

Ultrasonic Welding of Plasticized PLA Films

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

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

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

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

Correspondence to: N. Stoehr (E-mail: howarter@purdue.edu)

ABSTRACT: Poly(lactic acid) (PLA) is a commercially available biobased material that has become an ideal material in packaging applications because of its low toxicity along with its environmentally friendly characteristics. Unfortunately, PLA is rigid and brittle. These characteristics impede its wide application. The flexibility of PLA can be improved by plasticization. In addition, welding polymer films is essential in the packaging production. Therefore, the weldability by means of ultrasonic welding of the neat and with polyethylene glycol plasticized PLA films was analyzed in this study. Moreover, the study examines the influence of the material composition on the processing window, that is, the range of welding parameters which could be used to weld films efficiently, and on the weld quality. This research showed that all examined films can be welded by ultrasonic welding. Furthermore, it was discovered that the addition of a plasticizer has a strong influence on the processing window and on the weld quality. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41351.

KEYWORDS: biopolymers and renewable polymers; films; plasticizer

Received 22 May 2014; accepted 31 July 2014

DOI: 10.1002/app.41351

INTRODUCTION

Environmental concerns and a shortage of petroleum resources have inspired considerable engineering and scientific efforts devoted to the discovery, development, and modifications of biodegradable and renewably-derived polymers over the past several decades.¹ One such polymer is poly(lactic acid) (PLA). PLA is a thermoplastic aliphatic polyester that can be produced from renewable resources.² Its good clarity, high strength, moderate barrier properties, low toxicity, along with its environmentally friendly characteristics, has made PLA an ideal material for food packaging and film wrap, and for other consumer products.^{3–7} However, the main drawback of PLA is its brittleness, which limits its use in many applications. Because of its glass transition temperature (T_g) close to 55°C, it is rigid and brittle at room temperature.⁶ 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 application.^{8–11} Therefore, the modification processes that toughen PLA have drawn great attention.

PLA has been extensively modified using blending. Blending is the most widely used methodology to improve PLA mechanical properties. PLA is blended with different plasticizers and poly-

mers to achieve desired mechanical properties, such as bis(hydroxymethyl malonate) (DBM), polyethylene glycol (PEG), poly(propylene glycol) (PPG), poly(hydroxybutyrate) (PHB), poly(diethylene adipate) (PDEA), tributyl citrate-oligoester (TbC-oligoesters), polyvinyl acetate (PVA), or polycaprolactone (PCL).^{1,12–17}

From the multitude of possible plasticizer systems for PLA, PEG is one of the plasticizer most commonly used in film application.¹⁸

Recent studies of PLA plasticized with PEG^{19–23} have demonstrated an increase in the efficiency of plasticization with a decrease of PEG molecular weight. Because 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.⁸ Therefore, a high molecular weight PEG (4000 g/mol) was used as PLA plasticizer in this study. In addition, the plasticizer used has to be non-toxic to produce films which are suitable for food contact. As PEG has been approved for use in direct food contact, it meets these criteria.

As already mentioned, PLA is used in the packaging industry. The most important function of packaging is to ensure the protection and integrity of the product. This implies that the pack-

must be securely welded. Product protection and hence effective shelf life are a function of the quality of joining of the package.²⁴ In packaging industry there are many techniques available for joining thermoplastic materials, such as adhesive bonding and welding. Adhesive bonding suffers the disadvantage of adding a third component to the two parts to be joined. On the contrary, welding has the advantage of not requiring a third component.²⁵ In addition, there are many different welding methods suitable for industrial production of thermoplastic packages. The methods most frequently used for packaging are heat welding and ultrasonic welding.

The increase in the uses of the ultrasonic welding process results from several advantages over heat welding, such as much shorter process times. Moreover, unheated tools permit the widespread utilization of the ultrasonic welding technology especially in the packaging sector.

During ultrasonic welding high-frequency (typically 20, 30, 35, or 40 kHz), low-amplitude (typically between 10 and 60 μm) vibrations are used to generate heat at the joint interface of the parts being welded. The two parts to be welded are held together under pressure during the process and a bond forms upon the cooling of the molten polymer at the interface.^{26–28}

The weldability of polymers and the high quality of the weld are not only a function of the amount of mechanical energy delivered to the welding zone, but also the properties of the welded materials.^{29,30} Blending PLA with a plasticizer (PEG) affects the mechanical properties of the PLA. Therefore, it is to be expected that the addition of the plasticizer affects the weldability of PLA films.

Although there are a few publications^{31–33} dealing with ultrasonic welding of PLA films, there are no publications regarding the influence of the material composition on the weldability of PLA films. Therefore, this research is intended to consider the effects of the plasticizer amount on the mechanical properties and weldability of the plasticized PLA films. The purpose of this study is to provide background information regarding the weldability of plasticized PLA films via ultrasonic welding.

