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Cite as: AIP Conference Proceedings **2205**, 020019 (2020); https://doi.org/10.1063/1.5142934

Kübra Güzel, Marco Klute, Naci Kurgan, and Hans-Peter Heim

Influence of the Degree of Crystallinity and the Surface Free Energy on the Adhesion Properties of Different PLA/PBS Blends in Multicomponent Injection Molding

Kübra Güzel[1, 2a)], Marco Klute[2, b)], Naci Kurgan[1, c)] and Hans-Peter Heim [2, d)]

[1]*Ondokuz Mayıs University (Turkey)*
[2]*Kassel University (Germany)*
[a)]kubra.guzel@uni-kassel.de, [b)]marco.klute@uni-kassel.de, [c)]naci.kurgan@omu.edu.tr, [d)]heim@uni-kassel.de

Abstract Biocomposites made of biodegradable polymers have grown in interest due to their environmentally friendliness, considering that non-biodegradable polymers waste conduces to pollution, displaying high environmental impact in climatic changes. Therefore, in the presented study, biodegradable Poly (lactic acid) (PLA) and poly (butylene succinate) (PBS) were investigated as a series of PLA/PBS melt-blending compounds with the weight ratios of 50/50, 60/40, 70/30, 80/20 and 90/10. In a two-component injection molding process, they were used as the hard component to create hard-soft-combinations. Thermal properties, crystallinity and mechanical properties were examined with regard to the change in the adhesive bonding strength between the PLA/PBS compounds and thermoplastic polyurethane (TPU) under the influence of time and temperature (storage at room temperature and 100 °C in the course of 1, 3, 7 and 14 day(s)).The adhesion properties of the PLA/PBS blends were identified via Drop Shape Analysis (DSA) using a contact angle measurement device and corroborated with FTIR/ATR measurements. The attenuation in the interfacial tension between the blends and TPU with increasing amount of PBS content in the blend provided better bonding abilities. The maximal load required to disconnect these two components was measured by a universal tensile test machine. According to the results, the highest maximal load (552,69 N) was achieved with the PLA/PBS blend with a weight ratio of 60/40 wt% after being subjected to seven days of storage at 100 °C.

INTRODUCTION

In recent years, there is a growing interest to increase the sustainability of products by using bio-based polymers. According to the study of the Nova-Institute GmbH, the bio-based polymers have a share of 1,5 % in the field of construction polymers. This share represented a production of 3.5 million annual tons of the bio-based polymers in 2011 and it will be tripled to nearly 12 million tons by 2020 [1]. PLA is an aliphatic polyester that is obtained from renewable plant sources such as potatoes, sugar from beet and starch from corn. According to studies on PBS, films as well as molded objects show a significant biodegradation after a couple of months in soil, water with activated sludge or in the ocean [2]. Bhatia et al. investigated the possibility to replace commodity polymers with PLA/PBS blends for the use in packaging applications. It could be shown, that the tensile strength and the elastic modulus both decrease with increasing amount of PBS [3]. Ojijo et al. concluded that samples, that were tempered at 80 °C show a reduction in the yield strength for PLA-dominated blends since the crystallization of the PLA component during the annealing process causes a phase separation [4]. When it comes to the thermal characteristic of the PLA/PBS blends, the addition of PBS enhances the crystallization of the PLA and the DSC diagrams display two melting peaks over the entire composition range indicating that both polymers are semi-crystalline [5].

EXPERIMENTAL

The PLA used in this study is a commercial grade (PLA 2003D), that was purchased from Natureworks LLC. (Nebraska, USA), with an organic content of 100 %. On the other hand, PBS (bio PBS FZ71 PM), was obtained from Mitsubishi Chemical Co. (Tokyo, Japan) with an organic content of 50 %. As a soft component for the

Proceedings of the 35th International Conference of the Polymer Processing Society (PPS-35)
AIP Conf. Proc. 2205, 020019-1–020019-5; https://doi.org/10.1063/1.5142934
Published by AIP Publishing. 978-0-7354-1956-8/$30.00

hard- soft- combinations Elastollan N 95A 12 000 (TPU95) was used. It has an organic content of 43 % and was produced by BASF Polyurethanes GmbH (Lemförde, Deutschland). Since both, the PLA as well as the PBS have hydrophilic characteristics, they were dried for 4 hours at 60 °C prior to processing. The PLA/PBS blends were compounded in a twin-screw extruder (ZSE18 HPe, Leistritz Extrusionstechnik GmbH, Nürnberg, Germany) at different weight-ratios (50/50, 60/40, 70/30, 80/20, 90/10). The temperature (180 °C), throughout rate (6 kg/h) and the screw speed (200 rpm) were fixed for all experimental runs.

