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BLENDING CA WITH PBS TO INCREASE THE BONDING STRENGTH IN TWO-COMPONENT INJECTION MOLDING

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Abstract

Since CA shows no adhesive properties in the two-component injection molding process with bio based TPU, blends of CA and PBS were produced to decrease the interfacial tension between the materials. While the interfacial tension was calculated from the results of a drop shape analysis, the adhesion strength was measured in peel tests according to the guideline VDI 2019. The comparison of the results gave information about whether the drop shape analysis is a valid method to analyze the adhesive characteristics of material combinations for two-component injection molding. Moreover, tensile tests were performed, to characterize the mechanical properties of the CA/PBS blends. It could be shown, that decreasing the interfacial tension between the two components by blending the CA with the PBS increased the adhesion strength.

Introduction

The increasing variety and availability of bio-based polymers and the growing environmental awareness of the consumer lead to higher interests of using these materials in serial production. However, the rather new materials come along with significant uncertainties to manufacturers, especially when it comes to multi-component injection molding [1].

Much research and development regarding the use of bio-based polymers in different applications and processes has been done, as it is shown in [2]. However only few of these studies cover the topic of multi-component injection molding. [1] gives a basic overview of possible material combinations for hard-soft components manufactured in a two-component injection molding process. It is noticeable, that only few of the analyzed combinations show good adhesive characteristics.

When it comes to creating a good bonding between two polymers in multi-component injection molding, there are many theories about the bonding mechanisms [3]. These mechanisms and especially their interactions haven't been completely understood so far [4]. One of the theories implies that for a good adhesion the interfacial tension between the materials surfaces should be as low as possible, while the polar parts of the surface free energies should be high [5] [6] [7]. Recent studies show, that different methods of surface treatments allow the enlargement of the polar surface free energy of polymers and lead to higher adhesion strength in hard-soft combinations [8] [9].

The objective of this study is to use bio-based polymers with different surface free energies to create hard-soft composites. Blends of two different materials for the hard component were produced to create higher bonding abilities leading to higher adhesion strengths in two-component injection molding.

Experimental

Materials

To produce the hard-component blends, two different bio based thermoplastic polymers were used. The cellulose acetate (CA) was obtained from FKuR Kunststoff GmbH (Willich, Germany) and shows mechanical properties that are comparable to those of standard polystyrene [10]. The poly butylene succinate was obtained from Mitsubishi Chemical Co. (Tokyo, Japan).

For the soft-component in two component injection molding two types of bio based thermoplastic polyurethanes (TPU) were used. They were both obtained from BASF Polyurethanes GmbH (Lemförde, Germany) and differ in their Shore hardness. Table 1 gives a summary of the used materials and contains their organic content.

Table 1. Organic content of the used materials.

Material	Manufacturer	Shore A	Organic content
CA	FKuR Kunststoff GmbH	-	>60 %
PBS	Mitsubishi Chemical Co.	-	50 %
TPU75	BASF Polyurethanes GmbH	75	49 %
TPU95	BASF Polyurethanes GmbH	95	43 %

Compounding of the hard-component blends

The blends were produced on a twin-screw extruder (ZSE18 HPe, Leistritz Extrusionstechnik GmbH, Nürnberg, Germany) with a gravimetric metering system (Brabender GmbH & Co. KG, Duisburg, Germany). The L/D-ratio of the extruder was 40 and the diameter of the screw was 18 mm. Since the two materials were both available in granular form, they were mixed prior to the compounding and then dosed through the main feeder of the extruder. The weight percentage of the materials of each blend are shown in table 2. During the compounding of the different blends the machine parameters of the extruder were kept constant. To reach a throughput of 4 kg/h the screw speed was set to 200 rpm with a constant temperature setting of 210 °C for each zone. These parameters resulted in a mass temperature of 230 to 240 °C. The strands were cooled on a conveyor belt before they were granulated.

Table 2. Weight percentage of the blends.

Blend number	Amount of CA [%]	Amount of PBS [%]
1	90	10
2	80	20
3	70	30
4	60	40

Injection molding of the test specimen

To determine the mechanical properties of the blends, 1A dumbbell test specimen according to ISO 527-2 were injection molded [11]. Therefore, an all-hydraulic single component injection molding machine with a screw diameter of 25 mm was used (Arburg Allrounder 320C Gold Edition, Arburg GmbH + Co KG, Loßburg, Germany). For the injection molding not only the blends shown in table 2 were used, but also the pure CA and the pure PBS. The machine parameters were kept constant for each blend and the CA. To produce the PBS test specimen, the maximum temperature was reduced from 220 °C to 180 °C.