EXPERIMENTAL

Materials

The 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

Before processing, neat PLA granules were dried in a dry-air oven at 80°C until the required residual moisture content (under 250 ppm) was achieved. Compounds containing 0, 5.3, 7.9, and 10.6 phr (parts per hundred parts of resin based on 100 parts of PLA) plasticizer (PEG 4000) were prepared using a Leistritz corotating twin-screw extruder ($L/D = 45$; $D = 18$ mm). To maintain the stability of the compounds, Irga-

nox 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 to prevent premature melting of the plasticizer and reached a maximum of 200°C. The melt temperature was also 200°C. A vacuum was pulled on the vent port of the extruder to remove residual moisture. The used 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 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 a cast film a single-screw extruder from Dr. Collin with a diameter of 30 mm and an L/D ratio of 30 was used. The neat PLA granulates and the compound granulates containing 0 phr plasticizer were extruded with a screw speed of 90 rpm, whereas compound granulates containing 5.3, 7.9, and 10.6 phr were extruded with a screw speed of 60 rpm. The temperature in the feeding zone for the neat PLA granulates was 75°C and for the compound granulates containing 0 phr plasticizer the temperature in the feeding zone was 100°C reached a maximum of 200°C. The temperature of the water entering the chill roll was 50°C. For the granulates containing 5.3, 7.9, and 10.6 phr plasticizer 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. The adjustment of process parameters for each material composition was required to make good-quality films. By adjusting the speed on the rewind stand and chill roll it was possible to control the thickness of the polymer films. The thickness of the polymer films is set to be 50 μm .

Overview of the Investigated Films

As already defined, the compounds were prepared by an extrusion compounding technique (melt blending) where a material receives sufficient thermal and shear history to mix stabilizers and/or a plasticizer with the polymer matrix and to be configured into a shape (granules). Afterwards film extrusion was performed. Each step of processing, melt blending and film extrusion may influence the properties of the material, because structural changes may occur when the polymer is submitted to several processing steps.

To determine to which extent the processing of PLA (melt blending, film extrusion) on the one hand and the addition of PEG on the other changed the properties and weldability of the PLA films, the following films were examined (see Table I).

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 to 210°C to erase previous thermal history, then

Table I. Film Label as a Function of the Material Composition and the Processing Method

Description	Film composition			Processing method (step)	
	PLA content [phr]	Stabilizer content [phr]	Plasticizer content [phr]	Melt blending	Film extrusion
Film 1	100	0.0	0.0	-	+
Film 2	100	0.4	0.0	+	+
Film 3a	100	0.4	5.3	+	+
Film 3b	100	0.4	7.9	+	+
Film 3c	100	0.4	10.6	+	+

cooled to -70°C and finally heated to 210°C , at a cooling/heating rate of 10 K/min. Thermograms were recorded and, among others, glass transition temperatures, crystallization temperatures and melting temperatures evaluated.

Rheological Characterization

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

Ultrasonic Welding (Sealing) (US)

An ultrasonic welding system 2000 \times from Branson, operating at a frequency of 20 kHz, was used for the trials. An anvil with a diameter of 4.0 mm and a sonotrode with a width of 2.0 mm were used. The weldability of the material as a function of welding process variables like amplitude, welding pressure and welding time were analyzed. Because of the radius-shaped anvil welding pressure could not be calculated. For that reason the welding force, specified as force per length, was used as a relevant process variable. The ranges of amplitude, welding force, and welding time were 13–32 μm , 0.8–2.0 N/mm and 0.1–0.5 s, respectively. The holding time was kept constantly at 1.0 s and the holding force at 2.0 N/mm. All joints were made by welding a film to an identical film.

Tensile Testing

The tensile test is the commonly used test for determining mechanical properties of materials. Properties that are directly calculated using 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 neat and plasticized PLA films and 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 neat and 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.

RESULTS AND DISCUSSION

Influence of the Material Composition on the Processing Window (Suitable Range of Welding Parameters)

Initially a wide range of welding parameters (amplitude, welding time and welding force) was evaluated, to define a process window for the PLA films that were examined. The joint was considered sufficiently strong when it could withstand manual peeling without delamination. The amplitude, the welding time and the welding force were varied from 13 to 32 μm , from 0.1 to 0.5 s, and from 0.8 to 2.0 N/mm, respectively. Outside the ranges mentioned above no welds were generated. At the lower amplitudes, shorter welding times and lower welding forces material did not melt so that no joining could take place. At the higher amplitudes, longer welding times and higher welding forces films were not welded but cut through by the sonotrode.

As a result of the analysis it was discovered that the process window is individually dependent on the film composition. In addition, it was observed that the PLA films modified with PEG could be welded at lower amplitude compared with PLA films without a plasticizer, both film 1 (only one processing step; film extrusion) and film 2 (two processing steps; melt blending and film extrusion) (see Figure 1).

As seen from Figure 1, the addition of PEG leads to a decrease in minimum amplitude applied. On the other hand, the maximum amplitude applied remains constant and independent of the plasticizer content.

