INTERFACE PROPERTIES OF INJECTION MOLDED BIOPOLYMERS

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ABSTRACT

Rising prices for crude oil and the continuous trend of high complex technical products are good requirements to establish biopolymers in complex multicomponent applications. Currently a variety of industrial produced biopolymers are available such as the bio-based polymers Polylactide (PLA); Polyhydroxyalkanoate (PHA) and cellulosic plastic. Also “Drop In”-polymers are accessible e.g. Bio-Polyethylene (Bio-PE). To make the biopolymers available to more complex applications the material behavior regarding weld lines and binding behavior has to be investigated because the opportunity of weld lines rises with a more complex geometry of parts or more complex manufacturing processes. In case of multi component injection molding it is essential to know about the bond strength between the different materials. This work compares different thermoplastic biopolymers concerning the strength of hot-hot weld lines and the strength of hot-cold weld lines even in case of different material combinations. Whereas the variation of process parameters (melt temperature, mold temperature) does not show a significant influence of the generally high hot-hot weld line strength the influence on the hot-cold weld line strength is obvious. In case of a biobased PA 10.10 the tensile strength could be increased from 22 to 38 MPa. To purify the look and feel of plastics or to increase the resistance against scratches and other environmental impacts hard and/or self-healing PU-coatings are applied on the surface of a basic body. To minimize costs of production and reduce process time in-line surface coating is a valid method. Within these work the bonding strength between biobased thermoplastics and a PU-layer is investigated too.

Index Terms – biopolymer, weld line, in-line surface coating, interface

1. INTRODUCTION

Rising prices for crude oil and the continuous trend of high complex technical products are good requirements to establish biopolymers in complex multicomponent applications. Currently a variety of industrial produced biopolymers are available such as the bio-based polymers Polylactide (PLA); Polyhydroxyalkanoate (PHA) and cellulosic plastic. Also “Drop In”-Polymers are accessible e. g. Bio- Polyethylene (Bio-PE). Despite they have an identical chemical structure compared to their petrochemical pendants they are based on a regenerative biological feedstock (e. g. plants, bacteria, biological waste materials etc.).
The design complexity of technical parts and the merging of different manufacturing processes, e. g. the combination of thermoforming of composite sheets and injection-molding, lead to higher functional integration of technical products. The resulting material combinations create multiple interfaces and bondings (physical and chemical) between the different types of materials increasingly determine the overall structural strength of these parts as well as the strength of these interface connections.
Another impurity in structural parts are hot weld lines, which emerge because of the indifferent expansion of the molten plastic and the bonding of two or more melt fronts. The influence of the weld lines rises by increasing complexity of parts. Although the polarities of the surfaces and the melt temperatures are identical (because of the same type of plastic) hot-hot weld lines often show decreased strength.
Weld lines occur in multi component injection molding too. The structural strength of the part is determined by the bonding strength between the different materials as well.

