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Characterization of layer built-up and inter-layer boundaries in rotational molding of multi-material parts in dependency of the filling strategy

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Abstract: In rotational molding, shaping is achieved by elevating the temperature of polymer powder particles above their melting temperature, causing them to adhere to the mold wall. Multi-layer parts can be processed by sequential adding of different polymeric materials to the mold, while the thickness of each layer is defined by the amount of each material. In this work, the influence of adding time of a second component on the shape and development of the interface region between different materials for multi-layer rotational molding is investigated. Therefore, rotational molding experiments were conducted using an uniaxial rotating molding machine and a cylindrical mold. Varying the time of second material addition yielded different specific interface regions. The cross sections of the resulting multi-layer parts were analyzed using transmitted light microscopy and characteristic values were derived to describe the interfaces. Single-layer parts were produced to verify the built-up of the polymer layer and the development of the inner melt surface in rotational molding.

Keywords: adding time; interface; multi-layer; rotational molding.

1 Introduction

The rotational molding process is a primary shaping plastic processing technique developed in the 1940s [1]

and is shown schematically in Figure 1. In the first process step, a hollow mold is filled with powdery or liquid plastics. The filled and closed mold starts rotating about two axes. While maintaining the rotation, the mold is heated up in the second process step, often accomplished by convection within an oven. While heating the polymer, it successively forms a homogenous porous layer of polymer melt at the inner mold surface. This porous layer densifies while the polymer is held in the melt state. In the third step, the still rotating mold is cooled down by compressed air or water which is applied to the outer mold surface, causing the polymer to solidify within the mold and to form a solid hollow body. After reaching the demolding temperature, the mold is opened and the part is demolded in the last process step.

Large volume, hollow parts such as Kayaks, traffic barriers and storage tanks for various purposes with a volume up to 100,000 l are typical applications for rotational molding. In general, seamless hollow bodies with a high degree of design freedom and with very low residual stresses can be produced with this production technique [2, 3].

A total of 85–90% of the material processed by rotational molding is devoted to the different polyethylene (PE) types [4]. While this is on one hand based on historical developments, PE does on the other hand fulfill the material requirements of the rotational molding process, such as good flowability and resistance to thermal degradation. Other materials typically used are, in addition to others, polypropylene, polyvinyl chloride, polyamide and polycarbonate [1, 5].

The melting and densification processes during rotational molding were analyzed by Kontopoulou and Vlachopoulos [6] and Löhner and Drummer [7], as schematically shown in Figure 2.

The melting process starts with powder particles adhering to the mold wall the temperature of which is above the melting temperature of the polymer (Step 1). These powder particles plasticize after reaching the

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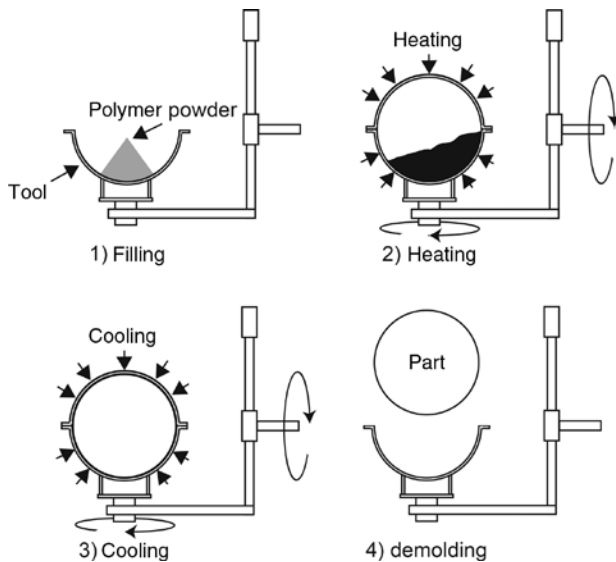


Figure 1: Process steps of rotational molding.

melting temperature of the polymer, followed by more powder particles adhering to the plasticized surface of these particles (Step 2). Inside the mold, free powder particles are moving during these process steps until the whole powder adheres to the mold wall (Step 4). The plasticized powder particles melt with increasing temperature and form a homogenous layer of polymer melt (Steps 3–5). While melting, a part of the air which is contained in the powder bulk is trapped in the polymer melt. The trapped air forms gas inclusions (Steps 3–6). By holding the polymer at an elevated temperature, the surface of the melt layer becomes uniform and the gas inclusions diffuse out of the polymer melt (Steps 6 and 7). These effects can be attributed to surface tension [7].

A process development which recently is increasingly recognized is the production of multi-layer parts by rotational molding which can generally be realized in rotational molding by sequentially adding different materials. Here, after spreading and melting of a first material, a second material is added to the process. A second layer forms on the inside of the first layer by adhering powder particles. By sequentially adding further materials, parts with complex, multiple-layer setups can be produced [8].