Furthermore, according to the differential scanning calorimetry measurements (corresponding thermograms could be seen in Ref. 8), the addition of PEG as a plasticizer resulted in a decrease in the glass transition temperature (T_g) because of improved chain mobility (see Figure 2).

These results reveal that improved chain mobility takes place at lower temperatures with increasing plasticizer concentration. Consequently, less energy is required to make polymer chains moving causing frictional forces between molecules and therefore frictional heat. Thus, less energy is required to get a

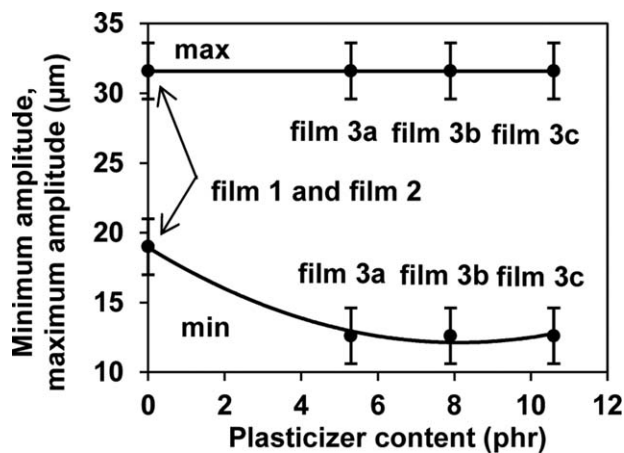


Figure 1. Minimum and maximum amplitude as a function of the plasticizer content.

sufficient amount of molten material necessary to achieve fusion at the interface between the films and thus sufficiently strong weld. Therefore, plasticized PLA films could be welded at lower amplitudes compared with PLA films without plasticizer, because by reducing the amplitude there is reduction in heating.

Besides during ultrasonic welding films undergo periodic mechanical load. This mechanical energy is partially used for internal friction of molecules, which causes a frictional heat. Damping factor ($\tan\delta$) is thereby an indicator of how efficiently the material converts mechanical energy into heat.

As observed from rheological measurements the presence of the plasticizer increased $\tan\delta$ (see Figure 3).

Because the plasticized PLA films have a greater $\tan\delta$ compared to the PLA films without the plasticizer, during ultrasonic welding of plasticized PLA films more mechanical energy will be converted into heat. Thus, the modified PLA films can be welded at lower amplitudes compared with PLA films without the plasticizer.

Moreover, it was possible to weld plasticized PLA films at the higher welding force comparing to the PLA films without the plasticizer, both film 1 and film 2 (see Figure 4).

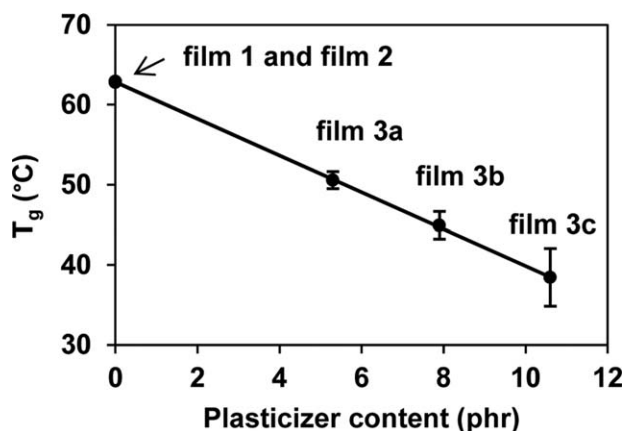


Figure 2. Glass transition temperature as a function of the plasticizer content.

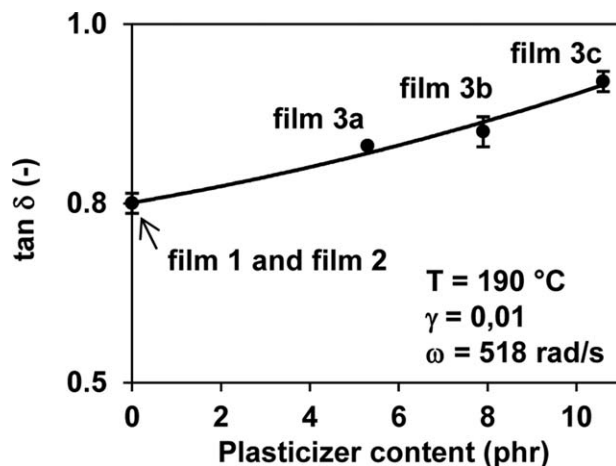


Figure 3. Damping factor as a function of the plasticizer content.

As shown in Figure 4 the addition of the plasticizer had no influence on the minimum welding force, whereas the maximum welding force was increased by the addition of PEG, although plasticized PLA films have higher $\tan\delta$.

The fact that the plasticized PLA films could be welded at lower amplitude and at the higher welding force compared with PLA films without the plasticizer indicates that the addition of PEG results in wider ultrasonic welding process window.