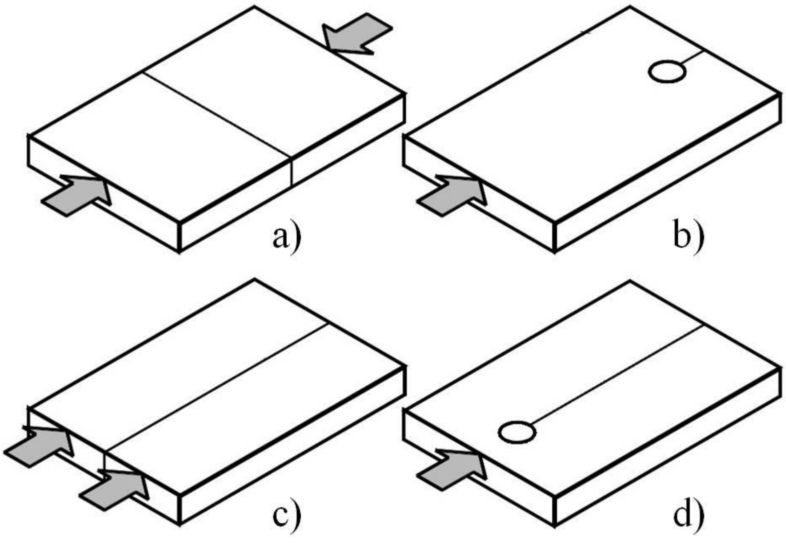
2. TEST SET-UP

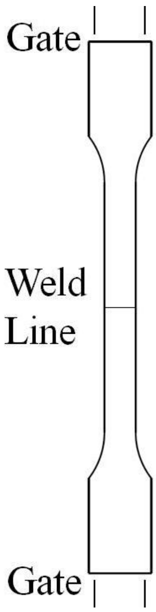
2.1 Hot-Hot Weld Lines

Hot-hot weld lines occur when several flow fronts of molten plastic join from different directions. A distinction of different types of weld lines can be made among their formation. First of all it must be separated between flowing and stagnating weld lines. Figure 1 shows these different types of weld lines. The more complex the parts are the greater the probability of occurring weld lines is. Because of the often decreased mechanical properties of weld lines they must be regarded as special weak points in part design [1].

For the following investigations tension bar mold that created a stagnating weld line with two streams of molten plastic (cf. Figure 1a) is used. During one filling of the mold tension bars with (cf. Figure 2) and withoud weld lines are produced simultaneously, which allows to compare the effects of high and low mold and melt temperatures directly. The tension bars features gates at both ends which guarantees the creation of a weld line in the middle of the rod (cf. Figure 2).
A KraussMaffei KM-250-1400-C2 was used for the injection molding of the tension rods. The molding tool, of dimensions 600 x 580 x 340 mm, has 4 main cavities that contain one falling dart plate, 8 flexural rods, 4 tension rods without weld lines and 2 tension rods with weld lines. Similar cavities can be blocked using a manifold located at the central gate. Only the tension rod cavities were used for the investigations of hot-hot weld lines. According to [2] a weld line factor *wf* can be calculated as follows:

$$wf = \frac{strength\ with\ weld\ line}{strength\ without\ weld\ line} \quad (1)$$





a) Stagnating weld line with two streams of molten plastic
b) Stagnating weld line after an obstacle
c) Flowing weld line between two melt flows
d) Flowing weld line after an obstacle

Figure 1: Different types of weld lines cf. [3]

Figure 2: Tension bar with gates and estimated position of weld line

For the investigations of the influence of the process parameters to the weld line strength the melt temperature and the mold temperature were varied between the minimum and maximum level according to the technical datasheets of the particular materials. Table 1 provides an overview of the variations. This means that $2^2 = 4$ various parameter settings for each material have to be processed.

Table 1: Overview of processing parameters

Polymer type	A…Mold temperature T_{mold} [°C]		B…Melt temperature T_{melt}[°C]	
	- min	+ max	- min	+ max
PLA	30	40	200	215
CP	40	80	190	230
PBS	30	50	170	190
HDPE	60	80	210	230

2.2 Hot-Cold Weld Lines

Hot-cold weld lines typically occur at multi component injection molding applications as well as multi color injection molding applications. To ensure a sufficient binding of process parameters melt temperature and mold temperature are varied.For the investigations of the hot-cold weld lines an Axxicon ISO Manufactured Test Mold System with two tensile bar cavities was used on an ARBURG All Drive 370 A full electric injection molding machine. To create the tensile bars an aluminum inlet was used that blocked half of each cavity (cf. Figure 3a). After the molding of the first half of the tensile bar the aluminum inlet was removed, the half of the tensile rod switched and the second component was injected. A schematic view is shown in Figure 4.


a)