Several technical implementations for this sequential adding of materials are known for the processing of multi-layer materials in rotational molding. For example polymeric bags filled with the material for the inner layer can be added to the process together with the material for the outer layer. These bags are designed in such a way that they will only melt after the material for the outer layer already adheres to the mold wall, resulting in the comprised material to be released and adhere to the layer formed by the first material [8].

Another possibility is the simultaneous adding of materials which differ significantly in properties which are relevant for the adhesion of the material to the mold wall, or, for the mixing and segregation within the process. Examples for these properties are particle size and melting temperature [8, 9].

A third possibility to realize the built-up of multi-layer structures is the usage of a so called drop box. Here, a thermally insulated container is placed inside or on the surface of the rotational molding mold which can be opened at a specific point of time during the process. The material in the container can be added to the mold and form a second, inner layer [10, 11].

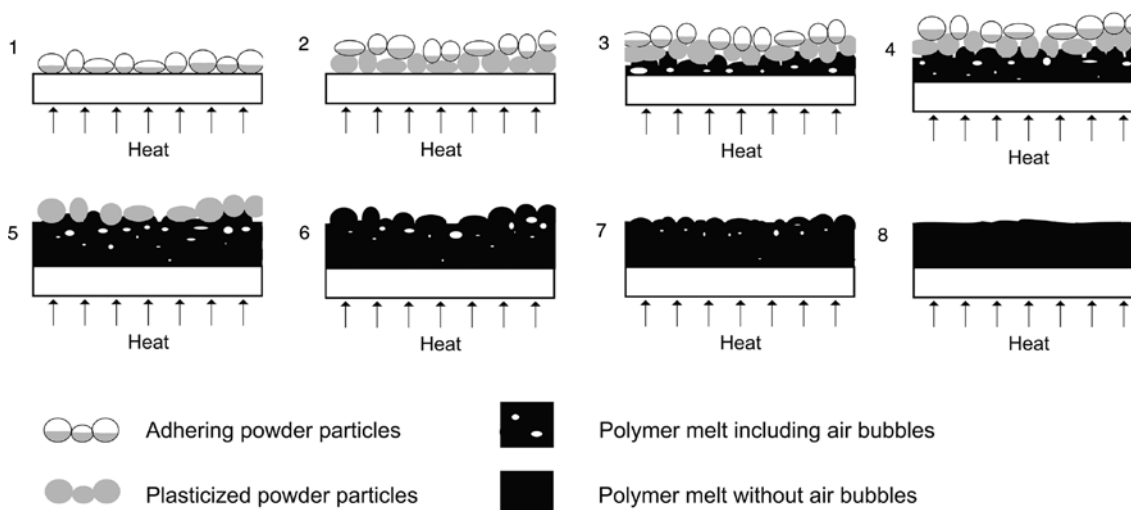


Figure 2: Melting and densification process in rotational molding according to Kontopoulou and Vlachopoulos [6].

2 Motivation

Multi-layer parts offer a wide range of advantages compared to single material constructions. By combining two materials, the advantages of both materials can be utilized at specific part areas. Cost reduction, for instance, can potentially be achieved by using recyclate for the inner structure and virgin material for the surface components. By using different polymers, additional integration of functions is possibly what leads to a broadening of the fields of application for rotational molded parts. Design aspects, haptics, wear resistance and tribological aspects can be improved or integrated in rotational molded systems.

Understanding the distribution of the materials over the part cross section in the process is crucial for controlling the resulting part properties, such as the bonding strength and overall mechanical properties. Due to the non-tool-based forming of the inner part surface in rotational molding, the interface layer between two different materials is significantly influenced by process parameters. The time when the second material is added and the condition of the outer layer at this time, for instance, are presumably important factors for the resulting interface layer. In this work, two-material rotational molded parts were investigated. The influence of the adding time of a second material to the system on the resulting cross section was analyzed and particular emphasis was put on the interface layer between the different materials.

3 Materials and methods

3.1 Material characterization

In this study, two medium density PE powders provided by LyondellBasell Industries (Rotterdam, Netherlands) were used, Lupolen K RM 4021 Powder (translucent material) and Lupolen K RM Black Powder (black material), two powdery rotational molding resins. Both materials were analyzed as described below.

The melt volume rate (MVR) was determined at a temperature of 190°C and with a load of 2.16 kg with a Zwick 4106 extrusion plastometer (Zwick GmbH & Co. KG, Ulm, Germany).

For further characterization of the melting behavior of the materials, differential scanning calorimetry (DSC, Q2000, TA Instruments, New Castle, USA) was conducted. The material was heated up to 220°C, cooled down to 0°C and then heated up again. The heating and cooling rates were set to 10°C min⁻¹.