Influence of the Welding Parameters on the Weld Quality

After a determination of the suitable range of the welding parameters (process window) for each film composition, a parameter study was carried out and the influences of welding parameters on the weldability of the examined films were conducted.

Through the examples of film 1 and film 3c, weld strength as a function of amplitude, welding force and welding time are shown in Figures 5–10. According to Figure 5 the amplitude and the welding force has a big influence on the weld strength at constant welding time (0.1 s). At a low welding force (0.8 N/mm) increasing the amplitude from 19 to 25 μm leads to an increase in weld strength. The weld strength remains rather constant, while increasing the amplitude from 25 to 32 μm . At

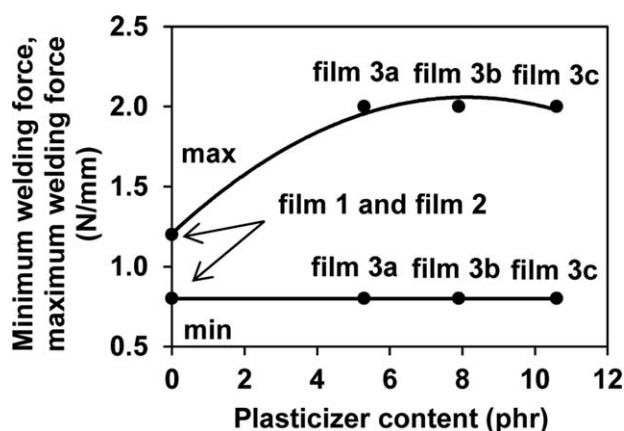


Figure 4. Minimum and maximum welding force as a function of the plasticizer content.

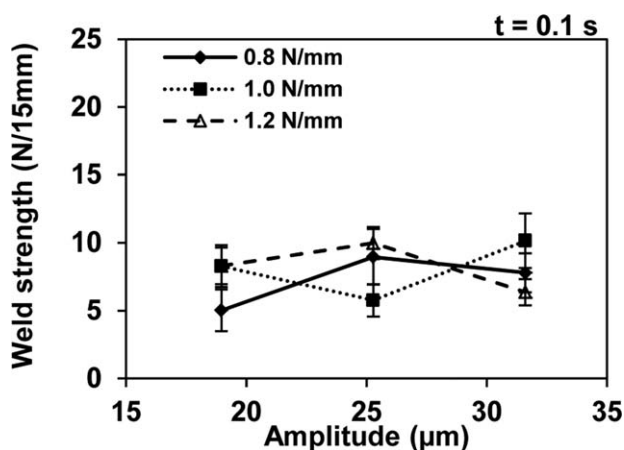


Figure 5. Weld strength at 0.1 s welding time, different welding forces and, amplitudes from welded film 1.

medium welding force (1.0 N/mm) there is a decrease in the weld strength with amplitude increasing from 19 to 25 μm . A further amplitude increase to 32 μm leads to an increase in weld strength. Moreover it was observed that increasing the amplitude from 19 to 25 μm at high welding force (1.2 N/mm) the weld strength slightly improves. In addition, a drop in the weld strength was noticed by increasing the amplitude from 25 to 32 μm .

Furthermore the welding time was increased to 0.2 s and the influences of the amplitude and the welding force on the weld strengths were studied (see Figure 6). As seen in Figure 6 the weld strength is almost independent from the amplitude at low (0.8 N/mm) and at medium (1.0 N/mm) welding forces, whereby the higher weld strength is reached at a low (0.8 N/mm) welding force. Increasing the amplitude to a high (1.2 N/mm) welding force leads to an increase in weld strength.

Additionally the weld strength as a function of the amplitude at various welding forces and at a constant welding time (0.4 s) for film 1 is shown in Figure 7. Independent from the welding force being examined (0.8, 1.0, and 1.2 N/mm) a comparable trend is noticeable. While increasing the amplitude from 19 to

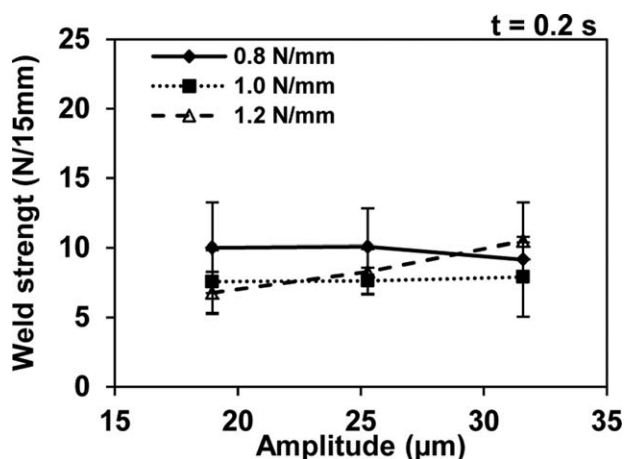


Figure 6. Weld strength at 0.2 s welding time, different welding forces and, amplitudes from welded film 1.