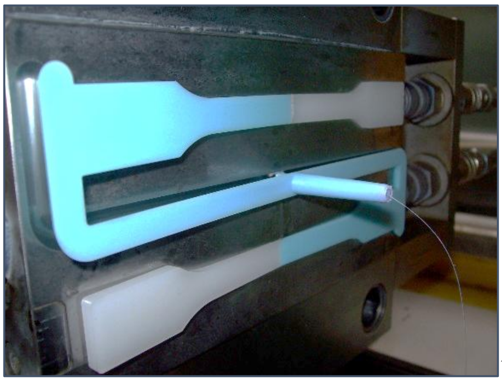
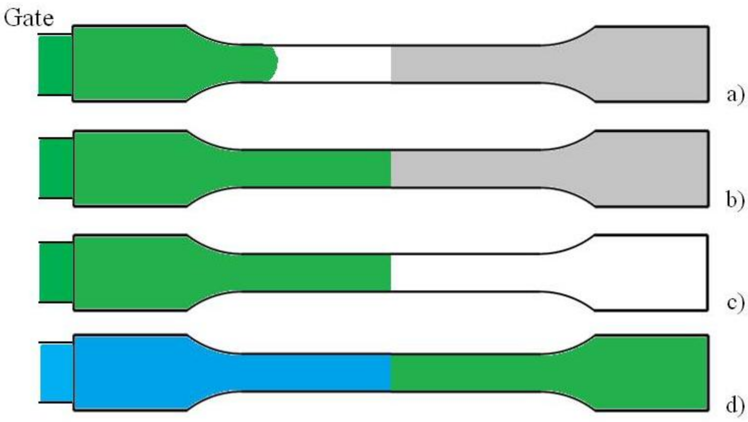

b)

Figure 3: Test set up of hot-cold weld lines



a) *Injection of first component against the aluminum inlet*
b) *Cooling time*
c) *Removal of the aluminum inlet*
d) *Switching of the first component and injection of second component*

Figure 4: Schematic view of injection molding of hot-cold weld line tensile rod

2.3 In-Line Surface Coating

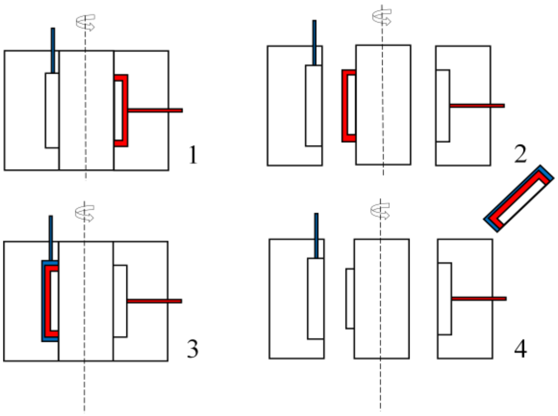
Different technologies are used and available on the market to purify the look and appearance of injection-molded plastic parts. The in-line surface coating of thermoplastic base bodies becomes increasingly important due to benefits in cost and process. The coating with a polyurethane layer is a typical application to gain a scratch resistant and high gloss surface.
A KraussMaffei KM 200-700/520 CZ WEN was used for the in-line surface coating tests. This injection molding machine is equipped with a turning plate which transports the part from one mold to the other. The polyurethane system, which was used for the coating, is provided by a KraussMaffei RimStar Hybrid-E-Tandem polyurethane coating system that can handle up to four different components. Figure 6 shows the demonstrator parts with the PU-layer.First of all the material for thermoplastic base body is injected in the first mold. After the cooling time the turning plate switches to the second mold and the polyurethane layer is applied. 1 molding of the thermoplastic base body

2 turning of the plate
3 injection of the PU-coating
4 opening of the mold

Figure 5 shows the schematic process operation. The tested material combinations are shown in Table 2

Table 2: Material combinations tested

Basic material	Surface coating
PLA Ingeo 3251D	Polyurethane system Ruehl puroclear 3109 JT (polyesterpolyol) Ruehl PUR 960-1 (isocyanate)
CP Albis Cellidor 300-10	
PHB Metabolix Mirel P1004	
HDPE Braskem SHC 7260	



1 molding of the thermoplastic base body
2 turning of the plate
3 injection of the PU-coating
4 opening of the mold