The one- and two-component test specimens were produced by using an injection molding machine (Allrounder 320 C Golden Edition, Arburg GmbH + Co KG, Loßburg, Germany). The sample geometry was chosen according to A1 tensile test specimen (ISO 527-1). The temperature of the barrel to produce the one-component specimens (composed of PLA/PBS blends) was set to 190, 185, 180, 175 and 170 °C from nozzle to hopper. The mold temperature was kept at 30 °C. While the holding time was set to 13 s, the cooling time and the injection velocity were adjusted to the amount of PBS in the blends (25-60 s and 30-40 cm³/s). To produce two-component test specimen, the one-component tensile test pieces of the PLA/PBS-blends were cut perpendicular to the melt flow direction in a distance of 80 mm from the sprue distant side. The halved test specimens were placed as inserts in the cavity of the injection mold, so that the second component (TPU 95) could be injected onto the cut surface to create a two- component tensile test specimen. For the injection molding of the TPU, barrel temperatures of 220, 215, 210, 205 and 200 °C were used from nozzle to hopper. The mold temperature of 30 °C, the holding time of 2 s, the injection velocity of 10 cm³/s and the cooling time of 20 s were selected.

To determine the influence of raised temperatures on the mechanical and thermal behavior, storage tests were carried out. The storage types consisted of the combination among 2 different temperatures (room temperature and 100 °C) and 5 different storage lengths (0, 1, 3, 7 and 14 day(s). The room temperature storage was carried out at a standardized climate of 23 °C and 50 % relative humidity (ISO 527-1).

On the purpose of measuring the maximal load that is needed to separate the two components from each other, tensile tests were carried out by using a universal testing machine (Zwick Z010, Ulm, Germany). According to ISO 527-1, the specimens that were stored at 100 °C were kept at 23 °C and 50 % relative humidity for at least 16 hours prior to the tensile test. The tests were conducted with a constant speed of 10 mm/min and 5 samples were tested for each combination of the storage length and the temperature.

Thermal analysis was performed by using the differential scanning calorimetry (DSC-Module Q 1000, TA Instruments, New Castle, DE, USA) under a nitrogen atmosphere The samples (~10 mg) were heated to 200 °C at a rate of 10 K/min, cooled down to 0 °C at the same rate and then reheated to 200 °C. Each combination of the storage type and composition ratio was tested. The degree of the crystallinity (Xc) of the samples was calculated by the following relationship:

$$X_C(\%) = \frac{\Delta H_f}{W_{PLA/PBS} \times \Delta H_f^0} \times 100 \tag{1}$$

Where ΔH_f is the heat of fusion of the PLA or PBS in the blend, ΔH_f^0 is the heat of the fusion for 100 % crystalline PLA (93 J g^{-1}) or PBS (110,3 J g^{-1}) [6] and W_{PLA} ,W_{PBS} are the weight fractions of the PLA and PBS in the blend.

A contact angle measuring device (Krüss GmbH, Hamburg, Germany) used to measure the left and right tangent angle of the fluid droplet on the material surface. As part of the two component model based on Fowkes [7] and OWRK [8] (Owens, Wendt , Rabel and Kaelble), the interfacial surface energy (γ_{LS}) was obtained by the sum of the surface free energies of the individual phases divided into their dispersive (D) and polar (P) interaction between phases. The equation is given as following:

$$\gamma_{LS} = \sigma_L + \sigma_S - 2\left(\sqrt{\sigma_L^D \times \sigma_S^D} + \sqrt{\sigma_L^P \times \sigma_S^P}\right) \tag{2}$$