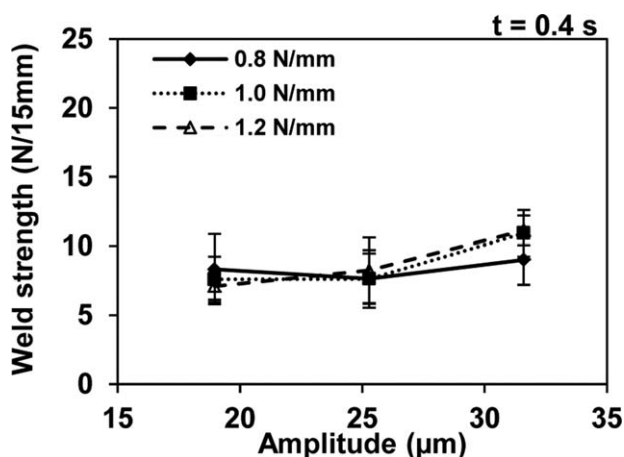


Figure 7. Weld strength at 0.4 s welding time, different welding forces and, amplitudes from welded film 1.

25 μm , there is no significant change in the weld strength. Moreover the weld strength was constant for all welding forces being examined (0.8, 1.0, and 1.2 N/mm) at a welding time of 0.4 s and amplitudes from 19 to 25 μm . A further amplitude increase to 32 μm leads to an increase in weld strength. In addition at welding forces 1.0 and 1.2 N/mm the similar weld strength was reached, being higher as the weld strength at welding force 0.8 N/mm.

Furthermore the weld strength as a function of amplitude, welding force and welding time for film 3c was examined.

First, the welding force was increased from 0.8 to 2.0 N/mm at constant amplitude (13 μm) and welding time (0.1 s) (see Figure 8). This increase of the welding force leads to an increase in weld strength. Nevertheless the standard deviation is extremely high indicating an unstable welding process. A further amplitude increase from 13 to 19 μm leads to an increase in weld strength at welding forces of 0.8 and 1.5 N/mm and in contrast to that to a decrease in weld strength at a welding force of 2.0 N/mm. Increasing the amplitude further to 32 μm leads to a decrease in weld strength with all welding forces being examined (0.8, 1.5, and 2.0 N/mm).

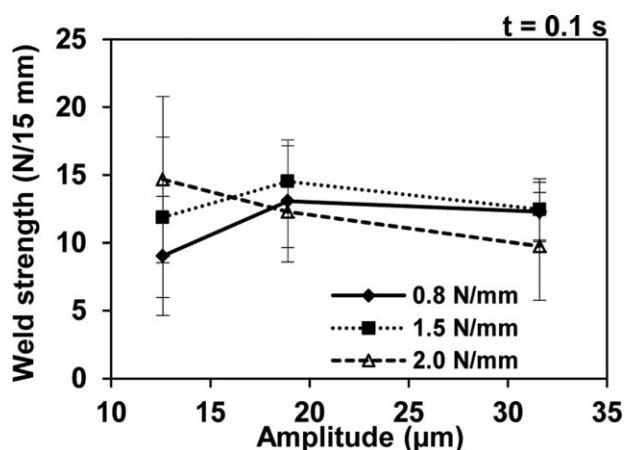


Figure 8. Weld strength at 0.1 s welding time, different welding forces and, amplitudes from welded film 3c.

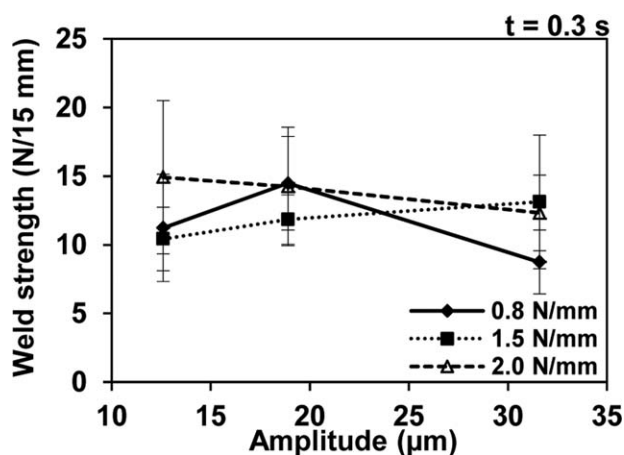


Figure 9. Weld strength at 0.3 s welding time, different welding forces and, amplitudes from welded film 3c.

Second, the welding time was increased to 0.3 s and the influences of welding force and amplitude on the weld strength were studied (see Figure 9). As seen in Figure 9 increasing the amplitude leads to a decrease in weld strength at a high (2.0 N/mm) welding force and to an increase in weld strength at a medium (1.5 N/mm) welding force. With a low (0.8 N/mm) welding force increasing the amplitude from 13 to 19 μm leads to an increase in weld strength. Furthermore, the weld strength decreases, while increasing the amplitude from 19 to 32 μm .