Figure 5: Schematic view of the in-line surface coating

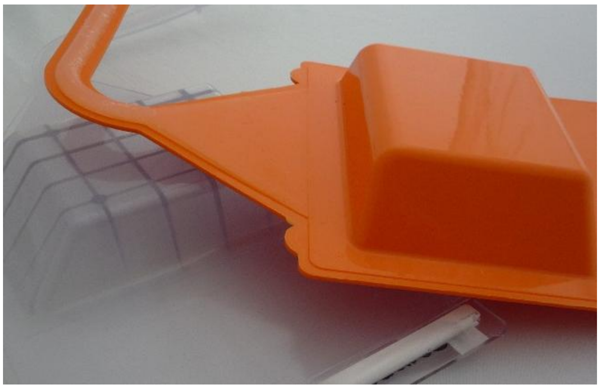


Figure 6: Demonstrator parts for the in-line surface coating

3. MATERIALS

3.1 Mechanical Properties

The mechanical properties of the materials investigated are summarized in Table 3. Apart from the polymer type the producer and the trading name of the material is specified. Some properties that are missing in the technical datasheets were completed with own testing.

Table 3: Selected mechanical properties of materials investigated

Polymer type	Tensile modulus [MPa]	Tensile strength at yield [MPa]	Strain at yield [%]	Charpy impact strength [kJ/m^2]	Charpy notched impact strength [kJ/m^2]	Density [g/cm^3]
PLA Ingeo 3251 D	3570*	62	3,5	15,8*	1,5*	1,25
CP Albis Cellidor 300-10	1950	45		no break	20	1,2
PA 10.10 Vestamid Terra DS16	1700	54	5	no break	7	1,05
HDPE Braskem SHC 7260	850*	18*	13*	no break*	2,1*	0,959
PHB	1600	24	3,5*	n. a.		1,3

Metabolix Mirel P 1004						
PBS Mitsubishi GS PLA FZ71PL	770*	40*	19	n. a.	4*	
Key	* Own testing, otherwise information from datasheets					

3.2 Thermal Properties

For the characterization of thermal properties the thermogravimetric analysis (TGA) and the differential scanning calorimetry (DSC) were used. With the use of the TGA (20 K/min; He) the peak temperature (T_{peak}) was determined. This temperature represents the maximum of material decomposition reaction. The DSC (20 K/min; N_2) at the second heating cycle delivers the glass transition temperature midpoint (T_g), the crystalline melting range and crystalline melting enthalpy (ΔH_m). The NETZSCH TG 209F1 Iris and the NETZSCH DSC 204F1 Phoenix are used for characterization of thermal material properties.

Table 4: Thermal properties of materials investigated

Polymer type	DSC			TGA
	T_g [°C]	crystalline melting range [°C]	ΔH_m [J/g]	T_{peak} [°C]
PLA	60,7	140-200	6,24	385,6
CP	112,5	amorph	/	412,2
PA 10.10	n. a.	120-210	66,13	449,1
HDPE	< -100°C	85-145	183,6	459,6
PHB	n. a.	105-175	31,65	302,8
PBS	n. a.	105-125	51,08	412,2

3.3 Surface Properties

For the investigations of the hot-cold weld line and the inline surface coating the surface tension serves as an indicator for good adhesion between the materials. According to the method of Owens, Wendt, Rabel and Kälble [4] [5] [6] the polar and disperse surface tension (SFT) were determined as shown in Table 5. Interferences can be drawn from an equal ratio of polar surface tension about the adhesion of the different polymers. Therefore it can be assumed that the HDPE will bond worse compared to the other polymers.

Table 5: Polar and disperse surface tension of market relevant biopolymers

Polymer type	Surface tension [mN/m]	Surface tension (disperse) [mN/m]	Surface tension (polar) [mN/m]
PLA	33,67	28,85	4,82
PHB	29,71	22,94	6,76
CP	32,41	29,09	3,31
HDPE	34,20	33,80	0,04

4. RESULTS

4.1 Investigations of Hot-Hot Weld Lines

The tensile testing of the hot-hot weld lines was done according DIN EN ISO 527. The tensile testing machine that was used is a Zwick/Roell Z010 ProLine. Table 6, Table 7, Table 8 and Table 9 show the results. According to the processing parameters shown in Table 1 the results for each material are revealed. In case of the PLA a tendency of an increased weld line strength can be seen with rising temperatures. The best overall weld line tensile strength shows the setting no. 3 which represents the injection of a hot melt into a cold mold. The other thermoplastics do not show a significant effect by variation of mold and melt temperature. Overall it can be said that the weld line factors of all investigated materials match approximately the tensile strength of the tensile rods without the weld line.