The particle size distribution was investigated using a Morphologi G3 particle characterization system (Malvern Instruments Inc., Malvern, England). Hereby, the powder particles were dispersed over a glass plate and the particle sizes were measured optically.

The particle shapes were analyzed using a scanning electron microscope Gemini Ultra-Plus (Carl Zeiss AG, Oberkochen, Germany).

3.2 Rotational molding experiments

Rotational molding experiments were conducted using a uniaxial rotating, cylindrical mold with a diameter of 211 mm. The heating was realized by contour-following infrared heaters which were located outside the mold and compressed air was applied to cool down the tool. The mold, which provided an axial opening enabling the feeding of material at random process times and a continuous process observation, was set to rotate with a speed of 5 min⁻¹. A rotatable feeding can be moved axially into the center of the rotation axis of the mold. By rotating the feeding, polymeric material can be added to the process. The material can thereby be distributed homogenously over the whole axial mold length. The temperature of the system was measured by infrared temperature measurement on the outside of the mold. Previous comparison measurements showed good accordance to the temperature on the inside of the mold wall. The cross section of the experimental setup (FILL Ges.m.b.H., Gurten, Austria) is shown schematically in Figure 3.

3.2.1 Single-layer experiment

A cycle time variation was conducted with a single material using the black material Lupolen 4021 K RM Black

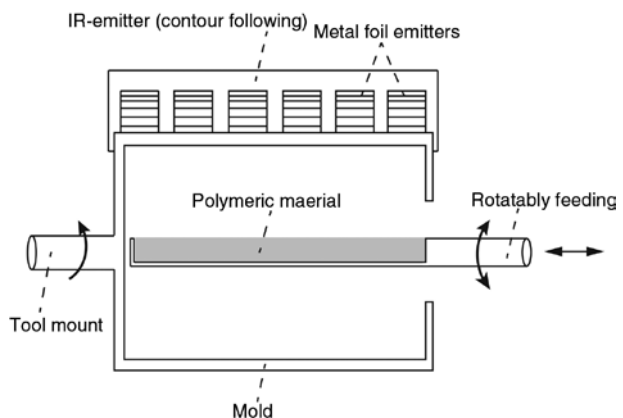


Figure 3: Cross section of the experimental setup.

Table 1: Process parameters, single material experiments.

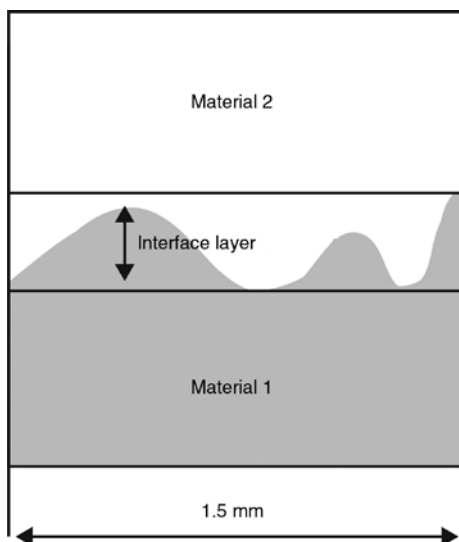
Test number	Heating time (s)	Maximum temperature (mold) (°C)
A	320	140
B	380	150
C	420	160
D	495	170
E	555	180

Powder. For this experiment, the material was placed in the cold mold and heated up. The heating was terminated at different times and the mold was then cooled without any holding time at an elevated temperature. The heating time and resulting maximum temperatures are shown in Table 1.

Thin sections of all parts were prepared and characterized using transmitted light microscopy focusing the center part of the resulting cylindrical. The surface roughness of the single layer parts was characterized by optically measuring the height of the surface irregularities on thin sections. The measuring length was 1.5 mm at three areas according to the measuring shown in Figure 4.

During the cycle time variations, the adhesion process of the black material was observed to define specific process steps. Here, the following specific process times could be identified:

- Start of adhesion: First powder particles adhere to the mold wall
- End of adhesion: The complete powdery material is molten and adheres to the mold
- Homogenous polymeric layer: Consistent polymeric layer with no unmolten powder particles occurs.

**Figure 4:** Measuring method for characterization of interface layer.**Table 2:** Process parameters, variation of adding time of second component.

Test number	Time of adding black material	Time of adding translucent material (s)
1	Before process start	200
2	Before process start	300
3	Before process start	360
4	Before process start	420
5	Before process start	500
6	Before process start	600
7	Before process start	1300

3.2.2 Multi-layer experiment

Multi-material samples were produced by adding different materials to the process at different points of time as shown in Table 2. The first material was added into the cold mold before the process start and the second material was added at the specified times during heating. The mold was heated up to 200°C for all experiments which took approximately 700 s. The temperature was then held constant for 20 min at 200°C. The mold was finally cooled down by compressed air for 15 min to approximately 65°C and the part was demolded. The amount of material added to the process was 137 g for each layer.