Finally, the welding time was increased to 0.5 s and the influences of welding force and amplitude on the weld strength were investigated (see Figure 10). It can be seen that at low (13 μm) amplitude the weld strength remains unaffected by increasing the welding force in the examined range (0.8, 1.5, and 2.0 N/mm). At medium (19 μm) amplitude increasing the weld force from 0.8 to 2.0 N/mm leads to an increase in weld strength. Furthermore, at high (32 μm) amplitude the highest weld strength has been achieved at high (2.0 N/mm) welding force, whereas there were no big differences between the weld strengths at medium (1.5 N/mm) and low (0.8 N/mm) welding forces.

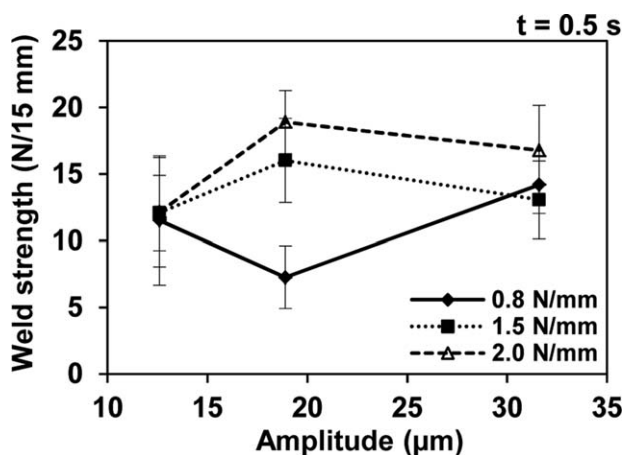


Figure 10. Weld strength at 0.5 s welding time, different welding forces and, amplitudes from welded film 3c.

Table II. Weld Parameters Used to Achieve the Maximum Weld Strength as a Function of the Material Composition and the Processing Method (Step)

Description	Amplitude [μm]	Welding time [s]	Welding force [N/mm]
Film 1	32	0.4	1.2
Film 2	32	0.4	1.2
Film 3a	32	0.3	0.8
Film 3b	13	0.3	2.0
Film 3c	19	0.5	2.0

As seen in Figures 5–10 there is no unambiguous dependency of welding parameters on the weld strength. Therefore a clear statement about the influence of the welding parameters on the weld strength could not be made but only described. This fact can be an indication that numerous factors such as, tolerance of the film thickness or fluctuation in the welding process make the evaluation of optimal weld quality difficult.

Influence of the Material Composition on the Weld Quality

The main aim of the parameter study was to find the right combination of welding parameters which result in the maximum weld strength for particular material composition. The weld parameters used to achieve the best weld strengths as a function of material composition are listed in Table II.

Furthermore, a kind of weld factor (Weld factor = tensile strength of the weld / tensile strength of the base material) as important factor regarding the weld quality was evaluated. Figure 11 shows the weld factor as a function of the plasticizer content.

According to Figure 11, it was discovered that the addition of a plasticizer leads to the improvement of the weld factor and thereby to the improvement of weldability. Furthermore, the weld factor seems to be dependent on plasticizer amount. Increasing the plasticizer content leads to an increase in weld factor and thus in weldability.

The increase in the weldability can be explained by the fact that the plasticized PLA films have a lower viscosity in comparison

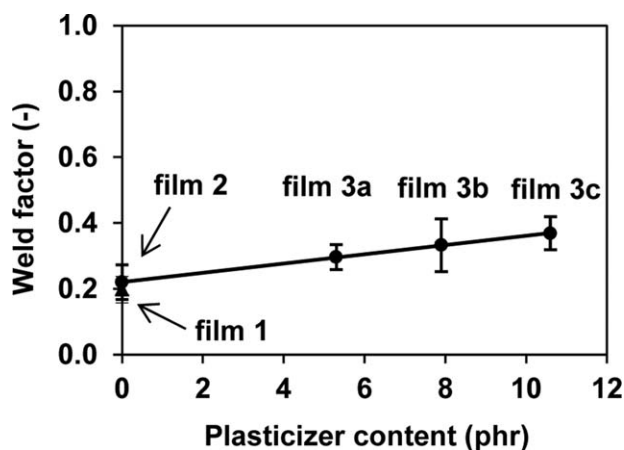


Figure 11. Weld factor as a function of the plasticizer content.

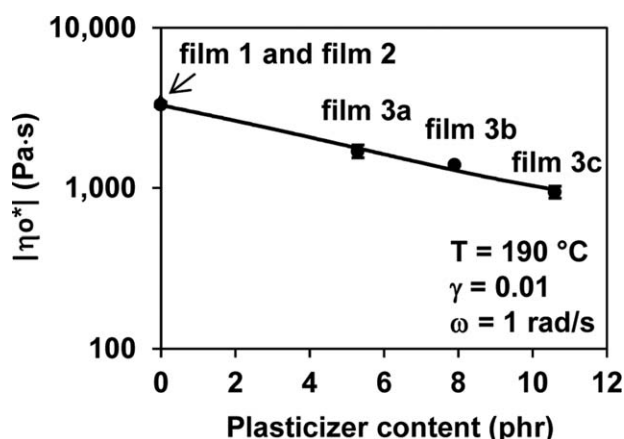


Figure 12. Zero shear viscosity as a function of the plasticizer content.

to the neat PLA films, both film 1 and film 2 (see Figure 12). The addition of PEG as a plasticizer resulted in viscosity decrease because of improved chain mobility.