For the determination of the bonding abilities of the blends, peel test specimen according to VDI 2019 [12] were produced on an all-hydraulic two component injection molding machine (Arburg Allrounder 470S, Arburg GmbH + Co KG, Loßburg, Germany). The two injection units were set up in a V-Layout, where the horizontal unit (screw diameter of 35 mm) injected the thermoplastic blends and the vertical unit (screw diameter of 25 mm) injected the TPU. The mold contained a hydraulically movable core, that opened a second cavity for the TPU after the substrate material was injected. The TPU was injected onto the substrate plate to create a tab, that can be pealed off during the peeling tests. The dimensions of the test pieces are shown in figure 1.

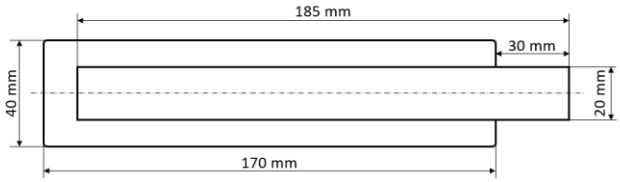

Figure 1. Dimensions of the peeling test pieces based on VDI 2019 [12].

For the measurement of the surface free energy of the blends, the substrate plates were injection molded as described above but without the TPU tab.

Tensile testing

The injection molded 1A tensile test specimen were tested on a universal testing machine (Z010, Zwick Roell, Ulm, Germany) according to ISO 527-1 [11]. The testing speed was set to 5 mm/min for each material. Prior to the tensile tests, the specimen were conditioned at standard conditions (23 °C / 50% relative humidity).

Peeling test according to VDI 2019

The peeling test pieces (figure 1) were tested on a tensile testing machine (Inspect table 5 kN, Hegewald und Peschke Meß- und Prüftechnik GmbH, Nossen, Germany) according to [12]. They were clamped in a test trolley that allows a horizontal movement to ensure a vertical peeling of the TPU tab orthogonal to the substrate plates surface during the whole peeling test. The TPU tab was peeled off the substrate plate with a speed of 100 mm/min.

Calculating the surface free energy using DSA

Drop Shape Analysis (DSA) can be used to measure the wetting behavior and the surface tension of substrate plates. A syringe that is filled with a test liquid injects a drop of that liquid onto the surface of the substrate plate. A highspeed camera records that process and a software calculates the contour of the drop to measure its two three-phase angles at the boundaries of the liquid, solid and gaseous phase. Figure 2 shows an example of the two three-phase angles measured between a water drop and a CA substrate plate, surrounded by air. In terms of wetting, a contact angle between 1° and 90° is considered to result from good to partial wetting abilities, while 0° resembles complete wetting [8].

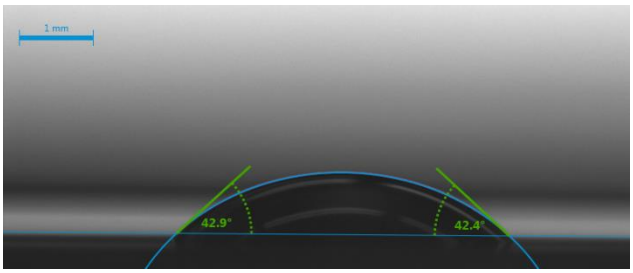

Figure 2. Contact angle of a water drop on a CA substrate.

The DSA measurements on the injection molded substrate plates were carried out with a contact angle measuring device (EasyDrop DSA 20B, Krüss GmbH, Hamburg, Germany). As test liquids water (H_2O) and diiodomethane (CH_2I_2) were used. The results of the contact angle measurement with those two liquids were used to calculate the surface free energy of the substrate plates with the method of Owens, Wendt, Rabel and Kaelble (OWRK) [13]. Therefor the Young's equation (1) for the interfacial tension between a solid (s) and a liquid (l) material (σ_{sl}) is extended by the dispersive part (σ^D) and the polar part (σ^P) of the surface free energy. This results in equation (2) [14].

$$\sigma_s = \sigma_{sl} + \sigma_l \cdot \cos\theta \quad (1)$$

$$\sigma_{sl} = \sigma_s + \sigma_l - 2\left(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^P \cdot \sigma_l^P}\right) \quad (2)$$

With two different liquids of known dispersive and polar surface tensions, this equation allows a calculation of the surface free energy of the substrate plate divided into the dispersive and polar parts. The surface tensions of the two used liquids are shown in table 3.

Table 3. Surface tension of the test liquids.