The interface layer between the two materials was analyzed by measuring the thickness of the interface layer orthogonal to the part surfaces, as shown in Figure 4, using thin sections and transmitted light microscopy. The height of the interface area was measured at six areas with a length of 1.5 mm for each experiment.

4 Results

4.1 Material characterization

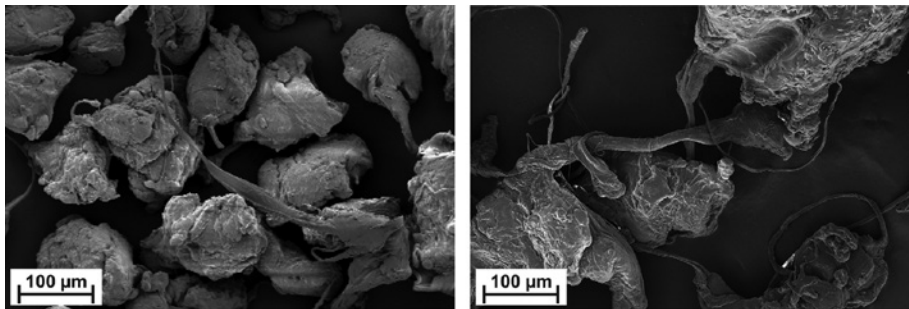
The relevant characteristic values of the DSC analysis are shown in Table 3. Additionally, the quantiles of the particle size and the average particle size, as well as the MVR of the materials, are included in Table 3.

The DSC analysis shows very similar values for both materials. Only the enthalpy of fusion during the first heating shows relevant differences. The average particle size of the two materials is similar to each other, whereas the translucent material shows slightly lower characteristic values. The 10% quantile and 90% quantile are about 30–40 µm smaller and the average particle size

Table 3: Measured characteristic values of medium density polyethylene (PE-MD) powders.

Characteristic value	Lupolen 4021 K RM Powder (translucent material)	Lupolen 4021 K RM Black Powder (black material)
Melting peak (1st heating) (°C)	126.5	126.7
Enthalpy of fusion (1st heating) (J g ⁻¹)	132.6	151.4
Melting peak (2nd heating) (°C)	126.0	127.7
Enthalpy of fusion (2nd heating) (J g ⁻¹)	146.9	151.1
Crystallization peak (°C)	114.2	117.9
Crystallization onset (°C)	116.4	119.0
10% quantile (volumetric) of particle diameter (μm)	194.7	224.8
90% quantile (volumetric) of particle diameter (μm)	611.9	654.9
Average (volumetric) particle diameter (μm)	374.6	455.7
MVR (g [10 min] ⁻¹)	5.2	6.0

MVR, Melt volume rate.

**Figure 5:** Scanning electron microscopy (SEM) analysis of medium density polyethylene (PE-MD) powders, left: Lupolen 4021 K RM Powder, right: Lupolen 4021 K RM Black Powder.

approximately 80 μm smaller compared to the black material. The MVR differs slightly from 5.2 g/10 min (translucent material) to 6.0 g/10 min (black material).

In Figure 5, the results of the scanning electron microscopy are shown. On the left side, Lupolen 4021 K RM Powder is shown and on the right side, Lupolen 4021 K RM Black Powder is shown. The particles show relatively low aspect ratios and are therefore generally suited for rotational molding. Partially, the particles have threads emerging from their surface. The surface of the particles shows mainly rough areas.

4.2 Rotational molding experiments

4.2.1 Single-layer experiment

In Table 4, the characteristic process times and resulting mold temperatures are shown for the characteristic process times specified above.

In Figure 6, the cross sections of the parts resulting from the cycle time variation with the black material are

Table 4: Specific process steps for the molding of the first material.

Specific process step	Process time (s)	Mold temperature (°C)
Start of adhesion	270	127
End of adhesion	420	153
Homogenous polymeric layer	500	168

shown. For short heating times, a rough inner surface appears with unmolten particles at the surface (320 s, 140°C maximum temperature). With increasing time and temperature, the inner surface melts continuously and a smoothing of the surface occurs. For heating times of approximately 495 s and above, a relatively even surface can be observed.

As shown in Figure 7, the thickness of the surface roughness of the single layer parts decreases significantly with increasing heating time and temperatures. After 555 s (180°C maximum temperature) no significant surface roughness was observed anymore.