While welding two films which both have symmetric interfaces, where the same polymer exists on both sides of the interface, their molten surfaces are brought into contact. During the welding process, the molecules near the surfaces become mobile and the weld strength develops by a combination of surface rearrangement, wetting, and diffusion. Thereby, wetting or close molecular contact (van der Waals) first occurs followed by interdiffusion of chain segments back and forth across the wetted interface.³⁴ A decrease in the viscosity enhances the mobility of the molecules. The increased chain mobility contributes to the more effective diffusion of polymer chains during welding and thus results in an increase of the weld strength and accordingly in an increase of the weld factor.

Moreover the material stiffness basically affects its ability to transmit the ultrasonic energy to the joint interface. The greater the material stiffness the better is its transmission capability. Young's modulus is often used as a measure of the material stiffness. As can be seen in Figure 13 there is a slight drop in

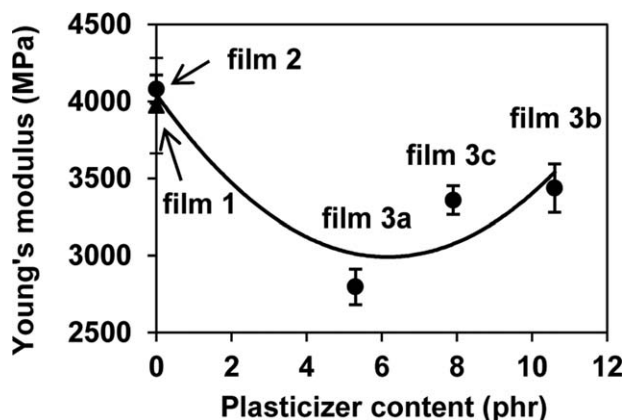


Figure 13. Young's modulus as a function of the processing step and the plasticizer content.

Young's modulus between film 2 and film 1. However, because of the high standard deviation of the Young's modulus for the film 1, it can be concluded, that there is no significant difference in the stiffness between film 1 and film 2. Furthermore the Young's modulus of film 2 was compared with Young's modulus of films modified with PEG (films 3a, 3b, and 3c). Thus, the influence of increasing plasticizer concentration on Young's modulus of plasticized films could be determined, because film 2 and films 3a, 3b, and 3c had the same previous processing history (melt blending and film extrusion). Additionally, the Young's modulus seems to be dependent on the plasticizer amount. Increasing the plasticizer amount leads to an increase in Young's modulus. According to Figure 13 film 2 and film 1 have the highest transmission capability for ultrasonic energy, followed by film 3a, 3b, and 3c respectively. However, as seen in Figure 11 plasticized PLA films have a higher weld factor as neat PLA film. Therefore, it could be concluded, that in the case of thin films (50 μm) due to a short transmission length of energy the material stiffness does not have crucial influence on the weld strength.

CONCLUSION

To test the weldability of PLA, the neat and plasticized PLA films were subjected to ultrasonic welding. It was discovered that it was possible to weld all the examined films, but their processing behavior seems to be affected by the material composition. The experimental research showed that the addition of a plasticizer resulted in wider process window, that is, it was possible to weld plasticized PLA films at lower amplitude and at the higher welding force compared with PLA films without a plasticizer. Because structural changes may occur when the polymer is submitted to several processing steps thus affecting the weldability and especially the processing window, it was examined if there are any differences in the processing window comparing two different unplasticized PLA films: film 1 (only one processing step; film extrusion) and film 2 (two processing steps; melt blending and film extrusion). The experimental research showed that both, film 1 and film 2, could be welded at the same welding conditions. In other words, the multiple processing stages didn't have any influence on the welding parameters.

Furthermore, it was determined that the addition of a plasticizer leads to the improvement of weld factor and thereby to the improvement of weldability. Additionally, the weld factor seems to be dependent on the plasticizer amount. Increasing the plasticizer content leads to an increase in weld factor and thus in weldability. Moreover, the weld factor of two different unplasticized PLA films, one of which was submitted to only one processing step (film 1) and the other one was submitted to two processing steps (film 2) was compared. However, the achieved weld factors seem to be independent of the processing steps.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from the German Parliament. The project (17623 N) is sponsored by AiF (Alliance of Research Associations) within the program to

promote Joint Industrial Research (IGF) by the Federal Ministry for Economic Affairs and Energy, based on a resolution of the German Parliament.