Table 6: Testing results of PLA

Setting No.	A	B	Tensile strength (without weld line) [MPa]	Tensile strength (weld line) [MPa]	Weld line factor
1	-	-	56	52	0,929
2	+	-	54	50	0,925
3	-	+	56	53	0,946
4	+	+	62	58	0,935
Standard deviation ~ 0,9…5,5					

Table 7: Testing results of CP

Setting No.	A	B	Tensile strength (without weld line) [MPa]	Tensile strength (weld line) [MPa]	Weld line factor
1	-	-	31	30	0,968
2	+	-	/	/	/
3	-	+	30	30	1
4	+	+	32	31	0,969
Standard deviation ~ 0,8…1,8					

Table 8: Testing results of PBS

Setting No.	A	B	Tensile strength (without weld line) [MPa]	Tensile strength (weld line) [MPa]	Weld line factor
1	-	-	37	36	0,973
2	+	-	38	36	0,947
3	-	+	37	36	0,973
4	+	+	38	37	0,973
Standard deviation ~ 0,2…1,7					

Table 9: Testing results of HDPE

Setting No.	A	B	Tensile strength (without weld line) [MPa]	Tensile strength (weld line) [MPa]	Weld line factor
1	-	-	19	19	1
2	+	-	19	19	1
3	-	+	20	20	1
4	+	+	19	19/	1
Standard deviation ~0,3…0,5					

4.2 Investigations of Hot-Cold Weld Lines

The results of the tensile testing according to DIN EN ISO 527 are shown in Figure 7. Over all the biopolymers show the tendency of an increased tensile strength by an increased mold temperature. Also a higher melt temperature influences the tensile strength in a positive way. Dependent on the material the enhancement of tensile strength varies from 25 % (CP) up to 72 % (PA).