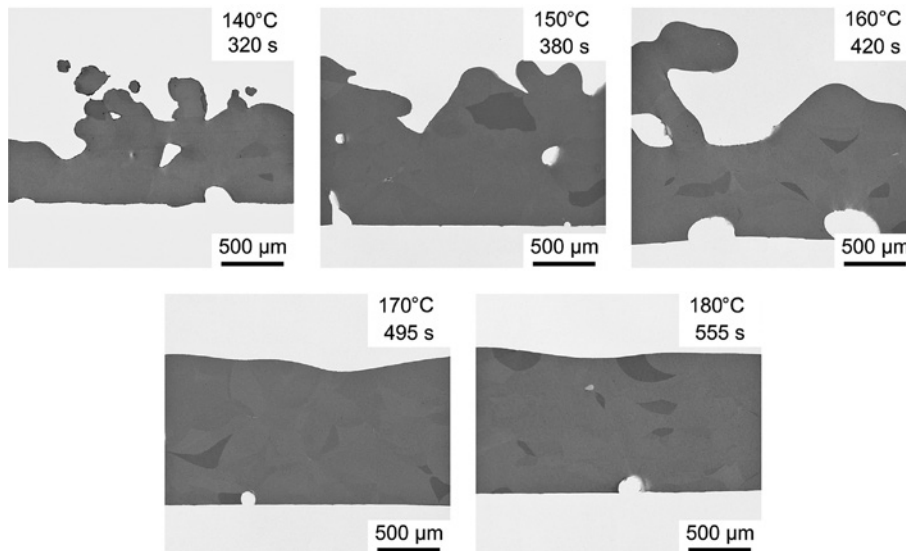


Figure 6: Cross sections of parts heated for different amounts of time and to different maximum temperatures.

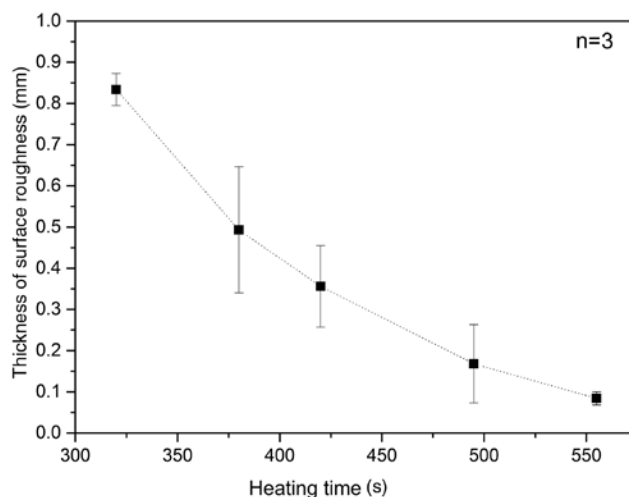


Figure 7: Surface roughness of single layer parts, measured over a length of 1.5 mm.

4.2.2 Multi-layer experiment

In Figure 8, exemplary cross sections of the two-material rotational molded parts for the different adding times of the second material are shown.

As shown in Figure 8, the resulting material distribution is strongly dependent on the adding time of the second component. By adding the translucent material after 200 s, approximately 70 s before the start of adhesion, a complete and homogenous mixing of the materials is observed. No agglomerations of single materials and no concentration gradient over the part diameter were observed. By adding the translucent material after the

adhesion of the black material on the mold wall started (300 s), a continuous layer of black material resulted on the mold wall. On the inner section of the part, a homogenous distributed blend of the two materials appeared, with no concentration gradient over the part thickness. A similar behavior was observed for an adding time of 360 s. Here, the thickness of the solid layer of black material has increased and the concentration of black material in the blend area has decreased.

A different behavior can be observed when the second material is added after the first material adhered completely to the mold wall. In this case, two separate layers with an irregular interface region form. The thickness of this interface layer was measured optically. The results of the thickness measurements on the interface layer are shown in Figure 9. The thickness of the interface layer slightly decreases, within the range of the standard deviation, for adding times between 420 s and 600 s. For later adding times, up to 1300 s, no further smoothing of the interface layer was observed.

5 Discussion

5.1 Comparability of material behavior

The characterization of the material properties revealed no major differences for the two investigated materials. The melting temperature differs by approximately 1.7°C (2nd heating) and the peak crystallization temperature by