REFERENCES

1. Rasal, R. M. Surface and bulk modification of poly(lactic acid), Ph.D. Thesis, Graduate School of Clemson University, **2009**.
2. 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**.
3. Li, H.; Huneault, M. A. *Polymer* **2007**, *48*, 6855.
4. Auras, R.; Harte, B.; Selke, S. *Macromol. Biosci.* **2003**, *4*, 835.
5. Rabetafika, H. N.; Paquot, M.; Dubois, P. *Biotechnol. Agron. Soc. Environ.* **2006**, *10*, 185.
6. Weber, C. J.; Haugaard, V.; Festersen, R.; Bertelsen, G. *Food Addit. Contam.* **2002**, *19*, 172.
7. Hassouna, F.; Raquez, J. M.; Addiego, F.; Toniazzo, V.; Dubois, P.; Ruch, D. *Eur. Polym. J.* **2012**, *48*, 404.
8. Stoehr, N.; Baudrit, B.; Haberstroh, E.; Nase, M.; Heidemeyer, P.; Bastian, M. *J. Appl. Polym. Sci.* **2014**, *131*, 40394; doi: 10.1002/app.40394.
9. Lim, L. T.; Auras, R.; Rubino, M. *Prog. Polym. Sci.* **2008**, *33*, 820.
10. Anderson, N. S.; Schreck, K. M.; Hillmyer, M. A. *Polym. Rev.* **2008**, *48*, 85.
11. Hassouna, F.; Raquez, J. M.; Addiego, F.; Dubois, P.; Toniazzo, V.; Ruch, D. *Eur. Polym. J.* **2011**, *47*, 2134.
12. Gajria, A. M.; Dave, V.; Gross, R. A.; McCarthy, S. P. *Polymer* **1996**, *37*, 437.
13. Park, J. W.; Im, S. S. *Polymer* **2003**, *44*, 4341.
14. Sivalingam, G.; Karthik, R.; Madras, G. *Polym. Degrad. Stab.* **2004**, *84*, 345.
15. Liu, H.; Zhang, J. *J. Polym. Sci. Polym. Phys.* **2011**, *49*, 1051.
16. Rasal, R. M.; Janorkar, A. V.; Hirt, D. E. *Prog. Polym. Sci.* **2010**, *35*, 338.
17. Meng, B.; Tao, J.; Deng, J.; Wu, Z.; Yang, M.; *Mater. Lett.* **2011**, *65*, 729.
18. Wypych, G. Handbook of Plasticizers; ChemTec Publishing: Toronto, **2004**; Chapter 11, p 312.
19. Baiardo, M.; Frisoni, G.; Scandola, M.; Rimelen, M.; Lips, D.; Ruffieux, K.; Wintermantel, E. *J. Appl. Polym. Sci.* **2003**, *90*, 1731.
20. Kulinski, Z.; Piorkowska, E. *Polymer* **2005**, *46*, 10290.
21. Jacobsen, S.; Fritz, H. G. *Polym. Eng. Sci.* **1999**, *39*, 1303.
22. Pillin, I.; Montrelay, N.; Grohens, Y. *Polymer* **2006**, *47*, 4676.
23. Hassouna, F.; Raquez, J. M.; Addiego, F.; Dubois, P.; Toniazzo, V.; Ruch, D. *Eur. Polym. J.* **2011**, *47*, 2134.
24. Kirwan, M. J.; Strawbridge, J. W. In Food Packaging Technology, Coles, R., McDowell D., Kirwan, M. J. Eds. Blackwell Publishing: New York, **2003**; Chapter 7, p 217.
25. Sancaktar, E.; Eric Walker, E. *J. Appl. Polym. Sci.* **2004**, *94*, 1986.
26. Truckenmüller, R.; Cheng, Y.; Ahrens, R.; Bahrs, H.; Fischer, G.; Lehmann, J. *Microsystem Technol.* **2006**, *12*, 1027.
27. Nonhof, C. J.; Luiten, G. A. *Polym. Eng. Sci.* **1996**, *36*, 1177.
28. Stokes, V. K. *Polym. Eng. Sci.* **1989**, *29*, 1310.
29. Gutnik, V. G.; Gorbach, N. V.; Dashkov, A. V. *Fibre Chem.* **2002**, *34*, 426.
30. Nase, M.; Bach, S.; Zankel, A.; Majschak, J.-P.; Grellmann, W. *J. Appl. Polym. Sci.* **2013**, *130*, 383.
31. Grewell, D.; Vogel, J.; Haubrich, K.; Srinivashan, G. Proceedings Society of Plastics Engineers (SPE) ANTEC; **2009**, 306.
32. Vogel, J.; Grewell, D. Proceedings Society of Plastics Engineers (SPE) ANTEC; **2010**, 1931.
33. Vogel, J.; Grewell, D.; Kessler, M. R.; Drummer, D.; Menacher, M. *Polym. Eng. Sci.* **2011**, *51*, 1059.
34. Wool, R.P.; Yuan, B.-L.; McGarel, O. J. *Polym. Eng. Sci.* **1989**, *29*, 1340.