

REFERENCES

- Li, H.; Huneault, M. A. *Polymer* **2007**, *48*, 6855.
- Auras, R.; Harte, B.; Selke, S. *Macromol. Biosci.* **2003**, *4*, 835.
- Rabetafika, H. N.; Paquot, M.; Dubois P. *Biotechnol. Agron. Soc. Environ.* **2006**, *10*, 185.
- Weber, C. J.; Haugaard, V.; Festersen, R.; Bertelsen, G. *Food Addit. Contam.* **2002**, *19*, 172.
- Hassouna, F.; Raquez, J. M.; Addiego, F.; Toniazzo, V.; Dubois, P.; Ruch, D. *Eur. Polym. J.* **2012**, *48*, 404.
- Lim, L.T.; Auras, R.; Rubino, M. *Prog. Polym. Sci.* **2008**, *33*, 820.
- Anderson, N. S.; Schreck, K. M.; Hillmyer, M. A. *Polym. Rev.* **2008**, *48*, 85.
- Hassouna, F.; Raquez, J. M.; Addiego, F.; Dubois, P.; Toniazzo, V.; Ruch, D. *Eur. Polym. J.* **2011**, *47*, 2134.
- Liu, H.; Zhang, J. *J. Polym. Sci. Polym. Phys.* **2011**, *49*, 1051.
- Rasal, R. M.; Janorkar, A. V.; Hirt, D. E. *Prog. Polym. Sci.* **2010**, *35*, 338.
- Meng, B.; Tao, J.; Deng, J.; Wu, Z.; Yang, M. *Mater. Lett.* **2011**, *65*, 729.
- Ljungberg, N. Plasticized Poly (lactic acid) Films- Preparation and Properties, Ph.D. Thesis, Department of Polymer Science & Engineering, Lund Institute of Technology, Lund University, **2003**.
- Jacobsen, S.; Fritz, H. G. *Polym. Eng. Sci.* **1999**, *39*, 1303.
- Hu, Y.; Hu, Y. S.; Topolkarav, V.; Hiltner, A.; Baer, E. *Polymer* **2003**, *44*, 5681.
- Hu, Y.; Rogunova, M.; Topolkarav, V.; Hiltner, A.; Baer, E. *Polymer* **2003**, *44*, 5701.
- Kulinski, Z.; Piorkowska, E.; Gadzinowska, K.; Stasiak, M. *Biomacromolecules* **2006**, *7*, 2128.
- Focarete, M. L.; Dobrzynski, M. S.; Kowalczyk, M. *Macromolecules* **2002**, *35*, 8472.
- Blumm, E.; Owen, A. J. *Polymer* **1995**, *36*, 4077.
- Okamoto, K.; Ichikawa, T.; Yokohara, T.; Yamaguchi, M. *Euro. Polym. J.* **2009**, *45*, 2304.
- Wypych, G. Handbook of Plasticizers, ChemTec Publishing, Toronto, **2004**, Chapter 11, p 312.
- Sungsanit, K.; Kao, N.; Bhattacharya, S. N.; Pivsaart, S. *Korea-Australia Rheol. J.* **2010**, *22*, 3, 187.
- Pillin, I.; Montrelay, N.; Grohens, Y. *Polymer* **2006**, *47*, 4676.
- Kulinski, Z.; Piorkowska, E. *Polymer* **2005**, *46*, 10290.
- Xiao, H.; Lu, W.; Yeh, J.-T. *J. Appl. Polym. Sci.* **2009**, *113*, 112.
- Fischer, E. W.; Sterzel, H. J.; Wegner, G.; Kolloid, Z. Z. *Polymers* **1973**, *251*, 980.
- Migliaresi, C.; Cohn, D.; De Lollis, A.; Fambri, L. *J. Appl. Polym. Sci.* **1991**, *43*, 83.
- Jiang, L.; Zhang, J.; Wolcott, M. P. *Polymer* **2007**, *4*, 7632.
- Yu, F.; Liu, T.; Zhao, X.; Yu, X.; Lu, A.; Wang, Y. *J. Appl. Polym. Sci.* **2012**, *125*, E99.
- Zhang, H.; Liu, N.; Ran, X.; Han, C.; Han, L.; Zhuang, Y.; Dong, L. *J. Appl. Polym. Sci.* **2012**, *125*, E550.