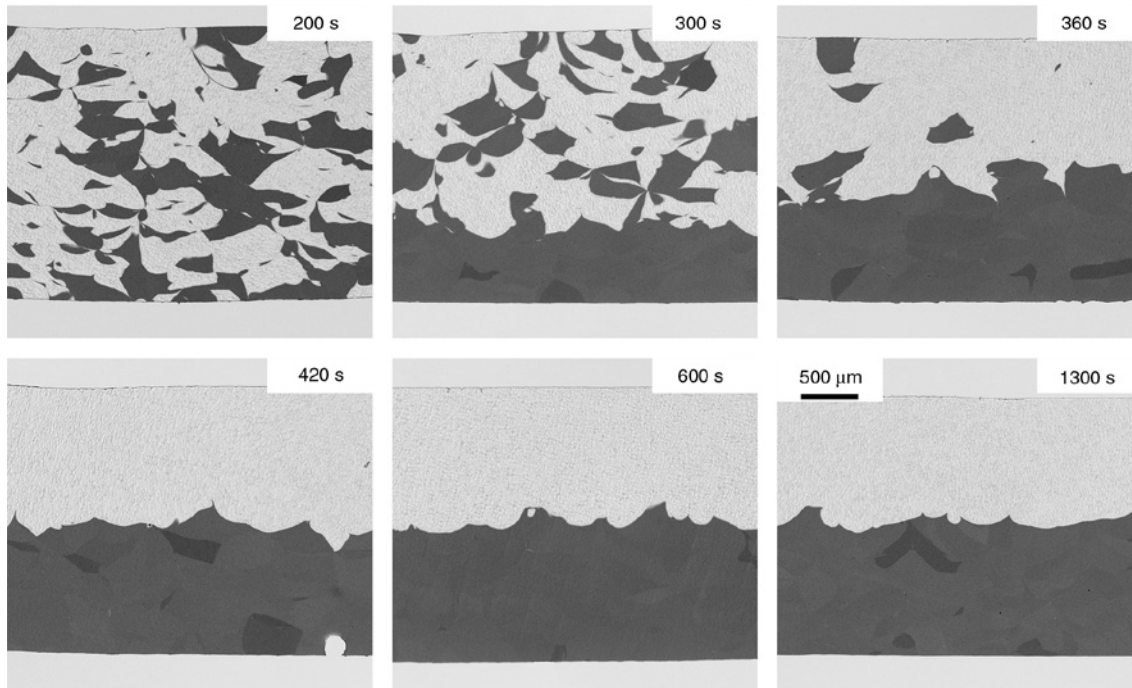


Figure 8: Representative cross sections of multi-layer parts with different adding times for the second component.

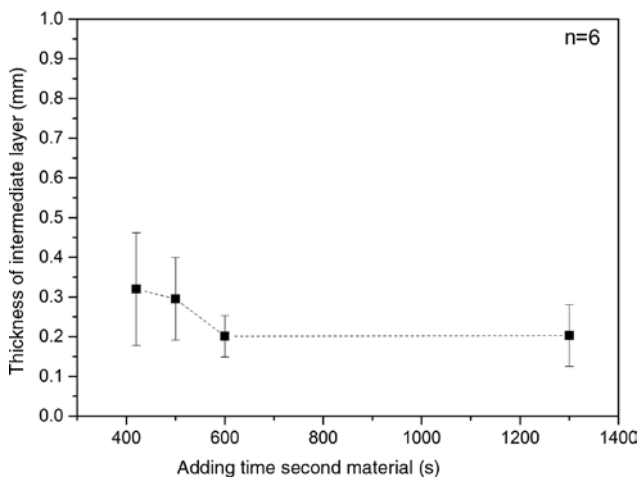


Figure 9: Thickness of interface layer for different adding times of the second, inner material.

3.7 K as shown in Table 3. The enthalpy of fusion at the first heating differs significantly (18.8 J g^{-1}). The lower enthalpy of fusion of the translucent material results presumably by a different thermal history and a resulting lower crystallinity. The enthalpy of fusion during the second heating shows good accordance. For the particle size distribution and the particle shape, high degrees of similarity could be measured for the two materials as well. The average particle size of the Lupolen 4021 K RM Black Powder was measured slightly (approximately $80 \mu\text{m}$) higher than for the Lupolen 4021 K RM Powder. It is not expected that this

difference has a significant effect on the processing behavior during rotational molding. The flowability (MVR) of the materials is similar. Therefore, it can be assumed that the behavior of the materials in the rotational molding process is comparable and no significant differences in particle movement, melting or densification appear.

5.2 Material arrangement

The single layer experiments showed a build of a porous melt layer with loose sintered particles on the inner surface during heating. The inner surface becomes smoother in the progress of heating, driven presumably by surface tension effects. The roughness of the inner surface, which occurs prior to the smoothening of the melt layer, is presumably significantly influenced by material properties. Especially smaller average particle sizes and lower aspect ratios of the particles could lead to a smoother inner surface already during sintering. Additionally, after complete adhesion of the powdery material, lower viscosities, higher surface tensions and higher processing temperatures, potentially could lead to a faster smoothening of the inner surface.