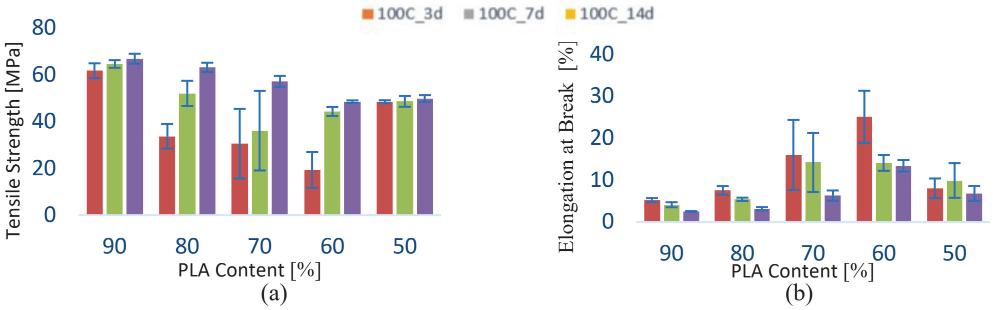
σ_L is the surface tension of the liquid and σ_S indicates the surface free energy of the solid. To calculate the dispersive and polar phase of the surface free energy of the samples, two liquids of known surface tensions had to be used. Almost purely dispersive diiodomethane (surface tension 50,8 mN/m, polar component 2,3 mN/m, dispersive component 48,5 mN/m [7]) and highly polar water (surface tension 72,8 mN/m, polar component 51,0 mN/m, dispersive component 21,8 mN/m [9]) were chosen as the test liquids.

Fourier transform infrared spectroscopy (FTIR spectroscopy) with an FTIR spectrometer (Shimadzu, IRAffinity - 1S, Kyoto, Japan) was used for further investigation. The specimens were examined using the attenuated total reflection (ATR) without prior preparation of the specimen.

RESULTS AND DISCUSSION

Mechanical Properties of Blends

The averaged tensile strength results are shown in Fig. 1 (a). It can be seen that with increasing content of PBS up to 40 wt%, a reduction in the tensile strength eventuates. This is indicative of the influence of the weaker PBS component on the strength of the material. The highest tensile strength of 67 MPa was obtained after 14 days storage of the PLA/PBS (90/10) at 100 °C. The longer storage time ensures a gradual drop in the strength with increasing amount of PBS. Fig. 1 (b) shows the results for the elongation at break as a function of the PLA content. According to the results, the highest elongation of 25 % occurred for the PLA/PBS (60/40) that was stored for 3 days at 100 °C. Analogous to the decrease in tensile strength, the increasing content of PBS leads to an increase in elongation at break up to a weight ratio of 40 wt% PBS. Moreover, it must be noticed that the highest standard deviation was measured at both plots in Fig. 1. when the PLA content was 70 wt%.

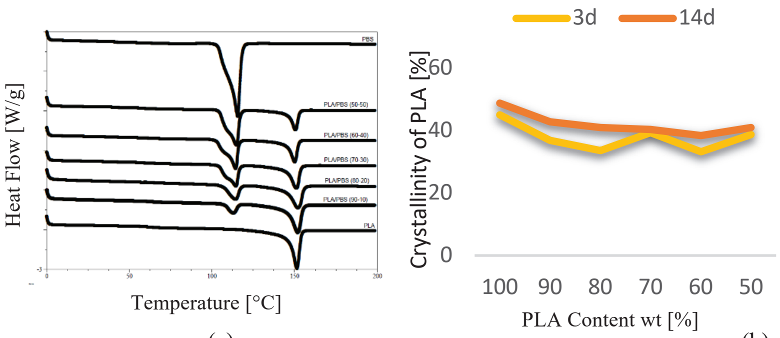


(a) (b)

FIGURE 1. Tensile strength (a) and elongation at break (b) of the PLA/PBS blends

Crystallinity and Thermal Analyses

Figure 2 (a) shows the results of the DSC measurements from the first heating scans. The first heating scan was used, to show the effects of the storage conditions. The none-stored pure PLA (not shown in Fig. 2 (a)) exhibited a glass transition at 61,25 °C and the crystalline melting at 148,09 °C. However, PLA and PLA/PBS blends did not show a noticeable glass transition after the storage at 100 °C. In addition, the melting peaks of PBS in the composition range of 30-50 % comprise a shoulder, verifying that the melting is overlaid by a recrystallization [10]. Referring to Fig. 2 (b), the longer storage length increased the crystallinity of the PLA in the blend. The fact, that the crystallinity of the PLA increases with weight ratios of 20-30 wt% PBS after 3 days storage at 100 °C, shows that the PBS works as a plasticizer for the PLA [11].



(a) (b)

FIGURE 2. (a) DSC traces of PBS, PLA and PBS/PLA blends after 14 days storage at 100 °C, (b) The crystallinity in the PLA after the storage 3- and 14-days at 100 °C as a function of PLA weight fraction.