Liquid	Surface tension [mN/m]	Polar part [mN/m]	Dispersive part [mN/m]	Source
Water	72,8	51,0	21,8	[15]
Diiodo-methane	50,8	2,3	48,5	[16]

Results and Discussion

Mechanical properties of the blends

Figure 3 shows the stress strain diagram of the different CA/PBS-blends. While the CA/PBS (90/10) shows a similar progression as the pure CA with decreased stress values, the other blends show less elongations at break. With increasing amount of PBS, the elongation at break of the blends declines steadily. This phenomenon is also visible in figure 4 showing the averaged elongation at break and the tensile strength of five tensile tests of each blend. Compared to the elongation at break, the tensile strength does not show a steady decrease with increasing amount of PBS. While each blend shows lower values than the pure CA, the CA/PBS (80/20) has the lowest averaged tensile strength of 37,6 MPa. It is also visible, that with an increasing amount of PBS in the blends, the standard deviation increases as well. The Young's modulus displayed in figure 5 shows similar characteristics as the tensile strength. While the standard deviation increases with a higher percentage of PBS, the Young's modulus does not show a steady decrease. The CA/PBS (70/30) blend shows the lowest modulus of 1726,4 MPa.

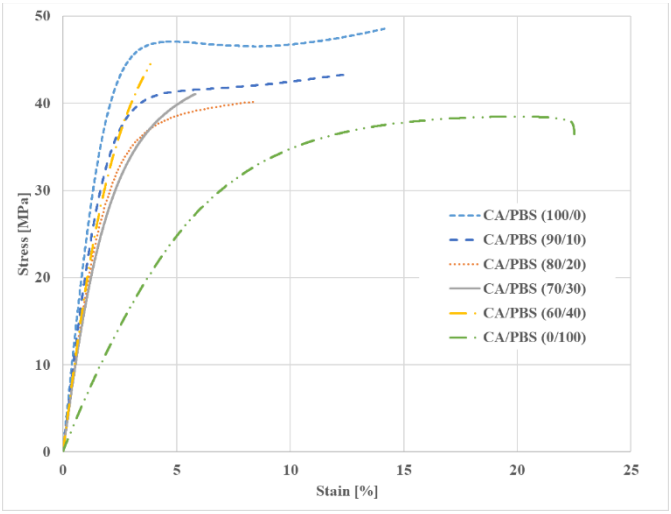

Figure 3. Strain stress diagram of the CA/PBS blends.

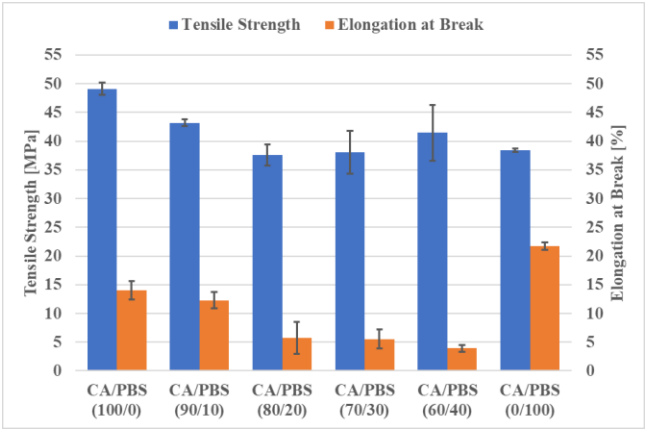

Figure 4. Tensile strength and elongation at break of the CA/PBS blends.

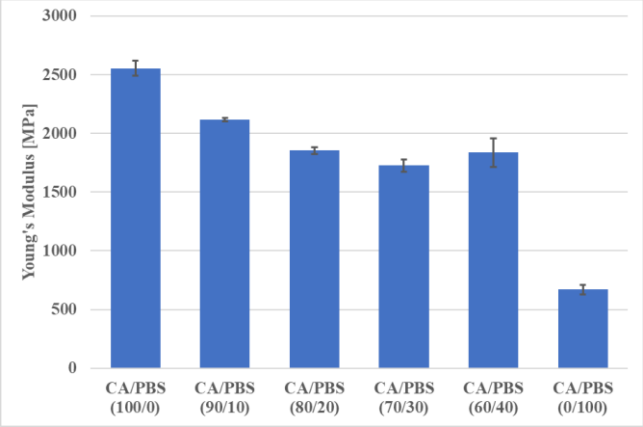

Figure 5. Young's modulus of the CA/PBS blends.

Surface free energy of the substrate plates

The mean contact angle of ten drops of each test liquid on a substrate plate of each material was used to calculate the surface free energy with the above described equation (2). The results of the energies divided into the polar and dispersive parts are shown in figure 6.