As shown in Figure 8, the characteristic cross sections of multi-layer rotational molded parts are strongly dependent on the adding times of the components. Different material arrangements can be accomplished by different times the second material is added to the process, as

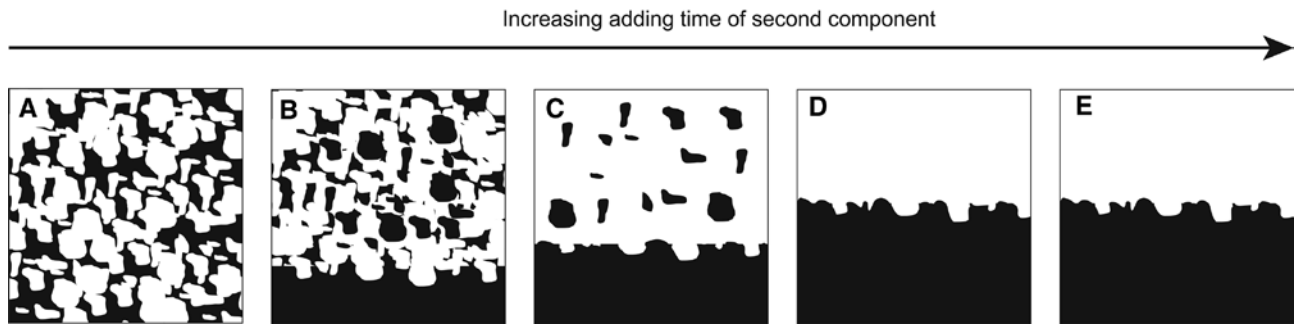


Figure 10: Layer setup depending on the adding time of the second material. (A) Adding of second material prior to adhesion of first material to mold wall. (B) Adding of second material during adhesion of first material. (C) Adding of second material during adhesion of first material. (D) Adding of second material after complete adhesion of first material, prior to smoothing of the inner surface of first material. (E) Adding of second material after complete adhesion of first material and after smoothing of the inner surface of first material.

schematically shown in Figure 10. The relevant factor for the resulting material distribution is the condition of the first material during adding of the second material.

If the second material is added while no adhesion of the first material has taken place, a complete distribution or blending of the two materials occurs (A). The experiments showed that a homogenous mixing of the materials already occurs when the second material is added to the process approximately 70 s before the start of adhesion of the material. If the second material is added during the adhesion process of the first material, two distinct layers occur; a continuous layer of the first material and a blend layer (B). The thickness of the solid layer thereby increases with increasing process time until the second material is added. Simultaneously, the concentration of the first material decreases within the blend layer (C). The particle size of the outer material determines the size of the inclusion within the blend layer. Two distinct but pure layers appear, when the first material has already formed a complete layer adhering to the mold surface before the second material is added (D). The smoothness of the interface layer is not significantly influenced by the adding time of the second material (E) as shown in Figures 8 and 9.

5.3 Interface layer

As shown in Figures 8 and 9, the interface between the two different materials shows a rough appearance. The thickness of the interface layer, which can be assumed to be an indicator for the roughness of the interface layer, slightly decreases for adding times shortly after the complete adhesion of the first material. For later adding times, no further smoothing of the interface layer was observed. No interface layer thickness below 200 μm occurred for

adding times of the second material between 200 s and 1300 s. In contrast to the results, the smoothing of a single material layer as shown in Figures 6 and 7 would normally suggest similar behavior and hence a smooth interface layer of the two materials, if the second material is added after a homogenous layer has already formed for the first material. This leads to the conclusion that the roughness of the first material is presumably not the critical factor for the actual shape of the interface layer. The measured roughnesses of the interface layer and of the single layer parts are compared for different process times in Figure 11.

For processing times of 495 s and 555 s, the surface roughness of the single layer is significantly lower than the resulting roughness of the interface area, for comparable adding times of the second material. After 555 s, the thickness of the measured surface irregularities of the single layer is already <0.10 mm. Therefore, the adding

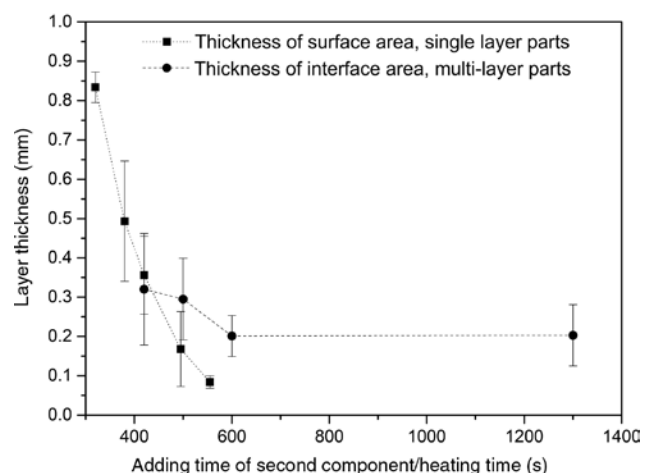


Figure 11: Comparison of surface roughness and height of interface area of one- and two-layered parts for different adding/heating times.

of the second material itself presumably leads to a significant roughening of the polymer layer of the first material. By comparing the cross section of the two-layer sample for an adding time of 600 s with the mono-layer sample for a heating time of 555 s, this effect can be illustrated as shown in Figure 12. The single material part shows a smooth surface with an insignificant, macroscopic surface structuring. The interface layer of the two-layered sample illustrates a structuring on a microscopic scale, approximately in the size range of the powder particles. The structuring additionally shows narrow radii and small concave areas.