Surface Free Energy and Interfacial Tension

The contact angle measurement was used to calculate the surface free energies of the PLA/PBS blends and the TPU95 under the influence of storage temperature and length. To reach a good bonding strength between the two components, the surface energies should have similar phase (dispersive or polar) interaction which eventuate in small interfacial tension [12] [13]. By comparing Fig. 3 and Table I, it can be observed that the calculated interfacial tension between PLA/PBS (60/40) and TPU95 correlates with the required load to disengage these two components. The highest interfacial tension (9,03 mN/m) was obtained after 1 day of storage at room temperature. This storage condition also leads to the lowest load (411,85 N). Moreover, Table I and Fig. 3 revealed that a longer thermal storage at 100 °C contributes to an increase in the adhesive bonding strength. Since the decrease in the polar phase of the soft component as well as hard component causes the attenuation in interfacial tension.

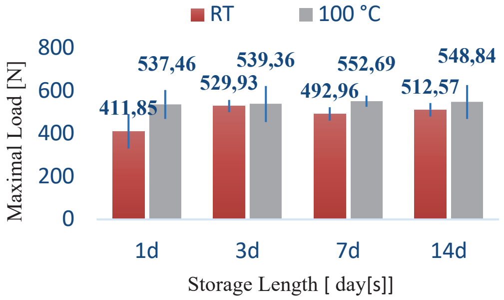


FIGURE 3. Load that was needed to separate the two-component test specimen (PLA/PBS (60/40) and TPU95)

TABLE I. Interfacial tension between the PLA/PBS (60/40) blend and TPU95, regarding storage temperature and length

	Interfacial Tension [mN/m]			
	1 day	**3 days**	**7 days**	**14 days**
RT (23 °C)	9,03	0,08	2,05	0,64
100 °C	0,6	0,63	0,54	0,46

Phase Morphology

Figure 4 illustrates the absorption peak shifts in specific region of pure PLA, pure PBS and the PLA/PBS (70/30) blend after the storage at 100 °C (3 and 14 days), measured by the ATR infrared spectroscopy to determine the intermolecular interactions.

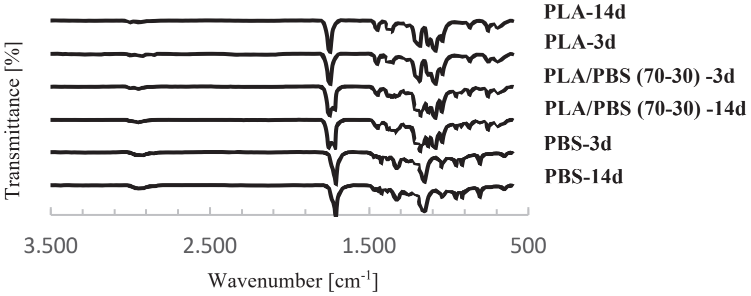


FIGURE 4. Infrared spectra in the 500-3,500 cm^{-1} region obtain from pure PBS, pure PLA and PLA/PBS (70-30) stored 3 and 14 days at 100 °C

The spectrum shows the C=O stretching for all samples with a single strong and sharp peak in the region of 1755- 1707 cm^{-1}. With increasing amount of PBS content, the stretching vibration of the C-O, C-C, and C-H groups signals appeared less but sharper in the region of 1100-1300 cm^{-1} indicating the increase in the polar phase of the PLA/PBS blend which results in the enhancement of the surface energy. According to calculation of the surface free energy and the tensile test results (not shown in the article), this increase contributed to the bonding strength.

CONCLUSIONS

PBS was added to the PLA to improve the crystallinity and the adhesive bonding strength in two component injection molding. The calculated interfacial tension between the PLA/PBS blends and the TPU estimates that the storage at 100 °C increases the bonding strength. These results also correlate with the increment in crystallinity of the PLA shown by the DSC measurement. The measurement of the reached maximal load needed to disengage the two- component test specimen complies with the calculated interfacial tension. The highest interfacial tension (9,03 mN/m) was obtained after 1 day of storage at room temperature. This storage condition also leads to the lowest load (411,85 N). The crystallization density and spherules' size of the PLA was affected by the addition of PBS regarding DSC measurement. In terms of mechanical properties, it was found that the tensile strength decreased with increased concentration of the PBS. The longer storage time ensures a less gradual drop in the strength with increasing amount of PBS. In contrast, the elongation at break shows an increase up to 40 wt% of PBS.

ACKNOWLEDGMENT

The author is grateful for the funding of this work from the polymer engineering department, University of Kassel.

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