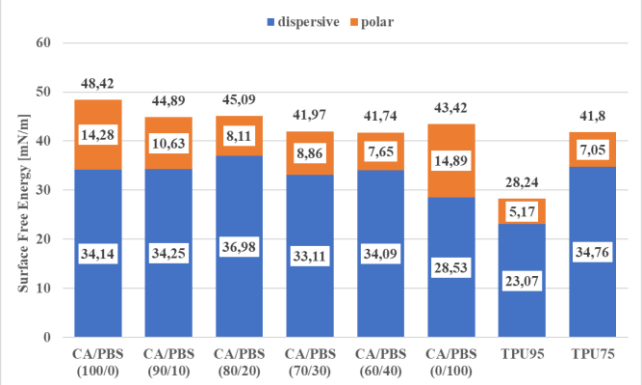

Figure 6. Surface free energy of the hard and soft components.

To achieve a good bonding strength, it is important that the hard and soft components have a similar ratio of polar and dispersive parts, where a higher polar part usually results in higher bonding abilities. Similar ratios of the polar and the dispersive surface energy result in small interfacial tensions [5] [7]. The calculated interfacial tension between the hard and soft components is shown in table 4.

Table 4. Calculated interfacial tension between the blends and the two TPU.

Blend	Interfacial Tension [mN/m]	
	TPU95	TPU75
CA/PBS (100/0)	3,347	1,266
CA/PBS (90/10)	2,074	0,368
CA/PBS (80/20)	1,963	0,071
CA/PBS (70/30)	1,398	0,123
CA/PBS (60/40)	1,315	0,016
CA/PBS (0/100)	2,802	1,756

Peel resistance of the two component test pieces

Table 5 and table 6 show the results of the peel tests for the different combinations of the CA/PBS blends with the TPU95 and the TPU75. As mentioned before, the pure CA shows no adhesive characteristics in combination with the two TPU. The TPU tab of the test piece gets separated from the CA substrate plate right after the overmolding. For this reason, these two combinations are listed with 0 N of adhesion strength. In combination with the TPU95, the CA/PBS blends show averaged adhesion strengths between 16,82 N and 22,06 N, where the CA/PBS (90/10) shows the lowest and the CA/PBS (80/20) the highest results. In all cases, the TPU tab was peeled off without residues. No peeling occurred during the test of the pure PBS in combination with the TPU95. At a load of 720,74 N the substrate plate showed a cohesive failure.

The CA/PBS (90/10) and the CA/PBS (80/20) in combination with the TPU75 show slightly higher results than in combination with the TPU95. However, the addition of 30 % PBS to the CA increases the adhesion strength of the blend to a value, that is higher than the tensile strength of the TPU75. Before a peeling occurred the TPU75 tab failed cohesively at a load of 147,26 N.

Table 5. Adhesion strength of the CA/PBS blends with TPU95 as the soft component.

Blend	Adhesion strength [N]	Standard deviation
CA/PBS (100/0)	0	-
CA/PBS (90/10)	16,82	0,09
CA/PBS (80/20)	22,06	0,37
CA/PBS (70/30)	20,02	1,23
CA/PBS (60/40)	19,68	0,54
CA/PBS (0/100)	720,74 (max)	22,57

Table 6. Adhesion strength of the CA/PBS blends with TPU75 as the soft component.

Blend	Adhesion strength [N]	Standard deviation
CA/PBS (100/0)	0	-
CA/PBS (90/10)	17,94	0,55
CA/PBS (80/20)	39,49	4,16
CA/PBS (70/30)	147,26 (max)	8,04

Conclusions

The blending of CA with PBS leads to a decrease of the interfacial tension between the blends and the two TPU. As it was shown in [7] lower interfacial tension leads to increased adhesive characteristics. This is also verified by the peel test results of this study. The adhesion strength of the two component test pieces of the CA/PBS blends and the TPU95 increases with decreasing interfacial tensions. The tensions between the blends and the TPU75 are constantly lower than the ones between the blends and the TPU95. This is also reflected in the higher adhesion strengths. This proves that the DSA is an applicable method to deliver information about the adhesive characteristics of two materials in two component injection molding. However, the results of this study do not allow a direct correlation between the interfacial tension and the adhesion strength.

The results of the tensile tests of the different CA/PBS blends show, that the tensile strength and the elongation at break both decrease with increasing amount of PBS in the blend. From the results can also be derived, that the blends are not compatible. This might also have an influence on the adhesive characteristics. The additional use of additives while compounding the blends could increase the compatibility and therefore result in better adhesion strength and smaller standard deviation of the results.

Even though the blends are not compatible, the adhesion strength of the CA/PBS (70/30) and the TPU75 was higher than the tensile strength of the TPU75. An addition of 30 % PBS to the CA results in an increase of the adhesive properties from no bonding at all to the cohesive failure of the soft component.

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