A possible reason for this effect is the penetration of the already smoothed first material layer by the solid powder particles of the second material. Due to the pressure resulting from the moving powder bed, solid particles of the second material are pressed into the already homogenized melt layer of the first material, as shown in Figure 13. After the particles of the second material are molten, an irregular interface between the materials occurs in the melt state. This irregular appearance is conserved during cooling and also occurs in the finished parts.

Therefore, parameters like the size and form of the particles of the inner material, the viscosity of the outer material, the amount of the second material and rotation speeds are likely to affect the interface layer in multi-layer rotational molded parts significantly. Bigger particles are likely to result in a coarser interlayer due to a deeper penetration of the melt layer. A higher MVR as well as higher processing temperatures (resulting in lower viscosities) have presumably a comparable effect on the interface due to the lower resistance of the outer melt layer against penetration.

The adding time of the second material only affects the interface layer during the initial phase, when the first material has not yet formed a homogenous melt layer (adding times lower than 495 s in this study). Therefore, later adding times are not sufficient to generate complete smooth interface layers in multi-layer rotational molded parts. The roughening of the melt layer of the outer material by powder particles of the second component has to be taken into account by designing rotational molding processes for multi-layer parts.

Possible approaches for a further smoothening of the interface layer of multi-layer rotational molded parts are based on the reduction of the penetration of powder particles into the melt layer of the outer material. This can on the one hand be accomplished by the reduction of the forces which act on the melt layer. Adding the inner material stepwise resulting in a smaller amount of powder being added at once and the usage of smaller and more spherical powder particles are possible approaches to reduce the resulting forces. On the other hand, a higher

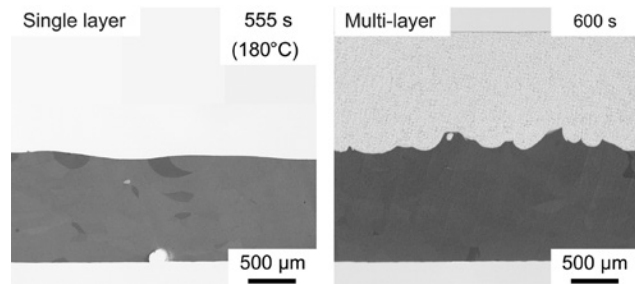


Figure 12: Comparison of the surface roughness of a single layer part (left, processing time: 555 s) and the interface layer of a multi-layer part (right, adding time of the second material: 600 s).

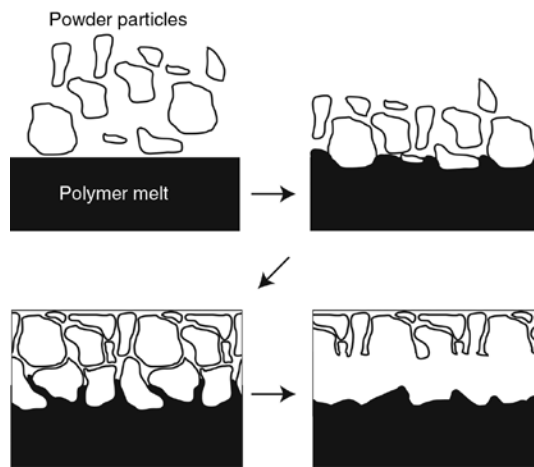


Figure 13: Roughening of the interface layer by penetration of the melt layer by solid powder particles.

resistance of the melt layer against mechanical penetration could result in smoother interfaces. As the usage of resins with higher viscosities would lead to unfavorable processing behaviors, for example during melt-densification and sintering, an adapted temperature profile could be used to increase the resistance of the melt during adding of the inner material. By reducing the melt temperature before adding the second material, the viscosity could be increased only in the critical step during adding of further materials, without influencing other process steps like densification and sintering.

6 Summary

In this work, the influence of adding time of the second material in two-component rotational molding on the layer built-up and resulting interface layers was investigated. Using different analyzing methods, the comparability of the two materials used was proven and material

effects on the results were precluded. By adding a second material while loose material is still present in the system, a blend develops in the inner part area. The mixing ratio within the blend and the thickness of the layers does here depend on the adding time. Two distinct, single material layers appear, if the second material is added to the system after the first material has completely adhered to the mold. The interface forming in this process is largely independent of the adding time of the inner material. It was shown, that the adding of the second material itself leads to a roughening of the interface area due to the deformation of the melt layer of the outer material. Based on the results, possible approaches to achieve a smoother surface in multi-layer rotational molded parts were deducted.

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