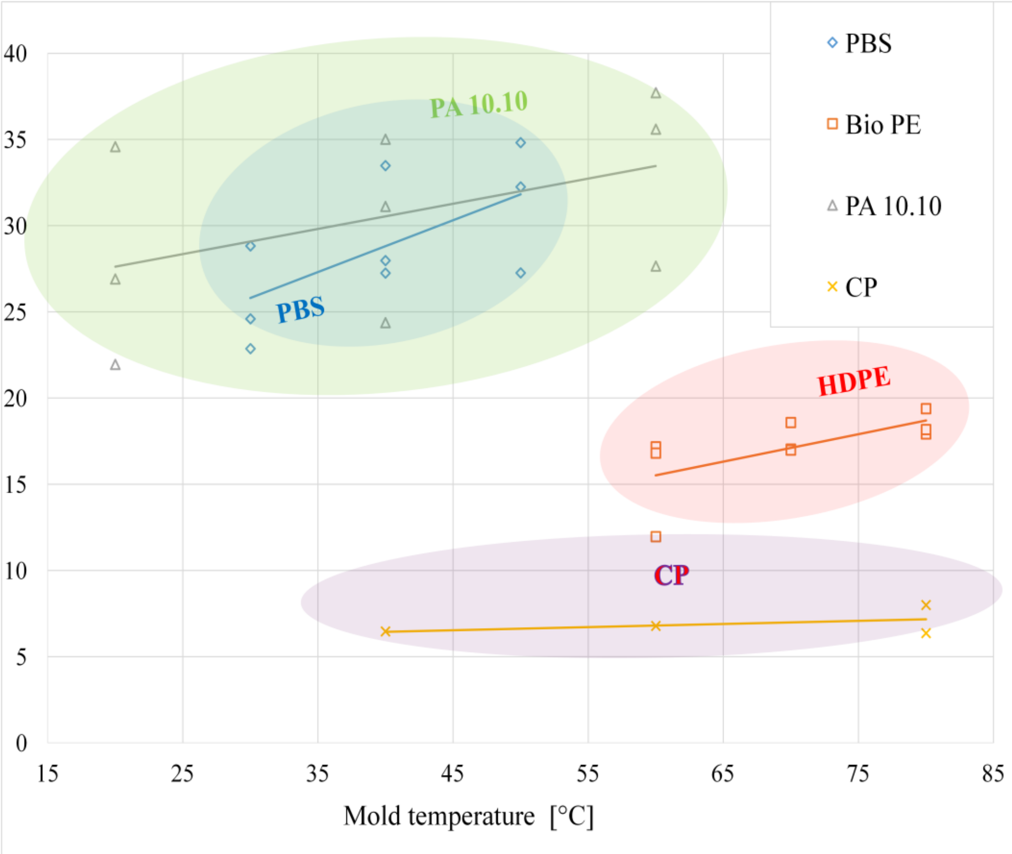


Figure 7: Bond strength of two-component tensile rods with hot-cold weld line

The tensile rods with the hot-cold weld line were tested according DIN EN ISO 527 as well. The results are shown in Table 10. It can be seen that the hot-cold weld lines composed of identical polymers (leading diagonal) feature tensile strengths of 80 % and above the tensile strength of the tensile rod without weld line. Even the PLA-PBS, PLA-PHB and PHB-PBS-combinations show a tensile strength of 40 % and above the tensile strength of the tensile rods without weld line. The HDPE shows no adhesion with other materials. The differences in polar surface tensions could be one explanation for that material behavior.

Table 10: Tensile strength of two component tensile rods with hot-cold weld line

	PLA	PBS	PHB	PA 10.10	HDPE
PLA	++	+	+	-	-
PBS		++	+	-	-
PHB			++	-	-
PA 10.10				++	-
HDPE					++
Key	++ good adhesion (σ_z > 80 % of one component tensile rods) + moderate adhesion (σ_z > 40 % of one component tensile rods) - no adhesion				

4.3 Investigations of Inline-Surface Coating

For the determination of the bond strength of the biopolymer-PU-interface plates with the dimension of 40 x 40 mm were cut out of the demonstrator parts (cf. Figure 6). The adapters for the tensile test machine were applied with a cyanoacrylate based adhesive. In the cases of PLA, CP, and PHB the maximum tensile force of 10 kN that can be delivered from the tensile test machine Zwick/Roell Z010 ProLine deployed, was not sufficient to separate the test specimens. In case of the HDPE the PU-layer could have been easily peeled of which shows that no sufficient bonding was achieved.

Table 11: Bond strengths of PU-coating on different basic materials

Basic material	PU-coating	Bond strength [MPa]
PLA Ingeo 3251D	Polyurethane system Ruehl puroclear 3109 JT (polyesterpolyol Ruehl PUR 960-1 (isocyanate)	› 6,25
CP Cellidor 300-10		› 6,25
PHB Mirel 1004		› 6,25
HDPE SHC 7260		no connection

5. SUMMARY

The investigations in this study show the influence of different processing parameters (melt temperature and mold temperature) to the tensile strength of hot-hot and hot-cold weld lines. In case of the hot-cold weld lines different material compositions are investigated as well. Furthermore a comprehensive material characterization regarding mechanical properties, thermal properties and surface properties is done. It has to be emphasized that the polar surface tension serves as a good criterion for the prediction of the bonding strength of different biopolymers. In case of HDPE, which has the greatest deviation of polar surface tension compared to other polymers, the bonding between HDPE and other thermoplastics is worst. Although the parameter variation does not show significant effects on tensile strength of hot-hot weld lines, the impact on hot-cold weld lines can clearly be seen. Especially the PA 10.10 shows an increase of tensile strength up to 72% if the mold and melt temperatures are raised. In case of the tensile rods with hot-hot weld line it has to be mentioned that the determined tensile strengths are on a higher level compared to petrochemical thermoplastics (cf. [2]). This can lead to the conclusion that biopolymers are not as vulnerable against weld line weaknesses as conventional polymers. Although this hypothesis has to be acknowledged by further testing and comparison. Last but not least the in-line surface coating experiments show good results. Only between HDPE and the PU-layer the bonding strength is not sufficient.

6. ACKNOWLEDGEMENT

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7. ILLUSTRATIONS, GRAPHS, AND PHOTOGRAPHS

7.1 List of Figures

7.2 List of Tables

7.3 References

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